

**PHYSICO-CHEMICAL CONDITIONS OF MINERALIZATION IN THE SABIE-PILGRIM'S
REST GOLDFIELD, EASTERN TRANSVAAL**

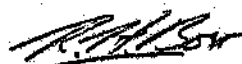
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DECLARATION

I declare that this research is my own work and that it has been conducted under the supervision of Professor L.J. Robb and Professor B.Th. Verhagen. No part of this research has been submitted in the past, or is being submitted, for a degree at another university.



R.H. Boer

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ABSTRACT

A different class of mesothermal gold deposit at Sable-Pilgrim's Rest is described which is probably associated with the Bushveld Igneous event in South Africa. Pressure and temperature estimates indicate that the ore-fluids of the Sable-Pilgrim's Rest Goldfield, which occurs within the early Proterozoic Transvaal Supergroup, were similar to those of mesothermal gold deposits. However, several features distinguish the Sable-Pilgrim's Rest ores from typical mesothermal deposits:- (1) the presence of ubiquitous Cu and Bi in addition to Au, Ag, As, Sb; (2) high salinities (mean ≈ 12 wt% eNaCl); (3) mean bulk CO_2 content is low (≈ 5 mole%); (4) veins are largely hosted within a platform carbonate sequence; and (5) mineralization occurs along both vertical and horizontal (stratiform) veins, showing a clear genetic link. Characteristic features of the Sable-Pilgrim's Rest Goldfield, which correspond to those within the spectrum of mesothermal gold deposits, include:- (1) a comparable light stable isotope (δD , $\delta^{18}\text{O}$, $\delta^{34}\text{S}$) ranges, together with a lack of isotopic evidence for meteoric water involvement; (2) high Au/Ag ratios; (3) presence of ore shoot structures, which are highly characteristic of mesothermal gold deposits; (4) variably deformed structures within individual sheeted veins which point towards cyclic opening and quartz accretion events separated by episodes of deformation; and (5) fluid inclusion properties which indicate high fluid pressures during entrapment.

Bushveld magmatism is thought to have been the main heat source responsible for generating the hydrothermal cell that resulted in the formation of the Sable-Pilgrim's Rest Goldfield. Mineralization involved an originally pristine fluid transporting metals that were probably derived from the same source, as well as a measure of connate waters from the granitic basement and the overlying sedimentary rocks. The fluid was relatively acidic and anoxic and equally efficient in transporting gold either as a bisulphide complex or a chloride complex. Gold precipitation took place as a result of (1) a decrease in sulfur activity within the ore-bearing fluid because of sulfide precipitation, and (2) changes in the fluid chemistry as a result of fluid immiscibility.

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Figure 4.9 Composite $^{207}\text{Pb}/^{206}\text{Pb}$ vs $^{208}\text{Pb}/^{204}\text{Pb}$ diagram of sulphide data for the Transvaal Sub-basin of the Transvaal Sequence (data from Duane, 1987; Duane *et al.*, 1991; Anderson, 1992), carbonate gangue (Anderson, 1992) and whole rock diabase samples from the Olifantsgeraamte Mine. The errorchron for the complete data set correspond to an "age" of 2219^{+8}_{-9}Ma ; MSWD=375.29.

Figure 4.10 A binary $^{207}\text{Pb}/^{204}\text{Pb}$ versus $^{208}\text{Pb}/^{204}\text{Pb}$ diagram of the lead isotopic composition of sulphides, gangue phases and host rocks from the Transvaal Basin (data from Duane, 1987; Duane *et al.*, 1991; Anderson, 1992 & this study). A characteristic feature of the data is the narrow clustering, compared to data from other ore deposits, eg massive sulphide deposits from the Noranda district (Franklin *et al.*, 1981; 1983).

Figure 5.1 Stability fields of minerals in the system $\text{K}_2\text{O} - \text{Na}_2\text{O} - \text{Al}_2\text{O}_3 - \text{SiO}_2 - \text{H}_2\text{O}$ plotted in terms of the activity ratios of Na^+/H^+ versus K^+/H^+ . The thermodynamic data for the mineral species are calculated using SUPCRT92 (Johnson *et al.*, 1992) with data from Helgeson *et al.*, (1978) (after Boer and Harley, 1994).

Figure 5.2 Composite $\log f\text{O}_2$ versus pH diagram for the SPRG conditions. Calculated using SUPCRT92; Johnson *et al.*, (1992). Shaded area represents an approximation of activities of vein forming fluids, based on average QMS gas analytical results.

Figure 6.1 Photomicrographs of quartz hosted fluid inclusions from western Transvaal auriferous veins.

Figure 6.2 Ternary $\text{CO}_2/10 - \text{HCl}/10 - \Sigma\text{S}_{\text{total}}$ diagram of QMS gas data from inclusion fluids of western Transvaal hydrothermal quartz specimens. Samples from the western Transvaal contain higher proportions of sulphur species, compared to the more HCl-rich fluids from the eastern Transvaal.

Figure 6.3 Ternary $\text{N}_2 - \text{Ar}/100 - \text{CO}_2/10$ diagram of QMS gas data of inclusion fluids from western Transvaal quartz. The scatter of data and lack of any positive correlation between N_2 and Ar suggest the absence of meteoric water involvement in the hydrothermal system. Low N_2 and Ar values also indicate that the samples were not contaminated with atmospheric air during analyses.

Figure 6.4 Ternary $\text{H}_2\text{O}/100 - \text{CO}_2/10 - \text{CH}_4$ diagram of the most common western Transvaal inclusion fluid gas species

Figure 6.5 Ternary diagram of the common carbonic species in western Transvaal inclusion fluids ($\text{CO}_2/10 - \text{CH}_4 - \text{C}_2\text{H}_6$).

Figure 6.6. A δD versus $\delta^{18}\text{O}$ plot depicting the stable isotope geochemistry of the western Transvaal hydrothermal quartz veins (empty squares), as well as the values for the Sabie-Pilgrim's Rest ore-bearing fluids (filled circles). MWL - Meteoric Water line.

Figure A1.1 Noble gas release patterns of ^4He , ^{36}Ar and ^{40}Ar from SPRG native gold samples, as a function of temperature. The numbers in the diagrams indicate the total amount (in $1\text{E}-08\text{ cm}^3\text{STP/g}$ [100%]) of the respective isotope.

Figure A1.2 (a) XRD trace of ralstonite and $\text{NaUZr}_2\text{F}_{12}$ obtained in this investigation along with the relevant JCPDS (1986) card data. (b) XRD trace of hieratite acquired in this investigation along with the relevant JCPDS (1986) card data.

Figure A1.3 SEM microphotographs of insoluble hieratite (a & b) and ralstonite (c & d) precipitates.

Figure A1.4 Chondrite-normalized REE distribution in hieratite and ralstonite. Chondrite values from Wakita et al., (1971).

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- Ek is opreg dankbaar teenoor my ouers vir my vroeëre opvoeding.
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It is great inconvenience for a man, in a haste, that there are three distinct roads between Calais and Paris; in behalf of which, there is so much to be said by the several deputies from the towns which lie along them that half a day is easily spent in setting which you'll take.

From Volume 7, Chapter III of Laurence Sterne's *Life and opinions of Tristram Shandy, Gent.*

CHAPTER 1 - INTRODUCTION AND GEOLOGICAL SETTING

1.1 Objectives and rationale

This project is aimed at investigating the nature of gold mineralizing fluids in the Sable-Pilgrim's Rest goldfield (SPRG), and the physico-chemical conditions that have resulted in the formation of ore within the eastern portion of the Transvaal Sub-Basin. The 600 km² area referred to here as the Sable-Pilgrim's Rest goldfield extends parallel to the Transvaal Drakensberg escarpment and include the towns of Sable, Pilgrim's Rest and Graskop (Fig. 1.1). The SPRG is found near the eastern margin of the Bushveld Complex, is roughly coeval with it and was probably covered by the complex when mineralization took place (Cheney and Twist, 1991). Although the SPRG has been overshadowed by the Barberton and Witwatersrand gold mining districts, it remains the third largest gold producer in South Africa and would be considered a large district in most other parts of the world. The size of this goldfield would place it among the top ten gold producers on the north American continent (Koschmann and Bergendahl, 1988), comparable to the well-known Juneau gold belt in Alaska (Redman, 1986).

Gold mineralization in the SPRG is epigenetic and confined to transgressive, vertical veins¹, stratabound flat veins, and sill/dyke-associated quartz-carbonate veins. Specific questions which are addressed in the present study relate to the nature of the ore-forming fluids, the source of these fluids, temporal fluid evolution, and the physico-chemical conditions under which the fluids precipitated metals. This study is regarded as relevant to the study of ore-genesis in general because the Sable-Pilgrim's Rest goldfield is unusual in terms of its geological setting, its mineral paragenesis, the characteristics of the mineralizing fluid, and because there is at present no consensus regarding the origin of these deposits.

Epigenetic vein systems have been important sources of gold for over a century (Lindgren, 1933). Most epigenetic precious metal deposits are found in metamorphic terranes, associated with subaerial or submarine volcanism, or sometimes near deep felsic intrusions and include the important greenstone gold deposits of the Archaean. The proximity of the goldfield to the Bushveld Complex is not a coincidence and may be related to the origin of the deposits. Layered igneous complexes (LIC) are not commonly thought to be associated with hydrothermal gold deposits and such a link suggests

¹ Within the Sable-Pilgrim's Rest goldfield, individual ore bodies or quartz-carbonate-sulphide-gold vein deposits are locally referred to as "reefs".

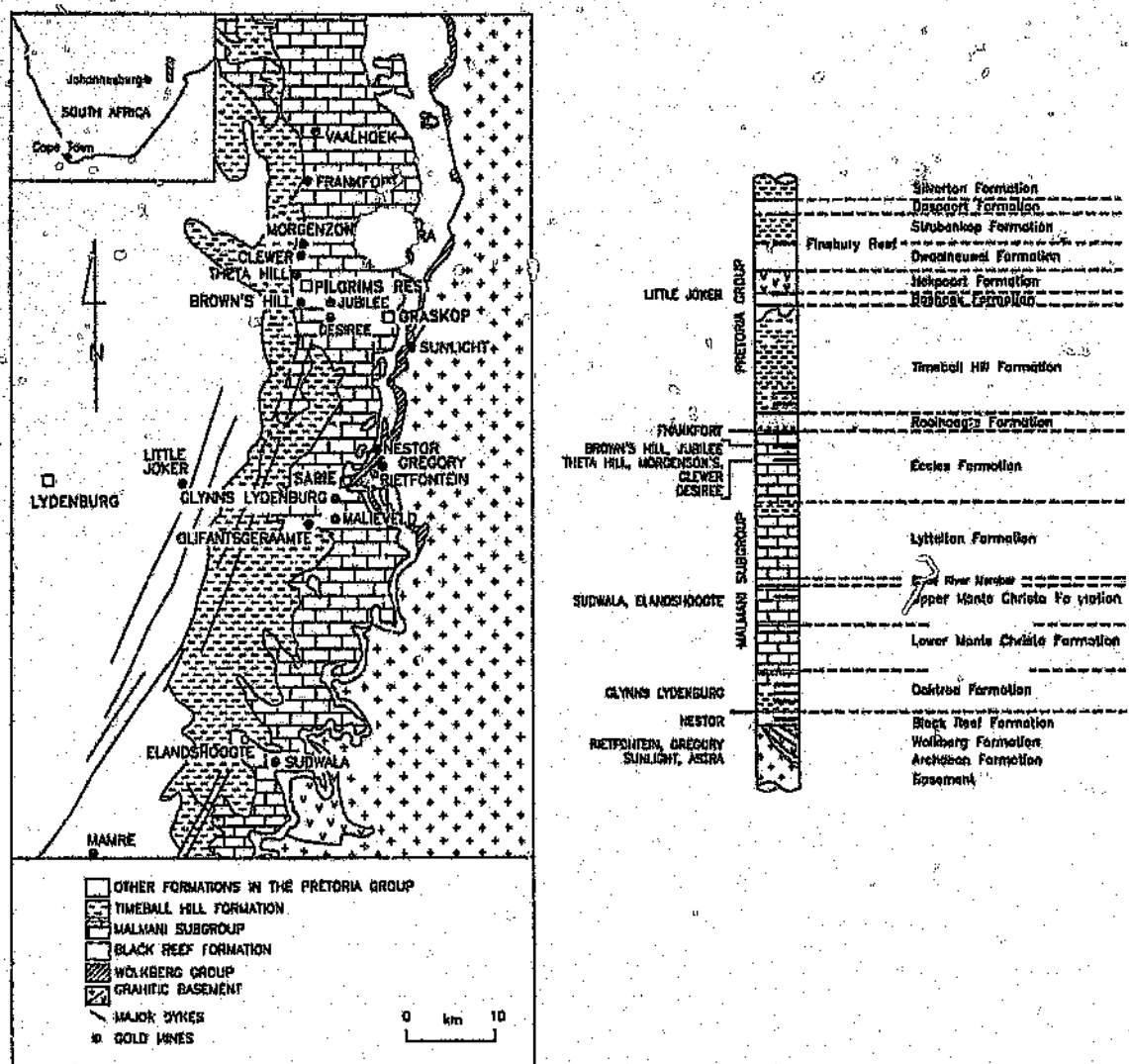


Figure 1.1 Geological map of the Sabie-Pilgrim's Rest goldfield with schematic stratigraphic column.

Position of mines are indicated (modified after Harley and Charlesworth, *in press*)

a new and very different setting for epigenetic gold mineralization. In view of the wide spread nature of mafic complexes, any such an association would be significant in terms of new exploration targets.

1.2 Methodology

The procedures and analytical techniques used to systematically study the ore-forming environment in the Sabie-Pilgrim's Rest goldfield are summarized in Figure 1.2. Sampling was aimed at obtaining a representative sample set in order to investigate vertical and lateral changes in fluid properties (Appendix 2). Detailed fluid inclusion petrography was undertaken to establish temporal relationships among the different fluid populations. Mineral petrography attempted to establish a paragenetic sequence for the sulphide minerals associated with gold mineralization, whereas electron microprobe analyses quantified chemical changes in sulphides and gold fineness. Cathodoluminescence studies were performed to identify different quartz domains related to specific fluid inclusion populations. Fluid salinities and densities were quantified by the acquisition of fluid inclusion microthermometric data and the application of various equations of state. Micro-Raman spectroscopy, as well as quadrupole mass spectrometry was used to quantify inclusion fluid composition. Thermodynamic modelling of these gas analyses enabled the quantification of the physico-chemical properties under which fluids were trapped as inclusions. Stable isotope compositions were determined for inclusion fluids ($\delta^{18}\text{O}$, δD , $\delta^{13}\text{C}$), as well as for vein quartz ($\delta^{18}\text{O}$). Radiogenic isotopes (Rb-Sr, Sm-Nd, Pb-Pb) were employed to model fluid flow, as well as attempting to determine an age of gold mineralization. These data were used to characterize the fluid properties of the Sabie-Pilgrim's Rest goldfield and synthesize a genetic model for gold mineralization. The Sabie-Pilgrim's Rest goldfield was also compared to other occurrences of gold mineralization in the Transvaal Basin, as well as similar deposits elsewhere in the world.

1.3 History

The history of gold mining in the eastern Transvaal started with the discovery of gold bearing rocks near Lydenburg by Karl Mauch in 1868. In 1869, Edward Button, Tom MacLachlan, J.L. Valentine and George Parsons found gold on the farm Spitzkop (195 JT), near the present Sabie. Their continued prospecting was rewarded by the finds on the farm Hendriksdal (216 JT), situated south of Sabie, and on 5 February 1873 the Landdrost of Lydenburg, A.F. Jansen, reported their results to Pretoria (Pretorius, 1994). Later that year Jan Muller found the precious metal on the farm Geelhoutboom (565 KT) (now called Mac Mac). Further occurrences of exploitable alluvial gold were located in early July of that year around Steenkampsberg by C. Evans and H. Helder. On 22 September 1873 William Trafford made

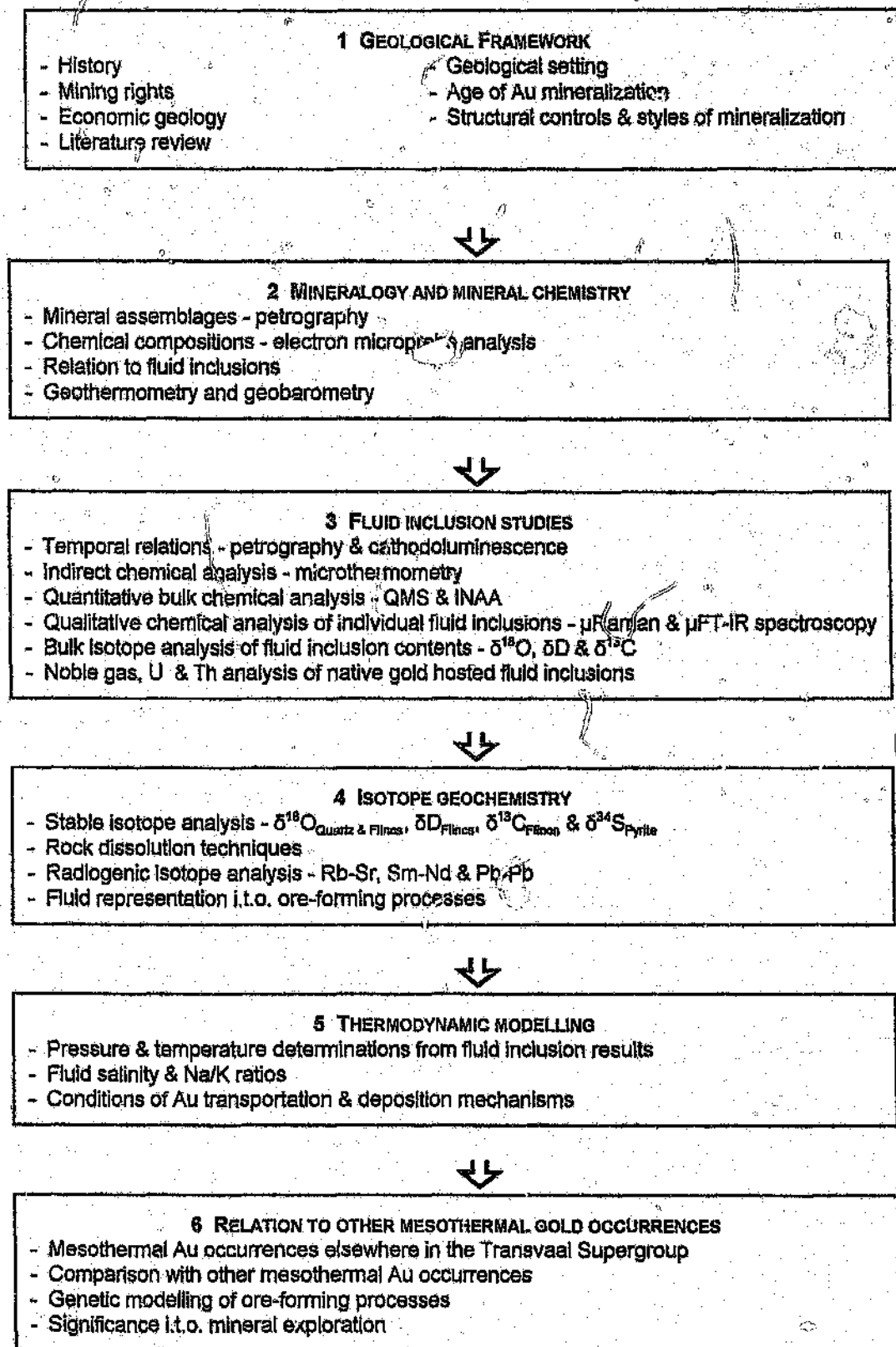


Figure 1.2 Schematic outline of research approach.

the big strike in the lower reaches of the Pilgrim's Creek and around the same time Alec Patterson found exceptional concentrations of gold higher up in the Pilgrim's Rest valley. The area was proclaimed a public goldfield on 14 May 1873 in terms of the 1872 Gold Law (Pretorius, 1994; Kaplan, 1985). One year after the discovery of gold some 1500 diggers were working their own claims, mainly in the area surrounding Jubilee. By the end of 1875, Pilgrim's Rest housed 21 stores, 18 canteens and 3 bakeries. This boom period coincided with gold production from lode mines, exceeding that from placer deposits in the United States (Koschmann and Bergendahl, 1968). Alluvial diggings provided the major portion of gold during the early seventies. In July 1875 the largest nugget weighing 283 ounces (8.802 kg) was recovered from the middle reaches of the Pilgrim's Creek. As deposits of alluvial gold waned, the prosperity of the alluvial diggers declined, but the discovery of gold along quartz rich vein horizons revived interests in the area. The British annexation of the Transvaal in 1877, the Sekukuni wars from 1876 to 1879 and the First War of Independence (Anglo-Boer war) in 1880 - 1881 brought the recovery of gold virtually to a standstill. The Transvaal regained her independence in 1881, but the war resulted in a depression. In an effort to stimulate industries, the reinstated Republican government of President Thomas Francois Burger instituted a policy of granting exclusive concessions to individuals or companies (O'Donoghue, 1884). This step was regarded by some to have been detrimental to the growth of the goldfield (Gillett, 1916). However, on 10 November 1881 David Benjamin was handed the mining rights on the farms Ponies Krantz (543 KT) (on which the village Pilgrim's Rest was established), Ledovine (507 KT), Waterhoutboom (567 KT), Driekop (542 KT), Grootfontein (562 KT) and Belvedere (382 KT). On November 20th, 1882 he registered the Transvaal Gold Exploration & Land Company and in 1895 several mining companies, including the Transvaal Gold Mining Company and H. Eckstein & Co., amalgamated to form the Lydenburg Gold Mining Estates Ltd. The name of this company was changed to the Transvaal Gold Mining Estates Ltd. (T.G.M.E.) in July 1896. Amalgamated companies included Clewer Estate and Gold Mining Co., Jubilee Mines Ltd. and Pilgrims Mining & Estate Co. At the time of the formation of the T.G.M.E. the freehold extended over 32 farms covering approximately 67000 hectares, together with various blocks and claims. A feature of the T.G.M.E. company was the control by two boards of directors (Williams, 1948), one in London and one in South Africa. The matter was settled in 1906 when the Johannesburg board gained the upper hand. The Glynn's Lydenburg company was formed in 1895 to work a small but rich area at Sabie. Numerous other companies were formed over the years. The Lisbon Berlyn Gold Mining Co. was founded in 1884 near Graskop, but had little success even after the main operations were moved north to Frankfort (509 KT). Among others in operation at the time were the Nestor Mining Co., Eastern Star Mining Co., Malleveld Gold Mining Co. and Sabie

Transvaal Gold Mines. These mines were generally short lived and were ultimately bought out or the claims taken over and incorporated into the operations of T.G.M.E. or Glynn's Lydenburg. In 1899-1902 the second Anglo-Boer war broke out between the Transvaal and Great Britain (Packenham, 1979). Although the area east of Lydenburg was never occupied by the British troops, the miners were deported to Delagoa Bay (Maputo), resulting in an interruption of mining activities. Although the mines had suffered, little damage had been done to the plants and operations were resumed immediately after the war. During the succeeding years, the fortunes of the mines fluctuated intensely, and generally it has been a battle for survival (Fowler, 1968; O'Donoghue, 1884; Bell, 1921; Moyle-Phillips, 1909). Good profits were made prior to the First World war 1914-1918, but then fell shortly afterwards. The situation improved after the abandonment of the gold standard in 1932, but profits gradually declined until in 1944 the operations were again marginal. Devaluation in 1949 gave further life to the mines, but costs soon caught up. Statutory notice of closure was given in 1967 when T.G.M.E. sold out to Rand Mines Properties (which subsequently in 1992 became Randgold & Exploration Company Ltd). In 1971 the last of the mines was closed and the T.G.M.E. handed over its final holdings to Rand Mines Properties. The history of production in the Sable-Pilgrim's Rest goldfield is one of increasing tonnage rates and falling grade. New ventures are currently underway by Randgold & Exploration Company Ltd to revive some of the underground operations at Clewer Mine, Morgenzon (525 KT) and Frankfort (509 KT).

1.4 Mining rights

Following the discovery of the Sable-Pilgrim's Rest goldfield (then called the Lydenburg goldfield), and subsequent proclamation under the 1872 Gold Law, a diggers committee, which existed until shortly after the annexation of the Transvaal by Britain in 1877, was appointed to regulate local affairs. Settlements of disputes regarding mining rights or related issues in the Sable-Pilgrim's Rest goldfield were closely related to the development of the South African Gold Law. Early disagreement between diggers on the farms Ponies Grantz (543 KT) and Driekop (542 KT), and the owner, H.W. Struben, concerned the high claim licence fees, which had been set by the ZAR Volksraad. Several types of claims existed during the early years (Kaplan, 1985), dimensions being in Cape feet: (1) "Quartz claims" of 150 feet by 400 feet along the vein; (2) "Creek claims" of 150 feet measured in the direction of the course of the stream and extending in width 50 feet from the centre of the river; and (3) claims of 150 feet square where the claim was situated on a hill or terrace. The latter type of claim could be extended in size to 200 feet square where the depth of the ground from the surface to the bedrock exceeded 25 English feet. Regulations determined that no more than four claims could be held by the

same owner, unless they were entitled to a discoverer's claim. As companies and syndicates (termed the "capitalist" faction in early news papers and reports) begun acquiring farms with a view both to speculation and gold mining, resentment begun to spread among the diggers. The 1875 Gold Law envisaged the acquisition of claims by companies with the same rights as individual diggers, and also introduced the "concession" type of mining title, which granted exclusive rights to mine for gold over large tracts of land. It also contained the first definition of "claims" as "dat gedeelte van land, waarop eenig persoon, personen, of compagniën gerechtigd zullen zijn te delven, of hetzelve te occupeeren onder de bepalingen van deze wet" (as reported in The Star newspaper of 2 May, 1925). Antagonism continued between the diggers and the "capitalist" faction during the Sekukuni War and after the annexation of the ZAR by Britain, as the 1875 Gold Law did not satisfy the needs of either group. The first Anglo-Boer War ended in July 1881 with the signing of the Pretoria Convention, which granted the Transvaal complete self-government. The new administration radically changed the policy concerning the development of the goldfield and repealed the 1873 proclamation of the Lydenburg goldfield, effectively closing the area off to the public and suspending the issuing of new claim licenses. The repeal was a direct consequence of the concession granted to David Benjamin. Under Benjamin's concession, and other subsequent concessions, the rights of existing claimholders were clearly overridden. Between 1881 and 1885 the Volksraad attempted to regulate gold mining almost exclusively by way of concession. The granting of concessions was very unpopular among the diggers and many of them left the district, some not even being compensated for their claims, as was required in terms of the concessions. The 1883 Gold Law allowed claims to be prospected, but a digger could not acquire a licence to enable him to mine. Once gold had been discovered in payable quantities, the landowner had the right to obtain a concession granting him the exclusive right to work the claims (Kaplan, 1985). This was also applicable to government owned ground. Amendments to the law in 1884 allowed diggers to obtain a licence from the State President under certain circumstances. In terms of this amendment a portion of the Lydenburg goldfields was opened to the diggers for pegging. The discovery of the Barberton goldfields in June 1884, put pressure on the government to reconsider the 1884 Gold Law, and a Gold Law Commission was appointed. The 1885 Gold Law somewhat strengthened the digger's rights and allowed for the granting of both prospectors and diggers licences. Only two types of claims were distinguished under this law, namely an alluvial claim of 150 feet square and a quartz vein claim of 150 feet by 400 feet. Three other types of claims were provided for, i.e. owners' claims, prospectors claims (a.k.a. discoverers' claims) and "vergunning" claims, which were distinguished by reference to the grantee and were allocated prior to public pegging. Between 1888 and 1907 the Gold Law contained cautious definitions

of "claims" (Kaplan, 1985). In the 1908 Gold Law the right to dig (i.e. the claim licence) was defined as a mining title, and treated separate from the definition of a "claim". Both "vergunning" and "owners" claims were abolished by the 1908 Gold Law, but "prospectors" claims were retained. Furthermore, the distinction between "reef" and "alluvial" claims was abolished, providing one claim size only of 150 x 400 feet. The 1908 Bill also made provision for penalty payments for claims not being satisfactorily worked. The 1908 Gold Law distinguished between "A" and "B" class districts, with class "A" districts encompassing mainly deep-level areas, while class "B" generally comprised areas where shallow vein and alluvial deposits occurred. The Sabie-Pilgrim's Rest goldfield was thus declared a class "B" goldfield in terms of the 1908 Bill, and had slightly different procedures for the pegging and administration of claims, compared to the class "A" deposits (see Kaplan, 1985). This division of mining areas was to be maintained in the 1967 Gold Law. Few amendments were made to the Gold Law during the period 1908 to 1967. Writings in The Pilgrim's Rest Goldfields Miners and Claimholders Quarterly indicate that the miners of Pilgrim's Rest and Lydenburg strongly pressed for changes to the law, especially between 1916 and 1917, but met with little success. Recommendations, which were to apply to the eastern Transvaal only, included reduced claim licence fees, and provision for alluvial and reef claims of 600 x 400 feet and 1200 x 600 feet, respectively. The granting of discoverers claims was eliminated from the Gold Law in 1934. By 1967 the Gold Law had reached a fairly mature and stable form, a summary and discussion of which can be found in Kaplan (1985).

1.5 Economic Geology

The economically important gold occurrences are all situated in the area around Sabie, Pilgrim's Rest and Graskop, except for the Mamre and Slaaihoek Mines near Machadodorp. Gold production reached its peak in 1912 when the annual production from all styles of gold mineralization in the Sabie-Pilgrim's Rest goldfield was 4.2 tons of gold at 15.1 gram/ton (calculated from unpublished data obtained by courtesy of V.W. Werrtmüller). A total of approximately 168 tons of gold was mined from the goldfield between 1897 and 1977 at an average grade of 8.3 g/ton (a complete catalogue of production figures for the Sabie-Pilgrim's Rest goldfield is available from the author on diskette).

Other mineral commodities that were either mined or processed as a by-product of the Sabie-Pilgrim's Rest goldfield include:-

- a) Silver which was recovered from the gold extraction process (Visser and Verwoerd, 1960). Although the fineness of gold varies significantly among the various gold occurrences, the average silver

production formed about 10 per cent of the gold production. Sable-Pilgrim's Rest ore contains no silver-bearing sulphide minerals, and silver occurs only in alloyed form as electrum.

b) Copper occurs mainly as chalcopyrite which is common in the veins, but usually not of any economic importance. However, copper was once produced as a by-product of gold mining from the Beta Mine near Pilgrim's Rest.

c) Pyrite occurs in large quantities in most of the auriferous veins. For a brief period during the Second World War, pyrite was mined from the Pyrite Blow in the Nestor Mine for the manufacture of sulphuric acid.

d) Chrysotile asbestos occurs in small quantities close to contacts with dykes and sills. The most important producers were the Olifantsgeraamte (198 JT) Asbestos Mine and the Graskop Chrysotile Mine (Zietsman, 1964).

e) Pyrolusite was mined on small scale from lenticular occurrences within the dolomite, in an area to the north of Graskop.

1.6 Review of relevant literature

The first scientific account of the Sable-Pilgrim's Rest area was by Cohen (1873) who described the alluvial workings along the Mac Mac River and around Spitzkop (195 JT) at a time when the auriferous quartz veins were not yet being worked. O'Donoghue (1884) recognized bedded quartz veins in the dolostones. Other papers of a descriptive nature followed (Penning, 1885; Bordeaux, 1897; Bousquet, 1897; Krause, 1897; Garnier, 1896; Kuntz, 1896) which dealt mainly with specific gold-bearing occurrences. Thord Gray (1905) was the first to give a general report on the geology and economic geology of the goldfield. The most comprehensive account on the geology of the Sable-Pilgrim's Rest goldfield was presented by Hall (1910), who also published the first geological map of the area covering the goldfield (Fig. 1.3). Wyberg (1925) elaborated on the economic geology of the goldfield and also produced a more detailed map (Fig. 1.3). Reinecke and Stein (1929) focused their attention on the location of the ore in terms of structure and stratigraphy, and were among the first to link the source of mineralizing fluids to the intrusion of a granitic batholith. The features of the Rietfontein Mine near Sable were described by Boxall (1938). Swiegers (1949) presented a detailed description of the orebodies and ore textures, as well as the mineralogy of both hypogene and supergene ores. Swiegers (1949), furthermore, gave an excellent account of the composition, distribution, mode of occurrence, mineral association and paragenesis of gold in the Sable-Pilgrim's Rest goldfield. Barnard (1958) described the structure and mineralization of the Bourke's Luck Mine, and reiterated what he believed to be an

involvement of the Bushveld Complex as a fluid source, as well as recognizing a mesothermal character of the orebody. In a compilation by Visser and Verwoerd (1980) details regarding the general geology of the area around Sabie and Mt. Anderson were presented as an explanation to the area mapped as Sheet 22 (Nelspruit) (Fig. 1.3). Zietsman (1964) dealt mainly with the general geology of the Pilgrim's Rest area, while Zietsman (1967) addressed structural controls on mineralization, as well as mineralization and ore-control in more detail. Zietsman (1967) recognized low-angle thrust faulting along vein planes, and inferred that they were the result of compressional forces due to emplacement of the Bushveld Complex. Two periods of mineralization were visualized; the first period was seen as a localized contact metasomatic event, caused by emplacement of the mafic sills, whereas the second period was seen as a metalliferous front originating from the "root" of the Bushveld Complex. Zietsman (1967) speculated on the origin of the gold, suggesting - with no substantiating evidence - that the metal was derived from both the "magma-chamber itself, as well as from the adjacent sedimentary rocks". Fowler (1968) contributed towards a complete description of the mining and metallurgical methods utilized by the T.G.M.E. in the Sabie-Pilgrim's Rest goldfield, and elaborated on general affairs concerning gold production.

It is only recently that researchers have started to investigate geochemical aspects of the gold-bearing veins and associated rocks. Based on preliminary fluid inclusion (Ash and Tyler, 1986) and stable isotope studies (Tyler, 1986b), Tyler (1986a) concluded that mineralization was a multiphase event with fluids being trapped at depths of 5.5 - 7.0 km. Four types of fluid inclusions were identified, but the authors were unable to distinguish between different fluid entrapment events, or to characterize the nature of the fluid associated with gold emplacement. Ash and Tyler's (1986) preliminary study on oxygen- and sulphur-isotope properties of quartz and pyrite pointed towards a common origin for the various gold-bearing veins within the goldfield. Ash and Tyler (1986) concluded that the mineralizing fluids were obtained either from a magmatic source related to late-Transvaal volcanism (i.e. Dullstroom lavas or Rooiberg Felsites), or from the Bushveld Complex, or by metamorphic devolatilization of the underlying rock-column.

Meyer et al. (1986) and Meyer (1988) identified three generations of gold mineralization, based on detailed ore-microscopy of the Bevetts and Theta veins. Ore-forming processes in the Olfantsgeraamte vein were seen to be less complex. Only one generation of gold precipitation was identified in the latter vein where quartz-veining is associated with and post-dates a dolerite sill. Whole

rock chemical analyses showed that the quartz lode systems had high Cu, As, S, Sb and Bi contents and moderate Zn, Pb, Co and Ni values. The shales, which often host gold-bearing quartz veins, exhibit high Cu, As and Au values. Various metallic elemental ratios were used to characterize pyrites occurring in the host rock and quartz veins and a genetic relationship between these different pyrite populations was suggested. REE patterns in carbonate minerals showed enrichment in heavy REE and were interpreted as indicative of remobilization of the carbonates. Meyer *et al.* (1986) inferred, from thermodynamic modelling, that gold was transported as a thiosulphide complex. The introduction of gold occurred in at least three stages and emplacement was considered to be related to structural deformation. Meyer *et al.* (1986) proposed a preliminary genetic model whereby gold was transported into the Transvaal Sub-Basin, together with clastic sediments. During intrusion of felsic dykes and sills into the sedimentary package, the "gold, sulphides, and gangue minerals" were remobilized and concentrated in "favourable lithological units, namely graphitic shale horizons".

Tyler (1989) investigated the cyclicity of sedimentation in the Malmman Subgroup. An outline of the sedimentological, depositional and structural characteristics of the Malmman Subgroup was given with the emphasis on the location of the ore-bodies. Tyler (1989) also recognized that a number of auriferous veins occur along shale horizons which formed during the termination of regressive and transgressive cycles during Malmman Formation deposition.

More recently, Anderson *et al.*, (1991; 1992) undertook fluid inclusion studies of auriferous quartz veins from a wide range of mineralized settings in the Transvaal Sequence. These authors identified two main sets of fluid inclusions, i.e. moderately saline, three phase CO₂-rich inclusions, with variable phase ratios and densities, and a highly saline aqueous inclusion population containing little or no CO₂. Anderson *et al.*, (1992) interpreted these inclusions to represent "heterogeneous trapping of two originally unrelated, partially immiscible, end-member fluids". Bulk leach methods were used to establish cation ratios, showing Na:K of inclusion fluids in samples from the Malmman Subgroup in the range 4 to 8. By contrast Na:K ratios of between 25 and 50 were reported for Pretoria Group hosted samples. The genetic model proposed by Anderson *et al.*, (1992) involved the mixing of a gold-bearing CO₂-rich fluid of deep-seated (metamorphic/magmatic) origin with a saline, basinal (connate/intraformational) brine (also see a discussion to Anderson *et al.*, 1992 by Boer and Harley, 1994 and a reply by Anderson, 1994).

Harley and Charlesworth (1991; 1992) addressed structural aspects of vein emplacement at the Elandschoogte (270 JT) Mine in the Sabie area, and emphasized that mineralization occurred in two stages, both of which are linked to bedding-parallel thrust faulting. Deformation, during early stages of vein-formation, is concentrated within shale horizons and evolved from shearing to later duplex faulting of the shales and associated quartz vein. Harley and Charlesworth (1993) dealt with the role of fluid pressure in the formation of these gold-bearing veins. Micro-structures within the veins indicate numerous episodic events of fluid infiltration. The authors used friction theory to suggest fault reactivation under low differential stress in the presence of over-pressured fluids (ie where fluid pressures approach or exceed lithostatic pressures).

The models and ideas concerning the origin of the gold and mineralizing solutions that have been put forward since exploitation of the goldfield started, can be categorized into mainly two groups. Reinecke and Stein (1929), Swiegers (1949), Barnard (1958), Visser and Verwoerd (1960), Zietsman (1967), Tyler (1986a) and Harley and Charlesworth (1991, 1992, 1993) all considered the ore to be of magmatic hydrothermal origin, with either Archaean granitic batholiths or the Bushveld Complex having supplied the fluids, as well as the requisite thermal energy to the hydrothermal system. Tyler (1986a) envisaged that metals were acquired, not only from a deep-seated magmatic provenance, but also from greenstone remnants through which these fluids may have passed. Anderson *et al.* (1992) drew attention to the spatial relationship with Archaean lode gold mineralization in the Barberton and Pietersburg greenstone belts and also suggested that the underlying Au-bearing quartz pebble conglomerate of the Black Reef Formation could have been the source of gold. Anderson *et al.*, (1991; 1992) proposed that mixing of a gold-bearing metamorphic/magmatic fluid with a high salinity basinal brine caused Au precipitation. An alternate genetic model was proposed by G.K. Joubert (in Visser and Verwoerd, 1960) which invoked a modified lateral secretion theory. Intrusion of the large diabase dyke swarm in the region was seen as the thermal heat source that caused mobilization of constituents already present within the Transvaal Sequence by connate waters. Arguments put forward in support of this hypothesis included; (i) the absence of a nearby felsic intrusion, (ii) the lack of mineralogical evidence for a temperature gradient within the goldfield, (iii) arguments for an initially undersaturated ore-bearing solution, (iv) compositional differences between quartz-sericite gangue in granite- and sediment-hosted veins, and (v) large volumes of potentially gold-bearing host-rock, compared to the volumetrically small veins. Minnitt *et al.* (1973) and Meyer (1988) both favoured a lateral secretion origin and argued that the gold could have been derived from the Transvaal strata.

1.7 Geological framework

The southern African shield consists of two cratons, namely the Zimbabwe and Kaapvaal cratons. These two cratons are separated by the high-grade metamorphic rocks of the Limpopo Belt and are rimmed by similar high-grade tectonothermal domains, including the Zambezi, Mozambique, and Namaqua-Natal metamorphic belts. From 3.1 to 2.2 Ga a series of Late Archaean and early Proterozoic successor basins developed on the Kaapvaal Craton, including the Dominion-Witwatersrand, Ventersdorp, Griqualand West and Transvaal depositional systems (Clendenin *et al.*, 1988). These basins are hosts to a major portion of the mineral wealth of the southern African subcontinent (Anhaeusser and Maske, 1986).

The Proterozoic Transvaal Sequence is developed in two structural basins, the first in the central Transvaal and the second in the northern Cape, extending into Botswana (Eriksson *et al.*, 1976). Broad correlations have been established between the Transvaal Sequence and the Griqualand West and Olifantshoek Sequences, situated in the northern Cape province of South Africa and in Botswana (Button, 1986; Eriksson *et al.*, 1976), and possibly also with units within the Pilbara and Yilgarn cratons of Western Australia (Button, 1976). The Mount Bruce Supergroup in western Australia, correlative of the Transvaal Sequence, is preserved as a single structural basin, referred to as the Hamersley Basin, which is situated on the Pilbara Block. The Nabberu Basin, a depository of similar age and general character, has been delineated around the northern and northeastern periphery of the Yilgarn Block (Button, 1976). The Transvaal Sequence comprises approximately 11 km of relatively undeformed, largely unmetamorphosed sedimentary and volcanic rocks (Button, 1986), extending over approximately 160 000 km². The lower part of the Transvaal Sequence is largely made up of volcanic and clastic units of the Wolkberg Group, overlain by non-detrital chemical sedimentary rocks of the Chuniespoort Group, made up predominantly of carbonates, chert and lesser amounts of shale.

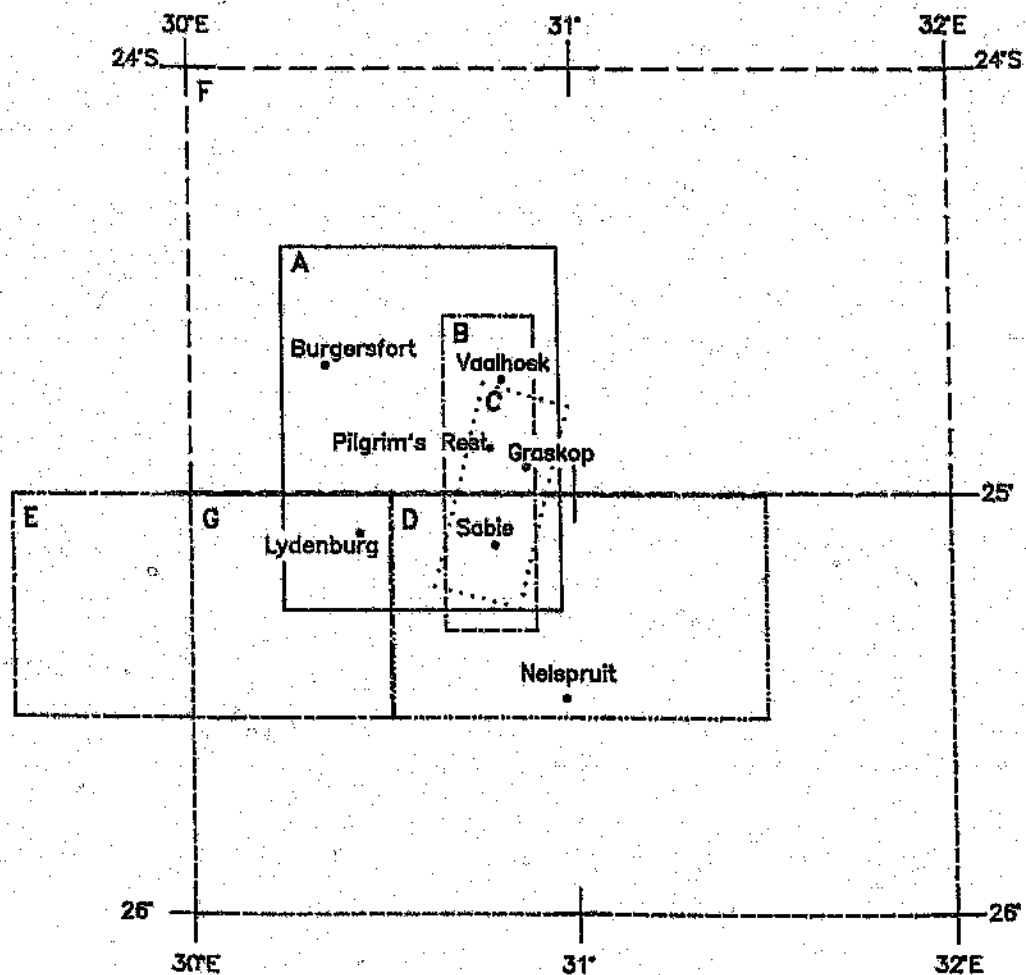


Figure 1.3 Published geological maps of the Sabie-Pilgrim's Rest goldfield. A - Hall (1910), scale 1:148750; B - Zietsman (1964), scale 1:50000; C - Wyberg (1925), scale 1:60000; D - S.A.G.S., scale 1:125000; E - S.A.G.S., scale 1:148750; F - S.A.G.S., scale 1:250000; G - S.A.G.S., scale 1:250000. (S.A.G.S. - South African Geological Survey).

Extensive weathering of these dolostones was followed by the formation of smaller, linked, fault-bounded basins forming the clastic sedimentary and volcanic depositories of the Pretoria Group. After a second major unconformity, deposition of the Transvaal Sequence was terminated by voluminous volcanism represented by the bimodal andesitic and rhyolitic Dullstroom Formation and rhyolitic Rooiberg volcanics, as well as subordinate sedimentary rocks.

1.7.1 Archaean granite basement and the Wolkberg Group

A complete succession of the Transvaal Sequence is developed in the eastern Transvaal. In the Sable-Pilgrim's Rest area (Fig. 1.1), the protobasinal Wolkberg Group forms the lower most part of the Transvaal Sequence and lies unconformably on the Archaean Nelspruit batholith. The 3105 Ma old Nelspruit batholith (Kamo and Davis, 1991) comprises a large composite body of granodiorite-adamellite which occurs mainly as massive, porphyritic granite, medium- to fine grained granodioritic bodies and K-rich gneisses and migmatites (Robb *et al.*, 1983). The batholith displays marked topographic relief with the more massive porphyritic phases forming a sheet-like crust which overlies the lower-lying migmatites and gneisses which, consequently, are considered to reflect a lower crustal level (Robb *et al.*, 1983). The medium- to fine-grained granodiorite occurs as two distinct pluton-like bodies (the Hebron and Berlin plutons) as well as innumerable veins and dykes within the porphyritic granite in the areas surrounding the two granite plutons. The origin of the Nelspruit batholith is poorly understood and suggestions include volatile-induced melting of pre-existing tonalite-trondhjemite crust (Collerson and Fryer, 1978), and partial melting of either tonalite-trondhjemite or high-grade gneiss (Cöndie, 1981). Initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratios, various trace element models and the presence of tonalitic gneiss fragments and/or cognate xenoliths in the Nelspruit batholith, support the derivation of the original magma by partial melting of older tonalitic-trondhjemitic gneisses (Robb *et al.*, 1983).

Maximum stratigraphic development of the Wolkberg Group occurs in the Selati Trough, situated to the north of the Sable-Pilgrim's Rest area, where it thins towards the north and south. The Wolkberg Group is regarded as a protobasinal stage of the Transvaal Sequence and consists predominantly of deltaic and fluvial coarse-clastic sedimentary rocks (Button, 1973). Periodic volcanic activity interrupted sedimentation within the Wolkberg Group (Button, 1973). The proportion of quartz-arenite in the Wolkberg Group decreases upwards, accompanied by an increase in mudstones (Tyler, 1989). Thickening of sediments in the Wolkberg Group could be related to troughs in the palaeotopography, as is evident at the Kowyn's Pass, near Graskop, and in the Blyde River canyon area.

1.7.2 Black Reef Formation and the Malmani Subgroup

Disconformably overlying the Wolkberg Group, are the siliciclastic sedimentary rocks of the Black Reef Formation which forms a major scarp step in the Drakensberg escarpment in the eastern Transvaal. A maximum thickness in excess of 500 m is attained in this region where it overlies the Wolkberg Group (Button, 1973). Generally the formation is much more thinly developed. The Black

Reef Formation consists of feldspathic quartzite with interlayered lenses of grit and conglomerate. These fluvially-deposited conglomerates are overlain by mature quartz arenites which are interpreted as a subtidal sheet sand (Button, 1973). In the Sabie-Pilgrim's Rest Area, the Black Reef Quartzite Formation is divided into two units, separated by a thin, volcanic tuffaceous horizon (Tyler, 1989).

The Malmani Subgroup (part of the Chuniespoort Group) (Fig. 1.1) conformably overlies the Black Reef Formation and is subdivided into five formations, based largely on chert content and type of algal structures found in the dolomite (Button, 1973; Clendenin, 1989); these are the Oaktree, Monte Christo, Lyttelton and Eccles Formations, with the uppermost Frisco Formation being absent in this area. The majority of Sabie-Pilgrim's Rest type stratabound gold-bearing quartz veins are hosted within the Malmani Subgroup. Stromatolites occur throughout the carbonates and cherts of the Malmani Subgroup. Forms vary from crinkly laminations, domal, columnar, thrombolitic and digitate stromatolites to elongated algal mounds (Eriksson and Truswell, 1973). Algal microstructures have been isolated and identified by Nagy (1974). Sedimentary structures are also common in the dolomites, including ripple marks, cross-laminations, oolites and intraclastic breccias (Button, 1973), as well as salt casts. In the Sabie-Pilgrim's Rest area the salt indentation casts are found in sedimentary rocks formed in the intertidal, supratidal and barred environments (Tyler, 1989), where salt growth occurred due to evaporation.

The Oaktree Formation reaches a maximum thickness of 245 meters in the Sabie-Pilgrim's Rest area (Tyler, 1989) and comprises iron- and manganese-rich dolomite, carbonaceous shale, and quartzite (Button, 1986). The Monte Christo Formation, whose maximum thickness is 320 metres in the Sabie-Pilgrim's Rest area, is characterised by a widely developed sequence of oolitic carbonates. Clastic sediments (quartzite and/or shale) of the Blyde River Member mark the base of the overlying, 10 metre thick, chert-poor Lyttelton Formation, which is composed mainly of dark-coloured quartz-arenite in the Sabie-Pilgrim's Rest area. This unit grades upwards into the upper dolomite and chert zone (Eccles Formation) which is capped by an unconformity. Detailed descriptions of the lithology and sedimentology of the Malmani Subgroup can be found in Tyler (1989) and Clendenin (1989). The upper two formations of the Chuniespoort Group, namely the Penge and Duitschland Formations, have not been developed in the eastern Transvaal.

1.7.3 Malmani Subgroup palaeoenvironment

An epeiric sea palaeoenvironment in which tidal processes predominated has generally been

inferred for the Malmari Subgroup (Button, 1973; Truswell and Eriksson, 1975; Eriksson *et al.*, 1976; Eriksson, 1977; Beukes, 1978; Tyler, 1989; Clendenin, 1990). The vast epicontinental sea, in which the carbonates and siliciclastics were deposited, spread over much of the Kaapvaal craton, stretching well beyond the preserved outcrops of the Transvaal and Griqualand West Sequences. The palaeoclimate is considered to have been tropical (Eriksson and Clendenin, 1990). This conclusion is supported by palaeomagnetic data (Windley, 1979), which indicate that southern Africa was at low latitudes during the time of deposition of the Chuniespoort Group. The distribution of lithofacies in this setting was largely determined by water depth (Eriksson and Clendenin, 1990). The absence of gravity flow deposits seaward of the shallow platform carbonates, and Beukes' (1977) interpretation that early carbonate tidal flats faced open ocean, support a distally steepened carbonate ramp depositional model (Eriksson and Clendenin, 1990). The latter authors inferred four palaeoenvironmental facies for the Malmari Subgroup: shallow siliciclastic, peritidal carbonate, periplatform carbonate and basinal facies. The peritidal carbonate facies represented an extended transition between the emergent peritidal carbonate and the basinal facies. The periplatform facies is subdivided into a shoaled flat subfacies, where planar laminated intraclastic and oolitic grainstones developed, and a more distal submerged shelf subfacies, characterized by stromatolitic boundstones. Estimated depositional palaeoslopes of a few dm.km^{-1} imply very gradual transition from the carbonate platform into a shallow basinal subfacies, characterized by mudstones associated with thrombolitic boundstones. A gradual contact between shallow and deep basinal subfacies is marked by interbedded ferruginous mudstones and shales, which pass into distal iron formations.

The Chuniespoort epicontinental sea had two principal stages of development. The first stage comprised the carbonates up to and including the lower portion of the Monte Christo Formation, which is succeeded by a marked erosive surface. This first stage was characterized by a dominantly north-northeastward transgressive depositional pattern as the depository expanded from an initial Griqualand West compartment. The Transvaal sea retreated off the Kaapvaal craton at the end of lower Monte Christo time, leading to relatively extensive erosion of the carbonates. The second stage of development of the Chuniespoort sea extended through to the Penge and Deutschland Formations; this stage was characterized by a re-initiation of the north-northeastward transgressive pattern, as well as a seesaw pattern of regression followed by deepening and depository expansion. The resultant cyclic pattern of sedimentation expanded out of and retreated into the Griqualand West compartment. Dolomitization of primary limestones apparently took place shortly after deposition (Eriksson *et al.*, 1975).

1.7.4 Pretoria Group

Following the chemical sedimentation, the strata were exposed and an extensive erosional period followed. This resulted in the formation of a widely developed chert breccia and chert pebble conglomerate at the base of the Pretoria Group, known as the Bevetts Conglomerate. Excluding the Rooiberg Felsite and Loskop Formation, the Pretoria Group is approximately 7000 metres thick (Button, 1986). The Pretoria Group comprises breccias, conglomerates, diamictites, sandstones and mudrocks. Deposition took place in an intracratonic basin setting, characterized by alluvial fans, fan-deltas, lacustrine deltas, and lake basin and margin palaeoenvironments. Subaerial and subaqueous andesitic volcanism also occurred (Eriksson et al., 1991). A half-graben structural setting is postulated by Eriksson et al. (1991) for the Pretoria Group. The proposed extensional rift-basin was bounded in the south by the Sugarbush-Barberton crustal lineament, and in the north by the Thabazimbi-Murchison lineament. A central submerged palaeohigh in the Pretoria Group basin probably reflects thermal updoming, possibly associated with deep-seated Bushveld magmatism (Eriksson et al., 1991).

A large number of basic sills has been intruded into the Transvaal Sequence in the eastern sub-basin. Most of these sills are probably Bushveld related (Button, 1986) and increase in frequency upwards (Sharpe, 1984). Sills low down in the stratigraphy are fairly altered and essentially undifferentiated. Stratigraphically upwards, some of the thickest sills are differentiated and comprise harzburgites which pass upwards through pyroxenite, feldspathic pyroxenite and norite to a diabasic upper zone (Button, 1986). The Transvaal sediments and volcanics are metamorphosed both by the intrusive sills and by the Bushveld Complex. The metamorphic effects of the Bushveld cut across stratigraphy and extend down to the Malmari Subgroup dolomite in places (Button, 1986).

1.7.5 Bushveld Complex

A vast literature exists on the Bushveld Complex (BC), none of which has been reviewed by Hunter (1976), Von Gruenewaldt (1979), Von Gruenewaldt et al. (1985) and various authors in Anhaeusser and Maske (1986). In brief, the BC is intrusive into the upper portion of the Pretoria Group, but its basal contact cross-cuts up to 5000 metres of Transvaal floor stratigraphy (Button, 1976a). The dolomites of the Malmari Subgroup have largely been unaffected by the intrusion of the BC (Button, 1986), but in areas where the BC is in direct contact with dolomite, recrystallization and decarbonation have occurred on a large scale (Schidlowski et al., 1975; Buchanan et al., 1981). It is thought that the original extent of the BC covered the SPRG during the time of mineralization and that folding and multiple

periods of erosion have reduced the extent of the BC and enclosing strata (Cheney and Twist, 1991). Thus, it is likely that the extent of metamorphism associated with emplacement of the BC may have been underestimated.

1.7.6 Diabase sills and dykes

Volumetrically the sills and dykes form a significant proportion of the stratigraphic pile in the Transvaal Sequence. Sharpe (1984) estimated that the aggregate thickness of these sills and dykes was over 2,5 km. Button (1973) and Sharpe (1984) pointed out that the diabase sills increase in thickness and frequency stratigraphically upwards. Hall (1932) was the first to speculate on a genetic link between these sills and the BC. This relationship was reiterated by Sharpe (1981). Willemse (1959) subdivided the mafic sills into two groups, namely the amphibolitic "Lydenburg type" and the noritic "Maruleng type". This subdivision was confirmed by Frick (1973), but Sharpe (1981) recognized multiple periods of sill emplacement on the basis of their chemical characteristics and the degree to which they had been affected by the mechanics of emplacement of the BC and its associated crystallization history. The syn-Bushveld intrusions are considered by Sharpe (1981; 1984) to form part of the marginal suite of the BC and display a diverse composition including noritic, gabbroic and harzburgitic sills. The pre-Bushveld sills are characterized by amphibolitic assemblages with no fresh orthopyroxene and some of these sills are truncated by the layered suite. Both tremolitic and hornblende-bearing sills are found and the nature of the amphibole present is ascribed to the relative importance of burial versus thermal metamorphism (Sharpe, 1984).

1.8 Age of gold mineralization associated with the Transvaal Supergroup

The Transvaal Supergroup rests unconformably on the Ventersdorp volcanic succession whose age is now well constrained. The most recent conventional U-Pb bulk zircon age determinations on the Maquassie Quartz Porphyry indicate an age of 2699 ± 50 Ma (Walraven, 1992) which is supported by the U-Pb zircon SHRIMP results of Armstrong *et al.* (1991) on the Klipriviersberg Formation and Maquassie Quartz Porphyry of 2714 ± 8 and 2709 ± 4 Ma respectively. Further support for a 2.7 Ga age for the Ventersdorp Supergroup is found in the zircon evaporation date of 2714 ± 3 Ma for the Zoetlief Group (Walraven *et al.*, 1991), a western outlier of quartz porphyry and clastic sediments correlated with the Ventersdorp Supergroup. Klein and Beukes (1990) have hypothesized, on the basis of sedimentological evidence, that deposition of the Transvaal Supergroup started as early as 2500-2600 Ma. This hypothesis now seems to have been corroborated by a Pb-Pb isochron age for stromatolitic

limestones from the Schmidtsdrif Formation in the Griqualand West basin (a facies equivalent of the Malmari Subgroup in the Transvaal; Eriksson *et al.*, 1976) of 2557 ± 49 Ma (Jahn *et al.*, 1990). Zircons from pre-Transvaal acid lavas of the Dornilton area have been dated at 2460 ± 120 Ma, using the U-Pb method (Coertze *et al.*, 1978). The Hekpoort Andesite Formation, which forms part of the Pretoria Group, is dated at about 2.2 Ga (Rb-Sr isochron age = 2224 ± 21 Ma, Burger and Coertze, 1974; Pb-Pb isochron age = 2239 ± 90 Ma for the Ongeluk lava, Walraven *et al.*, 1990; Rb-Sr whole rock age = 2208 ± 63 Ma; Hunter and Hamilton, 1978). This implies that the Transvaal Supergroup comprises a late Archaean Chuniespoort Group and a Proterozoic Pretoria Group, separated by a major hiatus of about 300 Ma (Jahn *et al.*, 1990). In short, age constraints of circa 2550 - 2250 Ma can be placed on deposition of the Transvaal Supergroup.

The mafic rocks of the Bushveld Complex postdate the Transvaal Sequence. This suite has been dated at 2095 ± 24 Ma by the Rb/Sr whole rock method (Hamilton, 1977). Walraven *et al.* (1990) have summarized the available data and recommended an age of 2060 ± 31 Ma for the mafic layered part of the Bushveld Complex. A slightly younger age, 2.05 Ga (Nebo Granite, 2052 ± 48 Ma; Makhutso Granite, 2046 ± 55 Ma) was obtained for the granitic phase of the Bushveld Complex (Walraven, 1988). These ages were confirmed by recent work which yielded an age of 2054.4 ± 1.8 Ma for the granitic phase of the Bushveld Complex, using the single zircon Pb-evaporation technique (Walraven and Hattingh, 1993). Various localities on the Kaapvaal craton yield Bushveld ages, both as coeval intrusions as well as metamorphic overprints of Bushveld age. These ages indicate that Transvaal sedimentation was terminated well before the Bushveld rocks were intruded.

Determination of the age of mineralization in the Sabie-Pilgrim's Rest goldfield has always presented a problem due to the lack of datable ore-stage material. Sharpe (1981; 1984) and Cawthorn *et al.* (1981) indicated that the emplacement of pyroxenitic and noritic sills predated the emplacement of the Bushveld complex (c. 2.05 Ga). Syn-Bushveld sills of similar composition have never been found to host mineralization and appear to be less altered than pre-Bushveld sills. This rather inadequate evidence restricts the age of mineralization to syn-Bushveld times. The highest stratigraphic limit where Pilgrim's Rest type gold mineralization occurs (the Finsbury vein) is at the contact of the Strubenkop and the Dwaalheuwel Formations of the Pretoria Group. The underlying basaltic Hekpoort Formation has been dated at 2224 ± 21 (Burger and Coertze, 1975), which indicates that quartz-vein gold mineralization must have occurred after this time. At the Olifantsgeraamte Mine, near Sabie, a metamorphosed

diabase sill is intersected by an auriferous quartz vein associated with pronounced wall-rock alteration. Samples unaffected by the vein-associated wall-rock alteration yielded an errorchron corresponding to an age of 2027 ± 39 Ma with an initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of 0.7042 ± 0.0003 (MSWD = 15.523). This age is interpreted as representing a maximum age limit for late gold mineralization in the Sable-Pilgrim's Rest goldfield (see comprehensive discussion in section 4.2.4).

1.9 Structural evolution of the Transvaal Sub-Basin

Clendenin *et al.* (1988a) suggested a three-stage rift system for a number of superimposed early Proterozoic basins which includes the Dominion-Witwatersrand, Ventersdorp and Chuniespoort/Ghaap depositional systems. These basins developed along lines of pre-existing tectonic weaknesses and resulted from a simple tectonic style of deformation in which neither extension nor compression dominated. Stresses that further modified individual successor basins was thought to be created by the collision of the Kaapvaal and Zimbabwean cratons. The three-stage rift system of Clendenin *et al.* (1988) consist of a pre-graben stage which influenced the Dominion Group, Witwatersrand Supergroup and the Klipriviersberg Group of the Ventersdorp Supergroup. A second stage involved graben development which superimposed the Platberg Group, Bothaville and Allanridge Formations of the Ventersdorp Supergroup, while a third stage of post-graben subsidence superimposed the Black Reef Formation and the Chuniespoort Group of the Transvaal Sequence. Clendenin and Maske (1986) recognized post-rift thermal subsidence in the Chuniespoort Group by using marginal unconformities passing basinward into conformable sequences, and sedimentary units thickening toward the basin centre. The Chuniespoort Group was deposited in an essentially transgressive environment as a result of almost continuous subsidence and accumulation. The major stage of subsidence was terminated by a rapid regression which led to the regional unconformity which separates the Chuniespoort Group from the overlying Pretoria Group. A SE-NW uplift resulted in the erosion of approximately 1000 metres of the dolomite stratigraphic pile in the southern portion of the sub-basin (Button, 1973). The development of the basin sequence was thus temporarily terminated prior to Pretoria Group deposition (Clendenin *et al.*, 1988b). Tankard *et al.* (1982) suggested that the dominantly terrigenous nature of the Pretoria Group indicated a dramatic change in the pattern of source area tectonics after Chuniespoort times. Eriksson and Clendenin (1990) proposed that the depositional palaeoenvironment of the Pretoria Group comprised an alternation of fan/fan delta/lacustrine delta and lacustrine basin/lake margin sedimentation. The uppermost sediments of the Pretoria Group are arkosic and Button (1986) interpreted these as representing the distal parts of braided fluvial wedges. Eriksson *et al.* (1991) state that a regressive

event terminated Pretoria sedimentation as the lacustrine depository became filled with sediments. The present shape of the Transvaal sub-basin has been largely controlled by the intrusion of the Bushveld Complex. Post-Bushveld thermal subsidence caused the Transvaal strata to dip towards the centre of the basin.

1.10 Structural controls and styles of Transvaal-related gold mineralization

A prominent series of north-northeasterly trending lineaments is visible on ERTS imagery, aerial photographs and maps of the goldfield (eg Zietsman, 1967). Mafic dyke emplacement, post-mineralization normal faulting, and limited graben development have occurred parallel to this trend. These north-northeasterly trending lineaments have also been exploited during emplacement of the vertical veins. Field relations (at Gregory and Rietfontein Mines; Fig. 1.1) show that the vertical veins divert along lithological contacts into a horizontal, stratabound, orientation, confirming the genetic correlation between the vertical and flat veins. Bedding in the goldfield strikes subparallel to the orientation of the northeasterly lineaments and dips typically between 4° and 7°, and sometimes as much as 15°, to the west (Harley and Charlesworth, 1993). Assay maps of mined out areas of the Dukes Hill, Clewer and Elandschoogte Mines, show mineralization to occur along a preferred orientation which parallels the north-northeasterly trending lineaments. In general, there are three styles of gold mineralization, namely (i) transgressive, vertical veins; (ii) stratabound flat veins, and (iii) sill/dyke-associated veins. Considerable evidence for south-eastward verging, bedding-parallel thrusting have been presented (Visser and Verwoerd, 1960; Zietsman, 1967; Harley and Charlesworth, 1992; 1993). The internal structure of the sill/dyke-associated and flat veins are complex and several superimposed episodes of deformation and mineralization can be recognized. The stratabound flat veins are composed of multiple sheets of quartz-carbonate, usually associated with thin slivers of carbonaceous shale and silicified dolomitic host rock. These inclusions of wall-rock material give rise to the typical sheeted nature (ribbon texture) of the flat veins.

Flat veins hosted within dolomites are commonly located at the contact with narrow carbonaceous shale layers interlayered within the carbonates (Tyler, 1989; Harley and Charlesworth, 1993). Examples of such occurrences can be found at the Frankfort Mine (ie the Theta vein), Malieveld Mine (ie the Glynn's vein). Veins also occur on lithological contacts eg the Formosa vein in the Little Joker and Mountain Mines is situated at the contact between the quartzite of the Boshhoek Formation and the shales of the underlying Timeball Hill Formation. A similar situation exists at the Frankfort Mine

where the auriferous quartz vein is positioned on the contact between the conglomerate of the Bevetts Formation and the overlying carbonaceous shales of the Rooihoogte Formation. The Finsbury vein is located on the contact between the quartzites of the underlying Dwaalheuvel Formation and the shales of the Strubenkop Formation. However, an obvious lithological control localizing vein emplacement is not always clear, such as in the case of the Sandstone vein (in the Nestor Mine) which occurs within the Black Reef Formation.

Throughout the goldfield there is a similarity in structural style displayed by the stratabound veins. Detailed structural work by Harley (1993) showed that the earliest deformation results in the formation of subhorizontal cleavages or micro-shear zones in the immediate wall-rocks to the veins. Narrow subhorizontal and steeply dipping vein sets frequently occur in the immediate vicinity of the veins. The arrangement of these associated veins are consistent with emplacement within dilated reidel and reidel conjugate fracture sets within the footwall and hanging wall to the main vein (Harley, 1993; Harley and Charlesworth, 1993). Asymmetric folds in shales within the zone of veining, such as at Frankfort Mine, have shallowly westward dipping axial planes, while the vergence of these structures is broadly to the east-southeast (Harley and Charlesworth, 1993). The final stage of vein development is characterized by the deformation of the vein in a bedding-parallel, blind thrust system which post-dates economic mineralization (Harley and Charlesworth, 1993). The whole deformation system is bounded within carbonaceous shale units. Narrow fault splays cut upsection from the sole to the roof thrust-forming ramps, transgressing the entire vein package, and commonly dip shallowly (15-30°) to the west or northwest (Harley, 1993). Subparallel spaced sets of splays constitute duplex arrays which could be developed on a cm to m scale (eg Elandschoogte Mine - cm scale; Morgenzon Addit - m scale). Antiformal stacks, consisting of narrow, folded slices of quartz and in some cases, shaley material also occurs within the vein horizons, on a variety of scales (Harley and Charlesworth, 1992). The fact that footwall ramps (Butler, 1988) are usually developed along the western margin of any one duplex, whereas the hangingwall ramp is localized at the eastern flank of the duplex horse, suggest eastward-directed thrust movement (Harley, 1993; Harley and Charlesworth, 1993).

CHAPTER 2 - MINERALOGY AND MINERAL CHEMISTRY

2.1 Nature and mineralogy of the veins

Sabie-Pilgrim's Rest-type gold mineralization is epigenetic and confined to transgressive, vertical veins, strata bound veins and sill/dyke-associated veins. Gold is also associated with structurally controlled quartz lens deposits (ie the "channel" deposits of the old timers, eg Dukes Hill Channel). The main gold producers are the stratiform veins which are mainly associated with the narrow shale horizons in dolomite of the Malmari Subgroup. Although the stratiform veins tends to pinch and swell down-dip and along strike, the average vein thickness ranges from 5 to 40cm. Typical stope dimensions of the old mines where stratiform veins were mined, are in the order of 700 by 300m. The Glynn's Lydenburg mine had the largest stoped area which extended approximately 7000 by 400m. The gold grade is highly variable and range from traces to $>60 \text{ g.ton}^{-1}$ (A.R.C. Fowler, pers. commun., 1993), with the overall district-wide grade being in the order of 8 to 9 g.ton^{-1} . In most deposits there are gradational differences in gold grade along strike so that alternating ore-grade and low-grade waste zones can be distinguished. This situation gives rise to a characteristic ore-shoot pattern (Wyberg, 1925; Zietsman, 1967), which exists despite there being little evidence of distinct mineralogical or elemental zoning. The auriferous veins of the SPRG are comprised of mainly three types of quartz. (i) The most abundant type of quartz, in general, is milky-white coarse grained "bull" quartz, also known as "buck" quartz (following the definition by Dowling and Morrison, 1989). "Buck" texture refers to milky to vitreous quartz that consists of tightly packed interlocking crystals of highly variable grain size and orientation. (ii) Comb-textured quartz in which individual terminated crystals can be recognized are fairly common and occur in both the strata bound and transgressive vertical vein settings. (iii) Ribbon-textured quartz, commonly found in the strata bound veins but virtually absent in the sill/dyke associated and vertical veins. Numerous sub-parallel orientated inclusions of wall-rock characterize this type of quartz and gives rise to the pronounced sheeted nature of the veins. The variable quartz textures reflect the factors influencing vein formation, and are not themselves indicative of gold potential, as was also noted by Dowling and Morrison (1989) for the North Queensland examples. Courtis (1889) was able to distinguish between gold-bearing quartz, also known as "kindly quartz", and barren quartz in the Mother Lode district, California. Such a characterization of quartz types in terms of potential gold content is not possible for the auriferous veins of the Sabie-Pilgrim's Rest goldfield. In general, however, the better gold grades tend to be associated with more complex vein textures, such as the presence of multiple quartz generations within sheeted veins.

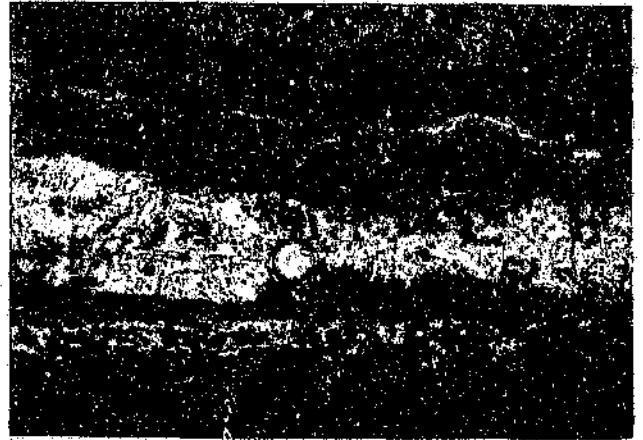
2.1.1 Strata bound veins

The strata bound horizontal veins are composed of multiple sheets of quartz-carbonate (Table 2.1), usually associated with thin slivers of carbonaceous shale and dolomitic host rock (Fig. 2.1a,b). Anhedral, coarsely granular, milky-white quartz, similar to that described by Dowling and Morrison (1989), comprises the bulk of the veins. Small vugs lined with zoned euhedral crystal of quartz are found locally (Fig. 2.1c). Dolomite appears to be the most common carbonate gangue phase occurring within the auriferous quartz veins (Fig 2.2). The scarcity of calcite or any of the other common minerals of the carbonate group, ankerite, is conspicuous. However, ferruginous calcite has been detected in a few samples (F.M. Meyer, pers. commun., 1991). There is a definite increase in carbonaceous material towards the periphery of the strata bound vein deposits. This increase in carbonate minerals within the veins is associated with a decrease in gold values. The old-timers referred to this phenomena as "calciting-out". Shales surrounding the quartz veins typically consist of fine-grained illite and hydromuscovite together with amorphous carbonaceous material, whereas the silt-size fraction comprises quartz, microcline, very rare plagioclase and chert together with interstitial dolomite and clay minerals (Meyer and Robb, 1993). The amorphous carbonaceous material was confirmed to be graphite, after combusting of the material in a ceramic crucible. The lack of a suitable mineral assemblage to determine the grade of metamorphism within the vein systems, is a complicating factor. However, the hydrous silicate minerals which occur in the surrounding shales, suggests a diagenetic metamorphic grade.

Stockworks and breccias, consisting of a mixture of vein material and silicified host-rock fragments, are locally abundant and economically significant (Fig. 2.1d). Dolomite-hosted veins commonly display silicification envelopes, between 0.5 and 1m in width, surrounding the vein. Within these silicified envelopes the dolomite is totally replaced by microcrystalline quartz. Sedimentary structures such as polites and stromatolites are obliterated and fine-grained muscovite and euhedral pyrite occur sparsely within the replaced rock. Harley and Charlesworth (1993) provide evidence for alteration pre-dating the main phases of vein emplacement at the Elandshoogte Mine. The horizontal veins associated with the Oaktree Formation, the upper Lytleton and Eccles Formations, as well as the vertical veins (Bray 1938), are characterized by a complex suite of ore minerals (i.e pyrite, arsenopyrite, fahlores, chalcopyrite, bismuth sulphosalts, bismuth and pyrrhotite), whereas the flat veins occurring at intermediate stratigraphic positions, in the Monte Christo and lower Lytleton Formations, contain predominantly pyrite with lesser amounts of chalcopyrite and sphalerite.



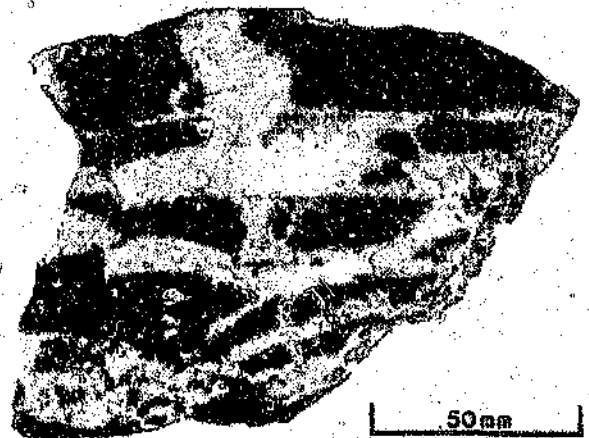
a



b



c



d

Figure 2.1 Underground exposure of auriferous quartz veins. (a). Typical quartz-carbonate vein with abundant coarse-grained pyrite, Elandshoogte Mine. (b). Sheeted appearance (ribbon texture) of vein with graphitic and dolomitic wall-rock inclusions, Glynns-Lydenburg Mine, Sheba Section. (c). Comb quartz, Clewer Mine. (d). Quartz cemented breccias, Elandshoogte Mine. (Photographs (a) & (d) courtesy of Michael Harley).

Table 2.1 X-ray diffraction results for carbonaceous material from selected samples of the Pilgrim's Rest goldfield. Samples were analysed using a Phillips PW1710 diffractometer with Cu LFF x-ray tube under 40kV and 20mA operating conditions

Sample No.	Sample Description	Minerals Identified
CLW014	Quartz/carbonate stringer from 1m below Rho Reef	Quartz Dolomite
CLW023	Mineralized Rho Reef	Quartz Dolomite
FKM074B	Mineralized Bevetts Reef	Quartz Dolomite
VLH040	Mineralized sample associated with dike	Quartz Dolomite
GLS053	Late stage quartz/carbonate vein, no sulphides associated	Quartz Dolomite
NSM098	Mineralized Sandstone Reef (C1 Face), 1cm graphitic layer below reef	Muscovite Katnohorite Quartz Pyrite Rutile

2.1.2 Vertical veins

Vertically oriented veins occur predominantly in the Archaean basement rocks, but are also found within the overlying sedimentary strata. Emplacement of the vertical veins is controlled by the prominent north-northeasterly trending lineaments in the area. A number of lucrative mines were situated along these veins, including the Gregory, Sunlight, Astra and Rietfontein Mines. The largest of the vertically orientated veins was the Bokwa-Stoltz vein which has a total strike length of approximately 47km (Harley and Charlesworth, 1993). The uneconomical Bokwa-Stoltz vein intersects stratigraphic units that are separated by 1000 metres true thickness, and has a maximum recorded thickness of 5 metres (Visser and Verwoerd, 1960). The most productive mine that exploited a vertical vein was the Rietfontein Mine which yielded 751kg of gold between 1912 and 1948. Sulphide mineralization within the vertical veins is more irregularly distributed compared to the overlying horizontal veins, but mineralogically the vertical veins are similar to the horizontal veins with pyrite, chalcopyrite, fahlores, bismuth sulphosalts and bismuth as the most common sulphide minerals (Boxall, 1938; Visser and Verwoerd, 1960).

2.1.3 Sill/dyke associated veins

The sill/dyke associated veins are closely related to diabase or pyroxenite sills and/or dykes, and are usually emplaced along the contacts of these sill/dykes. However, several occurrences are known where the mafic igneous rocks are transgressed by the quartz veining, such as the Olifantsgeraarte and Bourke's Luck Mines. The more productive sill/dyke associated deposits occur in the northern portion of the goldfield, eg Vaalhoek Mine, Bourke's Luck Mine and the New Chum Mine. Important occurrences in the central and southern part of the SPRG are the Mali Dyke and Nestor Dyke.

2.1.4 Lens deposits

Zietsman (1967) distinguished between two types of lens deposits (also called blows or leaders) namely (i) tabular blows that are developed between two strata bound veins, eg the Elandsdrift Blow, and (ii) ore-channels which are associated with "low-angle gravity-fault", eg Spitzkop and Dukes Hill channels. Surrounding such zones of vein thickening (commonly up to 3 metres) are sub-parallel, and occasional sub-vertical, stringer veins which are locally mineralized. In general, these stringers pinch out within tens of centimetres from the main vein component. Dense arrays of such stringers form the so-called "blows" (eg the "copper blow" and the "pyrite blow" at the Nestor Mine) which have been described from the area. The strike length of these "blows" is less than 100m and the mined height above the Sandstone vein (at Nestor Mine) was less than 10m (Harley and Charlesworth, 1993). Zietsman (1967) reported average dimensions for these lens deposits in the order of 1.5-6m high, up to 60m wide and over 900m long.

2.1.5 Sulphide paragenesis and paragenetic sequence

Despite limited variation in the modal proportions among various mine localities, three stages of sulphide mineralization have been identified (Meyer *et al.*, 1986): these are (i) early diagenetic pyrite from the wall rock associated with the gold mineralized veins, which are euhedral to subhedral and virtually free from mineral inclusions, apart from minor gold grains; (ii) a second stage of coarser-grained pyrite containing inclusions of chalcopyrite and gold. Contemporaneous, or slightly later, arsenopyrite containing inclusions of chalcopyrite and tetrahedrite and, in places, overgrowing and replacing pyrite also occurs. This mineralization episode was also accompanied by quartz and carbonate gangue deposition; and (iii) a final stage of mineralization followed brittle deformation, as indicated by fractures in pyrite and arsenopyrite and clasts of wall-rock found enclosed within quartz. These fractures and intergranular spaces in the early sulphide assemblage are also filled by a later suite of fahlores,

chalcopyrite, bismuth sulphosalts, native bismuth and gold. There is a distinct increase in gold content towards the later stages of sulphide mineralization, with the majority of gold being emplaced at a very late stage. The paragenetic sequence in siliceous associated deposits (ie Olifantsgeraamte and Vaalhoek Mines) appears to be less complex, with only one generation of pyrite and chalcopyrite developed, containing round inclusions of gold. Gangue minerals in the veins are dominated by quartz, with lesser amounts of ferruginous carbonate and local occurrences of muscovite, scheelite and rare rutile. Fe oxides in surface outcrops of auriferous quartz veins have been oxidized to a mixture of goethite, limonite and hematite, leaving behind a vuggy quartz. Other vein minerals that have been reported (Swiegers, 1948), include galena, bornite, sphalerite, scheelite, cubanite and galenobismutite. Additional gangue phases include chlorite and apatite, whereas the supergene component consists of chalcocite, covellite and marcasite. Non-sulphidic supergene minerals that were identified are native copper, malachite, cuprite, azurite, chrysocolla, tenorite, malaconite, cyanotrichite, anglesite, gypsum, sulphur and limonitic material (Swiegers, 1948). The dominance of Cu, As sulphides in the auriferous quartz veins of the SPRG is reflected in the trace element concentrations of whole rock analyses of veins from the Clewer West Mine (Table 2.2).

Table 2.2 Whole rock minor element analyses for selected samples from the Theta Reef at the Clewer West Mine. All values are in ppm unless stated otherwise. (Analyses presented with the permission of P.N. Bentley)

Element	MD276	PB101	PH103	PB104
Au	135.0	62.0	3.1	101.0
Ag	14.4	3.4	0.1	2.7
Bi	90	30	60	190
Cu, %	0.09	1.56	0.21	0.34
As, %	0.26	0.20	0.21	1.00
Sn	88	90	55	56
W	<20	<20	<20	<20
Sb	NA	<20	<20	<20
Pb	90	30	60	70
Zn	204	70	20	30
Ni	110	140	120	110
Co	40	NA	NA	NA
Mo	NA	<10	<10	<10
Hg, ppb	NA	110	60	110
S, %	NA	26.00	28.20	39.40

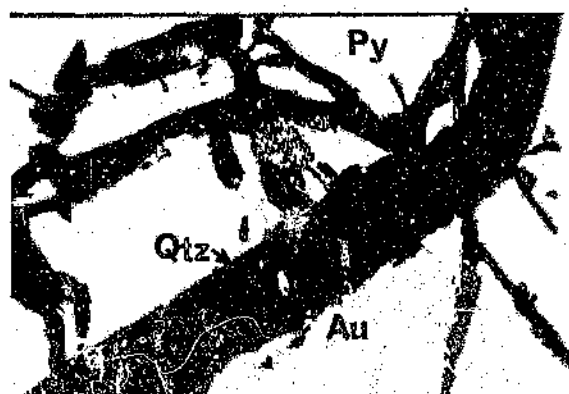
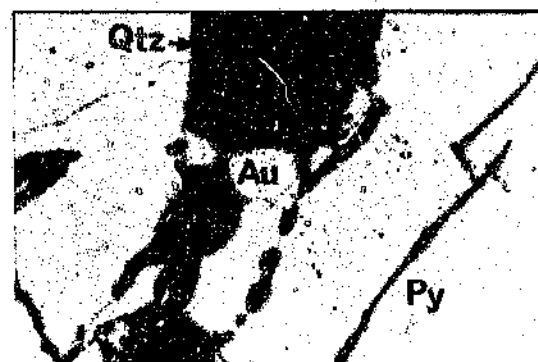
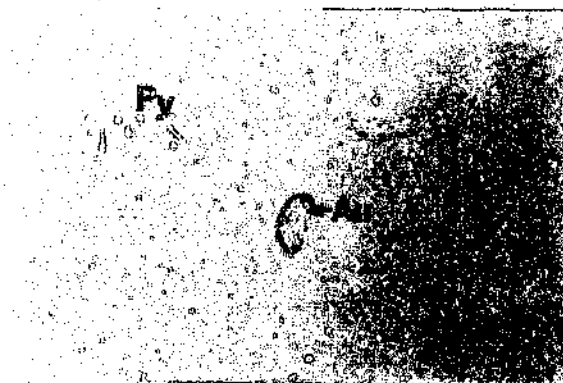
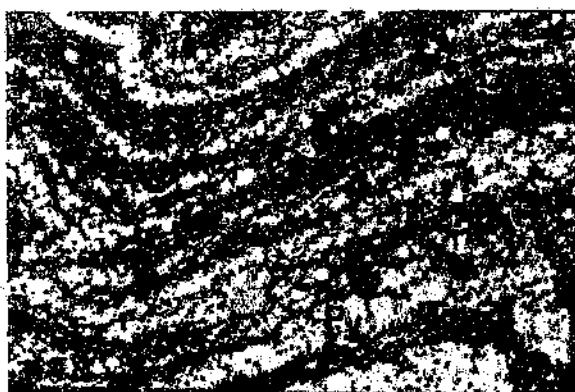
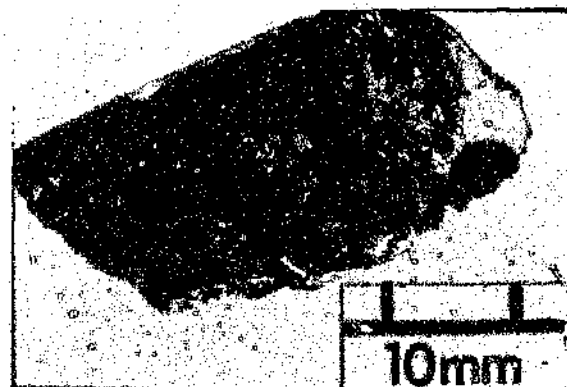


Figure 2.2 Photomicrographs of the typical ore mineral textures present in the Sable Pit in the Rest goldfield.

2.2 Mineral chemistry, geothermometry, and geobarometry

All mineral analyses were obtained by wavelength dispersion electron microprobe analyses (Cameca Camebax Microbeam), performed at the Department of Geology, University of the Orange Free State. The electron beam was operated with an accelerating voltage of 15kV and a beam current of 20 nA (on brass). Standards used are presented in Table 2.3. Matrix corrections were made using the ZAF correction (Potts, 1987), so called because of the influence of atomic number (Z), x-ray absorption (A) and secondary fluorescence (F) effects.

Table 2.3 Standards used for electron microprobe analyses.

Element	Spectrometer crystal	Line	Mineral Standard	Wt. fraction of elements in standard
S	PET	K α	Pentlandite	S: 0.3301 Ni: 0.3812 Co: 0.0010 Fe: 0.3077
Cl	PET	K α	Tugtupite	Cl: 0.0758 Al: 0.0577 Na: 0.1963 Be: 0.0193 O: 0.4105 Si: 0.2402
Fe	LIF	K α	Marcasite	Fe: 0.4654 S: 0.5346
Au	PET	M α	Au metal	
Ag	PET	L α	Ag metal	
Pb	PET	M α	Galena	Pb: 0.8660 S: 0.1340
Mg	TAP	K α	Olivine	Mg: 0.3110 Fe: 0.0506 Mn: 0.0009 Ni: 0.0016 Si: 0.1956 O: 0.4403
Mn	LIF	K α	Willemite	Mn: 0.0373 Si: 0.1313 Zn: 0.5374 O: 0.2940
Cu	LIF	K α	Cu metal	
Zn	LIF	K α	Willemite	Mn: 0.0373 Si: 0.1313 Zn: 0.5374 O: 0.2940
Ni	LIF	K α	Ni metal	
Co	LIF	K α	Co metal	
As	TAP	L α	Ga-As Alloy	As: 0.5180 Ga: 0.4820
Sb	PET	L α	Sb metal	
Bi	PET	M α	Bi ₂ Se ₃	Bi: 0.6383 Se: 0.3617

TAP: thallium hydrogen (acid) phthalate
PET: penta-erythritol
LIF: lithium fluoride

2.2.1 Pyrite

Pyrite is the most abundant metallic mineral in the quartz veins of the SPRG and serves as the major control on the activity of sulphur in the mineral phases and hydrothermal fluids. The high thermal stability (above 742°C pyrite undergoes a peritectic breakdown to hexagonal Fe pyrrhotite and sulphur, Kullerød and Yoder, 1959) and high physical strength ensure that it survived the low grade metamorphism which the SPRG has experienced. Two main characteristics dominate the physical behaviour of pyrite, namely its bond strength (reflected in the microhardness and the resistance to ductile deformation) and its tendency to form euhedral crystals. The Vickers hardness number for pyrite is 1605-1620 (Craig and Vokes, 1993), whereas those for the sulphides which are commonly associated with pyrite are much lower, eg chalcopyrite, 187-203; arsenopyrite, 715-1354; pyrrhotite, 230-318 and sphalerite, 218-227 (Vaughan and Craig, 1978). Graf and Skinner (1970) noted that pyrite behaves as a brittle substance under all conditions of deformation in the earth's crust. Siemes *et al.* (1991) confirmed the brittle behaviour of pyrite and showed that pyrite would remain rigid through a stress differential-temperature path of 60 MPa + 600°C. Although this conclusion was challenged by Mookherjee (1971) and although some ductile behaviour of pyrite has been demonstrated by Atkinson (1975) and Cox *et al.* (1981), the general observation by Graf and Skinner (1970) remains largely correct.

In the SPRG, three generations of pyrite can be recognized: (i) Fine-grained aggregates of pyrite formed during the diagenesis of shaley sediments; (ii) this variety of pyrite was remobilised and precipitated together with quartz and carbonate minerals and chalcopyrite, arsenopyrite and gold, during the early stages of the vein forming event (Fig. 2.3a); (iii) textural relations show that the latter type of pyrite was recrystallized into coarse-grained euhedral to sub-euhedral pyrite (Fig. 2.3b), this euhedral type of pyrite was used during EMP analysis. Thus, there seems to be a definite tendency to form coarser grained pyrite crystals, as the temperature of the mineralizing system was raised. Various authors (eg Templeman-Kluit, 1970; McClay and Ellis, 1983) have also documented a general increase in pyrite grain size with increasing temperature of recrystallization.

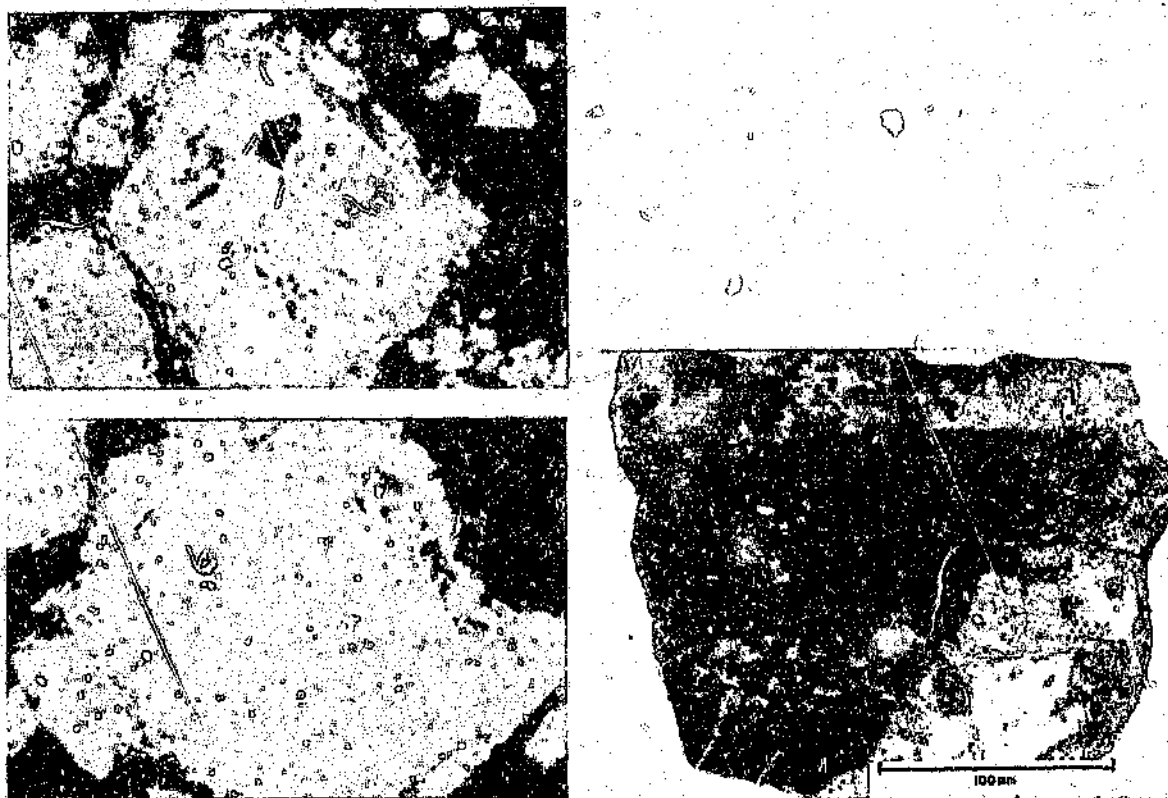


Figure 2.3 (a) Photomicrograph of euhedral pyrite crystal overgrown by secondary pyrite (magnification 400X). (b) Hand specimen from the Bevetts vein, Frankfort Mine, showing different generations of pyrite. See text for detailed description.

Pyrite from the SPRG veins exhibits various crystal morphologies, including pyritohedra (pentagonal dodecahedron), cubes and anhedral grains (Fig. 2.4a-h). The crystal habit of pyrite can be related to specific growth conditions. Amstutz and Ligasacchi (1958) were the first to record the systematic variation of pyrite habit within an ore body, but the mineralization and structure of the ore bodies was too complex to permit interpretation at the time (Amstutz, 1963). Several similar studies followed, amongst other Sunagawa (1957) and Bush *et al.* (1960), implying a relationship between degrees of sulphide supersaturation of the depositing solution and the morphology of the resulting pyrite crystals. Murowchick and Barnes (1987) also investigated the growth processes and resulting morphologies of hydrothermally grown pyrite. They were able to present a general sequence of forms indicative of increasing degree of sulphide supersaturation and temperature. Pyrite from the SPRG has been separated from the quartz matrix by dissolution in Teflon beakers using concentrated HF (45%) acid. The pyrite crystals were examined on a LINK[®]-JOEL[®] JSM 840 scanning electron microscope at the Electron Microscope Unit, University of the Witwatersrand (Fig. 2.4). The most common morphologies of vein pyrite from the SPRG show cubes with striated, as well as smooth surfaces. Following the

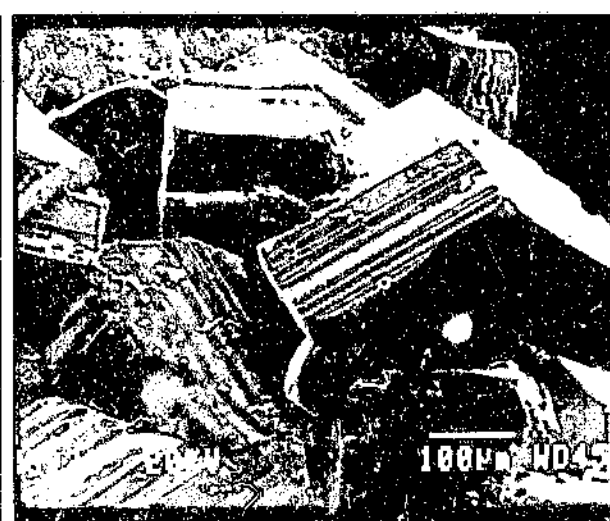
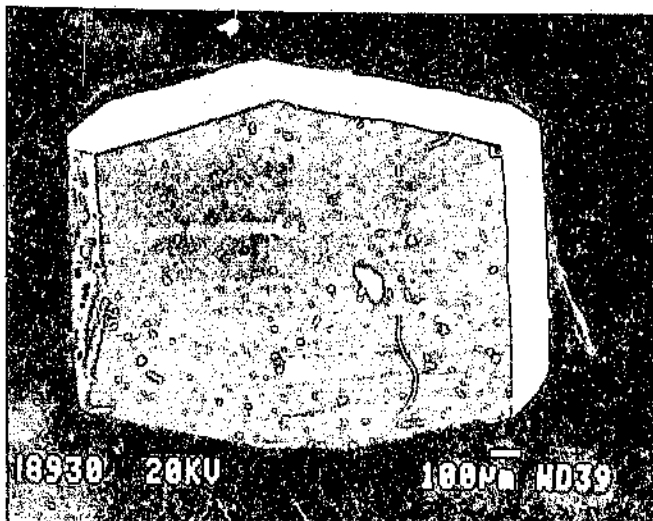
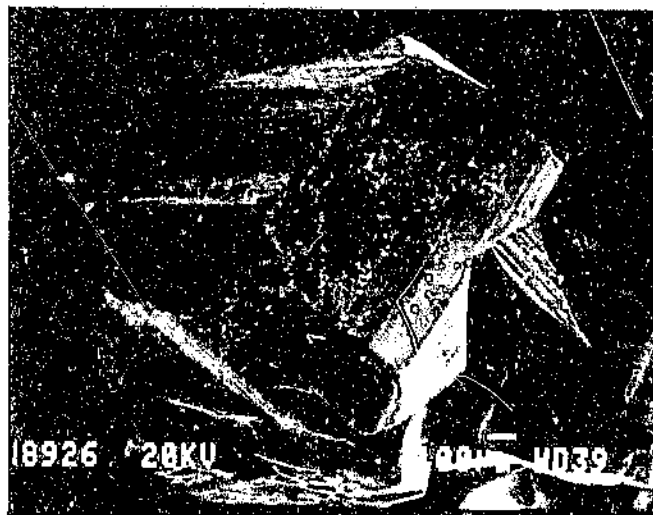
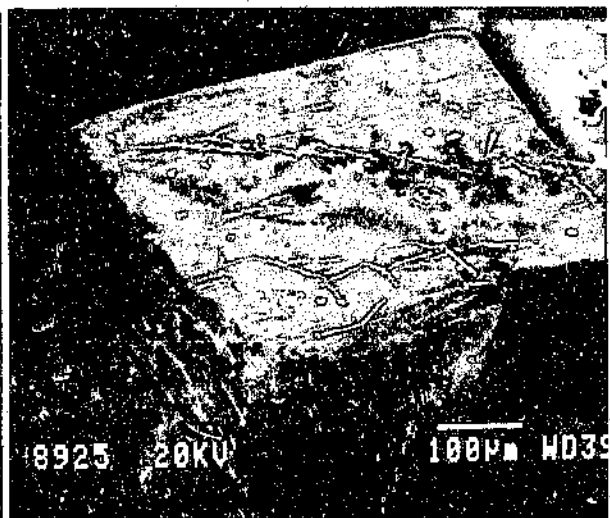
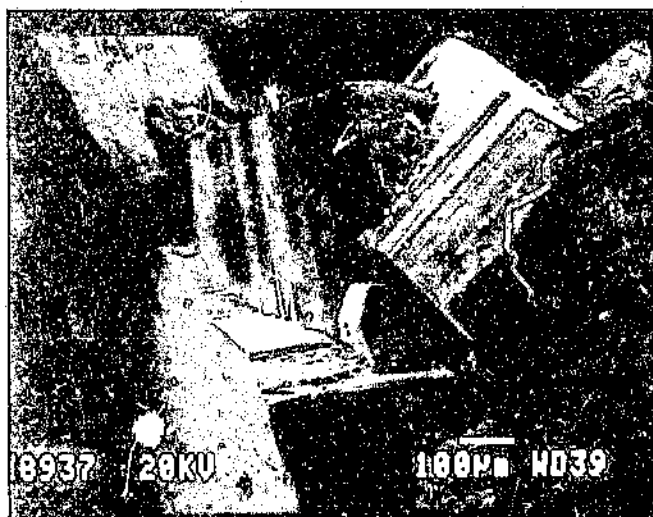


Figure 2.4. SEM photomicrographs of pyrite morphologies from different reef horizons and pyrite generations.

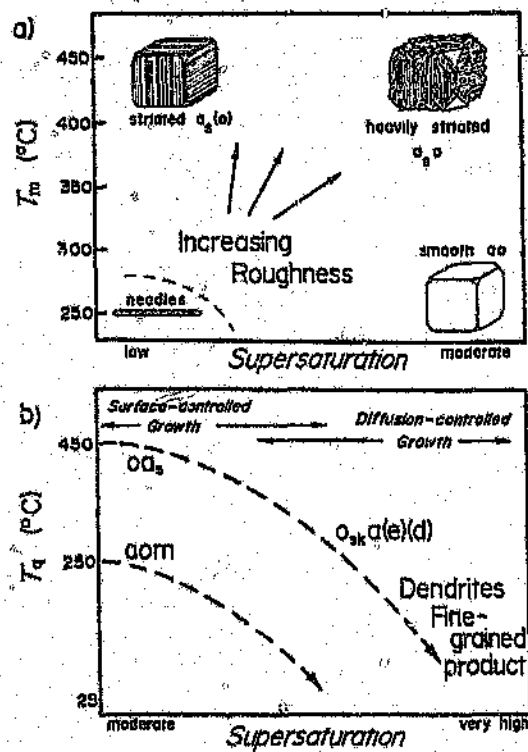


Figure 2.5 Morphologies of hydrothermally grown pyrite (after Murowchick and Barnes (1987).

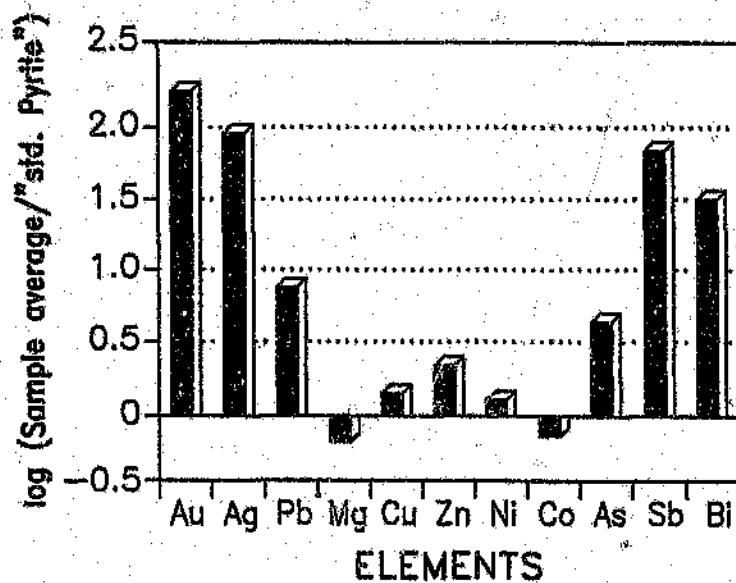


Figure 2.6 Trace element contents in pyrite from the SPRG auriferous veins, normalized to a "standard" pyrite. The "standard" pyrite represents an average of 1020 pyrite analyses which includes pyrite of diverse origin and genesis (Hallbauer, 1990).

classification system of Murowchick and Barnes (1987) for hydrothermal pyrites grown in steady-state conditions, SPRG type pyrite reflect growth conditions of intermediate temperature (300°-350°C) and moderate sulphur supersaturation (Fig. 2.5).

Quantitative electron microprobe (EMP) analyses of sixty-two pyrites from auriferous quartz veins of the Sable-Pilgrim's Rest goldfield, are presented in Table 2.4. Although a "primitive" or general "standard" pyrite (similar to a chondrite standard) does not exist in Nature, an attempt was made to compare pyrite from the SPRG with samples of various origins (Fig. 2.6). Data for a "standard" pyrite analyses was obtained from Hallbauer (1991), following Fleischer (1955). It is clear from Figure 2.6 that SPRG pyrite is significantly enriched in precious metal content, as well as in As, Sb and Bi, but contains "normal" Mg, Cu, Zn, Ni and Co concentrations. The mean Au and Ag concentrations in SPRG pyrites were 0.032wt% ($1\sigma = 0.029$) and 0.057wt% ($1\sigma = 0.026$), respectively. Co ($x = 0.008\text{wt}\%$) and Ni ($x = 0.028\text{wt}\%$) concentrations are slightly higher than average crustal values ($x_{\text{Co}} = 25\text{ppm}$; $x_{\text{Ni}} = 75\text{ppm}$; Rose *et al.*, 1979). However, the absolute Co values are much lower than values for Archaean-related magmatic sulphide ores which range between 0.22 to 0.34wt% (Naldrett, 1989). The Co/Ni ratio for SPRG pyrites ($x = 0.32$) is significantly higher than the range defined by magmatic sulphide deposits ($x = 0.031$; calculated from Naldrett, 1989) and correspond to the average values for normal shales ($x = 0.279$) as calculated from Turekian (1977). From Figure 2.7 there appear to be two groups of pyrites based mainly on As content. Because certain spot analyses falling in the two groups are from the same mineral grain, it was decided to micromap a single pyrite crystal for fourteen elements, using EMP. The EMP micromaps of the four most abundant elements, namely Fe, S, As and Cu are presented in Figure 2.8(a-d). A crude zonation pattern can be recognized from the arsenic micromap (Fig. 2.8c). This observation suggests that the distribution evident in Figure 2.7 could be ascribed to As zonation. A similar As zonation in pyrite was recognized by Anderson (1992) and by Fleet *et al.* (1988) for strata bound veins in the SPRG. However, no zonation could be recognized for any of the other elements analysed, which showed an irregular distribution pattern. Furthermore, the composition of pyrite from within auriferous quartz veins does not vary between the different vein horizons, nor does it change as a function of associated sulphide paragenesis. Meyer *et al.* (1986) compared trace element concentrations of pyrite determined by high precision instrumental neutron activation analyses from, shales within the Malmani Subgroup, wall-rock shales adjacent to the veins and vein associated pyrite. Pyrites obtained from the non-auriferous Malmani Subgroup shales contained high Co ($x=1540\text{ppm}$) and Ni ($x=1470\text{ppm}$) concentrations, with Co/Ni ratios ranging between 0.1 and 5 (Meyer *et al.*, 1986).

These pyrites showed very low Au concentrations ($\bar{x}=0.08\text{ppm}$). Pyrites from the vein associated shales and those occurring within the veins contained mean Au values of 2.7ppm and 7.9ppm, respectively (Meyer *et al.*, 1986), whereas the Co/Ni ratios varied between 0.2 - 0.4 and 0.01 - 0.3. Pyrites from the sill/dyke associated vein in the Olifantsgeraamte Mine near Sable, proved to be an exception to the narrowly defined Co/Ni ranges. These pyrites showed a mean Co/Ni ratios of 0.75 (Meyer *et al.*, 1986), as well as high Au concentrations ($\bar{x}=19.5\text{ppm}$), confirming the petrographic observation that gold is mainly associated with pyrite in the sill/dyke associated veins. Meyer *et al.* (1986) recognized a general trend on a Co versus Co/Ni diagram with values decreasing progressively "from shale pyrites through host rock pyrites to ore pyrites whereas the Au values tend to increase in the same direction", and concluded that this general trend indicate a genetic relationship between the different pyrites. This conclusion is, however, unfounded as any comparison between dependent variables, such as Co vs. Co/Ni, will inevitably show a positive correlation. The above data show a definite lithological control on trace element concentrations for pyrite from the various lithological settings. Furthermore, the differences in pyrite composition between the various veins, such as Theta and Beta, could also be explained in terms of host-rock control. Pyrites from the Sable-Pilgrim's Rest area, furthermore, display two different shades of reflectance, with one variety being distinctly paler than the other. No obvious reason could be found in the chemistry of the two pyrite types to explain this phenomenon.

Table 2.4 Quantitative EMP analyses of pyrite from the Pilgrim's Rest area.

Sample no.	S	Cl	Fe	Au	Ag	Pb	Mg	Cu	Zn	Ni	Co	As	Sb	Bi	Total
gls052	44.25	0.06	42.72									0.87			87.9
fkm075b	44.39	0.15	43.15						0.08	0.01		0.89			88.65
fkm075b	45.37	0.13	43.13			0.07			0.03			0.05			88.78
fkm075b	44.65	0.11	43.33			0.01			0.03	0.03		0.89			89.05
fkm075b	44.58	0.1	43.02				0.04					0.8			88.54
fkm075b	46.08	0.13	42.4						0.01	0.06	0.05	0.84			89.55
fkm075b	47.17	0.12	43.44		0.05			0.03		0.01		0.25			91.07
fkm077b	34.28	0.03	29.73			0.02	0.01	0.07	0.09	0.15		0.14		0.02	64.52
clw022	47.81	0.03	42.2		0.06			0.07	0.01			0.08		0.1	90.38
fkm076c	50.97	0.04	42.12			0.01		0.02			0.03	0.06			93.25
fkm076c	51.55	0.06	41.77		0.02					0.03		0.03		0.04	93.5
fkm076c	50.85	0.02	41.11		0.02			0.02		0.05				0.09	92.16
fkm076c	50.74	0.04	42.6									0.01			93.39
fkm076c	51.4	0.03	42.24			0.07		0.05	0.05	0.02		1			94.88
fkm076c	52.2	0.03	41.36		0.03				0.01	0.18	0.01	0.88		0.05	94.55
fkm076c	52.23	0.03	41.53		0.06							0.88			94.53
ofg12c	46.55	0.06	44.25									0.66			91.52
nestor2	46.31	0.01	44.27		0.03						0.01	0.7			91.33
shb2	50.13	0.03	43.33		0.03			0.02	0.05		0.01	0.34			93.94
pkb5a	49.66		43.58							0.28	0.03	0.05			93.6
pkb5a	45.97		41.39		0.02			0.05		0.13		0.11		0.08	87.73
shb3	51.21		43.23		0.03				0.04	0.06		0.31			94.88
shb3	46.81	0.01	42.28		0.06	0.1		0.05	0.01	0.07		0.09		0.08	89.56

Table 2.4 continue

Sample no.	S	Cl	Fe	Au	Ag	Pb	Mg	Cu	Zn	Ni	Co	As	Sb	Bi	Total
shb3	46.32	0.03	42.6		0.01			0.01		0.03	0.01	0.07		0.07	89.15
shb3	46.34	0.02	40.83			0.01						0.15			87.36
flm076c	62.76	0.01	42.33		0.16		0.01	0.09				0.98			106.3
flm076c	66.42	0.06	43.41		0.05					0.15		0.81	0.05	0.05	111
flm076c	62	0.03	43.42		0.12	0.16		0.03	0.19	0.07	0.02	0.91		0.27	107.1
flm076c	63.13	0.04	41.64		0.02	0.31			0.05			0.75		0.26	106.2
brf5	46.67	0.08	44.42		0.08			0.03		0.01	0.01	0.71			92.11
brf5	46.78	0.09	44.71					0.06		0.02	0.02	0.82			92.5
brf5	49.88	0.08	44.81		0.03			0.05	0.03	0.03	0.01	0.03	0.69		95.54
brf5	48.9	0.08	45.14		0.04					0.01	0.03	0.65			94.85
brf5	48.9	0.08	45.14		0.04					0.01	0.03	0.65			94.85
brf5	60.3		42.54	1.81					0.28		0.06	0.49		0.53	106
brf5	46.58	0.02	37.16		0.04	0.1			0.04			0.14		0.03	84.11
brf5	50.14	0.04	27			0.14		0.05	0.02	0.12		0.55			78.08
flm076c	43.56	0.03	41.19					0.03		0.05	0.03	0.03			84.92
gls050	45.14	0.01	42.02		0.04			0.05	0.03			0.76		0.09	88.14
thr046	44.99	0.04	45.15					0.16	0.04			1.11			91.49
thr046	44.74	0.03	45.36					0.02		0.01				0.04	90.2
cm2	44.67	0.09	44.91							0.05		0.74		0.1	90.56
pkb	47.94		43.57		0.01				0.07	0.03		0.01		0.01	91.64
bcl4a	49.61		42.15									0.07			91.83
bcl4a	50.03		42.27		0.01				0.07			0.63			93.01

Table 2.4 continue

Sample no.	S	Cl	Fe	Au	Ag	Pb	Mg	Cu	Zn	Ni	Co	As	Sb	Bi	Total
bcl4a	51.6		42.44		0.03			0.08	0.08			0.1		0.16	94.51
bcl4a	50.7	0.01	43.12					0.04		0.09	0.05				94.02
brf4	48.45	0.01	44.21		0.08			0.02	0.04			0.75		0.05	93.62
brf4	49.2	0.02	43.48					0.05			0.01	0.76			93.52
cm1	54.69	0.01	47.34						0.04			0.09			102.1
cm4	46.07	0.02	46.43	0.16		0.09		0.05		0.01	0.03			0.05	92.97
og2a	44.72		45.05					0.09				0.8		0.11	90.77
clw022	48.99	0.04	41.35			0.06			0.01			0.63		0.02	91.1
1	53.81		46.43		0.33			0.02	0.05			1			101.6
2	53.56		46.57		0.27			0.07	0.08			0.23			100.7
3	52.54		46.12			1.01			0.01				0.37		100.1
4	52.84		46.09		1.53				0.05			0.02			100.5
5	52.69		44.98			0.5			0.03			0.13			98.33
6	52.73		45.46			0.1		0.02	0.03			0.47			98.81
7	52.71		45.64					0.06	0.08			0.05	0.04		98.59
8	52.65		45.58		0.24			0.04				0.02			98.53
9	52.62		45.43					0.5	0.03			0.16			98.74
Aver. Py (wt%)	49.7	0.05	42.99	0.66	0.12	6.17	0.02	0.06	0.05	0.06	0.03	0.45	0.29	0.11	93.44
Std. Py (ppm)				36.7	12.5	218.5	251.8	471.5	257.8	538.1	398.3	1131	42.1	33.8	
log(sample average/standard pyrite)				2.25	1.97	0.88	-0.22	0.13	0.31	0.07	-0.19	0.6	1.83	1.49	

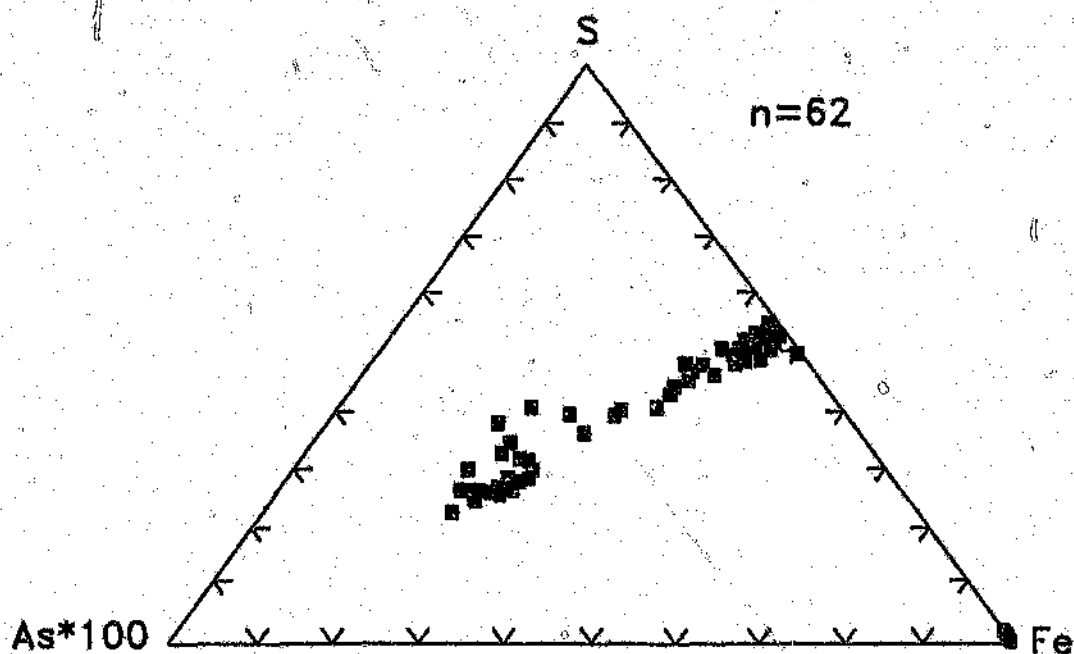


Figure 2.7 Ternary diagram (S - Fe - As*100) of pyrite, seemingly showing two pyrite types.

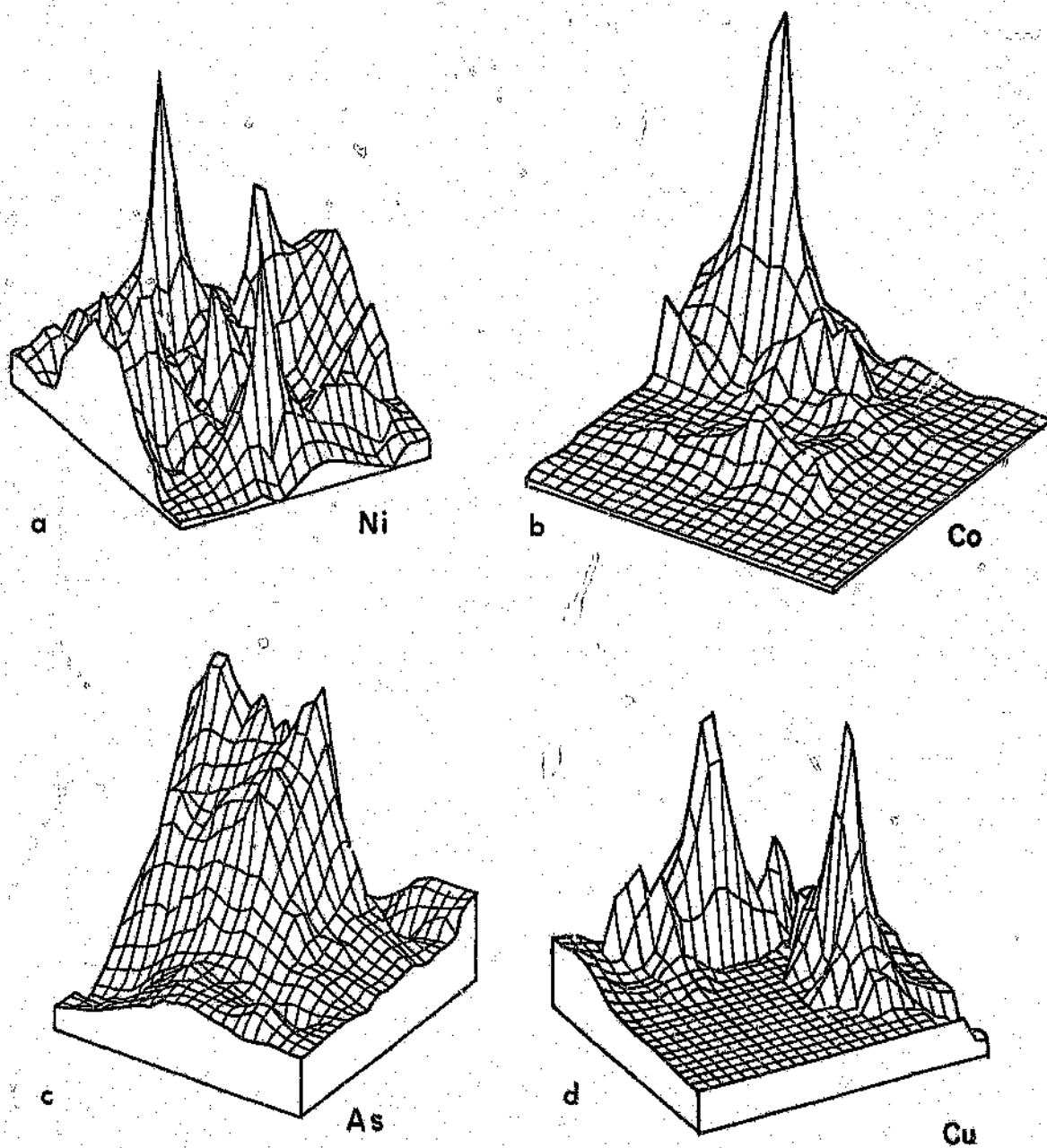


Figure 2.8 EMP micromaps of (a) Ni, (b) Co, (c) As and (d) Cu of an euhedral pyrite crystal from the Theta Reef in the Clewer Mine.

2.2.2 Chalcopyrite

Chalcopyrite compositions from the Pilgrim's Rest area show variation towards the pyrite end-member composition when plotted on a S-Cu-Fe ternary diagram (Table 2.5; Fig. 2.9). This spread of data plot within the intermediate solid solution (*iss*) field between chalcopyrite and pyrite, as delineated by Craig and Scott (1974), based "on data and discussions of several workers". Except for the unpublished study of Ueno (1981), phase relations in the Cu-Fe-S system are not well established for temperatures below 600°C. However, the field defined by the distribution of SPRG chalcopyrite encompasses the compositions of several minerals in the S-Cu-Fe system, but is sulphur-deficient relative to chalcopyrite, CuFeS_2 . Metastability or simple disequilibrium is common in many copper-iron sulphide assemblages, as is obvious from the many conflicting mineral parageneses in other reported deposits (eg pyrite + bornite or chalcopyrite + covellite). The reason for the observed sulphur-deficiency in the SPRG chalcopyrite is, however, not clear. No petrographic evidence exists which could indicate possible desulphidation or oxidation of the mineralized environment, such as was reported for Cu-Fe-S assemblages from the Okiep Copper District in Namaqualand, South Africa (Boer *et al.*, 1994). Barton (1973) has shown that the *iss* is a distinct phase which is structurally similar to chalcopyrite but which is, however, not an isomorphous phase. Chalcopyrite from the SPRG, furthermore, contains relative high Ag ($x_{\text{max}} = 0.36 \text{ wt\%}$; $x = 0.004 \text{ wt\%}$; $\sigma = 0.025$) and As ($x_{\text{max}} = 0.68 \text{ wt\%}$; $x = 0.07$; $\sigma = 0.04$) concentrations. The average Co/Ni ratio for SPRG chalcopyrite is 0.18.

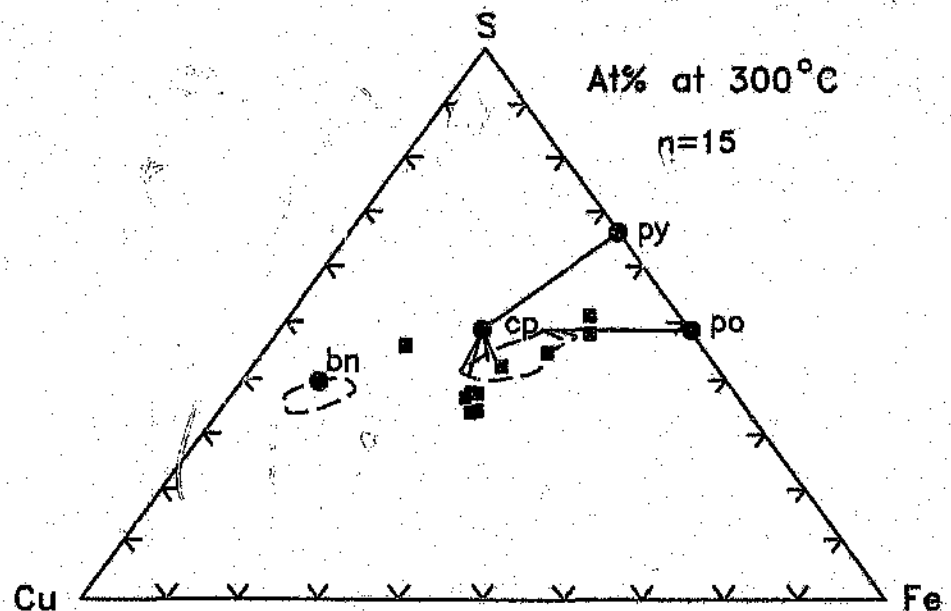


Figure 2.9 Ternary diagram (S-Fe-Cu) of chalcopyrite showing intermediate solid solution.

Table 2.5 Chalcopyrite electron microprobe analyses

Sample no.	S	Fe	Ag	Pb	Cu	Zn	Ni	Co	As	Bi	Total
CLW022	32.76	26.85		0.05	28.01			0.03	0.05	0.05	87.86
CLW022	50.04	39.86			21.83		0.02	0.05	0.02	0.02	111.96
FKM076C	50.81	40.34		0.15	13.67		0.01		0.69		105.71
MOB4	35.17	27.73	0.36		32.52		0.02		0.01	0.10	95.94
BRF5	45.13	31.27			9.41		0.03		0.01		85.86
FKM076C	29.22	26.82			30.13		0.02		0.02		86.36
THR46	32.41	29.58			31.64	0.08			0.04		93.91
THR46	31.50	29.21	0.09		32.57		0.02		0.04	0.06	93.56
DS1	29.6	21.16			18.35			0.04	0.06		69.31
DM2	31.85	29.39		0.07	31.01	0.02			0.01	0.08	92.49
PKB	31.13	28.53	0.10		31.39		0.01		0.01	0.15	91.34
BCL4A	35.76	28.20	0.04		31.06	0.02	0.01		0.01		95.11
BCL5A	39.58	14.80	0.03		31.91						86.40
BRF4	35.77	28.00	0.01	0.13	31.45	0.01			0.01		95.38
DM4	32.08	29.92			31.53						93.59
Average cpy	36.19	25.78			27.11				0.07		

2.2.3 Tetrahedrite-tennantite

Tetrahedrite¹ is a widely distributed phase in polymetallic base-metal sulphide deposits of the hydrothermal vein type and commonly also occurs in the SPRG. Johnson *et al.*, (1986) proposed a general formula of $(\text{Cu,Ag})_8\text{Cu}_4(\text{Fe,Zn,Cu,Hg,Cd})_2(\text{Sb,As,Bi,Te})_4(\text{S,Se})_{13}$ on the basis of a suite of 1271 natural tetrahedrite samples from selected localities worldwide, and 295 synthetic samples. This general formula differs somewhat from the earlier proposed tetrahedrite formula as described by Wuensch (1964), which can be written as: $^{\text{IV}}\text{M1}_6^{\text{III}}\text{M2}_6^{\text{III}}\text{X}^{\text{VI}}\text{Y}_4^{\text{VI}}\text{Z}$, where M1 represents Cu or Ag, M2 represents Cu, Fe, Zn, Hg or Cd, X stands for Sb, As, Bi or Te, and Y and Z could be either S or Se. Sack *et al.* (1987) devised a structural formulae for tetrahedrite of the following form: $(\text{Ag,Cu})_6^{\text{TRG}}[(\text{Cu,Ag})_{12}(\text{Fe,Zn})_{10}]_6^{\text{TET}}(\text{Sb,As})_4^{\text{SM}}\text{S}_{13}$. The latter structural formulae corresponds to full occupancy of the six trigonal planar (TRG), six tetrahedral (TET), and four semi-metal (SM) sites in the half-cell formula unit, with 208 valence electrons in the unit cell (Johnson *et al.*, 1986). Tetrahedrite compositions were calculated on the basis of 13 sulphur atoms per formula. Experimental studies by

¹ The term "tetrahedrite" is used to denote the entire solid solution series of tetrahedrite-tennantite, which is also referred to as "fahlore".

Johan and Kvacek (1971) and Brodin *et al.* (1979) have confirmed that Se substitutes for S, while Oen and Kieft (1976) and Mozgova *et al.* (1979) corroborated that Bi and Tl substitute for As and Sb. Other studies have reported the presence of Pb, Co, Ni, Au and Mn (Schroll and Azer Ibrahim, 1958; Bishop *et al.*, 1977; Patrick, 1978; Basu *et al.*, 1981, 1984). The composition of the solid solution series tennantite-tetrahedrite is complex and grades from pure As to pure Sb end-member compositions (Luce *et al.*, 1977). Natural tetrahedrite minerals are heterogeneous even within grain sizes smaller than 100 μm (Yui, 1971).

The chemical compositions of fifteen tetrahedrite samples from the SPRG are presented in Table 2.6, and plotted in Figure 2.10b. The data in Figure 2.10b are arranged in order of increasing Sb content. The increase in Sb is reflected by a corresponding decrease in the As content, implying that Sb substitutes for As in these samples. Zn and Fe concentrations remain constant (average $\text{Fe}+\text{Zn}=2.21\text{at\%}$; $\sigma=0.46$). A noticeable feature of SPRG tetrahedrite samples is their deficiency in Ag ($x=0.36\text{wt\%}$; $\sigma=0.018$). The Ag-poor nature of the SPRG tetrahedrite may be ascribed to the relative high Ag concentrations in native gold, or alternatively, indicate a deficiency in Ag content within the hydrothermal system. The presence of Ag-poor tetrahedrite in the SPRG veins also inhibits utilization of correlations between Ag and Sb in defining the direction of hydrothermal fluid flow. The (Sb+As) content varies in the narrow range 5.62 to 7.41at%. A small variation in Fe+Zn content ($x_{\text{Fe}}=1.62$ and $x_{\text{max}}=3.86\text{at\%}$; $\sigma=0.58$) is indicated, and the SPRG tetrahedrite corresponds to low Fe-Zn tetrahedrite (intermediate Fe-Zn: $\text{Fe}=4.83, 3.74\text{ at\%}$; Mishra and Mookherjee, 1991). Zn ($x=2.25\text{wt\%}$) and Bi ($x=0.54\text{wt\%}$) contents. From Table 2.6 it is apparent that there are significant variations in the tetrahedrite composition in the two strata bound veins analysed. Using the dominant exchange elements (Fig. 2.10a), the two can be distinguished unequivocally. The tetrahedrite from the Theta Reef is more As-rich (tennantite) than those of the Beta Reef (tetrahedrite). None of the other minerals in the tetrahedrite series e.g. freibergite (Ag-rich) or schwazite (Hg-rich), have been identified in the Sable-Pilgrim's Rest ores. The distribution of the tetrahedrite in the strata bound veins does not appear to be zoned, but rather seems to occur in an erratic fashion. In some hydrothermal deposits, tetrahedrite was found to exhibit an increase in (Ag/Cu) and (Sb/As) ratios along the direction of fluid flow (eg Wu and Petersen, 1977; Mishra and Mookherjee, 1991), in correspondence with the classic sequence of Cu-(Pb,Zn)-(Zn,Fe) zonation. Such a clear indication of the direction of fluid flow could not, however, be detected in the SPRG vein ores, although a distinct difference in the tetrahedrite composition from the Beta and Theta veins exist. However, it has to be borne in mind that the sampling would not allow for

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an investigation of mineralogical compositional variation on a mine/deposit scale. The chemical variation in individual fahlore grains from the SPRG appears to be random and the homogeneous areas in individual grains are of irregular shape and have sharp boundaries unrelated to zonal pattern or exsolution lamellae.

Table 2.6 Quantitative EMP analyses of SPRG tetrahedrite

Sample no.	S	Fe	Au	Ag	Cu	Zn	Ni	Co	As	Sb	Bi	Total
THR4C	26.89	9.19		0.24	39.50	0.53		0.01	12.43	10.79	0.98	100.59
THR4C	27.52	6.68	0.11	0.17	39.01	0.51	0.51		12.30	10.25	0.93	98.01
THR46	28.90	8.10		0.17	39.41	0.35	0.03		13.16	8.66	0.34	99.14
THR46	25.38	7.97		0.19	38.33	0.57		0.04	12.16	10.51	0.73	95.91
MOB4	25.55	7.13		0.20	38.48	0.50			11.91	10.25	0.36	95.68
MOB4	28.23	5.22		0.35	36.56	1.84			5.89	19.96	1.67	99.74
MOB4	20.46	10.7		0.60	35.95	1.72		0.04	5.90	17.25	1.77	94.41
MOB4	26.05	5.14		0.10	39.83	4.41			4.53	18.22		98.28
MOB4	27.31	5.88		0.09	41.58	4.09			8.36	11.65		98.96
MOB4	25.46	5.07		1.16	38.03	4.51			2.01	21.90		99.04
MOB4	26.06	4.96		0.60	40.42	4.56			3.11	19.32		99.03
MOB4	26.91	5.99		0.63	41.47	3.30			7.20	14.14		99.94
THR4	27.75	7.37		0.37	41.90	2.20			10.39	10.82		100.80
THR4	27.57	7.26		0.01	42.28	2.20			10.18	10.75		100.25
THR4	27.18	7.42		0.51	41.17	2.50			8.44	11.56		99.78
Average fahlore	26.48	6.84		0.36	39.66	2.25			8.60	13.73	0.54	

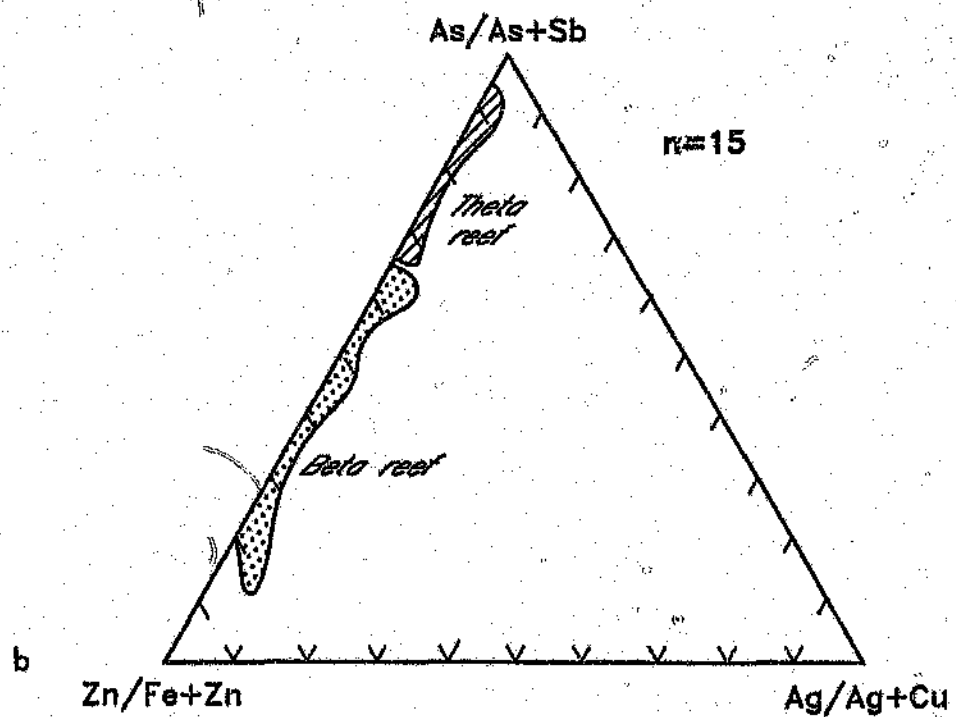
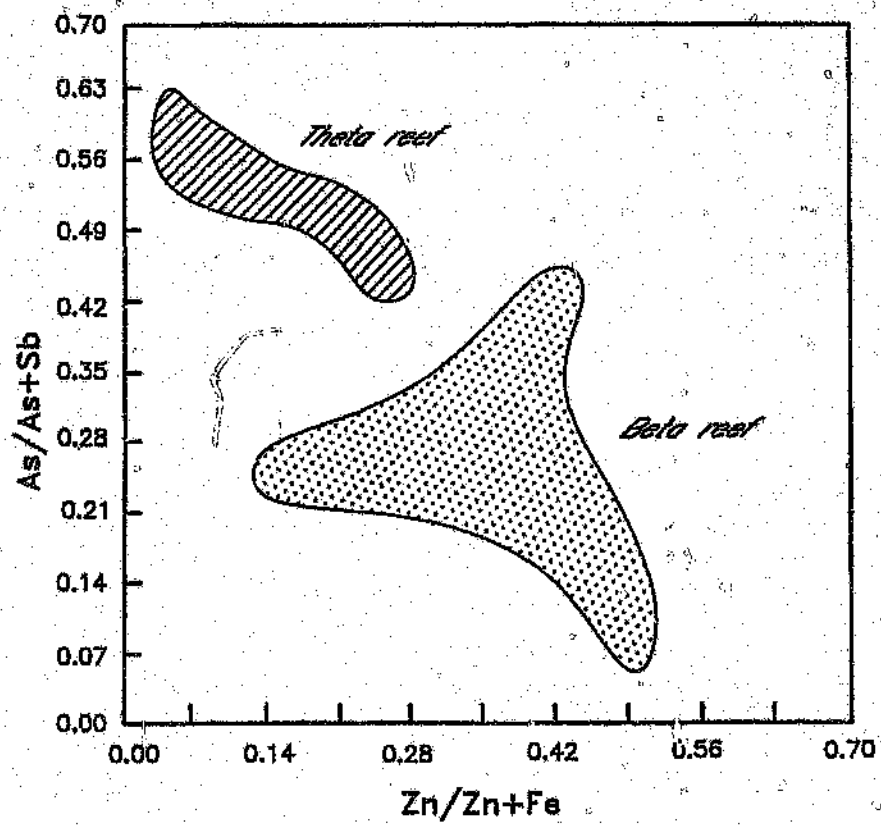


Figure 2.10 (a) Tetrahedrite from the Beta and Theta veins, respectively. (b) Chemical variation in tetrahedrite samples from the SPRG quartz veins.

2.2.4 Bi-Sulphosalts

Quantitative EMP analyses of SPRG Bi-sulphosalts (Table 2.7), most of which have been oxidized *in situ*, indicates that they are all members of the aikinite (PbCuBiS_3) - bismuthinite (Bi_2S_3) series. Previously these minerals were referred to as hammarite ($\text{Pb}_2\text{Cu}_2\text{Bi}_2\text{S}_6$), lindströmite ($\text{Pb}_3\text{Cu}_3\text{Bi}_3\text{S}_9$), and rezbayinite ($\text{Pb}_3\text{Cu}_2\text{Bi}_{10}\text{S}_{19}$), and have been detected in the Sabie-Pilgrim's Rest ores (Fig. 2.11). The names of these intermediate species have been discredited because they fall within the above mentioned solid solution series, aikinite (Kohatsu and Wuensch, 1971), is a packed derivative of the stibnite-type structure of bismuthinite. A Pb atom substitutes for the interior five-coordinated Bi in the stibnite chain. The Cu atom is added to a tetrahedral interstice in the structure. The lattice constants and atomic positions in aikinite remain remarkably similar to those of bismuthinite in spite of these substitutions (Wuensch, 1976). An interesting aspect is the presence of Pt in some of the Bi-sulphosalts. Pt has also been noticed in some pyrite, arsenopyrite and sphalerite from the Theta Reef.

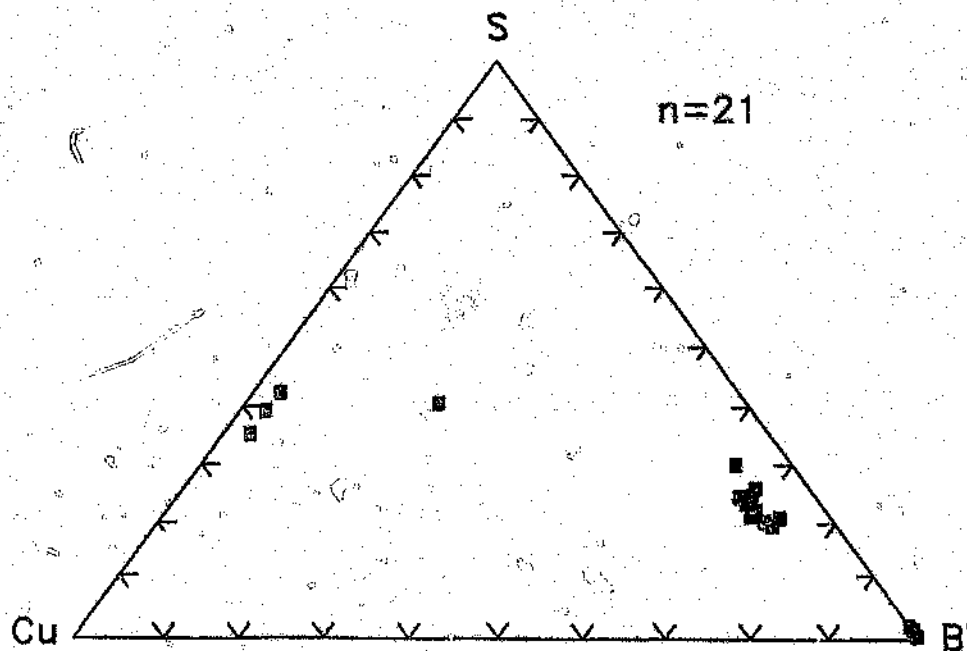


Figure 2.11 Ternary plot (S-Bi-Cu) of Bi-sulphosalts of the Pilgrim's Rest area.

Table 2.7 Chemical composition of Bi-sulphosalts from the Sable-Pilgrim's Rest area

Sample no.	S	Fe	Ag	Pb	Cu	Zn	As	Sb	Bi	Pt	Sn	Total
FKM075B	0.02		0.01	0.08	0.01	0.03			96.1			96.5
FKM075B	0.77	0.13				0.01			85.1			86.16
15	1.47	1.56	0.43		0.16	0.06	0.01	0.13	95.6		0.16	99.6
1	16.12	3.58	0.05	17.6	4.32		0.05	0.81	58.3			100.85
2	17.02	1.13		17.4	6.38			0.59	56.5		0.19	99.25
3	16.68	1.47	0.65	19.2	5.98	0.18	0.04	0.19	56.5			100.77
4	16.77	1.65		16	6.12		0.05	0.49	57.4	0.21	1.08	98.77
5	16.78	0.3	0.38	16.3	6.22		0.01	0.92	56.3		0.36	99.57
6	16.62	1.27		19.3	6.71		0.04		56.9		0.0	100.88
7	16.09	1.66	0.1	18.2	6.34			0.35	55.4	1.05	0.31	99.46
8	18.86	1.06	0.34	15.1	6.31			0.91	57.2		0.23	99.96
9	19.32	0.62	0.35	17.7	6.81	0.04	0.04	1.23	55.5		0.05	101.72
10	24.43	9.69		8.91	4.85		0.05	1.44	51.8			101.03
11	17.56	1.22	0.33	23.9	5.06		0.11	0.76	50.6		0.98	100.49
12	17.04	1.31	0.81	29.6	3.91		0.04	1.1	46.7			100.78
13	16.33	1.07		15.6	5.55			0.74	61.0		0.32	100.77
14	16.77	0.59		16.6	5.83		0.03	0.68	60.5	0.42		101.5

2.2.5 Gold fineness

Natural gold grains vary widely in composition, especially with respect to silver content, reflecting the complete range of solid-solution substitution in gold-silver alloys. Electron microprobe analyses of gold grains demonstrate that Bi, Fe, Sb, Ni, Cu, Pb and Co are common trace constituents and that a range of other elements may also be present (Antweiler and Campbell, 1977; Knight and McTaggart, 1986; Morrison *et al.*, 1991). As the proportion of components other than Au and Ag does not commonly exceed one percent, the composition of gold is normally expressed as fineness [$1000 \cdot \text{Au}/(\text{Au} + \text{Ag})$]. Gold-silver alloys with fineness greater than 800 are referred to as gold, those with fineness 200-800 as

electrum and less than 200 as silver. Since the significant studies of Fisher (1945), the fineness of gold grains and their trace-element contents have been used to classify hypogene gold deposits (Graton, 1933) and to identify the source of placer gold (Badalova and Badalov, 1967; Desborough et al., 1971; Fayzullin and Turhina, 1974; Ollrich and Saager, 1986).

A total of 37 different gold grains from various localities in the Sable-Pilgrim's Rest goldfield was analysed for fourteen elements using an EMP. The chemical analyses of these gold grains are presented in Tables 2.8 and 2.10. The size of the gold grains varied from $<5\mu\text{m}$ to $\pm 80\mu\text{m}$. The average size gold grain was in the order of 20 to $25\mu\text{m}$ and this size was consistent for the different modes of gold occurrences. Gold fineness for the Sable-Pilgrim's Rest ores ranges between 767 and 982 ($x=893$). Although average values show no consistent distribution pattern in terms of stratigraphic position (Fig. 2.12), a limited range of fineness values characterize each of the different stratigraphic horizons. A pattern of increasing fineness with increasingly complex sulphide paragenesis is generally apparent. The silver content in gold grains associated with the more complex sulphide parageneses is relatively high compared to those grains which occur simply as inclusions in early pyrite (Fig. 2.13). Despite the measure of overlap in fineness, average values show a decreasing fineness with increasing complexity of sulphide assemblage. This observation corresponds with the findings of Badalova and Badalov (1967), who showed that fineness varies as a function of specific mineral associations. In the case of the Sable-Pilgrim's Rest goldfield late stage gold contain lower fineness values. No obvious relationship exists between the size of the gold grains and Au chemistry, nor could any relationship be recognized between Ag content in pyrite and Au fineness. Cobalt and nickel concentration in gold seldom reaches above 0.1 %. Mercury values in ores from the Clewer West Mine range between 1.54 and 0.01 wt% compared to an average of 1.7 wt% Hg for gold from the Witwatersrand ores (Sellschop et al., 1986). The average Pilgrim's Rest gold-silver ratio of 10:1 is markedly higher than the crustal ratio of 0.06:1 (Levinson, 1974). This ratio also distinguishes the Sable-Pilgrim's Rest gold deposits genetically from Cenozoic volcanogenic (Au:Ag $\approx$ 0.02:1), Subvolcanic (Au:Ag $\approx$ 0.55:1) and Mesozoic volcanogenic (Au:Ag $\approx$ 0.4-0.83:1) deposits.

Following the approach of Fisher (1945), Morrison et al. (1991) ventured to classify average fineness of gold in terms of depositional environment (Table 2.9). The major deposit classes are characterized by a wide range of fineness values (Morrison et al., 1991). The Archaean (including Witwatersrand), Slate belt and Plutonic classes are characterized by a high and consistent average

fineness and a narrow fineness range. However, there is no clear subdivision within these classes according to deposit style or inferred genesis. The Porphyry, Volcanogenic and Epithermal classes have variable average fineness and also exhibit a wide range of fineness values. Morrison *et al.*, (1991) has shown that the ranges in gold fineness is not characteristic of a specific depositional environment, and thus, cannot be used as an indicator of transporting mechanisms. The fact that gold fineness in the Sabie-Pilgrim's Rest goldfield strongly reflects the paragenetic association may be attributed to complexities in the ore-deposition mechanisms. In earlier studies, the Au/Ag ratios in deposits have either been explained by the specific nature of the geological setting of these deposits (Tilley, 1987) or by the conditions of transportation and deposition of gold and silver (Cole and Drummond, 1988; Shimazaki and Shimizu, 1986, 1987; Morrison, *et al.*, 1991). Recently new thermodynamic data on gold- and silver-complexes have appeared (Sugaki *et al.*, 1987; Gammons and Barnes, 1989; Shenberg and Barnes, 1989; Hayashi and Ohmoto, 1992), and the relationship between gold chemistry and precipitation mechanism will be discussed further in (Chapter 5).

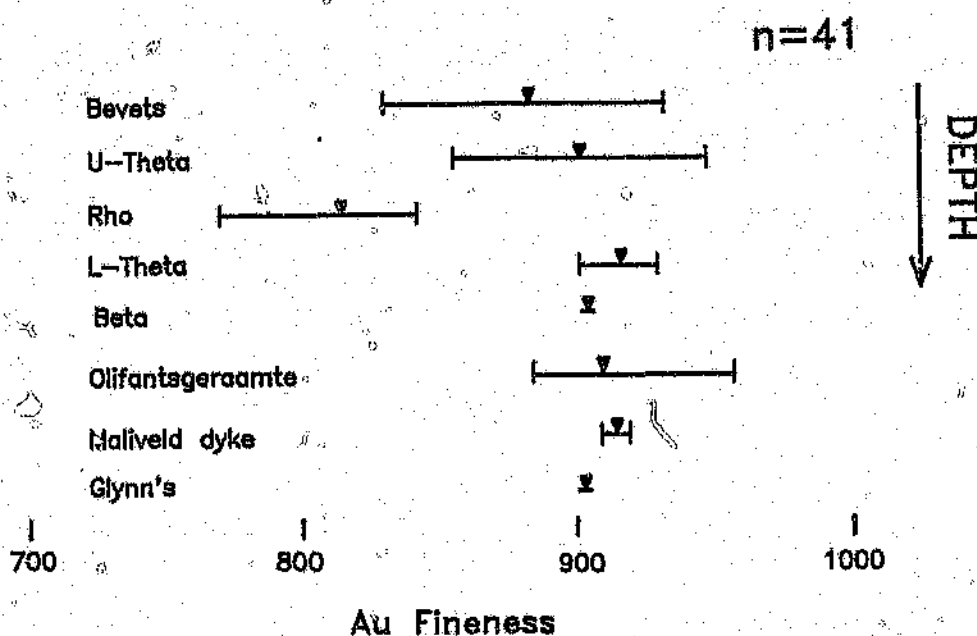


Figure 2.12 Variation in gold fineness with stratigraphic position in the Chuniespoort Group.

Au Paragenesis

Inclusions in Py

(952)

Fracture filling in Py

(903)

Py, Ccp

(889)

Thd→Tn, Apy, Ccp, Py, Bs, Bi

(871)

Quartz matrix

(825)

800

900

1000

Fineness

Figure 2.13 Variation in gold fineness in terms of sulphide paragenesis.

Table 2.8 Electron microprobe analyses of gold grains from different localities in the Pilgrim's Rest Goldfield.

Sample no.	Au	Ag	Fe	Pb	Cu	Ni	Co	As	Sb	Bi	Total	Fineness
fk075b	90.17	11.07	0.4	0.05	0.01		0.02	0.01	0.01	0.32	102.06	890.66
fk075b	91.43	11.32	0.5	0.03	0.03	0.04			0.01	0.62	103.98	889.83
fk075b	96.9	7.66	0.96	0.03	0.03				0.04	0.38	106	926.74
fk075b	87.66	15.43	1.02	0.05	0.01	0.02	0.01		0.01		104.21	850.32
fk075b	88.36	18.14	0.35		0.01		0.01			0.44	107.31	829.67
fk075b	90.8	18.32	0.55	0.04			0.02			0.41	110.14	832.11
fk077b	103.87	6.76	0.26		0.06	0.04			0.05	0.54	111.58	938.90
clw022	101.52	6.03	0.46		0.31	0.05	0.01	0.01		0.33	108.72	943.93
clw022	107.66	6.16	0.29		0.04					0.6	114.75	945.88
clw022	108.35	6.15	0.26	0.11			0.04		0.01	0.23	115.15	946.29
ofg12c	106.77	3.99	0.42	0.27	0.12	0.05	0.02			0.15	111.79	963.98
ofg12c	105.59	4.35	0.82		0.13			0.02		0.52	111.43	960.43
ofg12c	98.95	12.65	0.1					0.01		0.35	112.06	886.65
ofg12c	99.1	12.75	0.15	0.21	0.07	0.01	0.07	0.05	0.01	0.45	112.87	986.01
ofg12c	96.94	12.53	0.2							0.05	109.72	885.54
ofg12c	98.41	12.95	0.4	0.29		0.03				0.23	112.31	883.71
ofg12c	95.72	12.64	0.13	0.12		0.06		0.03	0.02	0.31	109.03	883.35

Table 2.8 (continue)

Sample no.	Au	Ag	Fe	Pb	Cu	Ni	Co	As	Sb	Bi	Total	Fineness
ofg12c	97.5	13.04	0.32	0.13	0.03			0.03			111.05	882.03
shb2	94.68	8.98	0.22	0.05		0.02				0.45	104.4	913.37
shb2	96.53	9.28	0.56	0.2	0.08		0.02			0.28	106.95	912.30
shb3	104.78	9.14	0.96	0.37	0.03	0.03	0.01	0.01		0.14	115.47	919.77
shb3	102.86	9.15	1	0.67			0.03			0.29	113.49	918.31
shb3	104.53	9.35	0.67		0.01			0.01		0.32	114.89	917.90
shb3	103.56	9.57	0.53	0.09	0.01		0.02		0.03	0.27	114.08	915.41
shb3	102.53	9.17	0.9		0.04	0.01			0.03	0.34	113.02	917.91
mob4	108.04	11.77	0.03		0.62	0.03				0.39	120.88	901.76
gls052	71.8	4.93	1.86		0.13	0.08		0.01		0.03	78.84	935.75
gls052	88	9.5	0.58	0.08				0.01		0.56	98.73	902.56
ds1	86.95	7	0.39			0.05				0.35	96.74	927.05
ds1	93.22	7.19	0.91	0.05						0.26	101.63	928.39
bcl4a	100.1	22.61	0.34	0.31				0.02		0.29	123.67	815.74
bcl4a	98.1	20.72	0.2	0.12	0.06	0.02	0.03	0.02		0.45	119.72	825.62
bcl4a	102.66	19.55	0.2	0.1						0.39	122.9	840.03
bcl4a	101.25	21.72	0.23	0.14	0.05					0.25	123.64	823.37
ofg2b	107.6	6.11	1.37	0.07	0.07	0.01			0.08	0.42	115.73	946.27

Table 2.8 (continue)

Sample no.	Au	Ag	Fe	Pb	Cu	Ni	Co	As	Sb	Bi	Total	Fineness
og2a	99.2	9.89	1.04		0.07	0.04				0.5	110.74	909.34
bcl5b	84.21	25.21	0.47		0.06			0.01			109.96	769.60

Table 2.9 Average fineness values for gold from different depositional environments (after Morrison *et al.*, 1991)

Archaean	940	(780-1000)
Slate Belt	920	(800-1000)
Plutonic	825	(650-970)
Porphyry	700-1000	(650-1000)
Volcanogenic	650-850	(520-870)
Epithermal	440-1000	(0-1000)

Table 2.10 Composition of SPRG gold samples determined by INAA. All values are presented in ppm, except when otherwise indicated. Analysis were performed at the Institute of geochemistry, University of Vienna by C. Koeberl

	Beta Mine	Elandsdrift Mine		Beta Mine	Elandsdrift Mine
Na	<1500	<1000	Sb	<40	<40
Sc	0.086	0.06	La	<5	<4
Cr	<50	<60	Ce	<10	<15
Fe	<500	<500	Eu	<0.2	0.03
Co	5.9	16.1	Yb	<8	<4
Ni	<500	<400	Lu	<0.5	<0.5
Zn	<50	<50	Hf	0.41	<0.2
Se	1	1.3	Ta	<0.05	<0.02
Rb	<50	<40	Ir	15	25
Sr	<500	<400	Hg	2890	2895
Ag (%)	1.14	4.06	Th	3.85	2.1
U	<1	<1			

2.2.6 Geothermometry and geobarometry

The auriferous veins of the SPRG suffer from a lack of suitable mineral assemblages that are amenable to geothermometry. A tenuous indication of mineralization temperatures is obtained from the habit of vein-related pyrite (see discussion in section 2.2.1), which suggests precipitation temperatures between 300° and 350°C. This semi-quantitative geothermometer suggests that coarser, striated pyrite surfaces formed at higher temperatures than smooth pyrite crystals, assuming a constant degree of sulphur saturation.

The only other mineral occurring in the SPRG that is relatively refractory and exhibits compositional solid-solution which could be calibrated in terms of temperature, is arsenopyrite. Arsenopyrite does not readily re-equilibrate on cooling and its composition reflects formation temperature, provided an estimate of the sulphur activity prevailing at the time of deposition can be made from coexisting minerals, such as pyrite, pyrrhotite and/or loellingite (Kretschmar and Scott, 1976; Clarke, 1960a,b). Kretschmar and Scott (1976) constructed a sulphur activity versus temperature diagram, based on the experimental work of Barton (1969) and Clarke (1960a,b). Sharp *et al.*, (1985) refined earlier versions of this arsenopyrite thermometer and corrected for the effect of pressure on As concentration. According to Sharp *et al.*, (1985) however, the composition of arsenopyrite when coexisting with pyrite, is largely unaffected by pressure. The most important consideration concerns the attainment of equilibrium within the Fe-As-S system which is characterized by slow sub-solidus reaction rates, as pointed out by Clarke (1960a) and Barton (1969). However, Ramdohr (1969) showed that only 5 of 98 natural arsenopyrite occurrences analysed were out of equilibrium (ie Fe-As-S assemblages not compatible at any temperature). Equilibrium conditions were thus assumed to have prevailed during formation of SPRG arsenopyrite and confirmed on the basis of textural appearance of arsenopyrite with other sulphide phases. Although natural arsenopyrite is commonly zoned, this could not be confirmed for SPRG arsenopyrite.

Arsenopyrite analyses presented in Table 2.11 were utilized for geothermometric determinations, using the calibration of Kretschmar and Scott (1976). Arsenopyrite from the Sabie-Pilgrim's Rest goldfield contained As in the range 29.03 to 29.75 atomic%. A minimum estimate for the activity of sulphur (a_{S_2}) was obtained from pyrite - pyrrhotite co-existence. Use of this reaction as a minimum estimate of sulphur activity is validated by the sporadic occurrence of pyrrhotite occurring together with pyrite in SPRG auriferous veins. The sulphur activity of this reaction is temperature dependant and at 320°C (average temperature adopted from the above discussion on the pyrite habit) yields a a_{S_2} of $10^{-10.6}$ (calculated using SUPCRT92; Johnson *et al.* 1992). Using these values a minimum temperature estimate of 300°C is obtained. This value is broadly compatible with values obtained by Anderson (1992), whose As values ranged between 28.8 and 31.7 atomic% ($\bar{x}=30.46$; $n=64$; $\sigma=0.67$), yielding a temperature range of 300° to 425°C ($\bar{x}=375^\circ\text{C}$), assuming a $\log a_{S_2}$ of -7.3.

An attempt was also made to use the composition of sphalerite from the SPRG as a geobarometer. Since the work of Kullerud (1953) it has been known that iron enrichment in sphalerite

is associated with decreasing pressure and increasing temperature. However, phase relations in the low temperature (<500°C) part of the Fe-Zn-S system is poorly constrained, and problems arise from the unappraised application of the sphalerite geobarometer (eg Lusk *et al.*, 1993; Toulmin *et al.*, 1991; Banno, 1988). It is imperative to establish that the required equilibrium assemblage (ie sphalerite - pyrite - hexagonal/monoclinic pyrrhotite) exists, as well as the post-formation history of the samples under study. The average element concentrations for SPRG sphalerite are as follows: Fe=1.68; Zn=64.51 and S=31.98 wt%. The average mole% FeS in sphalerite was calculated to be 2.98, which yield a pressure of 20.75 kbar, using the formulae of Lusk and Ford (1978), with a resulting $a_{\text{FeS}}^{\text{sp}}=0.085$. Such high pressures are unrealistic for the SPRG setting and are considered erroneous. Apart from the very low iron concentration in SPRG sphalerite, the high calculated pressures might also be an indication that sphalerite is not in equilibrium with pyrite and monoclinic pyrrhotite. Such an equilibrium paragenesis has produced sphalerite compositions consistently around 11 to 12 mole% FeS in a variety of ore deposits. These results indicate that low temperature (<500°C) assemblages in the system Fe-Zn-S are unlikely to yield useful geobarometric information, as was also concluded by various experimental studies (Lusk *et al.*, 1993; Toulmin *et al.*, 1991; Lusk and Ford, 1978).

A crude, but more reliable, indication of lithostatic pressure at the time of mineralization can be obtained from a reconstruction of the superjacent stratigraphy. The thickness of the Transvaal Sequence in the Transvaal sub-basin, at the time of quartz vein mineralization was approximately 7 to 8km (Barton, 1986). By using the density parameters determined by Smit and Maree (1966) for the lithologies of the Transvaal Sequence (ie Pretoria Group = 2.84 g.cm⁻³; Chuniespoort Group = 2.87 g cm⁻³), an average increase in pressure of 1kbar for each 3.2km of overburden is obtained. This corresponds to an lithostatic pressure of 2.2 to 2.5kbar at the time of vein emplacement in the SPRG.

Table 2.11 Electron microprobe analyses of SPRG arsenopyrite (Samples 2 and 3 obtained with courtesy of G. Smits and P.N. Bentley)

Sample	Fe	S	As	Ag	Pb	Cu	Zn	Bi	Co	Pt	Ir	Total
THR46	34.1	22.9	40.5	0.02	0.01		0.06	0.16	0.01			97.7
1	35.2	22.3	42.7			0.01	0.01				0.12	102
2	35.1	22.3	42.4			0.04	0.02			0.81		102

3.1 Fluid inclusion petrography

3.1.1 Cathodoluminescence

Identification of different types of quartz, and of individual crystal outlines is exceedingly difficult when dealing with massive buck quartz in which no grain boundaries or crystal surfaces are optically recognizable (also see section 2.1). In the auriferous veins of the SPRG, features such as terminated fluid inclusion trails and mineral/dust particles trapped on grain boundaries, are difficult to see and equivocal to interpret. For this reason cathodoluminescence (CL) was utilized in an attempt to distinguish between different quartz domains and to relate fluid inclusion populations to the various types of quartz.

Although the intensity of quartz CL is weak compared to the CL of feldspars, carbonates and other minerals (Marshall, 1988), the CL contrast between different types of quartz is more distinct than any optical examination. Zinkernagel (1978) classified three types of quartz based on CL, namely: (i) violet-luminescing quartz from plutonic, volcanic and contact metamorphic rocks, which have undergone fast cooling, (ii) brown-luminescing quartz from low grade metamorphic rocks and high grade metamorphic rocks which cooled slowly, and; (iii) non-luminescing authigenic quartz. No zonation was observed in brown CL and very rarely in violet-luminescing quartz. Three samples from the SPRG (ie GRR099, CLW017 and NSM093) were analysed by Dr. A.M. van den Kerkhof at the Institut für Geologie und Dynamik der Lithosphäre at the University of Göttingen. The equipment used for CL was a high-power ("hot") CL microscope, based on the design described by Zinkernagel (1978), which is particularly suitable for the study of quartz. The electron source operated at 15kV under high vacuum ($\sim 1\text{E-}05$ mbar), with a maximum beam current of 1 mA (average ~ 0.5 mA). The diameter of the illuminated spot on the sample surface was ~ 3 mm, corresponding to a beam intensity in the order of 100 W.cm^2 . Prolonged bombardment (3 to 7 minutes) of the quartz specimens was necessary for the photographic recording of CL, as the phenomenon was very short-lived in the SPRG samples. The temperature increase associated with prolonged electron bombardment is approximately 70°C , but is unlikely to cause decrepitation of the fluid inclusions.

The photomicrographs of SPRG samples, taken before and during CL experiments, are presented in Figures 3.1a-d and 3.2a-d. Sample GRR099 (Fig. 3.1b & d) exhibited a short-lived blue CL

(for a few seconds) diminishing to a dull violet-blue with time. A portion of the quartz shows brown CL and may also show fluid infiltration textures in the short-lived blue quartz. Locally, a patchy pattern (with no CL response), which is a typical indication of large decrepitated fluid inclusions, could clearly be observed during the first few seconds. However, these features fade away very quickly and are difficult to photograph (Fig. 3.1c & d). The blue band observed on Figure 3.1(d) is probably a synthetic artifact developed soon after switching on the electron beam, as luminescence is very intense during the first few seconds. These bands show a distinct contrast with the dark zones of decrepitated fluid inclusions. Sample CLW017 (Fig. 3.2a & b) shows a pronounced brown CL. Remnant grains, in greenish brown, are vaguely visible and might indicate growth zones. Sample NSM093 shows two clearly different quartz domains, with the darker variety displaying a pronounced brownish colouration.

Detailed fluid inclusion petrography revealed that there is no obvious petrographic difference in the types of fluid inclusions occurring in these quartz domains identified by CL. Furthermore, it would be misleading to suggest that the various CL colours are a reflection of different temperatures of quartz formation, as current research shows that there are many exceptions to the rudimentary classification scheme of Zinkmagerl (1978) (Dr. A.M. van den Kerkhof, pers. commun., 1994). However, the CL images in Figures 3.1 and 3.2 clearly indicated the presence of at least two generations of quartz, as colour/CL zonation was recognized in two of the three samples studied (i.e. samples CLW017 and NSM093). No evidence for differences in physical and chemical characteristics could be observed for fluid inclusions from the different quartz domains. Anderson (1992) also recognized two quartz generations, using CL, one brecciated, devoid of inclusions and yielding a high intensity CL, and the other a later quartz yielding a lower CL and containing the bulk of the fluid inclusions.

In summary, therefore, apart from the two types of quartz recognized in hand specimen, CL studies clearly indicate at least one further quartz variety confirming the presence of a minimum of three types of quartz in the SPRG veins. The late stage clear quartz can easily be identified in hand specimen, but it is exceedingly difficult to distinguish between the two quartz generations in massive buck quartz without the assistance of CL microprobes. As no optical or microthermometric difference could be identified between the fluid inclusions from the latter two quartz domains, these fluid inclusions were treated collectively.

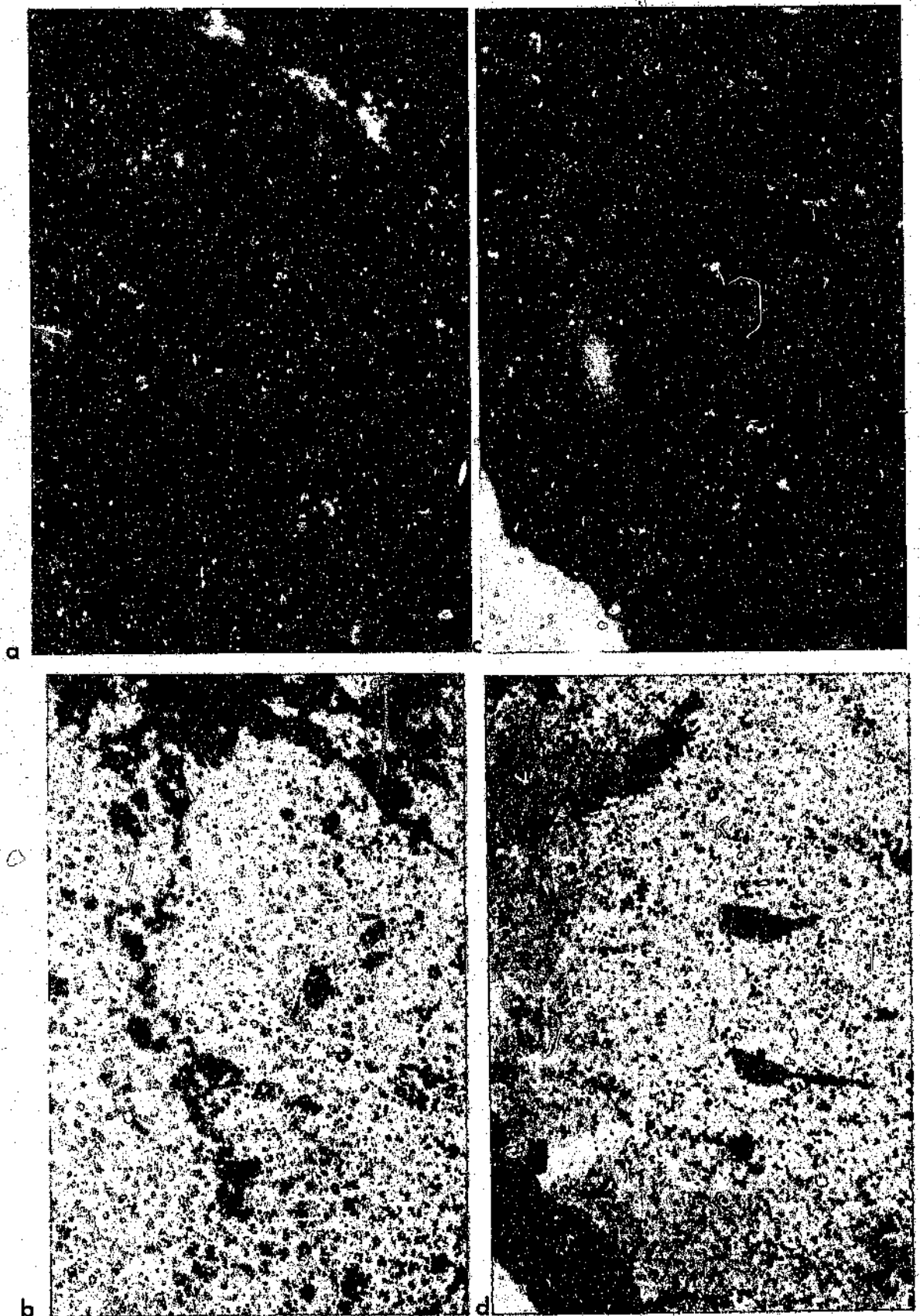


Figure 3.1 Cathodoluminescence photomicrographs of sample GRR099 (a to d), showing different quartz domains.

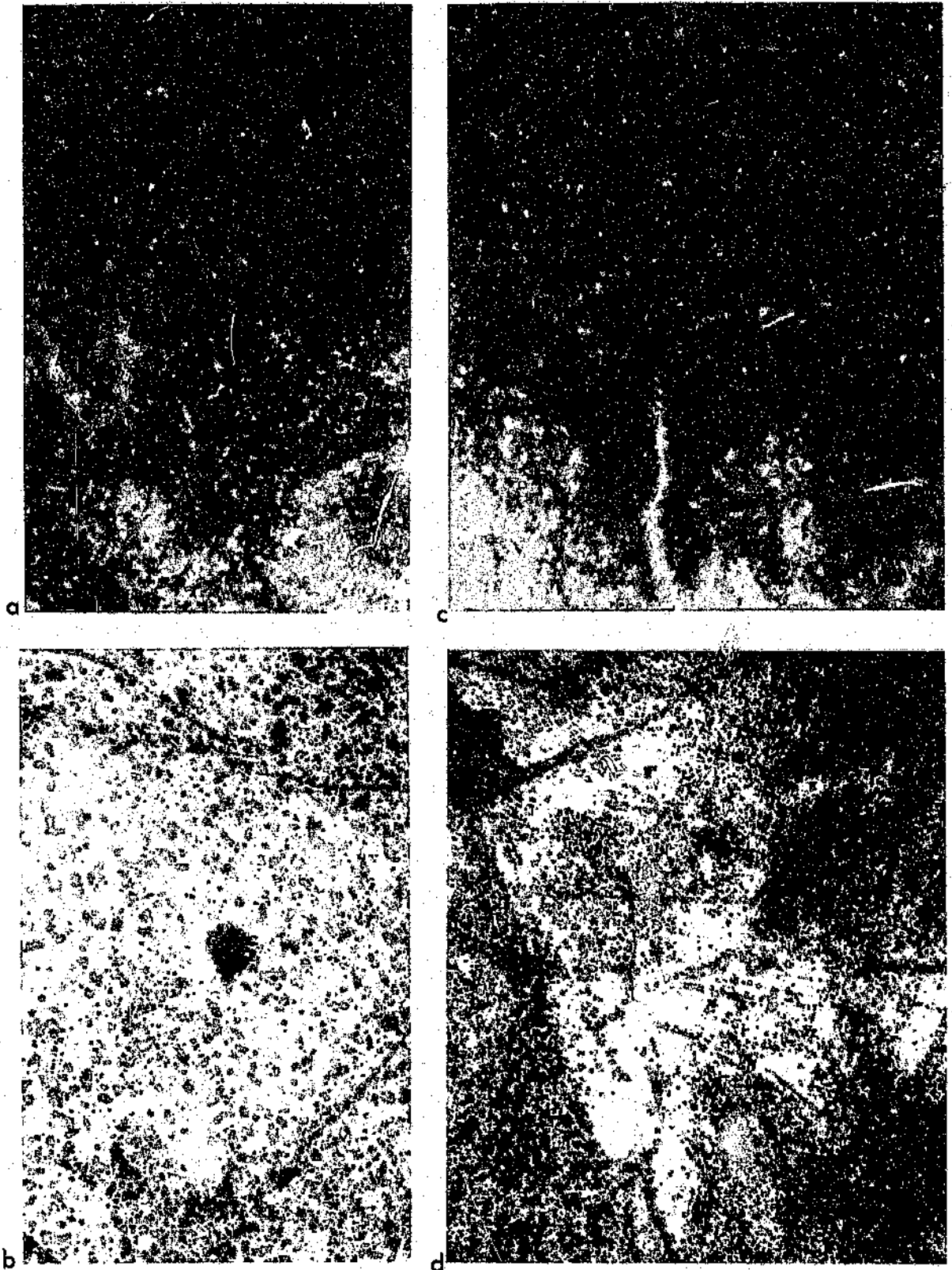


Figure 3.2 Cathodoluminescence photomicrographs of sample CLW017 (*a* & *b*) and sample NSM093 (*c* & *d*), showing different quartz domains.

3.1.2 Optical fluid inclusion petrography

All of the quartz veins examined experienced repeated fracturing in the presence of aqueous fluids as evident by abundant planes of secondary inclusions observed at low magnification. The high density of randomly oriented fractures decorated with fluid inclusions made it difficult to determine whether a given inclusion was fracture related or trapped during crystal growth. Furthermore, it was also not possible to relate fluid inclusion populations to the types of quartz recognized using CL (section 3.1.1), or to categorize the inclusions unequivocally as primary, secondary or pseudosecondary. For this reason, no attempt was made to classify fluid inclusion types according to the criteria of Roedder (1984), but groups of inclusions have been described in terms of their textural and compositional properties, which ultimately relate to the various stages of vein filling. Two optically distinct varieties of quartz were observed, namely an early, grey to milky translucent variety and a later transparent type which either engulfs or occurs along microfractures in the milky quartz, and is characterized by a distinctly different fluid inclusion population. The clear quartz is not associated with gold. In all of the samples studied from the horizontal veins, approximately 95% of the quartz is of the early, milky variety (also known as buck quartz). Quartz generally contains a number of apparently co-existing fluid inclusion populations within a single field of view. From detailed fluid inclusion petrography of numerous double polished thin sections, representing the entire vertical and regional extent of the SPRG, three types of fluid inclusions were recognized. The main features of these three fluid inclusion categories can be summarized as follows:

(i) *Type 1 inclusions.* This is the dominant fluid inclusion type and exhibits three phases, an aqueous liquid, a carbonic liquid, and a vapour bubble, at room temperature (Fig. 3.3a), with occasional daughter crystals. The liquid-to-vapour ratio, as well as $H_2O:CO_2$ ratios, vary to such an extent that the type 1 inclusions were subdivided into three categories: (i) aqueous inclusions contain an aqueous liquid, a small carbonic vapour bubble and occasionally a single cubic (Fig. 3.4), or less commonly a rectangular (probably anhydrite), daughter crystal; (ii) large single phase liquid carbonic inclusions with vapour bubbles that appear during cooling; and (iii) a spectrum of three phase inclusions with variable $H_2O:CO_2$ ratios, seldomly containing a daughter crystal. Fracture-related aqueous and carbonic fluid inclusions are contemporaneous, as they occur in the same quartz domain, feature that was confirmed by cathodoluminescence studies, which show that the range of Type 1 inclusions occur together within individual quartz domains (see section 3.1.1). Furthermore, aqueous and carbonic inclusions occasionally occur along the same healed fracture. This mode of occurrence, together with the

continuum in carbonic/aqueous ratios shown by these fluid inclusions strongly suggest a close genetic relation between the two fluids. The morphology of this inclusion type varies from irregular to rounded, with some equidimensional negative crystal shapes. The size of the inclusions ranges from 5 to 30 μm . Evidence for necking of fluid inclusions due to dissolution and reprecipitation is locally present, but does not appear to be a common phenomena in SPRG quartz. CL studies confirm the notion that SPRG quartz has undergone little recrystallization, as remnant crystal shapes are still visible.

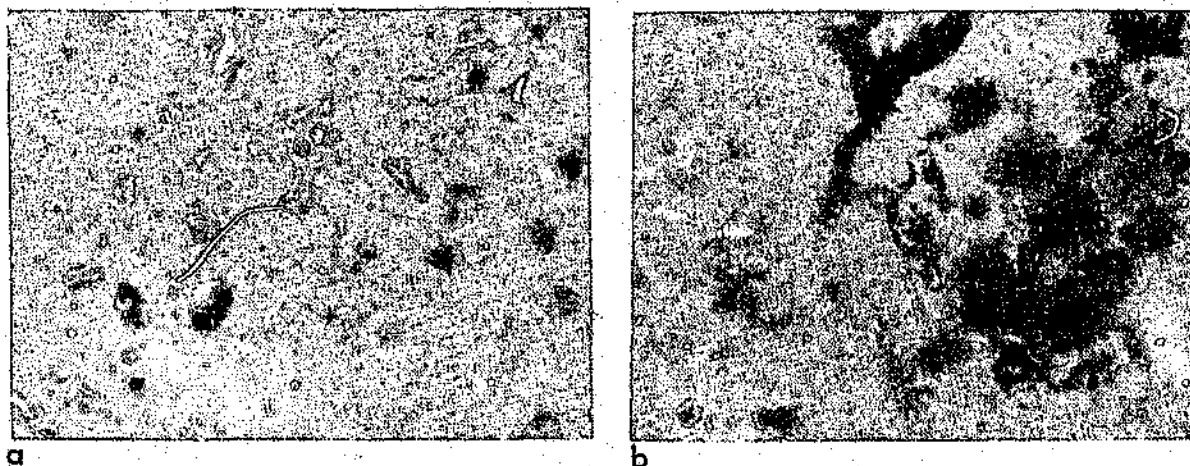


Figure 3.3 (a) Typical type 1 fluid inclusion arrangement. Sample CLW022 from Clewer West Mine. (50X magnification). (b) Type 2 fluid inclusion from Gregory Mine (50X magnification).

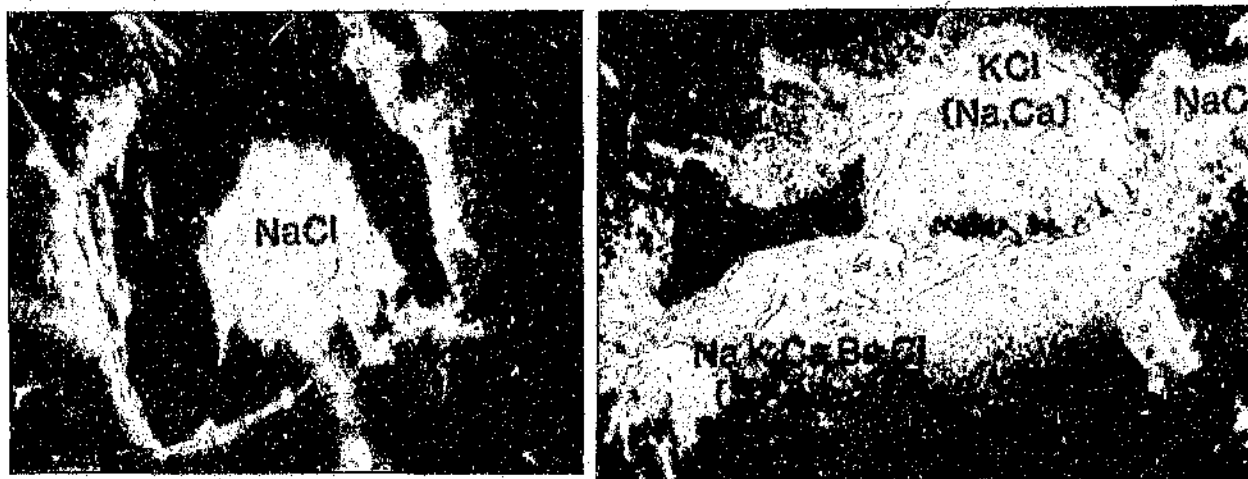


Figure 3.4 Scanning electron microscope image of cubic halite daughter crystal in opened fluid inclusion cavity (Image courtesy of F.M. Meyer)

(ii) *Type 2 inclusions*. This type of inclusion is less common, and is characterized by an aqueous liquid, a vapour bubble and at least one daughter crystal at room temperature (Fig. 3.3b). Daughter crystals display a variety of shapes and sizes, most commonly of cubic habit (probably halite and/or sylvite), but orthorhombic and monoclinic crystal habits also occur (probably indicating the presence of anhydrite, antarcticite and calcite). Carbonic species are frequently present, but are not visible and are only evident in the formation of clathrates (gas hydrates). This type of inclusion is common in the vertical veins, but do not appear to occur in the strata bound veins.

(iii) *Type 3 inclusions*. These inclusions contain an aqueous liquid, with or without a vapour bubble at room temperature, and are believed to be the last-formed inclusion type. They are found in both the milky and clear quartz varieties, occurring in well defined fluid inclusion trails. However, in the volumetrically minor late-stage clear quartz these inclusions predominate, while carbonic and aqueous saline inclusions are rare. Cross-cutting relations between type 3 and type 1 inclusions prove that the former post-date the carbonic-rich inclusions. The absence of vapour bubbles in many of these late fluid inclusions suggest low entrapment temperatures, and confirms the late temporal relations.

All fluid inclusions observed formed within annealed micro-fractures. No unambiguous temporal relation could be recognized between Type 1 and 2 fluids, but Type 3 fluids clearly cross-cut Type 2 inclusion trails. Type 1 fluids occur in milky quartz in both granite-hosted vertical veins and in sediment- and dyke-related horizontal veins, and has also been recognized by Ash and Tyler (1986) (Type I, II & IV) and Anderson *et al.* (1992) (Type I, II & III). Type 2 fluids were only observed in vertical veins, and correspond to the Type III inclusions of Ash and Tyler (1986). Type 3 fluids occur throughout, but form the predominant population in the paragenetically late transparent quartz.

3.2 Microthermometric fluid inclusion experiments

The fundamental assumption on which fluid inclusion studies are based is that the entrapped fluid phases are representative samples which can be used to characterize fluid compositions and *p-T* conditions associated with the formation of the host mineral. Indirect estimation of fluid inclusion properties, such as salinity, density and composition, were obtained by microthermometric heating and freezing experiments, using the standard techniques described by Roedder (1984) and Goldstein and Reynolds (1994). In this study, microthermometry was only used as a first approximation of fluid inclusion compositions. Temperatures of phase changes were obtained on a FLUID INC. adapted U.S.

Geological Survey heating-freezing system, with the thermocouple calibrated against synthetic fluid inclusions (Sterner and Bodnar, 1984) at the University of the Witwatersrand, as well as on a Chaixmeca heating-freezing system (Poty *et al.*, 1976) at the Centre de Recherches sur la Géologie des Matières Premières Minérales et Énergétiques (CREGU) in Nancy, France. The Chaixmeca stage was calibrated against pure chemical substances, over a temperature interval of -142.4° (methyl cyclopentane) to 398.3°C (potassium dichromate), using similar methods to those described by Boer (1987). Salinities are expressed relative to the equivalent weight percent NaCl (wt% eNaCl), with the latter being related to the depression of the freezing point through the equation: $\text{Salinity} = 0.00 + 1.78\theta - 0.0442\theta^2 + 0.000557\theta^3$, where θ is the depression of the freezing point in degrees Celsius (Bodnar, 1993). The latter equation may be used to obtain the salinity corresponding to a measured freezing temperature for any temperature between 0.0° and the eutectic temperature of the H₂O-NaCl system (ie -21.2°C). Microthermometric measurements were made on inclusions that could be confidently classified into any one of the above mentioned fluid inclusion types, and which were large enough to permit easy observation of phase changes. All microthermometric measurements were obtained during heating runs, as metastable effects prevent precise measurement of phase changes upon cooling (Roedder, 1984). Doubly polished wafers (100 to 150 μm thickness) were first thoroughly scrutinized for the presence of evolved hydrocarbon species, using ultraviolet microscopy. Ultraviolet microscopy was performed at the CREGU, as well as the Centre de Recherches Petrographiques et Geochimiques, (C.N.R.S.) in Nancy, France.

Table 3.1 List of microthermometric abbreviations following the usage after Roedder (1984)

T	Temperature (°C)
p	Pressure (kbar)
T _h	Temperature of homogenization
T _i	Temperature of trapping
T _d	Temperature of decrepitation
T _m	Temperature of melting
T _e	Temperature of eutectic
T _n	Temperature of nucleation
wt% eNaCl	Salinity expressed as weight percent NaCl equivalent

3.2.1 Clewer West Mine and Morgenzon Mine

Samples from the Clewer West Mine are typical buck quartz specimens obtained from the horizontal Rho vein, as well as perpendicular off-shoots into the footwall. The dominant fluid inclusion type belongs to the type 1 class, although approximately 5-10 % were type 3 inclusions. Final melting temperatures of ice in the type 1 fluid inclusions ranged from -15° to -8°C (Fig. 3.5a), corresponding to a salinity of 18.6 to 11.7 wt% eNaCl. However, the low first melting temperatures (see section 3.2.13) suggests that these inclusions may contain other cation species, such as CaCl_2 (Roedder, 1984). By superimposing the latter results on a ternary diagram of the $\text{NaCl}-\text{CaCl}_2-\text{H}_2\text{O}$ system it is apparent that the $\text{NaCl}:\text{CaCl}_2$ ratio varies between 5:1 and 12:1 (Fig. 3.8). Type 3 fluid inclusions melted around -4°C (Fig. 3.5a), indicating a lower salinity of ~6 wt% eNaCl. However, in many cases clathrates (gas hydrates, eg $\text{CO}_2 \cdot 5\frac{1}{2}\text{H}_2\text{O}$) were observed and a few clathrate melting temperature measurements fall in the range -2° to $+4.8^{\circ}\text{C}$. Clathrates incorporate a relatively large proportion of H_2O into their crystal structure, causing an overestimation of salinity when relying on the freezing point depression temperature for salinity estimation. Salinity calculations which are based on the freezing point depression, thus, present a maximum salinity estimate. However, it is possible to calculate salinities using clathrate melting temperatures (Diamond, 1990; Collins, 1979). Salinities determined from clathrate melting temperatures are slightly lower and range from 17.4 to 9.4 wt% eNaCl. The error on the latter salinity estimates are often large, as it is difficult to determine the precise final melting temperature of clathrates which have similar refractive indexes to that of ice. Total homogenization of type 1 inclusions are rarely observed, as these inclusions tend to decrepitate before complete homogenization (Fig. 3.6a). Such decrepitation of fluid inclusions before complete homogenization indicate that these fluid inclusions were trapped at high ambient pressures, although the actual pressure of entrapment is difficult to determine. By using the few T_h determinations available (homogenization invariably took place into the liquid phase) a density of 1.052 g.cm^{-3} was calculated for the low T_h populations around 120°C , and a density of 0.958 g.cm^{-3} for the higher T_h population around 225°C , using the equation of state (EOS) as defined by Brown and Lamb (1989) for the $\text{H}_2\text{O}-\text{NaCl}$ system. Isochoral calculations were performed using the computer program FLINCOR (Brown, 1989). First melting of solid CO_2 was observed in the temperature range between -59° to -56.6°C (Fig. 3.7). Suppression of the melting point temperature of pure CO_2 (-56.6°C), indicates the presence of other gaseous species, such as CH_4 ($T_e = -182.48^{\circ}\text{C}$) and/or N_2 ($T_e = -209.86^{\circ}\text{C}$), which have lower eutectic melting points. The presence of other gases are confirmed by quadrupole mass spectrometer analyses (section 3.5). A meaningful feature in the density distribution of carbonic species in the Clewer West Mine, is the

recognition of two distinctly different groups of inclusions. The one group yielded low CO_2 homogenization temperatures ranging between $+3^\circ$ to $+15^\circ\text{C}$, corresponding to high densities of between 0.910 and 0.813 g.cm^{-3} , whereas a second group of inclusions yield T_{hCO_2} of between $+22^\circ$ and $+28^\circ\text{C}$, corresponding with a lower density range of 0.752 to 0.657 g.cm^{-3} . However, these two groups of inclusion could not be distinguished optically.

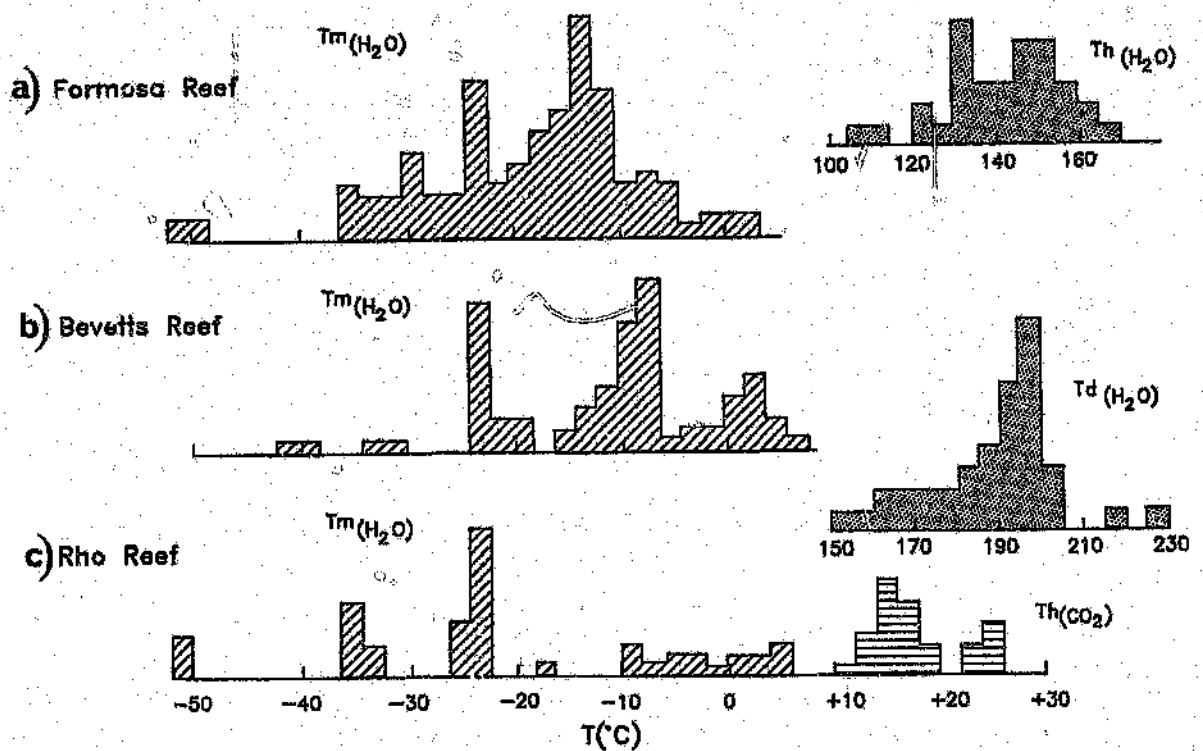


Figure 3.5 Summary of final melting temperatures for Clewer West Mine

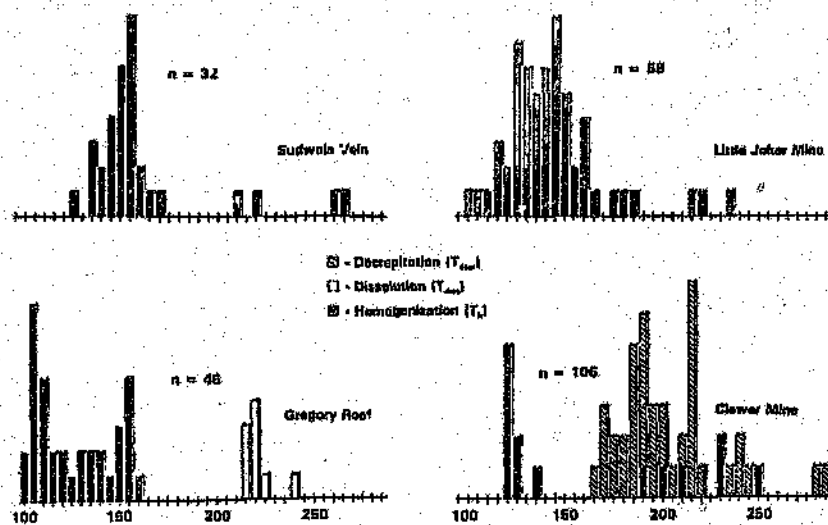


Figure 3.6 Summary of total homogenization (T_h), decrepitation (T_d) and daughter crystal dissolution (T_{dis}) temperatures for type 1 fluid inclusion.

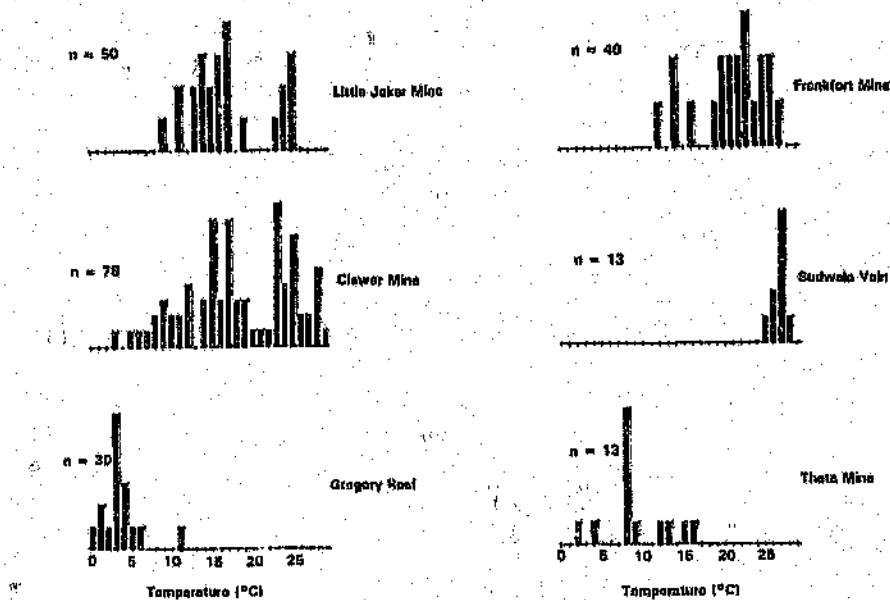


Figure 3.7 Summary of first melting (T_{m002}) and final homogenization (T_{h002}) temperatures for the carbonic species.

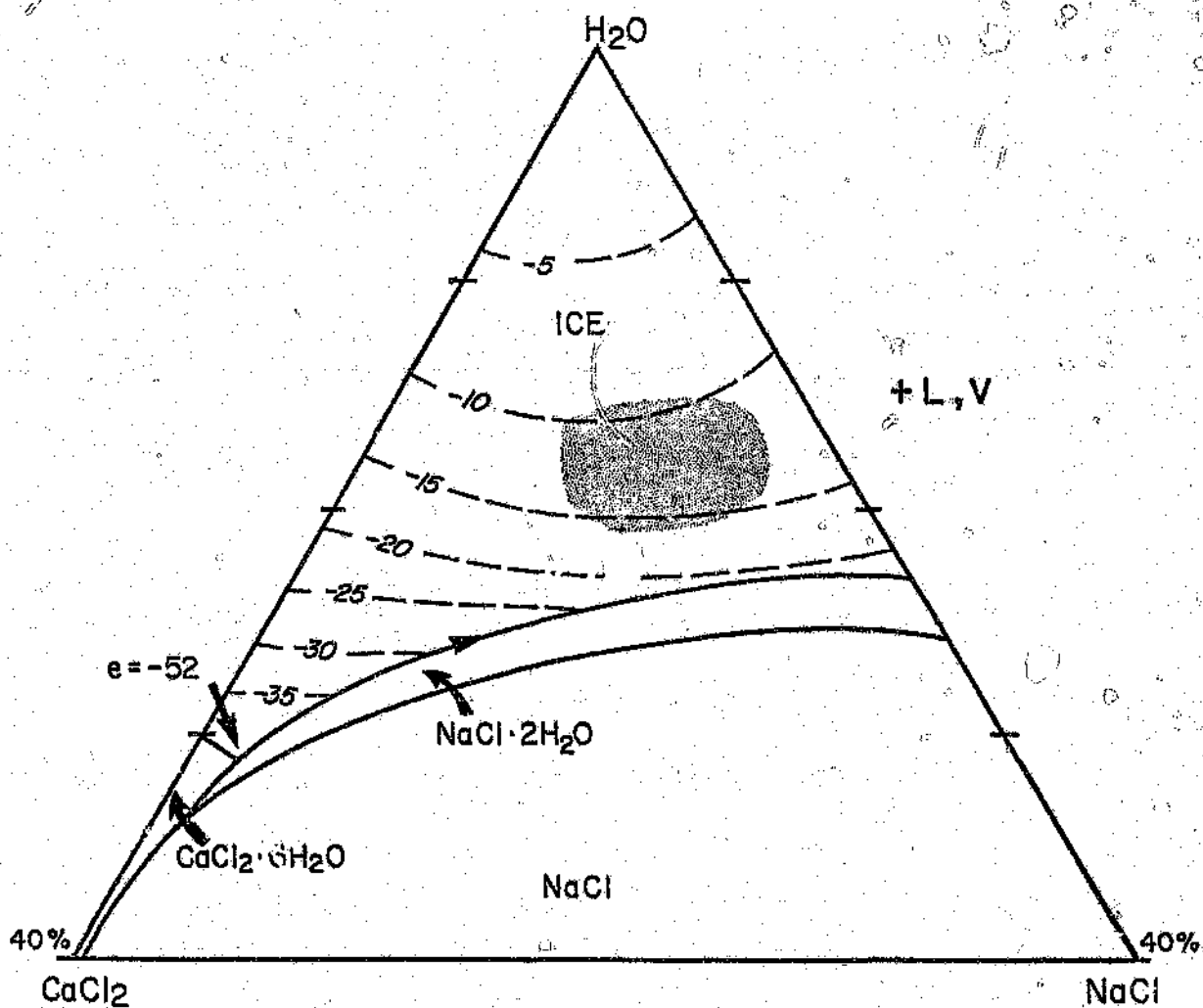


Figure 3.8 SPRG data superimposed on Isotherms of the ice liquidus at 1 atm total pressure in the system NaCl-CaCl₂-H₂O after Oakes *et al.*, (1990). The latter experimental data adequately approximate the SPRG fluid conditions.

3.2.2 Frankfort Mine

Samples were obtained from the Bevetts vein, which is a typical sheeted stratiform vein. A well defined shear plane divides the vein into an upper intensely folded part, and a lower undeformed portion (Fig. 2.1). Fluid inclusions from these two segments of the vein do not show any textural or chemical differences. Final melting temperatures for type 1 inclusions clustered around -23°C (Fig. 3.5). Such low final melting temperatures suggest that other divalent cation species are present, probably CaCl_2 , as the maximum freezing point depression in the system $\text{NaCl-H}_2\text{O}$ is 21.2°C . The dominant final melting point centred around -12°C , indicating an average salinity of 16 wt% eNaCl. Type 3 inclusions yielded final melting temperatures which range from 0° to -5°C , yielding salinities of approximately 3 wt% eNaCl. Clathrate melting temperatures ranged from 0° to $+6^{\circ}$, with a population peak at $+3^{\circ}\text{C}$, corresponding to a salinity of 12 wt% eNaCl for these inclusions. Total homogenization temperatures for type 2 inclusions ranged from $+150^{\circ}$ to $+205^{\circ}\text{C}$, indicating fluid densities of 1.019 to 0.967 g.cm^{-3} . CO_2 -rich fluid inclusions were less dense (0.813 to 0.678 g.cm^{-3}) with the bulk of homogenization (into the liquid phase) occurring between $+16^{\circ}$ to $+27^{\circ}\text{C}$.

3.2.3 Mountain and Little Joker Mines

The Mountain and Little Joker Mines are developed on the Formosa vein. Samples are of the typical buck quartz variety and do not have a sheeted appearance. This vein is dominated by type 1 fluid inclusions, although type 3 also occur. Fluid inclusion properties are very similar to those of the veins hosted in the carbonate rocks of the Charlesport Group, but the salinities are significantly higher. Type 1 fluid inclusion salinities range from 15 to 22 wt% eNaCl (average 17 wt% eNaCl), with final melting temperatures between -20° and -11°C (Fig. 3.5). Homogenization temperatures of type 3 inclusions were slightly lower, compared to the structurally lower Frankfort and Clewer West Mines, and range between 110° and 160°C (Fig. 3.6). The densities of these fluids were calculated to range between 1.050 and 1.010 g.cm^{-3} . CO_2 -rich fluid inclusions displayed the same two groups of inclusions which can only be distinguished in terms of their densities (Fig. 3.7). At the Clewer West Mine the two groups occurred in relatively equal proportions, whereas at the Frankfort Mine the lower density group dominated. However, at the Mountain and Little Joker Mines the high density group of carbonic fluid inclusions dominate.

3.2.4 Sudwala vein

The Sudwala vein (Clendenin, 1989; Harley and Charlesworth, 1990) is considered to be

uneconomical in terms of gold mineralization. The vein is exclusively made up of massive buck quartz, and is situated at the base of a sizable diabase s.d.. Fluid inclusion petrography revealed the dominance of type 3 inclusions, with very little visible CO_2 . The inclusions in this vein did not show a resemblance to the type 1 inclusions of the other localities. Fluid inclusions of the type 3 variety yielded final melting temperatures in the range -6° to -4°C , corresponding to salinities of 9 to 6.5 wt% eNaCl. Total homogenization temperatures centred around $+150^\circ\text{C}$, indicating densities in the order of 1.019 g.cm^{-3} . CO_2 -rich phases almost invariably were of the low density variety with homogenization temperatures clustering around $+28^\circ\text{C}$.

3.2.5 Nestor Mine

The vein system that was exploited at the Nestor Mine has a typical sheeted appearance in some parts. Samples were obtained from numerous localities throughout the mine and all yielded similar fluid inclusion properties. Final melting was in the range -14° to -10°C with an average salinity of 15 wt% eNaCl. Homogenization temperatures were in the range 110° to 180°C , conforming to a density range between 1.050 and 0.992 g.cm^{-3} . Dissolution of daughter crystals was measure in the temperature range between 220° and 280°C , and invariably occurred after homogenization of the gaseous phase into the liquid phase. The interpretation of this behaviour is that halite saturation during post-entrapment cooling was reached before the formation of a vapour bubble. By implication this suggests that the dissolution temperatures should be regarded as the minimum temperature of fluid entrapment. However, it is also possible, but very unlikely in the case of the SPRG fluid inclusions, that these crystals were trapped as foreign particles during fluid entrapment (Roedder, 1984), thereby rendering the deduced density and salinity estimates inapplicable.

3.2.6 Astra Mine

Samples were obtained from the vertical part of the Astra vein. Final melting temperatures centred around -10°C for type 1 inclusions, and at around -5°C for type 3 inclusions. These melting temperatures correspond to salinities of 14 and 8 wt% eNaCl, respectively. Homogenization temperatures peaked at around 150°C , with a large number of fluid inclusions decrepitating at temperatures above 210°C . These homogenization temperatures yielded densities of around 1.019 g.cm^{-3} for the low temperature homogenization and 0.963 g.cm^{-3} for the 210°C homogenization peak. CO_2 -rich fluid inclusions homogenized through a wide temperature range of $+3^\circ$ to 28°C , corresponding to densities for the carbonic phase varying between 0.910 g.cm^{-3} and 0.657 g.cm^{-3} .

3.2.7 Gregory Mine

Samples obtained from the Gregory Mine which occurs in the Archaean granitic basement were sampled a vertical vein of a 100 m vertical span. Quartz from the vertical veins typically display cockscomb textures, but are predominantly of the buck type quartz variety. Final melting temperatures for the type 1 inclusions centred around -18°C , indicating a salinity of 21 wt% eNaCl. Few type 2 inclusions were observed. Carbonic fluid inclusions were of the dense variety with homogenization temperatures clustering around 3.5°C , indicating a CO_2 density of 0.906 g.cm^{-3} . Total homogenization for the more aqueous type 1 inclusions occurred in the temperature range 105° to 155°C , although a number of inclusions homogenized between 290° and 360°C . However, the majority of type 1 inclusions decrepitated at temperatures above 200°C . Dissolution of daughter crystals, which were occasionally observed in type 1 inclusions, invariably occurred after total homogenization at temperatures around 220°C . This temperature is regarded as the minimum temperature of entrapment, and was used for density calculations which yielded an approximate density of 0.954 g.cm^{-3} . Type 2 fluid inclusions homogenized above 250°C , before dissolution of the large number (up to 7) of daughter crystals. Final melting temperatures, which centred around -20°C , were meaningless in the estimation of salinity, as the daughter crystals remain unidentified. However, the presence of rectangular shaped daughter crystals (probably anhydrite) suggest the presence of calcium, in addition to the other cations. No temporal relationship could be established between type 1 and 2 fluid inclusions, and they might have been trapped contemporaneously.

3.2.8 Summary of microthermometric properties

Type 1 inclusions. This is the dominant fluid inclusion type, with three phases (an aqueous liquid, a carbonic liquid, and a vapour bubble) at room temperature, and occasional cubic daughter crystals. Final melting temperatures (T_m) of the aqueous phase range from -21.2° to -4.3°C , corresponding to a salinity range of 23.5 to 5.5 wt% eNaCl. The most outstanding feature of type 1 fluid inclusions is the fact that those inclusions containing carbonic species normally decrepitate prior to bulk homogenization (T_h), in the temperature range between 170° and 290°C . This important observation suggests high internal fluid pressures. The T_h measurements obtained range from 105° to 255°C , corresponding to high bulk densities of 0.857 to 1.053 g.cm^{-3} . Comparison of homogenization and final melting temperatures for the various veins show different salinities for the three veins and confirm the salinity ranges within individual veins (Fig. 3.10). First melting temperatures for the carbonic phase are slightly below the value for pure CO_2 , and confirm the presence of other gaseous species, such as CH_4 .

and N_2 . Two distinct populations of carbonic inclusions were recognized on the basis of the CO_2 homogenization temperatures, with histogram peaks occurring at 10° and $23^\circ C$ respectively (Fig. 3.7). This suggests that two generations of carbonic fluid influx, of differing densities, occurred. It was not, however, possible to optically distinguish between the different density fluid inclusions.

The eutectic melting temperature of type 1 fluid inclusions was exceedingly difficult to determine, because of the small size of the inclusions and problems associated with observing the initial appearance of a liquid meniscus in an ice matrix. Figure 3.9 indicates that the majority of "apparent" eutectic melting temperatures were observed in the -25° to $-24^\circ C$ region. These temperatures do not correspond to the theoretical eutectic melting temperature of any of the systems involving a combination of the most common cation species (i.e. $NaCl$ & KCl) that are usually observed in fluid inclusions (Roedder, 1984). In larger fluid inclusions ($> 10 \mu m$ diameter) an eutectic temperature was observed at around $-22^\circ C$. These lower eutectic melting temperatures indicate the presence of a divalent cation (e.g. Ca^{2+} , Roedder, 1980; Crawford, 1981). Various studies have indicated that $CaCl_2$ is a major solute in hydrothermal brine solutions from a wide variety of geological environments (Schiffries, 1990; Keijy et al., 1983; Crawford et al., 1979). Fluid inclusions containing $CaCl_2$ are characterized by extremely low eutectic melting temperatures (T_e of the ternary $CaCl_2$ - $NaCl$ - H_2O is $-52^\circ C$; Bateman, 1946), and by the presence of hydrous phases such as antarcticite ($CaCl_2 \cdot 6H_2O$) and hydrohalite ($NaCl \cdot 2H_2O$). Experimental data for the system $CaCl_2$ - $NaCl$ - H_2O (Zhang and Frantz, 1989; Oakes et al., 1990) indicates that antarcticite melts at the eutectic temperature, whereas hydrohalite and ice are the next phases to melt.

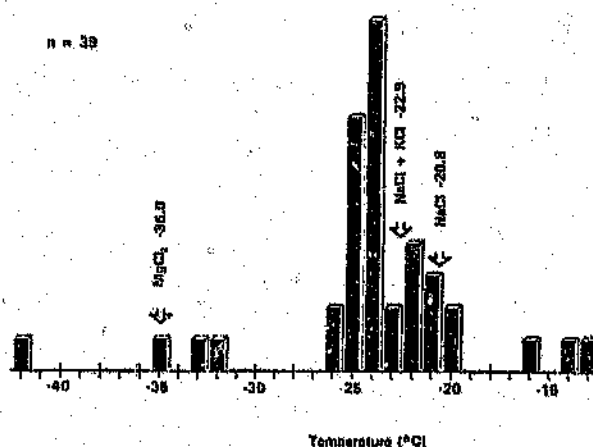


Figure 3.9 Eutectic melting temperatures for type 1 fluid inclusions from the SPRG

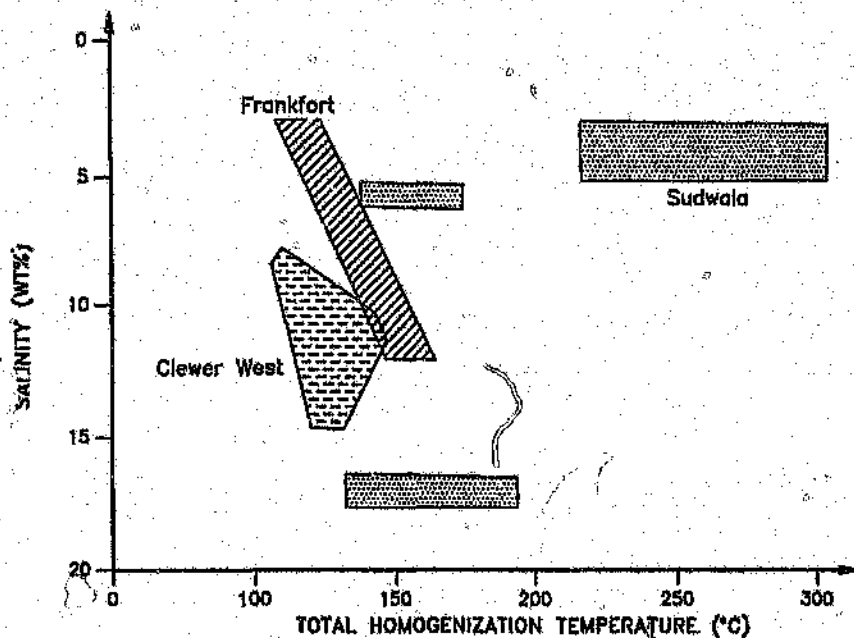


Figure 3.10 T_h versus T_m for SPRG veins

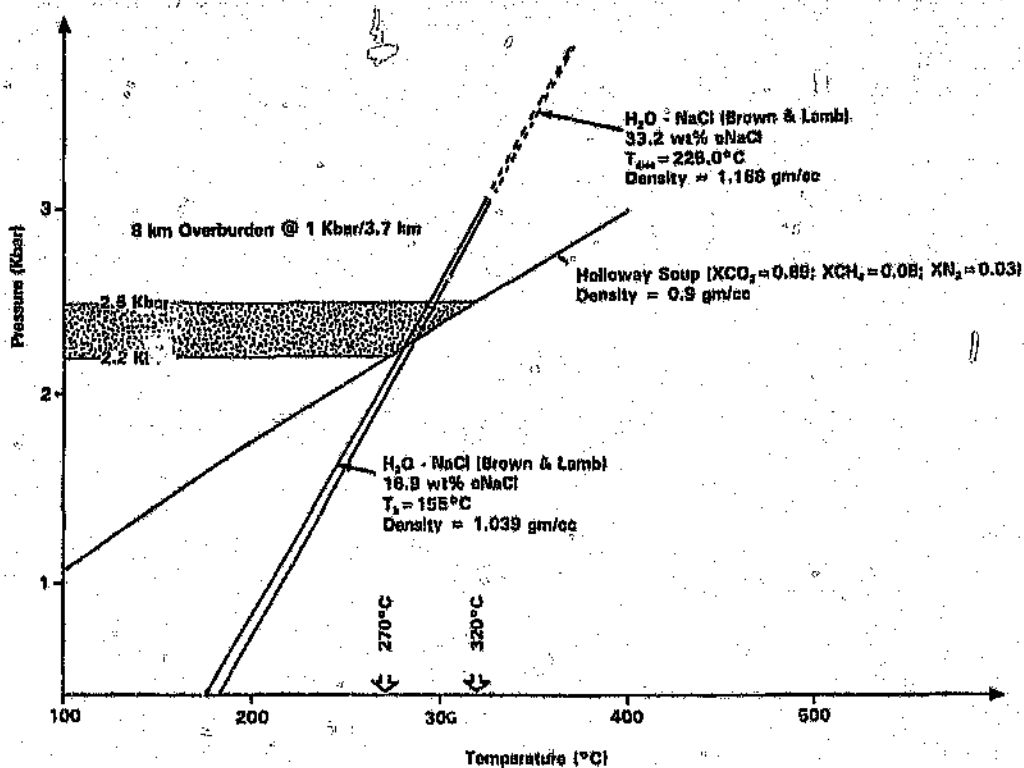


Figure 3.11 Isochore diagram intersecting pressure estimate

Type 2 inclusions - low CO₂ + high salinity. This type of inclusion is characterized by an aqueous liquid, a vapour bubble and at least one daughter crystal at +20°C. Low initial ice melting temperatures, plus the presence of rectangular daughter crystals (probably anhydrite) in addition to halite (or sylvite) indicate that calcium- or magnesium-chlorides are probably also present in these fluids. Carbonic species are frequently present, but are not visible and are only evident in the formation of clathrates that obscure accurate determination of final melting temperatures. This type of inclusion is common in the vertical veins, but has not been observed in the strata bound horizontal veins. Homogenization temperatures (gases into the liquid phase) in these inclusions range from 105° to 165°C while dissolution temperatures for the daughter phases (total homogenization) plot in the range 220° to 245°C, with salinities estimated in excess of 33 wt% eNaCl. It is very common for Type 2 fluid inclusions to decrepitate before total homogenization.

Type 3 inclusions - low CO₂ + low salinity. These inclusions contain an aqueous liquid, with or without a vapour bubble at room temperature, and are believed to be the last-formed inclusion type. They are found in both the milky and clear quartz varieties. However, in the volumetrically minor late-stage clear quartz these inclusions predominate, while carbonic and aqueous saline inclusions are rare. Cross-cutting relations between type 3 and type 1 inclusions suggest that the former post-date the carbonic-rich inclusions. Final melting temperatures centred around -4.5°C (corresponding to a salinity of about 7 wt% eNaCl), and homogenization temperatures ranged from 110° to 135°C (density range 1.00 - 0.98 g/cm³). The absence of vapour bubbles in many of these late fluid inclusions suggest low entrapment temperatures, and confirms the late temporal relations.

Fluid systematics. The main reason for selection of the H₂O-NaCl-CaCl₂ system for modelling of the SPRG fluid inclusion behaviour is the recognition of definite evidence for eutectic melting behaviour at temperatures below -40°C. In many cases melting has obviously taken place by -40°C, as indicated by ice rafts with well defined shapes and boundaries. The feasibility of identifying the fluid composition within this system relies on the recognition of the phase changes predicted by the experimentally constructed phase diagram of Crawford (1981) and Oakes *et al.*, (1990) using the data of Yanatleeva (1946). Upon super-cooling of the SPRG fluid inclusions, two significantly different styles of freezing were observed: (i) the inclusion froze with a sudden movement and the rest of the inclusion remained relatively clear, or; (ii) following the abrupt movement of the bubble the inclusion appeared dark, comprising a fine polycrystalline mass. Fluid inclusions mainly froze between -52° and -80°C. During slow heating of the

fluid inclusion, a mosaic texture appear at temperatures far below the stable eutectic temperature for the system $\text{H}_2\text{O}-\text{NaCl}-\text{CaCl}_2$. This texture could be due to recrystallization (Roedder, 1984), or crystallization of metastable phases in the presence of a liquid (Davis *et al.*, 1990; Spencer *et al.*, 1990), and is the source of much confusion when trying to determine the stable eutectic temperature. The stable eutectic is distinguished by identification of both the "orange peel texture" (T.J. Reynolds, pers. commun., 1991) and observation of a definite liquid at around -52°C . In most inclusions the unequivocal identification of a liquid was only possible several degrees above the actual eutectic temperature.

The next phase to disappear is hydrohalite. It is, however, difficult to distinguish between hydrohalite and ice, due to their similar refractive indexes. In large fluid inclusions (ie $> 10\ \mu\text{m}$ diameter) it was sometimes possible to cycle the temperature between -50° and -30°C , thus growing single crystals of hydrohalite and ice. However, in most cases this was not possible and numerous small crystals were present, making it impossible to recognize the hydrohalite melting temperature. Problems with the definite identification of the hydrohalite melting temperature impeded the determination of $\text{NaCl}/(\text{NaCl} + \text{CaCl}_2)$ ratios, as an error of a few degrees leads to significant misinterpretation of the $\text{NaCl}/(\text{NaCl} + \text{CaCl}_2)$ ratio (Fig. 3.9). In general, final melting of ice was easily recognized after a period of clearing in the inclusion during heating. This phase change can be refined by cycling of the temperature close to the final melting temperature. Despite the accurate determination of the final melting point, salinity is expressed relative as a function of the simpler $\text{H}_2\text{O}-\text{NaCl}$ system, thus, not taking into account the contribution of CaCl_2 to the suppression of the final melting temperature.

The uncertainty involved with the observations and data recorded above, as well as significant changes in phase behaviour that are caused by the presence of other species, places severe constraints on the usefulness of microthermometry as an analytical method for characterizing complex fluid compositions. It is therefore imperative to employ other, more quantitative analytical techniques to determine the gaseous composition of fluids, such as Raman spectroscopy, $\mu\text{FT-IR}$ spectroscopy, quadrupole mass spectroscopy, and gas chromatography. Cation compositions can also be determined using techniques such as ICP-MS and INAA of fluid inclusions (see Chapter 5 for INAA on SPRG fluid inclusions).

3.3. Micro-Raman spectroscopy

3.3.1 Micro-Raman spectroscopy results

Microthermometric data for inclusions from which reliable Raman spectra were obtained are presented in Tables 3.2, 3.3 and 3.4. Clathrate melting temperatures in type 1 inclusions range from 5.0 to 9.0°C, indicating salinities of between 9.1 and 2.0 wt% eNaCl (Bozzo *et al.*, 1973; Seitz *et al.*, 1992). In cases where clathrate melting temperatures could not be obtained, the salinity was determined from the final melting temperature, which for the inclusions in Table 3.2 ranged from -5.0° to -9.2°C, corresponding to salinities of 18.6 to 13.1 wt% eNaCl. The temperature of CO₂ melting lies between -58.8° and -56.6°C, indicating that small amounts of CH₄ and/or N₂ must be present in these inclusions. Molar volumes of the vapour phase in these inclusions range between 68.8 to 48.1 cm³ mol⁻¹.

Raman data for selected aqueous fluid inclusions are presented in Table 3.2, 3.3 and 3.4 and in Figures 3.12 and 3.14. Quantification of the Raman spectra (Table 3.4) indicates that CO₂ is the most abundant gaseous species in these inclusions, with CH₄ being the second most abundant phase. CO₂/CH₄ ratios range from 2.9 to 44.4 for the quartz-hosted fluid inclusions. Molecular water is a poor Raman scatterer and, thus, difficult to identify in fluid inclusions (Wopenka *et al.*, 1990), but its infrared absorption properties makes it easily recognizable using μ FT-IR (see section 3.4). A notable inconsistency in the spectra produced from the two Raman microprobes, is the presence of N₂ detected on the MICRODIL-28 instrument (Table 3.3) and the virtual absence of N₂ in the analyses produced by the DILOR-XY (Table 3.2). In both cases the background spectrum of the mineral host next to and at the same depth as the inclusion were obtained in order to determine the intensity of the Raman bands of atmospheric N₂ and O₂. This discrepancy cannot be explained geologically and points to possible differences in instrument calibration for Nitrogen. Fluid inclusion compositional data obtained from quadrupole mass spectrometer gas analyses also did not detect the presence of N₂ in the inclusions, casting doubt on the accuracy of the MICRODIL-28 results. For this reason data from the MICRODIL-28 (Table 3.3) are not being used for quantitative interpretation in this study. No evidence for the presence of ethane or other evolved hydrocarbon species were found in the Raman spectra. Data obtained for CO₂, using Raman spectrometry, showed two peaks, a stronger peak at $\Delta\nu=1382.6$ to 1385.1 cm⁻¹, and a weaker peak at $\Delta\nu=1278.2$ to 1281.8 cm⁻¹ (Fig. 3.12). No obvious relationship exists between the position of the Raman bands and the melting temperature of solid CO₂. The slight range in peak positions for specific molecular species is probably a function of variation in the internal fluid pressure of the inclusions, as was suggested for other instances by Wopenka *et al.*, (1990). Methane-rich fluids

analysed with the Raman microprobe yielded variable results, but generally showed a well developed peak at $\Delta\nu=2908.8$ to 2910.9 cm^{-1} (Fig. 3.12a). Using the experimental data of Fabre and Couty (1986) a pressure can be approximated from the CH_4 wavenumber. Given an accuracy of ± 0.5 wavenumbers, the accuracy of CH_4 pressure determination at lower pressures (ie 50 - 100 bars) is about ± 20 bar, and approximately ± 300 bar at higher pressures (ie above 500 bars) (Fabre and Couty, 1986). The CH_4 peak position for the SPRG samples at $\Delta\nu=2908.8$ to 2910.9 cm^{-1} correspond to inclusion pressures ranging between 400 and > 1600 bars (Fig. 3.13). The range in internal pressures may be a function of necking down of the inclusions with time, resulting in lower internal pressures. As it is not possible to increase the inclusion pressure by necking down, the Raman peak positions for CH_4 is interpreted as convincing proof for fluid entrapment at high pressures, ie > 1600 bars. This finding corresponds well with the calculation of overburden related lithostatic pressure which indicates pressures around 2.2 to 2.5 kbar.

Table 3.2 Micro-Raman spectroscopic data for samples from the SPRG. Data generated on a DILOR-XY Raman spectrometer at the Centre de Recherches sur la Géologie des Matières Premières Minérales et Énergétiques (CREGU) in Nancy, France

Sample no.	Microthermometric data	Molecular species	Peak position (cm ⁻¹)	Peak area	Mole Frac.	Remarks
FKM075b	$T_m = -56.7$, $T_h = +22.3$, $T_{fm} = -11.7$ $T_{ch} = +5.8$	CO ₂	1384.3	13741	0.1080	L:V = 70:30
		CO ₂	1280.1	5622		CO ₂ /CH ₄ peak area = 1.50
		CH ₄	2910.9	13085	0.0138	
		N ₂	2326.7	5886		N ₂ peak area in air = 6010
		H ₂ O			0.8803	
	$T_m = -57.0$, $T_h = +14.7$, $T_{fm} = -11.7$, $T_{ch} = +5.8$	CO ₂	1384.3	6981	0.2058	CO ₂ /CH ₄ peak area = 1.097
		CO ₂	1280.1	2432		
		CH ₄	2910.9	6365	0.0279	
		N ₂	2326.7	4641		High background values are due to fluorescent matter
		H ₂ O			0.7662	
FKM078a	$T_m = -56.9$, $T_h = +17.7$, $T_{fm} = -9.2$, $T_{ch} = +14.4$	CO ₂	1384.2	1381	0.1115	L:V = 80:20
		CO ₂	1278.2	638		
		CH ₄	2910.9	2212	0.0323	Very broad peak for CH ₄ suggest the presence of other C-H species. Overestimation of CH ₄ concentration due to peak shape.
		H ₂ O			0.8562	
		CO ₂	1278.2	608		
		CO ₂	2910.9	331		
		CH ₄	2910.9	1289		
		H ₂ O			0.8562	
		CO ₂	1278.2	608		
		CO ₂	2910.9	331		

Table 3.2 (continue)

Sample no.	Microthermometric data	Molecular species	Peak position (cm ⁻¹)	Peak area	Mole Frac.	Remarks
FKM064a	$T_m = -56.8$, $T_h = +28.7$, $T_{em} = -12.0$, $T_{ch} = +15.0$	CO ₂	1383.5	12343	0.0473	CO ₂ /CH ₄ =5.13
		CO ₂	1279.3	4320		
		CH ₄	2909.6	2404	0.0005	
		H ₂ O			0.9521	
		CO ₂	1383.5	8463		
MGL034	$T_m = -58.8$, $T_h = +2.3$, $T_{em} = -15.0$	CO ₂	1279.3	4089		CO ₂ /CH ₄ =5.24 L:V = 60:40
		CO ₂	1383.5	8631	0.0949	
		CO ₂	1279.3	3482		
		CH ₄	2908.9	4613	0.0079	
		N ₂	2326.7	5097		
		H ₂ O			0.8973	
		CO ₂	1383.5	3859	0.2289	
		CO ₂	1279.3	1194		
		CH ₄	2988.9	1999	0.0155	
		H ₂ O			0.7556	
LJM090 (Fig. 3.5)	$T_m = -56.8$, $T_h = +22.4$	CO ₂	1385.1	1676	0.0862	Isolated fluid inclusion, no obvious relationship to other inclusions
		CO ₂	1281.8	238		
		CH ₄			0.0041	
		H ₂ O			0.9087	
		CO ₂	1385.1	1697		
	$T_m = -55.7$, $T_h = +3.2$	CO ₂	1282.6	224		Fluid inclusion occurring along secondary trail

Table 3.2 (continue)

Sample no.	Microthermometric data	Molecular species	Peak position (cm ⁻¹)	Peak area	Mole Frac.	Remarks
THH029	$T_m = -57.8$, $T_h = +23.9$, $T_m = -11.4$, $T_m = +6.1$	CO ₂	1384.3	12304	0.0843	
		CO ₂	1280.1	5060		
		CH ₄	2910.9	10934	0.0063	
		N ₂	2326.7	4792		
	$T_m = -55.3$, $T_h = +5.7$, $T_m = -12.5$, $T_m = +5.0$	H ₂ O			0.9094	
		CO ₂	1384.3	9452		
		CO ₂	1280.1	4516		
		CH ₄	2910.9	5925		
		CO ₂	1384.3	20883	0.0959	
		CO ₂	1279.3	9362		
		CH ₄	2908.9	7461	0.0042	
		H ₂ O			0.8999	
		CO ₂	1384.3	14971		
		CO ₂	1279.3	7075		
CLW022a	$T_m = -57.8$, $T_h = +27.9$	CH ₄	2908.9	4661		
		CO ₂	1385.1	1561	0.0740	
		CO ₂	1280.1	707		
		CH ₄			0.0023	
		N ₂	2326.7	3581		
CLW022a	$T_m = -57.9$, $T_h = +3.4$	H ₂ O			0.9237	
		CO ₂	1384.3	7345	0.0827	
		CO ₂	1280.1	3338		
		CH ₄	2910.9	7322	0.0176	
		H ₂ O			0.8997	
		CO ₂	1384.3	5039		
		CO ₂	1280.1	2416		

Table 3.2 (continue)

Sample no.	Microthermometric data	Molecular species	Peak position (cm ⁻¹)	Peak area	Mole Frac.	Remarks
GLS052	$T_m = -56.5$, $T_h = +14.8$	CH ₄	2910.9	3456		
		CO ₂	1385.1	7395	0.3472	
		CO ₂	1280.1	3394		
		CH ₄	2909.2	1170	0.0116	
		H ₂ O			0.6412	
	$T_m = -56.8$, $T_h = +20.0$	CO ₂	1385.1	3407		
		CO ₂	1280.1	1432		
		CO ₂	1384.7	1732	0.2534	
		CO ₂	1280.4	421		
		CH ₄			0.0081	
VLH040	$T_m = -57.3$, $T_h = +11.4$	H ₂ O			0.7385	
		CO ₂	1383.5	13824	0.1994	
		CO ₂	1279.3	8284		
		CH ₄			0.0063	
		H ₂ O			0.7943	
		CO ₂	1383.5	11967		
		CO ₂	1279.3	5885		
		CO ₂	1382.6	14569	0.1384	
CLS038a	$T_m = -58.8$, $T_h = +20.5$	CO ₂	1279.3	6433		
		CH ₄	2908.9	9715	0.0127	
		H ₂ O			0.8488	
		CO ₂	1382.6	10943		
		CO ₂	1279.3	5316		
		CH ₄	2908.9	7272		

Table 3.3 Micro-Raman spectroscopic data for samples from the SPRG. Data generated on a MICRODIL-28 spectrometer at the Department of Earth Sciences, Free University of Amsterdam, The Netherlands

Sample no.	Microthermometric results	Molecular species	Peak position (lower limit)	Peak position (upper limit)	Peak area	Int. time	Remarks
SUN003		CO ₂	1072	578	1850	5	66 mole% CO ₂ ; CO ₂ /CH ₄ =3.3
		N ₂			137	5	14 mole% N ₂ ; N ₂ /CH ₄ =0.7
		CH ₄			1493	5	20 mole% CH ₄
		N ₂ (matrix)			-	5	
CLW022a	T _m =-57.8, T _b =+27.9	CO ₂	4573	2175	6748	3	98 mole% CO ₂ ; CO ₂ /CH ₄ =49
		N ₂			-	5	
		CH ₄			360	3	2 mole% CH ₄
		CH ₄			1067	3	4 mole% CH ₄ ; CO ₂ /CH ₄ =24
		N ₂			-	3	
VLH040	T _m =-57.3, T _b =+11.4	CO ₂	6050	2910	8976	3	96 mole% CO ₂
		CO ₂	4992	2462	7454	3	100 mole% CO ₂
		N ₂			38	3	
		CH ₄			-	3	
		N ₂ (matrix)			67	3	
LJM090	T _m =-56.8, T _b =+22.4	CH ₄			-	3	Pure H ₂ O
		N ₂			-	3	
		CO ₂			-	3	
FKM076a	T _m =-56.9, T _b =+17.7 T _{ch} =+14.4, T _f =9.2	CO ₂	2841	1410	4259	3	87 mole% CO ₂ ; CO ₂ /CH ₄ =8.7
		N ₂			104	5	3 mole% N ₂ ; N ₂ /CH ₄ =0.3
		CH ₄			1445	3	10 mole% CH ₄
		N ₂			-	5	

Table 3.3 (continue)

Sample no.	Microthermometric results	Molecular species	Peak position (lower limit)	Peak position (upper limit)	Peak area	Int. time	Remarks
THH029	$T_m = -57.8$, $T_h = +23.9$	CO ₂	7303	3923	11226	3	93 mole% CO ₂ ; CO ₂ /CH ₄ =23.3
	$T_{cs} = +6.1$, $T_f = -11.4$	N ₂			120	3	3 mole% N ₂ ; N ₂ /CH ₄ =0.75
		CH ₄			1569	3	4 mole% CH ₄
MGL034	$T_m = -58.8$, $T_h = +2.3$	N ₂ (matrix)			-	3	
	$T_f = -15.0$	CO ₂	2011	920	2931	3	almost pure CO ₂
		N ₂			-	3	
GLS052	$T_m = -56.8$, $T_h = +20.0$	CH ₄			32	3	traces <0.5 mole% CH ₄
		CO ₂	4540	2189	6729	3	98 mole% CO ₂ ; CO ₂ /CH ₄ =49
		N ₂			63	5	
FKM076b	$T_m = -56.7$, $T_h = +22.3$, $T_{cs} = +5.8$	CH ₄			486	3	2 mole% CH ₄
	$T_f = -11.7$	N ₂ (matrix)			77	5	
		CO ₂	2439	1266	3705	3	91 mole% CO ₂ ; CO ₂ /CH ₄ =10.1
OFG001		N ₂			-	5	
		CH ₄			1101	3	9 mole% CH ₄
		CH ₄			790	3	7 mole% CH ₄ ; CO ₂ /CH ₄ =13.3
		N ₂			-	5	
		CO ₂	2213	1020	3233	3	93 mole% CO ₂

Table 3.4 Micro-Raman spectroscopy results in mole%. Data generated using a DILOR-XY Raman spectrometer. All values are normalized to 100%

Sample no.	Molar volume (cm ³ /mole)	CO ₂	CH ₄
FKM076b	65	87.675	12.325
FKM076a	55	74.534	25.466
FKM064a	85	97.797	2.203
MGL034	50	94.391	5.609
LJM090	60	100.000	0.000
LJM090	50	100.000	0.000
THH029	80	88.418	11.582
THH029	50	95.121	4.879
CLW022	90	100.000	0.000
CLW022	50	87.527	12.473
GLS052	55	96.729	3.271
GLS052	60	100.000	0.000
VLH040	55	100.000	0.000

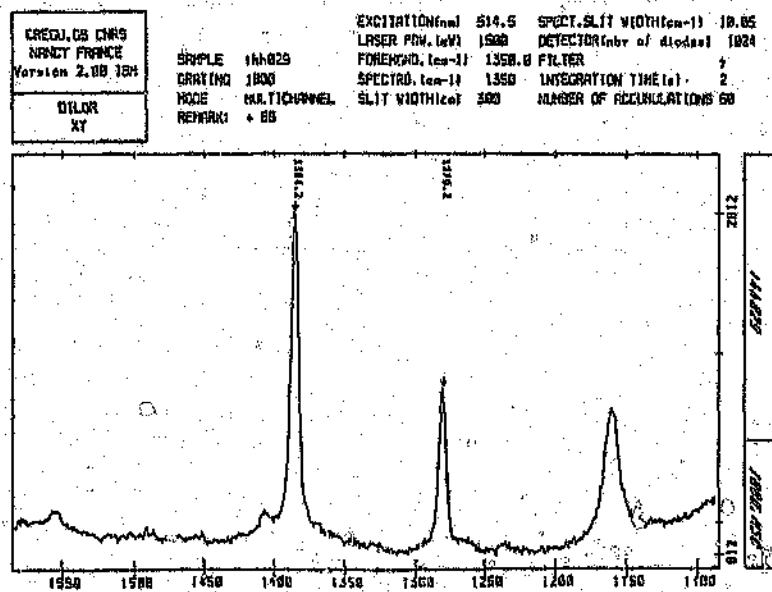
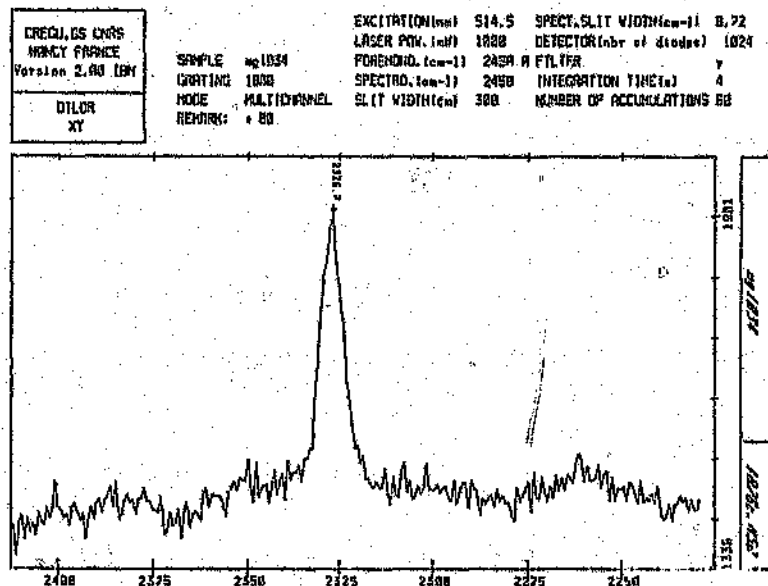


Figure 3.12 Selected Raman spectra for quartz hosted fluid Inclusions from various samples from the SPRG. A complete collection of Raman spectra for SPRG fluid Inclusions are presented in Appendix 3.

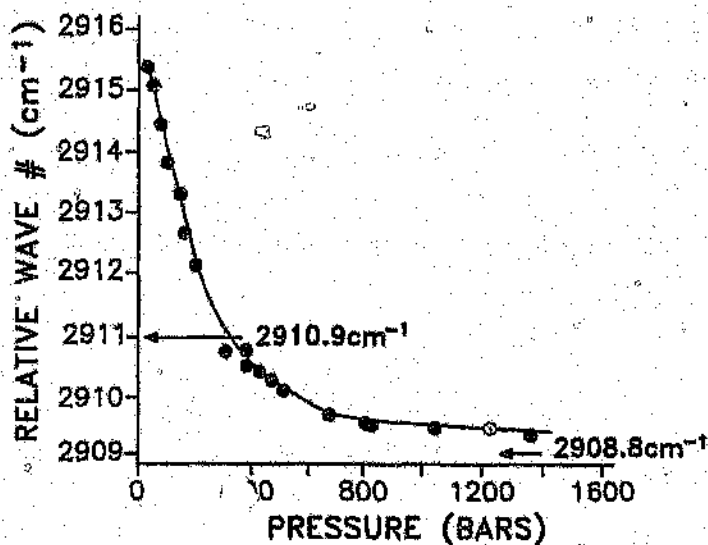


Figure 3.13 The relationship between the relative wavenumber of CH_4 , as determined from the laser micro-Raman spectroscopy, and the inclusion pressure for SPRG samples. Experimental data from Fabre and Couty (1986).

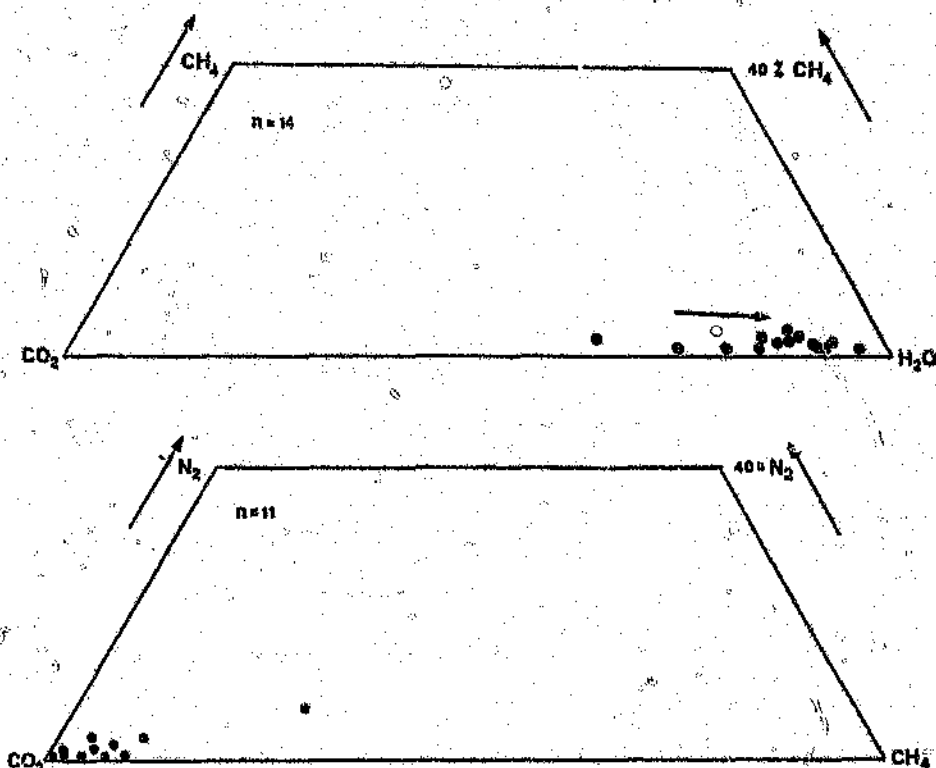


Figure 3.14 Fluid composition from Raman spectra (a) CH_4 - H_2O - CO_2 ternary diagram, and (b) N_2 - CH_4 - CO_2 ternary diagram.

3.4 Micro-Fourier Transform Infrared analysis (μ FT-IR)

Both micro-Raman and μ FT-IR are useful analytical techniques for studying fluid inclusion compositions qualitatively and quantitatively in a non-destructive manner. μ FT-IR is the preferred technique in the study of hydrocarbon-bearing fluid inclusions that tend to fluoresce under visible laser irradiation, and, where micro-Raman might cause heat-sensitive samples to thermally degrade. However, μ FT-IR cannot be used for the detection of IR-inactive diatomic homonuclear species such as H_2 , N_2 , or O_2 , nor can it detect species with very small IR absorptivities, such as H_2S . The main reason for undertaking the present μ FT-IR investigation was to scrutinize the CO_2 -rich type 1 fluid inclusions for the possible presence of hydrocarbon species not detected by Raman spectroscopy.

Infrared spectra were recorded with a Bruker IFS 88 Fourier transform infrared spectrometer, which is equipped with a Bruker A 590 microscope (Barres *et al.*, 1987). This microscope is fitted with a narrow band, mercury-cadmium-telluride (MCT) detector with a 100 μm diameter window cooled to $-196^\circ C$. The available spectral detection range lies between 5600 and 700 cm^{-1} . The diameter of the analysed section ranges from 20 to 80 μm , using a X15 objective magnification. Interferograms were obtained from 400 accumulations per 200 seconds with a 4 cm^{-1} spectral resolution. All the spectra are represented in terms of absorbance versus wave numbers ($\ln\text{ cm}^{-1}$). Two successive scans are necessary (reference and sample) because of the availability of only one beam. The ratio of the two spectra permits the determination of the transmission of the sample. Spectra of individual fluid inclusions were obtained through the microscope set with a 20 μm aperture and operated in transmission mode. The reference used for fluid inclusions is a single sylvite crystal, which is transparent in the infrared range (Pironon and Barres, 1990). Atmospheric H_2O and CO_2 are sometimes visible on the spectra, but their contributions are removed by peak subtraction of the relevant spectra.

An example of an infrared spectrum is presented in Figure 3.15. A complete collection of SPRG μ FT-IR spectra are presented in Appendix 3. The resolution of the obtained spectral information from inclusion fluids was affected by the infrared absorption characteristics of the quartz host. Quartz exhibits very low infrared absorbance from 4000 cm^{-1} to 2000 cm^{-1} , but starts to absorb strongly at lower wavenumbers (Fig. 3.15). It is relatively transparent in the important C-H stretch region at about $2800\text{--}3000\text{ cm}^{-1}$. The infrared spectra of individual quartz-hosted fluid inclusions from SPRG show a characteristically strong and sharp band at 2337 cm^{-1} , corresponding to the peak position of pressurized CO_2 (O'Grady *et al.*, 1989). The broad absorption band in the $3000\text{--}3800\text{ cm}^{-1}$ stretch is due to the

presence of water. The absence of any well defined spectral peaks in the 2800-3000 cm^{-1} C-H symmetric and asymmetric stretch of CH_3 and CH_2 , the 3000-3100 cm^{-1} C-H stretch of aromatic compounds, suggest that hydrocarbon species are absent. However, the shoulder of the strong absorption band produced by water is not always smooth and slight irregularities in the absorption curve (observed in samples CLW022, SUN003, LJM090) may indicate the presence of minor amounts of C-H species. The methane absorption band is obliterated by the strong absorbance of quartz which includes the 1300 cm^{-1} spectral band. Thus, the main conclusion to be drawn from the $\mu\text{FT-IR}$ study is confirmation of the absence of significant amounts of evolved hydrocarbon species in the SPRG fluid inclusions and reiterating the dominance of CO_2 as a gaseous phase.

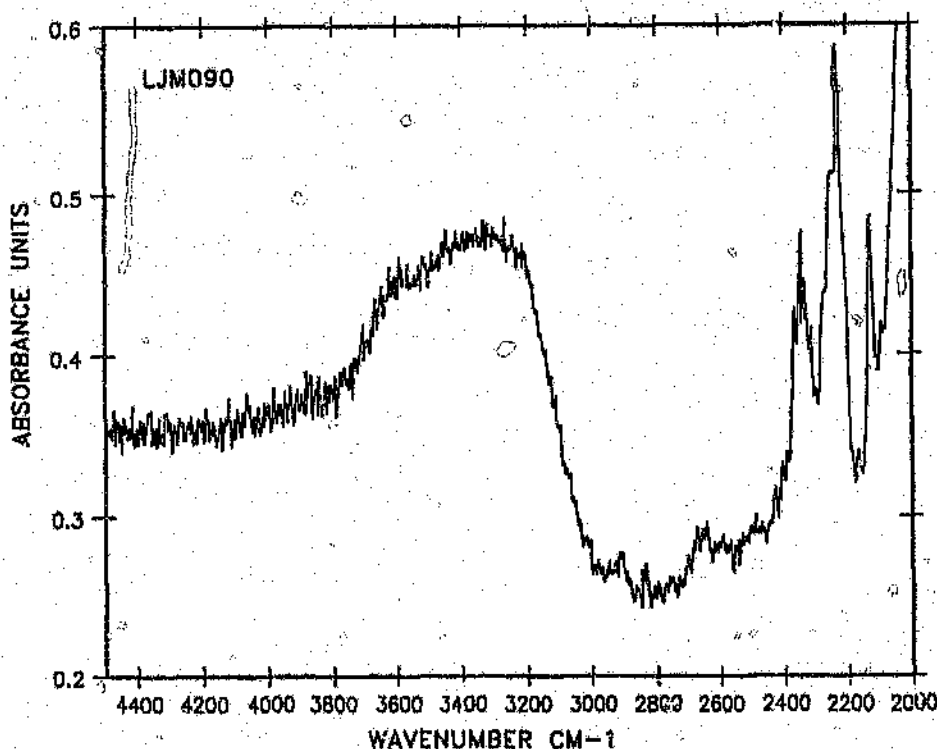


Figure 3.15 A selected micro Fourier Transform Infrared spectrum for quartz-hosted fluid inclusions from the SPRG.

3.5 Quadrupole Mass Spectrometer Fluid Inclusion Gas Analyses

3.5.1 QMS results

Results from bulk fluid inclusion gas analyses are presented in Table 3.5. H_2O is by far the dominant volatile component in the Sable-Pilgrim's Rest fluid inclusions and typically comprises 95 - 99 mole% of the inclusion fluid. CO_2 comprises most of the remaining volatile component (varying between 0.1 - 15 mole%), while the other gases are generally present in amounts smaller than 1 mole%. The vertical veins and the horizontal veins from lower down in the stratigraphy are relatively enriched in Ar and HCl, whereas the upper veins contain higher CO_2 and CH_4 concentrations (Fig. 3.16(a & b); Table 3.5). Furthermore, CH_4/CO_2 ratios for inclusion fluids from horizontal veins are significantly higher than vertical veins. High HCl concentrations in vertical veins (Fig. 3.17a) correlate well with high salinities, as indicated by microthermometric measurements, and are probably a result of the hydrolysis of NaCl at high temperatures (eg Hanf and Sole, 1970). The dominant fluid population in the SPRG goldfield exhibits variable CO_2/Ar ratios, and is depleted in N_2 . Comparison with normalized populations of present-day air and air-saturated water, suggests that large-scale fluid interaction with air-saturated meteoric water is unlikely. The average N_2/Ar ratio for the vertical veins is 13.5, which is significantly lower than values for air (84) or air-saturated ground water (38) (Heaton and Vogel, 1981). The N_2/Ar ratios for the horizontal veins are around 43.

Decrepitation analyses of individual fluid inclusions hosted within single gold grains (Fig. 3.18) yielded widely variable CO_2/H_2O ratios (Table 3.6) in spite of the fact that fluid inclusions decrepitated over a relatively restricted temperature range. These fluid inclusions are thought to represent a single fluid generation (see section 3.5.5), as it is unlikely that secondary fractures penetrated a mineral that is as malleable as gold. Thermal decomposition of minerals and organic compounds can also be a significant source of gases in some samples. A distinction between these two gas sources can be made, based on the differences in morphology of the gas release patterns. The time it takes for the signal response to return to background levels is significantly longer in the case of thermal decomposition of solid phases, than it is for individual inclusion fluids which immediately decay to background values (Fig. 3.19). A gradual release pattern has the potential to conceal fluid release from individual fluid inclusions. Organic inclusions or daughter crystals commonly start to decompose at low temperatures (ie around 350°C) yielding large amounts of CO_2 (Graney and Kesler, *in prep.*). Sulphide and carbonate phases thermally decompose at higher temperatures (> 750°C) yielding H_2S , SO_2 and CO , CH_4 , respectively. Detailed identification of the various solid phases responsible for liberation of these

gaseous phases, based on the thermal decrepitation temperatures is not yet possible (Graney and Kesler, *in prep.*) using the QMS method, although similar attempts, utilizing gas chromatography have been successful.

Evidence which support the contention that the quadrupole mass spectrometer response do indicate individual fluid inclusion bursts, are provided by scanning electron microscope images of freshly cut surfaces of gold grains that has been heated in the QMS to approximately 900°C (melting point of gold = 1064.43°C). These surfaces show bulges and craters that could only have been caused by the decrepitation of individual fluid inclusions (Fig. 3.18), thus, convincingly linking QMS response to the decrepitation of individual fluid inclusions.

Table 3.5. Composition of quartz hosted inclusion fluids in mole % as determined by quadrupole mass spectrometer gas analyses. Abbreviations for the different localities are as follow: AST - Astra; CLW - Clewer West; FKM - Frankfort; GLS - Glynns Lydenburg Sheba; GRR - Gregory; JBH - Jubilee; LJM - Little Joker; MGL - Morgenzon; NSM - Nestor; OGM - Olifantsgeraamte; SUD - Sudwala; SUN - Sunlight; VLH - Vaalhoek. Exact localities of samples obtained from the British Museum (Natural History) (BM) are unknown

Sample	H ₂ O	CO ₂	CH ₄	C _n H _{2m+2}	N ₂	Ar	H ₂ S	SO ₂	HCl	Total
AST109	98.641	3.216	0.078	0.000	0.0000	0.0065	0.0043	0.0007	0.0520	99.998
BM184A	99.538	0.249	0.053	0.069	0.0000	0.0067	0.0170	0.0091	0.0560	99.998
BM184B	99.744	0.127	0.050	0.008	0.0169	0.0019	0.0074	0.0019	0.0430	100.000
BM7384	98.635	1.088	0.157	0.008	0.0138	0.0009	0.0250	0.0005	0.0720	99.999
BRH112	91.748	7.945	0.070	0.018	0.187	0.012	99	5	72	
CLH040	86.922	12.526	0.049	0.016	0.348	0.026	0.024	23	0.020	
CLW016	96.969	2.814	0.128	0.017	0.0235	0.0021	0.0047	0.0020	0.0370	99.998
FKM075a	88.577	11.203	0.128	86	0.064	54	0.012	-	38	
FKM075B	84.634	14.930	0.394	0.007	0.0000	0.0009	0.0089	0.0029	0.0120	99.990
FKM076B	94.374	5.363	0.214	0.015	0.0000	0.0026	0.0043	0.0026	0.0210	99.997
GLS052	94.67	5.210	0.046	0.009	0.0181	0.0040	0.0059	0.0015	0.0310	99.996
GRR107	99.473	0.299	0.001	0.013	0.108	0.012	66	1	43	
GRR300	98.536	0.651	0.055	0.097	0.553	0.066	0.021	20	0.010	
GRR300	99.482	0.330	0.079	0.021	0.0251	0.0085	0.0085	0.0025	0.0430	99.999
JBH043	89.518	10.313	0.114	0.011	0.0000	0.0020	0.0051	0.0010	0.0290	99.993
LJM090	93.792	5.951	0.178	0.025	0.0000	0.0000	0.0045	0.0007	0.0330	99.984
MGL033	98.202	1.628	0.052	0.013	0.0820	61	0.011	5	44	
MGL204	88.824	0.982	0.043	0.079	0.0000	0.0017	0.0050	0.0031	0.0520	99.999

Table 3.5 continue

Sample	H ₂ O	CO ₂	CH ₄	C _n H _{2n+2}	N ₂	Ar	H ₂ S	SO ₂	HCl	Total
NSM093	99.340	0.529	0.053	0.019	0.0000	0.0048	0.0031	0.0008	0.0500	100.000
NSM098	83.758	15.422	0.240	0.035	0.505	0.024	94	-	56	
NSM098	88.794	10.534	0.561	0.023	0.0000	0.0077	0.0069	0.0024	0.0620	99.991
OGM078	96.491	1.147	0.081	0.074	0.1067	0.0108	0.0140	0.0027	0.0710	99.998
S1017	97.453	2.38	0.081	0.007	0.0181	0.0039	0.0055	0.0012	0.048	99.998
SUD211	99.010	0.758	0.029	0.047	0.0805	0.0041	0.0045	0.0019	0.0650	99.999
SUD211	96.765	2.566	0.048	0.120	0.422	0.049	0.018	17	90	
SUN003	98.661	0.883	0.047	0.017	0.146	0.015	0.060	79	1	
SUN003	99.150	0.733	0.031	0.019	0.0000	0.0036	0.0032	0.0002	0.0590	100.000
VLH040a	97.421	2.521	0.025	0.009	0.0000	0.0024	0.0041	0.0022	0.0130	99.998
VLH040b	93.265	6.607	0.021	0.014	0.0481	0.0036	0.0055	0.0017	0.0290	99.995
VLH040c	89.951	9.677	0.024	0.025	0.233	0.029	0.020	15	0.021	

Table 3.6. Quadrupole mass spectrometer gas analyses of individual fluid inclusions contained in pure gold, presented in mole %

H ₂ O	CO ₂	CO ₂ /H ₂ O
98.2	1.8	0.018
98.9	3.1	0.032
98.5	1.5	0.015
98.2	1.8	0.018
98.5	1.5	0.015
95.1	3.9	0.041
96.2	3.8	0.040
76.9	23.1	0.300
68.8	31.2	0.453
83.7	16.3	0.195
71.0	29.0	0.408
96.3	3.7	0.038
93.1	6.9	0.074
68.6	31.4	0.458
90.2	9.8	0.109
91.4	8.6	0.094
93.7	6.6	0.071
80.6	19.4	0.241
64.9	35.1	0.541
94.3	5.7	0.060
58.9	41.1	0.698
86.8	13.2	0.152

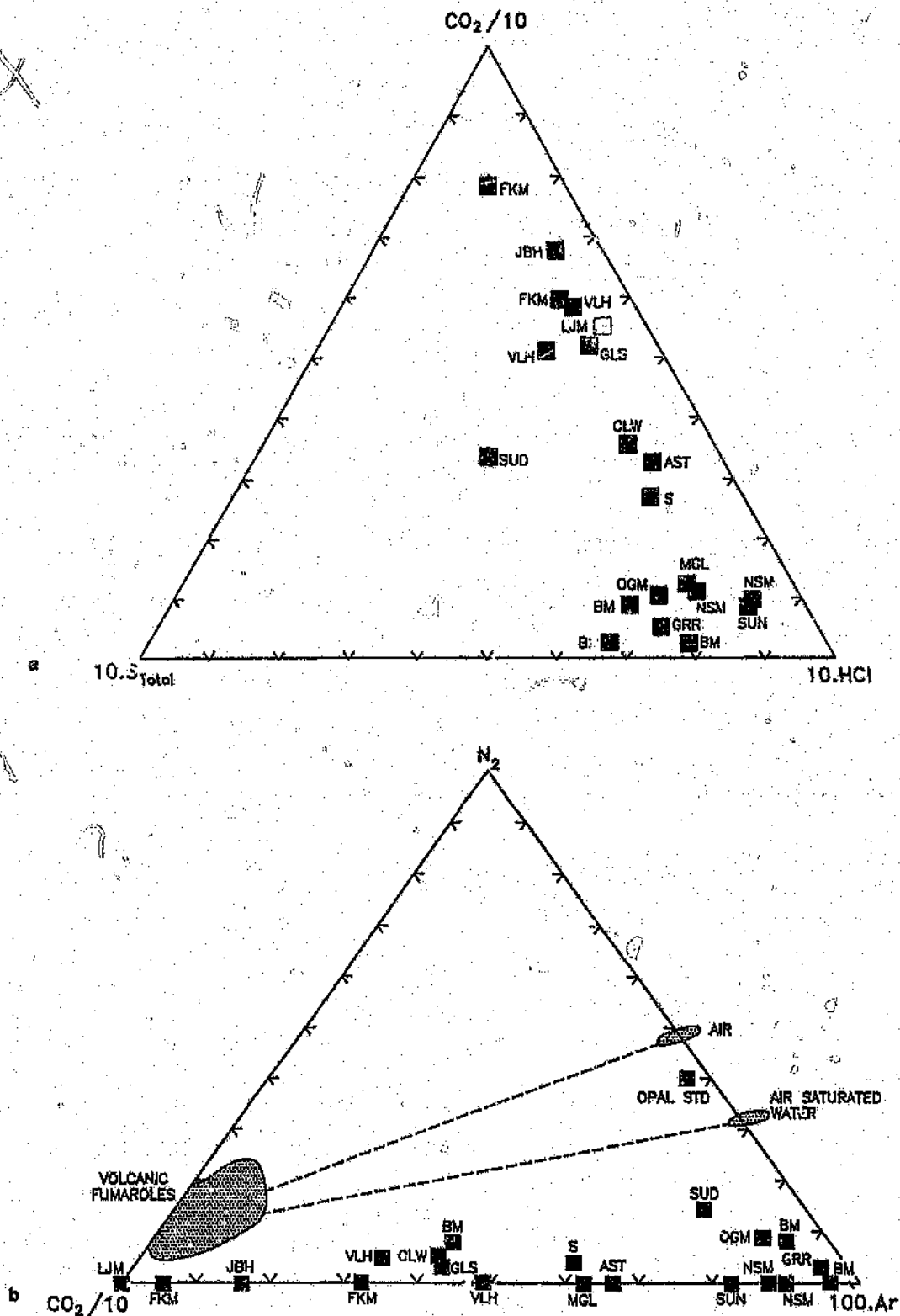


Figure 3.16 (a) Relative CO_2 , S_{Total} and HCl contents of hydrothermal gases from quartz specimens of the Sabie-Pilgrim's Rest goldfield. (b) Ternary diagram presenting the CO_2 , N_2 and Ar contents of inclusion fluids from the Sabie-Pilgrim's Rest goldfield.

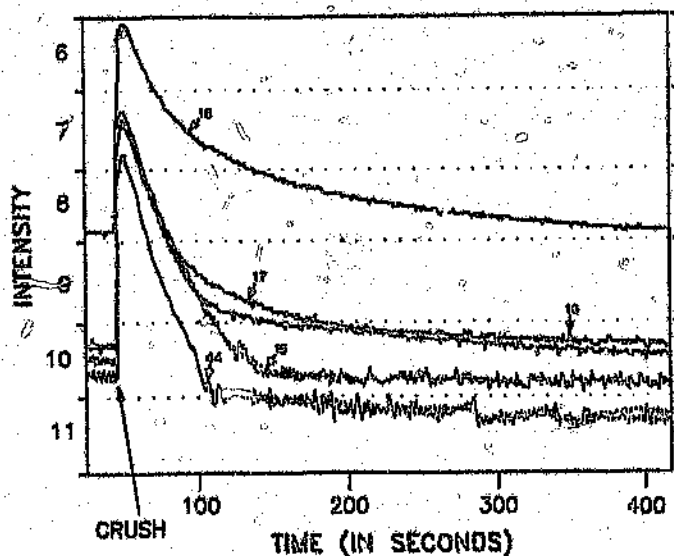


Figure 3.17 Signal response from bulk quadrupole mass spectrometer *crush* analyses from double polished quartz wafers (100 - 150 μm thickness)

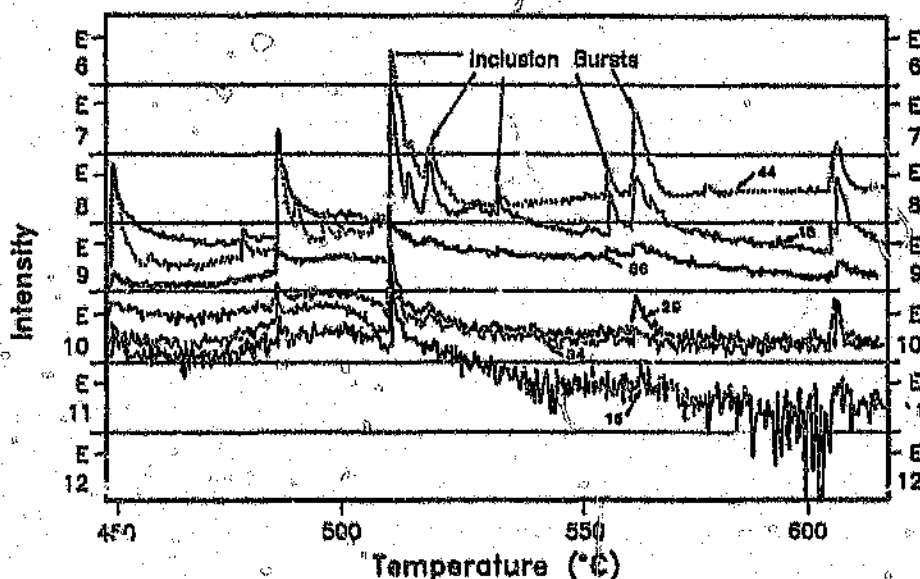


Figure 3.18 Signal responses from quadrupole mass spectrometer analyses of individual fluid inclusion bursts from a native gold grain, showing variable $\text{CO}_2/\text{H}_2\text{O}$ ratios (CO_2 - mass 44; H_2O - mass 18). Vertical scale is the negative logarithm of the SEM current. Horizontal scale indicate temperature (in $^{\circ}\text{C}$) relative to the number of QMS cycles. Other masses monitored are identified on the diagram.

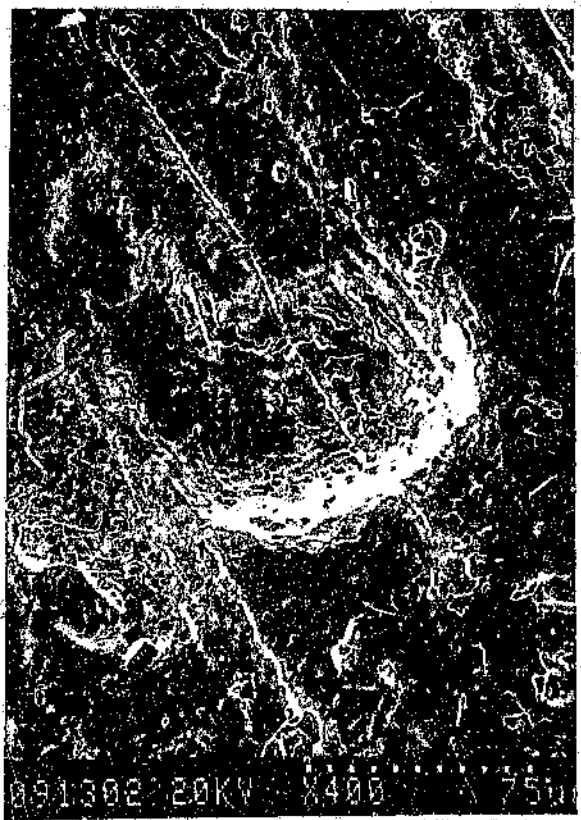


Figure 3.18a Scanning electron microscope images of decrepitated fluid inclusions on the surface of gold grains. Artificially formed striations have been deformed during heating in the QMS-linked Vycor® tube, suggesting that the QMS peak responses shown in Figure 3.18 actually relate to decrepitation of individual fluid inclusions.

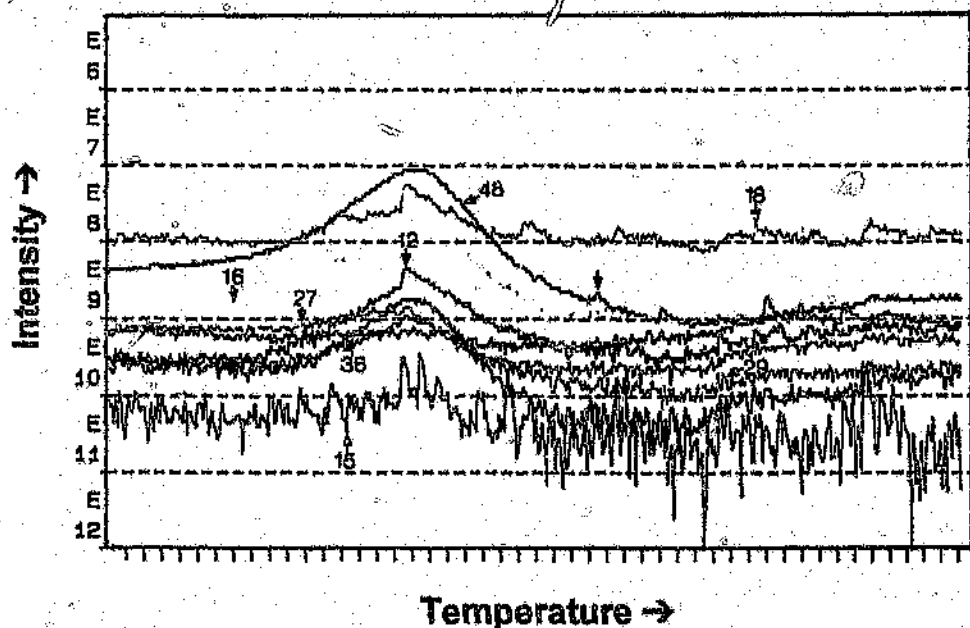


Figure 3.19 Signal responses from quadrupole mass spectrometer analyses of individual fluid inclusion bursts from a native gold grain. Vertical scale is the negative logarithm of the SEM current. Horizontal scale indicate temperature (in °C) relative to the number of QMS cycles. Masses monitored are identified on the diagram. The bell-shaped curve indicates the degassing of solid inclusions hosted within the gold.

3.5.2 Interpretation of QMS results

Few studies have been published on the gaseous components of Proterozoic ore deposits. In contrast there is much information available on meteoric and crust-derived rare gases in groundwaters and geothermal fluids (eg Norman and Musgrave, 1994; Giggenbach, 1986; Ozima and Podosek, 1983). A problem arises when trying to infer an origin for the QMS gas analysis in the SPRG by comparing the latter results with modern estimates of air-saturated ground waters, formation waters, magmatic waters or atmospheric compositions. A possible solution would be to evaluate the noble gas compositions, as noble gas compositions have not evolved significantly through time (eg Phinney, 1972; Alexander, 1975; Ozima and Podosek, 1983). Therefore, the early atmosphere either had a similar composition, in terms of the noble gases, compared to the modern atmosphere, or the observed concentrations actually represent modern air composition. The first option is not implausible as it may imply a very rapid

formation of the atmosphere (Ozima and Podosek, 1983), therefore comparison of SPRG noble gas QMS results with published gas data for more recent mineral deposits and modern atmospheric composition is not completely inappropriate. However, comparison of the other gases with modern examples in order to determine a fluid source, should be used with circumspection.

Giggenbach (1986) introduced the concept that N_2 -Ar-He ratios can distinguish between the magmatic, crustal and meteoric gaseous constituents in geothermal fluids. The most significant aspect of the Giggenbach (1986) proposal is that higher N_2 indicates magmatic gas components in geothermal fluids, except in the case of volatiles from basalts associated with divergent plate boundaries that are He rich (Giggenbach and Glover, 1992). The N_2 signature of magmatic gases were corroborated by Chiba (1991) in his definition of magmatic gases based on the composition of the volcanic discharge from Mt. Usu, Hokkaido, Japan. Groundwaters contain noble gas concentrations near those of pure meteoric waters (Mazor, 1972; Ozima and Podosek, 1983). Geothermal waters may have in addition to the average meteoric water noble gas concentrations, an increased radiogenic Ar content. In general the additional radiogenic Ar constitutes less than half of the dissolved Ar (Mazor, 1988; Kennedy *et al.*, 1985). As far as nitrogen in ground waters is concerned, it is only possible to specify the meteoric component. The N_2 /Ar ratio in air-saturated water (ASW) is approximately 38, but may be as high as 50 as a result of incorporated air (N_2 /Ar=84) (Heaton and Vogel, 1981). The average N_2 /Ar ratio for the vertical veins is 13 and for the horizontal veins the average ratio equals 43. A simple comparison suggests that SPRG data involves a significant meteoric water component, but not enough to explain the distinct difference in N_2 /Ar ratios between the vertical and horizontal veins. However, the average concentration of nitrogen in rocks are low: 21 ppm in granite; 30 ppm in basalt; 73 ppm in carbonate rocks; 120 ppm in sandstone, and; 602 ppm in shale (Wlotzka, 1972). These data suggest that the fluid inclusion gas chemistry may reflect the host rock composition, as the high N_2 /Ar ratios in the horizontal veins correspond to high N_2 values in shale and carbonate host rocks, whereas the lower ratios of the granite hosted vertical veins compare favourably with the low N_2 content in granites. In comparison, geothermal system associated with recent magmatic activity have N_2 /Ar > 100. This is the case for many of the geothermal systems in New Zealand (Giggenbach, 1986), Japan (Hedenquist and Aoki, 1991) and Ethiopia (Giggenbach and La Guern, 1976). Analyses of volcanic gases, using improved sampling methods which eliminates most air contamination (Hirabayashi, 1986), show N_2 /Ar ratios between 200 and 900 (Corazza, 1986). Norman and Musgrave (1994) showed that the N_2 /Ar ratio for typical sedimentary rock hosted ore deposits are slightly above the ASW value. When comparing the SPRG data with those data acquired for other

geological environments there seems to be no correlation. Apart from the indication that the SPRG ratios reflect host lithologies, the latter samples appear to be anomalously enriched in Ar, rather than depleted in N₂, which suggest that the N₂-Ar-He system is inappropriate as a fluid source tracer. Norman and Musgrave (1994) also stated that the use of the N₂-Ar-He ternary as a tracer is not definitive, and argued that supportive data in the form of light stable isotopes, noble gas isotopes and geological setting is essential.

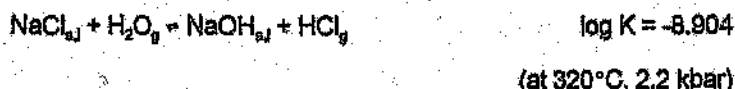
Another difference detected in the gas chemistry of vertical and horizontal veins is the higher CH₄/CO₂ ratios in the horizontal carbonate hosted veins compared to the granite hosted vertical veins. Higher CH₄/CO₂ ratios in the carbonate hosted horizontal veins suggests a contribution of carbonic species from the dolomitic host rock as a result of interaction with the hydrothermal fluid. Another possible source of CH₄ is thermocatalysis of organic matter within the vein-associated shale layers (Weiham, 1988). Although CH₄-rich fluids can be produced during low grade metamorphism of organic-rich sediment (Mullis, 1979; 1987) and at high grade metamorphic conditions (Hollister and Burruss, 1978), it seems more likely that the CH₄ within the SPRG quartz veins was produced *in situ* during fluid-rock interaction. Reaction between CO₂-bearing saline aqueous fluids and carbon within the host-rocks would produce CH₄ by a reaction such as:



Furthermore, the vertical veins show enhanced Ar and HCl concentrations compared to the horizontal veins. In theory the proportion of Ar resulting from the radiogenic decay of potassium, and its subsequent incorporation into fluid inclusions, would be much larger in granite hosted veins than in sediment hosted veins. This distribution pattern in the SPRG, also indicates that gas chemistry reflects the host lithologies. It is unlikely, however, that all the Ar could have been produced from the decay of potassium. Using the decay constants of Heaman and Ludden (1991) a concentration of ~100 ppm Ar would require decay of 100 000 ppm K over a period of 2000 Ma. Although the amount of self-generated Ar produced in this calculation seems significant, the K content in fluid inclusions, in general, is in the range of 1000 to 10000 ppm. In this perspective the contribution of radiogenic Ar is less significant, but still adequate to account for the difference between the vertical and horizontal veins.

High HCl concentrations in vertical veins (Fig. 3.16a) correlate well with high salinities, as indicated by microthermometric measurements. This relationship may be the result of the progressive

hydrolysis of NaCl at higher temperatures, the basis for which was experimentally demonstrated by Hanf and Sole (1970). The hydrolysis of sodium chloride at high temperatures may be described by the general equation:



The equilibrium partial pressure of the HCl/H₂O ratio is proportional to the activity of NaOH (Kazahaya and Shinohara, 1991), with a smaller a_{NaOH} yielding higher HCl partial pressures. However, the activity of NaOH may also be reduced by the presence of other acid gases such as CO₂ and SO₂ (Kazahaya and Shinohara, 1991). A typical reaction that controls the a_{NaOH} can be written as:



A reduction in a_{NaOH} with an increased CO₂ content should result in higher HCl concentrations. Such a relationship is not apparent in the horizontal veins of the SPRG which contain higher CO₂ concentrations than the vertical veins. By analogy with the industrial processes for HCl manufacture, silicates may also be important substances for reducing a_{NaOH} , but the ability of species to buffer the a_{NaOH} have not been established (Kazahaya and Shinohara, 1991). However, the significance of the abovementioned process is that circulating fluid which precipitate halite are also producing hydrochloric acid. The pattern of high HCl concentrations in the lower parts of the SPRG fluid system, suggest upward flow of these hydrothermal fluids, resulting in lower HCl content in the overlying horizontal veins.

Decrepitation analysis of individual fluid inclusions hosted within single gold grains (Fig. 3.18) yielded widely variable CO₂/H₂O ratios (Table 3.6) for fluid inclusions that decrepitated within a restricted temperature range. This characteristic is considered to reflect immiscibility from an originally homogenous fluid. The recognition of fluid immiscibility according to Ramboz et al., (1982) is that:

- (i) the two immiscible fluids must occur within the same region of the sample;
- (ii) the two types of fluid inclusions must homogenize within the same temperature range, because trapping is not an instantaneous and strictly isothermal-isobaric process; and
- (iii) although the internal pressures are different before homogenization because of variable liquid to vapour ratios, the pressures attain the same value at the homogenization temperature (trapping temperature). Therefore, the decrepitation temperatures should also reflect a restricted temperature range. Such a restricted temperature range for gold-hosted fluid inclusions is, however, influenced by

other factors such as the depth of the fluid inclusions beneath the surface of the gold grain. It is unlikely that more than one generation of fluid could have been trapped in a malleable mineral such as gold, which does not easily allow secondary fractures to penetrate. The fact that a single fluid population displaying variable $\text{CO}_2/\text{H}_2\text{O}$ ratios occurs in the same gold grain, together with a relatively restrict range of decrepitation temperatures is thought to be a good indication of fluid immiscibility during gold precipitation. The recognition of fluid immiscibility in native gold grains provides a mechanism whereby precipitation of gold could have taken place in the SPRG. Fluid immiscibility in native metals from a variety of geological settings, was first reported by Van Hees *et al.* (1992), using QMS data.

In summary, the QMS gas data indicate that the composition of quartz hosted fluid inclusion gases reflect the host lithologies, probably as a result of fluid-rock interaction during vein emplacement. Furthermore, variable $\text{CO}_2/\text{H}_2\text{O}$ ratios in gold hosted fluid inclusions indicate fluid immiscibility during gold precipitation.

3.6 Temporal and genetic interrelations of fluid inclusions

All fluid inclusions observed formed within annealed micro-fractures. No unambiguous temporal relation could be recognized between Type 1 and 2 fluids, but Type 3 fluids clearly overprint Type 2 inclusion trails. Type 1 fluids occur in milky quartz in both granite-hosted vertical veins and in sediment- and dyke-related horizontal veins, and have also been recognized by Ash and Tyler (1986) (Type I, II & IV) and Anderson *et al.* (1992) (Type I, II & III). Type 2 fluids were only observed in vertical veins, and correspond to the Type III inclusions of Ash and Tyler (1986). Type 3 fluids occur throughout, but form the predominant population in the paragenetically late transparent quartz.

The close association between the three categories of Type 1 fluids, and the compositional continuum between these types, suggests that the fluids may be genetically linked. Anderson *et al.* (1992) also recognized the existence of a compositional continuum in the fluids of the SPRG and attributed this to partial mixing between basinal brine and CO_2 -rich fluid of distinct origins. The interpretation presented in this study is that the fluids reflect unmixing of a single CO_2 - NaCl - H_2O fluid, since aqueous fluid inclusions, carbonic vapour-rich inclusions, as well as inclusions with variable $\text{H}_2\text{O}:\text{CO}_2$ ratios are present as the dominant types (Type 1 inclusions) in quartz. In addition, the QMS gas data also strongly support immiscibility in the gold-hosted fluid inclusions. Harley and Charlesworth (in prep.) presented evidence for variations in fluid pressure and accompanying crack seal behaviour

during ore deposition within the SPRG. Such a mechanism implies rapid and extreme fluctuations in pressure during ore deposition, which must have affected the position of the $\text{H}_2\text{O}-\text{CO}_2$ solvus in P-T-X space (Bowers and Helgeson, 1983; Bowers, 1991). Given an original, homogeneous fluid with 85 to 95 mole % H_2O , CO_2 = 5 to 15 mole % (Table 3.5) at 320°C and salinity ≈ 12 wt% eNaCl , fluctuations in fluid pressure between, say 2000 and 1000 bars would shift the solvus such that the fluid would move from a one-phase into a two-phase field (Fig. 3.20). The shape of the solvus dictates that unmixing would result in an aqueous component with high, but restricted salinity and low X_{CO_2} (Type 1_i fluid) and a CO_2 -rich, low salinity component (Type 1_{ii} fluid). Type 1 fluid exhibits widely varying $\text{H}_2\text{O}/\text{CO}_2$ properties because of the plateau-like geometry of the solvus, a feature which corroborates the compositional continuum observed in Type 1 fluids. Bowers and Helgeson (1983) have shown that a high salinity H_2O -fluid can be produced by unmixing of a relatively low salinity $\text{H}_2\text{O}-\text{CO}_2$ fluid, because the salt will fractionate into the H_2O -rich liquid phase rather than in the CO_2 -rich vapour phase. If pressure varies widely during repeated crack-seal events (Sibson *et al.*, 1988) then fluid entrapment during these events would reflect the changing position of the solvus resulting in variable $\text{H}_2\text{O}:\text{CO}_2$ proportions. Consequently, Type 1_i, 1_{ii} and 1_{iii} fluids are considered to be genetically related and formed from pressure-induced unmixing of the ore-bearing fluid during the principal period of gold and sulphide mineralization. However, the relevance of limited fluid mixing is being recognized, as is evident from the presence of a low density carbonic phase in Type 1 inclusions (Fig. 3.8). It is pertinent to note in this regard that the vertical veins are characterized by high density CO_2 with a restricted range in T_f , while all horizontal veins exhibit a much broader range of CO_2 densities, implying a contribution of low density basin-derived carbonic species.

The highly saline Type 2 fluid inclusions, which are confined to the granite-hosted vertical veins, are similar to the high salinity fluids recognized in granites of the Canadian Shield (Gascoyne *et al.*, 1987; Frapre *et al.*, 1984) and Cornwall (Edmunds *et al.*, 1984). The principal origins of the high salinity could be ascribed to acid hydrolysis of plagioclase, K-feldspar and biotite, but may also reflect evolved high density basinal brines which are concentrated at the bottom of the Transvaal Sub-basin.

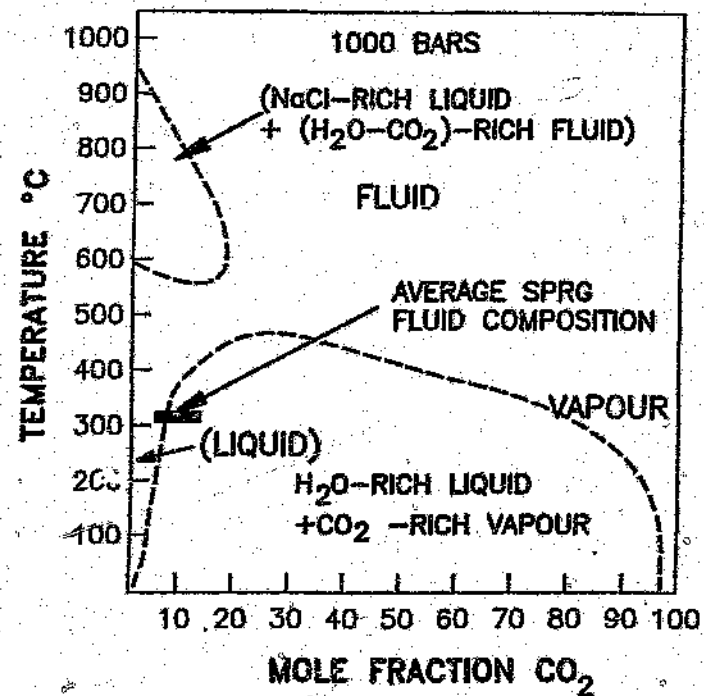
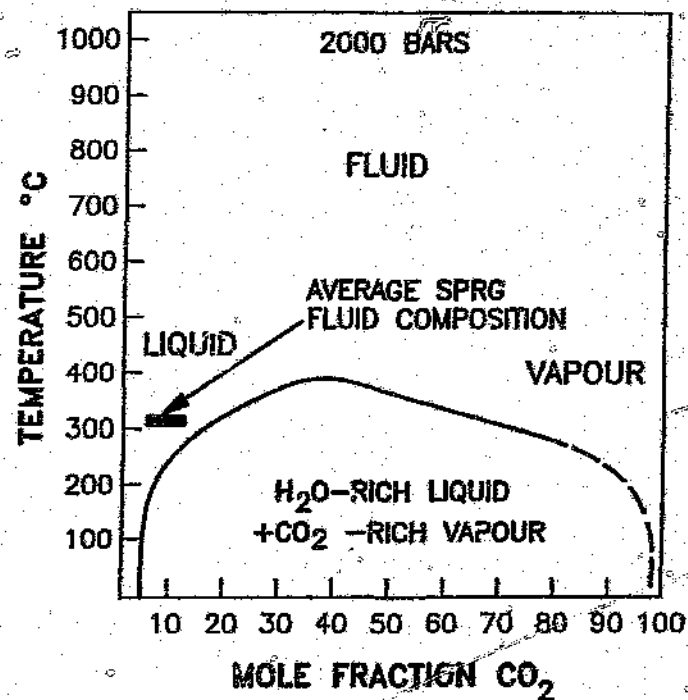


Figure 3.20 T - X diagrams for 12 weight percent NaCl relative to H₂O + NaCl after Bowers and Helgeson (1983). Variation in pressure result in fluctuation of the solvus across the compositional field defined for the Sabie-Pilgrim's Rest goldfield.

3.7 Gold-hosted noble gases, U and Th geochemistry

Noble gases have been shown to provide information on the source and history of inclusion-trapped fluids (eg Turner and Bannon, 1992). The absolute and relative concentrations of noble gases in inclusion fluids is dependant on the temperature, pressure and salinity of the fluid at incorporation. Assuming negligible diffusion loss, relative and absolute noble gas abundances in inclusion fluids can be related to different fluid sources and to p, T and X at entrapment (Ozima and Podosek, 1983). Subsequent fluid/rock interaction may lead to the incorporation of radiogenic ^4He and ^{36}Ar from U, Th and K decay, or from juvenile magmatic fluids, indicating the net pre-entrapment interaction. The solubilities of He, Ne, Ar, Kr and Xe in pure water have been measured from 0° to 300°C (eg Crovetto *et al.*, 1982). The presence of dissolved electrolytes, such as NaCl, reduces the solubility of the noble gases at high temperatures (Smith and Kennedy, 1983). Various studies have addressed the distribution of noble gas isotopes in silicate minerals, eg Lippolt and Weigel (1988), Staudacher and Allègre (1989), Karnensky *et al.*, (1990) and Turner and Stuart (1992), but as far as known no studies have yet been carried out on sulphides or native metals. This study appears to have been the first attempt to analyze for a number of the noble gas isotopes in native gold (also see Eugster *et al.*, submitted to *Journ. Geoph. Res.*).

Table 3.7 Native gold specimens used for noble gas, U and Th analyses

Sample no.	Sample weight (mg)	Locality
SB-A11	58.81	Beta Mine, Pilgrim's Rest
SB-B11	30.82	Beta Mine, Pilgrim's Rest
SB-C11	29.95	Elandsdrift Mine, North of Sable
SB-D11	8.55	New Chum Mine, Ledophine 469KT
SB-D12	264.77	New Chum Mine, Ledophine 469KT
SB-E11	8.84	Graskop 564KT, Pilgrim's Rest
SB-E12	10.20	Graskop 564KT, Pilgrim's Rest
SB-E13	20.67	Graskop 564KT, Pilgrim's Rest
SB-E14	65.97	Graskop 564KT, Pilgrim's Rest
SB-G11	11.92	Elandsdrift Mine 320JT, Sable
SB-H11	12.17	Sandstone vein, Sable
SB-J11	32.45	Elandsdrift 220JT, Sable

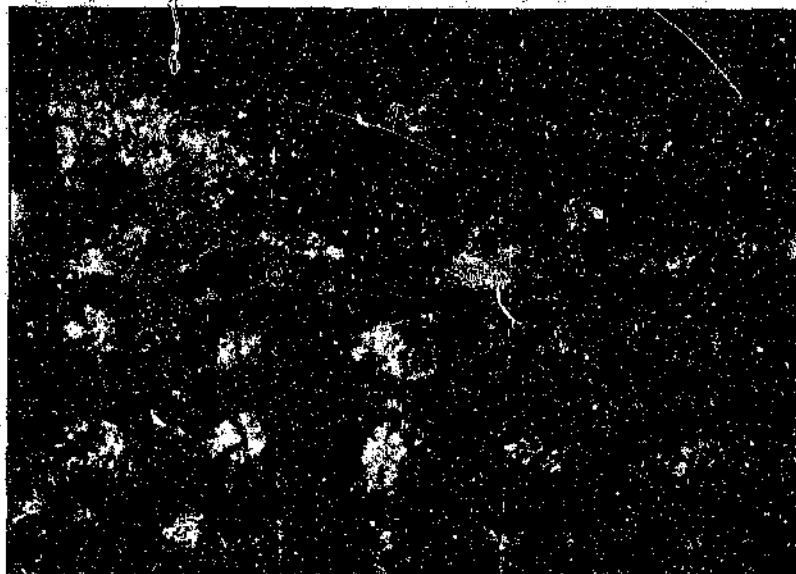


Figure 3.21 Selection of native gold specimens from the SPRG

3.7.1 Noble Gases - Results

The noble gas inventory in gold is a mixture of numerous components which have been categorized into two main groups, namely "trapped" and "*in situ*" gases. The term "trapped" gas denotes species that were present in the ambient fluid or gaseous phase and were incorporated into the gold at the time of formation, whereas *in situ* species are the daughter nuclei of radioactive or fissioning isotopes or nuclear reaction products, assuming that gold has remained a closed system since its formation.

Analytical results are presented in Tables 3.8, 3.9 and 3.10. The SPRG gold samples are enriched in trapped radiogenic ^4He and somewhat depleted in ^{20}Ne , with an average $^4\text{He}/^{20}\text{Ne}$ ratio of 18334. This ratio is much higher than the present day atmospheric $^4\text{He}/^{20}\text{Ne}$ ratio of 0.319, where ^4He originates mainly from the α -decay of U, Th and Sm in the Earth's crust. Helium, a minor constituent in air, is highly concentrated in groundwaters and geothermal fluids compared to ASW, because of input from crustal radiogenic sources (Torgersen and Clarke, 1985). Accumulation of He in ground waters increases at a constant rate with residence time (Andrews, 1985). Magmatic He has also been recognized in many geothermal systems associated with recent volcanic and intrusive activity (Welhan *et al.*, 1988), and concentrations (0.5 to 5 ppm) are generally four to five orders of magnitude higher than ASW. The average ^4He concentration for the SPRG is $887.68\text{E-}08 \text{ cm}^3 \text{ STP/g}$ (Table 3.8), which is markedly higher than the average atmospheric ^4He value of $0.35\text{E-}08 \text{ cm}^3 \text{ STP/g}$ (Ozima and Podosek,

1983). The average ^{20}Ne concentration for the atmosphere is $1.09\text{E-}08 \text{ cm}^3 \text{ STP/g}$. Thus, it is unlikely that ^4He enrichment in the SPRG was a result of the *in situ* decay of U and Th. Furthermore, most of the ^4He is liberated in the low temperature range (Fig. A1.1), suggesting that fluid inclusions may be the primary host. Compared to mantle material (ie Hamano and Ozima, 1978) the SPRG samples have lower $^4\text{He}/^{40}\text{Ar}$ ratios. Much has been said about the use of $^4\text{He}/^{40}\text{Ar}$ ratios as a geochemical tracer in identifying sources of radiogenic noble gases. However, the ranges defined for the various rock types and geological environments are considerable and the situation remains unresolved as there is no clear indication of the contents of $^4\text{He}/^{40}\text{Ar}$. Ratios of excess $^4\text{He}/^{40}\text{Ar}_{\text{rad}}$ in SPRG gold samples range between 0.76 and 27.2 (Table 3.9). These values are low compared to those for placer gold samples (25 to 137, Eugster *et al.*, in prep.), whereas samples from natural gas wells range from 2 to several hundred (Wasserburg *et al.*, 1963; Mamyrin and Tolstikhin, 1984). SPRG samples are somewhat depleted in ^{36}Ar ($x = 7.5\text{E-}10$) relative to the terrestrial atmospheric composition ($x = 2.08\text{E-}08$), whereas ^{86}Kr and ^{132}Xe concentrations appears to be similar to atmospheric content (Figures 3.22, 3.23, 3.24; Table 3.10). Furthermore, the $^{40}\text{Ar}/^{36}\text{Ar}$ ratios (Table 3.8) are all significantly higher compared to the value for air which is 296 (Ozima and Podosek, 1983). High $^{40}\text{Ar}/^{36}\text{Ar}$ ratios are not uncommon for igneous rocks (Ozima and Podosek, 1983). The $^{40}\text{Ar}/^{36}\text{Ar}$ values in Table 3.8 (average $^{40}\text{Ar}/^{36}\text{Ar} = 7428$) are broadly similar to the values for the lower zone of the Skaergaard intrusive ($^{40}\text{Ar}/^{36}\text{Ar} = 3800$, Smith, 1978). The decay of crustal ^{40}K is mainly responsible for Ar that is observed in relative high concentrations in SPRG samples (Table 3.8). By assuming 30 ppm as a typical K concentration in gold (Eugster *et al.*, submitted), the calculated concentration of $^{40}\text{Ar}_{\text{rad}}$ produced since the Archean should be approximately $90\text{E-}08 \text{ cm}^3 \text{ STP/g}$. This calculated $^{40}\text{Ar}_{\text{rad}}$ value is significantly lower than the average $^{40}\text{Ar}_{\text{rad}} = 274\text{E-}08 \text{ cm}^3 \text{ STP/g}$ concentration of the SPRG samples (Table 3.9), suggesting that a large portion of the observed $^{40}\text{Ar}_{\text{rad}}$ was trapped. This is also suggested by the low temperature ^{40}Ar liberation. The Kr and Xe isotopic ratios presented in Table 3.10 indicate that the $^{136}\text{Xe}/^{132}\text{Xe}$ ratio for the SPRG is enhanced relative to atmospheric Xe ($^{136}\text{Xe}/^{132}\text{Xe} = 0.3299$) by approximately 3%. This small enrichment, suggests trapping of Xe formed as a fission product, by SPRG gold. For the calculation of fissionogenic Kr and Xe, non-fissionogenic Kr and He were assumed to be of atmospheric composition (Nief, 1960; Podosek *et al.*, 1971).

SPRG samples were also analyzed for U concentrations by heating the samples to 1120°C , dissolve in aqua regia and analyzed with isotope dilution mass spectrometry. Th was analyzed using instrumental neutron activation analysis. U concentrations (Table 3.11) range between 0.0043 to 0.796

ppm, whereas Th varies between 0.011 and 0.0093 ppm. Due to limitations in sample size it was not possible to analyze for K, Na and Cl on the same sample material.

Table 3.8 Results of gold hosted ^4He , ^{20}Ne and ^{40}Ar analyses. An asterisk indicates noble gas extraction in several temperature steps (see Figures A1.1)

Sample no.	Extraction Temp. (°C)	^4He	^{20}Ne	^{40}Ar	$^{36}\text{Ar}/^{38}\text{Ar}$
		$10^{-9}\text{cm}^3\text{ STP/g}$			
SB-A11	1100	637±30	0.027±0.007	261±10	3660±1400
SB-B11	1100	32.4±1.0	0.046±0.010	33.3±1.2	587±60
SB-C11	1100	179.4±8.0	0.029±0.007	192.7±6.0	2610±280
SB-D12	1100	989±60	0.15±0.13	354±20	1520±150
SB-E11	1700	3470±200	0.04±0.02	152.7±6.0	1776±180
SB-E13	1120	80.2±4.0	0.88±0.05	58.7±6.0	4500±2000?
SB-E14	1120	1080±50	0.037±0.011	122.9±6.0	2110±500
SB-G11	1120	299±10	0.015±0.005	214±6	6630±2200
SB-H11	1100	1153±60	0.180±0.030	1012±40	48900±27000
SB-J11	1100	237±8	0.077±0.010	364±10	2090±120

Table 3.9 Results of gold hosted $^{40}\text{Ar}_{\text{rad}}$, $^4\text{He}/^{40}\text{Ar}_{\text{rad}}$ and $^{20}\text{Ne}/^{36}\text{Ar}_{\text{trapped}}$ analyses

Sample no.	Radiogenic		Trapped
	$^{40}\text{Ar}_{\text{rad}}$ $10^{-9}\text{cm}^3\text{ STP/g}$	$^4\text{He}/^{40}\text{Ar}_{\text{rad}}$	$^{20}\text{Ne}/^{36}\text{Ar}$
SB-A11	241±12	2.64±0.20	0.39±0.13
SB-B11	16.6±1.8	1.98±0.25	0.81±0.10
SB-C11	171±8	1.05±0.06	0.39±0.10
SB-G11	204±8	1.46±0.08	0.46±0.25
SB-J11	312±10	0.76±0.03	0.44±0.05
SB-D12	285±18	3.47±3.0	0.65±0.60
SB-E11	127±8	27.2±2.0	0.47±0.30
SB-E14	106±7	10.2±0.8	0.63±0.20
SB-H11	1006±40	1.15±0.07	8.7±5.0

Table 3.10 Result of ^{86}Kr and ^{132}Xe analyses

Sample no.	Extraction Temp. ($^{\circ}\text{C}$)	^{86}Kr	^{132}Xe	$^{62}\text{Kr}/^{68}\text{Kr}$	$^{134}\text{Xe}/^{132}\text{Xe}$	$^{136}\text{Xe}/^{132}\text{Xe}$
		$10^{-12}\text{cm}^3\text{ STP/g}$				
SB-D12	1100	15.6 ± 3.0	1.95 ± 0.50	-	0.400 ± 0.017	0.339 ± 0.012

Table 3.11 Results of U and Th concentrations (in ppm) of SPRG gold samples. For the determination of U concentrations the samples were heated in a vacuum to 1120°C , dissolved in aqua regia, and analyzed with isotope dilution mass spectrometry. Th was analyzed using instrumental neutron activation analysis

Sample no.	U	Th
SB-A11	0.0070 ± 0.0003	
SB-B11	0.0173 ± 0.0007	
SB-C11	0.0262 ± 0.0011	
SB-D11	-	0.011 ± 0.001
SB-D12	0.1051 ± 0.0070	
SB-E12		0.0093 ± 0.0010
SB-E13	0.796 ± 0.005	
SB-E14	0.0043 ± 0.0003	
SB-G11	0.062 ± 0.003	
SB-H11	0.0402 ± 0.00015	
SB-J11	0.0217 ± 0.0009	

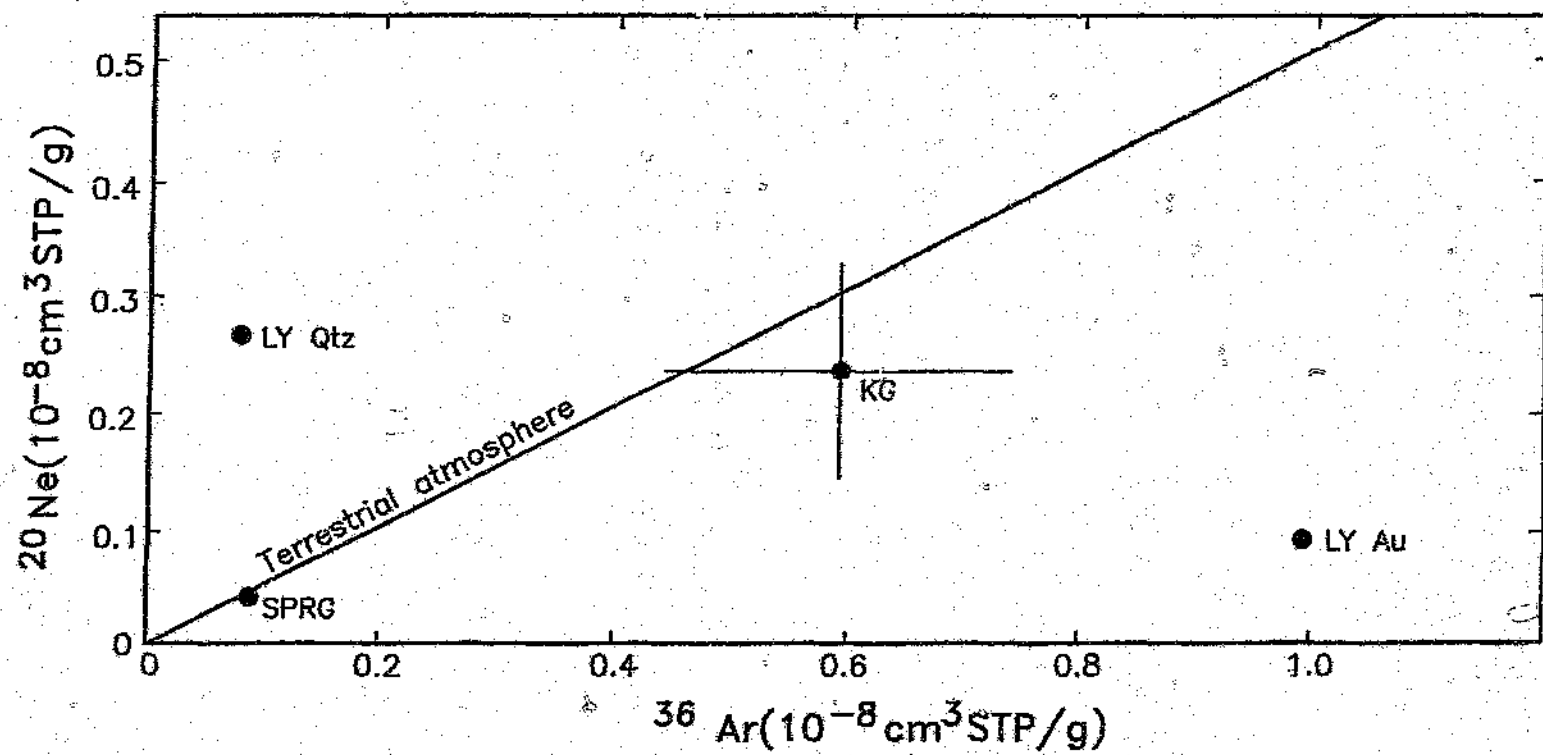


Figure 3.22 Binary plot showing ^{20}Ne versus ^{36}Ar .

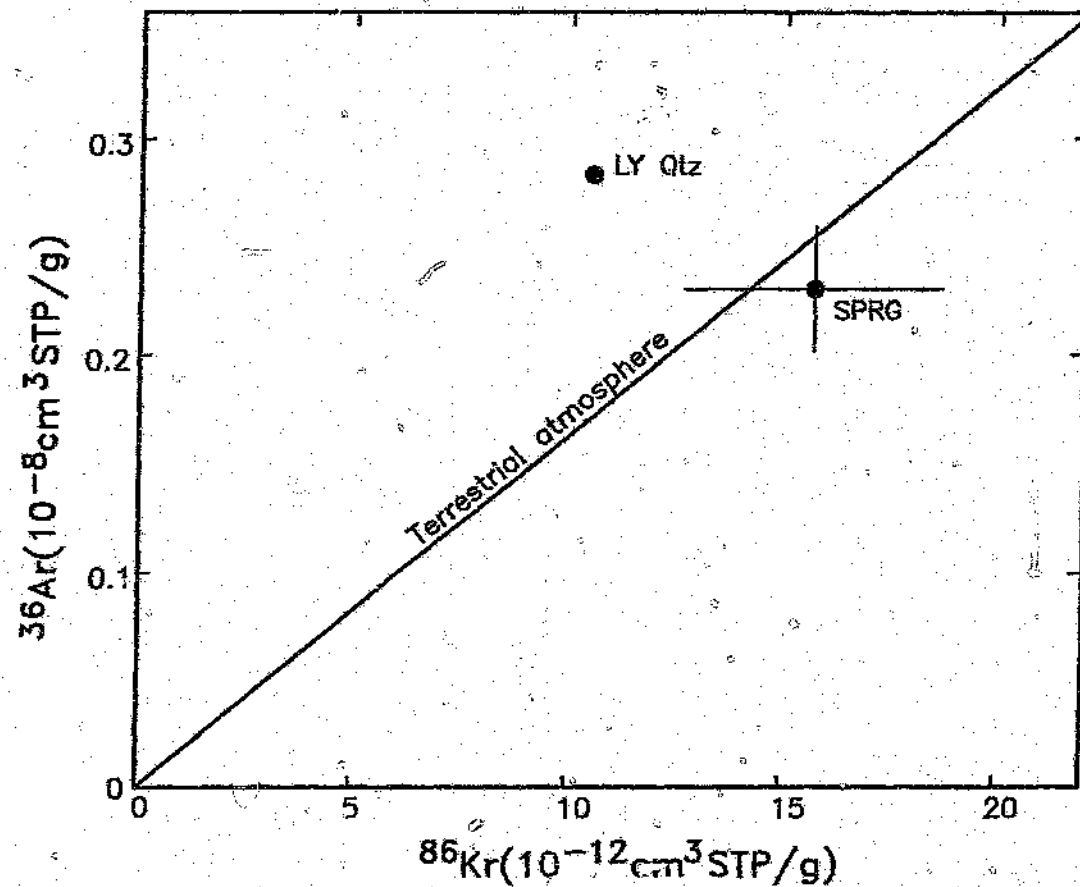


Figure 3.23 Binary diagram showing ^{36}Ar versus ^{86}Kr with the average values for the SPRG clearly plotting away from the terrestrial atmosphere average.

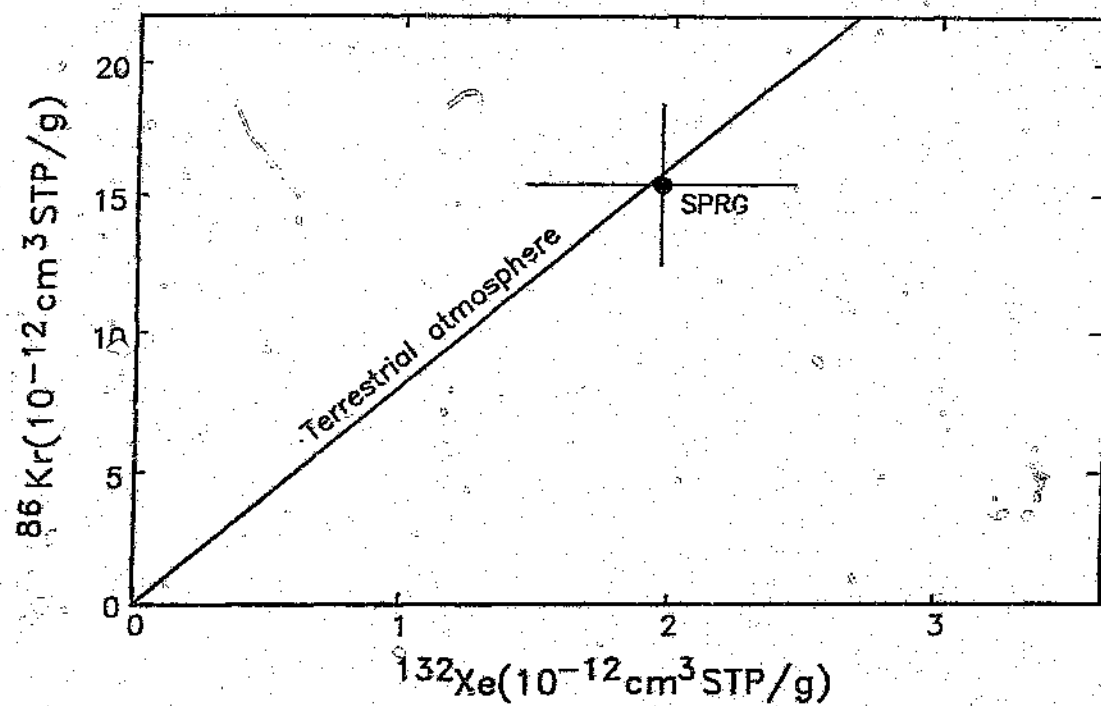


Figure 3.24 Binary diagram showing ^{86}Kr versus ^{132}Xe average values for the SPRG in relation to the average terrestrial atmosphere.

3.7.2 Noble Gases - Interpretation

From the data in Tables 3.8, 3.9, 3.10 and 3.11 it is clear that the U, Th and noble gas concentrations exhibit marked variations among the different gold samples analysed. As was noted in section 3.5, it is very difficult to establish an estimate of the composition of the Proterozoic atmosphere. It was also pointed out that the available literature is inconclusive with regard to evolutionary processes involving noble gases in the terrestrial atmosphere. Data obtained in this study show that the gold-hosted noble gas compositions of the SPRG are somewhat depleted in ^{36}Ar relative to the terrestrial atmosphere composition, whereas ^{86}Kr and ^{132}Xe concentrations appears to be similar to atmospheric content (Figures 3.22, 3.23 & 3.24; Table 3.10). Furthermore, the $^{40}\text{Ar}/^{36}\text{Ar}$ ratios (Table 3.8) are all significantly higher than the value for air, which is 296 (Ozima and Podosek, 1983). As presented in Tables 3.8, 3.9 and 3.10 the concentrations of the noble gases in SPRG samples are not significantly affected by contributions from nuclear decay. The observed ranges compare favourably with those values obtained for plutonic igneous rocks. For SPRG the observed ranges are (all concentrations in $\text{cm}^3\text{STP/g}$) $1.5\text{E}-10$ to $8.8\text{E}-09$ ^{20}Ne (sedimentary rocks $2\text{E}-10$ to $1\text{E}-05$, Ozima and Podosek, 1983; plutonic igneous rocks $2\text{E}-10$ to $2.7\text{E}-08$, Smith, 1978 & Kuroda *et al.*, 1977); $5\text{E}-11$ to $2.3\text{E}-09$ ^{36}Ar (sedimentary rocks $1\text{E}-09$ to $1\text{E}-05$; plutonic igneous rocks $2.4\text{E}-09$ to $3.3\text{E}-08$, Smith, 1978 & Kuroda *et al.*, 1977); $15.6\text{E}-12$ ^{86}Kr (sedimentary rocks $6\text{E}-12$ to $1\text{E}-06$); $1.95\text{E}-12$ ^{132}Xe (sedimentary rocks $1\text{E}-12$ to $1\text{E}-07$). Consequently the noble gas concentrations in SPRG gold samples seem to be analogous to igneous compositions and do not correspond with either atmospheric or sedimentary compositions.

Assuming that the present atmosphere has a similar noble gas composition to that in the Proterozoic (see discussion in section 3.5.5 as well as Phinney, 1972; Alexander, 1975; Ozima and Podosek, 1983), it can be concluded that gold did not form in the presence of atmospheric gases or air-saturated meteoric waters. Additional evidence for the lack of meteoric water or atmospheric involvement is provided by the extremely high $^{40}\text{Ar}/^{36}\text{Ar}$ ratios for the low temperature fractions, suggesting that trapped Ar was mainly produced from radioactive decay of crustal ^{40}K with negligible contributions from atmospheric Ar. Another important ratio is that of trapped radiogenic $^4\text{He}/^{40}\text{Ar}$. This ratio is governed by the U/K ratio of the source where the daughter nuclei are produced. Because of the longer half life of ^{238}U compared to ^{40}K the production ratio of $^4\text{He}/^{40}\text{Ar}$ increases with time, and at the present time the ratio is 3.0 times higher than 3000 Ma ago. Tertiary gold exhibits a trapped $^4\text{He}/^{40}\text{Ar}$ ratio of 3.93 (Eugster *et al.*, submitted), whereas gold from the SPRG has a ratio of 1.4 (Eugster *et al.*, submitted; Fig. 3.8). Figure 3.25 shows a plot of trapped ^4He versus trapped $^{40}\text{Ar}_{\text{rad}}$ for the low

temperature fractions of the SPRG samples. K and U tend to be geochemically coherent in crustal rocks, typically with a U/K ratio by weight of about $1\text{E-}04$ (Wasserbrugg *et al.*, 1964). Radiogenic gas produced from such a U/K ratio will have $^4\text{He}/^{40}\text{Ar} = 5.5$ (Ozima and Podosek, 1983). The fact that lower $^4\text{He}/^{40}\text{Ar}$ ratios are observed for the SPRG samples could be explained by addition of mantle-derived gases. Turner and Stuart (1992) and Turner (1988) showed that the mantle $^4\text{He}/^{40}\text{Ar}$ ratio is approximately 1.6. This value was corroborated by the study of Staudacher and Allègre (1989) working on glass samples from the archipelago of Tahiti. The good correlation between ^4He and ^{40}Ar demonstrate the retentive property of gold to ^4He and rule out any possibility that the $^4\text{He}/^{40}\text{Ar}$ ratio could have been affected by loss of ^4He . The significance of these results on the $^4\text{He}/^{40}\text{Ar}$ ratio for SPRG samples lies in the fact that gold represents an excellent carrier for crustal (and perhaps mantle) gases, including trapped ^4He . The retentive properties of gold for noble gases seems to be far superior to those of other silicate minerals from which, ^4He for example diffuses freely (Lippolt and Weigel, 1988). Fluid inclusions in gold are promising reservoirs of volatiles that were trapped as long ago as the late Archean or early Proterozoic epochs.

[Although Alexander (1975) made an early attempt to determine a palaeoatmospheric $^{40}\text{Ar}/^{39}\text{Ar}$ ratio, Cadogan (1977) provided the first value of 291.0 ± 1.5 for the 380 Ma argon dissolved in the Rhynie chert, a silicified peat bog from Scotland. Jones (1982) presented an $^{40}\text{Ar}/^{39}\text{Ar}$ ratio of 296.2 ± 1.5 for Phanerozoic cherts (mean age 70 Ma), whereas Turner (1988) presented $^{40}\text{Ar}/^{39}\text{Ar}$ ratios averaging 292 for 1700 Ma cherts from the Gunflint, a figure which is indistinguishable from the modern atmospheric value of 296. Unfortunately this simplistic pattern, showing an apparent lack of evolution in atmospheric noble gas content and isotopic ratios, does not extend to Proterozoic and Archean cherts. Jones (1982) indicated very low levels of atmospheric ^{39}Ar and high $^{40}\text{Ar}/^{39}\text{Ar}$ ratios dominated by either radiogenic ^{40}Ar or excess ^{40}Ar or both, similar to those values observed for the SPRG samples. It cannot be stated with any certainty whether the latter values represent early atmospheric compositions or reflect external contributions. Turner (1988) devised a way of unravelling multicomponent Ar mixtures, involving "cake mix diagrams" in which isotopic and elemental compositions are represented by the ratios $\text{K}/^{40}\text{Ar}$, $\text{Cl}/^{40}\text{Ar}$ and $^{39}\text{Ar}/^{40}\text{Ar}$. A significant finding of Turner's (1988) work is that both chlorine and excess Ar are predominantly brought into the silica by hydrothermal fluids which become subsequently trapped in the inclusions and in the structure.]

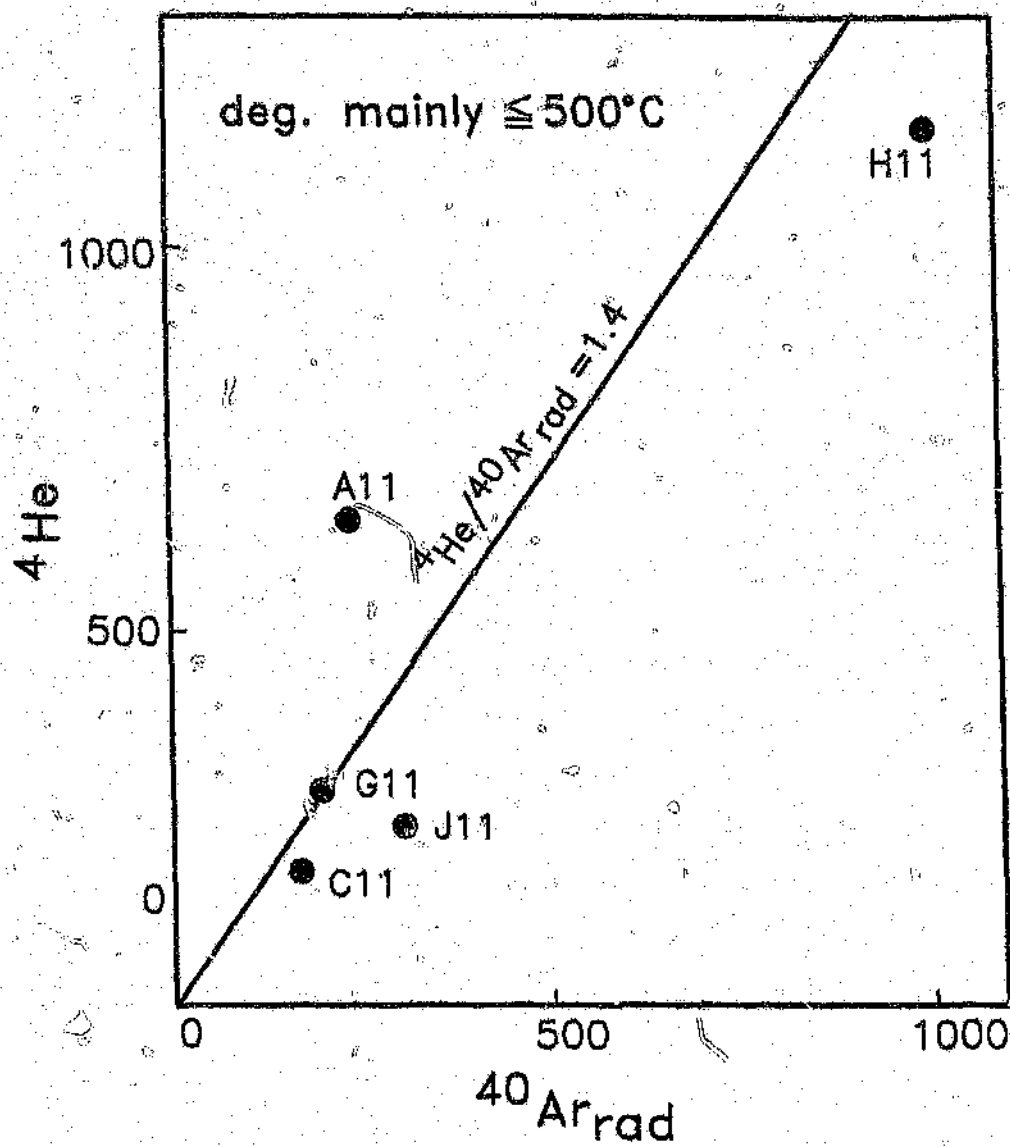


Figure 3.25 Binary diagram showing ^4He versus $^{40}\text{Ar}_{\text{rad}}$ for SPRG native gold samples, indicating an average $^4\text{He}/^{40}\text{Ar}_{\text{rad}}$ ratio of 1.4. The largest portion of ^4He and Ar_{rad} was liberated at temperatures below 500°C .

3.7.3 *In situ* produced noble gases: An attempt to directly date native gold

In view of the problems experienced with dating of the gold mineralizing event in the SPRG, as well as the lack of datable ore-stage material associated with the auriferous veins, an attempt was made to directly date native gold. Possible dating schemes are U,Th- ^4He , ^{40}K - ^{40}Ar and U-fission Xs. Eugster *et al.*, (1992) and Niedermann *et al.*, (1993) made the first attempt to directly date native gold and presented an age of 30 Ma for gold from hydrothermal veins at Brusson, Val d'Ayas, northwest Italian Alps, using the U,Th- ^4He system and assuming that all ^4He was produced *in situ* by U and Th decay. This age was in good agreement with the ^{40}K - ^{40}Ar age obtained on muscovites and biotites that are associated with the Brusson auriferous veins (Diamond and Wiedenbeck, 1986). However, it is clear from the data in the previous sections that most of the ^4He was trapped and only a small portion was acquired from the radiogenic decay of U and Th. Thus, the assumption by Eugster *et al.*, (1992) and Niedermann *et al.*, (1993) that all ^4He was produced *in situ* by U and Th decay is not valid and the similarity of the 30 Ma age with the age obtained by Diamond and Wiedenbeck, (1986) is merely fortuitous (also see Eugster *et al.*, in review).

In Figure 3.26 the $^4\text{He}/^{40}\text{Ar}_{\text{rad}}$ ratios are plotted versus the percentage of released He at temperatures above 600°C for the SPRG samples. It is clear from Fig. 3.26 that, with the exception of sample SB-E14, little ^4He is released at higher temperatures. The high $^4\text{He}/^{40}\text{Ar}$ ratios of this highly retentive gold sample (ie sample SB-E14) indicate that ^4He is not accompanied by trapped ^{40}Ar and, thus, must be *in situ* produced. However, ^4He in the SPRG samples is dominated by the trapped component. By assuming a $^4\text{He}/^{40}\text{Ar}$ ratio of 1.4 (Fig. 3.26) the concentration of *in situ* produced ^4He in sample SB-E14 is $9.32 \times 10^{-8} \text{ cm}^3 \text{ STP/g}$ with 0.0043 ppm U (Table 3.11). These values correspond to an apparent U,Th- ^4He age of > 6000 Ma. This absurd "age" is possibly a result of U loss during He extraction. Unfortunately, it is not possible to obtain ^4He , U and Th concentrations on a single grain, which is necessary in order to obtain an age, due to the extremely low concentration levels of the relevant nuclides (these problems are currently being addressed and collaboration with the researchers at the University of Bern is continuing). Furthermore, for a typical K concentration of about 40 ppm a radiogenic $^{40}\text{Ar}_{\text{rad}}$ content of $1.9 \times 10^{-8} \text{ cm}^3 \text{ STP/g}$ would be produced over a period of 3000 Ma. With the exception of sample SB-E11, the $^{40}\text{Ar}_{\text{rad}}$ contents in all the SPRG samples were much higher and, therefore, must have received a contribution from a trapped component. This interpretation is also consistent with the degassing pattern and the $^4\text{He}/^{40}\text{Ar}$ ratios of the samples. Theoretically the *in situ* produced $^{40}\text{Ar}_{\text{rad}}$ content in the Proterozoic SPRG samples could be relatively high. It is, however, not possible to

distinguish between trapped and *in situ* produced radiogenic $^{39}\text{Ar}_{\text{rad}}$, unless the $^{39}\text{Ar}/^{40}\text{Ar}$ method is employed. Calculation of $\text{U}-^{136}\text{Xe}$ fission ages is not meaningful at this stage, because of possible U losses during gas extraction and also the problem of establishing the contribution of trapped fission Xe. Consequently, all attempts at dating gold from its noble gas content have proved unsuccessful.

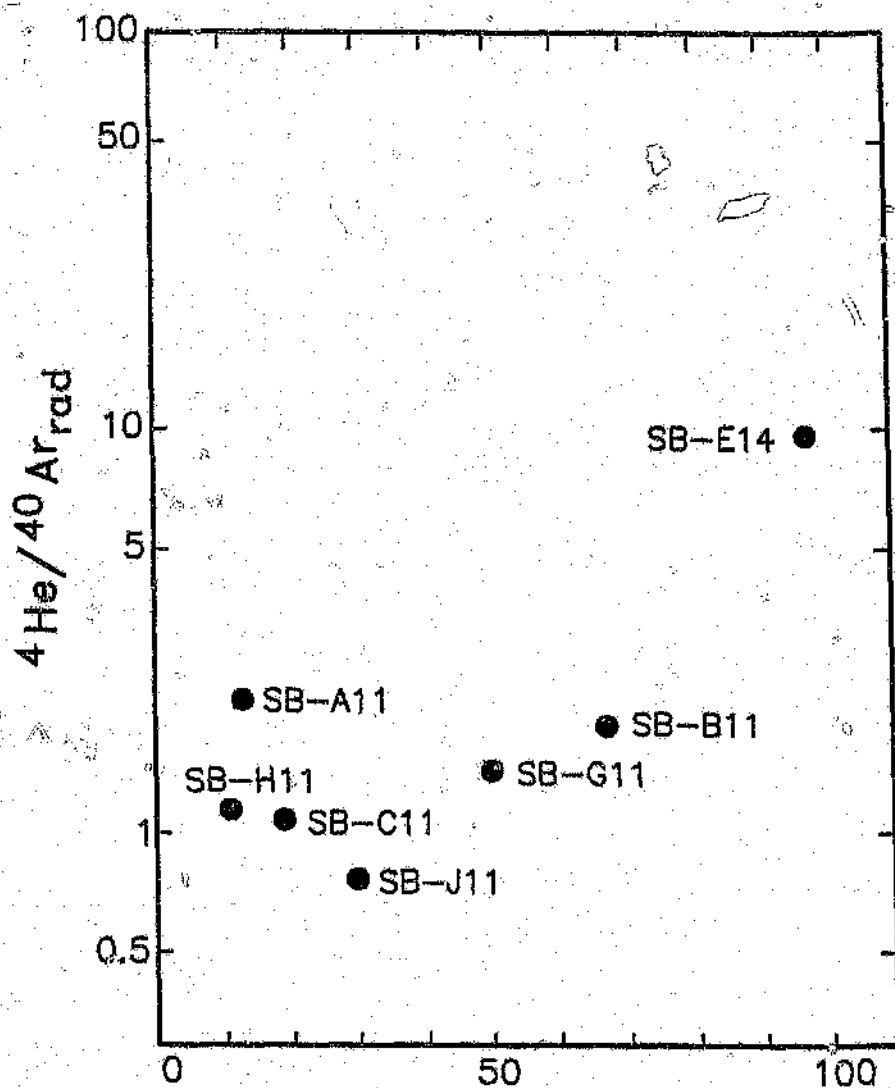


Figure 3.26 Binary diagram showing the percentage of ^{4}He released from SPRG samples at a cut-off temperature of 600°C versus $^{4}\text{He}/^{40}\text{Ar}_{\text{rad}}$ ratios. Only sample SB-E14 released most ^{4}He below 600°C .

4.1 Stable nonradiogenic isotopes

4.1.1 Oxygen isotopes

4.1.1.1 Oxygen isotope results

Thirty-two quartz samples (analysed in duplicate or triplicate) from both the vertical and horizontal veins as well as the sill/dike associated veins, covering a vertical stratigraphic span of approximately 1000 metres, were analysed for their $\delta^{18}\text{O}$ values (Table 4.1). The vertical veins yielded a mean $\delta^{18}\text{O} = 14.2\text{‰}$ ($S_x = 0.33$; $n = 14$), while the various horizontal veins yielded a slightly higher mean $\delta^{18}\text{O} = 16.0\text{‰}$ ($S_x = 1.56$; $n = 48$). The diabase sill/dike associated deposits yielded an average $\delta^{18}\text{O} = 20.4\text{‰}$ ($S_x = 1.14$; $n = 8$). The data in Figure 4.1 demonstrate a distinct difference in ^{18}O content between carbonaceous sediment- and granite-hosted quartz veins. Variations in $\delta^{18}\text{O}$ values amongst the vertical quartz vein systems are tightly constrained, whereas the $\delta^{18}\text{O}$ values for the horizontal veins are more variable (Table 4.1). However, oxygen isotopic values for individual mines are characterized by restricted compositional ranges, eg at the Frankfort Mine the average $\delta^{18}\text{O} = 16.3\text{‰}$, $S_x = 1.0$, $n = 16$. Fluid $\delta^{18}\text{O}$ values were calculated from quartz mineral values at a fractionation temperature of 320°C using the equation of Matsuhisa *et al.* (1979) (Table 4.1). These values ($\delta^{18}\text{O}_{\text{fluid}}$) ranged from 7.8 to 8.6‰ for the vertical veins, 5.3 to 12.3‰ for the flat veins and 13.3 to 16.0‰ for the dike/sill associated deposits, and generally overlap the range for both magmatic and metamorphic waters (5.5 - 9.0‰; Taylor, 1979).

The data presented above compare favourably with the oxygen isotopic values presented by previous workers: Tyler (1986b), $\delta^{18}\text{O}$ values ranging between +12.1 and +19.5‰; and Anderson (1992), $\delta^{18}\text{O}$ values ranging between +10.4 and +19.8‰. The $\delta^{18}\text{O}$ values obtained by Tyler (1986b) for the strata bound veins of the Malmani Subgroup clustered between +17 and +18‰, whereas the vertical veins yielded slightly lower values, ranging between +14.1 and +15.2‰. The $\delta^{18}\text{O}$ values for the veins in the siliciclastic Pretoria Group exhibit the lowest compositions, varying between +12.1 and +14.4‰. These low $\delta^{18}\text{O}$ values for the veins hosted in the Pretoria Group are confirmed by Anderson (1992) who reported compositions ranging between +10.4 and +13.9‰. Anderson (1992) also recognized a difference in the oxygen isotope composition of the siliciclastic rock hosted veins ($\delta^{18}\text{O} = +10.4$ to +13.9‰) and the carbonate rock hosted veins ($\delta^{18}\text{O} = +14.4$ to +19.8‰), and attributed these differences to "mineralized" as opposed to "barren" veins (although the criteria for classification of samples into the

latter categories are not clearly specified). Schidlowski *et al.*, (1975) analysed several carbonate samples covering the entire Transvaal Sequence. The oxygen isotope composition of dolomite host rock samples obtained in the vicinity of the SPRG range between +21.5 and +22.9‰, whereas $\delta^{18}\text{O}$ values of the carbonate gangue phases (dolomite and calcite) vary between +16.1 and +21.5‰ (Schidlowski *et al.*, 1975). Furthermore, Y.N. Shieh and X. Zhang (Department of Earth and Atmospheric Sciences, Purdue University; pers. commun. 1992) presented oxygen isotope data on the shales of the Black Reef Formation, ranging between +7.5 and +10.6‰.

Table 4.1 $\delta^{18}\text{O}$ and $\delta^{18}\text{O}_{\text{Fluid}}$ values for quartz from vertical and horizontal reefs as well as sill- associated gold mineralized localities. The $\delta^{18}\text{O}$ -values of 23 NBS-28 samples were within 0.12‰. NBS-30 yielded an average value of 5.1‰ V-SMOW. Average $\delta^{18}\text{O}_{\text{Fluid}}$ values were calculated from quartz mineral values using the equation of Matsuhisa *et al.*, (1979) for $T = 320^\circ\text{C}$. All values are expressed in per mil notation relative to V-SMOW. Abbreviations for the different localities are as follow: AST - Astra; BRH - Browns Hill; CLW - Clewer West; CLS - Clewer South; DRM - Desirée; FKM - Frankfort; GLS - Glynn's Lydenburg Sheba; GRR - Gregory; JBH - Jubilee; LJM - Little Joker; MAM - Mamre; MGL - Morgenzon; NSM - Nestor; OGM - Olifantsgeraamte; RFT - Rietfontein; SUD - Sudwala; SUN - Sunlight; THH - Theta Hill; VLH - Vaalhoek

Sample	$\delta^{18}\text{O}$	$\delta^{18}\text{O}_{\text{Fluid}}$	Sample	$\delta^{18}\text{O}$	$\delta^{18}\text{O}_{\text{Fluid}}$
Flat veins			Vertical veins		
FKM075A	16.3, 16.3 (15.7)	9.9	RFT113	14.7, 14.8	8.6
FKM075B	14.9, 14.4 (14.2)	8.3	SUN003	14.7, 13.6	8.0
FKM076A	17.5, 17.3	11.2	GRR099	14.3, 14.2	8.1
FKM076B	17.3, 17.0	11.0	GRR106	14.2, 14.0	7.9
FKM077A	16.6, 16.4, 17.0, 17.0	10.6	GRR107	14.2, 14.2	8.0
FKM077B	16.5, 16.5	10.3	GRR108	14.1, 14.3	8.0
LJM090	14.2, 14.4 (13.9)	7.8	AST109	13.6, 14.2	7.8
NSM093	14.4, 14.3 (14.1)	8.0	Sill/dike associated veins		
MAM103	15.3, 15.1	9.0	VLH040	22.1, 22.2	16.0
MAM104	14.7, 14.7	8.5	OGM082	19.4, 19.6	13.3
CLH110	11.4, 11.6	5.3	OGM083	20.8, 19.9	14.2
CLH111	16.1, 15.8	9.8	BRH112	19.7, 19.7	13.5
MGL032	16.0, 16.6	10.1	Nelspruit Granite		
MGL033	16.2, 16.1	10.0	NSG105	9.3, 9.3	3.1
CLS038	16.7, 16.8	10.6			
JBH043	18.6, 18.4	12.3			
DRM044	18.4	12.2			
GLS052	16.7, 17.0	10.7			
CLW013	16.6, 16.8	10.5			
CLW017	17.6, 18.0, (17.8)	11.8			
THH030	15.3, 15.4	9.2			

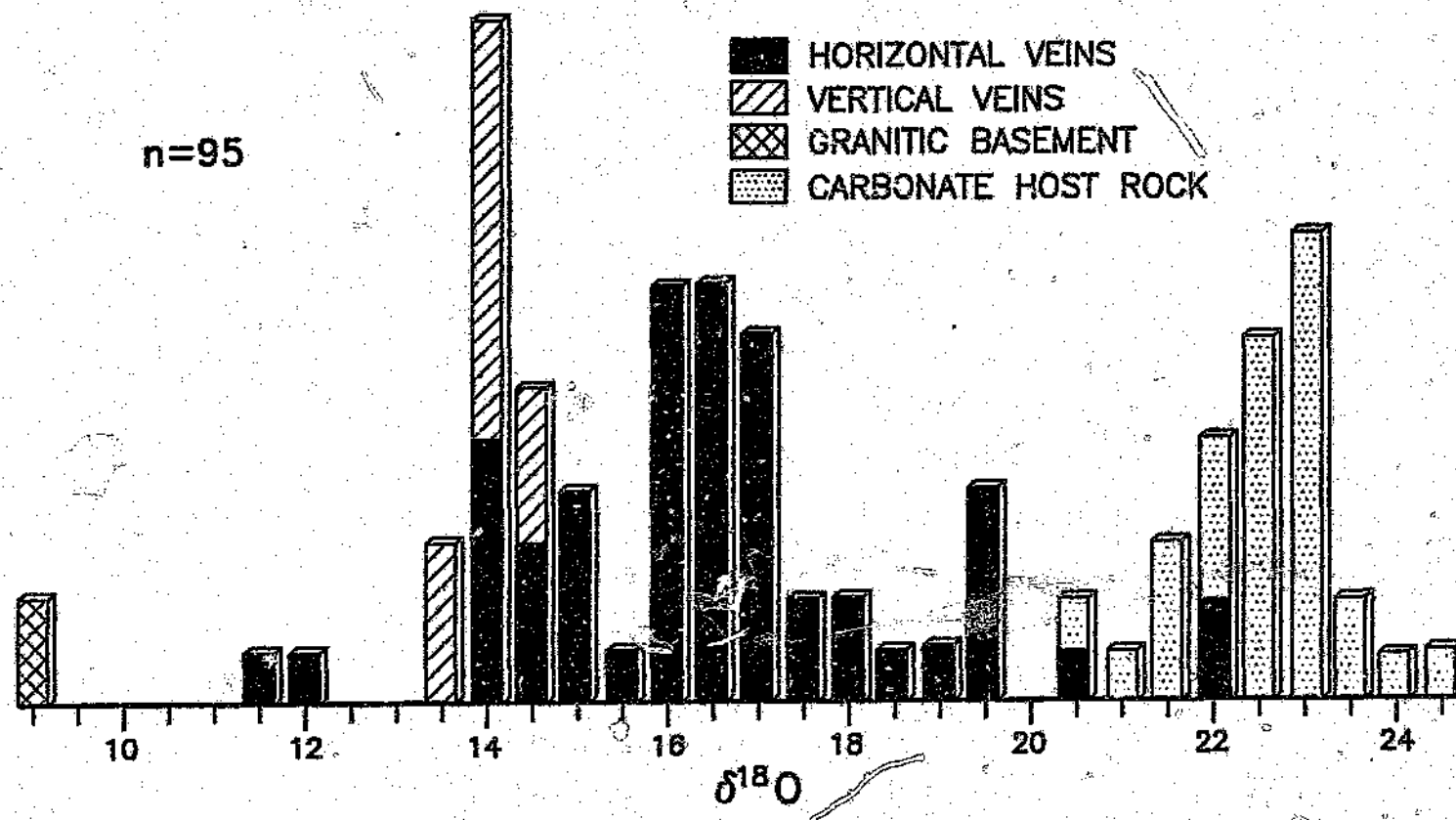


Figure 4.1 $\delta^{18}\text{O}$ values for quartz separates from various auriferous veins in the Sabie-Pilgrim's Rest goldfield. All values are presented in per mil notation, relative to V-SMOW. Data for the carbonate host rock are from Schidlowski *et al.*, (1975).

4.1.1.2 Oxygen isotope interpretation

Variations in the $\delta^{18}\text{O}$ values of hydrothermal quartz occur as a result of a number of independent parameters (eg. O'Neill, 1992). Quantitatively, the most important of these are the $\delta^{18}\text{O}$ value of the fluid and the ambient temperature at which fluid-mineral isotopic equilibrium is attained (eg. O'Neill, 1986). At the site of mineralization, the $\delta^{18}\text{O}$ of hydrothermal fluids may be modified by:

- (i) exchange reactions with wall rocks;
- (ii) precipitation or solution of an oxygen-bearing phase either depleted or enriched in ^{18}O with respect to the fluid;
- (iii) immiscible separation of CO_2 , or any other oxygen-bearing compound; and
- (iv) mixing with an isotopically distinct fluid reservoir.

In the SPRG a distinct correlation between the oxygen isotope composition of vein quartz and the associated host lithology is apparent (Figure 4.1) with increasing $\delta^{18}\text{O}$ values from the granite-hosted and siliciclastic sediment-hosted veins to the veins hosted in the overlying dolomite. The veins associated with diabase dykes/sills show the highest $\delta^{18}\text{O}$ values. Data from Tyler (1986b) and Anderson (1992) show that veins hosted in the siliciclastic Pretoria Group exhibit the lowest ^{18}O contents. Veins hosted in carbonate sediment of the Malmant Subgroup (average $\delta^{18}\text{O}=16.0\text{‰}$) tend to exhibit $\delta^{18}\text{O}$ values that are similar to the carbonate host rock itself, namely around 22.2‰ (Schidlowski *et al.*, 1975) (Fig. 4.1). Likewise, the $\delta^{18}\text{O}$ values for the Nestor Mine (Black Reef Formation hosted vein system) with an average $\delta^{18}\text{O}$ value of 14.3‰, approximates the oxygen isotope compositions of the shale host rock ($\delta^{18}\text{O}=7.5$ to 10.6‰). Furthermore, the granite hosted veins (average $\delta^{18}\text{O}=14.2\text{‰}$) have oxygen isotope values that resemble the lower values of the Nelspruit Granite ($\sim 9.3\text{‰}$; Table 4.1). The positive correlation between $\delta^{18}\text{O}$ values and host rock suggests that a strong lithological control (option (i) above) is exerted on the oxygen isotope composition of the veins in the SPRG. However, despite this, a difference still exists between the isotope composition of the host rock and the vein, indicating the existence of isotopic disequilibrium between the two. Fluid mixing can probably be eliminated as a first order effect, based on the observations that ore-forming solutions were close to, or greater than lithostatic pressure, during hydraulic fracture, fluid advection, vein forming events (see chapter 3), and from the consistency of paragenetic sulphide assemblages in successive vein stages (also see chapter 2). However, it cannot be ruled out completely that some mixing of pore water and metamorphic fluids might have occurred. Immiscibility of an oxygen bearing gaseous phase (eg CO_2) (also see chapter 3) may also have contributed to minor scatter in isotopic data. Separation of gaseous CO_2 from the aqueous hydrostatic fluid is a characteristic feature of most Au-Ag hydrothermal vein systems, and

Higgins and Kerrich (1982) have, for example, calculated that separation of 20 mole% CO₂ at 300°C would induce a 3‰ depletion in the δ¹⁸O of the residual fluid (given a CO_{2(gas)}-H₂O_(liquid) fractionation factor of 14‰ at 300°C; Bottinga, 1968). However, Smith and Kesler (1985) showed that fractionation on such an extensive scale is unlikely, and showed that for CO₂ molar proportions in the range 1 to 12%, the magnitude of the fractionation effect would be restricted to <2‰. This is consistent with the molar proportions of CO₂ that is typical for the SPRG veins (see chapter 5) and suggest that immiscibility probably did not affect oxygen isotopic compositions to a significant extent. Furthermore, precipitation of volumetrically small proportions of carbonate gangue minerals would also have caused only negligible shifts in the δ¹⁸O values of the fluid phase.

The uniformity of the δ¹⁸O values of quartz in the vertical Au-vein deposits, as well as the consistent paragenetic relations in most of the veins district-wide, implies a corresponding homogeneity in both the δ¹⁸O values of hydrothermal fluids, and a consistent ambient temperature of mineralization. The lithological control imposed by the host rock on oxygen isotopic compositions and the lack of knowledge on the extent of fluid/rock interaction at SPRG limit the calculation of the original oxygen isotopic signature of the mineralizing fluid. However, the reason for the consistent δ¹⁸O values in the SPRG veins appears to be somewhat different to those proposed for the characteristic consistency of oxygen isotope values in Archaean lode gold deposits (eg in the Abitibi subprovince of the Superior province, where δ¹⁸O values range between 12.5 and 15.0‰ for deposits distributed over a strike length of ~400km, and hosted by different lithologies, Kerrich, 1987). Oxygen isotope values of the Australian turbidite-hosted gold deposits of the Lachlan fold belt are also remarkably uniform (Stawell, δ¹⁸O=14.7±1.1‰; Bendigo-Ballarat, δ¹⁸O=17.5±1.3; Melbourne, δ¹⁸O=19.0±1.6; Tabberabbera, δ¹⁸O=16.3±1.9; Omeo, δ¹⁸O=14.4±1.0; Gray *et al.*, 1991). The restricted δ¹⁸O range for these deposits are interpreted as indicative of negligible shifts in δ¹⁸O of the mineralizing fluids, due to the high fluid/rock ratios in these deposits. In the case of the SPRG the fluid/rock ratios were not as high as Archaean lode gold systems (as indicated by limited wall-rock alteration and smaller volumetric size of the quartz veins compared to Archaean lode gold deposits of the Superior province, Ontario), and it is difficult to ascribe the consistency in δ¹⁸O values to a homogeneous mineralizing fluid. The consistency is rather, a case of homogeneous temperatures of mineralization throughout the vertical extent of the mineralized zone and emphasizes the predominant influence of host-rock lithologies on oxygen isotopic compositions. The remaining differences in isotopic composition, between host lithologies and veins, by implication rule out the lateral diffusion hypothesis for gold deposits (Boyle, 1979) as a viable ore-forming process. Given

that quartz is not affected by oxygen isotope exchange at $\leq 300^\circ\text{C}$ (Clayton *et al.*, 1968; Criss and Taylor, 1983), formation temperatures above this are implied for the veins of the SPRG.

4.1.2 Hydrogen isotopes

4.1.2.1 Hydrogen isotope results

The SPRG inclusion fluid stable isotope data are presented in Table 4.2. The hydrogen isotopic composition of water in quartz hosted fluid inclusions is variable and extends from -51 to -16‰, whereas the δD values for pyrite hosted inclusion fluids vary between -54 and -68‰. The magnitude of the observed dispersion cannot, however, be accounted for by mixing of fluids from depleted and enriched δD fluid reservoirs. Any such mixing would be reflected in shifts of both δD and $\delta^{18}\text{O}_{\text{fluid}}$, which is inconsistent with the relatively uniform $\delta^{18}\text{O}_{\text{fluid}}$ values. Rather, the observed range in δD may be due to the variable presence of H_2 and/or CH_4 in the aqueous fluid (see QMIS gas analyses; chapter 3). When plotted on a $\delta^{18}\text{O}$ vs δD diagram (Fig. 4.2), the Sable-Pilgrim's Rest data coincide with the primary magmatic, as well as metamorphic water field, and show no indication of any isotopic interaction with meteoric water (samples plot away from the meteoric water line defined as $\delta\text{D} = 8 \cdot (\delta^{18}\text{O}) + 10$). However, the Sable-Pilgrim's Rest δD and $\delta^{18}\text{O}$ data are distinctly different from epithermal Au-Ag, volcanic associated massive sulphide and Mississippi Valley Type deposits and predominantly plot in the area defined by mesothermal gold deposits (eg Ohmoto, 1986). To the best of the authors knowledge no other hydrogen isotope results are available for any of the lithologies of the Transvaal Sequence in the eastern portion of the Transvaal Sub-basin.

Table 4.2 Light stable isotope values (δD , $\delta^{13}C$ and $\delta^{18}O$) of extracted inclusion fluids from strata bound veins (Clewer West - CLW; Frankfort Mine - FKM; Mamre Mine - MAM; Morgenzon Mine - MGL), vertical veins (Gregory - GRR & Rietfontein - RFT) and sill/dyke associated veins (Olifantsgeraamte - OGM; Vaalhoek Mine - VLH; Browns Hill - BRH). Data are presented relative to per mil V-SMOW. $\delta^{18}O$ values are calculated from $\delta^{18}O_{\text{quartz}}$ using the equation of Matshuhisa et al. (1979) for $T = 320^{\circ}C$. * - values from pyrite-hosted fluid inclusions

Sample	δD_{H_2O}	$\delta^{13}C_{\text{Total}}$	$\delta^{18}O_{\text{Fluid}}$
OGM082	-47	-11.7	13.3
GRR107	-37	-2.3	8.0
CLW017	-53	-10.8	11.6
RFT001	-68	-4.8	6.5*
CLW017	-54	-1.4	15.4*
RFT113	-61	-5.7	8.8
CLW013	-47	-4.1	10.5
VLH040	-36	-0.3	15.9
FKM075A	-58	-8.2	9.8
MAM104	-17	-6.1	8.5
MGL033	-49	-8.4	10.0
GRR107	-47	-12.0	8.0
BRH112	-16	1.8	13.5

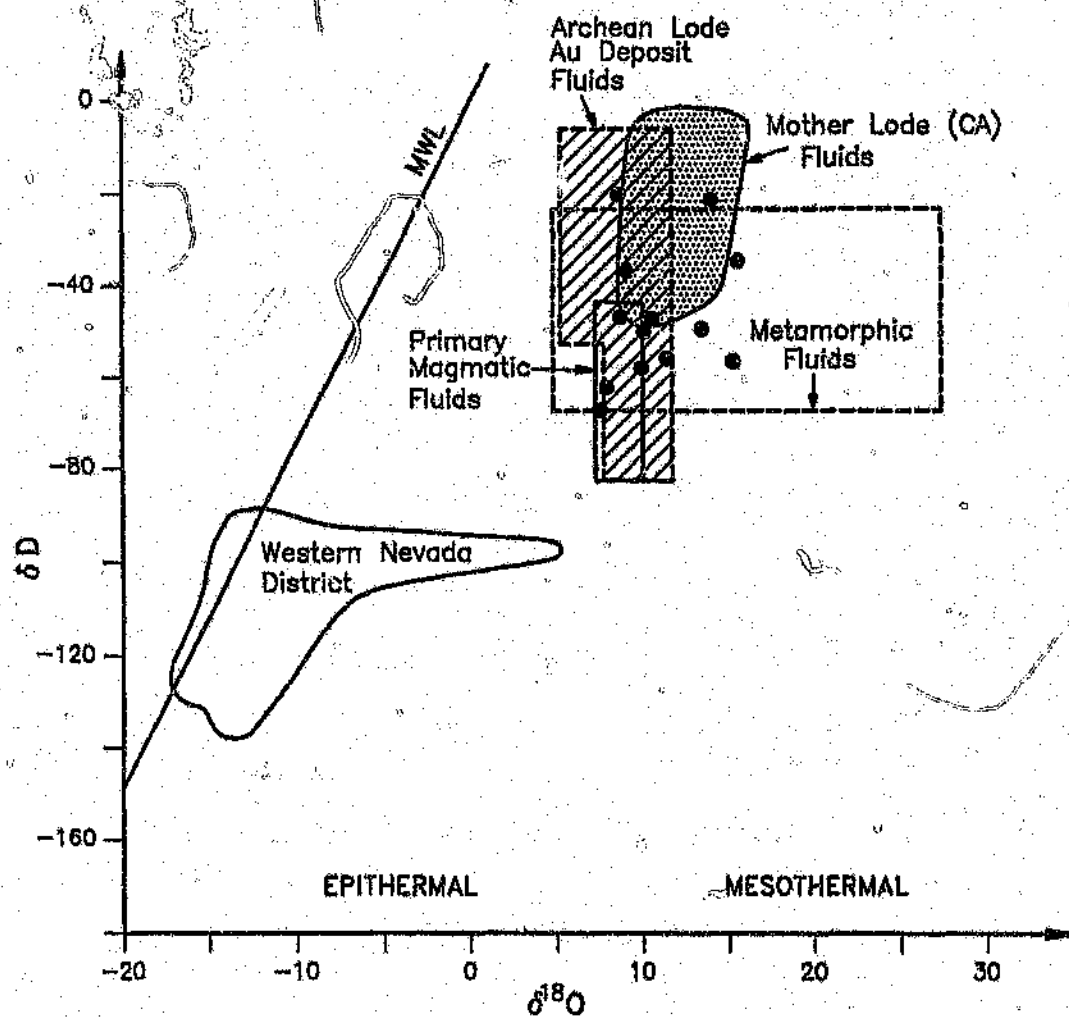


Figure 4.2 A δD versus $\delta^{18}O$ plot depicting the quartz hosted inclusion fluid stable isotope composition for Sable-Pilgrim's Rest goldfield. MWL - Meteoric Water line ($\delta D = 8 * (\delta^{18}O) + 10$).

4.1.2.2 Hydrogen isotope interpretation

Although the SPRG fluids plot within the magmatic and metamorphic fields, it is not possible to conclusively evaluate the origin of fluids, based on their hydrogen and oxygen isotopic composition alone, as has also been emphasized by various workers (eg Ohmoto, 1986; Kerrich and Watson, 1984; Boer *et al.*, in press). Formation brines with a significant meteoric water component may undergo extensive δD and $\delta^{18}O$ exchange and, thus, evolve into the areas defined by magmatic and metamorphic fluids (Fig. 4.2). Numerous examples exist where hydrogen and oxygen isotopic compositions of basinal fluids cover a broad range of values (Kyser and Kerrich, 1990). Furthermore, complexities arise when such evolved formation brines become involved in a hydrothermal system where low water/rock ratios prevail. Field and Ficarek (1985), as well as Taylor (1978), have shown that under these conditions fluids will evolve along J-shaped trajectories. Such evolved waters are invariably hypersaline, whereas fluids involved in the lode gold systems are characteristically dilute solutions (see chapter 3, Roedder, 1984). Thus, it is clear that other evidence, such as LILE associations and total dissolved solute content, is needed to establish the origin of mineralizing fluid in hydrothermal vein systems. Kyser and Kerrich (1990) subdivided the different genetic theories for saline formation brines into the following endmember models:

- (i) Formation waters which are predominantly of local meteoric origin, but the chemical and isotopic composition have been changed by interaction with the host lithologies (eg Banner *et al.*, 1989; Kharaka and Carothers, 1984);
- (ii) Formation waters which are variable mixtures of meteoric water and diagenetically modified seawater (eg Wiltrup and Kyser, 1990), and;
- (iii) Formation waters which represent variable mixtures of meteoric and evaporated seawater (eg O'Neill *et al.*, 1986; Knauth, 1986).

It is obvious that consensus has not been reached among workers involved in this field of research and one cannot expect to resolve the genesis of fluids involved in a hydrothermal system developed within such a sedimentary basin, using stable isotopic evidence alone. The δD and $\delta^{18}O_{\text{fluid}}$ data are clearly inconclusive with regard to the origin of the ore-bearing fluid, and cannot be used to adequately discriminate between the involvement of metamorphic-, magmatic- and/or basinal-derived fluids. The only constructive conclusion that arises from Figure 4.2 is the suggestion that meteoric waters did not play a major part in the mineralizing fluids of the SPRG, and if they were initially present, their isotopic composition have evolved to such an extent that they are not recognizable as meteoric waters anymore.

4.1.3 Sulphur isotopes

4.1.3.1 Sulphur isotope results

Eighty six pyrite specimens from within the horizontal quartz veins were analysed for $\delta^{34}\text{S}$, yielding a range from -4.6‰ to +3.3‰, and are presented in Table 4.3. $\delta^{34}\text{S}$ values for pyrite from the lower vein horizons fall into a restricted range close to 0‰, with low variance, characteristic of magmatic sulfur. The upper veins show a tendency towards more negative $\delta^{34}\text{S}$ values (Fig. 4.3). No sulphides were analysed from the vertical veins due to non-availability of fresh sulphide material. Tyler determined eight $\delta^{34}\text{S}$ values for pyrites from veins in the SPRG, which ranged between +0.5 to +4.0‰. Meyer *et al.*, (1990) presented $\delta^{34}\text{S}$ values ranging between 0 to 10‰ for pyrite from auriferous veins, whereas carbonaceous shales were characterized by sulphur isotope compositions in the order of 0 to -8‰. Liebenberg (1968) determined the sulphur isotope composition of a large number of host rock samples from the Transvaal Sequence, with values covering a wide range between -11.8 to +7.8‰. No pyrites from the vertical veins were analysed.

Table 4.3 Sulphur isotope composition of pyrite separates from the SPRG (in ‰ CDT)

Sample no.	$\delta^{34}\text{S}$ ‰	Sample no.	$\delta^{34}\text{S}$ ‰	Sample no.	$\delta^{34}\text{S}$ ‰
FKM058	+2.7, +2.4, +1.9, +2.3, +1.1, +1.1, +1.8, +2.1, +1.7	CLW012	+1.9, +1.5	CLS038a	-2.9
FKM054	+0.9	CLW013	+0.2, +0.6, +0.5, -0.1	MGL033	-1.0, -1.4
FKM064	-0.5, -0.4	CLW014	+0.0	MGL034	-1.6, -1.4, -1.6, -1.5
FKM066a	+0.5, +0.6	CLW016a	+0.2, -1.2	MAM103	-1.7, -2.6, -1.7, -2.3
FKM066b	-0.5	CLW016b	-1.5, -2.1	OGM078	-0.4, -0.4
FKM068a	-0.1, -1.8	CLW018	-4.6, -4.6	OGM082	-2.1
FKM068c	+0.3	CLW017	-2.2	OGM083	-0.2
FKM075a	+0.7	CLW023	-1.5, -1.4, -2.1, -1.8, - 1.2	MNM081	-1.7, -1.9
FKM076b	-0.3	CLW023a	-3.6	VLH039	+3.0
FKM076c	-0.6, -0.5, -1.2	CLW023b	-0.3, -0.4	VLH042	+2.7
FKM076b	+0.3	CLW019	-1.7, -1.7, -1.7	HSM092	+3.0, +2.5
GLS037	-3.7, -1.7				
GLS051	+2.9, +2.8, +3.0, +2.1, +3.3, +3.3	CLS037	-1.5, -2.3		
GLS050	+1.1	CLS037a	-4.0		
GLS052b	+3.1, +3.2, +2.8	CLS037b	-2.2		

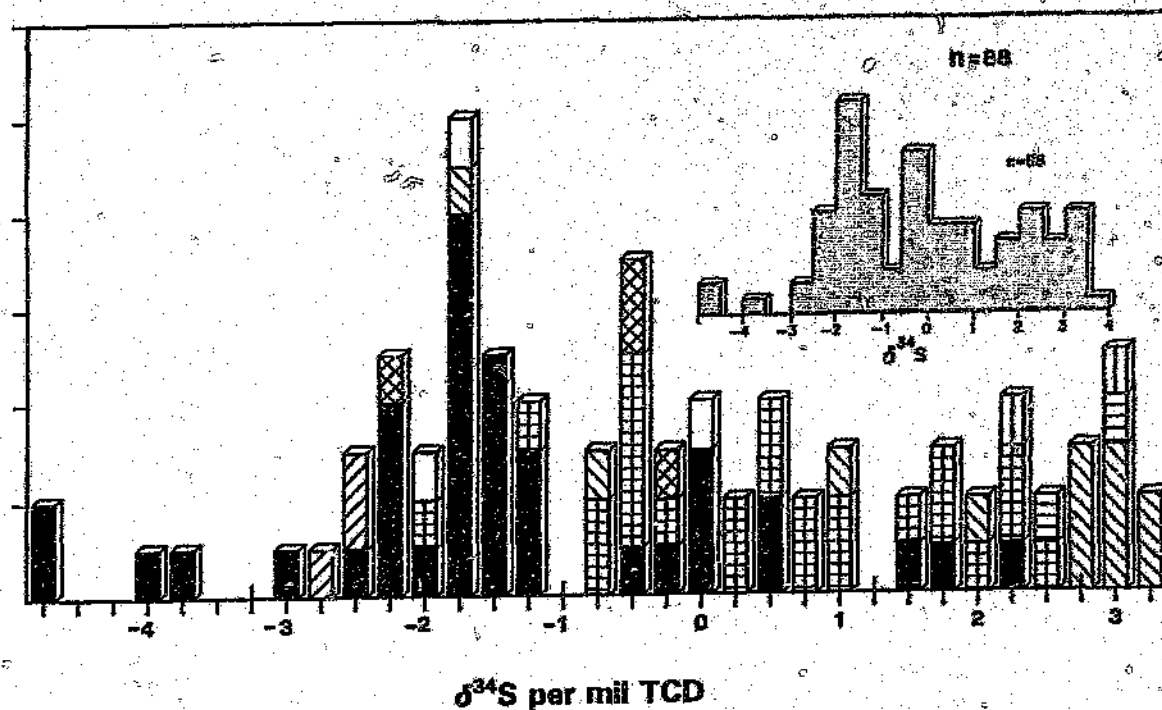


Figure 4.3 $\delta^{34}\text{S}$ values for pyrite separates from gold-bearing quartz veins, Sable-Pilgrim's Rest goldfield. All values are expressed in per mil notation relative to Canon Diablo Troilite (CDT).

4.1.3.2 Sulphur isotope interpretation

A feature of the sulphur isotope compositions of SPRG pyrites is the wide spread of data. Although the sulphur isotope values for the SPRG are distributed around 0‰, suggesting a typical magmatic signature, a distinct trend towards more negative sulphur isotope numbers exist among pyrites from the stratigraphically higher vein occurrences. This observed trend coincides with the trend toward negative $\delta^{34}\text{S}$ numbers in sulphides from host-rock sediments (Cameron, 1982). Cameron (1982) identified an isotopic transition zone in the lower Malmani Subgroup (Oaktree Formation), above which sulphides from interbedded shales were derived from sulphate reduction, involving both biogenic and inorganic processes. This abrupt decrease in $\delta^{34}\text{S}$ values was interpreted by Cameron (1982) as the earliest recorded sulphate reduction in the sedimentary record, and is important for several reasons. Firstly, it shows that sulphate-respiring bacteria was around at those times, and secondly, it indicates that sulphate was established as a major constituent of seawater (Cameron, 1982). The shift towards negative numbers in vein-associated sulphides could be ascribed to isotopic exchange with the latter group of shale hosted sulphides, suggesting a lithologic control on sulphur isotopic compositions. Along the same line of reasoning it could be argued that those samples that are enriched in ^{34}S could have gained their sulphur from evaporite minerals, such as anhydrite or gypsum. Textural evidence for the existence of evaporites occurring along the interbedded shale horizons is plentiful in the eastern portion of the Transvaal Sub-basin (Fig. 4.4a,b). Some of the oldest Proterozoic evaporites, dated at 1.3Ga, yielded $\delta^{34}\text{S}$ values of approximately 30‰ (Claypool et al., 1980). Thus, despite the variation within individual veins, the data suggest a lithological control on the distribution of sulphur isotopic composition of the vein hosted pyrites. Several other arguments can be put forward to interpret the variation in sulphur isotope composition, which seems to be a characteristic feature of sulphide mineralization in hydrothermal vein systems. The variable $\text{SO}_4/\text{H}_2\text{S}$ ratios in the inclusion fluids, hosted within the associated quartz (see chapter 3), would precipitate sulphides having variable $\delta^{34}\text{S}$ values (Ohmoto and Rye, 1979). Pyrites precipitated in an oxidizing environment yield $\delta^{34}\text{S}$ values that are considerably more negative compared to the mineralizing fluid (Schwarcz and Rees, 1985). This option can, however, be ruled out as a first order process responsible for the variation in $\delta^{34}\text{S}$ data, as the mineralizing fluids in the SPRG were reducing (see chapter 5). By implication the latter statement suggests that some of the $\delta^{34}\text{S}$ values of 0‰ or larger might have been a result of precipitation of sulphides from a reducing fluid (eg Golding and Wilson, 1983). A possible interpretation of the $\delta^{34}\text{S}$ data that can provisionally be ruled out is leaching of pre-existing sulphur-bearing minerals. Grinenko and Grinenko (1967) have indicated that sulphide mineral precipitated as a result of such a process yield little isotopic variation, and the $\delta^{34}\text{S}$

value of the precipitated sulphide could be up to 5‰ higher compared to the value of the leached source material. As SPRG $\delta^{34}\text{S}$ data for pyrite fall within the range defined for the host rock sulphur isotope data (Liebenberg, 1988), the latter leaching hypothesis as a mechanism in obtaining the required values, can be ruled out. Furthermore, this suggests that lateral secretion of gold from the sedimentary sequence, as a primary source of gold, is unlikely (see discussion in chapter 6).

The sulphur isotope data for the SPRG correspond broadly with the values presented for Archaean lode gold deposits (Cameron and Hattori, 1987; Colvine *et al.*, 1988). The negative $\delta^{34}\text{S}$ values of some Archaean lode gold deposits are, however, attributed to a control by oxygen fugacity ($f\text{O}_2$), which cannot apply to the sulphur isotope compositions of the SPRG where $f\text{O}_2$ is consistent and does not vary with the sulphur isotopic composition (see chapter 5 for $f\text{O}_2$ data). Thus, as in the case with other stable isotope systems, it is exceedingly difficult to unequivocally characterize the sulphur isotope values of the various potential reservoirs, as small changes in temperature, pH, ionic strength of the solution (I), and $f\text{O}_2$ (Ohmoto and Rye, 1979; Rye and Ohmoto, 1974; Ohmoto, 1972) induce profound changes on the isotopic compositions. These latter parameters have all been calculated for the SPRG fluids, using quantitative quadrupole mass spectrometer analyses on quartz hosted inclusion fluids (see chapter 5; Boer *et al.*, in press) and can be summarized as follow: average $f\text{O}_2 = 10^{-32.5}$; $f\text{H}_2\text{S}$ ranging between $10^{-2.5}$ and $10^{-2.8}$, pH=3.3 to 4.3 @ 320°C (neutral pH=5.1 @ 320°C); ionic strength=2.46, assuming $\sum \text{S}_{\text{Total}} \approx \text{X}_{\text{H}_2\text{S}}$ (see chapter 3). Ohmoto (1972) stated that the mean isotopic composition of sulphur in solution is a function of the proportional sum of all the sulphur species present (equation (1), Ohmoto, 1972), and deduce the equation $\delta^{34}\text{S}_i = f(\delta^{34}\text{S}_s, T, f\text{O}_2, \text{pH})$. In the interest of internal consistency, the older equilibrium constants, presented by Ohmoto (1972), were retained for the comparison. Equilibrium constants for data from this study were calculated using SUPCRT92 (Johnson *et al.*, 1992). When the above parameters are plotted onto the diagrams of Ohmoto (1972) the field that is defined, plots between the 0 and +1‰ $\delta^{34}\text{S}_i$ contours. This suggests that the measured deviation in sulphur isotope composition from the 0‰ average within individual vein systems at the different stratigraphic positions, may be a function of changes in pH, T, I and $f\text{O}_2$. Furthermore, this observation indicates that a magmatic origin for the ore-forming fluids cannot be disregarded. However, comparison of thermodynamic results calculated from different data sets should be used with circumspection. The fact that the above mentioned gas data plot in the wrong sulphide stability field is probably an indication of such data incompatibility. The variations in sulphur isotope compositions in other hydrothermal veins systems may also be a result of a variation in one or more of the above parameters, but this need to be

substantiated with quantitative data such as presented, before reliable comparisons are allowed.

In summary, the sulphur isotope composition of the SPRG pyrites show a wide scatter, with a distinct tendency towards more negative $\delta^{34}\text{S}$ values for pyrites from the stratigraphically higher vein occurrences. This deviation towards negative values coincides with the introduction of sulphate reduction as a viable fractionation mechanism for sulphur isotope ratios and, thus, implies equilibration between sulphur isotope compositions of the vein hosted pyrites and the host lithologies. The scatter in $\delta^{34}\text{S}$ values within individual veins are attributed to changes in external thermodynamic variables, such as pH, T, I and $f\text{O}_2$, and recalculation of the original sulphur isotope composition of the fluids yield $\delta^{34}\text{S}$ values around 0‰. This suggests that the fluids have retained a component of their original magmatic character. However, it is very difficult to unambiguously evaluate the origin of hydrothermal fluids on the basis of inferred sulphur isotope compositions alone.

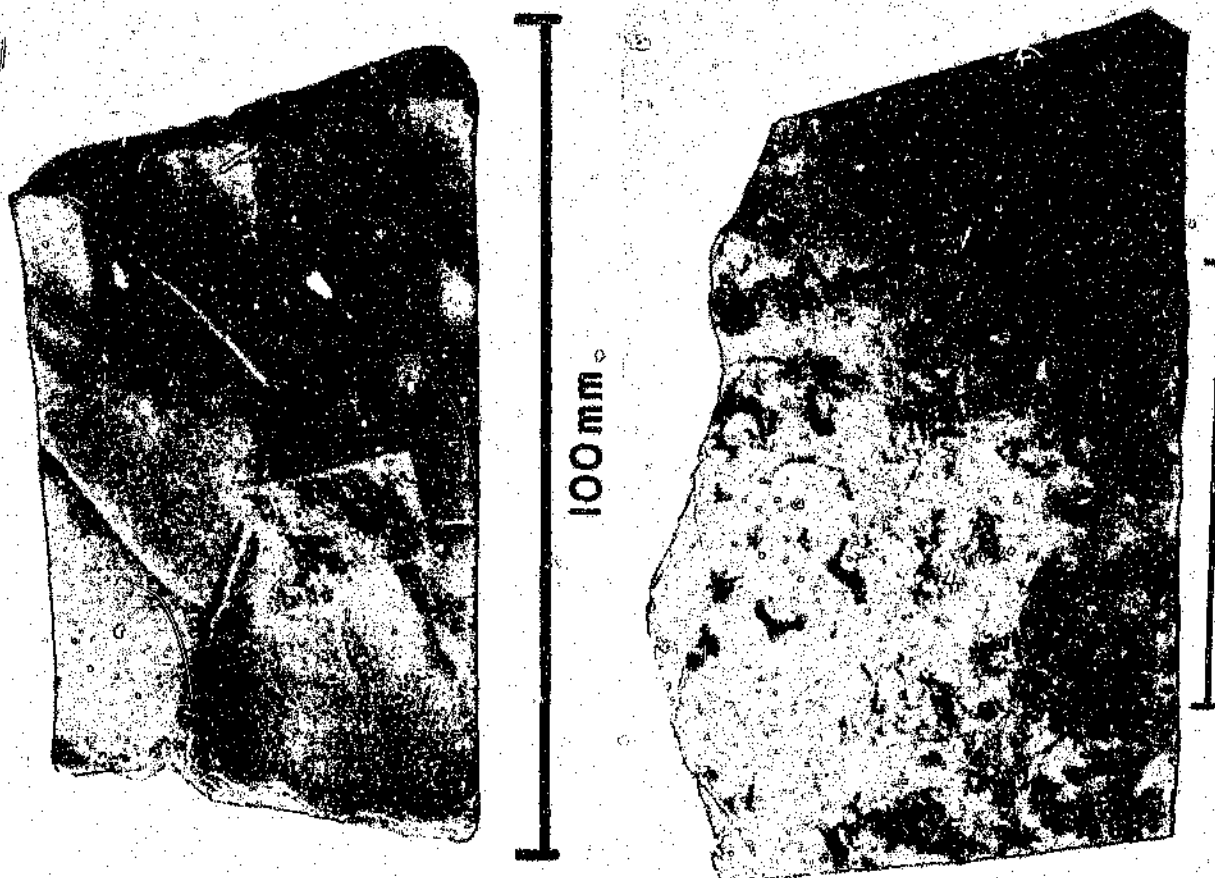


Figure 4.4 (a) Rectangular hopper crystal texture in dolomite, probably after anhydrite or gypsum, from the Transvaal Sequence, Transvaal Sub-basin. (b) cubic hopper crystals, probably halite or sylvite remnants, hosted in interbedded shales of the Chuniespoort Group.

4.1.4 Carbon Isotopes

4.1.4.1 Carbon Isotope results

^{13}C isotope values for quartz-hosted fluid inclusions fall within the range $+1.8$ to -12.0‰ (average $\delta^{13}\text{C} = -6.2\text{‰}$, $S_x = 4.6$, $n = 11$), whereas the values for pyrite hosted inclusion fluids vary between -4.8 and -1.4‰ . Carbon isotope compositions for inclusion fluids from stratiform and vertical veins overlap extensively (Table 4.2). The average value for vein hosted carbonate minerals is approximately -2.0‰ (Schidlowski *et al.*, 1975), whereas the average $\delta^{13}\text{C}$ value for the host sediments to the auriferous veins in the Transvaal Basin yield an average value of -0.85‰ ($n = 22$) (Schidlowski *et al.*, 1975; 1983).

4.1.4.2 Carbon Isotope Interpretation

A characteristic feature of the SPRG carbon isotope data is the coincidence in $\delta^{13}\text{C}$ values for gangue minerals (dolomite and calcite) and inclusion fluids hosted by vein quartz. As is the case with many of the other stable isotope systems, it is difficult to characterize a $\delta^{13}\text{C}$ value for specific carbon reservoirs. In general, $\delta^{13}\text{C}$ values of between -8 and -5‰ are considered as typical magmatic values (Kyser, 1986; Taylor, 1986). CO_2 -melt fractionation is approximately 3‰ , so that magmatic CO_2 is -5 to -2‰ (Taylor, 1986). It is, thus, clear that $\delta^{13}\text{C}$ values of approximately -3‰ are consistent with magmatic CO_2 , but not uniquely so. The assumption that $\delta^{13}\text{C}$ values of about -3‰ are uniquely diagnostic of a magmatic carbon reservoir is an unwarranted generalization (Kerrick, 1990). $\delta^{13}\text{C}$ values of -6.2‰ are difficult to interpret with regard to the carbon source, because magmatic, sedimentary and metamorphic rocks are all characterized by average $\delta^{13}\text{C}$ values in this range (Ohmoto and Rye, 1979). Furthermore, it should be kept in mind that the small data set presented in Table 4.2 is composed of samples from different localities, which may mask the real variations in the distribution of $\delta^{13}\text{C}$ values between vein systems which result from reactions with host rocks, gas immiscibility, or Rayleigh fractionation.

CO_2 with a $\delta^{13}\text{C}$ value of $-6.2 \pm 2\text{‰}$ would precipitate dolomite of $-4 \pm 2\text{‰}$ under the physico-chemical conditions summarized in section 4.1.3.3 (also see chapter 5). Fyon *et al.* (1984) argued that the $\delta^{13}\text{C}_{\text{H}_2\text{CO}_3}$ value of hydrothermal fluids could be shifted by $+2$ to $+3\text{‰}$ if small quantities of CH_4 (<10 mole%) were generated in the C-O-H fluid by a decrease of E_h , suffered by reactions with carbonaceous host rocks. However, this effect does not account for the enriched values observed in Table 4.2, where it is known that these samples occurred in close proximity to carbonate host rocks. Alternatively, positive ^{13}C shifts could be the result of a temperature decrease, but this possibility can be discounted based on the observation that the $\delta^{18}\text{O}$ values and calculated $\delta^{18}\text{O}_{\text{Fluid}}$, as well as the entrapment temperatures for

the various veins (see chapter 3) are remarkably uniform.

The SPRG carbon isotope data suggest that hydrothermal fluids may have acquired carbonic species (CO_2 , H_2CO_3 , HCO_3^-) from the carbonate host rocks. Under conditions where pressure = 2.2 to 2.5 kbar and temperature = 320°C , the $\delta^{13}\text{C}_{\text{Ca,Mg}(\text{CO}_3)_2} \approx \delta^{13}\text{C}_{\text{Fluid}}$ (Ohmoto and Rye, 1979), and fractionation between oxidized carbon species (CO_2 , H_2CO_3 , HCO_3^-) in solution is small (Bottinga, 1969). The calcite- HCO_3^- fractionation is $\sim +1\text{‰}$ at 320°C , so that calcite of -3‰ would have been precipitated from a fluid where $\delta^{13}\text{C}_{\text{HCO}_3^-} \approx -4\text{‰}$ (Kyser, 1987). The observed ranges and overlap in $\delta^{13}\text{C}$ values of gangue minerals and vein hosted inclusion fluids for the SPRG is consistent with the above mentioned values, thus, suggest dissolution and decarbonatization of the host dolomitic rocks. Although the $\delta^{13}\text{C}$ values of aqueous carbonate produced by such a process depends on a number of factors, it does appear as though isotopic equilibrium conditions were not obtained. Isotopic disequilibrium is apparent when the carbon isotope data are plotted onto a $\log f\text{O}_2$ vs pH diagram (after Ohmoto, 1972), using the external thermodynamic parameters calculated for the SPRG (see chapter 5). The SPRG data intersect the 21‰ $\delta^{13}\text{C}_{\text{H}_2\text{CO}_3}$ contour, clearly indicating isotopic disequilibrium in the carbon system. Ohmoto (1986) indicated that the isotopic effect between aqueous species and carbonate minerals are negligible, should disequilibrium conditions prevail. Under these conditions the $\delta^{13}\text{C}$ value of ΣCO_2 derived from carbonate rocks ranges between -8 and $+4\text{‰}$, coinciding with the range defined for the $\delta^{13}\text{C}$ values of the SPRG.

It is clear that the source, or sources, is not resolved with certainty, but dissolution and decarbonatization of the host rocks seem to be a plausible interpretation of the acquired carbon isotope data.

4.2 Radiogenic isotopes

Whole rock diabase samples were analysed for Rb, Sr, Sm, Nd and Pb by isotope dilution mass spectroscopy (ID-MS). Several whole rock dissolution procedures were used (Boer *et al.*, 1993; Appendix 1).

4.2.1 Rubidium-Strontium dating

4.2.1.1 Rb-Sr results

At the Olifantsgeraamte Mine, near Sable, a metamorphosed diabase sill is intersected by an auriferous quartz vein which is associated with a pronounced wall-rock alteration halo (Fig. 4.5a). Rubidium and strontium abundances and isotopic compositions of metamorphosed and altered diabase samples were analysed, following the procedure described by Boer *et al.* (1993), and the results are indicated in Table 4.4 and in Figure 4.5b. Whole rock Rb-Sr analyses of diabase from the Olifantsgeraamte Mine show variable Rb and Sr contents, with Rb concentrations in the range 71 - 120 ppm and Sr varying between 155 and 290 ppm, Rb and Sr concentrations in the unaltered samples range between 33 - 74 ppm and 150 - 262 ppm, respectively. $^{87}\text{Sr}/^{86}\text{Sr}$ ratios for altered samples range from 0.75169 to 0.76949, whereas the unaltered samples range from 0.71439 to 0.72974. These $^{87}\text{Sr}/^{86}\text{Sr}$ ratios, as well as Rb-Sr abundances, indicate that Rb has been introduced during vein-associated alteration. Samples affected by the vein-associated wall-rock alteration are widely scattered on a $^{87}\text{Sr}/^{86}\text{Sr}$ versus $^{87}\text{Rb}/^{86}\text{Sr}$ diagram (Fig. 4.5b), and were therefore not used in calculating an isochron. The remaining samples, away from the wall-rock alteration yield an errorchron corresponding to an age of 2927 ± 39 Ma with an initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of 0.7042 ± 0.0003 (MSWD = 15.523).

Table 4.4 Rb-Sr isotope abundance results for diabase sill from the Olifantsgeraamte Mine, near Sable.

A & U indicate altered and unaltered samples, respectively, whereas sp refer to spiked samples and nat refer to natural unspiked samples. Atomic $^{87}\text{Rb}/^{86}\text{Sr} = (^{87}\text{Rb}_{\text{ppm}}/^{86}\text{Sr}_{\text{ppm}}) \times 0.988494$.

Sample no.	$^{87}\text{Sr}/^{86}\text{Sr}$	^{87}Rb (ppm)	^{86}Rb (ppm)	^{87}Sr (ppm)	^{86}Sr (ppm)	$^{87}\text{Rb}/^{86}\text{Sr}$
2A/Fsp A	0.75355 ± 0.00002	25.54	90.21	19.58	202.75	1.2891
2A/Fsp A	0.75217 ± 0.00008			19.55		1.2909
2A/Fnat A	0.75226 ± 0.00002					
2A/Fnat A	0.75203 ± 0.00002					
2B/Hsp A	0.75987 ± 0.00002	20.29	71.68	16.51	171.95	1.2146
2B/Hsp A	0.75962 ± 0.00003			14.93	155.47	1.2431
2B/Hnat A	0.76028 ± 0.00002					
2B/Hnat A	0.76031 ± 0.00005					
2B/Hnat A	0.75988 ± 0.00001					
2C/Fsp U	0.72969 ± 0.00002	21.00	74.21	23.44	243.36	0.8657
2C/Fnat U	0.72974 ± 0.00005					
2C/Hsp U	0.72236 ± 0.00002	14.06	49.69	22.29	231.30	0.6235
2C/Hsp U	0.72228 ± 0.00004			17.57	182.29	0.7812
2C/Hnat U	0.72231 ± 0.00001					
2C/Hnat U	0.72241 ± 0.00002					
3A/Fsp A	0.76949 ± 0.00003	33.87	119.67	18.46	171.54	2.0342
3A/Fnat A	0.76919 ± 0.00002					
3B/Fsp U	0.71512 ± 0.00001	9.41	33.23	25.22	261.50	0.3886
3B/Fsp U	0.71439 ± 0.00003			14.44	149.69	0.6438
3B/Fnat U	0.71509 ± 0.00001					
4A/Hsp A	0.75774 ± 0.00004	29.88	105.58	17.97	187.10	1.6437
4A/Hsp A	0.75778 ± 0.00002			17.99	187.33	1.8417
4A/Hsp A	0.75774 ± 0.00002			15.09	157.07	1.9579
4A/Hnat A	0.75773 ± 0.00001					
4A/H1sp A	0.75169 ± 0.00002	32.09	118.20	27.85	289.76	1.1673
4A/H1nat A	0.75185 ± 0.00004					
4A/H1nat A	0.75192 ± 0.00004					
4A/H1sp A	0.75192 ± 0.00002			20.89	217.33	1.5563
4C/H1sp U	0.72644 ± 0.00002	15.84	55.96	21.48	222.92	0.7290
4E/H1nat U	0.72652 ± 0.00002					
4B/H1sp U	0.72650 ± 0.00002			21.01	218.07	0.7452
4C/Hsp U	0.71774 ± 0.00002	12.12	42.82	25.07	259.99	0.4779
4C/Hsp U	0.71764 ± 0.00002			18.65	193.44	0.6424
4C/Hnat U	0.71777 ± 0.00001					

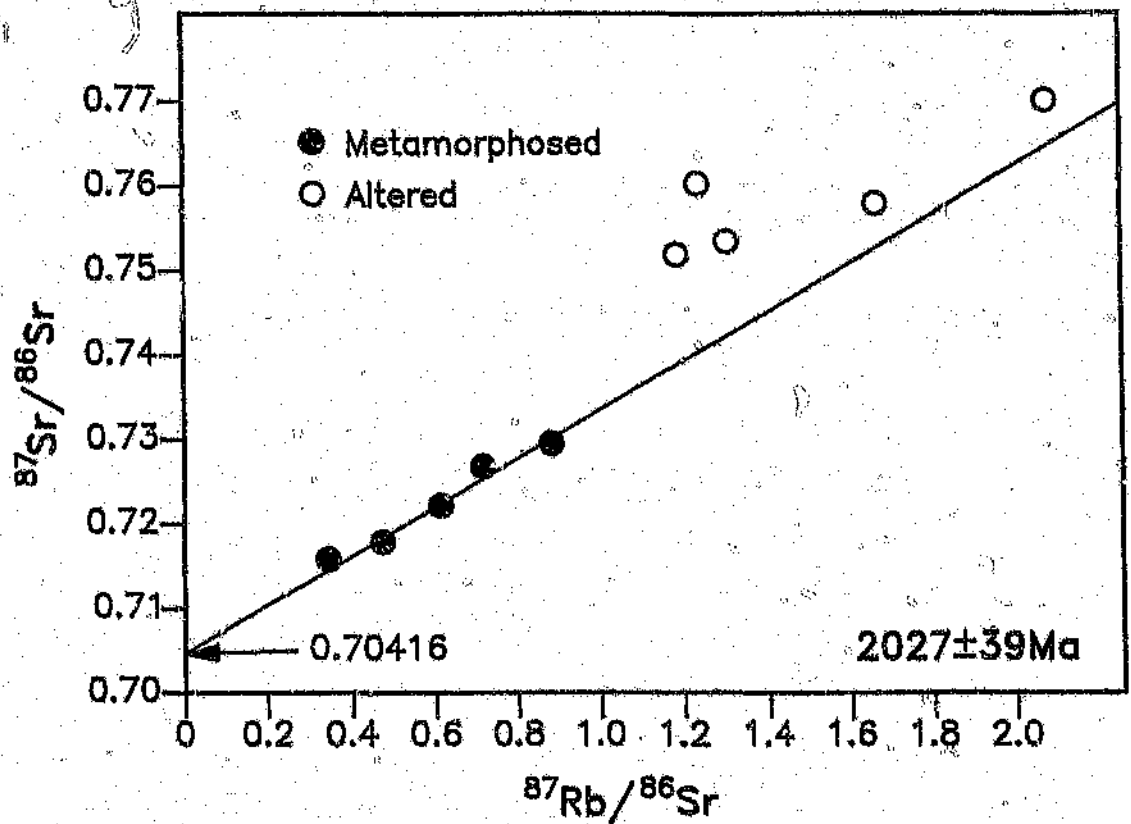


Figure 4.5 (a) Underground exposure at the Ollifantsgeraamte Mine, near Sabie, of an auriferous quartz vein, associated with a pronounced alteration halo, cross-cutting a dolerite sill. (b) Rb-Sr isochron of unaltered whole rock dolerite samples shown in (a). The isochron gives an age of 2027 ± 39 Ma with an initial $^{87}\text{Sr}/^{86}\text{Sr}$ of 0.71416 (MSWD = 15.5). The Rb-Sr ratios of altered samples have been completely reset.

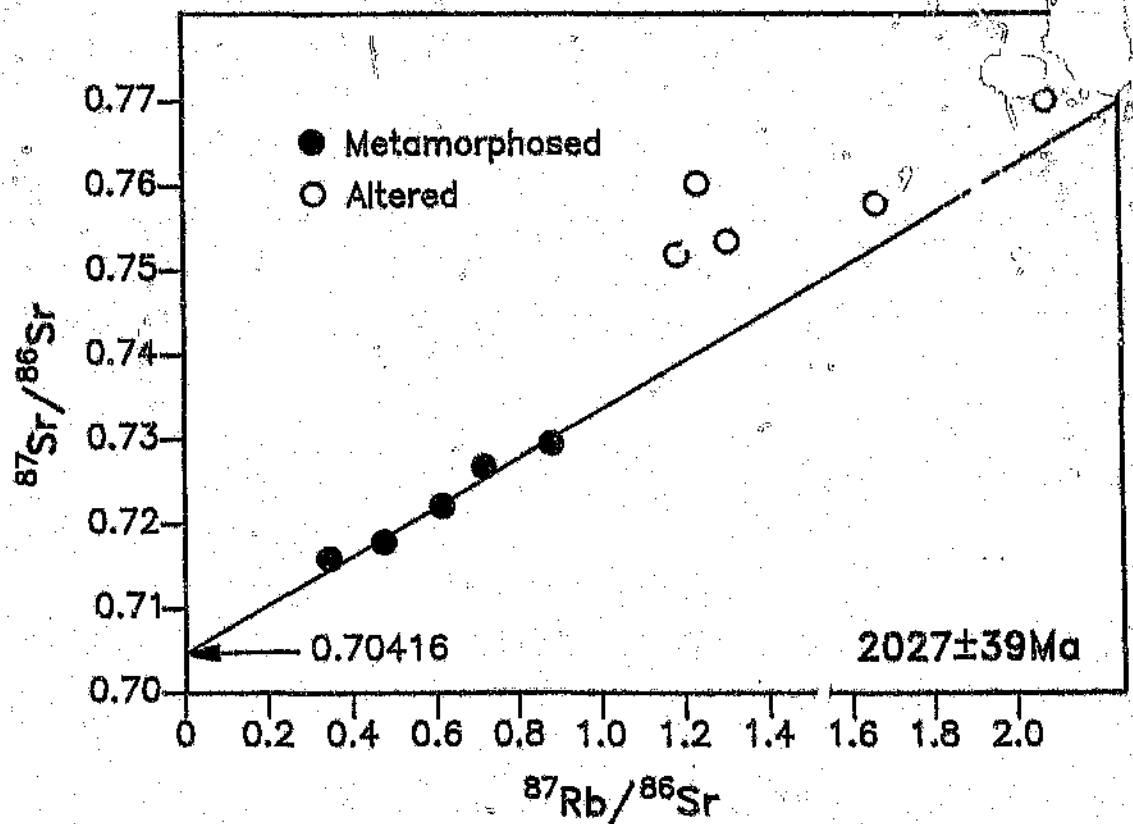


Figure 4.5 (a) Underground exposure at the Olifantsgeraamite Mine, near Sabie, of an auriferous quartz vein, associated with a pronounced alteration halo, cross-cutting a dolerite sill. (b) Rb-Sr isochron of unaltered whole rock dolerite samples shown in (a). The isochron gives an age of $2027 \pm 39 \text{ Ma}$ with an initial $^{87}\text{Sr}/^{86}\text{Sr}$ of 0.70416 (MSWD = 15.5). The Rb-Sr ratios of altered samples have been completely reset.

4.2.1.2 Interpretation of Rb-Sr data

These data may be relevant to the age of Pilgrim's Rest type gold mineralization, since the errorchron is interpreted to reflect the timing of metamorphism of the dolerite sill, brought about by emplacement of the mafic phase of the Bushveld Complex, which has been dated at 2061 ± 31 Ma (Walraven *et al.*, 1990). Interpretation of the Rb-Sr data for both hydrothermally altered and metamorphosed samples clearly shows that gold-vein associated alteration overprints the metamorphism, disturbing the metamorphic errorchron. This suggests that vein associated mineralization post-dates metamorphism, and by implication, the mafic phase of the Bushveld Complex. The age obtained from the metamorphosed dolerite samples thus represents a maximum age limit for Pilgrim's Rest-type gold mineralization. Furthermore, cross-cutting field relations between auriferous quartz veining with pre-Bushveld and syn-Bushveld diabase dikes (Sharpe *et al.*, 1981) yield the only dependable, albeit broad, age constraint. As is the case at the Olifantsgeraamte Mine, the pre-Bushveld diabase dikes/sills (Sharpe, 1981; Willemse, 1959) are intersected by gold mineralized quartz veins, whereas elsewhere the pyroxenitic syn-Bushveld dikes/sills cross-cut these mineralized quartz veins (eg Frankfort Mine). These field relations confine the age of mineralization to the early stages of emplacement of the Bushveld Complex, probably post-dating emplacement of the mafic phase. The age of the granitic phase of the Bushveld Complex have been dated at 2054.4 ± 1.8 Ma, using the single zircon Pb-evaporation technique (Walraven and Hattingh, 1993). Such field relations provide a minimum age limit, constraining the Pilgrim's Rest-type gold mineralization to syn-Bushveld age. An attempt was made to sample the latter diabase dyke at Frankfort Mine (upper adit), but the state of weathering prohibited reasonable Rb-Sr results. The Rb-Sr data show that no other significant thermal event had influenced the mineralized veins in the eastern Transvaal during post-Bushveld times, as such a thermal event would clearly be reflected in the susceptible Rb-Sr isotope systematics.

When comparing the Rb-Sr data of this study with those of the dolomite host-rock (Duane *et al.*, 1991) and interbedded shales (Meyer *et al.*, 1990; Dr. C.B. Smith, unpubl. data) (Fig. 4.6a) it is apparent that the radiogenic Rb-Sr composition of the diabase samples from the Olifantsgeraamte Mine and the dolomite host-rocks are distinctly different to that of the interbedded shales (Dr C.B. Smith, unpubl. data). Although the absolute Rb-Sr concentrations of the dolomite host-rock and diabase samples differ, they have very similar $^{87}\text{Rb}/^{86}\text{Sr}$ (0.0544 - 1.4137) and $^{87}\text{Sr}/^{86}\text{Sr}$ (0.71536 - 0.76679) ratios (Duane *et al.*, 1991), as is apparent from the overlapping distribution of data points on Figure 4.6b. Armstrong (1987) analysed nine hypersthene gabbros from the Rustenburg Layered Suite and showed that there is little

variation in the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios (0.70784 to 0.70742). The relatively low $^{87}\text{Sr}/^{86}\text{Sr}$ ratios for these Bushveld rocks, precludes them as a source for the high radiogenic values observed in the Olifantsgeraamte samples. This strongly suggest that the radiogenic strontium and rubidium content of the fluids associated with the vein-forming event is influenced by the dolomite host-rock composition. However, identification of a source for the vein-forming fluids, based on the available Rb-Sr data, requires an estimation of initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of the host sediment and the brine, as well as the degree and continuity of their isotopic interaction. Specific data for these parameters are not available. Furthermore, the assumption to use initial ratios of the shales, dolomites and brines that were equal to that of coeval seawater is pointless, as such data do not exist for Proterozoic seawater (Burke *et al.*, 1982). A third reason which make the absolute identification of a fluid source using Rb-Sr data unrealistic, is the uncertainty whether the vein-forming brines were predominantly influenced by evaporite dissolution or shale infiltration (Graf, 1982; Morton and Land, 1987), the latter having much higher $^{87}\text{Rb}/^{86}\text{Sr}$ ratios. In general, the most important water-rock reactions that modify brine compositions in a basin, including Rb-Sr content, involve feldspar alteration, illite formation, and calcite and evaporite dissolution (Gieskes *et al.*, 1986; Chaudhuri *et al.*, 1987). The relative importance of these reactions depend on the relative amounts of recrystallizing minerals and their Sr contents and on when the reactions occur. Thus, given these complicating factors, it is difficult to evaluate the degree of Rb-Sr isotopic exchange in the Transvaal Sub-basin. Furthermore, Morton (1985) showed that strontium isotopic exchange between pore water and illite is relatively rapid during early diagenesis, but as the basin matures and diagenesis is completed the isotopic compositions of water are less radiogenic compared to those of the host rock compositions. In fact, isotopic equilibrium has only been observed in cases where brines occupy isolated pockets in Precambrian basement rocks (McNutt *et al.*, 1984).

Because of these relative large uncertainties, it is not possible to quantify the source of the vein-forming fluids or to quantitatively evaluate the isotopic interaction between the ore-forming fluids and the dolomitic and shale host-rock.

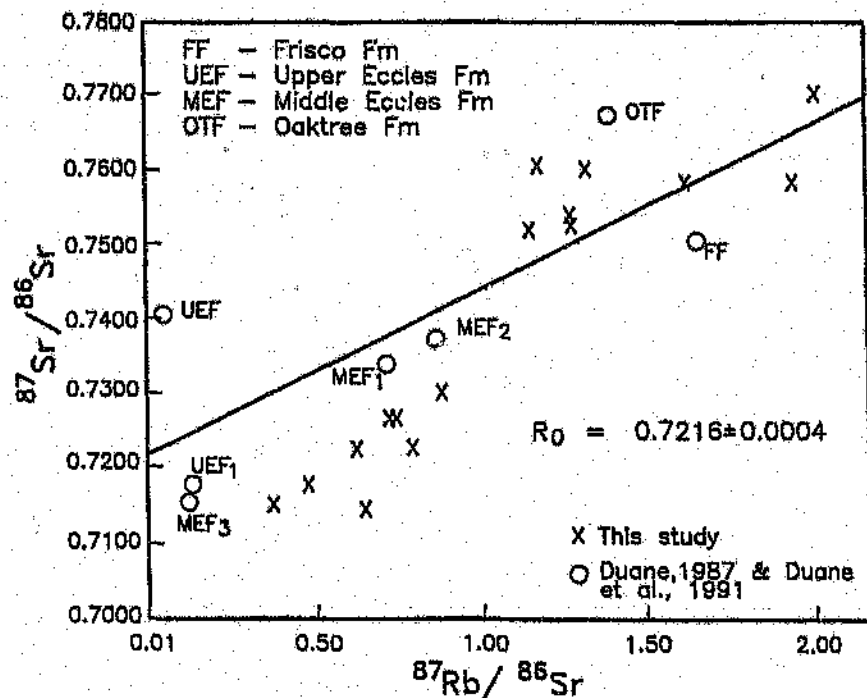
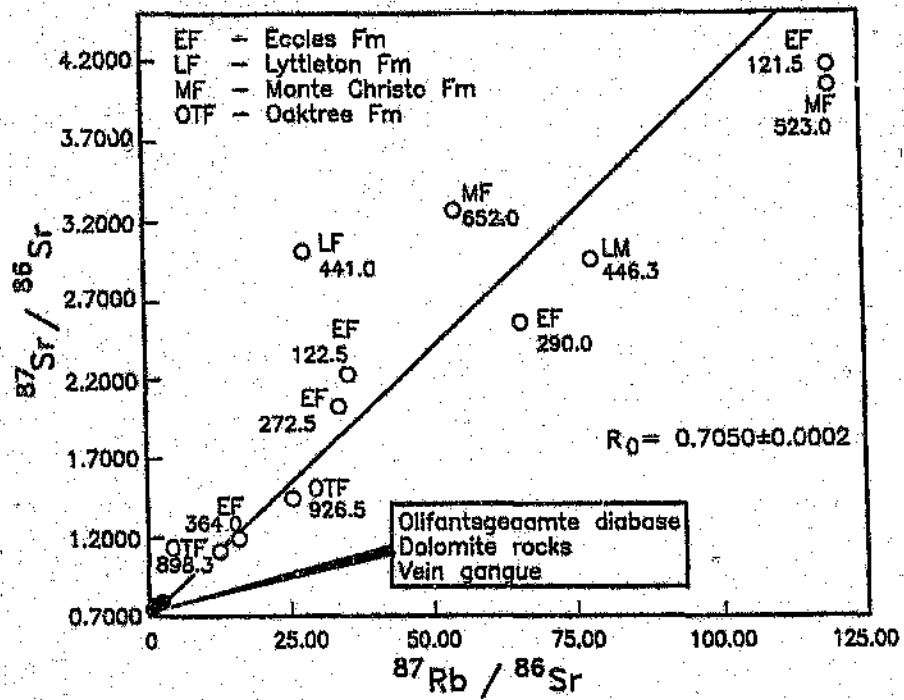


Figure 4.6 (a) Composite $^{87}\text{Sr}/^{86}\text{Sr}$ vs $^{87}\text{Rb}/^{86}\text{Sr}$ diagram of available data for the Transvaal Sequence dolomite (Duane *et al.*, 1991), shales (unpubl. data; C.B. Smith) and diabase (this study). $R_0 = 0.7050 \pm 0.0002$. (b) $^{87}\text{Sr}/^{86}\text{Sr}$ vs $^{87}\text{Rb}/^{86}\text{Sr}$ diagram illustrate interspersed data for dolomite host rock (Duane *et al.*, 1991) and diabase sill, Olifantsgeramte Mine. $R_0 = 0.7216 \pm 0.0004$.

4.2.2 Samarium-Neodymium System

4.2.2.1 Sm-Nd results and interpretation

Numerous duplicates of Sm and Nd analyses for 10 diabase samples are presented in Table 4.5. Problems were, however, encountered in obtaining consistent Sm and Nd concentrations and ratios for diabase samples from the Olifantsgeraamte Mine (see section 4.2.1; Table 4.6; Boer *et al.*, 1993). Comparison of ID-MS and INAA results show that for some samples (4B/H1, 2B/H, 4A/H1, 3B/F) the Sm analysis are in good agreement while in other cases the ID-MS results are between -20% and -50% lower. For Nd there is no agreement between the two methods and the ID-MS results are consistently lower. The Sm/Nd ratios determined by INAA vary in the narrow range between 0.159 to 0.187 while the ID-MS Sm/Nd ratios range from 0.200 to 0.354. These numbers clearly indicate fractionation of the solution to higher Sm/Nd values. These deviances cannot be explained by analytical uncertainties. Furthermore, it was not possible to duplicate any of the ID-MS Nd analyses, as is obvious from Table 4.5. Samarium did not present the same magnitude of error in duplicate ID-MS analyses (Table 4.6). The spurious ID-MS results are attributed to the presence of variable amounts of hieratite and ralstonite that take up the REE into their crystal structure. These precipitates preferentially incorporate the light REE (see section 4.2.1). Determination of model ages using the fractionated data was meaningless (Fig. 4.7) and a future age of -1033 ± 610 Ma ($R_0 = 0.5126 \pm 0.0005$; MSWD=0.86; $\epsilon_{Nd} = -26.79 \pm 9.70$) was obtained, using the DM model.

Table 4.5 Sm and Nd isotopes abundances for diabase from the Olifantsgeraamte Mine near Sabie

Sample no.	^{147}Sm (ppm)	Sm (ppm)	^{144}Nd (ppm)	Nd (ppm)	$^{147}\text{Sm}/^{144}\text{Nd}$	$^{143}\text{Nd}/^{144}\text{Nd}$
2A/F	0.68	4.44	5.71	24.01	0.1189	0.51179
	0.73	4.80	7.85	32.87	0.0937	
2B/H	0.62	4.08	3.95	16.61	0.1579	
	0.90	5.91	6.19	26.03	0.1460	
	0.72	4.73	6.52	27.39	0.1112	
	0.49	3.18	3.50	14.72	0.1388	
2C/F	0.75	4.92	6.60	27.72	0.1143	
	0.78	5.11	6.36	26.73	0.1229	
2C/H	0.96	6.27	6.33	26.62	0.1516	
	0.65	4.24	6.34	26.64	0.1024	
	2.54	16.57	5.01	21.05	0.4221	
	0.75	4.92	6.01	26.59	0.1090	
3A/F	0.88	5.74	6.91	29.06	0.1075	0.51161
			4.27	17.93		
3B/F	0.10	0.87	7.80	32.78	0.0132	0.51266
	0.81	5.33	1.29	5.44	0.6298	
	0.86	5.60	7.51	31.56	0.1141	
4A/H	0.48	3.15	7.63	32.05	0.1638	0.51151
			2.95	12.39		
			5.21	21.89		
			7.91	33.26		
4A/H1	0.48	3.12	3.30	13.87	0.1447	
	0.96	6.24	6.92	29.07	0.1383	
	0.78	5.13	5.94	24.95	0.1321	
			7.08	29.77		
4B/H1	1.16	7.56	2.24	9.18	0.1668	0.51163
			6.19	26.03		
			6.43	27.04		
			7.14	30.03		
4C/H	0.72	4.74	3.94	12.11	0.1493	
			4.85	20.40		
			6.05	25.42		
			5.22	21.94		

Table 4.6 Comparison of ID-MS and INAA analysis of samples where fluoride precipitates remained after acid digestion (all values are in ppm)

Sample No.	INAA	ID-MS	INAA	ID-MS	INAA	ID-MS
	Sm	Sm	Nd	Nd	Sm/Nd	Sm/Nd
2C/H	6.6	4.4	36.9	22.1	0.179	0.200
3B/F	7.3	7.7	42.0	34.6	0.174	0.223
4C/H	6.0	4.9	33.7	21.5	0.179	0.228
4B/H1	6.3	6.4	33.9	27.4	0.187	0.232
2B/H	5.7	6.2	33.4	17.5	0.171	0.354
4A/H	6.2	3.3	38.9	13.1	0.159	0.252
4A/H1	6.3	6.5	35.7	26.2	0.177	0.248

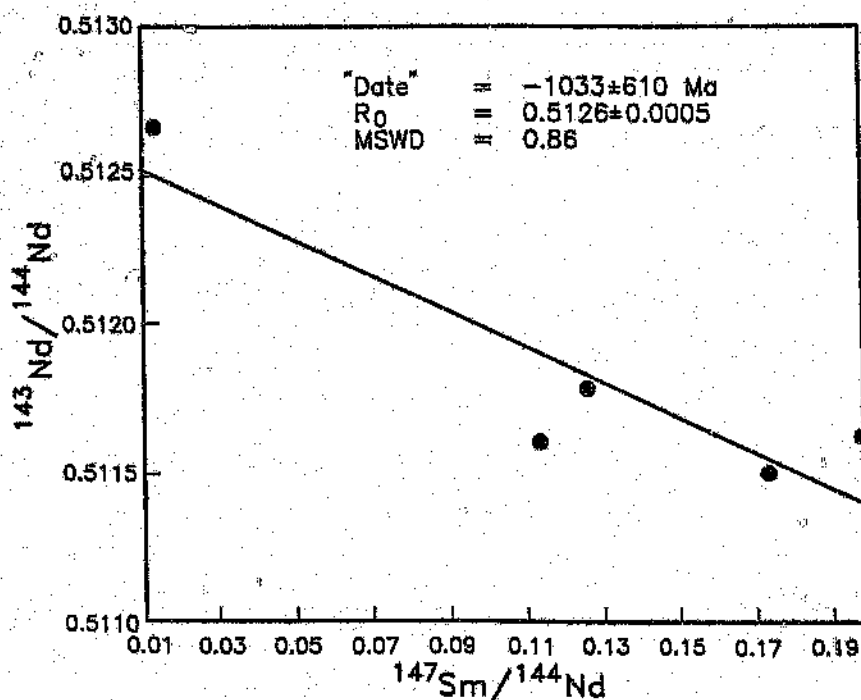


Figure 4.7 $^{143}\text{Nd}/^{144}\text{Nd}$ versus $^{147}\text{Sm}/^{144}\text{Nd}$ diagram for diabase samples (with fractionated Nd isotope compositions) from the Olifantsgeraamte Mine. The errorchron gives an "age" of -1033 ± 610 Ma; $R_0 = 0.5126 \pm 0.0005$; MSWD=0.86.

4.2.3 Lead-Lead System

4.2.3.1 Pb-Pb results

Eight diabase samples from the Olifantsgeraamte Mine were analysed for Pb isotopic ratios by Dr R.A. Armstrong at the University of Cape Town, Department of Geological Sciences, and the results are presented in Table 4.7. Six of the analyses (excluding OG 3B/F and OG 4A/H) conform to a secondary isochron (MSWD=1.73) with an "age" of 1636^{+172}_{-155} Ma (Fig. 4.8). The slope of the flat-lying regression line produced on the $^{207}\text{Pb}/^{204}\text{Pb}$ versus $^{208}\text{Pb}/^{204}\text{Pb}$ diagram (Fig. 4.8) is 0.1023 ± 0.0067 (1σ). The limited range in Pb isotope ratios, however, means that the uncertainty attached to the age data is large. The mean of the samples are slightly more radiogenic compared to those values that are presented by Duane (1987), Duane *et al.*, (1991) and Anderson (1992) for the Transvaal Sub-basin of the Transvaal Sequence (Fig. 4.9). The obtained Pb isotopic composition for the Olifantsgeraamte Mine is certainly more radiogenic than the values for the Griqualand West Sub-basin (Armstrong, 1987; Duane *et al.*, 1991). Comparison of the available Pb isotope data for the Transvaal Sub-basin (Fig. 4.10), as well as the Bushveld Complex, shows a restricted range in values and does not exhibit compositional differences, as for the lode gold deposits in the Abitibi belt, Ontario (Franklin *et al.*, 1981).

In general, initial Pb isotope ratios of Archaean and Proterozoic hydrothermal gold lode systems are more radiogenic than the supracrustal sequences which host the mineralization. Several workers have investigated the Pb isotopic composition of the eastern Transvaal gold lodes, among others Duane (1987), Duane *et al.*, (1988; 1991), Meyer *et al.*, (1990) and Anderson (1992). All the reported Pb isotopic compositions show a wide range of values. Duane *et al.*, (1991) recognized that Pb in sulphides from the Transvaal Sub-basin of the Transvaal Sequence becomes more radiogenic towards the north and east ($^{208}\text{Pb}/^{204}\text{Pb} = 14.53$ to 16.93). An important feature of Duane's *et al.*, (1991) data is the stratigraphic variation in Pb isotope composition, with the least radiogenic galena coming from the Oaktree Formation at the base of the carbonate sequence and the most radiogenic galena situated in the stratigraphically higher Frisco Formation in the northern Transvaal. Duane *et al.* speculated about possible sources for the radiogenic Pb isotope ratios, but failed to provide a conclusive interpretation. Meyer *et al.*, (1990) concluded that pyrites from the interbedded shales of the Transvaal Sequence represent a more radiogenic endmember, with the intermediate Pb isotopic composition of the veins-hosted sulphides being at least partially derived from the less radiogenic Bushveld Complex. None of the previous Pb isotope studies have provided convincing age constraints on the timing of vein emplacement.

Table 4.7 Pb-Pb isotope ratios for diabase from the Olifantsgeraamte Mine near Sable

Sample No.	$^{206}\text{Pb}/^{204}\text{Pb}$	$^{207}\text{Pb}/^{204}\text{Pb}$	$^{208}\text{Pb}/^{204}\text{Pb}$
OG 3B/F U	23.574	16.234	44.549
OG 3A/F A	19.571	15.588	38.861
OG 2C/F U	18.236	15.414	38.099
OG 4A/H A	18.316	15.619	38.146
OG 2C/H U	21.581	15.747	41.483
OG 2B/H A	18.630	15.454	38.238
OG 4B/H1 U	18.122	15.388	38.040
OG 4C/H U	20.555	15.646	40.610

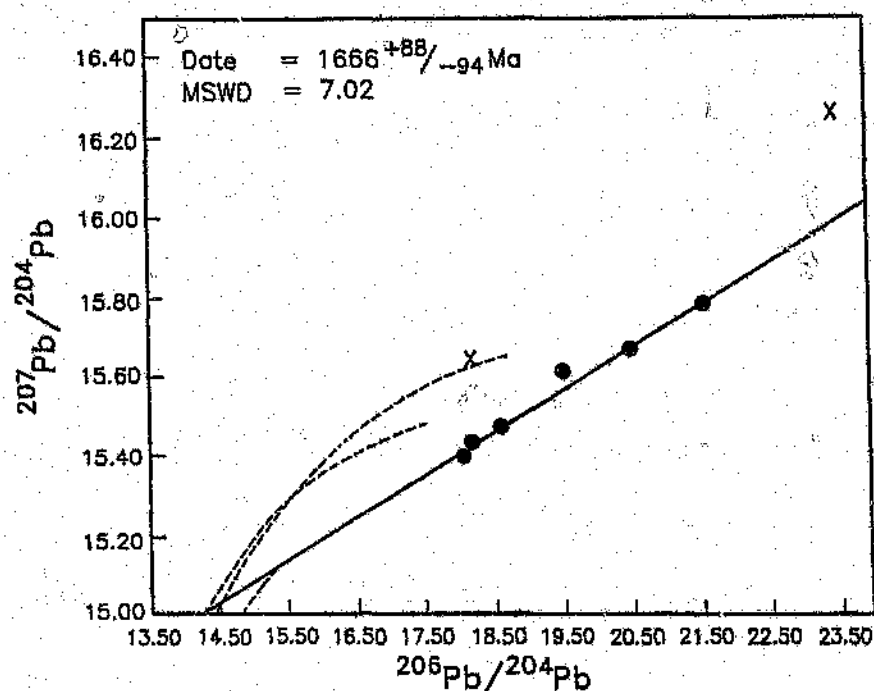


Figure 4.8 $^{207}\text{Pb}/^{206}\text{Pb}$ vs $^{206}\text{Pb}/^{204}\text{Pb}$ diagram of new whole rock data from a diabase sill at the Olifantsgeraamte Mine, near Sable. The Stacey and Kramers (1975) growth curve for crustal lead is also shown. The secondary isochron yields an "age" of 1666 $\pm$ 88 Ma; MSWD=7.02.

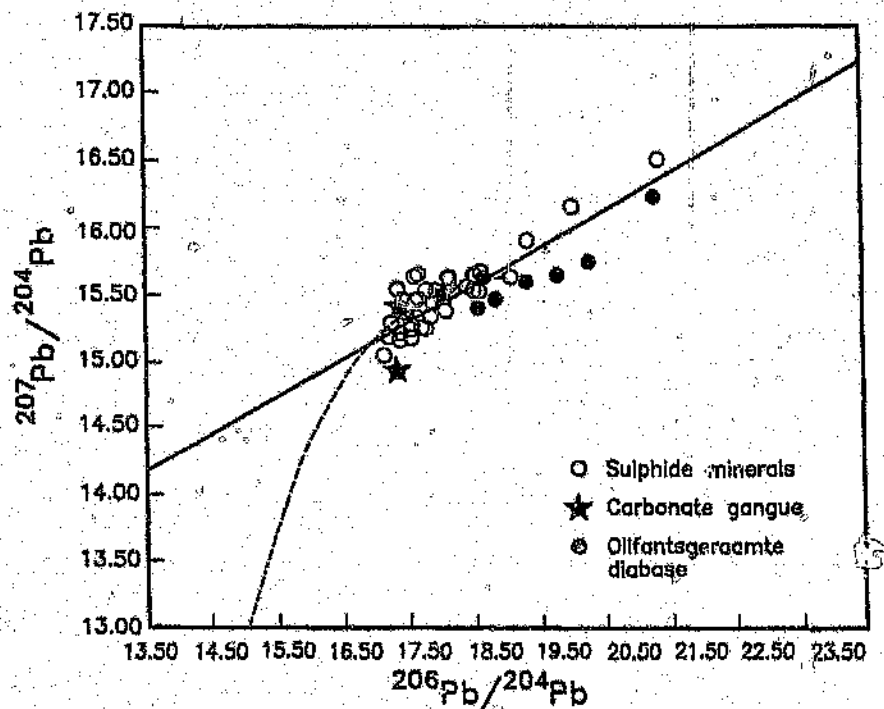


Figure 4.9 Composite $^{207}\text{Pb}/^{206}\text{Pb}$ vs $^{206}\text{Pb}/^{204}\text{Pb}$ diagram of sulphide data for the Transvaal Sub-basin of the Transvaal Sequence (data from Duane, 1987; Duane *et al.*, 1991; Anderson, 1992), carbonate gangue (Anderson, 1992) and whole rock diabase samples from the Olifantsgeraamte Mine. The errorchron for the complete data set correspond to an "age" of 2219^{+3}_{-3}Ma ; MSWD=375.29.

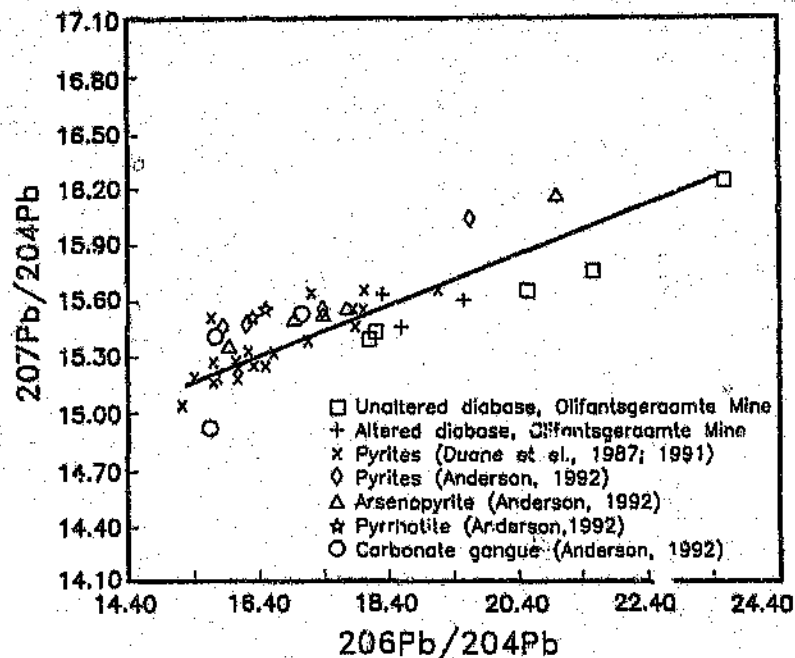


Figure 4.10 A binary $^{207}\text{Pb}/^{204}\text{Pb}$ versus $^{206}\text{Pb}/^{204}\text{Pb}$ diagram of the lead isotopic composition of sulphides, gangue phases and host rocks from the Transvaal Basin (data from Duane, 1987; Duane *et al.*, 1991; Anderson, 1992 & this study). A characteristic feature of the data is the narrow clustering, compared to data from other ore deposits, eg massive sulphide deposits from the Noranda district (Franklin *et al.*, 1981; 1983).

4.2.3.2 Pb-Pb interpretation

There seems to be no relation between the degree of alteration of the dolerite samples from the Olfantsgeraamte Mine and the Pb isotopic composition (Fig. 4.8). The flat-lying regression line acts as a connecting line between the low radiogenic values of hypersthene gabbro samples of the Rustenburg Layered Suite, Bushveld Complex (Armstrong, 1987), and the more radiogenic interbedded shales from the SPRG (F.M. Meyer, unpubl. data). Thus, the regression line calculated for the Olfantsgeraamte Mine diabase samples appears to be the result of mixing of two isotopically dissimilar sources, in this case a Bushveld component and the interbedded shales of the Transvaal Sequence. Therefore, the calculated regression line does not have any significance in terms of Pb isotope evolution and cannot be interpreted as an isochron. Data presented by Meyer *et al.*, (1990) also plot on regression lines with shallow slopes (varying between 0.140 and 0.165). The latter authors have also interpreted the data as indicative of mixing, rather than palaeo-isochrons. The interpretation presented above is similar to that suggested by (Meyer *et al.*, 1990) that the interbedded shales of the Transvaal Sequence provide the more radiogenic endmember of a mixing line, while the least radiogenic Pb isotope values are similar to Pb in galena from the Transvaal Sequence-hosted Pb-Zn deposits (Duane *et al.*, 1991), as well as the Pb in the Rustenburg Layered Suite of the Bushveld Complex (Armstrong, 1987). Anderson (1992) put that it is unlikely that the more radiogenic Pb compositions in the Transvaal Sequence could have been derived by closed system evolution as U concentrations are extremely low in samples from the Transvaal Sequence. The data on carbonate gangue phases (Fig. 4.9) confirm the suggestion that radiogenic Pb could not have been derived from the host-rock.

A number of preliminary conclusions follow from the Pb isotope data: (i) If Pb has been remobilised exclusively from a single carbonate sequence, such as the Transvaal Sequence, by implication, this source must have been laterally heterogeneous. However, the consistent Pb isotope ratios that have been published for the Transvaal Sequence carbonate rocks (Armstrong, 1987; Duane *et al.*, 1987, 1991; Anderson, 1992) show that this is not the case; (ii) It follows that more than one source of Pb is involved in the SPRG ores; (iii) The available Pb isotope data suggest mixing between endmember Pb isotope compositions, probably involving a Bushveld component and interbedded shales of the Transvaal Sequence.

CHAPTER 5 - THERMODYNAMIC MODELLING

To derive expressions for the fugacity and activity of a specific fluid, it is essential to first calculate the chemical potential of a fluid species in mixed fluids. Calculation of these quantities requires knowledge of the volume equations of state for pure fluids and fluid mixtures.

5.1 Evaluation of equations of state

Equations of state (EOS) for the principle fluid components encountered in the SPRG, ie H_2O , CO_2 , CH_4 and N_2 , were used in the thermochemical modelling of ore-forming fluids and the interpretation of fluid inclusions. An arbitrary selection of EOSs for the pure fluid components were evaluated following the guidelines set by Blencoe and Sterner (1992), Seitz *et al.*, (1994) and a straightforward comparison of results. Simulation of P-V-T properties of real systems using molecular dynamics (eg Belonoshko and Saxena, 1991, Duan *et al.*, 1992) was calculated with the computer program SUPERFLUID (Belonoshko, pers. commun., 1994). The latter results were not compared to experimental and empirically determined EOS, because of the large number of chemical species considered in the molecular dynamic modelling.

5.1.1 H_2O

The various EOS for H_2O developed by Burnham¹ *et al.*, (1969), Holloway (1977), Kerrick and Jacobs (1981), Bowers and Helgeson (1983), Haar *et al.*, (1984), Saul and Wagner (1989), Hill (1990) and Holland and Powell² (1991) were compared. These EOS can be divided into two groups, namely (1) equations developed mainly for the purpose of modelling the thermochemical properties of pure H_2O (eg Hill, 1990; Haar *et al.*, 1984; Burnham *et al.*, 1969; Saul and Wagner, 1989; Holland and Powell, 1991), and (2) equations formulated principally for thermodynamic modelling of fluid mixtures that contain H_2O (eg Hill, 1990; Bowers and Helgeson, 1983; Kerrick and Jacobs, 1981; Holloway, 1977). Sources for experimental data for H_2O are listed by Hill (1990). Blencoe and Sterner (1992) showed that isochores calculated with the first group of equations are in good agreement, but the second group of EOS yielded inconsistent isochores and do not compare favourably with those of the first group. This suggests that development of several of the second group EOS have been achieved at the expense of accuracy in representing experimental data for H_2O (Blencoe and Sterner, 1992). However, at high temperatures and low pressures the isochores of the two groups approach one another, an observation that is to be expected as the EOS are constrained mathematically to obey the restriction that $PV \rightarrow RT$ as $P \rightarrow 0$ (ideal gas law). Hill (1990) determined the triple point for H_2O to be at 0.00611 bars, 0.01°C

¹Actually, the EOS developed by Burnham *et al.*, (1969) consists of 6 discrete equations that mimic the mathematical behaviour of a single EOS (also see Blencoe and Sterner, 1992).

²The Holland and Powell (1991) EOS includes two terms that are only applied when $P > 2$ kbar; hence, the breaks in the slopes of the isochores calculated from this EOS.

and the critical point at 220.46 bars, 373.917°C, whereas the density of liquid H₂O decreases from 55.49 mol.litre⁻¹ at the triple point to 17.92 mol.litre⁻¹ at the critical point. Corresponding molar volumes for liquid H₂O at the triple point and for supercritical H₂O at the critical point are 18.02 and 55.81 cm³.mol⁻¹, respectively. The preferred EOS for H₂O are those developed by Saul and Wagner (1989) and Hill (1990).

5.1.2 CO₂

EOS for CO₂ can be divided into the same two groupings as those for H₂O EOS. EOS developed for thermochemical modelling of pure CO₂ systems include Shomakov and Shmulovich (1974), Bottinga and Richet (1981), Mäder and Berman (1991) and Holland and Powell³ (1991), whereas EOS developed for the thermodynamic modelling of mixtures involving CO₂ include Kerrick and Jacobs (1981), Bottinga and Richet (1981), Holloway (1977) and Saxena and Fei (1987). The principle sources of high P-T volumetric data for CO₂ are Juza *et al.*, (1965), Tsklis *et al.*, (1971) and Shomakov and Shmulovich (1974). Sources of phase-equilibrium data for reactions involving pure CO₂ have been compiled by Mäder and Berman (1991, Table 1). As is evident from the work of Blencoe and Sterner (1992), both groups show large discrepancies between the isochores calculated, particularly at high pressures (> 4 kbar) and low temperatures (< 400°C). For pure CO₂ the EOS developed by Bowers and Helgeson (1983) yields results similar to those derived from the Holloway (1977) EOS. Following the equations developed by Ely *et al.*, (1989) and Sterner and Bodnar (1991) the CO₂ triple point was calculated at 5.171 bars, -56.602°C and the critical point at 73.75 bars, 30.977°C. The density of liquid CO₂ decreases from 25.80 mol.litre⁻¹ at the triple point to 10.60 mol.litre⁻¹ at the critical point. Corresponding molar volumes for liquid CO₂ at the triple point and for supercritical CO₂ at the critical point are 37.31 and 94.34 cm³.mol⁻¹, respectively. According to Blencoe and Sterner (1992) the EOS by Kerrick and Jacobs (1981) is preferred for reproducing published P-V-T data for CO₂, whereas the EOS of Mäder and Berman (1991) is constraint by reversed phase-equilibrium data for subsolidus reactions involving pure CO₂, in addition to P-V-T data. The major source of error in calculated volumetric properties of fluid mixtures is the inability of equations of state to accurately predict the volumetric properties of the pure components (Seitz *et al.*, 1994).

³The Holland and Powell (1991) EOS for CO₂ includes two terms that are applied only when P > 5 kbar, thus the change on slope when calculating isochores using this EOS.

5.1.3 CH₄

EOS for CH₄ developed by Jacobs and Kerrick (1981 and Saxena and Fei* (1987) were compared to that of Redlich and Kwong (1949). The principal sources of high P,T experimental data for CH₄ are cited in Jacobs and Kerrick (1981) and Friend *et al.*, (1989). Isochores derived from these three EOS yield very similar results at $P \leq 5$ kbar and $T \geq 200^\circ\text{C}$ (Blencoe and Sterner, 1992). [CH₄: triple point is at 0.117 bars, -182.465°C , density at triple point = $28.145 \text{ mol.litre}^{-1}$; critical point situated at 45.992 bars, -82.599°C , density at critical point = $10.139 \text{ mol.litre}^{-1}$ (Friend *et al.*, 1989); corresponding molar volumes for liquid CH₄ at the triple point and for supercritical CH₄ at the critical point are 35.53 and 98.63 $\text{cm}^3.\text{mol}^{-1}$, respectively]. Blencoe and Sterner (1992) found that the EOS of Jacobs and Kerrick (1981) yields the most accurate calculated molar volumes for CH₄.

5.1.4 N₂

Thermodynamic properties of N₂ at P,T conditions up to 10 kbar and 1700°C were modelled using the EOS of Jacobson *et al.*, (1986) and an Redlich-Kwong equation (see Blencoe and Sterner, 1992). Representative Isochores from the two EOS formulations give similar results at low pressures and high temperatures, but at high pressures and low temperatures the isochores calculated from the two EOS are markedly different. Blencoe and Sterner (1992) ascribed this difference to the inability of the Redlich-Kwong equation to accurately represent the volumetric properties of N₂ when it is compressed to a "liquid-like" density. [N₂: critical point is at 33.978 bars and 399.343°C]

5.2 Pressure and temperature determinations from microthermometric fluid inclusion results

Pressure determinations based on fluid inclusions require compositional data on the inclusion contents and accurate P-V-T-X data on these compositions. In this study fluid compositions have been established with quantitative quadrupole mass spectrometer gas analyses, as well as semi-quantitative fluid inclusion microthermometry, Raman spectroscopy and $\mu\text{FT-IR}$, whereas the P-V-T-X data for the SPRG fluids are extrapolated using a selection of EOS as discussed in section 5.1. The pressure at the site of the inclusion is actually hydrostatic, although it has to be established whether the source of the pressure was hydrostatic, lithostatic or some intermediate value. In the case of SPRG a minimum pressure exerted on both the horizontal and vertical orientated veins is equal to the lithostatic pressure (see Roedder and Bodnar, 1980, Fig. 1, p.269), although the confining pressure is not well constrained.

*The Saxena and Fei (1987) EOS consists of two discrete equations, one for pressures above 1 kbar, the other for pressures below 1 kbar.

due to the lack of suitable geobarometers. Furthermore, the recognition of low-angle thrust deformation in the horizontal veins (Harley and Charlesworth, 1992), as well as the temporal and genetic interrelations of fluid inclusions (Boer *et al.*, in press), among other factors, necessitates that fluid pressures equal or exceed lithostatic levels. The SPRG horizontal veins record a vertical increment of dilation, suggesting that fluid pressures exceeded lithostatic levels for transient periods. It is conceptually difficult to see how lithostatic loading alone can be responsible for the formation of such overpressures in a deep crustal environment, such as was proposed by Anderson *et al.*, (1992). A reconstruction of the overburden at the time of quartz vein mineralization yields a thickness of approximately 7 to 8 km (Button, 1986). Using density data of Smit and Maree (1966) for the rock sequence involved, these thicknesses correspond to lithostatic pressures of 2.2 to 2.5 kbar (1 kbar per 3.2 km). Dissolution of daughter crystals after vapour homogenization, furthermore, indicates high minimum entrapment pressures. The abundance of two phase fluid inclusions also indicate that the hydrostatic pressure at the time of trapping was higher than the vapour pressure of the particular solution.

By plotting the above pressure values onto a P-T diagram showing various isochores for the different compositions and EOS (Fig. 3.11). From this diagram it is clear that the independently determined pressures (reconstruction of the overburden) and temperature (arsenopyrite geothermometer) are complimentary, indicating entrapment conditions around 320°C and 2.2 kbar for the SPRG mineralizing fluids.

Kalyuzhnyi and Kotun (1953) applied a method of intersecting isochores, calculated for separate CO₂ and H₂O inclusions, for the determination of entrapment pressures, first described by Nacker (1921). This method is discounted because there is no unambiguous evidence that the "pure" CO₂ and H₂O inclusions have been trapped simultaneously (ie under exactly similar P,T conditions), resulting in unacceptably large error limits.

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5.3 Salinity and Na/K ratios

The salinity of H₂O-salt inclusions are usually obtained by determination of the depression of the melting temperature of ice in the inclusion and application of the equation of Potter *et al.*, (1978). Hall *et al.*, (1988) experimentally redetermined the ice-melting temperatures of H₂O-NaCl-KCl solutions with compositions ranging from pure water to the ternary eutectic and to each of the two binary eutectics, i.e. H₂O-NaCl and H₂O-KCl. Bodnar (1993) regressed these H₂O-NaCl ice-melting temperatures using salinity as the dependent variable and yielded the following equation:

$$\text{Salinity} = 0.00 + 1.78\theta - 0.0442\theta^2 + 0.000557\theta^3$$

where θ is the depression of the freezing point in degrees Celsius.

Determination of the Na/K ratio is critical for the calculation of pH as well as a number of other related thermodynamic parameters. Two methods have been used to obtain a reliable estimate of the latter ratio.

(1.) Muscovite has been identified within most of the gold mineralized veins of the region, [eg Elandschoogte Mine (Harley & Charlesworth, 1991)]. XRD-patterns confirm the presence of 2M₁ and 1M muscovites, that occur as serrated intergrowths within the anhedral buck quartz that comprise the bulk of the vein (eg Dowling and Morrison, 1989). These micas are spatially and paragenetically related to late stage, fracture-hosted gold grains, which are developed within coarse-grained pyrite (Harley & Charlesworth, 1991). For this reason the chemistry of the micas is relevant to the composition of the gold-bearing fluid and, thus, chemical equilibrium between mica and the ore-fluid is inferred.

Electron probe micro-analyses of muscovite samples from the Elandschoogte deposit show that these micas have extremely low Na₂O contents [$x=0.10 \pm 0.03$ (2 σ) wt% Na₂O], and consistently high K₂O contents [$x=11.01 \pm 0.53$ (2 σ) wt% K₂O] (Harley, 1993; Boer and Harley, 1994). Calculation of the thermodynamic activity of stoichiometric endmember minerals is possible via homologous site mixing models for white micas (Aagaard and Helgeson, 1983). The equations describing the activity of stoichiometric paragonite and muscovite are as follows:

$$a_{\text{Paragonite}} = 9.4815(X_{\text{Na}}^{\text{XII}})(X_{\text{Al}}^{\text{VI}})^2(X_{\text{Al}}^{\text{IV}})(X_{\text{Si}}^{\text{IV}})^3$$

$$a_{\text{Muscovite}} = 9.4815(X_{\text{K}}^{\text{XII}})(X_{\text{Al}}^{\text{VI}})^2(X_{\text{Al}}^{\text{IV}})(X_{\text{Si}}^{\text{IV}})^3$$

These calculations give consistent activities for stoichiometric paragonite and muscovite ($a_{\text{paragonite}} = 1.002$; $a_{\text{muscovite}} = 0.686 \pm 0.077$) (Table 5.1; electron microprobe data from Harley, 1993). It is

noteworthy that the activity of muscovite exceeds that of paragonite by two orders of magnitude. In K^+/H^+ and Na^+/H^+ activity space, the composition of the muscovite (*sensu lato*) constrains the Na/K ratio of the equilibrium fluid from which such micas crystallized (Aagaard and Helgeson, 1983; Helgeson and Aagaard, 1985). Using this approach a $\log a_{Na^+/H^+}$ versus $\log a_{K^+/H^+}$ diagram was constructed (Figure 5.1) for the relevant phases, including the previously calculated activity contours for stoichiometric paragonite and muscovite. Na:K molal isopleths have been overlain on the diagram. These isopleths have been calculated using stoichiometric ion activity coefficients of Na^+ and K^+ computed from data of Helgeson (1969) and according to the relation:

$$a_i = \gamma_i m_i$$

where a_i is the activity of species i , γ_i is the stoichiometric ion activity coefficient of species i and m_i is the molality of species i .

The fluid in equilibrium with the muscovites from the Transvaal Sequence quartz vein deposits, and by inference, the gold (given the known relative timing of gold and muscovite within the vein) is indicated to have a Na:K ratio of 0.1. This is in sharp contrast to the bulk data of Anderson *et al.*, (1992) which suggest much larger Na:K ratios within the fluids (3.6 to 11.8 and 21.0 to 55.0 for the dolomite-hosted and clastic-hosted deposits, respectively). Na/K ratios around 28 (typical seawater ratio) are suggested as favourable for the formation of albite at temperatures above 150°C (Munha *et al.*, 1980), but albite is not developed in any of the Transvaal lode-gold deposits (Boer and Harley, 1994; Anderson, 1994). Rather, fluid conditions in the SPRG favoured the precipitation of muscovite, which is frequently the only silicate gangue phase present, besides quartz. It is clear that the use of bulk analytical data to characterize the solute composition of the ore-fluid yields results which are incompatible with the chemistry of the muscovite present in the veins. The muscovite records the chemistry of a specific fluid event, closely related to gold deposition. Bulk analyses present a time-integrated view of the fluid chemistry, and as such, the relevance of this data to ore genesis interpretations is questionable.

Table 5.1 Thermodynamic activities of stoichiometric muscovite, celadonite, pyrophyllite and paragonite, using the homologous site mixing models for white micas after Aagaard and Helgeson (1983). Electron microprobe analyses of white micas occurring as gangue in Transvaal gold lodes are from Harley, (1993). The a-X relationships used are as follow: $a_{\text{Muscovite}}$ = activity of $\text{KAl}_2\text{Si}_2\text{O}_{10}(\text{OH})_2$ in "Illite" = $9.4815(X_K^{XII})(X_{Al}^{VI})^2(X_{Al}^{IV})(X_{Si}^{IV})^3$; $a_{\text{Celadonite}}$ = activity of $\text{KMgAlSi}_4\text{O}_{10}(\text{OH})_2$ in "Illite" = $4(X_K^{XII})(X_{Mg}^{VI})^2(X_{Al}^{VI})(X_{Si}^{IV})^4$; $a_{\text{Pyrophyllite}}$ = activity of $\text{Al}_2\text{Si}_4\text{O}_{10}(\text{OH})_2$ in "Illite" = $(X_K^{XII})(X_{Al}^{VI})^2(X_{Si}^{IV})^4$; $a_{\text{Paragonite}}$ = activity of $\text{NaAl}_2(\text{AlSi}_3\text{O}_{10})(\text{OH})_2$ in "Illite" = $9.4815(X_{Na}^{XII})(X_{Al}^{VI})^2(X_{Al}^{IV})(X_{Si}^{IV})^3$, as presented in Aagaard and Helgeson (1983)

Sample	1	2	3	4	5	6	7	8	9	10
$a_{\text{Muscovite}}$	0.679	0.694	0.700	0.704	0.710	0.726	0.880	0.857	0.734	0.698
$\log a_{\text{Musc.}}$	-0.168	-0.159	-0.155	-0.154	-0.149	-0.139	-0.167	-0.182	-0.134	-0.156
$a_{\text{Celadonite}}$	0.180	0.158	0.157	0.144	0.144	0.124	0.169	0.170	0.133	0.170
$\log a_{\text{Cel.}}$	-0.744	-0.800	-0.804	-0.841	-0.841	-0.908	-0.722	-0.770	-0.876	-0.769
$a_{\text{Pyrophyllite}}$	0.020	0.015	0.015	0.024	0.018	0.014	0.029	0.020	0.020	0.025
$\log a_{\text{Pyro.}}$	-1.699	-1.823	-1.831	-1.617	-1.744	-1.842	-1.538	-1.704	-1.708	-1.603
$a_{\text{Paragonite}}$	0.002	0.002	0.001	0.001	0.002	0.002	0.002	0.002	0.002	0.002
$\log a_{\text{Parag.}}$	-2.699	-2.699	-2.000	-2.000	-2.699	-2.699	-2.699	-2.699	-2.699	-2.699

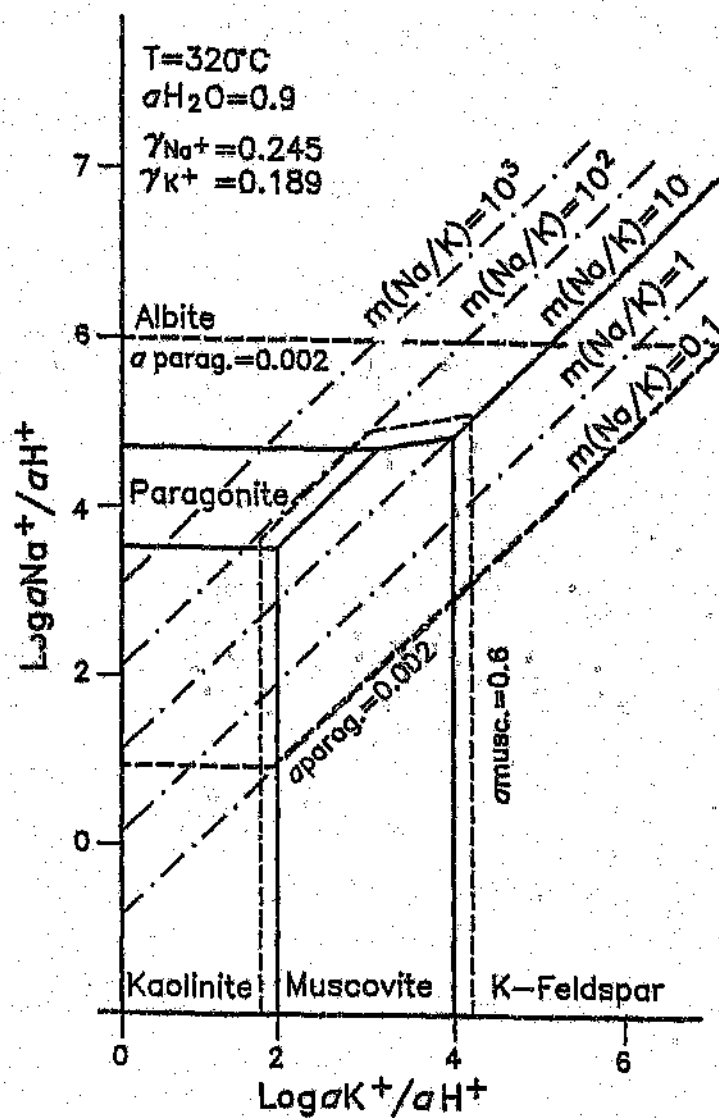


Figure 5.1 Stability fields of minerals in the system $K_2O - Na_2O - Al_2O_3 - SiO_2 - H_2O$ plotted in terms of the activity ratios of Na^+/H^+ versus K^+/H^+ . The thermodynamic data for the mineral species are calculated using SUPCRT92 (Johnson *et al.*, 1992) with data from Helgeson *et al.*, (1978) (after Eber and Harley, 1994).

(2.) An alternative method of determining the Na/K ratio in mineralizing fluids is to analyse pure vein quartz specimens, using high precision instrumental neutron activation analysis (INAA). Great care was taken to obtain pure quartz specimens. Samples were weighed and sealed into polyethylene vials. These samples were then irradiated (together with standards) for 1 hour in a TRIGA Mark II reactor, at the University of Vienna, in a neutron flux of about $1.5 \times 10^{12} \text{ n.cm}^{-2}.\text{s}^{-1}$. After cooling for about 16 hours, measurements were started. All samples were counted for 3 - 15 hours each on a 48% efficiency high purity Ge-detector. The elemental contents in the samples were evaluated in comparison with USGS G-2 and AC-E standard granites. All data are averages of 3 - 6 individual values. Accuracy in relative percentage are as follow: Na: 1; K: 2; As: 5; Br: 10; La: 5; Sm: 5. Precision in relative percentage: Na: 0.3; K: 1; As: 3; Br: 7; La: 5; Sm: 5. By implication bulk solute analysis presumes that only one generation of fluid inclusions was present in a given samples (Roedder, 1990). However, the predominance of type 1 fluid inclusions in the selected samples make the INAA data relevant. INAA data for six quartz samples from the SPRG are presented in Table 5.2. Na/K ratios for the dolomite-hosted horizontal veins yield values ranging from 0.8 to 3.7 ($\bar{x}=1.8$), whereas the granite hosted vein sample produce a value of 4.2 and the sill associated sample had the highest ratio of 4.9. These values are of a similar order than the ratios calculated using homologous site mixing models for white mica electron microprobe data presented above. Therefore, an average Na/K ratio of 1.8 will be used in thermodynamic calculations for the horizontal veins, 4.2 for the vertical veins and 4.9 for the sill/dyke associated veins.

5.4 Transport and deposition of ore

Data presented in this study allow the following summation to be made regarding the mineralizing fluid which formed the Sable-Pilgrim's Rest deposits (Table 5.3): Mineralization formed at a temperature of approximately 320°C and a pressure of 2.2 to 2.5 kbar; the mole fraction of carbonic species in the fluids is about 0.05 as determined by the QMS gas analyses, and fluid salinities ranging from 5.5 to 23.5 wt% eNaCl with an average salinity = 12 wt% eNaCl, as indicated by $T_{m,ice}$ measurements. Activities of ionic species in this fluid were $\log a_{Na} = -1.08$, $\log a_K = -0.32$, $\log a_{Cl} = -0.27$, with the ionic strength = 2.46, for a Na/K ratio of 0.1 (Boer and Harley, 1994). Activities of ionic species in the fluids of the various vein settings were $\log a_{Na} = -1.08$, $\log a_K = -0.32$, $\log a_{Cl} = -0.27$, with the ionic strength = 2.46, for INAA determined Na/K ratios of 1.8, 4.2 and 4.9, respectively. In terms of the reaction $\text{CaCl}_2 + \text{CO}_{2(aq)} + \text{H}_2\text{O} \rightleftharpoons \text{Ca}(\text{HCO}_3)^+ + \text{H}^+ + 2\text{Cl}^-$ ($\log K = -6.039$; calculated using SUPCRT92, Johnson *et al.*, 1992) an acidic pH of between 3.3 - 4.3 (neutral pH = 6.1 at 320°C) was calculated for the SPRG fluids (Table 5.3), for

Table 5.2 Composition of SPRG quartz samples, determined by INAA (Analyst: Professor C. Koeberl, Institute of Geochemistry, University of Vienna)

Sample	CLW-016	GLS-052	GRR-200	NSM-098	OFG-001	SUD-211
Na (ppm)	140	266	149	144	187	150
K (ppm)	166	159	35.1	178	37.8	40.1
As (ppm)	5.49	16.3	0.31	2.23	0.16	0.17
Br (ppm)	0.45	0.93	1.62	0.81	1.38	0.78
La (ppb)	140	31	<10	26	20500	92
Sm (ppb)	11.1	19.2	<3	5.1	530	1.0
Nb ^{III}	0.8	1.7	4.2	0.8	4.9	3.7
Weight (mg)	95.61	128.71	62.85	101.35	39.22	66.85

the range of 0.06 - 6.57 molal CO_2 concentration (Table 3.1; $\gamma_{\text{CO}_2} = 2.26$ [calculated from Patterson *et al.*, 1981]) as obtained from QMS gas data (Table 3.1). Although these calculated pH values correspond well with the range suggested by the gangue and sulphide mineral phase equilibria, the method of calculation is invalid, because the activity of the Ca species involved in the equation is unknown. Despite the lack of knowledge regarding the activity of the Ca species, the fact remains that the mineralizing fluids must have been slightly acidic, as indicated by the absence of K-feldspar in the gangue phase. QMS gas data were, furthermore, utilized to determine redox conditions: $f\text{O}_2$ was calculated using the reactions $\text{CH}_4 + 2\text{H}_2\text{O} = 4\text{H}_2 + \text{CO}_2$, assuming equilibrium between the carbonic gas species and organic carbon/graphite that are prevalent, and $\text{H}_2\text{O} = \text{H}_2 + \frac{1}{2}\text{O}_2$ which yielded values ranging from $10^{-32.9}$ to $10^{-31.5}$. The $f\text{H}_2\text{S}_g$ was determined, assuming $\Sigma S_{\text{total}} = X_{\text{H}_2\text{S}} + X_{\text{CO}_2}$, to range between 1.7 and 15.4 bars, which corresponds to $a\text{H}_2\text{S}_{\text{aq}}$ of between $10^{-2.5}$ to $10^{-3.4}$ (Table 5.3).

Using these fluid characteristics, inferences on the gold speciation and precipitation mechanism is possible. Experimental data on Au bisulphide complexes (Hayashi and Ohmoto, 1991; Shenberger and Barnes, 1989; Seward, 1973) for the conditions outlined above indicate solubilities between 1 and 10 ppb. Solubility calculations of Au as chloride complexes, using data of Henley (1973) and Shenberger and Barnes (1989) yield solubilities that are an order of magnitude less (Fig. 5.2). This implies that Sable-Pilgrim's Rest gold would have been more efficiently transported as a bisulphide complex than a chloride complex. The possible significance of the chloride complex may also explain the preponderance of Cu mineralization in the SPRG compared to other mesothermal lode gold deposits, as Cu is efficiently transported as a chloride complex. Precipitation mechanisms pertinent to a fluid transporting gold as a bisulphide complex include: a decrease in T at constant pH; oxidation of the complex; pH reduction; and reduction in sulfur activity in the fluid by sulphide precipitation. Oxidation may be ruled out as a first order control in gold precipitation since fluid CO_2/CH_4 ratios remain relatively constant throughout the Sable-Pilgrim's Rest goldfield. This situation differs from that at the Pamour Mine in the Timmins district in Canada for example, where widely variable CO_2/CH_4 ratios have been taken as an indication of the influence of changing oxidation states on gold precipitation (Walsh *et al.*, 1988). Given the predominant association of gold with various sulphides noted at many mines in the Sable-Pilgrim's Rest goldfield (Harley and Charlesworth, 1992; Meyer *et al.*, 1986), the role of sulphide precipitation may be critical to gold precipitation. However, as indicated by gas analyses from gold-hosted fluid inclusions, phase separation seems to be the principal controlling mechanism for both gold and sulphide precipitation. Thus, it is likely that gold precipitation was mainly controlled by (1) a decrease in sulfur activity within the

the range of 0.08 - 6.57 molal CO_2 concentration (Table 3.1; $V_{\text{CO}_2} = 2.26$ [calculated from Patterson *et al.*, 1981]) as obtained from QMS gas data (Table 3.1). Although these calculated pH values correspond well with the range suggested by the gangue and sulphide mineral phase equilibria, the method of calculation is invalid, because the activity of the Ca species involved in the equation is unknown. Despite the lack of knowledge regarding the activity of the Ca species, the fact remains that the mineralizing fluids must have been slightly acidic, as indicated by the absence of K-feldspar in the gangue phase. QMS gas data were, furthermore, utilized to determine redox conditions: $f\text{O}_2$ was calculated using the reactions $\text{CH}_4 + 2\text{H}_2\text{O} = 4\text{H}_2 + \text{CO}_2$, assuming equilibrium between the carbonic gas species and organic carbon/graphite that are prevalent, and $\text{H}_2\text{O} = \text{H}_2 + \frac{1}{2}\text{O}_2$ which yielded values ranging from $10^{-32.9}$ to $10^{-31.4}$. The $f\text{H}_2\text{S}_g$ was determined, assuming $\Sigma S_{\text{total}} = X_{\text{H}_2\text{S}} + X_{\text{CO}_2}$, to range between 1.7 and 15.4 bars, which corresponds to $a\text{H}_2\text{S}_{\text{aq}}$ of between $10^{-2.5}$ to $10^{-3.4}$ (Table 5.3).

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ore-bearing fluid because of sulphide precipitation, and (2) changes in the fluid chemistry as a result of fluid immiscibility. The fact that gold in the Sable-Pilgrim's Rest goldfield occurs in several ways does not distract from the controlling role of the latter two mechanisms. In the Sable-Pilgrim's Rest goldfield, gold occurs: (1) primarily as fracture fill within early sulphides (eg Elandschoogte, Clewer West, Malleveld); (2) as round co-genetic inclusions within sulphides, mainly pyrite (eg Olifantsgeraamte, Vaalhoek); and (3) as free gold within quartz (eg Morgenzon). All three styles of gold occurrence can be found within a single deposit, implying that several mechanisms of precipitation may have been operative, although phase separation was the more important mechanism. It cannot be ruled out that gold in late fractures was precipitated as a result of adsorption/reduction reactions (Schoonen *et al.*, 1992; Bancroft and Hyland, 1990).

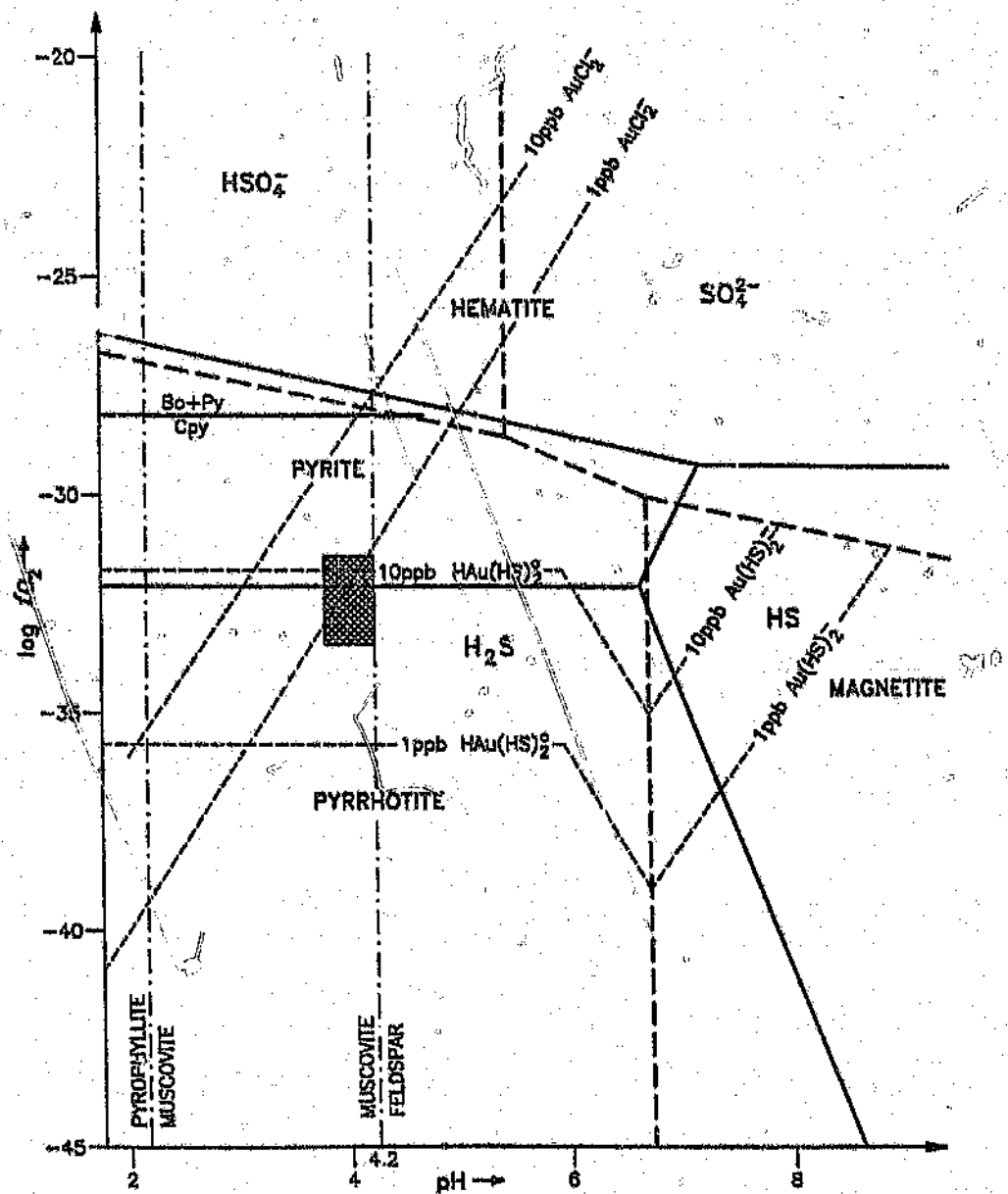


Figure 5.2 Composite $\log f_{O_2}$ versus pH diagram for the SPRG conditions. Calculated using SUPCRT92; Johnson *et al.*, (1992). Shaded area represents an approximation of activities of vein forming fluids, based on average QMS gas analytical results.

Table 5.3 pH and fugacities for the various species in quartz-hosted fluid inclusions, calculated using the approach of A.B. Belonoshko, P.F. Shi and S.K. Saxena (pers. commun., 1993; Uppsala University, Sweden). Equilibrium constants for the various reactions involved in the calculation of fugacities and pH were obtained using the SUPCRT92 software (Johnson et al., 1992). Densities were calculated for the species presented and do not take into account the effects of solid daughter phases.

	AST109	BM184a	BM184b	BM7384	BRH112	CLH040	CLW016	FKM075a	FKM075b
$\log f_{\text{H}_2\text{O}}$	2.04	2.45	2.10	2.31	2.42	2.27	2.47	2.25	2.28
$\log f_{\text{CO}_2}$	2.81	2.89	2.46	2.89	3.06	3.09	3.16	2.42	2.78
$\log f_{\text{CH}_4}$	1.72	2.32	1.57	1.04	1.13	1.10	1.76	1.08	0.85
$\log f_{\text{O}_2}$	1.37	1.69	1.65	1.77	1.63	1.45	1.59	1.40	1.17
$\log f_{\text{H}_2}$			0.27		0.78	0.88	0.07		0.19
$\log f_{\text{SO}_2}$			-2.86	-1.71	-1.85	-1.83	-1.79	-1.85	-1.79
$\log f_{\text{H}_2\text{S}}$	0.67	0.82	0.68	0.94	0.74	0.74	0.99	0.67	0.63
$\log f_{\text{N}_2}$	0.87	1.19	1.34	0.95	1.11	0.94	1.13	0.93	0.96
$\log f_{\text{Ar}}$	-0.25	-0.02	-0.07	0.08	-0.07	-0.21	-0.02	-0.27	-0.34
m_{CO_2}	1.41	0.11	0.05	0.48	3.49	5.51	1.24	4.93	6.57
pH	3.58	4.14	4.28	3.82	3.39	3.29	3.61	3.31	3.25
$\log f_{\text{O}_2}(\text{CO}_2)$	-32.07	-31.99	-32.43	-31.99	-31.83	-31.79	-31.73	-32.47	-32.11
$\log f_{\text{O}_2}(\text{CH}_4)$	-32.62	-33.22	-32.47	-31.94	-32.03	-32.00	-32.66	-31.98	-31.75
$f_{\text{CO}_2}/f_{\text{CH}_4}$	12.52	3.73	7.68	71.38	84.03	97.73	24.73	21.87	84.45
$\log f_{\text{O}_2}$	-32.35	-32.61	-32.45	-31.97	-31.93	-31.89	-32.19	-32.22	-31.93
Molar Mass (g.mol ⁻¹)	18.52	18.52	18.46	18.79	18.88	19.72	19.01	18.27	18.60
Density (g.cm ⁻³)	0.88	0.87	0.88	0.88	0.88	0.88	0.88	0.88	0.88

Table 5.3 (continue)

	FKM076 b	GLS052	GRR107	GRR300	GRR300	JBH043	LJM090	MGL033	MGL204
$\log f_{\text{H}_2\text{O}}$	2.11	2.28	2.46	2.19	2.23	2.30	2.46	2.39	2.16
$\log f_{\text{CO}_2}$	3.11	2.67	2.38	3.11	3.01	2.98	2.84	1.59	1.76
$\log f_{\text{CH}_4}$	1.84	1.29	0.99	0.96	1.99	1.70	1.09	2.35	2.40
$\log f_{\text{O}_2}$	1.64	1.12	1.56	1.73	1.14	1.83	2.04	1.57	1.42
$\log f_{\text{H}_2}$				0.71			0.26		
$\log f_{\text{SO}_2}$		-1.78	-1.49	-1.42		-1.89	-1.39		
$\log f_{\text{H}_2\text{S}}$	0.47	0.68	0.85	0.88	0.56	0.84	1.03	0.67	0.52
$\log f_{\text{N}_2}$	1.37	0.74	1.19	1.15	1.09	1.61	1.63	1.60	1.84
$\log f_{\text{Ar}}$	0.08	-0.26	0.01	0.17	-0.52	0.14	0.34	-0.06	0.17
m_{CO_2}	2.36	2.29	0.13	0.29	0.14	4.54	2.62	0.72	0.44
pH	3.47	3.48	4.09	3.93	4.08	3.33	3.45	3.73	3.84
$\log f_{\text{O}_2(\text{CO}_2)}$	-31.77	-32.22	-32.51	-31.78	-31.88	-31.91	-32.04	-33.29	-33.13
$\log f_{\text{O}_2(\text{CH}_4)}$	-32.74	-32.19	-31.89	-31.86	-32.89	-32.60	-31.99	-33.25	-33.30
$f_{\text{CO}_2}/f_{\text{CH}_4}$	18.69	24.15	24.41	140.99	10.43	18.85	56.07	0.18	0.23
$\log f_{\text{O}_2}$	-32.26	-32.20	-32.20	-31.82	-32.38	-32.26	-32.02	-33.27	-33.21
Molar Mass (g.mol ⁻¹)	23.87	18.45	18.16	20.69	19.44	19.08	18.49	18.07	18.18
Density (g.cm ⁻³)	0.89	0.88	0.86	0.88	0.88	0.88	0.88	0.87	0.87

Table 5.3 (continue)

	NSM093	NSM098	NSM098	OGM078	S1017	SUD211	SUD211	SUN003	SUN003
$\log f_{\text{H}_2\text{O}}$	2.46	2.32	2.48	2.33	2.46	2.28	2.19	2.25	2.39
$\log f_{\text{CO}_2}$	3.39	2.87	3.10	2.96	3.25	3.03	3.22	3.15	2.79
$\log f_{\text{CH}_4}$	2.71	2.84	1.57	1.85	2.64	2.27	2.30	2.73	2.19
$\log f_{\text{O}_2}$	2.24	2.04	1.53	1.41	2.39	1.99	1.08	1.24	1.95
$\log f_{\text{H}_2}$					1.15		-0.18		
$\log f_{\text{SO}_2}$			-1.79	-2.35					
$\log f_{\text{H}_2\text{S}}$	1.25	1.52	0.94	0.85	1.31	0.98	0.15	0.43	0.86
$\log f_{\text{N}_2}$	1.93	2.14	0.89	-0.18	2.13	2.02	1.58	1.49	1.75
$\log f_{\text{Ar}}$	0.84	0.97	-0.08	-0.22	0.87	0.55	-0.29	-0.19	0.18
m_{CO_2}	0.23	6.78	4.63	0.50	1.05	0.33	1.13	0.39	0.32
pH	3.97	3.24	3.32	3.81	3.65	3.89	3.63	3.86	3.90
$\log f_{\text{O}_2(\text{CO}_2)}$	-31.49	-32.02	-31.79	-31.92	-31.64	-31.86	-31.67	-31.74	-32.10
$\log f_{\text{O}_2(\text{CH}_4)}$	-33.61	-33.74	-32.47	-32.75	-33.54	-33.17	-33.20	-33.63	-33.09
$f_{\text{CO}_2}/f_{\text{CH}_4}$	4.86	1.07	33.50	12.88	4.10	5.77	8.33	2.59	3.97
$\log f_{\text{O}_2}$	-32.55	-32.88	-32.13	-32.34	-32.59	-32.51	-32.43	-32.69	-32.59
Molar Mass (g.mol ⁻¹)	21.88	18.95	18.85	18.87	19.82	19.51	26.20	20.82	18.53
Density (g.cm ⁻³)	0.88	0.87	0.88	0.88	0.88	0.88	0.88	0.86	0.88

Table 5.3 (continue)

	VLH040a	VLH040b	VLH040c	Average	Std. Dev.
$\log f_{\text{H}_2\text{O}}$	2.18	2.36	2.36	2.12	2.32
$\log f_{\text{CO}_2}$	2.79	2.98	2.98	2.88	2.85
$\log f_{\text{CH}_4}$	2.27	2.80	2.80	2.08	1.84
$\log f_{\text{O}_2}$	1.92	1.75	1.75	1.56	1.63
$\log f_{\text{H}_2}$	0.61	0	0	-0.02	
$\log f_{\text{SO}_2}$	0	0	0	-2.27	
$\log f_{\text{H}_2\text{S}}$	0.87	0.75	0.75	0.68	0.80
$\log f_{\text{N}_2}$	1.70	1.54	1.54	1.38	1.33
$\log f_{\text{Ar}}$	0.27	-0.99	-0.99	0.02	0.03
m_{CO_2}	1.11	2.91	4.26	1.88	1.95
pH	3.63	3.43	3.34	3.52	3.67
$\log f_{\text{O}_2}(\text{CO}_2)$	-32.19	-31.91	-31.91	-32.00	-32.04
$\log f_{\text{O}_2}(\text{CH}_4)$	-33.17	-33.70	-33.70	-32.98	-32.74
$f_{\text{CO}_2}/f_{\text{CH}_4}$	3.26	1.48	1.48	6.33	27.03
$\log f_{\text{O}_2}$	-32.64	-32.81	-32.81	-32.49	-32.39
Molar Mass (g.mol ⁻¹)	18.93	18.91	18.91	19.46	19.47
Density (g.cm ⁻³)	0.87	0.86	0.86	0.88	0.88

CHAPTER 6 - RELATION TO OTHER MESOTHERMAL GOLD DEPOSITS AND SUMMARY

6.1 Mesothermal gold occurrences in the western Transvaal portion of the Transvaal Supergroup

A peculiar aspect of gold mineralization in the Transvaal Supergroup is the virtual absence of economically viable deposits in the western Transvaal. Small gold occurrences have been mined in the past such as at Blaauwbank, west-north-west of Krugersdorp; the Batavia goldfield in the Rustenburg District; the Drylands occurrences in the Ventersdorp District, the Malmani Goldfield near Ottoshoop, the Magaliesburg Goldfield, as well as a few occurrences in the Klerksdorp and Potchefstroom Districts. These sporadic occurrences of gold were mainly found in the basal conglomerate of the Black Reef Formation, where the largest occurrences were mined in the east Rand area between Springs and Benoni. There are few known occurrences of auriferous quartz lodes in the western Transvaal. Furthermore, it appears that the gold occurrences in the north-western and western Transvaal have a transgressive relationship to the general stratigraphy of the Transvaal Supergroup.

6.1.1 Geological setting

The protobasinal Godwan Formation forms the lowermost part of the Proterozoic Transvaal Supergroup in the western Transvaal and lies unconformably on the Ventersdorp Supergroup. Disconformably overlying the Godwan Formation are the siliciclastic rocks of the Black Reef Formation. The Black Reef Formation consists of feldspathic quartzite with interlayered lenses of grit and conglomerate. The platform carbonates of the Malmani Subgroup (part of the Chuniespoort Group) conformably overlie the Black Reef Formation. The Malmani Subgroup consists of the Oaktree, Monte Christo, Lyttelton, Eccles and Frisco Formations. The Oaktree Formation is comprised of iron- and manganese-rich dolomite, carbonaceous shale, and quartzite, whereas the Monte Christo Formation is characterised by oolitic carbonate rocks (Button, 1986). Siliciclastic sediments (quartzite and/or shale) mark the base of the overlying chert-poor Lyttelton Formation, which is composed mainly of dark-coloured quartz-arenite. This unit grades upward to the upper dolomite and chert zone of the Eccles Formation. Following the deposition of these sediments, the strata were exposed and an extensive erosional period ensued. This resulted in the formation of a widely developed chert breccia and chert pebble conglomerate, known as the Bevetts Conglomerate Member, at the base of the siliciclastic dominated Pretoria Group. The Pretoria Group consists of alternating shale and quartz-arenites, with minor conglomerates, granulestones and interlayered volcanic units (Button, 1973a). The succession, as developed in the western Transvaal, is approximately 4000 m in thickness (S.A.S. 1980).

6.1.2 Sampling and nature of veins

Sampling was aimed at obtaining a representative stratigraphic and regional sample set in order to investigate vertical and lateral changes in fluid properties of the Transvaal Supergroup in the western Transvaal. Borehole material was the only source of samples. A total of 46 samples was obtained from 5 different boreholes (Table 6.1). In general three types of quartz veins were recognized: (1) vein samples which show a sheeted appearance; (2) vuggy quartz veins; and (3) quartz veins with brecciated wall-rock inclusions. Gangue minerals, other than quartz, include dolomite, ferrodolomite, calcite and muscovite, in decreasing order of abundance. Sulphides include pyrite and chalcopyrite with minor amounts of tetrahedrite-tennantite. Pyrite is sometimes oxidized to hematite/limonite. No feldspar minerals were recognized. Wall-rock alteration associated with the quartz veins appears to be limited in extent, and it was, therefore, difficult to quantify fluid/host-rock interaction. Where quartz veins are in contact with shales, a well-developed subhorizontal planar fabric, comprising a closely spaced cleavage, is developed within the shales. Cleavage surfaces often bear slickensides which indicate early faulting. Mineralogically the shales are composed of sericite with minor amounts of quartz and organic carbon.

Table 6.1 List of samples. A* sample material were obtained from borehole cores

Sample No.	Depth (m)	Stratigraphic Position	Sample No.	Depth (m)	Stratigraphic Position
BH1-1	2283	Black Reef Formation	BH3-1	19.2	Unknown
BH1-2	2283	Black Reef Formation	BH3-2	20.3	"
BH1-3	2271	Black Reef Formation	BH3-3	26	"
BH1-4	1948	Monte Christo Formation	BH3-4	28.5	"
BH1-5	1854.5	Monte Christo Formation	BH3-5	33	"
BH1-6	1784.5	Monte Christo Formation	BH3-6	44	"
BH1-7	1287.5	Eccles Formation	BH3-7	48.2	"
BH1-8	1409.5	Eccles Formation	BH3-8	59	"
BH1-9	1663	Monte Christo Formation	BH3-9	74	"
BH1-10	1143.5	Eccles Formation	BH3-10	82	"
BH1-11	1096	Eccles Formation	BH3-11	91	"
BH1-12	1001	Diabase Intrusive	BH3-12	101	"
BH1-13	733	Timeball Hill Formation			
BH1-14	717	Timeball Hill Formation	BH4-1	82.5	"
			BH4-2	72.6	"
BH2-1	2663	Monte Christo Formation	BH4-3	74.7	"
BH2-2	2990	Monte Christo Formation	BH4-4	61	"
BH2-3	1947	Eccles Formation	BH4-5	97.6	"
BH2-4	1349	Timeball Hill Formation	BH4-6	104.9	"
BH2-5	1351	Timeball Hill Formation	BH4-7	100	"
BH2-6	1379	Timeball Hill Formation			
BH2-7	1698	Timeball Hill Fm. (bottom cont.)	BH5-1	2313	Monte Christo Formation
BH2-8	1040	Hekpoort Formation	BH5-2	2012	Monte Christo Formation
BH2-9	851.4	Hekpoort Formation	BH5-3	1750	Eccles Formation
			BH5-4	1281	Rooihogte Formation (top contact)

6.1.3 Fluid Inclusion petrography and microthermometry

All of the quartz veins examined experienced repeated fracturing in the presence of aqueous fluids as evident by abundant planes of secondary inclusions observed at low magnification. The high density of randomly oriented fractures decorated with fluid inclusions made it difficult to determine whether a given inclusion was fracture related or was trapped during crystal growth. For this reason groups of inclusions were related to various stages of vein filling. Quartz specimens generally contains a number of apparently co-existing fluid inclusion generations within a single field of view (Fig. 6.1).

Type 1 inclusions

This is the dominant fluid-inclusion population and exhibits two phases, an aqueous liquid, and a vapour bubble, at room temperature, with occasional daughter crystals (NaCl?) also present. The liquid-to-vapour ratio varies to such an extent that the type 1 inclusions were subdivided into three categories, similar to the type 1 fluid inclusions occurring in the SPRG gold lodes: (i) aqueous inclusions appear as two phase inclusions, showing an aqueous liquid, a vapour bubble (liquid/vapour ratio = 65:35) and occasionally a single cubic daughter crystal (NaCl?); (ii) large dark single phase gaseous inclusions, with vapour bubbles appearing during cooling, and (iii) aqueous liquid-rich inclusions containing very small vapour bubbles. Clathrates (gas hydrates) were commonly observed in the type 1 inclusions, indicating the presence of carbonic species. Low initial ice melting temperatures indicate that additional fluid components are present (possibly calcium- or magnesium-chlorides). The size of the inclusions ranges from 5 to 30 μm . The morphology of this inclusion type varies from irregular to rounded, with equidimensional negative crystal shapes also developed.

Final melting temperatures (T_m) of the aqueous phase range from -22.9° to -3.5°C , corresponding to a salinity range of 28.3 to 5.6 wt% NaCl. Many inclusions contained carbonic species with clathrate melting temperatures ranging between 5 to 8°C . The T_h measurements obtained range from 80° to $>350^\circ\text{C}$, corresponding to high bulk densities of 0.88 to 1.13 g/cm^3 . Comparison of homogenization and final melting temperatures for the various samples show salinity ranges within individual samples. First melting temperatures for the carbonic phase are slightly below the value for pure CO_2 , and confirm the presence of other gaseous species, such as CH_4 and N_2 .

Type 2 inclusions

These inclusions occur in cross-cutting secondary trails and contain an aqueous liquid, with a small vapour bubble at room temperature, and are believed to be the last-formed inclusion type. They

are found in both the milky and clear quartz varieties. Cross-cutting relations between type 2 and type 1 inclusions prove that the former post-date the carbonic-rich inclusions. Final melting temperatures centred around -2.0°C (corresponding to a salinity of about 3.5 wt% eNaCl), and homogenization temperatures ranged from 100° to 200°C (density range 1.00 - 0.9 g/cm³). The absence of vapour bubbles in many of these late fluid inclusions suggest low entrapment temperatures, and confirms the late temporal relations.

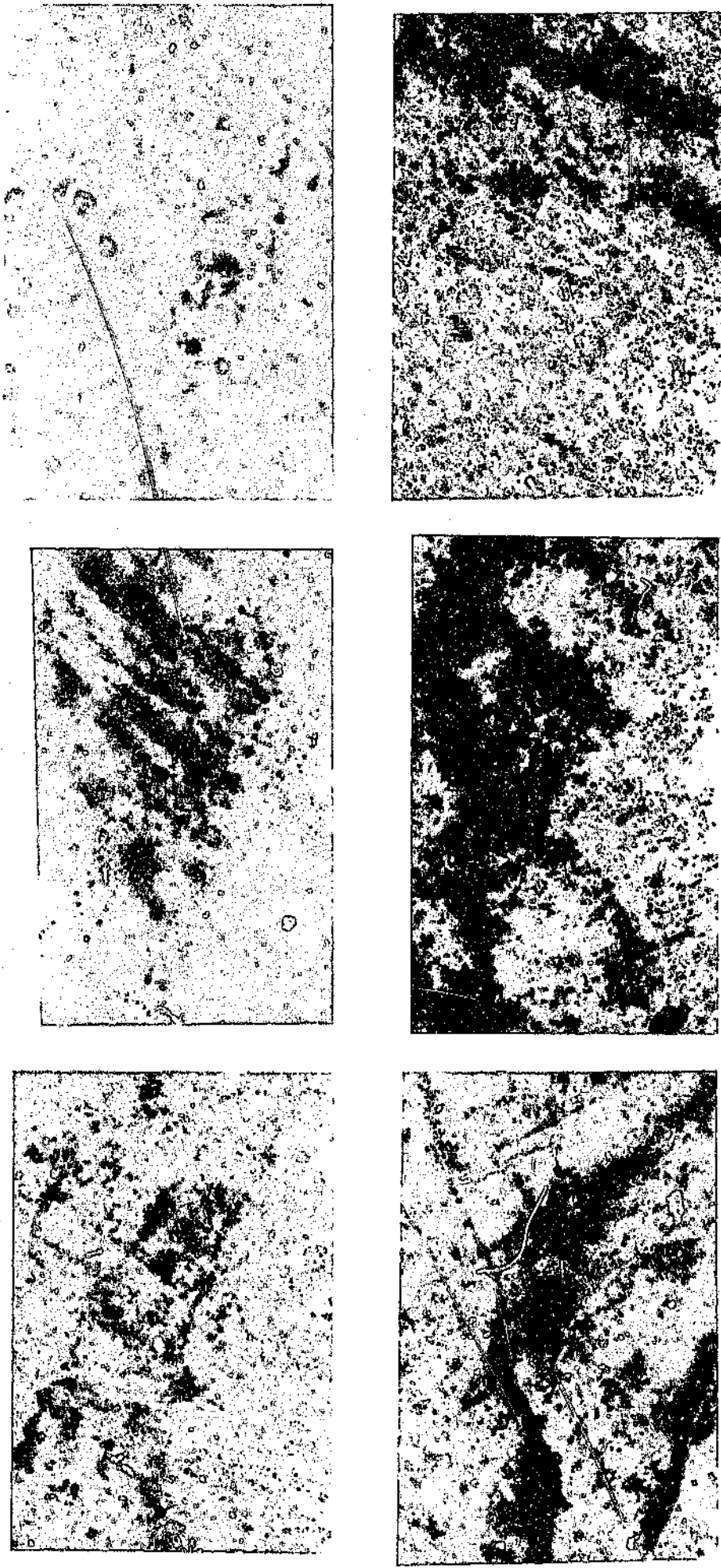


Figure 6.1 Photomicrographs of quartz hosted fluid inclusions from western Transvaal auriferous veins.

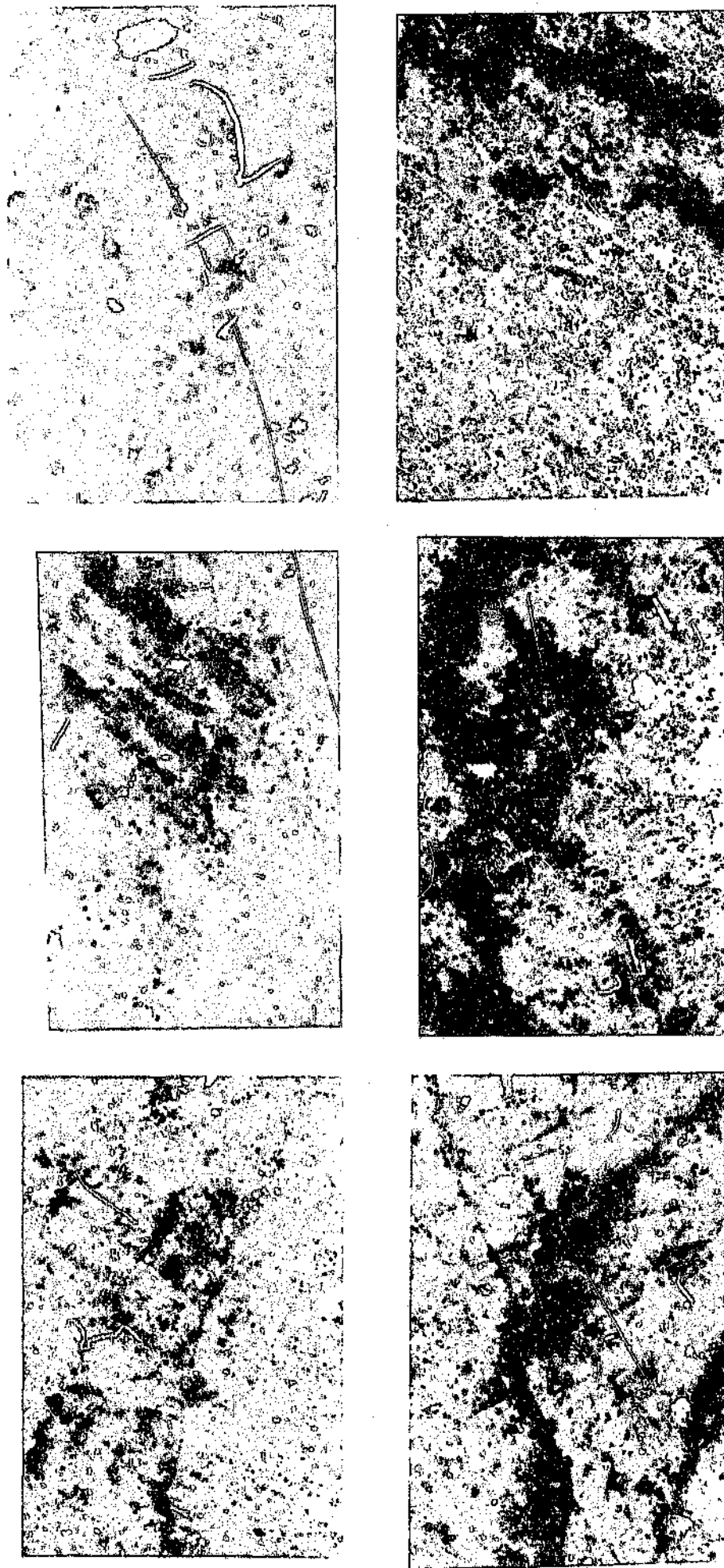


Figure 6.1 Photomicrographs of quartz hosted fluid inclusions from western Transvaal auriferous veins.

Pages 173 and 174 not included in the pagination, they do not exist.

6.1.4 Quadrupole mass spectrometer gas analyses

Results from bulk fluid inclusion gas analyses are presented in Table 6.2. Great care has been taken to ensure the dominance of Type I fluid inclusions within the pure quartz specimens. This was achieved by microscopic selection of doubly polished quartz chip fragments which were clearly dominated by Type I fluid inclusion trails. However, it is inevitable that this type of bulk analysis reflects contamination by other fluid populations (Roedder, 1990) and thus represent partially time-integrated fluid chemistry.

H₂O is by far the dominant volatile component in the western Transvaal fluid inclusions and typically comprises 95 - 99 mole% of the inclusion fluid. CO₂ comprises most of the remaining volatile component (varying between 0.1 - 31 mole%), while the other gases are generally present in amounts smaller than 1 mole%. N₂, He and Ar concentrations are relatively high for these quartz veins. Samples BH4-1 and BH4-7 show unusually high HCl concentrations. These high HCl concentrations correlate well with high salinities, as indicated by microthermometric measurements, and is probably a result of the hydrolysis of NaCl at higher temperatures. Furthermore, there seems to be a distinct stratigraphic control on the gaseous composition of the quartz samples. CO₂ content of Black Reef and the Monte Christo Formations are relatively low (0.5 - 3.3 mole% CO₂) compared to the CO₂ concentration in the Eccles and Timeball Hill Formations (2.2 - 10.1 mole% CO₂). The oxidized protore samples from the upper portion of both boreholes BH3 and BH4, yielded the highest average CO₂ contents (the CO₂-containing quartz vein of BH1-12 is hosted in an intrusive diabase rock) (Fig. 6.2 & 6.3; Table 6.2). A possible source for CH₄ is thermocatalysis of organic matter within the vein-associated shale layers (Welhan, 1988) (Fig. 6.4 & 6.5). Normalized proportions of inclusion hosted N₂, Ar and CO₂ indicate that the dominant fluid population in the western Transvaal exhibits variable CO₂/Ar ratios. Comparison with the normalized concentrations of present-day air and air-saturated water, suggests that large-scale fluid interaction with air-saturated meteoric water has not occurred. Such a comparison is justified, as Ozima and Podosek (1983) have shown that the noble gas ratios have not changed significantly through geological time. Average N₂/Ar ratios centre around 4.5 (maximum=19.6), which are well below those of air (84) or air-saturated ground water (38). The presence of Ar probably result from the radiogenic decay of potassium, with subsequent incorporation into fluid inclusions. The most important observation which is forthcoming from the study of gaseous concentrations in fluid inclusions from the western Transvaal quartz veins is that the variations in gaseous content strongly reflect the different host-rock lithologies.

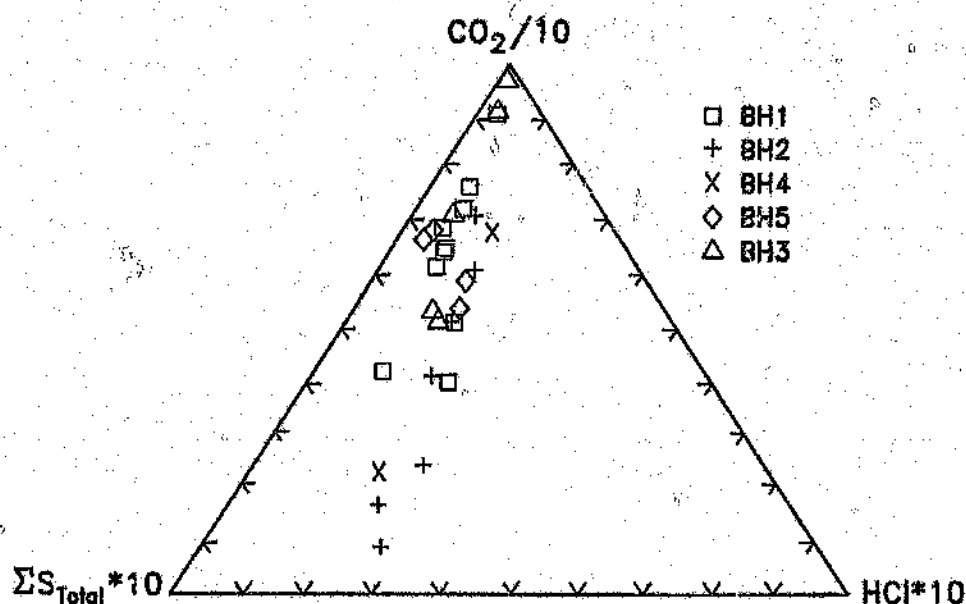


Figure 6.2 Ternary $\text{CO}_2/10$ - HCl^*10 - $\Sigma\text{S}_{\text{Total}}$ diagram of QMS gas data from inclusion fluids of western Transvaal hydrothermal quartz specimens. Samples from the western Transvaal contain higher proportions of sulphur species, compared to the more HCl -rich fluids from the eastern Transvaal.

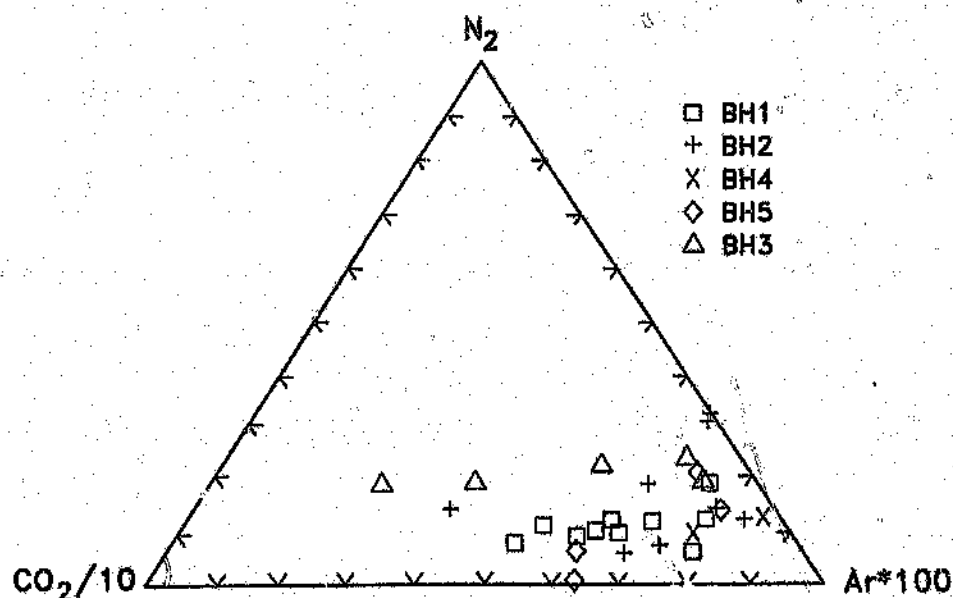


Figure 6.3 Ternary N_2 - Ar^*100 - $\text{CO}_2/10$ diagram of QMS gas data of inclusion fluids from western Transvaal quartz. The scatter of data and lack of any positive correlation between N_2 and Ar suggest the absence of meteoric water involvement in the hydrothermal system. Low N_2 and Ar values also indicate that the samples were not contaminated with atmospheric air during analyses.

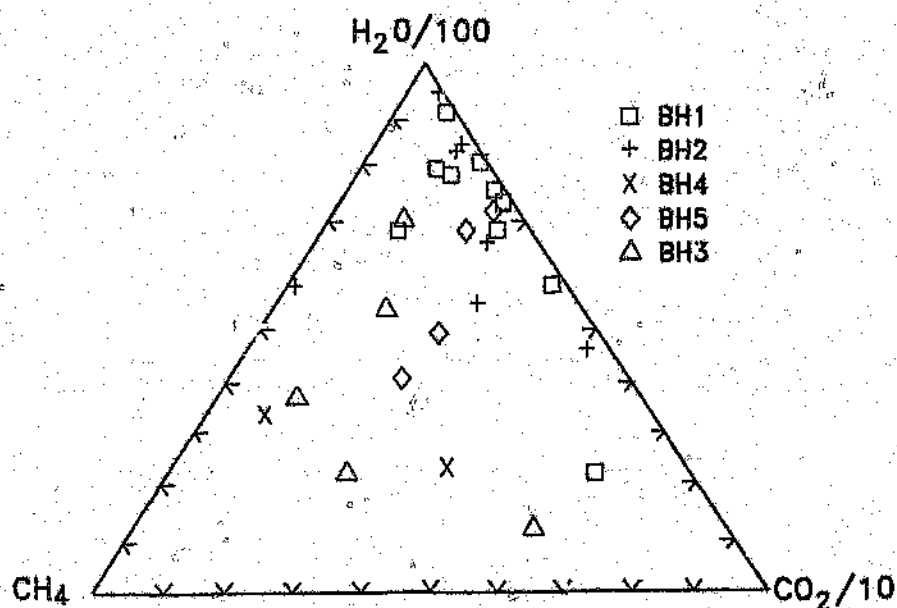


Figure 6.4 Ternary $H_2O/100$ - $CO_2/10$ - CH_4 diagram of the most common western Transvaal inclusion fluid gas species

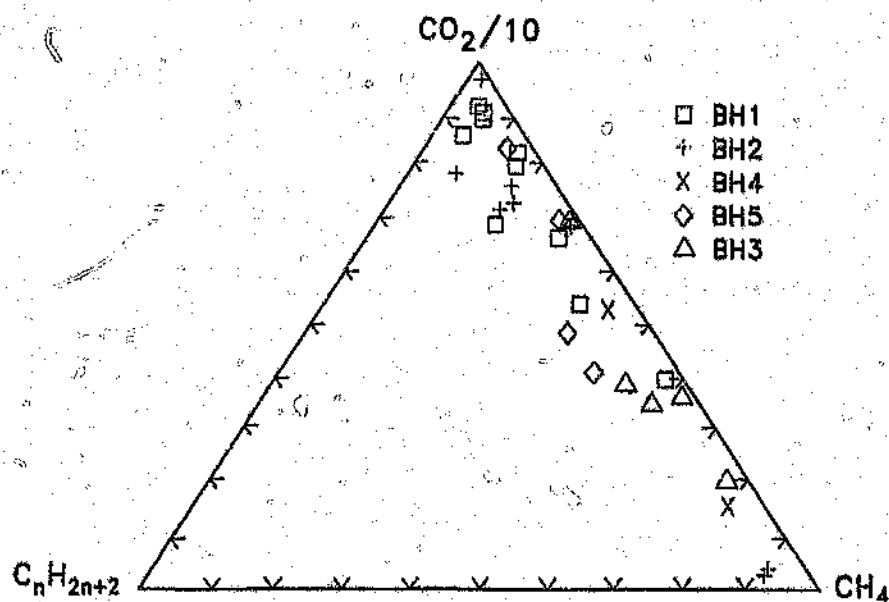


Figure 6.5 Ternary diagram of the common carbonic species in western Transvaal inclusion fluids ($CO_2/10$ - CH_4 - C_2H_6).

Table 6.2 Composition of quartz-hosted inclusion fluids (in mole.%) as determined by QMS gas analyses. Fugacities for the various species are calculated using the equation of state formulated by Belonoshko, A.B., Shi, P.F. and Saxena, S.K. (pers. commun., 1993; Uppsala University, Sweden). Equilibrium constants for the various reactions involved in the calculation of fugacities and pH were obtained using the SUPCRT92 computer programs (Johnson *et al.*, 1992). Densities were calculated for the species presented and do not take into account the effects of solid phases (e.g. NaCl, KCl, CaCO₃, etc.)

	BH1-1	BH1-2	BH1-3	BH1-4	BH1-5	BH1-7	BH1-8	BH1-9	BH1-11	BH1-12
H ₂ O	97.876	97.839	97.835	96.830	96.522	93.212	95.961	98.879	97.600	76.450
CO ₂	1.902	1.864	1.486	2.869	3.237	6.493	3.763	0.908	2.206	22.106
CH ₄	0.084	0.280	0.109	0.021	0.020	0.030	0.077	0.024	0.014	0.404
C _n H _{2n+2}	0.013	0.012	0.019	0.016	0.015	0.028	0.017	0.017	0.023	0.054
N ₂	0.067	0.114	0.363	0.097	0.106	0.113	0.099	0.097	0.103	0.655
Ar	0.0047	0.0066	0.0140	0.0130	0.0070	0.0079	0.0069	0.0061	0.0054	0.0330
H ₂ S	0.0081	0.0094	0.0150	0.0180	0.0088	0.0140	0.0140	0.0100	0.0090	0.0180
SO ₂	0.00001	0	0.0001	0.0009	0.0005	0.0008	0.0005	0.0007	0.0008	0
O ₂	0.041	0.070	0.141	0.124	0.069	0.072	0.056	0.055	0.032	0.273
H ₂	0	0	0.0069	0	0.0110	0.0230	0.0022	0	0.0038	0
HCl	23	25	81	93	35	53	29	23	27	61
He	14	15	22	12	7	12	9	5	7	18
Total	99.996	99.995	99.989	99.999	99.996	99.994	99.997	99.997	99.997	99.993

Table 6.2 (cont.)

	BH2-1	BH2-2	BH2-3	BH2-4	BH2-5	BH2-6	BH2-8	BH2-9	BH4-1	BH4-7
H ₂ O	98.220	99.307	89.353	94.101	95.387	97.843	99.170	97.956	82.953	93.475
CO ₂	1.616	0.494	10.086	5.417	3.822	1.601	0.091	0.238	14.287	2.851
CH ₄	0.037	0.012	0.029	0.245	0.102	0.016	0.319	0.660	1.162	1.545
C ₃ H ₈	0.015	0.008	0.016	0.012	0.041	0.029	0.021	0.036	0.121	0.094
N ₂	0.060	0.108	0.241	0.166	0.452	0.314	0.324	1.002	0.933	1.585
Ar	0.0057	0.0069	0.0250	0.0042	0.0150	0.0160	0.0070	0.0210	0.0730	0.1030
H ₂ S	0.0100	0.0094	0.0260	0.0097	0.0150	0.0150	0.0071	0.0090	0.0400	0.0730
SO ₂	0.0008	0.0010	0.0025	0	0.0006	0.0013	0	0	0	0
O ₂	0.028	0.049	0.184	0.037	0.151	0.153	0.057	0.073	0.403	0.246
H ₂	0	0	0.0210	0	0	0.0028	0	0	0	0
HCl	52	52	140	26	93	71	29	32	280	240
He	7	6	20	49	41	11	11	18	12	20
Total	99.993	99.995	99.984	99.992	99.986	99.991	99.996	99.995	99.972	99.972

Table 6.2 (cont.)	BH5-1	BH5-2	BH5-3	BH5-4	BH3-1	BH3-2	BH3-3	BH3-4	BH3-5	Average	Std. I
H ₂ O	96.648	96.502	91.106	92.728	86.357	86.878	97.355	95.243	94.916	92.359	8.26
CO ₂	3.162	3.272	6.230	5.089	31.117	10.682	1.697	3.121	3.324	6.310	7.78
CH ₄	0.049	0.131	0.730	0.432	1.326	1.846	0.241	0.52	1.245	0.527	0.56
C _n H _{2n+2}	0.015	0.014	0.185	0.131	0.034	0.017	0.037	0.056	0.029	0.047	0.04
N ₂	0.057	0.0069	1.166	1.297	1.058	0.498	0.490	0.749	0.351	0.553	0.46
Ar	0.0057	0.0056	0.0630	0.0430	0.0140	0.0100	0.0130	0.0270	0.0009	0.0237	0.02
H ₂ S	0.0120	0.0140	0.0350	0.0230	0.0093	0.0087	0.0120	0.0210	0.0110	0.0184	0.01
SO ₂	0.0005	0.0002	0	0	0	0	0	0	0	0.00037	0.00
O ₂	0.048	0.052	0.435	0.243	0.076	0.058	0.149	0.242	0.111	0.1476	0.12
H ₂	0	0	0.0290	0	0.0051	0	0	0.014	0	0.0036	0.00
HCl	20	19	190	130	27	23	45	69	27	79	75.46
He	7	7	17	19	10	5	11	6	14	15	11.22
Total	99.997	99.998	99.979	99.986	99.996	99.998	99.994	99.993	99.988	99.990	0.00

6.1.5 Light stable isotope results

6.1.5.1 Quartz oxygen isotope data

Fifteen quartz samples from four different boreholes, covering a vertical stratigraphic span from the Black Reef Formation to the Hekpoort Formation were analysed for their $\delta^{18}\text{O}$ values (Table 6.3). Average $\delta^{18}\text{O}$ values for veins within the various strata are as follow: $\delta^{18}\text{O} = 16.4\text{‰}$ ($S_x=0.71$; $n=3$) for the Black Reef Formation; $\delta^{18}\text{O} = 22\text{‰}$ ($S_x=0.91$; $n=4$) for the Monte Christo Formation; $\delta^{18}\text{O} = 21.9\text{‰}$ ($n=1$) for the Eccles Formation; $\delta^{18}\text{O} = 13.9\text{‰}$ ($n=1$) for the Rooihooft Formation; $\delta^{18}\text{O} = 10.2\text{‰}$ ($S_x=0.97$; $n=5$) for the Timeball Hill Formation; and $\delta^{18}\text{O} = 11.3\text{‰}$ ($S_x=1.44$; $n=6$) for the Hekpoort Formation. These data demonstrate a distinct difference in ^{18}O content between veins from the various stratigraphic units, whereas the veins from a specific stratigraphic unit fall within a restricted range. This internal consistency indicate a strong host rock control on the ^{18}O content of the quartz veins. Fluid $\delta^{18}\text{O}$ values were calculated from quartz mineral values for 320°C fractionation temperature using the equation of Matsuhisa *et al.* (1979) (Table 6.3). These values ($\delta^{18}\text{O}_{\text{Fluid}}$) range from 2.9 to 17.0 (average $\delta^{18}\text{O} = 8.5$ [$S_x=4.7$; $n=23$]).

Variations in the $\delta^{18}\text{O}$ values of hydrothermal quartz occur in response to a number of independent parameters. Quantitatively, the most important of these are the $\delta^{18}\text{O}$ value of the fluid and ambient temperature at which fluid-mineral isotopic equilibrium is attained (Kerrick, 1987). At the site of mineralization, the $\delta^{18}\text{O}$ of hydrothermal fluids may be modified by (1) exchange reactions with wall rocks; (2) precipitation or solution of an oxygen-bearing phase either depleted or enriched in ^{18}O with respect to the fluid, and in a closed system; (3) immiscible separation of CO_2 ; or (4) mixing with an isotopically distinct fluid reservoir. A strong lithological control (option 1 above) is exerted on $\delta^{18}\text{O}$ values as is evident from Table 6.3. This observed variation in $\delta^{18}\text{O}$ strongly argues for the dominant control of wall rock reactions on the oxygen isotopic composition of the quartz veins. Variations within stratiform quartz veins are probably the result of a combination of immiscibility of an oxygen bearing gaseous phase (eg CO_2) and mixing with an isotopically distinct fluid. Precipitation of volumetrically small proportions of gangue minerals, other than quartz, caused negligible shifts in $\delta^{18}\text{O}$ values of the fluid phase.

Sample BH2-8 showed distinct zonation within the quartz vein with a clear quartz variety in contact with the volcanic host rock (Hekpoort Formation), followed by a patchy white quartz, overgrown by a typical milky quartz, and topped by a vuggy quartz variety. Great care was taken to separate

material from these quartz varieties, which was then analysed for $\delta^{18}\text{O}$ composition. The vuggy quartz variety showed the highest $\delta^{18}\text{O}$ value of 12.1 ‰, milky quartz $\delta^{18}\text{O}$ value was 10.2 ‰, white patchy quartz $\delta^{18}\text{O}$ was 8.7 ‰, and the clear quartz $\delta^{18}\text{O}$ equalled 10.7 ‰. This variation in $\delta^{18}\text{O}$ composition within a single quartz vein reflect changes in fluid chemistry with time and reiterate the dominance of the host rock composition on the fluid composition.

6.1.5.2 Fluid Inclusion stable isotope data

Measurements of $\delta^{18}\text{O}$, δD and $\delta^{13}\text{C}$ were performed on fluids from decrepitated fluid inclusions in selected quartz samples. These data are presented in Table 6.4. The hydrogen isotopic composition of water in quartz hosted fluid inclusions is variable and extends from -80 to -18 ‰. The magnitude of the observed dispersion cannot, however, be accounted for by mixing of fluids from depleted and enriched δD fluid reservoirs. Any such mixing would be reflected in shifts in both δD and $\delta^{18}\text{O}_{\text{Fluid}}$, which is inconsistent with the relatively uniform $\delta^{18}\text{O}_{\text{Fluid}}$ values. Rather, the observed range in δD may be due to the variable presence of H_2 and/or CH_4 in the aqueous fluid, as confirmed by the gas chemistry data (Table 6.2). When plotted on a $\delta^{18}\text{O}$ vs δD diagram (Fig. 6.6), the western Transvaal data coincide with the metamorphic water field, and show no indication of any isotopic interaction with meteoric water. The δD and $\delta^{18}\text{O}_{\text{Fluid}}$ data are clearly inconclusive with regard to the origin of the ore-bearing fluid, and cannot be used to adequately discriminate between the involvement of metamorphic-, magmatic- and/or basinal-derived fluids. However, the western Transvaal δD and $\delta^{18}\text{O}$ data are distinctly different from epithermal, volcanic associated massive sulphide and Mississippi Valley Type deposits.

^{13}C isotope values for fluid inclusions fall within the range +4.7 to -12.9 per mil (Table 6.4). Schidlowski *et al.* (1975) determined the average $\delta^{13}\text{C}$ value for carbonate minerals from veins to fall around -2.4 ‰. These data suggest that hydrothermal fluids may have acquired carbonic species (CO_2 , H_2CO_3 , HCO_3^-) from the carbonate host rocks. Under conditions where pressure = 2.2 to 2.5 kbar and temperature = 320°C, the $\delta^{13}\text{C}_{\text{Ca,Mg}(\text{CO}_3)_2} = \delta^{13}\text{C}_{\text{Fluid}}$ (Ohmoto and Rye, 1979), and fractionation between oxidized carbon species (CO_3^{2-} , H_2CO_3 , HCO_3^-) in solution is small (Bottinga, 1969). The calcite-HCO₃⁻ fractionation is ~ +1 ‰ at 320°C, so that calcite of -3 ‰ would have been precipitated from a fluid where $\delta^{13}\text{C HCO}_3^- = -4$ ‰ (Kyser, 1987). The observed range in $\delta^{13}\text{C}$ for samples from the western Transvaal quartz veins suggest dissolution and decarbonatization of the host dolomitic rocks. Although the $\delta^{13}\text{C}$ values of aqueous carbonate produced by such a process depend on a number of factors, it seems as if isotopic equilibrium conditions was not obtained. The $\delta^{13}\text{C}$ values of ΣCO_2 derived from carbonate

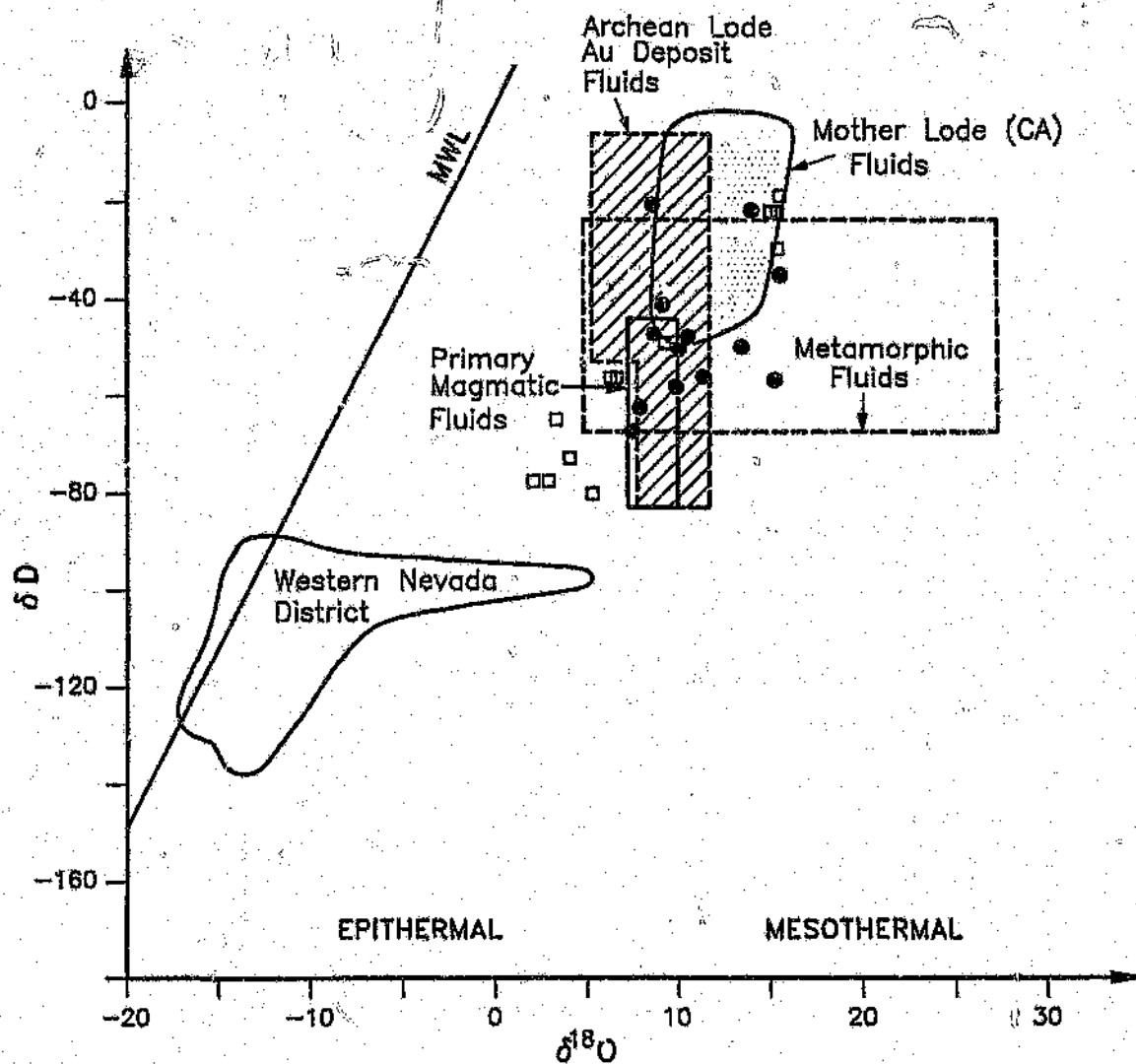


Figure 6.8. A δD versus $\delta^{18}O$ plot depicting the stable isotope geochemistry of the western Transvaal hydrothermal quartz veins (empty squares), as well as the values for the Sable-Pilgrim's Rest ore-bearing fluids (filled circles). MWL - Meteoric Water line.

Table 6.3 $\delta^{18}\text{O}_{\text{Quartz}}$ and $\delta^{18}\text{O}_{\text{Fluid}}$ values for specimens from the western Transvaal. $\delta^{18}\text{O}_{\text{Fluid}}$ values were calculated from $\delta^{18}\text{O}_{\text{Quartz}}$ using the equation of Matsuhisa et al., (1979) for $T=320^\circ\text{C}$. All values are expressed in per mil notation relative to V-SMOW. $\delta^{13}\text{C}$ values reflect the carbon isotope composition of the carbon rod used to convert O_2 to CO_2 for analysis in the Delta-S gas source mass spectrometer and give an indication of the consistency in operating conditions

Sample	Weight (mg)	$\delta^{18}\text{O}_{\text{Quartz}}$ (SMOW)	$\delta^{18}\text{O}_{\text{Fluid}}$ (SMOW)	$\delta^{13}\text{C}$ (PDB)
BH2-1	4.93	21.5	15.3	-26.48
BH2-1	4.63	21.1	14.9	-26.52
BH2-2	4.61	22.0	15.6	-26.55
BH2-3	5.18	21.9	15.7	-26.50
BH2-4	4.93	11.6	5.4	-26.55
BH2-5	8.83	9.1	2.9	-26.43
BH2-6	4.66	10.4	4.2	-26.41
BH2-8	5.00	12.4	6.2	-26.50
BH2-8	5.41	12.1	5.9	-26.51
BH2-8a	4.67	12.1	5.9	-26.41
BH2-8b	4.58	10.2	4.0	-26.47
BH2-8c	5.06	8.7	2.5	-26.49
BH2-8d	4.71	10.7	4.5	-26.43
BH1-1	4.30	15.6	9.4	-26.47
BH1-2	6.93	17.0	10.8	-26.50
BH1-2	4.70	16.5	10.3	-26.56
BH1-6	4.92	23.2	17.0	-26.47
BH1-13	4.64	10.4	4.2	-26.47
BH1-13	5.05	9.5	3.3	-26.51
BH5-4	4.86	13.9	7.7	-26.53
BH3-1	4.25	16.2	10.0	-26.43
BH3-2	6.29	15.5	9.3	-26.44
BH3-4	5.35	17.2	11.0	-26.47
NCSU Std	5.23	10.4	4.2	-26.48
NCSU Std	4.56	10.6	4.4	-26.43
NCSU Std	4.25	11.4	5.2	-26.52
NCSU Std	6.01	11.7	5.5	-26.48
NCSU Std	5.62	11.5	5.3	-26.45

Table 6.4 Light stable isotope values for quartz specimens from the western Transvaal. $\delta^{18}\text{O}_{\text{Fluid}}$ values were calculated from $\delta^{18}\text{O}_{\text{Quartz}}$ using the equation of Matsuhisa *et al.*, (1979) for $T=320^\circ\text{C}$. All values are expressed in per mil notation relative to V-SMOW.

Sample	δD (SMOW)	$\delta^{13}\text{C}$ (PDB)	$\delta^{18}\text{O}_{\text{CO}_2}$ (SMOW)	$\delta^{18}\text{O}_{\text{Quartz}}$ (SMOW)	$\delta^{18}\text{O}_{\text{Fluid}}$ (SMOW)	$\mu\text{mol CO}_2$	Comment
BH2-1	-22	1.5	20.4	21.5 (21.1)	15.3 (14.9)	1.2	
BH2-2	-18	0.3	20.5	22.0	15.8	0.8	
BH2-3	282	66	100	21.9	15.7	67.9	Bad trace for all
BH2-4	-80	-7.0	20.9	11.6	5.4	3.3	
BH2-5	-66	4.4	7.2	9.1	2.9	2.4	Bad trace for CO_2
BH2-6	-74	13.7	21.3	10.5	4.3	1.1	Bad trace for CO_2
BH2-8	-57	nd	nd	12.4 (12.1)	6.2 (5.9)	0.1	Too little CO_2
BH3-2	-49	-12.9	22.3	15.5	9.3	4.0	
BH3-4	168	54	62	17.2	11.0	24.8	Bad trace for all
BH1-2	+33	91	71	17.0 (16.5)	10.8 (10.3)	4.9	Bad trace for all
BH1-6	-32	-0.1	20.3	23.3	17.1	2.4	
BH1-13	-73	4.7	2.7	10.4 (9.5)	4.2 (3.3)	0.8	

rocks from the western Transvaal fall within the range specified by Ohmoto (1986).

6.1.6 Summary of fluid characteristics of the western Transvaal gold lodes

This study of the western Transvaal hydrothermal quartz veins has indicated the following:

1. Fluids associated with the western Transvaal hydrothermal quartz veins is capable of transporting gold, preferably as a bisulphide complex, in concentrations of ≈ 10 ppb. A strong positive correlation exists between CO_2 abundance and increased gold solubility;
2. Salinity range from 28.3 to 5.6 wt% eNaCl for aqueous fluid inclusions. Many inclusions contained carbonic species with clathrate melting temperatures ranging between 5 to 8°C . The T_h measurements obtained range from 80° to $>350^\circ\text{C}$, corresponding to high bulk densities of 0.88 to 1.13 g/cm^3 ;
3. H_2O is by far the dominant volatile component in the western Transvaal fluid inclusions and typically comprises 95 - 99 mole% of the inclusion fluid. CO_2 comprises most of the remaining volatile component (varying between 0.1 - 31 mole%), while the other gases are generally present in amounts smaller than 1 mole%. N_2 , He and Ar concentrations are relatively high for these quartz veins. The high HCl concentrations correlate well with high salinities, as indicated by microthermometric measurements, and is probably a result of the hydrolysis of NaCl at higher temperatures. There is a distinct stratigraphic control on the gaseous composition of the quartz samples. CO_2 content of Black Reef and the Monte Christo Formations are relatively low (0.5 - 3.3 mole% CO_2) compared to the CO_2 concentration in the Eccles and Timeball Hill Formations (2.2 - 10.1 mole% CO_2). The promising protore samples from the upper portion of both boreholes BH3 and BH4, yielded the highest average CO_2 contents (the CO_2 containing quartz vein of BH1-12 is hosted in an intrusive diabase rock). Large-scale fluid interaction with air-saturated meteoric water is ruled out, based on comparison with the normalized populations of present-day air and air-saturated water. The presence of Ar probably results from the radiogenic decay of potassium, with subsequent incorporation into fluid inclusions. Variations in gaseous content of the quartz veins in the western Transvaal strongly reflect the different host-rock lithologies;
4. Average $\delta^{18}\text{O}$ values for veins within the various strata are as follow: $\delta^{18}\text{O} = 16.4\text{‰}$ ($S_x=0.71$; $n=3$) for the Black Reef Formation; $\delta^{18}\text{O} = 22\text{‰}$ ($S_x=0.91$; $n=4$) for the Monte Christo Formation; $\delta^{18}\text{O} = 21.9\text{‰}$ ($n=1$) for the Eccles Formation; $\delta^{18}\text{O} = 13.9\text{‰}$ ($n=1$) for the Rooihooft Formation; $\delta^{18}\text{O} = 10.2\text{‰}$

($S_x=0.97$; $n=5$) for the Timeball Hill Formation; and $\delta^{18}\text{O} = 11.3 \text{ ‰}$ ($S_x=1.44$; $n=6$) for the Koppoort Formation. These data demonstrate a distinct difference in ^{18}O content between veins from the various stratigraphic units, whereas the veins from a specific stratigraphic unit fall within a restricted range. This internal consistency indicates a strong host rock control on the ^{18}O content of the quartz veins. The $\delta^{18}\text{O}_{\text{Fluid}}$ values range from 2.9 to 17.0 (average $\delta^{18}\text{O} = 8.5$ [$S_x=4.7$; $n=23$]).

The hydrogen isotopic composition of water in quartz hosted fluid inclusions is variable and extends from -80 to -18 ‰, ignoring the bad traces. The magnitude of the observed dispersion may be due to the variable presence of H_2 and/or CH_4 in the aqueous fluid, as confirmed by the gas chemistry data. The δD and $\delta^{18}\text{O}_{\text{Fluid}}$ data are inconclusive with regard to the origin of the ore-bearing fluid, and cannot be used to adequately discriminate between the involvement of metamorphic-, magmatic- and/or basinal-derived fluids. However, the western Transvaal δD and $\delta^{18}\text{O}$ data are distinctly different from epithermal, volcanic associated massive sulphide and Mississippi Valley Type deposits.

^{13}C isotope values for fluid inclusions fall within the range +4.7 to -12.9 per mil. These data suggest that hydrothermal fluids may have acquired carbonic species (CO_2 , H_2CO_3 , HCO_3^-) from the carbonate host rocks;

5.1.7 Comparison of fluid characteristics between eastern and western Transvaal gold lodes

The following features were apparent when hydrothermal fluids from the western Transvaal quartz veins were compared with the mineralizing fluids from the Sable-Pilgrim's Rest Goldfield:

- (1) The textural nature of the hydrothermal quartz veins in the eastern and western Transvaal are very similar, with both localities showing sheeted veins, brecciation and vuggy quartz.
- (2) All of the quartz veins examined experienced repeated fracturing in the presence of aqueous fluids as evident by abundant planes of secondary aqueous inclusions. The dominant type of fluid inclusion, in both the eastern and western quartz veins, is an aqueous inclusion with variable liquid to vapour ratios. This inclusion type commonly contains a carbonic phase and occasionally a cubic daughter crystal. Decrepitation invariably occurs before homogenization in this type of inclusion from the eastern Transvaal, whereas, the fluid inclusions of this sort from the western Transvaal homogenize around 150° to 250°C. This indicates a significant difference in the internal fluid pressures between inclusions from the eastern

and western Transvaal, and may reflect a difference in lithostatic pressure (as the overlying sedimentary pile is much thinner in the western Transvaal compared to the eastern Transvaal).

(3) Quantitative QMS gas analyses show that the bulk fluid chemistry of the quartz veins of the eastern Transvaal are very similar to those of the western Transvaal quartz samples. H_2O is the dominant species with CO_2 (average concentration ≈ 6 mole %) forming the bulk of remaining gaseous species. Other species that are present in reasonable concentrations, in both the east and west, are CH_4 , N_2 , C_2H_{6+2} , H_2S , Ar and HCl. In both areas the concentrations of gaseous species are mainly controlled by the composition of the host rocks.

(4) This observed variation in $\delta^{18}O$ strongly argues for the dominant control of wall rock reactions on the oxygen isotopic composition of the quartz veins. The dominant lithological control of the host rock on oxygen isotopic composition and a lack of knowledge of the extent of fluid/rock interaction, impede efforts aimed at determining the original oxygen isotopic signature of the mineralizing fluid. The δD and $\delta^{18}O_{fluid}$ data are clearly inconclusive with regard to the origin of the ore-bearing fluid, and cannot be used to adequately discriminate between the involvement of metamorphic-, magmatic- and/or basinal-derived fluids. However, the δD and $\delta^{18}O$ data are distinctly different from epithermal, volcanic associated massive sulphide and Mississippi Valley Type deposits. No indication of any isotopic interaction with meteoric water is apparent. $\delta^{13}C$ data suggest that hydrothermal fluids may have acquired carbonic species (CO_2 , H_2CO_3 , HCO_3^-) from the carbonate host rocks.

6.2 SPRG in relation to other mesothermal gold deposits

Mesothermal gold deposits can be classified into mainly three types:- (1) Greenstone hosted (Superior Province, Canada; Yilgarn and Pilbara cratons, Western Australia; Kaapvaal and Zimbabwean cratons, southern Africa); (2) turbidite hosted (Victoria, Australia; Nova Scotia, Canada); and (3) Cordilleran vein type deposits (felsic intrusion related). Low pressures (less than 3 kbar) are generally inferred for these mesothermal deposits, with temperatures around 300-400°C.

(1) The main characteristics of lode gold deposits hosted in greenstone belts of Archaean cratons and those in younger igneous-dominated terranes of oceanic affinities are as follows: (a) The metamorphic grade of these rocks ranges from sub-greenschist to middle amphibolite facies; (b) These deposits are not preferentially hosted by a specific greenstone lithology, but occur within ultramafic, mafic

and felsic metavolcanics, clastic metasediments, and mafic to felsic intrusions; (c) They are commonly found in regional composite shear systems in major tectonic zones; (d) Fluid inclusion and alteration studies of greenstone gold deposits have shown that auriferous fluids are generally H_2O-CO_2 dominated with lesser, but variable contents of $NaCl$, CH_4 , N_2 , S , K and other components; (e) Fluid salinities are generally low i.e. < -5 wt% $eNaCl$; (f) Fluid light stable isotope compositions fall within the ranges $\delta^{13}C = -1$ to -8 ‰ (PDB), $\delta^{18}O = 10$ to 16 ‰ (SMOW), and $\delta^{34}S$ around zero ‰ (CDT).

(2) Turbidite-hosted gold mineralization contained within true turbidites, iron formations, and impure carbonate rocks, occurs mainly in quartz veins, sheeted zones and saddle reefs in faults, fractures and shears and anticlinal parting planes. The host rocks are mainly marine sedimentary sequences, such as shale, sandstone and greywacke. Such sequences are invariably folded in a complex manner, metamorphosed, and invaded by granitic rocks, to form extensive areas of metasediments (Boyle, 1986). Although high grade mineral assemblages are developed close to the granitic intrusives, the gold mineralization is associated with the lower-grade greenschist facies. Wall rock alteration associated with the quartz veins and saddle reefs is limited and the quartz veins have sharp contacts with host lithologies. Fluid inclusion studies on rocks from the Ballarat Slate Belt (Cox *et al.*, 1983) indicate that both aqueous and carbonic fluids were present during auriferous reef formation. Salinities of aqueous solutions are low and trapping temperatures ranged from $250-300^\circ C$. Oxygen isotope values across the Australian turbidite-hosted gold deposits of the Lachlan fold belt are remarkably uniform, with $\delta^{18}O$ ranging between 14.4 and 19.0 ‰ (Gray *et al.*, 1991). Isotopic values of hydrogen range between -70 to -100 ‰.

(3) The main characteristic of Cordilleran vein type deposits are that they occur in compressive margin settings, and are generally associated with calc-alkaline igneous activity (Sawkins, 1972). Epigenetic quartz-carbonate vein emplacement is structurally controlled, and displays typically bilaterally-symmetrical wall-rock alteration (Gulbert and Park, 1986). Sulfide mineralization occurs as typical open-space fillings in silicate host rocks, and as replacements in carbonate hosts. Metal zonation is developed in the planes of the veins, with ore precipitation taking place at near surface crustal levels (Sawkins, 1972). Sulfur isotope ratios are close to zero per mil, with oxygen and hydrogen isotopic data indicating little or no demonstrable meteoric admixture during ore-formation stages (Rye and Sawkins, 1974). Various mechanisms have been proposed to account for generation of the mineralizing fluids involved in Cordilleran type mesothermal vein genesis, such as: (a) lateral secretion (Boyle, 1979); (b) mantle

degassing-granulitization (Colvine *et al.*, 1984); (c) meteoric water circulation (Nesbitt *et al.*, 1986; Shelton *et al.*, 1988); (d) metamorphic devolatilization (Kerrick and Fyfe, 1981; Goldfarb *et al.*, 1989); and (e) an orthomagmatic origin (Colvine *et al.*, 1984; Hattori, 1987). The most widely accepted model explaining the source of mineralizing fluids, involves the generation of H_2O and CO_2 during prograde metamorphism under greenschist to amphibolite facies conditions. This metamorphic devolatilization model has recently been questioned by Shelton *et al.* (1988) and Nesbitt (1990), based mainly on the stable isotopic data (Rushton *et al.*, 1993), who argued for the involvement of a significant meteoric water component.

Characteristic features of the SPRG that correspond to those within the above spectrum of mesothermal gold deposits, include:- (a) comparable light stable isotope ranges, together with a lack of isotopic evidence for meteoric water involvement; (b) high Au/Ag ratios; (c) presence of ore shoot structures, which are highly characteristic of mesothermal gold deposits (Colvine *et al.*, 1984); (d) variably deformed structures within individual sheeted veins (Harley and Charlesworth, in press) which points towards cyclic opening and quartz accretion events separated by episodes of deformation; and (e) fluid inclusion properties which indicate high fluid pressures during entrapment. However, several features also distinguish the Sable-Pilgrim's Rest ores from typical mesothermal deposits:- (a) The SPRG is spatially associated with a large layered mafic intrusion and its satellites, the Bushveld Complex, and overlies one of the two concentric structures along which feeder sites to the Bushveld Complex (such as Losberg and Uitkomst) are arranged (Sharpe *et al.*, 1981). Furthermore, the age of gold mineralization is broadly coeval with the emplacement age of the Bushveld Complex; (b) veins are largely hosted within a platform carbonate sequence; (c) high salinities (mean = 12 wt% eNaCl); (d) mean bulk CO_2 content is low (= 5 mole%), and; (e) the presence of ubiquitous Cu, Bi and lesser W in addition to Au, Ag, As, and Sb sulfides.

The observed characteristics of the SPRG contrast with those of epithermal gold deposits where temperatures of formation are almost similar, but inferred pressures of formation and $\delta^{18}O$ values are lower (Heald *et al.*, 1987), and the environment of ore deposition is markedly different. Furthermore, the consistent $\delta^{18}O$ values of the mineralizing fluids, along individual vein horizons, are also typical of those found in mesothermal systems of Archaean and Phanerozoic age, and contrast sharply with the relatively inhomogeneous stable isotopic data for epithermal gold systems (Kyser and Kerrich, 1990; Field and Fifiarek, 1985). The involvement of meteoric water characterize the formation of epithermal gold

deposits, whereas meteoric signatures are noticeably absent in the Sable-Pilgrim's Rest deposits.

Furthermore, the observed features are distinctly different from those observed in Mississippi Valley type deposits, which was interpreted by Anderson (1994) to be an analogue for the eastern Transvaal lode gold deposits. No evidence exists for the tectonic (deformation-linked) expulsion of basinal brines in the eastern Transvaal, such as was proposed by (Duane and Kruger, 1991; Duane and Saggerson, 1993) as there is no unequivocal evidence for large scale orogenic activity in the eastern Transvaal.

6.3 Genesis of the SPRG ores

Deposition of the SPRG ores is constrained between the emplacement of early Bushveld-aged pre-cl. or di. base intrusions which have been metamorphosed and then cut by mineralized vein systems, and unmetamorphosed pyroxenitic dykes, thought to be related to the Main Zone of the Rustenburg Layered Suite, which transgress mineralization. The Bushveld Complex was intruded over a relatively brief interval between 2061 ± 27 Ma (Rustenburg Layered Suite; Walraven et al., 1990) and 2054.4 ± 1.8 Ma (Lebowa Granite Suite; Walraven and Hattingh, 1993). Deposition of the SPRG ores is probably, therefore, broadly coeval with this interval, as also suggested by the Rb/Sr and Pb/Pb data for diabase from the Olifantsgeraamte Mine.

Besides its contemporaneity with the Bushveld igneous event, the SPRG is also spatially related to the Complex. The goldfield occurs over a restricted area (c. 10^3 km²) of the Transvaal sub-basin and, although several other small hydrothermal occurrences of gold are developed elsewhere in the Transvaal Sub-basin, this is by far the most important mineralized section. The SPRG occurs some 40-50 km east of the present limit of the Bushveld Complex, but falls on or close to two major concentric fracture zones which encompass and control the emplacement of the Bushveld Complex and its satellites (Sharpe, et al., 1981). The smaller Mamre-Slaaihoek goldfield, for example, which occurs to the south of the SPRG (Fig. 1.1), is spatially associated with the Uitkomst intrusion, a known Bushveld Complex satellite which also occurs on one of the concentric fractures which encircles the Complex. It is not known with certainty whether a mafic intrusion exists beneath the SPRG although geophysical indications suggest the presence of a number of magnetic anomalies in the general area of SPRG (P.N. Bentley, pers. commun.). These anomalies may be related to the presence of mafic intrusions at depth beneath the Transvaal sediments.

The occurrence of mineralized veins in the SPRG is observed at irregular intervals over at least

1000 metres of vertical extent, from the steeply dipping lodes in the granite basement beneath the Transvaal sedimentary cover, to flat-lying lodes well up into the Pretoria Group (Fig. 1.1). The nature of the fluids that are associated with the deposition of this extensively mineralized system are heterogeneous, but appear to have been derived at least partially from a deep-seated source. The hydrothermally altered diabasic wall-rock at Olifantsgeraamte mine is characterized by an enhanced radiogenic Sr isotope signature relative to unaltered diabase (Fig. 4.8), suggesting that the hydrothermal fluids themselves were enriched in ^{87}Sr . This supports the suggestion that the fluids interacted with a relatively high Rb/Sr rock such as the Nelspruit porphyritic granite (Rb typically 100-200ppm, Sr typically 300-500ppm) which occurs beneath the SPRG. Furthermore, Type 2 fluids, with low XCO_2 and high salinities, occur largely with the vertical granite-hosted veins in the SPRG, while the compositionally diverse Type 1 fluids occur throughout the mineralized successions. This pattern of fluid distribution indicates that the fluid chemistry reflect interaction with the host rock lithologies, but is also consistent with derivation of Type 2 fluids from a deep-seated, possibly an original magmatic, source, with incursion of this fluid with the host rocks during upward flow through the granite basement, into the overlying sedimentary sequences. Oxygen and sulfur isotope compositions clearly point to variable values which tend to range between the extremes of pristine juvenile signatures and values consistent with fluid/rock interaction. QMS gas analysis on quartz-hosted inclusion fluids indicate that carbonate-hosted veins have higher CO_2 and CH_4 abundances than, for example the vertical granite-hosted veins, confirming the influence of host rock on fluid composition. Low N_2/Ar ratios, as well as $\delta^{18}\text{O}$ and δD values, in the SPRG ore fluids suggests negligible interaction with a meteoric fluid component. However, we are not able to quantitatively evaluate the proportional contribution of fluid sources from either magmatic or sedimentary brines, to the SPRG hydrothermal system.

Mineralization in the SPRG was stimulated by a deep-seated heat source which initiated convective overturning of an originally pristine juvenile fluid transporting metals that were probably derived from the same source, as well as a measure of connate waters. The reconstituted remnants of such fluids are now preferentially preserved in the vertical granite-hosted vein systems. This fluid was relatively acidic and anoxic and equally efficient in transporting gold as either a bisulphide complex or a chloride complex, whereas copper may have been in solution as chloride complex. The volumetrically dominant SPRG ore fluid (Type 1), however, has been significantly modified by local fluid/rock interaction and is now represented by a fluid inclusion population exhibiting a variable continuum of $\text{H}_2\text{O}/\text{CO}_2$ ratios and salinities. These characteristics are confirmed by quantitative QMS gas analyses. This fluid

population is believed to have been derived by fluid unmixing that was initiated by periodic depressurization associated with crack-seal events in a fault-valve system formed by bedding plane slip during Bushveld related structural adjustments in the Transvaal Sub-basin. Periodic CO_2 effervescence associated with this unmixing event may have been responsible for a large measure of metal precipitation, especially the abundant native gold-in-quartz present in the SPRG. Fluid overpressures were instigated by the shale-rich cap rocks of the Pretoria Group, covering the more permeable carbonate sediments of the Chuniespoort Group. Phase separation was an important process during fluid evolution and is thought to be the principal controlling mechanism for both gold and sulfide precipitation. Gold precipitation was mainly controlled both by a decrease in sulfur activity within the ore-bearing fluid because of sulfide precipitation and changes in the fluid chemistry as a result of fluid immiscibility.

The SPRG is a predominantly sediment-hosted, Au-Cu-(Bi-As-Sb-W) metal province that represents an unusual member in the family of mesothermal ore deposits. As recognized in the past and confirmed in this study, the characteristics of the SPRG appear to be related to its close spatial, temporal and genetic association with the Bushveld Complex and its satellites. The minimum fluid volume required to account for all the gold (168 tons) in the SPRG is approximately 1.68×10^{13} litres which, assuming a gold solubility of 10ppb, could be derived from a Bushveld type magma of only 560 km^3 in size (containing 1 wt% H_2O ; density $\approx 3 \text{ g.cm}^{-3}$). In terms of the volume of magma associated with the Bushveld Complex which at the present levels of exposure covers an area of $67\,000 \text{ km}^2$ (Von Gruenewaldt *et al.*, 1985), the required volume is relatively small. However, pristine orthomagmatic fluids usually stay within the source intrusion. A calculation, similar to the one above, show that 840 km^3 of sedimentary rock with a total water content of 2%, including bound- and pore space water, is needed to account for the required fluid volume. Despite the abundance of potential mineralizing fluids around, there is no way to unequivocally define the fluid source. Numerous Bushveld related satellite intrusions of this magnitude exist in the central Kaapvaal Craton and, given the geophysical evidence, it is tempting to suggest that such an intrusion might be linked genetically to the formation of the SPRG. A relationship between mesothermal Au-Cu deposits and hidden or distant mafic-felsic intrusions has obvious exploration significance, not only to the vast expanse of Transvaal sediments on the Kaapvaal Craton, but also to similar geological settings elsewhere in the world.

6.4 Significance of the SPRG genetic model to exploration for mesothermal gold deposits

An understanding of the systematic inter-relationships of the geological characteristics of the Sabie-Pilgrim's Rest goldfield may be enhancing the probability of successful exploration for gold in similar geological settings elsewhere in the world. The attractiveness of Sabie Pilgrim's Rest as a modern-day exploration target is enhanced by the fact that the largest deposit in the district, the Theta Mine, produced about 1.68 million ounces of gold and that 9 mines produced more than 500 000 ounces of gold (Fowler, 1968). Furthermore, the form and distribution of mines in the area is controlled by structure, which could favour development of larger deposits in the area.

Emplacement of large igneous intrusions, such as the Bushveld Complex, are able to initiate large scale hydrothermal fluid circulation. The best studied example of such a hydrothermal system is the Skaergaard intrusion, east Greenland (Taylor and Forester, 1979; Bird *et al.*, 1986). Based on the work of Taylor (1977), Criss and Taylor (1986) have shown that the water/rock ratio for the Skaergaard intrusion was in the order of 0.05, with insignificant amounts of meteoric water involvement in the Precambrian basement gneiss. However, the major fractures acted as fluid conduits along which meteoric water circulated to depths of approximately 10 km beneath the Eocene surface (Criss and Taylor, 1986). Bird *et al.* (1991) have drawn attention to a gold-bearing horizon in the Skaergaard intrusion, but concluded that the gold was included into the silicate phases as a immiscible liquid metal. However, large volumes of fluid would be able to remobilise gold from such horizons and focused fluid flow could concentrated the metal into economically mineable deposits. A minimum estimate of the fluid volume associated with the Bushveld magmas would be 4.02×10^{15} litres, excluding the fluid volume hosted within the sedimentary rocks. Under ideal conditions such a volume of fluid with a gold transport capability of 10 ppb, as calculated above, could theoretically give rise to the precipitation of 40200 tons of gold. This should be a major incentive for any exploration geologist.

6.5 Brief summary of conclusions

The hydrothermal deposits of the SPRG are unusual in terms of geological setting and geochemical characteristics, and do not correspond to any of the known genetic models for typical mesothermal deposits.

This study of the SPRG has indicated the following:

1. age constraints indicate that gold mineralization in the SPRG is concurrent with the emplacement age of the Bushveld Complex;
2. mineralization occurred at temperatures around 320°C, at pressures in the range 2.2 to 2.5 kbar and at depths of 7 to 8 km. Vein textures indicate the involvement of high pressure (supralithostatic) fluids;
3. oxygen isotope values of quartz from the vertical veins are remarkably consistent (average $\delta^{18}\text{O} = 14.2\text{‰}$) and significantly different from those of the horizontal veins (average $\delta^{18}\text{O} = 16.1\text{‰}$) and sill/dike associated veins (average $\delta^{18}\text{O}$ value of 20.7 ‰). $\delta^{34}\text{S}$ values of vein pyrite range from -2.8 to +3.1 ‰. δD , $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values from inclusion fluids ($\delta\text{D}_{\text{Quartz}} = -37$ to -53‰ ; $\delta^{18}\text{O}_{\text{Pyrite}} = -54$ to -68‰ ; $\delta^{18}\text{O} = +6.5$ to $+15.4\text{‰}$, $\delta^{13}\text{C} = -11.7$ to -1.4‰) coincide predominantly with values of primary magmatic and/or metamorphic water, and exclude the involvement of meteoric water. Stable isotope data clearly suggest interaction of the ore fluid with the host rocks, and changes in stable isotope composition are largely host rock dominated.
4. the nature of the ore-bearing fluid was predominantly aqueous with <5 mole % carbonic species. Other gases, mainly CH_4 , C_2H_6 , N_2 , Ar, H_2S , SO_2 and HCl, were present in abundances <1 mole %. The strata bound veins contain significantly higher concentrations of CO_2 and CH_4 as oppose to the Ar- and HCl-rich vertical veins. The higher abundances of carbonic gas species (CO_2 and CH_4) in the carbonate hosted veins suggests decarbonatization of the dolomitic host rock by interaction with the hydrothermal fluid, as well as thermocatalysis of shale-hosted organic matter. However, the higher CO_2 and CH_4 contents in the upper veins could also be a direct result of H_2O - CO_2 phase separation. Evidence for phase separation is suggested by QMS results from individual native gold hosted fluid inclusions, showing varying $\text{CO}_2/\text{H}_2\text{O}$ ratios. High HCl concentrations in vertical veins correlate well with high salinities. The gaseous content of the veins, to some extent, reflect the host rock lithologies.

5. The noble gas concentrations and isotopic ratios of gold-hosted fluid inclusions appears to be analogous to igneous compositions and do not correspond as favourably with atmospheric values and sedimentary rock compositions. Available evidence (extremely high $^{40}\text{Ar}/^{39}\text{Ar}$ ratios; low $^4\text{He}/^{40}\text{Ar}$ ratios) indicate a lack of meteoric water or atmospheric involvement. The good retentive properties of gold for diffusive noble gases, such as ^4He , was shown convincingly.

6. the ore-bearing solutions were reducing ($f\text{O}_2 = 10^{-32.5}$) and the activity of the H_2S species was between 10^{-25} and 10^{-26} . Furthermore, the ore-fluids were acidic with salinities ranging between 5.5 and 23.5 wt% eNaCl for the horizontal veins and >30 wt% eNaCl for the vertical veins;

7. gold was equally soluble as a bisulphide complex or a chloride complex. Gold precipitation was enhanced by several mechanisms, including lowering of sulfur activity due to precipitation of sulfide minerals, changes in fluid chemistry due to unmixing within the fluid phase, and limited interaction with the sedimentary host-rock. However, the dominating mechanism for gold precipitation was phase separation as indicated by QMS results, as well as fluid inclusion petrography. Different styles of gold occurrence confirm that several mechanisms of precipitation may have been active, which makes the prediction of the siting of gold with respect to the vein components very difficult on a regional scale.

8. The SPRG proved to be a different type of mesothermal gold deposit associated with a Layered Igneous Complex, the Bushveld Complex. In view of the wide spread nature of such mafic complexes, this association could be significant in terms of opening new exploration targets.

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1. Micro-Raman Spectroscopic Technique

Micro-Raman spectroscopy involves the use of visible light to probe the vibrational behaviour of molecular systems, usually in the energy range $100 - 4200 \text{ Acm}^{-1}$. Raman scattering occurs when the energy of the incident beam is slightly raised or lowered by inelastic interaction with the vibrational modes, and is named after one of its discoverers, Raman and Krishnan (1928). Raman spectroscopy gives rise to a characteristic set of scattering peaks for each given sample, as a function of energy and can be made quantitative with suitable calibration. Micro-Raman spectroscopy enables non-destructive, direct molecular analysis of individual fluid inclusions, and is a vast improvement on the inferior indirect estimation of fluid inclusion properties using microthermometric heating-freezing experiments.

A micro-Raman analysis of an individual fluid inclusion involves the scattering of an incident monochromatic beam of visible light (eg 514.5 nm lines of an argon ion laser) during interaction with the fluid inclusion content. A small proportion of this scattered light interacts with the sample in such a way as to induce a vibrational mode. When this occurs, the energy of the scattered light is reduced by an amount corresponding to the energy of the vibrational transition. This type of inelastic scattering is known as Raman scattering, while elastic light scattering with no change in energy is known as Rayleigh scattering. The energy of the scattered light is analysed using a spectrometer, and the Raman lines appear as weak peaks shifted in energy from the Rayleigh line (which has the energy of the incident beam). The positions of these Raman peaks relative to the incident laser line correspond to the frequencies of Raman-active vibrations in the inclusion fluids. Raman activities of particular modes, with different relative intensities, are determined by the quantum mechanical selection rules for the vibrational transition (aka the change in polarizability; McMillan and Hess, 1988), and by the mode symmetry. Comprehensive accounts of the theory and application of micro-Raman spectroscopy to the study of individual fluid inclusions are given in Wopenka *et al.*, (1990), MacMillan and Hofmeister, (1988) and Touray *et al.*, (1985), among others.

Laser-excited micro-Raman analysis was conducted on SPRG samples in the laboratory of the Centre de Recherches sur la Géologie des Matières Premières Minérales et Énergétiques at Nancy, France, using a DILOR-XY, as well as at the Department of Earth Sciences, Vrije Universiteit in Amsterdam, The Netherlands, using a MICR0DIL-28. The DILOR-XY spectrometer was operated in

multichannel mode, allowing 30 accumulations over an integration time of 3 seconds, using 1024 diodes in the detector (slit width = 200 μm). The spectral resolution of the DILOR-XY is 2 cm^{-1} . An 514.6 nm wavelength Argon laser was used for excitation operation at 1000 mW, at the source. The MICRODIL-28 was operated at a slightly lower laser intensity of 700 mW at the source, slit width 300 μm , excitation line 514.5 nm. A complete description of the operating conditions and the method used to study fluid inclusions with the MICRODIL-28 are presented by Burke and Lustenhouwer (1987). Measured line positions of CO_2 , CH_4 , N_2 and C_2H_6 were identified by comparison of listed values by Dubessy *et al.*, (1989) and Van Den Kerkhof (1991). Peak areas were calculated using standard numerical integration methods and are related to relative concentration through the following equation:

$$\frac{C_a}{C_b} = \frac{A_a}{A_b} \cdot \frac{F_b}{F_a}$$

(Pasteris *et al.*, 1988), where C_a/C_b represents the molar ratio of species a and b, A_i is the Raman peak for species i and F_i the Raman quantification factor for species i. The Raman quantification factors are strictly instrument specific and represent a combination of the gas-specific scattering efficiencies, instrumental efficiency factors and are also dependent on the density (internal pressure) of the inclusion fluid (Pasteris *et al.*, 1988; Wopenka and Pasteris, 1987). As decrepitation at relatively low temperatures, as well as homogenization of the SPRG fluid inclusions into the liquid phase is a very common phenomena, high densities and high internal fluid pressures are indicated. These high internal fluid pressures distract from the accurate quantification of the Raman spectra and, thus, a 10% relative error for the minor components are assumed. Raman spectra were scrutinized for CO_2 , CH_4 , N_2 , H_2S , CO , C_2H_6 , H_2 , O_2 , SO_2 and H_2O .

2. Quadrupole Mass Spectrometry

Analysis of gases in fluid inclusions were made with a VG SXP600 quadrupole mass spectrometer at the Department of Geological Sciences, University of Michigan (for complete description of the instrument and operational procedures, see Graney and Kesler *in prep.*). Gases were passed for analysis through an inlet system designed to minimize the path distance between sample and ionizing filament. Source electron energy was 50 volts. Ionized molecules and molecular fragments were detected by a secondary electron multiplier operated at 1200 volts. For most samples, 16 masses were monitored, allowing simultaneous real time analysis for a number of compounds including H_2O , CO_2 , CH_4 , C_2H_6 , H_2 , N_2 , Ar, H_2S , SO_2 and HCl. Data were collected at a rate of approximately 100 cycles per

minute.

In a quadrupole mass spectrometer four rods are aligned parallel with a high degree of accuracy. Each pair of opposite rods is electrically connected, a positive dc voltage being applied to one pair and an equal, negative, dc voltage to the other pair. Superimposed on these dc voltages is a radiofrequency ac signal arranged so that the phase of this signal applied to one pair of rods is 180° different from that applied to the other pair. The ratio between the applied dc and ac fields is critical to successful operation. Quadrupole mass spectrometers have several advantages over an instrument that utilize an electromagnet: (i) The quadrupole mass spectrometer may be rapidly scanned to cover the entire mass range in a fraction of a second. In ICP-MS applications a spectrum is accumulated by superimposing data accumulated from many such scans. Magnetic sector analysers cannot be scanned anywhere near as rapidly; (ii) The spectrum obtained by scanning quadrupole mass filter is linear in mass, that from a magnetic sector analyser is exponential in mass; (iii) The quadrupole is capable of accepting ions for dispersion from a source over a wide solid angle. The lateral motion of ions entering the quadrupole is rapidly swamped by the induced magnetic fields. Ions entering a magnetic sector analyser must be tightly collimated to preserve adequate resolution; (iv) In quadrupole mass spectrometry there is a simple tradeoff between ion transmission intensity and resolution on a quadrupole mass spectrometer; (v) Construction of a quadrupole is relative compact and small; (vi) The main disadvantage which prevents more widespread use of the quadrupole is that the precision of isotope ratio measurements is about one to two orders of magnitude worse than can be obtained on a magnetic sector instrument (Jones and Kesler, 1992).

2.1 Gas Liberation Methods

Great care has been taken to ensure the preponderance of type I inclusions within the pure quartz specimens used for QMS analyses. This was achieved by microscopic selection of doubly polished quartz chip fragments which were clearly dominated by type I fluid inclusions. However, it is inevitable that this type of bulk analysis reflects contamination by other fluid populations (Roedder, 1990) and thus represents partially time-integrated fluid chemistry.

Quadrupole mass spectrometer (QMS) gas analyses were performed on pieces of fluid inclusion plates, $\sim 200 \mu\text{m}$ thick and less than 2 mm in diameter, with a total mass of less than 50 mg. Gases were released by crushing a double polished thin section of the host mineral at 110°C under vacuum in a

modified N₂ line. The crush analysis of specific inclusion types of SPRG quartz were performed on selected portions of fluid inclusion double polished plates that had been determined under the microscope to contain predominantly one type of fluid inclusion. In almost all instances, water mass response were 2 to 4 orders of magnitude above background. Smaller, but significant, signals were obtained for masses corresponding to less abundant gases. Despite the short path length on the inlet system, adsorption of water occurs, as indicated by the longer time required for masses 18, 17 and 16 to drop to background. Thus, the signal for each mass must be integrated across the entire scan between the crush and the time at which water peaks return to initial background levels, which typically requires 3 to 4 minutes.

In individual burst analyses, inclusions were released by heating small samples under vacuum in a Vycor[®] tube until their inclusions decrepitated. Gases liberated in this manner passed directly into the quadrupole source and produced episodic signal bursts that probably represent individual inclusions. To speed the cycling rate of the quadrupole, only masses corresponding to H₂O, CO₂ and CH₄ were monitored in these runs. The faster cycling rate ensured that inclusion bursts lasting only a few seconds spanned at least 10 to 20 cycles, which provides a clear record for analysis. Gas species from individual inclusions with abundances of less than 0.5 mole% cannot be reported quantitatively and were therefore omitted. Gas-rich or vapour inclusions will have low-sloped isochores and should survive without decrepitating to higher temperatures than aqueous inclusions.

2.2 QMS analytical considerations

Determination of the relative abundances (mole fraction) of gases in a complex gas mixture requires use of a matrix fitting procedure, provided as part of the operating software with the quadrupole. The program takes into account cracking patterns for each gas in the analyses and delineates multiple contributions to masses by a series of simultaneous equations in a matrix, with the one side of the matrix having a list of all gases considered in the analyses, whereas the other side has a list of all the masses that were monitored. In the appropriate cells are the known relative intensities of masses from each cracking pattern. These are compared to the overall signal detected for each mass and partitioned to the appropriate gases to determine the original composition in mole% (Lanals and Hofstra, 1991; Graney and Kesler, in prep.). A correlation coefficient determined for each analyses defines how well the reported final composition fits the original raw data; a low correlation coefficient indicates either a bad analyses or that the other gas component not accounted for in the data reduction was present. This last

possibility is discounted by initially performing full scans of all masses present in similar samples to determine whether we are analysing for the correct mixture of gases.

Comparing intensities of only parent peaks for individual gases will not yield an accurate overall gas composition for two reasons. Firstly, most gases are "cracked" to some extent into smaller fragments at the quadrupole analyser source. Secondly, some gases (e.g. N_2 and CO) share the same parent mass. Thus, if only mass 28 were analysed, N_2 and CO could never have been distinguished. Fortunately, the resulting cracked fragments are also ionized and detected, allowing one to determine the total amount of gas originally present. By knowing the cracking "pattern" (relative intensities of parent and cracked peaks at a particular pressure) of each gas, it is possible to distinguish among gases. In the case of N_2 and CO, monitoring the following masses allows us to obtain analysis of each: 28 (parent mass- N_2^+ and CO^+); 16 (O^+ from CO); 14 (N^+ and N_2^{2+} from N_2); and 12 (C^+ from CO). Masses monitored for the various species analysed are as follow: H_2O - 18, 16, 2; CO_2 - 44, 28, 16, 12; CO - 28, 16, 12; CH_4 - 16, 15, 14; C_nH_{2n+2} - 15, 27, 29; N_2 - 28, 14; O_2 - 32, 16; Ar - 40; H_2S - 34, 32, 2; SO_2 - 64, 48, 32, 16; H_2 - 2; HCl - 36, 2. While tables of cracking patterns for gases are available in the literature, the patterns are dependant on operating conditions and inlet/source geometry and are instrument specific. For all analyses, appropriate cracking patterns were used for the pressures generated by the fluid inclusion gases upon crushing or decrepitation. This method of data reduction works for most gases, because they fragment to different daughter masses in proportions characteristic for each gas. Graney and Kesler (in prep.) have shown that influences such as mass fragmentation and relative sensitivities have severe effects on detection limits of the various species. The latter authors considered a peak height of 5 times background (0.5 log units on the detector response profiles) as the minimum deflection necessary in order to measure a peak response quantitatively. Calibration of the quadrupole mass spectrometer at the University of Michigan show that masses which contribute to any reported gas concentrations above 5 ppm from a sample that contains at least $1E-3$ μ l of water are visible as peaks 5 times greater than background values (Graney and Kesler, in prep.). A 5ppm gas concentration correspond to $2.78E-13$ moles of water, which is equivalent to the amount of water contained in a 1 μ m radius H_2O inclusion. Therefore, the quantitative detection limits during crush analysis are $2.78E-13$ moles (Graney and Kesler, in prep.).

Confidence in the amount of H_2O reported in analysis is of particular importance, because of the high amounts of other gases (primarily CO_2 , CH_4 and N_2) obtained in the Pilgrim Rest samples, and the

trends of these gases with H_2O . These results could be artifacts of the analytical technique if either consistent over-reporting of the amounts of non- H_2O gases, or under-reporting the amount of H_2O took place. However, extensive investigation into the effects of variations of cracking patterns and relative sensitivities of gases on reported gas compositions (Jones and Kesler, 1992) makes it clear that there are no overestimation of non- H_2O gases in the analyses reported in Table 3.5. Because of the problem of adsorption, underestimation of H_2O is possible. Jones and Kesler (1992) state several reasons why it is not believed that analytical error due to H_2O adsorption is a serious concern.

3. Analytical considerations Gold-hosted noble gases, U and Th geochemistry

Two geochemical features make the noble gases extremely good tracers of fluid origins, namely its chemical inertness (noble gas interactions with other elements are of the van der Waals type) and the fact that noble gases are rare. Gold has the advantage of being extremely retentive for noble gases (Ozima and Podosek, 1983), in contrast to most minerals from which a large fraction of noble gases, particularly He, is usually lost. Eight gold specimens from the SPRG, obtained from the Museum of the Geological Survey/Transvaal Museum (with the courtesy of Mr. R. Dixon, Curator of the Museum of the Geological Survey of South Africa), was prepared for noble gas analysis and analysed by Professor O. Eugster and co-workers, Physikalisches Institut, University of Bern (Table 3.7; Fig. 3.21).

Gold was separated from the rock matrix by leaving the samples overnight in a 48% HF solution. The gold grains were then cleaned in 10% HCl at 50°C for 10 minutes, and afterwards placed in 40% HF for another 10 minutes. The samples were then rinsed with acetone and purified water, and were split for analyses. Samples were wrapped in Ni-foil (10 μm thickness, 50-80 mm^2 in a few cases Al- or Pt-foils were used). The noble gases were analysed using four different extraction and mass spectrometer systems. System A consists of a Mo crucible in a quartz vessel heated by radiofrequency up to 1820°C and the liberated gases were analysed using two sector-type 60° mass spectrometers with glass tubes. The spectrometer used for He, Ne and Ar analyses is equipped with a Faraday collector, whereas the spectrometer used for Kr/Xe analyses is equipped with an additional secondary electron multiplier. System B consists of a separate extraction line with Mo crucible in a 1720 corning glass vessel, heated by radiofrequency to 1820°C and two metal tube mass spectrometers equipped with secondary electron multipliers, with one spectrometer for He and Ne, and the other for Ar analyses. Eugster (pers. commun., 1994) found that U and Th were distributed heterogeneously in gold. This created a problem which required simultaneously analyses of the daughter products (fission Xe, ^4He and

^{40}Ar), as well as their parent nuclides (U, Th and K, respectively), within the same sample. For this purpose (System C) double walled (vacuum pumped) quartz tubes were used, with samples being placed inside the inner tube and recovered after melting and noble gas extraction, whereupon the chemical elements were analysed. The same mass spectrometers were used as for system A. System D also used heat resistant quartz tube, together with the system B mass spectrometer configuration. Mass spectroscopic techniques are described by Eberhardt *et al.*, (1970) and Eugster *et al.*, (1981), and techniques used for the determination of K, Th and U concentrations are outlined by Krähenbühl and Burger (1989). The following extraction blanks (in cm^3STP) were measured and the data were corrected accordingly: System A (at 1700°C) $3\text{E}-07$ ^4He , $1.5\text{E}-09$ ^{20}Ne , $1\text{E}-08$ ^{40}Ar , $2\text{E}-13$ ^{86}Kr , $3\text{E}-13$ ^{132}Xe ; System B (at 1700°C) $1.5\text{E}-10$ ^4He , $8\text{E}-12$ ^{20}Ne , $8\text{E}-09$ ^{40}Ar ; System C (at 1100°C) $3\text{E}-07$ ^4He , $1.5\text{E}-09$ ^{20}Ne , $3\text{E}-09$ ^{40}Ar , $1\text{E}-13$ ^{86}Kr , $2\text{E}-13$ ^{132}Xe ; System D (at 1100°C) $1\text{E}-10$ ^4He , $1\text{E}-11$ ^{20}Ne , $5\text{E}-10$ ^{40}Ar . The noble gas system blanks have atmospheric abundances. For corrections of isobaric interferences (eg doubly charged ions, hydrocarbons, etc.) see Eugster *et al.*, (1993). In order to realistically test the system blanks, 306 mg of commercial gold wire (H. Jeanmaire S.A. Biennne, Switzerland, stock # 505753, purity 99.99%) were analysed, yielding the following results, in $\text{cm}^3\text{STP/g}$: $<4\text{E}-10$ ^4He , $<3\text{E}-11$ ^{20}Ne , $1\text{E}-08$ ^{40}Ar . Except for an atmospheric Ar component in the gold wire, no He and Ne were detected. Technical details regarding the methodology of instrumental neutron activation analysis for U, Th and K, as well as isotope dilution mass spectrometry for U and Pb, are presented in Eugster *et al.*, (in review).

3.1 Noble gases - Degassing patterns

Degassing patterns for gold were studied by means of stepwise temperature increments. Gas release patterns for ^4He , ^{36}Ar and radiogenic $^{40}\text{Ar}_{\text{rad}}$ ($^{40}\text{Ar}_{\text{rad}} = ^{40}\text{Ar} - 295.5^{36}\text{Ar}$; Eugster *et al.*, 1992) from SPRG specimens are presented in Figure A1.1. All noble gases were liberated below 1100°C . Most of the ^4He is released below 600°C , although sample SB-E14 yielded a ^4He degassing peak at $\sim 1100^\circ\text{C}$. Sample SB-B11 from the Beta Mine yielded a peculiar ^4He release pattern over a temperature range between 400° and 1000°C . In comparison, the bulk of the ^4He from sample SB-A11, also from the Beta Mine, was released at $\leq 600^\circ\text{C}$. The latter sample contained twenty times more ^4He , apparently concentrated in a less retentive site. A similar bimodal gas release pattern can be observed for ^{36}Ar , particularly in sample SB-J11. The gas release pattern of sample SB-E14 differs somewhat from the others, as the bulk of the ^{36}Ar is released at $\sim 1100^\circ\text{C}$, whereas the other samples show a gradual ^{36}Ar release pattern. $^{40}\text{Ar}_{\text{rad}}$ is mainly released within the low temperature range (ie $< 600^\circ\text{C}$), except for sample SB-E14 which shows gradual $^{40}\text{Ar}_{\text{rad}}$ release. Thus, the gas release pattern for SPRG can be

divided into primarily two groupings, namely a low temperature release (400°-600°C) and a high temperature release of gases when the gold melts. These two populations of gases being liberated from gold have also been recognized in samples from other localities (Eugster *et al.*, 1993, 1992; Eugster *et al.*, in review).

Eugster *et al.*, (1993; in review) performed a series of experiments to determine the source of excess (also known as "parentless") noble gas concentrations (ie more noble gas than what can be attributed to ⁴⁰K, U or Th decay) in gold. A number of possible sources were considered, among others: (i) Implantation of ⁴He into gold grains from α -decay of U and Th in adjacent minerals; (ii) quartz inclusions in gold; (iii) silicate minerals or zircons that are attached to the surface of the gold grains and; (iv) gases trapped in fluid inclusions. (i) Noble gases may have been produced by *in situ* decay and fission of radionuclides (K, U, Th) that were incorporated in the crystal lattice of gold. Due to radiation damage the ⁴He retentivity would probably be low and degassing would start below the melting point of gold (ie 1064.43°C). Since gold and the radionuclides K, U and Th are incompatible elements, the concentration of these radionuclides are probably low. Another possibility is that He produced in neighbouring U- and Th-rich minerals may have been implanted in gold. As the range of α -particles in solids is about 20 - 40 μ m, this component is also expected to be released below the melting point of gold. A similar argument as the one presented for option (i) may also hold true for options (ii) and (iii), as solid inclusions, such as quartz and zircons, may also contain significant concentrations of K, U and Th. However, in this case a high temperature release of gases is expected, due to the higher melting temperatures of the solid inclusions. Option (iv) seems to be the most likely explanation for the abundance of gases liberated at low temperatures (Eugster *et al.*, 1993 & in review; Boer *et al.*, in press [Econ. Geol.]). Decapitation of the majority of gold hosted fluid inclusions analysed during quadrupole mass spectrometer analyses (see section 3.5; Fig. 3.19; Boer *et al.*, in press [Econ. Geol.]) occur in the temperature range 400° to 650°C, with a few small fluid inclusions releasing their gaseous content at temperatures as high as 900°C. These QMS results provide the required evidence needed to validate the presumption that the early degassing phase represent the release of fluid inclusion hosted gases. By implication, the gaseous populations liberated in the low temperature range should be avoided when direct dating of gold is attempted, because the excess noble gas concentrations would severely affect the relevant isotopic ratios.

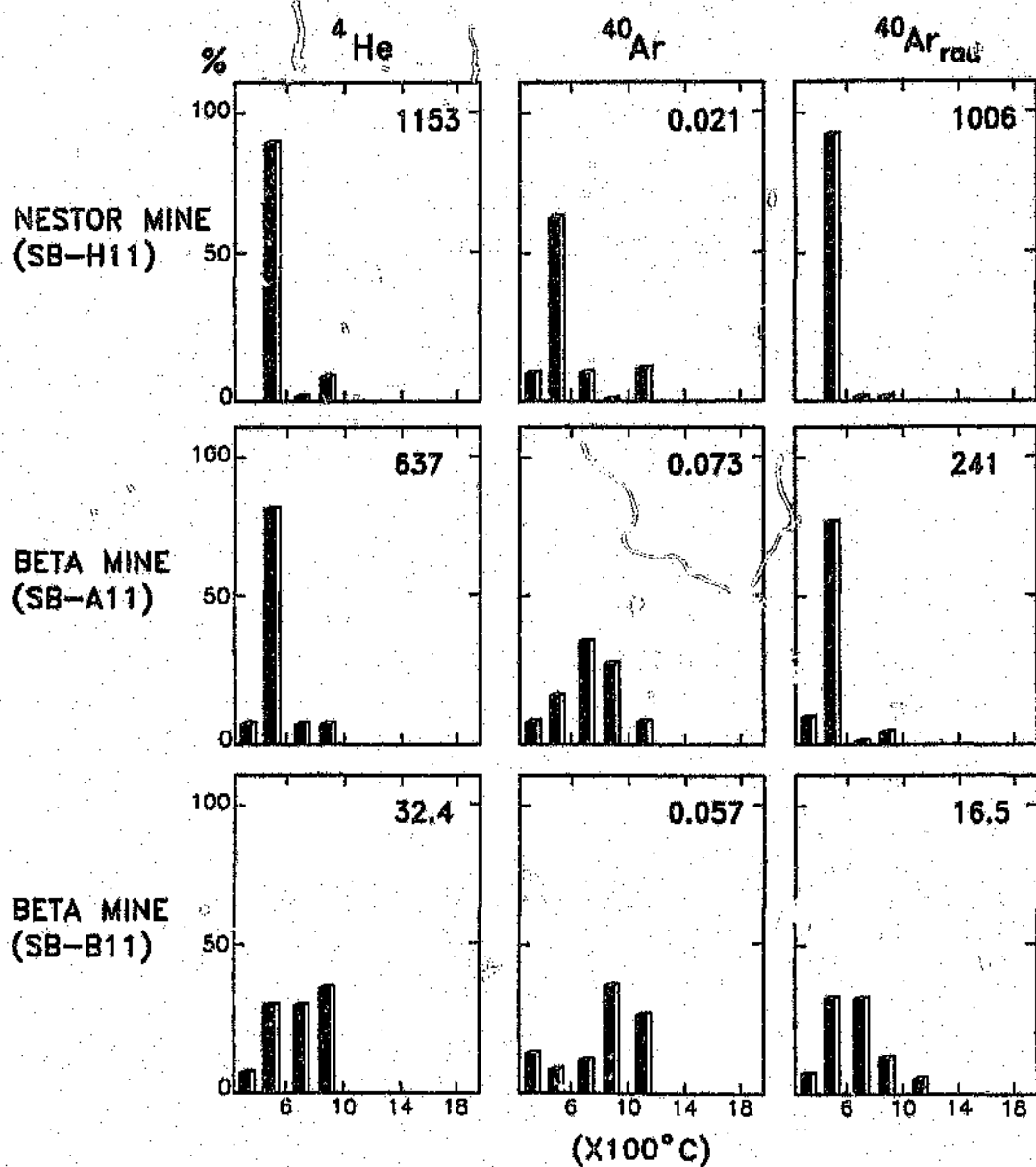


Figure A1.1a Noble gas release patterns of ^4He , ^{36}Ar and ^{40}Ar from SPRG native gold samples, as a function of temperature. The numbers in the diagrams indicate the total amount (in 1E-08 cm³STP/g [100%]) of the respective isotopes.

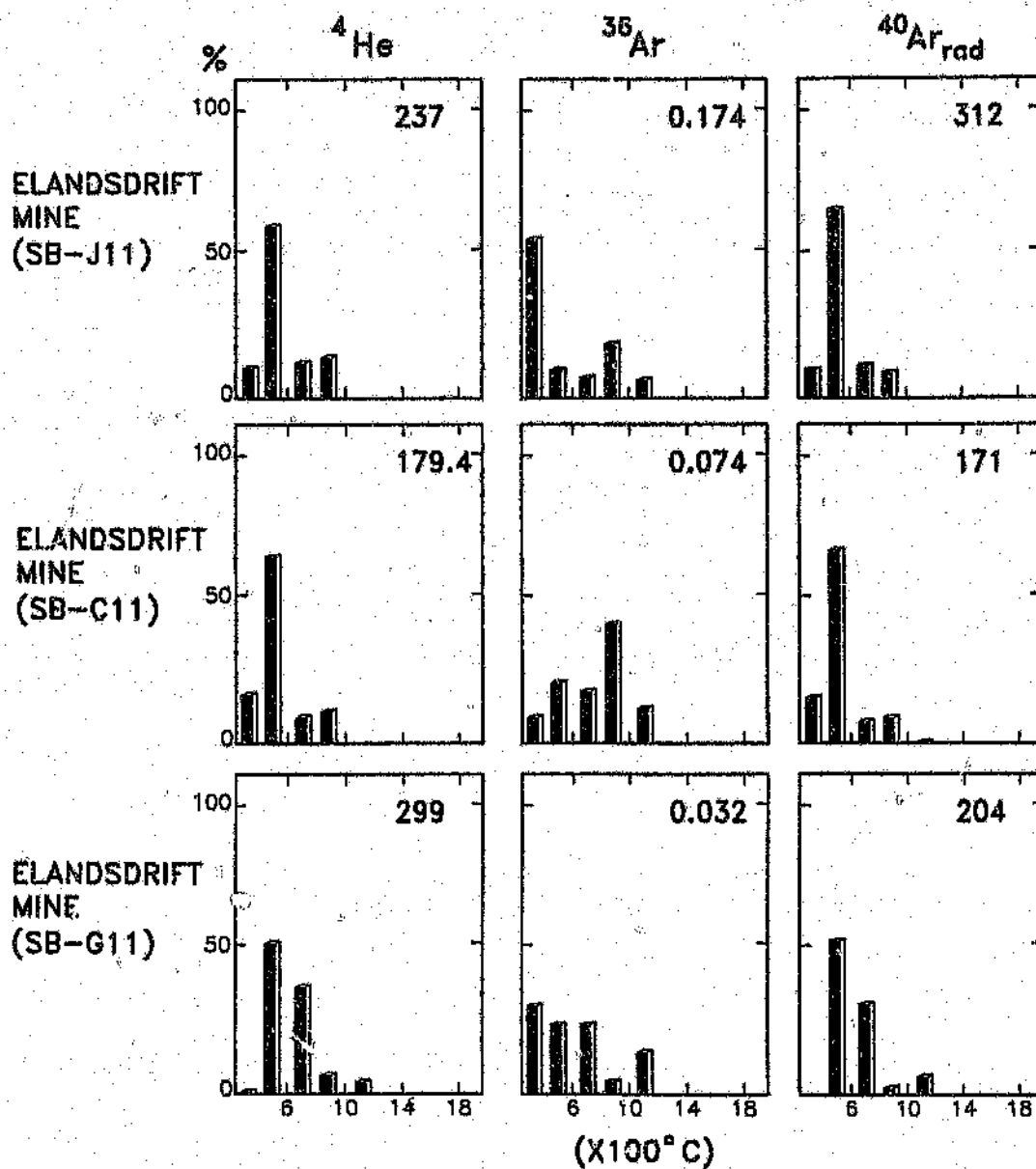


Figure A1.1b Noble gas release patterns of ^4He , ^{36}Ar and ^{40}Ar from SPRG native gold samples, as a function of temperature. The numbers in the diagrams indicate the total amount (in $1\text{E-}08 \text{ cm}^3\text{STP/g [100\%]}$) of the respective isotope.

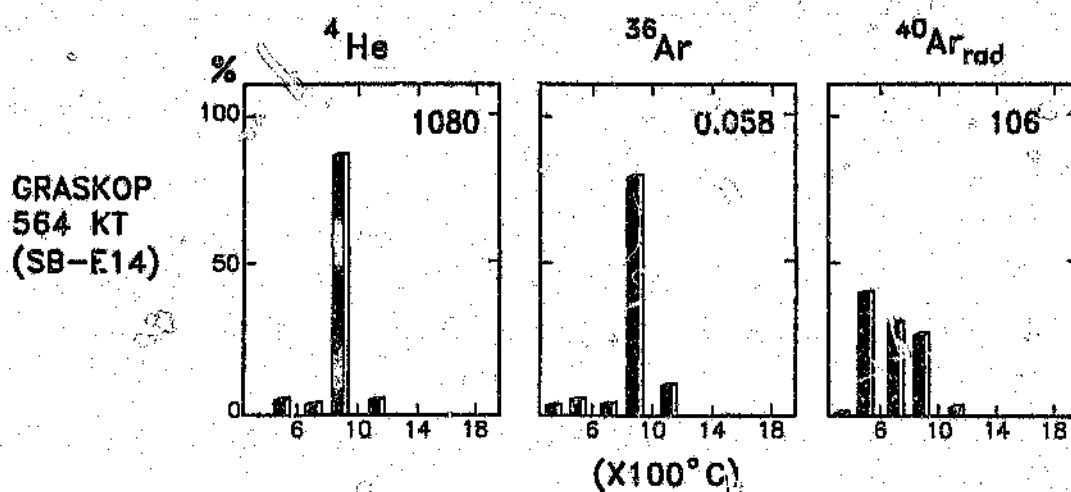


Figure A1.1c Noble gas release patterns of ^4He , ^{36}Ar and ^{40}Ar from SPRG native gold samples, as a function of temperature. The numbers in the diagrams indicate the total amount (in $1\text{E-08 cm}^3\text{STP/g [100\%]}$) of the respective isotope.

4. Oxygen isotopes

4.1 Conventional extraction technique

All silicate mineral separates used in the $\delta^{18}\text{O}$ isotope experiments were more than 95% pure. Oxygen extraction from silicates was performed in the Department of Geochemistry at the University of Cape Town, using the routine technique described by Borthwick and Harmon (1982) with ClF_3 as reaction agent (Vennemann and Smith, 1990). Between 10 and 20mg of sample were loaded into a nickel reaction vessel overpressured by analytically pure dry nitrogen. Once loaded the reaction vessels were evacuated and the sample allowed to degas at 200°C to approximately 10^{-5} mbar for a minimum period of 3hr. Reaction vessels were then charged with about seven times the stoichiometrically required amount of ClF_3 , isolated and heated to 600°C . Reaction times varied between 12 and 15hr. The extracted oxygen was converted to CO_2 by passing it over a hot platinized carbon rod. Manometric yields were accepted if they fell within 2% of 100% for samples providing between 50 and $200\mu\text{mol CO}_2$. Residual gases were passed over heated KBr crystals and frozen into a waste trap. CO_2 -gas was analysed in the Department of Archaeometry, University of Cape Town, using a VG Micromass 602E double collector ratio mass spectrometer. Average NBS-28 values were used to convert the raw data to the V-SMOW scale using the accepted value of 9.64‰ for NBS-28 (Coplen *et al.*, 1983; Harris and Erlank, 1992). The $\delta^{18}\text{O}$ -values of 23 NBS-28 samples were within 0.12‰. NBS-30 yielded an average value of 5.1‰ V-SMOW. All oxygen isotope values are reported in δ -notation in per mil units relative to V-SMOW (Vienna - Standard Mean Ocean Water).

4.2 Laser ablation extraction technique

Conventional extraction techniques present limitations on stable isotope geochemistry because of the large sample sizes that are required (eg Gileti and Shimizu, 1989) and the relative low spatial resolution attainable compared to other geochemical techniques. Limiting factors include:

- (i) the physical separation of small amounts of pure material;
- (ii) fractionation and contamination associated with chemical separation and purification of extracted gasses, and;
- (iii) extraction of sufficiently large volumes of gas for the mass spectrometer.

The principle of laser-based silicate analysis is identical to that of conventional fluorination (Clayton and Mayeda, 1963), whereby a mineral is heated in the presence of a BrF_3 , ClF_3 (Borthwick and Harmon, 1982; Vennemann and Smith, 1990) or F_2 (Bertschi and Silverman, 1951) atmosphere, quantitatively liberating O_2 . The main difference between laser fluorination and conventional fluorination is the method

of heating. The extreme temperatures generated during laser ablation allow for even the most refractory phases to be analysed (eg corundum, kyanite, olivine, zircon, garnet), and the spot heating makes *in situ* analyses possible. Both *in situ* analyses and complete analyses of mineral separates can be made with the laser extraction system (Sharp, 1990; Eisenheimer and Valley, 1992), although further technical refinement is still necessary to eliminate the consistently lower isotopic values obtained for *in situ* laser ablation analyses. Several approaches are used depending upon the material to be analysed:

- (i) the sample may be decomposed to release the element as a gas phase during heating, as in the case of CO₂ release from carbonate minerals (Smalley *et al.*, 1989) and H₂O release from hydrated minerals (Sharp, 1992);
- (ii) samples can be reacted with an oxidizing gas, as in the case of silicates (Sharp, 1990) (O₂ released from eg SiO₂ and subsequent conversion to CO₂), sulphur may be released from sulphides and converted to either SO₂ or SF₆ (Kelley and Fallick, 1990; Crowe *et al.*, 1990; Rumble *et al.*, 1991) and along similar lines carbon may be released from graphite and converted to CO₂ (Franchi *et al.*, 1986);
- (iii) samples can be reduced in the presence of graphite (Sharp and O'Neill, 1989), and; (iv) non-structural gasses such as nitrogen and noble gasses or those entrapped as fluid inclusions can be liberated from the crystal by heating (Megraw, 1967; Franchi *et al.*, 1986; Böhlke *et al.*, 1989; Gibson and Carr, 1989).

Several types of high-powered lasers are used in stable isotope geochemistry. These are CO₂, Nd-YAG (Nd-doped yttrium-aluminium garnet) or Nd-glass, Ar, Cu vapour and ultraviolet lasers (Andrews, 1990). The laser extraction system, used for the analyses of SPRG samples, at the Department of Geosciences, University of Michigan was a 20W, air-cooled Melles Griot CO₂ laser with a 12.7cm focal length, together with a coaxial He-Ne locating laser. An adjustable power control (0 to 100%) has been added, as well as a pulse generator so that the radiation can be delivered in pulses of 10µs to 1s over a wide range of pulse widths. The pulse generator can also be used to deliver a single laser shot of any duration. CO₂ lasers emit radiation at 10.6 and 9.6µm. This wavelength is well into the infrared and will be absorbed by all oxygen-bearing and most sulphur-bearing compounds. Virtually all minerals can be heated with a CO₂ laser. There are two disadvantages to the CO₂ laser. First, the long wavelength results in a minimum spot size of ~ 50µm, which is larger than that of other lasers. This problem was overcome by the insertion of a beam expander (Janos® ZnSe, AR-coated @ 10.6µm; Output diameter: 38.1mm) and focusing lens unit (plano mirror, diameter=76.2mm, 12.7mm thickness

coated with protected silver for 10.6 μ m radiation; plano convex lens ZnSe, AR/AR @ 10.6 μ m, EFL=127mm; BaF₂ window, diameter 38.1mm, 5mm thickness; with side-view Sapphire window, diameter 38.1mm, thickness 2.032mm), and was installed in the facility developed by the author at the Department of Geology, University of the Witwatersrand. A better focused laser beam has obvious advantages with regard to the selection of *in situ* mineral analyses. However, the amount of gas liberated from spots of <100 μ m is insufficient for conventional mass spectrometers. There are ~ 5.10⁻⁶ μ mol O₂ in a quartz cube with an edge of 1 μ m. A cube with an edge length of 10 μ m would, thus, contain 5E-05 μ mol O₂. A minimum of 0.1 μ mol is generally required for mass spectrometry. Therefore, it would take at least 1000 spots with a 10 μ m diameter to release the minimum amount of gas required for an analysis. Until further developments in mass spectrometers are made that allow for routine analyses of ultra-small quantities of gas, the larger beam diameter of the CO₂ laser does not effectively limit spatial resolution. The second disadvantage is that durable, readily available optical lenses and windows, such as those made of quartz, Pyrex® and sapphire cannot be used, as they absorb the radiation emitted by the laser. Window and lens materials that were used include BaF₂ and ZnSe, both of which are very fragile and sensitive to sudden changes in the intensity of the laser beam. BaF₂ readily dissolves in water and is extremely brittle. The laser is mounted on a pair of stacked X-Y motorized translation stages, so that the laser can be prepositioned over the sample. The very long focal length effectively eliminates deposition of vaporized material on the underside of the chamber window. Metals are extremely reflective to radiation at 10.6 μ m (Andrews, 1990), so that no heating and fluorination of the Ni sample holder occurs.

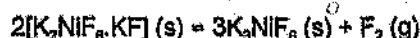
Following reaction, the halogen fluorides must be separated from the O₂ gas, using the same cryogenic separation method as employed during conventional extraction. Some non-condensable fluorine compound, presumably F₂, occasionally passes into the glass side of the line, resulting in a dark colouration and contamination of the borosilicate glass tubing. It is removed from the system either by a miniature mercury diffusion pump (Z.D. Sharp, pers. commun., 1992) or a KBr trap (D. Rumble III, pers. commun., 1992). In the mercury diffusion pump system, a trap on either side of the pump is necessary to prevent the Hg from diffusing through the whole line. The "upstream" trap is at liquid nitrogen temperature (-196°C) while the "downstream" trap is cooled by a mixture of dry ice and ethanol (-117.3°C).

The gasses used as oxidizing reagents, ClF₃, BrF₃ and F₂, are highly toxic and corrosive and

would react violently with most elements and organic compounds which are unsaturated in fluorine (Ostorero, 1970). Although most laboratories use BrF_3 , there are no real differences in the oxidizing properties of the three gases (Sharp, 1992). The above mentioned gases are commercially available and could be transported as a liquefied gas under its own vapour pressure. Care should be taken to ensure the use of only Inconel®, Monel®, nickel or 316 stainless steel material for tubing and containers for fluorine agents at high temperatures. However, these gases are expensive and cannot be recycled. Asprey (1976) devised a method of purifying fluorine gas from the usual gaseous contaminants which depends upon formation and decomposition of Ni(IV) complexes with K. By utilizing the oxidation potential of fluorine, a compound could be formed by fluorination with tank F_2 and then later decomposed upon heating to regenerate a more pure F_2 . In order for such a purification method to be generally useful, several criteria must be met (Asprey, 1976):

- (i) the compound to be fluorinated must be relative inexpensive;
- (ii) the compound should be non-volatile at operating temperatures, and;
- (iii) the compound should decompose, yielding reasonably high pressures of F_2 at somewhere below 500°C to avoid severe corrosion of the containers.

Complexes of heavy alkali metals with Ni(IV) meet the first two criteria, but are far too stable to yield useful pressures of F_2 at 500°C . By changing the stoichiometry one could thermally decompose K_2NiF_6 (potassium hexafluoronickelate (IV)-potassium fluoride, $\text{K}_2\text{NiF}_6 \cdot \text{KF}$) to K_3NiF_6 which would be present as a violet product. For the assumed reaction:



the equilibrium lies to the right. At 400°C the pressure of F_2 is in the order of 2.5×10^6 Pascals (19000 torr) compared to $\sim 3 \times 10^3$ Pascals for the pressure of F_2 over K_2NiF_6 . The ΔH for the decomposition has been approximated using the Clausius-Clapeyron relation to yield a value of 30 ± 3 kcal/mole of F_2 gas over the region of 289 – 402°C (Asprey, 1976). The 3:1 K:Ni(IV) salt is written in brackets since it is not known whether it is a mixture of K_2NiF_6 and KF or an actual compound. Based on the above mentioned, a very simple practical purifier has been constructed which is fully described by Asprey (1976).

The $\delta^{18}\text{O}$ values obtained on SPRG quartz samples, using laser ablation analyses are generally lower than the values obtained during duplication runs, utilizing the conventional extraction method

(Table 4.1). Uncertainties associated with the laser ablation analyses possibly come from:

- (i) fractionation associated with laser heating, as well as fluorination (if the sample grain is not approached carefully with the laser beam, a violent initial reaction takes place which scatters the sample all over the reaction chamber);
- (ii) contamination from fluid inclusions, and;
- (iii) true isotopic heterogeneities within the sample.

5. Hydrogen isotopes extraction technique

Quartz and pyrite hosted inclusion fluids were analysed for their δD composition at the Department of Geological Sciences, University of Michigan, following the method described by Vennemann and O'Neill (1993). The method involves a pure zinc reagent for the quantitative conversion of H_2O to H_2 . Zinc has been used successfully as an alternative reductant to uranium (Kishima and Sakai, 1980) for the conversion of H_2O to H_2 for D/H determinations of water samples (eg Coleman *et al.*, 1982; Kendall and Coplen, 1985). A few carefully selected quartz grains are placed in Pyrex[®] tubes containing zinc granules or shavings. About 30-50mg of Zn, or simply an excess amount, are used per expected milligram of H_2O . Prior to use, the Pyrex[®] are roasted at 500°C for a minimum of 1 hour and then stored at 110°C. For the reported analyses zinc laths supplied by the Biogeochemical Laboratory of the University of Indiana were used. Microlitre quantities of water of between 0.5-5 μl are liberated by decrepitation of the fluid inclusions in the quartz grains. The water is transferred by gentle heating of the lower portion of the tube which is at liquid nitrogen temperature. Any non-condensable gasses are pumped and the tube is sealed off with a gas-oxygen flame. Sealed tubes containing water and zinc are then placed in a muffle furnace for 10 minutes at 480°C. Under these conditions Zn spontaneously reacts with H_2O to give ZnO and a quantitative yield of H_2 . Subsequently the cooled tubes are cracked under vacuum on the mass spectrometer and the product H_2 is analysed for its hydrogen isotope composition. The reference gas was calibrated using V-SMOW and SLAP (Standard Light Antarctic Precipitation), analysed in the same fashion.

6. Sulphur isotopes extraction technique

The CuO_2 oxidation method of Fritz *et al.* (1974), Robinson and Kusakabe (1974) and Coleman and Moore (1978) was used for SO_2 extraction from sulphide samples. The function of the sulphur dioxide preparation line is to quantitatively convert the sulphur present in the sample, to sulphur dioxide. The extracted SO_2 must be free of air SO , H_2O and CO as considerable error can result from their

presence, probably because of SO_2 - CO_2 reactions in the source (Sakai and Yamamoto, 1966). The extraction line is constructed of borosilicate glass with the exception of the furnace tubes, which are quartz. Initially Quickfit Rotaflo Teflon taps have been used to minimize exposure of the sticky SO_2 gas to any grease-based connections. However, the use of these taps resulted in vacuum problems and were eventually replaced with ACE Glass Incorporated¹ stopcocks (cat. no. 3194-83). Sample vials are connected to the extraction line by ACE Glass Inc. threaded glass connectors (cat. no. 5027-05) and Nylon bushings (cat. no. 5029-10), fitted with Viton O-rings (cat. no. 7855-704). Yield is measured by a high precision vacuum gauge. The furnaces are calibrated using a Fluke digital thermometer fitted with a custom-made Monel[®] thermocouple.

Cuprous oxide is prepared by heating cupric oxide in quartz tubes under vacuum at 900°C for approximately 2 hours, until an insignificant volume of oxygen emerges. Commercial cuprous oxide is unsatisfactory as it often contains oil as a preservative. Quartz tubes are cleaned with *aqua regia*. Sulphide, sulphate and native sulphur samples can be run directly without any prior preparation. However, hydrous minerals such as gypsum need to be dehydrated at 200°C prior to use in order to prevent explosive dehydration. Samples that contain minerals such as serpentinite (water-rich) should not be analysed directly, but the sulphur content should instead be leached and re-precipitated as Ag_2S or BaSO_4 . Such samples should be washed in distilled water and then dissolved in boiling 1N HCl after which the dirty residue is filtered out. Sulphur is then precipitated as BaSO_4 by the addition of 10% BaCl_2 . The precipitate is recovered by filtering the solution through a Millipore filter. A more complex procedure is required if the oxygen isotope ratio of the barite is also to be determined (Claypool *et al.*, 1980). Sulphide samples can be run directly or can be purified by reaction to H_2S and precipitation of Ag_2S . Native sulphur can be run directly but extreme care must be taken when preparing sample charges. Small samples should be used together with an excess of Cu_2O in order to prevent sulphur contamination of the extraction line. Alternatively, native sulphur can be reacted with powdered silver metal in a sealed, evacuated tube to form Ag_2S . If necessary, the native sulphur can first be purified by dissolving it in hot benzene and filtering through a number 41 filter paper into a platinum basin. The benzene is then evaporated in a filter bath. Sulphur should not be overheated as it would become insoluble in benzene.

¹ ACE Glass Incorporated, Vineland, New Jersey, USA

The experimental procedure was designed to minimize SO_2 and sulphate production and also to limit any equilibrium fractionation between Cu_2O and SO_2 . This is achieved by using a large excess of oxygen over that required to form SO_2 (at least three times the required stoichiometric amount) and by running at temperatures above 1000°C . Sulphide charges commonly consist of 5mg of sulphur as sulphide, thoroughly mixed with 200mg of Cu_2O . However, the charge size may vary depending on the sulphur content of the mineral about to be analysed. The best reproducibility is obtained with more than 0.4mg of sulphur. At the time when the current data set was generated, a consistent precision of $\pm 0.5\%$ (1 σ) has been obtained in the laboratory at the Department of Geology, University of the Witwatersrand. It must be stressed that this was the first data produced on a new extraction line, constructed by the author, and the accuracy and precision has since been improved considerably. Currently the precision ($\sim 0.2\%$) is comparable with most other conventional laboratories and is satisfactory for all purposes (see Boer *et al.*, 1994), including geothermometry. Samples are reacted in the furnace and the resulting sulphur dioxide is purified on a separation line by sequential freezing. Water vapour is separated in a acetone-dry ice trap (-78.5°C - the sublimation point of CO_2 at atmospheric pressure), while CO_2 is removed from the sample in a second trap. This is achieved by differential sublimation of CO_2 and SO_2 during melting of n-pentane (-131°C) cooled by liquid nitrogen. Resulting SO_2 (and CO_2 , if required) is trapped, using liquid N_2 (-196°C) into glass vials, and isolated with a oxygen-gas flame. The sulphur isotope ratio of the purified sulphur dioxide is then measured on a Micromass MM602, dual inlet mass spectrometer, at the Schonland Research Centre for Nuclear Sciences, University of the Witwatersrand.

A dual inlet mass spectrometer compares the isotopic ratio in a sample gas with that in a standard reference gas. The minor collector receives mass 66 only, while the major collector encompasses two mass units, 64 and 65, thus, the mass ratio (R_{66}) is $R_{66} = 66/(64+65)$. The measured isotopic difference, $\delta 66$, between an unknown sample gas (x) and the standard reference gas is: $\delta 66 = (R_{66x}/R_{66}) - 1$, where $d = \delta/1000$. An equation can be established to relate the required value, $\delta 34$, the true sulphur isotopic difference of the reference gas, to the measured isotopic difference, $\delta 66$, and the true oxygen isotopic difference, $\delta 18$: $\delta 34 = (\delta 66 \cdot 2XY + \delta 18(R_{17} \cdot X - 2Y(X-Z)))/(2YZ - R_{33} \cdot X)$, where $X = R_{34} + R_{18} + R_{17}^2 + R_{33} \cdot R_{17}$, $Y = 1 + R_{17} + R_{33}$, and $Z = R_{34} + R_{17} \cdot 33/2$ (Coleman, 1980). Isotopic abundances are substituted in these equations. For a reference gas which contains the $\text{S}^{32}/\text{S}^{34}$ ratio of Canyon Diablo Troilite (CDT) and the $\text{O}^{16}/\text{O}^{18}$ ratio of Standard Mean Ocean Water (SMOW):

$$R_{17} = 0.0007385$$

$$R_{18} = 0.0040104$$

$$R_{33} = 0.007893$$

$$R_{34} = 0.04499$$

$$\delta_{34} = 1.094 \delta_{66} - 0.089 \delta_{18}$$

This result involves a relatively large correction for the sulphur term, as well as a significant correction for the difference in oxygen isotopic composition between the sample and standard. The oxygen term can be eliminated by preparing the sample and standard in such a way that they contain the same oxygen isotope composition. Alternatively, if more than one sulphur isotopic difference is measured the equations can be paired to eliminate the oxygen term.

Correctional procedures on the mass spectrometer are identical for both sulphide and sulphate samples. Coleman (1980) elaborated on the algebra associated with the isobaric correction of isotopic interferences. Minor interferences such as valve mixing (Deines, 1970) are usually small enough to be ignored. The isotopic composition of the reference gas is not considered and all standardization is with respect to a standard material which is included with each batch of samples. The steps involved are:

(i) The measurements of the standard material with respect to the reference gas are averaged and the average value is inverted to determine the δ_{66} of the reference gas with respect to the standard.

(ii) A correction equation is calculated using the isotopic abundance of the standard. These are derived from those for the Canon Diablo troilite and the $\delta^{34}\text{S}_{\text{CDT}}$ of the standard. Appropriate oxygen values, obtained for CO_2 which has been produced by oxidation of graphite with Cu_2O , are included. The graphite is oxidized in the same way as the sulphide samples and a similar stoichiometric excess of oxygen is used (eg 1.5 - 2.0mg of graphite and 200mg of Cu_2O).

(iii) The correction equation is applied to give a corrected value for the reference gas with respect to CDT. A new correction equation is calculated for the reference gas.

(iv) The measured δ_{66} values of the set of samples are corrected to produce δ_{34} compositions with respect to the reference gas. The corrected values are adjusted by the $\delta^{34}\text{S}_{\text{CDT}}$ value of the reference gas to relate all samples to CDT.

A number of in-house standards are used at the University of the Witwatersrand facility and their sulphur isotope compositions, relative to CDT are as follow: Broken Hill Ag_2S , $\delta^{34}\text{S}_{\text{CDT}} = +0.9\text{‰}$; Broken Hill BaSO_4 , $\delta^{34}\text{S}_{\text{CDT}} = +0.9\text{‰}$; Berg Aukas Ag_2S , $\delta^{34}\text{S}_{\text{CDT}} = +16.7\text{‰}$, and Kabwe Ag_2S , $\delta^{34}\text{S}_{\text{CDT}} = -16.8\text{‰}$.

7. Carbon isotopes extraction technique

Quartz-hosted inclusion fluids from the SPRG were analysed for carbon isotope compositions, i.e. $\delta^{13}\text{C}_{\text{CO}_2}$. Attempts were made to analyse for $\delta^{13}\text{C}_{\text{CH}_4}$, but the resulting values were unacceptable due to fractionation problems during extraction and the actual mass spectrometric measurements. Because of the high temperature of the mineralizing fluids (see chapter 3), isotopic equilibrium was assumed to exist between CH_4 and CO_2 (Ohmoto, 1972; 1986) and all carbon was, thus, treated as CO_2 . Fluid inclusions were thermally decrepitated under vacuum conditions and the liberated CO_2 , as well as CH_4 , was purified using cryogenic trapping procedures. The procedure was performed as part of the purification process whereby H_2O was liberated from fluid inclusions (see above section 4.1.2.1). All values are expressed relative to the international belemnite fossil standard from the Pee Dee Formation (PDB), North Carolina.

8. Rock Dissolution for radiogenic isotope analysis

Silicate rocks are usually dissolved in a solution of HF and a mineral acid (eg Potts, 1987; Chao and Sanzolone, 1992). The accompanying mineral acid is necessary in order to volatilize the SiF_4 and to remove excess F. The accompanying mineral acid, however, has little positive effect on the actual dissolution of the silicate (Langmyhr and Sween, 1965). The complete removal of the excess fluorine is important in order to prevent the formation of insoluble fluorides. The accompanying acid must sufficiently raise the boiling point of the HF- H_2O system in order to rapidly volatilize the excess F. The amount of HF removed in a single evaporation depends upon the mineral acid used and increases in the order: nitric - perchloric - sulphuric (Jeffrey, 1970). A double evaporation of perchloric acid is equivalent to a single evaporation of sulphuric acid (Cohen et al., 1975). Hydrochloric acid boils below the HF - H_2O azeotrope and is therefore unsuitable.

Several whole rock dissolution methods were applied to diabase samples from the Olifantsgeraamte Mine, near Sabie:

(1) The first procedure involved wetting 100 - 150mg of sample with 2ml HNO_3 (69%) and then adding 10ml of HF (48%). The solution was heated to 230°C in open PTFE Teflon beakers until it started to fume (Potts, 1987). This temperature is well above the azeotropic boiling point of HNO_3 - H_2O (121°C) as well as that of HF- H_2O (111.3°C) (Weast, 1972). Samples were then kept in covered beakers for 2-3 days at 100°C. Thereafter the solutions were evaporated to dryness in Perspex clean boxes under infrared lights;

(ii) The second method involved oxidation of the sample with 0.5ml perchloric acid (72% HClO_4) after which 3ml of HF was added. The main role of HClO_4 in the initial acid attack is to substantially raise the boiling point of the reaction mixture (the boiling point of 72% perchloric acid is 203°C), which has a dual purpose. Firstly, fluorosilicic acid that forms in solution by the attack of hydrofluoric acid on silicate materials, is efficiently decomposed at higher temperatures, leading to the volatilization of silica tetrafluoride:



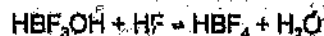
Secondly, hydrofluoric acid itself is progressively evaporated from the reaction mixture, since the HF-water azeotrope boils at 111.3°C . During this evaporation, it is expected that other elements that form volatile fluorides will also be lost. Langmyhr and Graff (1965) commented that sulphuric acid with its higher boiling point (338°C) is more efficient than perchloric acid in this role. (However, H_2SO_4 is normally avoided in modern flame techniques because of the serious interferences that can occur (Lee and Güven, 1975). Open PTFE Teflon beakers were placed on a 230°C hot plate and the solution was allowed to evaporate nearly to dryness before another 3ml of HF was added. Once the solution was clear the open beakers were left on a 100°C hot plate until complete evaporation.

Following dissolution the samples in both cases were re-dissolved in 10ml 6N HCl and the solution again heated to 230°C . The solution was then split into beakers and spiked with a known amount of reference isotope for quantitative ID-MS analysis.

Ten samples were prepared in triplicate and in at least 20% of the cases a white precipitate (consisting of microscopic size cubic crystals) formed. Precipitates did not form as readily when samples were taken up in 6N HCl before complete evaporation. None of the precipitates dissolved in HF, HNO_3 or HClO_4 even when heated to 235°C . The concentrations of elements such as Rb, Sr and Pb were unaffected by the presence of these insoluble compounds, but the REE's, especially Sm and Nd, were strongly fractionated as shown by subsequent instrumental neutron activation analyses (INAA);

(iii) As silicon concentration was irrelevant in the resultant solution there were considerable advantages if silicon (and fluorine) could have been removed completely by evaporation during the acid attack procedure. However, the complete removal of silicon and fluorine could not be attained with evaporation following the procedures described above. Because of these difficulties it was decided to make use of boric acid in addition to the procedures described above. Boric acid complexes with any free HF by a

two-stage exothermic reaction:



The resultant solution is far more stable and less hazardous to handle and may indeed be diluted to volume in glass volumetric flasks. The blank Nd and Sm concentrations of commercially available boric acid proved not to be a problem (Table A1.1) and determination of rare-earth element concentrations in USGS basalt standard BCR-1 yielded results that compared very favourably with those values presented by Hooker *et al.*, (1975) (Table A1.1). Under certain conditions, however, fluoroboric acid hydrolyses to release HF, a reaction which is promoted by increase of the hydrogen ion concentration. Calcium ions and probably other divalent ions have the same effect. Unfortunately, this scheme of analysis cannot be adopted uncritically for routine general silicate analysis, since many samples, such as the Olifantsgeraamte Mine diabbases, contain mineral phases (eg zircon, rutile, spinel) which are particularly resistant to acid attack. Furthermore, the undesired Si-F precipitates continued to form despite the presence of excess boric acid. In order to overcome the problems associated with dissolution of the refractory phases, Ingamells (1970) suggested the use of lithium metaborate ($\text{Li}_2\text{O} \cdot \text{B}_2\text{O}_3$ or LiBO_2) or lithium tetraborate ($\text{Li}_2\text{O} \cdot 2\text{B}_2\text{O}_3$ or $\text{Li}_2\text{B}_4\text{O}_7$) as fluxing agents. As lithium tetraborate have a higher acidity (ie a higher B_2O_3 content), Bennett and Oliver (1976) suggested that this acid is better for the dissolution of basic rocks, whereas lithium metaborate is a better flux for acidic (high silica) rocks. However, a combination of the two phases in a 2:1 ($\text{Li}_2\text{B}_4\text{O}_7$: LiBO_2) was found to be exceptionally effective for the dissolution of silicate rocks containing predominantly silica and aluminium (Yoshikuni, 1989).

Table A1.1 Sm-Nd values for USGS basalt standard BCR-1, as well as blank results for commercial analytical grade boric acid. The Nd and Sm results on the USGS basalt standard BCR-1 correspond very well with the values obtained by Hooker *et al.*, (1975): Nd=29ppm and Sm=6.6ppm

Sample No.	¹⁴⁴ Nd (ppm)	Nd (ppm)	¹⁴⁷ Sm (ppm)	Sm (ppm)	Sample wt. (g)
BCR-1	6.49	28.73			0.09983
BCR-2	6.51	28.82			0.10506
BCR-3	6.58	29.16	0.97	6.59	0.10052
BCR-4	6.44	28.53	0.96	6.56	0.11039
BCR-5	6.58	29.13	0.96	6.59	0.10534
Blank-1 (H ₃ BO ₃)	0.0003	0.0012			1
Blank-2 (H ₃ BO ₃)	0.0003	0.0013			1
Blank-3 (H ₃ BO ₃)	0.0003	0.0013			1
Blank-4 (H ₃ BO ₃)	0.0012	0.0052			3.12985
Blank-5 (H ₃ BO ₃)	0.0551	0.2440			0.10899

(iv) The dissolution properties of *m*-Benzene disulphonic acid (BDS) are superior to all the acids described above and furthermore do not present the undesired mineral precipitates during dissolution. The boiling point of BDS is higher than either perchloric or sulphuric acid and is thus more effective in removing F. This acid is better than sulphuric in the sense that there is less fuming of the acid during sample dissolution. Furthermore, the salts of BDS, including those of the alkali, alkaline-earth, transition and lanthanide elements, are all water soluble (Hemmes and Petrucci, 1969). *m*-Benzene disulphonic acid is presently available only in technical grade, but can easily be purified by the following procedure: Dissolve the solid technical grade acid in a minimum amount of water. Add carbon black to decolorize and filter. Add BaCl₂ solution (saturated) until BaSO₄ ceases to precipitate. Filter and retain the purified BDS solution. For still higher purities the BDS could be passed through an ion-exchange column. The use of *m*-benzene disulphonic acid together with hydrofluoric acid is recommended for a number of reasons (Cohen *et al.*, 1975). Firstly, the reaction mixture maintains a higher boiling temperature, which is above the HF-H₂O azeotrope. This will cause efficient decomposition of fluorosilicic acid and also volatilize the resulting silica tetrafluoride. The use of *m*-benzene disulphonic acid is, furthermore,

recommended because of the high solubility and non-complexing characteristics of virtually all salts of *m*-benzene disulphonic acid. Compared with other highly oxidizing acids such as perchloric acid, *m*-benzene disulphonic acid is relatively safe to work with.

In general, dissolution should be carried out in open beakers, allowing HF and SiF₄ to fume off. For this reason reactions in confined environments enhances the formation of precipitates (Boer *et al.*, 1993). Furthermore, the samples should not be allowed to evaporate to dryness (Croudace, 1980) during any stage of the dissolution procedure.

The white cubic precipitate phases which formed during the above mentioned dissolution procedures, were examined by X-ray diffraction, using a Philips model PW1051 diffractometer with Ni filtered Cu K_α radiation. All the results were obtained with Debye-Scherrer powder diffraction camera (57.3mm diameter), using the small sample mounting method of Hiemstra (1956). The XRD patterns are indicative of hieratite (Palache *et al.*, 1951), an isometric mineral phase with chemical composition of K₂SiF₆, and ralstonite (Pauly, 1965), a complex fluoride of the pyrochlore group with formula Na_{0.85}Mg_{0.85}Al_{1.12}(F,OH)₆·H₂O. An impurity is associated with ralstonite of which the diffraction lines resemble those of the chemical compound Na₂Zr₂F₁₂. Diffraction lines on the X-ray films were converted to diffractograms on a chart recorder connected to a X-ray film reader for reproduction purposes (Figures A1.2a and b). Pure hieratite occurred as cubic crystals and is often the only mineral precipitate present. Ralstonite, however, was often intimately associated with hieratite and occurred as a fine-grained white powder (Figure A1.3). In nature both ralstonite and hieratite are associated with fumarolic deposits occurring together with aluminium fluoride minerals (Palache *et al.*, 1951, Pauly, 1965). The mineral precipitates were examined in a LINK®-JOEL® JSM 840 scanning electron microscope, but due to the limitations of the technique no semi-quantitative analyses were possible on the small precipitate crystals. A white fine-grained material that could be seen clinging to the hieratite surface was identified as a chloride of Ca and Mg.

After recognizing that spurious radiogenic isotope ratios were probably a result of the formation of the above mentioned undesirable insoluble fluoride precipitates (see section 4.2.5 below), these fluoride precipitates were deliberately grown in order to obtain enough sample material for INAA analyses. The INAA technique is especially sensitive for the rare-earth elements La, Ce, Nd, Sm, Eu, Tb, Yb, Lu and Sc, Co, Cr, Cs, Hf, Ta, Th and U. INAA involves the irradiation and analysis of rock

powders that undergo no chemical treatment in the course of the analysis and are thus considered non-destructive. Neutron activation analysis has the advantage of being very sensitive for specified elements and virtually free of matrix interference effects (except overlap interferences in complex gamma spectra). The disadvantage is that the technique requires specialized irradiation facilities. Hieratite and ralstonite samples were analysed by C. Koeberl at the Institute of Geochemistry, University of Vienna and the results are presented in Table A1.2. Details of the method employed can be found in Koeberl (1992). Chondrite-normalized values (using the data of H. Wakita and D. Zellmar (unpubl.), quoted in Wakita *et al.*, 1971) for ralstonite and hieratite show distinct enrichment in Nd and to a lesser extent in Sm (Table A1.2; Fig. A1.4). The extent of LREE fractionation from HREE is demonstrated by the La/Lu ratios ($\text{La/Lu}_{\text{Hieratite}}=351.3$; $\text{La/Lu}_{\text{Ralstonite}}=32.9$). The LREE enrichment of these phases is also apparent when the difference in La/Sm (LREE) and Tb/Lu (HREE) ratios for the two minerals are compared: $\text{La/Sm}_{\text{Hieratite}}=6.3$, $\text{Tb/Lu}_{\text{Hieratite}}=3.0$; $\text{La/Sm}_{\text{Ralstonite}}=3.0$, $\text{Tb/Lu}_{\text{Ralstonite}}=2.5$. These ratios clearly indicate that hieratite is more LREE enriched compared to ralstonite. The REE data for the insoluble precipitates corroborate the suggestion that LREE, such as Nd and Sm, are being fractionated into the hieratite and ralstonite structure, disturbing the isotopic ratios of these elements. Fractionation of REE into these insoluble fluoride precipitates has severe effects on accurate determinations of these elements in the remaining solution.

Table A1.2 Instrumental neutron activation analyses of hieratite and ralstonite. Chondrite-normalized values were calculated using the data of H. Wakita and D. Zellmar (unpubl.), quoted in Wakita *et al.*, (1971)

	Hieratite (ppm)	Chondrite-normalized Hieratite	Ralstonite (ppm)	Chondrite-normalized Ralstonite
La	56.2	165.3	41.1	120.9
Ce	101	110.9	89	97.8
Nd	54	84.4	75	117.2
Sm	8.9	45.6	13.5	69.2
Eu	1.8	24.7	2.9	39.7
Tb	0.48	10.2	3.1	65.9
Yb	1	4.5	10.5	47.7
Lu	0.16	4.7	1.25	36.8

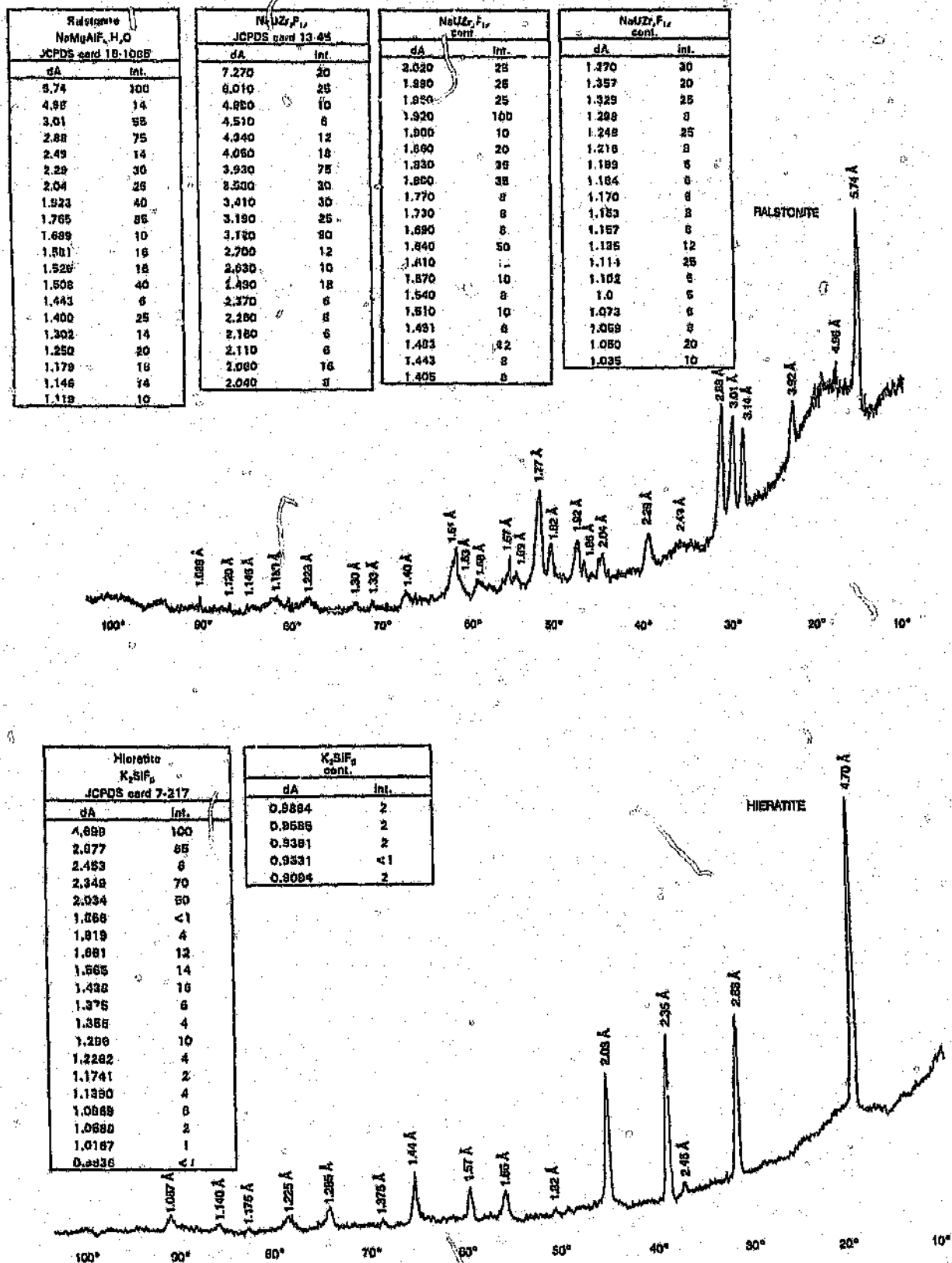
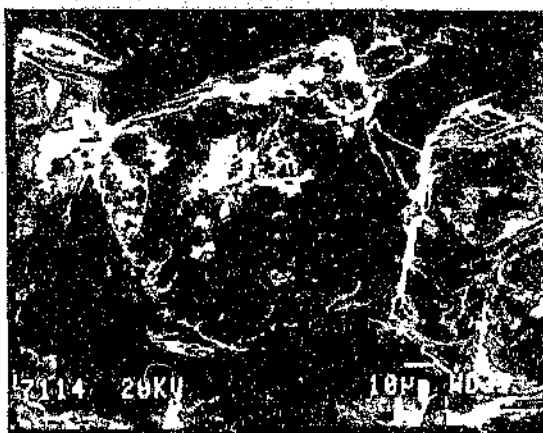
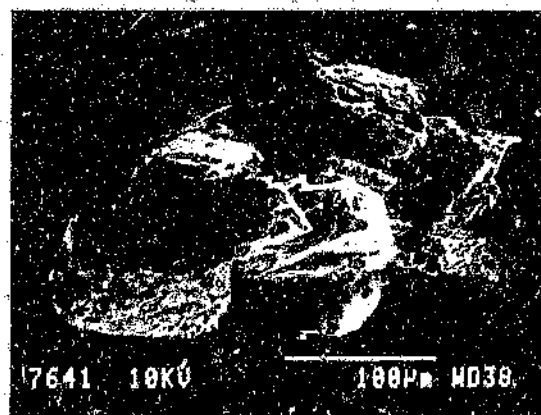


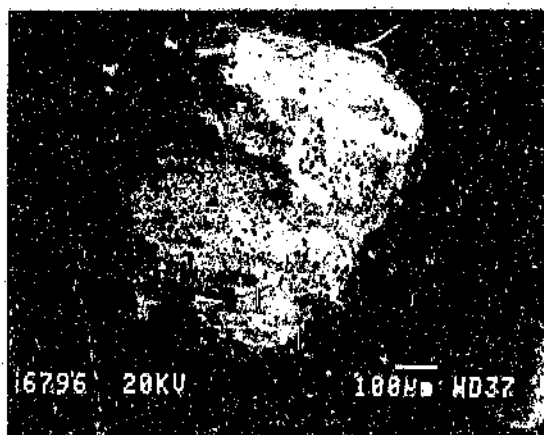
Figure A1.2 (a) XRD trace of ralstonite and NaUZr₂F₁₂ obtained in this investigation along with the relevant JCPDS (1986) card data. (b) XRD trace of hieratite acquired in this investigation along with the relevant JCPDS (1986) card data.



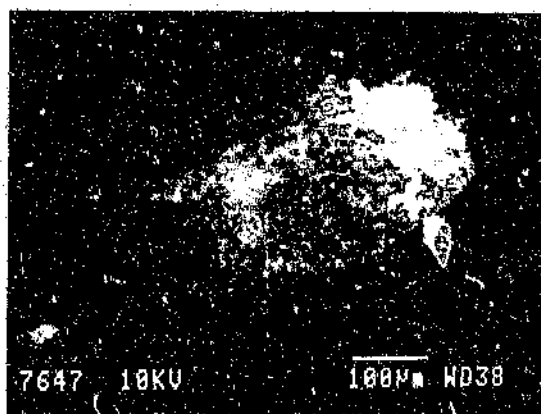
a.



b.



c.



d.

Figure A1.3 SEM microphotographs of insoluble hieratite (a & b) and reastonite (c & d) precipitates.

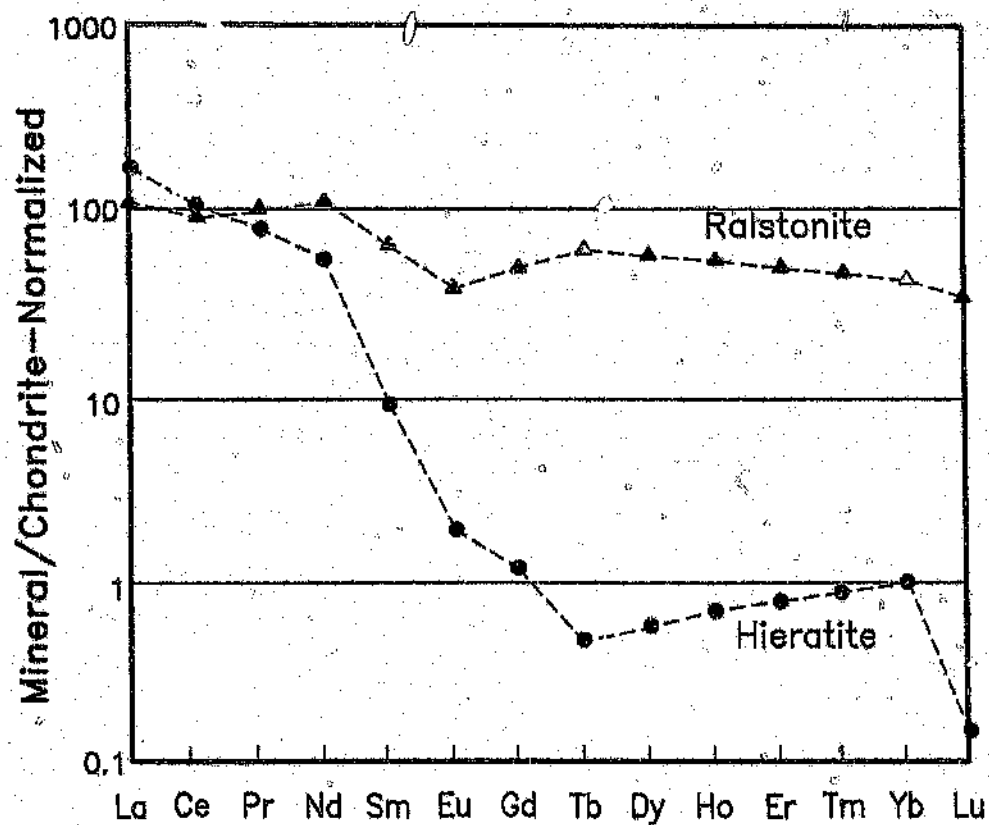


Fig. A1.4 Chondrite-normalized REE distribution in hieratite and ralstonite. Chondrite values from Wakita *et al.*, (1971).

3.1 Chemical Separation and INAA Techniques

Whole rock diabase samples were analysed for Rb, Sr, Sm and Nd by isotope dilution mass spectroscopy (ID-MS). Solutions were aliquoted into two parts for ID-MS. Roughly one-third was spiked with ^{148}Sm ($^{149}\text{Sm}/^{147}\text{Sm}=264.7$) and ^{148}Nd ($^{148}\text{Nd}/^{144}\text{Nd}=139.56$) for concentration determination. The remainder was used for Sm and Nd isotopic composition analyses. REE were separated using anion exchange columns (1cm diameter, with 20cm height; Biorad® AG50WX8, 200-400 mesh resin) conditioned with 2.59 N HCl. After addition of sample solutions (in 2.59 N HCl), the columns were washed with 126ml of 2.59 N HCl. REE were recovered by passing 20ml 6 N HCl through the columns. Sm and Nd separation columns (5mm diameter, with 9cm height; filled with di-2-ethylhexyl orthophosphoric acid [HDEHP] and Teflon®) were equilibrated with 10ml of 0.21 N HCl and washed with 3 x 0.25ml and 1 x 6ml of 0.21 N HCl after the samples were loaded. Nd was collected by adding 5ml of 0.21 N HCl after which the Sm fraction was recovered with 1ml of 2.59 N HCl.

The ID-MS results were compared to INAA, performed by F.M. Meyer on the same sample powders (Table A1.3). Rock samples were milled to a fine powder and 250 to 300 mg aliquots were sealed into high-purity SiO_2 glass (Suprasil AN) vials. Batches of 8 samples including 2 calibration standards (USGS BCR-1 and BVHO-1) were packed into Cd-containers and irradiated for 3 days in the SAFARI I reactor (Atomic Energy Corporation, Pelindaba, South Africa) in a thermal neutron flux of ca. $1.9 \times 10^{13} \text{ n/cm}^2/\text{s}$ and an epithermal flux of ca. $1 \times 10^{12} \text{ n/cm}^2/\text{s}$. Neutron flux variations were monitored by Fe-Ta wires attached to each of the sample vials as well as by the known Fe concentrations in the samples. Gamma-spectroscopy was performed by simultaneous counting with both a planar and a coaxial detector. The system configuration and the detector characteristics are similar to those described by Potts et al. (1985). Spectroscopy was carried out in 3 cycles. The first counting was started 3 days (for 1 hour) after end of irradiation, the second count 11 days (for 2.5 hours) and the third count 35 days (for 4 hours) after irradiation. Photopeak selections as well as corrections for peak interferences were carried out according to Potts et al. (1985). The error counting statistics was less than 5% for Sm and between 8 and 12% for Nd.

Table A1.3 Chemical analyses of diabase samples from the Olifantsgeraamte Mine near Sabie, utilizing XRF and INAA techniques, as well as Leco® analysers.

	S%	CO ₂ %	Sm (INAA)	Nd (INAA)	Rb (INAA)	Sr (INAA)	U (INAA)	Pb (INAA)	Rb (XRF)	Sr (XRF)
Unaltered										
2C/F	0.142	7.82	5.95	35.0	75.1	213	0.80	3	66	232
2C/H	0.258	6.28	6.63	36.9	43.6	214	0.87	5	43	222
3B/F	0.224	3.85	7.32	42.0	36.2	233	0.85	-	32	256
4C/H	0.159	3.83	6.03	33.7	41.7	207	0.77	-	36	254
4B/H1	0.141	4.28	6.34	33.9	60.3	183	0.75	-	64	229
Altered										
2A/F	2.58	13.5	5.01	28.1	91.5	191	1.01	4	88	203
2B/H	0.579	14.4	5.71	33.4	102.0	187	0.86	-	95	170
3A/F	2.68	13.7	7.07	39.4	112	170	1.07	-	109	172
4A/H	1.63	16.7	6.19	38.9	67.8	-	0.84	6	97	186
4A/H1	2.30	15.9	6.33	35.7	60.3	183	0.84	-	92	192

9 Thermal Ionization Mass Spectrometry

In thermal ionization mass spectrometry the sample is loaded on to a tantalum (for Rb and Sr ionization) or rhenium (for Nd, Sm, U and Pb ionization) ribbon filament and ionized by electrically heating the filament to a controlled temperature. Successful determination can normally only be made by chemically separating elements (as discussed in section 4.2.2) prior to analysis to remove all potential interferences. A simple magnetic sector is usually adequate for mass dispersion. At the Bernard Price Institute for Geophysical Research a single-collector type Alderton Micromass MM30 and a multi-collector type VG354 were used for mass spectrometric determinations. The technique is used in two distinct applications:

- (i) To determine to very high precision the relative isotopic abundances of the radiogenic elements;
- (ii) Very low detection limits can be achieved with isotope dilution analysis. The detection limits are mainly controlled by the procedural blank.

Isotope dilution analysis is based on the principle that when an amount of sample solution is mixed with a known amount of spike, the isotope composition of the mixture can be used to calculate the amount of the element in the sample solution. The relevant equation is as follows (after Faure, 1986):

$$N_w = \frac{S_w \cdot W_N}{W_S} \left[\frac{Ab_S^A - R_m Ab_N^B}{R_m Ab_N^B - Ab_N^A} \right]$$

where N_w ($N_w = N \cdot W_N / A$) and S_w ($S_w = S \cdot W_S / A$) (A is Avogadro's number, W_N and W_S are the atomic weights and N and S the numbers of atoms of the normal element and spike) are the weights of the normal element and the spike in the mixture in units of grams. Ab_N^A is the abundance of isotope A in the normal element, while Ab_S^B is the abundance of isotope B in the spiked element, and so forth, and R_m is the ratio of isotopes A and B in the mixture. The concentration of the normal element in the solution is obtained by dividing N_w by the weight of the sample solution. Good results are dependent on the accurate determination of the concentration and isotopic composition of the spike solution. Furthermore, it is essential that the normal element and spike must be completely homogenized.

Samples were loaded onto single Re or Ta filaments for mass-spectroscopic analysis, using dilute HCl and adding a small amount of 1M H₃PO₄. Mass-spectroscopic analysis was performed using either the Faraday cup collection (for ion beams of 10⁻¹²A or more) or a Daly-type scintillation detector with fast ion-counting electronics (Arden and Gale, 1974). Isotope ratios were determined by peak-switching with magnetic-field control. Emission behaviour was found to be perfectly reproducible even at very high filament temperatures.

9.1 Rubidium-Strontium systematics

The expression for the decay of ⁸⁷Rb to ⁸⁷Sr looks as follows:

$$^{87}\text{Sr} = ^{87}\text{Rb}(e^{\lambda t} - 1)$$

where λ is a constant characteristic of the decay of ⁸⁷Rb and t the time of formation of the sample. The total number of ⁸⁷Sr atoms in a mineral or rock sample will be:

$$^{87}\text{Sr}_{\text{measured}} = ^{87}\text{Sr}_{\text{initial}} + ^{87}\text{Rb}(e^{\lambda t} - 1)$$

where ⁸⁷Sr_{initial} represents atoms originally present and taken into the sample at the time of its formation.

This equation can also be expressed in the form:

$$\left(\frac{^{87}\text{Sr}}{^{86}\text{Sr}} \right)_{\text{measured}} = \left(\frac{^{87}\text{Sr}}{^{86}\text{Sr}} \right)_{\text{initial}} + \frac{^{87}\text{Rb}}{^{86}\text{Sr}} (e^{\lambda t} - 1)$$

In order to obtain the age of a sample, the present ⁸⁷Sr/⁸⁶Sr and ⁸⁷Rb/⁸⁶Sr ratios are required. By estimating the initial ⁸⁷Sr/⁸⁶Sr and finding a value for the decay constant, the above equation could be solved. The ⁸⁷Rb decay constant used was 1.42E-11. Ages for standard Isochron type techniques were calculated using the GEODATE software package of Eglington and Harmer (1989).

9.2 Sm-Nd systematics

The fact that samarium and neodymium retain their original Sm-Nd character during radiogenic decay make this system (as a geochronometer) resistant to "resetting" by metamorphism, unlike other radiogenic geochronometers such as Rb-Sr (eg O'Nions *et al.*, 1979; Hamilton *et al.*, 1979). The distribution of Nd isotopes and the REE in sedimentary and igneous environments has several potential applications to understanding the water-rock interaction history of pore fluids (Shaw and Wasserburg, 1985; Banner *et al.*, 1988; Banner *et al.*, 1989). Differences in isotopic ratios arise as a result of variations in depositional conditions and fractionations in aqueous environments. These differences may be imposed on the associated fluids during water-rock interaction and are, thus, useful in understanding

the genesis of the fluids involved, or to what extent these fluids have been modified. The chemical evolution of fluids in sedimentary basins and the associated effects of mineral-solution equilibria have mutually important consequences on sediment diagenesis and the formation of ore deposits (eg Sverjensky, 1986).

In the Sm-Nd system model ages can be calculated assuming that samples originated from either a source of chondritic composition (Chondritic Uniform Reservoir or CHUR of DePaolo and Wasserburg, 1976), or a source depleted in light REE relative to CHUR (Depleted Mantle or DM of DePaolo, 1981). The following expression is used for the calculation of CHUR model ages:

$$T_{CHUR} = \frac{1}{\lambda} \ln \left[1 + \frac{(^{143}\text{Nd}/^{144}\text{Nd})_s - 0.512638}{(^{147}\text{Sm}/^{144}\text{Nd})_s - 0.1967} \right]$$

where 0.512638 is the $^{143}\text{Nd}/^{144}\text{Nd}$ ratio for USGS standard basalt BCR-1, 0.1967 is the $^{147}\text{Sm}/^{144}\text{Nd}$ value, and $\lambda = 6.54 \times 10^{-12} \text{ a}^{-1}$. DM model ages are calculated by an iterative procedure between two curves in $^{143}\text{Nd}/^{144}\text{Nd} - t$ space, with:

$$(^{143}\text{Nd}/^{144}\text{Nd})_t = (^{143}\text{Nd}/^{144}\text{Nd})_{s,\text{present}} - (^{147}\text{Sm}/^{144}\text{Nd})_s (e^{\lambda t} - 1)$$

$$t = \frac{1}{\lambda} \ln(1 + ^{143}\text{Nd}/^{147}\text{Sm})$$

and

As the crustal processes of weathering, diagenesis and metamorphism do not significantly affect Sm-Nd systematics, model ages of diabase rocks from the Olifantsgeraamte Mine, near Sabie, should reflect their pristine origin. DePaolo (1981) showed that a depleted mantle source was more appropriate than CHUR for ~1800 Ma basement rocks to the Colorado Rocky Mountains, and suggested that crustal rocks were generally derived from depleted mantle. The degree of time-integrated light REE depletion or enrichment in petrogenetic sources is indicated by the ϵ_{Nd} parameter. Positive ϵ_{Nd} indicates a depleted mantle source, while negative ϵ_{Nd} suggests an enriched mantle or crustal source. The epsilon notation of DePaolo and Wasserburg (1976) describes deviations in initial ratio between sample (s) and CHUR, and is expressed as follows:

$$\epsilon_{\text{Nd}} = \left[\frac{(^{143}\text{Nd}/^{144}\text{Nd})_{s,T}}{(^{143}\text{Nd}/^{144}\text{Nd})_{\text{CHUR},T}} - 1 \right] \times 10^4$$

where T is the time of origin of the sample. Nd isotope evolution of DM may be related to that of CHUR as follows:

$$e_{Nd} = 0.25t^2 - 3t + 8.5$$

where t is age.

9.3 Pb-Pb systematics

Pb isotope evolution are treated according to several models. The single stage models that were originally proposed by Holmes (1946) and Houtermans (1946) have been superseded by models that take into account various degrees of mixing from crustal and mantle reservoirs. Because of the oversimplistic approach of the single-stage model, Stacey and Kramers (1975) developed a two-stage model in which a primordial Pb-isotope ratio at 4.57Ga is assumed, and which involves a chondritic growth curve ($U/Pb=7.19$) to 3.7Ga, and a lithospheric stage in a more radiogenic reservoir ($U/Pb=0.74$). Model ages are not solely dependant on the primordial Pb isotope ratio as the two-stage model also makes provision for subsequent changes in the $^{238}U/^{204}Pb$ and $^{232}Th/^{204}Pb$ ratios. The most important difference between the two-stage and single-stage models is that in the case of the former, the model age is determined by the slope of the isochron, and not on the $^{238}U/^{204}Pb$ ratio of the source from which it evolved. Cumming and Richards (1975) proposed a more realistic model of Pb isotope evolution which involves a continuous change in U/Pb ratios. The "plumbotectonics" model of Zartman and Doe (1981) and Zartman and Haines (1988) entails mixing of a progressively diminishing proportion of mantle Pb with an increasing amount of lower crustal Pb. According to Zartman and Doe (1981) Pb isotope evolution takes place in four reservoirs, (i) the lower crust, (ii) upper crust, (iii) mantle and (iv) the orogene. In general, several other influences affect the Pb-isotope ratio. Mixing in the form of magmatic assimilation, fluid mixing, or remobilisation of Pb by post-formation magmatism or metamorphism (Andrew *et al.*, 1984) are probably among the most important influences. Gulson (1986) have shown that the Pb-isotope system is relatively insensitive to chemical changes in the secondary environment eg weathering.

The common Pb method of dating in terms of a single stage history (eg Holmes-Houtermans model) assumes that Pb was produced by the decay of U and Th, after which it is then separated from the radiogenic source. Under such conditions the isotopic composition of Pb remains constant and is not influenced by the radiogenic breakdown of U and Th. These conditions could be expressed as follow:

$$\frac{{}^{206}\text{Pb}}{{}^{204}\text{Pb}} = \left(\frac{{}^{206}\text{Pb}}{{}^{204}\text{Pb}} \right)_i + \frac{{}^{238}\text{U}}{{}^{204}\text{Pb}} (e^{\lambda_1 T} - 1)$$

The ${}^{206}\text{Pb}/{}^{204}\text{Pb}$ ratio of Pb removed from a U-bearing system at time t would be:

$$\left(\frac{{}^{206}\text{Pb}}{{}^{204}\text{Pb}} \right)_t = \left(\frac{{}^{206}\text{Pb}}{{}^{204}\text{Pb}} \right)_i + \frac{{}^{238}\text{U}}{{}^{204}\text{Pb}} (e^{\lambda_1 T} - 1) - \frac{{}^{238}\text{U}}{{}^{204}\text{Pb}} (e^{\lambda_1 t} - 1)$$

where $({}^{206}\text{Pb}/{}^{204}\text{Pb})_i$ is the isotope ratio of common Pb of age t ,

$({}^{206}\text{Pb}/{}^{204}\text{Pb})_i$ is the isotope ratio of primeval Pb in the earth T years ago, ${}^{238}\text{U}/{}^{204}\text{Pb}$ is the isotope ratio in the source of the common Pb, T is the age of the earth (assuming $T = 4.55 \cdot 10^9$ a) and t is the time since removal of common Pb from the source. By substitutions and eliminations (as described in Faure, 1986) the following straight line equation, which forms the basis of the common Pb dating method, is derived:

$$\frac{\left(\frac{{}^{206}\text{Pb}}{{}^{204}\text{Pb}} \right)_t - b_0}{\left(\frac{{}^{206}\text{Pb}}{{}^{204}\text{Pb}} \right)_t - a_0} = \frac{1}{137.88} \left[\frac{e^{\lambda_2 T} - e^{\lambda_2 t}}{e^{\lambda_1 T} - e^{\lambda_1 t}} \right]$$

the slope of which can be expressed by the following equation:

$$m = \frac{1}{137.88} \left[\frac{e^{\lambda_2 T} - 1}{e^{\lambda_1 T} - 1} \right]$$

Further derivation of the equation to compensate for Pb growth curves are fully treated in Faure (1986).

In this study the age of a Pb-Pb regression curve was solved using the GEODATE program of Eglington and Harmer (1989). GEODATE makes use of Newton's iterative method:

$$x_{i+1} = x_i - \frac{f(x_i)}{f'(x_i)}$$

The solution for ${}^{207}\text{Pb}/{}^{206}\text{Pb}$ is therefore:

$$t_2 = t - \frac{\frac{(e^{d_{238}t} - 1)}{e^{d_{238}t} - 1} - 137.88 \text{ b}}{(e^{d_{238}t} - 1)(e^{d_{235}t}) d_{235} - (e^{d_{235}t} - 1)(e^{d_{238}t}) d_{238}}$$

Iteration continues until $(t_2 - t)$ is less than some chosen value eg 50000 a (Eglington and Harmer, 1989).

APPENDIX 2

Description of handspecimens used in this study, as well as sample positions

Sunlight vein	
SUN 001	Massive bull quartz, oxidized sulphides
SUN 002	ditto
SUN 003	ditto
Frankfort Mine	
FKM 004	Theta vein at Frankfort Mine, quartzite, unmineralized
FKM 005	ditto
FKM 006	ditto
FKM 007	Mineralized Theta vein, Frankfort Mine
Clewes Mine	
CLW 012	Quartzitic material occurring in vein forming part of quartz blow stringers terminating in vein, Rho vein
CLW 013	Relation between vein and quartz blow stringers Stratigraphic position 15-20m below Bevetts Conglomerate, Rho vein
CLW 014	Stringer of quartz 1 metre below vein, Rho vein
CLW 015	Stringer of vein right underneath Rho vein
CLW 016	Rho vein and blow quartz
CLW 017	Top portion of Rho vein, just above shear horizon
CLW 018	Bottom portion of Rho vein, below shear horizon
CLW 019	ditto
CLW 020	Rho vein
CLW 023	Rho vein, calcite and sulphides
CLW 024	Brecciated dolomite in calcite matrix parallel to vein and shear
CLW 026- CLW 028	Rho vein
Theta Hill	
THH 029	Quartzite from top of pyroxenite sill on Theta Hill. Quartzite occur in a lense like fashion.

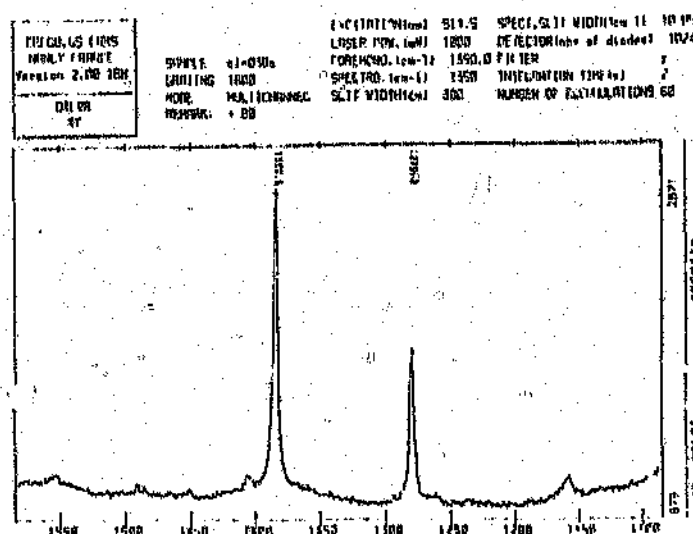
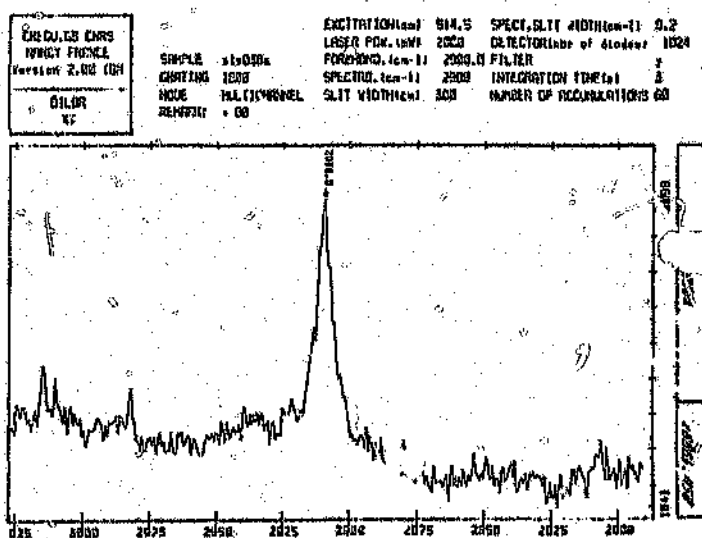
Morgenzon's Lense	
MGL031-MGL034	Late-late stage quartz emplaced after thrusting. Sampled near the entrance of the addit. Abundant sulphidic ore (mainly Py).
MGL035	Late stage quartz. Less oxidized. Abundant sulphides, stockwork- various phases of quartz in dolomite.
MGL036	Stockwork quartz with sulphides
Clewer South Mine	
CLS037	Contact between the breccia in quartz matrix (with sulphide ore) and later stage quartz on top.
CLS038	Later stage quartz including upper contact with dolomite.
Vaalhoek	
VLH039-VLH042	Samples taken from dump
Jubilee Mine	
JBH043	Lower Theta vein
Desire Mine	
DRM044	Portuguese vein
Theta South	
THS045-THS046	Shale vein. Graben structure. (Up to 300g/ton Au)
Beta Mine	
BTM047-48	Beta Central Section. Beta vein
Glynn's Lydenburg Mine	
GLS050-GLS052	Sheba section. vein quartz.
GLS053	Sheba section. Late stage quartz.

Frankfort Mine		
FKM054-FKM063	Upper Theta vein	
FKM064-FKM076	Bevetts vein	
Olifants-geraamte Mine		
OGM077-OGM084	Altered diabase sill.	
Mountain Mine		
MNM086-MNM087	Formosa vein, mineralization in the Pretoria Group shale.	
Little Joker Mine		
LJM088-LJM090	Formosa vein, same stratigraphic horizon as Mountain Mine.	
Nestor Mine		
NSM091	B7 Winch	
NSM092	B7 Winch 7N Gully	
NSM093	B7 Face	
NSM094+095	Raise no.1	
NSM096	A5 Face (fragmented piece)	
NSM097+098	C1 Face	
Gregory vein		
GRR099-102	Lower addit	
GRR106+107	Middle addit (lungy qtz)	
GRR108	Top addit	
Mamre mine		
MAM103	Top vein	
MAM104	Bottom vein	
NSG105	Quartz blow in Nelspruit Granite	

AST109	Astra Mine vertical vein
CLH110	Clewer Hill, Lense quartz
CLH111	Clewer Hill, Flower structure.
BRH112	Browns Hill, Lense deposit.
RFT113	Rietfontein Mine, vertical vein.

APPENDIX 3

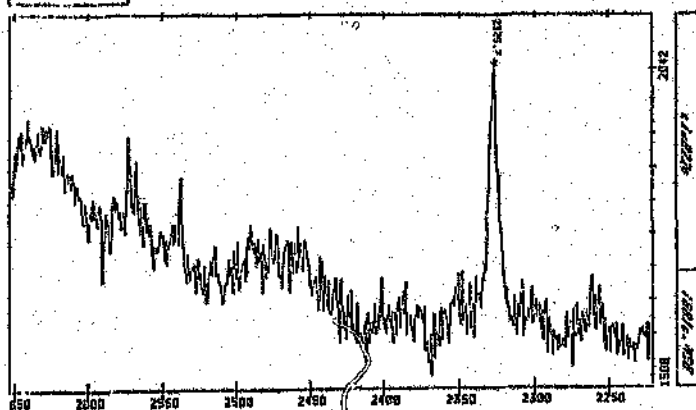
Micro-Raman spectroscopic data for individual quartz-hosted fluid inclusions from the SPRG. Data generated on a DILOR-XY Raman spectrometer at the Centre de Recherches sur la Géologie des Matières Premières Minérales et Énergétiques (CREGU) in Nancy, France. Peak positions relate to molecular species as indicated in Table 3.2.



CREOLIS SAS
WIMY FRANCE
Version 2.00 IRY
DILOR
XY

SAMPLE c1-022a
COATING 1600
MODE MULTICHANNEL
REPEAT: + 60

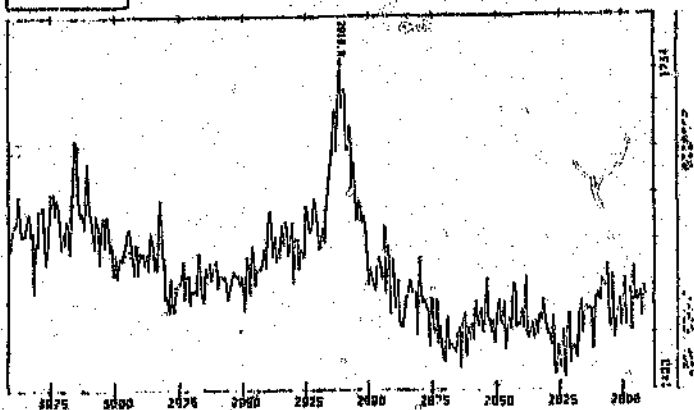
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LASER POW.(mW) 1500 DETECTOR(nm of diodes) 1024
FORENSIC.(nm-1) 2450.0 FILTER
SPECTRO.(nm-1) 2500 INTEGRATION TIME(s) 2
SLIT WIDTH(nm) 300 NUMBER OF ACCUMULATIONS 60



CREOLIS SAS
WIMY FRANCE
Version 2.00 IRY
DILOR
XY

SAMPLE c1-022a
COATING 1600
MODE MULTICHANNEL
REPEAT: + 60

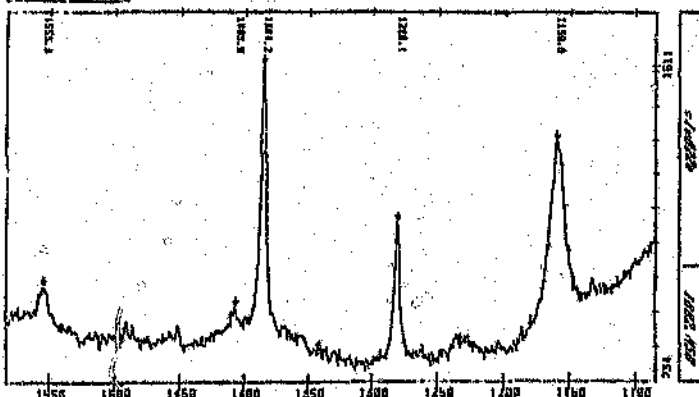
EXCITATION(nm) 514.5 SPECT.SLIT WIDTH(nm-1) 0.2
LASER POW.(mW) 2500 DETECTOR(nm of diodes) 1024
FORENSIC.(nm-1) 2000.0 FILTER
SPECTRO.(nm-1) 2500 INTEGRATION TIME(s) 3
SLIT WIDTH(nm) 300 NUMBER OF ACCUMULATIONS 60



CREOLIS SAS
WIMY FRANCE
Version 2.00 IRY
DILOR
XY

SAMPLE c1-022a
COATING 1600
MODE MULTICHANNEL
REPEAT: + 60

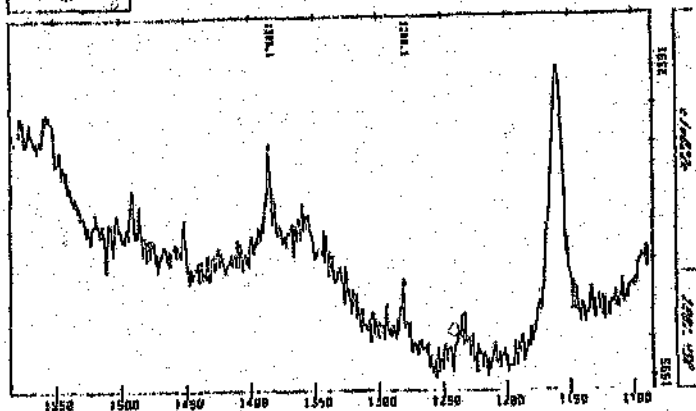
EXCITATION(nm) 514.5 SPECT.SLIT WIDTH(nm-1) 0.09
LASER POW.(mW) 1500 DETECTOR(nm of diodes) 1024
FORENSIC.(nm-1) 1350.0 FILTER
SPECTRO.(nm-1) 1350 INTEGRATION TIME(s) 2
SLIT WIDTH(nm) 300 NUMBER OF ACCUMULATIONS 60



TECHNICAL DATA
INSTRUMENT
Version 2.00.10M
DATE
XY

SAMPLE 1-022a
COATING 1000
MIXE MULTICHANNEL
REMARK: + 00

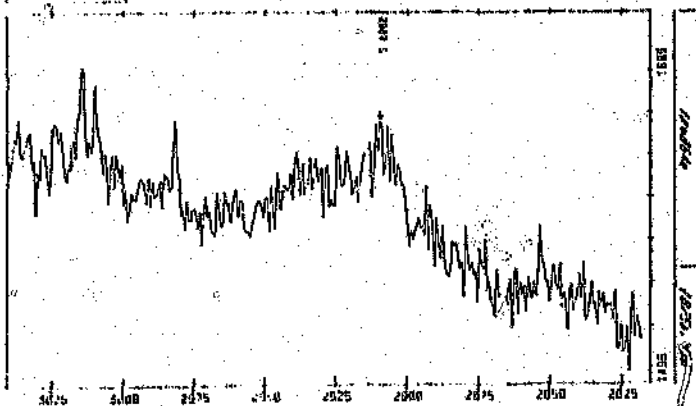
EXCITATION(wm) 514.5 SPECT. SLIT WIDTH(cm-1) 10.05
LASER PWR. (mw) 2200 DEFLECTION of diodes 1024
FOREWARD, (cm-1) 1550.0 FILTER
SPECTRO. (cm-1) 1550 INTEGRATION TIME(s) 2
SLIT WIDTH(cm) 300 NUMBER OF ACCUMULATIONS 60



TECHNICAL DATA
INSTRUMENT
Version 2.00.10M
DATE
XY

SAMPLE 1-022a
COATING 1000
MIXE MULTICHANNEL
REMARK: + 00

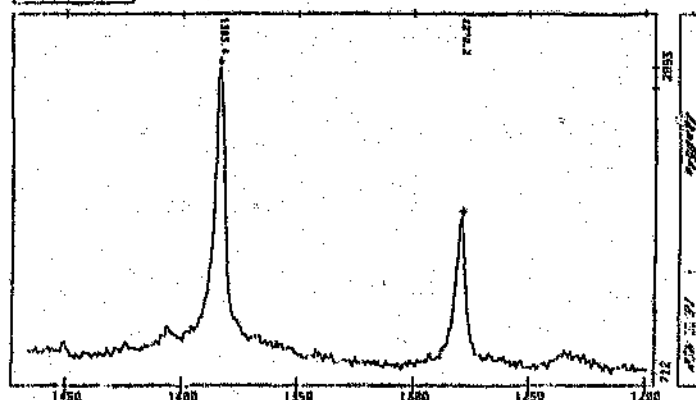
EXCITATION(wm) 514.5 SPECT. SLIT WIDTH(cm-1) 10.2
LASER PWR. (mw) 1000 DEFLECTION of diodes 1024
FOREWARD, (cm-1) 2000.0 FILTER
SPECTRO. (cm-1) 2000 INTEGRATION TIME(s) 2
SLIT WIDTH(cm) 300 NUMBER OF ACCUMULATIONS 60



TECHNICAL DATA
INSTRUMENT
Version 2.00.10M
DATE
XY

SAMPLE 1-0284a
COATING 1000
MIXE MULTICHANNEL
REMARK: + 00

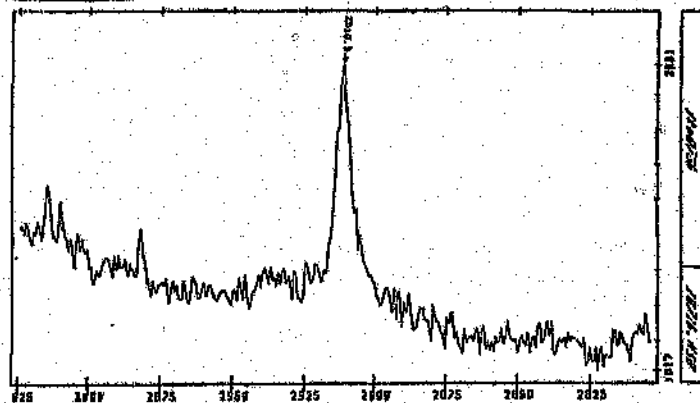
EXCITATION(wm) 514.5 SPECT. SLIT WIDTH(cm-1) 10.05
LASER PWR. (mw) 1000 DEFLECTION of diodes 1024
FOREWARD, (cm-1) 1550.0 FILTER
SPECTRO. (cm-1) 1550 INTEGRATION TIME(s) 1
SLIT WIDTH(cm) 300 NUMBER OF ACCUMULATIONS 60



CREOLAS CARS
INSTR FORCE
Version 2.00 10M
DILOR
XY

SAMPLE 1K0076A
GRATING 1000
MODE MULTICHANNEL
REMARK: * 00

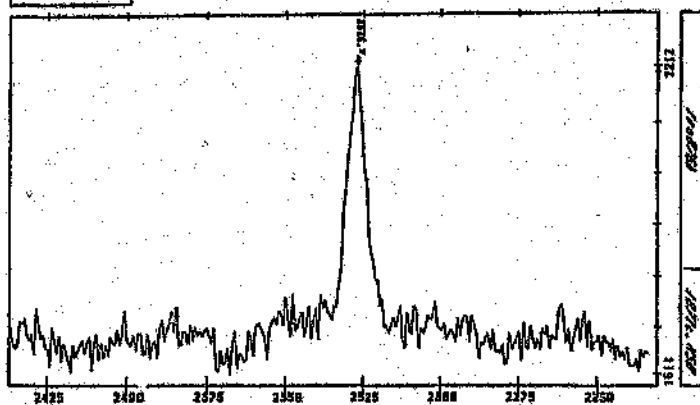
EXCITATION(w) 514.5 SPECT.SLIT WIDTH(mm-1) 0.2
LASER PWR.(w) 1000 DETECTOR(Inch of diodes) 1024
POTENTIAL (mm-1) 2450.0 FILTER
SPECTRO. (mm-1) 2450 INTEGRATION TIME(s) 3
SLIT WIDTH(mm) 500 NUMBER OF ACCUMULATIONS 50



CREOLAS CARS
INSTR FORCE
Version 2.00 10M
DILOR
XY

SAMPLE 1K0076A
GRATING 1000
MODE MULTICHANNEL
REMARK: * 00

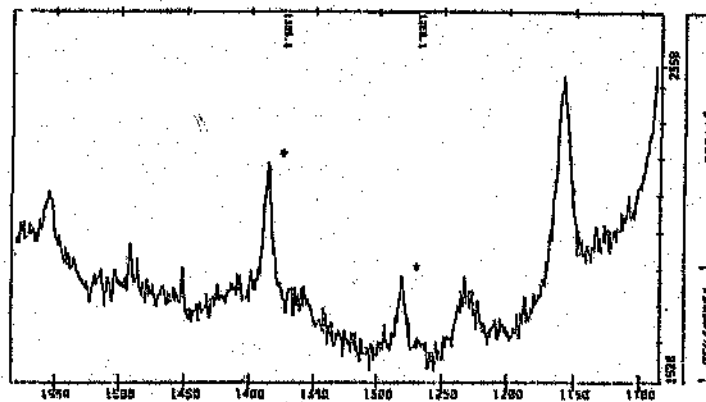
EXCITATION(w) 514.5 SPECT.SLIT WIDTH(mm-1) 0.22
LASER PWR.(w) 1000 DETECTOR(Inch of diodes) 1024
POTENTIAL (mm-1) 2450.0 FILTER
SPECTRO. (mm-1) 2450 INTEGRATION TIME(s) 3
SLIT WIDTH(mm) 500 NUMBER OF ACCUMULATIONS 50



CREOLAS CARS
INSTR FORCE
Version 2.00 10M
DILOR
XY

SAMPLE 1K0076A
GRATING 1000
MODE MULTICHANNEL
REMARK: * 00

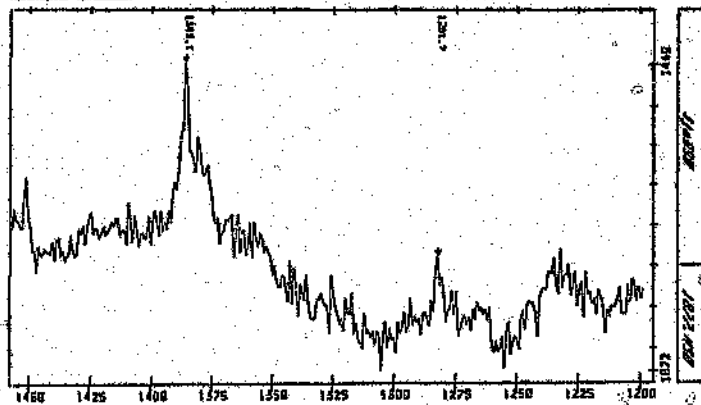
EXCITATION(w) 514.5 SPECT.SLIT WIDTH(mm-1) 0.15
LASER PWR.(w) 1000 DETECTOR(Inch of diodes) 1024
POTENTIAL (mm-1) 1950.0 FILTER
SPECTRO. (mm-1) 1950 INTEGRATION TIME(s) 3
SLIT WIDTH(mm) 500 NUMBER OF ACCUMULATIONS 50



CREGLIS CHS
RANCY FRANCE
Version 2.00 10M
DILOR
XT

SAMPLE 11-030
DATING 1800
MODE MULTICHANNEL
REMARK: * 88

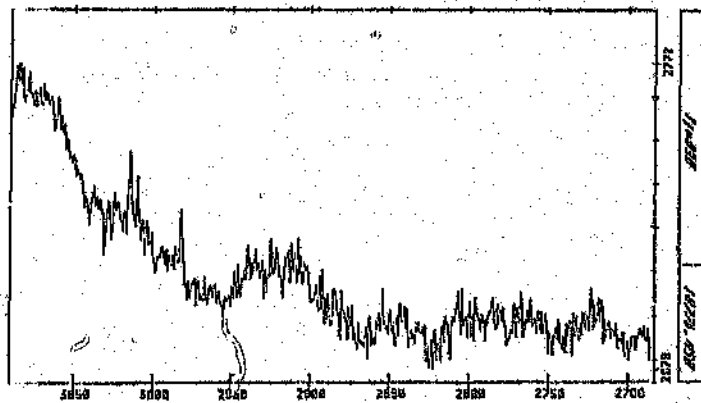
EXCITATION(mv) 514.5 SPECT.SLIT WIDTH(mm-1) 18.05
LASER PWR.(mW) 1250 DETECTOR(mv of d/decade) 1024
FORWARD, (cm-1) 1350.0 FILTER 7
SPECTRO. (cm-1) 1350 INTEGRATION TIME(s) 3
SLIT WIDTH(cm) 300 NUMBER OF ACCUMULATIONS 60



CREGLIS CHS
RANCY FRANCE
Version 2.00 10M
DILOR
XT

SAMPLE 11-030
DATING 1800
MODE MULTICHANNEL
REMARK: * 88

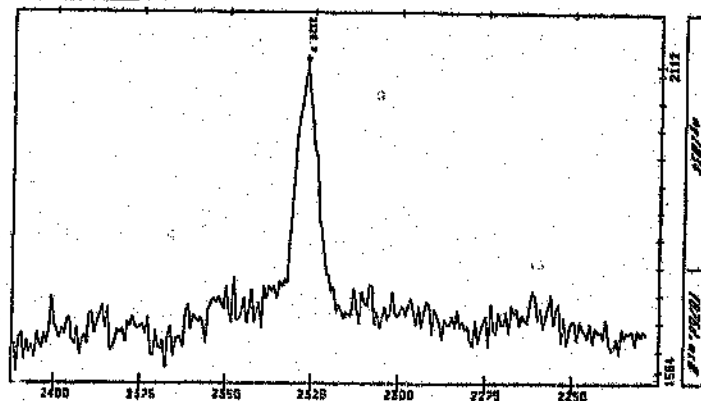
EXCITATION(mv) 514.5 SPECT.SLIT WIDTH(mm-1) 8.2
LASER PWR.(mW) 1500 DETECTOR(mv of d/decade) 1024
FORWARD, (cm-1) 2900.0 FILTER 7
SPECTRO. (cm-1) 2900 INTEGRATION TIME(s) 5
SLIT WIDTH(cm) 300 NUMBER OF ACCUMULATIONS 48



CREGLIS CHS
RANCY FRANCE
Version 2.00 10M
DILOR
XT

SAMPLE 091034
DATING 1800
MODE MULTICHANNEL
REMARK: * 88

EXCITATION(mv) 514.5 SPECT.SLIT WIDTH(mm-1) 8.72
LASER PWR.(mW) 1020 DETECTOR(mv of d/decade) 1024
FORWARD, (cm-1) 2450.0 FILTER 7
SPECTRO. (cm-1) 2450 INTEGRATION TIME(s) 4
SLIT WIDTH(cm) 300 NUMBER OF ACCUMULATIONS 60

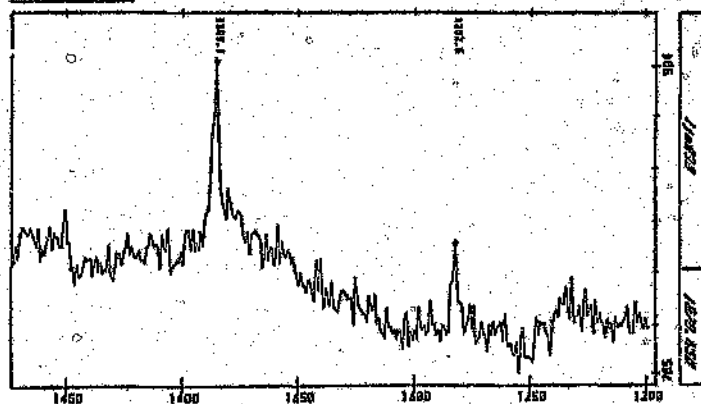


CREGG, CS CHRS
HARRY FROST
Version 2.10 10M

DILOR
XY

SAMPLE 1j0399
GRATING 1000
MODE MULTICHANNEL
REMARKS * 03

EXCITATION(wv) 514.5 SPECT.SLIT WIDTH(wv-1) 10.05
LASER POW.(wv) 1000 DETECTOR(wv of diodes) 1024
FORWARD(wv-1) 1350.0 FILTER
SPECTRO(wv-1) 1350 INTEGRATION TIME(s) 2
SLIT WIDTH(wv) 300 NUMBER OF ACCUMULATIONS 60

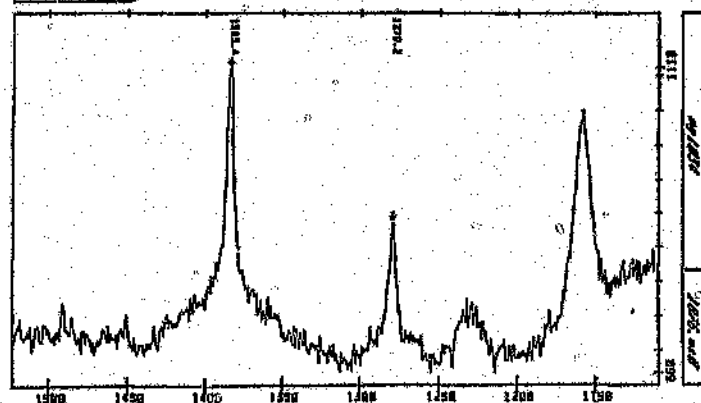


CREGG, CS CHRS
HARRY FROST
Version 2.10 10M

DILOR
XY

SAMPLE wj0354
GRATING 1000
MODE MULTICHANNEL
REMARKS * 03

EXCITATION(wv) 514.5 SPECT.SLIT WIDTH(wv-1) 10.05
LASER POW.(wv) 1000 DETECTOR(wv of diodes) 1024
FORWARD(wv-1) 1350.0 FILTER
SPECTRO(wv-1) 1350 INTEGRATION TIME(s) 2
SLIT WIDTH(wv) 300 NUMBER OF ACCUMULATIONS 60

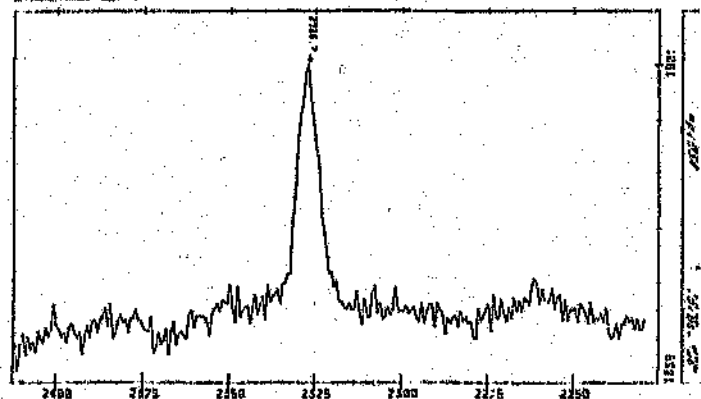


THO GLENN TAMS
HARRY FROST
Version 2.10 10M

DILOR
XY

SAMPLE wj0354
GRATING 1000
MODE MULTICHANNEL
REMARKS * 03

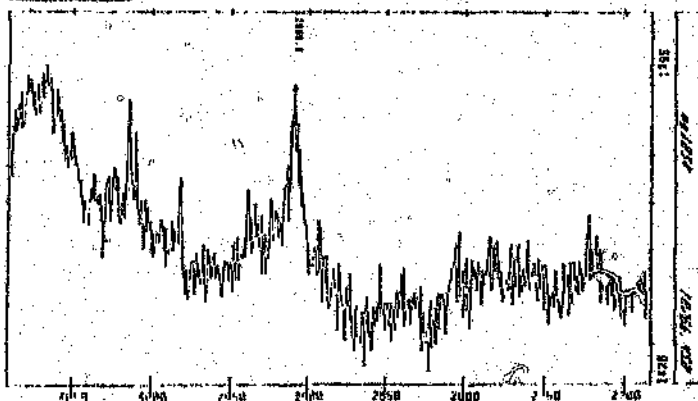
EXCITATION(wv) 514.5 SPECT.SLIT WIDTH(wv-1) 0.7
LASER POW.(wv) 1000 DETECTOR(wv of diodes) 1024
FORWARD(wv-1) 2400.0 FILTER
SPECTRO(wv-1) 2400 INTEGRATION TIME(s) 4
SLIT WIDTH(wv) 300 NUMBER OF ACCUMULATIONS 60



INTEGRALS FROM
1000.0 TO 1000.0
Version 2.00 1000
DILUTION
BY

SAMPLE 1000.0
DILUTION 1000.0
NAME 1000.0
REMARKS 1000.0

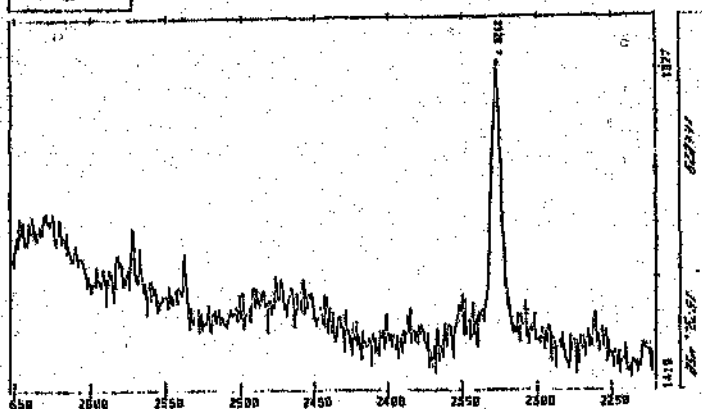
EXCITATION (nm) 514.5 SPECT. SLIT WIDTH (nm) 10.2
LASER POW. (mW) 1000 DETECTOR (nm of diode) 1024
FORWARD, (nm) 1000 FILTER 1000
SPECTRO. (nm) 1000 INTEGRATION TIME (s) 10
SLIT WIDTH (nm) 1000 NUMBER OF ACCUMULATIONS 10



INTEGRALS FROM
1000.0 TO 1000.0
Version 2.00 1000
DILUTION
BY

SAMPLE 1000.0
DILUTION 1000.0
NAME 1000.0
REMARKS 1000.0

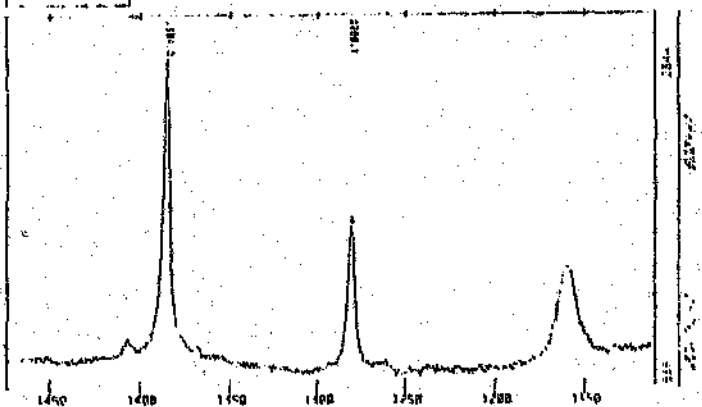
EXCITATION (nm) 514.5 SPECT. SLIT WIDTH (nm) 10.2
LASER POW. (mW) 1000 DETECTOR (nm of diode) 1024
FORWARD, (nm) 1000 FILTER 1000
SPECTRO. (nm) 1000 INTEGRATION TIME (s) 10
SLIT WIDTH (nm) 1000 NUMBER OF ACCUMULATIONS 10



INTEGRALS FROM
1000.0 TO 1000.0
Version 2.00 1000
DILUTION
BY

SAMPLE 1000.0
DILUTION 1000.0
NAME 1000.0
REMARKS 1000.0

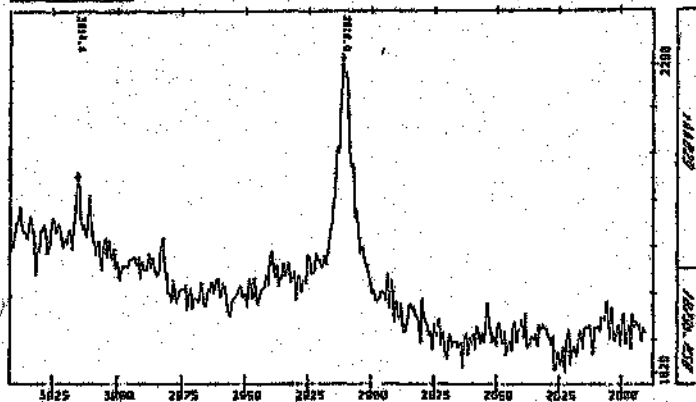
EXCITATION (nm) 514.5 SPECT. SLIT WIDTH (nm) 10.2
LASER POW. (mW) 1000 DETECTOR (nm of diode) 1024
FORWARD, (nm) 1000 FILTER 1000
SPECTRO. (nm) 1000 INTEGRATION TIME (s) 10
SLIT WIDTH (nm) 1000 NUMBER OF ACCUMULATIONS 10



CREDULUS DATA
NANCY FRANCE
Version 2.00 184

SAMPLE 164029
GRATING 1800
MODE MULTICHANNEL
REMARK: + 80

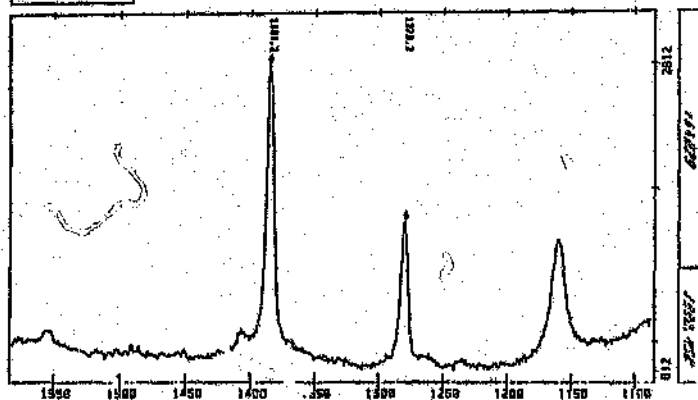
LASER POW. (mW) 1600 DETECTOR (nb. of diodes) 1024
FOREHAND. (cm-1) 2000.0 FILTER
SPECTRO. (cm-1) 2000 INTEGRATION TIME (s) 3
SLIT WIDTH (cm) 300 NUMBER OF ACCUMULATIONS 60



CREDULUS DATA
NANCY FRANCE
Version 2.00 184

SAMPLE 164029
GRATING 1800
MODE MULTICHANNEL
REMARK: + 80

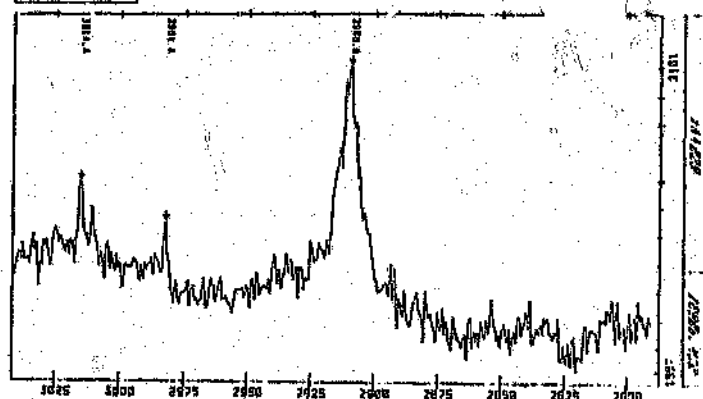
EXCITATION (nm) 514.5 SPECT. SLIT WIDTH (cm-1) 10.05
LASER POW. (mW) 1500 DETECTOR (nb. of diodes) 1024
FOREHAND. (cm-1) 1450.0 FILTER
SPECTRO. (cm-1) 1550 INTEGRATION TIME (s) 2
SLIT WIDTH (cm) 300 NUMBER OF ACCUMULATIONS 60



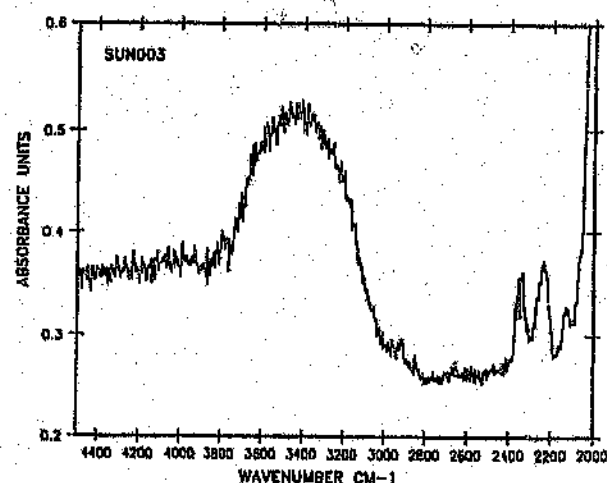
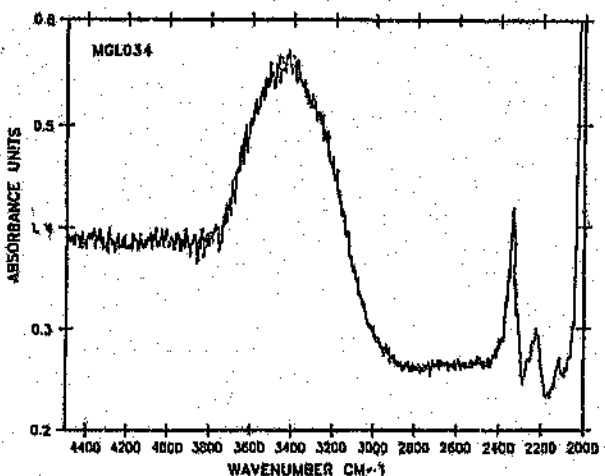
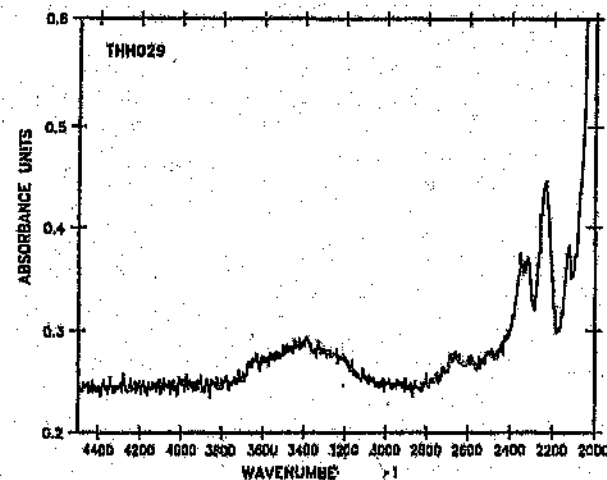
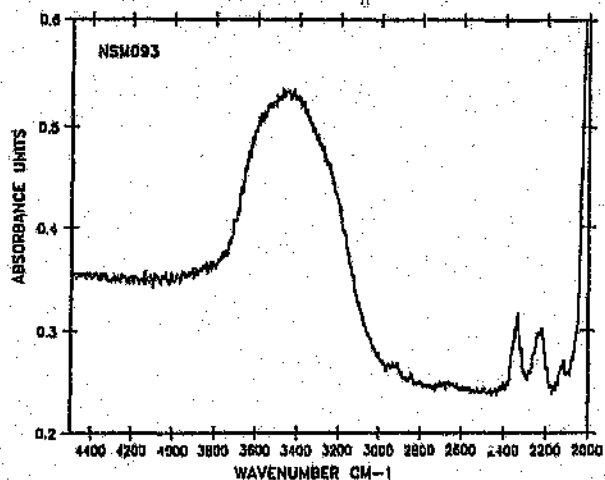
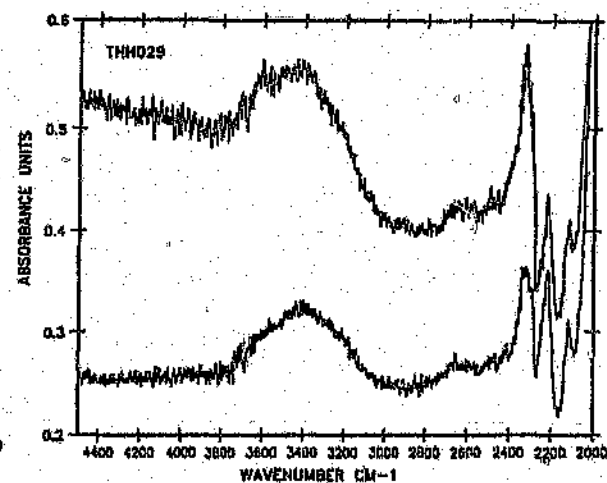
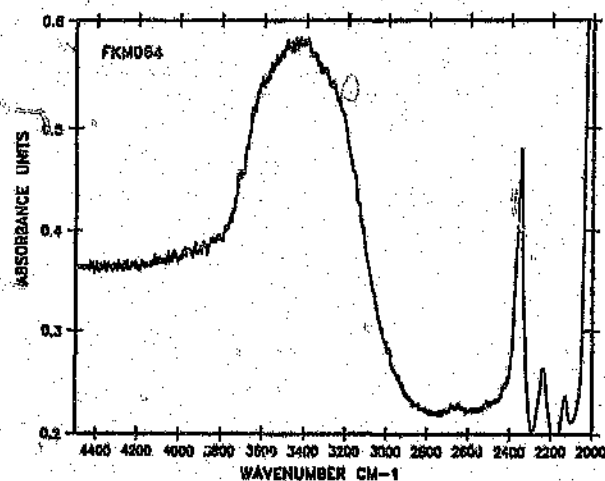
CREDULUS DATA
NANCY FRANCE
Version 2.00 184

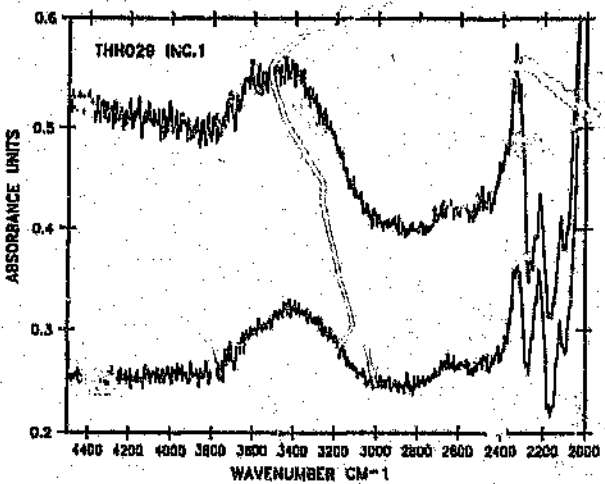
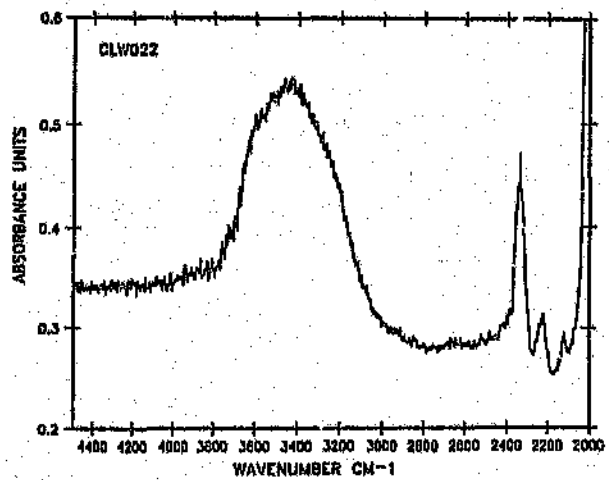
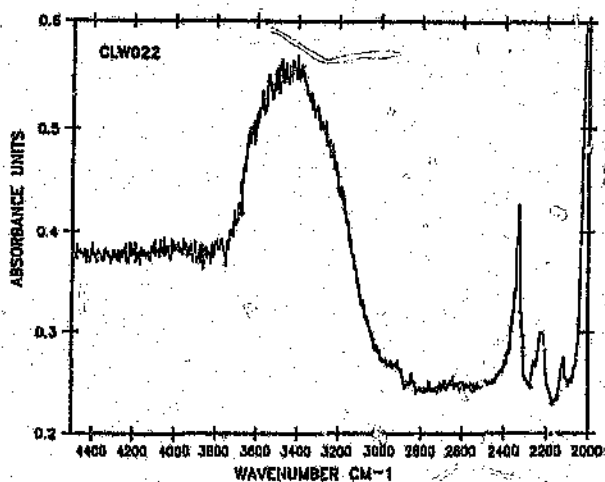
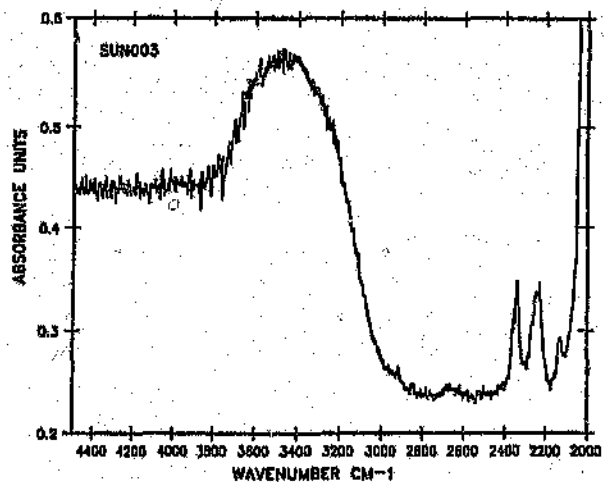
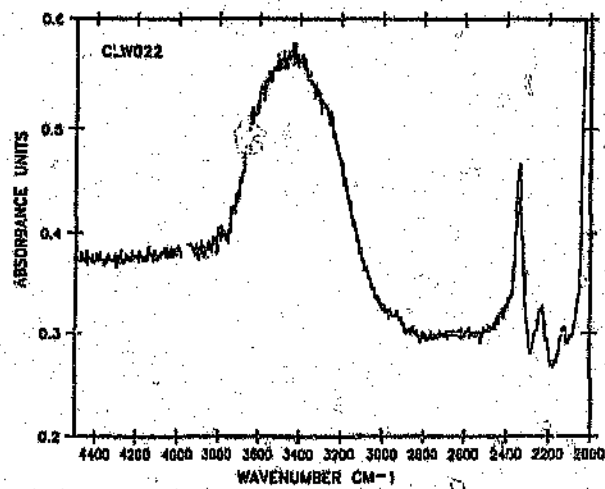
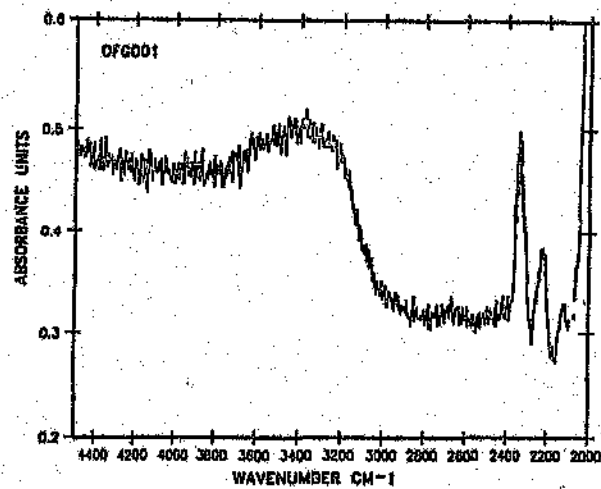
SAMPLE 164029
GRATING 1800
MODE MULTICHANNEL
REMARK: + 80

EXCITATION (nm) 514.5 SPECT. SLIT WIDTH (cm-1) 0.2
LASER POW. (mW) 1500 DETECTOR (nb. of diodes) 1024
FOREHAND. (cm-1) 2000.0 FILTER
SPECTRO. (cm-1) 2000 INTEGRATION TIME (s) 3
SLIT WIDTH (cm) 300 NAME ATOMS 60



Micr-Fourier Transform infrared spectra of individual quartz-hosted fluid inclusions from the SPRG. Spectra were recorded with a Bruker IFS 88 Fourier transform Infrared spectrometer, equipped with a Bruker A 590 microscope. The microscope is fitted with a narrow band, mercury-cadmium-telluride (MCT) detector with a 100 μm diameter window cooled to -196°C . Peak positions relate to molecular species as discussed in section 3.4.





Author: Boer R.H

Name of thesis: Physico-chemical conditions of mineralization in the sabie-pilgrims rest goldfield Eastern Transvaal

PUBLISHER:

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