

# Major element geochemistry and paleoclimatology of the Permo-Carboniferous glaciogene Dwyka Formation and post-glacial mudrocks in southern Africa

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## ABSTRACT

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A Chemical Index of Alteration (CIA) is used to quantify the degree of weathering of fine-grained materials in the glaciogenic Permo-Carboniferous Dwyka Formation and succeeding stratigraphic units of southern Africa. Diamictites in the Dwyka Formation have low CIA values compatible with their glaciogenic origin. Interbedded mudrocks show a wide scatter of values, suggesting that at least some of them were deposited during periods when ice had retreated from the source areas. Samples from the Prince Albert shale, which immediately overlies the Dwyka Formation, show high CIA values, suggesting a rapid transition to a much more intensive weathering regime (warmer climatic conditions?). Samples from the succeeding Whitehill shale have a low average value, so that weathering was once more inhibited, perhaps by a temporary return to a colder climate. The highest stratigraphic units sampled, the “upper shales”, have an average CIA value comparable to that of “average” shales, and suggesting “normal” weathering conditions. Major element geochemical data can supplement sedimentological and paleontological information and provide a valuable contribution to the detailed paleoclimatic interpretation of such glaciogenic successions.

## Introduction

The glacial origin of the Dwyka Formation which forms the basal unit of the Carboniferous to Jurassic Karoo Supergroup, was already established since the beginning of this century (Corstorphine, 1904; Du Toit, 1954). Despite their massive character, most of the diamictites of the Dwyka Formation were probably deposited by rain-out of glacial debris in a marine setting (Visser, 1989). The basal diamictite, which is overlying glacio-tectonised bedrock, may however, represent a true subglacial till. Widespread mudrock units in the formation have been interpreted as interglacial deposits (Du Toit, 1929; Visser, 1983). The upper contact of the glacial deposits with post-glacial mudrocks is remarkably sharp in the southern part

of the basin, suggesting a sudden change in depositional environment. However, in more proximal settings there is a facies change from stratified diamictite and dropstone argillite to post-glacial mudrock (Visser, 1982), which suggests a more gradual transition from glacial to non-glacial sedimentation in certain sectors of the basin.

The objectives of this study can be defined as:

- (1) To test the applicability of the chemical index of alteration (Nesbitt and Young, 1982) on well-established glacial and post-glacial rocks.
- (2) To establish whether the interbedded mudrocks represent true interglacial periods, with warmer climates even extending onto the source areas.
- (3) To establish the climatic conditions in the source areas following the rapid disintegration of

the marine ice sheet and the onset of mud deposition on the shelf during the late Permian.

### Stratigraphy

The Dwyka Formation, which unconformably overlies Precambrian basement and early Paleozoic sedimentary rocks, attains a thickness of about 800 m along the southern margin of the Karoo Basin (Fig.1). The formation consists of a shelf facies comprising predominantly massive diamictites with very subordinate sandstone and mudrock in the southern part of the basin (Figs.1 and 2). Clasts in the diamictite consist of plutonic, volcanic, metamorphic and sedimentary rock types and are predominantly distantly derived. The valley facies show an erratic distribution controlled by glacial topography along the northern basin margin (Fig.1). The glacial deposits attain a thickness of about 700 m in major valleys and consist of massive and stratified diamictites and mudrocks with subordinate sandstone and conglomerate. Clasts in the diamictites and conglomerates consist of plutonic, volcanic and sedimentary rock types and closely reflect the bedrock composition. A paleoescarpment defines the boundary between the shelf and the valley facies and major massive diamictite units of the shelf facies pinch out against this escarpment (Fig.3).

In the central and western part of the Karoo Basin and in the western part of the Kalahari Basin, mudrocks of the Prince Albert Formation, which forms the basal unit of the Permian Eccu Group, conformably overlie the glacial beds. The contact between the Dwyka and Prince Albert Formations is sharp over the paleo-shelf, whereas a marked transition consisting of debris-flow diamictites, turbidite sandstones and dropstone argillite (stratified diamictite of Fig.3) is commonly present in the valleys. The mudrocks overlap the glacial rocks onto basement. The Prince Albert Formation, which consists of dark-grey carbonaceous to olive green shale with very subordinate arenites and wackes, attains a thickness of about 200 m along the western and southern outcrop belt, but thins progressively towards the northeast. Chert and phosphatic nodules and lenses are present in the south. Remains of marine invertebrates and vertebrates, sponge spicules, foraminifera, radiolaria, acritarchs and plants were also found in the formation.

The Whitehill Formation which is a very useful white-weathering marker bed in the mudrock sequence, follows conformably on the Prince Albert Formation. Both upper and lower contacts are sharp. Along the western basin margin, the formation is up to 80 m thick, but towards the east and northeast it thins and loses its character

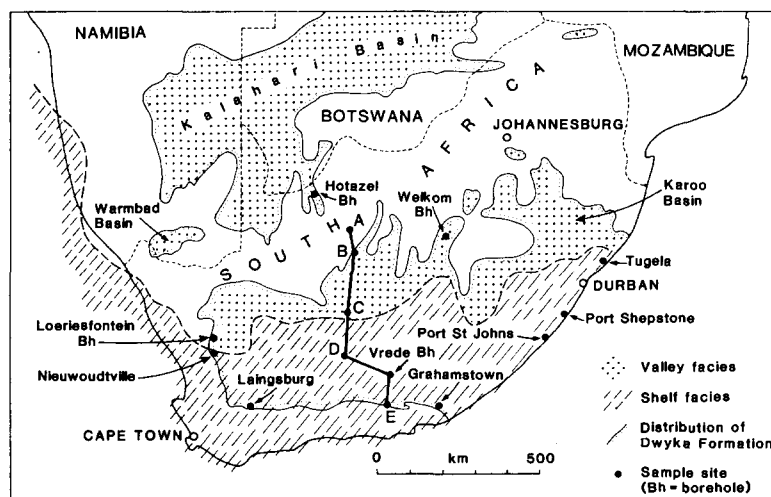


Fig.1. The distribution of the Permo-Carboniferous Dwyka Formation in southern Africa and the location of the sampling sites. A-E = location of section illustrated in Fig.3.

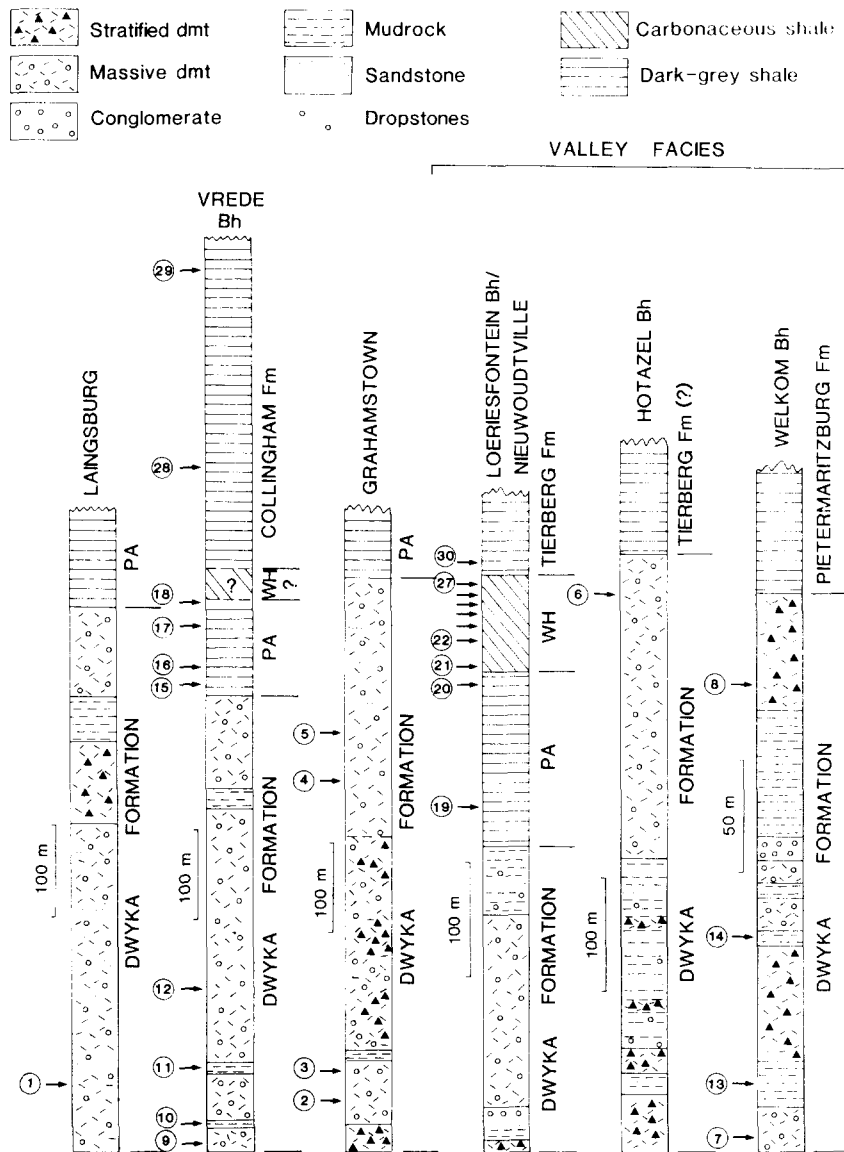


Fig.2. Stratigraphic sections with sample positions (arrows). Grahamstown section is a composite one for the eastern samples (5 = Tugela; 4 = Port Shepstone; 3 = Port St Johns; 2 = Grahamstown). Position of Whitehill Formation in the Vrede borehole uncertain. See Fig.1 for the location of the sections. PA = Prince Albert Formation (Fm); WH = Whitehill Formation; Bh = borehole.

so that the Prince Albert Formation becomes indistinguishable from the overlying mudrock units. The Whitehill Formation consists of carbonaceous shale with very subordinate silty beds. The restricted fossil species consist of a swimming reptile (*Mesosaurus*), paleoniscoid fish, arthropods and plant remains, and suggest synchronous deposition over the basin (Oelofsen, 1987).

A monotonous shale sequence belonging to the

Collingham, Tierberg and Pietermaritzburg Formations conformably overlies either the Whitehill or the Dwyka Formation (during further discussions in this paper these shales will be referred to as the "upper shales") (Fig.2). The "upper shales" are well-laminated, dark-grey to almost black in colour and more than 400 m thick. They are also carbonaceous and contain abundant pyrite. The Pietermaritzburg shale, like the Prince Albert shale,

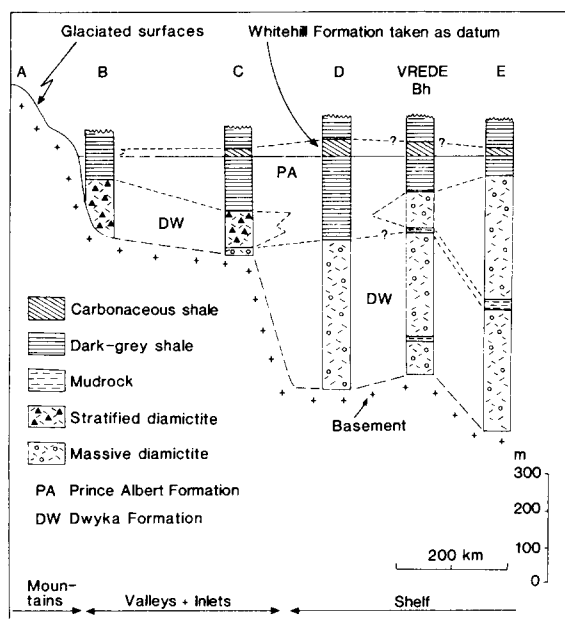


Fig.3. North-south section illustrating the basin topography and the relationship between the shelf and the valley facies of the Dwyka Formation. Note the pinch-out of the lower units of the shelf facies against the paleo-escarpment and the lateral facies change between the Dwyka and Prince Albert Formations. See Fig.1 for the location of the section.

also overlaps the glacial beds onto basement. On basement highs as well as in some valley heads in the northern part of the basin, the shale sequence is poorly developed or absent and coal-bearing strata, associated with reworked glacial deposits, locally directly follow on glacial beds.

### Chemical Index of Alteration method

Chemical weathering of source area rocks is climatically controlled. Nesbitt and Young (1984) suggested that 75% of the exposed minerals of plutonic and volcanic rocks is readily susceptible to chemical weathering. Degradation of these minerals resulted in the formation of clays. Calcium, sodium and potassium generally are removed from the feldspars by aggressive soil solutions so that the proportion of alumina to alkalis typically increases in the weathered product. With intensive weathering aluminous minerals such as kaolinite and beidellite are produced in quantity. Mass wasting of source areas in which chemical weathering is minimal, such as those produced under

glacial conditions, may supply fine-grained sediment containing less aluminous clay minerals and a high proportion of unaltered comminuted feldspar (Nesbitt and Young, 1982, 1989). Chemical analyses of argillaceous sediment derived from non-carbonate sources would thus reflect the prevailing climate in the source areas. Nesbitt and Young (1982) formulated an index of alteration to identify climate change in source areas. The method was first tested on the Huronian Supergroup in Canada (Nesbitt and Young, 1982) and was found potentially useful in the differentiation of cold and warm paleoclimates in a wide variety of sediments and sedimentary rocks (Young and Nesbitt, 1986).

The Chemical Index of Alteration (CIA) was calculated by Nesbitt and Young (1982) as follows:

$$CIA = [Al_2O_3 / (Al_2O_3 + CaO^* + Na_2O + K_2O)] \times 100$$

expressed as molar proportions.  $CaO^*$  is the amount of  $CaO$  in the silicate fraction so that, depending on the mineralogical make-up of the rock, a correction may have to be made for  $CaO$  in carbonates or phosphates. The CIA is a measure of alumina versus labile oxides and therefore gives an indication of the degree of weathering that the rock has undergone. Unweathered rocks give values of around 50, whereas higher values (up to 100) are obtained from rocks that have been subjected to strong weathering. For example, fresh granites give values between 45 and 55. "Average" shales range between about 70 and 75. The CIA value obtained from a sediment or sedimentary rock may also be a function of the grain size. In general, coarser-grained siliciclastic materials will contain a higher feldspar/clay ratio than those that are finer. Thus the coarser-grained sediment or rock should have a lower CIA value. Consequently, care should be taken to only compare results from materials of similar grain size.

The objectives of the study and the sensitivity of the method to subsequent rock weathering and to the presence of carbonate within the rock or in the source areas placed the following constraints on the sampling of the glacial and post-glacial strata in the Karoo Basin:

- (1) Experience showed that borehole samples

give much more reliable results than surface ones. Therefore sampling was confined to available borehole cores.

(2) Good stratigraphic control of the samples, especially in the mudrock sequences, was required.

(3) As dolomite rocks form a small part of the source areas, ice-flow directions, clast composition and paleocurrents had to be studied in advance to avoid sampling those deposits that might have been derived from such sources. In the case of the Hotazel borehole, the bedrock is dolomite and therefore a sample was taken only from near the top of the section (Fig.2).

(4) Only diamictites with an argillaceous matrix were sampled.

(5) In the case of the problematical Whitehill Formation (see below) a closely spaced series of samples from a single borehole was preferable to a random distribution of samples from a wider area.

(6) An effort was made to obtain representative samples from both the valley and the shelf facies.

### Results for the different stratigraphic units

The results of the calculations are plotted on ternary diagrams for the Dwyka diamictite, interbedded mudrocks in the Dwyka diamictite, Prince Albert shales, Whitehill shales and the "upper shales" (Fig.4 A–E). The triangular plot for matrix materials of the Dwyka diamictites (Fig.4A) shows a restricted and low range of CIA values ranging from 50 to 70. The generally low values agree with the glacial interpretation of these diamictites. Diamictite samples from the valley facies (no.6, 7 and 8) have higher values than those from the shelf facies. The interbedded mudrocks in the diamictite show a wide spread of values with two samples from the base of the glacial sequence in the Vrede borehole (no. 9 and 10) showing anomalously high  $K_2O$  contents (Fig.4B). Neither evidence of weathering (they were from a depth of about 3300 m) nor other abnormal characteristics (except that they were light grey in colour) was detected in the samples. Again samples from the valley facies (no. 13 and 14) have higher indices of chemical alteration than those from the shelf facies.

All the samples from the Prince Albert Formation have high CIA values and plot close together in a small field (Fig.4C). Plots of the Whitehill shale samples show a linear spread (Fig.4D) which appears to be related to their stratigraphic age. Samples from the lower part of the formation (no.22 and 23) have lower CIA values than those (no.25, 26 and 27) from near the top. Indices for the lower samples are similar to some of the values obtained from interbedded mudrocks in the diamictite (cf. Fig.4B and 4D). Samples from the "upper shales" have quite high CIA values. They plot in a small field (Fig.4E) that partly overlaps the field for the Prince Albert shales (cf. Fig.4C).

### Discussion

CIA values from the overlying shales are generally higher than those from the Dwyka Formation (Fig.5). The average value for the diamictite matrix is 60, for the interbedded mudrock 70, for the Prince Albert and "upper shales" 77 and 72, respectively, and for the Whitehill shale 67. The simplest interpretation of those numbers is as follows: (1) cold conditions existed in the source areas during deposition of the diamictites; (2) there were moderate climatic conditions with the possible presence of some ice in the source areas during sedimentation of the interbedded mudrocks and the Whitehill shales; (3) warm conditions prevailed during deposition of the Prince Albert and "upper shales".

Thus, the CIA values appear to support the existence of glaciated source areas during deposition of the Dwyka Formation and to provide a means of differentiating these from non-glaciated ones during post-Dwyka sedimentation. Visser (1989) suggested that the shelf facies of the Dwyka Formation was deposited under subpolar conditions, whereas the valley facies was laid down by temperate tidewater glaciers. This interpretation derives support from the major element geochemistry; the diamictite samples from the valley facies have higher CIA values than those from the shelf samples (cf. Fig.4A). Variable CIA values from the interbedded mudrocks in the diamictites (Fig.4B and 5) probably reflect variable climatic conditions present on the highlands during inter-

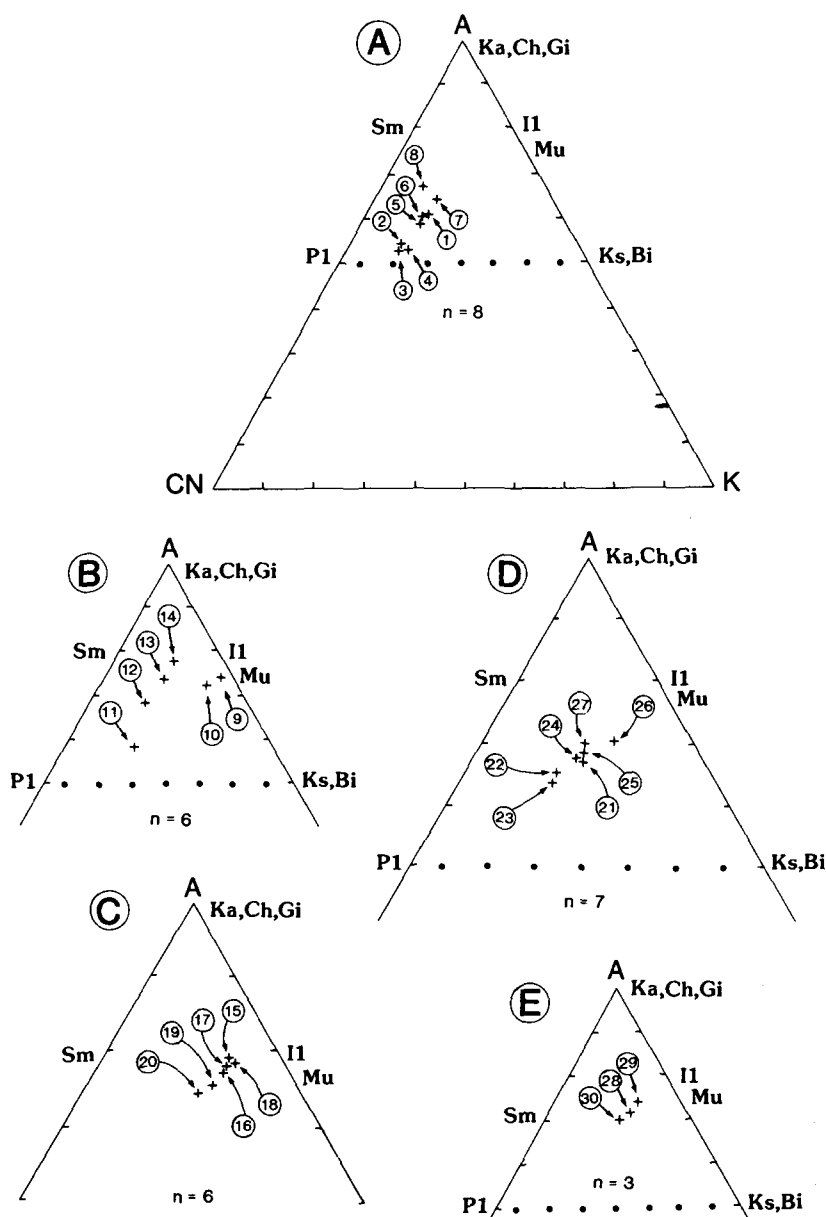


Fig. 4. Triangular plot (molar proportions), after Nesbitt and Young (1984), of A ( $\text{Al}_2\text{O}_3$ ), CN ( $\text{CaO}^* + \text{Na}_2\text{O}$ ) and K ( $\text{K}_2\text{O}$ ).  $\text{CaO}^*$  is  $\text{CaO}$  in silicates. Chemical Index of Alteration (CIA) values (0–100) may be read along a vertical axis drawn upward from the centre of the base of the triangle. Positions of some mineral species are shown; *Pl*=plagioclase; *Ks*=K-feldspar; *Bi*=biotite; *Il*=illite; *Mu*=muscovite; *Ka*=kaolinite; *Ch*=chlorite; *Gi*=gibbsite; *Sm*=smectite. See text for discussion. A. Diamictite matrix from the Dwyka Formation. B. Interbedded mudrocks in the Dwyka Formation. C. Prince Albert shales. D. Whitehill shales. E. "Upper shales".

glacial periods (Visser, 1983). Under certain circumstances, even mountain ice-caps could have melted (cf. correspondence between samples 9–14 and those of the post-glacial "upper shales"). On the whole, the CIA values confirm earlier inter-

pretations of the extensive interbedded mudrock units (some of them up to 60 m thick and traceable over distances of up to 400 km), as representing major interglacial periods.

CIA values for the Prince Albert and "upper

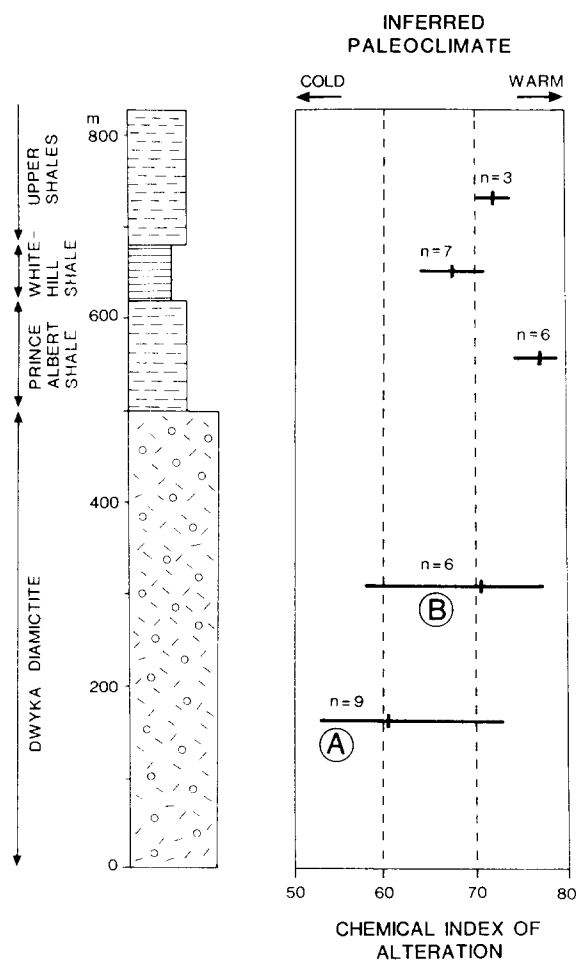


Fig. 5. Generalised stratigraphic sequence of the basal part of the Karoo Supergroup and the corresponding CIA values. A = diamictite matrix; B = interbedded mudrocks; n = number of analyses. Horizontal bar indicates the spread of the values and the vertical bar the average.

shales" suggest a fairly high degree of chemical weathering, consistent with wet, warm climatic conditions in the source areas. The change from relatively unweathered samples (glacial?) to weathered (warm conditions?) appears to be rapid (cf. results from diamictite sample 6 from near the top of the sequence and Prince Albert shale sample 19 from near the base of the formation). A similar sharp change is also suggested by the abrupt contact between the glacial beds and the post-glacial shale on the shelf. The assumption that warm climatic conditions succeeded glaciation in the source areas is contradictory to previous sedi-

mentation models as well as biostratigraphic correlations. Visser (1982) described lateral facies changes from post-glacial mudrock to glacial sediments in an upslope direction (cf. Fig. 3) and pollen analyses in the Kalahari and Karoo Basins confirm these stratigraphic transitions (Visser, 1990). The traditional sedimentary model for the Prince Albert Formation involves the presence of mountain ice-caps, maintained throughout most of the early Permian, following disintegration of the shelf ice sheet, and deposition, during this period, of a prism of marine muds on the shelf. This model is in sharp contrast with the warm climatic conditions in the source areas, supported by the chemical index of alteration.

Chemical data from the Whitehill shales suggest the influx of less-weathered material possibly under cooler climatic conditions. In the borehole at Loeriesfontein a complete set of samples from the Whitehill Formation was analysed (Fig. 2 and 6). CIA values from these samples suggest systematic changes. The basal samples (no. 21–23) suggest less weathering in the source areas than the upper ones

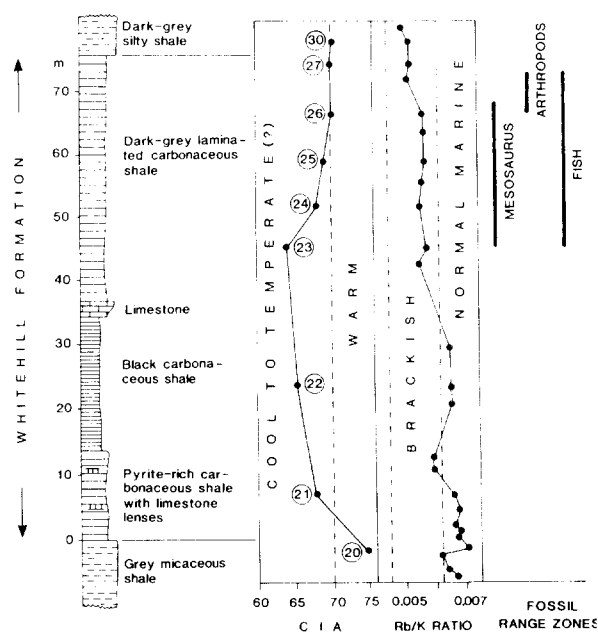


Fig. 6. Detailed section of the Whitehill Formation at Loeriesfontein with the corresponding geochemical and paleontological data. Interpretation of the Rb/K ratios after Campbell and Williams (1965) and fossil range zones after Oelofsen (1987). Sample numbers as in Figs. 2 and 4.

(no.25–27) (Fig.6). The early to late Permian Whitehill Formation is presently correlated with the coal-bearing beds in the Karoo Basin (Van Eeden, 1973; Visser, 1990), which are interpreted as of glaciolacustrine and fluvio-glacial deltaic origin (LeBlanc Smith and Eriksson, 1979). The restricted faunal species in the Whitehill Formation and the lack of input of any sediment coarser than fine mud over an extensive area also suggest possible cold conditions and sediment starvation. The CIA values therefore substantiate earlier climatic speculations on a cool environment, although these were never seriously considered as a result of the presence of fossil remains of a primitive free swimming reptile (*Mesosaurus*) in the Whitehill shales as well as in the Irati shales of the Paraná Basin (Oelofsen, 1987).

Detailed analysis of the Whitehill stratigraphy, vertical variation in CIA values, change in depositional environment and range zones of the fossils are all illustrated in Fig.6. *Mesosaurus* occurs in the upper part of the sequence where temperate climatic conditions can be inferred from other parameters. Although the climate was probably not yet warm, conditions became favourable for life to flourish in the brackish environment. Ancient reptiles are traditionally considered as ectothermic (i.e. obtained their body heat from the environment) (Colbert, 1961), but later views, for example on the dinosaurs, suggest the possibility of endothermy in some reptiles (cf. Bakker, 1972) and that these creatures may have been able to survive also in temperate to cold environments (cf. Rich and Rich, 1989). Thus, with our limited knowledge on the characteristics and behaviour of *Mesosaurus*, the presence of these fossils in the extensive Karoo, Kalahari and Paraná Basins of southwestern Gondwana, cannot be considered diagnostic of warm conditions during deposition of the Whitehill and Irati Formations.

Rubidium–potassium ratios in the Whitehill shales suggest normal marine conditions during deposition of the lower part of the formation and a brackish environment for its upper part (cf. Campbell and Williams, 1965) (Fig.6). Reducing bottom conditions may have been the result of stratification in the water during a lowering in sea-level when small ice caps rapidly expanded in the

source areas (cf. Thunneil and Williams, 1989). Subsequent warmer climatic conditions would have resulted in the melting of the ice and the addition of large volumes of fresh water to the depository, causing a change from marine to brackish conditions. It was in this latter environment that fishes, arthropods and swimming reptiles settled (Fig.6).

In this study we have attempted to use the chemical index of alteration derived from major element analyses of diamictites and mudrocks, as a paleoclimatic indicator. For the glaciogene Dwyka Formation and Whitehill Formation, there is reasonable correspondence between the geological and paleontological interpretations and those based on the chemical index of alteration. In the case of the immediately post-glacial Prince Albert shales, however, high CIA values are at variance with previous paleoclimatic interpretations. Because of the tentative nature of the present sedimentation model for the Prince Albert Formation and the poor time resolution in this formation, the CIA data should be considered as an additional input in future interpretations.

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