

Metallogenesis of germanium—A review

R. Höll ^{a,*}, M. Kling ^b, E. Schroll ^c

^a Department für Geo-und Umweltwissenschaften, Sektion Geologie, LMU München, Luisenstrasse 37, D-80333 München, Germany

^b Department für Geo-und Umweltwissenschaften, Sektion Mineralogie, Petrologie und Geochemie, LMU München, Theresienstrasse 41, D-80333 München, Germany

^c Institut für Mineralogie und Kristallographie, Universität Wien, Althanstrasse 14, A-1090 Wien, Austria

Received 5 November 2002; accepted 23 July 2005

Available online 15 June 2006

Abstract

Germanium (Ge) is a scarce, but not an extremely rare element in the Earth's crust (about 1.6 ppm Ge crustal average). Principal geochemical substitutions and mineral associations of Ge include Si, C, Zn, Cu, Fe, Sn, and Ag. Most Ge is dispersed through silicate minerals due to the substitution of Ge^{4+} for the geochemically similar Si^{4+} . Ge is unusual in that it exhibits siderophile, lithophile, chalcophile and organophile behaviour in different geologic environments. Only minor variations in Ge concentrations are known from different igneous rocks, siliceous sedimentary rocks, and their metamorphic equivalents. Carbonates and evaporites show a depletion to the crustal average of Ge. There is a tendency for Ge to be slightly enriched in silicate minerals of late magmatic differentiates (e.g., muscovite granites), rocks that crystallize in the presence of a high volatile concentration (e.g., pegmatites, greisens) and late hydrothermal fluids, accounting for ore deposits. Ge does not form specific ore deposits; rather it occurs in trace and minor amounts in various ore deposit types. Grades of a few tens to several hundred ppm Ge are known in sulphide deposits: volcanic-hosted, massive sulphide Cu–Zn(–Pb)(–Ba) deposits; porphyry and vein–stockwork Cu–Mo–Au deposits; porphyry and vein–stockwork Sn–Ag deposits; vein-type Ag–Pb–Zn deposits; sediment-hosted, massive sulphide Zn–Pb–Cu(–Ba) deposits; carbonate-hosted Zn–Pb deposits, and polymetallic, Kipushi-type Cu–Pb–Zn–Ge deposits. Low-iron sphalerite is the most important of all minerals containing Ge. Other sulphur minerals, e.g., enargite, bornite, tennantite–tetrahedrite, luzonite, sylvanite, and colusite, are significant Ge sources in some deposits. At high S activities, the thiocomplex $[\text{GeS}_4]^{4-}$ can give rise to the formation of thiogermanate minerals, e.g., argyrodite, briartite, renierite, and germanite, which can form elevated Ge concentrations, above all in Kipushi-type deposits. Ge concentrations due to sorption processes in iron hydroxides and oxides refer to those in oxidation zones of sulphide ore deposits, especially at the Apex Mine, USA, and Tsumeb, Namibia, as well as to iron oxide ores, particularly in banded iron formations (BIF). Lignite and coal deposits show germanium grades that vary by several orders of magnitude, both regionally and within particular deposits, from levels less than the Ge abundance in the Earth's crust up to a few thousands ppm Ge. This Ge enrichment is effected by chemisorptive processes on relatively stable organo-complexes, e.g., lignin and humic acids.

Currently, Ge is recovered as a by-product from sphalerite ores, especially from sediment-hosted, massive Zn–Pb–Cu(–Ba) deposits and carbonate-hosted Zn–Pb deposits, from polymetallic Kipushi-type deposits, and lignite and coal deposits in China and Russia. Figures for worldwide Ge reserves are not available.

© 2006 Elsevier B.V. All rights reserved.

Keywords: Germanium; Metallogenesis; Mineralogy; Geochemistry; Ore deposits

* Corresponding author. Tel.: +49 89 6414053.

E-mail address: rudolf.hoell@t-online.de (R. Höll).

Contents

1. Introduction	146
2. Distribution	148
2.1. Germanium hydrogeochemistry	148
2.2. Mineralogy and crystal chemistry	149
3. Geochemistry	152
4. Geological setting of Ge-bearing deposits	154
4.1. Volcanic-hosted massive sulphide (VHMS) Cu–Zn(–Pb)(–Ba) deposits	155
4.2. Porphyry and vein–stockwork Cu–Mo–Au deposits	158
4.3. Porphyry and vein–stockwork Sn–Ag deposits	159
4.4. Vein-type Ag–Pb–Zn(–Cu) deposits	159
4.5. Sediment-hosted massive sulphide (SHMS) Zn–Pb–Cu(–Ba) deposits	160
4.6. Carbonate-hosted base metal deposits	162
4.6.1. Mississippi Valley-type (MVT) Zn–Pb–Fe(–Cu)(–Ba)(–F) deposits	162
4.6.2. Irish-type (IRT) Zn–Pb(–Ag)(–Ba) deposits	163
4.6.3. Alpine-type (APT) Zn–Pb deposits	164
4.6.4. Kipushi-type (KPT) polymetallic deposits	165
4.6.5. Germanium in oxidation zones of Kipushi-type deposits	168
4.6.6. Sediment-hosted stratiform Copper (SSC) deposits	168
4.7. Germanium in non-sulphide Zn–Pb deposits	168
4.8. Germanium in Fe-oxide ores	169
4.9. Germanium in coal and lignite deposits	169
5. Summary and conclusions	170
Acknowledgements	171
References	172

1. Introduction

The element Ge was first detected by the German chemist Clemens Winkler in 1886 in the silver sulphide mineral argyrodite from Freiberg, Saxony, Germany (Weisbach, 1886). The existence of an element intermediate in properties between the metal Sn and the non-metal Si was predicted in 1871 and named eka-silicon by the Russian chemist Dmitrii Ivanovich Mendeleev. Ge is a chemical element in subgroup IVa of the periodic table (C–Si–Ge–Sn–Pb). It is greyish-white, metallic in appearance, and metallic in a number of physical properties. Its electrical properties are between those of a metal and an insulator; some of its compounds have properties similar to non-metals. The oxidation states of Ge are +2 and +4, with the +4 state forming the common and stable compounds; the tendency towards quadrivalency is very strong. Most divalent Ge compounds (e.g., GeO and GeS) are not stable under atmospheric conditions (Bernstein, 1985; Adams and Thomas, 1994).

Ge has no known biological role in humans; it is considered as an essentially non-toxic element, except for a few compounds (e.g., GeO₂, GeH₄, GeCl₄, and GeF₄). Ge dissolved in the ppm range in drinking water

can, however, cause chronic diseases (Gerber and Leonard, 1997). It has little or no effect upon the environment, because it usually occurs only as a trace element and is used in very small quantities in commercial applications (Brown, 2002; Buttermann and Jorgenson, 2005).

Ge occurs chiefly in Zn sulphide ores (sphalerite and wurtzite). Pyrometallurgical processing of Zn ores has now largely been replaced by hydrometallurgical Zn production (Fillipou, 2004). In the hydrometallurgical process, some elements, especially Ge, are intolerable impurities for the electrolytic recovery of Zn, and must be removed from the solution prior to Zn extraction. The permissible limit is 0.002 to 0.05 mg Ge/l in the liquid (Graf, 1996), allowing Ge recovery from Zn concentrates at Zn processing plants. Ge can be extracted by fractional distillation of the volatile GeF₄. Other technologies are used to extract Ge from Ge–Cu–Pb sulphide ores, coal ash, flue dust and slag.

World refinery production of primary germanium (from ores, coal ash and flue dust, generated in the combustion of Ge-bearing lignites and coals at power stations) (USGS, 2004, 2005):

Year	1998	1999	2000	2001	2002	2003	2004
Ge (t)	39	37	41	38	39	44	50

This primary supply of Ge from ores and coal ash and flue dust was well below the level of worldwide Ge consumption since about 35% of the total Ge consumed is produced from recycled materials. During the manufacture of most electronic and optical devices, more than 60% of the Ge metal used is routinely recycled as new scrap. Such recycled new scrap continued to grow and remained a significant supply factor (about 30 t of Ge worldwide). Little Ge returns as old scrap because there is a low unit use of Ge in most electronic and infrared devices. About 2 t of Ge were estimated to be consumed as old scrap in 2004. Germanium was also released from government and non-government stockpiles in recent years. Thus, about 1.8 t of Ge were released from the U.S. National Defense Stockpile in 2003 (George, 2004; USGS, 2005). Demand for Ge increased in 2004 because of increases in infrared applications, especially in automobiles as safety devices. World consumption matched the total supply (about 100 t Ge per year).

USGS (2005) reported price statistics for the United States as follows:

Price (US\$ per kg), producer, year-end,	2000	2001	2002	2003	2004
Ge metal zone refined	1250	890	620	380	640
GeO ₂ , electronic grade	800	575	400	245	410

Free-market prices for Ge and GeO₂ peaked in 1996 and declined until 2003.

Ge has the following uses, but in each case, only small amounts are required. The worldwide end use pattern for Ge was estimated to be as follows (George, 2004; USGS, 2004, 2005; Buttermann and Jorgenson, 2005):

- 35%: Polymerisation catalysts (GeO₂ is used mainly in Asia, e.g., Japan, as a polymerisation catalyst for the production of polyethylene terephthalate (PET), a commercially important plastic. New types of materials, e.g., Ti- and Al-based PET catalysts, are expected to replace the relatively expensive Ge as catalyst).
- 25%: Infrared optics (GeO₂ is added to glass to increase the index of refraction. Since the oxide is transparent to infrared radiation, it has found use in optical instruments, e.g., in microscope objective lenses and wide-angle camera-lenses. Infrared night-vision devices: Germanium lenses and windows can be used in infrared optical systems, principally for military guidance and weapon-sighting applications, in the same way that ordinary glass lenses and windows are used in visible-light optical systems. The use of Ge optics has increased in a wide range of applications, including television electronics as a component of diodes, satellite systems and personnel detection equipments in poor visibility environments, for fire department thermal-imaging systems, and for automobiles with Ge-based night-vision systems).
- 20%: Fiber-optic systems (Ge is used as a component (dopant) within the core of optical fibers for the telecommunication consumer sector).
- 12%: Electronics/solar electrical applications (SiGe-based chips are more energy-efficient than traditional Si-based chips. They offer high switching frequency and low energy consumption. The low-voltage operation of SiGe devices, coupled with high levels of integration achievable with SiGe technology, including more stability over a wider range of temperatures, have triggered their increased adoption in wireless devices, optical communication systems, hard disk drives, automotive chips and global positioning systems (GPS). Ge substrates are also used for space solar cells).
- 8%: Other uses (e.g., phosphors (in fluorescent lamps), metallurgy (numerous alloys containing Ge) and chemotherapy (toxic effects against certain microorganisms)).

The use pattern in the U.S.A. was significantly different from that worldwide; it was estimated to be fiber-optics, 40%; infrared optics, 30%; electronics/solar electrical applications, 20%; and others (phosphors, metallurgy, and chemotherapy), 10% (USGS, 2005). The significant shifts in the pattern of germanium use in the U.S.A. during the last two decades are documented by Buttermann and Jorgenson (2005).

Although some metallic compounds that contain Ga, In, Se, and Te, can be substituted for Ge, the pure element is more reliable than competing materials in many high-frequency and high-power electronics applications. There is growth potential for Ge in the thin-film application for digital video discs, SiGe chips, Ge-based semiconductors, and other electronic devices. The potential replacement of GaAs by SiGe in wireless telecommunication devices portends a bright, long-term future for Ge. A new metallic material consisting of Ge, Ga, and Yb, could be ideal for space probes that endure a wide range of temperatures. Research continues on Ge-on-insulator substrates as a replacement for Si on miniaturized chips and on Ge-base solid-state light-emitting diodes (LED). (George, 2004; USGS, 2004, 2005; Buttermann and Jorgenson,

Table 1
Germanium distribution on Earth and in major rock types

Material	Ge [ppm] (mean)	Reference
Earth	13.8	Dasch (1996)
Earth's core	37	Dasch (1996)
Primitive mantle	1.1	Dasch (1996)
Oceanic crust	1.5	Taylor and McLennan (1985)
Continental crust	1.6	Taylor and McLennan (1985)
Ultramafic rocks	1.3	Faure (1998)
Mafic rocks	1.4	Faure (1998)
Granite	1.3	Faure (1998)
Shale	1.6	Faure (1998)
Sandstone	0.8	Faure (1998)
Carbonate rocks	0.2	Faure (1998)
Deep-sea clay	2.0	Faure (1998)

2005; http://www.the-infoshop.com/study/fs22376_silicon_germanium.html).

2. Distribution

The first comprehensive study of the geochemistry of Ge was published by Goldschmidt and Peters (1933). This was followed by other important publications by Hörmann (1963, 1972) and Bernstein (1985). Dasch (1996) calculated contents of 13.8 ppm Ge for the total Earth, 37 ppm Ge for the Earth's core and 1.1 ppm Ge for the primitive mantle. Taylor and McLennan (1985) reported 1.5 ppm Ge for oceanic crust and 1.6 ppm Ge for continental crust (Table 1). Thus, on a weight basis, Ge is uncommon, but not an extremely rare element in the bulk continental crust. It is more abundant than W (1 ppm), Mo (1 ppm), Sb (0.2 ppm), Bi (0.06 ppm), and In (0.05 ppm) (Taylor and McLennan, 1985). Theoretically, the abundance of Ge in the Earth's crust should permit the formation of large (>14,000 t Ge), or even giant deposits (>140,000 t Ge), sensu Laznicka (1999), who reported a crustal abundance of 1.4 ppm Ge. However, the capacity of Ge to form deposits is limited because of its geochemical properties. The concentration of Ge in one of the largest Ge-bearing deposits, Tsumeb, with ~2160 t Ge (Lombaard et al., 1986), is not sufficient to allow Tsumeb to be classified as a 'large' deposit. The concentration of 14,000 t Ge would only be exceeded if the ore volume containing Ge were large enough, which might be possible in BIF ores or giant coal fields.

2.1. Germanium hydrogeochemistry

Ge concentrations in different types of water are shown in Table 2. Fresh (potable) water, river water and

seawater contain only 0.05 to 0.1 ppb Ge (Ershov and Shcheglova, 1958; Sarykin, 1977; Froelich and Andreae, 1981; Froelich et al., 1985; Mortlock and Froelich, 1986; Faure, 1998; Reimann and de Caritat, 1998). Goleva and Vorobyeva (1967) found Ge contents ranging from 0.001 to 0.1 ppm in mine waters from various types of sulphide ore deposits, predominantly dissolved as H_2GeO_3 . The highest concentrations were in waters with the lowest and highest pH values. Ge is lost from solution by sorption on hydrous iron oxides. In addition, Goleva and Vorobyeva (1967) reported high Ge concentrations (up to 48 ppb) and the presence of Ge humate complexes in some coalmine waters. Methyl-germanium species have been detected in seawater (Schink et al., 1975; Lewis et al., 1985). Oilfield waters have low Ge contents, similar to seawater. Ge can be transported as neutral hydroxide species $[\text{Ge}^{4+}(\text{OH})_4(\text{aq})]^0$ in dilute aqueous hydrothermal fluids at pH values <8 over a temperature range of 20 to 350 °C. The solubility of Ge and the Ge/Si ratios in thermal waters increase with temperature and salinity (Bernstein, 1985; Melcher et al., 2003). Pokrovski and Schott (1998) suggested that, in geological environments, Ge is transported mainly as hydroxide and chloro-complexes in hydrothermal fluids. In thermal water with high alkalinity, high Na and low Ca contents, Ge concentrations can be in excess of 100 ppb (El Wardani, 1957; Kraynov, 1967). Bernstein (1985) concluded that Ge will be most concentrated in hot, alkali-rich waters that pass through thermally metamorphosed, organic-rich (and Ge pre-enriched) sedimentary rocks. The distribution of Ge between melts and coexisting aqueous fluids was studied by Bai and Koster van Groos (1999), who concluded that the distribution coefficient D_{Ge}

Table 2
Germanium concentrations in water

Locality	Type of water	Ge [ppb]	Reference
Global	Sea water	0.07	Faure (1998)
Global	River water	0.06	Mortlock and Froelich (1986)
Former UdSSR	Mine water	0.5–48	Goleva and Vorobyeva (1967)
Massiv Central, France	Thermal water	<56	Criaud and Fouillac (1986)
Central Caucasus	Thermal water	33–140	Kraynov (1967)
Waimangu, New Zealand	Thermal water	46–94	Koga (1967)
Steamboat Springs, USA	Thermal water	293	El Wardani (1957)
Geyser field, Iceland	Thermal water	<24	Arnorsson (1984)
Azerbaijan	Oilfield water (NaCl–HCO ₃)	<85	Nuriyev et al. (1968)

[concentration of Ge in the aqueous fluid divided by concentration of Ge in the (granitic) melt] increases with pressure and more so with a carbonate-rich than with a (Na,K)Cl fluid. Glemser (1961) reported that Ge compounds are more volatile than Si compounds at high pressures in hot water vapour. The enrichment of Ge in topaz, and to a lesser extent in fluorite and white mica, associated with granitoids, and in F-bearing hot springs, suggest that aqueous F-bearing Ge species, perhaps $[\text{GeF}_6]^{2-}$ or related molecules, are present. Enhanced formation of Ge–F complexes may be only due to strongly acid ($\text{pH} < 3$) F-rich solutions (Bernstein, 1985). The compound GeF_4 is highly volatile (Rochow and Abel, 1975). The enrichment of Ge in hydrothermal sulphide deposits indicates that S-bearing Ge species may also form in some hydrothermal fluids (Bernstein, 1985). At high S activities, the thiocomplex $[\text{GeS}_4]^{4-}$ is responsible for the formation of thiogermanate minerals (Bernstein, 1985).

There is a considerable literature about the geochemistry of magmatic gases and condensates from (recently) active volcanos. Taran et al. (1995) reported among other data 27 ppb Ge in gas condensate from the highest-temperature fumarole of the Kudryavy Volcano, Iturup Island, Kuril Arc, Russia. Shaderman et al. (1996) informed about fumaroles from this volcano, indicating a potential source of rare (Ge, Re, In, Tl, and Bi) and noble (Au, Ag, and Pt) metals. Churakov et al. (2000) presented results obtained from thermodynamic numerical simulations for transport and deposition of elements, based on the data published by Taran et al. (1995) from the Kudryavy Volcano. Their results concerning Ge indicate: “At high temperatures, Ge is transported mainly as sulphide GeS_x The change of the predominant species takes place at 723 K, near which the GeF_2 , GeCl_2 , and GeS_2 species are almost equally important in Ge transport”. At intermediate to low temperatures, sulphide and chloride compounds are characteristic for the transport of Ge, Sn, Pb, and Bi, whereas Si, Al, and Be are transported mainly as fluorides and oxides. At low temperatures, GeCl_2 is substituted by GeCl_4 , while SiO is replaced by SiO_2 . This may imply a separation mechanism between Si and Ge.

2.2. Mineralogy and crystal chemistry

Table 3 summarizes Ge minerals currently recognised by the International Mineralogical Association (Strunz and Nickel, 2001), supplemented by recent data from Roberts et al. (2004) and Paar et al. (2004). In contrast to Si, the number of Ge minerals is very limited. Moreover, some of these minerals are extremely rare or

Table 3

Compilation of defined germanium minerals after Strunz and Nickel (2001), with supplements by Roberts et al. (2004) and Paar et al. (2004)

Mineral	Formula	Frequency
<i>Sulphides</i>		
Argyrodite	Ag_8GeS_6 (solid solution series with canfieldite, Ag_8SnS_6)	Common
Putzite	$(\text{Cu}_{4.7}\text{Ag}_{3.3})_{\Sigma 8}\text{GeS}_6$	Unique
Briartite	$\text{Cu}_2(\text{Fe,Zn})\text{GeS}_4$	Common
Barquillite	$\text{Cu}_2(\text{Cd,Fe})\text{GeS}_4$	Unique
Renierite	$(\text{Cu,Zn})_{11}\text{Fe}_2(\text{GeAs})_2\text{S}_{16}$	Common
Germanite	$\text{Cu}_{13}\text{Fe}_2\text{Ge}_2\text{S}_{16}$	Common
Germanocolusite	$\text{Cu}_{13}\text{V}(\text{Ge,As})_3\text{S}_{16}$	Rare
Ovamboite	$\text{Cu}_{10}(\text{Fe,Cu})_3\text{WGe}_3\text{S}_{16}$	Unique
Catamarcaite	Cu_2GeWS_8	Unique
“Ge-stannoidite”	$\text{Cu}_2\text{Fe}_2\text{ZnGe}_2\text{S}_{12}$	Unique
Morozeviczite	$(\text{Pb,Fe})_3\text{Ge}_{1-x}\text{S}_4$	Rare
Polkovicite	$(\text{Fe,Pb})_3\text{Ge}_{1-x}\text{S}_4$	Rare
<i>Oxides</i>		
Argutite	GeO_2	Rare
Brunogeierite	$\text{Fe}_2(\text{Ge,Fe})\text{O}_4$	Unique
Eyselite	$\text{FeGe}_3\text{O}_7(\text{OH})$	Unique
<i>Hydroxides</i>		
Stottite	$\text{FeGe}(\text{OH})_6$	Common
Manganostottite	$\text{MnGe}(\text{OH})_6$	Rare
<i>Sulphates</i>		
Itoite	$\text{Pb}_3[\text{GeO}_2(\text{OH})_2(\text{SO}_4)_2]$	Unique
Fleischerite	$\text{Pb}_3\text{Ge}[(\text{OH})_6(\text{SO}_4)_2] \cdot 3\text{H}_2\text{O}$	Unique
Schaurteite	$\text{Ca}_3\text{Ge}[(\text{OH})_6(\text{SO}_4)_2] \cdot 3\text{H}_2\text{O}$	Unique
Cararaite	$\text{Ca}_3\text{Ge}(\text{OH})_6(\text{SO}_4)(\text{CO}_3) \cdot 12\text{H}_2\text{O}$	Unique
<i>Germanates</i>		
Ottjumeite	PbGe_4O_9	Unique
Bartelkeite	$\text{PbFeGe}_3\text{O}_8$	Unique
Carboirite	$\text{FeAl}_2[(\text{OH})_2\text{OGeO}_4]$	Unique
Germanium–lepidomelane	$(\text{K,Na,H}_3\text{O})_2\text{Fe}_6[\text{Ge}_5\text{Al}_3\text{O}_{20}](\text{Cl}_2(\text{OH})_2)(?)$	Unique
<i>Silicates</i>		
Mathewrogersite	$\text{Pb}_7(\text{Fe,Cu})\text{Al}_3\text{Ge}[(\text{Si}_6\text{O}_{18})_2[(\text{OH}, \text{H}_2\text{O})_6]]$	Unique

even unique to one locality. Argyrodite (7% Ge), briartite (14% to 18% Ge), germanite (6% to 10% Ge), renierite (4% to 8% Ge), and stottite (32% Ge) are the only common Ge minerals. Argyrodite, the mineral in which Ge was first discovered, has since been found in several Ag-bearing deposits, e.g., in Sn–Ag deposits of Bolivia (Moh, 1976; Bernstein, 1985; Cunningham et al., 1991; Panteleyev, 1996). Briartite is the Ge equivalent of the Sn-minerals stannite $\text{Cu}_2\text{FeSnS}_4$ –kësterite $\text{Cu}_2\text{ZnSnS}_4$ solid solution. It has been found at Tsumeb, Namibia, and Kipushi, D.R. Congo, and a few other localities, occurring mainly as microscopic

Table 4

Germanium concentrations in minerals from pegmatites, greisens and skarns

Host mineral	Rock types	Ge [ppm]	n	Ref.
Topaz	Pegmatite, greisen	29–700	32	Ofteidal (1963), Schrön (1968), Seim and Schweder (1969)
Quartz	Pegmatite, greisen	0.85–7.1	9	Bernstein (1985)
Alkali feldspar	Pegmatite, greisen	2.4–7.8	26	Novokhatskiy et al. (1967)
Orthoclase	Pegmatite	2.2–6.0	3	Schrön (1968)
Plagioclase	Pegmatite	7.0–9.5	2	Bernstein (1985)
Muscovite	Pegmatite	16.5–62.7	4	Bernstein (1985)
Spodumene	Pegmatite	5–28	4	Novokhatskiy et al. (1967), Higazy (1953)
Lepidolite	Pegmatite	7.7–25	11	Novokhatskiy et al. (1967)
Pollucite	Pegmatite	15–18	2	Novokhatskiy et al. (1967)
Epidote	Skarn	1.1–10	21	Bernstein (1985)
Garnet	Skarn	0.9–180	271	Bernstein (1985)
Clinopyroxene	Skarn	1.1–80	67	Novokhatskiy et al. (1967)

n = number of analyses.

inclusions within tennantite (Bernstein, 1985). Germa-nite and renierite constitute the richest known ores of Ge at Tsumeb and Kipushi. Both minerals have also been found in numerous other localities worldwide, primarily in Cu-rich portions of dolomite-hosted Cu–Pb–Zn sulphide ores, as well as in other epigenetic Cu-rich sulphide ores. Associated minerals include chalcopryrite, bornite, tennantite–tetrahedrite, chalcocite, digenite, and sphalerite (Bernstein, 1985, 1986). Stottite was a major Ge mineral recovered in oxidized ore from Tsumeb.

Like Si, Ge is commonly in 4-fold (tetrahedral) coordination. Their ionic radii (Ge^{4+} 53 pm, Si^{4+} 40 pm) and covalent radii (Ge 122 pm, Si 117 pm) are similar. Germanates and silicates form isostructural compounds (Wittmann, 1966, 1972). Ge is incorporated preferably into weakly-bound $[\text{SiO}_4]$ -tetrahedra and it is largely camouflaged in silicate minerals (Goldschmidt and Peters, 1933). In the Earth's crust, most Ge is found in small amounts (up to a few ppm) in silicate minerals, due to isomorphous substitution of Ge^{4+} for the chemically similar Si^{4+} . The concentration of Ge within silicate minerals depends on the specific silicate group. The highest concentrations tend to be measured in nesosilicates (e.g., topaz, garnet, olivine, titanite), with Ge concentration decreasing in the following order: sorosilicates (e.g., epidote, allanite, zoisite), inosilicates (e.g., amphibole, pyroxene), phyllosilicates (e.g., muscovite, biotite,

chlorite) and tectosilicates (e.g., quartz, plagioclase, K-feldspar) (Hörmann, 1972; Bernstein, 1985) (Table 4). Ge is generally observed to be enriched in olivine and pyroxene relative to quartz and feldspar. However, the variation of the Ge content with the geological environment is of greater significance (Bernstein, 1985).

In contrast to Si, Ge has a stronger tendency for the 6-fold coordination. Thus, the oxide GeO_2 (argutite) crystallizes in the tetragonal rutile–(TiO_2) structure, and not in the trigonal quartz–(SiO_2) structure. Germanates are transformed to octahedral structures at lower pressures than equivalent silicates (Wittmann, 1966). The high electronegativities of $(\text{OH})^-$ and F^- favour octahedral coordination of Ge, e.g., in the minerals stottite $\text{FeGe}(\text{OH})_6$ and manganostottite $\text{MnGe}(\text{OH})_6$ (Strunz and Giglio, 1961). In goethite, FeOOH , Ge substitutes for the six-fold coordinated Fe. The solid solution in goethite probably occurs due to the coupled substitution $2 \text{Fe}^{3+} \leftrightarrow \text{Ge}^{4+} + 2\text{H}^{1+}$ (Bernstein and Waychunas, 1987). Fe^{3+} -hydroxides chemisorptively concentrate anion complexes, e.g., $[\text{VO}_4]^{3-}$, $[\text{AsO}_4]^{3-}$, $[\text{AsO}_3]^{3-}$, $[\text{PO}_4]^{3-}$, $[\text{SeO}_4]^{2-}$, $[\text{SeO}_3]^{2-}$, and also $[\text{GeO}_4]^{4-}$ (Goldschmidt and Peters, 1933; Li, 1982; Bernstein, 1985; Bernstein and Waychunas, 1987). In contrast, Mn-hydroxides only absorb cations. The Ge contents of ocean floor Mn-nodules and terrestrial Mn-oxides are attributed to the combined Fe-hydroxide (Fe-oxide) phases (Voskresenskaya et al., 1975; Voskresenskaya and Ufnarovskaya, 1978; Li, 1982) (Table 5).

Ge contents in vanadates, arsenates, phosphates, molybdates and tungstates have been summarized by Bernstein (1985). Ge concentrations of up to the several hundred ppm have been found in arsenates. Gutzmer and Cairncross (2001) reported 5.2 wt.% GeO_2 in beudantite $\text{PbFe}^{3+}[(\text{OH})_6(\text{SO}_4)(\text{AsO}_4)]$ from Tsumeb.

Table 5

Exceptional germanium concentrations in oxide and hydroxide minerals

Host mineral	Ge [ppm]	Type of mineralization	Reference
Hydrocassiterite	10,000	Porphyry and vein–stockwork Sn–Ag	Moh (1977)
Hematite	7000	Apex mine: oxidation zone	Bernstein (1985)
Goethite	5310	Apex mine: oxidation zone	Bernstein (1985)
Cassiterite	3000	Porphyry and vein–stockwork Sn–Ag	Bernstein (1985)
Magnetite	100	BIF and Lahn–Dill-type deposits	Lange (1957), Sarykin (1977)
Mn oxides and hydroxides	10	hydrothermal veins, oxidation zone	Voskresenskaya et al. (1975)

Vanadates and phosphates from Tsumeb and the Apex Mine, Utah, USA, contain lower Ge concentrations. Even less substitution would be expected in molybdates and tungstates, due to the much larger size of these ions.

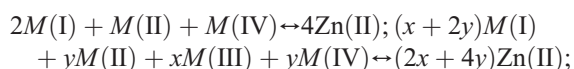
Divalent germanium (Ge^{2+} , ionic radius 73 pm) occurs in the structure of brunogeierite and four sulphate minerals (Table 3). Frondel and Ito (1957) suggested that Ge^{2+} substitutes for Pb^{2+} in anglesite and cerussite from Tsumeb (50 to 500 ppm Ge).

The electronegativity of Ge favours covalent bonding with many ligands; Ge–O bonds have about 31% ionic character and Ge–S bonds only 7% (Bernstein, 1985). The sp^3 -hybrid bonding of Ge^{4+} is combined with tetrahedral coordination in all structures of Ge sulphide compounds. Ge forms important copper–thiogermanate minerals with tetrahedral structures, e.g., germanite, renierite, and briartite. It is a minor to trace element in sulphide minerals, such as sphalerite and wurtzite, and other sulphide minerals, which have sphalerite- or wurtzite-derivative structures, which include enargite, tennantite–tetrahedrite, bornite, luzonite, sulvanite and colusite (Table 6).

Table 6
Exceptional germanium concentrations in sulphide minerals

Host mineral	Ge [ppm]	Type of mineralization	Reference
Enargite	5000	High-sulphidation mineralization	Vlassov (1964)
Sphalerite and wurtzite	3000	Low-temperature epigenetic Zn–Pb	Bernstein (1985)
Stannite	2830	Porphyry and vein–stockw. Sn–Ag	Moh (1976)
Tennantite	1500	Porphyry and vein–stockw. Cu–Mo–Au	Karamyan (1958)
Bornite	1000	Porphyry and vein–stockw. Cu–Mo–Au	Arsenijević (1958)
Sulvanite	1000	Porphyry and vein–stockw. Cu–Mo–Au	Vlassov (1964)
Chalcopyrite	900	Porphyry and vein–stockw. Cu–Mo–Au	Rose (1967)
Colusite	790	Porphyry and vein–stockw. Cu–Mo–Au	Vlassov (1964)
Teallite	690	Porphyry and vein–stockw. Sn–Ag	Moh (1976)
Franckeite	480	Porphyry and vein–stockw. Sn–Ag	Moh (1976)
Tetrahedrite	470	Vein-type Ag–Pb–Zn(–Cu)	Schroll and Azer (1959)
Luzonite	110	Porphyry and vein–stockw. Cu–Mo–Au	Terziyev (1966)
Herzenbergite	110	Porphyry and vein–stockw. Sn–Ag	Moh (1976)
Covellite	100	Porphyry and vein–stockw. Cu–Mo–Au	Arsenijević (1958)

Economically, sphalerite is the most important of all minerals containing relatively high amounts of Ge, up to 3000 ppm (Table 6). No differences in Ge concentrations within sphalerite and wurtzite have been identified (Schroll, 1953b). Enhanced Ge concentrations are obviously confined to low-iron sphalerite. Microprobe studies of Ge-rich sphalerite from the Saint-Salvy deposit (France) showed that Ge substitutes for Zn in the sphalerite structure (Johan et al., 1983; Johan and Oudin, 1986; Johan, 1988; Cassard et al., 1996). The presence of other elements, e.g., Ag, Cu, enhances this incorporation (Moh and Jäger, 1978). Johan (1988) proposed a coupled substitution mechanism for trivalent and tetravalent elements, including Ge^{4+} , in sphalerite, expressed in the following equations:



where $M(\text{I}) = \text{Ag}^+, \text{Cu}^+$; $M(\text{II}) = \text{Cu}^{2+}, \text{Fe}^{2+}, \text{Cd}^{2+}, \text{Mn}^{2+}, \text{Hg}^{2+}$; $M(\text{III}) = \text{In}^{3+}, \text{Ga}^{3+}, \text{Fe}^{3+}, \text{Ti}^{3+}$; $M(\text{IV}) = \text{Ge}^{4+}, \text{Sn}^{4+}, \text{Mo}^{4+}, \text{W}^{4+}$ and x and y are atomic proportions of $M(\text{III})$ and $M(\text{IV})$, substituting for Zn^{2+} , respectively. The equations indicate that the incorporation of trivalent and tetravalent trace elements into sphalerite is possible, owing to the formation of donor–acceptor pairs with monovalent ions (Johan, 1988). Moreover, Ge occupies the tetrahedral sites, rather than the interstitial octahedral positions in natural sphalerites. The incorporation of trace elements, including Ge, into the structure of sphalerite is likely to depend upon the diffusion/growth velocity ratio. Furthermore, the crystal chemistry of the sphalerite structure is important in order to understand the different substitution mechanisms, which may occur simultaneously in natural sphalerites (Möller, 1987; Johan, 1988). There is no evidence for direct substitution of Zn^{2+} by Ge^{2+} in sphalerite and wurtzite (Bernstein, 1985; Johan, 1988; Möller and Dulski, 1993).

Germanium can also be incorporated into sphalerite as micro- and submicrophases. A positive correlation between Ge and Cu suggests the presence of copper thiogermanates (e.g., renierite, and/or germanite, and/or briartite) and between Ge and Ag points to the presence of argyrodite. Such microphases are commonly interpreted as exsolution. Morales-Ruano et al. (1996) summarized, that Ge-rich inclusions may result either from exsolution or from trapping of solids grown independently in hydrothermal solutions. At Cerro del Toro, Spain, the observation of coalescent briartite and tetrahedrite included in sphalerite supports the second hypothesis.

The occurrence of Ge microphases in sphalerite has been confirmed by microprobe analysis (Johan et al., 1983; Johan and Oudin, 1986). They described Ge-

bearing minerals that occurred as microscopic inclusions in sphalerite in several metamorphosed sphalerite deposits from the French Pyrenees. These deposits contain argutite, brunogeierite, briartite, and the germanate equivalents of the silicates chloritoid (carboirite) and lepidomelane (Table 3); quartz, chlorite, zoisite, allanite, and titanite also display exceptionally high Ge concentrations. However, sphalerite from these deposits contains less than 150 ppm Ge (Geldron, 1983; Bernstein, 1985). Incorporation of Ge into Tl- and As-bearing Zn-sulphides is poorly understood. In situ SIMS analysis of banded Zn-sulphides indicates that there are positive correlations between Ge, Tl, As, Fe, and Pb (Pimminger et al., 1985). Kelley et al. (2004) concluded from geochemical studies on trace elements from the Red Dog Zn–Pb–Ag deposit, Alaska: “Elements most likely residing in the sphalerite lattice are Fe, Cd, Mn, Tl, Co, and Ge as suggested by their consistent distributions within and among different types of sphalerite”. However, Slack et al. (2004b) concluded from Zn-poor drill core samples from this deposit: “The coenrichment of Ge and SiO₂ and elevated Ge in the Zn-poor samples suggest that Ge is hosted mainly in quartz, although some could reside in other minerals and in fluid inclusions”. Möller (1987) suggested that the content of Ge in hydrothermal fluids may depend on the leaching temperature, and be roughly indicated by the Ga/Ge ratio in sphalerite. Mladenova and Valchev (1998) used the Ga/Ge ratio in sphalerite as a temperature indicator for hydrothermal fluids in the carbonate-hosted Sedmochislenitsi Deposit, Bulgaria. Occurrence and incorporation of Ge into other minerals associated with sphalerite, e.g., galena and iron sulphides, are poorly known. Ge-, As-, and Tl-bearing microphases in marcasite (up to 470 ppm Ge) were suggested by Duchesne et al. (1983). Ge enrichment in pure galena is unusual. Incorporation of Ge (up to 400 ppm) into galena, however, was observed by Moh and Jäger (1978). Wilkinson et al. (2005) reported Ge concentrations in galena from the Zn–Pb Lisheen Mine, Ireland, in the range 200 to 1300 ppm, determined by microprobe analysis.

The relationship between Ge⁴⁺ and isovalent Sn⁴⁺ is geochemically more important than that between Ge⁴⁺ and Ti⁴⁺. Sn is chemically similar to Ge; the major differences are due to its larger ionic size and its much greater tendency to divalency. The Ge–Sn relationship has been experimentally studied above all by Moh (1976), Moh and Jäger (1978) and Moh (1980) in sulphide, oxide and silicate mineral phases. Extensive substitution of Sn by Ge is known from

canfieldite, stannite, colusite, and cassiterite (Moh, 1976, 1977, 1980). Substitution of Ge²⁺ for Sn²⁺ is discussed in divalent Sn-bearing minerals by Bernstein (1985).

3. Geochemistry

Remarkably, Ge is widely an unreported trace element in geochemical analysis. Ge is unusual in that it exhibits *siderophile*, *lithophile*, *chalcophile*, and *organophile* (i.e., *biolithophile*) behaviour in different geologic environments (Bernstein, 1985).

The *siderophile* behaviour of Ge is reflected by the fact that it can achieve concentrations of up to 500 ppm in the iron phase of meteorites and telluric iron (Hörmann, 1972; Bernstein, 1985).

The *lithophile* behaviour is indicated by slight enrichments of Ge in the continental crust relative to the oceanic crust and the upper mantle (Hörmann, 1972). Igneous rocks commonly contain 0.5 to 6 ppm Ge. There is little variation in the Ge contents of mafic to felsic, and plutonic to volcanic rock types (Table 1). There is, however, a slight tendency for Ge to be concentrated in late magmatic differentiates (e.g., muscovite granites) and in other rocks that crystallize in the presence of a high volatile concentration (e.g., pegmatites, greisens and skarns; Shcherba et al., 1966), or in the presence of late hydrothermal fluids (e.g., hydrothermal sulphide ore deposits). Silicate minerals reported to have high Ge contents in these rocks include topaz (up to 700 ppm Ge), garnet, mica, spodumene, lepidolite, and pollucite (Table 4). The breakdown of mica (muscovite) in such differentiates (granites) may release a significant amount of Ge. This may contribute to the enrichment of Ge in coal, discussed below. Puzanov et al. (1973) described enrichment of Ge, up to 28 ppm, in fluorite from different localities, mainly in alkali granites. They found higher Ge concentrations in early-formed fluorite (220 to 140 °C) than that formed during later stages (130 to 70 °C). The Ge content of siliceous sedimentary rocks and their metamorphic equivalents is closely comparable to that of igneous rocks. Some shales are slightly enriched in Ge, especially those containing organic material (El Wardani, 1957; Burton et al., 1959). Carbonate minerals and rocks show depletion in Ge relative to the crustal average (Table 1). Ge data for evaporites are scarce, but available data indicate that they only contain small amounts (Bernstein, 1985).

The *chalcophile* behaviour of Ge is indicated by its separation from Si and the formation of Ge-sulphides. The chalcophile properties of Ge are evident in sulphur-

rich hydrothermal systems. High-sulphidation states favour Ge concentration through the formation of the thiocomplex $[\text{GeS}_4]^{4-}$ and thiogermanates, preferably as Cu- and Ag-sulphide minerals, e.g., germanite, renierite, briartite and argyrodite (Bernstein, 1985; Paar et al., 2004; Paar and Putz, 2005) (Table 3). Sn- and Cu-sulphides can display relatively high Ge grades (Table 6). In low-sulphidation Zn–Pb–Ag deposits, it seems to be characteristic that elevated Ge grades are associated with an Ag-enriched paragenesis; argyrodite is the common Ge mineral in this type of ore, and the content of Ge in sphalerite is low, mostly in the range of <1 ppm and <10 ppm (Paar and Putz, 2005). In Ag-poor (Ag-free) Pb–Zn deposits, low to moderate sulphidation states and low temperatures allow only minor enrichments in Ge and, above all, cause it to be incorporated preferably into Zn sulphides (sphalerite and wurtzite). Therefore, the highest Ge concentrations occur in non-silicate crustal environments, namely Ag–Pb–Zn-rich and Cu-rich sulphide ore deposits, as well as in coal and lignite (Bernstein, 1985).

The *organophile* behaviour of Ge is evident from its enrichment in organic matter, which is comparable with some Zn-sulphide ores (Table 7). Ge has one of the highest affinities for organic matter of all the elements commonly associated with carbonaceous sediments (Goldschmidt, 1930; Goldschmidt and Peters, 1933; Gluskoter et al., 1977; Bernstein, 1985). Organic matter in lignite and coal takes up various elements, e.g., Ge, B,

Be and U, and to some extent, also Mo and V (Finkelman, 1993). Spears and Zheng (1999) reported data for 24 British coals considered representative of the major U.K. coalfields. These coals, with 4.6% to 37.6% volatile matter, were analysed for 46 major and trace elements. Based on statistical analyses, Ge is the only element for which a consistent organic association can be demonstrated. The Ge enrichment is effected by chemisorptive processes on relatively stable organo-complexes, e.g., lignin and humic acids, onto which Ge can be precipitated as humate complexes (Glockling, 1969; Manskaya et al., 1972). Manskaya et al. (1972) and Bernstein (1985) described the absorption of Ge by humic acids in peat, and the subsequent formation of stable complexes with lignin-derivative compounds. In lignites, Ge will also be absorbed, forming chelates with lignin-derivatives. During coalification, highly condensed aromatic organo-germanium compounds will form; the latter are more stable due to a greater number of Ge–C bonds. The highest Ge concentrations in coals are commonly found in the vitrain fraction. Ge will be lost during progressive coalification processes with the formation of graphite. Only traces of Ge have been detected in graphites and their ashes from metamorphosed Carboniferous coal deposits. In such deposits, Ge is transferred into phyllosilicates during anthracite formation (Janda and Schroll, 1960; Weninger, 1965).

There are striking lateral and vertical differences in the Ge distribution in coal seams. Ge enrichments are

Table 7
Germanium in peat, coal and lignite, coal ash, and oil

Locality	<i>n</i>	Ge in peat, coal and lignite, and oil [ppm]	Ge in coal ash [ppm]	Reference
<i>Peat</i>				
Oldenburg, Germany	1	nr	8	Goldschmidt and Peters (1933)
<i>Coal and Lignite</i>				
Hartley Seam, England		100	Up to 11,000	Goldschmidt and Peters (1933)
US coal		5.7 (mean), 0.6 (median)	nr	Finkelman (1993)
Pennsylvania, USA	6	2–4	20–120	Stadnichenko et al. (1953)
West Kentucky, USA	31	6–12	4–1430	Stadnichenko et al. (1953)
Plzeň basin, Czech Rep.		5–40	Up to 3000	Bouška (1981), Laznicka (1985)
Kuznetsk basin, Russia	31	1.8–5.9	100–1000	Sarykin (1977)
Donetsk basin, Ukraine		3.4	52.7	Sarykin (1977)
Argun basin, Russia		8.2	62	Sarykin (1977)
Russian Far East		nr	100–1000 (max. 3000)	Seredin and Danilcheva (2001)
Assam, India		2.2	Up to 1600	Bouška (1981)
New South Wales, Australia	279	0.4–150	6–2000	Clark and Swane (1962)
<i>Oil</i>				
Azerbaijan	51	0.006–0.068		Kotova and Viktorova (1965)
Orenburg district, Russia	12	0.02–0.69		Guliyaeva and Lositskaya (1959)

n = number of samples, nr = not reported.

most pronounced in upper and lower few cm of seams, and along partings, first noticed by Zilbermints et al. (1936). Meanwhile, this distribution pattern has been observed in coal basins worldwide (Yudovic, 2003). The interior of a thick coal bed often contains less than 1 ppm Ge, while the margins of the same bed can contain several tens of ppm Ge. Thus, in a coal deposit, the average Ge grade is lower in thick seams, and higher in thin seams. Coal streaks and isolated coalified relicts mostly display the highest Ge grades. Breger and Schopf (1955) described thin coaly stringers within the Chattanooga shale (Tennessee, USA) that contain up to 760 ppm Ge; this black shale itself contains only up to 18 ppm Ge. Coal seams deposited on the edge of a sedimentary basin are richer in Ge than coals from the centre.

There is little doubt that the origin of Ge in lignite and coal deposits is mainly epigenetic, occurring during the peat and/or lignite stages of coal formation, due to migrating Ge-bearing fluids. The Ge in these fluids is likely to have been derived from adjacent rocks, especially those with pre-enrichments in Ge, such as differentiated granites (e.g., muscovite granites) or sediments containing organic material. Kaolinitization of Ge-enriched granite intrusions releases the Ge, which can then precipitate in coal and lignite. This has probably occurred in the coal of the granite-residuum-rich basin of Plzeň, Czech Republic. The coal has a high Ge content (up to 3000 ppm Ge in ash), linked to the neighbouring Ge-bearing granitic rocks (Zahradník et al., 1960; Bouška, 1981). A similar connection between granitic rocks and Ge enrichment in coal is reported from the Lincang Basin, Yunnan, China. Zhuang et al. (1998), Lu et al. (2000) and Qi Huawen et al. (2002) summarized, that the Ge mineralization is closely related to sedimentation, diagenesis and thermal processes. The maceral composition, inorganic minerals, trace element contents and huminite reflectance of the coal from the Lincang Basin suggest that the Ge source was mainly a muscovite granite. Ge leached from that granite was transported into the basin, where it was adsorbed by humic substances. Lignite from the Lincang Basin has undergone three thermal processes: (I) peatification, (II) early diagenesis, (III) hydrothermal transformation. During peatification, Ge was adsorbed or complexed by humic colloids. During early diagenesis, the Ge associated with humic acids was hard to mobilize or transport; most Ge was incorporated into the structure of huminite, and only a small amount of the Ge was fixed to residual humic acids as complex compounds or humates. During hydrothermal transformation hot water or fluids from the basement migrated through the coal predominantly along faults and

fractures. Sulphates were reduced by organic matter in the coal, resulting in the formation of pyrite and calcite. This hydrothermal process may also have been significant for the mineralization (redistribution) of Ge.

In contrast, some coal deposits are very poor in Ge, e.g., coal deposits in basins of the Internal Molasse facies, Eastern Alps. There, the surrounding and underlying metamorphic rocks show no evidence for any Ge concentration (Brandenstein et al., 1960).

The mixing of migrating, Ge-bearing fluids with fluids of magmatic origin is assumed to have caused enhanced Ge grades as well as enrichments of an As–Sb–Hg–Tl(–Au) association in coals of the Russian Far East near Vladivostok (Seredin and Danilcheva, 2001). There is no indication for significant Ge enrichment in sapropel and its diagenetic and metamorphic equivalents (Janda and Schroll, 1960). Oil is also poor in Ge (Guliyeva and Lositskaya, 1959; Kotova and Viktorova, 1965; Valković, 1978).

4. Geological setting of Ge-bearing deposits

Ge occurs in a variety of ore deposits of different ages (Fig. 1; Tables 8 and 9). There is still a need for further data to elucidate Ge enrichment processes in a regional and temporal context, but some influences on concentration processes of Ge during the Earth's history can nevertheless be inferred. Such processes coincide with the geologic evolution of hydrothermal base-metal deposits (Zn, Pb, and Cu), including an enrichment in Pb, and probably also geochemical anomalies of Ge, Tl, As in zinc sulphide deposits during time. The evolution of the atmosphere involved a change in the oxidation state of surficial iron at ~2.3 to 2.4 Ga. Since then, the oxidation of Fe²⁺ to Fe³⁺ and the formation of Fe³⁺-hydroxides have facilitated the chemisorptive concentration of Ge. The appearance of cellulose-producing eucariotes and the transformation of cellulose into lignin and humic acid in Proterozoic time gave rise to an enhanced adsorptive mechanism for the concentration of Ge in carbonaceous sediments, coaly black shales and coal. In the Phanerozoic, geochemical concentration processes for Ge were influenced by the change from prevailing dolostones to limestones and by the further evolution of the biosphere and organic matter (coal). Organisms (bacteria) and organic matter have also met the requirements for sulphate reduction, favouring predominantly Phanerozoic sulphide deposition in organic-rich sedimentary rocks (mainly shales) with slight Ge enrichments at low temperatures. Most of the Ge-bearing ore is derived from low-temperature, epigenetic deposits, especially those in sedimentary sequences. Moreover, present or future

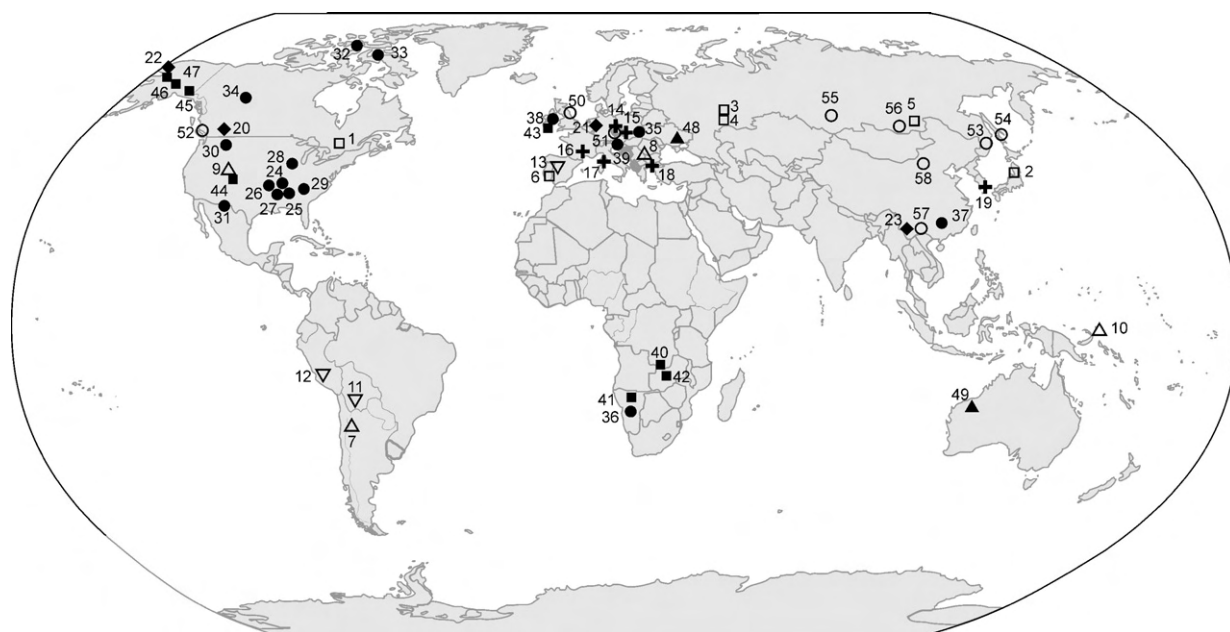


Fig. 1. Germanium-bearing ore deposits. □ Volcanic-hosted massive sulphide (VHMS) Cu–Zn(–Pb)(–Ba) deposits: 1 Abitibi–Belt: Kidd Creek, Noranda, Bousquet 2 Mine, Canada; 2 Kuroko-type (and Besshi-type) deposits, Japan; 3 Gaiskoje, Russia; 4 Bakr Tau, Russia; 5 Gorevskoe and Ozernoe, Russia; 6 Iberian Pyrite Belt: Neves Corvo, Portugal; △ Porphyry and vein–stockwork Cu–Mo–Au deposits: 7 Capillitas, Argentina; 8 Bor, Serbia, and Chelopech, Bulgaria; 9 Bingham, USA; 10 Lihir Island, Papua-New Guinea; ▽ Porphyry and vein–stockwork Sn–Ag deposits: 11 Potosi, Colquechaca, and Porco, Bolivia; 12 Sayapullo, Peru; 13 Barquilla, Spain; + Vein-type Ag–Pb–Zn(–Cu) deposits: 14 Freiberg, Germany; 15 Kutna Hora and Příbram, Czech Republic; 16 Noailhac-Saint Salvy, France; 17 Sardinia, Italy; 18 Kirki, Greece; 19 Wolyu, Korea; ♦ Sediment-hosted massive sulphide (SHMS) Zn–Pb–Cu(–Ba) deposits: 20 Sullivan, Canada; 21 Meggen, Germany; 22 Red Dog Mine, Alaska, USA; 23 Jinding, China; ● Carbonate-hosted base metal (Zn–Pb) deposits (Mississippi Valley-type, MVT; Irish-type, IRT; and Alpine-type, APT, deposits): 24 Central Missouri, USA; 25 Southeast Missouri (Old Lead Belt, Viburnum Trend, Indian Creek), USA; 26 Tristate District, USA; 27 Northern Arkansas, USA; 28 Upper Mississippi Valley (Illinois–Wisconsin), USA; 29 Elmwood–Gordonsville, USA; 30 Pend Oreille, USA; 31 Tres Marias Mine, Mexico; 32 Polaris Mine, Canada; 33 Nanisivik, Canada; 34 Pine Point, Canada; 35 Upper Silesia, Poland; 36 Mount Aukas, Namibia; 37 Fankou, China; 38 Irish-type: Navan, Lisheen, Silvermines, Galmoy and Tynagh, Ireland; 39 Alpine-type: Bleiberg, Austria; Cave de Predil, Italy; Mezica and Topla, Slovenia; ■ Carbonate-hosted base metal deposits: Polymetallic Cu–Pb–Zn–Ge deposits of the Kipushi-type: 40 Kipushi, Democratic Republic of Congo; 41 Tsumeb, Tsumeb West, Kombat and Tschudi, Namibia; 42 Kabwe, Zambia; 43 Gortdrum, Ireland; 44 Apex Mine, USA; 45 Kennecott Mine, Alaska, USA; 46 Ruby Creek, Alaska, USA; 47 Omar, Alaska, USA ▲ Iron oxide ores: 48 Kremenchuk–Krivoi Rog, Ukraine; 49 Hamersley Range, Australia; ○ Germanium in coal and lignite: 50 Durham Coalfield, England; 51 Plzeň, Czech Republic; 52 Lang Bay, Canada; 53 Shkotovskoye and Spetsugli, Russia; 54 Sakhalin Island, Russia; 55 Kuzbas Basin, Russia; 56 Chitinskaya Basin, Russia; 57 Lincang, China; 58 Xilinhaote, China.

sources for Ge are oxide and hydroxide ore deposits as well as lignite and coal.

4.1. Volcanic-hosted massive sulphide (VHMS) Cu–Zn(–Pb)(–Ba) deposits

Defining deposits as VMS (volcanogenic massive sulphide) and/or VHMS (volcanic-hosted massive sulphide) is not the principal focus of this paper. We choose one type name, which is widely recognised: VHMS. We are aware that some of the following deposits are described as VMS deposits elsewhere.

VHMS deposits occur in submarine volcanic rocks of different tectonic settings and of all ages, from Archean volcanic strata to currently active seafloor spreading

ridges. Usually, massive and/or banded to lens-like sulphide orebodies lie above strongly altered pyrite-dominated feeder-zones (Sangster, 1980, 1990; Large et al., 2001). The classification of VHMS deposits is based on ore composition (Zn, Cu, Pb, Ba), host lithology, and tectonic setting (Franklin et al., 1981): (I) Cyprus-type (Cu–Zn), hosted by ophiolites; (II) Abitibi-type, subdivided into IIa, Noranda-type (Cu–Zn), hosted in mafic–felsic volcanic sequences and IIb, Mattabi-type, similar to Noranda-type, but with significant Pb contents; (III) Kuroko-type (Cu–Zn–Pb(–Ba)), occurring in bimodal volcanic suites in island arc or back arc setting.

Ge concentrations of up to 100 ppm in recent ores, formed at the East Pacific Rise and hosted by MOR basalts, have been described by Bischoff et al. (1983).

Table 8
High-grade Ge concentrations in ores

Type of mineralization	Ge-bearing mineral phases	Ge [ppm] 1 < x < 10
<i>Sulphide ores</i>		
VHMS Cu–Zn(–Pb)(–Ba)	Sphalerite, (bornite, renierite, germanite)	100
(Thereof Kuroko-type)	Sphalerite, bornite, renierite	300
Porphyry and vein–stockw. Cu–Mo–Au	CuAs-sulphides, bornite, sphalerite, (renierite, germanite)	x * 10
Porphyry and vein–stockw. Sn–Ag	Argyrodite, (Sn–minerals, sphalerite)	x * 10
Vein-type Ag–Pb–Zn(–Cu)	Argyrodite, sphalerite	x * 100
SHMS Zn–Pb–Cu(–Ba)	Sphalerite, wurtzite	x * 10
MVT, IRT, APT Zn–Pb	Sphalerite, wurtzite	x * 100
KPT Cu–Pb–Zn–Ge	Ge-sulphides, CuAs-sulphides, bornite, (sphalerite)	1000
<i>Oxide ores</i>		
KPT oxidation zones	Iron oxides, iron hydroxides, sulphates, arsenates	1000
Oxidation zones of Sn-sulphides	Secondary tin hydroxide, tin oxide	x * 10
Non-sulphide Zn–Pb	Iron hydroxides; willemite–hemimorphite	x * 10
Iron oxide ores	Magnetite, hematite, martite, goethite	x * 10
<i>Coal and lignite deposits</i>		
Coal and lignite		x * 100
Coal and lignite ash		1000

Mortlock and Froelich (1986) and Mortlock et al. (1993) reported the hydrothermal input of Ge in the Pacific Ocean. Henry et al. (1995) studied the distribution of In and Ge in 180 hydrothermal sulphide samples from different oceanic sites. They found Ge in all environments, except in the Guaymas Basin, Gulf of California, Mexico. They concluded that Ge is an indicator of low temperature, whereas In indicates high temperature; In is coprecipitated with Cu, Zn, and Fe within active chimneys (black smokers) at temperatures between 350 and 260 °C (Schwarz-Schampera and Herzig, 2002). Tufar (1992) reported Ge contents (up to 80 ppm) in Zn–Pb–Cu-rich samples from massive sulphides at the Palinuro Seamount, Tyrrhenian Sea, Italy.

More data are required on the distribution of Ge in Cu–Zn ores of ophiolite-hosted Cyprus-type deposits.

The small amount of data for Ge concentrations in Archean Abitibi-type (Noranda-type and Mattabi-type) ore deposits does not indicate significant Ge enrichment. The giant, volcanic-hosted Kidd Creek massive sulphide deposit, Ontario, Canada, contains 150 Mt of pre-mining sulphide ores. This is partitioned into high-temperature Cu-rich and low-temperature Zn-rich ores, which contain only trace Ge (Walker and Mannard, 1974; Walker et al., 1975; Hannington et al., 1999). Tourigny et al. (1993) presented Ge data from the Bousquet 2 Mine in the southeastern part of the Abitibi Greenstone Belt, Quebec, Canada. Selected samples of Cu–Zn ores contained up to 85 ppm Ge (Table 6), present in Cu-rich ore containing renierite and mawsonite.

Some Ge data are available for Cu–Zn–Pb–Ba ores from Kuroko-type deposits in Japan (Ando, 1964; Nishiyama, 1974; Shimazaki, 1974; Eldridge et al., 1983; Tanimura et al., 1983; Shikazono, 2003). Grades up to 370 ppm Ge in sphalerite and the presence of renierite and Ge-bearing bornite are known for this type of ore deposits, e.g., in the Shakanai deposit. Komuro and Kajiwarra (2004) reported Ge-bearing colusite in the Ezuri Kuroko deposit, Japan; some data suggest local Ge enrichments (Table 7).

The Iberian Pyrite Belt (IPB), Spain and Portugal, comprises about 85 known ore deposits. It is truly a giant among Kuroko-type deposits, according to Misra (2000). The massive sulphide deposits are part of an Upper Devonian to Lower Carboniferous volcano-genic–sedimentary complex, consisting of calc-alkaline felsic volcanics, intercalated tholeiitic–alkaline mafic volcanics, sediments and sedimentary exhalites, and manganese deposits (Leistel et al., 1998). Ge has been reported in the giant Neves-Corvo polymetallic massive sulphide deposit in the Portuguese sector of the IPB. Besides high values in Cu, Sn and Zn, the Neves-Corvo deposit contains elevated levels of Ag, Se, In and Ge (10 to 60 ppm Ge) (Oliveira et al., 1997; Schwarz-Schampera and Herzig, 2002).

A few Ge data are available for VHMS deposits in the Ural Mountain Range (Russia): The Gaiskoye Cu–Zn deposit, 30 km north of Orsk, and the Bakr Tau Cu–Zn deposit, 120 km southeast of Magnitogorsk, are polymetallic and contain Ge. Avdonin and Sergeeva (1999) reported 25 ppm Ge in sphalerite from both deposits. Germanite is present in bornite-rich ore (Prokin and Buslaev, 1999).

The Gorevskoe Pb–Zn deposit, some 500 km east of Lake Baikal, with large reserves/resources, produces Pb and Zn concentrates, and Ge, Ag, Tl, Ga, and In as by-products. The neighbouring giant Ozernoe Zn–Pb deposit in Lower Cambrian volcano-sedimentary rocks represents

Table 9

Ge contents in sphalerite (sph), zinc ore (zo) and zinc ore concentrate (zconc) in hydrothermal ore deposits

Ore type and locality		<i>n</i>	Ge [ppm]		Reference
			Range	Mean	
<i>VHMS Cu–Zn(–Pb)(–Ba)</i>					
East Pacific Rise 21° N	zo	2	65	100	Bischoff et al. (1983)
Juan de Fuca Ridge	zo	2	27	120	Bischoff et al. (1983)
Galapagos Rift	zo	1			Bischoff et al. (1983)
Palinuro Seamount, Tyrrhenian Sea	zo	3	20	46	Tufar (1992)
Kuroko-type deposits, Japan	sph	132	<3	370	Ando (1964)
Bousquet 2 Mine, Quebec, Canada	Sulphide ore	2	<10	85	Tourigny et al. (1993)
Northern Norway	sph	10	<1	5	Oftedal (1941)
Skellefte district, Sweden	sph	32			Gabrielson (1945)
Alpine Paleozoic VHMS	sph	5	<1	16	Schroll (1954)
<i>Vein-type Ag–Pb–Zn(–Cu)</i>					
Freiberg, Germany	sph	9	0.6	1300	Schrön (1968)
Bad Grund, Germany	sph	12	16	110	Möller and Dulski (1993)
Pribram, Czech Republic	sph	3	1	1000	Schroll (1954)
Noailhac – Saint–Salvy, France					
Stratiform	sph	17		700	Barbanson and Geldron (1983)
Veins	sph	16	300	3000	Barbanson and Geldron (1983)
	zconc			750	Barbanson and Geldron (1983)
<i>SHMS Zn–Pb–Cu(–Ba)</i>					
Meggen, Germany	sph	1			Schroll (1954)
Rammelsberg, Germany	sph	1			Schroll (1954)
Graz Paleozoic, Austria	sph	4			Schroll (1997)
Red Dog Mine, Alaska, U.S.A.	zconc				Schmidt (1997)
<i>MVT Zn–Pb</i>					
Upper Mississippi Valley, U.S.A.	sph	6	<20	250	Hall and Heyl (1968)
Central Missouri, U.S.A.	sph	20	2	300	46
Southeast Missouri, U.S.A.	sph	154			11
Viburnum Trend, main stage, U.S.A.	sph	21	5	600	Viets et al. (1992)
East Tennessee, U.S.A.	sph	13			60
Elmwood–Gordonsville, Tennessee, U.S.A.	zconc				400
San Vincente, Peru	sph	6	11	62	18
Benue Trough, Nigeria	sph	13	42	220	
Fankou, China	sph	12	30	170	
Pomerzany, Poland	sph	9	30	800	85
				Median:	50
<i>IRT Zn–Pb</i>					
Tynagh, Ireland	sph	11	1	27	
Navan, Ireland	sph	3	1	72	
<i>APT Zn–Pb</i>					
Bleiberg, Austria	sph	146	22	1500	
	zconc				193
Mežica, Slovenia	sph	41	20	1100	
	zconc				190
Cave di Predil (Raibl)/Italy	sph	23	2	3000	
	zconc				544

n=number of analyses.

a major mining project for Zn, Pb, Ag, Au, Cu, and some other elements, including Ge (Tsarev, 1995; <http://cc.msnsnscache.com/cache.aspx?q=2059130177866> and <http://cc.msnsnscache.com/cache.aspx?q=2062452336093> and <http://www.portergeo.com.au/database/mineinfo.asp?mineid=mn272>).

Total reserves/resources of VHMS deposits are enormous, with 100 Mt estimated for Zn (Misra, 2000). They are a major source of the world's Zn, Cu, Pb, Ag and Au. They usually contain low to moderate amounts of Ge (average \ll 100 ppm). The refining of this type of ore generates Cd, In, Ga, Sn, Sb, Bi, and many other elements, including Ge as by-product.

4.2. Porphyry and vein-stockwork Cu–Mo–Au deposits

There is a large amount of data on porphyry ore deposits, which are the most important source of the world's Cu and Mo, and are also a major source of Au. By-products include Rh, Se, Te, and In. Ge has been reported in association with ores hosted in the peripheral zones of porphyry systems, including late-stage epithermal veins, stockworks and breccias. Ge has been identified in Cu, Sn and Zn minerals.

The “Capillitas diatreme” in Catamarca Province, northwestern Argentina, is located within the Farallon Negro Volcanic Complex. The latter is host to large porphyry Cu–Au deposits (Bajo de la Alumbrera, Agua Rica) (Sasso and Clark, 1998; Proffett, 2003) and genetically related epithermal vein-type deposits (Farallon Negro-Alto de la Blenda, Capillitas). The epithermal veins are hosted in rhyolite, ignimbrite and granite north and west of the Capillitas diatreme. Several stages of mineralization were identified (Marquez-Zavalía, 1999; Paar et al., 2004). These show a complex Cu–Pb–Zn–Fe–As–Sb–Au–Ag paragenesis with Bi, W, Sn, Te, Ge, Cd, In, V, Ni, Co and Tl in traces. Low- and high-sulphidation environments can be distinguished (Putz et al., 2002; Paar et al., 2004; Paar and Putz, 2005). The low-sulphidation assemblage occurs in veins remote from the diatreme; it comprises galena, Fe-poor sphalerite, chalcopyrite, pyrite, Ag-bearing minerals, rhodochrosite, barite and quartz. Ge is present as the mineral argyrodite (and an arsenian argyrodite) and is accompanied by native silver, acanthite, proustite and pearceite. A different Ge-bearing assemblage in dump samples near the “La Rosario vein” is characterized by a mineral assemblage typical for high-sulphidation state. It occurs in the zone of supergene enrichment of a hypogene Cu mineralization. The ore is composed of enargite, luzonite, tennantite, hübnerite, Sn-bearing

minerals (colusite–nekrasovite, stannoidite, mawsonite, stannite–kësterite) and Te-bearing phases (goldfieldite, hessite and various Au tellurides). A subtype of this assemblage contains the Ge-bearing phases putzite and unnamed $\text{Cu}_8\text{Fe}_2\text{ZnGe}_2\text{S}_{12}$ (“Ge-stannoidite”). Another subtype is represented by hübnerite-rich samples and catamarcaite, and in trace amount briartite.

Otherwise, Ge in porphyry Cu–Mo–Au deposits is commonly reported to be enriched in bornite (up to 1000 ppm Ge), enargite, tennantite, luzonite, stannite, and covellite (e.g., in Bor, Serbia (Arsenijević, 1958), in Chelopech, Bulgaria (Terziyev, 1966), in Bingham, Utah, USA (Rose, 1967) and in Chuquicamata, Chile) (Tables 5 and 7). Additionally, Cvetkovic et al. (1999) showed that Ge occurs in microphases (germanocolusite, germanite, and Ge-bearing arsenosulvanite) in the Bor deposit. The latter deposit is part of the 1500 km long Banatitic Magmatic and Metallogenic Belt of Romania, Serbia and Bulgaria (Ciobanu et al., 2002), part of the Alpine–Balkan–Carpathian–Dinaride geodynamic province (Heinrich and Neubauer, 2002). Although the belt has a dominant Cu–Au signature, several deposits feature a marked enrichment in Ge, Sb, Bi, Se, Te, Ag, Pb, Zn, Sn, In and Ga (Cook et al., 2002). Germanite, renierite, germanocolusite, and Ge-bearing arsenosulvanite are identified in the Chelopech deposit (Kovalenker et al., 1986; Petrunov, 1995; Bonev et al., 2002). Chelopech is a high-sulphidation epithermal Cu–Au deposit (Lips et al., 2004), which contains 25 Mt of 1.5% Cu, 4 ppm Au and 10 ppm Ag measured and indicated (Canby, 2005) and is situated in the Panagyurishte district, Bulgaria, where further high-sulphidation and low-sulphidation zones, e.g., at Petelovo, Breznia, Trun, Srebrna (Rakitovo), and Ada Tepe, are current exploration targets (Canby, 2005).

Müller et al. (2002) described microprobe analyses of selected sulphide phases from Landolam, Lihir Island, Papua New Guinea. They reported 550 ppm Ge in chalcopyrite from a hydrothermal breccia, and 120 ppm Ge in tennantite of a late-stage quartz–chalcedony–illite–adularia–pyrite vein. Landolam is considered as transitional between porphyry- and epithermal-style Au-mineralization by Müller et al. (2002) and Gemmell et al. (2004).

Germanium grade data for ore concentrates from porphyry Cu–Mo–Au deposits are unavailable. Ge can be recovered from the flue dust of copper smelters. However, this source probably only makes a minor contribution to total Ge production. We can conclude, therefore, that the worldwide Ge potential of porphyry Cu–Mo–Au deposits is difficult to assess. The peripheral zones of such porphyry deposits, enriched in bornite, tennantite, luzonite and sphalerite, may prove to be fruitful sources of Ge in the future.

4.3. Porphyry and vein-stockwork Sn–Ag deposits

Potosi/Bolivia-type Sn–Ag deposits (stockworks and arrays of ore veins) in subvolcanic, felsic intrusions (mainly dacite to rhyodacite; A-type to S-type) can be enriched in Ge (Ahlfeld and Schneider-Scherbina, 1964; Cunningham et al., 1991; Matthews, 1991; Panteleyev, 1996). Ge is an accessory component of ore deposits in the Bolivian “Ag–Sn belt”. At Colquechaca, ore shoots contained argyrodite in association with Ag-sulphides and -sulphosalts. Ge mineralization has also been reported to occur at Potosi (Cerro Rico), Chocoya-Animas and Tatatsi-Portugalete (Ahlfeld and Schneider-Scherbina, 1964). Mineralization includes argyrodite and Ge-bearing Sn minerals, e.g., canfieldite, stannite, cassiterite, teallite, franckeite and herzenbergite (Moh, 1976; Bernstein, 1985) (Tables 5 and 7). Paar and Putz (2005) reported Pb–Zn–Ag–Sn deposits of the Bolivian “Ag–Sn belt” may contain even high-grade Ge mineralization. Ge is present as the mineral argyrodite, which is usually associated with bonanza-grade silver mineralization composed of Ag-sulphosalts (pyrargyrite, stephanite, polybasite, miargyrite and diaphorite), native silver and acanthite. Paar and Putz (2005) detected a significant Ge anomaly in Ag-enriched ore shoots of the Porco deposit. The Ag–Zn–Pb–Sn deposit Porco, Department Potosi, Bolivia, consists of a swarm of ore veins within the Porco caldera. The Ag–Zn–Pb–Sn mineralization of two veins is significantly enriched in Ge; high-grade Ge ore can be ascribed to argyrodite, which is associated with a high-grade silver mineralization and galena; grab samples yielded up to 2000 ppm Ge (Paar and Putz, 2005). Soler (1987) reported up to 310 ppm Ge and 855 ppm Ga in samples from the Sn-bearing polymetallic Sayapullo ore deposit in the Cordillera Occidental, Peru.

Pascua et al. (1997) reported on Ge in the unique Cd-briartite mineral barquillite in Sn–Ge–Cd–Cu–Fe-bearing sulphides and sulfosalts from the vein-type deposit Barquilla, Salamanca, Spain. Low-temperature secondary ‘wood tin’ can contain up to 1% Ge (Moh, 1977).

The potential of these deposits for Ge exploration is difficult to constrain. Reliable data are not available for Ge grades in concentrates, the recovery of Ge, or for Ge reserves/resources in such deposits.

4.4. Vein-type Ag–Pb–Zn(–Cu) deposits

These deposits are heterogeneous and are hosted by (meta-)sedimentary and magmatic rocks in different tectonic settings. The locally abundant ore veins may be

up to a few m wide, more than 1 km in length, and may extend to depths of more than 1 km (Lefebvre and Church, 1996). The polymetallic Freiberg ore deposit in Saxony, Germany, where Ge was first identified, provides an example of Ag–Pb–Zn(–Cu) mineralization with Ge enrichment (Baumann, 1994; Baumann et al., 1999; Seifert, 1999). For 90% of the mined Zn ore, the Ge grade can be estimated at only 1 to 3 ppm. A substantial amount of Ge, estimated at about 100 ppm, in the remaining 10% of the Zn ore was restricted to a late-stage, low-temperature, Ag-rich mineralization (‘Edle Geschicke’). Ge was concentrated mainly in argyrodite and in botryoidal Zn sulphide (Schrön, 1968; Baumann, 1994).

Sphalerites from epithermal Ag–Pb–Zn vein-type deposits in the Harz Mountains, Germany (e.g., Bad Grund), contain only moderate amounts of Ge (Möller and Dulski, 1993) (Table 6). Variable concentrations of Ge have been analysed in veins of the polymetallic Ag–Pb–Zn Kutna Hora ore district, Czech Republic (Novák et al., 1962). The Ag–Pb–Zn vein-type Příbram ore district, Czech Republic, is situated at a major fault system. Four stages of mineralization are described (Pouba and Ilavský, 1986). Sphalerite formed in the first and second stages contains Ge.

The Noailhac-Saint Salvy Zn–Ge–Ag–Pb–Cd deposit, Tarn, France, was a major Ge source (reserves/resources 500 t Ge). A total of 547,300 t of Zn concentrate (55% Zn, 750 ppm Ge, 350 ppm Ag, 0.6% Pb) were produced between 1973 and 1990 (Cassard et al., 1996). Prior to 1980, this deposit produced 20% of the world’s Ge (Fogliérini et al., 1980; Barbanson and Geldron, 1983). The deposit is hosted within Cambrian sandstones and carbonaceous schists of the pre-Variscan basement, close to a late-Variscan granite batholith. The mineralized, subvertical vein structure is about 10 km long and has an average thickness of 25 m. Several stages, from skarn to low-temperature ore mineralization, are present. The economically important low-temperature, hydrothermal mineralization occurs as a stockwork with numerous veins up to 1 m thick and breccia bodies several m in width. It probably formed in Liassic time (Munoz et al., 1994; Marignac and Cuney, 1999). The main ore mineral is sphalerite, attaining grades of up to 2500 ppm Ge in hand specimen. The high Ge content of this deposit may be attributed to Ge from sphalerites in the Cambrian black shales and carbonates (up to 700 ppm Ge) and the influence of organic-rich fluids (Fogliérini et al., 1980; Barbanson and Geldron, 1983; Munoz et al., 1994).

The Pb–Zn province on Sardinia, Italy, comprises Pb–Zn–Ba ore deposits, hosted largely in Cambrian (meta-)sediments, and late- to post-Variscan Zn–Pb–

Ba–Ag–Cu skarn, vein and paleokarst deposits (Boni et al., 1996). The vein-type deposit at Monte Vecchio contains sphalerite with moderate Ge contents (Schroll, 1954).

The Kirki (St. Phillipi) Ag–Pb–Zn ore deposit in western Thrace, Greece, possibly represents the upper volcanic, base metal-bearing portion of a porphyry system. Sphalerite and wurtzite ores contain up to 70 ppm Ge and enhanced Ga concentrations (Skarpelis, 1995). Nikos Skarpelis (pers. comm., 2005) showed us data commonly in the range 1 to 60 ppm Ge (exceptionally 811 ppm Ge), mean <25 ppm Ge, for Pb–Zn ore samples. Moreover, such samples are significantly enriched in Cd, Ga, In, Sn, and Ag, resembling vein–stockwork Sn–Ag deposits.

Polymetallic ore veins in Cretaceous sedimentary and volcanic rocks at Wolyu (South Korea) contain galena, sphalerite, chalcopyrite and electrum. A late, low-temperature stage included the deposition of argyrodite (Yun et al., 1993), as with the Freiberg ore deposit.

Targets for Ge exploration among this heterogeneous group of ore deposits are preferably late-stage, low-temperature, Ag-rich veins, stockworks and breccia zones in (meta-) sediments (shales, carbonates).

4.5. Sediment-hosted massive sulphide (SHMS) Zn–Pb–Cu(–Ba) deposits

Corresponding to our statements about classification VMS versus VHMS (Sec. 4.1), defining deposits as SMS and/or SHMS (sediment-hosted massive sulphide) is also not the principal focus of this paper. We choose the type name SHMS. SHMS deposits are hosted in rocks formed in sedimentary basins (marine and clastic, including black shales) along continental margins or in intracratonic rift settings. They form massive to semi-massive accumulations of sulphide and sulphate (barite) minerals as stacked, lens-like, tabular bodies on or below the seafloor. They are concordant with their host rocks and continue laterally into a distal sedimentary facies, where they are characterized by minor sulphides, barite, iron oxide, chert and carbonates. Volcanic rocks (lavas and volcanoclastics) may be a minor component of the sediment-dominated associated strata, and intrusions (mafic dikes, sills) may also be present. However, a lack of clear magmatic affiliation is one of the distinguishing features between the SHMS-type deposits and the, otherwise often similar, VHMS-type deposits (Sangster, 1990; Goodfellow et al., 1993; Fontboté and Boni, 1994; Misra, 2000; Sangster, 2002; Kelley and Jennings, 2004).

SHMS deposits constitute a major global resource of Zn and Pb. They are among the largest Pb–Zn deposits,

and examples from the Proterozoic to the recent seafloor are known. Ge occurs as a trace element in Zn sulphides. Ge contents of sphalerite ores from Proterozoic SHMS deposits are commonly low (<10 ppm), e.g., in the polymetamorphic Broken Hill deposit, N.S.W., Australia (2 to 4 ppm Ge; Burton et al., 1959), compared to Phanerozoic deposits (Table 6). There are a few exceptions, e.g., the Sullivan ore deposit, hosted by Middle Proterozoic dominantly clastic metasediments. The Sullivan mine, B. C., Canada, in operation from 1909 to 2001, was a long-standing Ge source from zinc ore concentrates. Germanium dioxide was recovered at Cominco's metallurgical plant at Trail, B.C. (Teckcominco, 2002). Stikine Gold Corp. reported Ge grades in the range 2.6 to 20 ppm in massive sulphides from a drill-interval at the Sullivan Deeps, 4 km from the historic Sullivan mine, but not a fault-off portion of the historic orebody itself (Stikine Gold Corporation, 2004; Schroeter, 2005).

Zn sulphide ores of nearly all Phanerozoic deposits commonly contain <50 ppm Ge. For example, samples from Meggen, Germany, contain 10 ppm Ge; samples from Rammelsberg, Germany, indicated 3 ppm Ge (Schroll, 1954). Paleozoic Pb–Zn deposits near Graz, Austria, contain up to 10 ppm Ge in Zn ore concentrate (Schroll, 1997). Song (1994) reported average Ge contents of 1.4 to 55.5 in sphalerite from different SHMS deposits in China. Besshi-type deposits are similar to Kuroko-type (VHMS) deposits, but are hosted by sediments in volcanic terranes. Kuroko-type and Besshi-type deposits are usually Phanerozoic in age. We did not find data about significant Ge enrichments in Besshi-type deposits in Japan (Komuro and Kajiura, 2004; Kubota et al., 2004; Yakushi and Enjoji, 2004).

Barite and Zn–Pb–Ag massive sulphide deposits are regionally widespread in northern Alaska. The Red Dog Zn–Pb–Ag District, Western Brooks Range, Northern Alaska, contains numerous Zn–Pb–Ag sulphide and barite deposits (Kelley and Jennings, 2004). The Red Dog Zn–Pb–Ag strata-bound massive sulphide bodies are hosted by the Carboniferous Kuna Formation. This formation consists of finely laminated, black, siliceous and carbonaceous shale and mudstone with locally abundant carbonate turbidites (Moore et al., 1986; Dumoulin et al., 2004; Kelley et al., 2004). Deposition of the Kuna Formation took place in an extensional basin and slope setting characterized by anoxic or dysaerobic bottom waters and by high productivity of organic matter (Slack et al., 2004a; Kelley et al., 2004). Paleogeographic reconstructions suggest that mineralisation occurred along a passive continental margin.

The giant Red Dog deposits consist of a cluster of 4 ore bodies (Qanaiyaq, Main, Aqqaluk, and

Paalaaq) that lie within distinct thrust panels that offset a single ore deposit (Jennings and King, 2002; Leach et al., 2004). These four deposits have reserves and resources totalling 140.6 Mt at 16.6% Zn and 4.6% Pb (Jennings and King, 2002; Kelley and Jennings, 2004). Including resources of the Su-Lik (38 Mt at 9% Zn+Pb) and Anarraq deposits (18 Mt at 23% Zn+Pb, and 85 ppm Ag) northwest of Red Dog, the district has about 40 Mt of contained Zn+Pb (Kelley and Jennings, 2004). Massive sulphide mineralization in the Red Dog deposits consists mainly of sphalerite, galena, and lesser iron sulphides (pyrite+marcasite) with a quartz- or barite-rich gangue. Chalcopyrite is rare, except in the southern part of the Main deposit and at the Qanaiyaq deposit (Kelley et al., 2004; Leach et al., 2004; Slack et al., 2004b). A complex mineralization history is defined by four sphalerite types or stages (Kelley et al., 2004) for the Red Dog deposits. The stages are defined primarily by sphalerite type and summarized as follows: (1) early deposition of barite, early brown sphalerite, pyrite and minor galena on or immediately beneath the sea floor in unconsolidated mud; (2) deposition of yellow-brown sphalerite and hydrothermal recrystallization of previously formed barite; (3) deposition of barite, red-brown sphalerite and other sulphides in open space veins and replacement of barite; (4) postore sulphide deposition, including the formation of late tan sphalerite breccias in late veins and open vugs, due to thrusting, large-scale fluid flow and metal remobilization during Brookian orogeny in Jurassic–Cretaceous time. Stages 2 and 3 constitute the main ore-forming events and are volumetrically the most important. Kelley et al. (2004) reported Ge concentrations (ppm) in sphalerite of the four stages from the Red Dog deposits:

	Min	Mean	Median	Max
Stage 1	54	192	149	423
Stage 2	1.5	104	103	261
Stage 3	14	116	82	425
Stage 4	100	249	247	426

Late tan sphalerite has distinctly higher Ge relative to earlier sphalerite (Kelley et al., 2004).

Whole-rock geochemical analyses of unaltered and unmineralised Paleozoic sedimentary rocks from the western Brooks Range, Alaska, have been presented by Slack et al. (2004b). They report Ge concentrations in shales from different formations (range: 1.13 to 3.2 ppm Ge), for Kuna Formation black shale (range: <0.5 to 2 ppm Ge; mean: 0.67 ppm Ge), and for cherts, lithic turbidite and bedded siliceous rocks of the Kuna

Formation (mean: <0.5 ppm Ge). Moreover, Slack et al. (2004b) described Ge concentrations (in ppm) in altered wall rocks of the Red Dog District (Red Dog wall rocks: mean: 3.49; range: <0.5 to 10.5; Anarraq wall rocks: mean: 6.52, range: <0.5 to 75.4). Altered, sedimentary wall rocks in the Red Dog District are characterized by a distinctive suite of geochemical anomalies, especially for Zn, Pb, Tl, As, Sb, Ge and positive Eu anomalies. For mineral exploration (Zn–Pb–Ag) in the Brooks Range, Alaska, and in black shale elsewhere, Slack et al. (2004b) recommend: Ge anomalies (Ge>2.0 ppm), which are hallmarks of hydrothermal fluids in siliceous rocks and sediments, are best identified in district rocks having >85 wt.% SiO₂, and <3000 ppm Zn, to avoid the effect of Ge substitution in sphalerite.

All mining to date in the Red Dog deposits has been from the open pit of the Main deposit, which presently is the most productive Zn mine in the world (<http://www.teckcominco.com/investors/reports/aif-circ/tc-aif-01.pdf>). In 2004, the mine produced 554,200 t of zinc in concentrate (Freeman, 2005). From the opening of the mine in 1989 until 2002 some 29 Mt of ore containing greater than 20% combined Zn and Pb and 64 ppm Ag have been produced. Schmidt (1997) reported an average grade of 60 ppm Ge in zinc concentrate. The Red Dog mine is presently the largest source of Ge in the U.S.A., and Teck Cominco Ltd. as owner and operator of the Red Dog mine is the largest integrated germanium producer.

Sandstone-hosted Zn–Pb(–Ba)(–F) deposits are usually Pb-dominated [‘Laisval-type’ or ‘sandstone lead deposits’ (Misra, 2000)] and Ge-poor. An exception may be the giant Zn–Pb deposit Jinding (also known as Lanping) in northwest Yunnan, China (Kyle and Li, 2002). This deposit is considered to be the largest Zn–Pb deposit in China. It is hosted in Tertiary terrestrial red sandstones in the Lanping continental basin. Sphalerite, galena and pyrite are the predominant ore minerals; moreover, there are large celestine and barite resources. More than 380 orebodies, including 16 major orebodies, have been found. Proven reserves (metal contents) are reported as 2.5 Mt Pb and 12 Mt Zn. Additionally, there are probably very substantial resources. The average ore grade is 1.64% Pb and 8% Zn; the ore is rich in Cd, Tl, and Ag. A few tens ppm Ge have been analysed in sphalerite (Richard Kyle, pers.comm.).

Most SHMS-type deposits contain only low to moderate Ge concentrations. Zn sulphides with grades of at least several tens of ppm Ge can be economically recoverable Ge sources, because even moderate amounts may be removed prior to the hydrometallurgical process during large-scale Zn-production. The Red

Dog Mine is exceptional because of its size and Ge grade. The Jinding deposit may become another Ge source in the future.

4.6. Carbonate-hosted base metal deposits

High-temperature (>300 °C) carbonate-hosted Pb–Zn–Ag replacement deposits (mostly skarns) are formed by magmatic processes. Their commonly iron-rich sphalerites usually contain insignificant Ge concentrations only, but often display enhanced In concentrations (Schwarz-Schampera and Herzig, 2002).

Low-temperature carbonate-hosted Pb–Zn deposits are of interest concerning economically recoverable Ge concentrations in low-iron sphalerites. There is a vast amount of literature about this class of ore deposits, including distinguishing features with other classes of sediment-hosted deposits, e.g., SHMS-type deposits (e.g., Sangster, 1990; Leach and Sangster, 1993; Misra, 2000; Leach et al., 2001; Bradley and Leach, 2003; Wilkinson, 2003; Wilkinson et al., 2005; Symons et al., 2005). The host rocks of such base metal deposits are overwhelmingly unmetamorphosed platformal carbonates—limestones and dolostones—with a strong bias towards dolostones, but locally they can also be shales and are mostly devoid of contemporary igneous (volcanic) rocks. Orebodies may be elongate to lens-shaped, massive, stockwork-like or disseminated. Collapse and tectonic breccias, karst cavities and fault zones are locally mineralized. Discordant orebodies are associated with faults, fractures and breccia zones. Most of the ore occurred either as open-space fillings in breccias or as replacement zones adjacent to breccia zones and faults. It is in most cases clearly epigenetic, precipitated from low-temperature brines. Shale-hosted orebodies are usually concordant and stratabound and orebody dimensions are variable. The mineralogy is relatively simple, characterized by varying combination of sphalerite, galena, fluorite, barite, dolomite, calcite, and quartz. Cu- and Fe-sulphide minerals are of significance only in a few deposits. The assemblages may be complex due to repeated dissolution and precipitation of ore and gangue minerals. The deposits are not associated with or genetically related to igneous rocks, with a few exceptions. The fluids are commonly characterized by temperatures <250 °C (mostly 100 to 150 °C) and salinities in the range 10 to 30 wt.% NaCl equiv. A genetic model for this class of ore deposits can be based on large-scale migration of ore-forming hydrothermal fluids from deep sedimentary basins. They may be in part formation waters from oilfields or coalfields (Kesler, 1996). However, there is no indication

for enhanced Ge grades in Zn ores related to fluids from salt diapirs (Kyle and Saunders, 1996). Mixing with other fluids, e.g., seawater or meteoric water, may play an important role in the formation of such ore deposits. This genetic concept may be applicable in general. However, studies over the years have demonstrated a great diversity, and possibly in origin, among the deposits, which have been included in this class. Heijlen and Muchez (2003) supposed a relationship between paleohydrological conditions and lead isotope composition. We distinguish four types of deposits, namely Mississippi Valley-, Irish-, Alpine-, and Kipushi-type deposits.

4.6.1. Mississippi Valley-type (MVT) Zn–Pb–Fe(–Cu)(–Ba)(–F) deposits

Such carbonate- and locally shale-hosted sphalerite-rich sulphide deposits are distributed worldwide, and have been forming since the Proterozoic. A feature of MVT deposits is a significant age difference between host rock formation and ore mineralization (Sangster, 1990). Metal precipitation is usually due to thermal sulphate reduction. Kendrick et al. (2002), Bradley and Leach (2003), Kesler et al. (2004) and Bradley et al. (2004) have discussed the tectonic controls on MVT deposits. Although Bradley et al. (2004) suppose that favourable conditions for MVT mineralization are possible in extensional settings, the vast majority of MVT-type lead and zinc of the world has, however, come from orogenic forelands or adjacent thrust belts.

The classic major districts of MVT deposits in the USA are the Upper Mississippi Valley (Illinois–Wisconsin), Central Missouri, Southeast Missouri (Old Lead Belt, Viburnum Trend, Indian Creek), Tristate District and Northern Arkansas. Large orebodies are interconnected through weakly mineralized zones. Major ore districts with numerous individual orebodies can extend over several thousand km² (Sangster, 1990; Leach and Sangster, 1993; Appold and Garven, 2000; Leach et al., 2001; Symons et al., 2005).

MVT orebodies display distinctive mineralogies and metal contents. The orebodies contain sulphides of Zn, Pb, and Fe in different ratios, which dominate over sulphides of Cu, minor Ni, Co, Cd, As, Hg and negligible Ag contents. Barite and fluorite contents are very variable. Moderate Ge grades are reported from the classic major districts of MVT deposits in the U.S.A. (Table 6). Ge is hosted by sphalerite and wurtzite; distinct Ge minerals are rarely described. Grades up to 3000 ppm Ge in Zn ores have been reported (Jolly and Heyl, 1968), although Zn ores exceeding 1000 ppm Ge are uncommon. Viets et al. (1992) infer a parallel trend

in the enrichment of Ge (up to a few hundreds of ppm), Ga, and Cu in the depositional sequences of rosin jack sphalerite in Northern Arkansas, Tristate and Central Missouri samples.

The Elmwood-Gordonsville Zn–Pb district, Tennessee, USA, contained an average grade of about 400 ppm Ge in Zn ore concentrate (Misra et al., 1996). The Gordonsville mine near Nashville produced 45,000 t zinc per year, as well as a substantial amount of germanium (one of the largest sources in the world; <http://mbendi.co.za/indy/ming/ldzc/am/us/p0005.html>) prior to its shutdown in 2003.

The Pend Oreille deposit is located in the Selkirk Mountains in northeastern Washington State, USA. Production began in 2004 and the mine is expected to attain an annual output of 83,000 t Zn concentrate (rich in Ge) and 15,000 t of Pb concentrate (<http://www.teckcorp.com/operations/pendoreille/review.htm>). Pend Oreille will become a major US source for Ge, possibly second after the Red Dog mine, Alaska.

Tres Marias Mine in northernmost Chihuahua State, Mexico, is reported to have produced oxide and sulphide Zn ores on a small scale between 1952 and 1992 (average grade of 20% Zn, 6% Pb, and 400 ppm Ge) and is a focus of exploration and development for Zn/Ge in 2005. There are two zones containing Zn–Pb–Ge mineralized breccia in carbonate host rocks (<http://www.wareaglemining.com/s/>).

Zinc sulphides from MVT deposits in Arctic Canada, such as Polaris (closed in 2002), Nanisivik (closed in 2003) and Pine Point, show commonly moderate, rarely high Ge grades (Arne et al., 1991; Leach et al., 2001; Scoyer et al., 2001; Wilson et al., 2002). Zn ore concentrates from Nanisivik contained up to 400 ppm Ge, and were correlated with Ag (Harris and Sangster, 1991).

Zinc ore concentrates from the carbonate-hosted Zn–Pb deposits of the Upper Silesian district, Poland, show grades < 100 ppm Ge (Table 6); these deposits are close to the Carboniferous Upper Silesian Coalfield. The polystage ore mineralization is influenced by coal field water, indicated by local occurrences of dopplerite (Ca-humate). Ge is linked to sphalerite, and associated with Pb, Tl, and As (Sass-Gustkiewicz and Kwiecinsky, 1995; Leach et al., 1996; Sass-Gustkiewicz, 2001). The formation of Ge-humate may explain the low Ge grades of zinc ores. The $\delta^{34}\text{S}$ signatures in sulphides are consistent with bacterial reduction of sulphate.

The unusual MVT Mount Aukas V–Pb–Zn deposit, Otavi Mountainland, Namibia, close to Tsumeb and other Kipushi-type deposits (see below), is hosted by

Neoproterozoic carbonates. Zinc-rich sulphide ores contain up to 30 ppm Ge, 360 ppm Mo, 450 ppm Ag, and 64 ppm Hg; http://www.bgr.de/b423/b423_germanium.htm), and sphalerite 115 ppm Ge on average (Emslie and Beukes, 1981).

The Fankou Pb–Zn deposit, located 48 km NE of Shaoguan City, Guangdong Province, China, is hosted by Middle–Upper Devonian and Lower Carboniferous carbonate and argillaceous rocks, and has been classified as a carbonate-hosted, stratabound deposit (Song, 1984, 1994; Song and Tan, 1996). The Fankou Mine with high-grade ore and large reserves/resources has an annual production capacity of 150,000 t of (Pb + Zn) (<http://www.fkmine.com/>). The deposit contains about 15% Pb+Zn combined, but is also strongly enriched in Ag, Ge, and Ga, and can be entitled as a Pb–Zn–Ag–Ga–Ge ore deposit (<http://www.fkmine.com/>). Song (1984, 1994) reported trace element contents in different types of sphalerite in the range 30 to 170 ppm Ge, 70 to 540 ppm Ga, and 110 to 360 ppm Ag. There are at most traces of Ge in galena and pyrite separates. The Fankou Mine is probably a major Ge source.

In conclusion, most MVT deposits are poor in Ge. However, some MVT deposits contribute significantly to the world's Ge production, and large MVT deposits with enhanced Ge grades may be a prime target for Ge exploration.

4.6.2. Irish-type (IRT) Zn–Pb(–Ag)(–Ba) deposits

Irish-type (IRT) Pb–Zn(–Ag)(–Ba) deposits are hosted in Lower Carboniferous carbonate rocks of the Irish Midlands (Russell, 1978; Hitzman and Large, 1986; Andrew, 1993; Hitzman and Beaty, 1996; Anderson et al., 1998; Everett et al., 1999; Johnston, 1999; Misra, 2000; Fallick et al., 2001; Banks et al., 2002; Blakeman et al., 2002; Hitzman et al., 2002; Wilkinson, 2003; Wilkinson et al., 2005). Ireland contains one of the world's major ore districts, dominated by Zn- and in some cases Fe-sulphides. The largest Irish-type deposit is Navan, with pre-mining resources of some 9 Mt Zn+Pb; Lisheen has 2.8 Mt, Silvermines 1.6 Mt, Galmoy 0.9 Mt and Tynagh 0.6 Mt metals with significant Ge contents. Wilkinson (2003) discussed the validity of the “Irish-type” classification for such carbonate-hosted Zn–Pb(–Ag)(–Ba) deposits of the Irish orefield. He presented a summary of principal geological features of these deposits (p. 980, Table 3) in comparison with MVT deposits. Probably the most characteristic feature of these Irish-type deposits is that the sulphur source is dominantly bacteriogenic ($\delta^{34}\text{S} = -15 \pm 10$). There is a variety of carbonate-hosted base metal deposits in Ireland, some

are hosted in breccia pipes and have close affinities to MVT deposits (e.g., in the Kildara group). Others are characterized by stratabound and sometimes stratiform mineralization (e.g., Navan). A third group is associated with dolomite breccias and cavity fill mineralization (e.g., Lisheen; Johnston, 1999; Wilkinson et al., 2005). Moreover, the Irish orefield is regionally zoned. Published data regarding Ge are rare. The Ge grade of Zn ores from the northernmost deposit group (Navan group) is low (a few tens ppm Ge in sphalerite samples); it increases in the southern Silvermines–Lisheen group, reaching grades in sphalerite samples above 100 ppm Ge (Eyre, 1998). Wilkinson et al. (2005) reported Ge grades (ppm) from drill core samples within the Lisheen deposit, determined by microprobe analysis: 400 to 900 in sphalerite; 200 to 1300 in galena, and 200 to 1000 in tennantite. Besides Ge, Cu and Ag are more common in deposits of southern Ireland (Andrew, 1993; Wilkinson et al., 2005). Argyrodite is reported as a Ge carrier (Johnston, 1999). Furthermore, the ore mineralization changes locally to Cu–Ag–Hg–As–Sb–Ge parageneses, e.g., in the exploited Gortdrum ore deposit (Steed, 1986), which showed characteristics of the Kipushi-type deposits, described below. Kinnaird et al. (2002) reported an apparent temporal relationship between the Lower Carboniferous stratabound Cu–As–Ag–Zn–Pb polymetallic deposits in south-west Ireland, and the Zn–Pb deposits of the Irish Midlands during basin extension in the Carboniferous at 360 to 340 Ma. The difference in ore assemblages between the two areas might be caused by Cu derived from red beds in the south-west, where the limestones hosting the polymetallic deposits are underlain by several km of red beds. In contrast, the Zn–Pb deposits of the Irish Midlands are underlain by Lower Paleozoic greywackes where intervening red beds are either absent or of minimal thickness. Wilkinson et al. (2005) proposed a model for the Lisheen ore deposit and other economic Irish-type deposits: Main-stage ore was precipitated as a consequence of rapid supersaturation, caused by fluid mixing. This process involved relatively high temperature (ca. 240 °C), metal-bearing solutions derived from a basement-equilibrated fluid reservoir (carrying Zn, Pb, Fe, Cd), and shallow, saline (ca. 25 wt.% NaCl equiv.) formation waters rich in bacteriogenic H₂S. Minor metals (Cu, As, Ni, Co) (and in our opinion probably also Ge) are thought to have been stripped from the footwall Old Red Sandstone during hydrothermal alteration. The availability of abundant seawater sulphate, operation of open-system bacterial sulphate reduction, and episodic availability of free oxygen imply that ore formation cannot have occurred at significant depth below the paleoseafloor.

In conclusion, some IRT-type deposits contain elevated Ge grades, similar to some MVT-type and APT-type deposits.

4.6.3. Alpine-type (APT) Zn–Pb deposits

More than 200 Zn–Pb occurrences/deposits are known in Triassic carbonates of the Alps. The term “Alpine-type” (APT) is based on four large Alpine Zn–Pb deposits, that are now abandoned, at Bleiberg, Austria (total production 2.2 Mt Pb+Zn), Mežica, Slovenia (1.5 Mt Pb+Zn), Cave de Predil (Raibl), Italy (1.5 Mt Pb+Zn), Salafossa, Italy (0.5 Mt Pb+Zn) and many minor deposits/occurrences (Brigo et al., 1977). These deposits and most minor deposits/occurrences are hosted in Carnian carbonates and shales (Wetterstein limestone/dolomite and Raibl beds), a few, however, in older Anisian carbonates (Alpiner Muschelkalk: limestone/dolomite), e.g., Topla deposit, Slovenia. A syngenetic origin was formerly widely suggested, as summarized by Brigo et al. (1977). APT deposits show a distinctive Pb isotope composition (Köppel and Schroll, 1988; Schroll, 2005), and a light-sulphide sulphur, which points to a bacteriogenic reduction of coeval seawater sulphate (Schroll and Rantitsch, 2005). Concordant zinc ores show remnants of bacteriogenic activities, e.g., peloids and fossil bacteria (Kucha et al., 2000, 2002, 2005). However, there is evidence for an additional, non-bacteriogenic, hydrothermal sulphur source in discordant Zn–Pb ores at Bleiberg (Schroll and Rantitsch, 2005). Summarizing, the APT deposits show features more similar to IRT than to MVT deposits, e.g., sulphur source dominantly of bacteriogenic origin. Some Zn–Pb deposits/occurrences in Triassic carbonates, however, e.g., in Gorno district, Italy, display features of MVT deposits. Zeeh and Bechstädt (1994) claimed ore emplacement within an intermediate to deep burial environment at up to 250 °C for the Bleiberg ore deposit, which they also classified just as MVT deposit. Kuhlemann et al. (2001) suggested ore formation possibly in Late Triassic to Early Jurassic times. Schroll et al. (2005) conclude for the Bleiberg deposit, that Rb/Sr and Pb age data are consistent with geological evidence indicating a Triassic age of mineralization; they support a genetic model emphasizing the role of bacteriogenic sulphate reduction at low temperatures and at minor depth. This is in accordance with data by Möller and Dulski (1993), who concluded from Ga/Ge sphalerite geothermometry for Bleiberg, that the metals have been leached at low temperatures (about 100 °C). The APT deposits/occurrences were affected by burial and locally by metamorphism during the Alpine orogeny.

Extensive geochemical studies combined with field-work during active mining periods helped to elucidate the geochemical behaviour of Ge and other metals in these ore deposits (Schroll, 1996, 2005). Sphalerite and galena are the principal ore minerals in usually simple mineral assemblages in APT deposits. At Bleiberg, stratabound, locally banded ores are commonly composed of fine-grained sphalerite and colloform sulphides. Discordant ore bodies along faults are interpreted as due to former conduits for ore fluids.

There are discernible trends for Ge enrichments in sphalerites within particular ore deposits and between ore deposits from north to south in the Eastern/Southern Alps (Schroll, 1996, 2005). The Bleiberg deposit is exceptional in the Alpine Pb–Zn province and shows special features, obviously due to complex mineralization processes: Sphalerites from the four economically most important stratabound orebodies at Bleiberg yielded Ge grades of between 160 and 550 ppm (Schroll, 1996). These stratabound sphalerites are commonly richer in Ge compared to discordant and cavity-infill sphalerites (up to 200 ppm). Local Ge enrichments, especially in late stage botryoidal sphalerite (up to 1500 ppm) are in contrast to depletion in Ge in recrystallized, iron-poor sphalerite. Some unique massive and disseminated sphalerite ores in dolomite breccias displayed the lowest Ge grades, on average 160 ppm Ge in zinc concentrate, at Bleiberg. Remarkably, this decrease in Ge was accompanied by a decrease in As and Tl, and a slight increase in Ga and Cu (Schroll, 1996; Schroll et al., 2005). At Mežica, Kuhlemann and Zeeh (1995) reported higher Ge grades in fine-grained sphalerites from the first and last mineralising stages compared to other stages. At Cave di Predil, the last stage mineralization with redbrown botryoidal sphalerite displayed the highest Ge concentration (Schroll, 1954). Schroll et al. (1994) inferred a positive correlation between Ge, Tl and As, and a negative correlation between this association and Cd on a statistical basis from 150 ore samples from the Bleiberg deposit. The same is true for Cave di Predil, from where Brigo and Cerrato (1994) obtained positive correlations within the associations Ge, Tl and As, as well as Cd, Sb and Ga, and negative correlation between both associations, based on 111 sulphide-rich ore samples. Schroll (2005) used Pb isotope data from APT deposits and concluded on a statistical basis that Pb as well as Ge, As and Tl are derived from the upper crust, i.e., an old basement.

On a regional scale, sphalerite concentrates (about 57% Zn) from the Northern Tyrolean Limestone Alps contain on average 150 ppm Ge; from Bleiberg and

Mežica, both in the Drau Range district, some 200 ppm Ge; and from Cave de Predil in the Southern Alps, about 500 ppm Ge (Table 6). Orebodies in Anisian strata commonly contain lower Ge grades than those in Carnian strata (Schroll, 1996).

The combined pre-mining resources at Bleiberg, Mežica and Cave de Predil are estimated at 500 t Ge. Some 200 t Ge (174 t Ge from Bleiberg) have been recovered. The Austrian Ge reserves/resources in APT deposits, hosted in Triassic carbonate rocks, were estimated to be approximately 70 t Ge in 1985 (Cerny and Schroll, 1985). APT deposits have been an important source for the world's Ge production in the past, and remain a target for future Ge exploration.

Brigo et al. (2001) described a Zn–Pb–Ba–F mineralization in a pervasively silicified lithological unit capping an unconformity (old landscape) on top of Devonian carbonates in the Carnic Alps and Karavancs (Italy, Slovenia, and Austria). This Siliceous Crust Type (SCT) ore mineralization has supposedly formed by a diagenetic process at about 100 °C, involving fossil Devonian seawater. Sphalerite samples display moderate Ge concentrations, on average about 50 ppm (Peter Möller, pers. comm., 2005).

4.6.4. Kipushi-type (KPT) polymetallic deposits

Tsumeb, Kipushi and Kabwe are three major polymetallic sulphide deposits hosted by Neoproterozoic metacarbonates in the Pan-African Damara–Lufilian fold belt. Each deposit consists of epigenetic, massive, pipe-like orebodies. Trueman (1998) summarized data regarding the synonymous ‘Tsumeb-type’ or ‘Kipushi-type’ carbonate-hosted, polymetallic ore deposits as a class of Cu–Pb–Zn deposits. Cu, Pb, and Zn are commonly associated with rare chemical elements, e.g., Ge, Ga, Ag, In, As, Cd, Sn, Co, Ni, Sb, Mo, Re, V, W and Au (Lombaard et al., 1986; Melcher, 2003; Melcher et al., 2003). We use the term “Kipushi-type” for polymetallic, carbonate-hosted deposits with evidence for high sulphidization, i.e., including minerals, e.g., enargite, tennantite–tetrahydrite, colusite, and Ge-sulphides (Table 3). These deposits show some common characteristics: The ore mineralization is usually hosted by dolomite and/or limestone. Ore deposits are usually coincident with a zone of dolomitization. The pipe-like, tube-like or tabular ore deposits are irregular, discordant and often elongated in one direction up to more than 2000 m. Massive ores, stringer/stockwork ores, breccia and fracture fillings, as well as disseminated mineralization styles occur and grade into one another. Different breccia types may be present as a result of karst

environment (e.g., collapse breccias) and hydrothermal fracturing. The hosting carbonate rocks are embedded within a sequence, which typically includes clastic sediments and were deposited in shallow marine, intertidal, shabka, lagoonal or lacustrine environments; large ore deposits are commonly within thick sedimentary sequences. These host rocks represent intracratonic platform and rifted continental margin sedimentary sequences. KPT deposits form in proximity to a redox boundary between reduced carbonates and oxidized clastic sediments (sandstone–siltstone–shale). Evaporites (gypsum, anhydrite) in the sedimentary sequences seem to be widespread; they may have enhanced brine salinity and contributed sulphur. Chetty and Frimmel (2000) concluded that the distribution and availability of evaporites during basinal and orogenic fluid flow are crucial factors that control the nature and position of KPT deposits in Namibia. Magmatic rocks are absent or unrelated to ore mineralization. Most authors agree that KPT deposits formed from hot fluids (250 to 450 °C). Frimmel et al. (1996) and Chetty and Frimmel (2000) supposed that fluids at Tsumeb and Kombat were at 370 to 405 °C. Trueman (1998) suggested that different fluids could have prevailed in some deposits within oxidized and reduced strata leading to different metal assemblages. This could explain why only some deposits have a significant Ge component. KPT deposits often occur in clusters and/or in proximity to (in the same basin with) associated deposit types, e.g., carbonate-hosted MVT Zn–Pb and stratiform Cu deposits. Chetty and Frimmel (2000) proposed an orogenic brine model for KPT deposits in Namibia, and a possibly heat flow-driven circulation of basinal brines for the adjacent MVT Mount Aukas mineralization.

The principal ore minerals of KPT deposits are mostly galena, sphalerite, chalcopryrite, bornite, chalcocite, tennantite, and enargite. Sphalerite is typically not the major carrier of Ge; its Ge concentrations are usually moderate, mostly <100 ppm Ge (Lombaard et al., 1986; Trueman, 1998; Melcher et al., 2003). Important Ge carriers are Ge minerals (e.g., renierite, germanite, briartite, argyrodite and germanosulvanite), stannoidite, enargite and tennantite–tetrahedrite. Germanite and renierite-rich ores grading up to 0.83% Ge were formed in early stages of Cu sulphide precipitation (Melcher et al., 2003), and Ge ore enrichments are locally abundant, e.g., at Tsumeb (Intiomale and Oosterbosch, 1974). Pyrite may be common or virtually absent. Other common to rare minor minerals include arsenopyrite, marcasite, magnetite, gallite (CuGaS₂), Ni–Co arsenides, carrolite, molybdenite (Bernstein, 1985; Trueman, 1998).

Examples of Ge-bearing KPT deposits include Tsumeb, Tsumeb West, Khusib Springs, Kombat and Tschudi (Namibia), Kipushi (D.R. Congo), Kabwe (Zambia), Apex (Utah, USA), Kennecott, Ruby Creek and Omar (Alaska, USA), Gortdrum (Ireland) (Söhnge, 1964; De Vos et al., 1974; Intiomale and Oosterbosch, 1974; Bernstein, 1985, 1986; Bernstein and Cox, 1986; Folger and Schmidt, 1986; Hitzman, 1986; Innes and Chaplin, 1986; Lombaard et al., 1986; De Magnee and Francois, 1988; Schneider, 1989; Kamona and Friedrich, 1994; Frimmel et al., 1996; Trueman, 1998; Kamona et al., 1999; Chetty and Frimmel, 2000; Melcher, 2003; Melcher et al., 2003; http://www.bgr.de/b423/b423_germanium.htm).

The Tsumeb deposit consists of an irregular, sub-vertical, pipe-like orebody, proven to a depth >1700 m within Neoproterozoic dolomite (Söhnge, 1964; Lombaard et al., 1986; Melcher et al., 2003). The ore pipe consists of massive sulphide bodies concentrated mainly at the periphery of the deposit and low-grade disseminations in a dolomite breccia and feldspathic sandstones (Lombaard et al., 1986). The brecciation associated with the orebody is explained by hydraulic fracturing and fluidisation caused by overpressured hydrothermal fluids along a conduit formed at the intersection of two fracture planes (Theron and Beukes, 1995). Tsumeb is famous for its large number of partly unique minerals. Main ore minerals: Galena, sphalerite, tennantite, pyrite, digenite; minor ore minerals: enargite, bornite, chalcopryrite. Ge is enriched in different minerals, especially in germanite and renierite. Ge-rich ores display enrichments in Ga, In, As, Mo, and W (Melcher et al., 2003). Moreover, Tsumeb's oxidation zone contained high-grade Ge ore (see below). Mining at Tsumeb from 1905 to 1996 produced about 30 million t ore, and 5.4 Mt combined metals (1.7 Mt Cu + 2.8 Mt Pb + 0.9 Mt Zn, as well as Ge, Cd, As, Sb, Ag and Au; Kamona et al., 1999; Melcher, 2003; Melcher et al., 2003). Average ore grade: 10% Pb, 4.3% Cu, 3.5% Zn, 100 ppm Ag, 50 ppm Ge (Lombaard et al., 1986; http://www.bgr.de/b423/b423_germanium.htm). Prior to mining, the amount of Ge in the orebody was calculated to be 2160 t mostly in the form of germanite (Lombaard et al., 1986), but only 87 t Ge have been recovered during the mining period (Melcher, 2003). 2.9 million t of slags, grading 9% Zn, 2.05% Pb, 183 ppm Ge, 200 ppm Ga, and 170 ppm In, could yield about 800 t Ge, thus representing a major Ge source (http://www.zincoc.com/hr_pages/Tsumeb.htm; http://www.bgr.de/b423/b423_germanium.htm). ZincOx Resources plc reported on 30 September 2003: "The Tsumeb project represents the first of our slag recycling targets. ...We

are negotiating an extension to our option to purchase the slags in order to have sufficient time to test the behaviour of the slags, but particularly the germanium, using the Polykilm technology. ...The global resource now stands at 2,043,180 tonnes containing 9.03% Zn and 262 ppm Ge, of which the central part contains a measured resource of 744,500 tonnes with a grade of 9.52% Zn and 376 ppm Ge” (<http://cc.msnsocache.com/cache.aspx?q=2081925567277> and [lang=de-DE](http://cc.msnsocache.com/cache.aspx?q=2081925567277) and [FORM=CVRE2](http://cc.msnsocache.com/cache.aspx?q=2081925567277)). We found no data indicating there was any current Ge recovery at Tsumeb.

Data about other KPT deposits in Namibia have been reported as follows: Tsumeb West (3 km westwards Tsumeb City): Strong enrichments in Cu, Pb, Zn and Ag, but only minor concentration in Ge (<10 ppm). Khusib Springs: Massive Cu ore (500,000 t ore with 10% Cu, 1.8% Pb, 584 ppm Ag) composed of tennantite, enargite, galena and pyrite, with lesser amounts of sphalerite and Ag-rich sulphosalts. An average of 40 ppm Ge is mainly hosted by Ge-bearing colusite (Melcher, 2003). Tschudi (20 km westwards Tsumeb City): Sulphide copper deposit (57 million t, 0.76% Cu). Oxidised ores on farm Tschudi are enriched in Cu, Pb, Zn, As, V, Ge (up to 60 ppm), and in Ag, Ga, Hg, Sb, Sn, Tl, U, and W. (http://www.bgr.de/b423/b423_germanium.htm). Kombat: Pre-mining resources 27 million t Cu–Pb–Ag ore; Ge in bornite–chalcopyrite and rare colusite and renierite (Innes and Chaplin, 1986; Deane, 1995; Frimmel et al., 1996).

The ore lenses of the Kipushi Mine (30 km west of Lubumbashi) occur within cavities and collapse breccias along a fault between dolomitic shale and dolomite, and sulphide replacement zones extend along fracture zones and bedding planes. A primary Zn-dominated mineralization consists of sphalerite, galena, pyrite, and arsenopyrite, with locally abundant renierite, rare germanite and gallite; it is superimposed by a Cu-dominated mineralization of cobaltiferous chalcopyrite, Ge- and Ag-bearing bornite and molybdenite (Intiomale and Oosterbosch, 1974; Cox and Bernstein, 1986; De Magnee and Francois, 1988; Chabu, 1990). Pre-mining reserves/resources of Cu–Pb–Zn ores at Kipushi are estimated to have been 70 Mt averaging 4.8% Cu, 8.8% Zn and 0.5% Pb (Trueman, 1998). The mine at Kipushi produced between 1925 and 1986 3.8 Mt Cu, 5.9 Mt Zn, 0.4 Mt Pb, 45,000 t Cd, and 120 t Ge, as well as other elements, e.g., Ag and Co. (<http://www.portergeo.com.au/database/mineinfo.asp?mineid=mn261>). A project for a 20 t/y Ge recovery at Kokkola, Finland, from slag deposited at the Lubumbashi plant has been reported (Anonymous, 2002). There is a Ge recovery at Kokkola from alloys stemming from the refining of

cobalt tailings from Lubumbashi (<http://cc.msnsocache.com/cache.aspx?q=2078181101329> and [lang=de-DE](http://cc.msnsocache.com/cache.aspx?q=2078181101329) and [FORM=CVRE](http://cc.msnsocache.com/cache.aspx?q=2078181101329)).

The Kabwe deposit in Zambia (formerly known as Broken Hill) consists of four main pipe-like orebodies (Kamona, 1993; Kamona and Friedrich, 1994; Kamona et al., 1999). The primary mineralization is composed of massive sphalerite, galena and pyrite, with minor amounts of chalcopyrite and traces of briartite and renierite. Zn (1.8 Mt), Pb (0.8 Mt) and by-products of Cu, Ag, Cd, and V have been produced from the mine. We have no data about Ge recovery.

The Apex Mine, Utah, is unique, but displays characteristics of KPT deposits. A brecciated, tube-shaped orebody has been thoroughly oxidised to at least 425 m below surface (Bernstein, 1986). Only pieces of unreplaced primary ore contain pyrite, galena, sphalerite and chalcopyrite. Ge was concentrated in the oxidation zone (see below). Maximum grades of 0.5 wt.% Ge and 0.5 wt.% Ga, with an average grade of some 650 ppm Ge, have been reported (Bernstein, 1985, 1986; Bernstein and Cox, 1986; Bowling, 1988). The abundance of Cu, Ge, Ga and As in the supergene ore implies the former presence of sulphides and sulphosalts, e.g., renierite, germanite and gallite, containing these metals in the primary ore (Bernstein, 1986).

Resources at Ruby Creek, Alaska, are 90 Mt grading 1.2% Cu. The occurrence of Ge minerals (renierite, germanite) is described (Bernstein and Cox, 1986; Hitzman, 1986; Trueman, 1998). Kennecott, Alaska, production was at 12.4% Cu and 95 ppm Ag. Ge minerals are not reported from Kennecott and from Omar (Copper Hill), Alaska (Bateman and McLaughlin, 1920; Folger and Schmidt, 1986). However, both deposits contain minerals, such as tennantite–tetraedrite, bornite, carrollite, and digenite, which are often Ge carriers. The exploited Irish Gortdrum ore deposit with a Cu–Ag–Hg–As–Sb–Ge paragenesis (Steed, 1986) displays characteristics of KPT deposits, but is neighbouring and genetically related to IPT Zn–Pb (–Ag)(–Ba) deposits.

KPT deposits are mainly Neoproterozoic, in part Phanerozoic, in age and are frequently gently folded and locally intensely faulted. (Ge-rich) KPT deposits in southern Africa are discussed in the context of extreme climatic signature (“Snow ball Earth”) and increased production of organic matter in Neoproterozoic time (Trueman, 1998; Melcher, 2003). Kamona et al. (1999) report about age of ore formation of the three major KPT deposits: Emplacement of the mineralization took place during (Tsumeb and Kabwe) or after (Kipushi) periods of deformation related to orogenies. Fluid transport and

ore emplacement within host carbonates occurred as a result of fluid expulsion during tectonic movements associated with Pan-African orogenesis at about 530 and 680 Ma in the Owambo and Kabwe basins to form the Tsumeb and Kabwe orebodies, respectively. In the case of the Kipushi deposit, fluid transport and ore emplacement could be related to post-tectonic igneous activity at ~455 Ma. Thus, the different model ages of the deposits demonstrate that ore formation did not result from a single mineralizing event throughout the Pan-African fold belt. Moreover, Pb isotope data from the Tsumeb and Kabwe deposits indicate that the ore Pb was derived from upper crustal rocks. Pb isotope ratios from the Kipushi deposit are characteristic of ore Pb, derived from a mixture of crustal and mantle source reservoirs (Kamona et al., 1999).

KPT ore deposits are rare, but in some cases contain exceptional amounts of Ge. A few deposits display grades up to several hundreds ppm Ge and comparatively large Ge reserves/resources, usually in Cu-rich sulphide ores. Different Ge minerals, e.g., germanite, renierite and briartite, have been identified in such sulphide ores. KPT ore deposits and their slags at smelters are recommended targets for Ge exploration.

4.6.5. Germanium in oxidation zones of Kipushi-type deposits

High-grade Ge concentrations in oxidation zones are known from the Tsumeb orebody and the Apex Mine. Söhne (1964) described a fracture zone close to the Tsumeb orebody that extends from the surface to great depth. Meteoric water has caused an oxidation to occur at a depth below 900 m, forming a lower oxidized zone, where the fracture zone intersects the pipe-like, subvertical sulphide orebody. This oxidized zone is famous for its variety and beauty of secondary minerals. Within this oxidized zone, the primary minerals germanite and renierite have been altered to Ge oxides (brunogeierite, otjissimeite, bartelkeite), Ge hydroxides (stottite, manganostottite) and Ge hydroxy-sulphates (itoite, fleischerite, schaurteite), Pb-silicate (mathewrogersite) and Ge-rich beudantite (Söhne, 1964; Bernstein, 1985, 1986; Melcher et al., 2003), and eyselite (Roberts et al., 2004). Ge also occurs in willemite (up to 1280 ppm) and in arsenates, e.g., olivenite, adamite (up to 2800 ppm), duftite–bayldonite (up to 1100 ppm), mimetite (up to 500 ppm) and cerussite (Fronzel and Ito, 1957; Fronzel and Strunz, 1980; Lombaard et al., 1986; Melcher, 2003; Melcher et al., 2003). Fe-hydroxide samples are reported to be enriched in Ge (up to 2.5 wt.%) and Ga (up to 0.8 wt.%) (Melcher,

2003). At the oxidation zone of the Apex Mine, goethite is the most important ore mineral for Ge, containing up to 5310 ppm Ge, and hematite up to 7000 ppm Ge. These Ge grades exceed those in primary sulphides. Maximum grades of 5000 ppm Ge and 5000 ppm Ga in samples, and an average grade of some 650 ppm Ge have been reported (Bernstein, 1985, 1986; Dutrizac et al., 1986) (Table 8). Thus, significant amounts of Ge occur in the oxidation zones of the Ge-bearing sulphide deposits at the Tsumeb Mine and the Apex Mine. The oxidation zones of other Ge-bearing sulphide deposits may represent a target for Ge exploration.

4.6.6. Sediment-hosted stratiform Copper (SSC) deposits

Data about Ge concentrations in sediment-hosted stratiform copper deposits (SSC) are rare. Such data suggest that the sphalerites of the German Kupferschiefer contain 3 to 14 ppm Ge (Knitschke, 1966), and of the Marl Slate in Great Britain 5 to 20 ppm Ge (Shazly et al., 1957).

4.7. Germanium in non-sulphide Zn–Pb deposits

Oxidation zones of Ge-bearing Zn–Pb sulphide deposits are in part depleted in Ge (Schroll, 1953a). Ge is not retained in Zn-carbonate. However, it may be retained in goethite and hematite and in the Fe-hydroxide stottite and the Zn-silicate hemimorphite. Large non-sulphide zinc deposits are presently a target for exploration and mining, because high-grade zinc carbonates and zinc silicates can now be treated by hydrometallurgical processes. The Padaeng deposit in Thailand was the first non-sulphide deposit, where this extraction method was applied in 1984 (Fillipou, 2004). The Zn–Pb deposit Mehdiabad, Iran, (15.6 million t Pb–Zn ore, grading 7.2% Zn and 2.3% Pb) in Cretaceous carbonates is another example (Chapple, 2003).

Non-sulphide zinc deposits are divided into supergene and hypogene types (Hitzman et al., 2003). Such supergene non-sulphide deposits are formed primarily due to the oxidation of zinc sulphides. Zinc carbonates (smithsonite and hydrozincite) and zinc silicates (hemimorphite, willemite and sauconite) occur in the oxidized zone (gossan) of low-temperature, carbonate-hosted Pb–Zn and in high-temperature replacement deposits. Ge data from supergene zinc ores and minerals are rare. Zinc carbonate and zinc silicate minerals from Cave de Predil and Bleiberg show different capacities to retain Ge: zinc carbonates <10 ppm Ge, hemimorphite, however, up to 1000 ppm Ge (Schroll, 1953a). Supergene zinc ores (hemimorphite–smithsonite and Ge-bearing

clays) from the Shaimerden zinc deposit, Kazakhstan, contain 8 to 15 ppm Ge, compared to 35 ppm Ge in massive zinc sulphide ore (46 wt.% Zn) (Boland et al., 2003). Ge may also be absorbed by iron hydroxides in weathered iron sulphide-rich Pb–Zn deposits. Hypogene non-sulphide zinc deposits appear to be rare; they probably result from mixing of a reduced, zinc-rich, sulphur-poor fluid with an oxidised, sulphur-poor fluid (Hitzman et al., 2003). They contain willemite or willemite–franklinite–sphalerite assemblages, e.g., willemite–franklinite ores occur at the Franklin and Sterling Hill deposits, New Jersey, USA. Only <10 ppm Ge in willemite from Franklin, but 47 to 360 ppm Ge from some localities in New Mexico and Utah, have been reported (Scheffer, 1966).

Supergene non-sulphide Pb–Zn deposits account for some 10% of world's Zn reserves (Borg et al., 2002), and some may be derived from Ge-rich sphalerite. Nevertheless, the rare Ge data from non-sulphide zinc deposits has led us to believe that such deposits may not represent prime targets for Ge exploration, except willemite–hemimorphite-rich deposits.

4.8. Germanium in Fe-oxide ores

The enrichment of Ge in Fe-oxide ores has often been reported. However, no data have been found regarding significant amounts of Ge in Fe-oxide minerals of skarns. Vakrushev and Semenov (1969) noted an average Ge concentration of 10 ppm in magnetite from magnetite–hematite ores from (metamorphosed) 'volcanogenic–sedimentary deposits', and 2.5 ppm in 628 samples from skarn deposits. Bekmukhametov et al. (1973) reported Ge grades of up to 70 ppm in 'volcanogenic–sedimentary' magnetite–hematite, up to 20 ppm in magnetite from vein deposits, up to a few ppm in Fe-oxides from skarns, and up to several ppm from supergene limonites within Fe-deposits from Kazakhstan. Some data have also been presented from the Archean–Paleoproterozoic Algoma-type banded iron formations (BIF) and the predominantly Paleoproterozoic Superior-type BIF (Sarykin, 1977). BIF include giant and supergiant iron concentrations. They formed in sedimentary basins, in which four sedimentary facies are distinguished: (I) oxide facies (iron oxides and chert), (II) silicate facies (Fe-silicates, e.g., greenalite, thuringite), (III) carbonate facies (siderite), (IV) sulphide facies (pyrite-bearing black shales). The highest concentrations of Ge are in the oxide facies. Oxide ores containing up to 38 ppm Ge are reported in BIF from the Hamersley Range, Australia (Davy, 1983). Ores from Kremenchuk-Krivoi Rog, Ukraine, show similar Ge

contents, with average grades of 27 ppm in hematite and 43 ppm in magnetite (Sarykin, 1977). Hematite and magnetite from the small Lahn–Dill-type deposits in Germany contain up to 20 ppm Ge (average 8 ppm Ge) and up to 100 ppm Ge (average 40 ppm Ge), respectively (Lange, 1957; Schrön, 1968). In contrast, oolitic Fe-ores (e.g., Minette ores in France, and Salzgitter ores in Germany) are Ge-poor, containing <10 ppm Ge (Goldschmidt and Peters, 1933; Lange, 1957) (Table 8).

Giant and supergiant BIF deposits are an enormous potential resource for Ge. One billion t of ore containing 20 ppm Ge would yield 20,000 t of Ge. Aside from the recovery issue, the high costs of recovering Ge from such Fe-ores mean that at present and in the near future it is not economically viable to produce Ge from BIF deposits.

4.9. Germanium in coal and lignite deposits

The organophile (i.e., biolithophile) behaviour of Ge has been described in Sec. 3. Ge in coal and lignite is of interest, since Goldschmidt (1930) and Goldschmidt and Peters (1933) published data of high Ge concentrations in coal ashes, in particular from the Hartley Seam, Durham Coalfield, U.K. (up to 1.1% Ge). Coal and lignite deposits contain Ge, with grades that vary over several orders of magnitude, both regionally and within particular deposits (Bernstein, 1985; Laznicka, 1985) (Table 9). The Ge grades in some coal deposits are even lower than the abundance of Ge in the Earth's crust (1.6 ppm Ge). In general, coal contains inorganic material that after combustion becomes coal ash and flue dust. Reported maximum concentrations are 0.4 wt. % Ge in coal and 9 wt.% Ge in coal ash (Krejci-Graf, 1972). Sulphur-poor coal, used primarily in steam power plants, often contains about 1 ppm Ge. Upon combustion the ashes contain up to 10 ppm Ge, a 10-fold increase in concentration (Stadnichenko et al., 1953; Valković, 1983).

Germanium was first recovered from coal ash and flue dust generated by coal-fired power stations in Great Britain and the Soviet Union, and is currently recovered from coal both in Russia and in China. We did not find evidence for serious efforts for Ge recovery from coal in western countries, except in the Fargo Oil's Lang Bay property, Canada (Queneau et al., 1974).

In the former USSR, coal deposits have been the main source for Ge (Avdonin and Sergeeva, 1999). After the break-up of the USSR, the recovery of Ge from coal was shortly suspended in Russia. However, this

recovery is considered again as economically attractive (Kats et al., 1998; Seredin and Danilcheva, 2001). Ge is reported from 21 Russian deposits, mainly coal deposits, by Kats et al. (1998). Exceeding 50% of total Ge reserves in Russia are accumulated in Ge-bearing coals in Russian Far East (Novikovskoye deposit on Sakhalin Island; Shkotovskoye and Pavlovskoye (Spetsugli section) coal deposits northeast of Vladivostok in Primorsky Territory). Coal and coal argillites from the Novikovskoye deposit are strongly enriched in Ge, with Ge grades in coal and coal argillites on average at 276 ppm and 348 ppm, respectively (Kats et al., 1998). There is a promising coal-hosted Ge project at Shkotovskoye (about 50 km NE of Vladivostok), recovering Ge from an existing coal mine. Ge is concentrated in huge amounts of ash from this coal mine and stored at local power stations. Tselikova (2001) reported C2 category reserves were calculated at 888 t Ge and the average Ge grade in the coal ash was 1043 ppm, and the average ash content of 20.8%; <http://cc.msnsnscache.com/cache.aspx?q=2050278821396&lang=de-DE&FORM=CVRE3>). Moreover, the Pavlovskoye (Spetsugli) brown coal deposit, also in southern Primorsky Territory, is reported to be one of the major Ge resources. There, Ge is closely associated with Sb, and the coals of the Spetsugli deposit are qualified for an economic recovery for both Ge and Sb (Seredin, 2003). The remainder of the reserves are mostly in coal beds of the Kemerovo (Kuzbas) basin (east of Novosibirsk) and in brown coal beds of the Tarbagataiskoye deposit in the Chitinskaya basin (east of Lake Baikal) (Kats et al., 1998). There is obviously a recovery of germanium from ashes at least from the Novikovskoye and Shkotovskoye and Tarbagataiskoye deposits, and from the Kusbas basin.

China is a major Ge producer from coal. The Lincang lignite mine close to Lincang City, Yunnan Province, China, is an outstanding germanium source since 1971, and produces with a capacity of 16 t of high-grade (99.999%) GeO₂ annually, of which 90% are exported. Qi Huawen et al. (2002) refer to three “coal-bearing cycles” in the Lincang lignite basin; germanium occurs mainly in the lignite of the lower cycle, which is close to basement granites. The lignite reserves/resources are “huge” and the Ge grade is of “high quality” (www.sino-ge.com/english/company.htm). The germanium resources of Yunnan Province are estimated at 1112 t Ge (www.wsbyn.gov.cn/english/jryn/info.asp?id=88), the bulk of which is probably from the Lincang deposit. Brown (2001) provided information regarding a new coal/Ge project

in China. The Nei Mongol Coalfield Bureau has discovered a large Ge deposit at Xilinhaote in Nei Mongol (eastern Inner Mongolia). It is estimated to be up to 1600 t of Ge in this coal deposit. This would be the largest Ge deposit in China and account for 30% of China's Ge reserves. It is amenable to large-scale open pit mining. From the link <http://cc.msnsnscache.com/cache.aspx?q=2060253204888&lang=de-DE&FORM=CVRE>, we conclude for the year 2002: Coal exists in large quantities and is mined near Xilinhaote. A coal power station is planned. The mineral resources in the area include germanium. We did not find any information about Ge recovery.

5. Summary and conclusions

Ge is commonly an unreported trace element in geochemical analysis, and reliable Ge data even from large ore deposits are often lacking. The scarcity of Ge data in the scientific literature may be due to the lack of chemical methods that can be easily applied to evaluate Ge. Ge is uncommon, but not extremely rare in the bulk continental and oceanic crust. Ge is geochemically an unusual element; it is characterised by lithophile, chalcophile, siderophile and organophile behaviour. It is known to be enriched in some silicate, oxide, sulphide and organic compounds. Ge does not form specific ore deposits; rather it occurs in minor and trace amounts in various types of ore deposits. In a temporal context, some influences on the metallogenesis of Ge during the Earth's history can be concluded, due to the geologic evolution of the crust (mainly for Ge-bearing base metal deposits), atmosphere (inducing a change of the oxidation state Fe²⁺ to Fe³⁺), and biosphere (formation of lignite and coal). Most Ge-enriched deposits formed in Phanerozoic time.

By far, most Ge is found as Ge⁴⁺ in silicate minerals, where it substitutes for the ubiquitous Si⁴⁺. Igneous rocks and siliceous sedimentary rocks, and their metamorphic equivalents, display only a narrow range of low Ge grades, irrespective of their composition and genesis. There is only a slight tendency for Ge to be concentrated in late magmatic differentiates, and rocks that crystallize in the presence of high volatile concentrations or hydrothermal fluids, with Ge enrichments in a few minerals. A significant separation of Ge from Si in various geological environments is due to the different chalcophile features of both elements. Thus Ge can be incorporated above all in low-temperature, iron-poor sphalerite, as well as in some other sulphide minerals. At high S activities, the thiocomplex [GeS₄]⁴⁻ is responsible for the formation of thiogermanate

minerals, above all together with Cu, Ag and Sn, effecting locally special concentrations of Ge. In oxidation zones, Ge may be retained mainly in iron hydroxides and oxides, e.g., goethite and hematite, and in a number of rare to unique minerals. Ge enrichments in Fe-oxide ores, e.g., BIF, are commonly low; however, the total amount of Ge in BIF worldwide is enormous due to the huge BIF reserves/resources. Ge has a high affinity for organic matter. Ge grades in coal and lignite deposits vary over several orders of magnitude, from less than 1 ppm up to, in exceptional cases, 4000 ppm Ge. We believe, lignite and coal offer outstanding Ge resources worldwide (Paone, 1970). Therefore, we present some criteria for Ge exploration in lignite and coal: Low-grade coalification; coal basins with preferentially thin coal seams; country rocks pre-enriched in Ge (such as sediments containing organic material and/or differentiated, Ge-enriched granites); favourable paleo-climatic conditions for kaolinitization and release of Ge from granite minerals (e.g., muscovite) or from sediments into migrating fluids; flow of Ge-bearing fluids into sedimentary basins; Ge fixation by chemisorptive processes on relatively stable organo-complexes, onto which Ge can be precipitated as humate complexes, during the peat and/or lignite stages of coal formation. Major Ge enrichment processes in coal are favoured by the continuous, long-lasting flow of Ge-bearing fluids into the sedimentary basin where the coal is forming. The distribution of Ge in coal and host rocks changes during progressive metamorphism, with Ge being increasingly incorporated in silicate minerals and quartz. Anthracite commonly displays low Ge concentrations at about crustal average only.

Currently, the major source of Ge is iron-poor sphalerite. Most of the Ge-bearing ore is from low-temperature, epigenetic deposits, hosted predominantly in carbonate rocks; their Zn ore concentrates average a few hundred ppm Ge. The giant Red Dog Mine, Alaska, with the world's largest zinc concentrate output, is the major US source for Ge, despite relatively low Ge grades in the zinc concentrates. Zn sulphides from high-temperature vein deposits usually contain only a few ppm Ge. Polymetallic deposits of the Kipushi-type are rare, but commonly have relatively high average Ge grades of up to several hundred ppm, usually in Cu-rich sulphide ores. In addition, the Apex Mine and the Tsumeb deposit contain unusual Ge enrichments and unique Ge minerals in oxidized zones. Coal and lignite deposits in Russia and China (above all Lincang coal deposit) contribute significantly to the world's Ge supply.

Estimates of Ge reserves (and resources), even from ore-producing mines, are not widely available. Conservative calculations for world Ge reserves, in low-temperature hydrothermal Zn deposits and in polymetallic Kipushi-type ore deposits (including slags at Tsumeb and Kipushi (Lubumbashi plant)) suggest that there is a few thousand tons of recoverable Ge. Besides the actually Ge producing coal and lignite mines in Russia and China, additional lignite and coal deposits significantly enriched in Ge do exist. Further Ge-rich lignite and coal deposits in Russia and China may represent important Ge sources in the near future. In our opinion, coal offers the largest resource of Ge for the long-term future. We estimate, that in coal ash and flue dust produced annually at coal power stations worldwide, there are at least a few 1000 t of Ge contained; however, a Ge recovery from this source seems to be mostly uneconomic under present terms. Nevertheless, the worldwide reserves/resources should meet the requirements even for a significantly increasing Ge demand, at least for the next two decades.

Germanium is an important commodity in modern times, but generally only a by-product of mining. Ge sources should be preserved carefully. Ge-enriched slags at some mines and plants as well as Ge-enriched coal ash and flue dust at some coal power stations are such easily accessible sources.

Acknowledgements

A study by Kling et al. (2000) 'Review of germanium in rocks, ores, minerals, ore deposits and ore deposit provinces' (Literaturzusammenstellung und -auswertung zur Verteilung von Germanium in Gesteinen, Erzen, Mineralen, Lagerstätten und Lagerstättenprovinzen) was commissioned and funded by the German Federal Institute for Geosciences and Natural Resources (Bundesanstalt für Geowissenschaften und Rohstoffe (BGR), Hannover. It is a contribution to the research program 'BGR 2000—Metals with Short Lifetime Reserves'. We gratefully acknowledge the support of this study by Prof. Dr.-Ing. Dr. h.c. F.-W. Wellmer and his colleagues at the BGR. We sincerely thank Dr. Ian R. Jonasson (Geological Survey of Canada, Ottawa, Canada) and Prof. Dr. Peter Laznicka (Australian Mineral Foundation, Adelaide, Australia) for their reviews, constructive comments and helpful suggestions that have improved the earlier version of this paper. Dr. Alex Nicholls, Department für Geo-und Umweltwissenschaften, LMU München, is thanked for his help in improving the English style of a former version of the

manuscript. Detailed reviews and editorial comments by Prof. Dr. N.J. Cook significantly improved the final manuscript.

References

- Adams, J.H., Thomas, D., 1994. Germanium and germanium compounds. Kirk-Othmer Encyclopedia of Chemical Technology. 4th Edition, vol. 12. John Wiley and Sons, New York, pp. 540–555.
- Ahlfeld, F., Schneider-Scherbina, A., 1964. Los yacimientos minerales y de hidrocarburos de Bolivia. Boletín 5 (Especial), Departamento Nacional de Geología, Ministerio de Minas y Petróleo, La Paz, Bolivia. 388 pp.
- Anderson, I.K., Ashton, J.H., Boyce, A.J., Fallick, A.E., Russell, M.J., 1998. Ore depositional processes in the Navan Zn–Pb deposit, Ireland. *Economic Geology* 93, 535–567.
- Ando, A., 1964. Geochemistry of germanium in the metallic sulphide ore deposits in Japan. Geological Survey of Japan, Report 208, pp. 1–72 (in Japanese with English Abstract).
- Andrew, C.J., 1993. Mineralizations of the Irish Midlands. In: Patrick, R.A.D., Polya, A.D. (Eds.), *Mineralizations of the British Isles*. Chapman and Hall, London, pp. 208–269.
- Anonymous, 2002. *Erzmetall* 55 (2), 508.
- Appold, M.S., Garven, G., 2000. Reactive models of ore formation in the southeast Missouri District. *Economic Geology* 95, 1605–1626.
- Arne, D.C., Curtis, L.W., Kissin, S.A., 1991. Internal zonation in a carbonate-hosted Zn–Pb–Ag deposit, Nanisivik, Baffin Island, Canada. *Economic Geology* 86, 699–717.
- Amorsson, S., 1984. Germanium in Islandic geothermal systems. *Geochimica et Cosmochimica Acta* 48, 2482–2502.
- Arsenijević, M., 1958. Germanium and its distribution in some Yugoslavian ores. *Vesnik Zavoda za Geoloska i Geofizicka Istrazivanja NR Srbije* 16, 55–165 (in Serbocroat with English Abstract).
- Avdonin, V.V., Sergeeva, N.E., 1999. Rare metals in the evolutionary sequences of base-metal massive-sulfide deposits. *Moscow University Geology Bulletin* 54 (4), 43–53.
- Bai, T.B., Koster van Groos, A.F., 1999. The distribution of Na, K, Rb, Sr, Al, Ge, Cu, W, Mo, La, and Ce between granitic melts and coexisting aqueous fluids. *Geochimica et Cosmochimica Acta* 63, 1117–1132.
- Banks, D.A., Boyce, A.J., Samson, I.M., 2002. Constraints on the origins of fluids forming Irish Zn–Pb–Ba deposits: evidence from the composition of fluid inclusions. *Economic Geology* 97, 471–480.
- Barbanson, L., Geldron, A., 1983. Distribution du germanium, de l'argent et du cadmium entre les schistes et les minéralisations stratiformes et filonienues à blende-sidélite de la région de Saint-Salvy (Tarn). *Chronique de la Recherche Minière* 470, 33–42.
- Bateman, A.M., McLaughlin, D.H., 1920. Geology of the ore deposit of Kennecott, Alaska. *Economic Geology* 15, 1–80.
- Baumann, L., 1994. The vein deposit of Freiberg, Saxony. Monograph Series on Mineral Deposits 31, 147–167.
- Baumann, L., Kuschka, E., Seifert, T., 1999. Lagerstätten des Erzgebirges. Enke, Stuttgart. 300 pp.
- Bekmukhametov, A.E., Zamyatina, S.K., Kalinin, S.K., 1973. Geochemistry of germanium in iron deposits of Kazakhstan. *Geochemistry International* 5, 277–282.
- Bernstein, L.R., 1985. Germanium geochemistry and mineralogy. *Geochimica et Cosmochimica Acta* 49, 2409–2422.
- Bernstein, L.R., 1986. Geology and mineralogy of the APEX germanium–gallium mine, Washington County, Utah. United States Geological Survey Bulletin 1577, 1–9.
- Bernstein, L.R., Cox, D.P., 1986. Geology and sulphide mineralogy of the Number One Orebody, Ruby Creek Copper Deposit, Alaska. *Economic Geology* 81, 1675–1689.
- Bernstein, L.R., Waychunas, G.A., 1987. Germanium crystal chemistry in hematite and goethite from Apex Mine, Utah, and some new data on germanium in aqueous solution and in stottite. *Geochimica et Cosmochimica Acta* 51, 623–630.
- Bischoff, J.L., Rosenbauer, R.J., Aruscavaga, P., Baedeker, J., Philip, A., Crock, J.G., 1983. Sea floor massive sulphide deposits from 21°N, East Pacific Rise; Juan de Fuca Ridge and Galapagos Rift: bulk chemical composition and economic implications. *Economic Geology* 78, 1711–1720.
- Blakeman, R.J., Ashton, J.H., Boyce, A.J., Fallick, A.E., Russell, M.J., 2002. Timing of interplay between hydrothermal and surface fluids in the Navan Zn+Pb Orebody, Ireland: evidence from metal distribution trends, mineral textures, and $\delta^{34}\text{S}$ analyses. *Economic Geology* 97, 73–91.
- Boland, M.B., Kelly, J.G., Schaffalitzky, C., 2003. The Shaimerden supergene zinc deposit, Kazakhstan: a preliminary examination. *Economic Geology* 98, 787–796.
- Bonev, I.K., Kerestedijan, T., Atanassova, R., Andrew, C.J., 2002. Morphogenesis and composition of native gold in the Chelopech volcanic-hosted Au–Cu epithermal deposit, Srednogorie zone, Bulgaria. *Mineralium Deposita* 37, 614–629.
- Boni, M., Balassone, G., Iannace, A., 1996. Base metal ores in the lower Paleozoic of southwestern Sardinia. *Economic Geology* 75th Anniversary Volume, pp. 18–28.
- Borg, G., Kärner, K., Buxton, M., Armstrong, R., Van der Merve, S.W., 2002. Geology of the Skorpion supergene deposit, southern Namibia. *Economic Geology* 98, 749–772.
- Bouška, V., 1981. *Geochemistry of Coal*. Elsevier, Amsterdam. 284 pp.
- Bowling, D.L., 1988. The geology and genesis of the Apex gallium–germanium deposit, Washington County, Utah. M.S. Thesis, Utah University, Salt Lake City, U.S.A., 87 pp.
- Bradley, D.C., Leach, D.L., 2003. Tectonic controls of Mississippi Valley-type lead–zinc mineralization in orogenic forelands. *Mineralium Deposita* 38, 652–667.
- Bradley, D.C., Leach, D.L., Symons, D., Emsbo, P., Premo, W., Breit, G., Sangster, D.F., 2004. Reply to discussion on “Tectonic controls of Mississippi Valley-type lead–zinc mineralization in orogenic forelands” by S.E. Kesler, J.T. Christensen, R.D. Hagni, W. Heijlen, J.R. Kyle, K.C. Misra, P. Muchez, and R. van der Voo. *Mineralium Deposita* 39, 515–519.
- Brandenstein, M., Janda, L., Schroll, E., 1960. Seltene Elemente in österreichischen Kohlen- und Bitumengesteinen. *Tschermaks Mineralogisch-Petrographische Mitteilungen* 7, 260–285.
- Breger, I.A., Schopf, J.M., 1955. Germanium and uranium in coalfield wood from Upper Devonian black shale. *Geochimica et Cosmochimica Acta* 7, 287–298.
- Brigo, L., Cerrato, P., 1994. Trace element distribution of Middle–Upper Triassic carbonate-hosted lead–zinc mineralizations: the example of the Raibl Deposit (eastern Alps, Italy). In: Fontboté, L., Boni, M. (Eds.), *Sediment-Hosted Zn–Pb Ores*. SGA, Special Publication, vol. 10. Springer, Berlin, pp. 179–197.
- Brigo, L., Kostelka, L., Omenetto, P., Schneider, H.-J., Schroll, E., Struel, I., 1977. Comparative reflections on four Alpine Pb–Zn

- deposits. In: Klemm, D.D., Schneider, H.-J. (Eds.), *Time- and Stratabound Ore Deposits*. Springer, Berlin, pp. 273–293.
- Brigo, L., Camana, D., Rodeghiero, F., Potenza, R., 2001. Carbonate-hosted siliceous crust-type mineralization of the Carnic Alps (Italy, Austria). *Ore Geology Reviews* 12, 199–214.
- Brown, R.D., 2001. Germanium-2000. *United States Geological Survey Minerals Yearbook 2000*, pp. 33.1–33.3.
- Brown, R.D., 2002. Germanium. *United States Geological Survey, Mineral Commodity Summaries*, January 2002, pp. 70–71.
- Burton, J.D., Culkin, J.D., Riley, J.P., 1959. The abundance of gallium and germanium in terrestrial materials. *Geochimica et Cosmochimica Acta* 16, 151–180.
- Butterman, W.C., Jorgenson, J.D., 2005. Germanium. *USGS Open-File Report 2004-1218*, 19 pp. (<http://pubs.usgs.gov/of/2004/1218/2004-1218.pdf>).
- Canby, M., 2005. Exploration reviews. Europe. *SEG Newsletter* 61, 39 (April).
- Cassard, D., Chabod, J.C., Marcoux, E., Bourguine, B., Castaing, C., Gros, Y., Kosakevich, A., Moisy, M., Viallefond, L., 1996. Mise en place et origine des minéralisations du gisement à Zn, Ge, Ag, (Pb, Cd) de Noailhac-Saint-Salvy (Tarn, France). *Chronique de la Recherche Minière* 514, 3–37.
- Cerny, I., Schroll, E., 1985. Heimische Vorräte an Spezialmetallen (Ga, In, Tl, Ge, Se, Te und Cd) in Blei-Zink und anderen Erzen. *Archiv für Lagerstättenforschung der Geologischen Bundesanstalt*, Wien 18, 5–33.
- Chabu, M., 1990. Metamorphism of the Kipushi carbonate-hosted Zn–Pb–Cu deposit, Shaba, Zaire. In: Spry, P.G., Bryndzia, L.T. (Eds.), *Proceedings, 28th International Geological Conference*. VSP, pp. 27–47.
- Chapple, K., 2003. The Mehdiabad zinc deposit—a Tethyan giant. In: Eliopoulos, D.G., et al. (Eds.), *Mineral Exploration and Sustainable Development*. Millpress, Rotterdam, pp. 1149–1152.
- Chetty, D., Frimmel, H.E., 2000. The role of evaporites in the genesis of base metal sulphide mineralization in the Northern Platform of the Pan-African Damara Belt, Namibia: geochemical and fluid inclusion evidence from carbonate wall rock alteration. *Mineralium Deposita* 35, 364–376.
- Churakov, S.V., Tkachenko, S.I., Korzhinskii, M.A., Bocharnikov, R.E., Shmulovich, K.I., 2000. Evolution of composition of high-temperature fumarolic gases from Kudryavy Volcano, Iturup, Kuril Islands: the thermodynamic modeling. *Geochemistry International* 38, 436–451.
- Ciobanu, C.L., Cook, N.J., Stein, H., 2002. Regional setting and geochronology of the Late Cretaceous Banatitic magmatic and metallogenetic belt. *Mineralium Deposita* 37, 541–567.
- Clark, M.C., Swane, D.J., 1962. Trace elements in coal. I. New South Wales coals, Australia. *CSIRO, Coal Research, Technical Communications*, vol. 45, pp. 1–20.
- Cook, N.J., Ciobanu, C.L., Bogdanov, K., 2002. Trace mineralogy of the Upper Cretaceous Banatitic magmatic and metallogenetic belt, SE Europe. 11th Quadrennial IAGOD Symposium and Geocongress 2002, Windhoek, Namibia. CD Volume of Extended Abstracts. Geological Survey of Namibia.
- Cox, D.P., Bernstein, L.R., 1986. Descriptive model of Kipushi Cu–Pb–Zn. In: Cox, D.P., Singer, D.A. (Eds.), *Mineral Deposit Models*. United States Geological Survey Bulletin, vol. 1693, pp. 1–227.
- Criaud, A., Fouillac, A.M., 1986. Etude des eaux thermominérales carbogazeuses du Massif Central Français: II. Comportement de quelques métaux en trace, de l'arsenic, de l'antimoine et du germanium. *Geochimica et Cosmochimica Acta* 50, 1573–1582.
- Cunningham, C.G., McNee, J., Pinto-Vasquez, J., Ericksen, G.E., 1991. A model of volcanic dome-hosted precious metal deposits of Bolivia. *Economic Geology* 86, 415–421.
- Cvetkovic, L., Krajnovic, D., Zmic, B., Obradovic, L., 1999. Crystallochemical characteristics of colusite from the Bor copper deposit (eastern Serbia). *Geoloski Anali Balkanskoga Poluostrva* 63, 155–163.
- Dasch, E.J. (Ed.), 1996. *Encyclopedia of Earth Sciences*, vol. I. Macmillan Reference USA, New York. 563 pp.
- Davy, H., 1983. Contributions on the chemical composition of Precambrian iron formations. In: Trendall, A.F., Morris, R.C. (Eds.), *Iron Formation, Facts and Problems. Development in Precambrian Geology*, vol. 6. Elsevier, Amsterdam, pp. 325–344.
- De Magnee, I., Francois, A., 1988. The origin of the Kipushi (Cu,Zn, Pb) deposit in direct relation with a Proterozoic salt diapir, Copperbelt of Central Africa, Shaba, Republic of Zaire. In: Friedrich, G.H., Herzig, P.M. (Eds.), *Base Metal Sulphide Deposits in Sedimentary and Volcanic Environments*. SGA Special Publication, vol. 5. Springer, Berlin, pp. 74–93.
- De Vos, W., Viaene, W., Moreau, J., 1974. Mineralogie du gisement de Kipushi, Shaba, Zaire. In: Bartholome, P. (Ed.), *Gisements stratiformes et Provinces Cuprifères*. Société Géologique de Belgique, Liège, pp. 165–183.
- Deane, J.G., 1995. The structural evolution of the Kombat Deposits, Otavi Mountainland, Namibia. *Geological Survey of Namibia, Communications*, vol. 10, pp. 99–107.
- Duchesne, J.C., Rouhart, A., Schumacher, C., Dillen, H., 1983. Thallium, nickel, cobalt and other trace elements in sulphides from Belgian lead–zinc vein deposits. *Mineralium Deposita* 18, 303–313.
- Dumoulin, J.A., Harris, A.G., Blome, C.D., Young, L.E., 2004. Depositional settings, correlation, and age of Carboniferous rocks in the Western Brooks Range, Alaska. *Economic Geology* 99, 1355–1384.
- Dutrizac, I.E., Jambor, J.I., Chen, T.T., 1986. Host minerals of the gallium–germanium ores of the Apex Mine. *Economic Geology* 81, 241–281.
- El Wardani, S.A., 1957. On the geochemistry of germanium. *Geochimica et Cosmochimica Acta* 10, 321–322.
- Eldridge, C.S., Barton, P.B., Ohmoto, H., 1983. Mineral textures and their bearing on formation of the Kuroko orebodies. *Economic Geology Monographs* 5, 241–281.
- Emslie, D.P., Beukes, G.J., 1981. Minor- and trace-element distribution in sphalerite and galena from the Otavi Mountainland, South West Africa. *Annals of the Geological Survey of South Africa* 15 (2), 11–28.
- Ershov, V.M., Shcheglova, A.I., 1958. Germanium in mine waters of a coal basin. *Geochemistry International* 4, 490–492.
- Everett, C.E., Wilkinson, J.J., Rye, D.M., 1999. Fracture-controlled fluid flow in the Lower Palaeozoic rocks of Ireland: implications for the genesis of Irish-type Zn–Pb deposits. In: McCaffrey, K.J.W., Lonergan, L., Wilkinson, J.J. (Eds.), *Fractures, Fluid Flow, and Mineralization*. Geological Society of London Special Publication, vol. 155, pp. 247–276.
- Eyre, S.L., 1998. *Geochemistry of dolomitization and Zn–Pb mineralization in the Rathdowney Trend, Ireland*. Unpublished Ph.D. Thesis, University of London, 418 pp.
- Fallick, A.E., Ashton, J.H., Boyce, A.J., Ellam, R.M., Russell, M.J., 2001. Bacteria were responsible for the magnitude of the world-class hydrothermal base metal sulphide orebody at Navan, Ireland. *Economic Geology* 96, 885–890.
- Faure, G., 1998. *Principles and Applications of Geochemistry*, 2nd edition. Prentice Hall, New Jersey. 928 pp.

- Fillipou, D., 2004. Innovative hydrometallurgical processes for primary processing of zinc. *Mineral Processing and Extractive Metallurgy Review* 28, 206–252.
- Finkelman, R.B., 1993. Minor elements in coal. In: Engel, M.H., Macko, S.A. (Eds.), *Organic Geochemistry. Principles and Applications*. Plenum Press, New York, pp. 593–610.
- Fogliérini, F., Béziat, P., Tollon, F., Chabod, J.C., 1980. Le gisement filonien de Noailhac-Saint-Salvy (Tarn) Zn (Ag, Ge, Pb, Cd). 26th International Geological Congress, Paris. *Gisements Français*, Fascicule E, vol. 6, pp. 1–43.
- Folger, P.F., Schmidt, J.M., 1986. Geology of the carbonate-hosted Omar Copper Prospect, Baird Mountains, Alaska. *Economic Geology* 81, 1690–1695.
- Fontboté, L., Boni, M., 1994. Sediment-hosted zinc–lead ores—an introduction. In: Fontboté, L., Boni, M. (Eds.), *Sediment-Hosted Zn–Pb Ores*. SGA, Special Publication, vol. 10. Springer, Berlin, pp. 3–12.
- Fontboté, L., Gorzawski, H., 1990. Genesis of the Mississippi Valley-type Zn–Pb deposit of San Vicente, Central Peru: geologic and isotopic (Sr, O, C, S, Pb) evidence. *Economic Geology* 85, 1402–1437.
- Franklin, J.M., Lydon, J.W., Sangster, D.F., 1981. Volcanic-associated massive sulphide minerals. *Economic Geology 75th Anniversary Volume*, pp. 485–627.
- Freeman, C.J., 2005. Exploration reviews. Alaska. *SEG Newsletter* 61, 36 (April).
- Frimmel, H.E., Deane, J.G., Chadwick, P.J., 1996. Pan-African tectonics and genesis of base metal deposits in the northern foreland of the Damara Orogen, Namibia. In: Sangster, D.F. (Ed.), *Carbonate-Hosted Lead–Zinc Deposits*. Society of Economic Geologists Special Publication, vol. 4, pp. 204–217.
- Froelich, P.N., Andreae, M.O., 1981. The marine geochemistry of germanium: ekasilicon. *Science* 213, 205–207.
- Froelich, P.N., Hambrick, A.S., Kaul, L.W., Byrd, J.T., Lecointe, O., 1985. Geochemical behaviour of inorganic germanium in an unperturbed estuary. *Geochimica et Cosmochimica Acta* 49, 519–524.
- Frondel, C., Ito, J., 1957. Geochemistry of germanium in the oxydized zone of the Tsumeb Mine, South West Africa. *American Mineralogist* 42, 743–753.
- Frondel, C., Strunz, H., 1980. Fleischerit und Itoit, zwei neue Germanium–Mineralien von Tsumeb. *Neues Jahrbuch für Mineralogie, Monatshefte*, 132–142.
- Gabrielson, O., 1945. Studie över elemente ördelningen i zinkbländen från Svenska fyndorter. *Sveriges Geologiska Undersökning*, C468, Årsbok, 39, 1–52.
- Geldron, A., 1983. Le germanium: un élément valorisant des gisements hydrothermaux à Zn–Cu–(Pb). *Chronique de la Recherche Minière* 470, 25–32.
- Gemmell, J.B., Sharpe, R., Jonasson, I.R., Herzig, P.M., 2004. Sulfur isotope evidence for magmatic contributions to submarine and subaerial gold mineralization: conical seamount and the Ladolam gold deposit, Papua New Guinea. *Economic Geology* 99, 1711–1725.
- George, M.W., 2004. Germanium. *U.S. Geological Survey Minerals Yearbook 2003*, pp. 31.1–31.6 (<http://minerals.usgs.gov/minerals/pubs/commodity/germanium/germamb03.pdf>).
- Gerber, G.B., Leonard, A., 1997. Mutagenicity, carcinogenicity and teratogenicity of germanium compounds. *Mutation Research* 387, 141–146.
- Glemser, O., 1961. Ergebnisse und Probleme von Verbindungen der Systeme Oxyd–Wasser. *Angewandte Chemie* 73, 785–808.
- Glockling, F., 1969. *The Chemistry of Germanium*. Academic Press, New York. 234 pp.
- Gluskoter, H.J., Ruch, R.R., Miller, W.G., Cahill, R.A., Dreher, G.B., Kuhn, J.K., 1977. Trace elements in coal: occurrence and distribution. *Illinois State Geological Survey Circular*, vol. 499, 154 pp.
- Goldschmidt, V.M., 1930. Über das Vorkommen des Germaniums in Steinkohlen und Steinkohlenprodukten. *Nachrichten von der Gesellschaft der Wissenschaften zu Göttingen. Mathematisch-Physikalische Klasse* 28, 307–401.
- Goldschmidt, V.M., Peters, C., 1933. Zur Geochemie des Germaniums. *Nachrichten von der Gesellschaft der Wissenschaften zu Göttingen. Mathematisch-Physikalische Klasse* 31, 141–166.
- Goleva, G.A., Vorobyeva, I.N., 1967. The migration of germanium in the ground waters of ore deposits. *Geochemistry International* 4, 809–817.
- Goodfellow, W.D., Lydon, J.W., Turner, R.J.W., 1993. Geology and genesis of stratiform sediment-hosted (SEDEX) zinc–lead–silver sulphide deposits. In: Kirkham, R.V., Sinclair, W.D., Thorpe, R.I., Duke, J.M. (Eds.), *Mineral Deposit Modelling*. Geological Association of Canada Special Paper, vol. 40, pp. 201–251.
- Graf, G.G., 1996. Zinc. *Ullmann's Encyclopedia of Industrial Chemistry*. VCH, Weinheim, Germany, pp. 509–536.
- Guliyeva, L.A., Lositskaya, I.F., 1959. Investigation of germanium content in the petroleum of the Soviet Union. *Geochemistry* 1959, 186–195.
- Gutzmer, J., Cairncross, B., 2001. Germanium in beudantite from Tsumeb, Namibia. *The Mineralogical Record* 32, 304–307.
- Hagni, R.D., 1983. Minor elements in Mississippi Valley-type ore deposits. In: Shanks, W.C. (Ed.), *Cameron Volume on Unconventional Mineral Deposits*. American Institute of Mining, Metallurgical and Petroleum Engineers, New York, pp. 71–88.
- Hall, W.E., Heyl, A.V., 1968. Distribution of minor elements in ore and host rock. Illinois–Kentucky fluorite district and Upper Mississippi Valley zinc–lead district. *Economic Geology* 63, 655–670.
- Hannington, M.D., Bleeker, W., Kjaergaard, I., 1999. Sulphide mineralogy, geochemistry, and ore genesis of the Kidd Creek deposit. Part I: north, central, and south orebodies. *Economic Geology Monographs* 10, 163–224.
- Harris, D.C., Sangster, D.F., 1991. Minor element content of sphalerite, Nanisivik lead–zinc deposit, NWT. In: Richardson, D.G., Irving, M. (Eds.), *Project Summaries: Canada–Northwest Territories Mineral Development Subsidiary Agreement, 1987–1991*. Geological Survey of Canada, Openfile Report, vol. 2484. Geological Survey of Canada. 141 pp.
- Heijnen, W., Muchez, Ph., 2003. Palaeohydrogeology and geodynamic framework of carbonate-hosted Zn–Pb mineralisation in Europe and North America: insights from fluid composition and Pb isotope systematics. In: Eliopoulos, D.G., et al. (Ed.), *Mineral Exploration and Sustainable Development*. Millpress, Rotterdam, pp. 681–684.
- Heinrich, C.A., Neubauer, F., 2002. Cu–Au–Pb–Zn–Ag metallogeny of the Alpine–Balkan–Carpathian–Dinaride geodynamic province. *Mineralium Deposita* 37, 533–540.
- Henry, K., Fouquet, Y., Cambon, P., Etoubleau, J., Bohn, M., 1995. Indium and germanium in oceanic hydrothermal deposits. *Terra, EUG*, vol. 8, p. 209. Abstract Volume.
- Higazy, R.A., 1953. Observations on the distribution of trace elements in perthitic pegmatites of Black Hills, South Dakota. *American Mineralogist* 38, 172–190.
- Hitzman, M.W., 1986. Geology of the Ruby Creek copper deposit, Southwestern Brooks Range, Alaska. *Economic Geology* 81, 1644–1674.

- Hitzman, M.W., Beaty, D.W., 1996. The Irish Zn–Pb–(Ba) ore field. In: Sangster, D.F. (Ed.), *Carbonate-Hosted Lead–Zinc Deposits*. Society of Economic Geologists Special Publication, vol. 4, pp. 597–610.
- Hitzman, W.M., Large, D., 1986. A review and classification of the Irish carbonate-hosted base metal deposits. In: Andrew, C.J., Crowe, W.A., Finlay, S., Penell, W.M., Pyne, J.F. (Eds.), *Geology and Genesis of Mineral Deposits in Ireland*. Irish Association of Economic Geologists, Dublin, pp. 217–238.
- Hitzman, W.M., Redmond, P.B., Beaty, D.W., 2002. The carbonate-hosted Lisheen Zn–Pb–Ag deposit, County Tipperary, Ireland. *Economic Geology* 97, 1627–1655.
- Hitzman, M.W., Reynolds, N.A., Sangster, D.F., Allen, C.R., Carman, C.E., 2003. Classification, genesis, and exploration guides for nonsulfide zinc deposits. *Economic Geology* 98, 685–714.
- Hörmann, P.K., 1963. Zur Geochemie des Germaniums. *Geochimica et Cosmochimica Acta* 27, 861–876.
- Hörmann, P.K., 1972. Germanium. In: Wedepohl, K.H. (Ed.), *Handbook of Geochemistry*. Springer, Berlin. 32B1–O1.
- Innes, J., Chaplin, R.C., 1986. Ore bodies of the Kombat Mine, South West Africa/Namibia. In: Anhaeusser, C.R., Maske, S. (Eds.), *Mineral Deposits of Southern Africa*. Geological Society of South Africa, pp. 1789–1805.
- Intiomale, M.M., Oosterbosch, R., 1974. In: Bartholomé, P. (Ed.), *Géologie et géochimie du gisement de Kipushi, Zaire*. Société Géologique de Belgique, Liège, pp. 123–164.
- Janda, I., Schroll, E., 1960. Geochemische Untersuchungen an Graphitgesteinen. 21st International Geological Congress, Copenhagen, Session 1. *Geochemical Cycles*, pp. 40–53.
- Jennings, S., King, A.R., 2002. Geology, exploration history and future discoveries in the Red Dog District, western Brooks Range, Alaska. In: Cooke, D.R., Pongratz, J. (Eds.), *Giant Ore Bodies: Characteristics, Genesis, and Exploration*. CODES, University of Tasmania, Hobart Publication, vol. 4, pp. 151–160.
- Johan, Z., 1988. Indium and germanium in the structure of sphalerite: an example of coupled substitution with copper. *Mineralogy and Petrology* 39, 211–229.
- Johan, Z., Oudin, E., 1986. Présence de grenats, $\text{Ca}_3\text{Ga}_2(\text{GeO}_4)_3$, $\text{Ca}_3\text{Al}_2((\text{Ge}, \text{Si})\text{O}_4)_3$ et d'un équivalent ferrière, germanifère et gallifère de la sapphirine, $\text{Fe}_4(\text{Ga}, \text{Sn}, \text{Fe})_4(\text{Ga}, \text{Ge})_6\text{O}_{20}$, dans la blende des gisements de la zone axiale pyrénéenne. Conditions de la formation des phases germanifères et gallifères. *Comptes Rendus de l'Académie des Sciences. Series IIA (Earth and Planetary Science)* 303, 811–816.
- Johan, Z., Oudin, E., Picot, P., 1983. Analogues germanifères et gallifères des silicates et oxydes dans les gisements de zinc des Pyrénées centrales, France: argutite et carboirite, deux nouvelles espèces minérales. *Tschermaks Mineralogisch - Petrographische Mitteilungen* 31, 97–119.
- Johnston, J.D., 1999. Regional fluid flow and the genesis of Irish Carboniferous base metal deposits. *Mineralium Deposita* 34, 571–598.
- Jolly, J.I., Heyl, A.V., 1968. Mercury and other trace elements in sphalerite and wall rocks from central Kentucky, Tennessee, and Appalachian zinc district. *United States Geological Survey Bulletin* 1252-F, F1–F29.
- Kamona, A.F., 1993. The carbonate-hosted Kabwe Pb–Zn deposit, Central Zambia. Ph.D. Dissertation. Technical University of Aachen, Germany. 207 pp.
- Kamona, A.F., Friedrich, G., 1994. Die Blei–Zink–Lagerstätte Kabwe in Zentral Sambia. *Erzmetall* 37, 34–44.
- Kamona, A.F., Leveque, J., Friedrich, G., Haack, U., 1999. Lead isotopes of the carbonate-hosted Kabwe, Tsumeb, and Kipushi Pb–Zn–Cu sulphide deposits in relation to Pan African orogenesis in the Damaran–Lufilian fold belt of Central Africa. *Mineralium Deposita* 34, 273–283.
- Karamyan, K.A., 1958. Germanium-bearing sulphides of Dastakert copper–molybdenum deposit. *Doklady Akademii Nauk Armanjanskoy SSR* 27, 235–237 (in Russian).
- Kats, A.Y., Kremenetsky, A.A., Podkopaev, O.I., 1998. The germanium mineral resource base of the Russian Federation. *Mineral'nyye Resursy Rossii; Ekonomika i Upravleniye* 1998 (3), 5–9.
- Kelley, K.D., Jennings, S., 2004. A special issue devoted to barite and Zn–Pb–Ag deposits in the Red Dog District, Western Brooks Range, Northern Alaska. Preface. *Economic Geology* 99, 1267–1280.
- Kelley, K.D., Leach, D.L., Johnson, C.A., Clark, J.L., Fayek, M., Slack, J.F., Anderson, V.M., Ayuso, L.E., Ridley, W.I., 2004. Textural, compositional, and sulfur isotope variations of sulfide minerals in the Red Dog Zn–Pb–Ag deposits, Brooks Range, Alaska: implications for ore formation. *Economic Geology* 99, 1509–1532.
- Kendrick, M.A., Burgess, R., Leach, D.L., Patrick, R.A.D., 2002. Hydrothermal fluid origins in Mississippi Valley-type ore districts: combined noble gas (He, Ar, Kr) and halogen (Cl, Br, I) analysis of fluid inclusions from the Illinois–Kentucky fluorspar district, Viburnum Trend, and Tri-State districts, Midcontinent United States. *Economic Geology* 97, 453–470.
- Kesler, S.E., 1996. Appalachian Mississippi Valley-type deposits: paleoaquifers and brine provinces. In: Sangster, D.F. (Ed.), *Carbonate-Hosted Lead–Zinc Deposits*. Society of Economic Geologists Special Publication, vol. 4, pp. 182–194.
- Kesler, S.E., Chesley, J.T., Christensen, J.N., Hagni, R.D., Heijlen, W., Kyle, J.R., Muchez, P., Misra, K.C., van der Voo, R., 2004. Discussion of “Tectonic controls of Mississippi Valley-type lead–zinc mineralization in orogenic forelands” by D.C. Bradley and D.L. Leach. *Mineralium Deposita* 39, 512–514.
- Kinnaird, J.A., Ixer, R.A., Barreiro, B., Nex, P.A.M., 2002. Contrasting sources for lead in Cu–polymetallic and Zn–Pb mineralisation in Ireland: constraints from lead isotopes. *Mineralium Deposita* 37, 495–511.
- Kling, M., Höll, R., Schroll, E., 2000. Literaturstudie über Germanium in Gesteinen, Mineralien, Erzen und Lagerstätten. *Berichte zur Lagerstätten- und Rohstoffforschung*, vol. 39. Bundesanstalt für Geowissenschaften und Rohstoffe, Hannover. 117 pp.
- Knitschke, G., 1966. Zur Erzmineralisation, Petrographie, Hauptmetall- und Spurenelementführung des Kupferschiefers im SE-Harzvorland. *Freiberger Forschungshefte. C* 207, 1–147.
- Köppel, V., Schroll, E., 1988. Pb-isotope evidence for the origin of lead in strata-bound Pb–Zn deposits in Triassic carbonates of the Eastern and Southern Alps. *Mineralium Deposita* 23, 96–103.
- Koga, A., 1967. Germanium, molybdenum, copper and zinc in New Zealand thermal waters. *New Zealand Journal of Science* 10, 428–446.
- Komuro, K., Kajiura, Y., 2004. Germanium-bearing colusite in siliceous black ore from the Ezuri Kuroko deposit, Hokuroku District, Japan. *Resource Geology* 54, 447–452.
- Kotova, A.V., Viktorova, M.Y., 1965. Gallium and germanium contents in crude oils of the Emba Region. *Geochemistry International* 2, 1024–1027.
- Kovalenker, V.A., Tsonev, D., Breskovska, V.V., Malov, V.C., Troneva, N.V., 1986. New data on the mineralogy of the massive-sulphide deposits in the central Srednogie of Bulgaria. In: Korzhinsky, D. (Ed.), *Metasomatism, Mineralogy and Genesis*

- of Gold and Silver Deposits in Volcanic Series. Nauka, Moscow, pp. 91–110 (in Russian).
- Kraynov, S.R., 1967. Geochemistry of germanium in the thermal carbonate waters (illustrated by examples from the Pamirs and Greater Caucasus). *Geochemistry International* 4, 309–320.
- Krejci-Graf, K., 1972. Trace elements in sediments, oils, and allied substances. In: Fairbridge, R.W. (Ed.), *The Encyclopaedia of Geochemistry and Environmental Sciences*. Van Nostrand Reinhold Comp., New York, pp. 1201–1209.
- Kubota, H., Urabe, T., Yamada, R., Tanimura, S., 2004. Exploration indices and mineral potential map of Kuroko deposits in northeast Japan. *Resource Geology* 54, 387–398.
- Kucha, H., Schroll, E., Stumpf, E.F., 2000. Direct evidence for bacterial sulphur reduction in Bleiberg-type deposits. In: Piestrynski, A., et al. (Eds.), *Mineral Deposits at the Beginning of the 21st Century*. Balkema, Rotterdam, pp. 149–152.
- Kucha, H., Schroll, E., Stumpf, E.F., 2002. Bacteriogenic lead–zinc mineralization in the Bleiberg deposit, Austria. *Goldschmidt-Conference 2002, Abstracts. Geochimica et Cosmochimica Acta (Special Supplement, A688)*.
- Kucha, H., Schroll, E., Stumpf, E.F., 2005. Fossil sulphate-reducing bacteria in the Bleiberg lead–zinc deposit, Austria. *Mineralium Deposita* 40, 123–126.
- Kuhlemann, J., Zeeh, S., 1995. Sphalerite stratigraphy and trace element composition of East Alpine Pb–Zn deposits (Drau Range, Austria–Slovenia). *Economic Geology* 90, 2073–2080.
- Kuhlemann, J., Vennemann, T., Herlec, U., Zeeh, S., Bechstädt, T., 2001. Variations of sulphur isotopes, trace element compositions, and cathodoluminescence of Mississippi–Valley-type Pb–Zn ores from the Drau Range, Eastern Alps (Slovenia–Austria): implications for ore deposition on a regional versus microscale. *Economic Geology* 96, 1931–1941.
- Kyle, J.R., Li, N., 2002. Jinding: a giant Tertiary sandstone-hosted Zn–Pb deposit, Yunnan, China. *Society of Economic Geologists Newsletter* 50 (1), 9–16 (July).
- Kyle, J.R., Saunders, J.A., 1996. Metallic deposits of the Gulf Coast Basin: diverse mineralization style in a young sedimentary basin. In: Sangster, D.F. (Ed.), *Carbonate-Hosted Lead–Zinc Deposits*. Society of Economic Geologists Special Publication, vol. 4, pp. 218–229.
- Lange, H., 1957. Geochemische Untersuchungen an oxidischen Fe-Mineralen aus dem Elbingerode Komplex. *Geologie* 6, 610–639.
- Large, R.R., McPhie, J., Gemmell, J.B., Hermann, W., Davidson, G. J., 2001. The spectrum of ore deposit types, volcanic environments, alteration halos, and related exploration vectors in submarine volcanic successions: some examples from Australia. *Economic Geology* 96, 913–938.
- Laznicka, P., 1985. The geological association of coal and metallic ores—a review. In: Wolf, K.H. (Ed.), *Handbook of Strata-Bound and Stratiform Ore Deposits*, vol. 13. Elsevier, Amsterdam, pp. 1–72.
- Laznicka, P., 1999. Quantitative relationships among giant deposits of metals. *Economic Geology* 94, 455–473.
- Leach, D.L., Sangster, D.F., 1993. Mississippi Valley-type lead–zinc deposits. In: Kirkham, R.V., Sinclair, W.D., Thorpe, R.I., Duke, J. M. (Eds.), *Mineral Deposit Modelling*. Geological Association of Canada Special Paper, vol. 40, pp. 289–314.
- Leach, D.L., Viets, J.G., Koslowski, A., Kibitlewski, S., 1996. Geology, geochemistry and genesis of the Silesia-Cracow zinc–lead district, southern Poland. In: Sangster, D.F. (Ed.), *Carbonate-Hosted Lead–Zinc Deposits*. Society of Economic Geologists Special Publication, vol. 4, pp. 144–170.
- Leach, D.L., Bradley, M., Lewchuk, M.T., Symons, D.T.A., de Marsily, G., Brannon, J., 2001. Mississippi Valley-type lead–zinc deposits through geologic time: implications from recent age-dating research. *Mineralium Deposita* 36, 711–740.
- Leach, D.L., Marsh, E., Emsbo, P., Rombach, C.S., Kelley, K.D., Anthony, M., 2004. Nature of hydrothermal fluids at the shale-hosted Red Dog Zn–Pb–Ag deposits, Brooks Range, Alaska. *Economic Geology* 99, 1449–1480.
- Lefebvre, D.V., Church, B.N., 1996. Polymetallic vein Ag–Pb–Zn±Au. In: Lefebvre, D.V., Höy, T. (Eds.), *Selected British Columbia Mineral Deposit Profiles, Volume 2: Metallic Deposits*. British Columbia Geological Survey Open File Report 1996-13, pp. 67–70.
- Leistel, J.M., Marcoux, E., Thiéblemont, D., Quesada, C., Sánchez, A., Almodovar, G.R., Pascual, E., Sáez, R., 1998. The volcanic-hosted massive sulphide deposits of the Iberian Pyrite Belt. *Mineralium Deposita* 33, 2–30.
- Lewis, B.L., Froelich, P.N., Andreae, M.O., 1985. Methyl-germanium in natural waters. *Nature* 313, 303–305.
- Li, Y.H., 1982. Interelement relationship in abyssal pacific ferromanganese nodules and associated pelagic sediments. *Geochimica et Cosmochimica Acta* 46, 1053–1060.
- Lips, A.L.W., Herrington, R.J., Stein, G., Kozelj, D., Popov, K., Wijbrans, J.R., 2004. Refined timing of porphyry copper formation in the Serbian and Bulgarian portions of the Cretaceous Carpatho-Balkan Belt. *Economic Geology* 99, 601–609.
- Lombaard, A.F., Günzel, A., Innes, J., Krüger, T.L., 1986. The Tsumeb lead–copper–zinc–silver deposit, South West Africa/Namibia. In: Anhaeusser, C.R., Maske, S. (Eds.), *Mineral Deposits of Southern Africa*, Geol. Soc. South Africa, Johannesburg, vol. 2, pp. 1761–1782.
- Lu, J.L., Zhuang, H.P., Fu, J.M., Liu, J.Z., 2000. Sedimentation, diagenesis, hydrothermal process and mineralization of germanium in the Lincang superlarge germanium deposit in Yunnan Province, China. *Geochimica* 29 (1), 36–42 (in Chinese with English Abstract).
- Manskaya, S.M., Kodina, L.A., Generalova, V.N., Kraavitsova, R.P., 1972. Interactions between germanium and lignite structures in the early state of coal. *Geochemistry International* 8, 385–394.
- Marignac, C., Cuney, M., 1999. Ore deposits of the French Massif Central: insight into the metallogenesis of the Variscan collision belt. *Mineralium Deposita* 34, 472–504.
- Marquez-Zavalia, M.F., 1999. El yacimiento Capillitas, Catamarca. In: Zappettini, O. (Ed.), *Recursos Minerales de la Republica Argentina*. Instituto de Geología y Recursos Minerales SEGEMAR, Anales, vol. 35, pp. 1643–1652.
- Matthews, P.F.P., 1991. Bolivian mining—signs of recovery. *Mining Magazine* 164 (4), 226–230.
- Melcher, F., 2003. The Otavi Mountain Land in Namibia: Tsumeb, germanium and snowball earth. *Mitteilungen der Österreichischen Mineralogischen Gesellschaft* 148, 413–435.
- Melcher, F., Oberthür, T., Vetter, U., Gross, C.J., Vollbrecht, A., Braun, M., Haack, U., 2003. Germanium in carbonate-hosted Cu–Pb–Zn mineralization in the Otavi Mountain Land, Namibia. In: Eliopoulos, D.G., et al. (Eds.), *Mineral Exploration and Sustainable Development*. Millpress, Rotterdam, pp. 701–704.
- Misra, K.C., 2000. *Understanding Ore Deposits*. Kluwer Academic Publishing, Dordrecht. 845 pp.
- Misra, K.C., Gratz, J.C., Lu, Ch., 1996. Carbonate-hosted Mississippi Valley-type mineralizations in the Elmwood-Gordonsville deposits, Central Tennessee zinc district, a synthesis. In: Sangster, D.F. (Ed.), *Carbonate-Hosted Lead–Zinc Deposits*.

- Society of Economic Geologists Special Publication, vol. 4, pp. 58–73.
- Mladenova, V., Valchev, S., 1998. Ga/Ge ratio in sphalerite from the carbonate-hosted Sedmochislenitsi Deposit as a temperature indication of initial fluids. *Spisanie na Blgarskoto Geologicesko Druzestvo* 59 (2–3), 49–54.
- Moh, G.H., 1976. Experimental and descriptive ore mineralogy. *Neues Jahrbuch für Mineralogie, Abhandlungen* 128, 115–188.
- Moh, G.H., 1977. Ore minerals. *Neues Jahrbuch für Mineralogie, Abhandlungen* 131, 1–55.
- Moh, G.H., 1980. Ore synthesis, phase equilibria studies and applications. *Neues Jahrbuch für Mineralogie, Abhandlungen* 139, 114–184.
- Moh, G.H., Jäger, A., 1978. Phasengleichgewichte des Systems Ge–Pb–Zn–S in Relation zu Germanium–Gehalten alpiner Pb–Zn–Lagerstätten. *Verhandlungen der Geologischen Bundesanstalt (Wien)* 1978, 437–440.
- Möller, P., 1987. Correlation of homogenization temperatures of accessory minerals from sphalerite-bearing deposits and Ga/Ge model temperatures. *Chemical Geology* 61, 153–159.
- Möller, P., Dulski, P., 1993. Germanium and gallium distribution in sphalerite. In: Möller, P., Lüders, V. (Eds.), *Formation of Hydrothermal Vein Deposits—Case study of the Pb–Zn, Barite and Fluorite Deposits of the Harz Mountains*. Monograph Series on Mineral Deposits, vol. 30. Bornträger, Berlin, pp. 189–196.
- Moore, D.W., Young, L.E., Modene, J.S., Plahuta, J.T., 1986. Geologic setting and genesis of the Red Dog zinc–lead–silver deposit, Western Brooks Range, Alaska. *Economic Geology* 81, 1696–1727.
- Morales-Ruano, S., Touray, J.C., Barbanson, L., Hach-Ali, P.F., 1996. Primary cavities with incompatible fluid fillings in Ge-bearing sphalerite from Cerro del Toro, Alpujarride (Spain). *Economic Geology* 91, 460–465.
- Mortlock, R.A., Froelich, P.N., 1986. Hydrothermal germanium over the southern East Pacific Rise. *Science* 231, 43–45.
- Mortlock, R.A., Froelich, P.N., Feely, K.A., Massot, G.J., Butterfield, D.A., Lupton, J.F., 1993. Silica and germanium in Pacific Ocean: hydrothermal vents and plumes. *Earth and Planetary Science Letters* 119, 365–378.
- Müller, D., Kaminski, K., Uhlig, S., Graupner, T., Herzig, P.M., Hunt, S., 2002. The transition from porphyry- to epithermal-style gold mineralization at Ladolam, Lihir Island, Papua New Guinea: a reconnaissance study. *Mineralium Deposita* 37, 61–74.
- Munoz, M., Boyce, A.J., Courjault-Rade, P., Fallick, A.E., Tollon, F., 1994. Multi-fluid incursion in the Paleozoic basement-hosted Saint-Salvy ore deposit (NW Montagne Noire, southern France). *Applied Geochemistry* 9, 609–626.
- Nishiyama, T., 1974. Minor elements in some sulfide minerals from Kuroko deposits of the Shakanai mine. In: Ishihara, S. (Ed.), *Geology of Kuroko Deposits*. Society Mining Geologists of Japan, Special Issue, vol. 6, pp. 371–376.
- Novák, F., Tacl, A., Blüml, A., 1962. The distribution of indium in the Rejsy vein near Kutná Hora. *Sborník Geologických Ved* 2, 107–154 (in Czech with English Abstract).
- Novokhatskiy, I.P., Kalinin, S.K., Zamyattna, G.M., 1967. The germanium content of igneous and altered rocks of Kazakhstan. *Geochemistry International* 4, 1169–1192.
- Nuriyev, A.N., Lapshina, N.F., Dzhabarova, Z.A., 1968. Germanium in oil, water and rocks of oil deposits. *Geochemistry International* 5, 911–915.
- Oftedal, I., 1941. Untersuchungen über die Nebenbestandteile von Erzmineralen norwegischer zinkblendeführender Vorkommen. *Skrifter utgitt av det Norske Videnskaps-akademi i Oslo. Matematisk-Naturvitenskaplige Klasse* 8, 1–103.
- Oftedal, I., 1963. The germanium content of some Norwegian topaz specimen. *Norsk Geologisk Tidsskrift* 43, 267–270.
- Olade, M.A., Morton, R.T., 1985. Origin of the lead–zinc mineralisation in the Southern Benue Trough, Nigeria. Fluid inclusions and trace element studies. *Mineralium Deposita* 20, 76–80.
- Oliveira, J.T., Pacheco, N., Carvalho, P., Ferreira, A., 1997. The Neves–Corvo mine and the Paleozoic geology of Southwest Portugal. In: Barriga, F.J.A.S., Carvalho, P. (Eds.), *Geology and VMS Deposits of the Iberian Pyrite Belt*. Society of Economic Geologists Neves–Corvo Field Conference 1997. SEG Guidebook Series, vol. 27, pp. 21–71.
- Paar, W.H., Putz, H., 2005. Germanium associated with epithermal mineralization: examples from Bolivia and Argentina. In: Zhao, C.S., Guo, B.J. (Eds.), *Mineral Deposit Research: Meeting the Global Challenge*, vol. 3. China Land Publishing House, Beijing, pp. 48–51.
- Paar, W.H., Roberts, A.C., Berlepsch, P., Armbruster, T., Topa, D., Zagler, G., 2004. Putzite, $(\text{Cu}_{4.7}\text{Ag}_{3.3})_{\Sigma 8}\text{GeS}_6$, a new mineral species from Capillitas, Catamarca, Argentina: description and mineral structure. *Canadian Mineralogist* 42, 1757–1769.
- Panteleyev, A., 1996. Epithermal Au–Ag low sulphidation deposits. In: Lefebvre, D.V., Höy, T. (Eds.), *Selected British Columbia Mineral Deposit Profiles, Volume 2: Metallic Deposits*. British Columbia Geological Survey Open File Report 1996-13, pp. 45–48.
- Paone, J., 1970. Germanium. *Mineral Facts and Problems*. United States Bureau of Mines Bulletin, vol. 650, pp. 563–571.
- Pascua, M.I., Murciego, A., Pellitero, E., Babkine, J., Dusaouy, Y., 1997. Sn–Ge–Cd–Cu–Fe-bearing sulfides and sulfosalts from the Barquilla Deposit, Salamanca, Spain. *Canadian Mineralogist* 35, 39–52.
- Petrinov, R., 1995. Ore mineral paragenesis and zoning in the deposit of Chelopech (Bulgaria). *Geochemistry, Mineralogy and Petrology* 30, 89–98.
- Pimminger, M., Grasserbauer, M., Schroll, E., Cerny, I., 1985. Trace element distribution in sphalerites from Pb–Zn ore occurrences of the Eastern Alps. *Tschermaks Mineralogisch - Petrographische Mitteilungen* 34, 131–141.
- Pokrovski, G.S., Schott, J., 1998. Thermodynamic properties of aqueous Ge(IV) hydroxide complexes from 25 to 350 °C: implications for the behaviour of germanium and the Ge/Si ratio in hydrothermal fluids. *Geochimica et Cosmochimica Acta* 62, 1631–1642.
- Pouba, Z., Ilavský, J., 1986. Czechoslovakia. In: Dunning, F.W., Evans, A.M. (Eds.), *Mineral Deposits of Europe, Volume 3: Central Europe*. The Institution of Mining and Metallurgy and The Mineralogical Society, London, pp. 117–173.
- Proffett, J.M., 2003. Geology of the Bajo de la Alumbrera porphyry copper–gold deposit, Argentina. *Economic Geology* 98, 1535–1574.
- Prokin, V.A., Buslaev, F.P., 1999. Massive copper–zinc sulphide deposits in the Urals. *Ore Geology Reviews* 14, 1–69.
- Putz, H., Paar, W.H., Sureda, R.J., Roberts, A.C., 2002. Germanium mineralization at Capillitas, Catamarca Province, Argentina. *International Mineralogical Association, 18th General Meeting (Edinburgh), Abstract Volume*, p. 265.
- Puzanov, L.S., Koplus, A.V., Shmanenkov, I.V., El Khones, N.M., Poltarygina, T.V., 1973. The germanium and gallium contents of fluorite. *Geochemistry International* 10, 768–773.

- Qi Huawen, Hu Ruizhong, Su Wenchao, 2002. REE geochemistry of lignites in the Lincang germanium deposit, Western Yunnan Province, China. *Goldschmidt Conference Abstracts* 2002, p. A619 (www.the-conference.com/2002/abstracts/authors_Q.pdf).
- Queneau, P.B., Avotins, P.V., Farris, L.F., 1974. Germanium recovery from Fargo Oil's Lang Bay property. *CIM Bulletin* 79 (886), 92–97.
- Reimann, C., de Caritat, P., 1998. *Chemical Elements in the Environment*. Springer, Berlin, 398 pp.
- Roberts, A.C., Seward, T.M., Reusser, E., Carpenter, G.J.C., Grice, J.D., Clark, S.M., Markus, M.A., 2004. Eyselite, $\text{Fe}^{3+}\text{Ge}_3^{4+}\text{O}_7(\text{OH})$, a new mineral species from Tsumeb, Namibia. *Canadian Mineralogist* 42, 1771–1776.
- Rochow, E.G., Abel, E.W., 1975. *The Chemistry of Germanium, Tin, and Lead*. Pergamon Press, New York, 146 pp.
- Rose, A.W., 1967. Trace elements in sulphide minerals from the Central district, New Mexico, and the Bingham district, Utah. *Geochimica et Cosmochimica Acta* 31, 547–585.
- Russell, M.J., 1978. Downward-excavating hydrothermal cells and Irish-type ore deposits: importance of an underlying thick Caledonian prism. *Transactions, Institution of Mining and Metallurgy (Section B, Applied Earth Science)* 87, 168–171.
- Sangster, D.F., 1980. Quantitative characteristics of volcanogenic massive sulphide deposits. *Canadian Institute of Mining and Metallurgy Bulletin* 73, 74–81.
- Sangster, D.F., 1990. Mississippi Valley-type and sedex lead–zinc deposits: a comparative examination. *Transactions, Institution of Mining and Metallurgy (Section B, Applied Earth Science)* 99, 21–42.
- Sangster, D.F., 2002. The role of dense brines in the formation of vent–distal sedimentary–exhalative (SEDEX) lead–zinc deposits: field and laboratory evidence. *Mineralium Deposita* 37, 149–157.
- Sarykin, F.Y., 1977. Deposits of germanium. In: Smirnov, V.I. (Ed.), *Ore Deposits of the U.S.S.R.*, vol. III. Pitman Publishing, New York, pp. 442–451.
- Sass-Gustkiewicz, M., 2001. The Pomerzany Mine—characteristics of the ore deposit. In: Sawlowicz, Z. (Ed.), *Geological Excursion Guide, The Joint 6th Biennial SGA-SEG Meeting*, Krakow, Poland, pp. 64–78.
- Sass-Gustkiewicz, M., Kwiecinsky, B., 1995. Humic-source organic matter from the Upper Silesian Zn–Pb deposits (Poland). *International Journal of Coal Geology* 26, 135–154.
- Sasso, A.M., Clark, A.H., 1998. The Farallon Negro Group, northwest Argentina: magmatic, hydrothermal and tectonic evolution and implications for Cu–Au metallogeny in the Andean back-arc. *SEG Newsletter* 34, 1–18.
- Scheffer, H.-W., 1966. The occurrence of germanium in willemite. *Geochimica et Cosmochimica Acta* 30, 837–838.
- Schink, D.R., Guibasso, N.L., Fanning, K.A., 1975. Process affecting the concentration of silica at sediment–water interface of the Atlantic Ocean. *Journal of Geophysical Research* 80, 3013–3031.
- Schmidt, J., 1997. Shale-hosted Zn–Pb–Ag and barite deposits of Alaska. In: Goldfarb, R.J., Miller, L.D. (Eds.), *Mineral Deposits of Alaska. Economic Geology Monograph*, vol. 9, pp. 35–65.
- Schneider, G.I.C., 1989. The Tsumeb Mine, Excursion Guidebook, MINSA Excursion, SWA/Namibia. *Mineralogical Association of South Africa*, pp. 60–93.
- Schroeter, T.G., 2005. Exploration reviews. Western Canada. *SEG Newsletter* 60, 45 (January).
- Schroll, E., 1953a. Über Minerale und Spurenelemente, Vererzung und Entstehung der Blei-Zink-Lagerstätte Bleiberg-Kreuth, Kärnten in Österreich. *Mitteilungen der Österreichischen Mineralogischen Gesellschaft, Sonderheft* 2, 1–60.
- Schroll, E., 1953b. Über Unterschiede im Spurengehalt von Wurtziten, Schalenblenden und Zinkblenden. *Sitzungsberichte der Österreichischen Akademie der Wissenschaften, mathematisch-naturwissenschaftliche Klasse, Abteilung*, vol. I. Wien, pp. 21–32.
- Schroll, E., 1954. Ein Beitrag zur geochemischen Analyse ostalpiner Blei-Zink-Erze, Teil 1. *Mitteilungen der Österreichischen Mineralogischen Gesellschaft, Sonderheft* 3, 1–85.
- Schroll, E., 1996. The Triassic carbonate-hosted Pb–Zn mineralizations in the Alps (Europe). In: Sangster, D.F. (Ed.), *Carbonate-Hosted Lead–Zinc Deposits. Society of Economic Geologists Special Publication*, vol. 4, pp. 182–194.
- Schroll, E., 1997. Geochemische und geochronologische Daten und Erläuterungen. In: Weber, L. (Ed.), *Handbuch der Lagerstätten der Erze und Industriemineralien und Energierohstoffe Österreichs. Archiv für Lagerstättenforschung, Geologische Bundesanstalt*. Wien, pp. 395–542.
- Schroll, E., 2005. Alpine-type Pb–Zn deposits (APT) hosted by Triassic carbonates. In: Mao, J.W., Bierlein, F.P. (Eds.), *Mineral Deposit Research: Meeting the Global Challenge*. Springer, Berlin, pp. 175–178.
- Schroll, E., Azer, I.N., 1959. Beitrag zur Kenntnis ostalpiner Fahlerze. *Tschermaks Mineralogisch - Petrographische Mitteilungen* 7, 70–105.
- Schroll, E., Rantitsch, G., 2005. Sulfur isotope patterns in the Bleiberg deposit (Eastern Alps) and their implications for genetically affiliated deposits. *Mineralogy and Petrology* 148, 1–16.
- Schroll, E., Kürzl, U., Weinzierl, O., 1994. Geochemical studies applied to the Pb–Zn deposit Bleiberg/Austria. In: Fontbote, L., Boni, M. (Eds.), *Sediment-Hosted Zn–Pb Ores. SGA Special Publication*, vol. 10. Springer, Berlin, pp. 228–245.
- Schroll, E., Köppel, V., Cerny, I., 2005. Pb and Sr isotope and geochemical data from the Pb–Zn deposit Bleiberg (Austria): constraints on the age of mineralization. *Mineralogy and Petrology* 86, 129–156.
- Schrön, W., 1968. Ein Beitrag zur Geochemie des Germaniums: I. Petrogenetische Probleme. *Chemie der Erde* 27, 193–251.
- Schwarz-Schampera, U., Herzig, P.M., 2002. *Indium: Geology, Mineralogy, and Economics*. Springer, Berlin, 257 pp.
- Scoyer, J., Helian, G., Wolf, H.U., 2001. Germanium and germanium compounds. *Ullmann's Encyclopaedia of Industrial Chemistry* 2001. Wiley-VCH, Weinheim, Germany, pp. 351–363.
- Seifert, T., 1999. Relationship between Late Variscan lamprophyres and hydrothermal vein mineralization in the Erzgebirge. In: Stanley, C.J., et al. (Eds.), *Mineral Deposits: Processes to Processing*. Balkema, Rotterdam, pp. 429–432.
- Seim, R., Schweder, P., 1969. Untersuchungen zum Germaniumgehalt im Topas. *Chemie der Erde* 28, 83–90.
- Seredin, V.V., 2003. Anomalous trace elements contents in the Spetsugli germanium deposit (Pavlovka brown coal deposit), Southern Primorye: Communication 1. Antimony. *Lithology and Mineral Resources* 38, 154–161.
- Seredin, V.V., Danilcheva, J., 2001. Coal-hosted Ge deposits of the Russian Far East. In: Piestrzynski, A., et al. (Eds.), *Mineral Deposits at the Beginning of the 21st Century*. Balkema, Lisse, pp. 89–92.
- Shaderman, F.I., Kremenetsky, A.A., Volokh, A.A., Shteinberg, G.S., 1996. A recent gas-and-vapor system of the Kudryavyi Volcano: a new source of rare metals. 30th International Geological Congress, Beijing, China, August 4–14, 1996. *Abstract volume* 30/1, p. 426.

- (<http://cc.msnsnscache.com/cache.aspx?q=2082040220184&lang=de-DE&FORM=CVRE>).
- Shazly, E.M., Webb, J.S., Williams, D., 1957. Trace elements in sphalerite, galena and associated minerals from the British Isles. *Transactions, Institution of Mining and Metallurgy* 66, 271–341.
- Shcherba, G.N., Zamyatina, G.M., Kalinin, S.K., Mukhlya, K.A., 1966. Germanium in some greisens in Kazakhstan. *Geochemistry International* 6, 1091–1104.
- Shikazono, N., 2003. Geochemical and tectonic evolution of arc-backarc hydrothermal systems: implication for the origin of Kuroko and epithermal vein-type mineralizations and the global geochemical cycle. *Developments in Geochemistry*, vol. 8. Elsevier, Amsterdam. 463 pp.
- Shimazaki, Y., 1974. Ore minerals of the Kuroko-type deposits. *Mining Geology, Special Issue* 6, 311–322.
- Skarpelis, N., 1995. Minor elements in the base metal part of an epithermal system: the Kirki (St. Phillippe) Mine, Thrace, Northern Greece. *Terra—Proceedings of the 8th EUG Meeting, Strasbourg*, p. 293.
- Slack, J.F., Dumoulin, J.A., Schmidt, J.M., Young, L.E., Rombach, C.S., 2004a. Paleozoic sedimentary rocks in the Red Dog Zn–Pb–Ag district and vicinity, Western Brooks Range, Alaska: provenance, deposition, and metallogenic significance. *Economic Geology* 99, 1385–1414.
- Slack, J.F., Kelley, K.D., Anderson, V.M., Clark, J.L., Ayuso, R.A., 2004b. Multistage hydrothermal silicification and Fe–Ti–As–Sb–Ge–REE enrichment in the Red Dog Zn–Pb–Ag district, Northern Alaska: geochemistry, origin, and exploration applications. *Economic Geology* 99, 1481–1508.
- Söhne, P.C., 1964. The geology of the Tsumeb Mine. In: Houghton, S.H. (Ed.), *The Geology of Some Ore Deposits in Southern Africa*, vol. 2. Geological Society of South Africa, Johannesburg, pp. 367–382.
- Soler, P., 1987. Variations des teneurs en éléments mineurs (Cd, In, Ge, Ga, Ag, Bi, Se, Hg, Sn) des minerais de Pb–Zn de la province polymétallique des Andes du Pérou Central. *Mineralium Deposita* 22, 135–143.
- Song, X., 1984. Minor elements and ore genesis of the Fankou lead–zinc deposit, China. *Mineralium Deposita* 19, 95–104.
- Song, X., 1994. Sediment-hosted Pb–Zn deposits in China: mineralogy, geochemistry and comparison with some similar deposits of the world. In: Fontbote, L., Boni, M. (Eds.), *Sediment-Hosted Zn–Pb Ores*. SGA, Special Publication, vol. 10. Springer, Berlin, pp. 333–353.
- Song, X., Tan, H., 1996. Geochemical characteristics of the Fankou Pb–Zn deposits, northern Guangdong, South-China. In: Sangster, D.F. (Ed.), *Carbonate-Hosted Lead–Zinc Deposits*. Society of Economic Geologists Special Publication, vol. 4, pp. 350–355.
- Spears, D.A., Zheng, J., 1999. Geochemistry and origin of elements in some UK coals. *International Journal of Coal Geology* 38, 161–179.
- Stadnichenko, T., Murata, K.J., Zubovic, P., Hufschmidt, E.L., 1953. Concentration of germanium in the ash of American coals—a progress report. *U.S. Geological Survey Circular* 272, 1–34.
- Steed, G.M., 1986. The geology of the Gortdrum Cu–Ag–Hg orebody. In: Andrew, C.J., Crowe, R.W.A., Finlay, S., Pennell, W.M., Pyne, J.F. (Eds.), *Geology and Genesis of Mineral Deposits in Ireland*. Irish Association for Economic Geology, pp. 481–499.
- Stikine Gold Corporation, 2004. Interim financial statements for the nine months ended November 30, 2004, 22 pp. (<http://stikinegold.com/i/pdf/SKY-3Q2004.pdf>).
- Strunz, H., Giglio, M., 1961. Die Kristallstruktur von Stottit. *FeGe (OH)₆*. *Acta Crystallographica* 14, 205–208.
- Strunz, H., Nickel, E.H., 2001. *Strunz Mineralogical Tables*, 9th edition. Schweizerbart'sche Verlagsbuchhandlung, Stuttgart. 870 pp.
- Symons, D.T.A., Pannalal, S.J., Coveney, R.M., Sangster, D.F., 2005. Paleomagnetism of Late Paleozoic strata and mineralization in the Tri-state lead–zinc ore district. *Economic Geology* 100, 295–309.
- Tanimura, S., Date, J., Takahashi, T., Ohmoto, H., 1983. Geologic setting of the Kuroko deposits, Japan. *Economic Geology Monographs* 5, 24–38.
- Taran, Y.A., Hedenquist, J.F., Korzhinskii, M.A., Tkachenko, S.I., Shmulovich, K.I., 1995. Geochemistry of magmatic gases from Kudryavy Volcano, Iturup, Kuril Islands. *Geochimica et Cosmochimica Acta* 59, 1749–1761.
- Taylor, S.R., McLennan, S.M., 1985. *The Continental Crust: its Composition and Evolution*. Blackwell, Oxford. 312 pp.
- Teckcominco, 2002. Annual information form March 2002, 44 pp. (<http://www.teckcominco.com/investors/reports/aif-circ/tc-aif-01.pdf>).
- Terziyev, G.I., 1966. The conditions of germanium accumulation in hydrothermal mineralizations (as illustrated by Bulgarian deposits). *Geochemistry International* 3, 341–346.
- Theron, S.J., Beukes, N.J., 1995. Carbonate petrography and the origin of Neoproterozoic Tsumeb-type Cu–Pb–Zn mineralization in the Otavi Mountain land, Namibia. In: Barton, M.J., Copperthwaite, Y.E. (Eds.), *Centennial Geocongress, Extended Abstracts*, vol. I. Geological Society of South Africa, Johannesburg, pp. 115–117.
- Tourigney, G., Doucet, D., Bourget, A., 1993. Geology of the Bousquet 2 Mine: an example of a deformed, gold-bearing, polymetallic sulphide deposit. *Economic Geology* 88, 1578–1597.
- Trueman, E.A.G., 1998. Carbonate-hosted Cu±Pb±Zn. *Geological Fieldwork 1997*, British Columbia Ministry of Employment and Investment, Paper 1998-1, pp. 24B1–24B4.
- Tsarev, D.I., 1995. Ozernoe pyrite-polymetallic deposit. In: Laverov, N.P. (Ed.), *Deposits of Transbaikalia: GeoInformMark*, Moscow, vol. 1, book 1, pp. 94–100 (in Russian).
- Tselikova, Y., 2001. Mining Industry in Primorskiy Krai, The Russian Far East. (www.bisnis.doc.gov/bisnis/country/010209mining.htm) 5 pp.
- Tufar, W., 1992. Paragenesis of complex massive sulphide ores from the Tyrrhenian Sea. *Mitteilungen der Österreichischen Geologischen Gesellschaft* 84, 265–300.
- USGS, 2004. U.S. Geological Survey Mineral Commodity Summaries, January 2004: Germanium, pp. 70–71. prepared by M.W. George (<http://minerals.usgs.gov/minerals/pubs/commodity/germanium/germamcs04.pdf>).
- USGS, 2005. U.S. Geological Survey Mineral Commodity Summaries, January 2005: Germanium, pp. 70–71. prepared by M.W. George (<http://minerals.usgs.gov/minerals/pubs/commodity/germanium/germamcs05.pdf>).
- Vakrushev, V.A., Semenov, V.N., 1969. Regularities of germanium distribution in magnetite of iron-ore deposits (exemplified by the Altai-Sayan region and the Yenisey Ridge). *Geokhimiya* 6, 683–690 (in Russian with English Abstract).
- Valković, V., 1978. *Elements in Petroleum*. The Petroleum Publishing Company, Tulsa, Oklahoma. 298 pp.
- Valković, V., 1983. Trace elements in coal. Volumes I and II, CRC Press, Boca Raton, Florida, 210 and 281 pp.
- Viets, J.G., Hopkins, R.T., Miller, B.M., 1992. Variations in minor and trace metals in sphalerite from Mississippi Valley-type deposits of the Ozark region: genetic implications. *Economic Geology* 87, 1897–1905.

- Vlassov, K.A., 1964. Geochemistry and mineralogy of rare elements and genetic types of their deposits. Chapter Germanium, Volumes I and III. Academy of Sciences, U.S.S.R., Institute for Mineralogy, Geochemistry and Crystal Chemistry of Rare Elements, Moscow. Israel Program for Scientific Translation, 1966, p. 525–551 (in Russian).
- Voskresenskaya, N.T., Ufnarovskaya, G.P., 1978. Tl and Ge geochemistry in iron - manganese ores of the Karazhal Deposit, Central Kazakhstan. *Geokhimiya* 1978, 560–567 (in Russian with English Abstract).
- Voskresenskaya, N.T., Weimarn, A.B., Vinogradova, N.A., 1975. Thallium and germanium in manganese and iron ores of the Dzhezdinsk type (Central Kazakhstan). *Geokhimiya* 12, 61–66 (in Russian with English Abstract).
- Walker, R.R., Mannard, G.W., 1974. Geology of the Kidd Creek mine—a progress report. Canadian Institute of Mining and Metallurgy Bulletin 67 (572), 41–57.
- Walker, R.R., Matulich, A., Amos, A.C., Watkins, J.J., Mannard, G.W., 1975. The geology of the Kidd Creek Mine. *Economic Geology* 70, 80–89.
- Weisbach, A., 1886. Argyrodite, ein neues Silbererz. *Neues Jahrbuch für Mineralogie, Geologie und Palaeontologie* II, 67–71.
- Weninger, M., 1965. Über die Gehalte an Ge, Sn und einigen anderen Spurenelementen in ostalpinen Graphit- und Talkgesteinen. *Tschermaks Mineralogisch - Petrographische Mitteilungen* 13, 475–490.
- Wilkinson, J.J., 2003. On diagenesis, dolomitisation and mineralisation in the Irish Zn–Pb orefield. *Mineralium Deposita* 38, 968–983.
- Wilkinson, J.J., Eyre, S.L., Boyce, A.J., 2005. Ore-forming processes in Irish-type carbonate-hosted Zn–Pb deposits: evidence from mineralogy, chemistry, and isotopic composition of sulfides at the Lisheen Mine. *Economic Geology* 100, 63–86.
- Wilson, G.C., Rucklidge, J.C., Campbell, J.L., Nejedly, Z., Teesdale, W.J., 2002. Applications of PIXE to mineral characterization. *Nuclear Instruments and Methods in Physics Research. Section B, Beam Interactions with Materials and Atoms* 189, 387–393.
- Wittmann, A., 1966. Beiträge zur Strukturchemie des Germaniums. *Fortschritte der Mineralogie* 43, 230–272.
- Wittmann, A., 1972. Germanium 32, crystal chemistry. In: Wedepohl, K.H. (Ed.), *Handbook of Geochemistry*. Springer, Berlin, pp. 32-A-1–32-A-4.
- Yakushi, D., Enjoji, M., 2004. Chemical composition of ores from the Takara volcanogenic massive sulfide deposit, central Japan. *Resource Geology* 54, 437–446.
- Yudovic, Y.A., 2003. Notes on the marginal enrichment of germanium in coal beds. *International Journal of Coal Geology* 56, 223–232.
- Yun, S.-T., So, C.-S., Choi, S.-H., Shelton, K.L., Koo, J.-H., 1993. Genetic environment of germanium-bearing gold-silver vein ores from the Wolyu mine, Republic of Korea. *Mineralium Deposita* 28, 107–121.
- Zahradnik, L., Tyroler, J.L., Vondráková, M., 1960. Contribution to the geochemistry of germanium in the Pilzen Basin. *Věstník Ústředního Ústava Geologického, Praha* 18, 459–468 (in Czech).
- Zeeh, S., Bechstäd, T., 1994. Carbonate-hosted Pb–Zn mineralization at Bleiberg-Kreuth (Austria): compilation of data and new aspects. In: Fontboté, L., Boni, M. (Eds.), *Sediment-hosted Zn–Pb Ores*. SGA Special Publication, vol. 10. Springer, Berlin, pp. 271–296.
- Zilbermint, V.A., Rusanov, A.K., Kosrykin, V.M., 1936. On the question of Ge-presence in fossil coals. *Academician V.I. Vernadsky (up to the 50th Anniversary of His Scientific Activity)*, vol. 1. USSR Academy of Science, Moscow, pp. 169–190 (in Russian).
- Zhuang, H.P., Lu, J.L., Fu, J.M., Liu, J.Z., 1998. Lincang super-large germanium deposit in Yunnan Province, China; sedimentation, diagenesis, hydrothermal processes and mineralization. *Journal of China University of Geosciences* 9, 129–136 (in Chinese with English Abstract).