MITT.ÖSTERR.MINER.GES. 148 (2003)

THE OTAVI MOUNTAIN LAND IN NAMIBIA: TSUMEB, GERMANIUM AND SNOWBALL EARTH

by

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Vortrag vor der Österreichischen Mineralogischen Gesellschaft
gehalten am 25. 11. 2002 in Wien, am 26. 11. 2002 in Graz, am 27. 11. 2002 in Leoben
und am 29. 11. 2002 in Innsbruck

Abstract

Neoproterozoic carbonate successions in the Otavi Mountain Land, Namibia, host a large number of polymetallic (Cu-Pb-Zn) sulfide prospects and deposits, which may carry economic concentrations of rare elements such as germanium. Geochemical and mineralogical data are presented for Ge-bearing ores in the Tsumeb and Khusib Springs deposits, and are compared to the ores of Kombat and Berg Aukas. At Tsumeb, local pockets of germanite and reniérite-rich ore assaying up to 0.83 % Ge formed from hot, hydrothermal solutions in the early stages of Cu sulfide (tennantite) precipitation along a solution-induced collapse structure. Massive Cu ore at the Khusib Springs mine is composed of tennantite, enargite, galena and pyrite, with lesser amounts of sphalerite and Ag-rich sulfosalts. An average of 40 ppm Ge is mainly hosted by Ge-bearing colusite (4–6 wt.% Ge) forming euhedral crystals along ore-dolomite contacts. Ge-bearing ore replaces earlier sphalerite-pyrite-dominated mineralization and formed from saline, hot (> 300°C), acidic hydrothermal fluids during or postdating peak metamorphism in the area. At Tsumeb and Khusib Springs, Ge-bearing sulfide ores carry elevated concentrations of As, Sb, Ag, Ga, Mo, Sn, W and Re. Cu-Pb ores at Kombat and Zn-Pb ore at Berg Aukas generally carry lower concentrations of Ge, As, Mo and W. In the extensive oxidation zones of the Tsumeb deposit, Ge preferentially enters into iron hydroxides, but also into arsenates and carbonates, and forms rare secondary Ge minerals.

Zusammenfassung

In jungproterozoischen Karbonatabfolgen des Otavi Berglandes (Namibia) sind zahlreiche polymetallische (Cu-Pb-Zn) Sulfidvorkommen und Lagerstätten bekannt, die stellenweise ökonomische Gehalte an Germanium führen. In dieser Arbeit werden geochemische und mineralogische Daten aus den Lagerstätten Tsumeb und Khusib Springs präsentiert, und mit Erzen der Lagerstätten Kombat und Berg Aukas verglichen.

In der lösungsinduzierten Hohlraumstruktur (Karstschlauch) von Tsumeb bildeten sich lokale Anreicherungen von Germanit und Reniérit (bis zu 0.83 % Ge im Erz) aus heißen hydrothermalen Lösungen während der Frühphase der Cu-Sulfidbildung (v.a. Tennantit). Das massive Cu-Erz von Khusib Springs besteht aus Tennantit, Enargit, Galenit und Pyrit, mit wechselnden Gehalten von Sphalerit und Ag-Sulfosalzen. Idiomorphe Kristalle von Ge-haltigem Colusit (4–6 % Ge) treten gehäuft entlang von Erz-Dolomitkontakten auf und sind für durchschnittlich 40 ppm Ge im Erz verantwortlich. Das Ge-führende Sulfiderz verdrängt eine frühere Sphalerit-Pyrit Paragenese und setzte sich syn- oder postmetamorph aus salinaren, sauren und heißen (> 300°C) hydrothermalen Lösungen ab. In Tsumeb und Khusib Springs sind die Ge-führenden Sulfiderze mit Anreicherungen von As, Sb, Ag, Ga, Mo, Sn, W und Re verknüpft. Cu-Pb Erze von Kombat sowie Zn-Pb Erze von Berg Aukas weisen dagegen generell niedrigere Konzentrationen an Ge, As, Mo und W auf. In den ausgedehnten Oxidationszonen der Lagerstätte Tsumeb ist Ge vor allem in Eisenhydroxidphasen gebunden, aber auch in Arsenaten und Karbonaten, und in Form eigener sekundärer Ge-Minerale.

Introduction

Tsumeb – this is more than the name of a small town in Namibia and a polymetallic copper deposit: Tsumeb is renown for its variety and beauty of secondary minerals. More than 240 minerals have been described from Tsumeb until 2000, and Tsumeb is the type locality for about 55 minerals (JAHN, 2001). The reason for the spectacular number of mineral species is threefold: (1) the primary sulfide ore contains a large number of rare elements besides major Cu, Pb, Zn and As; (2) primary ore has been partly to pervasively oxidized to secondary ore in three oxidation zones; and (3) the deposit is hosted in a karst pipe structure which crosscuts carbonate rocks. For these reasons, about 28 % of the identified mineral species are phosphates and arsenates of Cu, Pb and Zn, 19 % are sulfides, 15 % silicates, 11 % sulfates, molybdates and vanadates and 9 % are carbonates.

It is less well known that the Tsumeb orebody represents the largest known single sulfidic accumulation of germanium (Ge). The original resource was estimated to 2,160 tons (LOMBAARD et al., 1986), but only 87 tons have been extracted during the mining period between 1907 and 1996, although the mine produced about 30 Mt of ore grading 10 % Pb, 4.3 % Cu, and 3.5 % Zn. Significant quantities of As, Sb, Ag, Cd, and Au have been extracted.

Germanium is a semiconductor metal and a rare element in the crust (average: 1.6 ppm). It is an important high-technology electronic metal, finding increasing use in fiber (50 %) and infrared optics (15 %), and as polymerization catalysts (20 %; BROWN, 2000). World refined Ge production (68 t in 2001) can no longer meet the demand (105 t in 2000) of the world market; the difference is balanced by recycling (25 t/y) and releases from US stockpiles. There is a strong demand for exploration and for innovative extraction techniques, because estimated global resources are a few thousand tons of recoverable Ge only. Germany is one of the leading importers of Ge oxide, from which ultrapure Ge is produced. In order to evaluate the potential of Tsumeb-type deposits for metals with a short lifetime of reserves (defined here as those high-technology metals having reserves of less than 25 years at constant demand), the German Federal Institute for Geosciences and Natural Resources (BGR) is conducting a geological research project in the Otavi Mountain Land (OML) of Namibia.

In this contribution a summary on the mineralogy and geochemistry of the sulfide ores from Tsumeb and Khusib Springs is given, with the main focus on the concentration, mineralogical siting and metallogenic position of Ge in the ores.

Geological background and Snowball Earth

The Neoproterozoic Damara Supergroup in the Otavi Mountain Land (Fig. 1) is subdivided, from bottom to top, into the Nosib (clastic sediments and volcanics), Otavi (mainly carbonates) and Mulden Groups (clastic molasse-type sediments) (Fig. 2). The Otavi Group, deposited between approximately 750 and 545 Ma and hosting most orebodies in the OML, is subdivided into the Abenab and Tsumeb Subgroups. Sedimentation in both subgroups started with glacial diamictites (the Chuos and Ghaub Formations), followed by carbonate sedimentation on a shallow shelf. Eight informal lithozones (T1 to T8) are distinguished within the Tsumeb Subgroup (Fig. 2). Sedimentological and carbon isotope studies indicate that the Maieberg Formation (T2-T3) has been deposited in relatively deeper water than the remaining Tsumeb Subgroup during a collision event in the Kaoko Belt further to the west (KAUFMAN et al., 1991; FRIMMEL et al., 1996), and in cold water following a glacial episode which is preserved in the underlying Ghaub Formation (T1). Deposition of lithozones T4-T8 reflects extensional tectonics and progressively warmer climate; the dolostones are characterized by the presence of chert, oolites and pisolites, silicified stromatolites and algal mats.

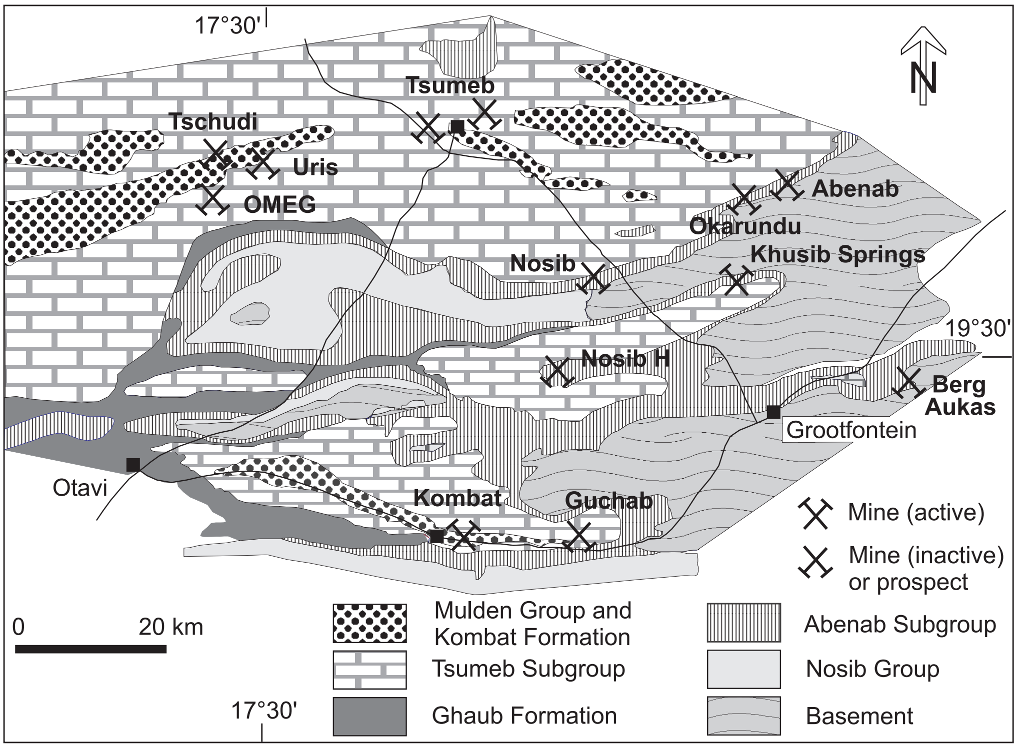


Figure 1

Geological sketch map of the Otavi Mountain Land with major mines and prospects (modified from CHETTY & FRIMMEL, 2000).

Group	Subgroup	Formation		Lithology
Mulden		Owambo		Pelite, marl, carbonate
		Kombat		Shale
		Tschudi		Arenite
Otavi	**Tsumeb**	Hüttenberg	T8	Dolomite, Pelite
			T7	
			T6	Dolomite, Chert
		Elandshoek	T5	
			T4	Dolomite
		Maieberg	T3	
			T2	Limestone
580 Ma		Ghaub	T1	Diamictite
	Abenab	Auros		Carbonate, Pelite
		Gauss		Dolomite
		Berg Aukas		
750 Ma		Chuos		Diamictite
Nosib		Askevold		Volcanics
		Nabis		Clastics
Grootfontein Basement Complex				

Figure 2

Stratigraphy of the Damara Supergroup in the Otavi Mountain Land.

There is ample field and geochemical evidence for multiple glaciation in the OML. This includes the presence of thick units of glacial diamictite, glaciogenic iron formation in the Chuos Formation, and negative excursions of $\delta^{13}C$ isotopes in carbonate units under- and overlying the diamictites. Following HOFFMAN et al. (1998, 1999), these features are observed globally ("Snowball Earth"; KIRSCHVINK, 1992) and may best be interpreted as indicating at least two global glaciations. The age of the glaciations is a contentious issue; while HOFFMAN et al. (1998) argue for a Sturtian age (760 to 700 Ma) of the whole Otavi Group, other authors (KENNEDY et al., 1998; FÖLLING & FRIMMEL, 2002) favour a syn-Marinoan/Varangian age (approx. 580 Ma) of the Ghaub Formation. The assembly of the super-continent "Rodinia" along the paleo-equator in the Neoproterozoic, in combination with as yet unknown solar-induced effects, triggered global glaciation on the continents followed by complete freezing of the oceans. Sudden deglaciation was probably induced by increasing volcanic activity causing a sudden greenhouse effect, resulting in deposition of typical "cap carbonates" on top of the diamictite units.

Continent-continent collision between the Congo and Kalahari Cratons resulted in deformation and regional metamorphism (D_2) in the Damara Belt approximately 545 Ma ago (FRIMMEL & FRANK, 1998). In the OML, D_2 deformation induced E-W-trending open to isoclinal F_2 folds and north-vergent thrusts with the intensity of deformation and metamorphism decreasing towards the north. Subsequent folding and thrusting onto the Kalahari Craton is documented by NE-trending open, upright cross-warps (D_3).

Ore deposits in the Otavi Mountain Land

About 600 occurrences of Cu-Pb-Zn-V mineralization are known in the OML. These can be grouped into at least four types: (1) "Berg Aukas-type” Zn-Pb deposits in carbonates; (2) "Tsumeb-type” Pb-Cu-Zn deposits in carbonates; (3) "Abenab-type” vanadium deposits in geologically young karst pipes and breccias, e.g. the Abenab Mine (1.85 Mt @ 1.03 % V_2O_5 mined; CAIRNCROSS, 1997); and (4) "Tschudi-type” low-grade Cu ores in sandstone and conglomerate of the basal Mulden Group. Types (3) and (4) are not dealt with in any detail here.

Carbonates of the Abenab Subgroup mainly host "Berg Aukas-type” Zn-Pb mineralization with appreciable supergene enrichment of vanadium (e.g., the former Abenab West and Berg Aukas mines; Fig. 1). These small to medium-size deposits can be grouped within the "Mississippi-Valley-type” (MVT) deposits (FRIMMEL et al., 1996) (Table 1). At Berg Aukas, 1.6 Mt of ore @ 4 % Pb, 17 % Zn and 0.93 % V_2O_5 has been mined, with another 1.6 Mt of similar grade still left in place (MISIEWICZ, 1988). Berg Aukas and Abenab West host large reserves of "non-sulfide zinc” ores as willemite, smithsonite and descloizite.

	Tsumeb	**Khusib Springs**	**Kombat**	**Berg Aukas-Type**
Host rocks	T4-T8 dolomite, Hüttenberg Fm.	T2 limestone, Maieberg Fm.	Upper Hüttenberg dolomite, sandstone, Fe-Mn ore, Kombat Fm. phyllite	Dolomites of Abenab SG and lower Tsumeb SG
Shape of orebody	Along margin and disseminated in discordant pipe with breccia and sandstone filling; structural control	Stratiform lensoidal body of massive sulfide ore, dolomite alteration, breccia; structural control?	Discordant sulfide lenses (roll structures), stringer mineralization, breccia; structural control	Stratiform orebodies, breccia common
Geochemistry	Pb>Cu~Zn; As Ag, Cd, Ge, Ga	Cu>Pb>Zn; As, Sb; Ag, Ge, Cd	Cu>Pb; low Zn, As, Ag, Ge	Zn>Pb; V supergene; low Cu, As, Ga, Ge, Cd
Major ore minerals	tn, ga, sph, py, bn, cp, dg, chc	tn, en, ga, py, sph, dg	cp, bn, ga (sph)	sph, ga (cp)
Ge minerals (primary)	Germanite, reniérite, briartite, germanocolusite	Ge-bearing colusite	Reniérite, colusite	Reniérite ?
Fluid composition	20-23 wt.% NaCl	17-23 wt.% NaCl		ca. 23 wt.% NaCl
P-T conditions	370-405°C, 2-3 kbar	>370°C	200-300°C (stage 1); 350-480°C (peak metamorphic)	137-255°C, 0.5 kbar
Fluid source	Orogenic	Orogenic	Hydrothermal and orogenic	Basinal brines
$\Delta^{34}S$ (sulfide ore)	Positive (+13 to +27‰)	Positive (+23 to +28‰)	Variable (-11 to +26‰)	Positive (+17 to +30‰)
$\Delta\,^{13}C$ (carbonate)	-4 to +2	-3 to +1	-9 to +10	+3 to +5
Pb isotopes (ore)	“Tsumeb-type”	“Khusib-type”	“Tsumeb-type”	“Berg Aukas-type”
Age of mineralization	Syn-D_2, 570-520 Ma?	Syn-D_2, or later?	Pre-D_2 and syn-D_2	Pre-D_2 , diagenetic?

Table 1

Major features of base metal deposits in the Otavi Mountain Land (data sources: CHETTY & FRIMMEL, 2000; FRIMMEL et al., 1996; HUGHES, 1987; INNES & CHAPLIN, 1986; LOMBAARD et al., 1986; MISIEWICZ, 1988).

The Tsumeb Subgroup mainly contains Cu-rich "Tsumeb-type” deposits, although Berg Aukas-type mineralization is known from several locations. The Tsumeb mine in the northern part of the OML (Fig. 1) is the largest "Tsumeb-type” deposit. The area was first prospected in 1893 by Mathew Rogers of the South West Africa Company, and the Tsumeb deposit was mined from 1907 to 1940 by the German OMEG (Otavi-Minen- und Eisenbahngesellschaft), which produced about 2.3 Mt @ 8.2 % Cu, 18 % Pb and 8.4 % Zn. From 1947 to 1996, Tsumeb Corporation Limited (TCL) mined further 28 Mt @ 4 % Cu, 12 % Pb and 5 % Zn. After liquidation of TCL in 1997, Ongopolo Mining and Processing Limited re-started the smelter operations at Tsumeb in 2000; since then small-scale selective mining of ore remnants continues in the upper levels of the Tsumeb mine.

The Tsumeb deposit has been described by a large number of workers (e.g., SCHNEIDERHÖHN, 1929; BARTELKE, 1976; KELLER, 1984; LOMBAARD et al., 1986; HUGHES, 1987; GEBHARD, 1991; SCHNEIDER & SEEGER, 1992). It forms a zoned pipe-like structure cross-cutting folded dolomites of the upper Tsumeb Subgroup (T4 to T8 lithozones; Fig. 2) close to the unconformity with the Mulden Group. The deposit has been exploited to a depth of 1700 m below surface (Fig. 3, Table 1). The ore-bearing pipe structure carries various types of carbonate breccia, altered dolomitic wall rock and irregular bodies of a feldspar-rich sandstone ("pseudoaplite" in the literature; LOMBAARD et al., 1986). Massive, high-grade sulfide ores are mainly distributed along the periphery of the pipe, whereas the central part usually has low-grade disseminated ore. Rich sulfide ores, including mantos into the dolomitic wall rock, are developed along the intersection of the pipe with the "North Break Zone", a unit of breccia that has been explained as a paleo-aquifer and original evaporite bed (LOMBAARD et al., 1986; THERON, 1994). Three oxidation zones are developed in the pipe structure, occurring from surface down to level 11 (310 m below surface), from level 24 (-720 m) to 35 (-1150 m), and below level 42 (-1380 m).

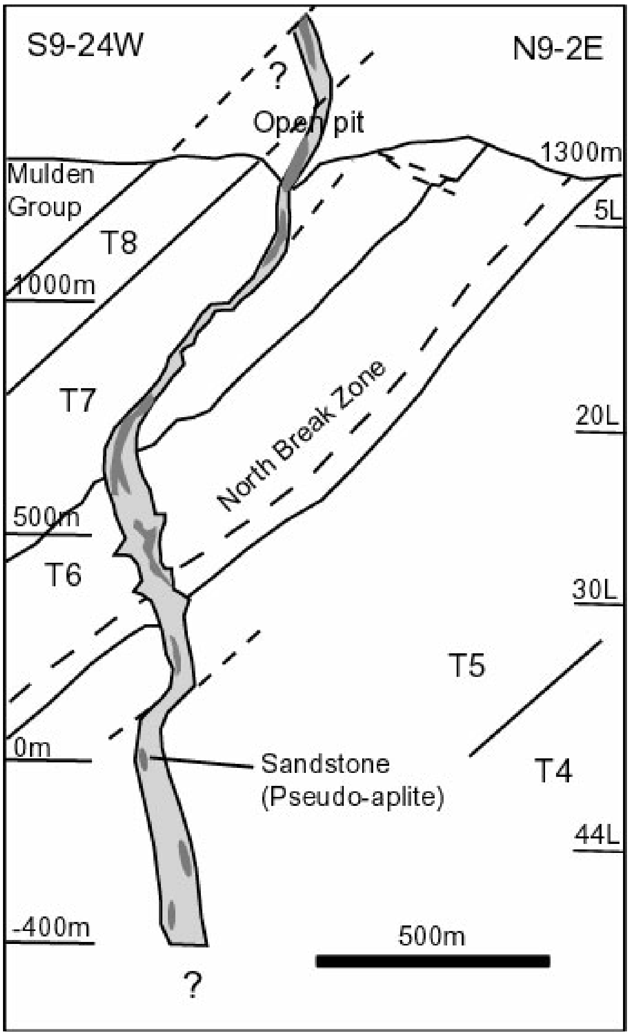


Figure 3
Geological cross-section of the Tsumeb deposit (modified from LOMBAARD et al., 1986).

The small, high-grade Khusib Springs deposit is located in laminated limestones of the Maieberg Formation (T2 lithozone) of the Tsumeb Subgroup, close to the contact with laminated dolomicrite of lithozone T3 (Fig. 2). It was discovered early in the 1990s by mapping and drilling, and went into production in 1995. Before liquidation of the TCL, 107,000 t of ore had been mined, from which 21,473 t Cu concentrates grading 26 to 28 % Cu have been produced (COAKLEY, 1997). Between October 2000 and August 2002, another 45,000 t ore has been mined by Ongopolo.

With proven reserves, in 2000, of 119,000 t grading 10 % Cu, 1.82 % Pb and 584 ppm Ag (COAKLEY, 2000), the deposit is nearing its end of production. The Khusib Springs mine is situated on the northern limb of a large NE-trending, westerly plunging synformal structure. The laminated limestones of the Maieberg Formation (T2-zone) dip approximately 25° to the south. In surface outcrop, a variety of breccias has been distinguished at Khusib Springs (VERRAN, 1996), including synsedimentary rip-up breccia and subordinate dolospar-supported polymictic breccia. Most conspicuous is a matrix (dolomite)-supported polymictic breccia along the T2/T3 contact. Open kink and box folds associated with local crackle breccias formed during E-W compression (D3). The most notable structural feature in the mine area is an offset of the T2 and T3 contacts by about 260 m (VERRAN, 1996). The orebody is oriented parallel to bedding, dipping 40° to the south (Fig. 4), forming a semi-continuous lens down to 300 m below surface that is separated into an upper and a lower body by a zone at 110 m depth where the orebody almost pinches out. The upper orebody reaches approximately 150 m in its longest dimension and a thickness of more than 10 m. A strata-bound zone of dolomite alteration and breccia surrounds the ore (Table 1).

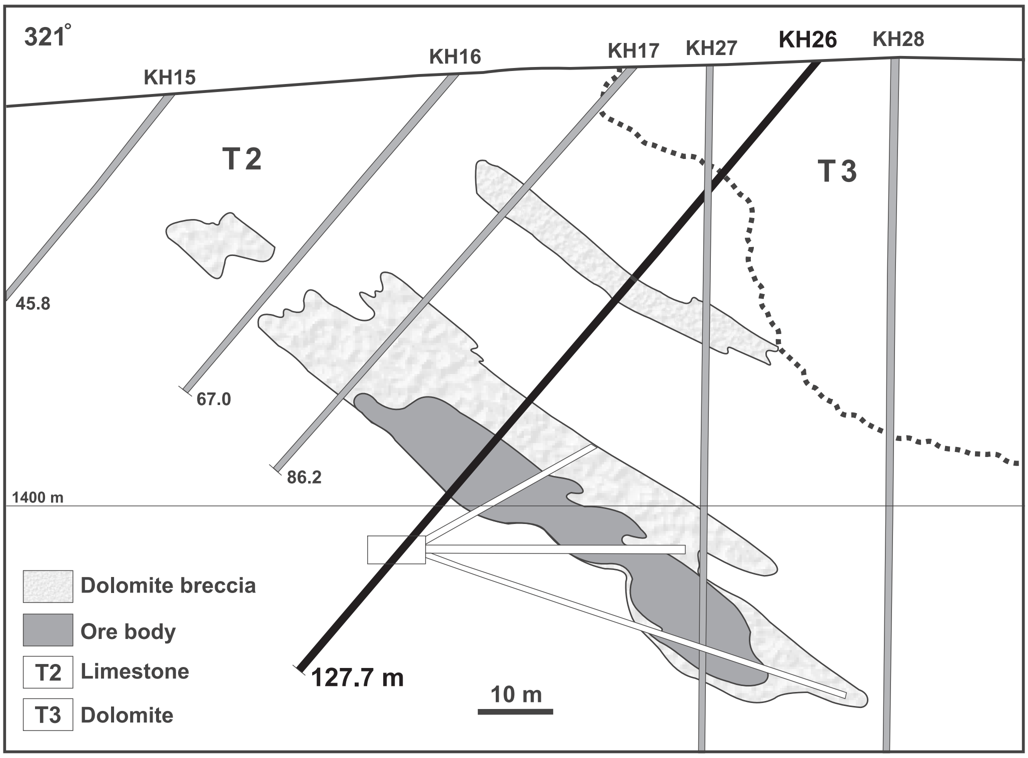


Figure 4
Geological cross-section of the Khusib Springs deposit.

In recent years, the Kombat mine in the Kombat valley of the southern OML (Fig. 1) was the largest producing mine in the area. About 8.7 Mt ore @ 3.1 % Cu, 1.1 % Pb and 26 ppm Ag have been mined from a number of orebodies between 1911–1925 and 1962–1991 (SCHNEIDER & SEEGER, 1992). Its total tonnage was estimated to 13.3 Mt (CAIRNCROSS, 1997); new orebodies have been discovered thereafter.

Starting from fall 2000, between 18,000 and 24,000 t grading 2.8–3.0 % Cu and 1.5–2.5 % Pb were mined per month. Although the deposit is classically regarded as a "Tsumeb-type" deposit, it differs from other examples in several ways (Table 1): (1) a large number of small to medium size deposits is developed along the contact of the upper Tsumeb Subgroup dolostones (Hüttenberg Formation) with clastic rocks (shales) of the Kombat Formation forming a prominent synclinal structure; (2) sulfide ores are accompanied by Fe- and Mn-rich silicate and oxide rocks of probable hydrothermal origin (FRIMMEL et al., 1996); (3) chalcopyrite and bornite are the major sulfide minerals, contrary to dominant tennantite at Tsumeb and Khusib Springs; (4) the sulfur isotope compositions differ from other deposits in the OML. Lenses of feldspathic sandstone ("pseudoaplite") are present along the dolomite-phyllite contact and are regarded as "intrusive" and karst-related (INNES & CHAPLIN, 1986; FRIMMEL et al., 1996).

Further Cu-rich "Tsumeb-type" deposits investigated by BGR, but not dealt with in detail here, include the Tsumeb West pipe, the Guchab deposit, the OMEG deposit and the Nosib mine (Fig. 1).

Ore geochemistry

Major and trace element geochemistry

Sulfide ores in the OML have highly variable compositions in terms of major element ratios and trace element concentrations. In general, Pb, Cu and Zn (in decreasing order of abundance) are the major metals at Tsumeb, whereas at Khusib Springs and Kombat, Cu > Pb > Zn. Berg Aukas-type deposits have Zn > Pb and little Cu. Highest concentrations of Ge (up to 0.83 wt.% in hand specimen) are found in some Tsumeb ores, and correlate well with Ga (up to 0.93 %), Mo (up to 0.93 %), W (up to 0.39 %), In (up to 65 ppm) and As (Table 2). Ge-rich samples also have high concentrations of Re (up to 79 ppm) and purely radiogenic ^{187}Os (up to 1240 ppt; HAACK et al., 2003). However, most Ge-bearing sulfide samples have between 100 and 500 ppm Ge (Table 2), and the bulk of the sulfide ore and the oxidized ore are relatively Ge-poor. Average run-of-mill ore for the period 1964-1974 graded 50 ppm Ge (LOMBAARD et al., 1986).

Massive sulfide ores from Khusib Springs average about 40 ppm Ge, with highest concentrations of 135 ppm. These ores are rich in As, Sb and Ag (up to 3350 ppm) (Table 2; MELCHER et al., 2003). Above-background Ge concentrations have been found in oxidized Cu ore from the OMEG prospect (up to 61 ppm), in sphalerite-filled tubes at Okarundu (up to 81 ppm), and in sphalerite ore from Berg Aukas (up to 30 ppm). Cu-Pb ores from Kombat and Tsumeb West are poor in germanium. However, high values of 200 ppm Ge have been reported from Kombat (INNES & CHAPLIN, 1986).

Sulfur isotopes

The sulfur isotope compositions of ores in the OML are invariably heavy (Fig. 5). Some samples from the Kombat mine are exceptionally light (range -11 to +26 ‰; HUGHES, 1987). δ^{34}S from the deposits of Tsumeb (range +17 to +27 ‰), Khusib Springs (range +21 to +28 ‰) and Berg Aukas (range +17 to +30 ‰) are indistinguishable and point to sulfur derivation from a common source, probably evaporite beds. The narrow range of sulfide δ^{34}S in most deposits suggests abiologic reduction processes. Evaporite horizons in the upper Nosib Group may be possible sources of the saline sulfate component. HUGHES (1987) recognized an evaporite horizon carrying sulfate minerals (gypsum and anhydrite with δ^{34}S from +31 to +33 ‰) in the T7 zone of the Tsumeb area, which may have acted as a source for sulfur in the Tsumeb deposit.

Sample	Ge-rich sulfide ore, Tsumeb (TS53e)	Ge-bearing sulfide ore, Tsumeb 30 level (DH2946/120 ft)	Ge-bearing oxidized ore, Tsumeb 30 level (DH2946/251 ft.)	Ge-bearing ore, Khusib Springs (KH26/85.6m)
Fe_2O_3 %	9.29	16.30	25.16	3.44
Al_2O_3 %	0.19	0.45	0.35	2.03
MnO %	0.022	0.05	0.01	0.097
MgO %	0.05	0.37	0.20	6.12
CaO %	0.18	0.80	17.22	8.19
S %	17.39	19.33	1.04	20.25
Cu %	41.26	13.31	18.55	29.79
Ag ppm	564	162	256	590
As ppm	30600	14500	1780	87100
Cd ppm	627	717	13	46
Co ppm	496	180	259	36
Ga ppm	1890	n.a.	n.a.	<3
Ge ppm	8290	376	128	109
Hg ppm	330	29	6	11
In ppm	26.8	4.4	0.3	n.a.
Mo ppm	9292	511	95	<2
Ni ppm	151	139	395	<3
Pb ppm	20730	5042	465	11957
Sb ppm	823	242	166	11827
Se ppm	105	138	23	63
Sn ppm	66	5.0	1.7	26
V ppm	<1	<1	336	28
W ppm	2700	156	709	9
Zn ppm	19100	104000	3320	14109

Table 2
Partial whole-rock analyses of Ge-rich Cu ores from the Tsumeb and Khusib Springs mines.

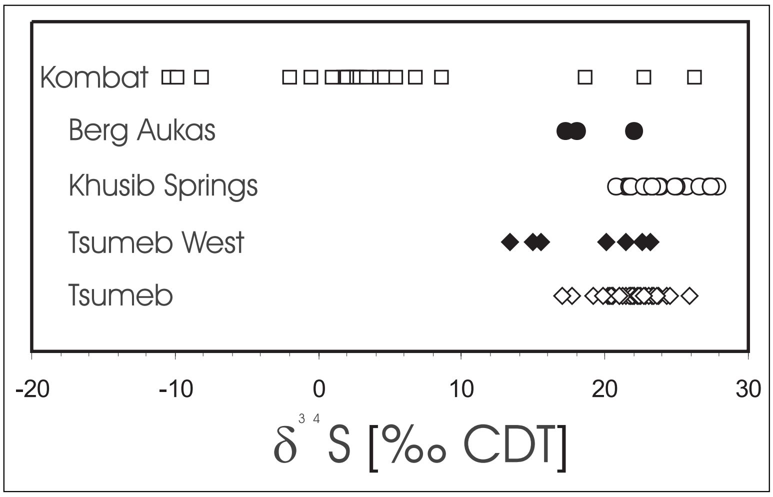


Figure 5
Sulfur isotope compositions of sulfide ores in the OML. Additional data sources: HUGHES (1987), INNES & CHAPLIN (1986), LOMBAARD et al. (1986).

Pb isotopes

Most samples from the Tsumeb and Kombat deposits follow a common Pb-isotopic trend (Fig. 6:a), which has already been established by ALLSOPP et al. (1981). Different trends for the Berg Aukas-type deposits (b) and sulfide ore from Khusib Springs (c) probably indicate mixing of a common hydrothermal end member with different source and/or aquifer rocks (HUGHES, 1987).

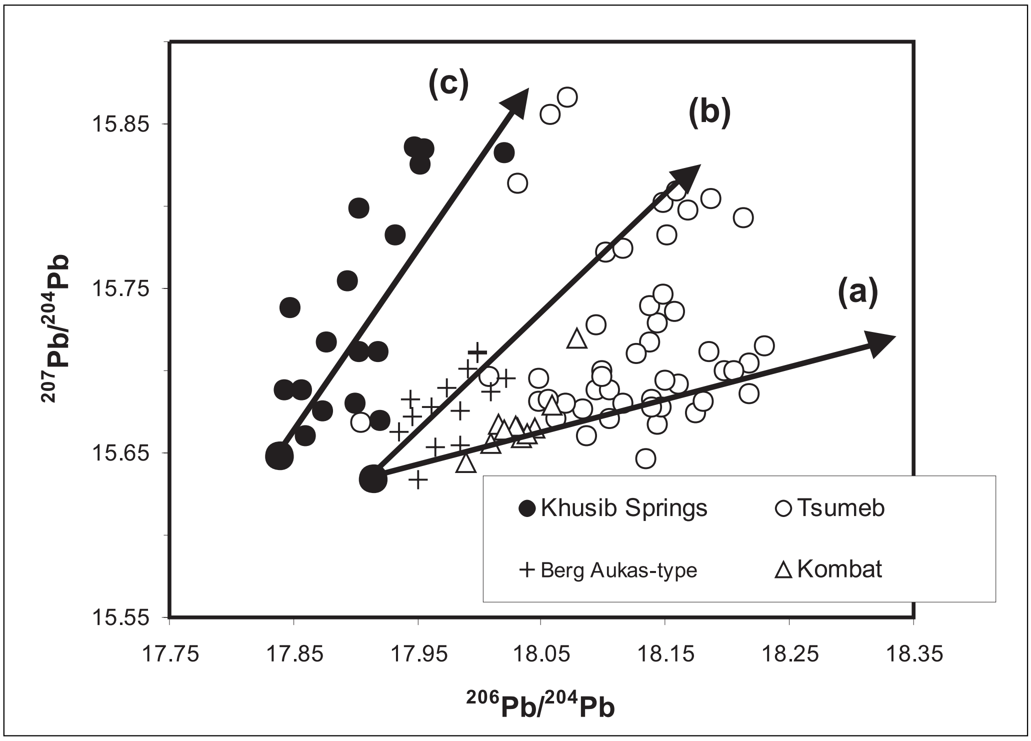


Figure 6

Lead isotope variation of sulfide ores from the Otavi Mountain Land. Additional data sources: HUGHES (1987), KAMONA et al. (1999), Ongopolo (unpubl. data).

Ore mineralogy

Sulfide ore

More than 40 sulfide minerals have been described from the Tsumeb deposit (BARTELKE, 1976; KELLER, 1984; LOMBAARD et al., 1986; GEBHARD, 1991). Most abundant are tennantite, sphalerite, galena, pyrite, chalcocite, digenite, with minor bornite and enargite. Minor and rare minerals include chalcopyrite, covellite, djurleite, umangite, gallite, luzonite, acanthite, stromeyerite, metacinnabarite, cinnabarite, mawsonite, sulvanite, wurtzite, greenockite, linneite, Ni-carrollite, glaucodot, molybdenite, tungstenite, seligmanite, betechthinite, gratonite, patronite, and realgar. The presence of cubanite, millerite and idaite is questionable. Stannoidite has been identified during the on-going investigation for the first time at Tsumeb.

Four named and two still unnamed Ge-rich sulfides (Table 3), and a number of Ge-bearing sulfides are known from Tsumeb. Most abundant are germanite and reniérite, which usually occur as small (10 to 100 µm) anhedral to subhedral crystals in association with tennantite, galena, sphalerite, bornite, chalcopyrite, digenite, pyrite and enargite. Germanite was present in the Tsumeb pipe from the surface down to 31 level, whereas reniérite is only known below level 15. Accordingly, germanite/reniérite ratios decrease with depth (LOMBAARD et al., 1986). GEIER & OTTEMANN (1970a,b) reported a number of minerals carrying both Ge and V, including Ge-bearing sulvanite [$Cu_3(Ge,V)S_4$] with 4.6 wt.% Ge and V-bearing germanite with 1.9–2.7 wt.% V. The "colour variant" of SCLAR & GEIER (1957) is tungsten-germanite carrying 7.4 to 10.3 wt.% W, which commonly develops crystal morphologies (GEIER & OTTEMANN, 1970a). Germanocolusite with a general formula of [$Cu_{26}V_2(Ge,As)_6S_{32}$] and Ge/(Ge+As) > 0.5 has been described from Tsumeb by SPIRIDONOV et al. (1992). SPIRIDONOV (1994) also identified Ge, Mo- and W-rich sulfides associated with germanocolusite, namely [$Cu_{20}(Fe,Zn,Cu)_6Mo_2Ge_6S_{32}$] and [$Cu_{20}(Fe,Zn,Cu)_6W_2Ge_6S_{32}$]. Reniérite, germanite, colusite (Fig. 7) and sulvanite are structurally closely related minerals of the fahlore group (e.g., BERNSTEIN, 1986; SPRY et al., 1994). Two Ge-bearing Cu-Sn sulfides have been reported from Tsumeb: the "Feuermineral" of GEIER & OTTEMANN (1970b) is Ge-bearing mawsonite [$(Cu,Ge)_7(Fe,Zn)_2(Sn,As)S_{10}$] with 3 % Ge and 7–12% Sn, occurring as inclusions in bornite and tennantite on level 30 (BARTELKE, 1976; KELLER, 1984). Ge-bearing stannite [$Cu_2(Fe,Ge)SnS_4$], the mineral "LU" of GEIER & OTTEMANN (1970b), carries 1.7 % Ge and 23.2 % Sn.

Mineral	Formula	wt.% Ge	Reference
Germanite	$Cu_{26}Fe_4Ge_4S_{32}$	9.10	PUFAHL, 1922
Reniérite	$(Cu,Zn)_{22}(Ge,As)_4Fe_8S_{32}$	6.58	SCLAR & GEIER, 1957
Briartite	$Cu_2(Fe,Zn)GeS_4$	18.57	GEIER & OTTEMANN, 1972
Germanocolusite	$Cu_{26}V_2(Ge,As)_6S_{32}$	10.15	SPIRIDONOV et al., 1992
Unnamed IMA 92-38	$Cu_{20}(Fe,Zn,Cu)_6Mo_2Ge_6S_{32}$	10.86	SPIRIDONOV, 1994
Unnamed IMA 92-39	$Cu_{20}(Fe,Zn,Cu)_6W_2Ge_6S_{32}$	9.70	
Brunogeierite	$Fe^{3+}{}_2(Ge,Fe^{2+})O_4$	22.31	OTTEMANN & NUBER, 1972
Bartelkeite	$PbFe^{2+}Ge_3O_8$	35.78	KELLER et al., 1981a
Otjisumeite	$PbGe_4O_9$	45.27	KELLER et al., 1981b
Stottite	$Fe^{2+}Ge(OH)_6$	31.50	STRUNZ et al., 1958
Fleischerite	$Pb_3Ge(SO_4)_2(OH)_6*3H_2O$	7.21	FRONDEL & STRUNZ, 1960
Itoite	$Pb_3Ge(SO_4)_2O_2(OH)_2$	7.62	FRONDEL & STRUNZ, 1960
Schaurteite	$Ca_3Ge(OH)_6(SO_4)_2*3H_2O$	13.42	STRUNZ & TENNYSON, 1965
Mathewrogersite	$Pb_7(Fe,Cu)Al_3GeSi_{12}O_{36}(OH)_6*6H_2O$	2.71	KELLER & DUNN, 1986

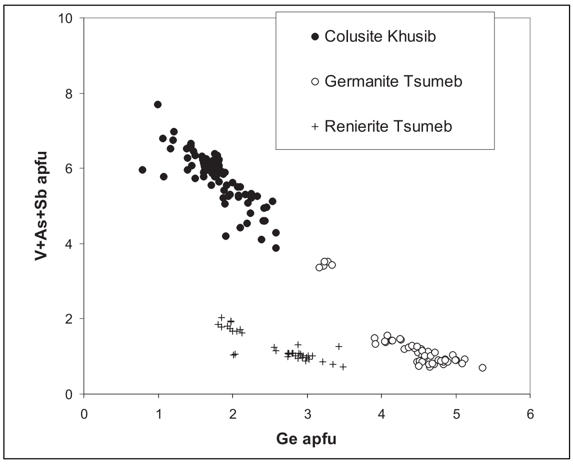
Table 3

List of Ge-rich minerals described from the Tsumeb deposit.

Germanite commonly forms typical "ovoid islands" in a matrix of tennantite and galena. From the 24 level (-730 m) of the Tsumeb mine, SCLAR & GEIER (1957) presented textural evidence that germanite precipitated as an early mineral with bornite and enargite, and is later replaced by reniérite. In four samples investigated from level 30 (drill hole 2946), reniérite frequently overgrows and rims germanite (Fig. 8 A); homogeneous single grains of reniérite, and commonly zoned single grains of germanite are also common.

Figure 7

Variation of Ge atoms per formula unit (apfu) and (V+As+Sb) in Ge-rich sulfides from the Tsumeb and Khusib Springs deposits.



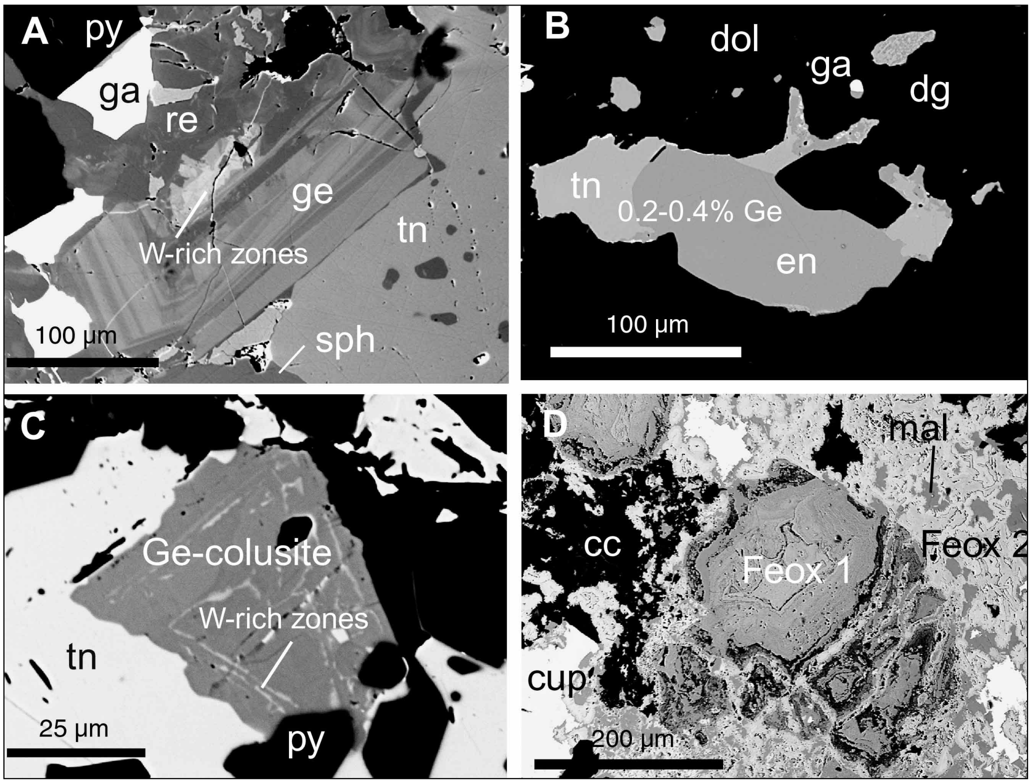


Figure 8

Back-scatter electron images of Ge-rich minerals from the Tsumeb and Khusib Springs deposits. A) Zoned germanite (ge) associated with reniérite (re), tennantite (tn), pyrite (py) and galena (ga). Tsumeb, 30 level. B) Ge-bearing enargite (en) and tennantite (0.2–0.4 wt.% Ge) with digenite (dg, 2.8 % Ag) and galena in dolomite (dol) veinlet. Footwall of the Khusib Springs orebody, KH26, depth 92.7 m. C) Ge-bearing colusite with zones rich in W, associated with tennantite and pyrite. Khusib Springs, KH26, depth 86.4 m. D) Ge-bearing oxidized ore carrying cuprite (cup), malachite (mal), calcite (cc), and a variety of Fe-hydroxides (Feox); Feox 1 has lower Ge, Ga and W concentrations than Feox 2. Tsumeb, 30 level.

Germanite (7.2–11.4 wt.% Ge) hosts a number of minor elements, such as V (<1.5 wt.%), Fe (0.6–9.7 wt.%), Zn (0.2–5.8 wt.%), Ga (< 0.14 wt.%), As (1.5–5.98 wt.%), Mo (< 5 wt.%), Ag (< 0.08 wt.%), Cd (< 0.14 wt.%), Sn (< 1.9 wt.%) and W (< 8.3 wt.%) (Table 4). In massive tennantite-galena-sphalerite-pyrite ore, germanite tends to be compositionally zoned with respect to Fe, Mo and W (Fig. 8 A). Germanite included in bornite carries higher V, As and Fe, and lower Zn, Ge, Mo, Sn and W. Zoning is rarely observed in reniérite (3.6–9.1 wt.% Ge), which has higher concentrations of Fe (9–16 wt.%) and Ga (0.1–0.3 wt.%) than germanite, similar contents of As, Zn, but less V, Mo, Sn and W (Table 4). Stannoidite [$Cu_8(Fe,Zn)_3Sn_2S_{12}$], previously not known from the Tsumeb mine, was identified in drill core from the 30 level and carries up to 2.2 wt.% Ge and 14.7–18% Sn (Table 5).

	Germanite		**Reniérite**		**Ge-rich colusite**	
	Tsumeb, level 30	N = 52	Tsumeb, level 30	N = 39	Khusib Springs	N = 93
	Average	Range	Average	Range	Average	Range
S	31.27	29.58-32.47	32.08	28.42-33.24	31.40	27.78-32.79
V	0.24	0.03-1.51	0.06	<0.61	2.86	1.24-3.41
Fe	3.71	0.65-9.68	12.94	8.83-16.17	0.63	0.01-3.28
Cu	47.27	39.57-50.71	44.08	41.65-51.67	50.22	45.06-53.79
Zn	2.10	0.23-5.82	1.73	<4.76	0.39	<2.67
Ga	0.06	<0.15	0.19	0.10-0.29	0.01	<0.10
Ge	9.78	7.25-11.35	5.98	3.64-9.11	3.94	1.72-5.66
As	2.61	1.46-5.98	2.93	1.52-5.36	9.00	5.96-13.20
Mo	2.09	<5.04	0.20	<1.26	0.14	<1.99
Ag	0.04	<0.08	0.08	<0.59	0.15	<2.44
Sn	0.40	<1.86	0.33	<0.71	0.59	<5.09
Sb	0.01	<0.06	0.01	<0.04	0.21	<1.99
W	1.43	<8.31	0.03	<0.59	0.77	<4.66
Hg	0.05	<0.71	0.02	<0.17	0.02	<0.66
Σ	100.61		100.52		100.44	

Table 4

Chemical composition (wt.%) of Ge-rich sulfides from the Otavi Mountain Land (CAMECA SX 100 electron microprobe data).

The mineralogical composition of sulfide ore from Khusib Springs is similar to primary sulfide ore from Tsumeb, although the relative abundances of minerals and their compositions may differ considerably. In decreasing order, tennantite, enargite, pyrite, galena and sphalerite are most abundant, followed by digenite, covellite, Ge-bearing colusite, chalcoyprite, bornite, Ag-rich tennantite, tetrahedrite, pearceite-polybasite, stannoidite, stromeyerite and molybdenite-tungstenite (MELCHER et al., 2003). Rutile and graphite are locally common constituents, accompanied by Mg-phengite, tourmaline and dolomite. Stannoidite carries 0.5–0.7 wt.% Ge (Table 5), and enargite and tennantite in rare cases contain between 0.2 and 0.4 wt.% Ge (Fig. 8 B). Ge-bearing colusite (1.7–5.5 wt.% Ge) is the major carrier of Ge in the ore, forming euhedral to subhedral crystals 5–50 µm in size along ore-dolomite contacts and within stylolites in tennantite-enargite ore (Fig. 8 C). Colusite carries up to 5 wt.% Sn and W, up to 2 wt.% Mo, Fe and Sb, and up to 2.7 wt.% Zn (Table 4). The chemical relation to other Cu-thiogermanate phases is illustrated in Fig. 7.

Mineral (N)	Ge ppm	Ga ppm	Ag ppm	Cd ppm
Tsumeb				
Tennantite I (20)	<30 to 130	140 to 352	124 to 2369	1131 to 2937
Tennantite II (2)	<30 to (2021)	690	2859 to 3347	n.a.
Sphalerite (11)	<30 to 68	1971 to 3120	<30	5337 to 8003
Bornite (4)	<30	n.a.	484 to 1264	n.a.
Digenite (1)	<30	n.a.	890	n.a.
Stannoidite (2)	254 to 2.27%	270 to 310	224 to 230	n.a.
Gallite (1)	176	32.43%	196	n.a.
Khusib Springs				
Tennantite (11)	<30 to 106	50 to 90	388 to 9637	<90 to 456
Tetrahedrite (1)	<30	<30	0.49%	<90
Enargite (8)	<30 to 64 (3710)	<30	441 to 8481	<90
Sphalerite II (6)	<30	725-896	<30 to 68	1130 to 1714
Sphalerite III (5)	<30	<30	716 to 1.8%	<90
Stannoidite (4)	0.51% to 0.69%	n.a.	181 to 215	n.a.

Table 5

Trace element concentrations in sulfides (CAMECA SX100, 30 kV, 300 nA sec on peak). Values in brackets probaly influenced by Ge minerals. Values quoted in % were measured using standard conditions. Number of measurements (N) in brackets.

Concentrations of trace elements in ore-forming sulfides from the Tsumeb and Khusib Springs deposits have been determined in a preliminary way using the electron microprobe (Table 5). Ge concentrations in tennantite, enargite, sphalerite, bornite and digenite are low (< 30 ppm), with few exceptions, notably in Fe-rich tennantite II from Tsumeb and in some enargites from Khusib. Stannoidite and gallite carry significant Ge. LOMBAARD et al. (1986) reported 60–700 ppm Ge in tennantite, up to 500 ppm in enargite, up to 50 ppm in chalcocite, up to 70 ppm in galena, and 70–140 ppm in sphalerite from the Tsumeb deposit. Ga and Cd concentrations are high in sphalerite and tennantite from Tsumeb, and moderate at Khusib. Ag concentrations are highly variable within samples, but significant (100 ppm to 1 %) in tennantite, bornite, enargite, digenite, stannoidite and gallite. Collomorphous Zn sulfide from Khusib Springs ("sphalerite III"; MELCHER et al., 2003) carries high concentrations of Ag, but low Ga, Ge and Cd.

In summary, distinct differences exist in the paragenesis and chemical composition of sulfide minerals at the Tsumeb and Khusib Springs deposits. Zincian tennantite, being the most abundant primary sulfide in both deposits, carries more Sb, Ag, Mn and less Cd at Khusib compared to fahlore from Tsumeb (Table 5). Galena is not a major carrier of Ag in both deposits, and pyrite is usually Cu-bearing but has low concentrations of Co, Ni and As. Sphalerite from Tsumeb is richer in Ga and Cd than sphalerite from Khusib. Three types of sphalerite occur at Khusib, discriminated by their Mn/Fe ratios, Cd, Cu and Ag concentrations (MELCHER et al., 2003). Variable Fe concentrations reported in the literature (EMSLIE & BEUKES, 1981) suggest that more than one sphalerite generation is developed at Tsumeb as well. X-ray fluorescence analyses of sphalerites separated from various prospects and mines in the OML gave the following ranges for trace elements: 8–427 ppm Ge, 6–310 ppm Ga, 1440–3896 ppm Cd, 87–219 ppm Ag, 175–1000 ppm Mn (EMSLIE & BEUKES, 1981). Thus, sphalerite is not a major carrier of Ge in the OML, despite significant Ge concentrations in sphalerites from many MVT deposits.

Oxidized ore

The presence of three oxidation zones in the sulfide-bearing pipe structure made Tsumeb unique, and is responsible for a large number of secondary minerals. Eight rare, secondary Ge-rich minerals are reported from the oxidation zones of Ge-rich sulfide ore (Table 3). The Fe-Ge hydroxide stottite was the first secondary Ge phase to be described, occurring in the second oxidation zone on level 30 with tennantite, leiteite and schneiderhöhnite (STRUNZ et al., 1958; KELLER, 1984); Mn- and Zn-rich stottite varieties are known (GEIER & OTTEMANN, 1970a). The Ge-ferrite-spinel brunogeierite was characterized in samples containing galena, tennantite with small reniérite blebs, stottite, smithsonite and cerussite on level 29. Bartelkeite and otjisumeite are further Ge-rich oxides first described from Tsumeb. The Ge sulfates fleischerite and itoite are associated with mimetite, kegelite, cerussite and plumbojarosite in the upper oxidation zone (levels 6 to 8), while schaurteite was found in the second oxidation zone associated with carbonates. The Pb silicate mathewrogersite occurs in paragenesis with other Pb silicates, willemite and mimetite in altered Pb-Zn ore on level 31. Recently, a Ge-rich beudantite variety ($H_2PbFe_2[(OH)_6/(SO_4)_{0.2}/(GeO_4)_{0.4}/(AsO_4)_{1.4}]$, with 5.2 wt.% GeO_2) has been described in a sample with quartz and wulfenite (GUTZMER & CAIRNCROSS, 2001).

FRONDEL & ITO (1957) showed that, apart from minor Ge^{2+} substituting for Pb in anglesite and cerussite (50–500 ppm Ge), the bulk of the Ge in secondary minerals is quadrivalent. It preferentially enters early formed Cu- and Pb-arsenates such as mimetite, olivenite and bayldonite (500–5000 ppm Ge). LOMBAARD et al. (1986) listed Ge concentrations for the following secondary minerals: up to 0.11 % in duftite-bayldonite, up to 500 ppm in mimetite, up to 0.28 % in olivenite-adamite, and 0.05–0.128 % in willemite.

Oxidized ore from level 30 (DH2946, 251 ft.; with cuprite, tenorite, malachite, Fe-hydroxide, konichalcite and rare mottramite) was investigated to characterize the mineralogical siting of Ge at some distance from primary sulfide ore; the sample contains 128 ppm Ge and concentrations of Co, Ni, V and W higher than in sulfide ore (Table 2). The Fe-hydroxides are in general rich in Cu, Zn and As (in the 1 to 3 wt.% range). Two textural types are distinguished (Fig. 8 D), (1) high-reflectance, euhedral to subhedral pseudomorphs (after pyrite?) have V, W, Mo, Sb and Pb concentrations below 0.5 wt.%; (2) low-reflectance hydroxides in the matrix form complex veins that are enriched in trace elements (up to 2.5 wt.% Ge and W, up to 0.8 wt.% Ga). In a further sample (8.4 ppm Ge) from the same drill core (DH2946, 216 ft.), having preserved islands of bornite with small inclusions of (V-bearing) germanite and reniérite, up to 0.2 wt.% Ge, 0.8–1 % Cu, 0.7–0.8 % Pb and 0.5 % Si have been detected in Fe hydroxide veinlets cutting into secondary chalcocite which replaces the bornite. In addition the sample carries wulfenite, Pb arsenate, Pb-Cu arsenate, cerussite, complexly zoned Pb dolomite and Ag-Hg alloy.

Detailed investigations as to the siting of Ge in oxidized portions of other deposits in the OML have yet to be carried out. From Khusib Springs, native silver and native copper have been determined during the ongoing study; a number of Cu arsenates and Cu carbonates are also present. Spectacular crystals of wulfenite have been found in the past (CAIRNCROSS, 1997; JAHN & NÄGELE, 2001).

In the Apex mine, Utah, 200 to 5300 ppm Ge are contained in goethite, and 1100 to 3500 ppm Ga are present in jarosite (BERNSTEIN, 1986; DUTRIZAC et al., 1986), representing the most important economic minerals in this unique Ga-Ge deposit (316,000 t of ore @ 0.04 % Ga, 0.09 % Ge, 1.65 % Cu, 1.47 % Zn; TAYLOR & QUINN, 1987). Apex is hosted by a solution collapse breccia and is considered an equivalent of a fairly oxidized "Tsumeb-type” deposit.

In combination with the data presented from the Tsumeb mine it is concluded that under favorable circumstances, mineable supergene Ge ores may form from Ge-rich sulfide ore.

Discussion

Tsumeb and Khusib Springs: the same mineralization type?

The mineralization at Khusib Springs shares many features with the Tsumeb deposit. Accordingly, CHETTY & FRIMMEL (2000) classify the deposit as a Tsumeb-type deposit, possibly representing the root zone of a much larger deposit higher up in the stratigraphic sequence and now eroded. Features similar between Tsumeb and Khusib Springs are (Table 1): (1) the relation to syn-D_2 structures, i.e. folding; (2) the general chemistry of the ores, which are dominated by Cu, with variable Pb, Zn, and have elevated concentrations of trace metals such as Ag, Ge, V, Sn, Mo, W; (3) the heavy sulfur isotope compositions (Fig. 5); (4) the major hypogene mineral assemblage consisting of tennantite, galena, sphalerite, pyrite, with low contents of chalcopyrite, (5) the presence, in trace amounts, of minerals typical of the primary and secondary Tsumeb assemblage. Major differences between Khusib Springs and Tsumeb are: (1) the lack, at Khusib, of a karst pipe structure with sandstone filling; (2) generally higher concentrations of Sb and Ag in fahlore and bulk ore at Khusib; (3) the presence of large amounts of enargite, being the second most abundant Cu mineral in the deposit – at Tsumeb enargite was present only in the upper part of the mine (LOMBAARD et al. 1986); (4) the virtual absence of bornite at Khusib; (5) the presence of Ag-sulfosalts unknown from Tsumeb; (6) the presence of Ge-bearing colusite as the major carrier of Ge instead of germanite and reniérite at Tsumeb; (7) the lack of pervasive oxidation below the surface at Khusib; (8) hydrothermal dolomite prevails at Khusib, whereas calcite and quartz are the dominant alteration minerals, syngenetic with sulfides, at Tsumeb.

Base metal mineralization in the OML: conditions and timing of ore formation

The conditions under which base metal deposits in the OML formed are a matter of considerable debate. Berg Aukas-type Zn-Pb deposits formed from basinal brines (~23 wt.% NaCl equivalent, < 240°C, $\delta^{18}O_{fluid}$ +13 ‰) moving along aquifers in the basal Damara Supergroup during an extensional period, probably during diagenesis (PIRAJNO & JOUBERT, 1993; FRIMMEL et al., 1996) (Table 1). Berg Aukas-type deposits thus resemble MVT deposits. In contrast, timing of ore deposition, fluid temperature and salinity data are controversially discussed for Tsumeb-type deposits. While HUGHES (1987) discusses a pre-D_2 mineralising event for Tsumeb, most authors agree that Tsumeb-type deposits formed during metamorphism and regional D_2 deformation (LOMBAARD et al., 1986) from hot fluids (350–450°C, $\delta^{18}O_{fluid}$ +18 ‰; FRIMMEL et al., 1996) that moved along regional structures and precipitated ores in traps such as karst structures. However, pre-D_2 ores have been found locally (e.g. Fe-Mn ores and stratiform Cu ores at Kombat; FRIMMEL et al., 1996). HAYNES (1984) interpreted the hypogene ore at Tsumeb to have resulted from interaction of Cu-As-rich, warm (210–280°C), moderately saline (6–12 wt.% NaCl equ.) circulating fluids with host dolomites. A confining pressure of 500–700 bars was estimated, and the age of the mineralization was thought to be 580–530 Ma (syn-D_2) based on Pb-Pb isotope compositions of galena (LOMBAARD et al., 1986; KAMONA et al., 1999). In contrast, CHETTY & FRIMMEL (2000) measured considerably higher salinities in fluid inclusions, i.e. 22 ± 3 wt.% NaCl equ. for Tsumeb and 20 ± 4 wt.% NaCl equ. for Khusib Springs.

A lithostatic pressure of 2.5 kbar and temperatures in excess of 300°C are reasonable estimates for the time of mineralization (FRIMMEL et al., 1996). Pressure corrections to the fluid inclusion data yield formation temperatures of 275°C for dolomite III at Tsumeb, and 370°C for dolomite II at Khusib Springs (CHETTY & FRIMMEL, 2000).

Stable isotope data ($\delta^{13}C$, $\delta^{18}O$) of ore-bearing dolomite II at Khusib Springs point to a metamorphic origin of the mineralising fluids (CHETTY & FRIMMEL, 2000). High concentrations of REE in carbonates suggest mineralising fluids having interacted extensively with rocks underlying the Otavi Group. The highly saline fluids are dominated by Ca- and Mg-chloride with subordinate NaCl, indicative of a large component of evaporitic residual brines (CHETTY & FRIMMEL, 2000). The heavy sulfur isotopes of the Khusib Springs, Tsumeb and Berg Aukas sulfides are unique among sediment-hosted base metal sulfide deposits, and most probably indicate derivation from sedimentary sulfate minerals, which precipitated from contemporaneous seawater. Evaporite horizons in the upper Nosib Group may be possible sources of the saline sulfate component. Based mainly on Pb isotope work, HUGHES (1987) favoured pelitic rocks of the Kombat Formation, metal-rich dolostone of the T8 zone and phosphoritic dolostone of the Hüttenberg Formation as sources of base metals and many other elements. Volcanic rocks and impure sandstones of the Nosib Group may also have contributed base metals to throughflowing brines, which moved along different aquifer systems to deposit the metals. CHETTY & FRIMMEL (2000) argue that the Grootfontein ultramafic-mafic body in the basement of the Otavi Mountain Land may have served as a source of base metals.

Genetic model for the Khusib Springs deposit

The lens-shaped orebody of Khusib Springs is developed along a breccia horizon attributed to hydrothermally induced solution-collapse preceding, or during regional D_2 deformation. The footwall mineralization with Fe-bearing sphalerite, chalcopyrite, pyrite and minor Fe-rich tennantite represents the earliest mineralization phase. The early-stage mineralization was replaced by main-stage enargite and tennantite, with Ge-bearing colusite, pearceite-polybasite, galena and some pyrite. Enargite and tennantite are replaced by chalcocite-group minerals (digenite), constituting the main minerals of the late stage and finally, by covellite. Digenite is associated with late-stage sphalerite (Cu, Ag-rich), tetrahedrite and pearceite-polybasite, which are associated with development of a considerable secondary porosity. The conditions of formation of the Khusib Springs orebody are governed by sulfide, silicate and carbonate equilibria (MELCHER et al., 2003). MÖLLER (1985) proposed the use of Ga/Ge ratios in sphalerite to estimate the conditions of sphalerite deposition under the assumption that Ga/Ge ratios in the fluid equal those in sphalerite. Sphalerite from the upper zone of the Khusib orebody (800 ppm Ga, < 30 ppm Ge) has log (Ga/Ge) > 1.4 corresponding to T > 260 ± 10°C. Temperature and sulfur fugacity are also constrained by the occasional presence of stannoidite in the presence of Fe-poor sphalerite and tennantite, which are stable at 200–300°C and log fS_2 –15 to –7 atm (SHIMIZU & SHIKAZONO, 1987). High temperatures and sulfur fugacities are also in accordance with the presence of Ge-bearing colusite. Furthermore, the pentavalent state of As and the tetravalent state of Ge in the colusite structure indicate that colusite forms under relatively high fO_2 conditions, similar to Ge-bearing colusite associated with pyrite, chalcopyrite and bornite in volcanogenic sphalerite-barite ores at the Yanahara mine, Japan (KASE et al., 1994). The physicochemical conditions of sulfide precipitation in the Tsumeb deposit were estimated to $10^{-39} < \log fO_2 < 10^{-33}$ atm, $\log fS_2 > 10^{-8.5}$, fluid pH = 3–6 and a minimum sulfur concentration of 10^{-1} m (HUGHES, 1987).

Main-stage sulfides are intergrown with iron-free, phengitic F-rich white mica and dravitic tourmaline, which differ chemically from sericitic mica and tourmaline in the dolomite host rock. It is thus assumed that an Mg-F-rich hydrothermal fluid replaced detrital or diagenetic silicates, and precipitated hydrothermal silicates. The fluid pH is fixed to values between 3 and 5 by the stability of muscovite, but may have changed to lower values due to the occasional presence of kaolinite. The zonation with tennantite + enargite in the central, and tennantite + sphalerite in the marginal parts of the Khusib Springs orebody would be best explained by pH increase due to interaction of an acid, hot, saline hydrothermal fluid with host carbonates.

Enrichment of germanium in Tsumeb-type deposits

Germanium and silicon are geochemically closely related and thus, Ge/Si ratios are fairly similar (10^{-6}) in the crust and in rivers, unless there is organic matter involved. However, significant fractionation may occur in hydrothermal fluids (Ge/Si = 10^{-5} to 10^{-3}; POKROVSKI & SCHOTT, 1998). Germanium is transported in dilute aqueous hydrothermal fluids as neutral hydroxide species [$Ge^{4+}(OH)_4^0(aq)$] at pH values < 8 over a wide range of temperatures (20–350°C). The solubility of Ge and Ge/Si ratios in thermal waters increase with temperature and salinity. Ge is also enriched in high-temperature hydrothermal systems associated with granitoids, e.g. in topaz, fluorite, and white mica (BERNSTEIN, 1985), suggesting Ge-transport as H_2GeF_6 complexes. However, experimental data show that significant formation of Ge-fluoride complexes may occur only in very acid (pH < 3) F-rich solutions. S-bearing Ge species possibly also form in S-rich hydrothermal fluids (BERNSTEIN, 1985).

Concentration through magmatic fractional crystallisation, or uptake from country rocks by fluids may be considered viable sources of Ge in a deposit. The latter is favoured for Khusib Springs and Tsumeb, because there are no time-equivalent magmatic rocks in the OML. Favourable country rocks from which Ge may be mobilised are sediments containing organic material, such as the Maieberg limestones and dolomites (T2-T3 zones) in the lower Tsumeb Subgroup. Organic matter of unknown origin has accumulated along stylolites, and is present in disseminated form throughout the succession. Lignin-derivative organic compounds as found in peat and lignite account for the concentration of Ge in coals and related organic material (BERNSTEIN, 1985). The strong biophile affinity of Ge makes some large coal deposits potential targets for future Ge production.

At Khusib Springs, textural and geochemical evidence indicates a close link between Cu-sulfosalts (enargite, tennantite) and Cu-thiogermanate minerals (Ge-bearing colusite) with F-rich phengitic mica, F-rich dravitic tourmaline, kaolinite, rutile and (semi)graphite; quartz is notably lacking. The element association of Ge with V, Sn, Mo and W probably points to the involvement of an organic compound. The sulfide ores precipitated at elevated oxygen fugacities from hot (> 300°C), saline, metal-rich fluids. Fluid inclusion data, analyses of fluid inclusion leachates, and sulfur isotope compositions indicate an evaporitic component to the fluids. This would also explain the concentration of fluorine in hydrothermally formed mica and tourmaline. The close association of F-rich silicates with Ge-bearing sulfides may point to the presence of Ge-fluoride complexes in the fluid; the necessary low pH values are corroborated by the presence of kaolinite. Destabilisation of Ge complexes in the fluid may be caused by a drastic pH increase along sulfide-dolomite contacts, where most of the Ge-bearing colusite is located.

The polyphase mineral assemblage and geochemical zoning of the Tsumeb, Khusib Springs and Kombat orebodies implies a complex model of ore formation. The early stage-mineralization of sphalerite, pyrite and minor galena and Fe-rich tennantite found at Khusib Springs formed from a hot, saline hydrothermal fluid at relatively lower fS_2 and fO_2 than the main stage Ge-rich mineralization dominated by tennantite and enargite. Early stage mineralization shares some aspects of mineralization commonly referred to as Berg Aukas-type in the OML, and with MVT deposits. Ample textural evidence of replacement of early stage ore by main stage ore indicates that an upgrading or enrichment process took place. The late stage mineralization with Ag- and Cu-rich Zn sulfide, digenite, pearceite-polybasite and tetrahedrite clearly postdates this replacement process, and must be attributed to fluid-induced remobilisation of parts of the orebody at lower temperatures. Future work will concentrate on a regional correlation of different mineralization events in the OML, and on mineralogical and geochemical proximity indicators to Ge-rich mineralization.

Mineralization and "Snowball Earth": a possible link?

There are only few radiometric data on the timing of sulfide mineralization in the OML. Pb model ages on galena (ALLSOPP et al., 1981; HUGHES, 1987; KAMONA et al., 1999) and a preliminary Re-Os isochron (HAACK et al., 2003) support a syn-orogenic age of sulfide mineralization at Tsumeb, in accordance with structural and petrological constraints (e.g., temperature-composition data of fluid inclusions). Pb-Zn mineralization of the Berg-Aukas type in the Abenab Subgroup formed from basinal brines and thus may predate Tsumeb-type mineralization (FRIMMEL et al., 1996); the host rocks were deposited between two global glaciations, the Sturtian (760–700 Ma) and Marinoan/Varangian glaciations (580 Ma). Metamorphism in this part of the Damara Orogen took place about 545 Ma ago, postdating the second glaciation (Ghaub Formation) by about 35 Ma. No direct connection has ever been made between "Snowball Earth" and base metal mineralization in sediments postdating global glaciations. However, such mineralization is globally distributed (see IGCP 450: Proterozoic sediment-hosted base metal deposits of Western Gondwana: Intra and intercontinental correlation of geological, geochemical and isotopic characteristics). During and after glaciation, active hydrothermal systems along mid-ocean ridges contributed large amounts of metals into ocean water, which was saline, reduced and relatively stagnant (BÜHN & STANISTREET, 1997) and thus capable of carrying metals in solution in reduced form (e.g., Fe^{2+}, Mn^{2+}). Some of the metals precipitated as sedimentary Fe- and/or Mn-rich sediments (e.g., the Otjosondu Mn ores, BÜHN et al., 1992; the Rapitan iron formation, KLEIN & BEUKES, 1993) during the Sturtian deglaciation, when surface waters became oxidizing. Synsedimentary, hydrothermal ores also formed after the climate had changed to conditions more fertile for life, such as the Fe-Mn(-Ba) ores in the upper Hüttenberg Formation at Kombat. In other parts of the Damara Orogen, sediment-hosted massive sulfides formed during synsedimentary faulting along basin margins (e.g., Zn-Pb(-Cu-Ag) ores at Rosh Pinah around 741 Ma; BORG, 2000; FRIMMEL, 2002) and as volcanogenic massive sulfides in the Khomas Ocean (e.g. pyritic Cu ores in the Matchless amphibolite belt). Their position is primarily determined by the basin-geometry during continental break-up. Future studies have to be devoted to a possible link between the "Snowball Earth" scenario and base metal mineralization in active and passive continental margin settings following deglaciation.

Acknowledgements

The support by Ongopolo Mining Ltd., especially by its manager, A. Neethling, and by geologists A. Günzel and A. Lombaard, is much appreciated. I gratefully acknowledge assistance by Dr. G. Schneider and V. Petzel from the Geological Survey of Namibia. Sincere thanks go to the members of the project team at BGR, T. Oberthür, U. Vetter, J. Lodziak and D. Rammlmair. C. Gross, A. Vollbrecht (University of Göttingen), M. Brauns and U. Haack (University of Giessen) contributed valuable data through cooperation projects. I would also like to thank the ÖMG, especially F. Koller and R. Brandstätter, and the responsible scientists from the Universities of Vienna, Graz, Leoben and Innsbruck for supporting the lecture tour and making this a memorable trip. It was good to be back!

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bei der Redaktion eingegangen:15. Mai 2003
Manuskript angenommen: 18. Mai 2003