The Classical Pb-Zn Deposits of the Eastern Alps (Austria/Slovenia) Revisited: MVT Deposits Resulting From Gravity Driven Fluid Flow in the Alpine Realm

Nov pogled na klasična svinčevo-cinkova rudišča v Vzhodnih Alpah (Avstrija/Slovenija) - nastanek MVT rudišč zaradi gravitacijskega toka rudonosnih raztopin na območju Alp

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Abstract

The stratabound East Alpine lead-zinc deposits in south Austria and northeast Slovenia are hosted by platform carbonates of Triassic age. Ore textures interpreted to be synsedimentary supported the model of syngenetic/synsedimentary ore formation, favored by many authors for a long time. These „synsedimentary" ore textures represent in our interpretation internal cavity infills.

Ore-formation commenced after the precipitation of shallow burial carbonate cements. The deep burial diagenetic stage includes two types of saddle dolomite and three types of blocky calcite. The Zn-rich first ore-phase occurred coeval with the first generation of saddle dolomite and shows a distinct succession of different sphalerite-types which can be distinguished by petrographical and geochemical characteristics. The mineralization of sphalerite is accompanied by pyrite, galena, fluorite, and barite.

The second ore-phase was Pb-dominated and appears distinctly after the precipitation of the first generation of saddle dolomite and before precipitation of the first generation of blocky calcite. This second ore phase contains only one type of sphalerite, which shows a characteristic yellow color in transmitted light. Sphalerite with the same optical characteristics and geochemical composition is also related to younger carbonate cements. Fluid inclusion studies indicate formation temperatures of 122 to 159 °C for saddle dolomite and sphalerite of the first ore phase. Formation temperatures of fluorite decreases from the first to the third generation.

The first generation of sphalerite and of saddle dolomite can be followed upsection into Late Triassic/Early Jurassic sedimentary rocks, giving a maximum age of ore emplacement for the first phase of Pb-Zn ore.

Geochemical data for the ore and the host rock indicate the origin of the metals in the crystalline basement rocks. It is suggested that fluids originating in the hinterland to the north (Vindelician-Bohemian massif) migrated southward by gravity driven flow. These fluids leached the metals from the crystalline basement rocks

and ascended, supported by a high heat flow resulting from the onset of rifting in the Alpine realm. Ores formed within the areas of high porosity under distinct geochemical conditions, e.g. the presence of Triassic sulfur.

Kratka vsebina

Svinčevo-cinkova rudišča v južni Avstriji in severovzhodni Sloveniji nastopajo v triasnih platformskih karbonatih. Rudne teksture, ki so jih razlagali kot sinsedimentne, so bile osnova za model singenetsko/sinsedimentnega nastanka rude, ki so ga dolgo časa zagovarjali mnogi avtorji. Po naši interpretaciji so te „sinsedimentne" rudne teksture interna zapolnitev odprtin.

Ruda je začela nastajati po izločanju diagenetskih cementov. Epigeneza vključuje dva tipa sedlastega dolomita in tri tipe debelozrnatega kalcita. Prva faza orudenja bogata s Zn je nastopila istočasno s prvo generacijo sedlastega dolomita in kaže jasno zaporedje različnih tipov sfalerita, ki jih lahko ločimo po petrografskih in geokemičnih značilnostih. Izločanje sfalerita spremljajo pirit, galenit, fluorit in barit.

V drugi rudni fazi prevladuje Pb; ta faza jasno nastopa po rasti prve generacije sedlastega dolomita in pred rastjo prve generacije debelozrnatega kalcita.

Ta druga rudna faza vsebuje samo en tip sfalerita, ki ima v presevni svetlobi značilno rumeno barvo. Sfalerit z enakimi optičnimi lastnostmi in geokemično sestavo se pojavlja tudi z mlajšimi karbonatnimi cementi.

Raziskave tekočinskih vključkov kažejo za prvo rudno fazo nastanka sedlastega dolomita in sfalerita temperaturo od 122 do 159 °C. Temperatura nastanka fluorita pada od prve proti tretji generaciji.

Prvi generaciji sfalerita in sedlastega dolomita v profilu lahko sledimo v zgornjetriasne in spodnjejurske sedimentne kamnine. Spodnja jura je s tem največja starost prve Pb-Zn rudne faze.

Geokemični podatki za rudo in prikamnino kažejo, da so metamorfne kamnine v podlagi izvorno področje kovin. Verjetno so rudonosne raztopine prihajale proti jugu iz dvignjenega severno ležečega prostora (Vindelicijsko-češki masiv) zaradi gravitacijskega toka.

Te raztopine so izluževale kovine iz metamorfne podlage in se dvignile, podprte z vročim toplotnim tokom, ki je posledica začetka razpiranja v alpskem prostoru.

Rude so nastajale v območjih z višjo poroznostjo, v specifičnih geokemičnih pogojih, kot je na primer prisotnost triasnega žvepla.

Introduction

The Pb-Zn deposits of the Eastern Alps hosted by Mid-Triassic carbonate rocks are believed to be different from Mississippi Valley-type deposits (MVT; S a n g s t e r, 1990), and have been summarized under the term „Bleiberg type" or „Alpine type" (M a u c h e r & S c h n e i d e r, 1967; S a n g s t e r, 1976; C e r n y, 1989). This distinction is mainly based on the occurrence of „sedimentary" ore textures (S c h u l z, 1964; M a u c h e r & S c h n e i d e r, 1967), believed to indicate a synsedimentary origin of these deposits. This paper presents petrographical and geochemical data, which indicate that the „Alpine" Pb-Zn deposits are normal MVT deposits, formed by precipitation from saline hot brines during burial diagenesis.

Geological setting

The study area in the Drau Range is located in south Austria and northeast Slovenia, where the economically important „Alpine" lead-zinc deposits, Bleiberg and Mežica, and many other small deposits occur (Fig. 1). These stratabound lead-zinc deposits occur within an approximately 1500 m thick, succession of Triassic carbonate rocks (Wetterstein Formation, Raibl Group; Fig. 2).
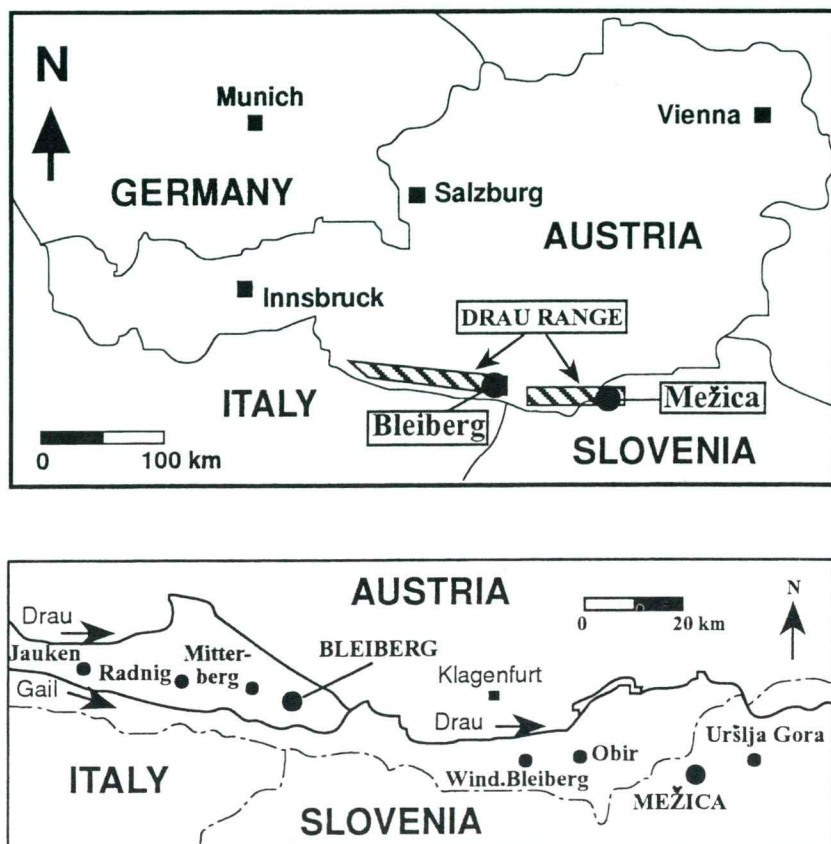
Fig. 1. Location of the studied area and the studied Pb-Zn deposits.

The carbonate rocks of the Wetterstein Formation were deposited on carbonate platforms. The Pb-Zn ores commonly occur in the so called „Bleiberg facies", which occurs at a distance of some hundreds of meters from a reefal facies and represents a cyclically exposed paleotopographic high within a lagoonal/tidal flat area (Z e e h & B e c h s t ä d t, 1994). The characteristic sediments and structures of the Bleiberg facies formed during emersions. They consist of greenish marls (soil products), sedimentary breccias with black pebbles, calcretes, and beds with microkarst porosity (B e c h s t ä d t, 1975a; B e c h s t ä d t & D ö h l e r - H i r n e r, 1983; Z e e h, 1994). They represent lithostratigraphic markers within the 60 m thick Bleiberg facies that facilitate exploration (H o l l e r, 1936; C e r n y, 1989). Sphalerite and galena are the main ore-components. Fluorite, barite, pyrite and blue colored anhydrite are the main accessory minerals (S c h r o l l, 1984).

Ore bodies also occur in stock-shaped dolomite breccias separated by faults from the Bleiberg facies. These breccias contain Zn-rich ores as networks and coarse masses of ore with a metal content of up to 40 % Zn and Pb (C e r n y, 1991).

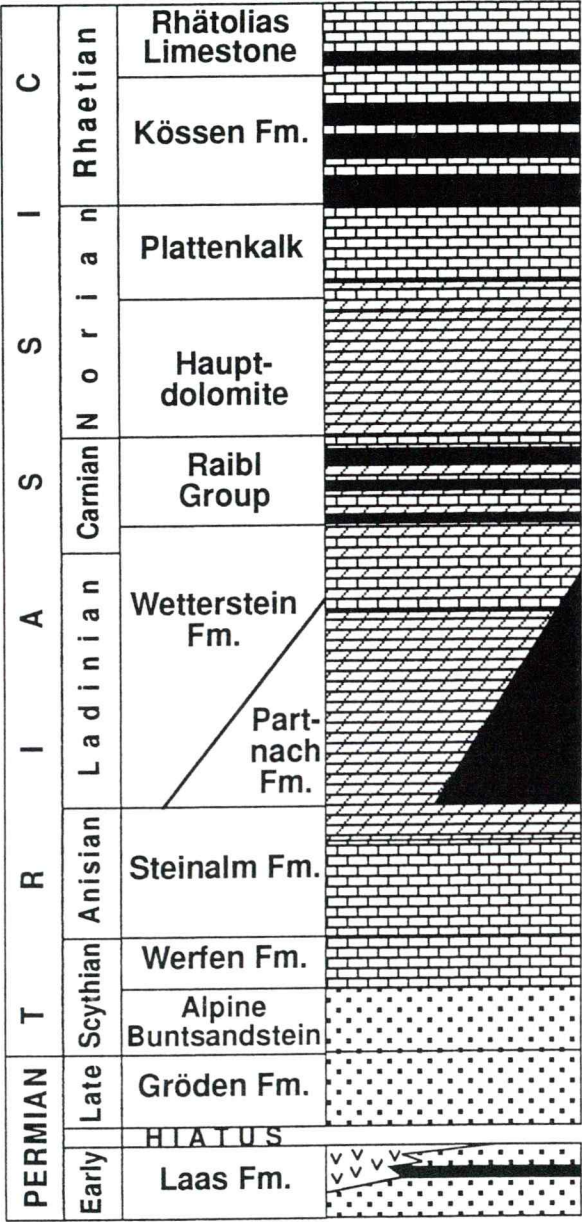|			
		Rhätolias Limestone	
C	Rhaetian	Kössen Fm.	
S	Norian	Plattenkalk	
S		Haupt-dolomite	
	Carnian	Raibl Group	
A	Ladinian	Wetterstein Fm.	
		Part-nach Fm.	
R	Anisian	Steinalm Fm.	
	Scythian	Werfen Fm.	
T		Alpine Buntsandstein	
PERMIAN	Late	Gröden Fm.	
		HIATUS	
	Early	Laas Fm.	

Fig. 2. Occurrence of the studied lead-zinc deposits within the Triassic sediments of the Drau Range.

    Ore occurrences within other facies of the Wetterstein Formation are rare. Reefal rocks contain Pb-Zn ores at Mežica (Š t r u c l, 1984), carbonate rocks of a lagoonal facies contain Pb-Zn ores at Jauken, and carbonate rocks of a lagoonal to tidal flat facies contain Pb-Zn ores at Radnig. The carbonate rocks of the Raibl Group also can host ore bodies, but only on top of the paleotopographic highs of the Wetterstein formation.

Methods

Petrographic analysis was done on polished thin sections. Cathodoluminescence (CL) microscopy was performed using a Technosyn 8200 Mk II cold cathode instrument employing a beam voltage of 15 kV and a current of about 550 µA.

Sulfur isotopic analysis were performed on sphalerite, galena, pyrite, barite, and anhydrite at the Institute Jožef Stefan Ljubljana (Slovenia). Analytical precision was better than 0.2 ‰.

Cold techniques were used for preparation of fluid inclusion samples to prevent overheating and reequilibration of the inclusions. Only a very small percentage of the samples actually contain fluid inclusions, which are also relatively small (<5 to 30 µm). Fluid inclusions within the various carbonate cements were studied with a Linkam heating/cooling stage. Measurements of homogenization temperature to liquid were made before freezing runs.

Carbonate cements

Carbonate cementation of near surface to shallow burial diagenesis depends on the paleotopography of the Wetterstein platforms (Z e e h et al., 1995). Some parts were always flooded by marine waters while other parts, e.g. Bleiberg facies, became cyclically emerged and were influenced by meteoric fluids. Therefore, the Bleiberg facies contains cements of meteoric and marine regimes (B e c h s t ä d t, 1975a; Z e e h et al., 1995), such as dripstone cements, radiaxial-fibrous calcites, and dogtooth cements.

The changing diagenetic conditions within the Bleiberg facies favor the development of several dolomite-types (H e n r i c h & Z a n k l, 1986). The shallow burial diagenesis terminated with the precipitation of an idiomorphic pore filling dolomite, which has also replaced the host rock. Carbonate cementation of these near surface to shallow burial diagenetic stages was very limited in the carbonate rocks of the Raibl Group and only some fibrous calcites can be distinguished.

Deeper burial cementation (Fig. 3) began with a first generation of saddle dolomite, represented by relatively small crystals, appearing clear in transmitted light and called „clear saddle dolomite" (CSD). The following „zoned blocky calcite" (ZBC) shows a zonation from non luminescing to red, orange, yellow and orange zones under CL. Dedolomitization of the earlier CSD is associated with the occurrence ZBC. „Cloudy saddle dolomite" (CLOSD) consists of relatively large crystals with a mostly cloudy appearance in thin sections. The subsequent two generations of blocky calcite cements show crystal sizes up to several mm. Corrosion of earlier cements and no luminescence or dull red/brown luminescence is typical for „post-corrosion blocky calcite" (PCBC). „Uniform blocky calcite" (UBC) shows a uniform red or orange color under CL.

These carbonate cements of deep burial diagenesis are followed by non luminescing blocky calcites, which contain brightly luminescing subzones. Smithsonite appears in fractures and other secondary pore types and replaces the carbonate host rock. These carbonate cements are interpreted to be formed after uplift of the host rock under telogenetic/meteoric conditions (K u h l e m a n n et al., 1993).

Formation of secondary porosity was active during all stages of diagenesis. Microkarst porosity formed when the Bleiberg facies was emergent and carbonate rock was

CARBONATE CEMENTATION	MINERALIZATION
Carbonate cements of near surface and shallow burial diagenesis	"grey" anhydrite barite framboidal pyrite

DEEP BURIAL DIAGENESIS

FIRST ORE PHASE

clear saddle dolomite (CSD)

SPHALERITE
PYRITE GALENA
FLUORITE BARITE

SECOND ORE PHASE

GALENA
PYRITE SPHALERITE
FLUORITE BARITE

zoned blocky calcite (ZBC)

cloudy saddle dolomite (CLOSD)

fluorite
sphalerite

post-corrosion blocky calcite (PCBC)

sphalerite

uniform blocky calcite (UBC)

"blue" anhydrite

TELO-GENESIS

smithsonite, meteoric blocky calcite

cerrusite, hemimorphite, hydrozincite, wulfenite

Fig. 3. Relative succession of ore mineralization within the sequence of deep burial carbonate cements.

leached before precipitation of late diagenetic blocky calcites. The cavities were filled with carbonate cements and with two types of internal sediments. The first type of internal sediment, which is associated with the carbonate cements of near surface

to shallow burial diagenesis, formed when material of the sedimentation surface in-filtrated the cavities. The second type of internal sediment is intercalated between the carbonate cements of deep burial diagenesis. These internal sediments are either micritic and mostly dolomitized or coarse crystalline and consists of crystal relics of former cements.

Ore structures

The Pb-Zn ores are arranged concordant or discordant to the bedding of the host rock. Concordant ore structures include single beds replaced by ore and occurrence of channel-like cavities arranged subparallel to the bedding filled with Pb-Zn ores and carbonate cements (Fig. 4a). Finely laminated units up to 50 cm thick and consisting of alternating layers of sphalerite and carbonate mud or cement commonly occur on the bottom of these „channels" (Fig. 4a). These laminated units sometimes show sedi-
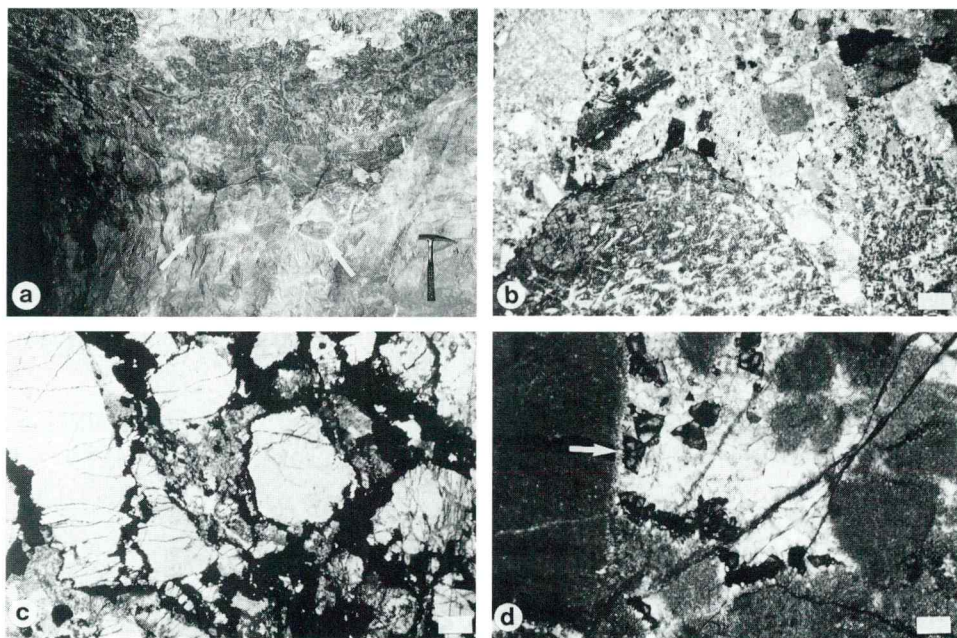
Fig. 4a. Channel-like cavity arranged subparallel to the bedding and filled with galena, sphale-rite and pyrite. Note the discordant contact of the orebody to the surrounding rock, indicating ore precipitation within cavities. The so called „ore rhythmites" occur below the massive Pb-Zn ore in small cavities (arrows). Konradi orebody, Bleiberg.

Fig. 4b. Ore breccia with ore fragments (sphalerite) and a saddle dolomite matrix. Scale bar = 0.4 cm.

Fig. 4c. Ore breccia with limestone fragments and a matrix consisting of galena. Fissures filled with galena crosscut the fragments and older fissures filled with saddle dolomite. Scale bar = 0.4 cm.

Fig. 4d. „Small" sphalerite is postdated (arrow) and predated by clear saddle dolomite. Scale bar = 0.3 mm.

mentary structures such as slumping or graded bedding and have been called „ore rhythmites" (S c h n e i d e r, 1964; S c h u l z, 1964; Š t r u c l, 1984).

Only discordant ore structures are economic. They include fractures/veins filled with lead-zinc ore and gangue minerals, which are fluorite, barite, and late diagenetic carbonate cements. Even more important are two types of ore breccias:

1) The clasts are ore-bearing (mostly sphalerite), the matrix consists of relatively coarse grained carbonate mud or clay similar to shale of the Raibl Group. Fractures filled with CSD crosscut the clasts, but do not crosscut the matrix. The matrix of other breccias with ore-bearing clasts consists of CSD (Fig. 4b) and/or younger carbonate cements. The clasts can be completely replaced by CSD, resulting in coarse crystalline dolomite breccias, which are typical for the stock-shaped dolomite breccias in the Bleiberg deposit. Clasts contain small solution cavities (Fig. 4d), in which the succession CSD - small sphalerite (see below) - CSD is present.

2) The matrix is ore and the clasts are mostly unmineralized (Fig. 4c). Fractures filled with CSD crosscut the clasts, but not the ore-matrix. This breccia-type with galena matrix is typical for ore breccias from Mežica („Graben" district).

Carbonate cements and lead-zinc ores

The different generations of carbonate cements enable relative dating of ore minerals by pore filling successions and/or crosscutting relationships. All carbonate cements of near surface and shallow burial diagenesis predate the lead-zinc ores (sphalerite, galena) and their accompanying minerals (fluorite, barite, „blue anhydrite"), with the exception of some synsedimentary or early diagenetic formed pyrite, anhydrite („grey anhydrite") and barite (cf. S c h u l z, 1968; S c h r o l l & W e d e - p o h l , 1972).

A first phase of Pb-Zn precipitation is closely linked to the formation of CSD, which predates and postdates sphalerite (Fig. 4d). Galena, fluorite and baryite are the accompanying minerals. The interfingering between ore mineralization and formation of CSD is also indicated by a close relation between the occurrence of Pb-Zn ores and the mineralogy of the host-rock. Most ores are associated with coarse crystalline dolomites, which formed as a replacement of limestone by CSD. This dependency can be observed in many ore deposits (e.g. Jauken) and was in general already shown by C e r n y (1989).

The first phase of ore precipitation is enriched in sphalerite and relatively poor in galena, while the second phase, which occurs distinctly after the precipitation of CSD and before ZBC, is rich in galena and poor in sphalerite. Pyrite, fluorite and barite are also accompanying minerals. The relationship of the ore minerals to CSD is illustrated by an ore breccia from the Graben area in Mežica (Fig. 4c), which consists of limestone and dolomite clasts containing a small amount of sphalerite. Fractures filled with CSD crosscut the clasts and the sphalerite, but not the galena-matrix. These fractures are crosscut by fractures filled with galena.

Both ore phases are economically important. The late precipitation of sphalerite and fluorite after CLOSD and before PCBC and of sphalerite after PCBC and before UBC is rare and uneconomic. Blue colored anhydrite follows UBC and is followed by oxidized minerals (e.g. smithsonite, cerussite).

Petrography and trace element content of the sphalerite

In hand specimens and in thin sections (transmitted light) sphalerite displays a variety of colors from yellow, green, red, violet, to brown without any distinct succession. Employing CL a distinct succession of sphalerite-types can be observed (K u h - l e m a n n et al., 1993; K u h l e m a n n & Z e e h, 1996). The first type of sphalerite crystals is small (20 to 40 μm) referred to as „small" sphalerite. This type luminesces similarly to the host rock or the gangue carbonate: dull, yellow or red. The following four types, which are called „light blue", „orange-red", „dark blue", and „brown" are characterized by their luminescence. The position of colloform sphalerite coincides with the light blue-type; light blue luminescing crystals occur in the center of colloform sphalerite as well as postdate it.

Formation of these types of sphalerite is closely related to the precipitation of CSD, which predates and postdates all sphalerite-types mentioned above. All later formed sphalerite shows no luminescence and has a uniform yellow color in transmitted light.

Geochemical analysis of trace elements by ICP-MS in the different sphalerite-types exhibit a characteristic distribution of Ag, As, Fe, Tl, Ge, Cd, and Cu, which support the optical discrimination based on their CL. These geochemical data were corroborated by electron-microprobe and proton-microprobe analysis (K u h l e - m a n n and Z e e h, 1996).

The small sphalerite-type is distinguished from other types by its relatively high Cu-, As-, Cd-, Tl- and Ge- contents and low Ag-contents. Colloform sphalerite contains the highest concentrations of Fe, As, Tl, and Ge, while both blue luminescing types of sphalerite are relatively poor in trace elements. The orange-red-type, which is intercalated between these two blue luminescing types, has the highest contents of Cu,
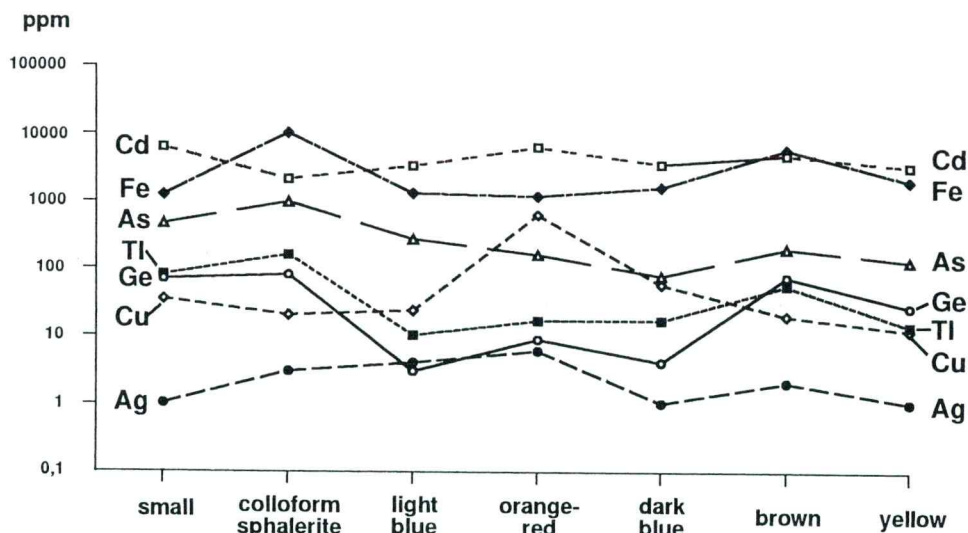

Fig. 5. Trace element (Ag, As, Cd, Cu, Fe, Ge, and Tl) content of sphalerite grains, measured by ICP-MS.

Ag, and Cd. The brown-type is relatively enriched in Fe, Cd, Tl, and Ge, while the yellow-type shows mean values for As, Cd, Fe, Ge, and Tl and a depletion in Ag and Cu.

The distribution of trace elements in the sphalerite-type succession (Fig. 5) shows an increase of the Ag-content from small to orange-red followed by a decrease. Cu-values are relatively low at the beginning and at the end of the succession with a strong maximum in the orange-red-type, while As, Ge and Tl reveal the opposite trend. The Fe- and Cd-contents of the sphalerite succession do not show a distinct trend.

Fluid inclusion and stable isotope studies

Fluid inclusion (FI) data are available from late diagenetic carbonate cements, fluorites, and brown sphalerite (Table 1). FIs from other sphalerite-types are too small for measurements. FIs in CSD, which was formed before small sphalerite (cf. Table 1, sample no. 90J10), show homogenization temperatures (T_h) of 83 to 109 °C and a salinity of the fluid of 15 to 16 wt% equivalent NaCl. FIs in sphalerite-type brown from the same sample have T_h of 92 to 129 °C and the final melting temperatures of ice Tm indicate a salinity of 8 to 12 wt% equivalent NaCl. FIs in CSD formed after brown sphalerite show T_h of 77 to 89 °C. Freezing temperatures could not be measured, because of the small FI size. Another sample of CSD with unknown relationship to Pb-Zn ores reveals T_h of 90 to 101 °C. The final melting temperatures of ice indicate a fluid salinity of 16 to 19 wt% equivalent NaCl.

Table 1. Fluid inclusion data of CSD, fluorite, and sphalerite.

sample no.	type	origin	stratigraphy	Th (°C)	Tfm (°C)	Tm (°C)	Thicknes of overljing sediment (m)	Pressure correction (Mpa)	Calculated temperature (°C)
90J10	CSD	Jauken	Watterstein Fm.	83-109	-52 to -51	-12 to -11	1500	20	122-147
90J10	sphalerite (brown)	Jauken	Watterstein Fm.	92-129	---	-8 to -5	1500	20	126-159
90C8	CSD	Bleiberg	Raibl Group.	77-89	---	---	1500	20	---
8/36	CSD	Bleiberg	Watterstein Fm.	90-101	-52	-15 to -12	1500	20	125-138
C5	Fluorite 1. Gen.	Bleiberg	Raibl Group.	170-195	-38 to -34	-18 to -15	1500	20	200-225
7/2	Fluorite 2. Gen.	Bleiberg	Watterstein Fm.	120-142	-52 to -49	-24 to -20	1500	20	150-175
90Rd2	Fluorite 3. Gen.	Radnig	Watterstein Fm.	76-100		-9 to -6	2000	30	124-145
90Rd5	Fluorite 3. Gen.	Radnig	Watterstein Fm.	79-117	-47 to -43	-9 to -5	2000	30	127-156
7/2	Fluorite 3. Gen.	Bleiberg	Watterstein Fm.	84-120	-23 to -20	-6 to -4	1500	20	130-165

FI in fluorite of the first mineralization phase, precipitated after brown sphalerite, reveal Th between 170 and 195 °C and a salinity of the fluid of 18 to 21 wt% equivalent NaCl. FI data of fluorite from the second mineralization phase show lower T_h of 120 to 142 °C and a salinity of 22 to 25 wt% equivalent NaCl. FI from three samples of the third fluorite generation show the lowest T_h of 76 to 120 °C with a salinity of the fluid between 6 and 10 wt% equivalent NaCl.

The first melting of ice (T_{fm}) occurred in CSD at temperatures of -52 to -51 °C. Similar values were measured for the second generation of fluorite. The first and the third generation show T_{fm} values between -47 and -20 °C.

The stable isotope data of the deep burial carbonate cements show a general decrease in the ^{18}O and ^{13}C content from CSD to CLOSD and from ZBC to UBC (Z e e h et al., 1995). $\delta^{18}O$ values of CSD are between -9.8 and -5.5 ‰ PDB and $\delta^{13}C$ values are between +1.9 and +3.8 ‰ PDB. Smithsonite and blocky calcite are distinctly different and show negative $\delta^{13}C$ values (K u h l e m a n n, 1995).

Stratigraphic occurrence of Pb-Zn ores and carbonate cements

Although the Carnian carbonate rocks of the Wetterstein Formation and the Raibl Group are the main ore-bearing strata, there are a few ore occurrences in rocks underlying and overlying these strata. The Pb-Zn deposit of Topla (Š t r u c l, 1974) is situated in Anisian carbonate rocks. These ores are somewhat different in their petrography and their geochemical composition to the Pb-Zn deposits described above and are not further discussed here. Some sphalerite crystals can also be found in carbonate rocks of Norian age. These sphalerites occur in fissures and show the same dark blue luminescence as observed in deposits hosted by Carnian rocks. Fluorite is also found in fissures crosscutting carbonate rocks of Rhaetian age.

Studies on the distribution of the above mentioned deep burial carbonate cements show that CSD can be traced in fissures of sedimentary rocks from Anisian up to Early Liassic in age (W a l t e r et al., 1994; K u h l e m a n n, 1995). CSD is also present in components of Early Jurassic conglomerates, but not in the matrix (Z e e h 1997). All other carbonate cements also occur in sedimentary rocks of Anisian to Miocene in age (W a l t e r et al., 1994, Z e e h et al. 1997, Z e e h 1997).

Lead and sulfur isotopes

Sulfur-isotope studies by S c h r o l l & W e d e p o h l (1972) and S c h r o l l et al. (1983) show a broad range of mostly negative $\delta^{34}S$ values for the sulfides and positive values for the sulfates. Our own sulfur isotope data corroborate these values, but show other features in detail (K u h l e m a n n, 1995). The $\delta^{34}S$ of different sphalerite types from the same sample decreases with decreasing age of the sphalerite. For example, sphalerite-type red and sphalerite-type dark blue from the same sample of Obir area have a $\delta^{34}S$ of -10.07 ‰ CD and of -12.99 ‰ CD, respectively. One sample from Mežica also shows a decrease of $\delta^{34}S$ in the sphalerite-type succession light blue (-13.22 ‰ CD), dark blue (-13.98 ‰ CD) and yellow (-14.89 ‰ CD). This trend towards more negative values is not present in the succession of sphalerite types, considering all sulfur isotope data of sphalerite.

Lead-isotope studies by K ö p p e l & S c h r o l l (1988) show a different isotopic composition of ore-lead and trace-lead of the host rock. The ore lead has homogeneous isotopic compositions, but the trace lead of the host rock has varying isotopic compositions.

Discussion

Ore structures

The channel-like cavities were interpreted as channels on the sea-floor (S c h n e i - d e r, 1964; S c h u l z, 1964) and used as a proof of the synsedimentary origin of the East Alpine Pb-Zn ores. S i e g l (1956) showed that the channels do not represent structures formed on the sea-floor, but instead are formed after lithification and burial of the host rock. This is indicated by the irregularity of the cavity-roofs (Fig. 4a) and the occurrence of clasts from the hanging wall within these cavities.

The laminated units on the bottom of the channel-like cavities were interpreted as another indication of a synsedimentary origin of the ores. The graded bedding and

slumping structures should be formed by transport processes on the sea-floor (S c h n e i d e r, 1964; S c h u l z, 1964; Š t r u c l, 1984), but internal sediments can also show lamination, slumping and graded bedding and these structures cannot be used as a proof of an origin on the sea-floor. Furthermore, internal sediments were formed at different times as shown by the relation to carbonate cements. However, the time of formation of the channel-like cavities and the ore-rhythmites is questionable. They could be formed during the synsedimentary karstification of the Bleiberg facies or during late diagenesis by aggressive fluids leaching carbonate rock in relation to the ore forming processes.

The economically important stock-shaped breccia bodies were interpreted to represent other paleotopographic highs (B e c h s t ä d t, 1975b; C e r n y, 1989), which were subaerially exposed most of the time, deeply karstified and brecciated. These breccias were later replaced by CSD. The formation of sphalerite in these stock-shaped dolomite breccias is closely linked to the formation of CSD as indicated by the succession CSD -small sphalerite - CSD in solution cavities.

Breccias with a matrix similar the Raibl shales have also been interpreted as indicative of a synsedimentary emplacement of the ores, because they are thought to be formed along fault scarps during sedimentation of the Raibl Group carbonates (C e r n y, 1989). A strong arguement against a synsedimentary origin is the occurrence of CSD within fractures, which crosscut the clast but not the matrix, indicating that brecciation occurred after formation of CSD in fractures.

The second type of ore breccias with an ore-matrix is dinstinctly formed after formation of CSD, as indicated by the crosscutting relationships of fractures filled with galena and CSD.

These examples and the observed relationship between Pb-Zn ores and gangue minerals show that a first emplacement of Zn-rich ores with a distinct succession of sphalerite types is closely linked with the formation of CSD. The second phase after the precipitation of CSD is Pb-rich.

Source rock for Pb and Zn

Isotopic similarity between feldspar-lead from the crystalline basement and ore-lead indicates a derivation of the metals from Paleozoic metasediments, with a possible minor amount of lead from Permian sandstones and Triassic volcanic rocks (K ö p p e l & S c h r o l l, 1988). Feldspars as the main source of lead might be further corroborated by the presence of barite and the high thallium content of ore minerals (K ö p p e l & S c h r o l l, 1988). In addition, Lower Paleozoic metasediments have in some parts high arsenic concentrations, which is one of the important trace element in the sphalerite (Köppel & Schroll, 1988). Therefore, the Paleozoic basement rocks seem to be the main source of Pb and Zn and trace elements of the sphalerite.

Time of ore formation

The stratigraphic distribution of CSD and sphalerite indicates a syn to post Late Triassic (Rhaetian) time of ore emplacement. Furthermore, CSD is present in components of Early Jurassic conglomerates, but not in the matrix (Z e e h, 1997), indicating that CSD and the related Pb-Zn ores were formed before or during Early Jurassic time.

Temperature of ore forming processes

Assuming a Late Triassic/Early Jurassic formation time for the first and second mineralization stage, the formation temperatures have to be corrected for an overburden pressure of 20 MPa, considering a lithostatic to hydrostatic conditions (Table 1). For late diagenetic blocky calcites, CLOSD, and the third generation of fluorite an overburden pressure of 30 MPa is assumed to prevail during the Tertiary.

The calculated formation temperatures show that brown sphalerite and fluorite of the first ore phase formed at higher temperatures than CSD. Formation temperatures increase from CSD (122 to 147 °C), formed before small sphalerite, to brown sphalerite (126 to 159 °C). CSD formed after brown sphalerite has the lowest Th, but Th could not be measured. Assuming a similar salinity of the fluid for this CSD as measured for other CSD, a formation temperature of 112 to 125 °C can be calculated. Fluorite formed after brown sphalerite shows the highest formation temperature of 200 to 225 °C and fluorite of the second ore stage show lower formation temperatures of 150 to 175 °C.

The third generation of fluorite, which postdates the formation of CLOSD show the lowest formation temperatures of 124 to 165 °C, which are also lower than the formation temperatures of CLOSD (175 to 194 °C; Z e e h et al., 1995). The blocky calcites, which predate and postdate the third fluorite generation show the highest formation temperatures (200 to 280 °C).

Fluid composition

The FI data indicate that the salinity of the fluid was higher during the precipitation of CSD than during the precipitation of sphalerite. The fluid-salinity increases from the first to second fluorite generation. The third generation of fluorite was precipitated from a fluid with the lowest salinity. The other carbonate cements were precipitated from fluids of low to high salinity (Z e e h et al., 1995). The Tfm values indicate $NaCl$-$CaCl_2$-$MgCl_2$ fluids during the precipitation of CSD and the second generation of fluorite. The first and third generation of fluorite were precipitated from $NaCl$-$CaCl_2$ fluids.

The calculation of the oxygen isotopic composition of the fluid precipitating CSD (Z e e h et al., 1995) reveal values between +6 and +10 ‰ (SMOW), which are characteristic for deep basinal brines enriched in salinity (cf. M ü l l e r & P a p e n - d i e c k , 1975; B a r k e r & H a l l e y, 1986).

The trace element composition of the sphalerite gives indications about the trace element content of the fluid. V i e t s et al. (1992) assumed that the trace element content of the sphalerite succession in the Ozark region reflects a time dependent leaching of trace elements from the source rock. The variations of the trace element content of the sphalerite could also reflect Eh- and/or pH-changes of the ore bearing fluid in the source and/or in the host rock (K u h l e m a n n & Z e e h, 1996).

Sulfur isotopes

S c h r o l l & W e d e p o h l (1972) and S c h r o l l et al. (1983) assumed Triassic sea water as the source of sulfur, due to the similar isotopic composition of the mea-

sured sulfates and Triassic sea water. The isotopic composition of the sulfides was ex-
plained by bacterial reduction of the sulfate-sulfur.

Assuming a bacterial reduction of sulfate-sulfur during ore-precipitation, the
most negative $\delta^{34}S$ values are expected for early formed sphalerite and less negative
$\delta^{34}S$ values for late formed sphalerite. Sulfur isotope data of different sphalerite-
types do not fit with this assumption. Early formed sphalerite show less negative va-
lues than late formed sphalerite in the same sample.

L e a c h & S a n g s t e r (1993) referred that bacterial reduction of sulphate must
occur separately in time or space from sulphide precipitation, because temperatures
during ore precipitation exceed those to which bacterial reduction is effective.
Reduction of sulphate-sulfur within the Bleiberg facies predating ore precipitation
could explain the contradiction between FI data and assumed bacterial reduction of
sulphate-sulfur. The observed sulfur isotope trends towards more negative $\delta^{34}S$ values
in sphalerite from the same sample might result from isotopic fractionation and mass
balance effects related to changing physicochemical parameters of the system (cf.
F o n t b o t é & G o r z a w s k i, 1990).

Pb-Zn ores within the Bleiberg facies

The concentration of ore deposits within the Bleiberg facies might result from:
1) The Bleiberg facies was rich in early formed secondary porosity developed du-
ring several emersion phases.
2) The occurrence of synsedimentary sulfates within this facies might have given a
potential source of sulfur.
3) The Wetterstein Formation is overlain by the first Raibl shale. The sealing effect
of this shale to ascending solutions (B e c h s t ä d t, 1979) is demonstrated by the only
local occurrence of Pb-Zn ores within the Raibl Group, where the intervening shale is
absent.

Model

The observations summarized in the present paper show that the East Alpine Pb-
Zn ores are distinctly different from SEDEX deposits and clearly result from epige-
netic mineralization. Considering the above mentioned data and reflections the follo-
wing model for the genesis of the East Alpine Pb-Zn deposits is proposed.

A source area for fluids during the Late Triassic/Early Jurassic may be the hinter-
land in the north (? Vindelician-Bohemian massif), where meteoric waters descended
(Fig. 6). A gravity driven flow might have been caused by the topographic difference
between the hinterland and the area of ore precipitation. The salinity of the solution
increased with depth and metals (Pb, Zn, and some trace elements) could have been
leached from the crystalline basement rocks along the migration path. The ascent of
the fluids might be supported by a thermal anomaly resulting from the onset of rif-
ting in the Alpine realm (B e r t o t t i et al., 1993). Brines rich in metals leached from
the crystalline basement and other possible source rocks ascended and migrated into
areas with high porosity, where they emplaced ores under distinct geochemical condi-
tions (e.g. presence of Triassic sulfur).

Ore-precipitation started with a Zn-rich phase closely linked with the precipitati-
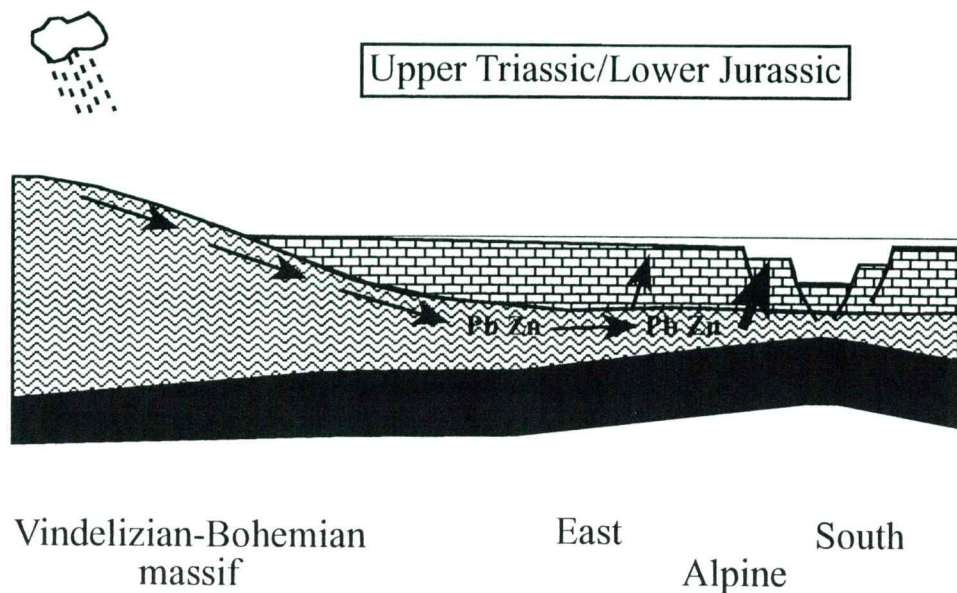
Fig. 6. Model for the Triassic/Jurassic fluid flow, which was responsible for the development of the Pb-Zn deposits in the Alpine realm.

on of CSD, which was formed at lower temperatures than the sphalerite. The first generation of fluorite, which was precipitated after CSD, shows the highest formation temperature at the end of the first ore formation stage. The second ore stage is Pb-rich and precipitated distinctly after CSD. The second and third generation of fluorite were precipitated at lower temperatures. The salinity of the fluid is high for the first and second ore phase and relatively low for the third phase of fluorite precipitation. Further precipitation of ore occurred during different stages and might result from mobilization processes, which were also assumed by D r o v e n i k (1983) for galena of the second ore phase.

The succession of deep burial carbonate cements after CSD seems to be of no direct relation to ore emplacement. These cements apparently formed during the Tertiary in relationship to metamorphism and uplift of the Alpine realm (Z e e h et al., 1997).

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