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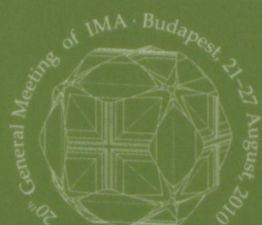
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MÁRTA POLGÁRI, WALTER PROCHASKA & ANTON BERAN

Alpine carbonate mining sites: Aspects of carbonate mineralizations related to the manganese mine of Úrkút, Hungary, the magnesite deposit of Veitsch and the siderite mine "Steirischer Erzberg", Austria

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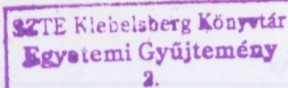
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*On the cover: Quartz veins crosscutting magnesite (Veitsch magnesite deposit, Styria, Austria).  
Photo: Walter Prochaska.*



# Alpine carbonate mining sites: Aspects of carbonate mineralizations related to the manganese mine of Úrkút, Hungary, the magnesite deposit of Veitsch and the siderite mine "Steirischer Erzberg", Austria

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## 1. The manganese mine at Úrkút, Hungary

### 1.1 Introduction

The Transdanubian Range (Hungary, ALCAPA Unit) hosts a series of black shale-hosted Mn-carbonate and cherty, Fe-rich

Mn oxide mineralizations in association with varicoloured metalliferous clays. The black shale-hosted Úrkút Mn mineralization is among the ten largest deposits in the world in its class. Its current reserve is 80 mln t of Mn carbonate ore (24 wt% average Mn and 10 wt% Fe content). The original deposit was much larger, a real giant with about 300 mln t of ore (32 mln t

of metal Mn, 26 mln t of Fe), but most of it eroded during geological times (Cretaceous and Eocene). The amount of eroded ore can be estimated from the amount of resedimented accumulations around the mineralization. Further, the Fe-rich chert part of the ore deposit exhibits approximately 5 mln t of SiO<sub>2</sub> and 1 mln t of Fe. In spite of its Jurassic age, the original features of the deposit were overprinted only by diagenesis.

The unmetamorphosed black shale-hosted manganese carbonate mineralization of the Úrkút Basin, Transdanubia, Hungary (Fig. 1) provides an excellent opportunity for complex

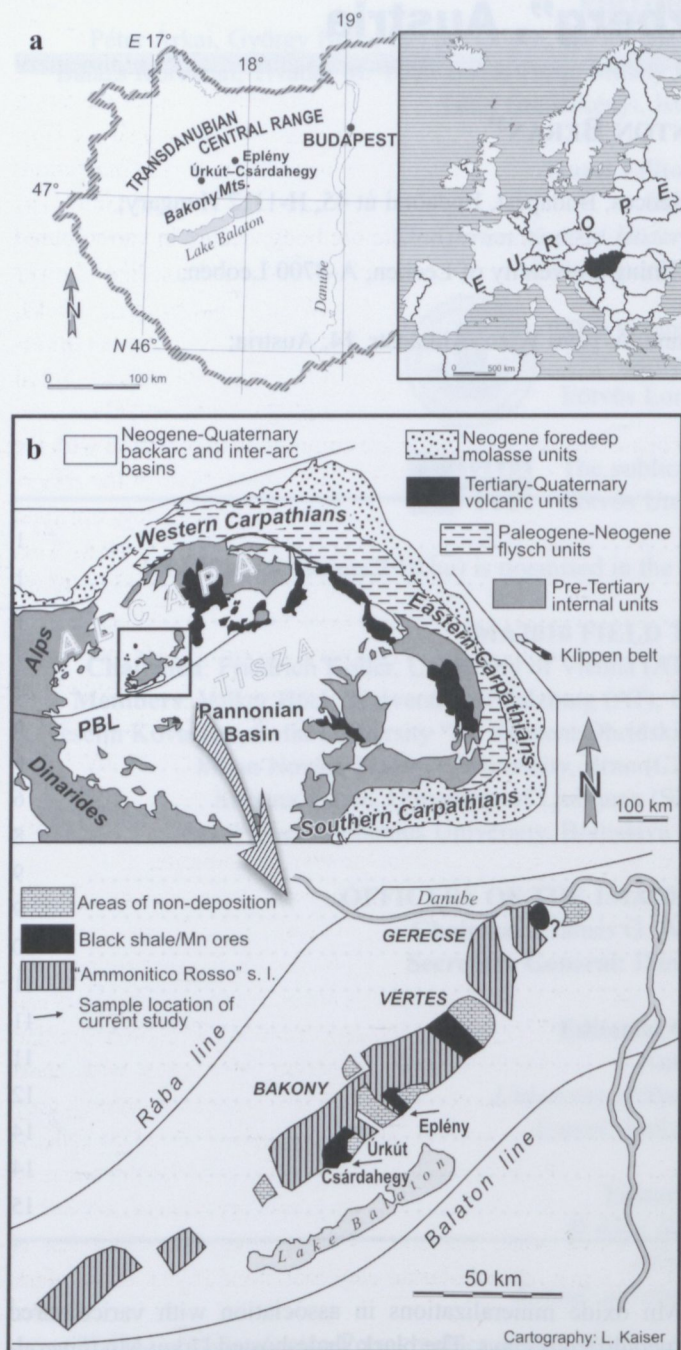
petrographic, mineralogical, geochemical, textural studies of early diagenetic Mn carbonates and primary oxides of Jurassic (Lias, Toarcian) age (Polgári *et al.*, 2000 and references therein).

*Metallogeny of black shale-hosted manganese deposits.* Sedimentary manganese deposits show a very wide range of distribution both in time and in space (Roy, 1981). Their formation extends through the greater part of the geological history and they are extensively distributed both on the continents and on the bottoms of the present-day oceans, shallow seas and lakes. Concentration of Mn ores was not uniform at all ages and major epochs of Mn ore deposition can be identified (Fig. 2a). Jurassic was an important epoch of Mn carbonate mineralization. Different factors controlling the evolution – tectonic activity, volcanism and climatic variations – have been invoked, individually or jointly, to explain the distribution of Mn ore deposits, but no unique model has yet been unambiguously recognized. Several attempts have been made to estimate the comparative extent of manganese deposition during geological ages but the variable parameters used (tonnage of ores of different grades, tonnage of metallic Mn in deposits unspecified in respect of ore and protore, etc.) and the incomplete information on the extent of the deposits prevent any precise comparative estimate. A number of Mn deposits are closely associated with organic carbon-rich beds. Mn carbonate deposits are typical of such associations. Many of the important sedimentary Mn deposits of older geological ages have been modified by regional and contact metamorphism, which hid the original character of the modes of formation (Roy, 1981).

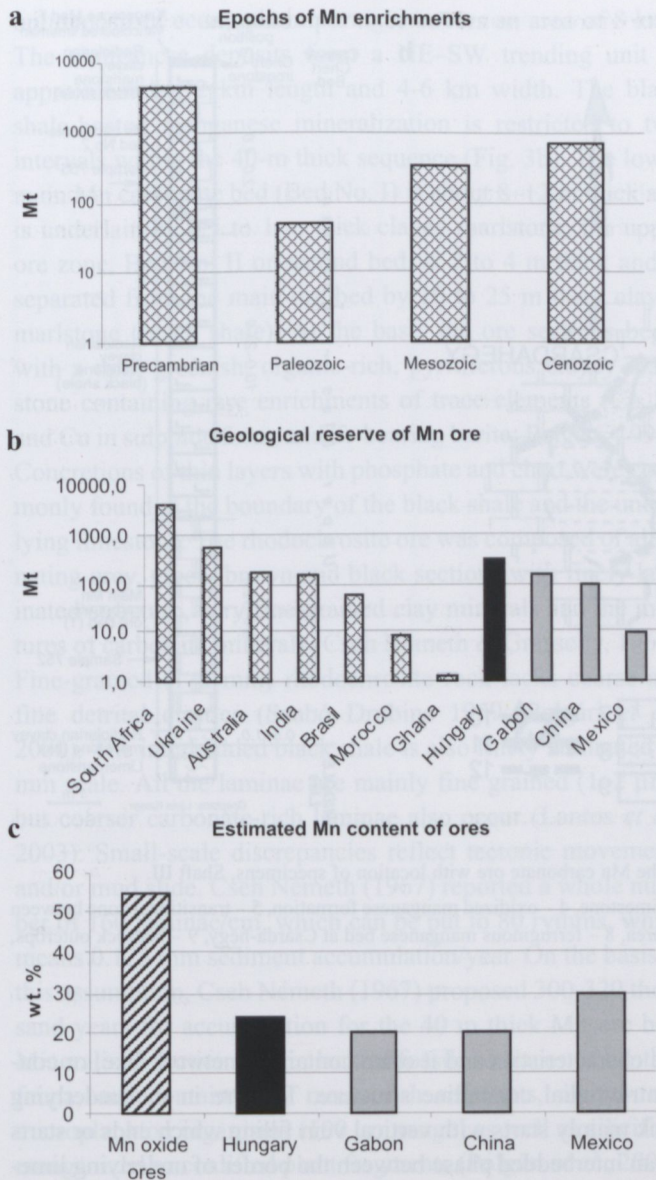
Among the black shale-hosted Mn carbonate mineralizations, Wafangzi, Gaoyan and Minle in China are Precambrian (Sinian), Moanda in Gabon are Precambrian; from Paleozoic (Cambrian), Tiantaishan, China, and Usinsk, Commonwealth of Independent States, and from Ordovician, Taojiang, China are worth to be mentioned among some smaller occurrences. Mesozoic (Jurassic) huge black shale-hosted Mn carbonate deposits are Molango, Mexico and Úrkút, Hungary. Most of these types of deposits represent huge reserves of manganese ore with 20–30 wt% Mn. Mn oxide deposits and secondary oxidized diagenetic Mn oxide formations contain much higher Mn content (around 50 wt% metal content). Geological reserves according to localities are shown on Fig. 2b. and Mn concentrations in ore beds represented by countries are summarized on Fig. 2c.

### 1.2 Geologic setting

The Úrkút Mn mineralization is located in the central Bakony Mountains (Transdanubia), in the North Pannonian unit of the Alpine-Carpathian-Pannonian region (ALCAPA, Figs. 1a–b). The history of development of the Mesozoic Transdanubian Range in the ALCAPA was determined from its palaeogeographic position in the Tethyan system. The Transdanubian



**Fig. 1.** Localization of Jurassic manganese deposits and indications in the Transdanubian Range, Central Europe. a) Location of the Jurassic Mn deposits in Hungary; b) Early Toarcian palaeogeographical sketch map (modified from Vörös & Galács, 1998); PBL – Periadriatic–Balaton Line.



**Fig. 2.** a) Epochs of manganese enrichments (Palaeozoic ore reserves are rough estimates); b) Geological reserve of manganese ores; c) Estimated manganese content of ores. Hungarian ore reserves are estimated before erosion (original occurrence).

Key to columns: grid – various types of Mn mineralizations; grey – black shale-hosted Mn carbonate mineralizations; black – Úrkút black shale-hosted Mn carbonate ore deposit. Note: In the case of China five deposits are given. Sources: Central Geological Office, Hungarian Geological Survey; Polgári *et al.* (2000); U.S. Geological Survey, Mineral Commodity Summaries, January 2008 <http://minerals.er.usgs.gov/minerals/pubs/commodity/manganese/mcs-2008-manga.pdf>; Roy (1981); Hein & Fan (1999).

terrane, part of the Tethyan shelf, was located between the Southern Alps and the Upper Austroalpine nappes during the complex development of the Mesozoic ocean. Its initial displacement started during the Eocene by way of NE lateral motion and it arrived at its present location in the Early Miocene (Csontos & Vörös, 2004). The Transdanubian Range Unit “Bakony” formed the highest Alpine nappe unit in Late Cretaceous, and can be interpreted as extensional allochthonous

unit (Fodor *et al.*, 2003). A Middle Jurassic palaeogeographic map (Haas, 1994) shows that the input of terrestrial detritus was blocked by the Ligurian-Penninic ocean and the Neotethys. Volcanic activity and oceanic spreading centres were widespread in the Neotethys and Ligurian-Penninic oceans.

### 1.3 Characteristics of the manganese ore deposit

The Mn carbonate ore beds lie conformably on Middle Lias cherty limestone (Tüzkövesárok Limestone Formation). Near the fracture zone the *underlying rock* is Lower Lias Hierlatz-type limestone.

The *manganese deposits* are within marine sedimentary rocks and composed mainly of bioclastic limestone, radiolarian clay marlstone and dark grey to black shale (Polgári, 1993).

Three main types of Mn deposits are in close connection. The (i) *primary Si-Fe-rich Mn oxide ore* as the proximal part of the much larger carbonate ore body, occurs in varicoloured metalliferous clays, on strongly dissolved “karst-like” Lower Lias Hierlatz type limestone footwall, in the form of blocks, nodules, wad beds, in close proximity to fracture zones (Úrkút-Csárdahegy, Csárdahegy-type ore). Sedimentary dykes filled with red limemud, varicoloured (red, green, brown) clays, carbonate debris or Mn oxide are common in association with the ores. The schematic geological map and sections of the mineralizations is shown in Fig. 3. The thickness of this ore type was 6–8 m on average, but its maximum was up to 15 m. This ore type represented an exploited ore volume of 436,000 m<sup>3</sup> and a “karst-like” open pit area of 181,300 m<sup>2</sup> (Fig. 4). The XRD mineralogy of the primary *cherty Fe-Mn oxide ore* (Csárdahegy) consists of hollandite, pyrolusite, cryptomelane, todorokite and manganite. Besides Mn minerals, goethite, quartz and 10Å-phyllsilicates occurs in main or moderate amounts. The ore bogs often are covered by a brown part, whose composition is goethite, manganite, 10Å-phyllsilicates, quartz traces, cristobalite (?) and hematite.

The (ii) *distal black shale-hosted Mn carbonate ore bed* occurs in black shale of Toarcian age (falciferum ammonite zone; Géczy, 1973), (Figs. 3a–b). From the underlying rock toward the manganese carbonate ore bed the following zones can be distributed: (a) typical red-grey mottled, thick Pliensbachian limestone (Tüzkövesárok Limestone Formation) with chert layers; (b) reddish grey limemarl with green to greenish grey layers, with fine texture, often containing calcified Belemnite rostrums and green clay filled fractures (the thickness of this zone is 1–1.2 m); (c) greenish brown limemarl, similar to the above zone, but more homogenous (the thickness is 0.2–0.5 m); (d) radiolarian clay marlstone (black shale), dark gray, pyritiferous (the thickness is 0–1.5 m); (e) Mn carbonate ore bed starting with greenish grey coarse laminated or brown-grey fine laminated ore type.

At the *contact zone* of the Mn carbonate ore bed and the underlying limestone–marlstone (iii) *Fe-Mn oxide ore* occurs. The Fe-Mn oxide ore is hard; metallic lustre and bluish colour

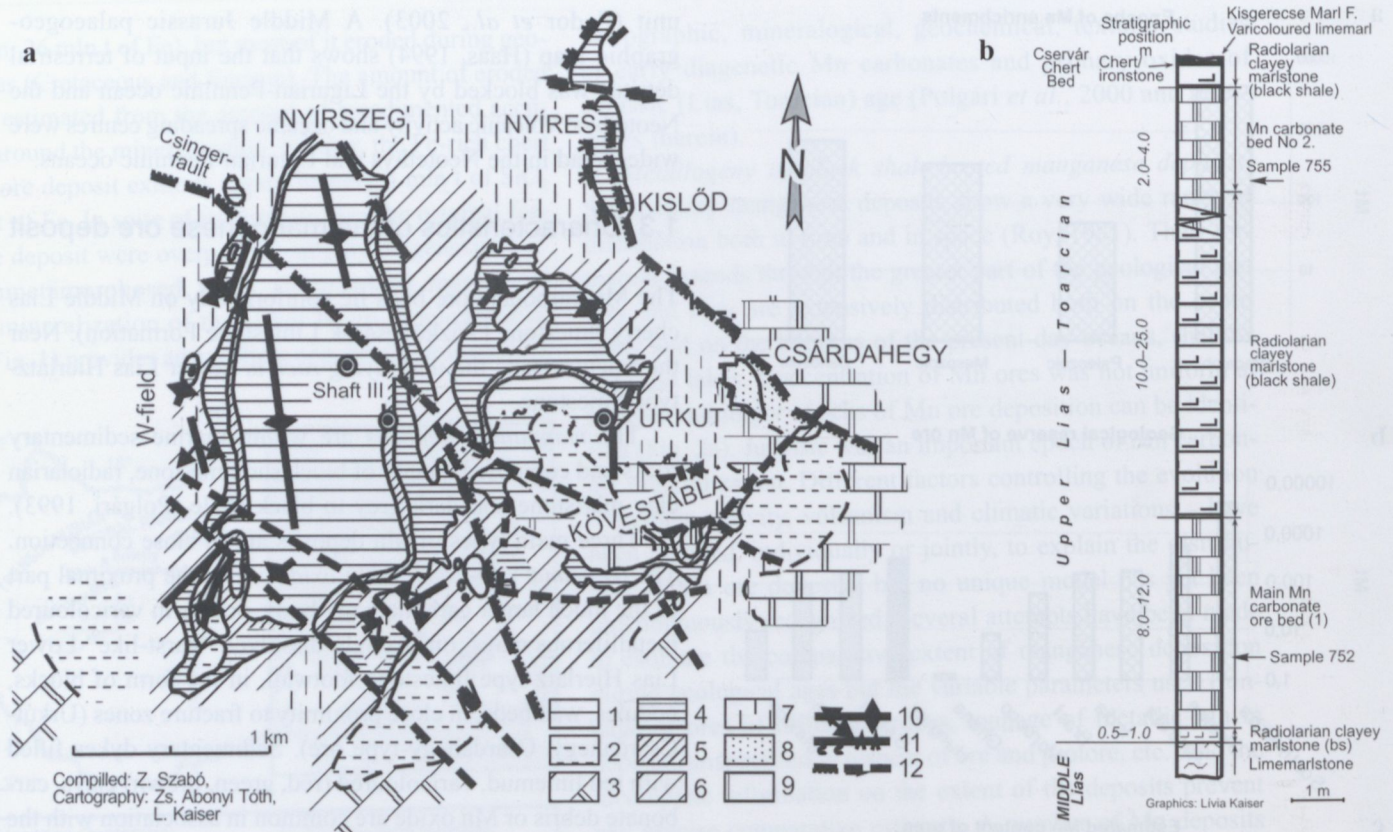


Fig. 3. a) Geological sketch map of the Úrkút deposit and b) the general profile of the Mn carbonate ore with location of specimens, Shaft III.

1 – Mn carbonate complex, 2 – Mn carbonate complex of reduced development, 3 – limestone, 4 – oxidized manganese formation, 5 – transitional zone between carbonate and oxide deposits, 6 – reworked manganese ore formation, 7 – denuded area, 8 – ferruginous manganese bed at Csárda-hegy, 9 – bedrock outcrops, 10 – anticline, syncline, 11 – flexure, 12 – fault.



Fig. 4. “Karst-like” open pit after total exploitation at Csárda-hegy.

are characteristics and it often contains a network-like, or concentric/radial crystalline structure. The ore in the underlying rock mainly starts with vertical vein filling which ends or starts as an interbedded phase between the border of underlying limestone and limemarl, forming “mound-like” up to 50 cm thick structures. Along these Fe-Mn oxide ore formations the host rock shows alteration (contact zone), which is represented by a changing colour of the limemarl (from red to greenish grey), by limonitization, clay alteration and/or silicification. The thickness of this contact zone is approximately 5 cm. The reddish brown layer around the Mn oxide mounds or interbeddings is 1–5 mm. In other cases this Mn oxide ore is in close connection with the Mn carbonate ore bed, or is interbedded in the brown Mn carbonate ore with sharp contact, where the signs of alteration are not visible. Signs of bacterial activity are common in a set of these samples. According to XRD, the black ore parts consist of cryptomelane, todorokite, manganite as main minerals, goethite, hematite, groutite, quartz, montmorillonite as moderate and rhodochrosite and kutnohorite as minor components. The brown parts contain goethite, hematite, quartz, K-feldspar, degraded illite/ montmorillonite and rarely groutite.

The distal black shale-hosted Mn carbonate ore bed is about 40 m thick at the centre of deposition and runs out towards the basin margins (Szabó *et al.*, 1981). Recently, the

ore deposit of economic importance covers an area of 8 km<sup>2</sup>. The manganese deposits form a NE–SW trending unit of approximately 12 km length and 4–6 km width. The black shale-hosted manganese mineralization is restricted to two intervals within the 40-m thick sequence (Fig. 3b). The lower main Mn carbonate bed (Bed No. I) is about 8–12 m thick and is underlain by 0.5 to 1 m thick clayey marlstone; the upper ore zone, Bed No. II or second bed, is 2 to 4 m thick and is separated from the main ore bed by 10 to 25 m thick clayey marlstone (black shale). At the base, the ore sections begin with a thin, greenish, organic-rich, pyritiferous clayey marlstone containing rare enrichments of trace elements (Co, Ni and Cu in sulphide form, and Sr-bearing barite; Polgári, 1993). Concretions of thin layers with phosphate and chert were commonly found at the boundary of the black shale and the underlying limestone. The rhodochrosite ore was composed of alternating grey, green, brown and black sections with finely laminated structure, very fine-grained clay minerals and the mixtures of carbonate minerals (Cseh Németh & Grasselly, 1966). Fine-grained (1–2 mm) rhodochrosite rock lacks coarse and fine detrital clastics (Szabó Drubina 1959; Polgári *et al.*, 2000). The interbedded black shale is also finely laminated on mm scale. All the laminae are mainly fine grained (1–2 µm), but coarser carbonate-rich laminae also occur (Lantos *et al.*, 2003). Small-scale discrepancies reflect tectonic movements and/or mud slide. Cseh Németh (1967) reported a whole number of 160 laminae/cm, which can be put to 80 rhythms, which means 0.125 mm sediment accumulation/year. On the basis of this assumption, Cseh Németh (1967) proposed 300–320 thousand years for accumulation for the 40 m thick Mn ore bed. Mineralized sections are in lack of fossils or traces of benthos fauna, and contain only rarely fish remnants, macro- and microplankton organisms (100 µm range) as well as silicified, manganized or coalified plant fragments (Polgári *et al.*, 2005).

The XRD mineralogical characterization of the Mn carbonate ore beds reveals various minerals: rhodochrosite (Ca-, Mg-bearing), siderite, kutnohorite, 10-Å phyllosilicates (celadonite), smectite (nontronite), goethite, quartz, apatite, pyrite, chlorite (traces), zeolites, feldspar (tr), manganite (tr), while the black shale consists of quartz, calcite, pyrite, smectite, 10-Å phyllosilicates (illite/celadonite), goethite, chlorite, zeolite (tr) and feldspar (tr).

The *overlying formation* of the Mn deposits is a chert/ironstone bed (Cservár Chert Bed). This bed is concordant with the underlying Mn ore and marks the termination of Mn accumulation in the area. Although there is no genetic connection between the two, the rocks adjacent to the contact record the oceanographic and bottom-water conditions that existed when the deposit ended the accumulation of Mn.

The regionally extensive greenish brown mottled chert/ironstone bed is a well-defined mostly 10–20 cm thick bed covering a large area (some 10 km<sup>2</sup>) and is composed of a bacterial mat sandwiched between two probably altered tuff layers (Polgári *et al.*, 2010). The bed formed in a submarine

environment below the photic zone based on the microfossils of the underlying and overlying formations (Sidó & Sikabonyi, 1953). The bed likely formed at the sediment/water interface. The chert/ironstone bed is Al-poor, K- and Mg-rich, and contains Fe-rich celadonite and Fe oxyhydroxide, and the mixture of these two phases. The temperature of the system was low (less than 40 °C) and oxidizing as the celadonite formation supports these conditions (Marescotti *et al.*, 2000). Silica and Fe mineralization of the bacterial mat can be attributed to sequestration of both elements by the bacterial mats and additionally to the acquisition of silica probably from alteration of the adjacent ash beds. The brown chert/ironstone bed does not contain terrestrial debris, microfossils, or other bioclasts.

The overlying marlstone still exhibits some MnO content, 1.9 wt% for the carbonate-rich parts (95.8 wt% CaO) and 2.6 wt% for the clay-rich parts (76.8 wt% CaO). This means that the manganese accumulation did not stop totally after the ore formation, and manganese substituted Ca in calcite. A pyroclastic origin for the chert/ironstone bed in the case of verification has a special significance for the Toarcian of Central Europe because sedimentary units there show only rare signs of coeval volcanism.

#### 1.4 Stable isotope investigations

Stable C and O isotope analyses of the Mn carbonate ore were carried out in order to obtain information on the source of C and Mn, on the enrichment mechanisms of Mn and on the formation temperature of the system. Mn carbonate ore bed samples represented  $\delta^{13}\text{C}$  values between –8.8 and –30.8‰ PDB and an average of –16.8‰ PDB for ore parts. This refers to an important organic carbon contribution to MnCO<sub>3</sub> carbon reservoir (more than 50%), which was formed via bacterially mediated early diagenetic processes (Polgári *et al.* 1991). These results raised the existence of Mn oxide (Mn oxyhydroxide) protore. The  $\delta^{18}\text{O}$  isotope results varied between –5.84 and +1.61‰ PDB, representing relatively constant values, which reflect the temperature of precipitation between 20 and 40 °C (Polgári *et al.*, 1991). For comparison of stable C and O isotope data, the results for huge Mn carbonate ore beds were summarized (Fig. 5). The joint evaluation of the deposits of Úrkút, Molango in Mexico (Okita *et al.*, 1988), Taojiang in China (Okita & Shanks, 1988) and Moanda in Gabon (Hein *et al.*, 1989) led to similar conclusions, and geochemical, mineralogical and isotopic features display many similarities. Almost all of these deposits are characterized by the occurrence of monomineralic ore zones consisting of rhodochrosite (often Ca-bearing rhodochrosite), by fine grain size (1–2 µm) and the lack of benthic fauna. The organic carbon contribution is similar in all deposits (average  $\delta^{13}\text{C}$  PDB values are –15‰ for Molango, –15.4‰ for Moanda), the O isotope data differ because of temperature elevation by metamorphic processes.

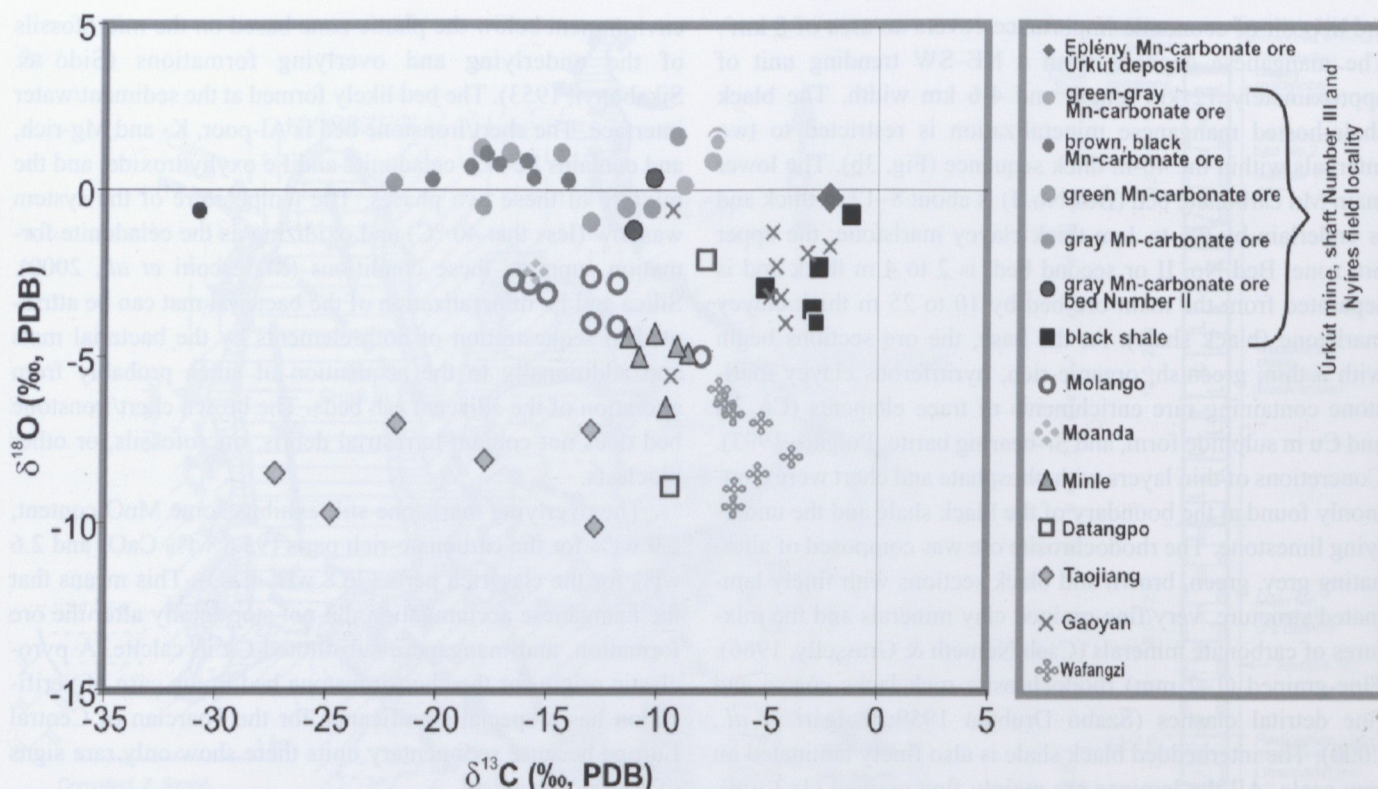


Fig. 5. Stable C and O isotope composition of Mn carbonate ores (Úrkút, Eplény: Polgári *et al.*, 1991, 2000; Molango, Mexico: Okita & Shanks, 1988; Moanda, Gabon: Hein *et al.*, 1989; Wafangzi, Minle-Datangpo, Gaoyan, Taojiang, China: Fan *et al.*, 1996).

### 1.5 Genetic considerations

Geochemical and mineralogical characteristics support the *hydrothermal source of metals*. The local feeding centre was probably the Csárdahegy locality, where stromatolite-like accretion growth of Fe-Mn oxide ore took place in metalliferous clay along feeding channels.

A new hypothetical approach was developed for the genesis of the Hungarian manganese ore deposits in sedimentary environments (Polgári *et al.*, 2004; Table 1). Accordingly, the carbonate manganese ore mineralization at Úrkút, in a black shale environment, is a manganese laminite of biogenic-bacterial, locally hydrothermal origin, deposited in a marine sedimentary environment. During formation of the ore deposit and in the enrichment of the elements, the main role was played by bacterial activity. The Úrkút-Csárdahegy area was the probable feeding centre (vent system) characterized by a strong mixing zone of hydrothermal fluids with seawater, causing autocatalytic Fe oxidation and Mn absorption on it, bacterial sulfide and MnOOH formation and also the bacterially mediated interaction of sulfides with reactive MnOOH. At distal position, the concentration decreased and this environment was favourable for aerobic chemolithoautotroph bacterial Mn<sup>2+</sup> oxidation causing a huge mineralization and organic matter accumulation on a relatively short geological period (primary aerobic bacterial cycle). The light C isotope signal of the Mn carbonate ore can be explained by a second-

ary anaerobic heterotrophic bacterial cycle during diagenesis (Polgári *et al.*, 1991). Mn<sup>4+</sup> and Mn<sup>3+</sup> oxides were reduced via bacterially mediated C<sub>org</sub> oxidation and this process overprinted the primary features of the deposit. Many features are characteristic for bacterial activity, *e.g.* very fine grain size, enrichment of bioessential elements, etc. The new approach discussed above allows a more uniform, less contradictory interpretation of the characteristic features of the ore deposits in the case of the black shale-hosted manganese carbonate ore mineralizations.

## 2. Sparry magnesite mineralization: The Veitsch type locality

### 2.1 Introduction

In 1850 the world's first deposits of magnesite were discovered in the province of Styria, Austria within Palaeozoic series of the Eastern Alps. Soon after the discovery, the first industrial application of magnesite was developed mainly for basic refractory lining of the blast furnaces of the local steel plants. The rapid application of this new raw material in a quickly growing steel industry triggered the scientific investigation and lead to a first general classification of magnesite deposits. In the following decades, different genetic models,



**Table 1.** Schematic model of mineralization at Úrkút (Polgári *et al.*, 2006)

<p><b>HYDROTHERMAL SOURCE</b> high Mn flux, as a need for mineralization</p>	<p>⇒ slow input, larger distance from source</p>	<p>⇒ decreasing concentration</p>	<p><b>Mn carbonate deposit (main bed, bed No. II., black shale layers)</b></p>
<p>⇓ quick intense input quick, sudden mixing autocatalytic chemical oxidation</p>			<p><b>aerob chemolithoautotrophic bacterial Mn oxidation</b> (+ further chemical oxidation)</p>
<p>Csárdahegy (Eplény)</p>			<p>huge amount of material accumulation due to very efficient bacterial activity</p>
<p><b>Ferruginous, siliceous Mn oxide ore + varicoloured metalliferous clays</b></p>			<p><i>Further evidences of bacterial activity:</i> high Mn/Fe ratio high plankton productivity high sediment accumulation rate (giant accumulation in a short time) Mg-enrichment enrichment of S, P, and other bioessential elements (Co, Ni, Zn, Ce, Sr, As) very fine grain size high N/C ratio</p>
<p>Fe – mainly chemical oxidation Mn – mainly microbial oxidation Varicoloured clay – bacterial sulfide formation MnOOH and metal-sulfide bacterial interaction <math>4.5\text{MnO}_2 + \text{FeS} + 7\text{CO}_2 + 4\text{H}_2\text{O} \rightarrow 4.5\text{Mn}^{2+} + \text{SO}_4^{2-} + 7\text{HCO}_3^- + \text{FeOOH}</math> (Aller &amp; Rude, 1988)</p>			<p><i>Original composition:</i> Mg-bearing todorokite, FeOOH (goethite) celadonite and other clay minerals bacterioplankton and normal plankton (Radiolaria) + organic matter of “higher animals” (Bivalvia, mussel – Bositra, fish etc.) biogene debris (calcite, opal)</p>

including a syndimentary origin, an Eoalpine metamorphic vein-type or metasomatic mineralization were proposed for this type of magnesite formation. However, up to now there is no consensus about a genetic model and the principal mechanisms of mineralization for “carbonate-hosted sparry magnesite”.

During the last years, new fluid inclusion and isotope data for the sparry magnesite deposit of the Eastern Greywacke zone provide strong evidence for formation of the magnesite deposits by metasomatic replacement due to infiltrating saline residual brines, which originated in the Upper Permian/Lower Triassic. These observations are considered to be of fundamental importance not only for the genetic aspects of carbonate-hosted sparry magnesite deposits but also hint towards a consanguineous origin of the magnesite and siderite deposits of the Eastern Alps in general. Earlier workers (*e.g.* Redlich, 1907; Petrascheck, 1932; Clar, 1953; Friedrich, 1968) already considered a consanguineous origin of the Alpine sparry magnesite mineraliza-

tions and the siderite deposits. In general they argued for hydrothermal fluids of different origin, like magmatic or metamorphic sources. Concerning the timing of the hydrothermal event and the corresponding geodynamic event, again different possibilities like Paleozoic (Variscan) and Cretaceous/Tertiary (Alpine) models had been considered. However, these concepts never gained general acceptance. A detailed overview on sediment-hosted magnesite deposits was given by Pohl & Siegl (1986). Möller (1989) published a monograph containing the different aspects of magnesite deposits of the Eastern Alps.

Within the excursion the Veitsch open pit mine will be visited. This site is the type locality of carbonate-hosted “sparry magnesite deposits”. Here in 1854 the world’s first magnesite deposit was discovered by geologists of the ‘k.k. Reichsanstalt’ (Imperial Geological Institute) and soon afterwards mining started. Redlich (1909) published the first genetic classification of magnesite deposits and the Veitsch mine became type locality of sparry magnesite deposits.

## 2.2 Geologic setting

The Eastern Alps are a fold and thrust belt formed in a collisional setting during the Alpine orogeny in late Mesozoic and Tertiary times. The Austroalpine nappe system which is a part of the Adriatic/African system overthrusts the Penninic units. All units consist of a low-grade metamorphosed pre-Alpine basement and a Permomesozoic cover. The Greywacke Zone, which hosts the most important magnesite mineralizations of the Eastern Alps, forms a Cretaceous stacked imbrication/nappe structure at the base of the Upper Austroalpine system. The rock series of the Greywacke Zone range from Ordovician to Carboniferous in age and comprise carbonates, metapelites and metamorphosed acid volcanics (Fig. 6).

In the Eastern Greywacke Zone carbonate-hosted sparry magnesite mineralizations occur mainly in Lower Carboniferous strata of the Veitsch nappe. A set of lens-shaped magnesite

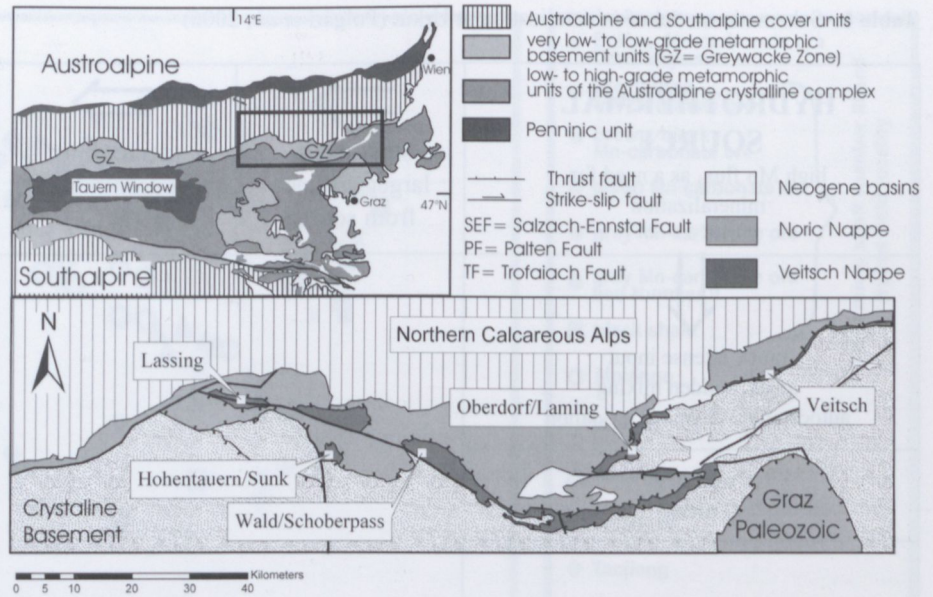


Fig. 6. Geological map showing the major magnesite mineralizations in the Eastern Greywacke Zone of the Eastern Alps.

bodies of various size can be found in a sequence of sericite schists, greywackes, conglomerates and metatuffs. Carbonate series hosting the magnesite bodies are of Upper Tournéan/Viséan age and exhibit

shallow water, marine environment. Neither Variscan internal deformation nor metamorphism was identified for the Veitsch nappe. The tectonothermal overprint is exclusively of Alpine (Cretaceous)

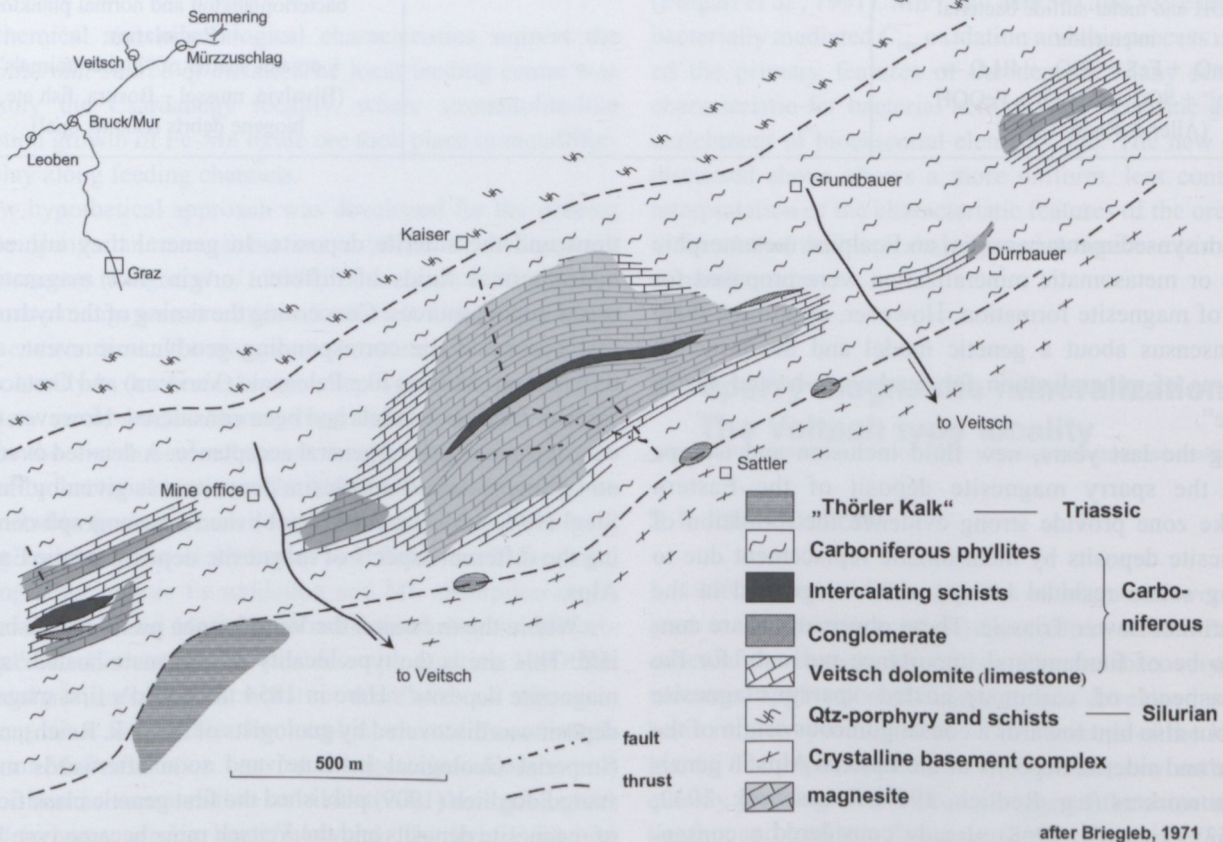


Fig. 7. Geologic sketch of the Veitsch magnesite deposit (modified after Briegleb, 1971).

age. The grade of the Eoalpine tectono-metamorphic events is generally of lower greenschist facies. Minor quartz veins in the magnesite bodies and the ubiquitous occurrence of talc are a consequence of the Alpine metamorphic overprint.

Other magnesite deposits in the Eastern Alps are the Breitenau mine, which is located in the “Graz Palaeozoic” and deposits in the Western Greywacke Zone which are in similar geotectonic positions as the magnesite mineralization of the Veitsch nappe. The magnesites of the Veitsch deposit are generally hosted by dolomitic carbonate series of Carboniferous age (Veitsch dolomite) and to a lesser extent by Carboniferous limestones, schists, conglomerates, quartzites and greywackes (Fig. 7). This host-rock lithology can also be found as inclusions of different size in the magnesite bodies. The chemistry of the inclusion fluids of the host-rock dolomites is very similar to the chemistry of the magnesite fluids (see below) thus indicating that this regional dolomitization occurred simultaneously with the formation of the magnesites. This is peculiar for the Veitsch deposit, in contrast to many other magnesite mineralizations of the Eastern Greywacke Zone, where dolomitic alteration zones usually are spatially limited.

### 2.3 Textural features of the sparry magnesites

Generally speaking, magnesite mineralizations tend to form irregular lenses and stocks (1000 × 450 m) whereas veins are very rare. Metasomatic replacement of the host-rock limestone by hydrothermal dolomite (alteration halo) is ubiquitous. Usually these dolomites are relatively finegrained and therefore the primary textures sometimes are often preserved. In the Veitsch type locality hydrothermal dolomites still exhibit very well preserved crinoids, which in some places are affected by transformation to magnesite (Friedrich, 1959; Briegleb, 1971). Usually in the coarse-grained magnesites no textures of the protolith are preserved. There is no consensus if the frequent bedding and layering in these rocks are primary sedimentary features or features due to diagenetic and hydrothermal recrystallization. Very low-grade alpine metamorphism is a regional phenomenon with very little effect on the magnesites.



Fig. 8. Quartz veins crosscutting the magnesite mineralizations are considered to be a secondary overprint of Alpine age.

Secondary dolomitization is ubiquitous in the Veitsch magnesite and coarse-grained dolomites of several cm in size can be found. The timing of this phenomenon is still unclear. A prominent secondary feature is the ubiquitous occurrence of quartz veins in the Veitsch magnesite deposit, which usually are considered to be of Alpine age. Associated with these quartz veins is a complex Cu sulfosalt mineralization, typical for all magnesite mineralizations of the Eastern Greywacke Zone (Fig. 8).

### 2.4 Inclusion fluid chemistry

The chemical composition of paleofluids can be used as geochemical tracer to investigate the original signature and origin of different kinds of inclusion fluids and can contribute substantially to the question of the origin of mineralizing fluids. The use of the Br content to characterize the origin of brines was introduced by Rittenhouse (1967). It is important that only very conservative systems that are not buffered and changed by ambient mineral reactions in the alteration zones are considered. Thus the Na–Cl–Br and to some extent I systematics are more suitable to provide clues to the identity of the highly saline fluids than other element ratios, which may be changed by wall rock alterations. Evidently Na–Cl–Br ratios are very difficult to be modified by fluid/rock reactions thus providing a tracer for hydrothermal fluids at least as “robust” as hydrogen isotope composition. Extensive studies on the evaporation path of seawater showed that in an initial state of evaporation, Na, Cl and Br are concentrated in a hypersaline environment and their ratios do not change. At an evaporation index of >10, halite is precipitated. Br has a very conservative behaviour and is not incorporated into the halite lattice. At an evaporation index of approximately 70, Mg salts start to precipitate and Br is still being enriched in the residual brines. In natural systems this process can lead to Cl/Br molar ratios as low as 90 (in seawater the ratio amounts to 655). At this stage K salts are being precipitated and the cation systematics of the corresponding brines changed from an original Na preponderance to Mg and K dominated systems.

The perfect positive correlation between Cl, Br and Na in the alteration dolomites of the Veitsch deposit as well as in the magnesites is of pivotal importance for the question of the mechanism of Br enrichment (Fig. 9). The coherent behaviour of Cl and Br and Na and Br proves that halite fractionation is the driving factor for the fluid composition and indicates that Br is not controlled by host rock reactions or supplied from external sources. The Na–Cl–Br numbers of the mineralized samples (hydrothermal dolomites as well as magnesites) are significantly lower than the seawater ratio and plot on the extreme end of the seawater evaporation trajectory, thus proving an evaporitic origin of the mineralizing fluids. The systematic difference in the Na/Br ratios between the host-rock marine limestones and the alteration dolomites marks the border of the hydrothermal alteration, thus indicating that dolomitization and magnesite formation belong to the same hydrothermal event.

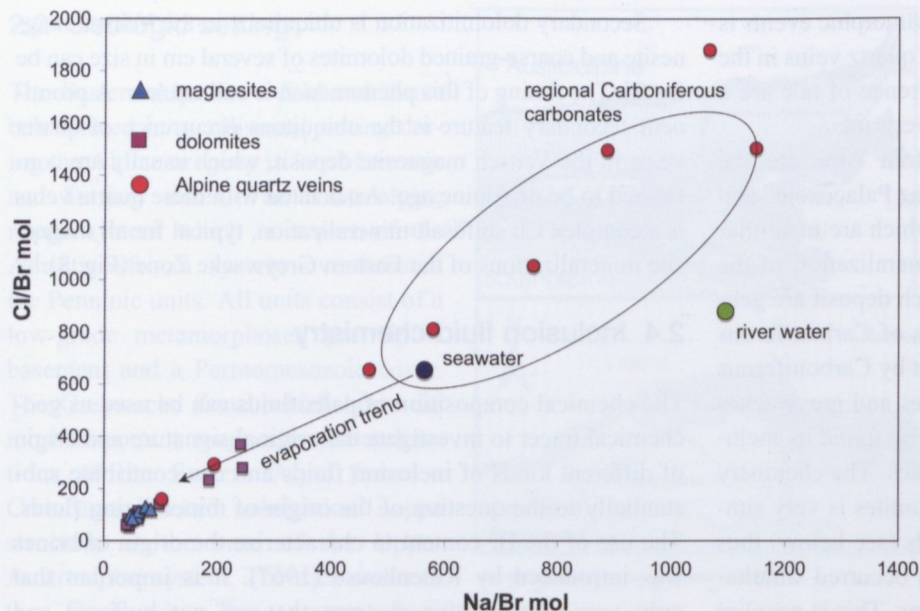


Fig. 9. Na–Cl–Br ratios in the profile ‘host-rock limestone – alteration dolomite – magnesite’ prove an evaporitic origin of the ore forming fluids.

Results obtained by the chemical analysis of the inclusion fluids were also applied on geothermometers based on semi-empirical cationic exchange reactions using Na/K, Na/Li or Na/K/Ca ratios. Different authors used these thermometers successfully (Kharaka & Mariner, 1989). In this study the best and most reliable results were obtained by the Na/K and the Na/Li thermometer. According to the geothermometric calculations the fluids in equilibrium with the hydrothermal dolomites and magnesites yielded temperatures of approximately 220 °C for the Na/K thermometer and 190 °C for the Na/Li thermometer.

## 2.5 Conclusion and genetic considerations

The regional dolomites as well as the magnesites of the Veitsch deposit exhibit low Na/Br and Cl/Br ratios plotting on the seawater evaporation trend, indicating that the fluids acquired their salinity by evaporation processes of seawater. Structural features and the totally different chemical signatures of the regional host-rock carbonates (platform carbonates of “normal” marine characteristics) prove an epigenetic origin of the mineralization (Prochaska, 2000). Temperature

calculations based on cation exchange thermometers indicate temperatures of the hydrothermal system of about 200 °C.

In an earlier study, Frimmel (1988) argued that Sr isotope data support a sedimentary origin of sparry magnesite deposits in the Eastern Alps. The Sr and Nd isotope investigations on the magnesites of the Eastern Greywacke Zone (presently being in progress) and the fluid chemistry data, however, require a different interpretation. The new data clearly document significant differences in isotope composition between the Carboniferous limestone and the magnesite deposit. Furthermore, the gradual increase in the Sr isotope ratio in the contact zone is a typical document for mixing processes whereby the original less radiogenic Sr of the limestone is gradually replaced by Sr of more evolved isotope composition in the course of a metasomatic replacement, triggered by infiltrating fluids. The relatively high-radiogenic Sr and Nd isotopic compositions in the main ore body are then interpreted as close estimates of the respective isotopic composition of the infiltrating fluid itself.

Based on the new inclusion fluid and Sr and Nd isotope geochemistry data and geologic observations, a genetic

model has to consider the following facts: (i) The mineralizing fluids exhibit all features of highly evolved seawater that suffered strong halite fractionation. (ii) The fluids of the regional Carboniferous host-rock limestones prove a “normal” marine sedimentary environment for the deposition of these rocks. (iii) Magnesite forming fluids necessarily have to have high Mg/Ca ratios and very low Fe contents (elsewhere dolomite or siderite would have been formed). (iv) Prominent alteration haloes around the magnesite mineralizations and the dramatic contrast in fluid composition between the mineralization and the host rocks prove the epigenetic origin of the mineralization.

In Upper Permian to lower Triassic times, very widespread and prominent evaporitic systems produced residual “bittern” brines with high concentrations in Mg, K, Br and SO<sub>4</sub> in the fluids. After the closure of the basins these fluids became formation waters and were mobilized by diagenetic processes due to the upland of the Triassic platform carbonates in Triassic times. Where these fluids came into contact with the adjacent Paleozoic carbonates, metasomatic stocks of sparry magnesite were formed because of the very high Mg/Fe ratio of these fluids. Longer migration distances of these fluids will result in an uptake of Ca and Fe and the fluids will lose their capacity to form magnesite and Fe-rich dolomites or siderite will form. This mechanism can lead to the formation of siderite. The siderite fluids of the Erzberg deposit (see Erzberg excursion) exhibit very similar chemical composition with high salinity and high Cl/Br ratios (conservative tracer!) compared to the magnesite fluids. The close resemblance of the magnesite and siderite fluids strongly suggests a consanguineous origin of their formation.

In this context it is also worth to note that the fluids of the Pb–Zn deposit Bleiberg, Carinthia, Austria which is of Triassic age also exhibit similar Na–Cl–Br ratios. It is conceivably that the Lower Triassic “magnesite fluids” took up Pb by fluid–rock interactions on their migration to shallower levels or

even to the seafloor consequently forming the Bleiberg Pb-Zn deposits. The originally high Mg/Ca ratios and the capacity to form magnesite gradually vanish by decreasing fluid-rock interaction along the migration path of the fluids.

### 3. The siderite mine "Steirischer Erzberg"

#### 3.1 Introduction

On a world-wide scale the economic importance of siderite deposits is fairly limited compared to oxidic iron ores and this mineral is hardly considered to be economic iron ore. Nevertheless, siderite is an important ore mineral and occurs in nearly all types of sedimentary iron ores and in many vein type mineralizations. In some European and Mediterranean countries siderite deposits are of national importance and are still in production.

Numerous siderite mineralizations of various sizes can be found in the tectonostratigraphic units of the Eastern Alps, many of them have been exploited in the past. Presently only the *Erzberg* siderite deposit, situated near the village

Eisenerz in the province of Styria, Austria, is operating. Currently the Austrian iron ore production of about 2 mln tpa is exclusively produced from this mine. The cut-off grade is 22% Fe and approximately 50% of the ore production has to be processed to a grade >30% Fe. The total volume of rock mined at the Erzberg is around 6 mln tpa.

Opinions concerning the genesis of the siderite mineralizations of the Greywacke Zone are inconsistent (Tollmann, 1977) and discussion about this topic is longstanding tradition. Different genetic models, including a synsedimentary origin or an Eoalpine vein type or metasomatic mineralization, have been proposed in the past. Early workers on this topic favoured syngenetic models but at the turn of the century, epigenetic models for the Erzberg type mineralization were proposed. More recent research has focused on the investigation of structural and geochemical features. In the 1970s syngenetic models were favoured mainly on the basis of detailed mineralogical studies of ankeritic rocks ("Rohwand") and because of the findings of minor banded ore structures that were interpreted as primary sedimentary ore bands (Beran,

1975, 1977, 1978, 1979; Beran & Thalmann, 1978). Following these arguments, Schulz *et al.* (1997) described ore textures of the Erzberg deposit and postulated a marine-synsedimentary origin for the mineralization. Recently an epigenetic genesis for siderite mineralization in the Greywacke Zone has been reintroduced on the basis of microthermometric, geochemical and isotope data (Frimmel, 1988; Prochaska, 1991, 1993; Spindler, 1992; Pohl & Belocky, 1994; Laube *et al.*, 1995). Nevertheless, the most important metallogenic features, the timing of the hydrothermal event, and the origin of the hydrothermal fluids are still enigmatic.

#### 3.2 Geologic setting

The *siderite mineralization* occurs in the Greywacke Zone, which is the Paleozoic basement of the Mesozoic platform carbonates of the Upper Austroalpine nappe. Fundamental overviews of the geology and tectonostratigraphy of the Greywacke zone were given by Schönlaub (1979, 1982) and Neubauer *et al.* (1993). The rock series of the Greywacke zone range from the Ordovician to the Carboniferous and comprise carbonates, metapelites and metamorphosed acid volcanics. The grade of metamorphism is generally lower greenschist facies and increases from east to west. Siderite mineralization is restricted to the tectonically highest segment of the Greywacke Zone, the Noric Nappe, and to the basis of the Northern Calcareous Alps (Fig. 10). The fact that these mineralizations do not occur in other, deeper tectonic units of the Greywacke Zone, supports a timing of

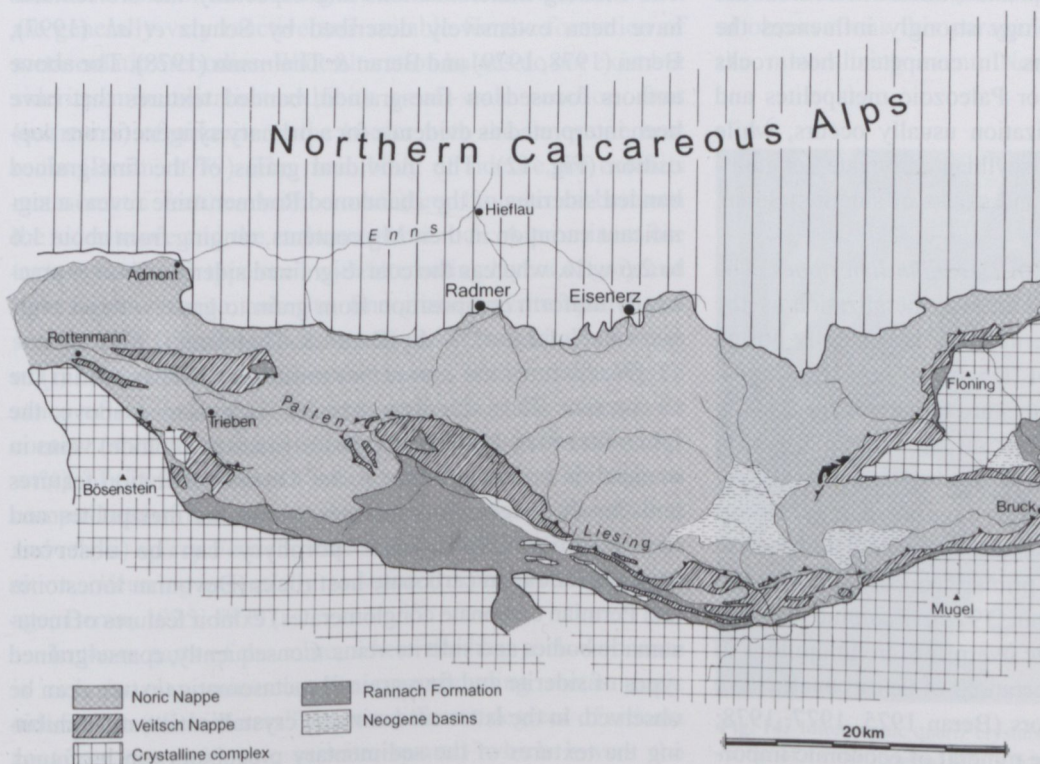


Fig. 10. Geological map showing the siderite deposits "Steirischer Erzberg" (village of Eisenerz) and Radmer in the Eastern Greywacke Zone (modified after Schönlaub, 1979). For outline map see Fig. 6.

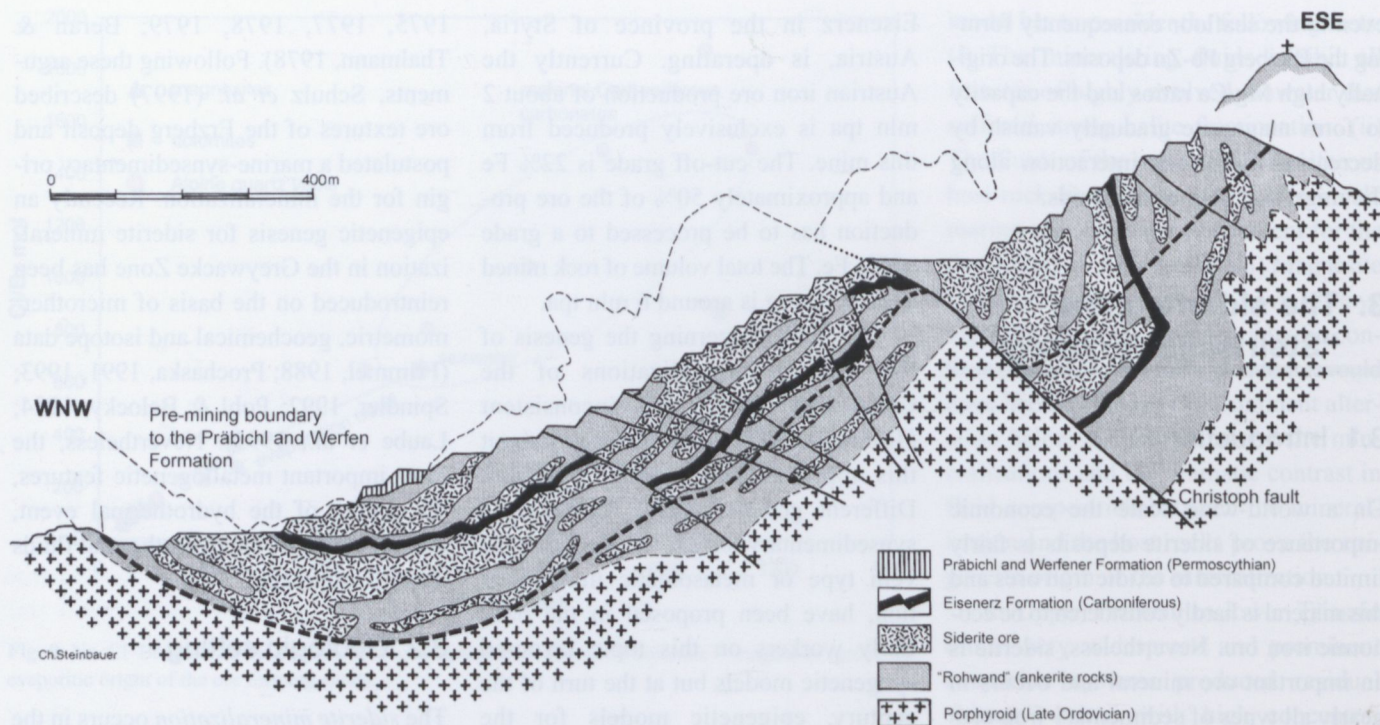


Fig. 11. Schematic cross-section through the Erzberg siderite deposit (modified after Holzer, 1980).

mineralization before the stacking of the Austroalpine nappes. Another significant feature is that this type of mineralization shows no indications of a continuation into the overlying Mesozoic carbonates of the Northern Calcareous Alps of the Upper Austroalpine Units.

The siderite occurrences in the Greywacke Zone are neither stratabound nor stratiform and exhibit different modes of occurrence. Host-rock lithology strongly influences the structure of the mineralizations. In competent host rocks (Ordovician quartz porphyries or Paleozoic metapelites and sandstones), vein-type mineralization usually occurs, while Devonian carbonates and Permoscythian carbonate conglomerates host metasomatic bodies and stocks of siderite (Beran, 1979; Prochaska, 1997).

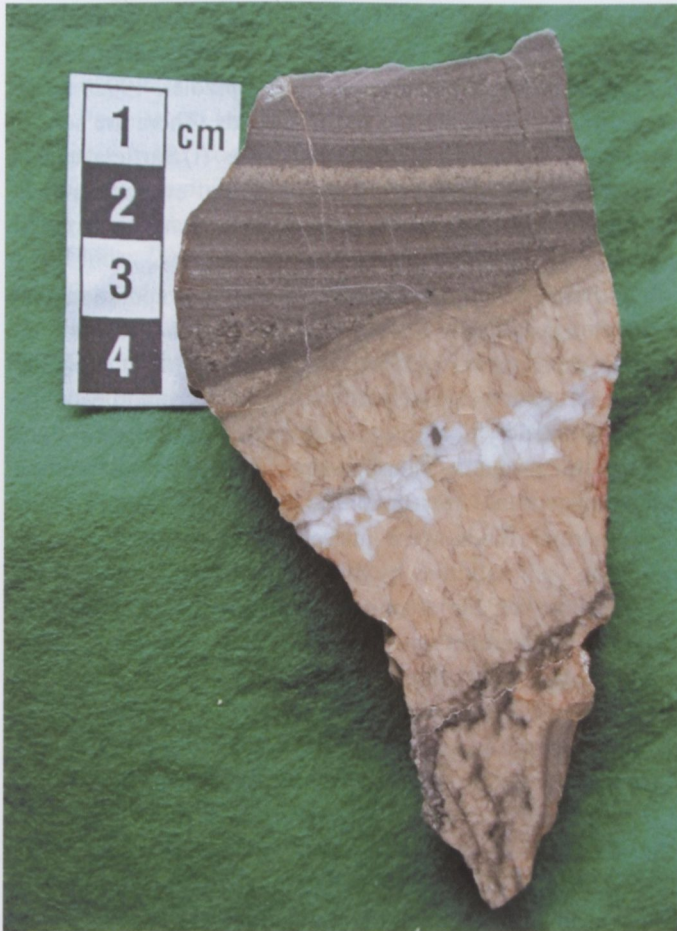
*Metasomatic siderite bodies in Devonian limestones.* The best example of this type of siderite mineralization is the Erzberg siderite mine. This siderite body is generally hosted by fine-grained limestones of Devonian age (Fig. 11). Metasomatic-epigenetic structures are dominant and usually coarse-grained siderite ore exhibits discordant contacts with the unmineralized limestones. In the nearby Radmer mine (for location see Fig. 10), the majority of the observed ore textures is the same, but very rarely banded ores occur. This leads to syngenetic interpretations of the primary genesis of these mineralizations (Beran & Thalmann, 1978). Eoalpine tectonic structures and weak metamorphic overprints are ubiquitous in the Erzberg deposit. Different generations of Fe carbonates have been described by various authors (Beran 1975, 1977, 1978; Schulz *et al.* 1997). The only ore mineral of economic impor-

tance is siderite but frequently ankeritic rocks with variable Fe contents can be found. Subordinate amounts of quartz, hematite, pyrite, chalcopyrite, fahlore, cinnabar and barite also occur.

### 3.3 Mineralogical features of the mineralizations

The Erzberg mineralizations and especially the ore textures have been extensively described by Schulz *et al.* (1997), Beran (1978, 1979) and Beran & Thalmann (1978). The above authors focused on fine-grained, banded textures that have been interpreted as evidence for a primary syngenetic ore deposition (Fig. 12). The individual grains of the fine-grained banded siderites of the abandoned Radmer mine reveal a significant variation in their Mg contents, ranging from about 1.6 to 2.6 wt%, whereas the coarse-grained siderites show a practically uniform composition from grain to grain with an average value of 2.2 wt% Mg (Beran & Thalmann, 1978).

Ore textures are varied but uniformly similar within the Greywacke Zone siderite province. As indicated above, the mineralizations usually are siderite-(quartz-sulphide) veins in metapelitic or volcanic host rocks. Distinct alteration features and clearly epigenetic structures within the metapelites and the metamorphosed quartz porphyry can be observed. Mineralizations in carbonate host rocks (Devonian limestones and Permian carbonate conglomerates) exhibit features of metasomatic bodies and siderite veins. Consequently, coarse-grained types of siderite and fine-grained metasomatic textures can be observed. In the latter case mimetic crystallization still exhibiting the textures of the sedimentary precursors can be found.



**Fig. 12.** Siderite vein with white ankerite crosscutting banded siderite ore from the abandoned Radmer mine.

The host rocks of the Erzberg are Devonian carbonates, which are generally very reactive and suitable for the formation of metasomatic orebodies. Wide alteration haloes do not exist but siderite mineralization exhibits small-scale reaction rims (some cm) of ankerite at the border with the limestone host rocks (Beran, 1979). The main body of siderite ore exhibits metasomatic features with crosscutting boundaries between the siderite ore and the carbonate host rock. A prominent ore texture is a “tiger type ore” with alternating layers of grey and light brown siderite, ankerite, fine-grained pyrite, quartz and sericite (Fig. 13). The above mentioned “Rohwand” consists of (i) fine-grained Fe-poor ankerite rocks with variable Mg/Fe ratios of the individual ankerite grains (*e.g.* the average Fe content amounts to 8.0 wt% with a standard deviation of 3.1 wt%), of (ii) fine-grained Fe-rich ankerite rocks with uniform composition of the individual grains (*e.g.* 16.5 (0.5) wt% Fe) and of (iii) sparry Fe-rich, white ankerites of uniform composition, occurring essentially as veins (of post-Permoscythian age; Beran, 1975, 1979).

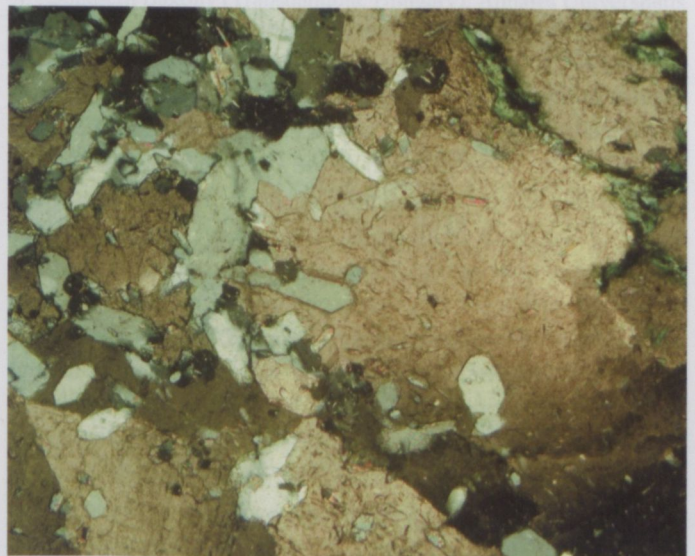
In those parts of the mine, where the host-rock carbonate is rich in clay minerals, the corresponding metasomatic siderite ore (“Schiefererz”) shows different degrees of silicate contamination (chlorite, sericite, quartz) which lowers the



**Fig. 13.** “Tiger-type ore”, showing banding of siderite, white ankerite and grey layers rich in fine-grained pyrite, organic matter, quartz and sericite.

grade of the ore. Veinlets and nodules of quartz in this type of ore are ubiquitous. Idiomorphic crystals of quartz are frequent in the siderite ore. In fine-grained massive ores (“silicate ore”), small hypidiomorphic quartz crystals with poikilitic carbonate inclusions frequently occur (Fig. 14).

Late stage mineralization in all lithologies comprises intense chloritization, the formation of quartz crystals, hematite and sulfides (chalcopyrite, cinnabarite). From textural observations this paragenesis occurs in the late stage of the mineralizing event. Nevertheless, O isotope equilibria



**Fig. 14.** Idiomorphic quartz crystals in siderites indicating the hydrothermal nature of the ore (crossed polars, width of field 3.5 mm).

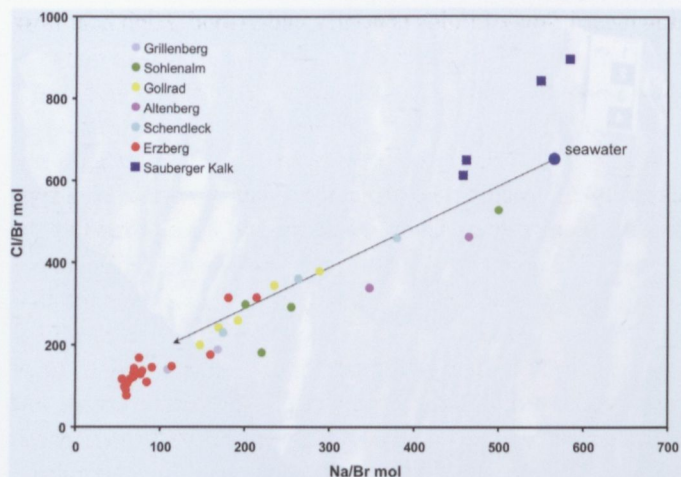


Fig. 15. Na-Cl-Br diagram showing the position of the siderites of the Eastern Greywacke Zone on the seawater evaporation trajectory, thus indicating that the ore forming fluids originally had been evaporative "bittern" brines.

(quartz-chlorite-hematite) yielding temperatures of 340 °C, are indicating that late-stage mineralization is part of the general epigenetic, siderite-forming hydrothermal activity (Prochaska, 1993; Prochaska *et al.*, 1996).

*Chemical characteristics of inclusion fluids.* In the Cl/Br and Na/Br molar ratio diagram (Fig. 15) the inclusion chemistry of none of the investigated samples from the mineralization matches the seawater composition. The molar ratios are characterized by low Na/Br (55–499) and low Cl/Br (78–530) numbers. Fig. 15 shows that all samples from the different localities are situated on the "evaporation trend", thus indicating an origin of the fluids from subaerial evapo-concentration of seawater. In addition, these fluids were modified by water-rock reactions after these surface waters penetrated into deeper crustal levels.

### 3.4 Discussion and conclusion

The analysis of the mineralizing fluids by the crush-leach method allows the investigation of the fluid evolution and the determination of the primary nature of the hydrothermal solutions. Thus it seems to be a key to elucidate genetic problems of the siderite mineralization in the Greywacke Zone. A first and obvious result is the identity of the chemical composition trends of the fluids of all investigated siderite mineralizations regardless of their host rock lithologies. This strongly suggests a common origin for all of these siderite deposits.

Total dissolved solutes analyses can help to distinguish between syngenetic, marine-sedimentary mineralizations and epigenetic-metasomatic origins. In the first case, no difference in the total dissolved solutes chemistry between the siderites and the marine host-rock carbonates next to the siderite ore is expected. In the case of an epigenetic, hydrothermal process, the Fe introducing fluid event should produce significantly different element ratios between the siderite ore and the unaffected marine host-rock limestone. Very important questions within

this context are the origin of the fluids, and the source of fluid salinity and the metals (Fe, Mg, Ba, etc.). Microthermometric data available so far (Belocky, 1992; Spindler, 1992) report high salinity values for the Erzberg fluids. There are several possibilities to generate highly saline brines: (i) Surficial evapo-concentration of seawater, (ii) dissolution of evaporite minerals and (iii) metamorphic fluids and concentrating retrograde reactions generated by the Cretaceous event.

Until now, brines generated by subaerial evaporation have not been considered to be the fluid source for the Austroalpine siderite deposits. Pohl (1993) and Belocky (1992) explained the observed high salinities as coming from evaporites which were dissolved by Eoalpine metamorphic fluids. For the North African metasomatic siderite deposits Ouenza and Jerissa, both situated in Cretaceous host rocks, the highly saline hydrothermal fluids were interpreted as diagenetic waters acquiring their salinities by dissolution of halite (Pohl *et al.*, 1986). However, the chemistry of the inclusion fluids is in very good agreement with residual "bittern" brines and definitely contradicts a halite dissolution trend.

*Source of Fe in the hydrothermal fluids.* Mineralogical alteration of the quartz porphyries hosting the siderites was described by different authors (Heinisch, 1980; Schönlaub, 1982; Schulz *et al.*, 1997). The existence of prominent chemical alteration haloes some tens of metres wide at the Greywacke Zone siderite mineralizations hosted by the Ordovician quartz porphyry was described by Prochaska (1991, 1997). A continuous decrease of Fe in the quartz porphyry approaching the deposits suggests the process of leaching and lateral secretion to be an efficient Fe source for the hydrothermal fluids percolating through the crust.

*Timing of the mineralizing event.* Timing of the mineralization is one of the most important pieces of information needed to establish a genetic model within the geodynamic frame of the Alpine or pre-Alpine orogenic cycles. The fact that the mineralized structures and the mineralizations cut Permomesozoic strata, exclude a syngenetic Devonian formation for these deposits. However, the Eoalpine metamorphic event is believed to be responsible by some authors for modification and remobilization of early syngenetic mineralizations finally producing epigenetic vein-type deposits. Studies of the chemistry of the ore forming inclusion fluids did not show any signs of two fundamentally different sets of fluid compositions (*e.g.* marine-sedimentary and Alpine-hydrothermal).

### 3.5 Genetic model

The genetic model is based on the following observations: (i) The nature of the mineralizations is hydrothermal-metasomatic. No indications of a synsedimentary concentration of Fe can be observed. (ii) According to their identical fluid characteristics the Greywacke Zone siderite mineralizations were formed during the same minerogenetic event. (iii) The mineralizing



event is post-Variscan and pre-Eoalpine. (iv) The mineralizing fluids were originally evaporitic brines, then modified by water-rock interactions while percolating through the crust.

In Permian (to Lower Triassic) times evaporitic basins are ubiquitous in the Austroalpine realm. Deposition of thick series of evaporites is widespread in the Permian strata of the Upper Austroalpine unit. High degrees of evaporation (evaporation index 20 to 90) produced residual "bitterns" with high salinities and high concentrations of Br, Mg, K, SO<sub>4</sub> in the fluids. The peculiar fluid composition of the siderites is in itself a strong argument for the Permian timing of the mineralization or at least of the formation of the ore forming fluids. The exact timing of the mineralizing event is still an open question.

Permian rifting provided channelways for these brines to infiltrate the deeper stratigraphic units although the

downward flow of fluids is poorly understood. High heat flow in the rift environment induced hydrothermal convection systems connected with the hydrosphere and the residual evaporitic brines. Diagenetic reactions and host rock alterations changed these brines into acid and reducing fluids with the capacity of leaching Fe from the country rocks. Vein-type siderite-hematite-sulfide mineralizations were formed in the metapelitic and metavolcanic host rocks. Within the Devonian platform carbonates metasomatic siderite bodies were formed. Metasomatism and mimetic crystallization of the marine host-rock carbonates often preserved primary sedimentary textures very well. Burial of the Permian evaporitic brines and mobilization during later closure of the basins and diagenetic processes, may be due to the sedimentary unroofing of the Triassic platform carbonates.

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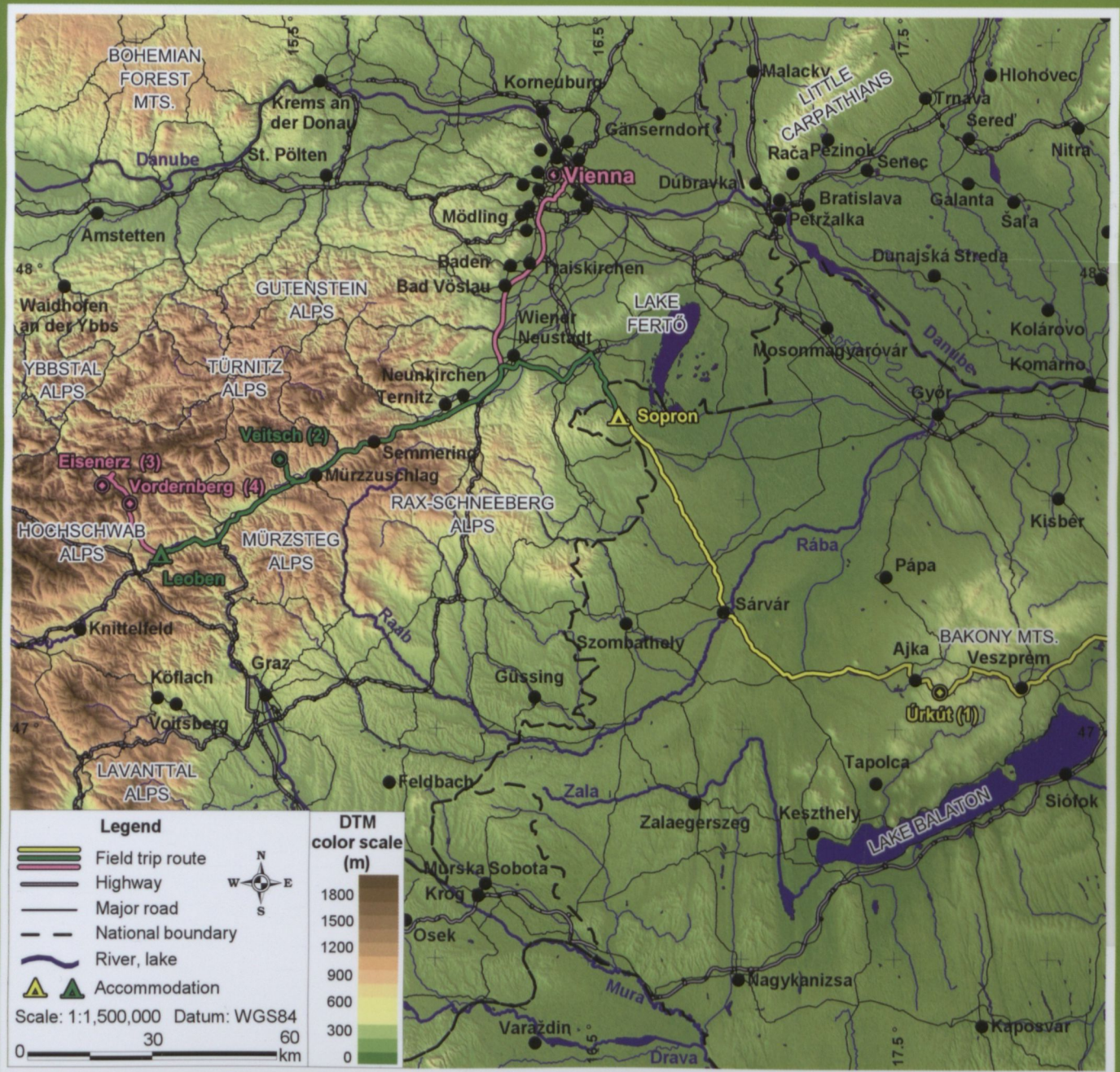
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