Comparative Metallogeny of Siderite Deposits

By W. POHL*)

Zusammenfassung

Es wird eine Aufstellung der genetischen Lagerstättentypen gegeben, in denen das Mineral Siderit als Hauptbestandteil auftritt. Im Mittelpunkt der Diskussionen stehen die sogenannten metasomatischen Lagerstätten vom Typus Erzberg und Bilbao. Ihr tektonisch-paläogeographisches Milieu ist das der Vorländer oder Plattformen. Chemische Indikatorelemente für ihre Herkunft gibt es kaum; der REE-Gehalt ist im Falle des Erzberges niedrig. Es fehlen weltweite chemische Daten für die Erkenntnisse der Genese.

Summary

A comparison of metallogenetic features of siderite deposits must remain limited to general features, as a broad base of modern geochemical and complementary data is not yet available.

Nearly all larger siderite deposits have traditionally been thought to be of hydrothermal origin, including veins, volcano-sedimentary and "metasomatic" types. The latter are still an important source of iron ore in many countries, but their metallogeny remains quite enigmatic.

In metasomatic siderite deposits the iron appears to be foreign to the original sedimentary environment of the enclosing carbonates, and is typically thought to have been introduced into its present location a long time after deposition of the country rocks. Precambrian to Tertiary deposits of this type are known, and they occur in unmetamorphosed to amphibolite facies metamorphic rocks.

Their alpidic plate tectonic setting is not related to active subduction zones, but appears restricted to continental crust undergoing tectonic strain, and is

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*) Institut für Geologie und Paläontologie, Technische Universität, Postfach 3329, D-33 Braunschweig, Germany.

variously accompanied by deep-seated basic intrusions or regional metamorphism; typically, however, the source of suspected hydrothermal solutions is unknown.

Non-hydrothermal genetic models for metasomatic siderite deposits invoke variously processes related to early or late diagenesis, karst-formation, or metamorphic mobilization affecting primary iron concentrations. Only broad comparative investigations of these ores and their country rocks with modern geoscientific methods will contribute towards a better understanding of their origin.

Introduction

At a worldwide scale actual mining of siderite deposits for iron ore is rather limited. In the Mediterranean-Alpine realm, however, siderite mines are more frequent as a locally or even nationally important source of iron. This economic interest, although of course secondary to oxidic iron ores, encourages continuing metallogenetic research.

The present review is conceived to summarize existing data on major siderite deposits and occurrences in the area covered by IGCP 169, to discuss their plate tectonic setting, and to encourage further geochemical and petrological work, supported by limited new data.

The Rôle of Siderite in Genetic Types of Iron ore Deposits

Iron ores occur in nearly all known geological environments, ranging from terrestrial bogs, rivers and lakes through shallow to deep seas. They are associated with many different types of magmas in plutonic and volcanic settings, forming within the magmas as an immiscible fluid or in their surrounding as a product of degassing and/or thermally introduced fluid convection. Many iron ore deposits, however, are not attributable to a clearly defined environment, and in such cases genetic explanations often range from telethermal "magmatic" through metamorphogenic to diagenetic fluids or even solutions derived from weathering rocks. Many siderite deposits belong to this enigmatic group, and command therefore a special scientific interest.

Because of the relatively narrow physico-chemical stability field of siderite in natural environments (GARRELS & CHRIST, 1965; SEGUIN, 1978; FROST, 1979) economic iron carbonate deposits are less frequent than oxidic ores (see Table 1). Siderite is practically absent from magmatic and contact-metasomatic iron ores, as its low dissociation temperature (~ 450° C) precludes formation from melts except under very high pressures (WYLLIE, 1966).

In nearly all types of sedimentary iron ore deposits siderite is ubiquitous, either as a primary or as a diagenetic constituent. In Precambrian banded iron formations (BIF), in continental-sedimentary settings, and even in marine sedimentary deposits ("Minette-type" in the widest sense) siderite is, however, hardly ever considered to be economic iron ore.

Nevertheless it should be noted here that siderite is a geologically important constituant in Paleozoic (Algeria, CSSR, France, Lybia, Maroc, Spain) and in Mesozoic (Lorraine/France, Germany) marine sedimentary iron ore deposits. Although karst-formation is often invoked for the origin of siderite deposits in carbonates there is only one larger undisputed example: The NE-Bavarian Cretaceous district (Pfeuffer, 1983; Gudden, 1984). There, fluvial transport of iron into non-marine karst-lakes and its deposition under oxidic and locally slightly reducing conditions has been demonstrated convincingly (Gudden, 1984; Ruppert, 1984).

Most siderite deposits of present or former economic significance have traditionally been called "hydrothermal". Those in direct relationship and proximal to submarine volcanism (the volcano-sedimentary "Lahn-Dill type") can be compared with recent Fe-carbonate precipitation near degassing volcanoes (for example Santorini/Greece: Puchelt et al., 1973). Rather distal situations (Vareš/Yugoslavia: Janković, 1967) of submarine exhalations related to volcanism are not infrequent. The same applies to siderite veins ("Siegerland-type"), which are of very local economic significance only. The epigenetic character of these veins, the often pronounced structural control, and geochemical data (Siegerland: Stahl, 1971) clearly indicate the hydrothermal origin. The source of the warm solutions, however, obviously need not be a magmatic body; metamorphic or deeply circulating formation waters could also be invoked.

The most disputed, economically important, and still enigmatic siderite deposits are those of the "hydrothermal"-metasomatic type. They comprise typically irregularly shaped ore-bodies within marine platform carbonates with conspicuous replacement textures, but also associated veins, stratiform lenses and sideritized breccias. Of the important examples cited in Table 1, however, probably not one single deposit has remained undoubted as being of hydrothermal origin.

Within this group, two sub-types are often differentiated (Bottke, 1981): The Erzberg-type (siderite only being mined), and the Bilbao-type (mainly oxidic iron ore mined, although most certainly derived by weathering of Fe-carbonates).

Metasomatic siderite deposits occur in quite different geological settings: non-metamorphic folded platform carbonates (Ouenza/Algeria), non-metamorphic faulted marine carbonates (Hüggel/NW-Germany), epimetamorphic carbonates (Erzberg/Austria) and amphibolite-fazies metamorphic carbonates (Batère/France). The sideritized carbonates may be dolomite or limestone, and include reef, lagoon and basinal fazies. Typically, the siderite bodies do not reflect any lateral or vertical facies zoning, which is so characteristic for nearly all sedimentary iron ores (James, 1954; Borchert, 1960). Many are surrounded by irregular shells of ankeritic carbonates, but direct siderite-limestone or -dolomite contacts are frequented.

Hydrothermal-Metasomatic Siderite Deposits?

Genetic models

Traditionally, warm ascending iron-rich solutions were thought to have replaced limestone and/or dolomite with siderite; that this may have happened before,

Table 1. Rôle of siderite in genetic types of iron ore deposits
(data from Walther & Zitzmann, 1977)

Genetic type of iron ore deposit	Occurrence siderite versus oxidic ores	Economic rôle of sid.	Important examples of siderite deposits
Magmatic	absent	–	–
Contact Metasomatic	very rare	–	–
Hydrothermal veins	equivalent	small, only local	○ Rudňani/CSSR, ○ Siegerland/FRG, △ Cercal do Alentejo/Port., ○ Madaras/Rom.
Metasomatic*)	predominant	locally important	● Ouenza/Alg., ● Eisenerz/Austria, ● Kremikovci/Bulg., ○ Batère/France, ○ Hüggel/FRG, ● Rudabánya/Hung., ● Shamsabad/Iran, ○ Delnita/Rom., ● Bilbao/Spain, □ Sierra Menera/Spain, ● Djerissa/Tun., ● Deveci/Turkey, □ Bakal/USSR, ● Ljubija/Jug.
Volcano-sedimentary	less frequent	only local	● Nisna Slaná/CSSR, ○ Ghelar/Rom., ○ Teliuc/Rom., ● Tajmište/Yug., ● Vareš/Jug.
Marine-sedimentary	less frequent	rather small	□ Gara Djebilet/Alg., ● Barrandian/CSSR, ● Normandie/France, □ Lorraine/France, □ Gifhorn/FRG, □ Salzgitter/FRG, □ Shatti Valley/Libya, ○ Ait Amar/Maroc., ○ Leon/Spain
Continental-sedimentary	rarely significant	unusual	● Ruhr/FRG, □ Lisakovsk/USSR
Karst	rarely significant	unusual	● NE-Bavaria/FRG
BIF	often present but secondary	–	–

Size of deposits: △ < 10 Mt ○ 10–100 Mt ● 100–1000 Mt □ > 1000 Mt of ore in virgin deposit

*) The existence of this type of genesis is now often disputed

during or after lithification of the country rocks has already been stated by REDLICH (1904). The source of such solutions may conceivably be quite variable:

- fluids derived from cooling deep intrusions of acidic, intermediate or basic magmas;
- degassing of subvolcanic magmatic bodies;
- intrusive magmatic bodies creating hydrothermal convection cells;
- ascending metamorphogenic fluids;
- ascending deeply circulating formation waters.

Rarely can the mineralizing solutions unequivocally be attributed to one of these classes. The only deposits of the metasomatic type with a plausible connection to a magmatic body appear to be the ones in Zechstein limestones about 5 kms above the top of the basic Cretaceous Bramsche intrusion (STADLER, 1971; WALTHER, 1983). Ordinarily, however, such links are quite cryptic and disputable.

Apart from the prevailing model of a hydrothermal-metasomatic origin (DAVYDENKO, 1972; WALTHER & ZITZMANN, 1977; BOTTKE, 1981; PETRASCHECK, 1982), various other processes have been invoked for the origin of different deposits of this type:

- volcano-sedimentary
  (Erzberg: lately again BERAN & THALMANN, 1978)
- marine-sedimentary, remobilization by subsurface karst formation
  (Sierra Menera/Spain: FERNANDEZ-NIETO et al., 1981)
- karst trapping continent-derived Fe
  (Djerissa/Tunisia: MAHJOUBI & SAMAMA, 1980)
- descending formation waters
  (Glamorgan/U.K.: SLATER & HIGHLEY, 1976)
- laterally migrating formation waters.

Later diagenetic or metamorphic remobilization are often an important aspect of some of these models. These recent trends of genetic thinking about metasomatic siderite deposits have been discussed succinctly and put into a regional metallogenetic perspective for Central and SE-Europe by W. E. PETRASCHECK (1982).

Geochemical investigations

Associated trace elements including REE, fluid inclusion chemistry (and thermometry) and stable isotope ratios are increasingly used as genetic indicators for rocks and mineral deposits. The regional and methodic coverage of metasomatic siderite deposits, however, is too limited to allow general conclusions.

Published analyses of the exploited ore (WALTHER & ZITZMANN, 1977) provide a very limited spectrum of elements only, which is little promising for genetic interpretation. On this base, a diagram linking the size of deposits or districts with %P is presented in Fig. 1. From this one might tentatively conclude, that deposits traditionally classed as hydrothermal have P-contents typically below 0.1%, while marine sedimentary and the NE-Bavarian karst ores range from 0.3–1.4%P. Volcano-sedimentary deposits vary from very low to very high P-contents.

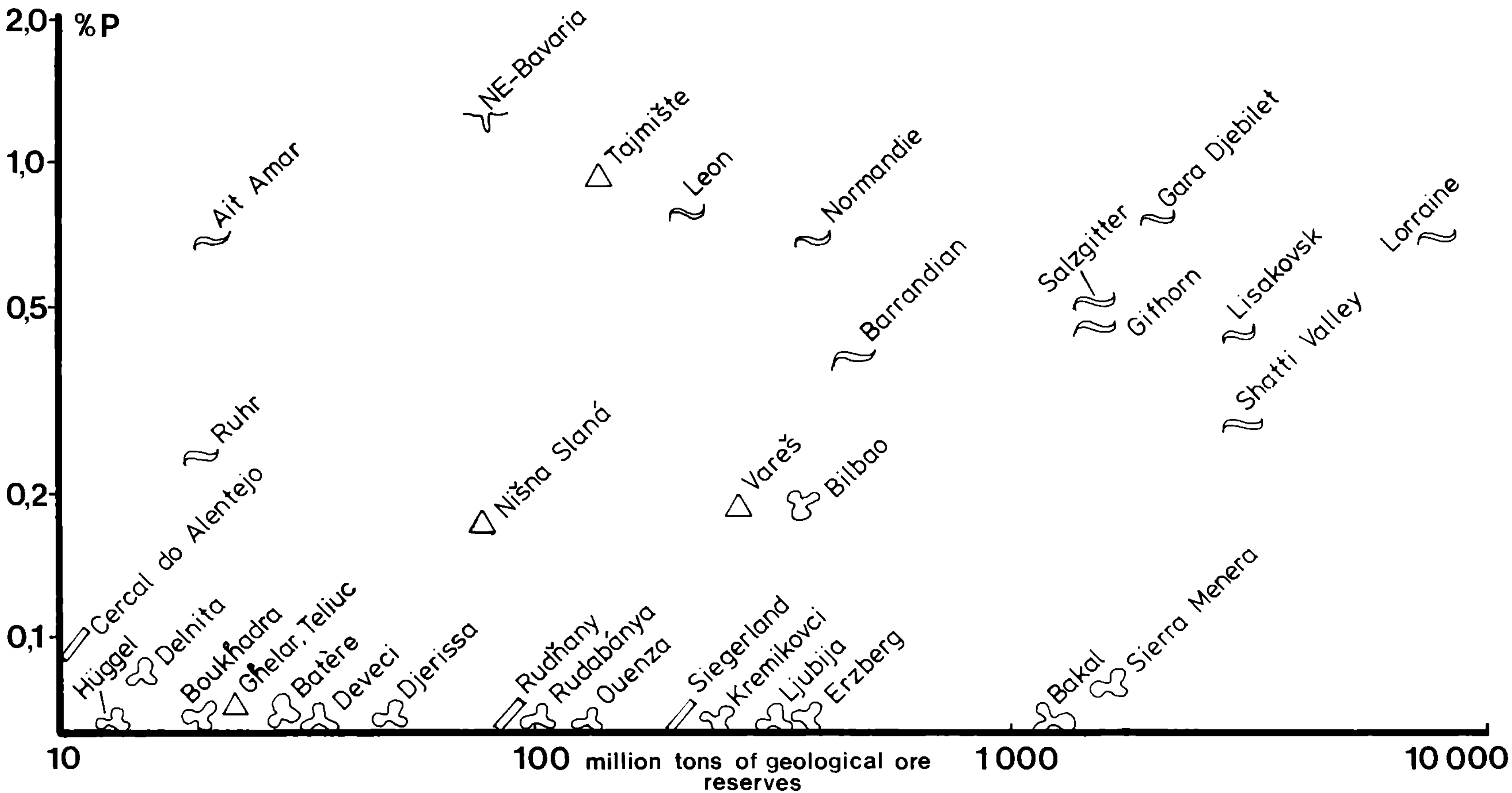

Fig. 1. Average P-contents versus size of major siderite deposits (data from WALTHER & ZITZMANN, 1977).

The siderite ores are usually monomineralic, and only traces of sulfides (pyrite, Cu, Pb, Zn, As, Sb, Hg) and baryte ± quartz are found in small, secondary veinlets. Mg, Mn, and a number of trace elements (Co, Sc, Ni etc.) in siderite have been determined by DOLEZEL & SCHROLL (1979) to characterize siderites of various sedimentary and hydrothermal environments. The results are not clearly conclusive, as stated by the authors themselves (ibid.).

Other methods mentioned above have only occasionally been applied to siderites, and accordingly the data base concerning REE-spectra, fluid inclusions and stable isotopes is too sketchy to allow meaningful comparison. Tentatively the REE-contents of two siderite samples from Erzberg/Austria have been determined (see Fig. 2). They are characterized by a low total REE-content, lower light REE (probably due to the restricted substitution of LREE for Fe), negative Ce and Eu-anomalies (the first either because of a marine environment, or the passage of the hydrothermal solutions through an oxidic rock mass; the second not surprisingly indicating low Eh at deposition—MÖLLER et al., 1976; MORTEANI et al., 1982). By itself, and compared with the data from Santorini (PUCHELT et al., 1973), these results remain inconclusive, especially without comparative analyses of the country rocks. They do not exclude a hydrothermal origin, however.

The Alpidic Plate Tectonic Setting of "Hydrothermal"-Metasomatic Siderite Deposits

Obviously it is of great interest to examine the plate tectonic setting of metasomatic siderite deposits. As all models of Paleozoic and Precambrian plate tectonics in the project area are still highly speculative (for ex. East Alpine Paleozoic: POHL, 1984), we exclude deposits of pre-Mesozoic age from the following discussion.

Unfortunately the age attribution of some of the remaining eleven deposits (see Fig. 3) is based on quite circumstantial arguments (for ex. Erzberg/Austria: the "geologically" indicated Middle-Upper Cretaceous age may only reflect metamorphic mobilization—see W. E. PETRASCHECK, 1982, for discussion). The age of mineralization is so difficult to establish, because the sideritized carbonatas as a rule are older or even much older than the event (orogeny, faulting, intrusion etc.) which is interpreted to be responsible for the rise of hydrothermal solutions. As at Ouenza/Algeria for example (THIBIEROZ & MADRE, 1976) it is, however, characteristic for most of these deposits, that the iron is foreign to the original sedimentary environment of the country rocks. In view of this situation, the traditional geologically indicated age attribution of the mineralization in the various deposits has been adopted for the purpose of this paper (as depicted in Fig. 3).

In a very simplifying approach, three tectonic environments are differentiated to examine the alpidic plate tectonic setting of "hydrothermal"-metasomatic siderite deposits (see Table 2):

- a folded foreland of Mesozoic platform carbonates,
- a zone of continental collision and/or crustal stacking, and a

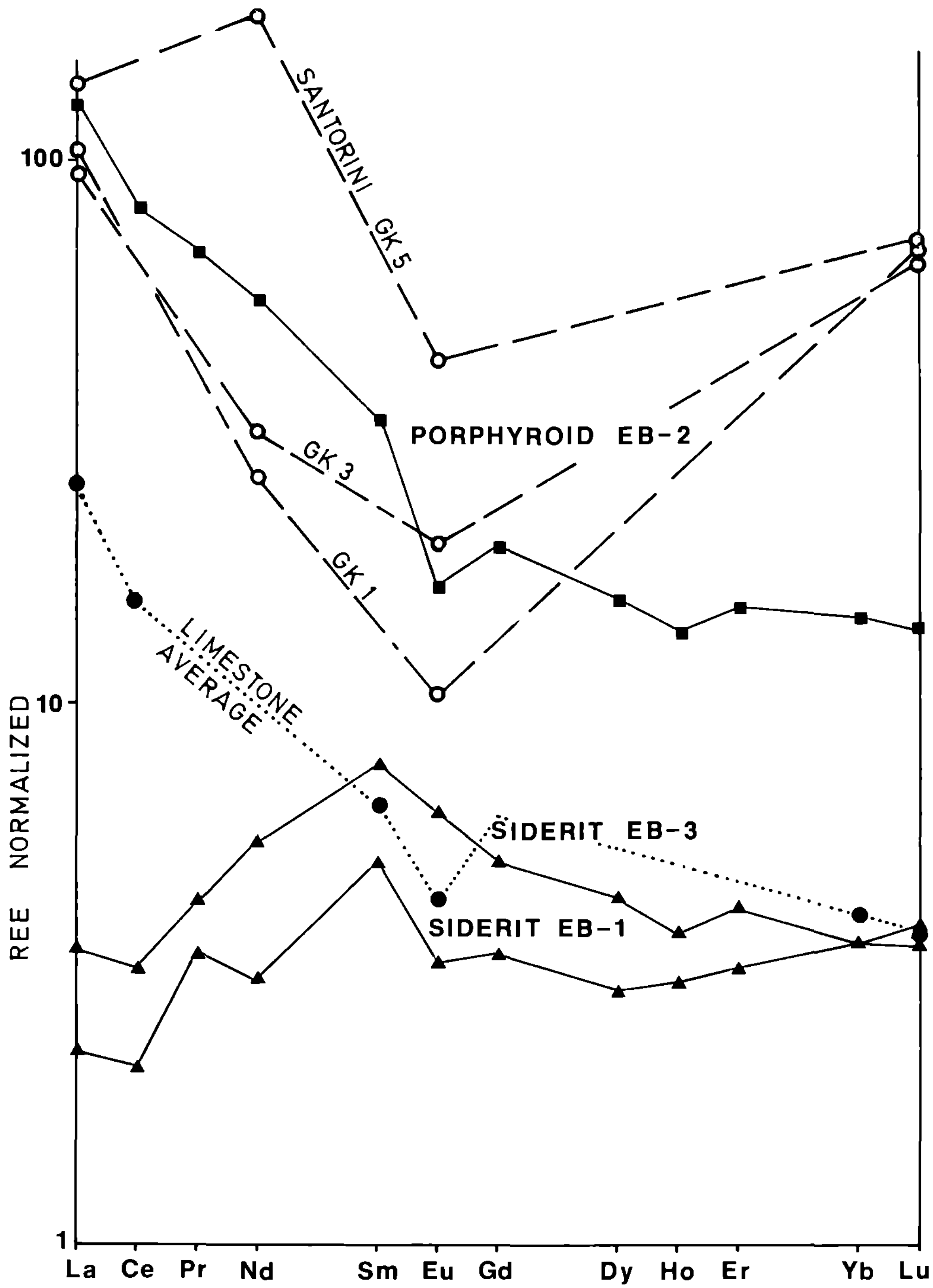

Fig. 2. Chondrite-normalised REE patterns in siderite and quartz-porphyry (Erzberg/Austria, analysed by Geomet Services, England 1983) compared with recent Fe-sediment from Santorini (from PUCHELT et al., 1973) and the limestone average (RONOV et al., 1974).

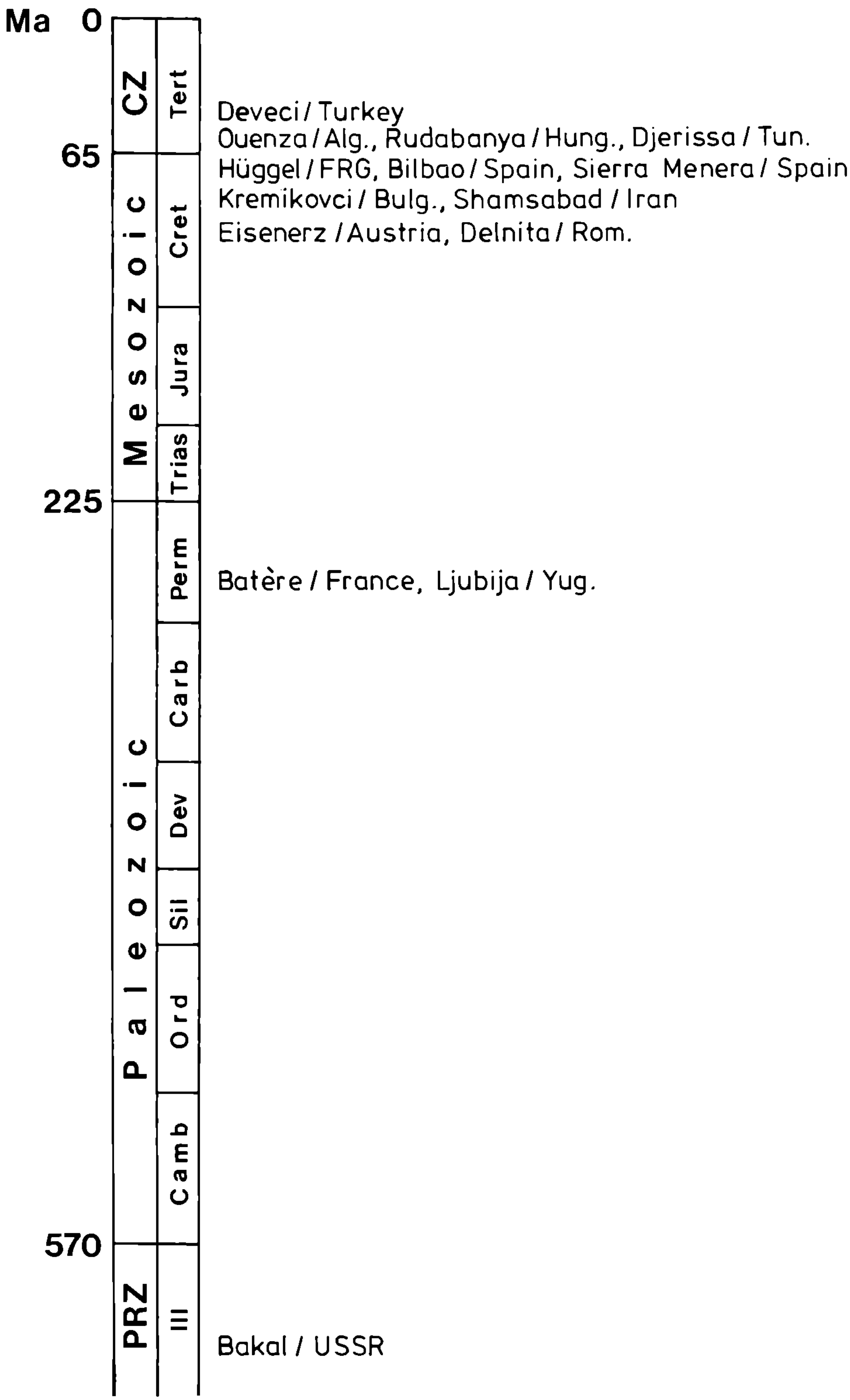

Fig. 3. Traditional age attribution of the formation of "hydrothermal"-metasomatic siderite deposits.

Table 2. Alpidic plate tectonic setting of "hydrothermal metasomatic siderite deposits (accepting the traditional age attribution of their formation)

Folded foreland (Carbonate platform)	Zone of continental collision or crustal stacking	Blockfaulted foreland (Carbonate platform)
Ouenza/Alg. (+ Ba, Cu, Zn, Pb, As)	Rudabanya/Hung. (+ Ba, Cu)	Hüggel/FRG (+ Cu, Ba, Pb, Zn)
Djerissa/Tun. (+ Cu, Pb, Zn, As)	Deveci/Turkey (+ Pb, As)	Sierra Menera/Spain (+ Ba)
Bilbao/Spain (+ Cu)	Kremikovci/Bulg. (+ Ba, Pb, Zn, Cu, Ag)	
	Eisenerz/Austria (+ Cu, Hg, Sb)	
	Shamsabad/Iran (+ Ba, Cu, Pb, Zn)	
	Delnita/Rom.	

– blockfaulted foreland, whose general nature during the supposed time of mineralization is a shallow marine (carbonate) platform, the sideritized rocks, however, being of Paleozoic age.

Far reaching conclusions on this base are certainly not justified. Keeping the above outlined limitations in mind one may state that the characteristic environment of metasomatic siderite deposits are not active subduction zones, but rather ± ordinary continental crust under tectonic stress possibly accompanied by magmatic or metamorphic heat domes.

Conclusions

Siderite occurs in a wide range of geological environments, but former or present economic ore bodies are restricted to volcano-sedimentary, hydrothermal vein and "hydrothermal"-metasomatic types of deposits, with very few exceptions only. In many respects similar to the latter, the clearly karst-related NE-Bavarian siderite-goethite district commands a special interest for comparative purposes.

The precise origin of the "hydrothermal"-metasomatic siderites in carbonates remains enigmatic. Deposits of this type have been formed from the Precambrian to Tertiary times, and they occur in non-metamorphosed to amphibolite fazies metamorphic rocks. The time of sideritization is typically thought to be much later than the original deposition of the carbonates, and the iron is obviously foreign to the original sedimentary environment. If of hydrothermal origin, many of these deposits must be called "telethermal"—a good example being the orebodies in Zechstein carbonates some 5 kms above the top of the Cretaceous Bramsche massiv/NW-Germany.

Of course, the sources of the iron are not necessarily fluids directly derived from cooling magmas, but may well be diagenetic, or deeply circulating formation waters, or metamorphic fluids. In addition, many different models based on non-hydrothermal sources have been proposed for various deposits of this type, but these are at present at least as vague in explaining all features observed as are the traditional hydrothermal-metasomatic ones.

Geochemical data on these ores are still insufficient to allow unequivocal genetic conclusions, but more modern, comparative research on their trace element contents, REE-spectra, fluid inclusions, and stable isotope ratios including country rocks is expected to enhance their understanding considerably. Additional genetic criteria may be derived from Mössbauer-effect studies (AMIGO & FORTUNE, 1981).

The plate tectonic setting of those of the metasomatic siderite deposits thought to have been formed during the Alpidic orogenic cycle is apparently not related to active subduction zones. They occur in the zone of continental collision and crustal stacking as well as in the folded and unfolded foreland. Their environment may be classified as ± ordinary continental crust, although under active stress, which is probably accompanied by magmatic or metamorphic heat domes producing large fluid convection cells.

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