Coordination of diagnostic features in ore occurrences of base metals in dolomites and limestones (Final report of IGCP-Project 6)

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Zusammenfassung

Die triassischen Blei-Zinkerz-Lagerstätten im mediterranen Raum können in zwei Gruppen eingeteilt werden: in endogene mit der höheren Bildungsenergie und in exogene mit der niedrigeren Bildungsenergie. Die zweite Gruppe überwiegt im betrachteten Bereich; ihre Lagerstätten sind an die Randzonen von transgredierenden Flachmeeren gegen Hochgebiete gebunden (Fig. 1) und zumeist in Kalk-Dolomitserien auftretend. Form und Gehalt der Erzkörper variieren sehr. Die Herkunft der Metalle ist meist diskutabel; submarine Tiefenbrüche, Durchpausen älterer Lagerstätten des Untergrundes oder Einschwemmung von Verwitterungsprodukten der Randgebiete kommen in Frage. – Die Isotopenverhältnisse werden ausführlich diskutiert. Die Blei-Isotopen der alpinen Lagerstätten weisen auf älteres Gesteinsblei, doch fehlt noch eine regionale vergleichende geochemische Bearbeitung der Lagerstätten des gesamten Mediterranraumes. Die Mannigfaltigkeit der Erscheinungen läßt trotz – oder wegen – der verschiedenartigen beschriebenen Fälle noch keine eindeutigen Merkmale für eine genetische Diagnose ableiten, aus der generelle Leitlinien für die Prospektion gefolgert werden können.

1. Introduction

The geographical area of research work stimulated during the period of the project has been limited to ore occurrences of the Mediterranean orogen and the bordering platforms of the European and African continents including Asia Minor. The

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observations are restricted mainly to ore occurrences of base metals hosted in Mesozoic, especially Triassic dolomites and limestones. However, extensive investigations by AMSTUTZ and his team (Heidelberg) about Pb-Zn mineralizations in carbonate rocks in South America, Peru and Argentina have been included in this report, too (AMSTUTZ, 1978; DAHLHEIMER, 1980; LEVIN et al., 1973; HIRDES et al., 1978; SAMANIOGO, 1982; SUREDA et al., 1984).

Comprehensive works on Eastern Alpine deposits were composed by ASSARETO et al. (1977 a, b, c), BRIGO et al. (1977), BRIGO et al. (1978), SCHULZ et al. (1977), OMENETTO (1978) and others. From local and special studies the papers of OMENETTO et al. (1977), BRUSCA (1978, HAGENGUTH et al. (1982), HAGENGUTH (1983) may be mentioned.

Beyond the region of the Eastern Alps research work about deposits in general should be mentioned, such as about strata-bound mineralizations in the Little Carpathians (ILAVSKY, 1979; KANTOR, 1977), about the polymetallic deposits of the Western Balkan by MINČEVA-STEFANOVA (1978), about the Swiss part of the Western Alps (SCHMIDT et al., 1983), and about strata-bound deposits of the Iberian Peninsula by FONTBOTÉ et al. (1983) and CASTROVIEJO (1982).

In addition to these there are comprehensive publications from Algeria and Tunisia (FUCHS, 1978; VASILEFF et al., 1977). In the Mediterranean area however a systematic investigation and listing of strata-bound deposits in carbonate rocks has still to be carried out, as for instance in Libya and Turkey, or have been set in motion in Greece. About Triassic ore mineralizations in connection with acid effusive rocks in the Dobrogea (Romania) is reported by VLAD (1978).

Investigations of lead-zinc occurrences hosted in Mesozoic rocks and covering the Hercynian Platform in France and Germany, are especially valuable for the comparison with the ore mineralizations of the Mediterranean geosyncline (AMSTUTZ et al., in press).

There are numerous publications about the mineral deposits in Upper Silesia available too, which give reason for new genetical interpretations (DZULINSKI et al., 1980; NIEC, 1980; PAWLOSKA et al., 1980; GRUSZINSKY, 1982).

Mainly as a result of organization problems methodical geochemical investigations were more or less confined to the Eastern Alps and for obvious reasons the large deposits of Bleiberg-Kreuth (Austria) and Mežica (Yugoslavia/Slovenia) were investigated most carefully.

Further contributions and special studies can be subdivided into the fields of general geological observations, lithogenesis and dolomitization, ore structures, mineralogy and geochemistry including isotope geochemistry.

Although considerable progress was achieved by the studies and correlated discussions within the working groups of the project, it must be confessed that the target, as outlined in the title, could not be attained. The complexity of the factors forming a single deposit and the varying significance of the heterogeneous features of the deposits prevented the set up of a system of features which could enable a geologist to discover a new deposit with a reasonable risk by following the schedule. This aim was too ambitious and a lucky chance will furthermore remain a most welcome compilation to careful geological studies while prospecting for a deposit.

2. Further contributions

2.1. General geological contributions

For the formation of hydrothermal ore mineralizations the following facts of a model are accepted:

a) a source, resp. source rock supplying the metals,

b) a hydrous medium for leaching and transport,

c) geological traps combined with geochemical barriers.

The leaching process is primarely controlled by the temperature and the chemical state of the leaching medium, especially solved gases or/and the salt content, mainly NaCl being in question.

Discussing the superpositions for the lead-zinc ore mineralization hosted in carbonate rocks, it is evident that at least two genetical groups can be distinguished:

a) ore deposits connected and formed by sedimentary or diagenetic processes,

b) ore deposits more or less directly related to volcanic or magmatic events.

The two types of deposits are showing significant differences with respect to the energy level which can be observed in connection with the ore occurrences. The lead-zinc deposits which are related to endogen processes have been formed at a much higher energy level, than the deposits produced by exogen events. The term energy is considered for the temperature level of the leaching process depending on energetically controled geotectonic events. Of course deposits exist which show features pointing to both types. It seems to be significant that the ambiguous observations correspond to the position of these deposits in the whole system between endogen and exogen dominated by the ranges of distribution. That apparently is the reason for the nearly endless discussions about syngenesis and epigenesis.

The different geoenergetic conditions in platforms, along their coastal margins and in areas of developing geosynclines, subduction and rifting zones, cause the conditions for different initial processes and the development of multiple ore mineralizations, ranging from the sedimentary preenrichment on platforms up to black smokers in zones of rifting.

A significant contribution to the understanding have been given by members of the working group, such as Fuchs (1981a) who set up a genetical system of base metal mineralizations hosted in carbonatic sediments and related to regional geotectonical events.

The region of the project had been directed originally to the area of the Mesozoic Mediterranean orogen including the bordering epicontinental sedimentary cover of adjacent platforms. All the mentioned geotectonic and geoenergetic situations are found in this part of the earth crust (Fig. 1). However, the most of the contributions to the project are related to the European platform and the Eastern Alps. Therefore the emphasis has been on the exogen type of ore mineralizations.

In the geotectonic stage of transgression epicontinental platforms are covered by the weathering products of older crystalline complexes forming horsts. If the climatic conditions exclude lateritization processes, the exogenic processes at first

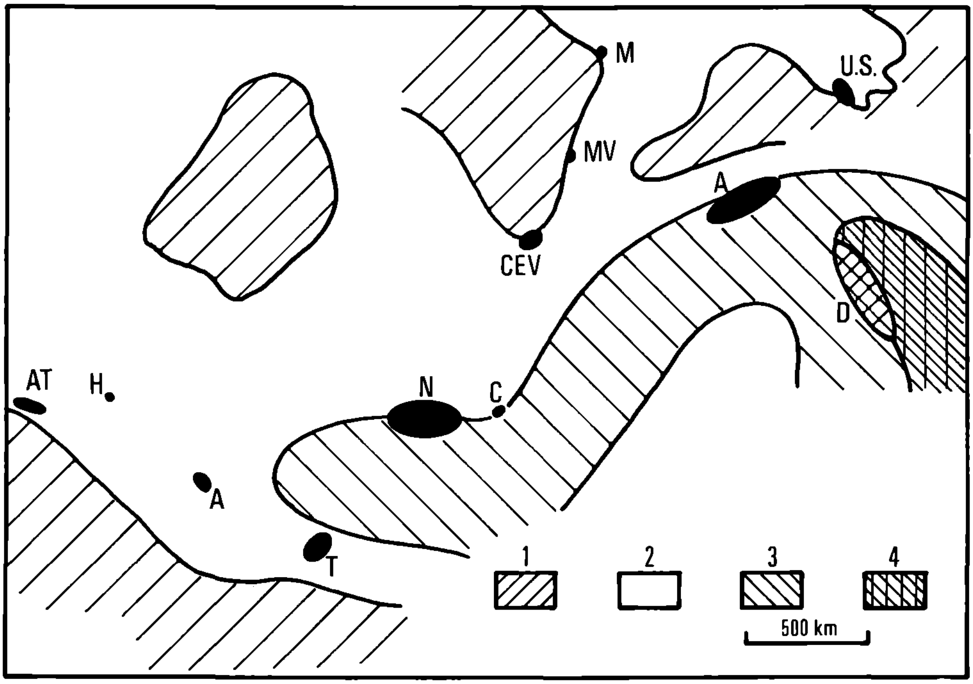

Fig. 1. Lead-zinc ore mineralizations of Triassic age in the Western Mediterranean system (after a schematic representation according to FONTBOTÉ et al., 1983)

Abbreviations:
1 = Horsts
2 = Transgressed platforms
3 = Thinned and faulted continental crust
4 = Oceanic crust of the Thetis

Ore districts:

AT, H	Atlas Mountains, Morocco	N	Betic Cordillera
A	Atlas Mountains, Algier	CEV	Cevennes
T	Atlas Mountains, Tunis	US	Upper Silesia
ALP	Eastern and Southern Limestone Alps	MV	Morvan
D	Dinarides	M	Mechernich-Maubach

supply clastic sediments. Chemical sediments follow in form of evaporitic intercalations and carbonatic rock series. The preenrichment of base metals can became apparented as well in the clastic sediments as in the superimposed carbonatic rock series or in intercalated pelitic schists. Generally geochemical anomalies can be found in the lowest carbonatic rock strata of mostly dolomitic composition. In many cases a widespread halo of metals can be observed distinctly above the Clark values, but richer metal concentrations are rather exceptional. The source in the metal content of the weathered crystalline complexes, such as apical parts of granitic intrusions or preexisting ore deposits (KÖPPEL et al., 1983). Fig. 1 clearly shows the connection of horsts with richer ore concentrations (FONTBOTÉ et al., 1983). Analogous to the Permian copper shale the distribution od lead and zinc is conditioned by the morphology; lead prefers swells and zinc basins (CERNY, 1977). In the carbonatic environment lead and zinc dominates and can be separated completely from copper and silver. For instance DROVENIK et al. (1983) reported that galena was purified by remobilization from some trace elements.

The further concentration of lead and zinc is determined by the geological development of the platform.

If the sediment cover is thin enough, the decomposition of biogenic substances into coal, oil and gas, salt diapirism and the activity of formation waters must be taken into consideration for late diagenetic and epigenetic metal concentrations. Younger magmatic activity in the crystalline basement is mostly an additional factor to exogenic heat (WALTHER, 1983). Tectonic events producing deep faults are the precondition for geothermal systems. Remobilization of metals from the basement were described by SCHNEIDERHÖHN (1953) at first. He called it "tracing of deposits" (Durchpausen). For instance the remobilization of fahlore from Old Paläozoic deposits into the superimposed mesozoic carbonate rocks was mentioned by GSTREIN (1983).

The migration of the elements happens in different ways (ROUTHIER, 1980). There is no doubt, that the evaporitic environment causes the migration of base metals during sedimentation and diagenesis (SCHNEIDER, 1972, 1978, 1980a, b, 1981a, b; FUCHS, 1976; LAGNY, 1980 etc.). Therefore the identification of brine relics in carbonate rocks and in the ore bodies could be used as a geochemical prospecting tool (see below in the following chapter Geochemistry).

The conditions for the formation of lead zinc deposits in the geosynclinal stage are similar to these in the overflooded platforms. Islands originated from the crystalline and Palaeozoic basement, coast-lines and reefs with lagoons are possible. An additional factor is the geosynclinal volcanism. The contribution of the Triassic volcanism to the formation of lead zinc deposits in the Eastern and Southern Alps seems to be still an unsolved problem. The mostly potassium-rich acid volcanites could be preferably the source of lead, barium, thallium or fluorine, but the lead isotope composition of the ore lead doesn't confirm this hypothesis. However, later tectonic processes forming the Alpine orogen have prevented oil formation and activities of formation waters. Only in the Eastern part of the Northern Limestone Alps indications for ore mineralizations being probably related to formation waters, could be found.

According to the platetectonics, the Eastern part of Mediterranean beginning with the Dinarides was influenced by the opening of the Tethys. The lead zinc deposits are often directly related to volcanogenic, resp. magmatogenic processes (ŠTRUCL, 1981). In the North of the Dinarides the first endogenic lead-zinc occurrences have been mined at Zavrh/Slovenia (DROVENIK et al., 1980). The ore occured in silicified and recristallized Ladinian reef limestone connected with hydrothermally altered keratophyric tuff. The high-hydrothermal volcano-sedimentary ores are similar to some ore occurrences of Middle Triassic age in Črna Gora (Montenegro). Other ore deposits are the siderite layers of Vareš combined with base metal mineralizations in the same area, Supleja Stijena, Podrinje etc. Ore structures and textures, mineralogy and geochemistry are significantly different from the exogenic type.

While the exogen type of lead zinc deposits usually occurs in well defined parts of more or less thick sequences of carbonatic rock series, the lithological situation of endogen deposits is mostly an extraordinary one. The alteration phenomena on the surface are often remarkable. Therefore this type is easier to be prospected. Endogen deposits are very often characterized by pretty high grade ores. Generally it can be observed that the limits of variablity of ore deposits related to plutonic or volcanogenic events are somehow smaller than patterns of the exogenic group. Naturally there are also deposits which can be classified as an intermediate type, showing features of both kinds of deposits, exogenic and endogenic ones. Submarine volcanogenic sources can be associated with sedimentary ore depositions in further distance. The same situation applies to hot solutions emanating from feeder faults, for instance very well described by MINČEVA-STEFANOVA (1978) for the ore deposits of the type Sedmočislenici (Stara Planina, Bulgaria).

Considering the suppositons for the formation of lead-zinc deposits in carbonate rocks we have to distinguish between regional and local factors:

The basic regional factor is the presence of the metals, the basic local factor the existence of suitable geological traps to collect the metal compounds.

The sources of the metals resp. their origin can be:

a) Magmatogenic lead and zinc originated during some phases of the geosynclinal stage. Mostly tuffites are the evidence for such events which often are not detectable at all. In that case sea water was very likely the medium for transport.

b) Feeders which have received their metal compounds from the crust mostly by deep reaching tectonic faults or lineaments.

c) Mobilization and re-deposition of lead and zinc pounced from elder deposits in an overlying younger sequence of strata.

d) Decomposition of elder geological units which contained Pb-Zn (or other metals) at least in parts and redeposition of these minerals.

The three suppositons a)–c) may have been efficacious and two or even all three of these phenomena may have been active with various intensity in the same deposit.

Besides the sources and the traps the processes connected with the lithification, resp. diagenesis, generally are of major importance for the formation of an exogen deposit. Locally concentration of metals may have been produced by karst-phenomena.

It is a consequence of these manifold genetical models and the often afterwards overlapping evolutionary components, that the selection of prospecting strategy is much more difficult than in case of deposits, the origin of which is directly detectable from endogen events.

Very likely this system of exogen and endogen deposits may occur in different areas and under varying conditions even in pre-Triassic sequences, but it certainly will be more difficult to distinguish these two types due to alterations originating from their even more complicated history.

Finally we can characterize these two types and can expect in the areas of their distribution that methods selected and adapted to the observed features will lead to optimal results. This may facilitate the set up of a prospecting strategy but not more. The real work still has to be done by geological, geochemical and geophysical methods.

2.2. Lithogenesis and dolomitization

The importance of facies bounderies for ore mineralization was reported by CERNY (1982). The microfacies is as revealing as macro-facial rock structures. In this respect the sedimentological interpretations of facial changes within the carbonate sequence is of vital importance, especially in the paleogeographic connection with reefs as proved by BECHSTÄDT (1875, 1979 a, b) in the Bleiberg-Kreuth deposit.

The importance of dolomitization for ore concentrations has already been mentioned to on several occasions.

A geochemical model for the processes of dolomitization was set up by MÖLLER et al. (1976). An investigation of the process of dolomitization by microprobe analysis was carried out by MINČEVA-STEFANOVA (1981).

2.3. Ore structures

The genetic interpretation of ore structures of this type of deposits was summarized by SCHULZ (1976). It was completed by FONTBONTÉ and AMSTUTZ (1980/1981) with respect to diagenetically crystallized rhythmites.

In the project the genetic conception of Bleiberg-Kreuth was put into question as a result of outdated suggestions and short-time observations question by reason of the comparability of some types of ore structures occuring in the Pb-Zn ore mineralization of Upper Silesia (DZULINSKY et al., 1977 a, b, 1978).

2.4. Mineralogy

Among contributions of ore mineralogy especially the results by MINČEVA-STEFANOVA (1979, 1980) should be emphasized. AMOURI et al. (1978) and DEVIGNE (1980) drew attention to the possible importance of sulphur-bacterial action in the formation of whisker-shaped galena. In the course of other investigations, such micro-crystallite formations were also found in the Eastern Alps (SCHROLL, 1980).

In-situ measurements with secondary mass spectrometry (SIMS) made for the first time in Vienna by PIMMINGER (1983) and investigations with the scanning electronic microscope (SCHROLL, 1981) showed that the insertion of important trace elements in sphalerites (such as germanium, gallium, thallium and arsenic) down to a range which cannot be resolved any more (ca. 1 μ^2), must be present in the form of micromineral phases or domaines, so that a substitution in the sphalerit lattice can be excluded.

2.5. Geochemistry

The geochemical knowledge about carbonate rock hosted lead-zinc ores was presented by SCHROLL (1978) at the beginning of the project. The geochemical characterization of the Bleiberg type in comparison with other carbonate hosted lead-zinc mineralizations has again been discussed by SCHROLL (1983) at the end of the project.

Geochemical investigations of the sedimentary rocks were connected with profiles of mineralized Triassic rock series (KRANZ, 1973, 1976; CERNY, 1977, 1978; HAGENGUTH, 1983). In green marls of lower Ladinian age tuffitic products could be identified (HAGENGUTH, 1983). Also in Raibl volcanogenic intercalations have been studied by JOBSTRAIBIZER, 1981).

The content of chlorine in carbonate rocks and in ore bodies was recently investigated by WOLTER et al. (1983) in the Bleiberg-Kreuth deposit. He reports on indications of halos with considerable brine concentrations in, as well as around the sulphidic ore bodies. This phenomenon can be interpreted as remnant of the transporting solutions. Moreover there are investigations going on whether this phenomenon could be used as a prospecting tool.

The distribution of fluorine in host rock sequences and especially its conspicuous linkage with comparatively few and thin layers indicate that the substance for the primary syndiagenetic formation of fluorine cannot originate from the host rock.

The lateral and vertical occurrence of fluorine anomalies and their spatial connexion with Pb-Zn mineralizations may be used as a proximity indicator which may be valuable for paleogeographic reconstructions. This was proved by the Berlin working team for numerous large deposits of the Eastern and Southern Alps.

The syndiagenetic origin of the fluorite is also proved by its characteristic content of the elements of the rare earth (REE) group, which is roughly the same as in the carbonate sediment. The subsequent diagenetic remobilization of fluorites can be shown by the fractionating in the REE content (SCHNEIDER et al., 1975, 1977; HEIN et al., 1983). MÖLLER et al. (1983) could interpret the distribution of gallium and germanium in sphalerites on the base of a physicochemical model. The results give evidence that the metals of Bleiberg type deposits have been leached at a low temperature range. Besides this, new data on the trace element distribution of galena and sphalerite are available but have only partly been published.

2.6. Isotope geochemistry

2.6.1. Carbon and oxygen isotopes

The investigation of carbon and oxygen isotopes of the carbonatic rocks and the gangue carbonate minerals informs us about the origin of the water participating in the ore forming processes and the origin of the carbon dioxide. Diagenetic processes influence the isotopic composition of oxygen preferably depending on the water-wallrock ratio. Hydrothermal ore fluids or meteoric waters can be recorded.

The distribution of the isotopes of both elements in the carbonates of the Bleiberg type show that diagenetic processes are operating up to late diagenesis (SCHROLL et al., 1978; KAPPEL et al., 1982; DOLENEC et al., 1983).

2.6.2. Sulphur isotopes

Systematical investigations of the sulphur isotope composition of sulphate and sulphide minerals support the evidence that in the Bleiberg type the sulphate is derived from the sea water sulphate and biogenic processes have influenced the sulphide sulphur during the early diagenesis. The remobilization of the sulphidic ores has mostly taken place in an open system (SCHROLL et al., 1983). Other investigations were carried out by DROVENIK et al. (1976, 1980) and PAK et al. (1980), SCHROLL et al. (1983).

The sulphur isotope composition reported from sulphidic ore minerals of the Bleiberg type alone however doesn't allow general statements about the admixture or the full evidence of volcanogenic sulphur. Ore mineralizations of endogenic origin show sulphur isotope distributions, which are distinctly different (SCHROLL et al., 1983). But a range of $\delta^{34}S$-values around zero was found too. In the case of a high temperature source and the existence of feeder faults transitions of $\delta^{34}S$-values to biogenic sulphur can be observed in some distance.

2.6.3. Lead isotopes

Extensive work for a better understandig of the origin of lead ore resulted from investigations of the lead isotopes in the area of the Eastern and Southern Alps. Abundant data of lead isotope compositions are available (KÖPPEL et al., 1976, 1979; KÖPPEL, 1983). Part of these data have to be published in detail. Not only the isotopic composition of the ore lead, but also of rock lead was studied. The resulting data indicate that in deposits of the type Bleiberg the ore lead doesn't correspond with the rock lead. This applies also for some investigated potassium-rich acid volcanites of Triassic age. The ore lead is isotopically very homogenous and must be introduced several times during a short period of time. The ore lead shows a model age of about little more than 300 my and it can be derived from ore lead and rock lead of the Old Paleozoic basement, originating from the Precambrian African platform. Ore lead from lead-zinc deposits of Morocco and Algier is comparable. Lead isotopes from the Hercynean platform and the Penninic area of the Alps are significantly different. This is true in the Alps for most of the lead ores of the Anisian and other Triassic mineralizations deviating in their chemical and/or mineralogical characteristics.

Lead isotope data are reported from the strata-bound polymetallic deposits of the Western Stara Planina Mountains (Bulgaria) (AMOV et al., 1979) and from Upper Silesia (PAWLOWSKA et al., 1980).

Endogen and exogen ore mineralizations can't be distinguished by the aid of lead isotopes alone. Well mixed homogeneous leads are found in both types. Mixing of the magmatic melt with pelitic substances is operating in the same manner. However, radiogenic ore lead is limited to the area of the Alps indicating uneconomic small ore occurrences (KÖPPEL et al., 1983).

2.7. Geochemical characterization

The geochemical characterization (SCHROLL, 1978, 1984) can be of practical importance as it turned out that relations to metal concentration seem to exist, but these relations have to be worked out for certain parts of the Earth crust which to their applicability in specific regions and at different times. The period of time necessary for carrying out our project (6) of the Correlation Programme was too short in relation to the amount of the problems as a whole. Standardized comparative investigations covering the whole Mediterranean area or other parts of the crust could not be achieved. On the basis of systematic geochemical and isotope-chemical data characteristic parameters for the Triassic lead-zinc ores of the crustal area of the Eastern and Southern Alps could be deduced.

Detailed geochemical investigations in the Eastern Alps suggest that in this part of the Earth crust larger Triassic deposits with high metal concentrations ($x \cdot 10^6$ t) are bound to a certain concentration of trace elements in lead-zinc ore, to a certain pattern of distribution of the sulphur isotopes in the sulphides and sulphates and, above all, to a well defined, very homogenous distribution of lead isotopes. These results were for the first time applied with good results in a regional study about prospecting of lead-zinc mineralizations in the Austrian part of the Karawanken mountains (CERNY et al., 1981).

It is necessary to continue this work in this direction, as the importance of this problem for the exploration of base metals is obvious, especially for the developing countries, and it seems likely that with modern methods and concepts the manifold problems can be solved.

3. Conclusions

Although it was not possible to find general "diagnostic features" for the mineralization of the base metals in carbonate rocks on a global scale, it turned out that in principle there do exist two types of deposits: one group which is related to exogen processes and a second group depending directly to endogen events. In the Mediterranean these two types do occur in seperate areas which are marked by their specific geological position. The deposits related to endogen processes are not at all occuring in carbonate rocks only so. They are characteristic for the active orogenic belt in the Dinarides. The deposits depending on exogen processes occur in Central Europe in the pre-Alpine and Alpine geosyncline in North Africa and on the epicontinental platforms as f. g. in Upper Silesia.

The methods of prospecting must be appropriate to the two differing genetical models which are owing to respective features of the deposits.

The mineralizations in carbonate rocks, from late pre-Cambrian onwards, are showing very similar phenomena even if they are different in origin and geologic evolution. Synchronous metallic deposits in carbonate rocks are confined to shallow water sediments with delta-reef- and lagoonal deposits.

On purpose we suggest the term "synchronous" instead of syngenetic or sedimentary, because it is only possible in very rare cases to verify that the ore has been deposited on the bottom of the sea, which would be the supposition when speaking of "sedimentary". Synchronous—as we understand the terminus—may also include the processes of lithification—or the events during diagenesis.

Acknowledgement

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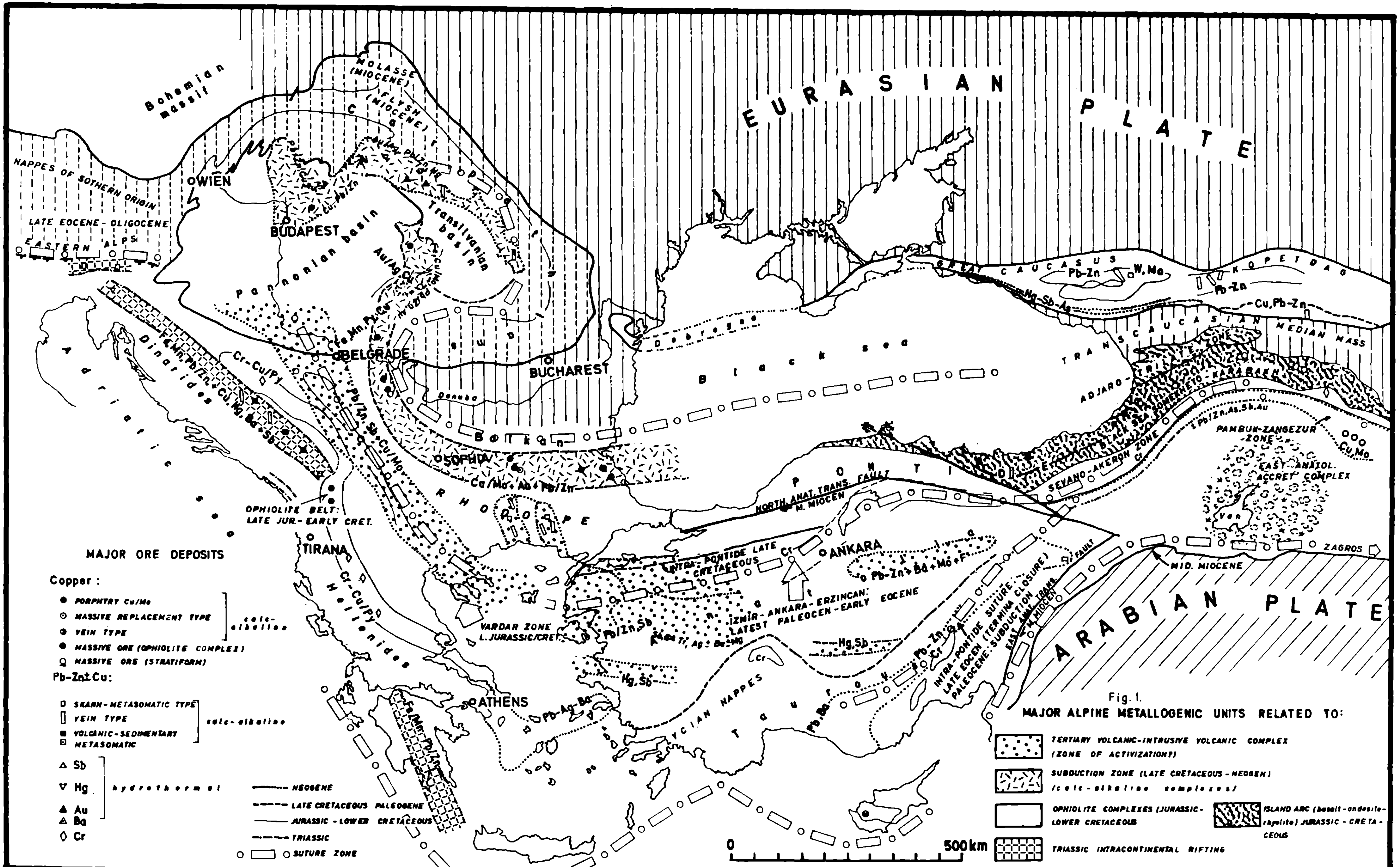

Fig. 1.
MAJOR ALPINE METALLOGENIC UNITS RELATED TO: