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Metallogeny, structural, lithological and time controls of ore deposition in anoxic environments

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Abstract. Accumulation of metals in anoxic environments occurs by sorption and precipitation from seawater, fossil brines or hydrothermal solutions. Metals can be remobilized during subsequent metamorphic and magmatic processes and form ore deposits. This type of mineralization is governed chiefly by the type of tectonic setting of the anoxic environment. Carbonaceous sediments of passive margins contain only subeconomic concentrations of uranium, vanadium and molybdenum. Cu-bearing black shales and the submarine-exhalative type of mineralization are confined to the environments of continental rifts and aulacogens or to back-arc basins of active margins. Metamorphogenic deposits are mainly connected with collision margins but they may also occur in other types of tectonic environments. The formation of Cu-bearing black shales was controlled by period of low sea-level during the break-up of supercontinents in the Earth's evolution. Increased contents of uranium and vanadium accumulated in black shales in periods of sea-level highstands. Lithological control is apparent in deposits of Cu-bearing and uraniferous black shales. On the contrary, the occurrence of polymetallic mineralization does not depend on the lithological maturity of carbonaceous sediments.

Discoveries of new industrial types of mineralization in sediments and metasediments rich in organic matter, especially deposits of gold (Radtke and Schneider 1970; Buryak 1975, 1982; Petrov 1988) and uranium (Rybalkov 1965), as well as new results in the investigation of the relation between mineralization and organic matter (Estep et al. 1980; Dean 1986; Pašava and Gabriel 1988) have generated a new wave of interest in the metallogeny of anoxic environments. With the aim of providing a theoretical basis for prospecting and exploration, the present paper summarizes the principles of metallogeny of anoxic environments, gives information on the types of such deposits whose occurrence is genetically or paragenetically associated with carbonaceous formations, and presents the definitions of some criteria used in determining their ore-bearing potential.

Metallogeny of an anoxic environment

A general review of the processes leading to the origin of ore deposition in carbonaceous formations is presented in Fig. 1. According to this scheme, mineralization in carbonaceous rocks (sediments and metasediments) could be connected with the processes of sedimentation, diagenesis, metamorphic and magmatic events, and weathering. Metals could be introduced to an anoxic environment or this environment could act as a source of metals in the processes of mineralization. Typical examples are given in the following sections.

Mineralization connected with the stage of sedimentation and diagenesis

Sorption and precipitation from seawater (Fig. 1, *arrow 1*), different types of brines (Fig. 1 *arrow 2*) and hydrothermal solutions directly or indirectly connected with the synchronous volcanicity (submarine-exhalative deposits, Fig. 1, *arrows 3* and *4*) could be regarded as a source of metals in this stage. Typical deposits that originated by the sorption of metals from a water environment are the uranium-bearing black shales of Sweden (Ranstadt deposit; Anderson et al. 1985), vanadium-bearing shales of Upper Proterozoic and Cambrian age of Kazakhstan (Kholodov 1968), Cambrian shales enriched in vanadium and several other elements in a number of Chinese provinces (Fan 1983) or Pennsylvanian metalliferous black shales of the central USA (Coveney et al. 1987).

In addition to the deposits mentioned above, the anoxic sediments are a host environment of pyrite and manganese ores produced by bacteriogenic activity, the origin of which may be connected with the activity of sulphate-reducing bacteria or of blue-green algae (Hein and Koski 1987; Ostwald 1988; Jinfra 1988). Large de-

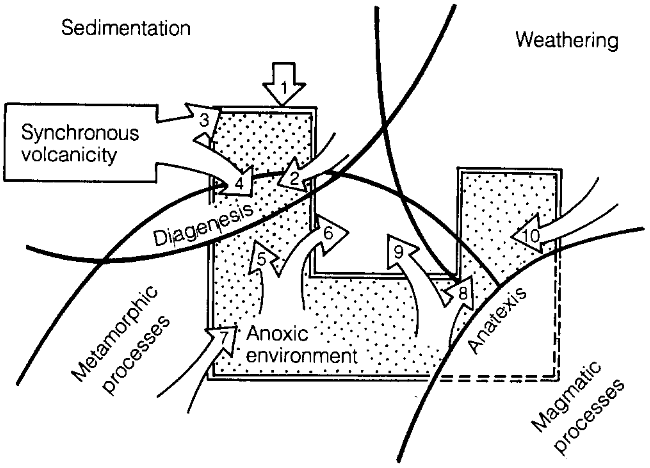

Fig. 1. Diagrammatic sketch of metallogeny of anoxic environment. Arrows indicate the processes leading to the origin of ore deposits. *1* Sorption and precipitation from seawater; *2* Remobilization of metals by formation waters and brines; *3–4* Submarine-exhalative deposits; *5* Metamorphic remobilization within carbonaceous formations; *6* Carbonaceous formations as a source of metals; *7* Carbonaceous formations as a host environment for metamorphic ores; *8* Remobilization of metals within the framework of anatexis and during the ascent of granites; *9* Carbonaceous formations as a mineralization source in hydrothermal postmagmatic processes; *10* Infiltration processes. Examples of the different types of mineralization are given in text

posits of manganese mostly occur at the boundary between oxic and anoxic sediments. Force and Cannyon (1988) explain this finding by the mixing of anoxic waters with high managanese solubility with shallower oxygen-bearing water with low manganese solubility. The deposits of stratabound barite ores are often situated in the same area.

The stratabound copper mineralization of the "Kupferschiefer" type is also a typical mineralization of anoxic sediments. These deposits, originally considered as synsedimentary (Wedepohl 1971), are now regarded by most authors (Renfro 1974; Jowett 1986; Kucha and Pawlikowski 1986) as a product of metal remobilization by brines during diagenesis and at the beginning of epigenesis. A redox-precipitated model is proposed to explain the platinum group elements (PGE) mineralization of the "Kupferschiefer" in Poland (Kucha 1983) and Ni-Mo-PGE-Au mineralization of the lower Cambrian black shales in southwest China (Tian Eshan deposit, Guishou province; Coveney and Chen 1989).

Carbonaceous sediments also contain deposits formed by hydrothermal solutions of different origin (submarine-exhalative deposits). These develop either at the water/sediment boundary (volcanic-hosted massive sulphidic deposits) or in the diagenetic stage of the development of anoxic sediments (SEDEX type deposits). In the former case the mineralization is usually located at the boundary between volcanites and black shales. This may be exemplified by the Finnish Cu-Ni deposits – Kotalantai and Hitura (Isokangas 1978); Swedish deposits in the Skellefte area (Boliden, Langstele, Langdal; Grip 1978); and Norwegian deposits in the Caledonides (Folldal, Killingdal, Løkken, Twerrffellet; Bugge 1978). In cases like this the spatial relation between thin layers of carbonaceous rocks overlying mineralization can be interpreted in terms of local anoxia associated with the outflow of hydrothermal solutions. Solutions supplying a considerable amount of hydrogen sulphide may cause the exhaustion of the oxygen potential of water environments as it occurs in recent volcanic lakes of Kamchatka (Jerosheev et al. 1985).

Somewhat different is the relation between mineralization and anoxic sediments in SEDEX type Pb-Zn sulphide mineralizations. Examples are the deposits of the Soviet Far East (Kholodinskoe and Lineinoe deposits; Rukhkin 1980); the deposits of Queensland (Mount Isa, Hilton, McArthur River; Sawkins 1984); the deposits in Canada (Howard Pass and Sullivan; Gustafson and Williams 1981); and the deposits in Germany (Meggen, Rammelsberg; Gehlen 1985). On the basis of time coincidences of the occurrence of these deposits with the anoxic events in the history of the world ocean, Goodfellow (1987) suggested that they originated during periods of anoxia when the developing sulphidic mineralization was shielded from subsequent oxidation. Using the example of the Selwyn basin (Canada) the same author demonstrated that the carbonaceous sediments were also a source of sulfur needed for mineralization.

Besides Pb, Zn and Cu deposits, there are other types of submarine-exhalative mineralization associated with carbonaceous sediments (e.g. manganese ores: Wafanzi, Guo Shiqin and Sun Wenhong deposits in China, Woodstock in Canada and Aroostock in the USA, Lienne in Belgium and Les Cabesses in France; Láznička 1985). Obviously also of a submarine-exhalative origin are some Sb-Hg-As deposits in black shales (Stadt Schlaning in Austria and Nigde in Turkey; Láznička 1985). Black shales commonly host tungsten mineralizations which may also be connected with the submarine-exhalative activity. Examples are the Kleinarital and Felbertal deposits in Austria (Höll and Maucher 1976), the Jerrois Range deposit in Australia, Wolfram schist in the Republic of South Africa, Amutara deposit in Bolivia; Láznička 1985), and the Barum-Shivenskoe deposit in the USSR (Apeltsyn 1981).

Metamorphic types of mineralization in anoxic sediments

During metamorphic processes the metals accumulated in anoxic sediments may be locally remobilized in carbonaceous formations (Fig. 1, *arrow 5*), which may be a source of metals and sulphur for rocks which do not contain a larger amount of organic matter (Fig. 1, *arrow 6*) or may act only as a suitable lithological environment of metamorphic mineralization (Fig. 1, *arrow 7*). In the first case uranium and gold deposits are concerned. The uranium deposits of this type are in essence polygenetic. Uranium accumulated during sedimentogenesis by organic matter is remobilized under conditions of very low-grade contact or regional metamorphism into zones of brittle deformation. A typical mineralization of this kind is found in low-grade metamorphic carbonaceous sediments in the Ronneburg area, Germany (Rybalkov 1965).

The metamorphogenic gold deposits in black shales are, in contrast to the uranium deposits, located in the areas of higher-grade metamorphism (upper part of the greenschist facies). These deposits (an example of which are the Sukhoi Log and Muruntau in the USSR) are characterized by veinlet and disseminated types of mineralization, spatial connection with the zones of brittle ductile deformation and a rapid rise of metamorphic grade in the area (Buryak 1976; Sozinov 1981). They are frequently accompanied by extensive zones of alterations, a supply of potassium, and development of Fe-Mn carbonates. Simultaneously with gold remobilization, carbon-rich metasomatites originate (Ivankin and Nazarova 1984). Analogous association of gold with bitumens has been recognized in many metamorphic deposits linked up with the graphitized shear zones. The Timmins Camp mines in Quebec and Au-W deposit Macraes, East Otago, New Zealand are given as an example (Downes et al. 1984; Springer 1985; McKeag et al. 1989).

The metamorphogenic uranium deposits in the Moldanubian region of Central Europe are also linked up with the graphitized shear zones of the same structural type (Dill 1983; Křibek and Jedlička 1986).

It may be that metamorphic processes from deposits of other metals in carbonaceous sediments. For example, Reedman (1973) suggested that tungsten deposits in carbonaceous metamorphites of Uganda formed by metamorphic remobilization. Apeltsyn (1978) thought the scheelite mineralization in carbonaceous aleuropelites of Karelia, Yenisei and Aldan ridges in the USSR to be of metamorphic origin and White et al. (1973) described what they called metamorphogenic remobilization during tectonic processes of Sb, Hg and Sb in deposits of West California.

Mineralization of carbonaceous formations associated with the processes of ultrametamorphism, partial melting and rising of intrusive-extrusive magmatic complexes

In magmatic processes a very intricate interaction of magmatic and volcanic rocks with carbonaceous sediments and metasediments takes place (Fig. 1, *arrows 8* and 9). The assimilation of carbonaceous rocks during anatexis processes can also cause the enrichment of melts in metals and sulphur. In this way Campbell (1965), for example, explained the origin of graphitic granite with increased gold contents in the Victoria Goldfield (Australia) or Golovanov (1977) the genesis of prophyry copper ores of the Almalyk deposit (northern Tyan Shan, USSR). The origin of the uranium deposits in shear zones of high-grade metamorphic terrains of northwest Canada may also be connected with anatexis and migmatization of carbonaceous formations (Fay Verna and Gunar Mines deposits; Tremblay and Růžička 1984). Leroy (1978) assumed that the uranium vein deposits of France (Bois Noirs-Limouzat, Margnac, Fanay and La Crouzille) formed by the enrichment of granitoids in uranium during the anatexis of carbonaceous sediments and the following extraction of uranium due to circulation of hot meteoric waters. The extraction of metals from carbon-rich sediments by meteoric water whose circulation is controlled by the increased thermal flow above intrusive complexes gave rise to mineralizations of various types. Such origins may apply to Carlin-type gold deposits (Carlin, Cortez, Gold Acres, Jerritt Canyon; Radtke et al. 1980), where the mineralization occurs particularly in bituminous limestones with interlayers of carbonaceous shales and chert. The Soviet deposits of gold and silver of the "Kazakhstan type" (Bakyrchinskoe deposit) occurring in the carbonaceous Proterozoic and Lower Paleozoic lava- and tuff-breccias are believed to be formed by remobilization of metals as a result of the thermal front of Carboniferous magmatites (Mavchenko et al. 1981). Other epigenetic deposits of this type may include Hg-Sb-As mineralizations in black shales and bituminous carbonates of Kirgizia (Kadamdzhai deposit; Magakyan 1968) or the San Antonio deposit of Sb-W-Hg ores in Spain (Arribas and Guniel 1984) situated in Lower Paleozoic graphitized shear zones, the genesis of which is associated with the thermal front of Carboniferous granitoids.

Infiltration ore mineralization in anoxic sediments and metasediments

In weathering processes and in the formation of infiltration mineralization the carbonaceous sediments – that is, the reduction and sorption characteristics – play an important role in forming deposits of uranium, copper and other metals (Fig. 1, *arrow 10*). The role of organic matter in the origin of the sandstone-type uranium mineralization was discussed many times in the past (Langford 1977; Rackley 1976) as well as the role of graphite in deposits of "unconformity type" (Dahlkamp and Adams 1981; Needham and Stuart-Smith 1980; Langford 1978). The genesis in the copper mineralization in black shales in the Marsberg deposit in the Rheinisches Gebirge can also be explained by supergene processes (Stribrny 1987).

The controls of ore mineralization in carbonaceous formations

Geostructural position of ore mineralization in carbonaceous formations

Anoxic sediments originate in basins of all geotectonic types. Their mineralization is consequently controlled to a considerable degree by the geostructural position of sedimentary basins as is shown in Fig. 2 and in the following overview.

1. Mineralization of the anoxic sediments of oceanic basins

Deep-water oceanic sediments containing a major amount of organic carbon are poor in metals, yet some are enriched in uranium, vanadium and other elements, which may be connected with hydrothermal emanations (Boström and Fisher 1971). This is in agreement with higher metal contents in anoxic sediments, which fre-

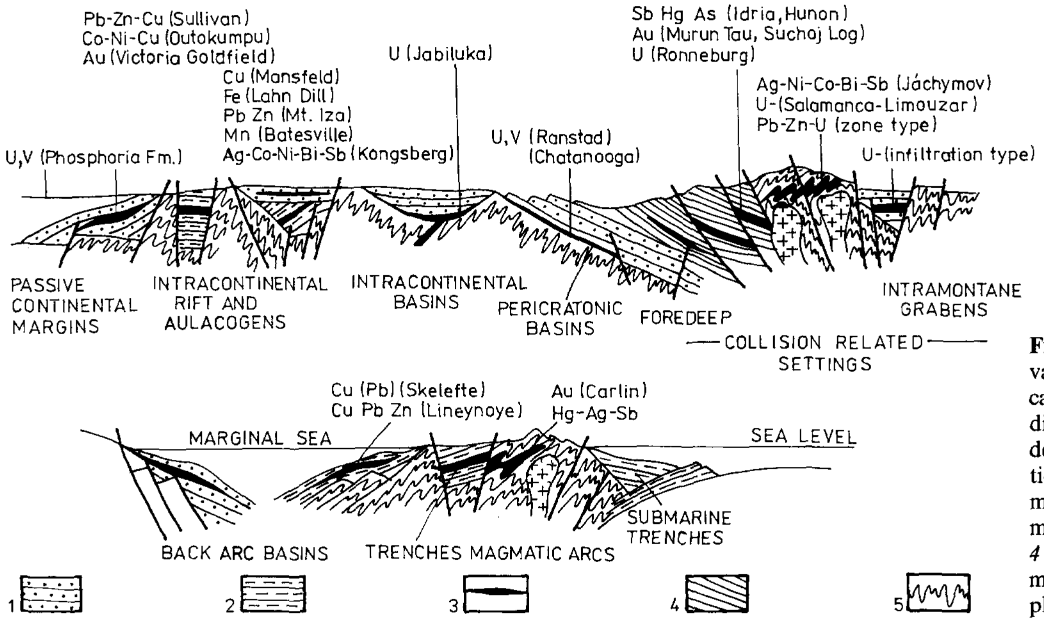

Fig. 2. Geotectonic position of various mineralization types in carbonaceous formations with indications of examples of typical deposits. *1* Sedimentary formations; *2* Volcanosedimentary formations; *3* Carbonaceous sediments and metasediments; *4* Epizonally metamorphosed formations; *5* High-grade metamorphosed formations

quently accompany the deposits of massive sulphides in the rift valleys as for example, the carbonaceous sediments overlying the Løkken and Hoydal deposits in Norway (Stephens et al. 1984).

2. Mineralization of the anoxic sediments of active continental margins

In the environment of active continental margins a significant ore mineralization of carbonaceous sediments is associated with magmatic arcs, viz. magmatic and nappe zones in the sense of Dickinson (1976). The carbonaceous sediments and metasediments of the ancient continental crust are frequent components of these zones. The "inherited" carbonaceous formations are very often a source of epigenetic mineralization, which develops in a period of tectonic reactivation usually connected with increased thermal flow. The most prominent mineralization of this type is the "Carlin type" gold mineralization, which Radtke et al. (1980) classified with the deposits of a magmatic arc and Sawkins (1984) with a rift of a magmatic arc. In the same geotectonic position there exist a number of epigenetic vein deposits the genesis of which may also be connected with the remobilization of metals in carbonaceous sediments (Hg-Ag-Sb and Pb-Zn-Cu deposits in many places of the North American Cordillera; Jensen 1971, or Co-Ni-Ag-U mineralization in the Andes in Peru; Kobe 1982).

Within the scope of the development of active continental margins the carbonaceous sediments are often deposited in trenches of various types, in and near magmatic arcs, intra-arc basins and back-arc basins. They comprise many submarine-exhalative sulphide deposits, such as, for example, the ore deposits in the Skelefte area in Sweden (Sawkins 1983) and sulphide deposits of "terrigenous geosynclines" of the Soviet authors (Kholodninskoe in Trans-Baikalia and Lineinoide in the Yenisei ridge, Rukhkin 1980).

3. Mineralization of the anoxic sediments of collision margins

The carbonaceous sediments of collision margins may be divided into "inherited" ones, i.e. formed in other tectonic regimes, and formations produced during the collision itself. An example of mineralization in the inherited carbonaceous formations may be the metamorphogenic uranium deposits (Ronnenburg, Germany; Rybalkov 1965) or gold deposits (Sukhoi Log, Muruntau, USSR; Buryak 1976). The parent rocks of these gold deposits were evidently the carbonaceous sediments of "terrigenous geosynclines" corresponding to the back-arc basins of active continental margins (Rukhkin 1980); the genesis of metamorphogenic mineralization may tentatively be ascribed to the collison of the island-arc with the continent. The remobilization of metals in the collision environment may also serve for an explanation of a number of epigenetic Sb-Hg-As ore deposits in Yugoslavia and China, and – under the conditions of higher-grade metamorphism – the Ag-Ni-Co-Bi-Sb deposits in southern England and in the Krušné hory Mts. (Badham 1976), and uranium deposits in the graphitized shear zones in Bavaria (Dill 1985).

The carbonaceous formations proper of active margins are accumulated in the foreland (molasse) basins and margian (flysch) basins and in the intermontane troughs. They are the host rocks of some uranium deposits of the infiltration type (Turner 1985).

4. Mineralization of the anoxic sediments of passive continental margins

The anoxic formation of passive continental margins are mostly formed from shallow-water sediments and often contain increased amounts of uranium, vanadium and other metals which, however, usually do not attain an economic concentration. Organic carbon, together with silicites, phosphates and dolomite, accumulated primarily in zones of upwelling. This type of mineralization is represented, for example, by increased U and V contents in the Phosphoria Formation (Heckel 1977).

5. Mineralization of the anoxic sediments of pericratonic and intracratonic basins

The anoxic sediments of pericratonic and intracratonic basins whose origin is apparently connected with eustatic movements and changes of the level of the world ocean host a number of deposits of the uranium- and vanadium-bearing black shales, such as U-bearing Chattannoga shales (Suppe 1985) V-bearing shales of Estonia (Getseva et al. 1981) and Lower Paleozoic V-bearing schists of Kazakhstan (Kholodov 1968). Mitchell and Garson (1981) range to this group also the U deposits of "unconformity type" associated with the graphitized shear zones.

6. Mineralization of the anoxic sediments of continental rifts and aulacogens

Robbins (1983) was among the first who noticed a high ore potential and mutual contingency of the occurrence of carbonaceous sediments and several types of mineralization in continental rifts and aulacogens. In this geotectonic environment the following deposits are most significant: deposits of copper-bearing black shales, submarine-exhalative Pb-Zn deposits in sediments (deposits of SEDEX type), submarine-exhalative ores of the Lahn-Dill type, metamorphogenic gold deposits and various types of epigenetic vein deposits of Co-Ni, Pb-Zn, Sb-Hg and As ores. The origin of the last ones may be connected with the remobilization of metals in anoxic sediments by the effects of the thermal front of intrusive rift complexes.

Most deposits of copper-bearing shales date from the earliest stage of the development of rift systems, occurring in carbonaceous sediments of shallow-water rift complexes (Permian deposits of Europe, deposits of the Roan group in Zambia; Sawkins 1984); the deposits produced during the final (inactivation) stage of the rift are subordinate (White Pine; Ensign et al. 1968).

On the contrary, the submarine-exhalative Pb-Zn and barite deposits are connected with the advanced stage of the rift structure development (Sawkins 1984). Mineralization occurs both in shallow-water sediments (Mount Isa and McArthur River deposits in Australia; Dunnett 1976; Raybould 1976; Devonian Rammelsberg and Meggen deposits in Germany; Hannak 1980; Krebs 1981) and deep-water complexes (Sullivan, Canada; Sawkins 1976; Broken Hill, Australia; Stevens et al. 1980). The iron ore deposits in the Lahn and Dill areas, Germany, and a number of manganese ore deposits (Batesville) are also of submarine-exhalative origin. The increased heat flow in the region of rifts and aulacogens often causes heating of buried waters and remobilization of sulphur and trace elements in black shales. As a result, veinlet-disseminated deposits of uranium (Gabelman 1977; Robbins 1983) and possibly also of gold are produced (Abitibi zone in Canada; Groves and Batt 1966, or Ballarata, Bendigo and Wedderburn deposits in Australia; McAndrew 1965). The genesis of the Kongsberg deposit of Co-Ni-As-Ag ores in Norway (Bugge 1944) and of vein Pb-Zn ores in West Africa may be related to such processes (Upkong and Olabe 1979).

Distribution of some mineralization types of carbonaceous formations during the geological history of the Earth

In the geological history of the Earth the origin of mineralization in carbonaceous formations was controlled by irreversible events (development of the atmosphere and biosphere) and reversible processes. During the Upper Proterozoic and Phanerozoic the most important reversible processes were of a tectonic character, which induced a periodic formation of supercontinents and their subsequent fragmentation (Windley 1977, Condie 1982). The recurrent tectonic fragmentation of supercontinents (e.g. Pangea) is mostly thought to be due to the heat-isolation activity and restraint of the heat flow in the Earth's interior by the mass of supercontinents, which led to their partial melting and fragmentation (Anderson 1981). The periods of the origin of supercontinents, their fragmentation in the timespan of the whole-planetary rifting, of the opening of the oceans of Atlantic type and of the following collisions are illustrated in Fig. 3 for the past 1100 Ma, according to Worsley et al. (1984). The periodicity of this cycle predetermines a series of other geological events, such as, for example, the principal orogenic eras (Condie 1976) or changes in the levels of the world ocean. These changes in the Phanerozoic times (Vail et al. 1978) and their interpolation into the Late Proterozoic, inferred from the general laws as expressed by Worsley et al. (1984), are presented in the same figure. It demonstrates that the world ocean level rises markedly always following periods of whole-planetary extensions, i.e. during the opening of the oceans of the Atlantic type. The rise of the oceal level is usually believed to be connected with the thermal extension of the continental crust, with the uplift of oceanic ridges and the deposition of sediments in the new oceans (Heller and Angevine 1985). The same figure shows the distribution of metal reserves in some deposit types whose genesis is mainly limited to carbon-rich sediments (U, V and Cu-bearing shales and submarine-exhalative deposits in sedimentary formations of SEDEX type).

The pattern of U-V shale distribution demonstrates that their origin is connected with the rise of the sea level in the stage of ocean opening (Cambrian and Cretaceous deposits) or with the partial level culminations (Vail's cycles of second order), as is the case of the Devonian Chattanooga Formation or the Permian Phosphoria Formation in the USA. In these periods the ancient eroded peneplanes became flooded, anoxia was induced as a result of the nutrient supply and eutrofication of the water environment, and metals were supplied from the continent or deeper parts of the ocean.

The distribution of the deposits of copper-bearing shales within the range of the Earth's geological history is quite different. Their appearance goes back to the time of a low level of the world ocean before or immediately after the periods of global rift structure opening. In other words, they were formed in the initial continental stage of the rift development or in the final stage of rift inactiva-

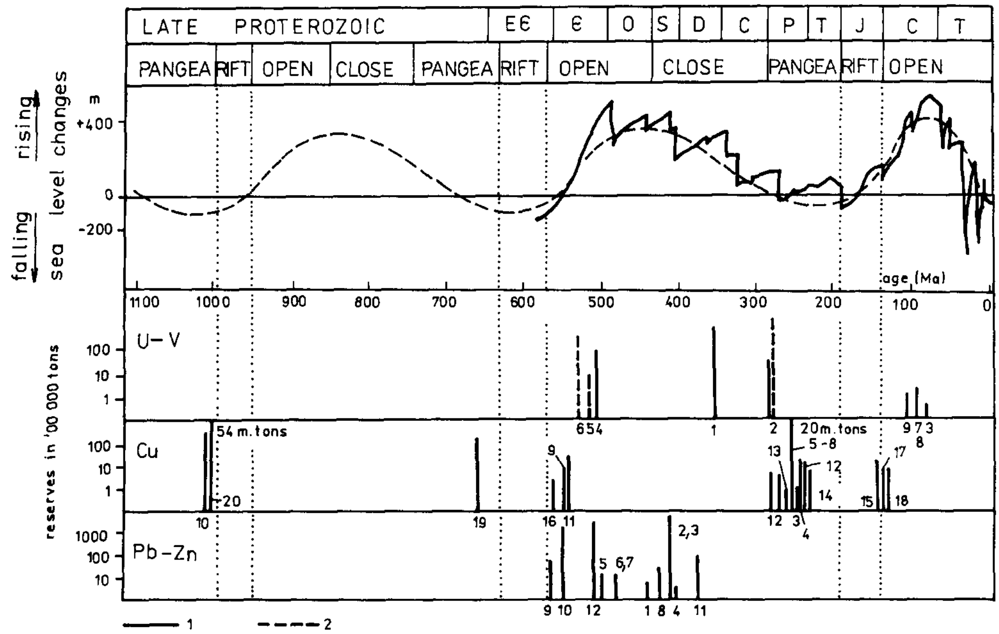

Fig. 3. Distribution of uranium and vanadium deposits in carbonaceous sediments, copper-bearing black shales and Pb-Zn submarine exhalative deposits in carbonaceous sediments in the Upper Proterozoic and Phanerozoic Age in dependence on all-planetary tectonic megacycles and the world ocean water level changes. Stages of planetary rifting, opening of oceans of an Atlantic type, and of supercontinents origin according to Nance et al. 1986, sea-level changes according to Vail et al. 1978. Resources of individual deposits according to Lážnička 1985. Deposits of uranium- and vanadium-bearing black shales: *1* Chattanooga, USA; *2* Phosphoria formation, USA; *3* Recife-Olinda, Australia; *4* Alum shales, Sweden; *5* Baikonur, USSR; *6* Talass-Karatau, USSR; *7* Joussofia, Morocco; *8* Khourigba, Morocco; *9* Calinda, Morocco. Deposits of copper-bearing black shales: *1* Creta, USA; *2* Mangum, USA; *3* Dona Brasilia, Peru; *4* Kirovsk, USSR; *5* Richelsdorf, Germany; *6* Mansfeld, Germany; *7* Zajaczik, Poland; *8* Sieroszowice, Poland; *9* Yenisei, USSR; *10* White Pine, USA; *11* Lena, USSR; *12* Myngyshalk, USSR; *13* Dzirgalan, USSR; *14* Luchang, China; *15* Yunan depression, China; *16* Talate d'Ouamame, Morocco; *17* Ain Sefra, Morocco; *18* Cachoeivas, Angola; *19* Burra, Australia; *20* Deposits in Zimbabwe (Roan-Antelope, Mufulira, Chambishi and others). Submarine exhalative Pb-Zn deposits in carbonaceous sediments: *1* Deposits in Sardinia, Italy; *2* Meggen, Germany; *3* Rammelsberg, Germany; *4* Arshinskoe, USSR; *5* Sentein, France; *6* Carboire, France; *7* Arzberg, Austria; *8* Kuchke, Iran; *9* Taro, Japan; *10* Faro-Anvil, Canada; *11* Tom and Jason, Canada; *12* Howard's Pass, Canada. Explanation: *1* Uranium deposits; *2* Vanadium deposits

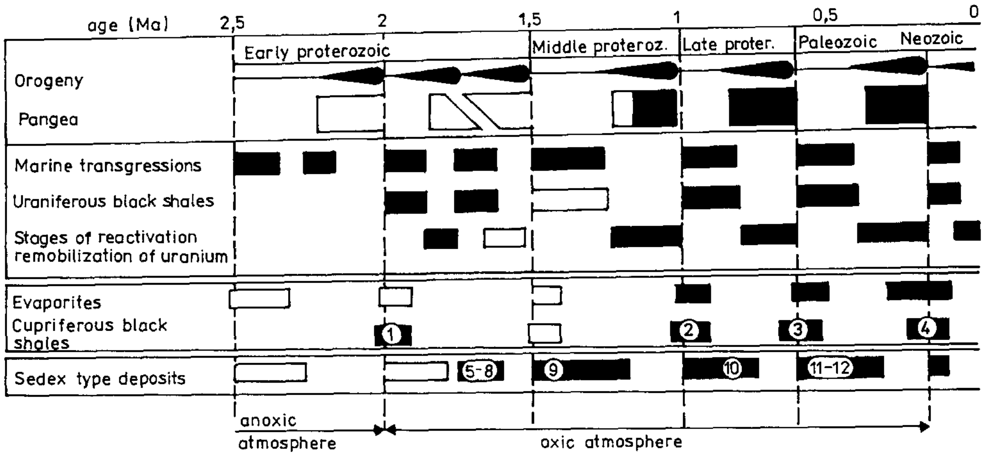

Fig. 4. Model of time distribution of uranium, copper and submarine-exhalative deposits in carbonaceous sediments in the 2.5 Ma timespan. Main stages of orogeny, stages of all-planetary rifting (dot and dash line), timespan of supercontinents origin, and main transgression stages according to Nance et al. 1986. Reactivation and mobilization stages of uranium according to Robertson et al. 1978. Explanation: Deposits of copper-bearing black shales: *1* Udokan, USSR; *2* White Pine, USA and deposits in Zimbabwe; *3* Burra, Australia and Yenisei, USSR; *4* Mansfeld, Germany, Sieroszowice, Poland and several others. Pb-Zn submarine-exhalative deposits; *5* Broken Hill, Australia; *6* Lady Loreta, Australia; *7* McArthur, Australia; *8* Mt. Isa, Australia; *9* Sullivan, Canada; *10* Ducktown, USA; *11* Meggen, Germany; *12* Rammelsberg, Germany. *Open oblongs:* hypothetic stages and processes

tion, or through the processes of extraction and remobilization of metals by buried brines under the conditions of load metamorphism of sediments.

The chronologic distribution of submarine-exhalative Pb-Zn deposits in carbonaceous sediments differs from that of copper-bearing black shales. Their distribution is independent of the periods of the whole-planetary rifting and their origin may tentatively be put into connection with the coincidence of local extension structures with the intervals of total ocean anoxia at the beginning of the Cambrian, in the Ordovician and the Lower and Upper Devonian (Goodfellow 1987).

The absence of similar Pb-Zn deposits in the Mesozoic and Tertiary may be explained as due to very short anoxic intervals in these eras (< 5 Ma) relative to the Lower Paleozoic (15–20 Ma; Arthur and Schlanger 1979).

In the periods of longer duration (2.5 Ma) the mineralization processes in anoxic environment were influenced not only by reversible but also by irreversible changes (Fig. 4), the most important of which is the origin of the oxic atmosphere during the timespan of 2.2 to 2.0 Ma. It was only this event which made possible the mobilization of uranium, vanadium and copper in weathering processes. Therefore, the appearance of highly increased uranium and vanadium contents in the carbonaceous sediments during the interval of 2.8 to 2.1 Ma is not fortuitous (Robertson et al. 1978; Toens 1981; Belevcev and Danceva 1985), in the same way as the oldest mineralization of copper-bearing shales (Udokan deposit, USSR; Samonov and Pozharski 1977). Figure 4 also presents the periods of principal orogeneses, according to Condie (1976), and the assumed periods of the origin of supercontinents, their fragmentation and of marine transgressions, according to Nance et al. (1986). The periods of the whole-planetary rifting are expressed by a dashed line. The main periods of the occurrence of vanadium and uranium-bearing black shales, according to Kříbek (1989), agree in time with the intervals of marine transgressions, similarly as in the preceding figure. In contrast, the dates of the genesis of the major part of epigentic uranium mineralization (deposits of "unconformity type" in the early formations and of metamorphic and vein types in the later formations) correspond with the periods of major orogeneses. This supports the idea of Belevcev and Danceva (1985) that uranium accumulated in an anoxic environment and becomes a protore in the next stages of the tectono-magmatic reactivation.

Of interest is the relationship between the distribution of copper-bearing black shales and the occurrence of principal evaporite formations, which is apparent in Fig. 4. The genesis of large evaporite deposits in the rift structures after their flooding by sea is universally accepted (Mitchel and Carson 1981). This implies that the presence of evaporites is a prerequisite for the origin of this type of mineralization.

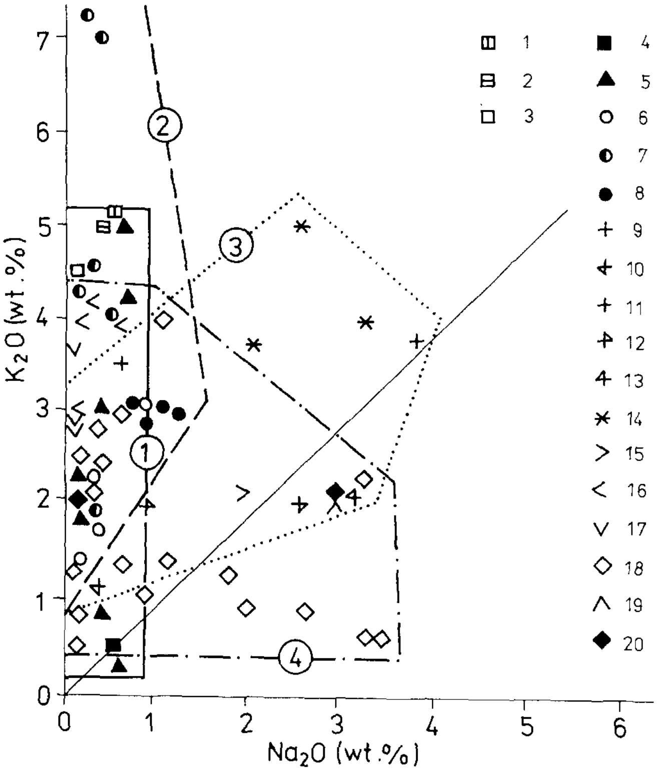

Fig. 5. K_2O–N_2O plot of uranium- and vanadium-bearing carbonaceous sediments (1), copper-bearing carbonaceous sediments (2), oil shales without mineralization (3) and carbonaceous sediments that host submarine-exhalative Pb-Zn mineralization (4). Explanation: *1–5* Uranium- and vanadium-bearing black shales: *1* Alum shales, Sweden; *2* Chattanooga shales, USA; *3* Estonian uranium-bearing black shales, USSR; *4* Julia Creek Formation, Australia; *5* Cambrian uranium and vanadium-bearing shales of China. *6–8* Copper-bearing black shales: *6* Kupferschiefer, Poland; *7* Cu deposits in Zimbabwe; *8* Kapunda deposit, Australia. Oil shales without mineralization: *9* Kimmeridge Formation, England; *10* Mowry Formation, USA; *11* Green River Formation, USA; *12* Kreyenhagen Formation, Denmark; *13* Monterey Formation, USA; *14* Irati Formation, Brazil. *15–20* Carbonaceous sediments that host submarine-exhalative Pb-Zn deposits: *15* Outokumpu, Finland; *16* Stekkenjok, Sweden; *17* Woodlawn, Australia; *18* Submarine-exhalative Pb-Zn deposits of Karelia, USSR; *19* Kambalda, Australia; *20* Yukon submarine-exhalative deposits, USA. According to Kříbek 1989

Lithologic criteria of the origin of mineralization in the anoxic sediments

Of great importance for the appreciation of the ore-bearing potential of carbonaceous sediments is the study of their chemical composition. In Fig. 5 there is one of many diagrams used for this purpose, i.e. the K_2O/Na_2O plot, determined in the selected ore-bearing types of aleuropelites. The figure demonstrates that the sediments with high organic carbon contents but lacking mineralization ($C_{org} > 5\%$, oil shales) cover an extensive field with a wide range of K_2O/Na_2O values. In contrast, the uraniferous carbonaceous sediments (Fig. 5, field 1) or copper-bearing black shales (field 2) are characterized by high K_2O/Na_2O values. These sediments are dominantly illitic and their plausible sources are continental weathered rocks. High values of the ratio provide evidence of the absence of basic tuffaceous material, whose existence in sedimentary rocks is expressed by high Na_2O values and the variability of the K_2O/Na_2O ratio. The predominance of potassium over sodium and the high homogeneity of this ratio demonstrate that the U, Cu and V mineralizations

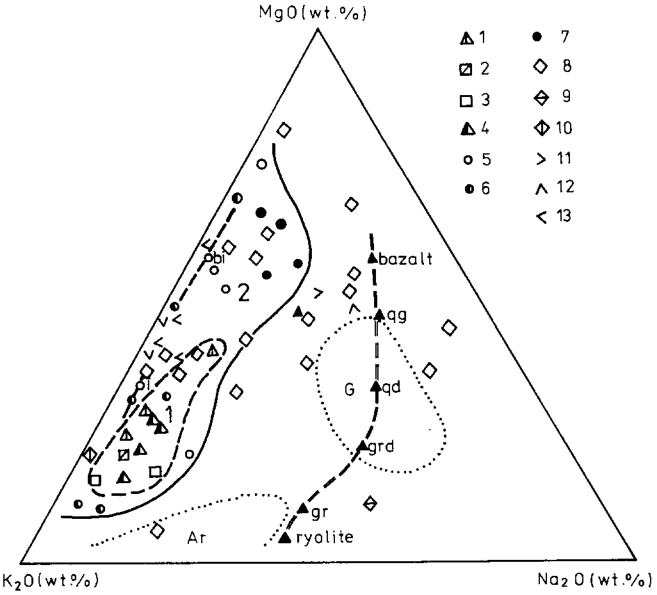

Fig. 6. $K_2O-MgO-Na_2O$ plot of uranium- and vanadium-bearing black shales (*field 1*), cupriferous black shales (*field 2*) and carbonaceous sediments that are host rocks of submarine-exhalative sulphidic deposits (field is not indicated with regard to considerable dispersion of data). In the plot the trend line of some volcanic and magmatic rocks, greywackes, arkoses and sandstone are indicated. Explanation: *1–4* Uranium- and vanadium-bearing black shales: *1* Alum shales, Sweden; *2* Chattanooga shales, USA; *3* Estonian uraniferous black shales, USSR; *4* Vanadiferous black shales of Cambrian, China. *5–7* Copper-bearing black shales: *5* Black shales of Zimbabwe; *6* Kapunda deposit, Australia; *7* Kupferschiefer, Poland. *8–12* Black shales which host submarine-exhalative Pb-Zn deposits: *8* Submarine-exhalative deposits of Karelia, USSR; *9* Deposits of Pilbara block, Australia; *10* Submarine-exhalative deposits of Yukon area, USA; *11* Outokumpu, Finland; *12* Kambalda, Australia; *13* Stekenjokk, Sweden. According to Kříbek 1989. *G* – graywackes; *Ar* – arkoses, sandstones; *bi* – biotite; *g* –gabbros; *qg* – quartz gabbros; *qd* – quartz diorites; *gr* – granites; *grd* – granodiorites; *i* – illite

develop without a direct dependence on volcanic activity. For comparison, the K_2O/Na_2O ratios in black shales (which are host rocks or accompany the submarine-exhalative sulfide mineralization) are plotted in the same figure. In this case the ratio of the two oxides is highly variable, being controlled by the mixing of potassium-rich continental weathered rocks with the products of synchronous basin volcanism. These results are also confirmed by the K_2O-MgO-Na_2O ternary diagram (Fig. 6). The figure additionally indicates that the U- and V-bearing anoxic sediments have essentially lower MgO contents relative to the Cu-bearing black shales.

Conclusions

From the above overview it may be summarized that sediments and metasediments of the anoxic environment are, with respect to their chemical properties, an unusually appropriate environment for the location of the most varied mineralization types.

During sedimentation anoxic sediments become a reservoir of trace elements and sulfur. The accumulated metals, however, attain economically significant concentrations only under very specific conditions, e.g. when the sediments were enriched in metals by submarine hydrothermal activity.

The economically important types of deposits form only subsequent in the processes of diagenetic, metamorphic or infiltration remobilization under favourable structural conditions. Therefore most of the ore deposits of carbonaceous formations can be designated as polygenetic.

The carbonaceous formations participate in their formation in two ways: directly, e.g. by sorption of metals by organic matter, by the formation of organometallic complexes or by the reduction of ore-bearing solutions; and indirectly, when the already formed deposits (chiefly sulfidic), are protected in the anoxic environment from subsequent oxidation and destruction.

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