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GEOCHEMISTRY AND MINERALOGY OF PROTEROZOIC METAL-RICH BLACK SHALES FROM THE BOHEMIAN MASSIF, CZECH REPUBLIC, WITH A DESCRIPTION OF POSSIBLE NEW MOLYBDENUM SELENIDE AND TELLURIDE PHASES

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Abstract

The black shales associated with basic volcanogenic rocks at the Hromnice locality, in the Barrandian Upper Proterozoic (Bohemian Massif, Czech Republic) show heavy-metal enrichment. Maximum values of 0.4% Zn, 0.1% Cu, 0.12% Ni, 0.1% Cr, 0.06% As, 0.02% Mo, 15 ppm Ag and 132 ppb Au are compared with normal black shales of the monotonous sequence. Detailed mineralogical investigations of metal-rich facies reveal the following assemblage of ore minerals: granular and framboidal pyrite, sphalerite, chalcopyrite, molybdenite and galena. Rare native gold, berthierite, clausthalite, and two new minerals, molybdenum selenide (Mo_3Se_4) and molybdenum telluride (Mo_3Te_4), were identified. The latter form small grains (about 4 μm) closely associated with abundant organic carbon and framboidal pyrite. Monazite, xenotime, rhabdophane and ningyoite were recognized as accessories in addition to rutile, zircon, the Cd-carbonate otavite and anglesite. Molybdenum values are often elevated in many occurrences of black shale worldwide. Mo enrichment is commonly associated with organic matter and framboidal pyrite, manifest as jordisite and only sporadically as molybdenite. "Castaingite" is very rare. The discovery of a new molybdenum selenide and a molybdenum telluride in the Proterozoic metal-rich black shales of the Bohemian Massif brings new important data on mineralogy of molybdenum in low-temperature hydrothermal (volcanogenic) processes in anoxic environment.

Keywords: new mineral species, molybdenum selenide, molybdenum telluride, metal-rich black shales, geochemistry, electron-microprobe data, sulfide mineralogy, Bohemian Massif, Czech Republic.

Sommaire

Les shales noirs associés aux roches volcanogéniques basiques à Hromnice, dans la séquence protérozoïque barrandienne du massif bohémien, en République Tchèque, font preuve d'un enrichissement important en métaux (jusqu'à 0.4% de Zn, 0.1% de Cu, 0.12% de Ni, 0.1% de Cr, 0.06% d'As, 0.02% de Mo, 15 ppm d'argent et 132 ppb d'or) en comparaison des shales noirs normaux de la série monotone. Une étude approfondie de la minéralogie des facies métallifères a mis en évidence l'assemblage suivant: pyrite granuleuse et framboïdale, sphalérite, chalcopyrite, molybdénite et galène. Parmi les espèces plus rares sont: or natif, berthierite, clausthalite, et deux espèces nouvelles, un séléniure et un tellurure de molybdène, Mo_3Se_4 et Mo_3Te_4, respectivement. Ces deux espèces se présentent en grains très petits (4 μm, environ), étroitement associés au carbone organique et à la pyrite framboïdale, qui sont abondants. Les phosphates monazite, xénotime, rhabdophane et ningyoïte sont accessoires, tout comme rutile, zircon, otavite (carbonate de Cd) et anglésite. Il semble que des teneurs élevées en Mo soient courantes dans de telles roches. Cet enrichissement en Mo, étroitement associé à une accumulation de matière organique et de pyrite framboïdale, est exprimée sous forme de jordisite, et plus sporadiquement sous forme de molybdénite. La "castaingite" est rarissime. La découverte des deux espèces nouvelles dans ces shales noirs apporte des précisions nouvelles sur l'expression minéralogique du molybdène dans des milieux volcanogéniques hydrothermaux à faible température.

(Traduit par la Rédaction)

Mots-clés: nouvelles espèces minérales, séléniure de molydène, tellurure de molydène, shale noir métallifère, géochimie, données à la microsonde électronique, minéralogie des sulfures, massif bohémien, République Tchèque.

INTRODUCTION

The International Geological Correlation Programme IGCP #254 on "Metalliferous Black Shales" has generated interest in the mineralogy and the distribution of metals in black shales. Special attention has been given to a new type of Mo–Ni–PGE–Au ore deposit recently identified in

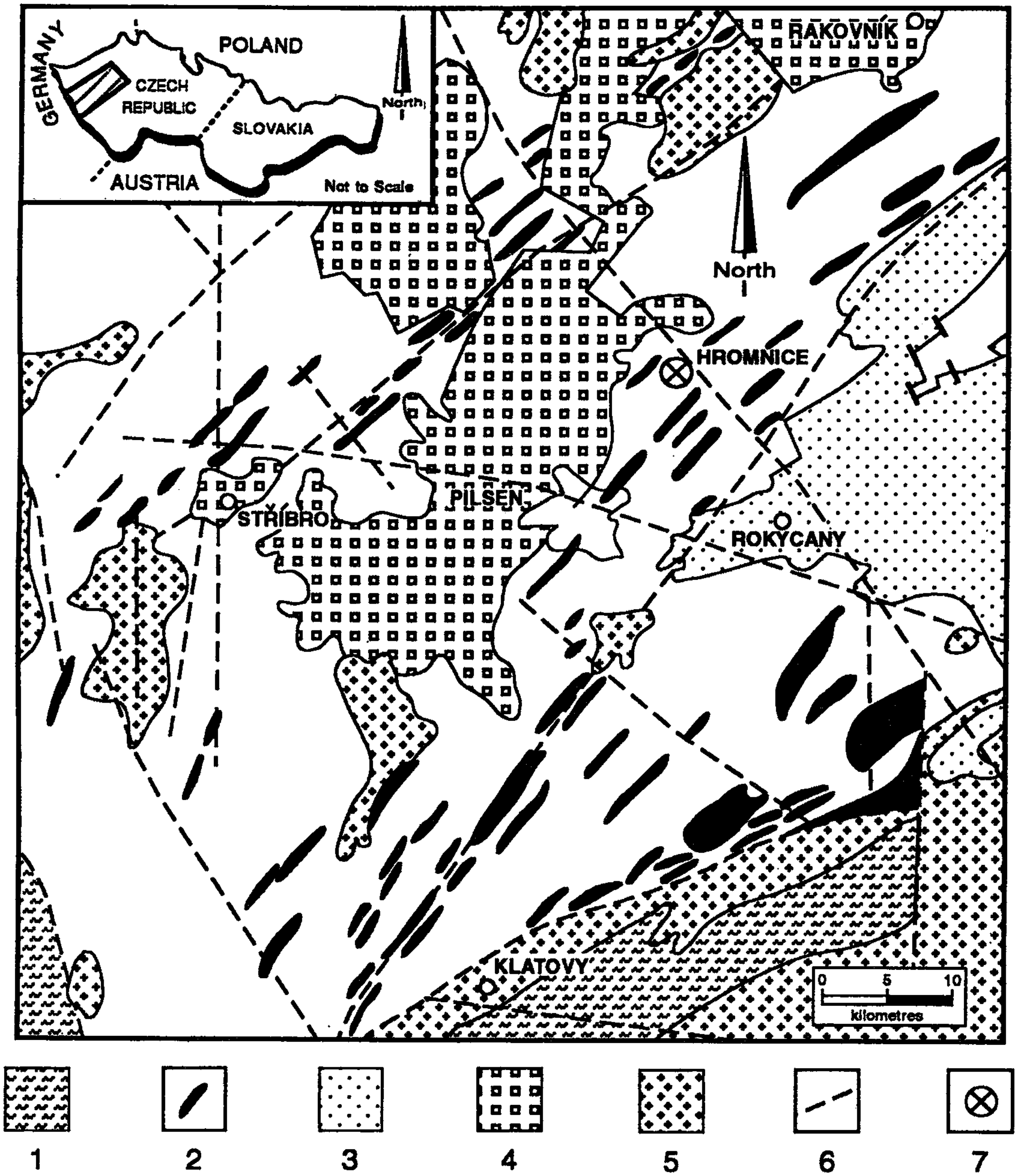

FIG. 1. Geological and tectonic map of the Barrandian Proterozoic, with location of Hromnice n. Pilsen locality (after Kovalova 1991). Symbols: 1 Moldanubicum (gneiss and migmatites), 2 Upper Proterozoic series with basic volcanic rocks, 3 Lower Paleozoic sedimentary series, 4 Permo-Carboniferous and Tertiary platform sediments, 5 granitic rocks (Variscan), 6 deep-seated faults (geophysically indicated), 7 locality studied.

southwestern China (Chen *et al.* 1982, Fan 1983, Chen 1988, Coveney & Chen 1991), and also in Canada (Hulbert *et al.* 1990), Czechoslovakia (Pašava 1990), Finland (Loukola-Ruskeeniemi *et al.* 1991), U.S.A. (Coveney & Chen 1989) and the former U.S.S.R.

A detailed mineralogical investigation of Upper Proterozoic metal-rich black shales from a 300-m-deep (HRM–3) borehole drilled by the Czechoslovak Uranium Enterprise at the Hromnice locality, Bohemian Massif, Czech Republic, has resulted in the discovery of two new Mo-bearing mineral phases described in this paper.

Geological and Metallogenic Framework

The Hromnice locality is situated in western Bohemia, about 12 km northeast of Pilsen, in a classical region of the Barrandian Upper Proterozoic (Fig. 1). This geological unit belongs to the Moldanubicum of the Variscan Belt of central Europe and consists of a complex of eugeosynclinal sandy and silty wackes and abundant submarine mafic flows and pyroclastic material. The Proterozoic sequence exhibits a simple structure, with alternating anticlinal and synclinal NE–SW-trending belts (Holubec 1966). Isolated or semi-isolated marine basins with limited circulation of water enhanced deposition of black shale. Two different tectonic models have been proposed for the basin: a rift model (Pouba & Zoubek 1986) and a collisional model (Behr *et al.* 1984).

Low-grade metamorphism has affected the host rocks of the mineral occurrence, which is located within the Teplá-Barrandian metamorphic region, a classical terrane of the Cadomian regional metamorphism in the Bohemian Massif.

The whole region has a long history of mining, and pyritic black shales represent one of the most widespread types of Precambrian mineralization in the Bohemian Massif. They were intensively worked at many locations from the 16th through 19th centuries for the production of sulfuric acid. At the best-known locality, Hromnice, 766 000 t of ore were mined between 1833 and 1872, and only an open pit (190 × 130 × ~ 50 m) remains.

Systematic geochemical investigations made in the Bohemian Massif by the Czech Geological Survey in Prague at a scale of 1: 50 000 has shown several anomalies in stream sediments (Zn, Cu, Ni, Mo, Pb, Ag, *etc.*) on Barrandian Proterozoic bedrock. A hole (HRM–3) drilled to test one such geochemical anomaly 3 km northwest of the Hromnice mine site intersected alternating black shales and basic tuffs, and showed that the source of the anomaly was in metal-rich black shales (Pašava *et al.* 1989). Samples collected during the above project and from a nearby borehole HRM–1 form the basis of this paper.

Methods

Geochemical and mineralogical studies of black shale samples were carried out. Samples from the HRM–1 and HRM–3 boreholes were homogenized in laboratories of the Research Institute of the Czechoslovak Uranium Enterprise in Straz n. Ralsko. The trace elements were determined by the X-ray fluorescence method on a Philips TW 1404 instrument in laboratories of the UNIGEO Enterprise in Brno (analyst: Ing. Janáčkova). Geochemical results for the Upper Proterozoic black shales are summarized in Table 1.

TABLE 1. DISTRIBUTION OF SELECTED TRACE ELEMENTS IN THE PROTEROZOIC NORMAL BLACK SHALES (HRM-1 BOREHOLE) AND METAL-RICH FACIES (HRM-3 BOREHOLE) AT HROMNICE

Drill hole	HRM-1 n = 33	HRM-3 n = 17		Ave. black shale
Element	x	x	x_{max}	
Zn (ppm)	383	950	4170	<300
Cu	93	256	1044	70
Ni	88	293	1200	50
Mo	33	67	200	10
Pb	25	25	72	20
As	56	148	597	n.d.
Co	12	21	46	10
Cr	156	317	1230	65
V	570	938	2020	100
Ag	0.38	2.3	15	1

n = number of samples, x = arithmetic mean, x_{max} = maximum value, n.d. = not determined. Average black shale: data from Vine & Tourtelot (1970).

Only three quantitative analyses of each of the possible new Mo-minerals were done; results are listed in Table 2. There was no drysdallite ($MoSe_2$) sample

TABLE 2. RESULTS OF ELECTRON-MICROPROBE ANALYSES OF Mo MINERALS FROM HROMNICE

	Mo selenide			Mo telluride		
	1	2	3	4	5	6
Mo wt.%	44.39	46.54	46.27	33.94	33.56	33.21
Te				62.06	63.71	58.56
Fe	0.80	0.66	1.24	1.04	0.74	1.18
Si	2.14	0.84			0.86	0.33
Se	44.46	47.44	46.76			
Al	2.21	1.69				0.32
Cu	1.15	1.06	1.20			
K						0.21
Ca						2.90
Ti						0.33
Total	95.15	98.23	95.47	97.04	98.87	97.04

Inferred stoichiometry: 1) $Mo_{3.28}Se_{4.00}$, 2) $Mo_{3.23}Se_{4.00}$, 3) $Mo_{3.26}Se_{4.00}$ 4) $Mo_{2.94}Te_{4.00}$, 5) $Mo_{2.80}Te_{4.00}$, 6) $Mo_{3.02}Te_{4.00}$. Ideal formulae: Mo_3Se_4 Mo_3Te_4.

available for a comparative study. Physical properties such as color, reflectivity, hardness, X-ray data, *etc.* could not be determined because of the small grain-size. Quantitative analyses of mineral phases were performed at 20 kV on an EDAX–LINK system and using internal analytical standards in the Research and Development Institute in Stráž p. Ralskem (analyst: Dr. P. Sulovský).

Geochemistry and Origin of Black Shales

Metal-rich black shales from the Hromnice locality, Bohemian Massif hosted in the volcanosedimentary sequence (HRM–3 borehole) are strongly enriched in Zn, Cu, Ni, As, Cr, V, Ag if compared to "normal" black shales of the abandoned mine (HRM–1 borehole) and to "normal" black shale of Vine & Tourtelot (1970). The maximum concentrations, 0.4% Zn, 0.1% Cu, 0.12% Ni, 0.1% Cr, 0.2% V, 0.02% Mo, 15 ppm Ag and 132 ppb Au, are very close to those (0.54% Zn, 0.26% Ni, 0.15% Cu, 0.01% Mo and 0.006% Se) reported by Loukola-Ruskeeniemi *et al.* (1991) for the Precambrian metal-rich black schists of the Talvivaara deposit in eastern Finland.

Metal-rich black shales at the Hromnice locality originated under specific conditions (Pašava 1990, 1991). In partially isolated basins, an alternation of oxidized and reduced layers within the water column may have existed. The metals, contributed from volcanogenic–hydrothermal exhalations, could have been fixed either as organometallic complexes by abundant organic matter or could have precipitated directly as sulfides, selenides or tellurides. During diagenesis and low-grade metamorphism, unstable organometallic bonds disintegrated, and ore minerals were recrystallized and remobilized into newly formed quartz, carbonate and quartz–carbonate veinlets.

Distribution and Mineralogy of Molybdenum and Selenium in Different Metal-Rich Black Shales

Molybdenum is commonly enriched in anoxic or organic-matter-rich sediments. There are two major mechanisms for its accumulation. The first is coprecipitation of Mo-sulfides with FeS or other metal sulfides. The occurrence of Mo-sulfide in sediments was early established by observation of molybdenite and jordisite (MoS_2) and later "castaingite" ($CuMo_2S_5$) in the Permian Kupferschiefer of Germany (Schüller & Ottemann 1963, Fleischer & Mandarino 1991). The second is fixation of Mo by adsorption, reduction and other mechanisms in organic phases, especially in black shales (Wedepohl 1972). Gavshin (1991) suggested that molybdenum in marine organic-matter-rich rocks precipitated mostly from the ocean waters in an H_2S-rich reducing environment. On the other hand, elevated concentrations of molybdenum, together with anomalous levels of zinc, iron and vanadium, have been found in modern hydrothermal springs from the Playton on Salitre, in the Ahuachapan thermal area in Salvador (Barnes 1979).

Tellurium, selenium and sulfur in nature are closely associated and commonly found in pyritic ores. In contrast to selenium, which substitutes isomorphously for sulfur in structures, tellurium forms distinct mineral species present as microscopic segregations in the sulfide minerals (notably in copper sulfides). The deposition of tellurium and selenium in concentrations of economic significance is associated with the formation of magmatic and postmagmatic sulfides (Fairbridge 1972).

The average molybdenum content in shales ranges from 2 ppm (Vinogradov 1962), through 2.6 ppm (Turekian & Wedepohl 1961) and 10 ppm (Vine & Tourtelot 1970), to 134 ppm in SDO–1 (USGS Devonian Ohio Shale from Kentucky), which has been proposed as a "normal black shale" (Huyck 1991). Only limited data are available on the average distribution of Se in black shales; the midpoint of the range for Huyck's (1991) normal black shales is 4.9 ppm. In low-calcium marine black shales, the mean concentration of Se, 5.6 ppm, has been established by Quinby-Hunt *et al.* (1989). The Lower – Middle Cambrian and Upper Jurassic black shales from the Siberian platform contain 12.7 ppm and 26.0 ppm Se, respectively (Gavshin 1991). The tellurium content of graywackes and shales is less than 0.1–1 ppm (Wedepohl 1972), and there are no other data available on its distribution from metal-rich black shales.

The maximum concentrations of Mo (18.28 wt.%) known in shales occur in the Lower Cambrian marine polyelement black shales of southern China (Fan 1983). The mine at Tian Eshan, close to Zunyi in Guizhou province, is the only one in the world in which molybdenum is recovered from black shales. Sulfide beds contain about 4% Mo, up to 4% Ni, 2% Zn, 0.01–0.04% Se, 0.7 ppm Au, 50 ppm Ag, 0.3 ppm Pt, 0.4 ppm Pd, 30 ppb Ir. These beds originated as exhalites from low-temperature submarine springs (Coveney & Chen 1991). Their mineralogy is complex. Molybdenum occurs as jordisite, and ore minerals include framboidal and granular pyrite, the Ni sulfides millerite, vaesite, violarite, polydymite and pentlandite, and gersdorffite. Selenium is bound in pyrite, according to Fan (1983). Recent studies by Grauch *et al.* (1991) showed the presence of a Hg selenide phase (probably tiemannite).

High concentrations of molybdenum (0.716 wt.%) have been described by Hirner *et al.* (1990) from the Upper Cretaceous Julia Creek Oil Shale of the Eromanga Basin, Queensland, Australia. Observations by electron microscopy revealed a presence of cyanobacteria with Mo. The authors concluded that molybdenum is associated with V, Ni, Cu and B in the mobile organic fraction.

Enriched Mo values, ranging from 0.14 to 0.29%, with the selenium concentrations in the range 0.06 – 0.24%, have recently been reported by Hulbert *et al.* (1990) from epithermal Ni–Zn–PGE mineralization hosted by the Devonian black shales of the Selwyn Basin in the Yukon. Selenium is selectively partitioned into vaesite and pyrite, respectively, whereas molybdenum occurs in some of the organic matter and as a Mo sulfide phase (probably jordisite: Grauch *et al.* 1991).

A close relationship of molybdenum and selenium with organic matter also has been documented in the Middle Pennsylvanian Mecca Quarry Shale Member of the Linton Formation in Indiana by Coveney *et al.* (1987) and in the Upper Pennsylvanian Stark Shale Member of the Dennis Limestone in east-central Kansas by Desborough *et al.* (1991). For example, in Indiana, near-shore Desmoinesian black shales typically contain in excess of 1000 ppm Mo and 162 ppm Se, and similar values for Mo occur in near-shore facies in South Dakota (Coveney *et al.* 1991). Mo-rich shales also have abundant Zn, U and V values. Framboidal pyrite and marcasite are the most common sulfide minerals. The main hosts of Zn, Cu and Pb are sphalerite, chalcopyrite, and clausthalite (PbSe), respectively. Mo is associated with pyrite framboids and organic-matter-rich layers within the groundmass. Neither molybdenite nor jordisite has been observed (Coveney & Glascock 1989).

Sequential chemical analyses and electron-microprobe studies of the Mississippian metal-rich New Albany Shale of southern Indiana have shown that Mo (average 170 ppm) is held as a sulfide (about 70%) and within kerogen (20%). The presence of molybdenite was stronly suggested, although no Mo minerals have been identified. Zn, Cu and Cd occur as sulfide minerals, Pb as selenide, and Ni is distributed between kerogen (about 50%) and sulfide (about 45%) (Ripley *et al.* 1991).

For metal-rich Cambrian Alum Shales in Scandinavia, a very good correlation between Mo and C_{org} has been demonstrated by Leventhal (1991), as well as in the low-temperature Permian copper ores of the Kupferschiefer type in Poland (Mayer & Piestrzynski 1985). In the German Kupferschiefer, "castaingite" may form the interior of the colloidally precipitated globules (Schüller & Ottemann 1963).

Petrography and Mineralogy of Proterozoic Black Shales from the Bohemian Massif

Petrographically, the metal-rich black shales are black metasandstones and siltstones with a laminated structure (an irregular alternation of dark layers rich in organic matter and framboidal pyrite, with lighter layers composed predominantly of volcanoclastic material). There are also numerous younger veinlets and microslump-fragments of quartz, carbonate and quartz–carbonate. The phosphates monazite, xenotime, rhabdophane and ningyoite occur as accessory minerals, in addition to rutile, zircon, the Cd carbonate otavite, and anglesite.

The following mineral assemblage, identified using an EDAX-LINK system, is present: granular and framboidal pyrite, sphalerite and chalcopyrite, and sporadically, galena and molybdenite. Very rarely, native gold, berthierite, clausthalite, a Mo selenide and a Mo telluride were recognized. The results of quantitative analyses of new molybdenum minerals are listed in Table 2.

Granular pyrite

This conspicuous sulfide is irregularly disseminated in rocks. It usually forms anhedral grains (5–150 μm)

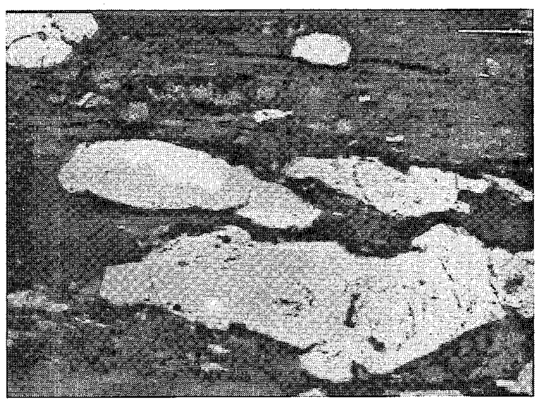

FIG. 2. Granular pyrite (large light xenomorphic grains) with inclusions of chalcopyrite (white spots) bound to quartz–carbonate veinlet in metal-rich black shale from the HRM – 3/53 m drill hole; Hromnice. Scale bar: 30 μm.

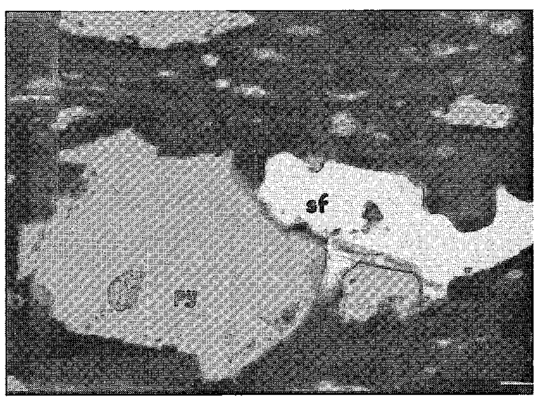

FIG. 3. Granular pyrite (py) intergrown with sphalerite (sf) related to quartz–carbonate veinlet in metal-rich black shale from the HRM – 3/53 m drill hole; Hromnice. Scale bar: 10 μm.

in quartz and quartz–carbonate veinlets, commonly with sphalerite and chalcopyrite inclusions (Figs. 2, 3). It also occurs with framboidal pyrite. The Co/Ni ratio is high in this phase. We interpret this coarse-grained pyrite to have originated from framboidal pyrite by recrystallization. Depletion of Ni in pyrite during its recrystallization and mobilization was demonstrated in the Barrandian Upper Proterozoic by Breiter & Pašava (1985).

Framboidal pyrite

This syngenetic to early diagenetic pyrite, nearly as common as granular pyrite, occurrs mostly as small framboids, with diameter up to 10 μm in organic-carbon-rich layers (Fig. 4), and as disseminations in the groundmass and in microslump-fragments (Fig. 5). The Co/Ni ratio is low.

FIG. 4. Framboidal pyrite disseminated in C_{org}-rich layers in metal-rich black shale from the HRM – 3/85 m drill hole; Hromnice. Scale bar: 3 μm.

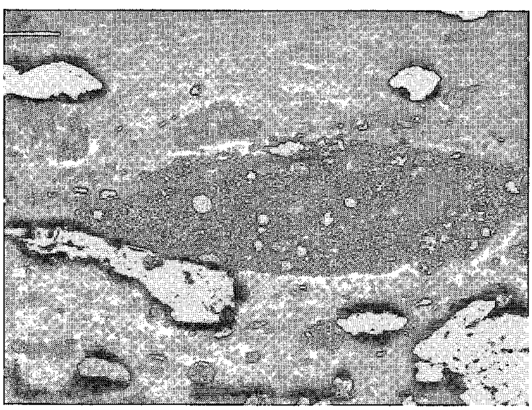

FIG. 5. Framboidal pyrite (white, globular) in greywacke fragment. Granular pyrite (light xenomorphic grains) is mostly associated with quartz veinlets. Metal-rich black shale from the HRM – 3/53 m drill hole; Hromnice. Scale bar: 30 μm.

Sphalerite

Sphalerite is a relatively common sulfide found in a variety of associations. It occurs predominantly as anhedral grains (diameter 5–60 μm) either intergrown with, or forming inclusions (2–40 μm) in, granular pyrite (Fig. 3), generally within relatively late veinlets of quartz and quartz–carbonate. Its chemical composition is similar in both modes of occurrence: Fe values range from 2.5 to 4.5 wt.%, and Cd contents are 0.4 – 0.7 wt.%. Sphalerite occurs more rarely in close association with framboidal pyrite and molybdenite at the boundary between quartz veinlets and the groundmass (Fig. 6). Very small (up to 10 μm) subhedral grains also are present in intergrowths with siderite. They are richer in Fe (7.1 wt.%) and chemically purer than sphalerite associated with framboidal pyrite and molybdenite.

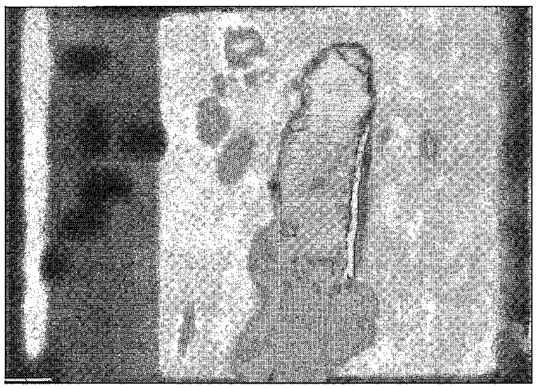

FIG. 6. Framboidal pyrite (deformed smaller globular and larger grey, more massive aggregate in the lower part of the picture) intergrown with sphalerite (larger elongate light grey grain in the upper part of the picture) and molybdenite (lamellar grain) at the boundary between quartz–carbonate vein (left part) and groundmass (right part) in metal-rich black shale from the HRM – 3/53 m drill hole; Hromnice. Scale bar: 10 μm.

Chalcopyrite

This mineral is much scarcer than sphalerite. Only a few anhedral to subhedral grains up to 20 μm were found intergrown with siderite in quartz–carbonate veinlets; rare small inclusions up to 10 μm can be recognized in coarser pyrite (Fig. 2) and sphalerite grains.

Galena

Galena was found as fracture fillings (up to 1 μm in width) in granular pyrite. Some galena contains 17.6 wt.% Se (member of galena – clausthalite group).

Molybdenite

Molybdenite occurs very sparsely as plates (1 × 25 μm) in association with sphalerite and framboidal pyrite (Fig. 6). Only one euhedral grain (1 × 10 μm) intergrown with granular pyrite in younger quartz veinlets was detected (Fig. 7).

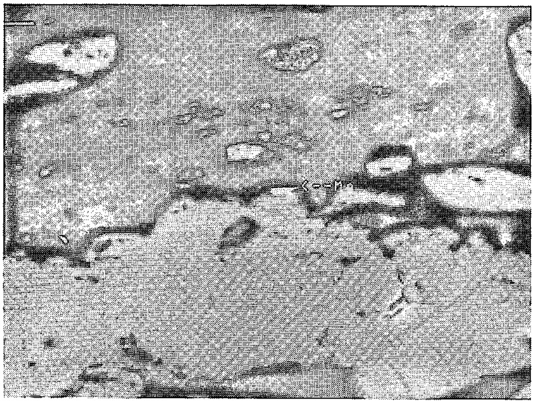

FIG. 7. Granular pyrite (large light grey grains) scarcely intergrown with molybdenite (Mo) related to quartz–carbonate veinlet in metal-rich black shale from the HRM – 3/53 m; Hromnice. Scale bar: 10 μm.

Molybdenum telluride phase

Small (3–4 μm) globular grains of molybdenum telluride (Mo_3Te_4) are bound to the organic matter and framboidal pyrite-rich layers and also occur with granular pyrite and sphalerite (Fig. 8). The results of quantitative analyses are summarized in Table 2. This is the first description of a natural molybdenum telluride. An unnamed nickel telluride phase, Ni_3Te_4, with the same stoichiometry as our Mo telluride, has been identified in the Wellgreen Ni–Cu–PGE deposit, Yukon (L.J. Cabri, oral comm.).

Molybdenum selenide phase

Grains of a molybdenum selenide, Mo_3Se_4 (about 4 μm) are related to framboidal pyrite (Fig. 9). The results of electron-microprobe analyses are listed in Table 2.

The only known molybdenum selenide, drysdallite ($MoSe_2$), has been reported from Kapijimpanga in Zambia (Ramdohr 1980). The mineral trüstedtite, a cubic spinel-type nickel selenide, Ni_3Se_4, with a stoichiometry similar to that of our Mo-selenide phase, has been identified with other Ni selenides in veinlets associated with uranium mineralization from Kuusamo, eastern Finland (Vuorelainen *et al.* 1964). A tellurium selenide, Te_3Se_4, again of the same stoichiometry as our molybdenum selenide, has been described from the Prasodov occurrence, Kurile Island, in the former U.S.S.R., an example of epithermal sulfide – selenide – telluride mineralization (Kovalenker *et al.* 1989). There, the tellurium selenide forms a margin 4–6 μm wide between segregations of clausthalite and native Te, which are intergrown with each other, sylvanite, and naumannite. These fill interstices among quartz grains (Kovalenker *et al.* 1989).

The mineralogy of molybdenum in the Bohemian Upper Proterozoic metal-rich black shales differs somewhat from the above-mentioned examples. Molybdenum-bearing minerals occur both in layers rich in organic matter and in layers rich in framboidal pyrite, in the form of a sulfide (molybdenite), but also as a selenide and a telluride. Considering that the

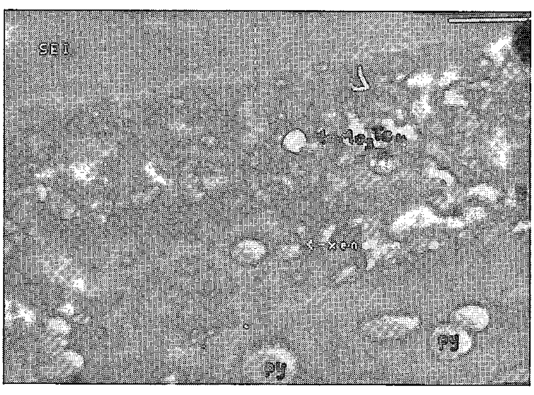

FIG. 8. Small globular grain of Mo-telluride, of inferred stoichiometry Mo_3Te_4, associated with framboidal pyrite in organic-matter-rich layers in metal-rich black shale from the HRM – 3/53 m drill hole; Hromnice. Scale bar: 10 μm.

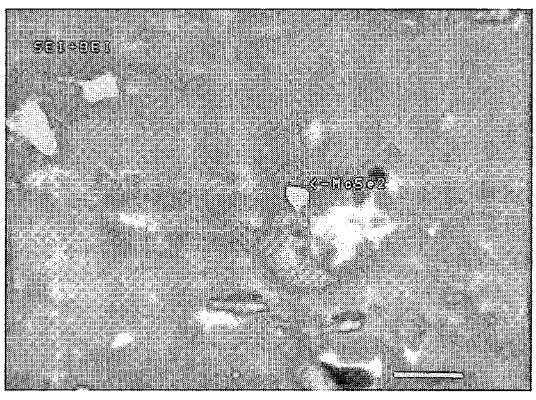

FIG. 9. Small xenomorphic grain of Mo-selenide, of inferred stoichiometry Mo_3Se_4, closely associated with framboidal pyrite in organic-matter-rich horizon in metal-rich black shale from the HRM – 3/53 m drill hole; Hromnice. Scale bar: 10 μm.

Proterozoic metal-rich black shales from the Bohemian Massif originated in the presence of significant submarine volcanic activity, it seems probable that the source of Mo, Se, and Te was low-temperature volcanogenic–hydrothermal springs (Dobeš & Pašava 1990), as proposed for the other metals by Pašava (1991).

Conclusions

As shown, the mineralogy of molybdenum and selenium is very simple in most of world occurrences of metalliferous black shale. The most common carrier of Mo is jordisite, the amorphous molybdenum disulfide, which is generally intimately associated with organic matter and framboidal pyrite. Molybdenite occurs much more rarely, and is usually connected with granular pyrite and other base metal sulfides, *e.g.* sphalerite and chalcopyrite. "Castaingite" is very rare; it has been found only in the copper-rich black shales of Mansfeld, Germany.

Possible new molybdenum selenide (Mo_3Se_4) and molybdenum telluride (Mo_3Te_4) phases have been identified in the Proterozoic metal-rich black shales from the Bohemian Massif. They both form very small grains (about 4 μm) closely associated with layers rich in organic matter and layers rich in framboidal pyrite. The discovery of two possible new Mo-bearing minerals raises new possibilities concerning the mineralogy of molybdenum in low-temperature hydrothermal (volcanogenic) processes in an anoxic environment. To explain sufficiently anomalous concentrations of Mo in world occurrences of black shales and to clarify the role of organic matter in associated processes of mineralization, more attention should be paid to their detailed mineralogical investigations, followed possibly by studies of sulfur isotope geochemistry.

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References

Barnes, H.L., ed. (1979): *Geochemistry of Hydrothermal Ore Deposits* (2nd edition). John Wiley & Sons, New York.

Behr, H.-J., Engel, W., Franke, W., Giese, P. & Weber, K. (1984): The Variscan Belt in central Europe: main structures, geodynamic implications, open questions. *Tectonophys.* **109**, 15-40.

Breiter, K. & Pašava, J. (1985): Distribution of trace elements in black shales and pyrites from Barrandian Upper Proterozoic. *Sbor. III. Cykl. seminar CSVTS, Usti n. Labem*, 63-69 (in Czech).

Chen, Nansheng (1988): The Cambrian hydrothermal sedimentary molybdenum and nickel ore deposits in south China. *In* IAS Int. Symp. on Sedimentology Related to Mineral Deposits (Beijing), 29 (abstr.).

———, Yang, Xiuzhen, Liu, Dehan, Xiao, Xuejum, Fan, Delian & Wang, Lianfang (1982): Lower Cambrian black argillaceous and arenaceous rock series in south China and its associated stratiform deposits. *Mineral. Dep.* **1**(2), 39-51 (in Chinese).

Coveney, R.M., Jr. & Chen, Nansheng (1989): Nickel and molybdenum-rich black shales of southern China: a new ore type with possible analogues in the Pennsylvanian of the U.S.A. *Int. Geol. Congress, 28th* **1**, 335-336 (abstr.).

——— & ——— (1991): Ni–Mo–PGE–Au-rich ores in Chinese black shales and speculations on possible analogues in the United States. *Miner. Deposita* **26**, 83-88.

——— & Glascock, M.D. (1989): A review of the origins of metal-rich Pennsylvanian black shales, central U.S.A., with an inferred role for basinal brines. *Appl. Geochem.* **4**, 347-367.

———, Leventhal, J.S., Glascock, M.D. & Hatch, J.R. (1987): Origins of metals and organic matter in the Mecca Quarry Shale Member and stratigraphically equivalent beds across the Midwest. *Econ. Geol.* **82**, 915-933.

———, Watney, W.L. & Maples, C.G. (1991): Contrasting depositional models for Pennsylvanian black shale discerned from molybdenum abundances. *Geology* **19**, 147-150.

Desborough, G.A., Hatch, J.R. & Leventhal, J.S. (1991): Geochemical and mineralogical comparison of the Upper Pensylvanian Stark Shale Member of the Dennis Limestone, east central Kansas, with the Middle Pennsylvanian Mecca Quarry Shale Member of the Carbondale Formation in Illinois and of the Linton Formation in Indiana. *In* Metalliferous Black Shales and Related Ore Deposits – Proceedings (R.I. Grauch & H.L.O. Huyck, eds.). *U.S. Geol. Surv., Circ.* **1058**, 12-30.

Dobeš, P. & Pašava, J. (1990): Preliminary fluid-inclusion study of quartz–carbonate veinlets at Kamenec and Hromnice, Barrandian Proterozoic. *Geol. Surv. Czechoslovakia, Unpubl. Rep.* (in Czech).

Fairbridge, R.W., ed. (1972): *The Encyclopedia of*

Geochemistry and Environmental Sciences. Vol. IVA. Van Nostrand Reinhold, New York.

FAN, DELIAN (1983): Polyelements in the Lower Cambrian black shale series in southern China. *In* The Significance of Trace Metals in Solving Petrogenetic Problems and Controversies (S.S. Augustithis, ed.). Theophrastus Publications S.A., Athens, Greece (447-474).

FLEISCHER, M. & MANDARINO, J.A. (1991): *Glossary of Mineral Species 1991.* The Mineralogical Record, Inc., Tucson, Arizona.

GAVSHIN, V.M. (1991): Sea water and a source of metals in black shales. *In* Source, Transport and Deposition of Metals (M. Pagel & J.L. Leroy, eds.). A.A. Balkema, Rotterdam, The Netherlands (519-522).

GRAUCH, R.I., MUROWCHICK, J.B., COVENEY, R.M. & CHEN, NANSHENG (1991): Extreme concentrations of Mo, Ni, PGE and Au in anoxic marine basins, China and Canada. *In* Source, Transport and Deposition of Metals (M. Pagel & J.L. Leroy, eds.). A.A. Balkema, Rotterdam, The Netherlands (531-534).

HIRNER, A.V., KRITSOTAKIS, K. & TOBSCHALL, H.J. (1990): Metal-organic associations in sediments. I. Comparison of unpolluted recent and ancient sediments and sediments affected by anthropogenic pollution. *Appl. Geochem.* **5**, 491-505.

HOLUBEC, J. (1966): Stratigraphy of the Upper Proterozoic in the core of the Bohemian Massif. *Rozpr. Čs. Akad. věd ř. mat-př.* **76**(4), 3-62 (in Czech).

HULBERT, L., CARNE, R., GRÉGOIRE, C. & PAKTUNC, D. (1990): Sediment hosted Ni–Zn–PGE mineralization in the Selwyn Basin, Yukon: a new environment for nickel and platinum group element mineralization. *Eighth IAGOD Symp. (Ottawa), Program Abstr.* A-111.

HUYCK, H.L.O. (1991): When is a metalliferous black shale not a black shale? *In* Metalliferous Black Shales and Related Ore Deposits – Proc. (R.I. Grauch & H.L.O. Huyck, eds.). *U.S. Geol. Surv., Circ.* **1058**, 42-56.

KOVALENKER, V.A., NEKRASOV, I.Y., SANDOMIRSKAYA, S.M., NEKRASOVA, A.N., MALOV, V.S., DANCHENKO, V.Y. & DMITRIEVA, M.T. (1989): Sulfide – selenide – telluride mineralization of epithermal manifestations of the Kurile–Kamchatka volcanic belt. *Am. Mineral.* **77**, 208-210.

KOVALOVÁ, M. (1991): Evaluation of uranium potential in black shale of the Barrandian Proterozoic, Bohemian Massif, Czechoslovakia. Czechoslovak Uranium Industry, Příbram, Internal Rep. (in Czech).

LEVENTHAL, J.S. (1991): Comparison of organic geochemistry and metal enrichment in two black shales: Cambrian Alum Shale of Sweden and Devonian Chattanooga Shale of the United States. *Miner. Deposita* **26**, 104-112.

LOUKOLA-RUSKEENIEMI, K., HEINO, T., TALVITIE, J. & VANNE, J. (1991): Base-metal-rich metamorphosed black shales associated with Proterozoic ophiolites in the Kainuu schist belt, Finland: a genetic link with the Outokumpu rock assemblage. *Miner. Deposita* **26**, 143-151.

MAYER, W. & PIESTRZYNSKI, A. (1985): Ore minerals from Lower Zechstein sediments at Rudna Mine, Fore-sudetic Monocline, SW Poland. *Geologica Transacta, Prace Mineral.* **75**.

PAŠAVA, J. (1990): *Anomalous Black Shales – a New Type of Mineralization in the Barrandian Upper Proterozoic, Bohemian Massif, Czechoslovakia.* Ph.D. thesis, Charles Univ., Geological Surv. Czechoslovakia, Prague (in Czech with English abstr.).

______ (1991): Metal-rich black shales from the Barrandian Proterozoic (Bohemian Massif, Czechoslovakia). *In* Source, Transport and Deposition of Metals (M. Pagel and J.L. Leroy, eds.). A.A. Balkema, Rotterdam, The Netherlands (577-580).

______, KOVALOVÁ, M. & HLADÍKOVÁ, J. (1989): Black shales and associated mineralizations as a result of development of the semi-isolated basin in the Barrandian Proterozoic. *In* Symp. on Mineralizations in Black Shales (Cracow; W. Mayer, ed.), 30-31 (abstr.).

POUBA, Z. & ZOUBEK, V. (1986): Upper Proterozoic Metallogeny of the Bohemian Massif. *In* Proc. Conf. Metallogeny of the Precambrian (Z. Pouba, ed.). Geol. Surv. Czechoslovakia (23-35).

QUINBY-HUNT, M., WILDE, P., ORTH, C.J. & BERRY, W.B.N. (1989): Elemental geochemistry of black shales – statistical comparison of low-calcic shales with other shales. *In* Metalliferous Black Shales and Related Ore Deposits, Program and Abstracts (R.I. Grauch & J.S. Leventhal, eds.). *U.S. Geol. Surv., Circ.* **1037**, 8-15.

RAMDOHR, P. (1980): *The Ore Minerals and their Intergrowths* (2nd ed.). Pergamon Press, Berlin, Germany.

RIPLEY, E.M., SHAFFER, N.R. & GILSTRAP, M.S. (1990): Distribution and geochemical characteristics of metal enrichment in the New Albany Shale (Devonian – Mississippian), Indiana. *Econ. Geol.* **85**, 1790-1807.

SCHÜLLER, A. & OTTEMANN, J. (1963): Castaingit ein neues mit Hilfe der Elektronen-Mikrosonde bestimmtes Mineral aus den Mansfelder "Rücken". *Neues Jahrb. Mineral. Abh.* **100**, 317-321.

TUREKIAN, K.K. & WEDEPOHL, K.H. (1961): Distribution of the elements in some major units of the Earth crust. *Geol. Soc. Am. Bull.* **72**, 175-191.

VINE, J.D. & TOURTELOT, E.B. (1970): Geochemistry of black shale deposits – a summary report. *Econ. Geol.* **65**, 253-272.

VINOGRADOV, A.P. (1962): Average content of chemical elements in the principal types of igneous rocks of the Earth's crust. *Geochemistry* **7**, 641-664.

VUORELAINEN, Y., HUHMA, A. & HAKLI, A. (1964): Sederholmite, wilkmanite, kullerudite, makineite and trustedtite, five new nickel selenide minerals. *Bull. Soc. Géol. Finlande* **36**, 114-125.

WEDEPOHL, K.H., ed. (1972): *Handbook of Geochemistry.* Springer-Verlag, Berlin.

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