Timing and composition of stratiform pyrite mineralization in black shales at Liblín (Teplá Barrandian Unit, Bohemian Massif)

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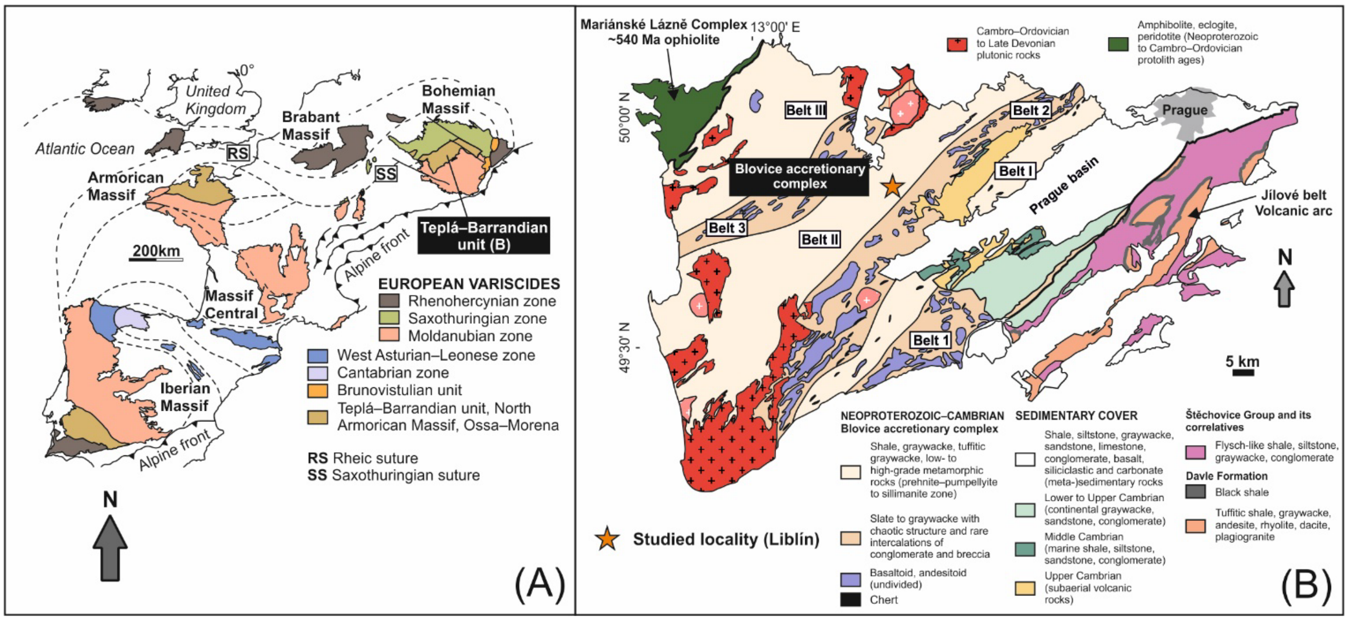

Figure 1. (A) Inferred paleogeographic position of the Teplá–Barrandian unit in the Avalonian–Cadomian belt on the northern active margin of Gondwana during the late Neoproterozoic. (B) Overview geologic map showing basement outcrop areas and principal lithotectonic zones of the Variscan belt in Europe. The Blovice accretionary wedge constitutes a major portion of the supracrustal Teplá–Barrandian unit in the center of the Bohemian Massif. (C) Simplified geologic map of the Blovice accretionary complex, emphasizing coherent belts (Belts I–III) alternating with ophiolitic mélanges (Belts 1–3). Modified from Hajná et al. (2013). Location of black shales hosting Fe stratiform mineralization at Liblín is shown by asterix.

Abstract. Pyritic black shales represent one of the most widespread types of mineralization in the Bohemian Massif which were mined in the past for the production of the Bohemian sulfuric acid. They were considered to be of Neoproterozoic age. Here, we present new geochemical, geochronological and laser ablation ICP-MS data from pyritic black shales at Liblín - a part of the Teplá–Barrandian Unit (TBU). We suggest that these normal (non-highly metalliferous) black shales were deposited in suboxic/anoxic depositional environment during early Cambrian (Re-Os dating on pyrite - 505 ± 21 Ma), coinciding with the Cambrian explosion. Syn-sedimentary pyrite has significantly higher As, Ag, Cr, Mn, Pb, Sb and V concentrations when compared to recrystallized type, which is, however characterized by much higher Co, Cu and Se contents.

1 Introduction

The Bohemian Massif, a remnant of Middle-Late Paleozoic Variscan belt, is composed of four major units (Teplá–Barrandian, Moldanubian, Saxothuringian and Moravo-Silesian) characterized by different compositional and temporal tectonostratigraphic evolution (Kroner and Romer 2013 and references therein).

The Teplá–Barrandian Unit (TBU) includes predominant Neoproterozoic to Cambrian basement (~550–500 Ma) metamorphosed at low grade, intruded by volumetrically minor Cambro–Ordovician plutons and covered by Late Cambrian to Devonian sedimentary and volcanic rocks (e.g., Hajná et al. 2017 and references therein). The Cadomian basement of the TBU is represented by the Blovice accretionary complex (BAC) and Jílové belt (JB). The BAC developed during subduction of an oceanic plate beneath the northern margin of Gondwana (Linnemann et al., 2014 and references therein) and exposes a complete section across an ancient subduction–volcanic arc system active from about 650–620 to ca. 480 Ma (Hajná et al. 2017 and references therein). The most notable feature of the BAC is that it consists of six fault-bounded linear belts, where three coherent domains of arc-derived and multiply recycled deep-marine siliciclastic rocks (Belts I–III; Fig. 1) represented by siltstones, slates, greywackes and (black)shales accompanied by cherts alternate with belts of ocean-floor-bearing (ophiolitic) mélanges (Belts 1–3; Hajná et al. 2013; Fig. 1) with basaltic rocks of highly variable composition. The Liblín locality belongs to the Kralovice–Rakovnik belt (Belt II) characterized by very low-grade monotonous succession of graywackes rhythmically alternating with minor slates and siltstones interpreted as deep-water turbidites (Cháb and Pelc 1968). This belt is devoid of volcanic rocks except for only a few NE–SW-trending km-scale elongated bodies of alkali basalt and trachybasalt to trachyandesite. Well-preserved shallow-dipping bedding, syn-sedimentary textures, and general lack of pervasive deformation suggest that the Kralovice–Rakovnik belt is the least deformed unit of the accretionary wedge (Hajná et al. 2013).

The region of the TBU has a long mining history of pyritic black shales, considered to be of Neoproterozoic/Ediacaran age, representing one of the most widespread types of mineralization in the Bohemian Massif (Kurzweil et al. 2015). Many locations including Liblín were exploited intensively from the 16th to 19th century for the production of the sulfuric acid (Slavík 1905; Pašava et al. 1996). Between 1833 and 1872, about 766,000 t of ore were mined at Hromnice, where an open pit remains.

Here, we present new geochemical characteristics of black shales and pyrite paralleled by Re-Os pyrite geochronology, developed in suboxic/anoxic environment and well preserved at the accretionary wedge. Our data provide new constraints on palaeoenvironment and metallogeny and timing of evolution of subduction process at the northern margin of Gondwana.

2 Results and discussion

2.1 Samples and methods

Eleven representative samples of black shales were collected in accessible gallery at the former pyrite deposit at Liblín. Major oxides were determined using a wet-chemistry method and selected trace elements were measured on an ICP-MS at the laboratories of the Czech Geological Survey in Prague. The polished sections with different types of pyrite grains were studied using an optical microscope and a FE–SEM Tescan Mira3 GMU, both housed at the Czech Geological Survey. Re–Os geochronology of the pyrite was carried out at the University of Alberta using protocols described in detail elsewhere (e.g., Morelli et al. 2010). The method includes decomposition in a concentrated $HCl–HNO_3$ mixture in Carius Tubes with the presence of $^{185}Re–^{190}Os$ spike and Re and Os separation by ion exchange chromatography and solvent extraction, respectively. Both Re and Os fractions were analyzed for their isotopic compositions using negative thermal ionization mass spectrometry (N-TIMS). Fine pyrite microcrystals and framboids (272 analyses), and coarse-grained pyrite (analyses), have been analyzed *in-situ* for selected trace elements using an Element 2 high-resolution mass spectrometer coupled with a 193 nm ArF Analyte Excite excimer laser ablation system (Teledyne/Cetac), located at the Institute of Geology of the Czech Academy of Sciences (Prague).

2.2 Geochemistry of black shale

Concentrations of selected major oxides and trace elements (TE) are listed in Table 1. Based on average metal values, these facies can be considered normal black shales (e.g., Pašava 1996).

Table 1. Selected major (wt.%) and trace (ppm) elements in early Cambrian pyritic black shales from Liblín.

	min	max	mean
SiO_2	67.0	73.9	70.3
TiO_2	0.3	0.7	0.5
Al_2O_3	6.7	16.4	12.5
Fe_2O_3	0.2	4.4	1.6
FeO	0.1	0.6	0.3
MgO	0.6	1.8	1.2
MnO	0.008	0.023	0.015
CaO	0.01	0.09	0.04
Na_2O	0.1	3.1	1.6
K_2O	1.7	3.8	2.9
P_2O_5	0.026	0.046	0.035
TOC (wt.%)	0.8	7.0	3.2
S(pyrite)	0.01	3.1	0.6
As	12	52	23
Co	0	9	2
Cr	35	114	74
Cu	10	44	23
Mo	7	90	28
Ni	6	60	24
Pb	9	93	27
Sb	6	24	16
Se	0.2	10	2
U	8	25	14
V	231	983	575
Zn	5	154	62
Zr	93	204	159
V/Cr	5	11	7

It was documented by Pašava et al. (2018) that the positive correlation between TOC and V/Cr in both Ediacaran highly metalliferous black shales and normal black shales from the TBU justifies the use of this ratio as an indicator of paleoredox changes. Median value of V/Cr

~7 in our sample set indicates suboxic to anoxic conditions (Jones and Manning 1994) which were reported from different Cambrian locations worldwide (e.g. Sperling et al. 2015). Calculated Spearman correlation coefficients (r) indicate a significant relationship between TOC and Cr (r=0.81), V (r=0.79), Mo (r=0.78), S (r=0.72) and U (r=0.71). Sulfur shows the highest positive correlation with Fe and with Se (r=0.78), Co (r=0.743), Mo (0.72), U (r=0.66), and V (r=0.63).

2.3 Re-Os geochronology

Eight pyrite separates yield a Re–Os age of 505 ± 21 Ma (MSWD = 39) with initial $^{187}Os/^{188}Os$ value of 0.87 ± 0.12 (Fig. 2).

This age is younger than previously thought Neoproterozoic age (Pb–Pb age of 635 ± 45 Ma for black shales, Pašava and Amov 1993; U-Pb zircon age of 559.8 ± 3.8 Ma from tuffitic intercalations in black shale, Kurzweil et al. 2015). Our new age is, however, consistent with outcomes of the recent study of Hajná et al. (2017) who suggested that Ediacaran-aged orogeny was not abruptly terminated at the Neoproterozoic-Cambrian boundary, but represents succession of multiple, episodic accretion, deformation, and magmatic events and basin development from Ediacaran to early Ordovician.

It is also important to note that this new age coincides with the Cambrian explosion which was triggered by oxygenation (e.g., Canfield et al. 2008 and references therein) and/or other environmental, developmental and ecological causes (Zhang et al. 2014).

2.4 Geochemistry of pyrite

Basically, two types of pyrite were identified. Fine pyrite microcrystals and framboids concentrated in sedimentary bed (Fig 3A) and coarse-grained pyrite aggregates dispersed in matrix (Fig. 3B). Both types significantly differ in chemical composition (Fig. 3A, B).

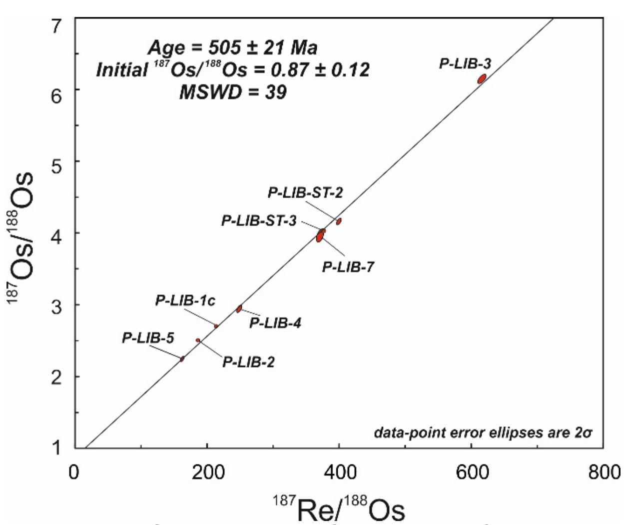

Figure 2. Re–Os regression age for eight pyrites from pyritic black shales at Liblín.

Levels of As, Ni, Pb, and Cu concentrations in our syn-sedimentary pyrite (Fig. 3A) are well comparable with those of average sedimentary pyrite reported by Gregory et al. (2015), however, pyrite from Liblín shows slightly higher Ag and Cd and much higher Sb and Zn values. Similarly, aged syn-sedimentary pyrite from the Que River Shale (505 Ma; Gregory et al. 2015) has almost identical mean As and Se values, much higher mean Co and Ni values and significantly lower mean Sb and V values. In syn-depositional pyrite from Liblín, Mo, Se and U are mostly homogeneously distributed while other TE show some zoning.

Large et al. (2019) used redox sensitive elements in synsedimentary pyrite for estimation of oxygen level through Proterozoic and Phanerozoic. Following this methodology and calculations after Yeung et al. (2017), we suggest that the mean concentration at the time of deposition of our black shales was about 16 wt% which is consistent with results reported by Large et al. (2019) and Berner et al. (2007).

3 Conclusions

The following outcomes resulted from the study of pyritic black shales at Liblín (TBU, Bohemian Massif):

1. Based on the chemistry of major and trace elements, they represent normal black shale (non-highly metalliferous facies), deposited in suboxic/anoxic environment.
2. Re-Os pyrite age of 505 ± 21 Ma indicates lower Cambrian deposition, which has an important geotectonic, palaeoenvironmental and metallogenetic implications.
3. Syn-sedimentary pyrite has higher mean As, Ag, Cr, Mn, Pb, Sb and V concentrations when compared to recrystallized one, which is, however characterized by higher mean Co, Cu and Se contents. Calculations based on redox-sensitive elements in synsedimentary pyrite indicate mean atmosphere O_2 value of ~16 wt.%.

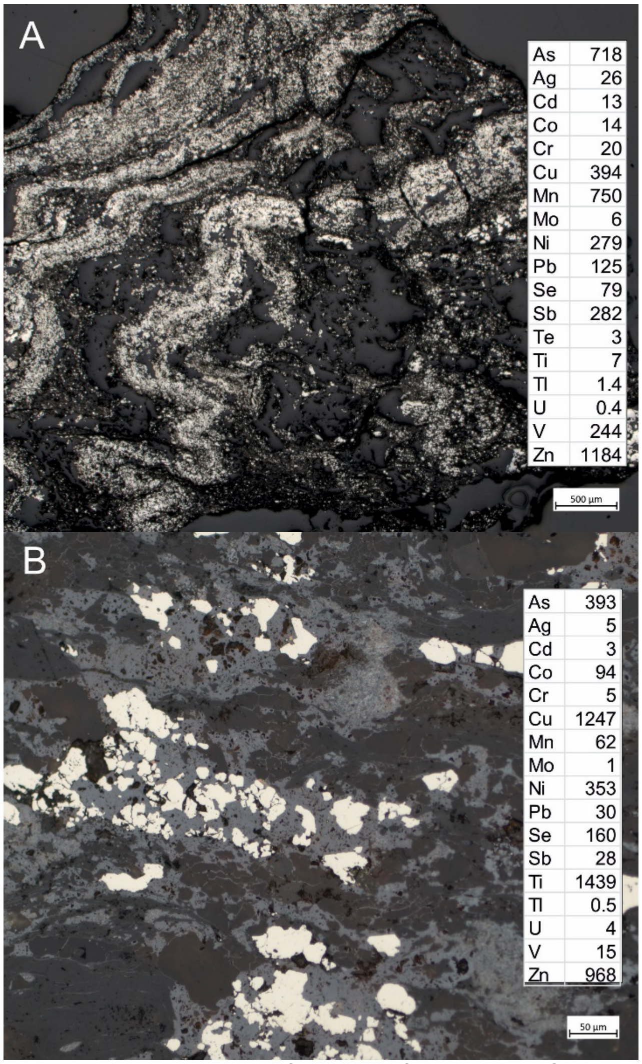

Figure 3. Photomicrographs of two types of pyrite in lower Cambrian black shales at Liblín with mean TE contents (in ppm). (A) Syn-sedimentary pyrite beds, (B) coarse grained pyrite aggregates (recrystallized). Axio Imager A2m, Carl Zeiss, Reflected light image, A. Vymazalová.

Acknowledgements

This study is a contribution to the Czech Science Foundation project 17-15700S and to the Institutional support RVO67985831 of the Inst Geol Czech Acad Sci and the Strategic Research Plan (DKRVO) of the Czech Geological Survey (2018-2022).

References

Berner RA, Vandenbrooks JM, Ward PD (2007) Oxygen and evolution. Science 316:557-558

Canfield DE, Poulton SW, Knoll AH, Narbonne GM, Ross G, Goldberg T, Strauss H (2008) Ferruginous conditions dominated later Neoproterozoic deep-water chemistry. Science 321: 949–952

Cháb J, Pelc Z (1968) Lithology of Upper Proterozoic in the NW limb of the Barrandian area. Krystalinikum 6:141–167

Gregory DD, Large RR, Halpin JA, Baturina EL, Lyons TW, Wu S, Bull SW (2015) Trace element content of sedimentary pyrite in black shales. Econ Geol 110:1389-1410

Hajná J, Žák J, Kachlík V, Dörr W, Gerdes A (2013) Neoproterozoic to early Cambrian Franciscan-type mélanges in the Teplá–Barrandian unit, Bohemian Massif: Evidence of modern-style accretionary processes along the Cadomian active margin of Gondwana? Precambrian Res 224:653–670

Hajná J, Žák J, Dörr W (2017) Time scales and mechanisms of growth of active margins of Gondwana: A model based on detrital zircon ages from the Neoproterozoic to Cambrian Blovice accretionary complex, Bohemian Massif. Gondwana Res 42:63–83

Jones B, Manning DAC (1994) Comparison of geochemical indices used for the interpretation of palaeoredox conditions in ancient mudstones. Chem Geol 111:111–129

Kroner U, Romer RL (2013) Two plates - Many subduction zones: The Variscan orogeny reconsidered. Gondwana Res 24:298–329

Kurzweil F, Drost K, Pašava J, Wille M, Taubald H, Schoeckle D, Schoenberg R (2015) Coupled sulfur, iron and molybdenum isotope data from black shales of the Teplá-Barrandian unit argue against deep ocean oxygenation during the Ediacaran. Geochim Cosmochim Acta 171:121–142

Large RR, Mukherjee I, Gregory D, Steadman J, Corkrey R, Danyushevsky LV (2019) Atmosphere oxygen cycling through the Proterozoic and Phanerozoic. Miner Depos 54:485-506

Linnemann U, Gerdes A, Hofmann M, Marko L (2014) The Cadomian Orogen: Neoproterozoic to Early Cambrian crustal growth and orogenic zoning along the periphery of the West African Craton-Constraints from U-Pb zircon ages and Hf isotopes (Schwarzburg Antiform, Germany). Precambrian Res 244:236–27

Morelli RM, Bell CC, Creaser RA, Simonetti A (2010) Constraints on the genesis of gold mineralization at the Homestake Gold Deposit, Black Hills, South Dakota from rhenium–osmium sulfide geochronology. Miner Depos 45:461–480

Pašava J, Amov B (1993) Isotopic composition of lead in Proterozoic anoxic metasedimentary and volcanogenic rocks from the Bohemian Massif (Czech Republic) with metallogenetic implications. Chem Geol 109:293–304

Pašava J, Hladíková J, Dobeš P (1996) Origin of Proterozoic Black Shales from the Bohemian Massif, Czech Republic. Econ Geol 91: 63–79

Pašava J, Chrastný V, Loukola-Ruskeeniemi K, Šebek O (2018) Nickel isotopic variation in black shales from Bohemia, China, Canada, and Finland: a reconnaissance study. Miner Depos, DOI 10.1007/s00126-018-0839-8

Slavík F (1905) O kamenečných a kyzových břidlicích západočeských. Rozpr Čes Akad, č. 26, Praha.

Sperling EA, Wolock CJ, Morgan AS, Gill BC, Kunzmann M, Halverson GP, Macdonald FA, Knoll AH, Johnston DT (2015) Statistical analysis of iron geochemical data suggests limited late Proterozoic oxygenation. Nature 523: 451–454

Zhang X, Shu, DG, Han J, Zhang ZF, Liu JN, Fu DJ (2014) Triggers for the Cambrian explosion: Hypotheses and problems. Gondwana Research 25: 896–909