Genetic aspects of barite mineralization related to rocks of the teschenite association in the Silesian Unit, Outer Western Carpathians, Czech Republic

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Abstract: Barite is a relatively uncommon phase in vein and amygdule mineralizations hosted by igneous rocks of the teschenite association in the Silesian Unit (Western Carpathians). In macroscopically observable sizes, it has been reported from 10 sites situated only in the Czech part of the Silesian Unit. Microscopic barite produced by the hydrothermal alteration of rock matrix and also by the supergene processes is more abundant. We examined four samples of barite by mineralogical and geochemical methods. Electron microprobe analyses proved pure barites with up to 0.038 *apfu* Sr and without remarkable internal zonation. Fluid inclusion and sulphur isotope data suggests that multiple sources of fluid components have been involved during barite crystallization. Barite contains primary and secondary aqueous all-liquid (L) or less frequent two-phase (L+V) aqueous fluid inclusions with variable salinity (0.4–2.9 wt. % NaCl eq.) and homogenization temperatures between 77 and 152 °C. The higher-salinity fluid endmember was probably Cretaceous seawater and the lower-salinity one was probably diagenetic water derived from surrounding flysch sediments during compaction and thermal alteration of clay minerals. The $\delta^{34}S$ values of barite samples range between −1.0 ‰ and +16.4 ‰ CDT suggesting participation of two sources of sulphate, one with a near-zero $\delta^{34}S$ values probably derived from wall rocks and another with high $\delta^{34}S$ values being most probably sulphate from the Cretaceous seawater. All results underline the role of externally derived fluids during post-magmatic alteration of bodies of rock of the teschenite association.

Keywords: Silesian Unit, teschenite, barite, fluid inclusions, stable isotopes.

Introduction

For more than 150 years, the Podbeskydí (Beskydy Piedmont) area lying at the eastern edge of the Czech Republic near the border with Poland and Slovakia (Fig. 1) has been known for the occurrence of a special group of mostly alkaline basaltic igneous rocks, which are often referred to as teschenites (*sensu* Hohenegger 1861), rocks of the teschenite association (Šmíd 1978; Kudělásková 1987), or teschenite-picrite formation (Hovorka & Spišiak 1988). In southern Poland, where small bodies of these rocks also occur, the term rocks of the Cieszyn magmatic province (Smulikowski 1930, 1980; Włodyka 2010) is used. Picrite (Tschermak 1866) and teschinite *sensu stricto* (Rosenbusch 1887) were described for a first time in the Podbeskydí Piedmont area.

One of the specific features of teschenites is intense hydrothermal alteration of primary rock-forming minerals to a mixture of zeolites (analcime), phyllosilicates, and carbonates (Pacák 1926; Smulikowski 1930; Šmíd 1978; Dolníček et al. 2010a,b, 2012; Urubek et al. 2014; Kropáč et al. 2015). In addition, cementation of fissures and vesicles by hydrothermal minerals gave rise to abundant hydrothermal veins and amygdules. Recent studies (Dolníček et al. 2010a,b; Dolníček et al. 2012; Urubek et al. 2014; Kropáč et al. 2015) revealed that multiple stages of hydrothermal activity occurred in this rock environment. The most important event was early post-magmatic alteration, which took place immediately after solidification of the host rock, when fluid circulation was allowed due to heat flow associated with the host intrusion (e.g., Dolníček et al. 2010a,b). Later alteration events occurred during subsequent deeper burial (Dolníček et al. 2012; Kropáč et al. 2015) and thrusting during the Alpine Orogeny (Dolníček et al. 2010a; Urubek et al. 2014).

Along with carbonates, chlorites, zeolites, quartz, fluorite, glauconite, and sulphide minerals, barite is also observed in the hydrothermal paragenesis of veins and amygdules. In macroscopically observable sizes, it is relatively uncommon mineral, reported from 10 sites situated only in the Czech part of the Silesian Unit (Table 1). Both amygdule- and vein-hosted examples have been described, but the exact geological position of some historical finds is unknown today (cf. Table 1). Barite in microscopic size, as crystals and grains up to 50 μm in size and filling of fissures, is abundant (Fig. 2). The origin of such barite is connected to the hydrothermal alteration of
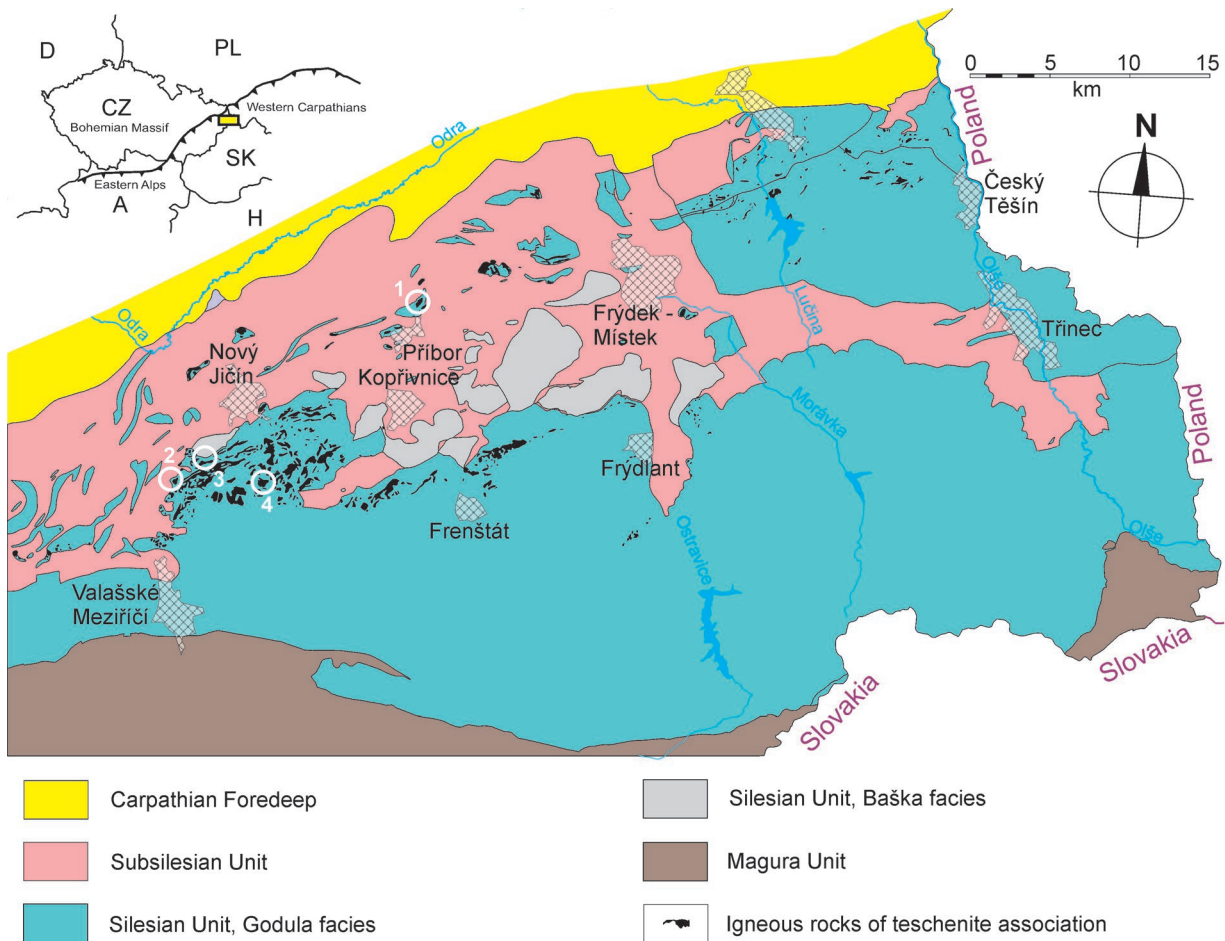
Fig. 1. Schematic geological map of the occurrences of rocks of the teschenite association in the Czech part of the Podbeskydí area (compiled after Czech Geological Survey 2014 and Matýsek & Jirásek 2016). Position of the studied localities: 1 — Skotnice, 2 — Palačov, 3 — Kojetín, 4 — Hodslavice.

rock matrix (Matýsek 2013) and also with supergene processes (Matýsek, unpublished data).

The aim of this study is to characterize the most important teschenite-hosted occurrences of barite mineralogically and genetically. We have studied four archive samples in terms of fluid inclusions and stable isotopes. Barite is a sink for sulphate dissolved in the hydrothermal fluids and its isotopic composition together with the nature of the parent fluids enclosed in fluid inclusions are useful tracers of the origin of fluids (e.g., Majzlan et al. 2016). Moreover, these independent data can further help to verify the reliability of existing interpretations of sources of hydrothermal fluids. Magmatic, marine, and diagenetic fluid sources have been suggested by previous works in this area (cf. Pacák 1926; Šmíd 1978; Dolníček et al. 2010a,b, 2012; Urubek et al. 2014).

Geological setting

Eastern Moravia and Silesia belong to an area built up by nappe units of the Outer Western Carpathians, thrusted over the SE part of the Bohemian Massif during the Tertiary (Fig. 1). Predominantly flysch sediments of the Upper Jurassic-to-uppermost Palaeogene were transformed during several stages of the Alpine Orogeny into discrete tectonic units. Based on the superposition, the following units were distinguished in the studied area: the Subsilesian Unit, Silesian Unit, and Magura Unit (Menčík et al. 1983; Fig. 1). The Silesian Unit, which hosts the study sites, consists of two basic facial developments. The Godula facies represents sediments of the ocean floor, while the Baška facies is considered to be deposited on a frontal continental slope. The differentiation is likely to have occurred during the Cenomanian. The occurrence of igneous rocks of the teschenite association is almost exclusively bound to the sediments of the Hradiště Formation (terminology by Eliáš et al. 2003) belonging to the lower part of the Silesian Unit; they are also rarely situated in the Vendryně Formation and in the Těšín Limestones, underlying the Hradiště Fm. (e.g., Włodyka 2010). The Hradiště Formation is composed of typical flysch sediments and consists of unmetamorphosed calcareous claystones, siltstones, and sandstones (Eliáš 1970) of the Late Valanginian to Early Aptian age (Skupien & Vašíček 2002).

Table 1: An overview of to-date known occurrences of barite mineralization hosted by igneous rocks of the teschenite association in the Silesian Unit.

Locality	Description	References
Choryně	One small crystal of barite was found in a vug of a magmatic rock in the bed of the Bečva River near the village of Choryně.	Matýsek, unpublished data
Hodslavice	Small white barite crystals occur in thin veinlets hosted by altered picrite in the Palackého lom Quarry	Bobková (1936), Burkart (1953)
Kojetín (1)	Small free fragments of milky white barite are from a creek springing between the Požáry and Hory Hills, near junction with a creek springing below the Kojetín village.	Melion (1855), Šmíd et al. (1964)
Kojetín (2)	Fragments of barite, coarse grained calcite, and chalcedony covered by quartz crystals were found on a tilth near the southern margin of the village. Host rock is a strongly altered amygdaloid volcanite.	Šmíd et al. (1964)
Kunčice pod Ondřejníkem	Calcite veins hosted by amphibole fourchite in the Maralův lom Quarry contain younger witherite which is corroded and overgrown by small tabular crystals of barite.	Kudělásek et al. (1989)
Nový Jičín (1)	Tabular barite crystals overgrowing drusy quartz are from the Gimpelberg Hill (today called Hýlovec Hill) situated between the Bludovice and Žilina villages. A fragment of barite was also found in a creek south of the Hill.	Melion (1855), Sapetza (1864), Šmíd et al. (1964)
Nový Jičín (2)	Fragments of barite together with calcite and analcime were found at the locality Čerťák, south of the town of Nový Jičín, in the vicinity of water reservoir Čerťák	Tschermak (1860)
Palačov	Barite was found in the Pavlíkův lom Quarry. No further details are given by original author.	Kučera (1926)
Příbor	Barite was found on building site of new by–pass road of the town of Příbor. It represents one of the youngest phases filling the fissures in a rock of teschenite association.	Kynický (2010)
Skotnice	Colorless, bluish, white or grey–white crystalline aggregates of barite occur in central parts of carbonate geodes in strongly altered picrite in the quarry at the Hončova hůrka Hill. Also found as monomineral fillings of amygdules up to several kg in weight. The 2–4 mm big tabular crystals were found in a small veinlet in picrite.	Rusek & Vališek (1968), Dolníček et al. (2010b)

Rocks of the teschenite association usually form sills, rarely dykes or lava pods (Matýsek & Jirásek 2016). In the Czech part, subaquatic effusive types such as lava flows, pillow lavas, tuffs, and tuffites are relatively common (Šmíd 1978). Shallow subvolcanic intrusions prevail over effusive types (Szopa et al. 2014). Radiometric dating carried out by Lucińska-Anczkiewicz et al. (2002; Ar–Ar method) and Szopa et al. (2014; U–Pb method on apatite) gave ages of 120.4–122.3 Ma and 103.0–126.5 Ma, respectively. These dates are consistent with palaeontological evidence from the syngenetic sediments of the Hradiště Fm. (Valanginian to Aptian; Vašíček 1972; Eliáš et al. 2003; Skupien & Pavluš 2013).

Rocks of the teschenite association are characterized by widely variable mineral composition, variable structural and textural features, and extremely variable intensity of post-magmatic alterations. There are many classification schemes of these rocks (Pacák 1926; Smulikowski 1930; Šmíd 1978; Hovorka & Spišiak, 1988; Włodyka 2010). The most frequent rock types include teschenites, picrites, monchiquites, and alkali basalts; gradual transitions are often observed among them (Machek & Matýsek 1994). Leucocratic components in these rocks are represented by alkali feldspars, plagioclase, analcime, zeolites, and nepheline, mafic minerals comprise pyroxene (Ti-rich diopside and hedenbergite, rarely augite) and amphibole (usually kaersutite). Olivine (Fo$_{-90}$) occurs mainly in picrites and Ti-rich biotite was identified in lamprophyric varieties. Accessory minerals include pyroxenes of aegirine-augite series, fluorapatite, Ti-rich magnetite or Cr-rich spinels (in picrites), titanite, sulphides, and others. Post-magmatic alterations are a characteristic feature of rocks of the teschenite association. Šmíd (1978) described a variety of alterations which include analcimization, chloritization, smectitization, serpentinization, and carbonatization.

Rocks of the teschenite association belong to basic, alkaline-to-subalkaline rocks with elevated concentrations of TiO_2, P_2O_5, alkalis, and incompatible trace elements (REE, Zr, Nb, Y, Ba, and Sr — Dostal & Oven 1998). The contents of Ba are abnormally high and highly variable. From published data (30 analyses; Włodyka 2010; Dostal & Oven 1998; Dolníček et al. 2010a,b, 2012), the contents of Ba vary between 125 and 2164 ppm. Unpublished XRF data of the authors (50 analyses performed by D. Matýsek) revealed <600−4614 ppm Ba. Ba does not provide statistically significant correlations with other components of rocks, which may be related to the occurrences of Ba-minerals or with the redistribution of this element during the post-magmatic alterations (cf. Fig. 2). There are known mineralogical occurrences of harmotome, hyalophane, Ba-rich alkali feldspars with up to 8 wt. % BaO (Włodyka 2010), slawsonite with variable content of celsiane component, celsiane (Matýsek & Jirásek 2016), witherite, and barite (Table 1).

The origin of rocks of the teschenite association is related to short-term rifting of the continental crust (Oszcypko 2004; Ivan et al. 1999; Hovorka & Spišiak 1993; Narebski 1990). Dostal & Owen (1998) suggested that the magma was of mantle origin and its composition resembles that of ocean island basalts and some continental alkaline basalts.

Material and methods

We have studied four samples of barite hosted by rocks of the teschenite association from locations illustrated in Fig. 1. The sample from Skotnice originated from an abandoned quarry on the western slope of the Hončova hůrka Hill (N 49° 39.590' E 18° 09.180'), which had exploited strongly
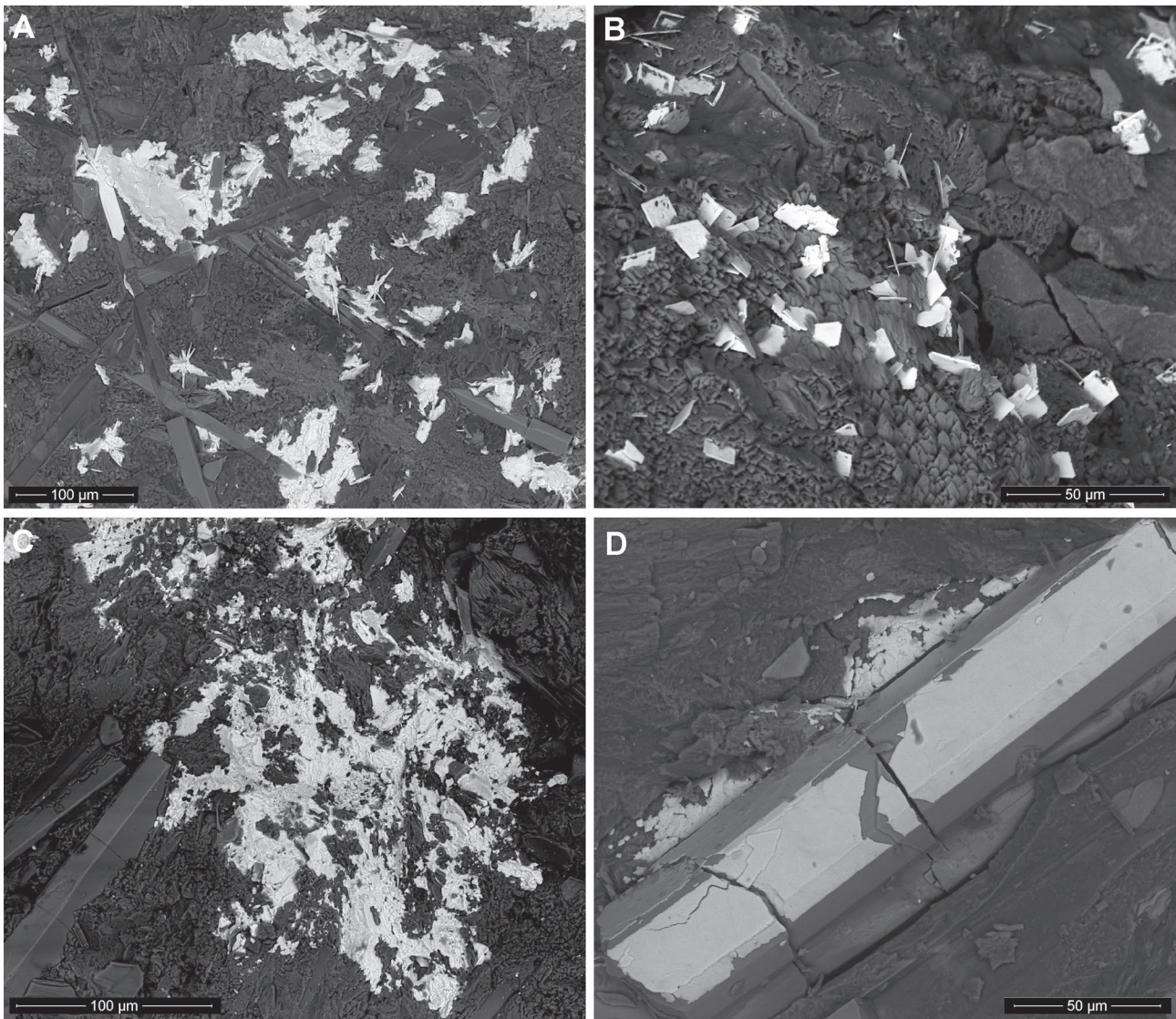
Fig. 2. Backscattered electron (BSE) images of microscopic barites (white) on a fracture surfaces. **A** — barite impregnation in rock matrix, fourchite, Bruzovice; **B** — isometric euhedral barite crystals, amygdaloidal picrite, Baška; **C** — barite impregnation in rock matrix, fourchite, Kunčice pod Ondřejníkem; **D** — barite coating on prismatic apatite crystal, teschenite, Řepiště near Paskov.

altered effusive picrite (Rusek & Valošek 1968). Abundant amygdules and fissures are filled up by low-temperature hydrothermal mineralization formed by dolomite, magnesite, siderite, quartz, calcite, fluorite, aragonite, glauconite, chlorite, sulphides, and barite (Dolníček et al. 2010b; Kropáč et al. 2015). The studied sample is a fissile piece of grey-white barite overgrowing calcite in a spherical geode representing the filling of an amygdule. The sample was collected in 1966 by D. Matýsek.

The sample from Palačov is from the collection of the Moravian Museum in Brno (inventory number A1579). It is a specimen described by Kučera (1926), from whose collection it originated. Locality is the Pavlíkův lom Quarry situated in a "dyke/sill of a picritic igneous rock". At present the quarry does not exist, but according to Frejková (1952) it can approximately be situated at the coordinates N 49° 33.000'

E 17° 56.000'. The studied sample is a white-grey fissile piece of barite without associated minerals or wall rock.

The sample from Kojetín is from the collection of the Moravian Museum (inventory number 2684). It is probably a sample collected by Melion (1895), but no additional information on its geological position is available today. Samples of identical appearance were collected by Šmíd et al. (1964) at a site with the coordinates N 49° 33.555' E 17° 58.306'. At this place and on the slope above, there are outcrops of various types of amygdaloid picrites, monchiquites, tuffs, and tuffites (Šmíd 1978). The studied sample is a white fissile piece of barite without other minerals or wall rock.

The sample from Hodslavice came from the Moravian Museum (inventory number 15477). It is a find described by Bobková (1936) and Burkart (1953), which originated from the Palackého lom Quarry (N 49° 33.127' E 18° 01.669')

situated in a body of picrite to diabase picrite (Klvaňa 1897; Pacák 1926; Šmíd 1978). The studied sample is formed by white tabular crystals of barite up to 2 mm in size, developed on a fissure of host picrite. Barite is associated with minor calcite.

The chemical composition of barite was studied with an electron microprobe Cameca SX 100 at the Faculty of Science, Masaryk University in Brno (analyst R. Škoda). The following conditions were used: wavelength-dispersive analysis, accelerating voltage 15 keV, beam current 10 nA, beam diameter 5 μm. Well defined minerals and synthetic phases were used as standards: Sr (Lα, SrSO$_4$), Na (Kα, albite), Si (Kα, sanidine), Mg (Kα, Mg$_2$SiO$_4$), P (Kα, fluorapatite), Ca (Kα, fluorapatite), Fe (Kα, almandine), Mn (Kα, spessartine), Ba (Lα, barite), S (Kα, barite), Cl (Kα, vanadinite), Pb (Mα, vanadinite), Zn (Kα, gahnite). The counting time on each peak was 20 s in the case of major elements and 40 s in case of minor elements, the same as on the background.

Fluid inclusions were investigated by means of petrography and optical microthermometry in cleavage fragments of barite. The distinguishing of individual genetic types of fluid inclusions was made according the criteria given by Roedder (1984) and Shepherd et al. (1985). Inclusions were checked for the presence of petroleum under ultraviolet (UV) radiation at 365 nm excitation wavelength. Microthermometric parameters were measured using the Linkam THMSG 600 stage mounted on the Olympus BX-51 microscope (Palacký University, Olomouc). The temperature of final homogenization (Th), freezing temperature (Tf), and melting temperature of ice (Tm$_{ice}$) were measured. The stage was calibrated between –56.6 and 374.1 °C with inorganic standards and synthetic fluid inclusions. The reproducibility is within 0.1 °C for temperatures between –56.6 and 0 °C, and within 1 °C for temperature up to 374.1 °C. The cryometric data of one phase L inclusions were measured after heating to a temperature of 200 °C which led to stretching of inclusions and subsequent bubble nucleation. Salinity of fluids was calculated from measured Tm$_{ice}$ values according to Bodnar (1993).

Sulphur isotope analyses of barites were conducted in the laboratories of the Czech Geological Survey in Prague, using a Finnigan MAT 251 mass spectrometer (analyst Z. Lněničková). The SO$_2$ gas for isotope analysis was produced by heating of powdered barite with a SiO$_2$+V$_2$O$_5$ mixture (Ueda & Krouse 1987) at 1050 °C in vacuum. Results of isotope analyses are conventionally expressed in delta (δ) notation as per mil (‰) deviation from the commonly used CDT standard. Uncertainty involving the whole analytical procedure is better than ±0.3 ‰.

Results

Chemical composition of barite

Electron microprobe analyses (Table 2) revealed that all samples belong to rather pure barite without remarkable internal zonation. The highest contents of strontium were found in samples from Hodslavice (up to 0.038 *apfu*) and Kojetín (up to 0.010 *apfu*). The contents of calcium were with one exception (sample Hodslavice containing up to 0.014 *apfu*) always below the detection limit of the microprobe. In addition, some samples contained slightly elevated contents of zinc (up to 0.005 *apfu*), iron (up to 0.002 *apfu*), and silica (up to 0.006 *apfu*). The concentrations of other analysed elements (Mg, Cl, P, Na) were always below the detection limits.

Fluid inclusions

Fluid inclusions suitable for microthermometric analysis were found in all studied barite samples. Samples contain abundant primary fluid inclusions showing essentially constant sizes ranging between 5 and 8 μm. They are mostly solitary with regular rounded isometric shapes, sporadically slightly elongated inclusions occur along growth zones. At room temperature, the studied primary inclusions are one-phase (L-only) in most cases. Two-phase (L+V) inclusions with essentially constant liquid-vapour ratios (gaseous phase takes about 5 to 10 vol. %) are less frequent and are spatially associated with L-inclusions (Fig. 3a). Frequent irregular flattened or isometric secondary inclusions arranged in trails along healed microfractures (Fig. 3a) usually reach very small sizes (up to 3 μm). Somewhat larger secondary inclusions are present in the sample from Palačov (Fig. 3b) and contain aqueous solution only (L-inclusions). No fluorescence has been observed in the UV-microscope in any type of fluid inclusion.

The homogenization temperatures of two-phase primary fluid inclusions range between 77 and 152 °C (Table 3, Fig. 4a). However, a narrower variability (within ca. 30 °C) is usually observed for most samples with an exception of fluid inclusions from Skotnice which range within 55 °C (77 to 133 °C).

Fluid inclusions have generally similar cryometric parameters (Table 3, Fig. 4). In all cases, the inclusions freeze at temperatures between –38 and –43 °C. The frozen fluid inclusions usually remain colourless, sometimes slight darkening of the inclusion content is observed. Eutectic melting as well as salt hydrate melting was never observed due to observation complications caused by small sizes of the fluid inclusions. The last ice melts at temperatures between –0.2 and –1.7 °C (Table 3, Fig. 4b) indicating bulk fluid salinities between 0.4 and 2.9 wt. % NaCl eq. There is no systematic difference between associated L+V and L-only primary inclusions in terms of their salinity. The secondary inclusions showed slightly higher Tm values (–0.3 to –1.0 °C) than the primary inclusions in the same sample (Table 3, Fig. 4b).

Sulphur isotopes

The following δ^{34}S values have been determined for the studied barite samples: Hodslavice –1.0 ‰ CDT, Skotnice +8.0 ‰ CDT, Kojetín +14.2 ‰ CDT, and Palačov +16.4 ‰ CDT.

Table 2: Average chemical composition of barite (oxides in wt. %) and recalculation of coefficients of empirical formulae to 4 atoms of oxygen.

Spots	Skotnice 6			Palačov 7			Kojetín 6			Hodslavice 5		
	average	max.	min.	average	max.	min.	average	max.	min.	average	max.	min.
BaO	65.26	65.62	65.04	65.02	65.65	64.39	64.50	64.90	64.09	63.33	64.57	62.80
SrO	0.04	0.06	0.00	0.09	0.11	0.04	0.39	0.43	0.35	1.32	1.69	0.19
CaO	0.00	0.01	0.00	0.01	0.02	0.00	0.01	0.02	0.00	0.13	0.34	0.05
ZnO	0.04	0.10	0.00	0.03	0.09	0.00	0.05	0.16	0.00	0.03	0.10	0.00
FeO	0.03	0.06	0.00	0.01	0.03	0.00	0.01	0.04	0.00	0.01	0.10	0.00
SiO_2	0.07	0.16	0.00	0.00	0.14	0.00	0.04	0.12	0.00	0.06	0.09	0.00
SO_3	33.75	34.31	33.17	33.94	34.49	33.28	33.84	34.55	33.15	34.50	34.65	34.15
Total	99.20			99.14			98.85			99.37		
Ba^{2+}	1.005	1.016	0.994	0.999	1.011	0.980	0.993	1.006	0.976	0.959	0.974	0.950
Sr^{2+}	0.001	0.001	0.000	0.002	0.003	0.001	0.009	0.010	0.008	0.030	0.036	0.004
Ca^{2+}	0.000	0.001	0.000	0.000	0.001	0.000	0.001	0.001	0.000	0.005	0.014	0.002
Zn^{2+}	0.001	0.003	0.000	0.001	0.003	0.000	0.001	0.005	0.000	0.001	0.003	0.000
Fe^{2+}	0.001	0.002	0.000	0.001	0.001	0.000	0.000	0.001	0.000	0.000	0.001	0.000
Si^{4+}	0.003	0.006	0.000	0.000	0.001	0.000	0.002	0.006	0.000	0.002	0.003	0.000
S^{6+}	0.995	1.002	0.990	0.999	1.005	0.994	0.997	1.002	0.992	1.000	1.003	0.997
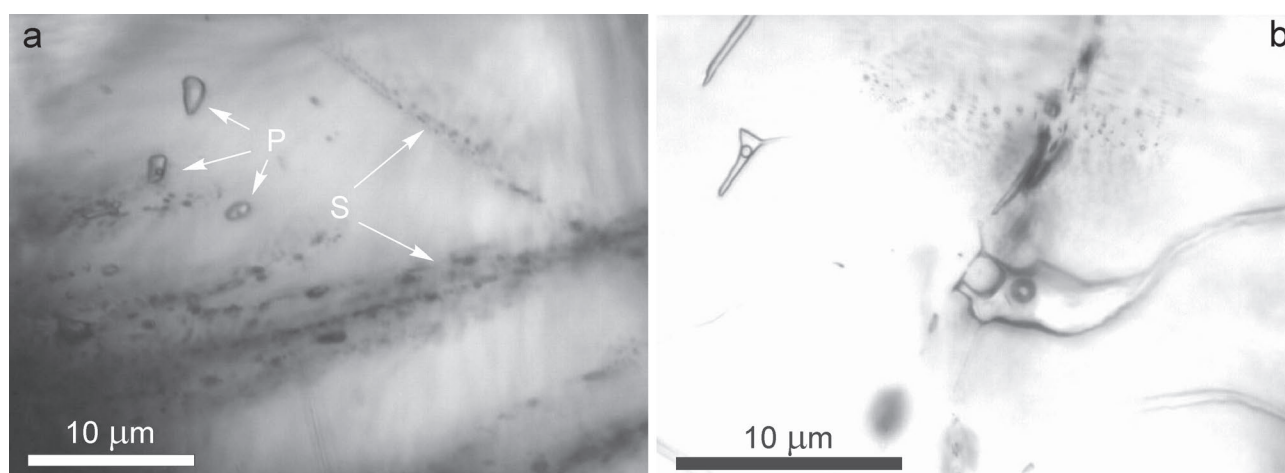
Fig. 3. Microphotographs of fluid inclusions hosted by the studied barite. **a** — A group of L and L+V primary (P) fluid inclusions neighbouring with trails of very small secondary (S) fluid inclusions in the sample from Kojetín. **b** — Larger flat irregularly shaped originally all-liquid secondary inclusions after overheating to 200 °C which resulted to stretching of most inclusions and nucleation of vapour bubbles. Sample from Palačov.

Discussion

Fluid inclusions

Constant liquid-vapour ratios in primary L+V fluid inclusions confirmed by rather narrow ranges of measured homogenization temperatures suggest trapping of a homogeneous fluid phase in the studied barite-hosted fluid inclusions. Therefore, the measured homogenization temperatures of primary inclusions should represent the minimum possible formation temperatures (Goldstein & Reynolds 1994). Moreover, narrow ranges of Th values together with often well-defined trends in the Th-Tm$_{ice}$ plot (Fig. 4c) in individual samples imply good preservation of fluid inclusions in barite host which is usually reported to be very sensitive to post-entrapment leakage and stretching of fluid inclusions (e.g., Ulrich & Bodnar 1988). In contrast, the occurrence of numerous one-phase aqueous inclusions would indicate very low formation temperatures not exceeding ca. 50 °C (Goldstein & Reynolds 1994) which contradicts the information given from L+V inclusions. The absence of vapour bubbles is often observed in smaller inclusions (with sizes below about 6 μm) implying that metastability of the bubble nucleation could play a role. The idea about a metastable nature of the liquid inclusions is supported by the fact that there are no systematic differences in cryometric parameters of L-only and associated L+V inclusions.

Different trends for different samples can be observed in the Th-Tm$_{ice}$ plot (Fig. 4c). Fluid inclusions from Palačov, Kojetín,

Table 3: Results of fluid inclusion microthermometry on teschenite-hosted barites from the Silesian Unit. n.a. — not applicable

Sample	Genesis	Phase composition	Th (°C)	Tf (°C)	Tm$_{ice}$ (°C)	Salinity (wt. % NaCl eq.)
Hodslavice	Primary	L, L+V	92–118	–39/–43	–0.5/–1.2	0.9–2.1
Kojetín	Primary	L, L+V	103–140	–38/–43	–0.3/–1.7	0.5–2.9
Palačov	Primary	L, L+V	120–152	–39/–41	–0.8/–1.3	1.4–2.2
Palačov	Secondary	L	n.a.	–38/–42	–0.3/–1.0	0.5–1.7
Skotnice	Primary	L, L+V	77–133	–39/–43	–0.2/–0.5	0.4–0.9
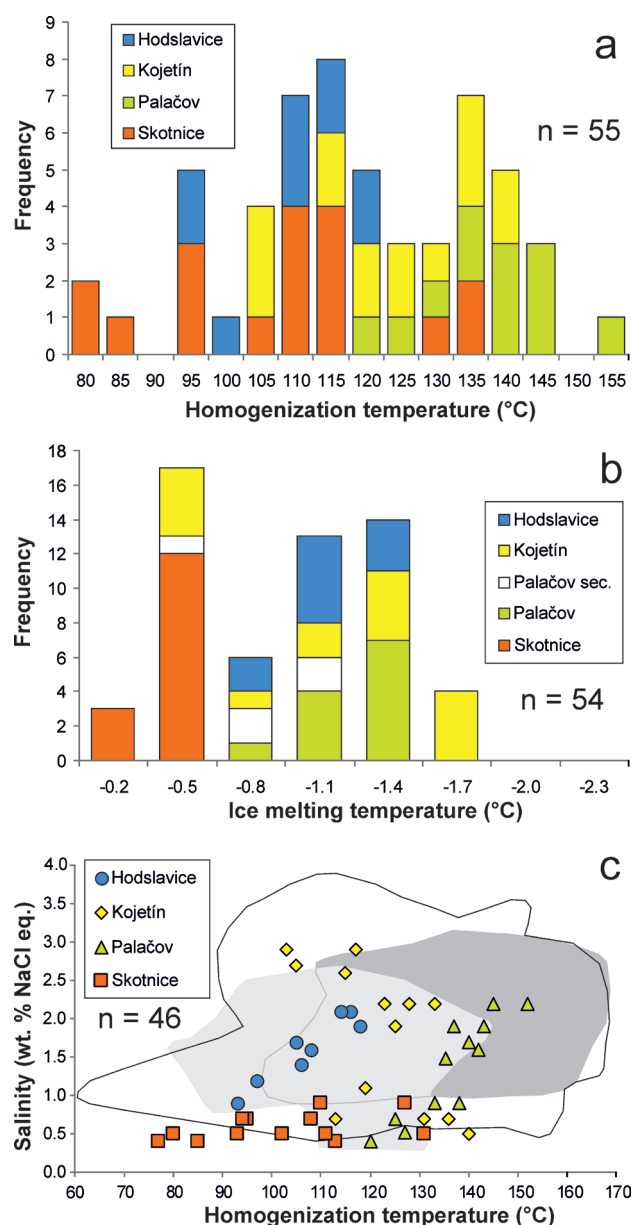
Fig. 4. Graphical presentation of results of microthermometry of fluid inclusions in the studied barites. **a** — Histogram of homogenization temperatures of L+V fluid inclusions. **b** — Histogram of melting temperatures of last crystal of ice. **c** — Th vs. salinity plot. Outlined are comparative data from the Silesian Unit (Urubek et al. 2014 and references therein): *white field* refers to post-magmatic teschenite-hosted carbonate-rich mineralizations, *light grey field* is syntectonic teschenite-hosted mineralization, and *dark grey field* are diagenetic and post-tectonic vein mineralizations hosted by sedimentary rocks.

and Hodslavice define diagonal or subvertical trends which have to be interpreted in terms of mixing of fluids with different salinities and/or temperatures. By contrast, the sample from Skotnice yielded a subhorizontal distribution which can be interpreted in terms of (i) mixing of two fluids with the same salinity and different temperatures; (ii) changes of temperature of a single fluid; (iii) changes of pressure of a single fluid; (iv) post-entrapment damage to fluid inclusions caused by necking-down; (v) a combination of the above mentioned possibilities. The variations of pressure seem to be unlikely alone to explain the observed variability in Th values, because decrease from 130 °C to 75 °C requires increase of pressure by 1.3 kbars (modelling in the Flincor software using an isochore calibration by Zhang & Frantz 1987), which is unlikely for a post-magmatic mineralization developed in a body of effusive picrite which originated in a marine basin with a depth more than the CCD (cf. also Dolníček et al. 2010b). Larger variability in Th values has been reported for some amygdule-hosted aqueous fluid inclusions from Skotnice by Dolníček et al. (2010b); these authors presupposed damage to fluid inclusions by necking-down. In any case, various trends observed for individual samples clearly suggest mixing of contrasting types of fluids related to the local low-temperature hydrothermal systems.

The lower salinity of secondary fluid inclusions suggests decrease of salinity of hydrothermal fluids during evolution of the hydrothermal system. Such a trend is very characteristic for low-temperature post-magmatic hydrothermal mineralizations hosted by teschenites in the Silesian Unit (e.g., Dolníček et al. 2010a,b; Urubek et al. 2014).

Sulphur isotopes

The wide observed range of δ^{34}S values of the studied barite (–1.0 to +16.4 ‰ CDT) can be interpreted by involvement of either multiple sources of sulphur or various processes affecting fractionation of sulphur isotopes. Fig. 5 summarizes available data on isotopic composition of possible sources of sulphur. Sulphidic minerals disseminated in teschenites showed δ^{34}S values between –7.4 and +2.4 ‰ CDT, whereas sulphides from post-magmatic vein and amygdule mineralizations hosted by teschenites have δ^{34}S values between –23.6 and +6.8 ‰ CDT; the isotopic composition of sulphur from flysch sediments of the Hradiště Fm. adjacent to teschenites has not been studied yet. The teschenite-related sources are not heavy enough to explain the observed highest δ^{34}S values of the studied barites. The increase of δ^{34}S values of sulphate dissolved in a hydrothermal fluid can be potentially caused by partial reduction of sulphate to H$_2$S resulting in shift of δ^{34}S values of residual sulphate due to kinetic isotope effects (Hoefs 2005). However, two of three principal mechanisms of sulphate reduction operate at temperatures which are out of the range suggested by our fluid inclusions (inorganic sulphate
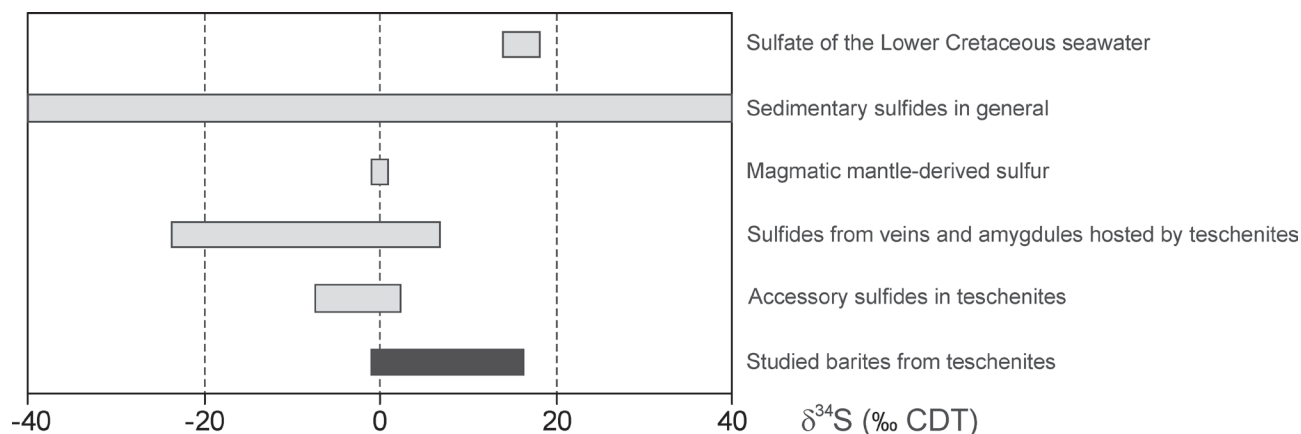
Fig. 5. Comparison of δ³⁴S values of the studied barites and possible sources of sulphur. Comparative data are from Strauss (1997), Hoefs (2005), Urubek & Dolníček (2008), and Dolníček et al. (2010b, 2012). Unpublished data of the authors are also included.

reduction: above ca. 250 °C; bacterial sulphate reduction: below ca. 80 °C; Hoefs 2005; Desrocher et al. 2004). Thermochemical reduction of sulphate by organic matter cannot be a dominant source because of the lack of higher hydrocarbons in the parent fluids which is indicated by the absence of fluorescence in an UV-microscope. Therefore, our data rather suggest involvement of an additional source of isotopically heavy sulphate, which can most probably be found in seawater sulphate showing δ³⁴S values of ca. +16±2 ‰ CDT during the Lower Cretaceous period (Strauss 1997; Hoefs 2005).

Genetic model

Crystallization of barite occurred from aqueous fluids with salinities ranging between 0.4 and 2.9 wt. % NaCl eq. In the given setting, such wide variability in fluid salinity was very common during post-magmatic hydrothermal activity and cannot be explained by a single fluid source (cf. Dolníček et al. 2010a,b; Dolníček et al. 2012; Urubek et al. 2014). The available fluid inclusion data (cf. Fig. 4c) suggest participation of at least two types of fluid. The low-salinity fluid endmember cannot be considered to be meteoric water because of submarine position of the host igneous rocks. Similarly, low-salinity fluid cannot have a magmatic source with respect to the rather shallow nature of the basin (above CCD) which results in production of high-salinity fluids during the final stages of magmatic crystallization (cf. Cline & Bodnar 1991). The likely source of low-salinity fluid can be found in diagenetic waters, produced by compactional and thermal dewatering of clayey sediments spatially and temporarily associated with the rocks of teschenite association. Such diagenetic fluids are frequently described from both teschenite- and sediment-hosted minerogenetic environments in this area (Dolníček et al. 2010a,b; Dolníček et al. 2012; Jarmolowicz-Szulc et al. 2012; Urubek et al. 2014). The higher-salinity fluid endmember can be found in either magmatic fluids (with salinities

reaching up to several tens of wt. % NaCl eq. in the given area; cf. Dolníček et al. 2010a) or seawater (with salinity of 3.5 wt. % NaCl eq.). With respect to the rather low temperatures of the fluid mixture requiring substantial previous cooling of the host igneous rocks (which was dominantly mediated by fluids circulating along fractures), we suggest that seawater was the crucial source of salinity in the hydrothermal fluid. Nevertheless, the contribution of the higher-salinity fluid decreased with time, as indicated from decreasing salinity of secondary fluid inclusions. Barium can be leached from rocks along the fluid pathways (from teschenites and/or clayey sediments). Adamová (1983) states that barium contents range between 146 and 560 ppm in the sediments of the Hradiště Formation. The source of sulphate can dominantly be found in Cretaceous seawater (in case of high δ³⁴S values) or rocks (in the case of near-zero δ³⁴S values; again possibly derived from both teschenites and/or clastic sediments). Both Ba and sulphate can be brought by the individual fluid endmembers and mixing of compositionally different fluids (having often different temperatures) at the site of deposition resulted in barite crystallization. A possible genetic scenario is illustrated in Fig. 6.

Conclusions

Barite is a relatively uncommon phase in vein and amygdule parageneses hosted by igneous rocks of the teschenite association in the Czech part of the Silesian Unit. The available data suggest that multiple sources of fluid components have been involved during barite crystallization. Fluid inclusions reveal mixing of at least two fluid endmembers differing in salinity and sometimes also in temperature. The higher-salinity endmember was probably Cretaceous seawater and the lower-salinity one was probably diagenetic water derived from surrounding flysch sediments during compaction and thermal alteration of clay minerals. The wide range of δ³⁴S values of
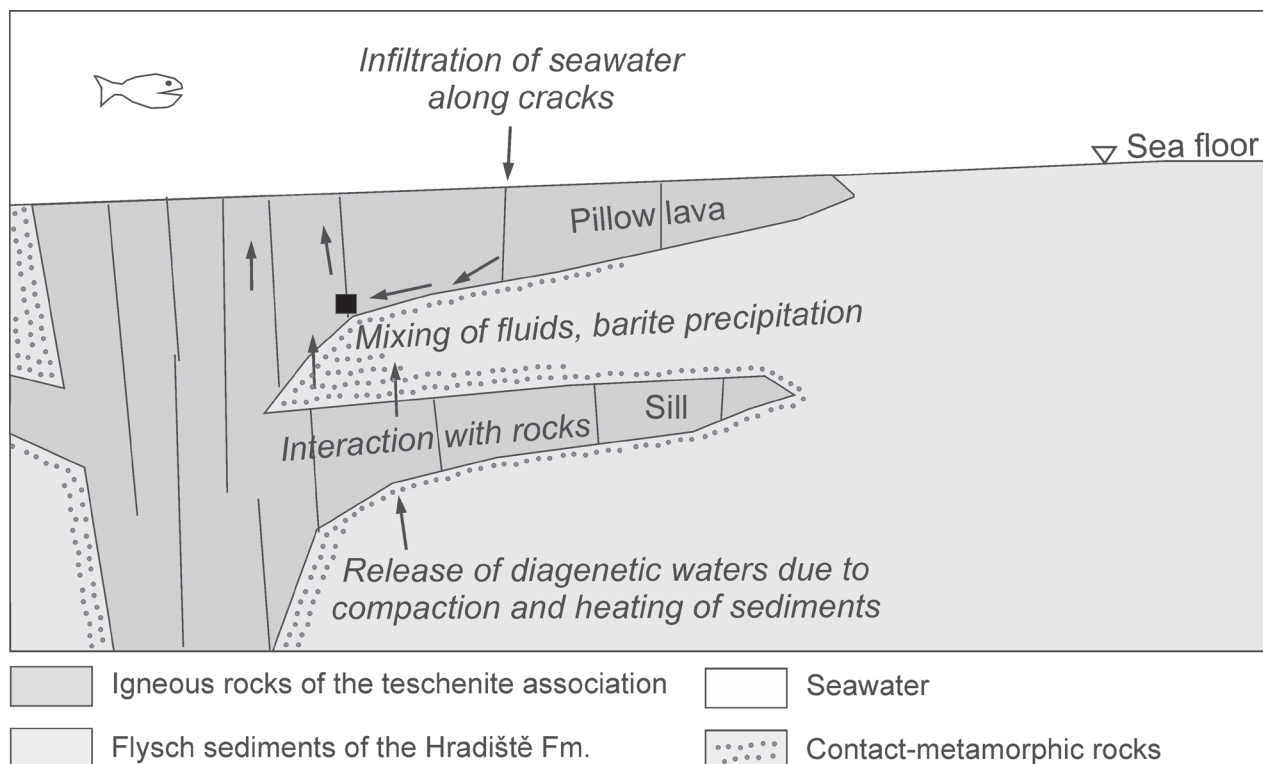
Fig. 6. Schematic drawing illustrating the suggested genetic environment of the studied barite mineralization. Arrows indicate directions of movement of fluids.

barite also suggests mixing of two sources of sulphate, one with near-zero $\delta^{34}S$ values probably derived from wall rocks (either teschenites or sediments) and another with high $\delta^{34}S$ values (up to +16 ‰ CDT) being most probably sulphate from the Cretaceous seawater. These findings underline the role of externally derived fluids during post-magmatic alteration of bodies of rock of teschenite association and the significance of leaching of specific wall rocks for mineral paragenesis precipitating from circulating fluids.

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