



Rapid ore classification for real-time mineral processing optimisation at the Niederschlag multi-generation hydrothermal barite-fluorite vein deposit, Germany

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Introduction

Fluorite is currently viewed as a critical raw material (CRM) by the European Commission (2017) as it is the main source of fluorine which is vital as a flux for metal ore smelting and the manufacture of hydrofluoric acid. In addition, it also contributes to the manufacture of fluorine-containing chemicals and their products. Due to supply risks and increasing industrial demand, investment in exploration and mining of European fluorite deposits has been encouraged to support European markets. The opening of the Niederschlag fluorite mine in the Erzgebirge, Germany, by Erzgebirgische Fluss- und Schwerspatwerke GmbH (EFS) in 2013, is a positive outcome of this initiative. EFS produces a fine-grained acid grade concentrate containing greater than 97% CaF₂.

The Niederschlag barite-fluorite mineralisation is a complex, multi-generation (Permian and Mesozoic) vein-type deposit which has been modified by multiple syn- and post-genetic shearing and in the Paleogene-Neogene, local hydrothermal alteration and replacements caused by the emplacement of phonolite dykes and sills (Kuschka et al. 2002; Haschke et al. 2021). Each generation has its specific mineral paragenesis with distinctive mineral abundances and diversity, grain shapes and sizes and micro-scale mineral intergrowths. The combination of these complex

features has greatly complicated the design and operation of mineral processing operations at the mine.

The major aim of this study was to establish criteria for the rapid ‘real-time’ identification of the main vein generation in the ore to allow crucial adjustments and refinements to be made to the processing flowsheet, to achieve the best possible quality of fluorite concentrate. In addition, the trace element compositions of fluorite from the main generations were determined by laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) to confirm that they are genetically different, i.e. formed during separate phases of hydrothermal alteration and mineralisation. This information could also be used to further develop the deposit model for Niederschlag to aid in exploration for near-mine extensions or similar deposits in the area or worldwide. The study does not aim to provide insights into methodologies for fluorite processing.

Geology of the Niederschlag deposit

The Niederschlag barite-fluorite deposit, which is part of the Niederschlag-Bärenstein ore district in the central Erzgebirge, is situated 12 km south of the German town of Annaberg-Buchholz, close to the border with the Czech Republic (Fig. 1). The major mineralised fault, which was named Magistralnaya by Russian geologists during U mining operations (1948–1954), is c. 2.5 km long, up to 15 m wide, strikes NNW-SSE and dips 80° towards WSW (Fig. 2). The Niederschlag deposit hosts 3.1 Mt of raw ore reserves containing 1.34 Mt of CaF₂ (Kuschka et al. 2002).

Vertically, the deposit can be divided into an upper part, which hosted the U mineralisation (exploited), and a lower part from the 765-m level downwards, in which the U mineralisation disappeared (Kuschka et al. 2002). The lower part of the Magistralnaya is the target for fluorite mining today. The mineralisation was formed from

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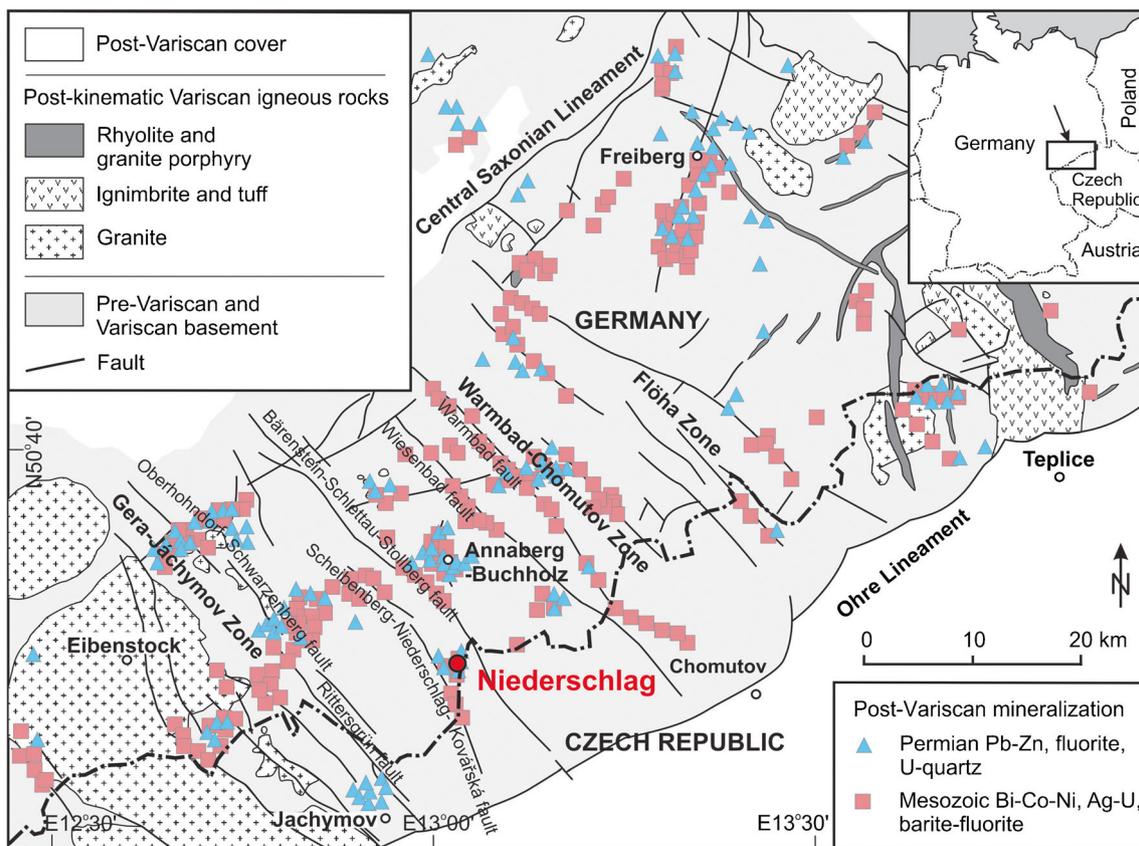


Fig. 1 Map of the major fault zones in the central Erzgebirge (Czech: Krušné Hory) according to Hösel (1972), Leonhardt (1995) and Kuschka et al. (2002). Localities of Post-Variscan mineralisation and their general classification is according to Romer et al. (2010)

the late-Variscan (Permian) to recent times. According to Kuschka et al. (2002), the major fluorite-forming stages dominating the lower part of the Magistralnaya comprise the Permian fluorite-quartz stage and the Mesozoic haematite-barite and barite-fluorite stages (Fig. 3). The classification bases on visual identification of mineral paragenesis. Haschke et al. (2021) proposed a two-stage formation of the deposit based on fluid inclusion and fluorite composition studies. These authors suggest that the haematite-barite and barite-fluorite stages should be considered as one stage, stage II, due to similar origin and chemistry of the ore-forming fluids. The entire mineralisation underwent intense syn- to post-genetic shearing, and in the Paleogene-Neogene, several phonolite dykes and sills intruded the deposit to cause local hydrothermal alteration and replacements (Kuschka et al. 2002). The wall rocks within the mine and below are amphibolite-facies two-mica gneisses and muscovite schists of the Preßnitz Supergroup (Rusová and Měděnc Formation) and of the younger Niederschlag Supergroup. Protoliths of these rocks are Neoproterozoic greywackes (c. 570–540 Ma) with interlayered conglomerates, carbonates and extrusive rhyolites. The entire sequence was metamorphosed under MP-MT conditions

during the Variscan orogeny (c. 340 Ma; e.g. Tichomirova 2003). The foliation in the schists and gneisses plunges 10 to 35° SW. More information about the geological setting of the deposit is provided by Haschke et al. (2021).

Results

Refined characterisation of the Niederschlag barite-fluorite mineralisation

The visual identification of the fluorite-quartz (stage I according to Haschke et al. 2021) and haematite-barite and barite-fluorite (stage II according to Haschke et al. 2021) assemblages during ongoing underground mining is mainly based on the scheme for vein-type mineralisation in the central Erzgebirge introduced by Kuschka et al. (2002), which is a comprehensive synthesis of earlier works by Baumann (1967, 1968), Baumann and Rösler (1967), Rösler and Pilot (1967) and Kuschka (1972, 1994), and observations made during active mining in the Erzgebirge before 1990. In the following years, however, the skills to identify the different vein

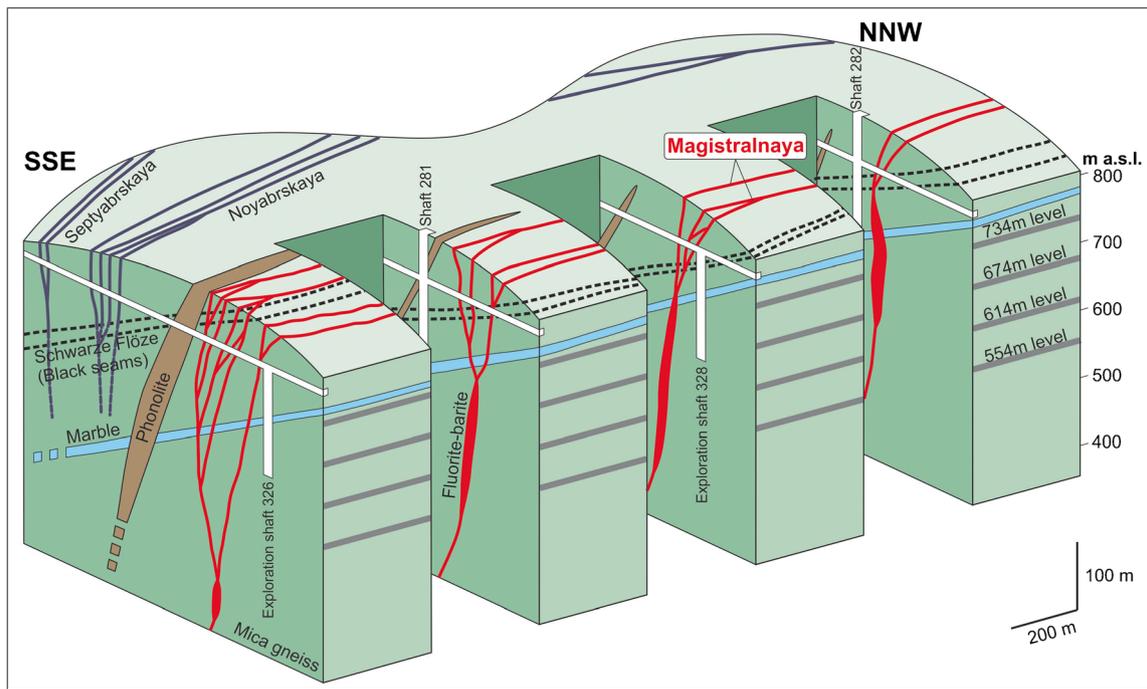


Fig. 2 Block diagram of the Niederschlag barite-fluorite deposit. The barite-fluorite mineralisation (Magistralnaya) is shown in red. The tunnels and shafts shown in white are from the Russian U mining period (1948–1954), and thick grey lines correspond to current and planned major

mining levels. Schwarze Flöze (Black seams) is a mining term referring to sheets (0.1 to 2 m in thickness) of black schist containing accessory graphite and pyrite. With permission of EFS

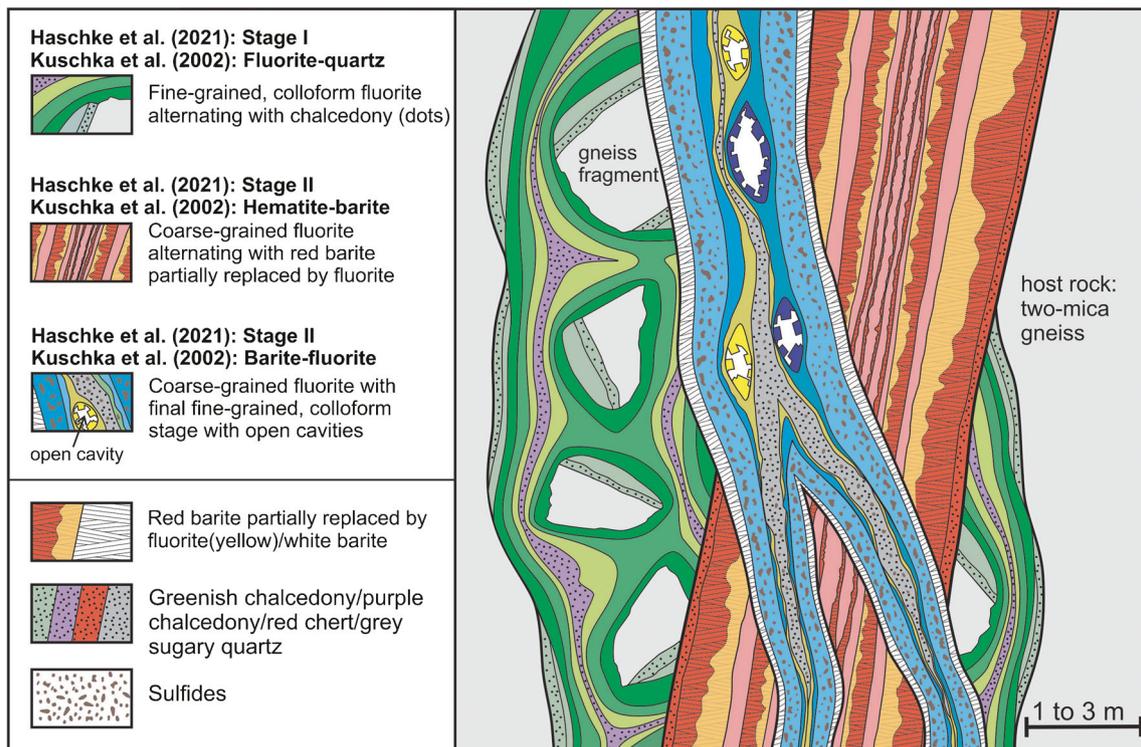


Fig. 3 Simplified scheme for the juxtaposition of the three major fluorite-mineralising generations which make up the Niederschlag deposit, as observed at 662-m to 682-m mine levels (c. 120 to 140 m below surface).

The chosen colours correspond to the dominant fluorite and barite colour in the stage. All stages are associated and overprinted by intense shear tectonics, which are not illustrated due to their complexity

generations were almost entirely lost. This was until 2013 when the fluorite mine was reopened and new observations were made in combination with a review of the literature and performing new research, such as Haschke et al. (2021). In the following, the haematite-barite and barite-fluorite assemblages are named substages of stage II according to the new findings by Haschke et al. (2021). A new scheme for identifying the different generations is given in Fig. 3 and described below.

The stages and substages are highly distinctive in terms of their mineralogy and textures which requires real-time adjustments of the ore processing depending on the predominant generation in the mined ore (Fig. 3): (1) the fluorite-quartz stage is rich in microfibrinous chalcedony with common micro-scale fluorite-chalcedony intergrowths, (2) the haematite-barite substage is rich in haematite-bearing (red) barite and chert ('roter Hornstein') and fine- to micro-grained Fe- and Mn-(hydr)oxides and (3) the barite-fluorite substage is rich in sulphides and sugar-textured quartz (Figs. 3 and 4). The primary sulphides in the barite-fluorite

substage, which comprise predominantly (in order of abundance) of chalcopyrite, galena and sphalerite, as well as subsidiary tennantite, tetrahedrite, pyrite, marcasite, arsenopyrite and bornite, were commonly altered post-mineralisation, remobilised and precipitated as cerussite, pyromorphite, phosphohedyphane, hemimorphite, mimetite, azurite, malachite, duftite, chrysocolla, etc. These non-fluorite alteration products tend to form smaller mineral grains and aggregate at grain boundaries and in intra-crystal micro fractures which are difficult to remove and therefore may contaminate the concentrate. Figure 4 summarises the main features of the stages and substages with examples of contaminating grains found in the processed fluorite concentrate. Two new observations have been made which require modifications to Kuschka's scheme (Kuschka et al. 2002). Firstly, the haematite-barite substage contains a higher proportion of coarse-grained fluorite (in relation to barite), mainly due to replacement of red barite by late-haematite-barite substage fluorite (fluoritisation; Figs. 3 and 4). Secondly, the main sulphide mineralisation during the barite-fluorite substage began

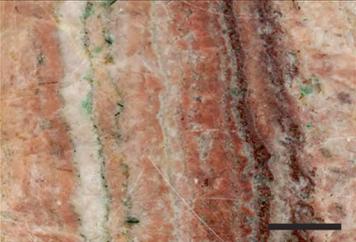
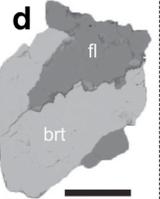
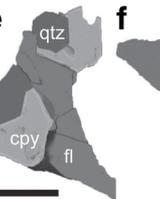
Mineralization stages according to Haschke et al. (2021)		Stage I	Stage II	
Mineralization stages according to Kuschka et al. (2002)		fluorite-quartz	hematite-barite	barite-fluorite
Representative hand specimen of the mineralization stage				
Main mineral paragenesis	Fluorite	green-white-violet; colloform	reddish-white; coarse-grained	white-blue-yellow; coarse to colloform; cavities
	Barite	chalcidony	red	white
	Quartz	chert	fluoritization	sugary
	Hematite
	Mn oxides
	U oxides
	Sulphides*
BSE image of fluorite-concentrate-contaminating grains typical for the mineralization stage		a  b 	c  d 	e  f 

Fig. 4 Characteristics of major fluorite-forming stages of the Niederschlag barite-fluorite deposit, as observed in the 662-m and 682-m levels. Scale bars on the hand specimen photographs correspond to 2 cm and those on the backscattered electron (BSE) images to 50 μ m. **a** and **b** Fluorite (fl) intergrown with chalcedony (qtz); **c** chert-haematite

intergrowth; **d** fluorite-red barite (brt) intergrowth; **e** fluorite-chalcopyrite(cpy)-sugary quartz intergrowth; **f** fluorite with tennantite (tnt) inclusions. * primary sulphides: chalcopyrite, galena, sphalerite, tennantite, tetrahedrite, pyrite, marcasite, arsenopyrite and bornite

after the precipitation of white barite; only a small proportion of the galena seems to be contemporaneous with the crystallisation of white barite.

Volumetric proportions of the three vein generations change vertically and horizontally within the mineralised zone. Thus, their identification and visual and photographic estimation of their proportions within the run-of-mine are essential for successful processing.

Trace element chemistry of fluorite

Fluorite from all stages has low trace element concentrations in particular for the rare earth elements (REE) (Table 1) compared with fluorite from other deposits (e.g. Schwinn and Markl 2005). Values for Σ REE are 54 ± 30 ppm for flq, 133 ± 48 ppm for the haematite-barite substage and 75 ± 24 ppm for the barite-fluorite substage. Distinct differences between these fluorites are as follows: (1) low Y, light (L)REE and middle (M)REE and high Sr of the fluorite-quartz stage; (2) elevated concentrations of Y, LREE and Na of the haematite-barite substage; and (3) very low LREE of the barite-fluorite substage (Fig. 5). Some of the haematite-barite substage fluorites (named barite-fluorite late in Fig. 5c) inherited the Tb/La ratio and the REE pattern of the older fluorite-quartz generation as a result of their partial replacement/reworking. The majority of fluorite has a hydrothermal signature according to the Tb/Ca* versus Tb/La discrimination diagram of Möller et al. (1976). The haematite-barite substage fluorite, which plots across the boundary into the pegmatitic field, close to the fluorite-quartz stage fluorites, partially inherited the trace element signature of fluorite-quartz stage fluorites.

In the chondrite-normalised REE plots on Fig. 5c, two types of pattern can be distinguished: (1) those with an enrichment of LREE compared to heavy (H)REE with negative Ce and Eu anomalies (fluorite-quartz stage, late haematite-barite substage) and (2) patterns showing a strong depletion in LREE and enrichment of MREE with less pronounced negative Ce and Eu anomalies (early haematite-barite and barite-fluorite substages). The occurrence of Ce anomalies in REE patterns for fluorite is rare, restricted to only a few localities worldwide such as the Clara fluorite deposit in Schwarzwald, Germany (Schwinn and Markl 2005).

As illustrated in Fig. 5, the fluorite generations are easily distinguishable from their trace element contents and patterns. The older fluorite-quartz stage fluorites are very different to the younger haematite-barite and barite-fluorite substage fluorites in particular in the REE contents and patterns. These findings confirm the results by Haschke et al. (2021) that fluorite at Niederschlag was formed by two different fluid types: low to medium saline fluids with homogenisation temperatures of 140–180 °C forming the fluorite-quartz stage and

younger high salinity fluids with homogenisation temperatures of 80–120 °C forming the haematite-barite and barite-fluorite substages.

The main processes which control the trace element signatures of hydrothermal fluorite are as follows: (1) leaching of source rocks, (2) *P-T* evolution of the fluid phase, (3) precipitation paragenesis of fluorite and co-existing phases, (4) fluid mixing and interaction with wall rocks and (5) remobilisation and reprecipitation and/or reworking of pre-existing fluorite (Richardson and Holland 1979; Schwinn and Markl 2005). The REE patterns of fluorites from the Niederschlag deposit are mostly controlled by their source rocks as evidenced by the fluorite-quartz stage fluorite having a distinct granite source pattern characterised by an enrichment of HREE and a negative Eu* anomaly. Their REE pattern is very similar to early-stage granites of the Eibenstock-Nejdek and Kirchberg plutons in the Western Erzgebirge (e.g. Breiter et al. 1999) and to the Altenberg-Frauenstein microgranite and Teplice rhyolite of the Eastern Erzgebirge (e.g. Müller and Seltmann 2002; Müller et al. 2018). Granite xenoliths found in the Paleogene-Neogene phonolith dykes crosscutting the Niederschlag mineralisation indicate the existence of a hidden granite intrusion at greater depth, below the deposit. The negative Ce anomaly is the only feature which distinguishes the fluorite-quartz stage fluorite pattern from granite REE patterns. The Ce anomaly resulted from Ce loss from the fluorite-forming fluid during migration, which may have been due to a higher reactivity of Ce and greater potential to adsorb to surfaces due to its increased oxidation stage compared with the other REEs. The REE patterns of the haematite-barite and barite-fluorite fluorite generations predominantly reflect the composition of the fluids from which they precipitated, which were controlled by varying interactions/equilibration with surrounding metamorphic rocks.

Mining and processing implications

In this study, we provide a practical guide for the rapid/real-time identification of the main vein generations in mined ore from the Niederschlag barite-fluorite deposit. The visual classification of the vein generations is based primarily on the scheme for the central Erzgebirge introduced by Kuschka et al. (2002). New identification criteria are established by combining literature data with observations made since the opening of the Niederschlag fluorite mine in 2013 and by including new results on the deposit genesis by Haschke et al. (2021).

Variations in the volumetric proportions of the three vein generations during mining change the types and

Table 1 Average trace element concentrations (in ppm) of fluorite of different mineralisation stages determined by LA-ICP-MS

	Haschke et al. (2021)		Stage II		Stage II	
	Stage I		Stage II		Stage II	
	Kuschka et al. (2002)		Haematite-barite		Barite-fluorite	
	Fluorite-quartz <i>n</i> = 24		<i>n</i> = 8		<i>n</i> = 7	
	Mean	STD	Mean	STD	Mean	STD
Na	48.7	22.4	209.9	133.4	52.2	25.6
Mn	<0.2	–	0.9	0.8	0.4	0.2
Sr	214.0	46.1	157.8	103.8	142.2	60.6
Y	22.0	17.3	231.1	106.7	173.8	54.8
Zr	<0.1	–	0.7	0.7	0.5	0.7
Ba	0.2	0.1	2.7	2.3	0.9	0.8
La	15.9	9.4	14.6	14.4	2.4	1.3
Ce	10.3	13.4	26.8	24.5	5.6	2.3
Pr	3.5	2.0	4.7	4.1	1.4	0.6
Nd	15.9	7.8	25.7	20.4	9.2	3.9
Sm	2.5	1.1	8.2	3.2	5.5	1.8
Eu	0.4	0.2	2.0	0.6	1.6	0.6
Gd	1.9	1.0	13.9	5.5	12.2	4.4
Tb	0.2	0.2	2.5	1.3	2.3	0.9
Dy	1.6	1.2	17.2	9.3	16.8	7.8
Ho	0.3	0.2	3.0	1.4	3.4	1.4
Er	0.9	0.7	7.8	4.1	7.6	3.1
Tm	0.1	0.1	0.9	0.4	1.0	0.5
Yb	1.0	0.8	4.8	1.9	5.5	2.6
Lu	0.1	0.1	0.6	0.2	0.6	0.3
Pb	0.8	0.9	6.3	6.3	5.4	7.2
U	0.9	0.8	0.6	1.1	0.3	0.3
LREE	45.5	28.4	71.8	62.6	18.5	7.8
MREE	4.7	2.2	24.0	8.0	19.4	6.5
HREE	4.3	3.2	36.9	18.4	37.2	16.2
ΣREE	54.4	29.9	132.7	47.6	75.1	24.0
Eu/Eu*	0.46	0.06	0.56	0.06	0.60	0.10

Concentrations of Al, Cu and K are below the limits of detection, which are 120, 0.6 and 5.5 ppm, respectively. *n* number of analyses, *STD* standard deviation

proportions of mineral phases contaminating the fluorite concentrate. The main contaminating phases are micro-scale fluorite-chalcedony ingrowths in the fluorite-quartz stage, barite-fluorite intergrowths and Fe and Mn (hydr)oxide inclusions in fluorite from the haematite-barite substage, and fluorite- and barite-quartz intergrowths, inclusions of sulphides and their alteration products in fluorite from the barite-fluorite substage. In order to produce the highest quality of fluorite concentrate, the processing has to be continuously adjusted to the mineralogical composition of the mined ore.

LA-ICP-MS is a useful tool for distinguishing fluorite generations from their trace element contents and allows conclusions to be made as to the source of the

mineralising fluids. It also adds to our understanding of the nature and genesis of the Niederschlag deposit which may aid in the exploration and discovery of similar such deposits close by or in other geological terranes. Visual observations confirm the existence of three fluorite mineralisation stages and substages supposed by Kuschka et al. (2002). Differences in REE patterns of the Permian quartz-fluorite stage fluorites, indicating a fluid source with granitic fingerprint, and the Mesozoic haematite-barite and barite-fluorite substage fluorites, reflecting an increasing interaction/equilibration with the metamorphic wall rocks, verify the two-stage source model of fluids by Haschke et al. (2021) for the Niederschlag barite-fluorite mineralisation.

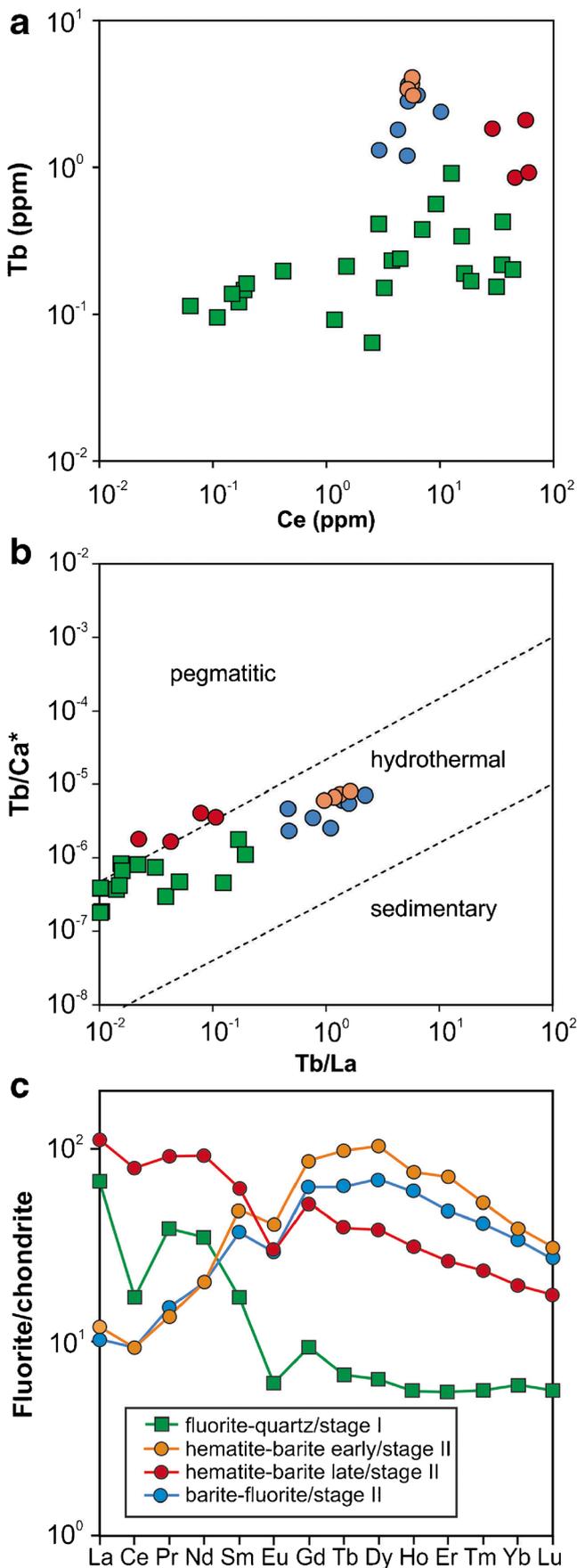


Fig. 5 Trace element variation plots for fluorite from the Niederschlag barite-fluorite deposit. **a** Ce versus Tb diagram for discrimination of the fluorite-forming stages of the Niederschlag deposit. **b** Tb/Ca* versus Tb/La discrimination plot for fluorite according to Möller et al. (1976). Ca*, stoichiometric abundance of Ca in fluorite. **c** Chondrite-normalised REE pattern fluorite. Average concentrations of the different fluorite concentrations are plotted. REE chondrite values used are from Anders and Grevesse (1989)

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Data availability All data related to the study are accessible.

Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

Code availability Not applicable.

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