



Nano-structural features of barite crystals observed by electron microscopy and atom probe tomography

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ABSTRACT

For the first time a barite sample was investigated by applying electron microscopy and atom probe tomography in a complementary approach to characterize its inner microstructure. Pores covering the size range from a few nanometers to a few micrometers were identified inside particles of a commercially available high purity barite. The barite matrix appeared to be a single crystal. A particular feature of the observed porous structure is a system of layers containing a high number of homogeneously distributed nano-scale pores, alternating with layers containing a limited number of larger pores. High-resolution chemical analyses indicate that the pores contain a solution of water and sodium chloride. The filling of these nano-scale inclusions was interpreted as residua of the initial supersaturated solution used for particle growth by precipitation. These findings explain the high reactivity observed in previous Ra uptake studies on the same type of barite and provide further implications for the interpretation of these results. Our results offer a new analytical approach and necessary reference data for future investigations on changes of the internal barite structure during these Ra uptake experiments.

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1. Introduction

Barite (BaSO_4) is the most common barium mineral formed at low temperatures (Deer et al., 2013; Röslér, 1991) and is characterized by a very low solubility (Hanor, 2000). In nature, barite occurs as a gangue mineral in hydrothermal veins or as cavity filling in limestones, sandstones, shales and clays. It is also present as surface deposits and as a residual of limestone weathering (Deer et al., 2013). Solid solution formation between BaSO_4 and other sulfates such as SrSO_4 , PbSO_4 , and RaSO_4 or by exchange of the anion, e.g. by CrO_4 , has been investigated repeatedly over decades due to the potential environmental implications (Becker et al., 2000; Bosbach et al., 2010; Boström et al., 1967; Burkhard, 1973; Ceccarello et al., 2004; Grahmann, 1920; Prieto et al., 1993, 1997; Putnis et al., 1992; Sabine and Young, 1954; Takano and Watanuki, 1974).

The formation of the $(\text{Ba,Ra})\text{SO}_4$ solid solution raises problems in a number of industrial processes, leading to the contamination by naturally occurring radioactive material (NORM) (Grundl and Cape, 2006; Minster et al., 2004; Zielinski and Otton, 1999). On a global scale, NORM created by the $(\text{Ba,Ra})\text{SO}_4$ solid solution dominates the radioactivity originating from the production of gas and oil and geothermal

energy (Eggeling et al., 2013; Zielinski et al., 2001). Recently, barite scale formation during hydraulic fracturing was observed. Here, Ra contamination of the barite scale plays an important role in a minority of wells (Zhang et al., 2014, 2015; Renock et al., 2016). Beginning with the early works of Doerner and Hoskins (1925), Gordon and Rowley (1957) and Marques (1934) up to recent publications (Curti et al., 2010; Rosenberg et al., 2011; Zhang et al., 2014), the fate of Ra in contact or during co-precipitation with barite has been studied. A very specific case in this context is the replacement of a pre-existing barite by a $(\text{Ba,Ra})\text{SO}_4$ solid solution, which has been recently investigated with regard to safety assessments for the direct deep geological disposal of spent nuclear fuel (Bosbach et al., 2010; Brandt et al., 2015; Curti et al., 2010; Klinkenberg et al., 2014; Norrby et al., 1997; SKB, 2011). In both cases, the barium concentration is typically orders of magnitude higher than the Ra concentration. Therefore the precipitation of a mixed $(\text{Ba,Ra})\text{SO}_4$ phase lowers the concentration of Ra compared to the case of pure RaSO_4 precipitation (Jaremalm et al., 2013; Vinograd et al., 2013).

Starting from a pure barite in contact with a Ra-bearing solution, the formation of homogeneous $(\text{Ba,Ra})\text{SO}_4$ particles in batch experiments has been demonstrated at the resolution of time-of-flight secondary ion mass spectrometry (Brandt et al., 2015; Klinkenberg et al., 2014). Scanning electron microscopy (SEM) observations on two different barites have shown that this reaction displays the typical features of a

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replacement reaction, i.e. the morphology and grain size of the barite after Ra uptake remain similar (Klinkenberg et al., 2014). The kinetics of the Ra uptake of the same barite types as in Klinkenberg et al. (2014) were described in Brandt et al. (2015). The latter study indicated a higher reactivity of the coarser grained barite compared to the other, fine grained barite with a much higher specific surface area. Brandt et al. (2015) concluded that normalizing the rate of Ra uptake to the surface area as determined by the BET method (Brunauer et al., 1938) may not be appropriate for describing the dissolution–reprecipitation processes controlling the replacement of pure barite by (Ba,Ra)SO₄.

A complete re-arrangement of the internal structure of the original barite particles can be expected for this process (Ruiz-Agudo et al., 2014). In order to characterize and understand the internal features of the barites which may contribute to their reactivity during the replacement, the application of true-nanometer scale resolution techniques is required. Recently, the combination of transmission electron microscopy (TEM) and atom probe tomography (APT) have provided new data in the case of glass dissolution. Based on these results the consideration of glass dissolution as a dissolution–reprecipitation process was further strengthened (Geisler et al., 2015; Gin et al., 2013; Hellmann et al., 2015; Putnis, 2015).

Here, we have applied a range of electron microscopy techniques for the detailed investigation of the internal microstructure of the same type of barite, which was the coarse barite with high reactivity used for Ra uptake experiments in several earlier studies (Bosbach et al., 2010; Brandt et al., 2015; Curti et al., 2010; Klinkenberg et al., 2014). Barite is known to contain different degrees of impurities of anions and cations, which are often associated with fluid inclusions (Bao, 2006). We therefore have accompanied the electron microscopy characterization in a complementary approach with APT. The elemental composition information obtained by APT is to a certain degree superior compared to energy-dispersive X-ray spectroscopy (EDX) as it provides near to atomic chemical and spatial resolution in particular for elements with low atomic numbers.

2. Materials and methods

2.1. Barite sample

The material studied in this work is a commercially available high-purity barite (Blanc Fixe XR-10, Sachtleben GmbH, Germany) synthesized by precipitation according to the manufacturer information (Sachtleben, 2015). A high purity of the material with >99.9% BaSO₄ content was verified by X-ray diffraction (XRD) and SEM–EDX. Subsequently, the barite particles were separated to obtain a grain size fraction of ~6–45 μm. Finally, the material was equilibrated as described for the Ra-free reference sample named “reference SL” in Klinkenberg et al. (2014). First, the barite powder was equilibrated in pure water for 6 weeks. Afterwards, the grain size fractionation was performed by sedimentation using Atterberg cylinders. In a second equilibration step the barite powders were equilibrated in a suspension with 10 mL of 0.2 N NaCl solution for 4 weeks. The barite of the present study will be referred to as SL barite throughout this study and represents the starting condition of the barite before the uptake of Ra.

2.2. Sample preparation

Barite samples were extracted from an isopropanol suspension, dried on a Si-wafer, and coated with a carbon layer of approximately 20 nm thickness using a Quorum Q150T E sputter coater (Quorum Technologies Ltd., U.K.). For the structural characterizations TEM lamellae and needle-shaped APT specimen, so-called APT tips, were cut from the barite particles using a focused ⁶⁹Ga⁺ ion beam (FIB) instrument. TEM lamellae were prepared in two different orientations: (i) cross-sections perpendicular and (ii) plane view lamellae parallel to the particles surface. A thickness < 100 nm is required of the TEM lamellae in

order to achieve electron transparency (Williams and Carter, 2009). Due to the high sensitivity of the barite towards the Ga⁺ ion beam, the milling conditions had to be adapted to obtain lamellae fulfilling the thickness requirements of TEM. These adapted milling conditions applied with each working step are summarized in Table 1. The APT analysis requires a sample in the shape of a very sharp needle with an apex diameter of 50–100 nm in order to enable field evaporation of atoms (Kelly and Larson, 2012). Different types of FIB instruments were used depending on the availability and on the suitability of the equipment for the individual desired sample preparation procedure. The specification of the applied FIB instruments is given in the descriptions of the preparation procedures.

2.2.1. Preparation of cross-section TEM lamellae

Cross-section lamellae were extracted from the barite particles perpendicular to a selected surface. In general, the cross-section sample preparation was performed according to well-established procedures (Giannuzzi and Stevie, 1999; Mayer et al., 2007) using a Zeiss NVision 40 Cross Beam workstation (Carl Zeiss AG, Germany). The instrument is equipped with a GEMINI high-resolution field emission electron gun and a high performance S II NT zeta FIB column, thus providing a combination of ion milling and sample characterization by SEM. Additionally, the instrument comprises an INCA EDX detector (Oxford Instruments, U.K.). Regions with one cross-section axis parallel to the longest particle axis were chosen in order to obtain cross-sections of maximum area. A protective layer of around 3 μm thickness of either carbon (C) or platinum (Pt) was deposited on the region of interest. Afterwards, a ~ 1.5 μm thick slice was cut out of the bulk material and attached to the middle post of an Omniprobe TEM-grid (Oxford Instruments, U.K.). The lamella was thinned to < 100 nm in three steps, where the inclination angle and the beam current were reduced with each step. Subsequently, the lamellae were finalized with a low kV polishing to reduce amorphization and Ga implantation at the sample surface. Finally, the thinned cross-section lamellae had a size of 15 ± 5 μm × 7 ± 5 μm and were electron transparent in most areas.

2.2.2. Preparation of plan-view TEM lamellae

Plan-view lamellae are thin slices cut out parallel to the crystal surface. The plan-view preparation was generally performed according to Stevie et al. (1998) with an FEI Helios Nanolab 400S (FEI Company, The Netherlands) dual beam instrument equipped with the necessary flip-stage for this preparation procedure. The milling conditions adapted for the barite particles are given in Table 1. In contrast to the cross-section preparation described in the previous section, where a preliminary lamella was cut out, a thick wedge is removed from the particle in the plan-view preparation procedure. First, a protective Pt

Table 1
Milling conditions for the preparation of cross-section and plan-view TEM lamellae of barite particles.

Working step	Milling conditions	Sample tilt
Cross-section TEM lamellae		
Cut out of the lamella <1.5 μm		
Trapezia	30 kV, 300 pA	
Rectangle	30 kV, 300 pA	1.0°
Thinning of the lamella <100 nm		
Step 1	30 kV, 80 pA	1.0°
Step 2	30 kV, 40 pA	0.8°
Step 3	30 kV, 60 pA	0.6°
Low kV polishing	2 kV, 25 pA	2.0°
Plan-view TEM lamellae		
Cut out of the wedge		
	30 kV, 6.5 nA	
Thinning of the lamella <100 nm		
Step 1	30 kV, 460 pA	1.5°
Step 2	30 kV, 280 pA	1.2°
Step 3	30 kV, 93 pA	0.8°
Low kV polishing	5 kV, 47 pA	2.0°

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