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ORIGINAL ARTICLE

Gypsum whiskers in Messinian evaporites identified by μ-XRD^2

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Abstract The gypsum mineralogy of hair-like, so-called whisker crystals was determined by micro X-ray diffractometry equipped with a focusing X-ray optic and a two-dimensional detector (μ-XRD^2). Gypsum whiskers typically form by efflorescence on surfaces that are in contact with water. The delicate whiskers studied here formed within a Messinian evaporite mostly consisting of anhydrite. They project from alabastrine gypsum into former cavities. The gypsum resulted from hydration of anhydrite. Whiskers were finally engulfed by biogenic, native sulphur, which filled the cavities in the course of microbial alteration of the host lithology. The sulphur protected the delicate whisker crystals from destruction, including a period of exposure to weathering on a dumping site of a former mine where the rocks have been sampled. To the best of our knowledge, this is the first report of gypsum whiskers in evaporites. More significantly, this study reveals that μ-XRD^2 has great potential for sedimentary petrology, allowing the in situ identification of minute mineral phases that cannot be identified with conventional techniques.

Keywords Gypsum whisker · Anhydrite · Native sulphur · Gypsum efflorescence · Micro XRD

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Introduction

Gypsum crystals exhibit various growth forms including tabular, prismatic, and acicular habits, but also granular and fibrous masses have been described (Nesse 2004). Fibers or filaments, usually composed of gypsum, have been recognized as speleothems forming cave hair, cave cotton, and other delicate crystal forms (Hill and Forti 1997). Hair-like crystals are commonly referred to as whiskers, which are defined as filamentary single crystals with a length-to-diameter ratio of at least five and a diameter between 20 nm and 100 µm (Evans 1972). Gypsum whiskers have been found to grow from aqueous solution (Strickland-Constable 1968; Hünger and Henning 1988), particularly from solutions with low supersaturation ($\alpha \leq 2$; Hünger and Henning 1988) where growth is inhibited in two dimensions (Strickland-Constable 1968).

Within Messinian evaporitic rocks from Sicily, we recognized similar peculiar hair-like, fibrous crystals, closely resembling gypsum whiskers. The whisker-like crystals are associated with anhydrite and alabastrine gypsum and are surrounded by native sulphur. Because such whiskers have not been previously recognized in evaporites (C. Pierre, J.M. Rouchy, and B.C. Schreiber, pers. comm.), we tried to determine their mineralogy, applying optical and electron microscopy, conventional X-ray diffractometry (XRD), as well as energy-dispersive X-ray spectrometry (EDX) for qualitative element analysis. Unfortunately, none of these techniques was successful due to the size of crystals and their entombment in native sulphur. Because of these difficulties, we used a micro-X-ray diffractometer equipped with a focusing X-ray-polycapillary microlense, which provided the opportunity to analyze mineral phases with a local resolution in the hundred-µm range (cf. Berthold et al. 2009). This new technique allowed the identification of the whiskers as gypsum crystals.

Geological context and materials

Loose blocks of sulphur-bearing anhydrite were sampled from a dumping site of the former sulphur mine at Monte Capodarso, northeast of the town of Caltanissetta, Sicily. The evaporites belong to the sulphate-bearing strata of Sicily, which formed during the Late Miocene (Messinian) salinity crisis (Colalongo and Pasini 1997 and references therein). A sea-level drop caused by the cutoff of the Mediterranean Sea from the Atlantic Ocean resulted in the apparent desiccation of the Mediterranean Sea between 5.96 and 5.33 million years ago (Hsü et al. 1973b; Krijgsman et al. 1999; Duggen et al. 2003). The development of restricted conditions led to the deposition of evaporitic series including evaporitic carbonate, sulphate, halite, and bittern salts in deeper Messinian basins (Hsü et al. 1973a) as well as in Sicily (Decima and Wezel 1973). Besides primary evaporitic carbonate, a second type of carbonate rock is present in the Messinian sequence of Sicily. Apart from carbonate minerals, rocks of this type contain variable amounts of sulphate minerals and in some places, native sulphur. Such parageneses have been described in evaporitic strata worldwide and are linked to the former presence of crude oil or methane. The carbonate minerals and native sulphur have been found to result from microbial sulphate reduction using locally derived sulphate ions and organic compounds that infiltrated the host lithology (Thode et al. 1954; Feely and Kulp 1957; Davis and Kirkland 1970; Pierre and Rouchy 1988; Böttcher and Parafiniuk 1998; Peckmann et al. 1999). Such secondary carbonates and native sulphur are particularly abundant in Messinian strata at different sites in Sicily (Dessau et al. 1962; Ziegenbalg et al. 2010). With respect to the location Monte Capodarso, microbial sulphate reduction was found to have been coupled to oxidation of methane during sedimentation and early diagenesis, resulting in secondary carbonates with $\delta^{13}C$ values as low as −52‰ V-PDB (Ziegenbalg et al. 2010). The accompanying native sulphur yielded rather low $\delta^{34}S$ values (as low as +1‰ V-CDT), corroborating that it formed as a consequence of microbial sulphate reduction (Ziegenbalg et al. 2010).

Methods

Thin-sections were studied with transmitted light and fluorescence microscopy using a Zeiss Axioskop 40 optical microscope (lamp: HBO 50, filters: BP 365/12 FT 395 LP 397 and BP 450–490 FT 510 LP 515). Standard X-ray diffraction (XRD) was performed on powdered samples with a Philips X'Pert Pro MD. A LEO 1530 Gemini and an attached energy-dispersive X-ray spectrometer (EDX) Oxford Inca 400 were used for field-emission scanning-electron microscopy (FE-SEM) and qualitative element identification. The micro-scale phase determination of the whisker crystals was performed directly on uncovered thin-sections by micro X-ray diffraction. In order to make the crystals accessible for the analysis, the sulphur entombing the whiskers was dissolved beforehand with hexane. We used the Bruker D8 DISCOVER GADDS XRD^2-micro diffractometer at the IFG-Tübingen equipped with a focusing polycapillary microlens and two-dimensional HI-STAR detector (cf. Berthold et al. 2009). The spotsize of the used microlens was approximately 50 µm. Due to the fixed incident angle of 10° and sample rotation, the analyzed area on the thin-section had a diameter of approximately 400 µm.

Results

Tabular to acicular anhydrite crystals represent the dominant phase in the studied rocks. Anhydrite is partly altered to alabastrine gypsum (Fig. 1a, b). Bundles of fluorescent, thin fibrous crystals project from the alabastrine gypsum into former cavities, which are now filled by native sulphur and minor spheroidal dolomite. Electron microscopy indicates that the thin fibrous crystals are also directly associated with anhydrite (Fig. 1c). The crystal fibers are apparently single crystals, which are several hundred micrometers long (Fig. 1b), flat shaped with a width of approximately 1 µm, and a height in the nanometer scale (Fig. 1c, d). They are consequently characterized by a length-to-width ratio considerably higher than 100 and are therefore referred to as whisker crystals.

Bulk XRD measurements of powdered samples revealed the presence of anhydrite, gypsum, and sulphur (data not shown). EDX analyses showed that whiskers contain calcium, oxygen, and sulphur (Fig. 2). For micro X-ray analysis, the X-ray spot was focused on crotches between anhydrite crystals (Fig. 3a), where whiskers are particularly abundant, forming bundles of fibers. Anhydrite as well as gypsum was detected (Fig. 3b), but no other minerals. These two minerals showed distinctly different diffraction patterns on the two-dimensional HI-STAR detector. The

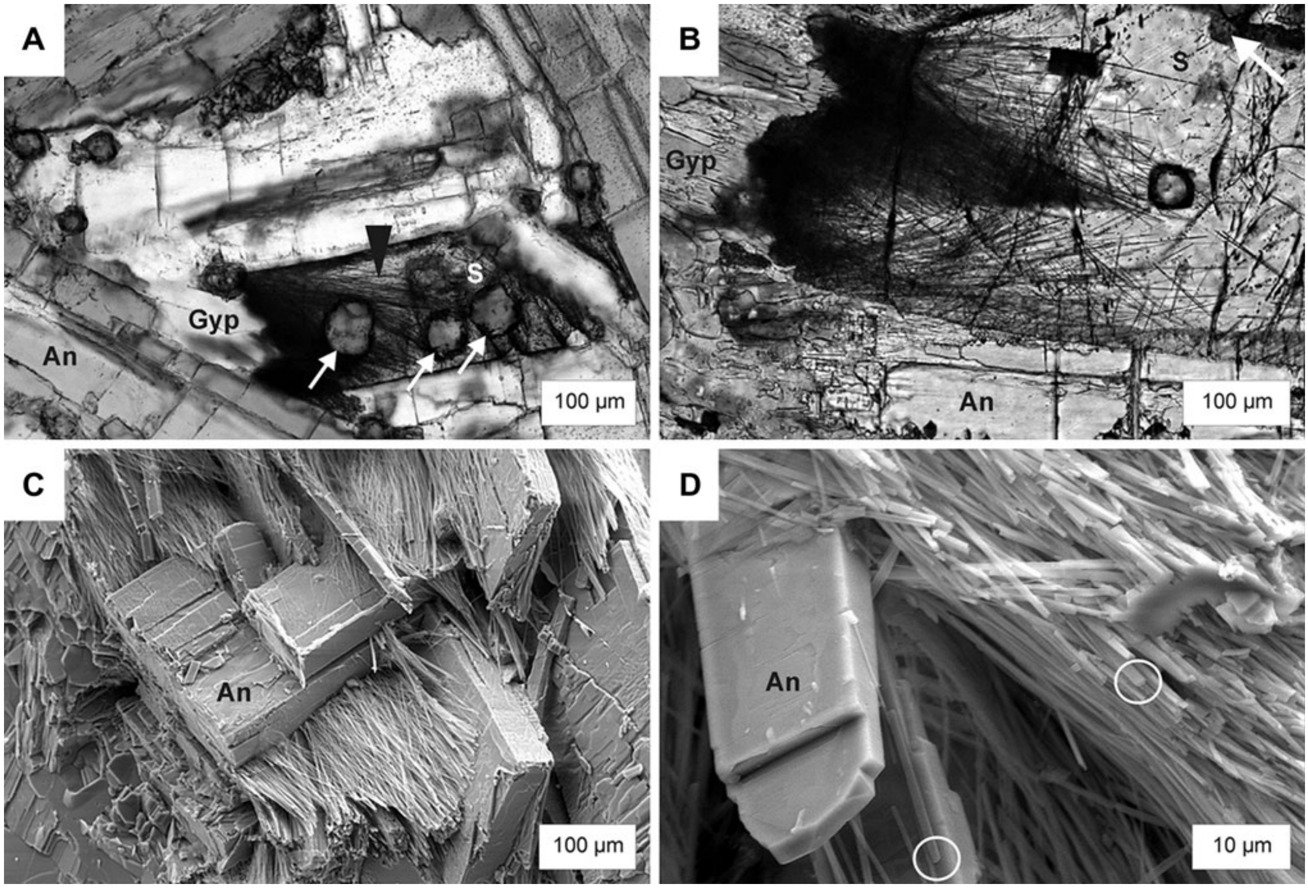

Fig. 1 Photomicrographs of gypsum whiskers and associated phases (*An* anhydrite; *Gyp* gypsum, *S* sulphur). **a** Gypsum whiskers (*black arrowhead*) associated with dolomite (*white arrows*) within a sulphur-filled cavity surrounded by gypsum and anhydrite; plane-polarized light. **b** Gypsum whiskers (*black*) originating on gypsum and projecting into a former cavity now filled by native sulphur and minor dolomite (*white arrow*); plane-polarized light. **c** Gypsum whiskers between anhydrite; FE-scanning electron micrograph. **d** Gypsum whiskers showing an angular profile. *Circles* mark two angular crystal terminations with high width-to-height ratios; FE-scanning electron micrograph

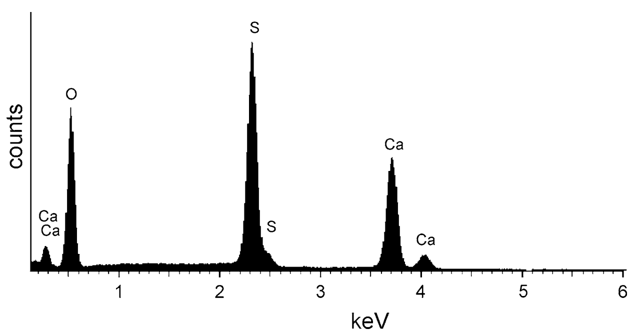

Fig. 2 EDX spectrum of gypsum whiskers

anhydrite generated only few intense spots on the corresponding peak positions (Fig. 3c), typical for large single crystals. In contrast to this, the gypsum showed a pattern with typical diffraction rings of a powder for each (hkl)-reflection (Fig. 3c), caused by the random orientation of many small whisker crystals.

Discussion

Conventional techniques including optical microscopy, electron microscopy coupled with EDX, and standard XRD failed to identify the mineralogy of whisker crystals enclosed in Messinian evaporites from Sicily. Optical microscopy did not allow the mineralogy to be determined due to limited crystal diameter and the entombment of crystals in native sulphur. Although EDX measurements revealed that the whiskers are comprised of calcium, oxygen, and sulphur, this did not unequivocally constrain mineralogy. Based on the paragenetic sequence and EDX results, different mineralogies still appeared feasible, including anhydrite, bassanite (calcium sulphate hemihydrate; cf. Allen and Kramer 1953; Bundy 1956; Peckmann et al. 2003), and gypsum. Under these circumstances, conventional XRD-techniques require either sufficient amounts of fine-ground material of the respective mineral phase or separation of single crystals. Because the whiskers were

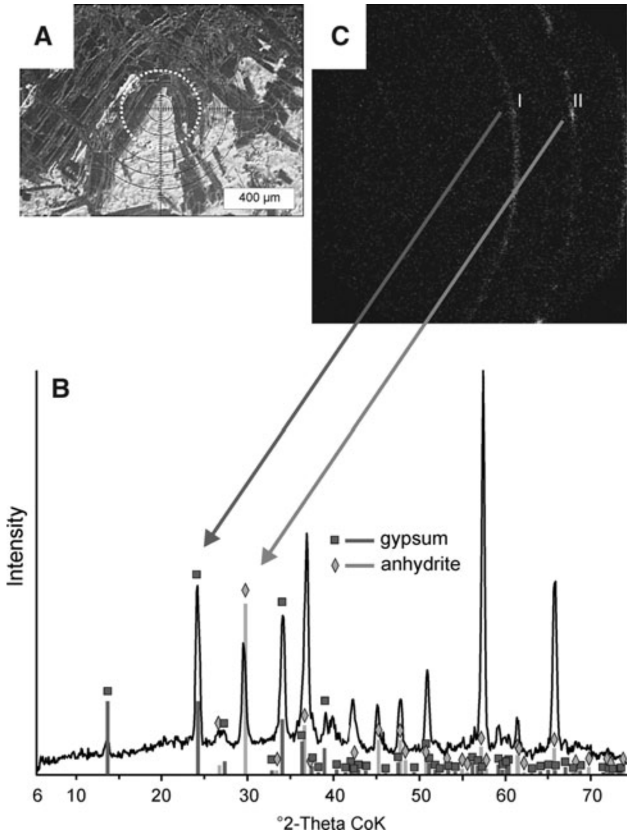

Fig. 3 **a** Position of the X-ray spot on the thin-section. **b** Diffraction pattern of the spot shown in (**a**) with peaks of gypsum whiskers and anhydrite. **c** Diffraction image from the two-dimensional HI-STAR detector with a spotty diffraction of anhydrite (*II*) and evenly *filled diffraction rings* of gypsum whiskers (*I*) in the cone section

only recognized in limited amounts in few thin-sections, neither bulk analyses nor their separation were feasible.

With the advent of μ-XRD^2 equipped with focusing microlenses, it is now possible to identify even small amounts of mineral phases in situ on uncovered thin-sections (Berthold et al. 2009). A problem that needed to be overcome with respect to the whiskers in the Sicilian samples was their entombment in native sulphur. Surficial dissolution of sulphur by hexane caused the surface of the thin-section to become uneven, with the whiskers now being exposed, but situated within a depression. This situation was not ideal for μ-XRD^2, which benefits from even and polished surfaces, but no relevant negative effect was observed by this surface topology, confirming the great potential of this technique.

To the best of our knowledge, this study is the first report of gypsum whiskers in evaporitic lithologies. Similar hair-like structures, however, have been recognized in gypsum and halite deposits of modern and Permian acid saline lakes (Benison et al. 2008). These structures were found to be a composite of gypsum and carbon, prompting Benison et al. (2008) to interpret them as remains of acidophilic microorganisms. No carbon was found to be associated with the Sicilian whiskers. Despite their distinct fluorescence, which appears to be caused by crystal boundaries, a microbial origin seems unlikely. Gypsum whiskers are typically formed by efflorescence on moist porous surfaces (Evans 1972) or as speleothems (Vidal Romani and Rodriguez 2007). In the Sicilian evaporites, the gypsum whiskers formed predominantly on alabastrine gypsum, growing into cavity spaces. The gypsum obviously originated from the hydration of anhydrite (Fig. 1). Water consequently penetrated into the pore space of the Messinian evaporites and this water most likely contained significant amounts of dissolved sulphate. As part of the water was consumed in the gypsification of the anhydrite, the sulphate concentration of the solution necessarily increased. As the formation of gypsum whiskers starts even at very low rates of supersaturation (cf. Strickland-Constable 1968; Hünger and Henning 1988), gypsification of anhydrite may have been sufficient to induce crystal growth. Whisker precipitation apparently preceded sulphur emplacement, as indicated by the paragenetic sequence with sulphur filling the residual pore space after whisker growth. Because sulphur formation was syngenetic at the studied location, occurring during early diagenesis (Ziegenbalg et al. 2010), the whiskers would have to be of Neogene age. A later formation of whiskers, however, cannot be excluded. If the sulphur was remobilized at some point, the whiskers may have formed epigenetically, possibly even in the course of mining activities or afterwards. Independent of the time of whisker formation, the entombment by hydrophobic sulphur efficiently protected the delicate gypsum crystals from dissolution during the exposure of the evaporites on the dumping site.

Conclusions

Because micron-sized mineral phases are often difficult to analyze and identify with conventional techniques, the use of micro X-ray diffractometry with focusing microlenses and a two-dimensional detector promises a substantial advancement for sediment petrology. We applied μ-XRD^2 to uncovered thin-sections of Messinian evaporites from Sicily that contain peculiar delicate hair-like crystals, revealing their gypsum mineralogy. With a length-to-width ratio considerably higher than 100, these crystals can be referred to as gypsum whiskers. The whiskers formed by efflorescence from alabastrine gypsum, which resulted from the hydration of anhydrite. The entombment by biogenic sulphur finally enabled the preservation of the delicate whisker crystals.

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