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BERNALITE FROM THE CLARA MINE, GERMANY, AND THE INCORPORATION OF TUNGSTEN IN MINERALS CONTAINING FERRIC IRON

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ABSTRACT

The very rare mineral bernalite is a ferric iron hydroxide with a structure related to that of perovskite. The present description of only the second known occurrence focusses on two samples from the Clara mine, central Black Forest, Germany. X-ray powder diffraction, scanning electron microscopy, and optical microscopy are used to characterize the mineral. The bernalite is polysynthetically twinned, with the twinning seen both microscopically, in the case of apparently "single" crystals, and macroscopically, in crystallographically oriented intergrowths of crystals. The samples investigated contain small amounts of tungsten and trace amounts of silicon. Crystal-chemical considerations suggest that W^{6+} ions in bernalite and in other ferric iron minerals substitute for Fe^{3+} ions.

Keywords: bernalite, occurrence, twinning, crystal chemistry, tungsten, ferric iron, Clara mine, Germany.

SOMMAIRE

La bernalite, minéral rarissime, est un hydroxyde de fer ferrique ayant une structure semblable à celle de la pérovskite. Ici, on présente une description du deuxième exemple connu, découvert à la mine Clara, dans la Forêt Noire centrale, en Allemagne. L'étude repose sur des spectres de diffraction X, la microscopie électronique à balayage, et un examen des deux échantillons disponibles par microscopie optique. La bernalite est maclée de façon polysynthétique, et ces macles sont visibles sous le microscope, dans le cas des cristaux apparemment uniques, et macroscopiquement dans les intercroissances cristallographiquement orientées. Les échantillons étudiés contiennent de faibles quantités de tungstène et des traces de silicium. D'après les considérations cristallochimiques, les ions W^{6+} dans la bernalite et autres minéraux de fer ferrique remplaceraient le Fe^{3+}.

(Traduit par la Rédaction)

Mots-clés: bernalite, indice, macle, chimie cristalline, tungstène, fer ferrique, mine Clara, Allemagne.

INTRODUCTION

Bernalite is an orthorhombic (pseudocubic) modification of ferric iron hydroxide, $Fe(OH)_3$. It was discovered by Birch *et al.* (1992, 1993) from the oxidized zone of the Proprietary mine, Broken Hill, New South Wales, Australia. It forms pseudo-octahedral, bottle-green crystals up to 3 mm on edge, partially embedded in a layer of goethite. The crystals sit on a matrix of coronadite and are coated with a thin black layer of goethite (Birch *et al.* 1992).

Interestingly, the orthorhombic structure of bernalite [space group *Immm*: Birch *et al.* (1993), or *Pmmm*: McCammon *et al.* (1995)] is that of a slightly distorted perovskite or ReO_3 type, and consists of a three-dimensional framework of corner-shared, almost ideal $Fe^{3+}(OH)_6$ octahedra. Bernalite is a member of the söhngeite, $[Ga(OH)_3]$, group, and closely related to the stottite $[Fe^{2+}Ge^{4+}(OH)_6]$ and schoenfliesite $[Mg^{2+}Sn^{4+}(OH)_6]$ groups. Chemical analyses of this unusual mineral reveal the presence of very small amounts of Si, Pb, Zn, H_2O and CO_2 (Birch *et al.* 1992, 1993, McCammon *et al.* 1995). Recent spectroscopic investigations revealed that the Si detected in these crystals (2–6 wt.% SiO_2) may be considered an essential constituent of the structure (McCammon *et al.* 1995). The small amounts of molecular carbon dioxide were assumed to be located in a large void site of the structural framework. The empirical formula $[(H_2O)_{0.04}(CO_2)_{0.03}Pb_{0.01}](Fe_{0.93}{}^{3+}Si_{0.06}Zn_{0.01})(OH)_{2.95}O_{0.04}$ has been derived (McCammon *et al.* 1995). The magnetic structure of bernalite was investigated by McCammon *et al.* (1996).

The present contribution provides data on bernalite from the Clara mine, central Black Forest, Germany.

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This mine is worked as a barite – fluorite deposit and consists of a system of hydrothermal veins hosted mainly by paragneiss. Among both mineral collectors and scientists, it is known for its wealth of unusual and rare minerals (*e.g.*, Molon 1990; Walenta 1992, 1997, Kolitsch 1997, 1998). More than 320 different mineral species have been found there, including rarities such as cyanophyllite, doyleite, prosopite, rankachite, tungstibite and uranosphaerite. The element tungsten plays an important role in this deposit. Brief accounts of the occurrence of bernalite at the Clara mine have been given by Walenta (1995a) and Kolitsch (1997).

DESCRIPTION OF THE SAMPLES

Samples of bernalite were kindly provided by M. and W. Zapf, Ingolstadt, Germany (sample A) and R. Bayerl, Stuttgart, Germany (sample B). Both samples were found on the dumps of the Clara mine, where collecting is permitted for a small fee. In sample A, found in 1993, the bernalite forms bright olive-green to dark bottle-green crystalline aggregates, closely intergrown with brownish black goethite. Voids in mamillary goethite host small (up to ~0.1 mm), blocky (pseudotetragonal, rarely pseudocubic) crystals that are perfectly transparent and have a glassy luster (Fig. 1). All crystals are slightly elongate, resembling tetragonal prisms, and are invariably somewhat thicker toward the crystal terminations. They also exhibit a faint striation perpendicular to their elongation. The prisms are commonly intergrown either in a subparallel way or by forming a "boxwork" of crystals oriented at right angles to each other (Fig. 2). Both bernalite and goethite cover milky quartz and colorless, slightly corroded fluorite. Older, whitish barite also is present, but not in contact with the iron minerals.

Sample B, found in 1989, is rather similar in appearance to sample A and shows olive-green to yellowish green crusts of bernalite on mamillary, dark brownish black goethite. Closer inspection revealed thin (<0.5 mm), fine-grained layers of bernalite between thick (1–5 mm) layers of goethite, thus suggesting simultaneous growth. Rare, single, prismatic crystals up to 0.1 mm have a square or slightly rectangular cross-section and perfectly flat top, thus resembling bricks. As for sample A, a faint striation perpendicular to the crystal elongation was noted.

In contrast with the Clara mine samples, the much larger crystals of bernalite from the type locality in Australia exhibit a pseudo-octahedral habit (Birch *et al.* 1992), a feature that may reflect different contents of impurity elements and their influence on crystal growth and morphology (see Discussion).

EXPERIMENTAL

X-ray powder diffractometry (Siemens D5000, Cu *K*α radiation, position-sensitive detector) was used to identify the bernalite and determine its unit-cell dimensions. The compositions of both bernalite and associated goethite were investigated by scanning electron microscopy (SEM; Cambridge Stereoscan 200 and 250 Mk3 instruments), using energy-dispersion (EDS) and wavelength-dispersion (WDS) X-ray analyses. During spot analysis of the top face of a single prism of bernalite, dehydration cracks parallel to the face diagonal developed after a short time. This dehydration is in accord with the low thermal stability of bernalite already observed by Birch *et al.* (1993) and McCammon *et al.* (1995) during electron microprobe and transmission electron microscope investigations. After losing H_2O at ~190°C, bernalite decomposes to hematite.

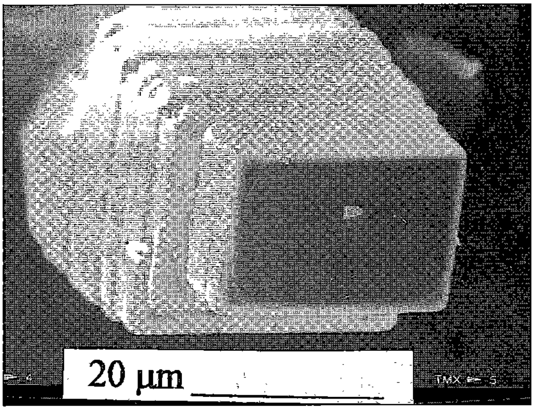

FIG. 1. SEM micrograph of an elongate "single" crystal of bernalite. The striation perpendicular to the elongation is related to the polysynthetic twinning (see text).

Optical properties of apparently single crystals and of aggregates of crystals were investigated in white light using Cargille immersion liquids.

RESULTS

Crystallography and twinning

The refined "pseudocubic" unit-cell parameters of the two samples are quite close to the value given for the type-locality bernalite [a_p = 7.568(1) Å: Birch *et al.* (1992, 1993)]. Sample A, for instance, has a_p = 7.56(1) Å.

Apparent single, elongate crystals from both samples were investigated under the polarizing microscope. In agreement with the orthorhombic symmetry proposed for this mineral, no deviation from straight extinction was observed. Growth features resembling the upper part of an hourglass were seen, obviously related to the greater thickness of the crystals toward their terminations. Birefringence is nearly zero down the elongation axis, but shows maximum values perpendicular to it.

The extinction itself is strongly inhomogeneous. "Single" crystals invariably show band-like regions perpendicular to their elongation, which are alternatively in an extinction position or 90° away from it. The optical elongation of these regions is consequently either positive or negative. The bands vary considerably in width, from immeasurably thin to ~5% of the crystal's length, and all bands have sharply defined boundaries. The banding feature clearly demonstrates that a "single" crystal of bernalite actually is composed of polysynthetically twinned individual crystals, with the single bands representing differently sized and oriented single-crystal domains. The width of the bands (domains) probably depends on local constraints such as variations in composition or mechanical strain. The twinning is undoubtedly the cause of the striation of the crystals perpendicular to their elongation. The fact that the top face of a typical prism of bernalite is perfectly flat suggests that the polysynthetic twinning may be only two-dimensional, *i.e.*, restricted to two of the three axes of the orthorhombic system. Consequently, the shorter dimension, a, equal to 7.544(2) Å, would be the elongation axis, whereas the two longer and similar dimensions, b = 7.560(4) and c = 7.558(2) Å (Birch *et al.* 1993), would be perpendicular to the direction of elongation. This proposed orientation would also be in agreement with the direction of the maximum birefringence.

The octahedral crystals from the type locality, when viewed in thin section or under a transmission electron microscope, were also found to be polysynthetically twinned, resulting in a cross-hatched texture (Birch *et al.* 1993). The individual "fibrous" crystallites of bernalite were found to be approximately 30 μm in length (Birch *et al.* 1992). The electron-diffraction experiments of McCammon *et al.* (1995) showed that polysynthetic twinning in this bernalite is along $\{100\}_p$ planes, with twin domains ranging from 3 to 20 nm in thickness.

The widely variable thickness of domains does not suggest that the bernalite from the Clara mine has formed as a cubic modification at a somewhat higher temperature, followed by a transformation to a lower-symmetry modification stable at ambient temperature. It would be worthwhile to gently heat a polysynthetically twinned sample of bernalite to verify a possible phase-transition from the (distorted) orthorhombic room-temperature symmetry to a hypothetical cubic (or tetragonal?) symmetry typical of perovskite at some higher temperature less than 190°C.

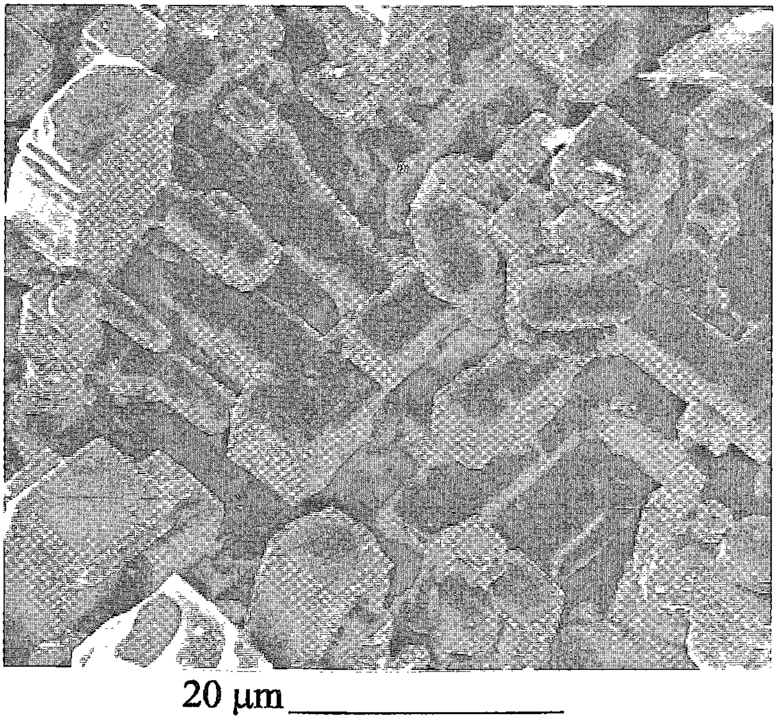

FIG. 2. Right-angle intergrowths of orthorhombic, pseudotetragonal crystals of bernalite (SEM micrograph).

The polysynthetic twinning of bernalite is also expressed macroscopically by the observed "boxwork" of intergrown crystals oriented at perfectly right angles to each other (Fig. 2). This might be interpreted as a second-order twinning superposed on the microtwinning of the "single" crystals.

On account of the polysynthetic twinning, the prism faces of the elongate crystals can only be described in terms of a "composite" tetragonal form, which could be either $\{010\}_t$ or $\{011\}_t$. There are two indications that the form is in fact $\{010\}_t$. First, the observed features of twinning are in accordance with $\{100\}_t$ as the twin plane, *i.e.*, parallel to the flat top face of the crystals. Second, the observed beam-induced dehydration cracks parallel to the face diagonal of the top face indicate that the evaporated molecules of H_2O have formed from the hydroxyl groups that are arranged approximately parallel to the $\{011\}_t$ planes (Birch *et al.* 1993).

With the SEM, some rare "single" crystals were found to show very small faces bevelling the edges of the top face (compare Fig. 1). These probably are the forms {110} and {101}.

Composition

Results of semiquantitative SEM–EDS analyses of both samples A and B show unexpectedly high contents of W (approximately 3 to 5 at.% of the total metal content; estimated error ~1 at.%) and very minor Si contents (between zero and ~1.5 at.%; estimated error 0.5 at.%). No other elements with an atomic number greater than 9 were detected. Since *K* peaks of Si are rather difficult to differentiate from *M* peaks of W owing to a very marked overlap, wavelength-dispersion measurements were conducted to evaluate the Si contents. These measurements confirm the presence of significant amounts of W. They also show that very small amounts of Si are detectable in sample A, but Si is present in sample B only as a trace. The derived formula is $(Fe^{3+},W,Si)(OH)_3$. The specimen investigated by Walenta (1995a) seems to contain Si only in small amounts. However, bernalite from the type locality contains Pb, Zn and carbonate in addition to Si (Birch *et al.* 1992, 1993, McCammon *et al.* 1995). The latter authors showed, by transmission electron microscopy, that the Si is present within domains, but that domain boundaries are enriched in Si. By comparison with thaumasite, a mineral with $Si(OH)_6$ groups in the structure (Effenberger *et al.* 1983), and using bond-valence arguments, Birch *et al.* (1993) gave convincing evidence that Si replaces Fe in bernalite and can occur in six-fold coordination. In both bernalite and thaumasite, the $R(OH)_6$ octahedron is highly regular.

The present results confirm that Si replaces Fe in bernalite, but it may not be an essential constituent of the structure since only trace amounts were found in sample B.

The underlying matrix of goethite in both samples A and B contains small amounts of W, with sample B showing additional traces of Mn, Cu and Cl. EDS analyses and back-scattered electron images of the fracture surface of a worm-like aggregate of goethite with internal radiating structure (from sample B) shows that the W content increases toward the center of the radiating structure. This would indicate that at the beginning of goethite crystallization, a rather large number of tungsten ions was present in the solution; tungsten possibly was preferentially incorporated in goethite.

DISCUSSION

Tungsten in minerals containing ferric iron

The relatively high tungsten content of the bernalite from the Clara mine is interesting in view of the fact that a number of other Fe^{3+} oxide minerals from the Clara mine also contain appreciable tungsten (see below). The valency of tungsten is undoubtedly 6+, as all tungsten minerals formed in more or less oxidizing environments contain W^{6+} ions (Sahama 1981, Williams 1990). A review of the crystal-chemical behavior of hexavalent tungsten in ferric iron minerals shows that in various minerals, tungsten substitutes for iron and does not occupy vacant sites.

Crystals of akaganéite, β–$Fe^{3+}(O,OH,Cl)$, from the Clara mine contain up to 14% W (17.7% WO_3) (Walenta 1982). Akaganéite has the basic structure-type of hollandite, with large channels parallel to [001]. Walenta (1982) assumed that the W atoms are situated in these channels. However, in both natural and synthetic hollandite compounds, only molecules of water and monovalent or divalent cations are known to occupy the channels (*e.g.*, Downs *et al.* 1995). As with the bernalite described here, the unit-cell parameters of the W-bearing akaganéite do not show significant deviation from the literature values. The accompanying goethite was found to contain only a very minor amount of W.

Feroxyhyte, δ–$Fe^{3+}O(OH)$, recently reported from the Clara mine, contains considerable amounts of tungsten (Fe:W ~1:0.14; Walenta 1997). In addition, the analysis revealed small amounts of aluminum and vanadium. Walenta (1997) proposed that the feroxyhyte was stabilized by its tungsten content. Feroxyhyte grew on a goethite matrix that contained only minor amounts of tungsten.

Tungsten-bearing goethite also has been reported from Bulgaria (Tarasov *et al.* 1994). Reports on tungsten- and uranium-bearing hollandite and cryptomelane from a low-temperature iron–manganese-oxide vein deposit suggest that tungsten may also replace (trivalent or tetravalent) manganese (von Gehlen 1958).

The generally close geochemical association of tungsten with iron (Evans & Krauskopf 1974) may be explained by laboratory evidence that tungsten ions are strongly adsorbed on colloidal $Fe(OH)_3$ (Mao 1985). High tungsten contents were also found in oxysalt minerals containing ferric iron. In a tungsten-bearing variety of the iron–calcium phosphate–arsenate walentaite, hexavalent tungsten was reported to substitute for trivalent iron (Nickel 1987). The 14.5 wt.% WO_3 detected did not have an appreciable effect on the unit-cell parameters of the walentaite.

Ferric iron in tungsten minerals

The reverse substitution, *i.e.*, that of Fe^{3+} for W^{6+}, occurs in the following three secondary tungsten minerals: ferritungstite, a member of the pyrochlore group with the structural formula $([H_2O],Ca,Na)_{0.67}(W,Fe^{3+})_2(O,OH)_6([H_2O],K)$ (Machin & Süsse 1975, Ercit & Robinson 1994), jixianite, $Pb(W,Fe^{3+})_2(O,OH)_7$, a lead-dominant member of the pyrochlore group (Liu 1979), and russellite, $(Bi_{1.59}Pb_{0.05})_{\Sigma 1.64}(W_{0.85}Fe_{0.15})_{\Sigma 1.00}O_6$ (Anthony *et al.* 1997). It is noteworthy that other trivalent cations such as V^{3+} and Cr^{3+} are also known to occur in natural, iron-free ferritungstite and in jixianite, where they presumably substitute for the tungsten ions (Walenta 1995a, b, Kolitsch 1997, 1998).

Concluding statements

The above data and observations suggest that in bernalite and at least in the majority of ferric iron minerals, W^{6+} substitutes for Fe^{3+}. The very high (formal) charge of the W^{6+} ion would make it very difficult to incorporate it into any channel or vacant sites in a given structure.

As noted by Birch *et al.* (1992), bernalite belongs to the söhngeite group and is closely related to compounds adopting the ReO_3 structure type such as $Sc(OH)_3$, $Lu(OH)_3$, as well as the non-stoichiometric tungsten-bronze-type phases such as H_xWO_3, H_xMoO_3, and β–H_xMoO_3 (Wiseman & Dickens 1973, Wells 1975). The structural relationship with H_xWO_3 corroborates the substitution of W^{6+} for Fe^{3+} in bernalite, idealized as $Fe(OH)_3$ or H_3FeO_3. Bond-valence calculations, assuming a complete substitution of W^{6+} for Fe^{3+} and neglecting hydrogen-bond contributions, yielded 4.7 valence units for the tungsten ion, and oxygen valence units increased by 50 to 60% compared to ideal $Fe(OH)_3$. Therefore, a partial or complete solid-solution series of bernalite with H_xWO_3 may exist.

Simple crystal-chemical considerations provide additional evidence for the proposed substitution. A comparison of ionic radii shows that the radius of $^{VI}W^{6+}$, 0.60 Å, is quite close to that of $^{VI}Fe^{3+}$, 0.645 Å (Shannon 1976). Not surprisingly, on average, the coordination number of $^{VI}W^{6+}$ in inorganic compounds is 5.6 (Brown 1988), almost identical with that of $^{VI}Fe^{3+}$, 5.69. The similarity of the ionic radii explains that an incorporation of relatively large amounts of W does not result in significant changes of the unit-cell parameters of a given ferric iron mineral.

It is obvious that an $Fe^{3+} \Leftrightarrow W^{6+}$ substitution requires concomitant charge-balance. This can be achieved by a decrease in hydroxyl groups and molecules of H_2O in the respective structure (as also suggested by the structural relationship with H_xWO_3), simultaneous substitution of monovalent or divalent cations for Fe^{3+}, or introduction of vacancies according to the scheme $2Fe^{3+} \Leftrightarrow W^{6+} + \square$.

As a final conclusion, and as already pointed out by Birch *et al.* (1992, 1993) and McCammon *et al.* (1995), synthesis experiments are needed to elucidate the conditions leading to the formation of bernalite. Preliminary efforts in this direction were unsuccessful (Birch *et al.* 1993), although bernalite is thought to form in the pH range from 8 to 10 (A. Pring, pers. commun., 1998). Such experimentation may also be used to establish the extent of substitution of W in ferric iron hydroxides, oxyhydroxides and other Fe^{3+} minerals.

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