Bernalite, Fe(OH)₃, a new mineral from Broken Hill, New South Wales: Description and structure

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ABSTRACT

Bernalite is a new iron hydroxide from the Proprietary mine at Broken Hill, New South Wales, Australia. The mineral occurs as flattened pyramidal to pseudo-octahedral crystals up to 3 mm on edge with concretionary goethite and coronadite. The crystals are dark bottle green, with a vitreous to adamantine luster. Bernalite has a pale green streak and is brittle with no cleavage but an uneven to conchoidal fracture and a Mohs hardness of 4. Optical data are incomplete due to the effects of twinning; the indices of refraction are in the range 1.92–1.94. Chemical analysis gave Fe₂O₃, 65.53; SiO₂, 2.99; ZnO, 1.13; PbO, 2.70; H₂O, 25.2; CO₂, 1.0; total 98.55 wt%. The simplified formula is very close to Fe(OH)₃. Bernalite is pseudocubic but single-crystal studies gave an orthorhombic cell with a = 7.544(2), b = 7.560(4), c = 7.558(2) Å, V = 431.0(3) Å³. The density is Dcalc = 3.35 g/cm³. The crystal structure was solved by Patterson methods, but full refinement was not possible because of the effects of polysynthetic twinning. The best refinement in space group Immm with Z = 8 gave R = 0.106, R = 0.112, using a set of 785 reflections, of which 462 were considered observed [I > 3σ(I)]. Bernalite has a distorted ReO₃-like structure, consisting of a three-dimensional network of corner-connected Fe(OH)₆ octahedra.

The strongest lines in the X-ray powder pattern are [d calc (Å), I calc, hkl] 3.784 (100) (200, 020, 002); 2.676 (15) (220, 202, 022); 2.393 (16) (310, 130, 013, 031, 301, 103); 1.892 (10) (400, 040, 004); 1.692 (17) (420, 240, 204, 402, 024, 042); 1.545 (9) (422, 242, 224). The name is for the British crystallographer J. D. Bernal (1901–1971).

INTRODUCTION

While visiting the Proprietary mine at Broken Hill, New South Wales, Australia, in the early 1920s, R. T. Slee collected specimens containing dark green octahedral crystals on concretionary goethite and coronadite. Slee passed the specimens on to the noted Australian geologist Frank Stillwell for identification. Stillwell (1927) suggested that the crystals were limonitic replacements of arsenopyrite coated with scorodite. The specimens were subsequently deposited in the research collections of the Department of Geology at the University of Melbourne, where they remained unnoticed for many years. In 1990 the collections of the Department of Geology were transferred to the Museum of Victoria, and during this process the specimens were rediscovered and examined. Preliminary examination by powder X-ray diffraction and electron microprobe analysis suggested that the mineral forming the octahedral crystals was a new member of the stottite group. A single-crystal structure determination was undertaken to resolve fully the composition and stoichiometry of the mineral. The new species is ferric trihydroxide and has been named bernalite in honor of John Desmond Bernal (1901–1971), eminent British crystallographer and historian of science. Bernal made outstanding contributions across the field of crystallography, including the investigation of the crystal chemistry of iron oxides and hydroxides (Bernal et al., 1959). The mineral and the name were approved by the Commission on New Minerals and Mineral Names. Type specimens (cotypes) are in the collections of the Museum of Victoria, Melbourne, and the South Australian Museum, Adelaide.

OCCURRENCE

At least two specimens containing bernalite, which were originally one piece, were collected in the upper levels of the Proprietary mine at Broken Hill, New South Wales.
Unfortunately, accurate locality data for the material were not recorded, so the exact occurrence in the Proprietary mine sequence cannot be established. However, the nature of the mineral and the goethite-coronadite matrix are consistent with the specimens having come from the near-surface portion of the oxidized zone. At the Proprietary mine the secondary zone extends to depths of up to 150 m from the original surface (Birch and Van der Hayden, 1988; King, 1983). All this area of the lode, within the original Proprietary mine leases, has been opencut, and no further specimens of bernalite, either recently collected or in old collections, are known.

**PHYSICAL AND OPTICAL PROPERTIES**

Bernalite occurs as flattened pyramidal to pseudo-octahedral crystals up to 3 mm on edge (Fig. 1). The crystal faces are rough and slightly concave. The outer surface is yellow green with a resinous luster, but the inner portions are transparent, dark bottle green with a vitreous to adamantine luster. A thin layer of dark brown fibrous goethite occurs on most crystals, which gives them a glossy, nearly black appearance. The streak of bernalite is apple green. In thin section the crystals are yellowish bottle green and when viewed under crossed nicols show a fine-scale crosshatched texture due to polysynthetic twinning. The crystallographic orientation of the twinning could not be determined, but it is probably on \{100\}, \{010\}, and \{001\}. Strings of small goethite inclusions occur roughly parallel to the outer margins of the crystals. The mineral has no prominent cleavage or parting but is brittle with an uneven to conchoidal fracture. The Mohs hardness is 4, and the density, measured by suspension in a mixture of diiodomethane and chloroform, is 3.32(2) g/cm³ (mean of five determinations), which is within experimental error for the calculated density 3.35 g/cm³ for the empirical formula (see below). Complete optical properties could not be determined because of the twinned nature of the mineral. Grain mounts gave refractive indices in the range 1.92–1.94. It was not possible to determine more than one refractive index on any grain, and therefore optical orientation could not be established.

**CHEMISTRY**

Bernalite was analyzed using a Jeol electron microprobe operating at 15 kV with a specimen current of 20 nA. The mineral is quite stable in the electron microprobe beam. The standards employed were hematite (Fe), wollastonite (Si), sphalerite (Zn), and galena (Pb). No other elements with atomic number >8 were detected by wavelength spectroscopy. H₂O and CO₂ were determined separately using a Perkin Elmer 240 Automatic C/H/N analyzer on a 7-mg hand-picked sample. Eight microprobe analyses were obtained, for which the average is given in Table 1. The empirical formula calculated on the basis of one cation is \[\text{Fe(OH)₃(CO₃)}_{0.05}\text{Pb}_{0.01} \cdot \text{Si}_{0.06} \text{Zn}_{0.01} \text{(OH)}_{2.96}\], with the simplified formula being Fe(OH)₃.

The small amount of Si in the analysis has been assigned to the same site as the Fe, an octahedral site in this structure. White and Nelen (1973) and Kampf (1982) adopted a similar assignment in their respective descriptions of the closely related minerals tetrawickmanite and jeanbandyite. The presence of Si in octahedral coordination with O in minerals and compounds formed at low temperature and pressures is exceedingly unusual, although a small number of synthetic compounds and at least one mineral are known (Finger and Hazen, 1991). An alternative explanation is that the bernalite crystals contain submicroscopic inclusions of silica. Other, perhaps less likely, locations for the Si (e.g., a tetrahedral site associated with the A cation site) are also possible. However, the limitations associated with effects of twinning in fully refining the crystal structure and the rapid decomposition of the mineral in the electron beam of the electron microscope unfortunately prevent clarification of the role of Si in bernalite.

**POWDER X-RAY DIFFRACTION**

The powder X-ray diffraction pattern was recorded using a Philips automatic powder diffractometer with Fe-filtered CoKα radiation (\(λ = 1.79026 \text{ Å}\)). Line intensities (peak areas) were estimated from the diffractometer trace.

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**Fig. 1.** Pseudo-octahedral crystals of bernalite on goethite from the Proprietary mine, Broken Hill, New South Wales. Scale bar is 3 mm.

**TABLE 1. Chemical analysis of bernalite**

<table>
<thead>
<tr>
<th></th>
<th>Bernalite* (wt%)</th>
<th>Fe(OH)₃ (wt%)</th>
<th>Bernalite** (atomic proportion)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe₂O₃</td>
<td>65.53</td>
<td>74.73</td>
<td>0.92</td>
</tr>
<tr>
<td>SiO₂</td>
<td>2.99</td>
<td>0.06</td>
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</tr>
<tr>
<td>ZnO</td>
<td>1.13</td>
<td>0.01</td>
<td></td>
</tr>
<tr>
<td>PbO</td>
<td>2.70</td>
<td>0.01</td>
<td></td>
</tr>
<tr>
<td>H₂O</td>
<td>25.2</td>
<td>25.27</td>
<td>3.12</td>
</tr>
<tr>
<td>CO₂</td>
<td>1.0</td>
<td>3.12</td>
<td>0.03</td>
</tr>
<tr>
<td>Total</td>
<td>98.55</td>
<td>100.0</td>
<td></td>
</tr>
</tbody>
</table>

* Average of eight microprobe analyses. H₂O and CO₂ determined separately on a 7-mg sample.

**Note:** Bernalite of Proprietary mine, Broken Hill, New South Wales.
TABLE 2. Powder X-ray diffraction data for bernalite

<table>
<thead>
<tr>
<th>2θ (°)</th>
<th>d_{hkl} (Å)</th>
<th>θ (°)</th>
<th>hkl</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>3.784</td>
<td>20</td>
<td>002</td>
</tr>
<tr>
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<tr>
<td>16</td>
<td>2.676</td>
<td>202</td>
<td>022</td>
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<tr>
<td>17</td>
<td>2.676</td>
<td>202</td>
<td>022</td>
</tr>
<tr>
<td>5</td>
<td>2.393</td>
<td>231</td>
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<tr>
<td>6</td>
<td>2.185</td>
<td>213</td>
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<td>7</td>
<td>2.185</td>
<td>213</td>
<td>321</td>
</tr>
<tr>
<td>10</td>
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<td>240</td>
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<td>040</td>
</tr>
<tr>
<td>9</td>
<td>1.545</td>
<td>242</td>
<td>224</td>
</tr>
<tr>
<td>18</td>
<td>1.545</td>
<td>242</td>
<td>224</td>
</tr>
</tbody>
</table>

Note: The pseudocubic cell parameters refined from the data above are $a = b = c = 7.568(1)$ Å; $V = 433.4(2)$ Å$^3$.

The powder pattern was initially indexed on a cubic unit cell, and least-squares refinement was undertaken using the eight reflections with $d > 1.4$ Å ($2\theta < 80^\circ$). The cubic cell has $a = 7.568(1)$ Å. Subsequent structural studies using single-crystal X-ray diffraction methods showed the symmetry to be orthorhombic, with the true cell only slightly distorted from a body-centered cubic, perovskite-like structure. The powder pattern indexed on the orthorhombic (pseudocubic) cell is presented in Table 2.

MOßSBAUER SPECTROSCOPY

The room temperature Mössbauer spectrum of bernalite was recorded on a 20-mg hand-picked sample. The spectrum is shown in Figure 2, and the spectral parameters are given in Table 3. The isomer shifts are typical for Fe$^{3+}$ and show that all Fe in bernalite is present in the Fe$^{3+}$ rather than the Fe$^{2+}$ oxidation state. The spectrum was fitted with two magnetically ordered fields of six lines and one quadrupole split doublet. Because the isomer shifts and the electric-field gradients for the magnetic fields are very similar, the spectrum probably involves only one site, which is not fully ordered at room temperature. The isomer shift and quadrupole splitting of the small central doublet suggest that it is related to the same site (J. Brown, personal communication). Unfortunately the specimen was accidentally lost before low temperature spectra were recorded. In view of the very limited amount of material on the type specimens, it was decided not to remove further material to complete the Mössbauer studies.

A considerable number of Mössbauer studies have been undertaken on iron oxy-hydroxides and iron hydroxides; however, none so far shows magnetic ordering at room temperature (Mathalone et al., 1970; Au-Yeung et al., 1984; Coey and Readman, 1973; Persoons et al., 1986).

THERMAL ANALYSIS

Differential thermal analysis revealed that bernalite dehydrates to form hematite. This strongly exothermic reaction occurs in a single step between 190 and 200 °C:

$$2\text{Fe(OH)}_3 \rightarrow \text{Fe}_2\text{O}_3 + 3\text{H}_2\text{O}.$$ 

The dehydration of bernalite was also observed in a Philips CM 30 transmission electron microscope operating with an accelerating voltage of 300 kV. When exposed to the focused electron beam, bernalite underwent dehydration within seconds to form microcrystalline hematite. No orientational relationship between the original bernalite lattice and the hematite was observed.

CRYSTAL STRUCTURE

Experimental

Crystal fragments suitable for detailed study were sought by examination under polarized light. Although most did not extinguish uniformly, three fragments showing only slight undulose extinction were selected. Precession and Weissenberg photography showed a distribution of strong and weak reflections assignable to a pseudocubic body-centered perovskite-like lattice with observed reflections $h + k + l = 2n$. However, some very weak reflections that violated this condition were also observed. Intensity data were obtained from all three fragments using a CAD-4 single-crystal diffractometer, and the structure was solved by Patterson methods using SHELXS-86 (Sheldrick, 1986). However, as no satisfactory refinement emerged, further measurement of intensities was undertaken on one of the crystal fragments, and a full sphere of data was measured within the limits $-13 < h < 13$; $-13 < k < 13$; $-13 < l < 13$. A total of 10760 reflection intensities was obtained using an $\omega-2\theta$ scan technique. The scan rate varied between 1.03 and 16.48°/min, and

<table>
<thead>
<tr>
<th>Table 3. Mössbauer parameters for bernalite at room temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Isomer shift</strong> (mm/s)</td>
</tr>
<tr>
<td>Field 1</td>
</tr>
<tr>
<td>0.36</td>
</tr>
<tr>
<td>Field 2</td>
</tr>
<tr>
<td>0.37</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>Doublet</td>
</tr>
</tbody>
</table>
the maximum measuring time per reflection was 80 s. Three standard reflections were monitored every 3 h of measuring time, and no loss of intensity was noted. The orientation of the crystal was checked every 400 reflections through remeasurement of the standard reflections. Some 4409 reflections having negative intensities were excluded from the data set. A numerical absorption correction based on six indexed but not perfect crystal faces was applied with the program SHELXTL (Sheldrick, 1976). Data were also corrected for Lorentz and polarization effects. The Laue symmetry of the data set was found to be 2/m which suggested the space groups P2_1/m, I112, or I11m. Data reduction of 6351 reflections led to a set of 2637 unique reflections (R \_\_r = 0.0722) with the assumption of the monoclinic space group P2_1/m. Of this data set only 785 reflections were considered observed with I > 3\sigma(I), \sigma(I), on the basis of counting statistics.

**Structure refinement**

Refinements of the structure were undertaken in a number of space groups, including P1, I112, I11m, and P2_1/m. All refinements were characterized by splitting of the O positions, suggesting that the crystal fragment used for data measurement was twinned. Orthorhombic symmetry was clearly shown by unit-cell projections calculated by STRUPL84 (Fischer, 1985) for geometrically correct FeO_6 octahedra (O-O distances approximately 2.7 Å). On this basis two trial models for the bernalite structure were derived in the orthorhombic space group Pmmn. An electron density peak on the perovskite A cation site in difference Fourier maps was tentatively assigned to H_2O on the basis of the chemical analysis and included in the structural models. The two models differed only in the O positions, and both suggested higher symmetry than Pmmn. The difference perpendicular to the c direction between the n glide of Pmmn and the mirror of the body-centered space group I11mm was found to be minimal when comparing O positions of the octahedra. This small difference was in accordance with 90 very weak reflections, which did not belong to the body-centered cell. The reflections were in the parity groups oee = 24, eoe = 17, eeo = 21, and oeo = 28, where o represents odd and e even values of h, k, and l.

In order to continue the refinement in a higher symmetry the absorption correction and the data reduction were repeated in space group I11mm. The 3852 reflections were merged for the body-centered space group, and the weak reflections inconsistent with the space group were omitted, giving 785 unique reflections (R \_\_r = 0.1069), of which 462 were significant with I > 3\sigma(I). The R value excluding the O position for that of H_2O at that stage of the refinement was 13%. The electron densities for the two O atoms associated with H_2O in the Pmmn models were 6.85 and 6.54 e/Å^3, respectively. They were included in the refinement together with split O parameters. Fe was refined with anisotropic displacement parameters, whereas all O atoms were refined with isotropic displacement factors. Four reflections were omitted because secondary extinction was suspected. The remaining 458 reflections were used in the final refinement of one Fe position and three octahedral O positions with site occupancies of 0.5 and the O of the H_2O molecule with a site occupancy of 0.125. This suggested an idealized formula, [Fe(OH)_6]_x \_2H_2O. However, it is likely that the small amount of Pb found in the analysis would also occupy the A site accounting for part if not all of the scattering of the H_2O site. Refinements of the occupancy of the A site were undertaken, but the results were inconclusive, as it was not possible to identify positively the contents of the site. Attempts were also made to refine the occupancy of the Fe site in accord with the stoichiometry found by chemical analysis; however, such refinements were characterized by marked increases in R, and the isotropic temperature factors for O remained unrealistically low.

Because other closely related metal hydroxide structures with cubic symmetry are known [e.g., In(OH)_3], which has space group Im3 (Christensen et al., 1967), an attempt was also made to refine the bernalite structure in Im3. As the data are not cyclically permutable, R \_\_r was very high (R \_\_r = 0.22) after data reduction and resulted in 266 unique reflections, of which 163 were considered observed with I > 3\sigma(I). According to the cubic symmetry the refinement needs only one O atom position for the FeO_6 octahedra. Again, other split positions near the O were seen in the difference Fourier map. The R value of this refinement converged at 0.094, for 163 reflections and nine varied parameters. Although this may appear to be a better refinement, fewer parameters are involved, and the H_2O/Pb position cannot be accommodated in this cubic model without destroying the symmetry. The distances between O and the O in H_2O ranged between 1.96 and 2.04 Å, whereas the result of the orthorhombic refinement shows distances between the O of H_2O and the O of octahedra of 2.68 and 2.72 Å, which is in agreement with H bonding of the form O-H⋯OH or HOH⋯OH.

The value of R for the refinement in I11mm is 10.6%. This high value of R reflects a number of problems associated with the bernalite structure. The chosen body-centered structure models represent only two of at least six orientations in the orthorhombic cell. It is clear that even the preferred data set represents an intergrowth of lattices in all three crystallographic directions in the unit cell. The fact that the FeO_6 octahedra are slightly rotated from the idealized perovskite structure explains the ease with which microtwinning may occur. Twinning of the pseudocubic unit cell results in the Fe sites being superimposed and in the splitting of the O positions. Additional uncertainties arise from the unresolved nature of the contents of the A cation and the probable measurement errors in the absorption corrections rendering the temperature factors associated with the O positions unrealistically low.
TABLE 4. Crystal data and results of crystal-structure refinement for bernalite

<table>
<thead>
<tr>
<th>Crystal size</th>
<th>0.10 x 0.12 x 0.025 mm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unit-cell dimensions</td>
<td>a (Å) 7.544(2)</td>
</tr>
<tr>
<td>v (Å³)</td>
<td>431.0(3)</td>
</tr>
<tr>
<td>Z</td>
<td>8</td>
</tr>
<tr>
<td>Space group</td>
<td>Immm</td>
</tr>
<tr>
<td>Density (g/cm³)</td>
<td>3.32(2)</td>
</tr>
<tr>
<td>μ (cm⁻¹)</td>
<td>66.70</td>
</tr>
<tr>
<td>Radiation</td>
<td>MoKα</td>
</tr>
<tr>
<td>Collection limit</td>
<td>2θ(MoKα) 80°</td>
</tr>
<tr>
<td>Unique reflections</td>
<td>785</td>
</tr>
<tr>
<td>Reflections / &gt;3σ</td>
<td>462</td>
</tr>
<tr>
<td>Transmission factors</td>
<td>Max 0.8179</td>
</tr>
</tbody>
</table>

In conclusion, structural models found in all lower symmetry refinements showed only small deviations from body-centered orthorhombic symmetry. Despite the relatively high R values for the final orthorhombic refinement in space group Immm, we feel it is the best, albeit imperfect, model for the structure of bernalite. It is not possible to refine completely the structure with the available crystals. Experimental details for the most satisfactory refinement are summarized in Table 4, and the final list of observed and calculated structure factor amplitudes is given in Table 5.¹ The final atomic parameters and their standard deviations for the best body-centered orthorhombic refinement, estimated assuming 0.25 H₂O in the A cation site, are given in Table 6.

Structure description

The structure of bernalite is depicted in Figures 3 and 4. The structure consists of FeO₆ octahedra, which are linked by corner sharing to form a three-dimensional network containing large 12-fold coordinated cavities, which

¹ A copy of Table 5 may be ordered as Document AM-93-530 from the Business Office, Mineralogical Society of America, 1130 Seventeenth Street NW, Suite 330, Washington, DC 20036, U.S.A. Please remit $5.00 in advance for the microfiche.
may accommodate a small amount of H₂O or Pb. The structure is derived from the perovskite or ReO₃-type structures (Hyde and Andersson, 1989). In the bernalite structure the octahedra are rotated or tilted about each of the three fourfold axes of the octahedra in such a way so as to reduce the symmetry from cubic (Im3) to orthorhombic (Immm). The distortion of the perovskite or ReO₃-type structures by the tilting and rotation of the octahedra has been extensively studied, and the symmetry relationship established (Deblieck et al., 1985). The A cation site of the perovskite structure in bernalite is partially occupied; however, the exact chemical nature of site is unresolved. It may contain up to 0.25 of a H₂O molecule or a mixture of a small amount of Pb and H₂O.

The small amount of Zn found during the electron microprobe analysis would occupy the octahedral site.

The Fe-O distances fall within a small range, 1.984(5)-2.035(7) Å, with a mean of 2.011 Å, and the O-Fe-O bond angles show only small departures from 90°; they range from 86.0(9) to 90.4(7)°. The Fe-O bond lengths are typical for Fe³⁺-O contacts in ferric oxysalts (see, for example, Szymanski, 1988).

**RELATIONSHIP TO OTHER MINERALS**

Bernalite is fundamentally different from the ferric oxy-hydroxide minerals goethite, lepidocrocite, and akaganeite in a number of ways, and these differences can be directly related to structural differences. Whereas in bernalite the octahedra are joined by corner sharing, the ferric oxy-hydroxides have structures based on pairs of edge-sharing octahedra, which link by corner sharing. Edge sharing results in large distortions to the octahedral coordination, with a shortening of some of the Fe-O bonds and a lengthening of others; for example goethite has three Fe-O bonds at 1.95 Å and three at 2.09 Å (Szytuta et al., 1968). In contrast, bernalite has nearly perfect octahedral coordination, and this regularity results in a small crystal-field stabilization energy and the absorption of light being shifted to the red end of the spectrum. Hence bernalite is green rather than red or yellow, like the ferric oxy-hydroxide minerals.

It is clear from the Mössbauer and structural data that bernalite and amorphous Fe(OH)₃ gels are structurally distinct. There is considerable evidence suggesting that the Fe(OH)₃ gels are structurally related to gibbsite and thus have structures based on sheets of edge-sharing octahedra (van der Giessen, 1968; Au-Yeung et al., 1985; Coey and Readman, 1973).

There are a number of metal hydroxide minerals that also have the distorted perovskite or ReO₃-type structure, including those in the stottite and schoenfliesite groups (Fleischer and Mandarino, 1991), together with söhngeite and dzhalindite (Table 7). Ross et al. (1988) refined the structure of stottite, FeGe(OH)₆, in a tetragonal space
group and, like the present authors, encountered considerable problems with twinning and uncertainties in space group assignment. Jeanbandyite is the other metal hydroxide of this structure type that contains significant Fe in the ferric oxidation state (Kampf, 1982), and it is possible that a compositional field between bernalite and jeanbandyite may exist in nature. Considerable solid solution of the divalent cations has been reported for some of the schoenfliesite group minerals (Marshukova et al., 1984; Nefedov et al., 1977), and it appears that the full extent of chemical substitutions in the metal hydroxide minerals of this structure type is yet to be established.

For the present, bernalite is assigned to a group with söhngeite and dzhalindite, as the stottite and schoenfliesite groups have mixed occupancy of the octahedral site. Bernalite appears to be the only orthorhombic metal hydroxide mineral, the others being cubic or tetragonal. However, it must be pointed out that many of the structures have not been studied in detail.

**Paragenesis**

The oxide and hydroxide mineral relations of the Broken Hill deposit have not been thoroughly investigated. The dominant minerals in the near-surface gossan are coronadite and goethite, and there are reports of lepidocrocite and chalcohenite, but the existence of other manganese and iron oxides or hydroxides can only be predicted. The chemical and structural complexity of the oxidized zone (Plimer, 1984; van Moort and Swenson, 1981) suggests that a wide range of microenvironments, some of them possibly unusual, was present at times during its formation. Bernalite appears to occupy such a microchemical niche.

At an early stage in this investigation, it was considered that bernalite may have been one of the long sought-after, naturally occurring green-rust compounds. However, it is clearly distinct from these synthetic pyroaurite-like phases (Taylor, 1973). Because of direct association with concretionary goethite, which pre- and postdates it, bernalite almost certainly crystallized from a ferric hydroxide gel. A variety of these gels has been synthesized over a range of pH by either precipitation from solutions of ferric salts by addition of a base, or by oxidation of Fe$^{2+}$ in basic aqueous solutions (Au-Yeung et al., 1985). Magnetic and X-ray diffraction properties of the products vary, often depending on particle size, but none matches those of bernalite.

It is not possible to distinguish among these alternative possible origins for bernalite. Whereas the environment of the oxidized zone strongly suggests that all near-surface Fe would already be Fe$^{3+}$ when the bernalite precursor precipitated, it is possible that reaction of the aqueous salts with a strong oxidizing agent such as H$_2$O$_2$ (Williams, 1990) could have occurred on a limited scale. Similarly, diffusion of atmospheric O$_2$ into concentrated Fe$^{3+}$-bearing solutions could also result in the precipitation of ferric hydroxide phases (Thorber, 1975).

In assessing the formation and stability of bernalite, several factors may be considered.

1. An upper temperature limit of 50–60 °C is likely from the geological setting. There is no geological evidence for any higher temperature, such as may have occurred during metamorphism.

2. Estimates of the pH during formation of bernalite cannot be constrained on the basis of the published synthesis conditions for ferric hydroxide gels, in which the pH ranged from 4.5 to 9.

3. The bernalite crystals contain small but significant amounts of Pb, Si, and Zn. These are presumably, with the possible exception of Si, in solid solution, suggesting they were originally absorbed or scavenged elements that were not expelled during crystalization of the gel. They may have played a role both in the initial precipitation of the gel and in stabilizing the bernalite crystal structure.

Preliminary attempts to synthesize bernalite by crystalization from Fe(OH)$_3$ gels have been unsuccessful, and the synthesis of this mineral appears to pose a considerable challenge.

**Acknowledgments**

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**References Cited**


Christensen, A.N., Broch, N.C., von Heidenstam, O., and Nilsson, A. (1967) Hydrothermal investigation of the system In$_2$O$_3$-H$_2$O-Na$_2$O and In$_2$O$_3$-D$_2$O-Na$_2$O. The crystal structure of rhombohedral In$_2$O$_3$, and of In(OOH)$_3$. Acta Chemica Scandinavica, 21, 1046–1056.


