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Bearthite, $\text{Ca}_2\text{Al}[\text{PO}_4]_2(\text{OH})$, a new mineral from high-pressure terranes of the western Alps

by Christian Chopin¹, Fabrice Brunet¹, Walter Gebert², Olaf Medenbach² and Ekkehart Tillmanns³

Abstract

Bearthite occurs associated with lazulite in synmetamorphic quartz segregations of the Monte Rosa massif, where it has been partly described as a probably new Ca-phosphate by Peter Bearth (1952); it also occurs as an accessory rock-forming mineral in metapelite and magnesian schist of the coesite-bearing terrane, Dora Maira massif. Textural relationships suggest that it formed during the early, high-pressure stages of the Alpine metamorphic evolution; it was later replaced by lazulite and then apatite in Monte Rosa, by apatite + monazite(?) in Dora Maira. Bearthite is close to ideal $\text{Ca}_2\text{Al}[\text{PO}_4]_2(\text{OH})$ in Monte Rosa, with some $\text{Sr} \rightleftharpoons \text{Ca}$ substitution toward its Sr-homologue, goedkenite. In the Dora Maira material, up to one third Al may be replaced by Mg through the coupled substitution $\text{Ca Al} \rightleftharpoons \text{RE Mg}$. Bearthite is optically biaxial positive, n_x 1.662(1), n_y 1.671(1), n_z 1.696(1), $2 V_m$ 65.0(3)°, dispersion $r < v$, X/b . It is monoclinic, space group $\text{P}2_1/m$, a 7.231(3), b 5.734(2), c 8.263(4) Å, β 112.57(8)°, $Z = 2$, D_{calc} 3.28. The structure, refined to a conventional R of 5.8% from 1499 independent reflections, is that of the brackebushite group, with infinite chains of edge-sharing $\text{AlO}_5(\text{OH})$ octahedra extending parallel to b . In this group bearthite has the smallest cation in each structural position, which may account for its stability at high pressure. It has been synthesized at 4 kbar water pressure, 500–600 °C, and 24 kbar, 820 °C.

Keywords: Bearthite – new mineral, phosphate, crystal structure, goedkenite, high-pressure metamorphism, REE, Monte Rosa, western Alps.

Introduction

In the course of petrological studies in the coesite-bearing metamorphic terrane of the Dora Maira massif, western Alps, Italy, one of us found a new calcium-aluminium phosphate as an accessory mineral in several rock types (CHOPIN, 1987). It became apparent that this mineral was the Ca-homologue of goedkenite $(\text{Sr,Ca})_2\text{Al}(\text{OH})[\text{PO}_4]_2$ (MOORE et al., 1975) and might be identical with the "probably new Ca-phosphate" reported and optically characterized by BEARTH (1952) from a lazulite occurrence in the Monte Rosa massif. The reinvestigation of BEARTH's original samples confirmed the identity of both minerals.

The name of the new mineral (pronounced BE as in *best*, ARTH as in *artist*) honours Prof. Dr. PETER BEARTH (1902–1989) for his pioneering

petrographic work in the high-pressure terranes of the western Alps. For P. Bearth as for his contemporary F. Ellenberger, the combination of the free spirit and of the extremely keen observer resulted in interpretations that went well beyond established schools of thought. As a matter of fact, after 30 years their papers (*e.g.* BEARTH, 1952, 1959, 1967; ELLENBERGER, 1958) are still the basis of our understanding of the western Alps and of their metamorphism.

Mineral and name were approved by the IMA Commission on New Minerals and Mineral Names. The holotype material is sample PB 100f, originally studied by BEARTH (1952) and reinvestigated here; it is preserved at the Mineralogisch-Petrographisches Institut, Universität Basel. The new thin section of this sample from which all the data reported here were obtained is preserved at

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the Musée de Minéralogie, Ecole des Mines de Paris, together with the co-type specimens from the Dora Maira massif (84DM54, 85DM45, 85DM70). The crystal drilled out of the holotype thin section is deposited at the Museum d'Histoire naturelle, Paris.

Occurrence

The Monte Rosa occurrence is situated on the western ridge of the Stockhorn, Zermatt valley, Switzerland, at about 3400 m elevation; it has been thoroughly described by BEARTH (1952). Bearthite and lazulite occur as primary phases in quartz segregations that are concordant with the foliation of the surrounding garnet-albite gneiss and quartz-phengite schist of the Stockhorn series. Up to centimetre-size light-blue lazulite crystals occur in the veins, often close to the margins, and also in the immediately adjacent rock. In hand specimen, the very subordinate yellowish bearthite is not easily distinguished from the abundant cream-coloured apatite. It has so far only been observed in the quartz veins. It forms rarely up to millimeter-size aggregates of partly euhedral, flat prismatic crystals associated with lazulite and minor primary apatite and paragonite; usually it occurs as smaller anhedral grains corroded by lazulite, both aluminophosphates being deformed, partly recrystallized and then corroded, sometimes pseudomorphed, by late abundant post-kinematic apatite.

The enclosing Palaeozoic crystalline series may have undergone Late Palaeozoic metamorphism and certainly underwent early-Alpine high-pressure metamorphism followed by a lower-pressure thorough overprint (FREY et al., 1976). Considering textural evidence and the exclusively Alpine character of the mineral assemblages in the surrounding rocks, we favour the idea that bearthite and lazulite formed during early Alpine times.

In the Dora Maira massif bearthite has been found exclusively in the coesite-bearing terrane, which extends between the Po and Varaita valleys (CHOPIN et al., 1991). It occurs as an accessory rock-forming mineral both in metapelite and in the pyrope-bearing phengite-quartzite in which coesite was first found there (CHOPIN, 1984). In metapelite sample 84DM54 (from Val Po), bearthite is included in a large primary flake of phengite-3T ($\text{Si}_{3.5}$ p.f.u.) and so was most likely part of the early high-pressure paragenesis together with almandine garnet, kyanite, phengite, rutile, jadeite (now pseudomorphed by albite) and coesite (still preserved as inclusions in garnet

rim and kyanite but entirely replaced by quartz in the matrix, CHOPIN et al., 1991). In the pyrope-phengite quartzite, bearthite occurs as discrete, sometimes granulated crystals both in the rock matrix and as inclusion within pyrope megacrysts. In the matrix (sample 85DM45, from Val Gilba) the high-pressure early assemblage comprises pyrope garnet, kyanite, phengite-3T ($\text{Si}_{3.55}$), quartz (formerly coesite) and rutile (cf. CHOPIN, 1984; SCHERTL et al., 1991). Textural relationships show that bearthite was part of this paragenesis, as also suggested by a polycrystalline quartz inclusion in bearthite that may be a recrystallised pseudomorph after coesite (Fig. 1). Bearthite is typically surrounded by a symplectitic rim of apatite containing highly refringent blebs of a rare-earth phosphate (monazite? Fig. 1). This feature, just like the incipient chloritisation of pyrope, is most likely retrogressive and decompression-related. In pyrope megacryst 85DM70 (from Val Gilba) bearthite occurs as inclusion together with kyanite, talc, rutile; wagnerite and apatite also occur as inclusions but were not observed in contact with bearthite.

From these occurrences bearthite appears as a mineral stable at high pressures, about 30 kbar and 700–750 °C in Dora Maira (CHOPIN, 1984, 1986; SCHERTL et al., 1991) and near 15 kbar, 500 °C in Monte Rosa (CHOPIN and MONIE, 1984; DAL PIAZ and LOMBARDO, 1986).

Chemistry

Bearthite is soluble in cold HCl (BEARTH, 1952). Electron-microprobe work revealed Al, P, Ca and Sr as the major cations in the Monte Rosa material, with Mg and rare-earth elements (RE) in addition in the Dora Maira samples. The presence of hydroxyl groups suggested by low analytical totals could not be directly demonstrated because of the material paucity, but it is clear from the structure refinement. Analyses were performed in the wavelength-dispersive mode with the Cameca Camebax instrument at Université Paris 6, 15 kV acceleration voltage, 15 nA beam current, using fluorapatite (Ca, P, F), forsterite (Mg, Si), anorthite (Al), SrSiO_3 (Sr), monazite (Ce) and rare-earth rhenates (La, Nd) as standards, with ZAF data reduction.

The average of four analyses in holotype sample PB 100f (Tab. 1) shows that crystals are homogeneous and very close to the end-member composition $\text{Ca}_2\text{Al}[\text{PO}_4]_2(\text{OH})$. In other samples from the same locality substitution of Sr for Ca toward goedkenite, $\text{Sr}_2\text{Al}[\text{PO}_4]_2(\text{OH})$, extends to 39 at.% – goedkenite type-material is in fact a calcian vari-

ety, with $\text{Sr}/(\text{Sr}+\text{Ca}) = 0.61$. The Dora Maira material shows the same spread of Ca/Sr ratios but two additional, strictly correlated substitutions, of Ca+Sr by RE and of Al by Mg (Tab. 1). Bearing in mind that only the major RE have been analysed (hence the decrease of the analytical totals and of the sums of the large-size cations with increasing RE), we may consider that these two substitutions are in a one-to-one ratio; they represent the charge-balanced substitutional mechanism $\text{Ca Al} \rightleftharpoons \text{RE Mg}$ as known, for instance, in the epidote group. Interestingly, RE are not incorporated through the substitution $\text{Ca P} \rightleftharpoons \text{RE Si}$, although the compound $\text{RE}_2\text{Al}[\text{SiO}_4]_2\text{OH}$ is structurally allied to bearthite (see below).

Bearthite has been synthesized with nearly 100% yields from a stoichiometric mixture of $\text{CaHPO}_4 \cdot 2 \text{H}_2\text{O}$ and $\gamma\text{-Al}_2\text{O}_3$ at water pressures of 4 to 24 kbar, between 500–600 and 820 °C, respectively. A strong band near 3400 cm^{-1} in its Raman spectrum is evidence for the presence of an OH group in the structure.

Physical properties

Bearthite is yellowish in hand specimen, with uneven fracture and white streak. According to BEARTH (1952), Mohs' hardness is less than 5 and there may be one faint prismatic cleavage. The mineral is transparent and colourless in thin section (but often clouded by tiny fluid (?) inclusions), biaxial positive, dispersion $r < v$ distinct. Optical data were obtained with a spindle-stage refractometer (MEDENBACH, 1985) on the crystal drilled out of a thin section from holotype sample PB 100f and on a synthetic crystal; they are compared with Bearth's original data and those for goedkenite in table 2. Obviously both minerals cannot be distinguished simply on the basis of optical data.

Bearth also mentioned the optical similarity of bearthite with the Ca-phosphate spodiosite. In spite of its distinctive orthorhombic morphology (and optical properties? LARSEN, 1921), the material described by TIBERG (1885) and NORDEN-

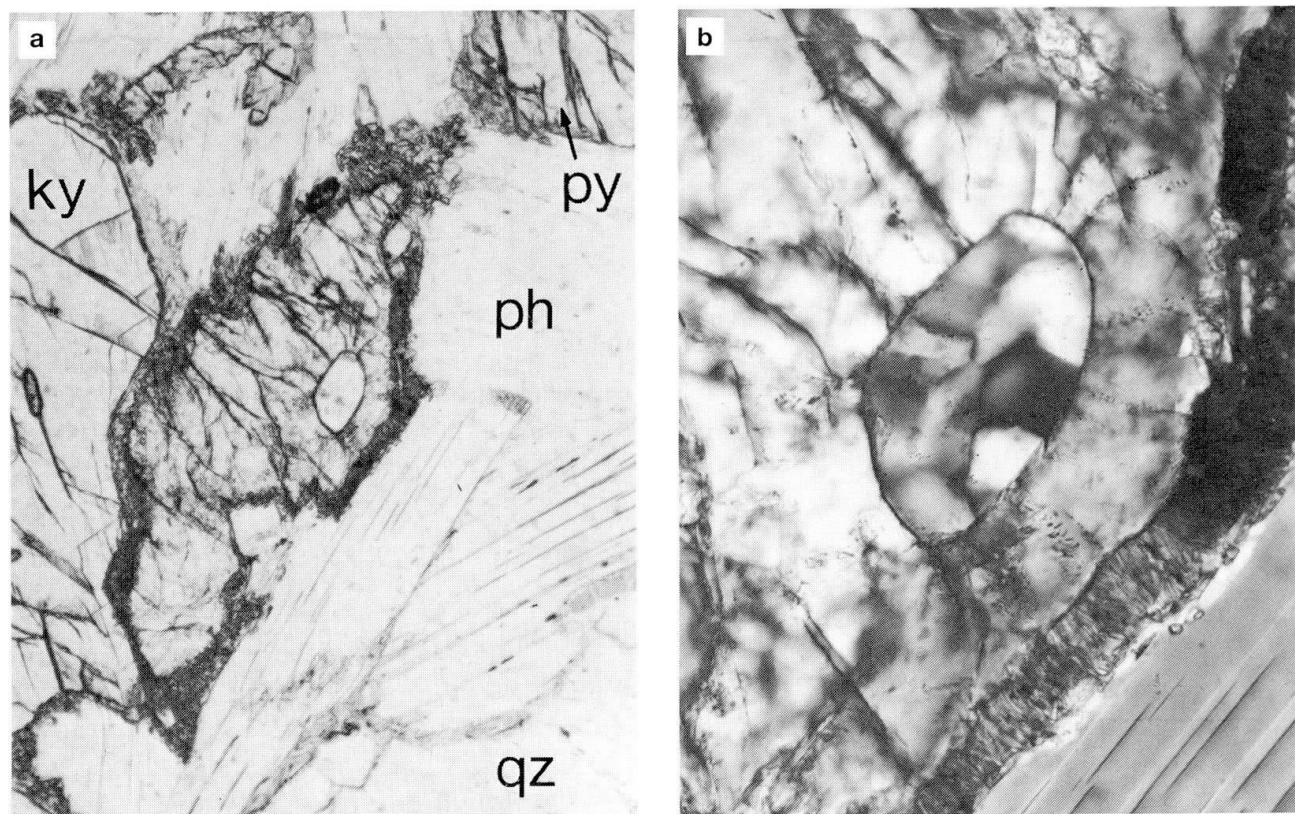


Fig. 1 a) Lozenge-shaped section of a bearthite crystal in pyrope (py) – phengite (ph) – kyanite (ky) – quartz (qz) – schist from the Dora Maira massif (sample 85DM45a). SrO contents increase from 3.5 to 7.6 wt% from core to rim. Photomicrograph, plane polarized light; picture width represents 900 μm . b) Close-up view showing the symplectite rim (of strontian apatite (Tab. 1) plus a highly refringent RE phosphate) and the polycrystalline quartz inclusion with radial cracks around it, suggesting the former presence of coesite (relics of which were found in neighbouring samples). Crossed nicols.

Tab. 1 Microprobe analyses of bearthite and coexisting phosphates. Structural formulae are calculated on the basis of P+S+Si = 4, 4 and 6 for bearthite, lazulite and apatite, respectively.

| | Bearthite | | | | | Lazulite | | Apatite | |
|--------------------------------|--------------|---------|--------|---------|--------|----------|---------|---------|---------|
| | PB 100f | PB Laz2 | 84DM54 | 85DM45a | 85DM70 | PB 100f | PB 100f | PB Laz2 | 86DM45a |
| P ₂ O ₅ | 44.32 (0.56) | 42.34 | 41.64 | 39.85 | 38.39 | 46.22 | 46.32 | 41.95 | 40.67 |
| SO ₃ | 0.01 (0.01) | 0.00 | 0.00 | 0.00 | n.a. | 0.17 | 0.01 | 0.00 | 0.00 |
| SiO ₂ | 0.30 (0.11) | n.a. | 0.26 | 0.27 | n.a. | n.a. | n.a. | n.a. | 0.14 |
| Al ₂ O ₃ | 15.91 (0.14) | 14.88 | 13.00 | 10.36 | 9.49 | 32.25 | 33.52 | 0.00 | 0.05 |
| FeO | 0.03 (0.03) | 0.00 | 0.19 | 0.03 | 0.16 | 2.46 | 0.90 | 0.54 | 0.05 |
| MgO | 0.12 (0.12) | 0.21 | 1.64 | 3.13 | 3.47 | 11.59 | 12.56 | 0.10 | 0.16 |
| SrO | 3.53 (0.16) | 17.25 | 2.30 | 5.72 | 12.06 | 0.52 | 0.00 | 0.86 | 3.49 |
| CaO | 33.04 (0.10) | 23.34 | 29.32 | 23.95 | 18.23 | 0.87 | 0.02 | 54.23 | 51.36 |
| Ce ₂ O ₃ | 0.04 (0.07) | 0.07 | 3.15 | 5.97 | 5.62 | n.a. | n.a. | 0.00 | 0.18 |
| La ₂ O ₃ | 0.03 (0.04) | 0.00 | 1.52 | 2.95 | 2.75 | n.a. | n.a. | 0.04 | 0.04 |
| Nd ₂ O ₃ | n.a. | n.a. | 0.82 | 1.57 | 2.39 | n.a. | n.a. | 0.00 | 0.08 |
| H ₂ O | | | | | | | | | |
| F | 0.48 (0.06) | 0.52 | 0.60 | 0.64 | 0.61 | 0.49 | 0.42 | 1.35 | 3.20 |
| Cl | 0.02 (0.01) | 0.02 | 0.00 | 0.01 | n.a. | 0.02 | 0.02 | 0.24 | 0.19 |
| Total O = F,Cl | 97.62 (0.51) | 98.41 | 94.19 | 94.18 | 92.91 | 94.38 | 93.59 | 98.69 | 98.22 |
| P | 3.97 | 4.00 | 3.97 | 3.97 | 4.00 | 3.99 | 4.00 | 6.00 | 5.98 |
| S | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.01 | 0.00 | 0.00 | 0.00 |
| Si | 0.03 | 0.00 | 0.03 | 0.03 | 0.00 | 0.00 | 0.00 | 0.00 | 0.02 |
| P+S+Si | 4.00 | 4.00 | 4.00 | 4.00 | 4.00 | 4.00 | 4.00 | 6.00 | 6.00 |
| Al | 1.98 | 1.96 | 1.73 | 1.44 | 1.38 | 3.87 | 4.03 | 0.00 | 0.01 |
| Fe | 0.00 | 0.00 | 0.02 | 0.00 | 0.02 | 0.21 | 0.08 | 0.08 | 0.01 |
| Mg | 0.02 | 0.03 | 0.28 | 0.55 | 0.64 | 1.76 | 1.91 | 0.03 | 0.04 |
| | 2.00 | 1.99 | 2.02 | 1.99 | 2.03 | | | | |
| Sr | 0.22 | 1.12 | 0.15 | 0.39 | 0.86 | 0.03 | 0.00 | 0.08 | 0.35 |
| Ca | 3.74 | 2.79 | 3.54 | 3.02 | 2.40 | 0.09 | 0.00 | 9.82 | 9.55 |
| Ce | 0.00 | 0.00 | 0.13 | 0.26 | 0.25 | 0.00 | 0.00 | 0.00 | 0.01 |
| La | 0.00 | 0.00 | 0.06 | 0.13 | 0.12 | 0.00 | 0.00 | 0.00 | 0.00 |
| Nd | 0.00 | 0.00 | 0.03 | 0.07 | 0.11 | 0.00 | 0.00 | 0.00 | 0.00 |
| | 3.96 | 3.91 | 3.91 | 3.86 | 3.75 | 5.97 | 6.02 | 10.00 | 9.98 |
| F | 0.16 | 0.18 | 0.21 | 0.24 | 0.24 | 0.16 | 0.14 | 0.72 | 1.76 |
| Cl | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.07 | 0.06 |
| REE | 0.00 | 0.00 | 0.23 | 0.45 | 0.48 | | | 0.00 | 0.02 |
| Mg | 0.02 | 0.03 | 0.28 | 0.55 | 0.64 | | | 0.03 | 0.04 |
| Ca/(Ca+Sr) | 0.945 | 0.714 | 0.959 | 0.886 | 0.736 | | | 0.991 | 0.965 |

Tab. 2 Optical data for bearthite and goedkenite.

| | Bearthite | | | Goedkenite |
|------------------|--------------|----------|-----------|--------------------|
| | Bearth, 1952 | PB 100f | Synthetic | Moore et al., 1975 |
| n _x | 1.660(3) | 1.662(1) | 1.663(1) | 1.669(2) |
| n _y | 1.671(3) | 1.671(1) | 1.672(1) | 1.673(2) |
| n _z | 1.690(3) | 1.696(1) | 1.693(1) | 1.692(2) |
| 2 V _m | 64–66° | 65.0(3)° | 65.0(3)° | 45–50° |
| Orient. | | X//b | X//b | X//b |
| Ca/(Ca+Sr) | | 0.95 | 1.0 | 0.39 |

Tab. 3 Calculated and observed (single crystal, Gandolfi-camera 114.6 mm, Cu $K\alpha$) powder pattern for bearthite.

| dc | Ic | h | k | l | do | Io | dc | Ic | h | k | l | do | Io |
|-------|-----|----|---|---|-------|-----|-------|----|----|---|---|-------|----|
| 6.68 | 3 | 1 | 0 | 0 | 6.63 | 30 | 2.075 | 1 | 3 | 1 | 0 | | |
| 6.38 | 3 | -1 | 0 | 1 | 6.31 | 50 | 2.024 | 7 | -2 | 0 | 4 | | |
| 4.58 | 22 | 0 | 1 | 1 | 4.58 | 10 | 1.986 | 12 | -1 | 2 | 3 | 1.985 | 50 |
| 4.35 | 8 | 1 | 1 | 0 | 4.37 | 40 | 1.946 | 4 | 3 | 0 | 1 | | |
| 4.27 | 14 | -1 | 1 | 1 | | | 1.934 | 5 | -1 | 1 | 4 | 1.939 | 10 |
| 4.05 | 2 | -1 | 0 | 2 | | | 1.909 | 1 | -2 | 1 | 4 | 1.918 | 10 |
| 3.82 | 2 | 0 | 0 | 2 | 3.83 | 10 | 1.908 | 2 | 0 | 0 | 4 | | |
| 3.61 | 2 | -2 | 0 | 1 | 3.62 | 10 | 1.840 | 1 | -3 | 2 | 1 | 1.837 | 10 |
| 3.43 | 1 | 1 | 1 | 1 | 3.43 | 30 | 1.805 | 7 | -4 | 0 | 2 | 1.809 | 20 |
| 3.34 | 10 | 2 | 0 | 0 | 3.34 | 30 | 1.751 | 6 | -3 | 1 | 4 | 1.755 | 15 |
| 3.18 | <1 | 0 | 1 | 2 | 3.17 | 5 | 1.734 | 4 | -4 | 0 | 3 | 1.737 | 15 |
| 3.05 | 100 | -2 | 1 | 1 | 3.06 | 100 | 1.729 | 1 | 2 | 0 | 3 | | |
| 2.872 | 2 | 1 | 0 | 2 | | | 1.714 | 2 | 2 | 2 | 2 | | |
| 2.867 | 61 | 0 | 2 | 0 | 2.849 | 50 | 1.709 | 4 | -3 | 2 | 3 | | |
| 2.789 | 13 | -2 | 1 | 2 | 2.790 | 15 | 1.705 | 3 | 1 | 2 | 3 | 1.704 | 10 |
| 2.754 | 27 | -1 | 0 | 3 | 2.771 | 50 | 1.689 | 6 | -2 | 3 | 1 | 1.681 | 20 |
| 2.702 | 6 | 2 | 0 | 1 | 2.717 | 10 | 1.670 | 4 | -1 | 2 | 4 | | |
| 2.684 | 11 | 0 | 2 | 1 | 2.671 | 10 | 1.670 | 4 | 4 | 0 | 0 | | |
| 2.634 | 21 | 1 | 2 | 0 | | | 1.640 | 1 | -2 | 3 | 2 | 1.631 | 5 |
| 2.615 | 5 | -1 | 2 | 1 | 2.607 | 15 | 1.610 | 12 | 3 | 2 | 1 | 1.610 | 50 |
| 2.568 | 39 | 1 | 1 | 2 | 2.570 | 70 | 1.596 | 2 | -4 | 0 | 4 | | |
| 2.549 | 1 | -2 | 0 | 3 | | | 1.591 | 7 | 1 | 3 | 2 | 1.587 | 50 |
| 2.544 | 1 | 0 | 0 | 3 | | | 1.560 | 1 | 2 | 3 | 1 | | |
| 2.483 | 3 | -1 | 1 | 3 | | | 1.548 | 2 | -3 | 2 | 4 | | |
| 2.444 | 19 | 2 | 1 | 1 | 2.450 | 30 | 1.527 | 6 | -4 | 2 | 2 | | |
| 2.381 | 8 | 1 | 2 | 1 | 2.375 | 30 | 1.515 | 2 | -3 | 1 | 5 | | |
| 2.329 | 13 | -2 | 1 | 3 | 2.334 | 25 | 1.433 | 6 | 0 | 4 | 0 | 1.443 | 10 |
| 2.292 | <1 | 0 | 2 | 2 | 2.288 | 10 | 1.417 | 2 | -1 | 2 | 5 | 1.423 | 40 |
| 2.226 | 2 | 3 | 0 | 0 | | | 1.377 | 2 | -2 | 0 | 6 | | |
| 2.213 | 6 | -3 | 1 | 1 | 2.217 | 10 | 1.370 | 1 | -5 | 1 | 1 | | |
| 2.179 | 2 | -3 | 1 | 2 | | | 1.325 | 2 | -3 | 3 | 4 | | |
| 2.175 | 5 | 2 | 2 | 0 | 2.171 | 50 | 1.301 | 2 | 5 | 1 | 0 | | |
| 2.139 | 2 | 2 | 0 | 2 | | | 1.284 | 3 | 2 | 2 | 4 | 1.287 | 20 |
| 2.128 | 2 | -3 | 0 | 3 | 2.134 | 25 | 1.272 | 3 | -1 | 4 | 3 | | |
| 2.122 | 4 | 1 | 0 | 3 | | | 1.241 | 2 | -2 | 2 | 6 | 1.243 | 25 |

SKIÖLD (1893) as spodiosite yields an apatite X-ray diffraction pattern (STRUNZ, 1939; B. LINDQVIST, pers. comm. 1992) and remains of uncertain status. In addition, a component with bearthite composition and X-ray pattern has been identified beside predominant attakolite in a cirrolite specimen of a kyanite-lazulite rock from Västana, Bromölla, Sweden (B. LINDQVIST, comm. pers., 1992). As analysed by BLOMSTRAND (1868), cirrolite ($\text{Ca}_3\text{Al}_2(\text{PO}_4)_3(\text{OH})_3$), is thus most likely a mixture of bearthite with some lazulite and kyanite (plus attakolite to account for the 2.2 wt% MnO?).

Synthetic bearthite forms short flat prismatic crystals, up to 150 μm in size; at variance with goedkenite, these are elongated parallel to b , with the pinacoids $\{001\}$ and $\{100\}$ (and Z almost perpendicular to $\{001\}$).

Crystallography

Table 3 shows observed and calculated powder patterns for bearthite. The calculated pattern is based on the results of the crystal structure refinement, the observed pattern was recorded on a Gandolfi camera with the *single crystal* drilled out of thin section PB 100f. It is obvious that the observed intensities are grossly in error, which is probably due to the limitations of the Gandolfi method. Table 4 gives crystal data and experimental details of X-ray intensity data collection; the results of the crystal structure refinement are contained in tables 5 and 6. A table of observed and calculated structure factors is available from the authors on request.

Like goedkenite (MOORE et al., 1975), tsumebite (NICHOLS, 1966), As-tsumebite (BIDEAUX et

Tab. 4 Crystal data and details of data collection.

| | |
|-------------------------|---------------------|
| Space group | P 2 ₁ /m |
| a [Å] | 7.231(3) |
| b [Å] | 5.734(2) |
| c [Å] | 8.263(4) |
| β [°] | 112.57(8) |
| V [Å ³] | 316.4 (6) |
| Z | 2 |
| Dx [Mg/m ³] | 3.25 |
| scan mode | ω-scan |
| Θ max [°] | 37.5 |
| Independent reflections | 1499 |
| Refl. with I > 2.5 σI | 1303 |
| weighting scheme | unit weights |
| conventional R | 0.058 |

Tab. 5 Fractional atomic coordinates and equivalent isotropic displacement factors.

| Atom | x/a | y/b | z/c | U _{eq} * |
|------|-----------|-----------|-----------|-------------------|
| Ca1 | 0.2293(2) | 0.75 | 0.2539(2) | 0.019 |
| Ca2 | 0.8280(2) | 0.75 | 0.4175(2) | 0.016 |
| Al | 0.5 | 0.5 | 0.0 | 0.016 |
| P1 | 0.9373(2) | 0.25 | 0.1730(2) | 0.015 |
| P2 | 0.5249(2) | 0.25 | 0.3391(2) | 0.016 |
| O1 | 0.5251(4) | 0.5277(5) | 0.7808(4) | 0.019 |
| O2 | 0.7452(6) | 0.25 | 0.4519(6) | 0.024 |
| O3 | 0.4003(7) | 0.25 | 0.4495(6) | 0.024 |
| O4 | 0.9929(4) | 0.0314(4) | 0.2894(4) | 0.019 |
| O5 | 0.0284(6) | 0.25 | 0.0356(6) | 0.023 |
| O6 | 0.7001(6) | 0.25 | 0.0642(5) | 0.017 |
| OH | 0.3269(6) | 0.25 | 0.9138(5) | 0.017 |

$$* U_{eq} = 1/3 [U_{22} + 1/\sin^2\beta (U_{11} + U_{33} + 2U_{13}\cos\beta)]$$

al., 1966), arsenbrackebuschite (HOFMEISTER and TILLMANN, 1978), gamagarite (HARLOW et al., 1984; BASSO et al., 1987) and synthetic (Nd,La)₂-Al[GeO₄]₂OH (JARCHOW et al., 1981), bearthite belongs to the group of minerals with a brackebuschite-type structure (DONALDSON and BARNES, 1955), to which fornacite and vauquelinite (FANFANI and ZANAZZI, 1968), törnebohmit (SHEN and MOORE, 1982) and its synthetic equivalent Nd₂Al[SiO₄]₂OH (JARCHOW et al., 1982) are very closely allied (cf. HAWTHORNE, 1985). Basic principle is a one-dimensional array of AlO₆ octahe-

dra and PO₄ tetrahedra. AlO₆ octahedra form infinite chains along [010] via common edges. Four PO₄ tetrahedra per unit cell are connected via common corners to each octahedral chain to form units of composition [Al₂(PO₄)₄(OH)₂], which are linked to each other via common corners with the irregular coordination polyhedra around calcium (Fig. 2). The same building block [Al₂(SiO₄)₄(OH)₂] is present in törnebohmit and in the Ca-silicates clinozoisite (DOLLASE, 1968), lawsonite (BAUR, 1978), pumpellyite (GALLI and ALBERTI, 1969) and vuagnatite (McNEAR et al.,

Tab. 6 Selected interatomic distances [Å] and angles [°] for bearthite. Estimated standard deviations are less than 0.005 Å and 0.3°, respectively.

| | | | | | |
|--------|-------------|----|-----|-------|-------|
| Ca1-O2 | 2.366 | O4 | O6 | 108.5 | 2.548 |
| -O5 | 2.403 | O4 | O4 | 109.3 | 2.507 |
| -O4 | (2x) 2.449 | | | | |
| -O1 | (2x) 2.482 | P2 | -O2 | | 1.506 |
| -O3 | 2.853 | | -O3 | | 1.508 |
| -O6 | 2.863 | | -O1 | (2x) | 1.569 |
| | | O2 | O3 | 111.2 | 2.487 |
| | | O2 | O1 | 108.9 | 2.502 |
| Ca2-O3 | 2.308 | O3 | O1 | 109.6 | 2.515 |
| -O4 | (2x) 2.473 | O1 | O1 | 108.7 | 2.549 |
| -OH | 2.529 | | | | |
| -O4 | (2x) 2.590 | Al | -OH | (2x) | 1.856 |
| -O2 | 2.852 | | -O1 | (2x) | 1.895 |
| -O1 | (2x) 2.920 | | -O6 | (2x) | 1.960 |
| -O2 | (2x) 2.965 | OH | O1 | 89.8 | 2.647 |
| | | OH | O1 | 90.2 | 2.658 |
| | | OH | O6 | 81.9 | 2.501 |
| P1 -O5 | 1.516 | OH | O6 | 98.1 | 2.884 |
| -O4 | (2x) 1.537 | O1 | O6 | 89.3 | 2.710 |
| -O6 | 1.602 | O1 | O6 | 90.7 | 2.742 |
| O5 O4 | 112.6 2.539 | | | | |
| O5 O6 | 105.0 2.474 | OH | O5 | | 2.709 |

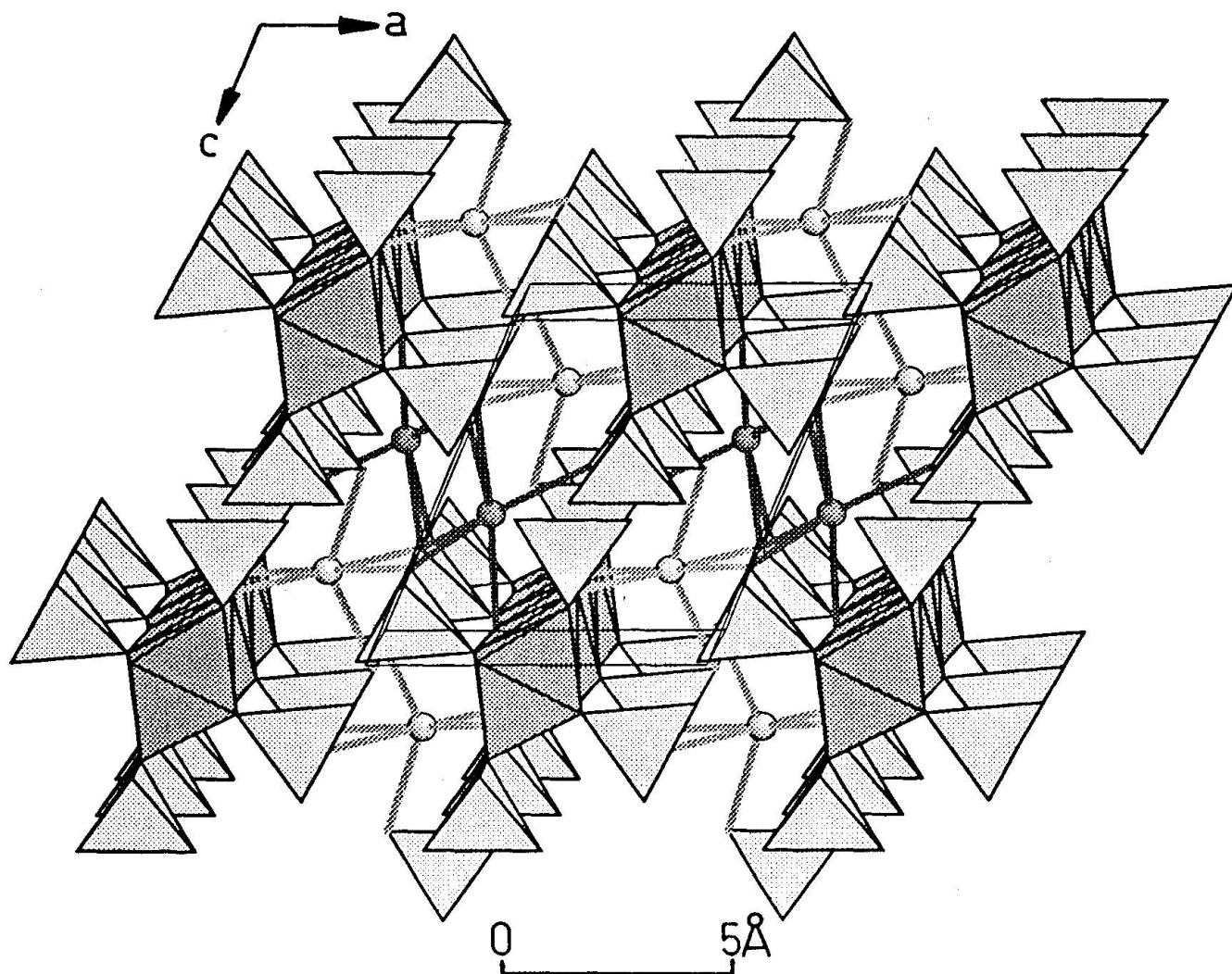


Fig. 2 The crystal structure of bearthite, with emphasis on the polyhedral arrangement. Circles represent Ca atoms (drawn with ATOMS, Shape Software).

1976), but in the latter three minerals the chains are directly connected to each other via common tetrahedra, so that a denser structure results. The same is true for the $[\text{M}_2((\text{As},\text{V})\text{O}_4)_4(\text{OH})_2]$ chains in the conicalcite and tsumcorite-mawbyite series (QURASHI and BARNES, 1963; TILLMANN and GEBERT, 1973 and PRING et al., 1989, respectively).

As for Pb in arsenbrackebuschite and Ba in gamagarite the coordination of Ca1 in bearthite can be considered 6-fold or 8-fold with six Ca–O distances between 2.366 and 2.482 Å and two additional oxygen atoms at 2.853 and 2.863 Å respectively. The latter distances are about 17% larger than the mean distance of the [6]-coordination, the distances of four further oxygen atoms at 3.290 and 3.402 Å are about 30% larger than the mean distance of the [8]-coordination. Ca2 has an irregular [11]-coordination.

The slight difference in mean T–O distances for the P1 and P2 positions has also been observed for the vanadium atoms V1 and V2 in gamagarite and attributed to ordering of As in the V2-position (BASSO et al., 1987); in the case of bearthite it is due to the difference in coordination numbers and individual bond strengths sums of the coordinating oxygen atoms, since the tetrahedral positions are occupied only by phosphorus.

The hydrogen atom could not be localized with certainty in the final difference synthesis, which showed maxima of $\pm 1 \text{ e}/\text{\AA}^3$ close to the positions of the heavier atoms. An inspection of bond strength sums shows clearly, however, that the OH-molecule occupies the same position as in brackebuschite, gamagarite and arsenbrackebuschite (and the Ca-silicates mentioned above), and that a hydrogen bond is formed to oxygen atom O5 at a distance of 2.709 Å from OH.

For those minerals of the brackebuschite group in which the octahedral position is partly occupied by a divalent cation like Zn in arsenbrackebuschite and perhaps Mn^{2+} in gamagarite, HARLOW et al. (1984) have suggested an interpretation as a partially acid arsenate or vanadate. In arsenbrackebuschite where the octahedral position is occupied by 35% Zn and 65% Fe^{3+} , an additional proton with a site occupancy of 0.175 would have to be present for charge balance and the formula $\text{Pb}_2(\text{Fe}^{3+}, \text{Zn})(\text{OH}, \text{OH}_2)(\text{AsO}_4)_2$ given by HOFMEISTER and TILLMANN (1978) could lead to the impression that the OH-position be statistically occupied by OH and H_2O . This is not likely, however, since the OH position is already roughly tetrahedrally coordinated by three cations and oxygen atom O5, which is acceptor of the hydrogen bond. Until a member of the brackebuschite family with divalent octahedral cation is found and becomes available for crystal structure analysis, the case of the missing proton can probably not be solved. For arsenbrackebuschite, the interpretation given by HARLOW et al. (1984) for gamagarite is certainly more likely, although gamagarite itself probably does not contain any additional protons since the crystal structure refinement by BASSO et al. (1987) showed a mean octahedral distance of 2.014 Å, which is typical for Fe^{3+} and Mn^{3+} and excludes the presence of 40% Mn^{2+} in the octahedral position.

A high-pressure phase?

From the occurrences known so far, it is clear that bearthite is stable at high pressures. This is consistent with the fact that, among the brackebuschite-group minerals, bearthite has the smallest cation in each structural site. Despite the occurrence of calcian goedkenite as a late phase in pegmatite (MOORE et al., 1975), the question is now whether bearthite has a lower-pressure stability limit and so can become a petrological index mineral. An experimental study is presently being undertaken.

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