Zeitschrift für Kristallographie 201, 253–262 (1992)

Crystal chemistry of beryllophosphates: The crystal structure of moraesite, $Be_2(PO_4)(OH) \cdot 4H_2O$

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Received: July 12, 1991, in revised form: September 16, 1991

Moraesite / Humaita (Brazil) / Beryllophosphate / Crystal structure / Hydrogen bonds

Abstract. Moraesite, $Be_2(PO_4)(OH) \cdot 4H_2O$, is a hydrated beryllophosphate mineral. The crystal structure of moraesite from Humaita, Brazil has been solved and refined in the space group $C2/c$, $a = 8.553(6)$, $b = 12.319(6)$, $c = 7.155(8)$ Å, $\beta = 97.93(9)°$, up to $R = 0.062$ for 262 reflections. The structure is characterized by infinite double chains, running along c, formed by $[PO_4]$ and $[BeO_2(OH)H_2O]$ tetrahedra. Within such chains three- and four-membered rings of tetrahedra occur. Additional water molecules, not linked to any cation, fill the large channels of the structure. Within each channel, the hydrogen bonds assume either of two schemes. Evidences were obtained that the true unit cell of moraesite is three times larger, with a b parameter of 36.96 Å and space group symmetry Cc. It is suggested that the ordering of the hydrogen bond system, concerted with minor adjustments of the structure, could be responsible for the triplication of the b axis.

Introduction

In the last years the interest in the beryllophosphate minerals has significantly grown up, mainly since phosphorus and beryllium were used as substitutes for silicon and aluminum in tetrahedral frameworks, with the aim to prepare new kinds of molecular sieves.

With regard to phosphorus a large variety of aluminophosphates has been synthesized and thoroughly studied (Flanigen, Lok, Patton and Wilson, 1986). The interest in the use of beryllium as T-atom in molecular sieves was raised by the indication of Meier (1986) that very open frameworks may be induced by the presence of three-membered rings of tetrahedra and by the observation that the only known zeolite-like material presenting three-membered rings was a beryllosilicate, lovdarite (Merlino, 1984, 1990). These considerations stimulated successful attempts to synthesize beryllophosphates with zeolite-like structure by Harvey and Meier (1989). Examples of beryllophosphate minerals with a zeolite-like framework are already known [*e.g.* tiptopite (Peacor, Rouse and Ahn, 1987) and pahasapaite (Rouse, Peacor and Merlino, 1989)].

The crystal chemical relationships between beryllophosphates and aluminosilicates extend well beyond the materials with zeolite-like tetrahedral framework. In fact chain-like [*e.g.* väyrynenite (Mrose and Appleman, 1962)] and sheet-like beryllophosphates [*e.g.* herderite (Lager and Gibbs, 1974)] have been found. To deepen the study of these relationships a large amount of structural informations on beryllophosphates in the various classes is necessary. We therefore felt useful to undertake a series of structural and crystal-chemical studies of beryllophosphate minerals. A wide structural knowledge of beryllophosphate compounds does not only present interest from the mineralogical point of view, but can also be relevant in the molecular sieves technology, suggesting possible secondary building units for the synthesis of materials with new framework topologies.

Moraesite is a hydrated beryllium phosphate firstly described from the Sapucaia pegmatite mine, Minas Gerais district, Brazil, by Lindberg, Pecora and Barbosa (1953), who presented a detailed mineralogical description and gave morphological, physical, chemical and X-ray data for the new mineral. According to Lindberg et al. (1953), moraesite has composition $Be_2(PO_4)(OH) \cdot 4H_2O$, is monoclinic, space group Cc or $C2/c$, with unit cell parameters $a = 8.55$, $b = 36.90$, $c = 7.13$ Å, $\beta = 97°41'$. They also observed that all the reflections with $k = 3n$ are very weak, pointing to a smaller pseudo-cell with $b = 12.3$ Å.

Since then moraesite has been reported, among other localities, from a number of ocurrences in the Minas Gerais area, Brazil (Cassedanne and Cassedanne, 1987), and additional chemical data were presented for moraesite from Mulundu (Cassedanne and Cassedanne, 1985) and from Humaita (Cassedanne and Cassedanne, 1987). In these occurrences a substantial substitution of Be by [Ca + Mn + Fe] (Humaita) or by [Ca + Mg] (Mulundu) is proposed. Moreover Cassedanne and Cassedanne (1987), while confirming the monoclinic symmetry, space group Cc or $C2/c$, indicated a unit cell parameter $b = 12.286$ Å for moraesite from Humaita.

Such differences in both the unit cell parameters and the chemical composition between two samples from Sapucaia and Humaita, both referred as "moraesite", gave a further incentive to undertake a structural study of moraesite.

Experimental

A careful comparison of long-exposed ($hk0$) Weissenberg photographs of crystals of moraesite from Humaita and Sapucaia revealed that be b axis of approximately 37 Å represents a common feature of moraesite from both occurrences, and reasonably from all the other samples of the mineral. However, the extremely small dimensions of moraesite from Humaita made it very difficult to reveal the additional spots, and only with the help of the analogue Weissenberg spectrum of the Sapucaia specimen a few of them were detected, although very weak. However, owing to the very low intensity and the limited number of the additional detectable reflections, we decided to perform a structural analysis of moraesite on the basis of the sub-cell with $b = 12.3$ Å.

A small crystal of moraesite from Humaita (dimensions *ca.* $0.5 \times 0.05 \times 0.03$ mm), previously tested by Weissenberg method, was chosen for the intensity data collection, which was carried out on an Ital Structures four-circle automatic diffractometer using graphite-monochromatized Mo$K\alpha$ radiation ($\lambda = 0.71069$ Å). Only the independent reflections were collected in ω-2θ scan mode up to $2\theta = 55°$, scan range $(1.2 + 0.3 \tan \theta)°$, scan speed $1° \min^{-1}$. Notwithstanding the extended collection time, only 262 out of the 905 measured reflections were considered observed, having $I > 3\sigma(I)$, and were used in the least-squares calculations after reduction for Lorentz and polarization factors. The following unit cell parameters were obtained by least-square fitting of 2θ values of the few reflections whose intensity was high enough to allow an accurate centering: $a = 8.553(6)$, $b = 12.319(6)$, $c = 7.155(8)$ Å, $\beta = 97.93(9)°$.

The structure of moraesite was solved in the $C2/c$ space group through direct methods by means of the SHELXS86 system (Sheldrick, 1986). The maxima of the E-map were interpreted on the basis of their intensity and bondings as due to P, Be and four oxygen atoms (O1 to O4). The fifth oxygen (O5) was found after two least-squares cycles and a Fourier synthesis. After an empirical correction for the absorption effects through DIFABS program (Walker and Stuart, 1983), the refinement was completed with anisotropic thermal parameters for all the atoms. The final difference Fourier synthesis did not reveal the presence of any other atom: therefore calcium is not a constituent of moraesite. With regard to the hydrogens, it should be stressed that their negligible contribution to the scattering of X-rays is even lowered because of their disordered distribution in the average cell with $b = 12.3$ Å, as it will be discussed in the following of the present paper. The refinement was carried out with the SHELX76 system (Sheldrick, 1976). Neutral atomic scattering factors were those incorporated in SHELX76; that of Be was taken from *International Tables for X-ray Crystallography* (1974). The final R factor, using unit weights, was 0.062.[1]

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[1] A list of observed and calculated structure factors and the anisotropic thermal parameters can be ordered from the Fachinformationszentrum Energie-Physik-Mathematik, D-7514 Eggenstein-Leopoldshafen 2, Federal Republic of Germany. Please quote reference no. CSD 55712, the names of the authors and the title of the paper.

Table 1. Final fractional coordinates and equivalent isotropic thermal parameters given in Å^2 for moraesite. $U_{eq} = 1/3\ \Sigma\Sigma\ U_{ij}\ a_i^* a_j^*\ (\mathbf{a}_i \cdot \mathbf{a}_j)$.

Atom	x	y	z	U_{eq}
P	1/2	0.5753(4)	1/4	0.014(1)
Be	0.623(2)	0.625(1)	0.624(2)	0.024(6)
O1	0.623(1)	0.5064(7)	0.176(1)	0.017(3)
O2	0.578(1)	0.6517(6)	0.404(1)	0.027(3)
O3	0.805(1)	0.6624(8)	0.696(1)	0.038(4)
O4	1/2	0.685(1)	3/4	0.037(5)
O5	0.398(1)	0.091(1)	0.052(1)	0.060(4)

Table 2. Bond distances (Å) and angles (°) in moraesite. Distances and angles marked with an asterisk occur twice.

P –O1	1.508(9)*	O1 –O1^a	2.49(1)	111.5(5)
–O2	1.530(8)*	O1 –O2	2.49(1)*	110.0(5)*
		O1 –O2^a	2.50(1)*	110.5(5)*
Average	1.519	O2 –O2^a	2.41(1)	104.0(4)
Be –O1^b	1.66(2)	O1^b–O2	2.74(1)	114(1)
–O2	1.60(2)	O1^b–O3	2.59(1)	103(1)
–O3	1.64(2)	O1^b–O4	2.67(1)	107(1)
–O4	1.65(2)	O2 –O3	2.66(1)	110(1)
		O2 –O4	2.69(1)	111(1)
Average	1.64	O3 –O4	2.71(1)	111(1)
P–O1–Be^c	130.2(9)	P–O2–Be	127.0(8)	Be–O4–Be^d 127(1)
O1 –O1^e	3.05(1)	O1–O5^f	2.82(1)	
O2 –O3^g	2.64(1)	O3–O5^h	2.70(1)	
O4 –O5^b	3.17(2)	O5–O5^i	2.99(2)	
O5 –O5^a	3.12(1)			

Symmetry code for equivalent positions:
^{a} $-x+1, y, -z+1/2$; ^{b} $x, -y+1, z+1/2$; ^{c} $x, -y+1, z-1/2$; ^{d} $-x+1, y, -z+3/2$; ^{e} $-x+1, -y+1, -z$; ^{f} $x+1/2, y+1/2, z$; ^{g} $-x+3/2, -y+3/2, -z+1$; ^{h} $x+1/2, y+1/2, z+1$; ^{i} $-x+1, -y, -z$.

Description of the structure

The final fractional coordinates and equivalent isotropic thermal parameters are listed in Table 1. Selected interatomic distances are listed in Table 2. A drawing of the structure of moraesite in terms of coordination polyhedra in presented in Figure 1.

As it can be argued by the drawing, the structure of moraesite is characterized by insulated modules, which may be described as consisting of double tetrahedral chains, running along [001]. Each single chain has a

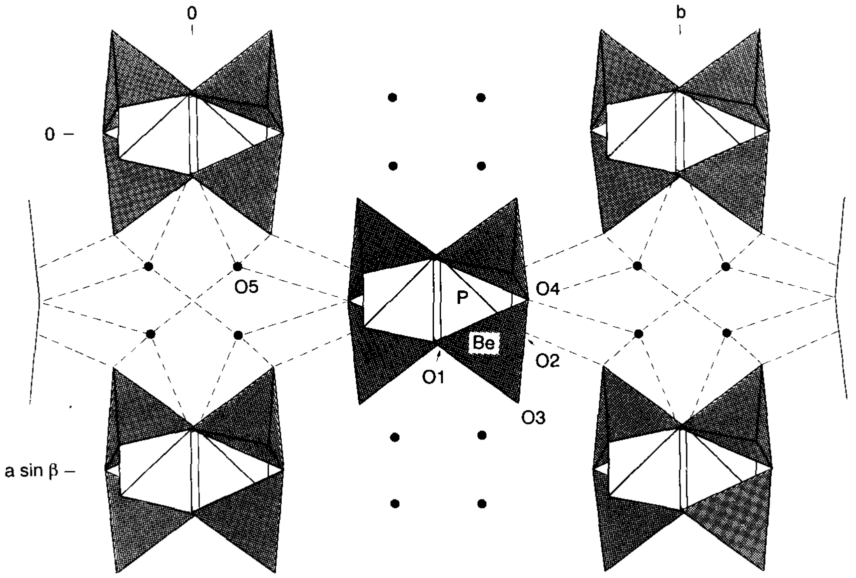

Fig. 1. The crystal structure of moraesite, as seen along *c*. Different grey tones denote $[PO_4]$ and $[BeO_2(OH)(H_2O)]$ tetrahedra. The insulated water molecules labelled O5 are indicated by black circles. The other water molecules (O3) and the hydroxyls (O4) belong to the Be-centered tetrahedra. Dashed lines indicate the traces of the hydrogen bondings.

repeat period of three tetrahedra, and is formed by a P-centered tetrahedron followed by two Be-centered tetrahedra. Adjacent chains are linked through sharing of O1 atoms. The resulting double chain has composition $[Be_4(OH)_2(H_2O)_4(PO_4)_2]$, and is internally charge-balanced. Therefore the channels of the structure are filled by water molecules only.

Each P is coordinated by four oxygen atoms (O1 and O2), whereas each Be is coordinated by two oxygen atoms (O1 and O2), a hydroxyl (O4) and a water molecule (O3). The four oxygen atoms which build up the $[PO_4]$ tetrahedron are shared with four $[BeO_2(OH)H_2O]$ tetrahedra. The hydroxyl oxygen (O4) is shared by two $[BeO_2(OH)H_2O]$ tetrahedra.

The connection of adjacent chains gives rise to three-membered rings of tetrahedra, as shown in Fig. 1. Neighbour three-membered rings are stacked in the [001] direction by sharing of two O2 atoms.

In both P- and Be-centered tetrahedra the T—O and O—O distances, as well as the O—T—O angles, are within the normal values (Table 2), indicating that the tetrahedra are essentially regular and undistorted, the only exception being represented by the short O2—O2 edge of 2.41 Å in the $[PO_4]$ tetrahedron, and the correspondingly small O2—P—O2 angle of 104°. As regards the T—O—T angles, unexpectedly, all the values are very

Table 3. Bond valence balance for moraesite, computed following Brese and O'Keeffe (1991). $\Sigma_a v$ = valence sum of bonds emanating from cation. $\Sigma'_c v$ = valence sum of bonds (other than H-bonds) reaching anion. $\Sigma_c v$ = valence sums of bonds reaching anion, corrected for the contribution of the hydrogen bonds (Ferraris and Ivaldi, 1988). O5 and O5′ differ between each other in the hydrogen bonds only. The figures have been approximated at the third digit.

	P	Be	$\Sigma'_c v$	H-bonds		$\Sigma_c v$
O1	1.296[a]	0.470	1.767	+0.176		1.942
O2	1.221[a]	0.549	1.770	+0.263		2.034
O3		0.491	0.491	−0.263	−0.225	0.003
O4		0.483[b]	0.967	+0.105	−0.105	0.967
O5				+0.225 −0.176	+0.105 −0.131	0.023
O5′				+0.225 −0.176	+0.131 −0.105	0.076
$\Sigma_a v$	5.035	1.994				

[a] Two bonds for each cation. [b] Two bonds for each anion.

similar (lying in the range between 127° and 130°), no matter whether they are involved in the three-membered or in the four-membered rings.

Hydrogen bond system

In Table 2 all the O...O distances shorter than 3.30 Å between oxygen atoms not belonging to the same polyhedron are listed. A plausible hydrogen bond system – which is sketched in Fig. 1 by dashed lines – has been assessed, on the basis of the O...O distances, taking into account the valence balance calculations computed according to Brese and O'Keeffe (1991) (*cf.* Table 3), and assuming a regular tetrahedral environment for the donor and acceptor atoms around the O5 water molecules.

For all the H-bonds involving O1, O2 and O3 donor and acceptor oxygen atoms can be unambiguously indicated: O1 is an oxygen atom, being linked to 1 P + 1 Be, and is acceptor of an O5–H...O1 bond. O2 is an oxygen atom, too, being linked to 1 P + 1 Be, and is acceptor of an O3–H...O2 bond. O3 is a water molecule, being linked only to 1 Be. O3 is donor of two hydrogen bondings towards O5 and O2.

On the contrary, with regard to the hydrogen bonds involving only O4 (a hydroxyl, linked to two Be cations) and O5 (a water molecule not linked to any cation), two different hydrogen bond schemes are possible, as indicated in Figure 2, where the arrows go from the donor towards the acceptor oxygen atoms. The common part in both systems is indicated with light dashes, whereas heavy dashes indicate the part which is different in the two systems. In Fig. 2 at left a chain of hydrogen bonds O–H...O–

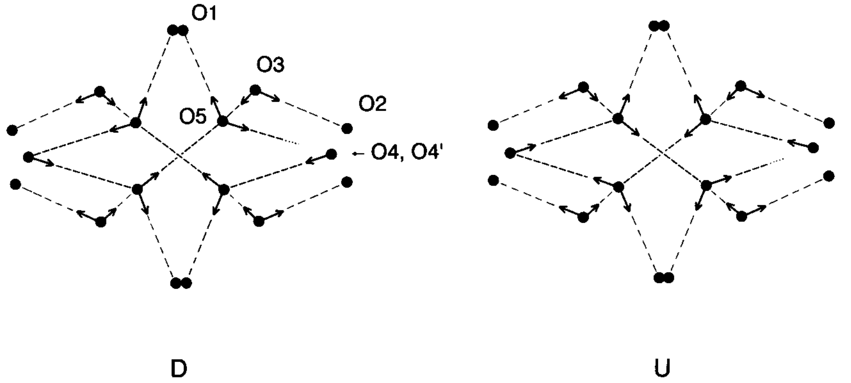

Fig. 2. The two kinds of hydrogen bond schemes, as seen along *c*, conventionally referred as D and U. Only one of the symmetry-equivalent oxygen atoms has been labelled, with the exception of O4 and O4′, which are superimposed in the [001] projection, lying at the distance of a *c* translation, and represent the starting and ending point of the loop of the hydrogen bonds involving O4 and O5 atoms (heavy dashes).

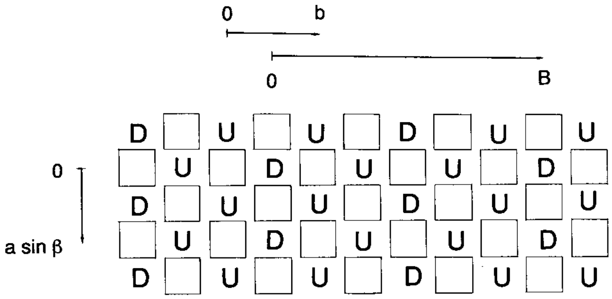

Fig. 3. Suggested ordering scheme of U and D systems of hydrogen bonds, which gives rise to the true unit cell of moraesite, with space group *Cc* and $B = 3b$.

H...runs downwards along *c* (D-chain), starting from O4 at 1/2, *y*, 3/4, passing through O5, O5, O4, O5, O5, and returning to O4′ at 1/2, *y*, −1/4. The chain at right, obtained from the previous one by reversing the donor-acceptor role in each hydrogen bond of the chain, runs upwards along *c* (U-chain), starting again from O4 at 1/2, *y*, 3/4, passing through O5, O5, O4, O5, O5, and returning to O4′ at 1/2, *y*, 7/4. The two chains are equivalent and related one to the other through a twofold axis parallel to *b*.

A statistical distribution of D- and U-chains result in a structure with $b = 12.3$ Å and space group symmetry *C*2/*c* (average structure or substructure). The ordering of the hydrogen bonds according to a single scheme is not compatible with the twofold axis, as clearly indicated by Fig. 2, and results in a descent in space group symmetry from *C*2/*c* to *Cc*.

Different distributions of U- and D-chains give rise to different possible structures: small adjustments of the heavy atoms, mainly O5 water molecules, related to the ordering of the hydrogen bonds, may result in the appearence of weak superstructure reflections. Actually the observations of Lindberg et al. (1953) on samples from Sapucaia and our observations on samples from Humaita indicate that moraesite has an unit cell parameter *b* of 36.9 Å and a *C*-centered monoclinic cell. A distribution of U- and D-chains as represented in Figure 3 is consistent with such observations.

Conclusions

The results of our structural analysis gave convincing proof that the chemical composition of moraesite from Humaita is closely similar to that indicated by Lindberg et al. (1953) for moraesite from Sapucaia and corresponds to the ideal stoichiometry $Be_2(PO_4)(OH) \cdot 4H_2O$. The presence of Ca, Mn, and Fe claimed by Cassedanne and Cassedanne (1987) for moraesite from Humaita is not confirmed.

Therefore, if we look at the chemical composition of a "Ca—Mn—Fe^{2+}-bearing moraesite" from Humaita (Cassedanne and Cassedanne, 1987), and of a "Ca—Mg—Fe^{3+}-bearing moraesite" from Mulundu (Cassedanne and Cassedanne, 1985), we may confidently assume that the analyzed specimen consisted of intergrowths of two or more phases. As regards the anomalous chemical data presented by Cassedanne and Cassedanne (1987) for moraesite from Humaita and Mulundu, it seems plausible that they could result from impurities, *e.g.* intergrowth of moraesite with other phosphates. For instance, if we assume that moraesite is the only Be-bearing phase, and thus correct the analytical data of the Humaita and Mulundu samples for the fraction due to the ideal moraesite, we obtain a residual analysis which could point to the occurrence of calcium and Mg—Mn—Fe phosphates, like anapaite, $Ca_2Fe^{2+}(PO_4)_2 \cdot 4H_2O$, collinsite, $Ca_2(Mg,Fe)(PO_4)_2 \cdot 2H_2O$, fairfieldite, $Ca_2(Mn,Fe)(PO_4)_2 \cdot 2H_2O$.

The differential thermal analysis studies on moraesite samples (Bhaskara Rao, 1965; Cassedanne and Cassedanne, 1987) could now be interpreted on structural grounds. In fact the total water content of moraesite is displayed in three different ways, namely as water molecules not linked to any cation, as well as water molecules and hydroxyls linked to Be^{2+} cations. This could be related to the presence of three distinct endothermal peaks in the DTA curve.

As a final remark we would stress the possible role of the double beryllophosphate chains found in the crystal structure of moraesite as building modules in large-pore molecular sieves. In fact the chains may be connected by sharing O3 atoms, which correspond to water molecules in the "free" chains and would become bridging hydroxyls in the resulting framework. The schematic reaction n $[Be_4(OH)_2(H_2O)_4(PO_4)_2]$ = $[Be_4(OH)_4(OH)_4(PO_4)_2]_n^{-2n}$ + $2n$ $(H_3O)^+$ should be favoured by alkaline solutions: large tetralkylammonium cations could lead to the formation of open frameworks.

Acknowledgements. We are indebted to R. Kristiansen (Torp, Norway), who stimulated our interest in moraesite and provided us with the sample from Humaita. P. J. Dunn (National Museum of Natural History, Smithsonian Institution) kindly provided with the sample *no.* NMNH 106577 of moraesite from Sapucaia. Financial support has been supplied by M.U.R.S.T. (60% and 40% grants to S. Merlino).

References

Bhaskara Rao, A.: Note on the DTA study of some rare Brazilian phosphate minerals. Mineral. Mag. **35** (1965) 427–428.

Brese, N. E., O'Keeffe, M.: Bond-valence parameters for solids. Acta Crystallogr. **B47** (1991) 192–197.

Cassedanne, J. P., Cassedanne, J. O.: Présence d'une moraesite à Ca – Mg dans le champ pegmatitique de Itinga-Taquaral. Anais Acad. Bras. Ciências **57** (1985) 319–323.

Cassedanne, J. P., Cassedanne, J. O.: La moraesite de la mine de tourmaline de Humaita, Minas Gerais, Brésil. Can. Mineral. **25** (1987) 419–424.

Ferraris, G., Ivaldi, G.: Bond valence *vs* bond length in O...O hydrogen bonds. Acta Crystallogr. **B44** (1988) 341–344.

Flanigen, E. M., Lok, B. M., Patton, R. L., Wilson, S. T.: Aluminophosphate molecular sieves and the periodic table. In: *New developments in zeolite science and technology* (Eds. Y. Murakami, A. Iijima, J. W. Ward), pp. 103–112, Tokyo, Kodansha 1986.

Harvey, G., Meier, W. M.: The synthesis of beryllophosphate zeolites. In: *Zeolites: Facts, Figures, Future* (Eds. P. A. Jacobs, R. A. van Santen), pp. 411–420, Amsterdam, Elsevier Science Publishers B. V. 1989.

International Tables for X-ray Crystallography: Vol. IV. Birmingham, Kynoch Press 1974.

Lager, G. A., Gibbs, G. V.: A refinement of the crystal structure of herderite, $CaBePO_4OH$. Am. Mineral. **59** (1974) 919–925.

Lindberg, M. L., Pecora, W. T., Barbosa, A. L. de M.: Moraesite, a new hydrous beryllium phosphate from Minas Gerais, Brazil. Am. Mineral. **38** (1953) 1126–1133.

Meier, W. M.: Zeolite and zeolite-like materials. In: *New developments in zeolite science and technology* (Eds. Y. Murakami, A. Iijima, J. W. Ward), pp. 13–22, Tokyo, Kodansha 1986.

Merlino, S.: Recent results in structural studies of zeolites and zeolite-like materials. In: *Proceedings of the Sixth International Zeolite Conference — Reno, USA 10–15 July 1983* (Eds. D. Olson, A. Bisio), pp. 747–759, Guildford, Butterworths 1984.

Merlino, S.: Lovdarite, $K_4Na_{12}(Be_{18}Si_{18}O_{72}) \cdot 18H_2O$, a zeolite-like mineral: structural features and OD character. Eur. J. Mineral. **2** (1990) 809–817.

Mrose, M. E., Appleman, D. E.: The crystal structure and crystal chemistry of väyrynenite, $(Mn,Fe)Be(PO_4)(OH)$, and euclase, $AlBe(SiO_4)(OH)$. Z. Kristallogr. **117** (1962) 16–36.

Peacor, D. R., Rouse, R. C., Ahn, J.-H.: Crystal structure of tiptopite, a framework beryllophosphate isotypic with basic cancrinite. Am. Mineral. **72** (1987) 816–820.

Rouse, R. C., Peacor, D. R., Merlino, S.: Crystal structure of pahasapaite, a beryllophosphate mineral with a distorted zeolite rho framework. Am. Mineral. **74** (1989) 1195–1202.

Sheldrick, G. M.: SHELX76. *Program for crystal structure determination.* Univ. of Cambridge, England 1986.

Sheldrick, G. M.: SHELXS86. *Program for the solution of crystal structures.* Univ. of Göttingen, Germany 1986.

Walker, N., Stuart, D.: An empirical method for correcting diffractometer data for absorption effects. Acta Crystallogr. **A39** (1983) 158–166.