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HYDROXYL GROUPS AND H_2O MOLECULES IN PHOSPHATES: A NEUTRON DIFFRACTION STUDY OF EOSPHORITE, $MnAlPO_4(OH)_2 \cdot H_2O$

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Minerals belonging to the eosphorite $[MnAl(PO_4)(OH)_2 \cdot H_2O]$ - childrenite $[FeAl(PO_4)(OH)_2 \cdot H_2O]$ series are widespread secondary phosphates occurring in medium to strongly evolved rare-element granitic pegmatites, ranging from the beryl to the petalite subtype in the classification of Černý and Ercit (2005). Eosphorite is a low-temperature metasomatic mineral in Lithium-Cesium-Tantalum (LCT) granitic pegmatites that frequently crystallizes in open cavities occurring in platy albite (cleavelandite) units of zoned pegmatitic dikes (Simmons *et al.* 2003). Eosphorite constitutes one of the low temperature products of alteration of primary phosphates, mainly lithiophilite or triplite. The unit-cell constants and the possible space groups of childrenite (*Bbam* or *Bba*2) were first reported by Barnes (1949). The crystal structure of childrenite was later solved by Giuseppetti and Tadini (1984) by means of X-ray single-crystal diffraction. The authors refined the crystal structure in the acentric space group *Bba*2, with $a = 10.395(1)$, $b = 13.394(1)$, and $c = 6.918(1)$ Å ($Z = 8$). The crystal-structure of eosphorite was first solved by Hanson (1960) in the centric *Bbam* space group, with $a = 10.52$, $b = 13.60$, and $c = 6.97$ Å ($Z = 8$) using a sample from Newry, Maine and later reinvestigated by Hoyos *et al.* (1993) using a sample from Taquaral, Brazil, by means of X-ray single-crystal diffraction, in the *Cmca* space group, with $a = 6.928(1)$, $b = 10.445(1)$, and $c = 13.501(2)$ Å [eosphorite composition: $(Mn_{0.76}Fe_{0.24})Al(PO_4)(OH)_2 \cdot H_2O$]. The crystal structure of both eosphorite and childrenite consists of chains parallel to the *a*-axis (in the *Cmca* space group) constituted by (Mn,Fe)-distorted octahedra, sharing opposite O-O edges, and chains of Al-octahedra. The two types of chains are connected, via corner-sharing, to form a set of (100) sheets held together by $[PO_4]$ tetrahedra (and hydrogen bonds) to form a three-dimensional network.

The crystal structure of eosphorite has been reinvestigated by means of single-crystal neutron diffraction. A gemmy single-crystal of eosphorite up to 14 mm in length and 5 mm in diameter from a granitic pegmatite outcropping in the area of Chamachhu (Changmachhu), Skardu district, Baltistan, Pakistan, was used for the diffraction experiment and for the chemical analysis. The specimens from Chamachhu show eosphorite crystals perched on white platy albite (cleavelandite) or directly on pollucite or topaz crystals up to 20-30 cm contained in large miarolitic cavities. The mineralogical association of these pegmatites is fairly evolved and consists of muscovite, lepidolite, spessartine, gem elbaite, gem topaz, beryl (gem aquamarine and morganite), pollucite, tantalite-(Mn), fluorapatite, eosphorite, and väyrynenite. The WDS electron-microprobe analysis shows that our sample of eosphorite is homogeneous and approaches an almost ideal composition with the following empirical formula: $(Mn^{2+}_{0.95}Fe^{2+}_{0.02}Al_{0.10})_{\Sigma 1.07}$ $AlPO_4(OH_{1.93}F_{0.07})_2 \cdot H_2O$. Our single-crystal neutron structure refinement, based on diffraction data collected at 20 K, provides a general structural model in agreement with the one reported by Hoyos *et al.* (1993). The building block units of the eosphorite structure consists of chains of (Mn,Fe)-octahedra (sharing opposite O-O edges) running along the *a*-axis, and chains of Al-octahedra. The two types of chains are connected, via corner-sharing, to form a set of (100) sheets held together by P-tetrahedra (and hydrogen bonds) to form a three-dimensional framework. Distorted channels, confined by 6-membered ring of polyhedra, run along [100]. The (Mn,Fe)-octahedron is significantly distorted, with $\Delta(O\text{-}O)_{max} \sim 0.81$ Å, as the O-O distance of the shared edge is significantly shorter than the non-shared ones. We cannot exclude that this effect is due to the cation-cation repulsion, as $M\text{-}M \sim 3.46$ Å. The Al-octahedron and the P-tetrahedron appear to be less distorted, with $\Delta(O\text{-}O)_{max} \sim 0.15$ Å and $\Delta(O\text{-}O)_{max} \sim 0.03$ Å. The low-*T* structure refinement does not show any evidence of (Mn, Fe)-octahedral ordering, which should lead to a lowering of the symmetry. In addition, the principal root-mean-square components of the atomic displacement parameters do not show any pronounced displacement about the equilibrium position, compared with those of the other atomic sites, suggesting the absence of a local split. The Fe-content deduced on the basis of the structure refinement is 0.165 *a.p.f.u.* where the chemical

analysis shows a Fe-content of about 0.025 *a.p.f.u.* This difference can be ascribed to a multi-element population at the *M* site, in which Mn, Fe and Al might coexist. In fact, the EPMA-WDS data show an excess of Al, as often reported in other eosphorite analyses (*e.g.* samples from Black Mountain and Buckfield, Maine; Hurlbut 1950). The neutron structure refinement of this study allowed an unambiguous location of the H-sites along with the description of the H-bonding scheme in eosphorite structure. We can now describe the structure as made by (Mn, Fe) $O_4(OH, H_2O)_2$ and $AlO_2(OH)_2$ $(OH, H_2O)_2$ octahedra (Figure 1). The *O3* site is the OH$^-$ group (*i.e.* *O3-H3*) oxygen, whereas *O4* is the oxygen of OH$^-$ group (*i.e.* *O4-H1*) and H_2O molecules (*i.e.* *H2-O4-H1*). In particular, H_2O molecules have site occupancy of 50%, so that the two H_2O molecules generated by the mirror plane are mutually exclusive. In other words, the two equivalent *O4* sites generated by the mirror plane are respectively the oxygen of one OH group and one H_2O molecule, with a local breaking of the symmetry. Among the three independent Al-O bond distances of the $AlO_2(OH)_2(OH,H_2O)_2$ octahedron, the Al-OH bond distance (*i.e.* Al-O3) is the shortest and the Al-(OH,H_2O) distance (*i.e.* Al-O4) the

longest. In the (Mn, Fe)$O_4(OH,H_2O)_2$ polyhedron, the *M*-(OH,H_2O)$_2$ bond distance (*i.e. M-O4*) is the longest. The geometry of the H_2O molecule and the OH group, along with the hydrogen bonding scheme in eosphorite, are now well defined. The *O4-H1* and *O4-H2* distances, corrected for "riding motion", are ~1.003 and ~1.071 Å, respectively, and two strong energetically favorable hydrogen bonds occur: *O4···O5* = 2.711(1) Å, *H1···O5* = 1.757(1) Å and *O4-H1···O5* = 161.9(1)°; *O4···O4* = 2.504(1) Å, *H2···O4* = 1.454(1) Å and *O4-H1···O4* = 170.9(1)° (Fig. 1). In other words, symmetry-related *O4* act as *donor* and as *acceptor* of the H-bond. The *H1-O4-H2* angle approaches the ideal value (*i.e.* 107.2(1). The OH-group shows: *O3-H3* distance, corrected for "riding motion", of ~ 0.995 Å, *O3···O1* = 2.836(1) Å, *H3···O1* = 1.930(1) Å and *O3-H3···O1* = 154.0(1)°. The *O1* site (*i.e.* the *acceptor* of the H bond of the *O3-H3* group) is *under-bonded*, as it is shared by two (Mn, Fe)- octahedra and one P-tetrahedron (Fig. 1). The anisotropic structure refinement shows that the principal root-mean-square components of the atomic displacements parameters of the *H3* site (belonging to the OH group) are larger in magnitude than those of the *H1* and *H2* sites.
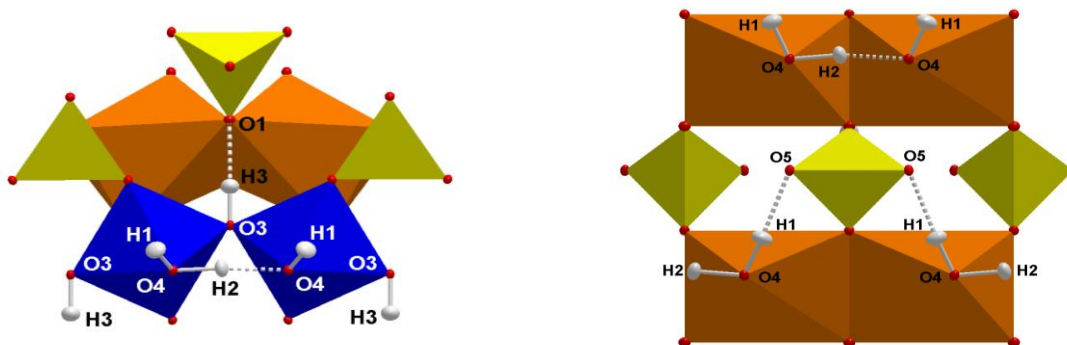
Fig. 1: Hydrogen location, configuration of OH groups and H_2O molecules, along with the H-bond scheme, in the structure of eosphorite. The occupancy factor of the H2 site is 50%.

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