

FA2-MS01-P06**Crystal Chemistry of the Divalent Cations in Solid-State Synthesized Fillowite-type Phosphates.**

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Minerals of the fillowite group are Na-, Mn- and Fe-bearing phosphate minerals, with a chemical composition corresponding to the simplified formula $\text{Na}_2\text{Ca}(\text{Mn,Fe,Mg})_7(\text{PO}_4)_6$. They occur as primary phases in granitic pegmatites, in meteorites, and in some metamorphic rocks. Araki and Moore [1] determined the crystal structure of fillowite from Branchville Pegmatite (Connecticut), in the R-3 space group, with $a = 15.51$, $c = 43.51$ Å, and $Z = 18$.

In order to better understand the role of the divalent cations in the fillowite structure, the solid solutions $\text{Na}_2M^{2+}(\text{Mn}_{7-7x}\text{Mg}_{7x})(\text{PO}_4)_6$ ($M^{2+} = \text{Ca}$ and Cd ; $x = 0$ to 1), $\text{Na}_2M^{2+}_2(\text{Mn}_{6-6x}\text{Mg}_{6x})(\text{PO}_4)_6$ ($M^{2+} = \text{Ca}$ and Cd ; $x = 0$ to 2/3) and $\text{Na}_2(\text{Mn}_{8-8x}M^{2+}_{8x})(\text{PO}_4)_6$ ($M^{2+} = \text{Ca}$, Cd and Mg ; $x = 0$ to 1) were synthesized by solid state reactions in air between 650 and 970°C at 1 bar.

In the $\text{Na}_2M^{2+}(\text{Mn}_{7-7x}\text{Mg}_{7x})(\text{PO}_4)_6$, $\text{Na}_2M^{2+}_2(\text{Mn}_{6-6x}\text{Mg}_{6x})(\text{PO}_4)_6$ ($M^{2+} = \text{Ca}$ and Cd) and $\text{Na}_2(\text{Mn}_{8-8x}\text{Mg}_{8x})(\text{PO}_4)_6$ solid solutions, the incorporation of Mg immediately induces the crystallization of $\text{Mg}_2\text{P}_2\text{O}_7$. However a temperature increase causes the depletion or the disappearance of this impurity. Moreover, the presence of fillowite-type phosphate for the composition $\text{Na}_2M^{2+}\text{Mg}_7(\text{PO}_4)_6$ ($M^{2+} = \text{Ca}$ and Cd), even with the Mg-rich impurity, confirms the significant role of Mg in the fillowite structure.

In the $\text{Na}_2\text{Cd}(\text{Mn}_{7-7x}\text{Mg}_{7x})(\text{PO}_4)_6$ ($x = 4/7$ to 1) and $\text{Na}_2\text{Cd}_2(\text{Mn}_{6-6x}\text{Mg}_{6x})(\text{PO}_4)_6$ ($x = 1/3$ to 2/3) solid solutions, an alluaudite-type phosphate appears at low temperature (about 700°C), while a fillowite-type compound is identified at high temperature (about 900°C).

Interestingly, the compositions $\text{Na}_2(\text{Mn}_{8-8x}\text{Cd}_{8x})(\text{PO}_4)_6$ (with $x = 0$, 1/8 and 1/4) produce single-phase fillowite-type compounds, whereas the compositions with $x = 3/4$ and 1 produce another pure compound with a powder X-ray diffraction pattern similar to that of $\text{NaCd}_4(\text{PO}_4)_3$ synthesized by Ben Amara et al. [2]. The composition $\text{Na}_2(\text{Mn}_4\text{Cd}_4)(\text{PO}_4)_6$ gives both compounds.

The incorporation of Ca into the structure is limited. Only $\text{Na}_2\text{Ca}_2\text{Mn}_6(\text{PO}_4)_6$ is constituted by pure fillowite. An increasing of the Ca amount induces the systematic crystallisation of whitlockite, $\text{NaCa}_9\text{Mn}(\text{PO}_4)_7$

[1] Araki, T. & Moore, P.B., 1981, *Am. Mineral.* 66, 827-842. [2] Ben Amara M., Olazuaga R., le Flem G., Vlasse M., 1979, *Acta Cryst.* B35, 1567.

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Thermal Expansivity and Dehydrogenation in Amphiboles. Roberta Oberti^a, Michele Zema^b, Serena Tarantino^b, Massimo Boiocchi^c. ^aCNR-IGG,

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Few data exist on the thermal expansivity of amphiboles, and they refer to rather exotic compositions which either are not useful to model geologic processes or undergo phase transition. Indeed, amphiboles are not crystal-chemically inert during annealing. Whereas symmetry changes involve only compositions with Mg_2 or (NaMg) at the B sites, important changes in cation distribution are frequent during annealing. Moreover, at high T dehydrogenation processes coupled with oxidation of Fe^{2+} may become significant, and may induce crystal collapse. Both these processes strongly affect the evolution of the unit-cell parameters, and thus quantification of expansivity in amphiboles is tricky. On the other end, amphiboles play a crucial role in the deep crust and upper-mantle regions, especially concerning constraints to their water budget. Thus information of HT-HP behaviour of amphiboles is crucial. This work is part of a systematic project aimed at modelling the HT-HP behaviour of amphiboles, which is based on a long-term expertise in amphibole crystal-chemistry and in situ HT crystallography of anhydrous minerals acquired in Pavia. We started with amphiboles peculiar of upper mantle geological contexts, such as kaersutite and pargasite. Progressive in situ annealing up to the experimental limit of 1050 °C was done on well-characterised crystals with similar overall composition but with different OH and Fe^{2+} contents, as well as on a fully dehydrogenated Fe^{2+} -free kaersutite where cation disorder is impossible. Measurements of the evolution of the unit-cell parameters were coupled with HT structure refinement to monitor changes in cation ordering and site geometries as well as crystal-chemical signals of increasing dehydrogenation. Thus the different processes could be discriminated, and their effects accurately evaluated by difference. The unit-cell edges of the kaersutite increase linearly up to 1050 °C ($b > c > a$), while the beta angle decreases linearly; the unit-cell volume increases by 3%. Those of the partially to totally hydrogenated amphiboles have a similar behaviour until 600-700 °C (depending on composition). When the dehydrogenation process starts, the unit-cell edges decrease (a in a quite dramatic way), and the β angle increases. When the isothermal reaction is complete, the reversal path measured during cooling has quite similar expansivity values. Structure refinement results confirm that: a) during annealing, the tetrahedra do not expand, but both the geometry of the 6-membered rings and the stacking of the double chains of tetrahedra change (yielding a stretching along c and an increase in $a \sin\beta$); b) with ongoing dehydrogenation, a rearrangement of the double chains around a more compressed A site is observed, as well as an increased transfer of Fe^{2+} from the B to the C sites; c) dehydrogenation is coupled with oxidation of Fe at the $M(1)$ and $M(3)$ sites (which both shrink significantly), and its amount can be estimated based on proper geometrical parameters even at high T .

Keywords: high-temperature crystallography; thermal expansion; dehydrogenation