

Crystal chemistry of natural and synthetic fillowite-type phosphates

F. HATERT^{1*}, P. KELLER², E. S. GREW³, M. RONDEUX¹
AND A.-M. FRANSOLET¹

¹Univ. Liège, B-4000 Liège, Belgium

(*correspondence: fhatert@ulg.ac.be)

²Univ. Stuttgart, D-70569 Stuttgart, Germany

³Univ. Maine, Orono, ME 04469, USA

The fillowite group comprises complex phosphate minerals that occur in granitic pegmatites, high grade metamorphic rocks, and in meteorites. The fillowite crystal structure is rhombohedral, space group *R*-3, with *a* = 15.28, *c* = 43.51 Å, and *Z* = 18. The formula for fillowite is $\text{MnNa}_8(\text{Ca}_4\text{Na}_4)\text{Mn}_{43}(\text{PO}_4)_{36}$. Ca, Na, Fe or Y (REE) substitute for Mn at the (0,0,0) site; Mg or Fe^{2+} substitute for Mn at the M sites and Ca/Na ratio is variable [1,2,3]. In order to better understand the crystal chemistry of fillowite-type phosphates, natural minerals and synthetic compounds were investigated by single-crystal and powder X-ray diffraction techniques.

Natural fillowite from the Buranga pegmatite, Rwanda [$\text{Na}_{10.78}\text{Ca}_{4.94}\text{Mn}_{24.46}\text{Fe}^{2+}_{14.92}\text{Fe}^{3+}_{2.16}\text{Mg}_{0.34}\text{Zn}_{0.30}(\text{PO}_4)_{36}$, *a* = 15.122, *c* = 43.258 Å, *R*₁ = 0.0796], and from the Kabira pegmatite, Uganda [$\text{K}_{0.26}\text{Na}_{11.42}\text{Ca}_{5.38}\text{Mn}_{23.42}\text{Fe}^{2+}_{16.94}\text{Fe}^{3+}_{1.56}(\text{PO}_4)_{36}$, *a* = 15.125, *c* = 43.198 Å, *R*₁ = 0.0463], johnsomervilleite from Loch Quoich, Scotland [$\text{Na}_{8.48}\text{Ca}_{6.42}\text{Fe}^{2+}_{20.96}\text{Mg}_{17.84}\text{Mn}_{4.00}(\text{PO}_4)_{36}$, *a* = 15.036, *c* = 42.972 Å, *R*₁ = 0.0413], as well as the synthetic compounds $\text{Na}_2(\text{Na},\text{Mn})_{14}\text{Mn}_{44}(\text{PO}_4)_{36}\cdot\text{H}_2\text{O}$ [*a* = 15.274, *c* = 43.334 Å, *R*₁ = 0.0728 [4]], $\text{Na}_{14.36}\text{Mn}_{44.51}(\text{PO}_4)_{36}$ [*a* = 15.305, *c* = 43.672 Å, *R*₁ = 0.0802], and $\text{Na}_{15.66}\text{Mn}_{37.12}\text{Fe}^{3+}_{4.80}\text{Fe}^{2+}_{1.86}(\text{PO}_4)_{36}$ [*a* = 15.216, *c* = 43.291 Å, *R*₁ = 0.0770], were investigated by single-crystal X-ray diffraction. Accurate cationic distributions were established and confirmed by bond-valence calculations. In two synthetic compounds was observed a supplementary position O25, that was not previously reported in natural fillowite-type phosphates [1, 2]. This position corresponds to molecular water, the presence of which is confirmed by infrared spectroscopy.

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Phosphate alteration on Mars

E.M. HAUSRATH, D.C. GOLDEN, R.V. MORRIS AND
D.W. MING

NASA Johnson Space Center, 2101 NASA Parkway, Houston,
TX 77058 (Elisabeth.M.Hausrath@nasa.gov)

Analyses by the Mars Exploration Rover Spirit suggest the loss of a phosphate-containing mineral from rock surfaces [1]. In addition, the highly altered Paso Robles deposit contains ~5% P₂O₅, modeled as 8-10 % phosphate [2]. Phosphate may therefore be a useful tracer of alteration conditions on Mars.

Acid vapor experiments were performed (c.f. [3]), except samples were suspended on Teflon instead of quartz beads in solutions of sulfuric (85% and 98%) and hydrochloric (30%) acid. Mineral substrates, which included San Carlos forsterite, Durango fluorapatite, and basalt glass (Stapafjell Volcano, courtesy of S. Gislason, University of Iceland [4, 5]), were prepared as thick sections and powdered grains (individual minerals and as a mixture). Reacted samples were analyzed by X-ray diffraction (XRD), Scanning Electron Microscopy (SEM) and Energy Dispersive Spectroscopy (EDS). Hygroscopic chlorides were dried at 60°C and analyzed by XRD and SEM when possible.

Preliminary results show formation of sulfates including kieserite, hexahydrate, and anhydrite, and anhydrous and hydrated monocalcium phosphate (XRD). Al and Ca sulfates, amorphous silica and Fe-phosphates were detected by SEM and EDS. Preliminary results from the HCl reactions suggest the presence of monocalcium chlorophosphate ($\text{CaClH}_2\text{PO}_4\cdot\text{H}_2\text{O}$), $\text{CaCl}_2(\text{H}_2\text{O})_4$, bischofite ($\text{MgCl}_2(\text{H}_2\text{O})_6$), chloraluminite ($\text{AlCl}_3\cdot 6\text{H}_2\text{O}$), and tachyhydrite ($\text{CaMg}_2\text{Cl}_6\cdot 12\text{H}_2\text{O}$) (XRD). Monocalcium chlorophosphate is expected to alter to brushite in water and monetite on exposure to air [6].

Future experiments will explore the effects of variables such as humidity, parent mineralogy, solid:liquid ratio, acidity, temperature, time, and oxidation state on phosphate reactions relevant to the Martian surface.

[1] Hurowitz J.A. *et al.* (2006) *JGR*, **111**, E02S19 [2] Ming D.W. *et al.* (2006) *JGR*, **111**, E02S12 [3] Golden D.C. *et al.* (2005) *JGR*, **110**, E12S07 [4] Oelkers E.H. & Gislason S.R. (2001) *GCA*, **65**, 3671-3681 [5] Gislason S.R. & Oelkers E.H. (2003) *GCA* **67**, 3817-3832. [6] Crystallographic Properties of Fertilizer Compounds National Fertilizer & Environmental Research Center Bulletin Y-217 1991 Tennessee Valley Authority.