

SPECTRA OF PHOSPHATE MINERALS AS OBTAINED BY VISIBLE-NEAR INFRARED REFLECTANCE, THERMAL INFRARED EMISSION, AND MÖSSBAUER LABORATORY ANALYSES.

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Introduction: Here we present an initial survey of phosphate minerals using three spectroscopic techniques including visible-near infrared (VNIR) reflectance, thermal infrared (TIR) emission, and Mössbauer spectroscopies. We are studying both common and unusual terrestrial phosphate samples in order to establish multi-technique libraries of well-characterized samples. These spectral libraries will be used for analysis of remote-sensing data, including the phosphate-rich, bright soil at Paso Robles, Mars.

Visible-Near Infrared: Reflectance spectra of several phosphate minerals are shown in Figure 1. The spectra of apatite ($\text{Ca}_5(\text{PO}_4)_3(\text{F},\text{Cl})$) and hydroxyl-apatite ($\text{Ca}_5(\text{PO}_4)_3(\text{OH})$) powders were acquired at RELAB/Brown University from 0.3 to 5.0 μm by splicing visible/near-infrared bidirectional spectra (measured relative to Halon) with FTIR spectra measured under H_2O -purged conditions (relative to a rough gold surface). The splice was made near 1.2 μm . FTIR-only spectra of plumbogummite ($\text{PbAl}_3(\text{PO}_4)_2(\text{OH})_5 \cdot \text{H}_2\text{O}$) and amblygonite ($(\text{Li},\text{Na})\text{Al}(\text{PO}_4)(\text{F},\text{OH})$) powders also were acquired at RELAB. Reflectance spectra of the ferrolaueite ($\text{Fe}^{2+}\text{Fe}^{3+}_2(\text{PO}_4)_2(\text{OH})_2 \cdot 8\text{H}_2\text{O}$) powder and the coconite-spotted ($\text{Fe}^{3+}_2\text{Al}_2(\text{UO}_2)_2(\text{PO}_4)_4(\text{SO}_4)(\text{OH})_2 \cdot 20\text{H}_2\text{O}$) rock surface were measured using an ASD spectrometer (from 0.3-2.5 μm) under ambient conditions at the SETI Institute.

Fig. 1: Visible-near infrared reflectance spectra of several phosphate minerals.

The apatite spectra include a strong feature due to the OH stretching vibration near 2.8 μm . The OH-apatite also exhibits water bands near 1.4, 1.9 and 3

μm . Many apatite spectra also have a sharp band at 3.47 μm and a doublet at 3.98 and 4.03 μm . These were also observed in spectra of fluoro-apatite (not shown). Some phosphate spectra also contain a band near 4.2 μm as in the case of amblygonite. Coconite and ferrolaueite contain some Fe and show electronic absorption bands due to Fe from 0.6 to 1 μm .

Thermal Infrared: Emissivity spectra of several phosphates (Figure 2) were measured in the emission lab at the Arizona State University Mars Space Flight Facility. The samples of apatite, metavariscite ($\text{AlPO}_4 \cdot 2\text{H}_2\text{O}$), turquoise ($\text{Cu}^{2+}(\text{Al},\text{Fe}^{3+})_6(\text{PO}_4)_4(\text{OH})_8 \cdot 4\text{H}_2\text{O}$), pyromorphite ($\text{Pb}_5(\text{PO}_4)_3\text{Cl}$), and wavellite ($\text{Al}_3(\text{PO}_4)_2(\text{OH},\text{F})_3 \cdot 5\text{H}_2\text{O}$) were either hand samples or encrustations of crystals on a hand sample. The hot-sonite ($\text{Al}_5(\text{PO}_4)(\text{SO}_4)(\text{OH})_{10} \cdot 8\text{H}_2\text{O}$) sample consisted of a few small flakes (hence, the data are noisier), and the ferrolaueite was a bulk particulate sample.

Fig. 2: Thermal emission spectra of several phosphates.

Phosphate mineral structures are based on the PO_4 tetrahedron (Figure 3). The P-O asymmetric stretching vibrations (ν_3) of the PO_4 tetrahedra produce dominant spectral features in the range of ~ 1200 to 900 cm^{-1} . The symmetric stretch, (ν_1) feature appears when the molecular symmetry of the tetrahedron is reduced and occurs at ~ 900 to 1000 cm^{-1} , occurring at longer wavelengths relative to the ν_3 modes, as occurs in sulfates. Additional features at ~ 400 - 600 cm^{-1} are attributable to the ν_4 (asymmetric bending) vibrations. Hydroxyl- and H_2O -bearing phosphates produce many additional features due to their associated vibrational modes.

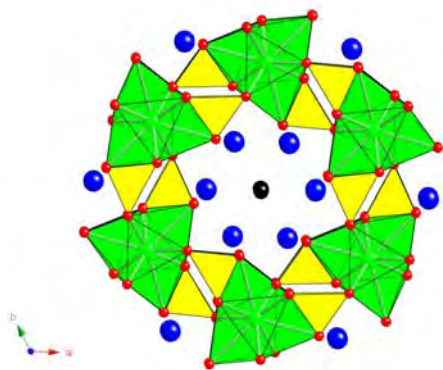


Fig. 3: The structure of fluorapatite from [1] projected onto its *ab*-plane and centered on the ring with the F atom (black sphere). The Ca1 site is represented by green translucent polyhedra and the Ca2 site by blue spheres. The yellow PO_4 tetrahedra are formed by four oxygens at their vertices (small red spheres) and link the other structural elements. In other phosphate minerals, the PO_4 tetrahedra cross-link octahedral chains and/or form many diverse geometries quite analogous to sulfate, arsenate, and silicate structures.

Mössbauer: Mössbauer spectra were collected at 293K on a WEB Research Co. model 302 spectrometer at Mount Holyoke College, using α -Fe foil for calibration.

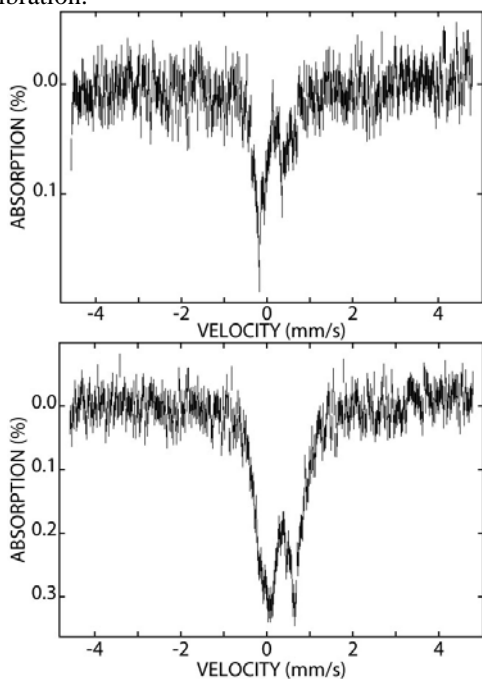


Fig. 4: Preliminary Mössbauer spectra of hotsonite (top) and coconinoite (bottom).

Very few Mössbauer spectra of phosphates exist in the present literature, especially for Fe^{3+} . Our preliminary spectra of hotsonite and coconinoite are shown in Figure 4. Mössbauer parameters for the Fe^{3+} phosphates shown in Figure 5 are based on several available published spectra along with preliminary data acquired for coconinoite, hotsonite, and ferrolaueite. It

is likely that trends in parameters will emerge as additional comprehensive data are acquired and studied. However, it is already apparent that these phosphate parameters are quite similar to those of many Fe^{3+} -sulfates (see companion abstract, this volume [2]), which is not surprising given that the mineral structures are analogous (because S and P are both small, highly charged, and occupy tetrahedral sites that form the basis for their crystal structures).

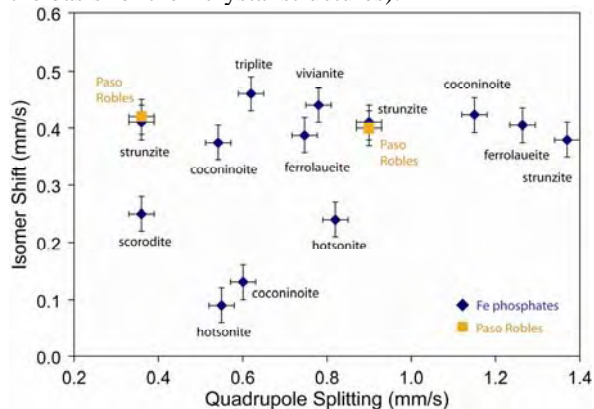


Fig. 5: Mössbauer parameters for Fe-bearing phosphate minerals collected from the literature and this study. Diamonds are Fe-phosphates and squares represent Fe^{3+} doublets fit to the sol 429A light soil at Paso Robles.

It is interesting to note that the two Fe^{3+} doublets observed in the Paso Robles light soil (see companion abstract, this volume [2], for discussion) are an excellent match to the MB parameters for strunzite ($Mn^{2+}Fe^{3+}_2(PO_4)_2(OH)_2 \cdot 6H_2O$) (for which we do not yet have VNIR or TIR spectra). Strunzite group minerals have structures in which corner-sharing Fe^{3+} octahedra form chains that are linked by PO_4 tetrahedra. Other phosphate minerals with chain structures (e.g., metavauxite ($Fe^{2+}Al_2(PO_4)_2(OH)_2 \cdot 8H_2O$)) are expected to have quite similar Mössbauer spectra to those of strunzite. Furthermore, the strunzite structure is also closely related to the sulfate minerals butlerite ($Fe^{3+}(SO_4)(OH) \cdot 2H_2O$), parabutlerite, slavikite ($NaMg_2Fe^{3+}_5(SO_4)_7(OH)_6 \cdot 33H_2O$), and fibroferrite ($Fe^{3+}(SO_4)(OH) \cdot 5H_2O$), making them possible candidates for the sulfate component of the bright Paso Robles soils.

Final Remark: We are continuing to obtain a broad range of phosphate mineral samples for our ongoing study of phosphate (and sulfate [2]) minerals using a coordinated multi-technique analysis strategy, and will continue to expand our spectral libraries.

References: [1] Hughes J M, et al. (1989) *Amer. Min.*, 74, 870-876. [2] Lane, M. D., Bishop, J. L., Dyar, M. D., Parente, M., King, P. L., and Hyde, B. C. (2007) *this volume*.