

PHOSPHATE MINERALS MEASURED IN THE VISIBLE-NEAR INFRARED AND THERMAL INFRARED: SPECTRA AND XRD ANALYSES. Melissa D. Lane¹, Stanley A. Mertzman², M. Darby Dyar³, and Janice L. Bishop⁴. ¹Planetary Science Institute, Tucson, AZ (*lane@psi.edu*), ²Franklin and Marshall College, Lancaster, PA (*stan.mertzman@fandm.edu*), ³Mount Holyoke College, South Hadley, MA (*mdyar@mtholyoke.edu*), ⁴SETI Institute/NASA-Ames Research Center, Mountain View, CA (*jbishop@seti.org*).

Introduction: The occurrence of phosphate minerals on Mars is implied both by their presence in Martian meteorites and by high levels of P in Martian soils, float rocks, and bedrock. Phosphates commonly occur together with sulfates because both mineral classes are based on tetrahedral anion groups of similar size and charge. Sulfates are widespread on Mars; hence, it is likely that phosphate minerals will continue to be identified at many locations on Mars, too. The purpose of this work is to analyze and characterize a large suite of phosphate minerals using a wide variety of techniques including electron microprobe, X-ray diffraction, extended visible/near-infrared/mid-infrared reflectance spectroscopy, thermal emission spectroscopy, and Mössbauer spectroscopy. Such a complete study of phosphates will provide spectra of well-characterized samples that will be critical for interpreting past and future data from Mars. The results of this work lay the necessary groundwork for future mission data and meteorite data interpretation that will allow for the determination of which phosphates exist on Mars and their environments of formation. Here, we report specifically on thermal emission spectroscopy data.

Samples and Methods: We have assembled a suite of >200 phosphate samples from museums and private collections. Many have been hand-picked and separated into various particle sizes. We are currently undergoing XRD analyses of these samples to confirm the phase identification and purity. XRD spectra are being acquired at Franklin and Marshall College with a PANalytical X'Pert PRO X-ray diffractometer equipped with a 15-position sample changer, a ceramic Cu X-ray tube, and the most current software available. Reflectance spectra were acquired at RELAB/Brown University from 0.3 to 50 μm by splicing visible/near-infrared bidirectional spectra (measured relative to Halon) with FTIR spectra measured under H₂O-purged conditions (relative to a rough gold surface). The spectra were spliced near 1.2-1.4 μm . Emissivity spectra were obtained at Arizona State University using a Nicolet Nexus 670 E.S.P. FT-IR interferometer modified for emission measurements. This spectrometer is equipped with a DTGS detector and a CsI beam splitter that allows the measurement of emitted radiation over the range of ~ 2000 to 220 cm^{-1} (5 to 45 μm). To reduce and maintain the amount of water and CO₂ vapor inside the spectrometer and external sample chamber and glove box, the entire system was continuously scrubbed using a Parker Balston compressed air and gas in-line filter.

Visible-Near Infrared: Spectra are shown in Figure 1 from 0.3-3.2 μm of several finely particulate phosphate minerals. All of the phosphate spectra shown here exhibit Fe absorptions from 0.6-1.2 μm . The baricite and chalcociderite spectra both include water bands near 2 μm . Ferroalluaudite ($\text{NaCaFe}^{2+}(\text{Fe}^{2+}, \text{Mn}^{2+}, \text{Fe}^{3+})_2(\text{PO}_4)_3$) has a water band at 1.93 μm and another absorption at 2.52 μm . The spectra of childrenite ($\text{Fe}^{2+}\text{Al}(\text{PO}_4)(\text{OH})_2 \cdot \text{H}_2\text{O}$), kulanite ($\text{Ba}(\text{Fe}^{2+}, \text{Mn}, \text{Mg})_2\text{Al}_2(\text{PO}_4)_3(\text{OH})_3$), chalcociderite ($\text{Cu}^{2+}(\text{Fe}^{3+}, \text{Al})_6(\text{PO}_4)_4(\text{OH})_8 \cdot 4\text{H}_2\text{O}$), and gormanite ($\text{Fe}^{2+}_3\text{Al}_4(\text{PO}_4)_4(\text{OH})_6 \cdot 2\text{H}_2\text{O}$)/souzalite ($\text{Mg}, \text{Fe}^{2+}_3(\text{Al}, \text{Fe}^{3+})_4(\text{PO}_4)_4(\text{OH})_6 \cdot 2\text{H}_2\text{O}$) all include multiple sharp absorptions in the range 2.1-2.5 μm that are characteristic of overtones and combinations of OH and PO₄ vibrations, similar to the OH/SO₄ features in the spectra of jarosite and alunite [1]. Sharp OH stretching bands are observed near 2.7-2.9 μm for childrenite, kulanite, chalcociderite and gormanite, and broad water features are observed from 2.8-3.2 μm for ferroalluaudite, chalcociderite, and baricite. We are still in the process of performing XRD analyses on these and many other samples to verify their compositions.

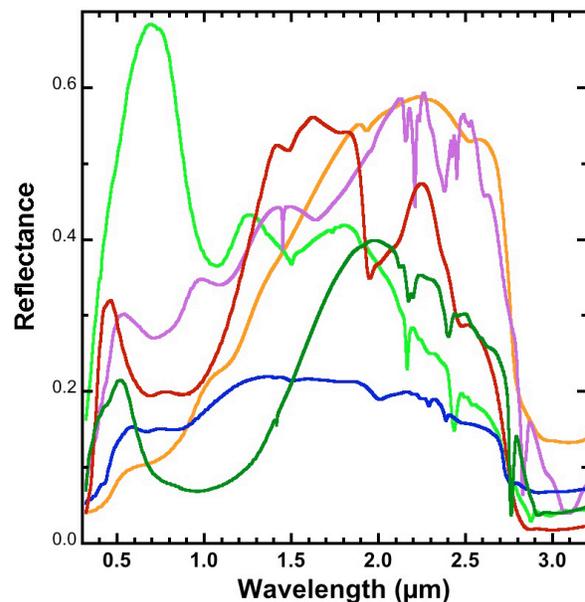


Figure 1. Visible-near infrared reflectance spectra of phosphates: childrenite, P29 (light green); kulanite, P32 (purple); baricite, MDD11 (red); ferroalluaudite, P14 (orange); chalcociderite, P39 (blue); gormanite/souzalite, MDD13 (dark green).

Thermal Emission (Vibrational) Spectroscopy:

Phosphate mineral structures are based on the PO_4 tetrahedron (Figure 2). Spectral features in the phosphates predominantly arise from oscillations of the P-O bonds within the phosphate anion [3]. Emission measurements of some phosphate samples (Figure 3) show that the P-O asymmetric stretching vibrations (ν_3) of the PO_4 tetrahedra produce dominant spectral features

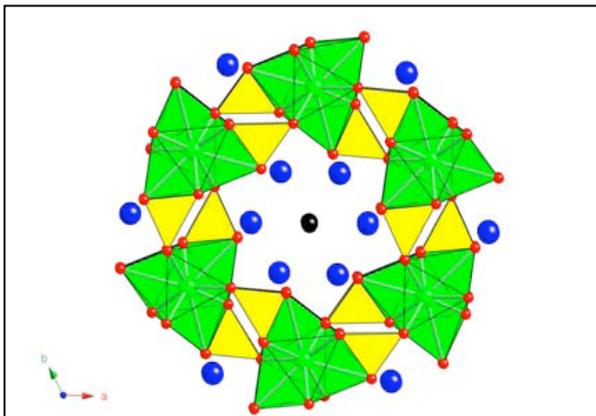


Figure 2. The structure of fluorapatite [2] projected onto its ab -plane and centered on the ring with the F atom (black sphere). The Ca1 site is represented by green translucent polyhedra and the Ca2 site by blue spheres. The yellow PO_4 tetrahedra are formed by four oxygens at their vertices (small 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 analogous to sulfate, arsenate, and silicate structures.

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. Phosphate mineral structures are based on various combinations of the PO_4 tetrahedron.

Final Comments: These spectra are just a few of the many VNIR and TIR spectra we have. These phosphate samples, whose spectra are presented here, and others to follow currently are being analyzed by XRD and their identifications will be known by LPSC. Many phosphates in our collection are also being studied using Mössbauer spectroscopy [4].

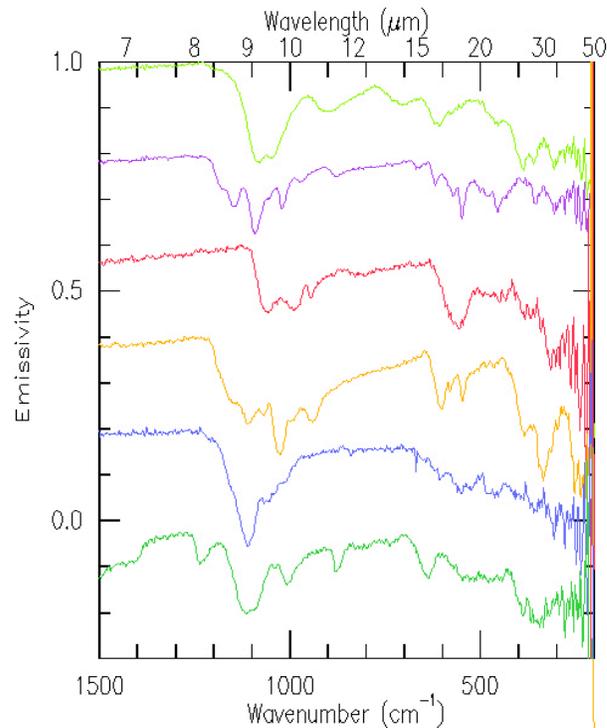


Figure 3. Emissivity spectra of phosphates: childrenite, P29 (light green); kulanite, P32 (purple); baricite, MDD11 (red); ferroalluaudite, P14 (orange); chalcociderite, P39 (blue); gormanite/souzalite, MDD13 (dark green). The feature at $\sim 878\text{ cm}^{-1}$ in the MDD13 sample is due to contaminant siderite.

References:

- [1] Bishop, J. L. and E. Murad (2005) *Am. Mineral.*, 90, 1100-1107. [2] Hughes, J. M. et al. (1989) *Am. Mineral.*, 74, 870-876. [3] Ross, S. D. (1974) in *The Infrared Spectra of Minerals*, 423-444. [4] Jawin, E. et al. (2011) this volume.