

**INTER-RELATIONSHIPS AMONG MÖSSBAUER PARAMETERS OF PHOSPHATE MINERALS AND CRYSTAL STRUCTURES.** E. R. Jawin<sup>1</sup>, M. D. Dyar<sup>1</sup>, M. D. Lane<sup>2</sup>, J. L. Bishop<sup>3</sup>, and G. J. Marchand<sup>1</sup>. <sup>1</sup>Dept. of Astronomy, Mount Holyoke College, South Hadley, MA 01075, mdyar@mtholyoke.edu., <sup>2</sup>Planetary Science Institute Tucson, AZ 85719, <sup>3</sup>SETI Institute/NASA-Ames Research Center, Mountain View, CA 94043.

**Introduction:** Martian meteorites are known to contain phosphate minerals, and high levels of P have been observed 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. Spectroscopic characteristics of phosphate minerals deserve careful study in order to lay the necessary groundwork for interpretation of future mission and meteorite data that will enable determination of which phosphates exist on Mars and their environments of formation. Here, we report specifically on Mössbauer spectroscopy data of phosphates.

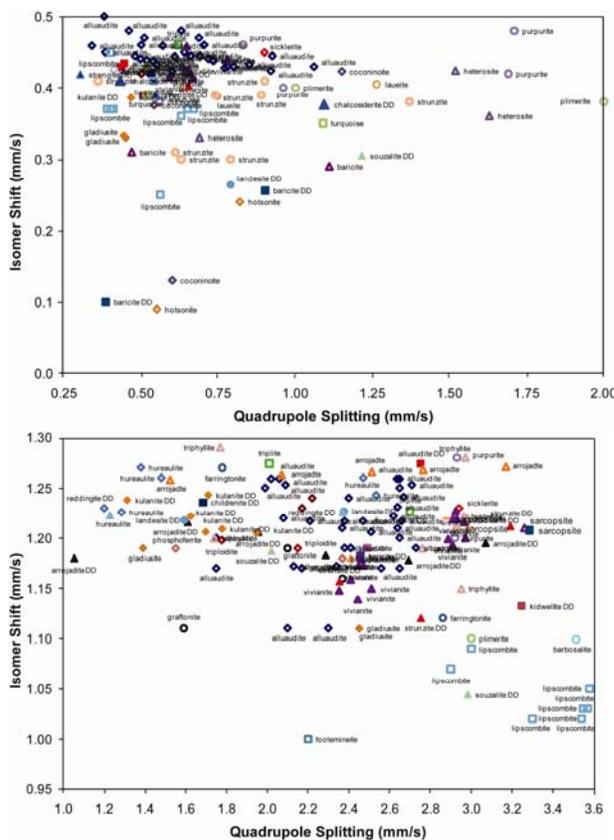
**Samples and Methods:** We have assembled a suite of >200 phosphate samples from museums and private collections. A subset of these was prepared for Mössbauer spectroscopy by mixing with sucrose. Spectra were acquired with a WEB Research Co. constant acceleration MB spectrometer equipped with a Janis Research Co. model 850 closed-cycle He refrigerator at Mount Holyoke. A  $\leq 100$ -30 mCi <sup>57</sup>Co in Pd source and 24-hour run times were used, and the data are referenced to the midpoint of an  $\alpha$ -Fe foil. Data reported here are 295K spectra only, though acquisition of data at temperatures down to 4K is in progress.

**Table 1. Phosphate Structure Groups**

T $\phi_4$ clusters*
T $\phi_4$ chains*
T $\phi_4$ sheets*
T $\phi_4$ frameworks*
Unconnected T $\phi_4$ *
Infinite tetrahedral and octahedral chains
Infinite tetrahedral and octahedral sheets
Infinite tetrahedral and octahedral frameworks
Large-cation phosphates
Apatite-related structures
* $\phi$ is O <sup>2-</sup> or OH <sup>-</sup>

**Context:** Interpretation of these Mössbauer data requires an understanding of the various structure types assumed by phosphate minerals. Phosphate mineral structures are based on various combinations of the P $\phi_4$  tetrahedron, in which  $\phi$  is either an O<sup>2-</sup> anion or an OH<sup>-</sup> (Table 1) and described in detail in [1,2]. It is expected that spectroscopic characteristics of minerals within each group should be similar, in a manner analogous to silicates. For example, just as olivine (iso-

lated SiO<sub>4</sub> tetrahedra), pyroxene (SiO<sub>4</sub> tetrahedra in single chains), amphiboles (SiO<sub>4</sub> in double chains), and phyllosilicates (SiO<sub>4</sub> in sheets) have diagnostic spectral features within those mineral groups, so too should phosphate minerals within groups in Table 1 have spectral features that are alike. Such similarities would be most pronounced for spectral techniques that measure interatomic bond distances and angles and less pronounced for those that probe the local environments around transition metals (e.g., VNIR and Mössbauer).

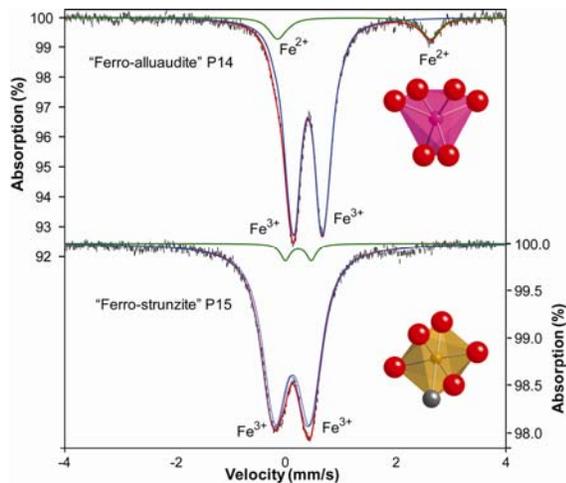


**Figure 1:** Mössbauer parameters for Fe<sup>3+</sup> (top) and Fe<sup>2+</sup> (bottom) doublets in Fe-bearing phosphate minerals. Solid symbols are from this study; hollow symbols are from the literature.

Where possible, we have studied at least one sample from each of the groups listed in Table 1, with several species represented in the two largest groups with the most diversity: minerals based on infinite sheets of tetrahedra and octahedra, and those based on infinite frameworks of tetrahedra and octahedra. A large number of Mössbauer spectra also exist in the literature,

though nearly all studies focused on a single species without relating it to others in its structure group.

**Results:** Mössbauer parameters for 295K spectra are shown graphically as solid symbols in Figure 1, along with other parameters from the literature. As with silicates, phosphate Mössbauer spectra show a broad range of doublets representing varying distortion in the coordination polyhedral surrounding the  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  cations. Many phosphate minerals have multiple sites for  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$ , and thus have as many as five superimposed Mössbauer doublets (e.g., ferro-lauzeite).

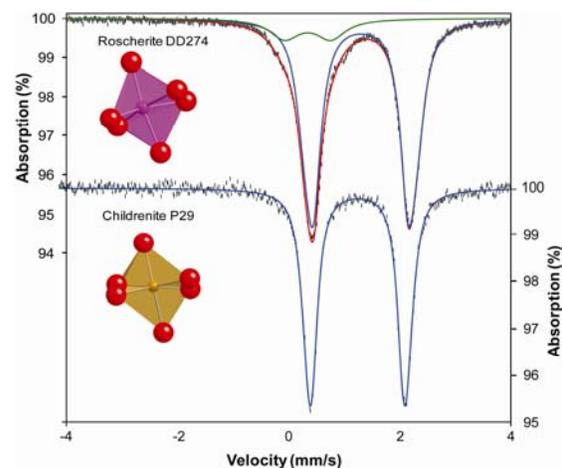


**Figure 2:** 295K Mössbauer spectra of “ferro-alluaudite” from the Pleasant Valley pegmatite in Custer Co., SD and “ferrostrunzite” from Blaton Hainaut, Belgium. The former is 90%  $\text{Fe}^{3+}$  and 10%  $\text{Fe}^{2+}$ , and the latter is completely  $\text{Fe}^{3+}$  in two different sites. Note that because the structures are different, the spectral peak positions are also different.

Very few of our samples were completely reduced or oxidized; most contained both  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  as is common for natural samples. We suspect that ferro-phosphate minerals, in particular, have often been unintentionally mis-represented due to lack of chemical analyses (Figure 2).

Mössbauer parameters of phosphates in which the symmetry of the Fe coordination polyhedra is similar will be consistent, and this trend is observed across phosphate groups. Consider the case of roscherite and zanzaziite, which both have structures with rings of four alternating  $\text{BeO}_4$  and  $\text{PO}_4$  tetrahedra arrayed in chains parallel to [101] ( $T\phi_4$  chains). Although their IR spectra might be similar because stretching and bending modes in the chains would be the same, the resultant local polyhedra are very different, as are their Mössbauer spectra. In contrast, the  $\text{Fe}^{2+}$  doublet in childrenite (infinite tetrahedral and octahedral chains), which contains Fe in octahedra with edge-sharing chains, has a geometry similar to that of the Mn site in roscherite; their Mössbauer parameters are identical.

**Discussion:** An unexpected result of this study is the wide range of  $\text{Fe}^{3+}/\text{Fe}^{2+}$  ratios observed in many of the phosphates studied. It is apparent that naturally-occurring phosphate minerals rarely have the pure  $\text{Fe}^{2+}$  or  $\text{Fe}^{3+}$  composition predicted by end-member stoichiometry. For example, we have yet to find an example of true ferro-strunzite, and we measured very few minerals that were completely reduced. These trends are also seen in literature data on naturally-occurring samples. It appears that the Fe redox state in each sample is responding to the oxidation state of the mineral assemblage in which it forms (as is the case for silicates), and that assumptions regarding the presence of  $\text{Fe}^{3+}$  or  $\text{Fe}^{2+}$  cannot be safely made without corroboration from Mössbauer spectroscopy or wet chemistry.



**Figure 3:** Comparison of 295K Mössbauer spectra of roscherite and childrenite, which have similar Fe coordination polyhedra, and thus similar Mössbauer doublets and parameters.

Moreover, it was noted from the literature data that in many cases,  $\text{Fe}^{2+}$ -Mg solid solutions, along with other cation substitutions, are common. It is therefore unlikely that phosphate samples in other types of spectral databases (e.g., NIR and mid-IR reflectance), except where samples have been chemically characterized, are true end-members. Deviations from end-member stoichiometry of phosphate minerals may complicate use of spectral and thermodynamic data to infer formation conditions on planetary surfaces.

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**References:** [1] Huminicki D. M. C. and Hawthorne F. C. (2002) *Revs. Mineral. Geochem.*, 48, 123-253. [2] Hughes J. M. and Rakovan J. (2002) *Revs. Mineral. Geochem.*, 48, 1-12. [3] Hughes J. M. et al. (1989) *Amer. Mineral.*, 75, 295-304.