WHAT LURKS IN THE MARTIAN ROCKS AND SOIL? INVESTIGATIONS OF SULFATES, PHOSPHATES, AND PERCHLORATES

Mössbauer parameters of iron in phosphate minerals: Implications for interpretation of martian data‡

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ABSTRACT

Phosphate minerals, while relatively rare, show a broad range of crystal structure types with linkages among PO4 tetrahedra mimicking the hierarchy of polymerization of SiO4 tetrahedra seen in silicate minerals. To augment previous Mössbauer studies of individual phosphate species and groups of species, this paper presents new Mössbauer data on 63 different phosphate samples, and integrates them with data on more than 37 phosphate species in 62 other studies from the literature. Variations in Mössbauer parameters of different sites in each mineral are then related to both the local polyhedral environment around the Fe cations and the overall structural characteristics of each species. The entire aggregated Mössbauer data set on phosphate minerals is juxtaposed against parameters obtained for spectra from the MIMOS spectrometers on Mars. This comparison demonstrates that signatures from many different phosphate or sulfate mineral species could also be contributing to Mars Mössbauer spectra. Results underscore the conclusion that unique mineral identifications are generally not possible from Mössbauer data alone, particularly for paramagnetic phases, although combining Mössbauer results with other data sets enables a greater level of confidence in constraining mineralogy. This study provides a wealth of new data on Fe-bearing phosphate minerals to bolster future analyses of Mössbauer spectra acquired on Mars.

Keywords: Mossbauer, Mars, phosphates, alluaudite, arrojadite, vivianite, triphylite

INTRODUCTION

Phosphate minerals have tremendous economic importance owing to their roles as components of fertilizer and animal feed supplements, lending significance to the many minerals in this class. Phosphorus (P) is also used in food products as a preservative, stabilizer, and thickener, and phosphoric acid is used in many carbonated drinks. Li phosphates are rapidly emerging as excellent candidates for producing batteries for green energy storage and transportation uses (e.g., Takahashi et al. 2002; Yang et al. 2003; Deniard et al. 2004; Kang and Ceder 2009), so this group of minerals has been increasingly studied in recent years.

From a more theoretical perspective, phosphate minerals are significant for their broad array of crystal structures, which are grouped by composition and designated on the basis of the cation that occupies the tetrahedral sites. Thus by definition (Huminicki and Hawthorne 2002), normal phosphates contain P in 4-coordination with O (PO4), hydrated normal phosphates have PO4 as well as H2O, anhydrous phosphates contain PO4 and OH, while hydrated phosphates contain PO4, OH, and H2O.

Finally, phosphate minerals are key indicators of rock paragenesis because their variable oxidation and hydration states make them valuable markers of oxidation/reduction and pH in geological environments. The latter characteristic is particularly useful to planetary explorations.

Phosphates commonly occur together with sulfates because both mineral classes are based on tetrahedral anion groups of similar size and high charge. There is ample evidence for the presence of phosphate minerals on Mars, based on their presence in martian meteorites, their identification in remotely sensed data, and on the high levels of P seen in chemical analyses of martian soils, float rocks, and bedrock. Knowledge of the specific minerals present will provide critical information about the diverse environments in which they formed (e.g., acidic/alkaline, hydrated/dehydrated, degree of oxidation, etc.). Sulfates are widespread on Mars, hence, it is likely that phosphate minerals will continue to be identified at many locations on Mars as well.

The authors of this paper are united in a broad research effort aimed at analyzing and characterizing a broad range of the 549 known phosphate mineral species, using a wide variety of techniques including electron microprobe, X-ray diffraction, extended-visible/near infrared/midinfrared reflectance spectroscopy, thermal emission spectroscopy, and Mössbauer spectroscopy. Such a complete study of phosphates will provide well-characterized sample spectra that will be critical for...