American Mineralogist, Volume 98, pages 1943–1965, 2013

What Lurks in the Martian Rocks and Soil? Investigations of Sulfates, Phosphates, and Perchlorates

Mössbauer parameters of iron in sulfate minerals†

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Abstract

Although Fe-sulfate minerals occur only rarely on Earth as alteration products of sulfidic basalts or in hydrothermal systems, multiple lines of evidence point to the importance of Fe- (and other) sulfate minerals on the surface of Mars. One such martian data set comes from the MIMOS II Mössbauer spectrometers on the Mars Exploration Rovers, which acquired hundreds of spectra from the martian surface at two locations. Interpretation of those spectra has been limited by the lack of a comprehensive set of laboratory analog spectra of the broad range of naturally occurring sulfate minerals. Accordingly, this study reports Mössbauer data of 98 samples representing 47 different sulfate mineral species, all containing six- or higher-coordinated Fe. The resultant Mössbauer parameters are related to the local polyhedral environment around the Fe cation in each mineral to explain variations in spectral characteristics. Results show that the size of the coordination polyhedron is the best predictor of quadrupole splitting, which increases with both octahedral volume and mean bond length. Species within groups of structurally similar minerals are shown to have comparable spectral peaks that generally fall within small ranges. Although coordination polyhedron geometry is not necessarily unique to any particular mineral species or group, Mössbauer data can be used to help constrain mineral identifications from martian spectra. The number of mineral species is large, but the range of crystal structures and hyperfine parameters may be small, so that in many cases, individual minerals cannot be uniquely fingerprinted. Examples would include quenstedtite, coquimbite, kornelite, and lausenite, which have indistinguishable spectra, as do apjohnite, bilinite, dietrichite, and römerite. Overlap of Mössbauer parameters is a particular complication for identification of Fe^{3+}-rich phases because the range of Mössbauer parameters for Fe^{3+} in any coordination number is so small. Previous analyses of martian Mössbauer spectra reported the presence of jarosite (Klingelhöfer et al. 2004; Morris et al. 2004) and an unspecific ferric sulfate (Morris et al. 2008). New data presented here indicate that botryogen, metasideronatrite, and slavikite exhibit Mössbauer spectra similar to those attributed to jarosite at Meridiani Planum. Fibroferrite and rhomboclase have parameters similar to those observed at Arad Samra, and copiapite and parabutlerite could be present at Tyrone Mount Darwin and Berkner Island. 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 new expansive data set for future interpretation of iron sulfates on Mars.

Keywords: Mössbauer, sulfate, jarosite, Mars