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

Synthesis and characterization of the Mars-relevant phosphate minerals Fe- and Mg-whitlockite and merrillite and a possible mechanism that maintains charge balance during whitlockite to merrillite transformation‡

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Abstract

Merrillite [$Ca_9NaMg(PO_4)_7$] occurs as a dominant primary Ca-phosphate mineral in martian meteorites and therefore presumably also on Mars. The mineral is an important phase in exploring differences in geologic processes between Earth and Mars, and also has astrobiological implications due to its potential role as a significant source of the bio-essential nutrient phosphate. Merrillite does not occur terrestrially as a discrete mineral phase, making it difficult to obtain for Mars-relevant studies. It can, however, be synthesized from a similar terrestrial mineral, whitlockite (natural or synthetic), through dehydrogenation. Here we present methods for synthesizing relatively large quantities (0.5 g or greater per batch) of coarse crystalline (75 μm+) Mg-whitlockite, Fe-whitlockite, mixed Fe/Mg-whitlockites, and from these synthesized minerals produce Mg-merrillite, ferrous and ferric Fe-merrillite, and ferrous and ferric mixed Fe/Mg-merrillite. Chemistry and atomic structures of synthesized Fe- and mixed Fe/Mg-whitlockite and ferrous and ferric Fe- and mixed Fe/Mg- merrillite resulting from single-crystal X-ray diffraction, infrared spectroscopy, and electron microprobe analyses are presented. We also present a mechanism for maintaining charge balance during the formation of merrillite from whitlockite. Our results shed light on these mineral structures for future martian studies, and provide methods for creating coarse crystalline merrillite for use in Mars-relevant thermodynamic, kinetic, soil/dust simulant, crystallographic, astrobiological, and other studies.

Keywords: Whitlockite, merrillite, Mg, Fe, structures, synthesis, dehydrogenation, phosphate, Mars, astrobiology