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 \([\text{Ca}_9\text{NaMg(PO}_4\text{)}_2]\) 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 \(\mu\text{m}\)+) 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

Introduction

Merrillite is an anhydrous calcium phosphate mineral that occurs in lunar samples and meteorites, including martian meteorites (Jolliff et al. 1993; McSween et al. 1996; Xie et al. 2002; Terada et al. 2003). The IMA formula for merrillite is \(\text{Ca}_9\text{NaMg(PO}_4\text{)}_2\), though merrillite can also be iron-bearing (Jolliff et al. 2006). Synthetic merrillite also lacks Na\(^+\) and charge balance is maintained by additional Ca\(^{2+}\) [i.e., \(\text{Ca}_9\text{Mg(PO}_4\text{)}_2\)]. Merrillite is of particular interest to martian studies because it is the dominant primary phosphate mineral in martian meteorites (McSween et al. 1996; McSween and Treiman 1998), and thus presumably also on Mars. This is in contrast to Earth where fluorapatite \([\text{Ca}_9\text{(PO}_4\text{)}_3\text{F}]\) is the dominant terrestrial primary phosphate mineral and the nearest analog to merrillite, the mineral whitlockite \([\text{Ca}_9\text{Mg(PO}_4\text{OH})(PO}_4\text{)}_3\]), occurs as a component of teeth and bones in vertebrates, but outside of biological systems is a rare alteration product of phosphates pegmatites. Merrillite is also the major carrier of Rare Earth Elements (REE) in martian meteorites (McSween et al. 1996; McSween and Treiman 1998; Shearer et al. 2011a) and likely one of the major sources of the phosphorus observed in phosphorus rich martian soils and dust (Goetz et al. 2005; Greenwood and Blake 2006; Brückner et al. 2008). Phosphate minerals such as merrillite and apatite are thought to react in late-stage martian magmas (McCubbin and Nekvasil 2008; Filiberto and Treiman 2009; Gross et al. 2013b), and their presence and intergrowth relationships with each other within martian rocks (or meteorites) can be useful indicators of crystallization and melt evolution, including the evolution of both water and halogen budgets over time (Patiño-Douce and Roden 2006; Patiño-Douce et al. 2011; Gross et al. 2013a, 2013b). Such use of merrillite/apatite intergrowth relationships may also be applicable to other differentiated bodies outside of Mars (Shearer et al. 2011b). Phosphate minerals have also been shown to be altered in acid vapor environments, potentially recording important characteristics of the reacting environment (Lane et al. 2008; Hausrath et al. 2013; Haustrath and Tschauner 2013). In addition, phosphate is a required component in fundamental biologic reactions, and phosphorus, either as phosphate or a