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LETTER

Chemical composition and crystal structure of merrillite from the Suizhou meteorite

XIANGE XIE1,4, HEXIONG YANG2,*, XIANGPING GU3 AND ROBERT T. DOWNS2

1Key Laboratory of Mineralogy and Metallogeny, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, 511 Kehua Street, Guangzhou, 510640, China
2Department of Geosciences, University of Arizona, 1040 East 4th Street, Tucson, Arizona 85721-0077, U.S.A.
3School of Geosciences and Info-Physics, Central South University, Changsha, Hunan, 410083, China
4Guangdong Key Laboratory of Mineral Physics and Materials, Guangzhou, 510640 China

ABSTRACT

Merrillite, ideally Ca9NaMg(PO4)7, is an important accessory phosphate mineral in many different groups of meteorites, including martian meteorites, and a major carrier of rare earth elements (REE) in lunar rocks. By means of electron microprobe analysis, single-crystal X-ray diffraction, and Raman spectroscopy, we present the first structure determination of merrillite with a nearly ideal chemical composition, Ca9.00Na0.98(Mg0.95Fe0.06)0.02(PO4)7, from the Suizhou meteorite, a shock-metamorphosed L6-chondrite. Suizhou merrillite is trigonal with space group R3c and unit-cell parameters a = 10.3444(3), c = 37.0182(11) Å, and V = 3430.5(2) Å3. Its crystal structure, refined to R1 = 0.032, is characterized by a structural unit consisting of a [(Ca3Mg)3(PO4)6]6+ complex anion that forms a “bracelet-and-pinwheel” arrangement. Such structural units are linked by interstitial complexes with a formula of [Ca3Na(PO4)6]6+, which differs from that of [Ca9(PO3)[OH]]16+, [Ca9(PO3F)]16+, [Ca9(Ca0.5REE0.5)(PO4)]16+, or [Ca9(xREE)2(Na1–x,REE)(PO4)]16+ in terrestrial whitlockite, terrestrial/extraterrestrial bobdownsite, meteoritic Ca-rich merrillite, or lunar REE-rich merrillite, respectively. The Suizhou merrillite is found to transform to tuite at high pressures, pointing to the likelihood of finding REE-bearing tuite on the Moon as a result of shock events on REE-merrillite.

Keywords: Merrillite, whitlockite, Suizhou meteorite, crystal structure, Raman spectroscopy

INTRODUCTION

Merrillite, ideally Ca9NaMg(PO4)7, is a primary accessory mineral in many different groups of meteorites, including martian meteorites, and a major storage of rare earth elements (REE) in lunar rocks (e.g., Jolliff et al. 1993; McSween et al. 1996; Xie et al. 2002; Shearer et al. 2015; Adcock et al. 2014). It is considered to be an important phase in exploring the differences in petrogenesis, mantle evolution, and other geologic processes among Earth, Mars, and other planetary bodies (McSween et al. 1996; Shearer et al. 2015 and references therein). Merrillite was originally proposed by Wherry (1917) in honor of George P. Merrill, who first described this mineral from four meteorites (Merrill 1915). However, owing to the chemical and structural similarities between merrillite and terrestrial whitlockite, ideally Ca3Mg(PO4)6(PO3OH), there has been a considerable overlap in the use of these two mineral names in the literature. Fuchs (1962) noted the strong resemblances in powder X-ray diffraction data among merrillite, whitlockite, and synthetic 3Ca2(PO4)3, leading him to argue that these three phases were actually the same and the term “merrillite” should be abandoned in favor of “whitlockite.” Subsequent investigations, nevertheless, demonstrated that the structures of merrillite and synthetic 3Ca2(PO4)3 are similar, but not identical to that of terrestrial whitlockite, especially in terms of their lack of an essential hydrogen component that is found in whitlockite (e.g., Calvo and Gopal 1975; Prewitt and Rothbard 1975; Dowty 1977). Early work on lunar samples also suggested that “lunar whitlockite” is actually more similar in structure to meteoritic merrillite than to terrestrial whitlockite (Fuchs 1971). Thus, Dowty (1977) recommended “merrillite” for the H-free form found in meteorites and “whitlockite” for the terrestrial form. However, because of the lack of definitive structural data for merrillite due to its small crystal size in meteorites, the term “whitlockite” continues to occasionally be used synonymously or interchangeably when describing extraterrestrial merrillite (e.g., Jolliff et al. 1993; McSween et al. 1996; Xie et al. 2002, 2013).

Another confusion about merrillite arises from its chemical variations. In addition to the ideal chemical formula approved by the Commission on New Minerals, Nomenclature and Classification of the International Mineralogical Association (IMA), there are also two other ideal end-members commonly found in meteorites and lunar rocks: a Na-free but Ca-excess form, Ca3(REE)(PO4)2(H2O); and a Na-free but REE-bearing form, (Ca3REE)(PO4)2(H2O) (e.g., Dowty 1977; Jolliff et al. 1993, 2006; Shearer et al. 2015). These two phases are isostructural with merrillite, but have no official names approved by IMA. To facilitate the following discussion, we will temporarily follow the proposal by Jolliff et al. (2006), whenever it is necessary, by calling the three forms Ca9NaMg(PO4)7, Ca3(REE)(PO4)2(H2O), and (Ca3REE)(PO4)2(H2O) as Na-, Ca-, and REE-merrillites, respectively.

Although there have been several structure determinations on