Chemical composition and crystal structure of merrillite from the Suizhou meteorite

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ABSTRACT

Merrillite, ideally Ca9NaMg(PO4)3, 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, Ca9.00Na0.00(Mg2.00Fe0.06)2.01(PO4)3, 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 [(Mg,Fe)(PO4)34+] complex anion that forms a “bracelet-and-pinwheel” arrangement. Such structural units are linked by interstitial complexes with a formula of [Ca9Na(PO4)3]16+, which differs from that of [Ca9(PO4)(OH)]16+, [Ca9(PO4,F)]16+, [Ca9(Ca9,REE)(PO4)]16+, or [(Ca9,REE)6(Na9,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)3, 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 Ca9Mg(PO4)3(PO4OH), 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 β-Ca9(PO4)2, 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 β-Ca9(PO4)2 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, Ca9(Ca9,REE)(Mg,Fe2+)4(PO4)3, and a Na-free but REE-bearing form, (Ca9,REE)4(Mg,Fe2+)4(PO4)3 (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)3, Ca9(Ca9,REE)(Mg,Fe2+)4(PO4)3, and (Ca9,REE)4(Mg,Fe2+)4(PO4)3 as Na-, Ca-, and REE-merrillites, respectively.

Although there have been several structure determinations on
synthetic or heat-treated merrillites (e.g., Malozov et al. 1997; Hughes et al. 2008; Adcock et al. 2014), the first high-quality single-crystal X-ray structural refinement from a natural sample was only conducted recently by Hughes et al. (2006) using a REE-rich but Na-poor lunar merrillite with the chemistry \( \text{Ca}_7 \text{REE}_{6.90} \text{Na}_{2.11} \text{Mg}_{9.06} \text{Fe}^{2+}_{0.78} \text{Mn}_{0.03} \text{O}_{32} \text{Cl}_{1.06} \text{P}_1 \text{Na}_{2} \text{O}_4 \). Based on this study, Hughes et al. (2006) illustrated the detailed structural differences among lunar merrillite, merrillite reported from meteorites, and terrestrial whitlockite. Jolliff et al. (2006) further suggested that significant structural differences between terrestrial whitlockite and lunar (and meteoritic) varieties warrant the use of “merrillite” for the H-free extraterrestrial material, and the systematic enrichment of REE in lunar merrillite warrants the use of “REE-merrillite.” Yet, there has been no crystal structure report on any, natural or synthetic, Na-rich merrillite to date. This paper presents the first single-crystal X-ray diffraction and Raman spectroscopic study on a natural merrillite with nearly ideal chemistry, \( \text{Ca}_9 \text{Na}_{0.09} \text{Mg}_{0.06} \text{Fe}^{2+}_{0.78} \text{Cl}_{1.01} (\text{P}_1 \text{Na}_{2} \text{O}_4) \), from the Suizhou meteorite.

The Suizhou meteorite is a shock-metamorphosed L6-chondrite, (Xie et al. 2011). The meteorite contains shock-produced melt veins ranging from 20 to 200 μm in width with a bulk chondritic composition. Major rock-forming minerals in the host meteorite are olivine, pyroxene, plagioclase, kamacite, taenite, and troilite. Accessory minerals include chromite, ilmenite, merrillite, and apatite. Both olivine and pyroxene display moderate mosaicism texture, and most of the plagioclase grains were shock-melted and quenched to maskelynite. The shock veins contain abundant high-pressure minerals (e.g., ringwoodite, majorite, akimotoite, vitrified perovskite, lingunite, tuite, xieite, CF-phase, magnesiowüstite, majorite-pyrope garnet solid solution), for which the shock-produced pressure and temperature of 24 GPa and 1900~2000 °C is inferred (Xie et al. 2011).

**EXPERIMENTAL METHODS**

Merrillite in the Suizhou meteorite makes up about 2 vol% of the chondritic portions (Xie et al. 2002). It occurs as single grains of irregular shape up to 0.5 mm in length (Fig. 1). The grains of merrillite are heavily fractured by shock. The merrillite sample used in this study was selected from a polished section of the shock vein-bearing fragment, which was deposited in the RRUFF Project with the deposition number R150063 (http://rruff.info/R150063). Its chemical composition measured from the chemical composition analysis. Final coordinates and displacement parameters of atoms in merrillite are listed in Table 2, and selected bond distances in Table 3. (CIF available.)

**RESULTS AND DISCUSSION**

**Crystal structure**

The crystal structure of merrillite from the Suizhou meteorite is directly comparable with that reported by Hughes et al. (2006) for the REE-rich lunar merrillite. It is characterized by a structural unit consisting of a \((\text{Mg,Fe})\text{(PO}_4)_3\) complex anion that forms a “bracelet-and-pinwheel” arrangement (Moore 1973) (Fig. 2). The central octahedral cation and the six-coordinating phosphate tetrahedra form a pinwheel, which is characteristic of whitlockite-type compounds. Such structural units are linked by interstitial complexes with a formula of \(\text{Na} \text{PO}_4\). The major structural difference between the Suizhou merrillite and the lunar REE-rich merrillite is that, due to the coupled substitution of \((\text{REE}^{3+}+\text{Na}^+\) ↔ \((\text{Ca}^{2+}+\text{Na}^+)\), the Na site in lunar REE-merrillite is only about 20% occupied, resulting in an average Na-O bond distance (2.71 Å)

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**TABLE 1. Comparison of crystallographic data for various merrillite**

<table>
<thead>
<tr>
<th>Sample source</th>
<th>Merrillite</th>
<th>REE-Merrillite</th>
<th>Ca-Merrillite</th>
</tr>
</thead>
<tbody>
<tr>
<td>Suizhou meteorite</td>
<td>(\text{Ca}<em>9 \text{Na}</em>{0.09} \text{Mg}<em>{0.06} \text{Fe}^{2+}</em>{0.78} \text{P}<em>1 \text{Na}</em>{2} \text{O}_4)</td>
<td>(\text{Ca}_{9} \text{REE}^{3+} \text{Fe}^{2+} \text{P}<em>1 \text{Na}</em>{2} \text{O}_4)</td>
<td>(\text{Ca}_{9} \text{REE}^{3+} \text{Fe}^{2+} \text{P}<em>1 \text{Na}</em>{2} \text{O}_4)</td>
</tr>
<tr>
<td>Apollo 14 lunar rocks</td>
<td>(\text{Ca}_{9} \text{REE}^{3+} \text{Fe}^{2+} \text{P}<em>1 \text{Na}</em>{2} \text{O}_4)</td>
<td>(\text{Ca}_{9} \text{REE}^{3+} \text{Fe}^{2+} \text{P}<em>1 \text{Na}</em>{2} \text{O}_4)</td>
<td>(\text{Ca}_{9} \text{REE}^{3+} \text{Fe}^{2+} \text{P}<em>1 \text{Na}</em>{2} \text{O}_4)</td>
</tr>
<tr>
<td>Angra dos Reis achondrite</td>
<td>(\text{Ca}_{9} \text{REE}^{3+} \text{Fe}^{2+} \text{P}<em>1 \text{Na}</em>{2} \text{O}_4)</td>
<td>(\text{Ca}_{9} \text{REE}^{3+} \text{Fe}^{2+} \text{P}<em>1 \text{Na}</em>{2} \text{O}_4)</td>
<td>(\text{Ca}_{9} \text{REE}^{3+} \text{Fe}^{2+} \text{P}<em>1 \text{Na}</em>{2} \text{O}_4)</td>
</tr>
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**Figure 1.** Backscattered electron image showing a large merrillite (Mer) grain in the Suizhou meteorite. Ol = olivine, Pyx = Low Ca-pyroxene, Mas = maskelynite, M = FeNi metal.
slightly longer than that (2.625 Å) in the Suizhou merrillite. According to Hughes et al. (2006, 2008) and Jolliff et al. (2006), the Na site in the interstitial complex unit plays a critical role in maintaining the charge balance in various merrillites. In Ca-merrillite (Calvo and Gopal 1975; Prewitt and Rothbard 1975; Dowty 1977), the Na-O3 bond is slightly longer than that (2.625 Å) in the Suizhou merrillite. Acid-base or synthetic, which exhibits an asymmetric single peak or a very poorly resolved doublet (Jolliff et al. 2006). The Raman spectrum of the Suizhou merrillite contains a well-resolved strong doublet at 960 and 976 cm⁻¹, which are attributable to the ν₁ symmetric stretching vibrations of the P-O bonds within the PO₄ tetrahedra. The weak bands between 1018 and 1106 cm⁻¹ correspond to ν₃ asymmetric stretching vibrations of the PO₄ groups. The bands ranging from 561 to 524 cm⁻¹ are due to the O-P-O bending modes within the PO₄ tetrahedra and those below 479 cm⁻¹ to the lattice mode (Jolliff et al. 1996).

Raman spectroscopy

There have been several investigations on merrillite with Raman spectroscopy and the detailed assignments of major Raman bands have been proposed (e.g., Chen et al. 1995; Jolliff et al. 1996, 2006; Wang et al. 2004). The Raman spectrum of the Suizhou merrillite is displayed in Figure 3, which resembles that of weakly to moderately shocked merrillite in the Sixiangkou meteorite (Chen et al. 1995), merrillite from martian meteorites (Wang et al. 2004), and synthetic REE-poor merrillite (Jolliff et al. 2006). The spectrum of the Suizhou merrillite contains a well-resolved strong doublet at 960 and 976 cm⁻¹, which are attributable to the ν₁ symmetric stretching vibrations of the P-O bonds within the PO₄ tetrahedra. The weak bands between 1018 and 1106 cm⁻¹ correspond to ν₃ asymmetric stretching vibrations of the PO₄ groups. The bands ranging from 561 to 524 cm⁻¹ are due to the O-P-O bending modes within the PO₄ tetrahedra and those below 479 cm⁻¹ to the lattice mode (Jolliff et al. 1996).

The Raman spectrum of the Suizhou merrillite is, however, obviously different from that of the REE-rich merrillite, natural or synthetic, which exhibits an asymmetric single peak or a very poorly resolved doublet (Jolliff et al. 2006). The Raman spectrum of terrestrial whitlockite is similar to that of the REE-rich merrillite, but exhibits an additional weak peak at ~924 cm⁻¹ (Fig. 3) that...
is not observed in the spectra of the H-free merrillite. This peak, according to Jolliff et al. (2006), is attributable to the $v_1$ symmetric stretching vibrations of the $\text{PO}_2(\text{OH})$ group.

**IMPLICATIONS**

The Suizhou merrillite has a simple composition with 0.98 Na apfu. This value is much higher than that (0.05–0.20 Na apfu) in lunar merrillites (Hughes et al. 2006; Jolliff et al. 2006), most of which exhibit characteristic enrichment in REE. In comparison, on the one hand, martian merrillite contains significantly higher Na concentrations (up to 0.86 apfu) and much lower REE concentrations (Shearer et al. 2015 and references therein). On the other hand, meteoritic merrillite has relatively low REE contents, but exists in both Ca-rich and Na-rich varieties. Clearly, the simple chemical formula for merrillite, $\text{Ca}_9\text{Mg}(\text{PO}_4)_2$, approved by IMA is insufficient and inadequate to describe various merrillites documented thus far. Accordingly, Jolliff et al. (2006) proposed three merrillite end-member compositions: $\text{Ca}_9\text{Mg}(\text{PO}_4)_2$, $\text{Na}-\text{merrillite }\text{Ca}_9\text{NaMg}(\text{PO}_4)_2$, and $\text{REE-merrillite }[\text{Ca}(\text{REE})]\square\text{Mg}(\text{PO}_4)_2$. These merrillite end-members are linked by coupled substitutions: $0.5\square_{\text{Na-site}} + 0.5\square_{\text{Ca-site}} \leftrightarrow \text{Na}-\text{merrillite }\text{Ca}_{9}\text{NaMg}(\text{PO}_4)_2 + 0.5\text{Ca}_{\text{Na-site}} \leftrightarrow \text{REE-merrillite }[\text{Ca}(\text{REE})]\square\text{Mg}(\text{PO}_4)_2$. The nomenclature proposed by Jolliff et al. (2006) for various merrillites appears to have its merits, as it reflects their chemical differences and provides considerable conveniences in their descriptions.

Tuite, ideally $\text{Ca}_9(\text{PO}_4)_2$, was first discovered from the Suizhou meteorite as the high-pressure polymorph of merrillite (Xie et al. 2002) or the high-pressure decomposition product of chlorapatite (Xie et al. 2013). It is stable at Earth’s mantle temperature-pressure conditions and is proposed to be a potential host for REE and incompatible elements, such as Na, Sr, and Ba (Murayama et al. 1986; Xie et al. 2002). Based on chemical analyses of numerous tuite grains from the Suizhou meteorite, Xie et al. (2013) noticed that tuite converted from merrillite retains similar amounts of MgO and Na$_2$O as merrillite, whereas that formed through the decomposition of chlorapatite contains little MgO or Na$_2$O, but significant Cl, suggesting that the Na$_2$O, MgO, and Cl contents in natural tuite may serve as good indicators for distinguishing its precursor phosphate mineral, merrillite or chlorapatite. It thus begs the question whether REE-bearing tuite could be found on the Moon as a consequence of the REE-merrillite transformation under impacts, as only lunar merrillite exhibits high REE concentrations of all extraterrestrial merrillites documented thus far.