The atomic arrangement of merrillite from the Fra Mauro Formation, Apollo 14 lunar mission: The first structure of merrillite from the Moon

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ABSTRACT

The atomic arrangement of lunar merrillite has been refined to $R = 0.0452$ in $R3c$ using X-ray diffraction data recorded on a CCD detector; previous attempts at structure solution using a point detector were not successful because of the poorly crystallized nature of the lunar material. The atomic arrangement of merrillite has a structural unit of $[(\text{Mg,Fe})(\text{PO}_4)_6]^{2+}$ that forms a “bracelet-and-pinwheel” unit that is common in hexagonal-closest-packed layers. The individual structural units are not polymerized and exist in layers at $z = 1/6, 1/3, 1/2, 2/3, \text{and } 5/6$. In lunar merrillite, the $[(\text{Mg,Fe})(\text{PO}_4)_6]^{2+}$ structural units are linked by a $[(\text{Ca,REE}),_3\text{Na}_2(\text{PO}_4)_3]^{12-}$ interstitial complex, formed of $\text{CaO}_8, \text{Ca}_2\text{O}_8, \text{Ca}_3\text{O}_8, \text{NaO}_6,$ and $\text{P}_2\text{O}_7$ polyhedra.

There has long been speculation regarding the relationship between merrillite and terrestrial whitlockite, and the solution of the Fra Mauro merrillite atomic arrangement allows the characterization of the lunar phase. Lunar merrillite and terrestrial whitlockite have largely similar atomic arrangements, but the phases differ due to the presence or absence of hydrogen. In whitlockite, H is an essential element and allows the charge balance. Hydrogen is incorporated into the whitlockite atomic arrangement by disordering one of the phosphate tetrahedra and forming a $\text{PO}_3(\text{OH})$ group. Lunar merrillite is devoid of hydrogen, and thus no disordered tetrahedral groups exist. Charge balance for substituents Y and REE (for Ca) is maintained by Si ↔ P tetrahedral substitution and □ ↔ Na at the Na site. The structure solution demonstrates the effectiveness of the CCD detector in unraveling previously intractable diffraction data and urges that previously analyzed lunar material be reexamined using this instrumentation.

Keywords: Merrillite, Moon, atomic arrangement, chemistry

INTRODUCTION

With the return of the Apollo lunar landing missions (Apollo missions 11, 12, 14, 15, 16, and 17), direct observation of lunar samples provided the first significant insight into lunar mineralogy and petrology. In the Apollo missions, 382 kg of rocks were returned from the Moon, and an unprecedented national (U.S.) scientific initiative was undertaken to characterize the samples. Using the entire array of scientific instrumentation available at the time, lunar samples were characterized as completely as possible. Most lunar minerals were found to be similar to terrestrial minerals. However, those lunar minerals whose terrestrial analogs contain H and/or Fe$^+$ necessarily differ from their terrestrial counterparts.

One phase that was tentatively identified from the Moon was whitlockite, ideally $\text{Ca}_3(\text{Mg,Fe}^{2+})(\text{PO}_4)_3(\text{PO}_4(\text{OH})), a phosphate that contains essential hydrogen. Jolliff et al. (1993) provided detailed chemical analyses of lunar “whitlockite” from Apollo 14. Those authors recognized that lunar “whitlockite” differs from the terrestrial phase, but the small crystal size of the rare specimens precluded structure investigations. The recognition of differences between the terrestrial and extraterrestrial phases has a long history, but lacked definitive data (Tschermak 1883; Merrill 1915; Mason 1971; Dowty 1977), and the name “merrillite” was given to the extraterrestrial phase—in this case meteoritic—by Wherry (1917).

Prewitt and Rothbard (1975) also noted the inability to identify a crystal of lunar “whitlockite” suitable for structure studies, but provided an abstract report of the atomic arrangement of extraterrestrial “whitlockite” from the Estacado meteorite; extensive details regarding crystal data and the results of the crystal-structure refinement were not offered in that work. Dowty (1977) offered the atomic arrangement of “whitlockite” from the Angra dos Reis meteorite, and presciently demonstrated the similarity of the atomic arrangement of meteoritic Ca$_3$(PO$_4$)$_2$ phases to that of synthetic $\beta$-Ca$_3$(PO$_4$)$_2$. In the 1990s, a grain separated from Apollo 14 sample 14161,7373 (Jolliff et al. 1993) was found to be large enough for structure determination by single-crystal methods. However, data collected from a single-crystal diffractometer with a point-detector showed that the material was poorly crystallized, almost certainly from metamictization due to decay of substituent ac-