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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 $[(Mg,Fe)(PO_4)_6]_2^{16-}$ 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, and 5/6. In lunar merrillite, the $[(Mg,Fe)(PO_4)_6]_2^{16-}$ structural units are linked by a $[(Ca,REE)_{18}Na_2(PO_4)_2]^{32+}$ interstitial complex, formed of $Ca1O_8$, $Ca2O_8$, $Ca3O_8$, NaO_6, and $P1O_4$ 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 $PO_3(OH)$ 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 $\square \leftrightarrow$ 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^{3+} necessarily differ from their terrestrial counterparts.

One phase that was tentatively identified from the Moon was whitlockite, ideally $Ca_9(Mg,Fe^{2+})(PO_4)_6[PO_3(OH)]$, 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 β-$Ca_3(PO_4)_2$.

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-

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tinides, and diffractions were broad and diffuse. The sample was analyzed using an Enraf-Nonius CAD4 diffractometer, and the data were not sufficiently resolvable to even determine the unit cell. We report here the successful structure refinement of lunar merrillite using X-ray data recorded on a CCD (charge-coupled device) detector, demonstrating the efficacy of that method in unraveling previously intractable atomic arrangements.

CHEMISTRY

Jolliff et al. (1993) presented the results of electron and ion microprobe analyses of 10 lunar merrillite crystals, including four analyses from sample 14161,7373 of this work; those four analyses are contained in Table 1. Those analyses yielded an average formula of:

$(Na_{0.39})$ $(Mg_{1.43}Fe^{2+}_{0.62}Mn^{2+}_{0.02})_{\Sigma 2.07}[Ca_{16.83}(Y,REE)_{1.38}]_{\Sigma 18.21}$ $(P_{13.90}Si_{0.05})_{\Sigma 13.95}$ O_{56}. The empirical formula is in remarkable agreement with the ideal formula obtained from the crystal structure, which is idealized as:

(Na_{2-x}) $(Mg, Fe^{2+}, Mn^{2+})_{\Sigma 2}$ $[Ca_{18-x-z}(Y,REE)_{x+z}]_{\Sigma 18}$ $(P_{14-z}Si_z)_{\Sigma 14}$ O_{56}, with $Z = 3$.

EXPERIMENTAL PROCEDURES

Heating experiments and Raman spectroscopy

Given the possibility of radiation damage over the several-billion-year lifetime of the crystal, we subjected the grain to heating in a silica-tube using an Ar flow-through furnace in an attempt to anneal it in an inert atmosphere. Several heatings at different temperatures were made and the grain was analyzed before and after each heating episode with a Raman spectrometer to monitor any changes in structure. Raman spectra of metamict minerals have been shown to vary systematically in terms of parameters such as peak broadening with degree of metamictization (Wopenka et al. 1996). At the maximum temperature step, the grain was heated for 40 h at 658 °C (±1). Raman spectra, however, did not show any significant change from the original spectra taken prior to heating (see Jolliff et al. 1996). X-ray diffraction results taken with the Enraf-Nonius CAD4 diffractometer before and after heating also did not show any detectable change.

TABLE 1. Chemical analyses of merrillite sample 14161,7373 (from Jolliff et al. 1993)

wt%	1	2	3	4	Avg.
P_2O_5	43.32	43.61	43.27	42.94	43.29
SiO_2	0.13	0.12	0.13	0.14	0.13
FeO	1.97	1.89	2.03	1.9	1.95
MnO	0.01	0.06	0.07	0.09	0.06
MgO	2.6	2.54	2.45	2.54	2.53
CaO	41.27	41.33	41.52	41.54	41.42
Na_2O	0.61	0.52	0.49	0.49	0.53
Y_2O_3	2.42	2.55	2.49	2.57	2.51
Sum Ln_2O_3	6.33	6.62	6.41	6.78	6.54
Total	98.66	99.24	98.86	98.99	98.94
Formula proportions based on 56 O atoms					
P	13.916	13.942	13.898	13.825	13.895
Si	0.049	0.045	0.049	0.053	0.049
Sum (tet)	13.965	13.987	13.947	13.878	13.944
Fe^{2+}	0.625	0.597	0.644	0.604	0.618
Mn	0.003	0.019	0.022	0.029	0.018
Mg	1.471	1.43	1.386	1.44	1.432
Ca	16.778	16.721	16.878	16.926	16.826
Na	0.449	0.381	0.36	0.361	0.388
$Y+Ln^{3+}$	1.339	1.398	1.364	1.434	1.384
Sum (other)	20.665	20.546	20.654	20.794	20.665

Optical properties

Optical data were collected on merrillite to determine if optical methods are an effective way of distinguishing whitlockite and merrillite and to fully characterize the lunar material. A polarizing light microscope (Leitz Ortholutz) equipped with a spindle stage was used to determine the optical properties.

Crystal structure

Subsequent to point-detector experiments, the same fragment of merrillite from Apollo 14 sample 14161,7373 was re-analyzed using a single-crystal diffractometer (Bruker Apex Platform goniometer) equipped with a CCD detector. A remarkable peak-broadening was observed, thus confirming the poor diffraction quality of the lunar sample. A sphere of diffraction data was collected using Mo*K*α radiation. Table 2 contains crystal data and the results of the structure refinement of lunar merrillite.

The atomic arrangement was refined with the Bruker SHELXTL V. 6.14 (Bruker AXS, Inc. 2000) package of programs using the starting parameters from Prewitt and Rothbard (1975); neutral-atom scattering factors and terms for anomalous dispersion were employed throughout the solution and refinement. Refinement was performed with anisotropic thermal parameters for all atoms, and the structure was refined on F^2. In Table 3, we list the atom parameters, using the atom nomenclature of Prewitt and Rothbard (1975), and in Table 4, we present selected interatomic distances. During refinement, two oxygen atoms (O6, O7) refined to non-positive-definite values; those anisotropic displacement factors are listed in Table 5[1]. Given the poor quality of the data, however, we consider the refinement a remarkable success, and the efficacy of the CCD detector in unraveling previously intractable structure data is affirmed. Phosphorous and Ca sites were refined with unconstrained occupancy, to reflect the substitution of Si and REEs, respectively; the Mg site was constrained to (Mg + Fe) = 1. Values of cation occupancy in Table 3 allow calculation of the site scattering (mean electron numbers) as follows: Ca1, 22.3(3); Ca2, 20.4(2); Ca3, 20.6(3); Mg, 14.8(2); Na, 2.5(3); P1, 13.95(30); P2, 13.2(2); P3, 13.4(2). Table 6[1] contains observed and calculated structure factors from the crystal structure.

RESULTS

Optical properties

An extinction data set was collected for a single crystal of merrillite and used to determine the optical class of the mineral, as well as the spindle stage and microscope stage settings required to measure the principal refractive indices of the mineral. Graphical output from the newest version of EXCALIBR (Gunter et al. 2005) confirmed merrillite to be uniaxial, which is in agreement

TABLE 2. Crystal data and results of structure refinement for lunar merrillite

Crystal size: 0.06 × 0.16 × 0.24 mm
Unit cell by least squares (space group: *R*3*c*, 4, 645 reflections):
a (Å) 10.2909(10); *c* (Å) 36.8746(68)
Frame width (ω), scan time, no. of frames, no. of runs: 0.20°, 30 s, 4500, 7
$-13 \leq h \leq 13$; $-13 \leq k \leq 13$; $-48 \leq l \leq 48$; $2\theta \leq 57°$
Temperature: 20 °C
Detector-to-crystal distance: 5 cm
Effective transmission: 0.3189–1.000
R_{int} (before–after SADABS absorption correction): 0.0976–0.0513
Measured reflections, full sphere: 10,015
Refined parameters: 147, refined on F^2
$R1 = 0.0452$ for 922 Fo > 4sig(Fo) and 0.0632 for all 1103 data
$wR2 = 0.1130$, GooF = S = 1.055
Largest difference peaks: +0.77, –0.69 e^- $Å^3$

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[1] Deposit items AM-06-027, Tables 5 and 6. Deposit items are available two ways: For a paper copy contact the Business Office of the Mineralogical Society of America (see inside front cover of recent issue) for price information. For an electronic copy visit the MSA web site at http://www.minsocam.org, go to the American Mineralogist Contents, find the table of contents for the specific volume/issue wanted, and then click on the deposit link there.

TABLE 3. Atom positions and equivalent isotropic displacement factors for atoms in lunar merrillite

Atom	x	y	z	U_{eq}	Occ.
Ca1	0.2763(3)	0.1398(10)	0.67489(14)	0.0247(8)	$Ca_{1.113(15)}$
CaIb	*0.2887*	*0.1545*	*0.67371*		
Ca2	0.2745(2)	0.1376(11)	0.56760(13)	0.0195(8)	$Ca_{1.019(12)}$
CaIIB1	*0.2794*	*0.1457*	*0.56639*		
Ca3	0.3805(3)	0.1887(15)	0.76925(13)	0.0251(9)	$Ca_{1.030(13)}$
CaIIB2	*0.3871*	*0.1794*	*0.76866*		
Mg	0	0	0	0.0144(12)	$Mg_{0.80(2)}$
Fe	0	0	0	0.0144(12)	$Fe_{0.20}$
M	*0*	*0*	*0*		
Na	0	0	0.8137(19)	0.07(2)	$Na_{0.23(3)}$
CaIIA′	*0*	*0*	*0.8125*		
P1	0	0	0.73247(16)	0.0193(15)	$P_{0.93(2)}$
PA′	*0*	*0*	*0.7344*		
P2	0.3151(4)	0.1390(11)	0.86556(14)	0.011(2)	$P_{0.879(16)}$
PB1	*0.3166*	*0.1426*	*0.86517*		
P3	0.3429(4)	0.1539(14)	0.96904(14)	0.016(3)	$P_{0.892(15)}$
PB2	*0.3501*	*0.1570*	*0.96832*		
O1	0	0	0.6905(4)	0.027(3)	O_1
OIA′	*0*	*0*	*0.6934*		
O2	–0.0075(12)	0.1375(11)	0.7450(3)	0.032(3)	O_1
OIIA′	*–0.0001*	*0.1374*	*0.7499*		
O3	0.2713(11)	0.0915(12)	0.8262(3)	0.031(2)	O_1
OIB1	*0.2728*	*0.0910*	*0.8261*		
O4	0.247(2)	0.233(2)	0.8792(5)	0.029(4)	O_1
OIIB1	*0.2456*	*0.2317*	*0.8788*		
O5	0.2717(19)	–0.001(2)	0.8881(4)	0.021(3)	O_1
OIIB3	*0.2729*	*0.0014*	*0.8874*		
O6	0.4887(9)	0.245(3)	0.8694(2)	0.029(2)	O_1
OIIB5	*0.4889*	*0.2417*	*0.8698*		
O7	0.3776(9)	0.189(3)	0.0092(2)	0.028(2)	O_1
OIB2	*0.4013*	*0.1951*	*0.0080*		
O8	0.3993(18)	0.0509(18)	0.9564(4)	0.028(3)	O_1
OIIB2	*0.3991*	*0.0475*	*0.9550*		
O9	0.4141(17)	0.3040(16)	0.9491(4)	0.026(3)	O_1
OIIB4	*0.4158*	*0.3034*	*0.9476*		
O10	0.1723(9)	0.084(6)	0.9622(2)	0.026(3)	O_1
OIIB6	*0.1779*	*0.0783*	*0.9642*		

Note: For comparison, equivalent atoms of whitlockite (Calvo and Gopal 1975) are given in italics; see text for discussion.

TABLE 4. Selected interatomic distances (Å) in lunar merrillite

Ca1-O8	2.32(2)	Ca2-O9	2.34(2)
Ca1-O4	2.40(2)	O7	2.343(9)
Ca1-O5	2.43(2)	O8	2.42(2)
Ca1-O7	2.51(3)	O2	2.43(1)
O1	2.529(4)	O6	2.43(2)
O7	2.54(3)	O5	2.45(2)
O9	2.65(1)	O6	2.45(3)
O3	2.70(1)	O4	2.82(2)
Mean	2.51	Mean	2.46
Ca3-O5	2.26(2)	Mg-O6	2.069(8)
O3	2.36(1)	O6	2.069(8)
O2	2.37(1)	O6	2.069(8)
O10	2.41(6)	O10	2.074(8)
O10	2.44(5)	O10	2.074(8)
O8	2.51(2)	O10	2.074(8)
O4	2.52(2)	Mean	2.072
O9	2.73(2)		
Mean	2.45		
Na-O3	2.50(2)	P1-O2	1.527(9)
O3	2.50(2)	O2	1.527(9)
O3	2.50(2)	O2	1.527(9)
O2	2.92(6)	O1	1.549(13)
O2	2.92(6)	Mean	1.533
O2	2.92(6)		
Mean	2.71		
P2-O3	1.52(1)	P3-O8	1.51(2)
O5	1.53(2)	O7	1.522(7)
O4	1.54(2)	O9	1.53(2)
O6	1.567(8)	O10	1.550(9)
Mean	1.539	Mean	1.528

with the structural refinement described herein. Bloss (1981) and Gunter et al. (2005) both pointed out that stereographic projections of the extinction curves for uniaxial minerals result in a great circle projection that coincides with the one circular section of the uniaxial indicatrix, and its pole plots on the other extension curve and locates the single optic axis. Such a relationship was confirmed for merrillite.

In addition to the graphical output, EXCALIBRW (Gunter et al. 2005) also provides the spindle stage and microscope stage settings to determine n_ε and n_ω for merrillite, as well as to determine the optic sign by use of an interference plate to ascertain the relative magnitude of the two principal indices of refraction. In the case of merrillite, $n_\varepsilon < n_\omega$, and thus merrillite is uniaxial (–). Output from EXCALIBRW was also used to orient both n_ε and n_ω to determine their refractive indices by use of the double-variation method (Su et al. 1987). This method found $n_\varepsilon = 1.6336(5)$ and $n_\omega = 1.6353(5)$. On the basis of these values, the chemical data presented in Table 1, and the cell parameters presented in Table 2, the density of merrillite was calculated to be 3.34 g/cm^3. Given the density and the mean refractive index $(n_\varepsilon + 2n_\omega) / 3 = 1.6347$, the Gladstone-Dale compatibility index was calculated to be 0.026. This index was used to determine the relationship between the measured refractive index and crystal structure, which for merrillite shows excellent agreement (Mandarino 1981).

Crystal structure

The structural data obtained in this study demonstrate that the lunar sample examined crystallizes with the β-$Ca_3(PO_4)_2$ atomic arrangement and therefore it can be classified as merrillite. On the whole, the structure is quite similar to that of the meteoritic "whitlockites" reported by Prewitt and Rothbard (1975) and Dowty (1977). The atomic coordinates of lunar merrillite are listed in Table 3, and equivalent atoms for terrestrial whitlockite are also given; the concordance of the atomic positions is evident. However, there are atoms in whitlockite that do not have equivalents in the merrillite atomic arrangement, as will be discussed subsequently. The P1 tetrahedron (our nomenclature as well as that of Prewitt and Rothbard 1975) is the component of the whitlockite/merrillite atomic arrangement that affects the structural accommodations that distinguish between merrillite and whitlockite. Below we elucidate the structural disorder in that tetrahedron occurring in whitlockite that accommodates hydrogen, disorder that is not present in merrillite.

Hawthorne (1983) recognized two distinct parts of complex mineral structures: (1) the *structural unit*, usually the anionic portion of the structure that contains bonds of higher bond-valence; and (2) the *interstitial complex*, usually the cationic part of the structure, with bonds of lower bond-valence between alkaline and alkaline-earth cations and H_2O, OH, and/or Cl groups. The merrillite atomic arrangement, like that of whitlockite, is formed of an $[(Mg,Fe)(PO_4)_6]_2^{16-}$ structural unit forming a "bracelet-and-pinwheel" arrangement (Moore 1973). Moore defined a bracelet as a mathematical object, a loop with n nodes involving m symbols, where $m < n$. For the pinwheel, $n = 6$ (a hexagonal ring) and $m = 2$. Thus, the central octahedral cation and the six coordinating tetrahedra form a pinwheel, and in the case of merrillite, the pinwheels are not polymerized. Moore described bracelet-and-pinwheel structures in Ca-orthosilicate and alkali sulfate structures, and Hughes et al. (1987) described similar structural units in a vanadate structure.

Figure 1 displays the array of the structural units projected down **c**, and also illustrates the topology of a single bracelet and pinwheel. Such a pinwheel topology is known most commonly in structures with hexagonal-closest-packed arrays of O atoms; the P atoms in merrillite occupy tetrahedral interstices in the closest-packed arrays, and (Mg, Fe) in merrillite occupy octahedral interstices of the closest-packed sheet. In merrillite, the bracelet-and-pinwheel structural unit is formed of the (Mg, Fe) atoms in the central octahedron, with P2- and P3-centered tetrahedra decorating that octahedron, and coordinating oxygen atoms O3, O4, O5, O6, O7, O8, O9, and O10 (our atom nomenclature).

The pinwheels in merrillite are centered on the (Mg, Fe) octahedra, which form the center of the pinwheel, at $z = 0$, 1/6, 1/3, 1/2, 2/3, and 5/6. The pinwheels are linked by the interstitial complex, formed of $[(\mathrm{Ca,REE})_{18}\mathrm{Na}_2(\mathrm{PO}_4)_2]^{32+}$ units; we here use the term "interstitial complex" as in Hawthorne (1983), but recognize that the term traditionally is used for units that contain hydroxyl and/or water, unlike lunar merrillite. As in the traditional usage, however, the interstitial complex is a cationic unit. The $[(\mathrm{Ca,REE})_{18}\mathrm{Na}_2(\mathrm{PO}_4)_2]^{32+}$ interstitial complex is formed of $\mathrm{Ca1O_8}$, $\mathrm{Ca2O_8}$, $\mathrm{Ca3O_8}$, $\mathrm{NaO_6}$, and $\mathrm{P1O_4}$ polyhedra; oxygen atoms O1 and O2 are unique to the interstitial complex, and the interstitial complex cements the structure by sharing the O atoms of the pinwheel structural unit.

A comparison of merrillite and whitlockite atomic arrangements

For all atoms in merrillite, there are concordant atoms in whitlockite (with the caveat that the partially occupied Na site in merrillite is matched by a partially occupied Ca site in whitlockite), but the converse is not true. Whitlockite has three additional atoms, P(A), O(IA), and O(IIA) in the nomenclature of Calvo and Gopal (1975), in addition to the hydrogen atom [bonded to O(IA) of Calvo and Gopal] that was not located in that study.

The difference between the atomic arrangements of merrillite and whitlockite results from the presence of H in terrestrial whitlockite, illustrated in Figure 2. In whitlockite, the "extra" phosphate group [P(A)] relative to merrillite occurs because the fully occupied P1 site in merrillite is split into two sites in whitlockite, the $\mathrm{P(A')O_4}$ and $\mathrm{P(A)O(IIA)_3O(IA)H}$ (atom nomenclature of Calvo and Gopal 1975). Hydrogen in terrestrial whitlockite is accommodated in the atomic arrangement by reorientation of the $\mathrm{P(A)O(IIA)_3O(IA)H}$ phosphate tetrahedron. The reorientation of the P(A) phosphate group is necessitated by the

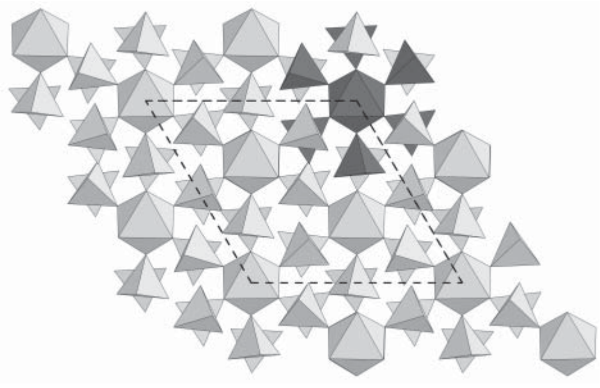

FIGURE 1. The arrangement of the bracelet-and-pinwheel structural units in lunar merrillite, projected on (001). One $[(\mathrm{Mg,Fe})(\mathrm{PO}_4)_6]_2^{16-}$ structural unit is highlighted.

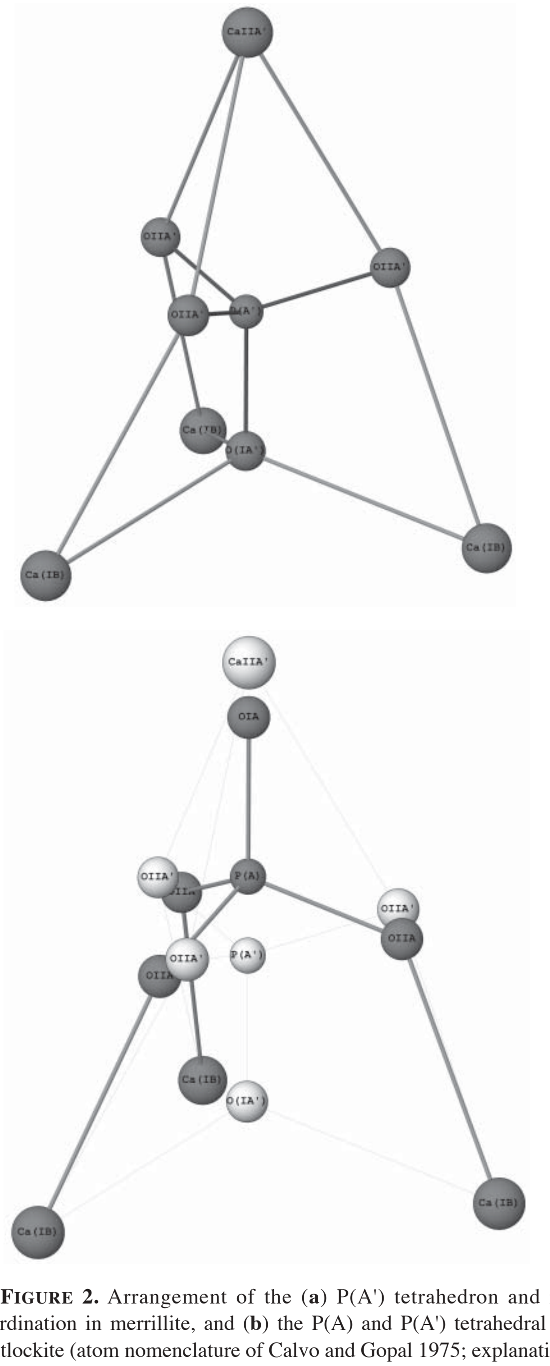

FIGURE 2. Arrangement of the (**a**) P(A') tetrahedron and its coordination in merrillite, and (**b**) the P(A) and P(A') tetrahedral in whitlockite (atom nomenclature of Calvo and Gopal 1975; explanation in text). In whitlockite, both the dark and light phosphate groups exist in a disordered manner; the inverted P(A) phosphate group occurs to accommodate the hydroxyl OIA. Where the OIA hydroxyl occurs, the CaIIA' site is vacant.

presence of the H atom, and thus atoms P(A), O(IA), and O(IIA) of the disordered tetrahedron exist in whitlockite, but not in the H-free merrillite. The structural adjustments necessary to accommodate H distinguish the terrestrial phase whitlockite from the extraterrestrial phase merrillite.

Gopal and Calvo (1972) examined the structural relationships of whitlockite and the β-$Ca_3(PO_4)_2$ atomic arrangement by heating terrestrial whitlockite at 1200 °C "overnight" and refining the atomic arrangement. They found that, upon heating, the whitlockite atomic arrangement no longer had atoms in the P(A), O(IA), and O(IIA) positions, and assumed the β-$Ca_3(PO_4)_2$ atomic arrangement. Clearly, the heated whitlockite had evolved its H, and thus the reorientation of the $P(A)O(IIA)_3O(IA)H$ phosphate tetrahedron is no longer necessary to accommodate H in the atomic arrangement. The atomic arrangement of heated whitlockite assumes the β-$Ca_3(PO_4)_2$ atomic arrangement, and that structure is identical to that of merrillite (Dowty 1977).

The solution of the atomic arrangement of the lunar sample confirms the role of H in distinguishing whitlockite from merrillite, and allows the distinction of whitlockite, meteoritic merrillite, and lunar merrillite. We here urge a reexamination of the nomenclature of the whitlockite and merrillite phases in light of the elucidation of their distinct chemistry and atomic arrangements of the terrestrial and extraterrestrial phases.

As noted previously, maintenance of charge balance in merrillite is attained through several substitutions, and the Na site is critical to the charge balance. The Na site is partially occupied, and the occupancy refined to $(Na_{0.23}\square_{0.77})$. The Na site in merrillite corresponds to the CaIIA' site in terrestrial whitlockite and meteoritic merrillite (Calvo and Gopal 1975; Prewitt and Rothbard 1975; Dowty 1977), a site that is also partially occupied, primarily by Ca in some meteorites and Na in others. However, the charge-balance mechanisms in the phases are decidedly different, and here we elucidate those differences. The lack of H in the lunar phase distinguishes it from terrestrial whitlockite, and the presence of REEs, in contrast to meteoritic merrillite and terrestrial whitlockite, provides a unique charge-balance mechanism in lunar merrillite.

Crystal chemistry of merrillite

The structure analysis reported above demonstrates that the Na site is partially occupied, and effects, in conjunction with $(Y,REE)^{3+} \leftrightarrow Ca^{2+}$ and $Si^{4+} \leftrightarrow P^{5+}$ substitutions, charge balance in lunar merrillite. In an unsubstituted Na-bearing merrillite structure with a theoretical formula of $Na_2(M^{2+})_2Ca_{18}(PO_4)_{14}$, the charge is balanced. However, as $(Y,REE)^{3+}$ substitute for Ca^{2+}, charge is gained, and as Si^{4+} substitutes for P^{5+}, charge is lost. The overall charge-balance is maintained by balance of the charge-adding $(Y,REE)^{3+} \leftrightarrow Ca^{2+}$ substitution and the charge-reducing $\square \leftrightarrow Na$ and $Si^{4+} \leftrightarrow P^{5+}$ substitutions.

Of all extraterrestrial merrillites studied, only lunar merrillite has high REE concentrations, perhaps owing to intrinsically low Na concentrations in lunar materials (and in the Moon in general), and to the fact that when lunar magmas become sufficiently concentrated in P for merrillite to crystallize, REE concentrations of residual melts tend to be high. High Na and relatively low REE concentrations characterize Martian merrillite (Lundberg et al. 1988, 1990), indicating that Na occupancy is preferred over vacancy on the Na site if sufficient Na is available (see Jolliff et al., this volume).

Using complex quadratic programming methods, Wright et al. (2000) devised a method of optimizing cation site occupants in compounds containing multiple occupants on cation sites. The method essentially minimizes the differences between the formula obtained from the results of the chemical analysis and that obtained by single-crystal structure refinement. In the case of merrillite, the optimization was highly constrained because of the relatively poor quality of the structure data, yet the optimization yielded excellent results. The optimized cation site occupancies of merrillite are: $^{Na}(Na_{0.44}\square_{1.56})^{Mg}(Mg_{1.54}Fe_{0.46})^{Ca1}(Ca_{5.52}RE_{0.48})^{Ca2}(Ca_{5.82}RE_{0.18})^{Ca3}(Ca_{5.65}Y_{0.28}RE_{0.07})^{P1}(P_{1.87}Si_{0.05}\square_{0.08})^{P2}(P_{6.00})^{P3}(P_{6.00})\,O_{56}$. As shown by the optimization, the rare-earth elements (modeled using Ce, the most abundant REE) are concentrated in the Ca1 site, and Y was found to order into the Ca3 site. Among the phosphate tetrahedra, the P1 site concentrates the substituent Si and vacancies, whereas P2 and P3 are occupied by P.

Terrestrial and extraterrestrial "whitlockites" were long thought to be identical, and the early literature used the names interchangeably. However, this study illustrates the structural differences between the terrestrial and lunar phases, and also allows distinction among lunar merrillite, merrillite reported from meteorites, and terrestrial whitlockite.

Hydrogen is an essential element in terrestrial whitlockites, but is obviously absent from meteoritic and lunar merrilites. Thus, lunar merrillite and terrestrial whitlockite are indeed chemically distinct phases, as H is essential in whitlockite, but absent in merrillite. In addition, lunar merrillite differs from previously described meteoritic merrillites (Prewitt and Rothbard 1975; Dowty 1977), as Na is found in the partially occupied metal alkali/alkaline earth site as opposed to the half-occupied Ca-site in the meteoritic phase. Meteoritic and lunar merrillite possess the same atomic arrangements, but the phases differ chemically by the abundant REE in the lunar phase. Earlier conjecture on a vacant metal alkali/alkaline earth site in the lunar material is now confirmed (Dowty 1977), as that site is vacant in some samples of the lunar phase reported by Jolliff et al. (this volume).

CONCLUDING REMARKS

Lunar merrillite has resisted structure determination because of the lack of suitable samples. With the advent of the CCD-detector for detecting diffracted X-radiation, samples that were previously untenable for structure study now yield data of sufficient quality for solution of the atomic arrangements. We urge a reexamination of all lunar phases using this technology, as those studies are certainly more expedient than collecting new samples.

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