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The crystal chemistry of whitlockite and merrillite and the dehydrogenation of whitlockite to merrillite

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ABSTRACT

The atomic arrangements of two natural samples of whitlockite, a synthetic whitlockite specimen, a synthetic whitlockite specimen heated at 500 °C, and a synthetic merrillite specimen (formed through dehydrogenation of synthetic whitlockite by heating at 1050 °C for 24 h) have been determined in space group $R3c$ by X-ray diffraction methods; the high-quality structure refinements yielded $R < 0.019$. Whitlockite, ideally $Ca_{18}Mg_2(PO_4)_{12}[PO_3(OH)]_2$ and merrillite, ideally $Ca_{18}Na_2Mg_2(PO_4)_{14}$, are similar phases that differ by the lack of hydrogen and the concomitant addition of charge-balancing sodium (or calcium) in merrillite. The atomic arrangements of whitlockite and merrillite contain a structural unit consisting of a $[(Mg,Fe)(PO_4)_6]_2^{16-}$ complex anion that forms a "bracelet-and-pinwheel" arrangement. The central octahedral cation and the six coordinating phosphate tetrahedra form a pinwheel, and in whitlockite and merrillite the pinwheels are not polymerized; the structural units are linked by interstitial complexes. In unsubstituted merrillite (assuming no Na or REE substituents for Ca), the interstitial complex has a formula of $[Ca_{19}(PO_4)_2]^{32+}$, and in whitlockite, the terrestrial phase in which hydrogen is accommodated, the interstitial unit has the formula $[Ca_{18}(PO_3[OH])_2]^{32+}$, yielding the charge-balancing relationship $[H_{(whit)} \leftrightarrow Ca_{0.5(merr)}]_2$. Whitlockite and merrillite are perhaps the only phases that form a solid solution with terrestrial and extra-terrestrial end-members that differ by structural adjustments that result from the accommodation of hydrogen in the terrestrial phase. The results of the study also suggest that in terrestrial samples of whitlockite, a merrillite component of the solid solution is common, but that extraterrestrial samples of merrillite are devoid of any whitlockite component.

Keywords: Whitlockite, merrillite, structures, dehydrogenation

INTRODUCTION

Among naturally occurring phosphates of biological importance, the complex crystal chemistry of whitlockite and its relationship with merrillite have not been examined in detail. Whitlockite occurs in dental calculi and other abnormal calcifications in the human body (Gopal and Calvo 1972), and also has been found in terrestrial rocks and ostensibly in meteorites. Gopal and Calvo (1972) examined the structural relationship of whitlockite to synthetic β-$Ca_3(PO_4)_2$ using X-ray powder diffraction data measured at STP and at elevated temperatures. Their results showed that upon elevating the temperature of whitlockite to 900 °C the transformation from whitlockite to the β-$Ca_3(PO_4)_2$ atomic arrangement was complete, although the charge-balancing mechanism was not elucidated. Dowty (1977) examined extraterrestrial "whitlockite" from the achondritic Angra dos Reis meteorite, and found that the phase, although very similar to whitlockite, was devoid of the essential hydrogen found in whitlockite and that it adopted the β-$Ca_3(PO_4)_2$ atomic arrangement. Confusion has existed regarding the relationship between terrestrial and extraterrestrial "whitlockite." The contradiction of essential hydrogen in whitlockite and the purported existence of the phase in meteoritic and lunar rocks that are known to crystallize in environments in which hydrogen is rare or absent has not been addressed with high-quality structure descriptions of the two phases. Numerous previous studies have examined aspects of the whitlockite and merrillite structures (Belik et al. 2002a, 2002b; Morozov et al. 1997; Bigi et al. 1996; Dickens et al. 1974; Schroeder et al. 1977; Ionov et al. 2006), but this study is believed to be the first to juxtapose high-quality structure refinements of the two phases and examine the dehydrogenation reaction of whitlockite to merrillite.

Hughes et al. (2006) reported the atomic arrangement of lunar merrillite (Jolliff et al. 1993), and demonstrated that the phase is similar to meteoritic merrillite and, predictably, devoid of hydrogen. Jolliff et al. (2006) summarized the chemistry of lunar and other extraterrestrial whitlockite in detail. As noted by Hughes et al. (2006), there has been controversy surrounding the distinction between merrillite and whitlockite, and no detailed comparison of the two phases based on modern analyses has been offered. In this work we report the atomic arrangements of two natural samples of whitlockite, of synthetic whitlockite, and of samples of synthetic whitlockite that were heated at 500 and 1050 °C for 24 h (the latter treatment resulting in the dehydrogenation of whitlockite to form merrillite), and compare the crystal chemistry and crystal structures of the phases.

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EXPERIMENTAL DATA

Samples

Natural samples of whitlockite were obtained from the Palermo Mine, North Groton, Grafton Co., New Hampshire, U.S.A. (Harvard University sample 103359; subsequently labeled "Palermo") and from the Tip Top Pegmatite, Custer Co., South Dakota, U.S.A. (subsequently labeled "Tip Top"). The synthetic samples are labeled Syn STP, Syn 500, and Syn 1050, indicating their synthetic nature and the temperature (°C) to which they were heated before X-ray diffraction and structure determination. Two separate synthetic crystals, analyzed after the same heating sequence, yielded identical results.

Synthetic samples of whitlockite were prepared from hydrothermal solution (sample R46). Hydroxylapatite powder was first synthesized by mixing phosphoric acid and calcium hydroxide solutions in a beaker at 90 °C. The solution-precipitate mixture was stirred continually at this temperature until the solution evaporated. Powder X-ray diffraction confirmed that the resulting phase was hydroxylapatite.

A 0.0514 g sample of the synthetic hydroxylapatite was added to 10 mL of distilled water and stirred for 10 min. The pH of the mixture after stirring was 5.98. This was adjusted to 2.79 by the addition of phosphoric acid. The suspension was then sealed in a 23 mL polytetrafluoroethylene-lined acid digestion vessel (Parr Instrument Company), and heated at 240 °C for five days in an Isotemp oven. The result of the hydrothermal treatment was well-formed, elongate, recrystallized hydroxylapatite and a small number of euhedral, pseudo-octahedral, colorless, transparent crystals of whitlockite (Fig. 1). At the core of each whitlockite crystal is a cluster of inclusions.

The presence of whitlockite in the synthesis was unexpected because no Mg was intentionally added to the experiment. The volume of whitlockite produced is very small compared to the volume of hydroxylapatite, indicating a minor amount of Mg in the system. Although the source of Mg is undetermined, it is speculated that it may have leached from components of the reaction vessel. Electron microprobe analysis of the synthetic whitlockite confirmed the presence of the contaminants that effected the crystallization of whitlockite.

Crystal structure

Crystals for structure refinement were mounted on a Bruker Apex CCD diffractometer equipped with graphite-monochromated Mo$K\alpha$ radiation. Refined cell parameters and other crystal data are listed in Table 1. Redundant data were collected for a sphere of reciprocal space, and were integrated and corrected for Lorentz and polarization factors using the Bruker program SaintPlus (Bruker AXS Inc. 2001).

The structures were refined by standard methods using whitlockite and merrillite starting-models and the Bruker Shelxtl v. 6.10 package of programs, with neutral-atom scattering factors and terms for anomalous dispersion. Refinement was performed with anisotropic thermal parameters for all atoms. In Table 2

TABLE 1. Crystal data and results of structure refinements for whitlockite and merrillite samples

	Individual samples				
	Palermo	Tip Top	Syn STP	Syn 500	Syn 1050
a	10.3612(6)	10.3477(2)	10.3571(2)	10.3597(5)	10.3499(2)
c	37.096(4)	37.077(1)	37.138(1)	37.161(4)	37.115(1)
No. frames	4500	4500	7200	4500	7200
Total refl.	25542	24710	40629	25506	40590
Unique refl.	2232	2226	2228	2229	2226
R_{int}	0.0161	0.0288	0.022	0.0167	0.0231
Parameters	149	149	150	156	143
$R1$	0.0183	0.0186	0.0179	0.0144	0.0172
$wR2$	0.0506	0.0515	0.0495	0.0414	0.0481
GooF	1.178	1.084	1.096	1.152	1.114
Difference peaks					
(+), $e^-/Å^3$	0.47	0.45	0.44	0.35	0.45
(–), $e^-/Å^3$	0.61	0.39	0.32	0.30	0.62

Note: For all samples: Frame width (ω) = 0.20°, scan time = 15 s, full sphere. Space group *R*3*c*; Temperature 20 °C; Detector-to-crystal distance 5 cm, 2θ max = 60°.

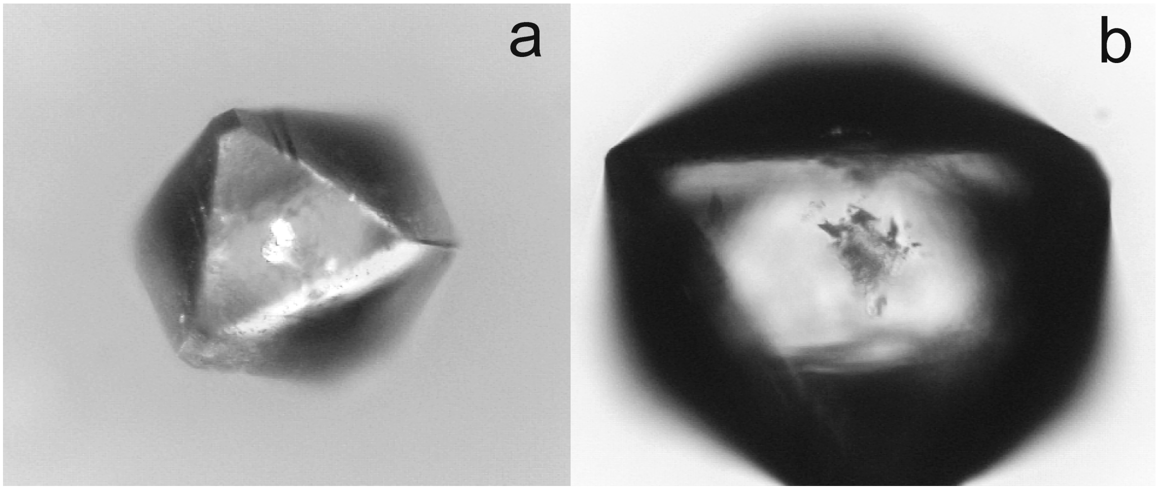

FIGURE 1. Optical photomicrographs of a synthetic crystal of whitlockite (in reflected light **a**, and transmitted light **b**) showing reagents entrained within the crystal. Entrained reagents are the source of the charge-balancing Ca for the dehydrogenation reaction of whitlockite to merrillite. The crystal measures approximately 300 μm on edge.

TABLE 2. Atomic parameters for whitlockite and merrillite samples

Atom	Palermo	Tip Top	Syn STP	Syn 500	Syn 1050
Mg	$Mg_{0.571(5)}Fe_{0.429}$	$Mg_{0.986(6)}Fe_{0.014}$	$Mg_{0.921(5)}Fe_{0.079}$	$Mg_{0.916(4)}Fe_{0.084}$	$Mg_{0.935(6)}Fe_{0.065}$
x	0	0	0	0	0
y	0	0	0	0	0
z	0	0	0	0	0
U_{eq}	0.0089(2)	0.0092(4)	0.0086(3)	0.0080(3)	0.0086(3)
CaIIB1	$Ca_{1.00}$	$Ca_{1.00}$	$Ca_{1.00}$	$Ca_{1.00}$	$Ca_{1.00}$
x	0.27895(5)	0.28086(4)	0.28103(4)	0.28105(4)	0.27347(4)
y	0.14521(5)	0.14684(4)	0.14681(3)	0.14678(3)	0.14232(3)
z	0.56616(3)	0.56524(3)	0.56524(3)	0.56529(3)	0.56805(3)
U_{eq}	0.01015(9)	0.01064(8)	0.01046(8)	0.01021(7)	0.00999(8)
CaIIB2	$Ca_{1.00}$	$Ca_{1.00}$	$Ca_{1.00}$	$Ca_{1.00}$	$Ca_{1.00}$
x	0.38756(5)	0.38857(4)	0.38774(4)	0.38763(4)	0.38364(4)
y	0.17949(5)	0.18041(4)	0.18010(3)	0.18007(3)	0.17687(3)
z	0.76821(3)	0.76783(4)	0.76772(3)	0.76769(3)	0.76923(3)
U_{eq}	0.01128(9)	0.01180(8)	0.01083(8)	0.01061(7)	0.01083(8)
CaIB	$Ca_{1.00}$	$Ca_{1.00}$	$Ca_{1.00}$	$Ca_{1.00}$	$Ca_{1.00}$
x	0.28589(7)	0.29316(5)	0.29481(5)	0.29466(5)	0.27226(5)
y	0.15301(6)	0.15677(5)	0.15772(4)	0.15765(4)	0.14701(4)
z	0.67340(3)	0.67249(4)	0.67220(3)	0.67217(3)	0.67506(3)
U_{eq}	0.02297(11)	0.02103(10)	0.02000(10)	0.02021(9)	0.01981(9)
P(B1)	$P_{1.00}$	$P_{1.00}$	$P_{1.00}$	$P_{1.00}$	$P_{1.00}$
x	0.31608(7)	0.31789(5)	0.31784(5)	0.31784(5)	0.31343(5)
y	0.14232(7)	0.14369(5)	0.14377(5)	0.14377(5)	0.13900(5)
z	0.86487(3)	0.86415(4)	0.86425(3)	0.86430(3)	0.86563(3)
U_{eq}	0.00908(11)	0.00928(9)	0.00902(9)	0.00866(8)	0.00944(9)
P(B2)	$P_{1.00}$	$P_{1.00}$	$P_{1.00}$	$P_{1.00}$	$P_{1.00}$
x	0.34973(7)	0.35105(6)	0.35115(5)	0.35111(5)	0.34384(5)
y	0.15633(6)	0.15782(5)	0.15823(5)	0.15826(5)	0.15160(5)
z	0.96794(3)	0.96743(4)	0.96727(3)	0.96727(3)	0.96931(3)
U_{eq}	0.00909(10)	0.00905(9)	0.00883(9)	0.00865(8)	0.00837(8)
O(IB1)	$O_{1.00}$	$O_{1.00}$	$O_{1.00}$	$O_{1.00}$	$O_{1.00}$
x	0.2719(2)	0.27590(16)	0.27767(15)	0.27761(15)	0.26151(16)
y	0.0913(2)	0.09227(17)	0.09381(16)	0.09418(15)	0.08320(17)
z	0.82566(5)	0.82502(5)	0.82512(4)	0.82513(4)	0.82711(5)
U_{eq}	0.0199(3)	0.0176(3)	0.0179(2)	0.0180(2)	0.0210(3)
O(IIB1)	$O_{1.00}$	$O_{1.00}$	$O_{1.00}$	$O_{1.00}$	$O_{1.00}$
x	0.24554(19)	0.24752(15)	0.24695(14)	0.24689(14)	0.24269(15)
y	0.23150(19)	0.23409(16)	0.23366(14)	0.23367(14)	0.22849(15)
z	0.87850(5)	0.87751(5)	0.87756(4)	0.87760(4)	0.87966(4)
U_{eq}	0.0154(3)	0.0153(2)	0.0145(2)	0.0143(2)	0.0182(2)
O(IIB3)	$O_{1.00}$	$O_{1.00}$	$O_{1.00}$	$O_{1.00}$	$O_{1.00}$
x	0.27315(17)	0.27268(14)	0.27216(13)	0.27196(12)	0.27624(12)
y	0.00089(17)	0.00219(14)	0.00147(13)	0.00130(13)	–0.00043(12)
z	0.88698(5)	0.88649(5)	0.88632(4)	0.88626(4)	0.88827(4)
U_{eq}	0.0118(3)	0.0119(2)	0.0118(2)	0.0116(2)	0.0114(2)
O(IIB5)	$O_{1.00}$	$O_{1.00}$	$O_{1.00}$	$O_{1.00}$	$O_{1.00}$
x	0.48750(19)	0.48953(15)	0.48960(15)	0.48942(14)	0.48536(14)
y	0.24141(18)	0.24215(13)	0.24229(13)	0.24224(12)	0.24023(12)
z	0.86869(5)	0.86839(5)	0.86891(5)	0.86896(4)	0.86822(5)
U_{eq}	0.0139(3)	0.0127(3)	0.0146(2)	0.0146(2)	0.0148(2)
O(II)B2	$O_{1.00}$	$O_{1.00}$	$O_{1.00}$	$O_{1.00}$	$O_{1.00}$
x	0.39897(18)	0.39930(14)	0.39967(13)	0.39968(13)	0.39666(13)
y	0.04698(18)	0.04797(14)	0.04862(13)	0.04875(13)	0.04391(13)
z	0.95475(5)	0.95395(5)	0.95375(4)	0.95375(4)	0.95679(4)
U_{eq}	0.0138(3)	0.0141(2)	0.0141(2)	0.0139(2)	0.0140(2)
O(IIB4)	$O_{1.00}$	$O_{1.00}$	$O_{1.00}$	$O_{1.00}$	$O_{1.00}$
x	0.41720(19)	0.41485(15)	0.41517(14)	0.41539(14)	0.41985(14)
y	0.30286(19)	0.30319(15)	0.30397(14)	0.30422(13)	0.30068(14)
z	0.94715(5)	0.94625(5)	0.94640(4)	0.94649(4)	0.94937(4)
U_{eq}	0.0170(3)	0.0158(2)	0.0158(2)	0.0157(2)	0.0163(2)
O(IIB6)	$O_{1.00}$	$O_{1.00}$	$O_{1.00}$	$O_{1.00}$	$O_{1.00}$
x	0.17844(18)	0.17944(14)	0.17978(14)	0.17993(13)	0.17435(13)
y	0.07904(18)	0.07920(13)	0.07952(13)	0.07962(12)	0.07693(12)
z	0.96333(5)	0.96426(5)	0.96382(5)	0.96367(4)	0.96245(4)
U_{eq}	0.0121(3)	0.0110(2)	0.0126(2)	0.0129(2)	0.0112(2)
O(IB2)	$O_{1.00}$	$O_{1.00}$	$O_{1.00}$	$O_{1.00}$	$O_{1.00}$
x	0.3989(2)	0.40594(17)	0.40528(16)	0.40458(15)	0.37816(14)
y	0.19368(18)	0.19802(14)	0.19756(13)	0.19726(13)	0.18167(13)
z	0.00765(5)	0.00678(6)	0.00669(5)	0.00667(5)	0.00954(5)
U_{eq}	0.0174(3)	0.0145(3)	0.0149(2)	0.0149(2)	0.0130(2)
O(IA)	$O_{0.693(14)}$	$O_{0.890(16)}$	$O_{0.870(14)}$	$O_{0.831(14)}$	NA
x	0	0	0	0	
y	0	0	0	0	
z	0.7974(3)	0.79603(13)	0.79590(10)	0.79602(13)	
U_{eq}	0.034(2)	0.0281(11)	0.0259(10)	0.0261(18)	
P(A)	$P_{0.725(7)}$	$P_{0.961(6)}$	$P_{0.943(5)}$	$P_{0.926(5)}$	NA
x	0	0	0	0	
y	0	0	0	0	
z	0.75472(6)	0.75338(5)	0.75349(4)	0.75359(4)	
U_{eq}	0.0128(5)	0.0137(3)	0.0112(3)	0.0111(3)	
O(IIA)	$O_{0.57(4)}$	$O_{0.66(5)}$	NA	NA	NA
x	–0.0230(7)	–0.0254(5)			
y	0.1290(4)	0.1266(4)			
z	0.7409(3)	0.7394(2)			
U_{eq}	0.0111(12)	0.0115(9)			
Ca(IIA')	$Ca_{0.181(8)}$	$Ca_{0.061(12)}$	$Ca_{0.060(12)}$	$Ca_{0.036(8)}$	$Ca_{0.443(5)}$
x	0	0	0	0	0
y	0	0	0	0	0
z	0.8111(4)	0.804(4)	0.785(4)	0.794(3)	0.81260(5)
U_{eq}	0.038(3)	0.16(5)	0.21(7)	0.09(5)	0.0147(1)
P(A')	$P_{0.275(7)}$	$P_{0.039(6)}$	$P_{0.057(5)}$	$P_{0.074(5)}$	$P_{0.964(6)}$
x	0	0	0	0	0
y	0	0	0	0	0
z	0.73290(11)	0.7306(6)	0.7305(3)	0.7308(3)	0.73451(4)
U_{eq}	0.0048(11)	0.000(6)	0.001(4)	0.002(3)	0.0092(3)
O(IA')	$O_{0.307(14)}$	$O_{0.110(16)}$	$O_{0.130(14)}$	$O_{0.169(14)}$	$O_{1.00}$
x	0	0	0	0	0
y	0	0	0	0	0
z	0.6923(3)	0.6900(10)	0.6889(11)	0.6889(7)	0.69336(8)
U_{eq}	0.011(3)	0.035(10)	0.049(10)	0.048(7)	0.0169(4)
O(IIA')	$O_{0.43(4)}$	$O_{0.34(5)}$	$O_{1.00}$	$O_{0.76(8)}$	$O_{1.00}$
x	–0.0068(10)	–0.0111(12)	–0.02053(14)	–0.0200(3)	–0.00408(16)
y	0.1359(6)	0.1350(8)	0.12951(13)	0.1305(3)	0.13809(13)
z	0.7484(4)	0.7463(5)	0.74144(4)	0.74108(17)	0.74822(5)
U_{eq}	0.0115(15)	0.0138(16)	0.0172(2)	0.0105(18)	0.0224(2)

we list the atom parameters, and in Table 3 we present selected interatomic distances. Table 4[1] contains observed and calculated structure factors for the five structures presented herein.

Chemistry

Natural whitlockite from the Palermo and Tip Top pegmatites has been well analyzed, and the results of those analyses are presented in Table 5. Analytical details and the results of the chemical analysis of the synthetic phase are also contained in that table.

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[1] Deposit item AM-08-039, Table 4 (observed and calculated structure factors for whitlockite and merrillite samples). 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. Selected interatomic distances in natural and synthetic whitlockite and synthetic merrillite specimens (Å)

		Palermo	Tip Top	Syn STP	Syn 500	Syn 1050
Mg-	O(IIB5) × 3	2.075(2)	2.052(2)	2.066(1)	2.069(1)	2.078(1)
	O(IIB6) × 3	2.104(2)	2.087(2)	2.102(1)	2.107(1)	2.097(1)
Mean		2.090	2.070	2.084	2.088	2.088
CaIB-	O(IIB2)	2.380(2)	2.378(1)	2.379(1)	2.380(1)	2.383(1)
	O(IIB3)	2.389(2)	2.380(1)	2.376(1)	2.376(1)	2.414(1)
	O(IIB1)	2.435(2)	2.388(1)	2.391(1)	2.394(1)	2.505(1)
	O(IB2)	2.456(2)	2.457(1)	2.471(1)	2.473(1)	2.483(1)
	O(IB1)	2.582(2)	2.532(2)	2.531(1)	2.536(1)	2.615(2)
	O(IB2)	2.524(2)	2.535(1)	2.548(1)	2.551(1)	2.554(1)
	O(IIB4)	2.657(2)	2.668(1)	2.658(1)	2.654(1)	2.617(1)
	O(IIA)	2.853(11)	2.856(9)	NA	NA	NA
	O(II')	NA	NA	2.958(1)	2.948(6)	3.063(1)
Mean		2.535	2.524	2.539	2.539	2.579
CaIIB1-	O(IIB4)	2.313(2)	2.312(1)	2.316(1)	2.317(1)	2.320(1)
	O(IB2)	2.423(2)	2.440(2)	2.444(1)	2.444(1)	2.366(1)
	O(IIB5)	2.465(2)	2.456(1)	2.454(1)	2.482(1)	2.476(1)
	O(IIB2)	2.455(2)	2.461(1)	2.457(1)	2.457(1)	2.467(1)
	O(IIB5)	2.489(2)	2.486(1)	2.481(1)	2.482(1)	2.498(1)
	O(IIA)	2.490(4)	2.489(3)	NA	NA	NA
	O(IIA')	NA	NA	2.464(1)	2.454(4)	2.443(1)
	O(IIB3)	2.505(2)	2.512(1)	2.517(1)	2.519(1)	2.481(1)
	O(IIB1)	2.786(2)	2.752(1)	2.760(1)	2.762(1)	2.828(1)
Mean		2.491	2.489	2.487	2.490	2.485
CaIIB2-	O(IB1)	2.391(2)	2.371(1)	2.372(1)	2.374(1)	2.434(1)
	O(IIB3)	2.370(1)	2.372(1)	2.372(1)	2.372(1)	2.373(1)
	O(IIA)	2.378(3)	2.397(3)	NA	NA	NA
	O(IIA')	NA	NA	2.383(1)	2.385(3)	2.363(1)
	O(IIB6)	2.431(2)	2.440(1)	2.443(1)	2.443(1)	2.420(1)
	O(IIB1)	2.447(2)	2.465(1)	2.464(1)	2.463(1)	2.444(1)
	O(IIB6)	2.450(2)	2.468(1)	2.470(1)	2.470(1)	2.439(1)
	O(IIB4)	2.654(2)	2.627(1)	2.631(1)	2.634(1)	2.686(1)
	O(IIB2)	2.649(2)	2.644(1)	2.647(1)	2.648(1)	2.631(1)
Mean		2.471	2.473	2.473	2.474	2.474
P(B1)-	O(IIB1)	1.523(2)	1.527(1)	1.528(1)	1.529(1)	1.531(1)
	O(IB1)	1.537(2)	1.532(1)	1.529(1)	1.530(1)	1.535(1)
	O(IIB3)	1.538(2)	1.537(1)	1.540(1)	1.539(1)	1.543(1)
	O(IIB5)	1.551(2)	1.552(1)	1.556(1)	1.555(1)	1.552(1)
Mean		1.537	1.537	1.538	1.538	1.540
P(B2)-	O(IIB4)	1.526(2)	1.524(1)	1.523(1)	1.523(1)	1.528(1)
	O(IIB2)	1.537(2)	1.536(1)	1.538(1)	1.537(1)	1.538(1)
	O(IIB6)	1.549(2)	1.544(1)	1.544(1)	1.543(1)	1.544(1)
	O(IB2)	1.543(2)	1.545(2)	1.547(1)	1.546(1)	1.531(1)
Mean		1.539	1.537	1.538	1.537	1.535
P(A')-	O(IA')	1.505(11)	1.51(4)	1.55(4)	1.56(3)	1.527(3)
	O(IIA')	1.555(6)	1.57(1)	1.514(4)	1.515(4)	1.537(1)
	O(IIA')	1.555(6)	1.57(1)	1.514(4)	1.515(4)	1.537(1)
	O(IIA')	1.555(6)	1.57(1)	1.514(4)	1.515(4)	1.537(1)
Mean		1.542	1.555	1.523	1.526	1.534
Ca(IIA')-	O(IB1)	2.541(4)	2.64(4)	2.94(8)	2.78(5)	2.455(2)
	O(IB1)	2.541(4)	2.64(4)	2.94(8)	2.78(5)	2.455(2)
	O(IB1)	2.541(4)	2.64(4)	2.94(8)	2.78(5)	2.455(2)
	O(IIA')	2.738(17)	2.59(11)	2.17(11)	2.46(1)	2.795(2)
	O(IIA')	2.738(17)	2.59(11)	2.17(11)	2.46(1)	2.795(2)
	O(IIA')	2.738(17)	2.59(11)	2.17(11)	2.46(1)	2.795(2)
Mean		2.640	2.615	2.555	2.620	2.625
P(A)-	O(IA)	1.583(10)	1.582(5)	1.575(4)	1.577(5)	NA
	O(IIA)	1.557(5)	1.549(4)	NA	NA	NA
	O(IIA)	1.557(5)	1.549(4)	NA	NA	NA
	O(IIA)	1.557(5)	1.549(4)	NA	NA	NA
	O(IIA')	NA	NA	1.526(1)	1.538(4)	NA
	O(IIA')	NA	NA	1.526(1)	1.538(4)	NA
	O(IIA')	NA	NA	1.526(1)	1.538(4)	NA
Mean		1.564	1.557	1.538	1.548	NA

TABLE 5. Chemical analyses of whitlockite and merrillite

	Tip Top*	Palermo†	Ideal whitlockite‡	Ca-substituted merrillite§	Synthetic whitlockite‖
P_2O_5	46.0	45.81	47.28	46.44	46.3
SiO_2	<0.02	–			
Al_2O_3	<0.01	–			0.21
FeO	<0.06	2.13			0.75
MnO	<0.06	0.38			
MgO	3.61	2.22	3.84	3.77	2.59
CaO	46.6	46.87	48.03	49.80	48.3
SrO	0.31	–			
Na_2O	0.46	–			
H_2O	0.84	0.57	0.86		0.84
Y_2O_3	<0.05	–			
Ce_2O_3	<0.09	–			
SO_3	0.07	–			
F	0.43	–			
Total	98.4	98.95			
–O = F	0.18				
Rem.	–	0.93			
Total	98.2	99.88	100.01	100.01	99.0

* Formula on the basis of $(P_{14}O_{56})$; H_2O was calculated as 2.0. Formula: $(Ca_{17.8}Sr_{0.06}Na_{0.3})_{\Sigma 18.16}Mg_{1.9}(PO_4)_{12}[PO_3(OH)]_2$. Analyses were done on a polished mount with a JEOL 733 electron microprobe at 15 keV and 20 nA, using *Probe for Windows* data reduction; F was analyzed using a TAP crystal; for Y and Ce, $L\alpha$ lines were measured, for all others, $K\alpha$.

† Average of two analyses (analyses 2, 3) from Palache et al. (1957, p. 685). Water was analyzed in both analyses. Formula: $Ca_{18.13}(Mg_{1.20}Fe^{2+}_{0.64}Fe^{3+}_{0.13}Mn_{0.18})_{\Sigma 2.15}(PO_4)_{12.62}[PO_3(OH)]_{1.38}$.

‡ Ideal whitlockite, $Ca_{18}Mg_2(PO_4)_{12}[PO_3(OH)]_2$.

§ Ideal Ca-substituted merrillite, $Ca_{19}(Mg)_2(PO_4)_{14}$.

‖ Average of six analyses of synthetic whitlockite. H_2O calculated from ideal formula, metals by electron microprobe. Formula: $Ca_{18.44}(Mg_{1.37}Fe_{0.23}Al_{0.09})(PO_4,PO_3OH)_{13.98}$. Analyses were done on an unpolished crystal face with a JEOL 8200 electron microprobe operating at 15 keV and 25 nA using *Probe for Windows* data reduction; F was analyzed using an LDE1 crystal, and volatile-element corrections were made for Na and F.

RESULTS AND DISCUSSION

As noted previously, earlier studies suggested that whitlockite occurred in terrestrial and extraterrestrial samples. However, the determination of essential hydrogen in the terrestrial samples, an element generally absent in extraterrestrial samples, demonstrated that the extraterrestrial phase must differ chemically, and presumably structurally, from terrestrial whitlockite. The gross atomic arrangements of whitlockite and merrillite have been previously elucidated in separate works (whitlockite: Calvo and Gopal 1975; merrillite: Dowty 1977); we here highlight the structural similarities and differences between the phases, and provide high-quality structure refinements ($R_1 < 0.019$) of both natural and synthetic whitlockite and synthetic merrillite.

Common structural components of whitlockite and merrillite

Using a lunar sample of the phase that was collected and returned to Earth (an Apollo 14 sample), Hughes et al. (2006) described the merrillite atomic arrangement by elucidating the structural unit and the interstitial complex (Hawthorne 1983). In both whitlockite and merrillite, the structural unit (the anionic portion of the atomic arrangement) consists of a $[(Mg,Fe)(PO_4)_6]_2^{16-}$ anionic unit that yields a "bracelet-and-pinwheel" arrangement (Moore 1973). Moore defines 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 phosphate tetrahedra form a pinwheel, and in whitlockite and merrillite the pinwheels are not polymerized. Moore described bracelet-and-pinwheel structures in calcium orthosilicate and alkali sulfate structures, and Hughes et al. (1987) have described similar structural units in a vanadate structure. The array of the structural units projected down *c* is depicted in Figure 1 of Hughes et al. (2006), which also highlights the topology of a single bracelet and pinwheel. The pinwheels in whitlockite and merrillite are centered on the (Mg, Fe) octahedra at $z = 0$, 1/6, 1/3, 1/2, 2/3, and 5/6. In both whitlockite and merrillite, the structural unit consists of the (Mg, Fe) octahedral cation, phosphate tetrahedra that decorate that octahedron centered on P(B1) and P(B2), and octahedron/tetrahedron bridging oxygen atoms O(IIB5) and O(IIB6). The remaining O atoms coordinating the P(B1) and P(B2) tetrahedra [O(IIB1), O(IB1), O(IIB3) on P(B1); O(IB2), O(IIB2), O(IIB4) on P(B2)] bridge the structural unit and the interstitial complex.

The pinwheels in whitlockite and merrillite are linked by the interstitial units. In whitlockite the interstitial unit is formed of $CaIBO_8$, $CaIIB1O_8$, $CaIIB2O_8$, $Ca(IIA')O_6$, and $PA'O_4$ polyhedra [and, in whitlockite, its disordered equivalent, the $P(A)O_3(OH)$ tetrahedron]. The interstitial complexes (the cationic portion of the structure) differ slightly between whitlockite and merrillite as a result of incorporation of hydrogen in the whitlockite, as detailed below. In lunar merrillite, the interstitial complex has the formula $[Ca_{19}(PO_4)_2]^{32+}$, as the Ca(IIA') site in merrillite is half-occupied (as opposed to fully occupied with Na at that site in ideal merrillite). In whitlockite, in which hydrogen is accommodated, the interstitial unit has the formula $[Ca_{18}(PO_3[OH])_2]^{32+}$, yielding the charge-balancing relationship $H_{2(whit)} \leftrightarrow Ca_{(merr)}$. The $H_{2(whit)} \leftrightarrow Ca_{(merr)}$ substitution occurs at or near the Ca(IIA') site, as detailed below. In ideal merrillite, with Na occupying the Ca(IIA') site of Hughes et al. (2006), the charge-balancing relationship is $H_{2(whit)} \leftrightarrow Na_{2(merr)}$.

Structural components that distinguish whitlockite and merrillite

For all atoms in merrillite there are concordant atoms in whitlockite, but the converse is not true (Hughes et al. 2006). Figure 2 of Hughes et al. (2006) depicts the portion of the atomic arrangement that distinguishes whitlockite and merrillite.

As noted above, the structural units in whitlockite and merrillite are identical, but the interstitial units differ by the relationship $H_{(whit)} \leftrightarrow Ca_{0.5(merr)}$ in lunar merrillite or $H_{(whit)} \leftrightarrow Na_{(merr)}$ in ideal merrillite. Whitlockite and merrillite are perhaps the only phases in which the terrestrial and extraterrestrial "equivalents" are structurally similar, and differ only by structural adjustments that result from the accommodation of hydrogen in the terrestrial equivalent. The phases demonstrate the ability of the whitlockite/merrillite atomic arrangement to transcend extraterrestrial and terrestrial geochemical environments. The structural adjustments that allow the whitlockite/merrillite atomic arrangement to transcend those geochemical environments are illustrated by the high-quality structures described herein. Figure 2 of Hughes et al. (2006) depicts the portion of the atomic arrangement that distinguishes whitlockite from merrillite.

As noted in Table 2, there are three atoms in whitlockite that do not occur in merrillite [P(A), O(IA), and O(IIA)]. As seen in Figure 2a of Hughes et al. 2006, in merrillite the P(A') tetrahedron is occupied, and the central P atom is coordinated to 3 × O(IIA') and O(IA'). In the whitlockite component, the P(A') tetrahedron is inverted. Figure 2b of Hughes et al. (2006) displays the inverted P(A) tetrahedron, which bonds to 3 × O(IIA) and O(IA)H, the hydroxyl. The disordering of the O(IIA) and O(IIA') atoms to effect the inversion is subtle, as the two atom positions in natural whitlockite are only ~0.3Å apart. Indeed, in the synthetic phases, no disordering of the O(IIA') atoms was observed, and no O(IIA) atoms were observed. In the refinements, the concordance of the occupancies of P(A) and O(I) is reassuring, particularly as the O(I) oxygen is used to model a hydroxyl.

The inversion of the P(A') tetrahedron in merrillite to the P(A) tetrahedron in whitlockite effects the $H_{(whit)} \leftrightarrow Ca_{0.5(merr)}$ substitution in lunar merrillite. In the inverted tetrahedron in whitlockite, the P(A)-O(IA) distance is ~1.58 Å, the long P-O distance resulting from the fact that the O(IA) oxygen is a hydroxyl oxygen. The Ca(IIA') position (half-occupied) present in the merrillite configuration would be 0.54 Å distant from that O(IA) atom and thus 0.42 Å from the attendant hydroxyl H atom. The half-occupied Ca(IIA') site in the merrillite component is thus vacated for the hydroxyl hydrogen in the whitlockite component, effecting the $H_{(whit)} \leftrightarrow Ca(IIA')_{0.5(merr)}$ charge-balancing substitution. In ideal merrillite, all the (IIA') sites are filled with Na, as opposed to half-occupied by Ca in extraterrestrial merrillite.

Solid solution between whitlockite and merrillite

Solid solution occurs between whitlockite and merrillite, at least in terrestrial samples. To illustrate the solid solution, the formulas can be recast as $Ca_{18}(Mg,Fe)_2(PO_4)_{14}H_{2whit}$ and $Ca_{18}(Mg,Fe)_2(PO_4)_{14}Ca_{merr}$, illustrating the $(H \leftrightarrow Ca_{0.5})_2$ substitution that accompanies the disordering of the $P(A')O_4$ tetrahedron by inversion to create the $P(A)O_3(OH)$ tetrahedron. The formula could also be written to substitute Na for $Ca_{0.5,}$ as would occur in "ideal" merrillite. The extent of the solid solution can be measured by refining occupancy of the P(A) and P(A') atoms with the constraint that P(A) + P(A') = 1, with the fractional component of P(A) indicating the whitlockite component and the fractional component of P(A') indicating the merrillite component. In the natural structures reported herein, the Tip Top sample is of the composition $Whit_{0.725(7)}Merr_{0.275}$, and the Palermo sample is of composition $Whit_{0.961(6)}Merr_{0.039}$. In the synthetic sample, at STP the sample is of composition $Whit_{0.946(5)}Merr_{0.054}$. Although extraterrestrial samples of the solid solution that are typically devoid of hydrogen are necessarily of composition $Merr_{100}$ (as found in the lunar sample of Hughes et al. 2006), the two samples of terrestrial origin analyzed herein suggest that solid solution in terrestrial phases is common.

Dehydrogenation of whitlockite to form merrillite

Gopal and Calvo (1972) examined the structural relationships of whitlockite and β-$Ca_3(PO_4)_2$ 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 hydrogen, and thus the reorientation of the $P(A)O(IIA)_3O(IA)H$ phosphate tetrahedron was no longer necessary to accommodate H in the atomic arrangement. It is not clear from their description, however, what elements are present as the charge-balancing substituents to balance the evolution of hydrogen.

To document the structural response to the dehydrogenation of whitlockite and address the source of the charge-balancing Ca, we subjected synthetic whitlockite to heating experiments. As the exchange reaction between whitlockite and merrillite is H ↔ $Ca_{0.5}$, mere heating of whitlockite in the absence of substituent cations would not necessarily lead to the completion of the reaction, as the presence of substituent Ca to occupy the CaIIA' site is necessary to effect the reaction. However, we found that heating of synthetic whitlockite at 1050 °C for 24 h yielded the dehydrogenation of whitlockite to form merrillite, the hydrogen-free phase. Examination of the whitlockite synthesized by the procedures outlined above, however, showed that there were entrained reagents in the synthesized crystals (Fig. 1); the results of the crystal structure refinements demonstrate that reagents entrained in the synthetic whitlockite crystals yielded Ca sufficient to balance the evolution of hydrogen from synthetic whitlockite, and thus the merrillite end-member is obtained upon dehydrogenation. The atomic arrangement of the merrillite obtained from the dehydrogenation of whitlockite is detailed herein. The charge-balancing mechanism of the whitlockite ↔ merrillite dehydrogenation experiments of Gopal and Calvo (1972) remains unclear.

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