Appendix A

Supplemental Information for paper titled Synthesis and characterization of the Mars-relevant phosphate minerals Fe- and Mg-whitlockite and merrillite and a possible mechanism that maintains charge balance during whitlockite to merrillite transformation. Christopher T. Adcock*, Elisabeth M. Hausrath, Paul M. Forster, Oliver Tschauner, and Kirellos J. Sefein.

Effects of parameter variation during whitlockite synthesis.

In order to synthesize Mg-whitlockite, the Hughes et al. (2008) experiment was replicated, but Mg^{2+} was intentionally supplied to the system in the form of magnesium nitrate hexahydrate ($Mg(NO_3)_2·6H_2O$) (J. T. Baker, ACS grade). To simplify the method, 40 mesh reagent grade calcium hydroxyapatite (HAP) powder (Spectrum, reagent grade) was used rather than pre-synthesizing this phase. The ratio of HAP to magnesium nitrate hexahydrate by mass was generally 3.33: 1 to provide sufficient Mg^{2+} based on whitlockite stoichiometry, but not excess Mg^{2+} that might lead to the formation of additional Mg phases. Variables during the preliminary experiments included incubation time at 240 °C (5-14 days), adjusted pH (2.1 to 2.8), and the total concentration of solids used in the experiments (6.7 to 90 g/L). Early experiments were run in 23 ml Teflon lined acid digestion vessels (Parr 4749) and later scaled up to 125 ml vessels (Parr 4748). Preliminary experiments were carried out with the goal of first producing Mg-whitlockite crystals, and then refining the synthesis method for phase purity, larger crystal size, and sufficient output mass to carry out crystallographic and chemical characterization as well as supply Mg-whitlockite for use in the synthesis of Mg-merrillite.

Insight gained during synthesis of Mg-whitlockite was used to develop a procedure for Fe-whitlockite synthesis. Initially, $FeCl_2$ was used as a source of Fe^{2+} in place of the $Mg(NO_3)_2·6H_2O$ used in Mg-whitlockite synthesis. After experiments using $FeCl_2$ failed to produce significant whitlockite, Fe(II)S was utilized as the Fe^{2+} source and whitlockite crystals were produced along with hydroxyapatite and opaque phases (presumably Fe phases). Variables during the preliminary experiments included incubation time at 240 °C (5-9 days), and total concentration of solids (9.0 to 17.8 g/L). In addition, the production of iron sulfide phases prompted varying the ratio of HAP to Fe(II)S from 9.6:1 (near stoichiometric ideal) to 28.6:1 by mass to limit their formation. The pH value was not significantly varied from 2.8 as results from Mg-whitlockite synthesis indicated it had no effect.

Although endmember whitlockite and merrillite are useful for different studies, natural whitlockite and merrillite generally contain both Mg^{2+} and Fe^{2+}. We therefore applied the results of endmember synthesis experiments to synthesize non-endmember whitlockites and from them mixed Fe/Mg-merrillite. Variables included the ratio of Mg and Fe, as well as the concentration of total solids in solution (10.2 to 17.8 g/L). Sodium (as NaCl) was also included in some experiments. Though sodium is not typical within terrestrial whitlockite, it is present in most natural merrillite, particularly martian merrillite, in what is a partially filled calcium site in synthetic merrillite (Jolliff et al., 2006). The methods documented in the accompanying paper are those which successfully produced the material characterized and used for mixed Fe/Mg-merrillite synthesis in this study and include sodium (as NaCl), however, sodium was not incorporated into the whitlockite structure in any of multiple attempts. Additional experiments showed sodium to neither inhibit nor aid the production of mixed Mg/Fe-whitlockite. Deposited Table A1 contains parameter values for all whitlockite synthesis experiments in this study, including those used to make mixed Fe/Mg-whitlockite and subsequent Fe/Mg-merrillite.

Table A1. Batch parameters for whitlockite synthesis experiments. For paper titled Synthesis and characterization of the Mars-relevant phosphate minerals Fe- and Mg-whitlockite and merrillite and a possible mechanism that maintains charge balance during whitlockite to merrillite transformation. Christopher T. Adcock*, Elisabeth M. Hausrath, Paul M. Forster, Oliver Tschauner and Kirellos J. Sefein.

ID	Vessel Size	$MgNO_3 \cdot 6H_2O$ (g)	$FeCl_2$ (g)	FeS (g)	NaCl (g)	HAP (g)	Mass Tot (g)	DI (mL)	g/L*	pH start	Days	pH end	Mass Out (g)	Note
Mg-1	23 ml	0.0153				0.0518	0.0671	10	6.7	2.70	5	-	-	Whit.
Mg-2	23 ml	0.2210				0.7716	0.9926	11	90.2	2.78	5	-	-	Monetite
Mg-3	23 ml	0.0159				0.0519	0.0678	10	6.8	2.66	10	2.80	0.016	Whit.
Mg-4	23 ml	0.0461				0.1541	0.2002	10	20.0	2.69	11	2.80	0.113	Whit.
Mg-5	23 ml	0.1093				0.3630	0.4723	13.5	35.0	2.81	14	2.16	0.189	Monetite
Mg-6	23 ml	0.2190				0.7280	0.9470	13.5	70.1	2.80	14	1.92	0.607	Monetite
Mg-7	125 ml	0.4599				1.5432	2.0031	90	22.3	2.80	7	2.09	1.150	Monetite
Mg-8	125 ml	0.4588				1.5423	2.0011	90	22.2	2.78	6	1.85	1.320	Monetite
Mg-9	125 ml	0.4595				1.5452	2.0047	90	22.3	2.80	5	1.86	1.370	Monetite
Mg-10	125 ml	0.4601				1.5426	2.0027	90	22.3	2.77	5	1.85	1.300	Monetite
Mg-11	125 ml	0.4595				1.5423	2.0018	90	22.2	2.80	5	1.90	1.220	Monetite
Mg-12	125 ml	0.2298				0.7709	1.0007	90	11.1	2.70	7	2.10	0.240	Whit.
Mg-13	125 ml	0.3890				1.2813	1.6703	90	18.6	2.79	5	2.01	0.834	Crypto-xtal mix
Mg-14	23 ml	0.0158				0.0512	0.0670	10	6.7	2.10	7	1.85	0.030	Whit.
Mg-15	23 ml	0.2006				0.0000	0.2006	10	20.1	2.70	5	2.12	0.125	Whit.
Mg-16	125 ml	0.3004				1.0014	1.3018	90	14.5	2.77	7	1.70	1.131	Whit.
Mg-17	125 ml	0.3000				1.0000	1.3000	90	14.4	2.76	7	1.84	0.899	Whit.
Mg-18	125 ml	0.3000				1.0000	1.3000	90	14.4	2.74	7	-	-	Whit.
Mg-19	125 ml	0.3000				1.0000	1.3000	90	14.4	2.78	7	-	-	Whit.
Mg-22	125 ml	0.3004				1.0000	1.3004	90	14.4	2.72	7	1.78	0.800	Whit.
Mg-23	125 ml	0.3000				1.0070	1.3070	90	14.5	2.79	7	2.10	0.555	Whit.
Mg-24	125 ml	0.3000				1.0000	1.3000	80	16.3	2.74	7	2.11	0.588	Leaked/Failed

Mg-25	125 ml	0.3004	1.0007	1.3011	90	14.5	2.73	7	1.97	0.510	Whit.
Mg-26	125 ml	0.3005	1.0011	1.3016	90	14.5	2.70	7	1.98	0.480	Whit.
Mg-27	125 ml	0.3003	1.0010	1.3013	90	14.5	2.79	7	1.81	0.720	Whit.
Mg-28	125 ml	0.3000	1.0000	1.3000	90	14.4	2.78	7	1.88	0.699	Whit.
Mg-29	125 ml	0.3000	1.0000	1.3000	90	14.4	2.65	7	1.74	0.702	Whit.
Mg-31	125 ml	0.3026	1.0004	1.3030	90	14.5	2.65	12	1.76	0.810	Whit.
Mg-32	125 ml	0.3016	1.0006	1.3022	90	14.5	2.69	12	1.77	0.710	Whit.
Mg-33	125 ml	0.2997	1.0012	1.3009	90	14.5	2.71	12	1.72	0.730	Whit.
Mg-34	125 ml	0.2994	0.9996	1.299	90	14.4	2.74	6	1.78	0.770	Whit.
Mg-35	125 ml	0.3013	0.9998	1.3011	90	14.5	2.80	6	1.75	0.720	Whit.
Mg-36	125 ml	0.2997	1.0009	1.3006	90	14.5	2.75	6	1.74	0.810	Whit.
Mg-37	125 ml	0.3004	1.0005	1.3009	90	14.5	2.68	7	1.89	0.730	Whit.
Mg-38	125 ml	0.3002	1.0001	1.3003	90	14.4	2.72	7	1.82	0.700	Whit.
Mg-39	125 ml	0.3003	1.0001	1.3004	90	14.4	2.40	7	1.78	0.760	Whit.
Mg-40	125 ml	0.3004	1.0004	1.3008	90	14.5	2.74	8	1.89	0.665	Whit.
Mg-41	125 ml	0.2994	0.9999	1.2993	90	14.4	2.78	8	1.82	0.706	Whit.
Mg-42	125 ml	0.3008	1.0002	1.301	90	14.5	2.75	8	1.78	0.825	Whit.
Mg-44	125 ml	0.3002	1.0012	1.3014	90	14.5	2.73	7	-	0.632	Whit.
Mg-45	125 ml	0.3003	1.0008	1.3011	90	14.5	2.76	7	1.83	0.676	Whit.
Mg-46	125 ml	0.3005	1.0005	1.3010	90	14.5	2.74	7	1.77	0.775	Whit.
Mg-47	125 ml	0.2998	1.0003	1.3001	90	14.4	2.74	7	1.77	0.723	Whit.
Mg-48	125 ml	0.2998	1.0005	1.3003	90	14.4	2.76	7	1.76	0.726	Whit.
Mg-49	125	0.2990	1.0000	1.2990	90	14.4	2.75	7	1.69	0.813	Whit.

	ml												
Mg-50	125 ml	0.3002			1.0001	1.3003	90	14.4	2.66	8	1.80	0.627	Whit.
Mg-51	125 ml	0.3003			1.0001	1.3004	90	14.4	2.73	8	1.73	0.734	Whit.
Mg-52	125 ml	0.3001			1.0000	1.3001	90	14.4	2.75	8	1.68	0.776	Whit.
Mg-53	125 ml	0.3008			1.0000	1.3008	90	14.5	2.66	6	1.84	0.594	Whit.
Mg-54	125 ml	0.3009			1.0003	1.3012	90	14.5	2.79	6	1.75	0.690	Whit.
Mg-55	125 ml	0.3412			1.0006	1.3418	90	14.9	2.76	6	1.74	0.715	Whit.
Mg-56	125 ml	0.3003			0.9994	1.2997	90	14.4	2.69	7	1.85	0.702	Whit.
Mg-57	125 ml	0.3002			0.9995	1.2997	90	14.4	2.76	7	1.74	0.715	Whit.
Mg-58	125 ml	0.2999			1.0003	1.3002	90	14.4	2.74	7	1.70	0.734	Whit.
Mg-59	125 ml	0.3002			0.9998	1.3000	90	14.4	2.77	7	1.83	0.460	Whit.
Mg-60	125 ml	0.2998			0.9998	1.2996	90	14.4	2.74	7	1.85	0.437	Whit.
Mg-61	125 ml	0.3003			1.0012	1.3015	90	14.5	2.74	7	1.83	0.566	Whit.
Fe-1	23 ml		0.0287		0.2307	0.2594	16	16.2	2.68	9	2.26	0.148	No Whit.
Fe-2	23 ml		0.0290		0.2311	0.2601	16	16.3	2.77	9	2.20	0.143	No Whit.
Fe-3	23 ml	0.0356	0.0173		0.2312	0.2841	16	17.8	2.74	8	2.11	0.114	No Whit.
Fe-4	23 ml	0.0357		0.0129	0.2311	0.2797	16	17.5	2.77	8	2.00	0.173	minor Whit.
Fe-5	23 ml			0.0249	0.2334	0.2583	16	16.1	2.75	8	1.80	-	aggregates Whit.
Fe-6	23 ml			0.0183	0.1739	0.1922	16	12.0	2.74	8	1.80	-	Cleaner Whit
Fe-7	125 ml			0.0763	0.7300	0.8063	90	9.0	2.76	7	2.06	0.427	Fe-Whit.
Fe-8	125 ml			0.0769	1.0012	1.0781	90	12.0	2.77	7	2.10	0.520	Fe-Whit.
Fe-9	125 ml			0.0600	0.9994	1.0594	90	11.8	2.78	7	2.05	0.630	Fe-Whit.
Fe-10	125 ml			0.0500	1.0001	1.0501	90	11.7	2.77	7	2.17	0.520	Fe-whit+agg.
Fe-11	125 ml			0.0347	1.0009	1.0356	90	11.5	2.78	7	1.87	0.500	
Fe-12	125			0.0392	1.0000	1.0392	90	11.5	2.69	7	1.96	0.471	Lg xtals Fe-

	ml													whit.
Fe-13	125 ml			0.0450		1.0000	1.0450	90	11.6	2.74	7	1.87	0.785	Lg xtals Fe-whit.
Fe-14	125 ml			0.0767		1.0008	1.0775	90	12.0	2.75	7	1.90	0.731	Fe-whit+agg.
Fe-15	125 ml			0.1003		1.0004	1.1007	90	12.2	2.72	7	1.92	0.846	Fe-Whit.
Fe-16	125 ml			0.0349		0.9999	1.0348	90	11.5	2.69	7	1.89	0.609	Fe-Whit.
Fe-17	125 ml		0.0800			1.0003	1.0803	90	12.0	2.75	7	1.94	0.451	No-Whit.
Fe-18	125 ml			0.0849		1.1003	1.1852	90	13.2	2.75	7	1.89	0.726	Fe-Whit.
Fe-19	125 ml			0.1101		1.2004	1.3105	90	14.6	2.68	7	1.97	0.845	Fe-whit+agg.
Fe-20	125 ml			0.0549		1.0004	1.0553	90	11.7	2.76	7	1.95	0.419	Fe-Whit.
Fe-21	125 ml			0.0558		1.0001	1.0559	90	11.7	2.69	7	1.92	0.452	Fe-Whit.
Fe-22	125 ml			0.0544		1.0004	1.0548	90	11.7	2.71	7	1.96	0.444	Fe-Whit.
Mix-1	125ml	0.0500		0.0500	0.0667	1.0000	1.1667	90	13.0	2.64	7	2.05	0.761	Whit.
Mix-2	125ml	0.1000		0.0500		1.0000	1.1500	90	12.8	2.73	7	2.15	0.694	Whit.
Mix-3	125ml	0.1000			0.1000	1.0000	1.2000	90	13.3	2.78	7	-	-	No Whit.
Mix-4	125ml	0.1000		0.0495		0.9997	1.1492	90	12.8	2.78	7	2.2	0.688	No Whit. (HAP)
Mix-5	125ml	0.1103		0.0403		1.0000	1.1506	90	12.8	2.70	7	2.01	0.821	No Whit. (HAP)
Mix-6	125ml	0.1207		0.0305		1.0005	1.1517	90	12.8	2.78	7	2.27	0.591	Rare Whit.
Mix-7	125 ml	0.0505		0.0499	0.0668	1.0000	1.1672	90	13.0	2.75	7	1.8	0.811	Whit.
Mix-8	125 ml	0.0505		0.0499		1.0005	1.1009	90	12.2	2.74	7	1.84	0.915	Whit.
Mix-9	125 ml	0.1505		0.0500		1.2000	1.4005	90	15.6	2.78	7	2.1	0.974	No Whit.
Mix-10	125 ml	0.1000		0.0500		1.0000	1.1500	90	12.8	2.72	7	2.05	0.700	Rare Whit.
Mix-11	125 ml	0.0800		0.0400		0.8000	0.9200	90	10.2	2.78	7	2.04	0.550	Rare Whit.
Mix-12	125 ml	0.0900		0.0300		0.8000	0.9200	90	10.2	2.78	7	2.02	-	Minor Whit.
Mix-13	125 ml	0.0500		0.0501		1.0002	1.1003	90	12.2	2.75	7	1.89	0.799	Whit. (lg)
Mix-	125	0.0399		0.0601		0.9999	1.0999	90	12.2	2.78	7	-	0.765	Whit.

14	ml												
Mix-15	125 ml	0.0600	0.0400		1.0000	1.1000	90	12.2	2.77	7	2.04	0.707	Whit.
Mix-16	125 ml	0.0501	0.0500	0.0601	1.0001	1.1603	90	12.9	2.77	7	1.99	0.785	Whit. well fm.
Mix-17	125 ml	0.0251	0.0501		0.9000	0.9752	90	10.8	2.76	7	-	0.556	Whit.
Mix-18	125 ml	0.0300	0.0700		1.0000	1.1000	90	12.2	2.77	7	2.01	0.644	Whit.
Mix-19	125 ml	0.0351	0.0501		1.0001	1.0853	90	12.1	2.77	7	1.98	0.689	Whit.
Mix-20	125 ml	0.0350	0.0502		1.0000	1.0852	90	12.1	2.78	7	1.96	0.674	A.W./Whit.
Mix-21	125 ml	0.0901	0.0302		0.9002	1.0205	90	11.3	2.78	7	2.2	0.470	Rare Whit.

Vessel Size = the volume of the Teflon lines Parr reaction vessel used. All chemistry weights are in grams. Mass Tot = Total mass of solids in grams used in the experiment. DI = volume of 18 MΩ water used in experiment. g/L = ratio of total mass of solids (g) in solution (L). pH Start = the adjusted pH at the start of the experiment. Days = number of days of incubation. pH end = measured pH at end of experiment. Mass Out = total mass (g)of material recovered after experiment including impurities. Abbreviations in notes: Whit.=whitlockite, agg. = polycrystalline aggregates, lg = large, HAP = hydroxyapatite, well fm. = well formed crystals. Crypto-xtal mix = mix of microcrystalline phases. A.W. = reaction vessel underwent additional cleaning including additional acid washing to investigate any affect on nucleation.

Table A2. Microprobe analyses of Mg/Fe-whitlockite synthesized with varied Fe: Mg ratios. For paper titled Synthesis and characterization of the Mars-relevant phosphate minerals Fe- and Mg-whitlockite and merrillite and a possible mechanism that maintains charge balance during whitlockite to merrillite transformation. Christopher T. Adcock*, Elisabeth M. Hausrath, Paul M. Forster, Oliver Tschauner and Kirellos J. Sefein.

	Mg/Fe-Whitlockite Synthesis Experiment ID					
	Mix-6		***Mix-21***		***Mix-1***	
CaO	48.40	(0.26)	47.73	(1.31)	46.54	(0.59)
P_2O_5	45.83	(0.28)	45.59	(0.92)	45.83	(0.36)
MgO	3.43	(0.32)	2.63	(0.05)	1	(0.20)
FeO	0.18	(0.24)	1.92	(2.51)	4.62	(0.71)
Na_2O	B.D.	-	B.D.	-	B.D.	-
H_2O^a	0.86	-	0.86	-	0.86	-
Total	98.69	(0.42)	98.73	(0.79)	98.85	(0.49)
n	11		7		18	
Stoic.	$Ca_{9.2}Fe_{0.0}Mg_{0.9}(PO_3OH)(PO_4)_{5.9}$		$Ca_{9.1}Fe_{0.3}Mg_{0.7}(PO_3OH)(PO_4)_{5.9}$		$Ca_{9.0}Fe_{0.7}Mg_{0.3}(PO_3OH)(PO_4)_6$	

Fe:Mg Soln.[b]	0.74	0.98	2.91
Fe:Mg Prod.[c]	0.00	0.43	2.33

Parenthetical values are 1 standard deviation. n = number of analyses averaged chemistry is based on. B.D. = below detection.
[a]*H_2O is based on ideal whitlockite (Hughes et al., 2008) and is included in these EMP totals.*
[b]*The molar ratio of Fe: Mg added to the solution of the experiment.*
[c]*The molar ratio of Fe: Mg in the stoichiometry of the resulting whitlockite.*

Table A3. Atomic parameters for synthesized whitlockite and merrillite. For paper titled Synthesis and characterization of the Mars-relevant phosphate minerals Fe- and Mg-whitlockite and merrillite and a possible mechanism that maintains charge balance during whitlockite to merrillite transformation. Christopher T. Adcock*, Elisabeth M. Hausrath, Paul M. Forster, Oliver Tschauner and Kirellos J. Sefein.

Atom	Fe-whitlockite	Fe/Mg-whitlockite	Ferric Fe-merrillite (Pt cruc.)	Ferrous Fe-merrillite (SiO_2 tube)	Ferric Fe/Mg-merrillite (Pt cruc.)	Ferrous Fe/Mg-merrillite (SiO_2 tube)
Fe(1)	$Fe_{1.00}$	$Fe_{0.637}$	$Fe_{1.00}$	$Fe_{1.00}$	$Fe_{0.754}$	$Fe_{0.646}$
x	0.6667	0.6667	0.6667	0.6667	0.6667	0.6667
y	0.3333	0.3333	0.3333	0.3333	0.3333	0.3333
z	0.1137(1)	0.1138(1)	0.1151(1)	0.1142(1)	0.1149(1)	0.1150(1)
U(eq)	0.008(1)	0.003(1)	0.005(1)	0.006(1)	0.002(1)	0.004(1)
Mg(1)		$Mg_{0.363}$			$Mg_{0.246}$	$Mg_{0.354}$
x	NA	0.6667	NA	NA	0.6667	0.6667
y	NA	0.3333	NA	NA	0.3333	0.3333
z	NA	0.1138(1)	NA	NA	0.1149(1)	0.1150(1)
U(eq)	NA	0.002	NA	NA	0.002	0.004
Ca(1)	$Ca_{1.00}$	$Ca_{1.00}$	$Ca_{1.00}$	$Ca_{1.00}$	$Ca_{1.00}$	$Ca_{1.00}$
x	0.7191(1)	0.7192(1)	0.7224(1)	0.7245(1)	0.7226(1)	0.7239(1)
y	0.8534(1)	0.8534(1)	0.8547(1)	0.8571(1)	0.8548(1)	0.8566(1)
z	0.2150(1)	0.2150(1)	0.2140(1)	0.2133(1)	0.2140(1)	0.2144(1)
U(eq)	0.005(1)	0.004(1)	0.004(1)	0.005(1)	0.004(1)	0.005(1)
Ca(2)	$Ca_{1.00}$	$Ca_{1.00}$	$Ca_{1.00}$	$Ca_{1.00}$	$Ca_{1.00}$	$Ca_{1.00}$
x	0.5125(1)	0.5122(1)	0.5081(1)	0.5099(1)	0.5088(1)	0.5103(1)
y	0.0542(1)	0.0537(1)	0.0442(1)	0.0502(1)	0.0451(1)	0.0509(1)
z	0.1792(1)	0.1793(1)	0.1798(1)	0.1785(1)	0.1796(1)	0.1794(1)
U(eq)	0.005(1)	0.005(1)	0.004(1)	0.005(1)	0.004(1)	0.006(1)
Ca(3)	$Ca_{1.00}$	$Ca_{1.00}$	$Ca_{1.00}$	$Ca_{1.00}$	$Ca_{1.00}$	$Ca_{1.00}$
x	1.1580(1)	1.1573(1)	1.1483(1)	1.1495(1)	1.1489(1)	1.1506(1)
y	0.8643(1)	0.8646(1)	0.8714(1)	0.8731(1)	0.8709(1)	0.8717(1)
z	0.1080(1)	0.1080(1)	0.1072(1)	0.1064(1)	0.1071(1)	0.1074(1)
U(eq)	0.012(1)	0.011(1)	0.006(1)	0.015(1)	0.007(1)	0.016(1)

P(2)	$P_{1.00}$	$P_{1.00}$	$P_{1.00}$	$P_{1.00}$	$P_{1.00}$	$P_{1.00}$
x	0.4761(1)	0.4761(1)	0.4745(1)	0.4713(1)	0.4746(1)	0.4725(1)
y	-0.0162(1)	-0.0160(1)	-0.0175(1)	-0.0201(1)	-0.0174(1)	-0.0193(1)
z	0.0827(1)	0.0827(1)	0.0841(1)	0.0820(1)	0.0837(1)	0.0830(1)
U(eq)	0.005(1)	0.004(1)	0.003(1)	0.005(1)	0.003(1)	0.005(1)
P(1)	$P_{1.00}$	$P_{1.00}$	$P_{1.00}$	$P_{1.00}$	$P_{1.00}$	$P_{1.00}$
x	0.8606(1)	0.8601(1)	0.8562(1)	0.8602(1)	0.8564(1)	0.8601(1)
y	0.6848(1)	0.6841(1)	0.6761(1)	0.6794(1)	0.6767(1)	0.6798(1)
z	0.1464(1)	0.1464(1)	0.1459(1)	0.1455(1)	0.1458(1)	0.1464(1)
U(eq)	0.004(1)	0.004(1)	0.003(1)	0.004(1)	0.003(1)	0.005(1)
P(3A)	$P_{0.890}$	$P_{0.840}$	$P_{0.029}$	$P_{0.239}$	$P_{0.065}$	$P_{0.309}$
x	0.3333	0.3333	0.3333	0.3333	0.3333	0.3333
y	-0.3333	-0.3333	-0.3333	-0.3333	-0.3333	-0.3333
z	0.1934(1)	0.1934(1)	0.2178(1)	0.2138(1)	0.2170(1)	0.2146(1)
U(eq)	0.005(1)	0.005(1)	0.004(1)	0.005(1)	0.005(1)	0.006(1)
P(3B)	$P_{0.110}$	$P_{0.160}$	$P_{0.971}$	$P_{0.761}$	$P_{0.935}$	$P_{0.691}$
x	0.3333	0.3333	0.3333	0.3333	0.3333	0.3333
y	-0.3333	-0.3333	-0.3333	-0.3333	-0.3333	-0.3333
z	0.2160(2)	0.2165(1)	0.1952(13)	0.1932(2)	0.1933(5)	0.1936(1)
U(eq)	0.005	0.005	0.004	0.005	0.005	0.004(1)
O(10A)	$O_{0.890}$	$O_{0.840}$	$O_{0.029}$	$O_{0.239}$	$O_{0.065}$	$O_{0.309}$
x	0.3333	0.3333	0.3333	0.3333	0.3333	0.3333
y	-0.3333	-0.3333	-0.3333	-0.3333	-0.3333	-0.3333
z	0.1508(1)	0.1508(1)	0.2594(1)	0.2555(2)	0.2586(1)	0.1523(2)
U(eq)	0.013(1)	0.012(1)	0.006(1)	0.009(1)	0.007(1)	0.015(3)
O(10B)	$O_{0.110}$	$O_{0.160}$	$O_{0.970}$	$O_{0.761}$	$O_{0.935}$	$O_{0.691}$
x	0.3333	0.3333	0.3333	0.3333	0.3333	0.3333
y	-0.3333	-0.3333	-0.3333	-0.3333	-0.3333	-0.3333
z	0.2568(8)	0.2579(3)	0.1549(15)	0.1520(2)	0.1511(8)	0.2560(2)
U(eq)	0.013	0.004(2)	0.007	0.009	0.007	0.011(1)
O(6)	$O_{1.00}$	$O_{1.00}$	$O_{1.00}$	$O_{1.00}$	$O_{1.00}$	$O_{1.00}$
x	0.5657(2)	0.5658(1)	0.5682(2)	0.5602(3)	0.5677(2)	0.5620(2)
y	-0.0877(2)	-0.0872	-0.0826(2)	-0.0930(3)	-0.0831(2)	-909(2)
z	0.0696(1)	0.0695(1)	0.0696(1)	0.0684(1)	0.0691(1)	0.0694(1)
U(eq)	0.008(1)	0.007(1)	0.006(1)	0.016(1)	0.006(1)	0.013(1)
O(9)	$O_{1.00}$	$O_{1.00}$	$O_{1.00}$	$O_{1.00}$	$O_{1.00}$	$O_{1.00}$
x	0.3533(2)	0.3526(1)	0.3444(2)	0.3420(3)	0.3436(2)	0.3431(3)
y	-0.1832(2)	-0.1834(1)	-0.1866(2)	-0.1882(3)	-0.0187(2)	-0.1876(2)
z	0.2056(1)	0.2054(1)	0.2050(1)	0.2018(1)	0.2044(1)	0.2030(1)
U(eq)	0.009(1)	0.008(1)	0.007(1)	0.016(1)	0.009(1)	0.017(1)

O(8)	$O_{1.00}$	$O_{1.00}$	$O_{1.00}$	$O_{1.00}$	$O_{1.00}$	$O_{1.00}$
x	0.3344(2)	0.3345(1)	0.3365(2)	0.3317(3)	0.3356(2)	0.3325(2)
y	-0.0606(2)	-0.0606(1)	-0.0552(2)	-0.0575(3)	-0.0559(2)	-0.0579(2)
z	0.0604(1)	0.0604(1)	0.0606(1)	0.0594(1)	0.0605(1)	0.0604(1)
U(eq)	0.006(1)	0.005(1)	0.005(1)	0.006(1)	0.005(1)	0.006(1)
O(5)	$O_{1.00}$	$O_{1.00}$	$O_{1.00}$	$O_{1.00}$	$O_{1.00}$	$O_{1.00}$
x	0.5754(2)	0.5756(1)	0.5763(2)	0.5746(3)	0.5762(2)	0.5750(2)
y	0.1551(2)	0.1556(1)	0.1589(2)	0.1516(3)	0.1582(2)	0.1529(2)
z	0.0774(1)	0.0778(1)	0.0808(1)	0.0781(1)	0.0803(1)	0.0792(1)
U(eq)	0.007(1)	0.007(1)	0.005(1)	0.009(1)	0.004(1)	0.010(1)
O(2)	$O_{1.00}$	$O_{1.00}$	$O_{1.00}$	$O_{1.00}$	$O_{1.00}$	$O_{1.00}$
x	0.8747(2)	0.8737(1)	0.8599(2)	0.8660(3)	0.8613(2)	0.8670(2)
y	0.7381(2)	0.7360(1)	0.7100(2)	0.7168(3)	0.7119(3)	0.7198(3)
z	0.1068(1)	0.1068(1)	0.1058(1)	0.1054(1)	0.1057(1)	0.1063(1)
U(eq)	0.009(1)	0.009(1)	0.006(1)	0.010(1)	0.007(1)	0.013(1)
O(3)	$O_{1.00}$	$O_{1.00}$	$O_{1.00}$	$O_{1.00}$	$O_{1.00}$	$O_{1.00}$
x	1.0193(2)	1.0188(1)	1.0161(2)	1.0204(2)	1.0161(2)	1.0203(2)
y	0.7337(2)	0.7330(1)	0.7289(2)	0.7308(3)	0.7291(2)	0.7311(2)
z	0.1598(1)	0.1597(1)	0.1589(1)	0.1580(1)	0.1590(1)	0.1590(1)
U(eq)	0.007(1)	0.006(1)	0.006(1)	0.007(1)	0.006(1)	0.007(1)
O(1)	$O_{1.00}$	$O_{1.00}$	$O_{1.00}$	$O_{1.00}$	$O_{1.00}$	$O_{1.00}$
x	0.7795(2)	0.7792(1)	0.7803(2)	0.7857(3)	0.7800(2)	0.7846(2)
y	0.7504(2)	0.7499(1)	0.7482(2)	0.7538(3)	0.7486(2)	0.7528(2)
z	0.1674(1)	0.1672(1)	0.1665(1)	0.1657(1)	0.1663(1)	0.1667(1)
U(eq)	0.008(1)	0.007(1)	0.006(1)	0.009(1)	0.007(1)	0.009(1)
O(4)	$O_{1.00}$	$O_{1.00}$	$O_{1.00}$	$O_{1.00}$	$O_{1.00}$	$O_{1.00}$
x	0.7675(2)	0.7671(1)	0.7619(2)	0.7656(3)	0.7623(2)	0.7655(2)
y	0.5128(2)	0.5122(1)	0.5034(2)	0.5096(3)	0.5041(2)	0.5093(2)
z	0.1506(1)	0.1506(1)	0.1519(1)	0.1523(1)	0.1516(1)	0.1524(1)
U(eq)	0.007(1)	0.007(1)	0.005(1)	0.007(1)	0.005(1)	0.008(1)
O(7)	$O_{1.00}$	$O_{1.00}$	$O_{1.00}$	$O_{1.00}$	$O_{1.00}$	$O_{1.00}$
x	0.4261(2)	0.4260(1)	0.4214(2)	0.4176(3)	0.4222(3)	0.4189(2)
y	-0.0543(2)	-0.0550(1)	-0.0610(2)	-0.0657(3)	-0.0616(2)	-0.0650(3)
z	0.1219(1)	0.1219(1)	0.1227(1)	0.1208(1)	0.1224(1)	0.1218(1)
U(eq)	0.009(1)	0.008(1)	0.006(1)	0.014(1)	0.008(1)	0.0015(1)
Ca(4A)				$Ca_{0.148}$		$Ca_{0.098}$
x	NA	NA	NA	0.3333	NA	0.3333
y	NA	NA	NA	-0.3333	NA	-0.3333
z	NA	NA	NA	0.1360(1)	NA	0.1041(3)
U(eq)	NA	NA	NA	0.011(1)	NA	0.019(3)

Ca(4B)				$Ca_{0.296}$		$Ca_{0.264}$
x	NA	NA	NA	0.3333	NA	0.3333
y	NA	NA	NA	-0.3333	NA	-0.3333
z	NA	NA	NA	0.1028(3)	NA	0.1369(1)
U(eq)	NA	NA	NA	0.013(3)	NA	0.007(1)

Parenthetic values are standard deviations. Pt cruc. = merrillite produced by heating in open air in a platinum crucible. SiO_2 tube = merrillite produced in a triple argon purged and sealed silica glass tube.

Table A4. Bond lengths for synthesized whitlockite and merrillite in angstroms. For paper titled Synthesis and characterization of the Mars-relevant phosphate minerals Fe- and Mg-whitlockite and merrillite and a possible mechanism that maintains charge balance during whitlockite to merrillite transformation. Christopher T. Adcock*, Elisabeth M. Hausrath, Paul M. Forster, Oliver Tschauner and Kirellos J. Sefein.

		Fe-whitlockite	**Fe/Mg-whitlockite**	**Ferric Fe-merrillite (Pt cruc.)**	**Ferrous Fe-merrillite (SiO_2 tube)**	**Ferric Fe/Mg-merrillte (Pt cruc.)**	**Ferrous Fe/Mg-merrillite (SiO_2 tube)**
Ca(1)-	O(1)	2.3062(14)	2.3115(11)	2.308(2)	2.313(3)	2.310(2)	2.3128(19)
	O(2)#6	2.4348(17)	2.4268(13)	2.340(2)	2.386(3)	2.345(2)	2.385(2)
	O(3)#8	2.4482(15)	2.4548(11)	2.468(2)	2.456(2)	2.467(2)	2.4568(19)
	O(5)#7	2.4401(14)	2.4445(11)	2.511(2)	2.449(3)	2.506(2)	2.449(2)
	O(5)#9	2.4724(14)	2.4763(11)	2.495(2)	2.487(3)	2.484(2)	2.485(2)
	O(6)#7	2.7753(15)	2.7703(11)	2.740(2)	2.849(3)	2.741(2)	2.823(2)
	O(8)#9	2.5050(14)	2.5065(11)	2.470(2)	2.469(2)	2.474(2)	2.4742(19)
	O(9)#2	2.4570(14)	2.4530(11)	2.409(2)	2.437(3)	2.409(2)	2.437(2)
Ca(2)-	O(1)#14	2.6522(15)	2.6481(11)	2.638(2)	2.627(3)	2.631(2)	2.630(2)
	O(10B)#15	2.717(7)	2.699(3)	2.5360(11)	2.544(2)	2.578(2)	2.542(2)
	O(2)	2.5441(15)	2.5465(11)	2.586(2)	2.475(3)	2.492(2)	2.469(2)
	O(2)#14	2.4649(14)	2.4675(11)	2.492(2)	2.377(2)	2.389(2)	2.3720(18)
	O(3)	2.3727(14)	2.3736(11)	2.388(2)	2.564(2)	2.5518(12)	2.5888(17)
	O(6)#1	2.3934(15)	2.4009(12)	2.458(2)	2.484(3)	2.463(2)	2.468(2)
	O(7)#13	2.5186(16)	2.5251(12)	2.609(2)	2.573(3)	2.610(2)	2.567(2)
	O(8)#13	2.3717(15)	2.3762(11)	2.418(2)	2.399(3)	2.412(2)	2.3957(19)
	O(9)#16	2.9456(15)	2.9483(11)	2.899(2)	2.998(3)	2.926(2)	2.994(3)
Ca(3)-	O(1)#1	2.6373(15)	2.6345(11)	2.634(2)	2.681(3)	2.638(2)	2.669(2)
	O(3)#2	2.6570(14)	2.6507(11)	2.602(2)	2.633(2)	2.602(2)	2.6348(18)
	O(4)#1	2.4591(14)	2.4612(11)	2.501(2)	2.439(2)	2.497(2)	2.4444(19)
	O(4)#2	2.4278(14)	2.4313(11)	2.463(2)	2.414(3)	2.458(2)	2.4191(19)
	O(6)#12	2.4604(14)	2.4616(11)	2.473(2)	2.450(3)	2.468(2)	2.449(2)

	O(7)	2.3600(15)	2.3633(11)	2.345(2)	2.407(3)	2.350(2)	2.401(2)
	O(8)#11	2.3685(14)	2.3691(11)	2.378(2)	2.368(2)	2.374(2)	2.3675(18)
	O(9)	2.3782(14)	2.3748(11)	2.320(2)	2.358(3)	2.327(2)	2.360(2)
Ca(4A)-	O(6)#18	NA	NA	NA	2.736(5)	NA	2.758(6)
	O(6)#19	NA	NA	NA	2.736(5)	NA	2.758(6)
	O(7)#18	NA	NA	NA	2.541(4)	NA	2.541(4)
	O(7)#19	NA	NA	NA	2.541(4)	NA	2.541(4)
Ca(4B)-	O(6)#18	NA	NA	NA	2.516(3)	NA	2.518(2)
	O(6)#19	NA	NA	NA	2.516(3)	NA	2.518(2)
	O(7)#18	NA	NA	NA	2.846(5)	NA	2.851(4)
	O(7)#19	NA	NA	NA	2.846(5)	NA	2.851(4)
Fe(1)-	O(4)	2.1131(16)	2.1067(13)	2.046(2)	2.122(3)	2.048(2)	2.104(2)
	O(4)#1	2.1130(16)	2.1068(13)	2.046(2)	2.122(3)	2.048(2)	2.104(2)
	O(4)#2	2.1130(16)	2.1068(13)	2.046(2)	2.122(3)	2.048(2)	2.104(2)
	O(5)	2.0893(16)	2.0806(12)	2.011(2)	2.108(3)	2.023(2)	2.092(2)
	O(5)#1	2.0893(16)	2.0806(12)	2.011(2)	2.108(3)	2.023(2)	2.092(2)
	O(5)#2	2.0893(16)	2.0806(12)	2.011(2)	2.108(3)	2.023(2)	2.092(2)
P(1)-	O(1)	1.5281(15)	1.5257(11)	1.528(2)	1.528(3)	1.530(2)	1.528(2)
	O(2)	1.5484(16)	1.5456(13)	1.521(2)	1.532(3)	1.523(2)	1.535(2)
	O(3)	1.5393(14)	1.5382(11)	1.535(2)	1.537(2)	1.535(2)	1.5377(18)
	O(4)	1.5512(16)	1.5497(12)	1.562(2)	1.546(3)	1.561(2)	1.546(2)
P(2)-	O(5)	1.5538(16)	1.5552(12)	1.588(2)	1.556(3)	1.583(2)	1.558(2)
	O(6)	1.5261(15)	1.5260(12)	1.527(2)	1.537(3)	1.526(2)	1.531(2)
	O(7)	1.5284(15)	1.5256(12)	1.516(2)	1.529(3)	1.520(2)	1.529(2)
	O(8)	1.5385(15)	1.5381(11)	1.544(2)	1.543(2)	1.546(2)	1.5422(19)
P(3A)-	O(10A)	1.582(3)	1.578(3)	1.540(4)	1.530(3)	1.57(3)	1.530(7)
	O(9)	1.5297(14)	1.5291(11)	1.5366(19)	1.493(3)	1.518(6)	1.500(2)
	O(9)#18	1.5298(14)	1.5292(11)	1.5366(19)	1.493(3)	1.518(6)	1.500(2)
	O(9)#19	1.5298(14)	1.5292(11)	1.5366(19)	1.493(3)	1.518(6)	1.500(2)
P(3B)-	O(10B)	1.51(3)	1.534(14)	1.49(3)	1.546(7)	1.543(5)	1.535(6)
	O(9)	1.512(3)	1.5187(16)	1.507(12)	1.526(2)	1.534(2)	1.5209(19)
	O(9)#18	1.512(3)	1.5187(16)	1.507(12)	1.526(2)	1.534(2)	1.5209(19)
	O(9)#19	1.512(3)	1.5187(16)	1.507(12)	1.526(2)	1.534(2)	1.5209(19)

Parenthetic values are standard deviations. Pt cruc. = merrillite produced by heating in open air in a platinum crucible. SiO_2 tube = merrillite produced in a triple argon purged and sealed silica glass tube.