The Crystal Structure and Chemistry of Natural Giniite and Implications for Mars

Supplemental Online Data

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Supplementary Tables

Table S1. EMP standards configuration for Giniite

Element	Xtal	Standard	Composition wt%
Mg Ka	TAP	Olivine Fo92	Si: 19.13, Al: 0.02, Fe: 6.36, Mn: 0.09, Mg: 30.33, Ca: 0.07, Ni: 0.32, O: 43.74
Fe Ka	LLIF	Fayalite	Si: 13.84, Ti: 0.01, Al: 0.05, Fe: 52.24, Mn: 1.55, Mg: 0.06, Ca: 0.21, Zn: 0.38, O: 31.45
P Ka	LPET	Synthetic Apatite	F: 3.77, P: 18.43, Ca: 39.74, O: 38.07
Mn Ka	LLIF	Rhodochrosite	Si: 21.66, Ti: 0.01, Al: 0.02, Fe: 2.1, Mn: 36.14, Mg: 0.58, Ca: 2.69, O: 37.28

Note: 2 µm beam. 15 KeV at 10na.

Table S2. Crystallographic data for giniite

Empirical chemical formula	$(Fe^{2+}_{0.80}Mn_{0.11}Mg_{0.02})_{\Sigma=0.93}Fe^{3+}_4(PO_4)_{4.03}(OH)_2{\cdot}2H_2O$
Ideal chemical formula	$Fe^{2+}Fe^{3+}_4(PO_4)_4(OH)_2{\cdot}2H_2O$
Crystal symmetry	Monoclinic
Space group	*P*2/*n*
a (Å)	10.3472(6)
b (Å)	5.1497(2)
c (Å)	14.2338(7)
β (°)	111.175(6)
V(Å^3)	707.24(7)
Z	2
ρ_{cal}(g/cm^3)	3.424
2ϑ range for data collection	≤67.482
No. of reflections collected	12223
No. of independent reflections	2518
No. of reflections with $I > 2\sigma(I)$	1991
No. of parameters refined	144
R(int)	0.041
Final R_1, wR_2 factors [$I > 2\sigma(I)$]	0.032, 0.075
Goodness-of-fit	1.025

Table S3. Fractional atomic coordinates and anisotropic and equivalent isotropic displacement parameters (Å^2) for giniite

Fe1				**Fe2**				**Fe3**			
x	0.97559 (4)	U_{11}	0.0098(2)	*x*	0.75000	U_{11}	0.0053(2)	*x*	0.75558 (4)	U_{11}	0.00517(18)
y	−0.24625 (7)	U_{22}	0.01023(18)	*y*	1.21898 (9)	U_{22}	0.0063(2)	*y*	0.48901 (7)	U_{22}	0.00782(18)
z	0.25478 (3)	U_{33}	0.01112(18)	*z*	0.75000	U_{33}	0.0067(2)	*z*	0.51184 (3)	U_{33}	0.00680(16)
U_{eq}	0.01006 (10)	U_{23}	-0.00070(13)	U_{eq}	0.00619 (11)	U_{23}	0.00000	U_{eq}	0.00646 (9)	U_{23}	-0.00126(13)
		U_{13}	0.00499(15)			U_{13}	0.00197(19)			U_{13}	0.00266(13)
		U_{12}	0.00082(14)			U_{12}	0.00000			U_{12}	-0.00078(13)
P1				**P2**				**O1**			
x	0.55670 (7)	U_{11}	0.0039(3)	*x*	0.93837 (7)	U_{11}	0.0045(3)	*x*	0.4001 (2)	U_{11}	0.0054(9)
y	0.72166 (12)	U_{22}	0.0046(3)	*y*	0.24451 (12)	U_{22}	0.0062(3)	*y*	0.7325 (3)	U_{22}	0.0090(8)
z	0.62842 (5)	U_{33}	0.0050(3)	*z*	0.37905 (5)	U_{33}	0.0067(3)	*z*	0.57249 (15)	U_{33}	0.0116(9)
U_{eq}	0.00450 (13)	U_{23}	-0.0002(2)	U_{eq}	0.00566 (13)	U_{23}	-0.0012(2)	U_{eq}	0.0094 (4)	U_{23}	-0.0016(7)
		U_{13}	0.0017(2)			U_{13}	0.0025(2)			U_{13}	0.0005(7)
		U_{12}	-0.0001(2)			U_{12}	-0.0004(2)			U_{12}	-0.0007(7)
O2				**O3**				**O4**			
x	0.59412 (19)	U_{11}	0.0084(9)	*x*	0.6371 (2)	U_{11}	0.0111(10)	*x*	0.59566 (19)	U_{11}	0.0076(9)
y	0.4765 (3)	U_{22}	0.0070(8)	*y*	0.7158 (3)	U_{22}	0.0103(9)	*y*	0.9636 (3)	U_{22}	0.0076(8)
z	0.69647 (14)	U_{33}	0.0108(8)	*z*	0.55790 (14)	U_{33}	0.0107(9)	*z*	0.69697 (13)	U_{33}	0.0098(8)
U_{eq}	0.0085 (3)	U_{23}	0.0035(6)	U_{eq}	0.0096 (4)	U_{23}	0.0016(7)	U_{eq}	0.0086 (3)	U_{23}	-0.0043(6)
		U_{13}	0.0045(7)			U_{13}	0.0078(7)			U_{13}	0.0024(7)
		U_{12}	0.0017(7)			U_{12}	0.0021(7)			U_{12}	-0.0031(7)
O5				**O6**				**O7**			
x	1.0955 (2)	U_{11}	0.0056(9)	*x*	0.8746 (2)	U_{11}	0.0091(9)	*x*	0.8771 (2)	U_{11}	0.0103(9)
y	0.2688 (3)	U_{22}	0.0114(9)	*y*	0.3004 (4)	U_{22}	0.0153(9)	*y*	0.4384 (4)	U_{22}	0.0131(9)
z	0.41791 (15)	U_{33}	0.0135(9)	*z*	0.45726 (15)	U_{33}	0.0124(9)	*z*	0.28939 (14)	U_{33}	0.0102(9)
U_{eq}	0.0103 (4)	U_{23}	-0.0021(7)	U_{eq}	0.0111 (4)	U_{23}	-0.0028(7)	U_{eq}	0.0117 (4)	U_{23}	0.0050(7)
		U_{13}	0.0030(7)			U_{13}	0.0080(8)			U_{13}	0.0019(7)
		U_{12}	-0.0019(7)			U_{12}	0.0012(7)			U_{12}	0.0008(7)
O8				**O9H**				**O10W**			
x	0.8975 (2)	U_{11}	0.0101(9)	*x*	0.80558 (19)	U_{11}	0.0107(9)	*x*	0.8022 (2)	U_{11}	0.0089(10)
y	−0.0307 (3)	U_{22}	0.0078(8)	*y*	1.2337 (3)	U_{22}	0.0063(8)	*y*	−0.2174 (4)	U_{22}	0.0093(9)
z	0.33714 (14)	U_{33}	0.0161(9)	*z*	0.62760 (13)	U_{33}	0.0071(8)	*z*	0.11126 (14)	U_{33}	0.0104(9)
U_{eq}	0.0109 (4)	U_{23}	-0.0031(7)	U_{eq}	0.0077 (3)	U_{23}	-0.0003(6)	U_{eq}	0.0091 (4)	U_{23}	0.0006(7)
		U_{13}	0.0065(7)			U_{13}	0.0044(7)			U_{13}	0.0051(7)
		U_{12}	-0.0013(7)			U_{12}	0.0004(7)			U_{12}	0.0009(7)
H1				**H2**				**H3**			
x	0.806 (3)	U_{11}	-	*x*	0.826 (4)	U_{11}	-	*x*	0.729 (5)	U_{11}	-
y	1.071 (7)	U_{22}	-	*y*	−0.077 (7)	U_{22}	-	*y*	−0.175 (8)	U_{22}	-
z	0.603 (3)	U_{33}	-	*z*	0.095 (3)	U_{33}	-	*z*	0.121 (4)	U_{33}	-
U_{eq}	0.017 (9)*	U_{23}	-	U_{eq}	0.016 (9)*	U_{23}	-	U_{eq}	0.047 (13)*	U_{23}	-
		U_{13}	-			U_{13}	-			U_{13}	-
		U_{12}	-			U_{12}	-			U_{12}	-

Table S4. Giniite Oxide Wt. % by EMP.

	MgO	Fe_2O_3	P_2O_5	MnO	Total
1	0.1093	51.24	38.38	1.020	90.77
2	0.0957	50.88	38.36	1.236	90.60
3	0.1043	51.28	38.25	0.993	90.68
4	0.0833	51.35	38.61	1.180	91.26
5	0.1079	50.79	38.09	1.312	90.33
6	0.1094	51.41	38.42	1.058	91.03
7	0.0816	50.94	38.39	1.158	90.62
8	0.1136	52.15	38.53	0.662	91.47
9	0.0676	51.42	38.21	0.738	90.48
10	0.0689	51.15	38.46	1.278	91.00
11	0.1016	51.44	37.62	1.092	90.34
12	0.1130	51.26	38.18	1.219	90.80
13	0.0965	50.87	38.41	0.835	90.23
14	0.0809	51.45	38.65	0.945	91.16
15	0.1062	51.05	38.50	1.267	91.02
Ave.	**0.0960**	**51.25**	**38.34**	**1.066**	**90.79**
S.D.	**0.0157**	**0.34**	**0.25**	**0.201**	**0.37**
D.L.	**0.0444**	**0.19**	**0.12**	**0.151**	**-**

S.D. = Standard Deviation. D.L. = Detection Limit. Na_2O and K_2O analyses were below detection.

Table S5. Comparison of stoichiometries of this work and Keller (1980a) using EMP data fit to the ideal formula and a best fit for the analyses in this work..

Calculated Stoichiometry	
Keller:	$(Fe^{2+}_{0.67}Mn_{0.07}Mg_{0.13})_{\Sigma=0.87}Fe^{3+}_{4.00}(PO_4)_{4.05}(OH)_{2.00}\cdot 2H_2O$
This Study:	$(Fe^{2+}_{0.80}Mn_{0.11}Mg_{0.02})_{\Sigma=0.93}Fe^{3+}_{4.00}(PO_4)_{4.03}(OH)_{2.00}\cdot 2H_2O$
This Study Best Fit	$(Fe^{2+}_{0.89}Mn_{0.11}Mg_{0.02})_{\Sigma=1.02}Fe^{3+}_{3.93}(PO_4)_{4.05}(OH)_{1.92}\cdot 2.08H_2O$
Ideal:	$Fe^{2+}Fe^{3+}_4(PO_4)_4(OH)_2\cdot 2H_2O$

Table S6. A range of stoichiometry fits from EMP data in this study for different Fe valence ratios.

x	Chemistry								Stoichiometry						
	Fe_2O_3	FeO	MgO	MnO	P_2O_5	OH	H_2O	Total	Fe3+	Fe2+	Fe Sum	(PO4)3-	OH-	H2O	$Fe^{3+}:Fe^{3+}+Fe^{2+}$
0.35	51.25	0.00	0.096	1.07	38.34	3.82	2.54	97.12	4.55	0.12	4.67	3.83	2.65	1.00	0.97
0.70	46.94	3.88	0.096	1.07	38.34	2.83	4.19	97.35	4.30	0.52	4.82	3.95	2.30	1.70	0.89
0.80	45.54	5.14	0.096	1.07	38.34	2.69	4.40	97.28	4.20	0.65	4.85	3.98	2.20	1.80	0.87
0.90	44.16	6.38	0.096	1.07	38.34	2.55	4.62	97.22	4.10	0.79	4.89	4.01	2.10	1.90	0.84
1.00	42.74	7.66	0.096	1.07	38.34	2.41	4.83	97.15	4.00	0.93	4.93	4.03	2.00	2.00	0.81
1.05	42.12	8.22	0.096	1.07	38.34	2.35	4.93	97.12	3.95	0.99	4.94	4.04	1.95	2.05	0.80
1.06	41.98	8.34	0.096	1.07	38.34	2.41	4.82	97.06	3.94	1.00	4.94	4.04	1.94	2.04	0.80
1.07	41.85	8.46	0.096	1.07	38.34	2.32	4.97	97.11	3.93	1.01	4.94	4.05	1.93	2.07	0.80
1.08	41.73	8.57	0.096	1.07	38.34	2.31	5.00	97.11	3.92	1.03	4.95	4.05	1.92	2.08	0.79
1.10	41.45	8.82	0.096	1.07	38.34	2.28	5.04	97.10	3.90	1.05	4.95	4.06	1.90	2.10	0.79
1.20	40.12	10.02	0.096	1.07	38.34	2.14	5.24	97.02	3.80	1.19	4.99	4.09	1.80	2.20	0.76
1.30	38.80	11.21	0.096	1.07	38.34	2.01	5.44	96.96	3.70	1.32	5.02	4.11	1.70	2.30	0.74
1.40	37.28	12.57	0.096	1.07	38.34	1.64	5.61	96.61	3.60	1.48	5.08	4.17	1.60	2.40	0.71

Note: Fe Sum includes Mg and Mn cations.

Supplementary Figures

Figure S1. Giniite sample RO60765 used for characterization. Image credit: RRUFF.info, Photo 8567 M

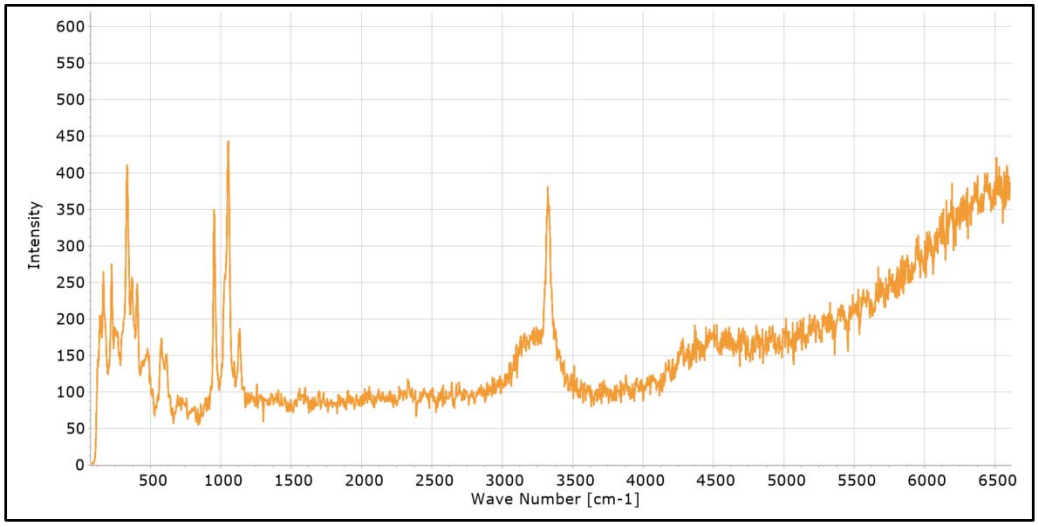

Figure S2. Raw broad scan Raman data plot of giniite.

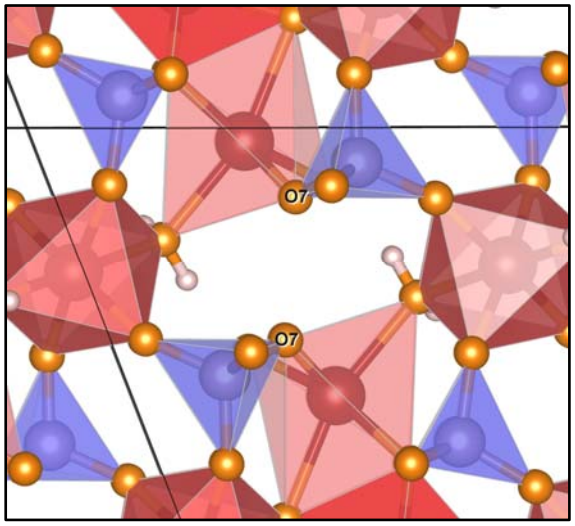

Figure S3. Close up of O7 "void" viewed down the *b* axis.