

Online Materials

Synthesis and structure analysis of CaFe_2O_4 -type single crystals in the NaAlSiO_4 - MgAl_2O_4 - Fe_3O_4 system

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Table OM1. Compositions of calcium ferrite single crystals.

Run no.	H5477	S7759	H5469	S7760
Na ₂ O	18.99(34)	14.04(82)	12.62(39)	12.15(38)
MgO	0.15(4)	7.82(93)	5.10(14)	5.30(26)
Al ₂ O ₃	35.67(81)	42.32(80)	40.17(82)	43.00(75)
SiO ₂	40.96(62)	31.92(139)	27.74(56)	26.55(62)
FeO	0.02(2)	0.22(5)	11.78(46)	10.27(55)
Total	95.79(71)	96.32(69)	97.41(36)	97.27(60)
Fe ³⁺ /ΣFe	-	-	0.32(1)	0.34(1)
Na	0.900(12)	0.663(36)	0.620(19)	0.594(18)
Mg	0.006(1)	0.284(35)	0.193(5)	0.199(10)
Al	1.028(21)	1.216(28)	1.200(25)	1.277(21)
Fe	0.000(0)	0.004(1)	0.250(10)	0.216(12)
Si	1.001(16)	0.778(30)	0.703(13)	0.669(15)
O	4	4	4	4
Cations	2.935(11)	2.945(9)	2.967(12)	2.954(9)
Vacancies	0.065(11)	0.055(9)	0.033(12)	0.046(9)
Components				
NaAlSiO ₄	0.90(1)	0.66(4)	0.62(2)	0.59(2)
Mg ₂ SiO ₄	0.00(0)	0.00(2)	0.00(0)	0.00(0)
Fe ₂ SiO ₄	0.00(0)	0.00(0)	0.02(1)	0.00(0)
MgAl ₂ O ₄	0.00(0)	0.28(2)	0.19(1)	0.20(1)
FeAl ₂ O ₄	0.00(0)	0.00(0)	0.10(1)	0.14(1)
Fe ₃ O ₄	0.00(0)	0.00(0)	0.04(1)	0.03(1)
□Al _{8/3} O ₄	0.04(1)	0.00(2)	0.00(1)	0.00(2)
□Si ₂ O ₄	0.05(1)	0.06(3)	0.03(1)	0.04(1)

Components were calculated as follows.

1. Na, Al and Si form NaAlSiO₄ component.
2. Mg and remaining Al form MgAl₂O₄ component.
3. In case of excess Mg and excess Si, Mg₂SiO₄ component is formed.
4. In case of excess Si, □Si₂O₄ component is formed.
5. In case of excess Al and presence of Fe²⁺, FeAl₂O₄ component is formed.
6. Fe³⁺ and remaining Fe²⁺ form Fe²⁺Fe³⁺₂O₄ component.
7. In case or excess Fe²⁺ and Si, Fe₂SiO₄ component is formed.
8. In case of excess Al or Fe³⁺, □Al_{8/3}O₄ or □Fe³⁺_{8/3}O₄ components are formed.

Table OM2a. Chemical compositions of recovered phases (wt.%).

	Na ₂ O	FeO	SiO ₂	MgO	Al ₂ O ₃	H ₂ O	Total
<u>H5474 (24 GPa, 1100 °C)</u>							
δ	0.07(4)	16.07(53)	9.96(82)	5.65(12)	52.31(130)	15.38(137)	84.62(137)
ε	0.19(9)	55.81(540)	5.61(105)	2.46(77)	16.62(538)	18.89(120)	81.11(120)
L	31.55(879)	6.35(311)	9.27(386)	5.89(226)	10.13(433)	-	63.23(324)
<u>H5462 (24 GPa, 1700 °C)</u>							
St	0.32(42)	0.41(6)	93.87(59)	0.01(1)	4.71(26)	-	99.89(88)
Cor	0.12(3)	9.77(47)	4.41(15)	2.74(12)	81.48(81)	-	99.05(131)
LN*	0.51(13)	41.02(85)	19.72(98)	10.15(64)	24.55(76)	-	96.20(76)
L	22.87(274)	8.61(130)	3.50(41)	8.49(137)	3.63(49)	-	47.63(135)
<u>H5471 (24 GPa, 2000 °C)</u>							
Cor	0.07(7)	11.67(27)	5.87(20)	3.44(10)	76.51(92)	-	97.84(105)
St	0.04(3)	0.38(5)	93.27(114)	0.03(3)	4.79(80)	-	98.93(71)
L	10.17(155)	16.29(228)	17.50(335)	9.54(39)	7.63(68)	-	61.49(397)

Abbreviations: Cf, calcium ferrite phase, δ, AlOOH-rich hydrous phase δ; ε, FeOOH-rich

hydrous phase ε; St, stishovite; Cor, corundum; L, melt. Note that no compositional

analysis was performed for NaAlSiO₄ samples (I1195 and S7759).

Table OM2b. Chemical compositions of recovered phases (cation number).

							Cat.	
	Na	Fe	Si	Mg	Al	H	Total	O*
<u>H5474 (24 GPa, 1100 °C)</u>								
δ	0.001(1)	0.140(5)	0.104(9)	0.088(3)	0.64(2)	1.07(8)	2.04(6)	2
ε	0.004(2)	0.53(6)	0.06(1)	0.04(1)	0.22(7)	1.42(9)	2.28(6)	2
<u>H5462 (24 GPa, 1700 °C)</u>								
St	0.006(8)	0.003(1)	0.954(3)	0.000(0)	0.056(3)	-	1.021(6)	2
Cor	0.004(1)	0.145(6)	0.078(3)	0.072(3)	1.702(5)	-	2.001(2)	3
LN	0.020(5)	0.69(2)	0.39(2)	0.30(2)	0.58(2)	-	1.983(5)	3
<u>H5471 (24 GPa, 2000 °C)</u>								
Cor	0.003(2)	0.175(4)	0.106(3)	0.092(3)	1.621(8)	-	1.997(2)	3
St	0.001(1)	0.003(0)	0.955(8)	0.000(1)	0.058(1)	-	1.017(3)	2

Abbreviations: Cf, calcium ferrite phase, δ, AlOOH-rich hydrous phase δ; ε, FeOOH-rich hydrous phase ε; St, stishovite; Cor, corundum.

*Oxygen number was fixed.

Table OM3. Results of EPMA analysis using acquisition times of 5, 10 and 20 s.

	H5477			S7759			H5469		
Acquisition time (s)	5	10	20	5	10	20	5	10	20
Na ₂ O	18.9(5)	19.0(3)	18.8(5)	14.0(5)	14.0(8)	13.5(6)	12.3(3)	12.6(4)	11.8(3)
MgO	0.14(4)	0.15(4)	0.13(4)	7.2(10)	7.8(9)	7.5(8)	5.2(2)	5.1(1)	5.1(1)
Al ₂ O ₃	36.0(9)	35.7(8)	36.3(8)	41.8(7)	42.3(8)	42.1(8)	41.2(5)	40.2(8)	41.4(7)
SiO ₂	40.7(11)	41.0(6)	41.0(8)	32.4(10)	31.9(14)	32.0(12)	27.6(5)	27.7(6)	27.5(3)
FeO	0.0(0)	0.0(0)	0.0(0)	0.13(4)	0.22(5)	0.19(3)	11.8(3)	11.8(5)	11.7(4)
Total	95.8(6)	95.8(7)	96.3(3)	95.4(8)	96.3(7)	95.3(8)	98.0(6)	97.4(4)	97.4(4)
Na	0.897(22)	0.900(12)	0.886(21)	0.664(23)	0.663(36)	0.644(27)	0.597(16)	0.620(19)	0.576(10)
Mg	0.005(2)	0.006(1)	0.005(2)	0.263(35)	0.284(35)	0.275(32)	0.194(6)	0.193(5)	0.192(5)
Al	1.037(30)	1.028(21)	1.039(23)	1.209(18)	1.216(28)	1.219(24)	1.220(13)	1.200(25)	1.230(16)
Fe	0.001(1)	0.000(0)	0.001(0)	0.003(1)	0.004(1)	0.004(1)	0.247(8)	0.250(10)	0.247(10)
Si	0.995(24)	1.001(16)	0.997(19)	0.795(22)	0.778(30)	0.785(25)	0.695(10)	0.703(13)	0.695(10)
O	4	4	4	4	4	4	4	4	4
Cations	2.935(19)	2.935(11)	2.927(18)	2.933(14)	2.945(9)	2.927(10)	2.954(10)	2.967(12)	2.939(8)
Vacancies	0.065(19)	0.065(11)	0.073(18)	0.067(14)	0.055(9)	0.073(10)	0.046(10)	0.033(12)	0.061(8)

Table OM4. Crystallographic data of calcium ferrite single crystals.

H5477		
Crystal color	Colorless	
Crystal system	Orthorhombic	
Lattice parameter	$a = 10.1448(2) \text{ \AA}$ $b = 8.67304(19) \text{ \AA}$ $c = 2.73648(6) \text{ \AA}$ $V = 240.772(9) \text{ \AA}^3$	
Z	4	
Space group	<i>Pbnm</i> (no. 62)	
Chemical composition*	$\text{Na}_{0.90(1)}\text{Al}_{1.03(2)}\text{Si}_{1.00(2)}\text{O}_4$	
Measurement temperature	293(2) K	
Refinement strategy	1	2
Measured/unique reflections	6269/1163	6269/1163
Unique reflections with $F_o > 4\sigma(F_o)$	1033	1033
Index ranges	$-20 \leq h \leq 20$ $-13 \leq k \leq 17$ $-5 \leq l \leq 5$	$-20 \leq h \leq 20$ $-13 \leq k \leq 17$ $-5 \leq l \leq 5$
Number of parameters	43	48
F(000)	277	277
θ max	45.6936°	45.6936°
R_{int}	0.0363	0.0363
R1	0.0384	0.0369
wR2	0.0938	0.0866
Goodness-of-fit (S_{fit})	1.082	1.07
Weight for refinement	$a = 0.0575$ $b = 0.0032$	$a = 0.0575$ $b = 0.0032$
S7759		
Crystal color	Colorless	
Crystal system	Orthorhombic	
Lattice parameter	$a = 10.0928(3) \text{ \AA}$ $b = 8.6336(2) \text{ \AA}$ $c = 2.75882(8) \text{ \AA}$ $V = 240.394(12) \text{ \AA}^3$	
Z	4	
Space group	<i>Pbnm</i> (no. 62)	
Chemical composition*	$\text{Na}_{0.66(4)}\text{Mg}_{0.28(4)}\text{Al}_{1.22(3)}\text{Si}_{0.78(3)}\text{O}_4$	
Measurement temperature	293(2) K	
Refinement strategy	1	2
Measured/unique reflections	6222/1156	6222/1154
Unique reflections with $F_o > 4\sigma(F_o)$	989	987
Index ranges	$-20 \leq h \leq 20$	$-20 \leq h \leq 20$

	-13 ≤ <i>k</i> ≤ 17	-13 ≤ <i>k</i> ≤ 17
	-3 ≤ <i>l</i> ≤ 5	-3 ≤ <i>l</i> ≤ 5
Number of parameters	43	48
F(000)	278	278
θ max	45.6444°	45.6444°
<i>R</i> _{int}	0.0419	0.0419
<i>R</i> 1	0.04	0.0388
<i>wR</i> 2	0.0896	0.086
Goodness-of-fit (<i>S</i> _{fit})	1.125	1.096
Weight for refinements	a = 0.0446 b = 0.0228	a = 0.0474 b = 0
H5469		
Crystal color	Light brown	
Crystal system	Orthorhombic	
Lattice parameter	<i>a</i> = 10.12087(16) Å <i>b</i> = 8.64079(15) Å <i>c</i> = 2.76864(5) Å <i>V</i> = 242.124(7) Å ³	
<i>Z</i>	4	
Space group	<i>Pbnm</i> (no. 62)	
Chemical composition*	Na _{0.59(2)} Mg _{0.20(1)} Fe _{0.22(1)} Al _{1.28(2)} Si _{0.67(2)} O ₄	
Measurement temperature	293(2) K	
Refinement strategy [§]	1	2
Measured/unique reflections	6304/1156	6304/1161
Unique reflections with <i>F</i> _o > 4σ(<i>F</i> _o)σ	1066	1071
Index ranges	-20 ≤ <i>h</i> ≤ 20 -17 ≤ <i>k</i> ≤ 17 -3 ≤ <i>l</i> ≤ 5	-20 ≤ <i>h</i> ≤ 20 -17 ≤ <i>k</i> ≤ 17 -3 ≤ <i>l</i> ≤ 5
Number of parameters	43	51
F(000)	292	292
θ max	44.9488°	44.9488°
<i>R</i> _{int}	0.0326	0.0326
<i>R</i> 1	0.031	0.0344
<i>wR</i> 2	0.097	0.084
Goodness-of-fit (<i>S</i> _{fit})	1.095	1.094
Weight for refinements	a = 0.0648 b = 0.0319	a = 0.0561 b = 0

$$R_{\text{int}} = \sum | |F_o|^2 - |F_o|^2(\text{mean}) | / \sum |F_o|^2, R1 = \sum | |F_o| - |F_c| | / \sum |F_o|, wR2 = \{ \sum w (|F_o|^2 - |F_c|^2)^2 / \sum |F_o|^2 \}^{1/2}, S_{\text{fit}} = \{ \sum w (|F_o|^2 - |F_c|^2)^2 / (n - p) \}^{1/2}, w = 1 / \{ \sigma^2 (|F_o|^2) + (a \times P)^2 + b \times P \} \text{ and } P = ([\text{Maximum } (|F_o|^2 \text{ or } 0)] + 2 \times |F_c|^2) / 3,$$

where F_o and F_c are the observed and calculated structure factors, respectively. w , n and p , are the statistical weight, the number of reflections and the total number of parameters refined, respectively. Maximum (F_o^2 or 0) is replaced by 0 when the observed F_o^2 value is negative because the background is higher than the peak.

*Chemical composition from EPMA.

§In refinement strategy 1, the site occupancies and total atomic concentrations are fixed according to the end members molar fractions reported in Table OM1. In refinement strategy 2, the site occupancies and total atomic concentrations were refined using chemical restraints from EPMA data.

Table OM5. Summary of site occupancy factors for each cation in the A, B1 and B2 sites and total atomic concentration refined or fixed in different refinement strategies and experimental.

	H5477		S7759		H5469	
Refinement strategy ^a	1	2	1	2	1	2
Si(B1)	<i>0.50</i>	0.57(2)	<i>0.40</i>	0.50(3)	<i>0.35</i>	0.42(2)
Al(B1)	<i>0.50</i>	0.42(2)	<i>0.60</i>	0.48(3)	<i>0.60</i>	0.56(2)
Fe(B1)	-	-	-	-	<i>0.05</i>	0.02(1)
Si(B2)	<i>0.50</i>	0.43(2)	<i>0.40</i>	0.29(3)	<i>0.35</i>	0.30(2)
Al(B2)	<i>0.50</i>	0.57(2)	<i>0.60</i>	0.71(3)	<i>0.60</i>	0.66(2)
Fe(B2)	-	-	-	-	<i>0.05</i>	0.04(1)
Na(A)	<i>0.90</i>	0.940(4)	<i>0.66</i>	0.684(4)	<i>0.62</i>	0.58(3)
Mg(A)	-	-	<i>0.28</i>	<i>0.28</i>	<i>0.19</i>	<i>0.19</i>
Fe(A)	-	-	-	-	0.15	0.19(2)
Al(A)	<i>0.03</i>	<i>0.03</i>	-	-	-	-
Al _{tot}	<i>1.03</i>	1.02(2)	<i>1.22</i>	1.19(2)	<i>1.20</i>	1.21(1)
Si _{tot}	<i>1.00</i>	1.00(2)	<i>0.78</i>	0.79(2)	<i>0.70</i>	0.72(1)
Fe _{tot}	-	-	-	-	<i>0.25</i>	0.25(2)
B1 _{tot}	<i>1.00</i>	0.99(1)	<i>1.00</i>	0.99(1)	<i>1.00</i>	1.00(1)
B2 _{tot}	<i>1.00</i>	1.00(1)	<i>1.00</i>	1.00(1)	<i>1.00</i>	1.00(1)
A vacancies	<i>0.07</i>	0.030(4)	<i>0.06</i>	0.032(4)	<i>0.04</i>	0.04(2)

^a In refinement strategy 1, the site occupancies and total atomic concentrations are fixed according to the end members molar fractions reported in Table OM1. In refinement strategy 2, the site occupancies and total atomic concentrations were refined using chemical restraints from EPMA data. Uncertainties determined in the refinement strategy 2 are determined using the full covariance matrix to account for the high correlation coefficients between site occupancy factors. Numbers in italics were fixed during the refinement.

Table OM6. Results of structure analyses of crystals (H5477, S7759, and H5469). All values are reported in Å.

H5477		
Refinement strategy ^a	1	2
B1-O2 x2	1.8258(6)	1.8256(6)
B1-O4 x2	1.8333(6)	1.8342(6)
B1-O2	1.9129(9)	1.9130(9)
B1-O1	1.9400(10)	1.9390(9)
B1-O av	1.862(2)	1.862(2)
B2-O3 x2	1.8321(6)	1.8322(6)
B2-O1 x2	1.8660(6)	1.8665(6)
B2-O3	1.8723(9)	1.8722(9)
B2-O4	1.9507(9)	1.9497(9)
B2-O av	1.870(2)	1.870(2)
A-O3 x2	2.2756(8)	2.2748(7)
A-O2 x2	2.2768(8)	2.2769(7)
A-O4	2.3986(8)	2.3981(9)
A-O4	2.3997(9)	2.4003(9)
A-O1 x2	2.4425(8)	2.4427(8)
A-O av	2.349(2)	2.348(2)
S7759		
Refinement strategy ^a	1	2
B1-O2 x2	1.8403(7)	1.8400(6)

B1-O4 x2	1.8553(7)	1.8555(6)
B1-O2	1.9087(9)	1.9101(9)
B1-O1	1.9148(10)	1.9156(10)
B1-O av	1.869(2)	1.869(2)
B2-O3 x2	1.8618(6)	1.8617(6)
B2-O1 x2	1.8887(7)	1.8880(6)
B2-O3	1.8752(11)	1.8761(11)
B2-O4	1.9198(10)	1.9205(9)
B2-O av	1.883(2)	1.883(2)
A-O3 x2	2.2408(8)	2.2404(8)
A-O2 x2	2.2428(9)	2.2419(8)
A-O4	2.3935(11)	2.3937(10)
A-O4	2.3993(11)	2.3995(10)
A-O1 x2	2.4177(10)	2.4178(9)
A-O av	2.324(3)	2.324(2)

H5469

Refinement strategy ^a	1	2
B1-O2 x2	1.8471(6)	1.8471(5)
B1-O4 x2	1.8664(6)	1.8660(5)
B1-O2	1.9077(10)	1.9074(9)
B1-O1	1.9113(9)	1.9125(8)
B1-O av	1.874(2)	1.874(2)
B2-O3 x2	1.8767(6)	1.8763(5)

B2-O1 x2	1.8930(9)	1.8932(6)
B2-O3	1.8831(7)	1.8834(8)
B2-O4	1.9256(9)	1.9258(7)
B2-O av	1.891(2)	1.891(2)
A-O3 x2	2.2407(7)	2.2403(6)
A-O2 x2	2.2478(7)	2.2478(6)
A-O4	2.3941(9)	2.3934(8)
A-O4	2.4010(10)	2.4022(8)
A-O1 x2	2.4145(8)	2.4146(7)
A-O av	2.325(2)	2.325(2)

^a In refinement strategy 1, the site occupancies and total atomic concentrations are fixed according to the end members molar fractions reported in Table 2. In refinement strategy 2, the site occupancies and total atomic concentrations were refined using chemical restraints from EPMA data. Uncertainties determined in the refinement strategy 2 are determined using the full covariance matrix to account for the high correlation coefficients between site occupancy factors.

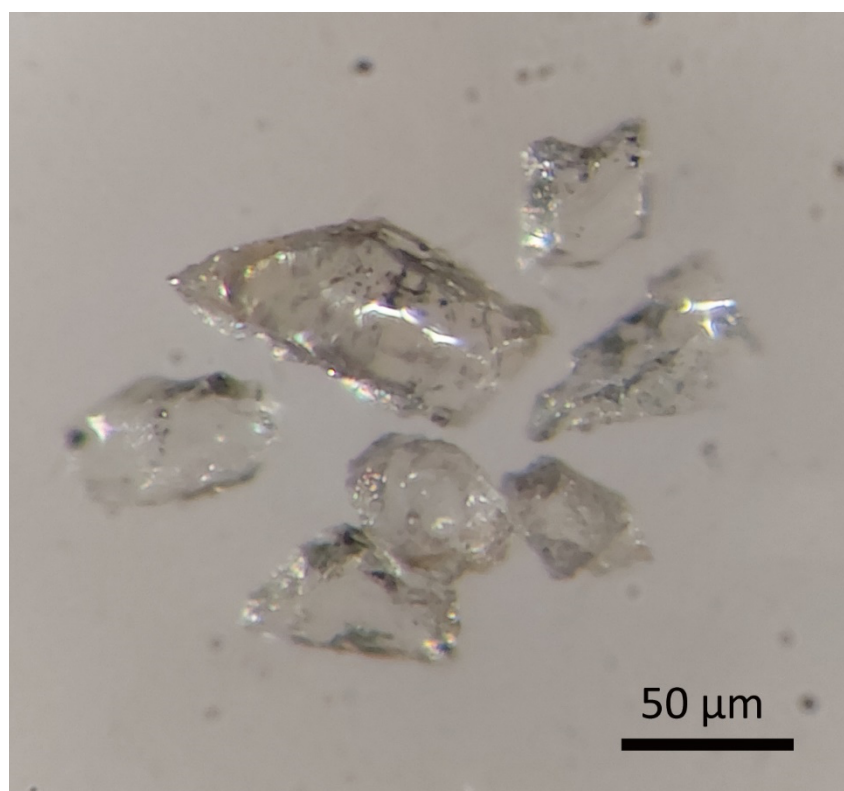


Figure OM1. A photograph of NaAlSiO₄ calcium ferrite single-crystals (H5477).

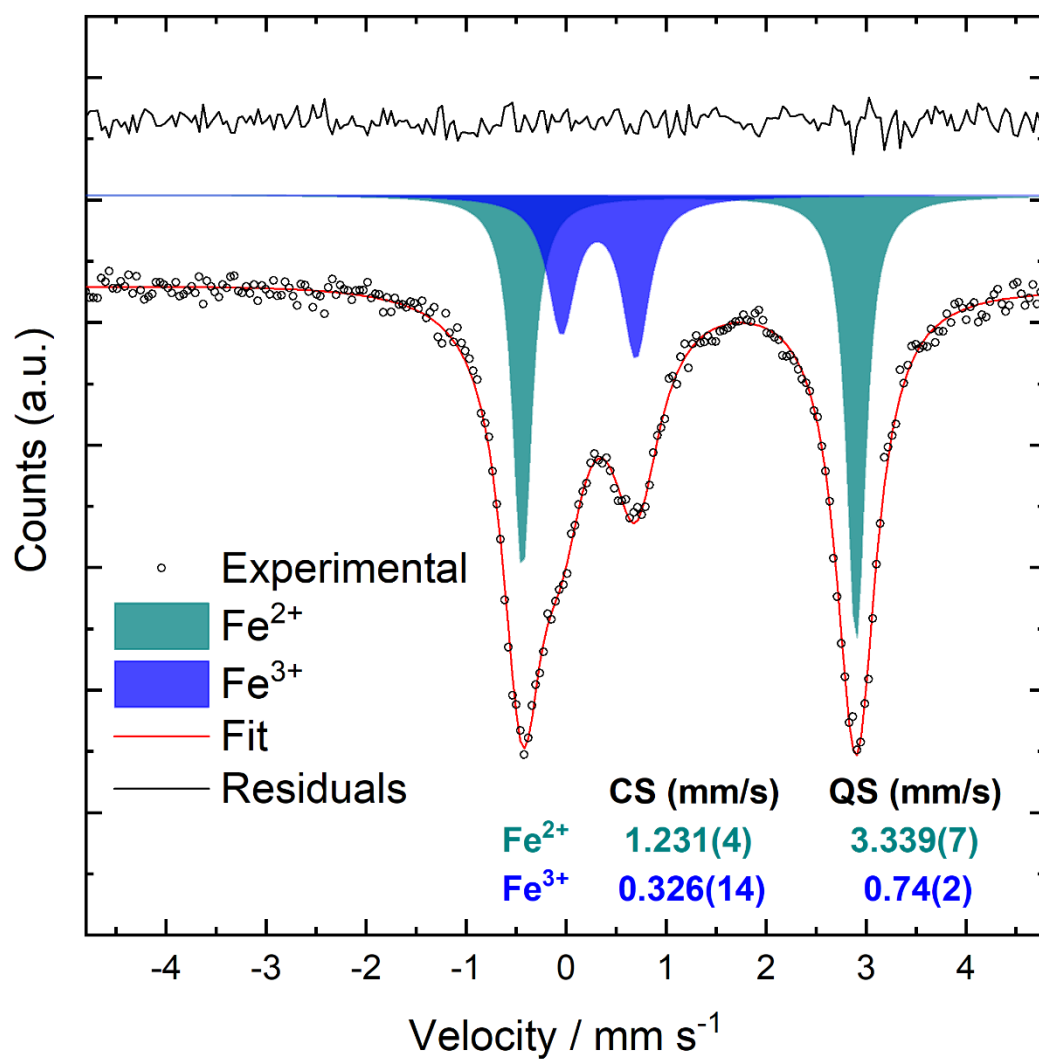


Figure OM2. A Mössbauer spectrum of recovered Fe-bearing calcium ferrite sample (S7760). CS, center shift; QS, quadrupole splitting.

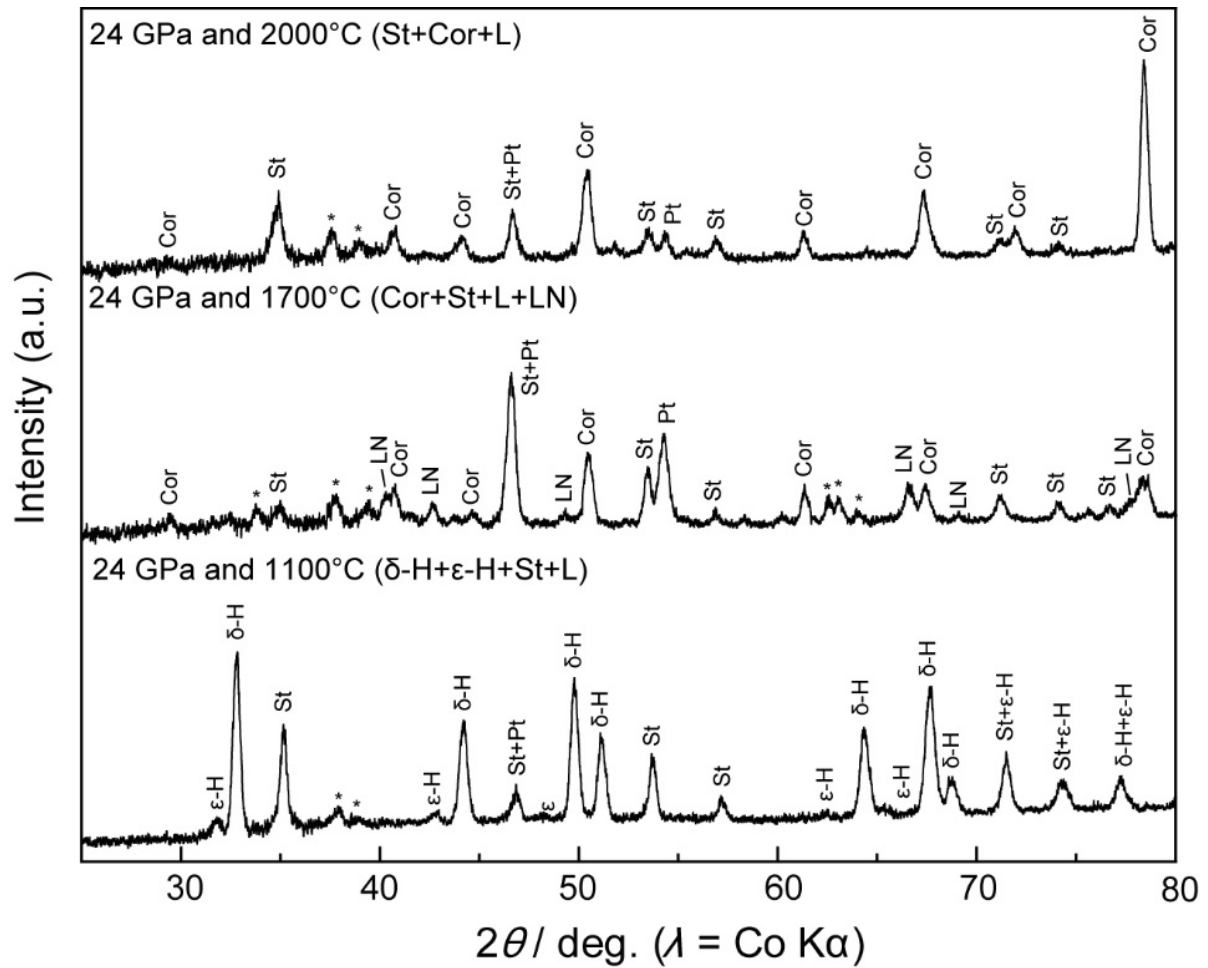


Figure OM3. Representative micro-focus X-ray diffraction patterns of the recovered hydrous samples at 24 GPa and 1100, 1700 and 2000 °C. δ-H, AlOOH-rich hydrous phase δ; ε-H, FeOOH-rich hydrous phase ε; St, stishovite; Cor, corundum; Ln, lithium niobate phase; L, liquid phase; Pt, Pt capsule. Stars (*) are unknown peaks, which are probably from quenched melt (see text).

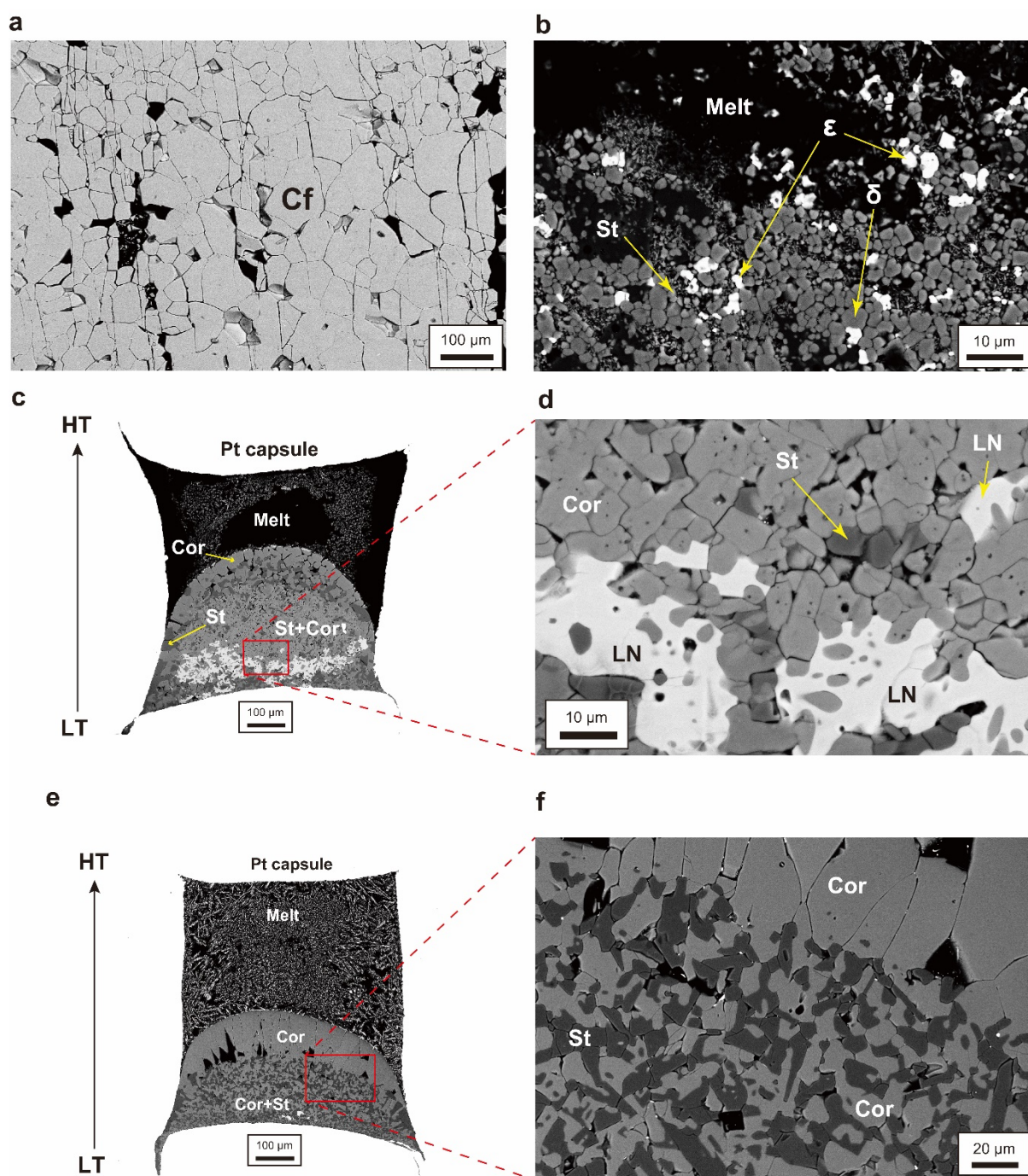


Figure OM4. Representative back-scattered electron images of recovered samples at (a) 23 GPa and 2000 °C in the $\text{NaAlSiO}_4\text{-MgAl}_2\text{O}_4\text{-Fe}_3\text{O}_4$ system (H5469) and (b) 24 GPa and 1100 °C (H5474), (c,d) 24 GPa and 1700 °C (H5462) and (e,f) 24 GPa and 2000 °C (H5471) in the $\text{NaAlSiO}_4\text{-MgAl}_2\text{O}_4\text{-Fe}_3\text{O}_4\text{-H}_2\text{O}$ system. Cf, calcium ferrite phase; δ , AlOOH -rich hydrous phase δ ; ϵ , FeOOH -rich hydrous phase ϵ ; St, stishovite; Cor, corundum; LN, lithium niobate phase; HT, higher temperature; LT, lower temperature.

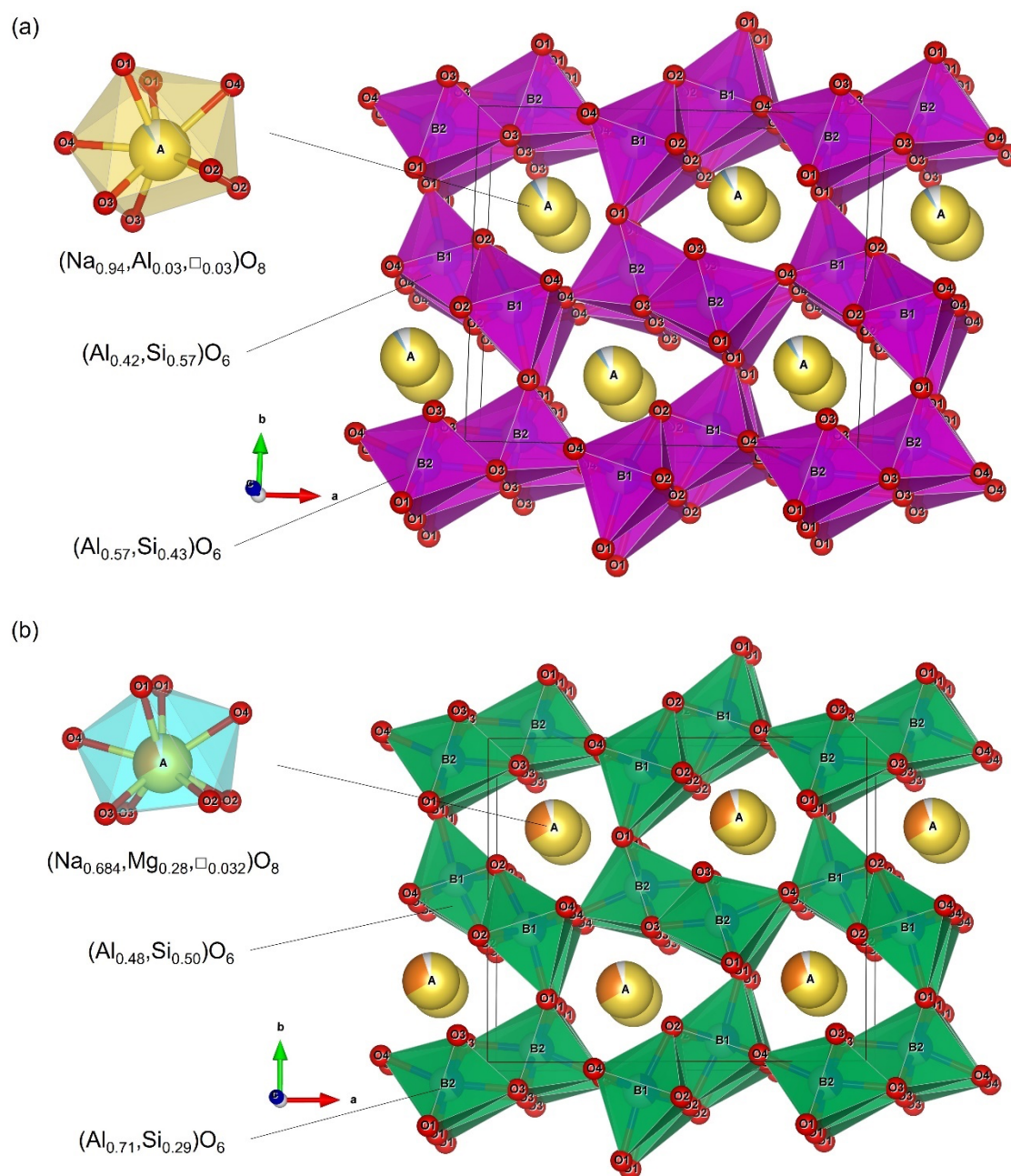


Figure OM5. Crystal structures of (a) $\text{Na}_{0.90(1)}\text{Al}_{1.03(2)}\text{Si}_{1.00(2)}\text{O}_4$, (b) $\text{Na}_{0.66(4)}\text{Mg}_{0.28(4)}\text{Al}_{1.22(3)}\text{Si}_{0.78(3)}\text{O}_4$ for H5477 and S7759, respectively. Different color areas in the spheres of A, B1 and B2 sites show the ratio of constituent atoms. \square : vacancy. The crystal structure was drawn with the VESTA software (Momma and Izumi, 2011).

Supplementary text

Detailed description of analytical methods

All phases in the recovered samples were first identified using a micro-focused X-ray diffractometer (Bruker, D8 DISCOVER) equipped with an I μ S source of Co-K α radiation operated at 40 kV and 500 μ A, and a two-dimensional solid-state detector (VÅNTEC500). The compositions of the phases in the recovered samples were measured using an electron microprobe analyzer (EPMA) with wavelength-dispersive spectrometers (JEOL, JXA-8200), operated at an accelerating voltage and probe current of 15 kV and 5 nA, respectively. The samples were generally measured for acquisition times of 10 s, except for run products from H5469, H5477 and S7759, which were measured for 5, 10 and 20 s each. Enstatite was used as standard for Mg and Si, corundum for Al, albite for Na and iron metal for Fe. Sample textures were observed using a field-emission-type scanning electron microscope (SEM) (Zeiss LEO 1530 Gemini) with a detector for backscattered electron (BSE) imaging and an energy dispersive X-ray spectrometer (Oxford X-Max^N).

The oxidation state of iron in the recovered Fe-bearing Cf-type phases was determined by Mössbauer spectroscopy. A mosaic of large inclusion free single-crystals of the Cf-type phase with a total dimension of about 500 μ m in diameter and 100 μ m in height was prepared and sandwiched between plastic films. A piece of Ta foil with a 500 μ m hole was placed in front of the sample mosaic to select the desired area to measure. Mössbauer spectra were obtained at room temperature in transmission mode on a constant acceleration Mössbauer spectrometer with a nominal 370 MBq ⁵⁷Co high specific activity source in a 12- μ m-thick Rh matrix. The velocities in all spectra were calibrated using a reference spectrum of a 25- μ m-thick α -Fe foil certified by National Bureau of Standards (now referred to as the National Institute of Standards and Technology, standard reference material no. 1541) at room temperature. Spectra were collected for 4-6 days and fitted with full transmission integrals using the MossA software (Prescher et al. 2012). Two pseudo-Voigt doublets were used to fit the contribution of Fe²⁺ and Fe³⁺ in the Cf-type phases to the transmission spectra.

High-quality crystals of Cf-type phases with no inclusion and sharp optical extinction checked under a polarizing microscope were mounted on glass fibers and analyzed on a kappa-geometry Xcalibur single-crystal diffractometer (Rigaku, Oxford

Diffraction). The diffractometer was equipped with graphite-monochromatized $\text{MoK}\alpha$ radiation operated at 50 kV and 40 mA and a Sapphire2 CCD detector. Intensity data were acquired upon ω -scan rotations up to $2\theta_{\text{max}} = 90^\circ$ so that unique reflections in the Laue group mmm were measured with an average redundancy of 5. Integration of intensity, correction for Lorentz and polarization factors, frame scaling and empirical absorption correction using spherical harmonics were carried out using CrysAlisPro (Rigaku, Oxford Diffraction).

References for Online Materials

- Momma, K., and Izumi, F. (2011). VESTA 3 for three-dimensional visualization of crystal, volumetric and morphology data. *Journal of Applied Crystallography*, 44, 1272-1276.
- Prescher, C., McCammon, C., and Dubrovinsky, L. (2012). MossA: a program for analyzing energy-domain Mössbauer spectra from conventional and synchrotron sources. *Journal of Applied Crystallography*, 45, 329-331.