Supporting Information for

Crystal structure of calcium-ferrite type $NaAlSiO_4$ up to 45 GPa

Fei Qin[1,5*], Ye Wu[2], Shengchao Xue[1], Dongzhou Zhang[3], Xiang Wu[4], Steven Jacobsen[5]

[*[1]School of Earth Sciences and Resources, China University of Geosciences (Beijing), Beijing, China*
[2]School of Science, Wuhan University of Technology, Wuhan, China
[3]School of Ocean and Earth Science and Technology, Hawai'i Institute of Geophysics and Planetology, University of Hawaii at Manoa, Honolulu, Hawaii, USA
[4]State Key Laboratory of Geological Processes and Mineral Resources, China University of Geosciences, Wuhan, China
[5]Department of Earth and Planetary Sciences, Northwestern University, Evanston, Illinois, USA]

Corresponding author: Fei Qin

Email: fei.qin@cugb.edu.cn

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Text S1

To determine the axial compressibility of *a*, *b* and *c*, we used a linearized BM3 fitting to quantify the pressure-axial length relations, where each axial dimension is cubed and treated as volume in the BM formulation (Angel et al., 2014). The zero-pressure axial compressibility of linear dimension *l*, defined as $\beta_{l0} = -(l^{-1})(\delta l/\delta P)_{P=0}$, is related to the linear modulus (linear incompressibility) by $M_{l0} = (\beta_{l0})^{-1}$. Consequently, our fitted linear moduli to *a*, *b* and *c* axes are 158(5), 180(8) and 338(9) GPa Fe-free CF phase, and 158(11), 181(7) and 306(16) GPa for Fe-bearing CF, which are corresponding to axial compressibility values of $\beta_a = 6.33(1) \times 10^{-3}$, $\beta_b = 5.56(3) \times 10^{-3}$, and $\beta_c = 2.96(5) \times 10^{-3}$ GPa^{-1} for Fe-free CF, while $\beta_a = 6.33(1) \times 10^{-3}$, $\beta_b = 5.52(2) \times 10^{-3}$, and $\beta_c = 3.27(5) \times 10^{-3}$ GPa^{-1} for the Fe-bearing sample, respectively.

Figure S1 Single-crystal X-ray diffraction patterns of (a) Fe-free CF phase at 1.7 and 41.0 GPa and Fe-bearing CF phase, and (b) Fe-bearing CF phase at 1.7 and 44 GPa, respectively.

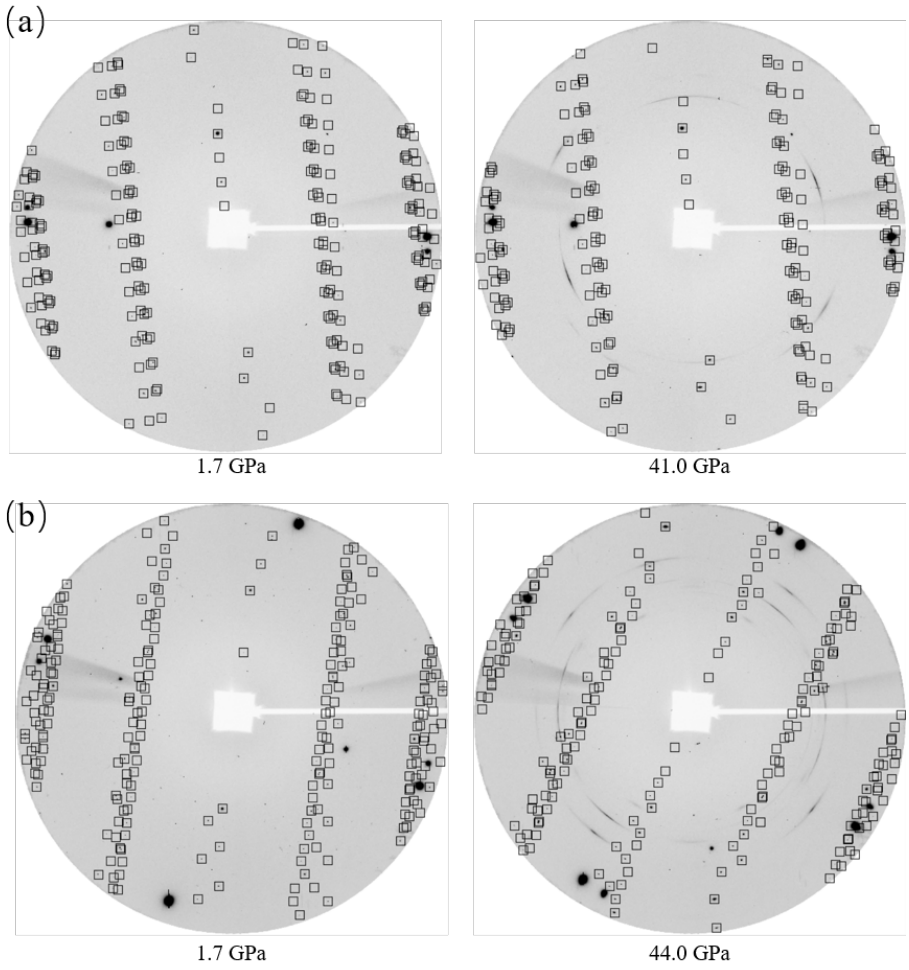

Figure S2 Pressure dependence of distortion indices of the $M1O_6$, $M2O_6$ octahedra and NaO_8 polyhedra.

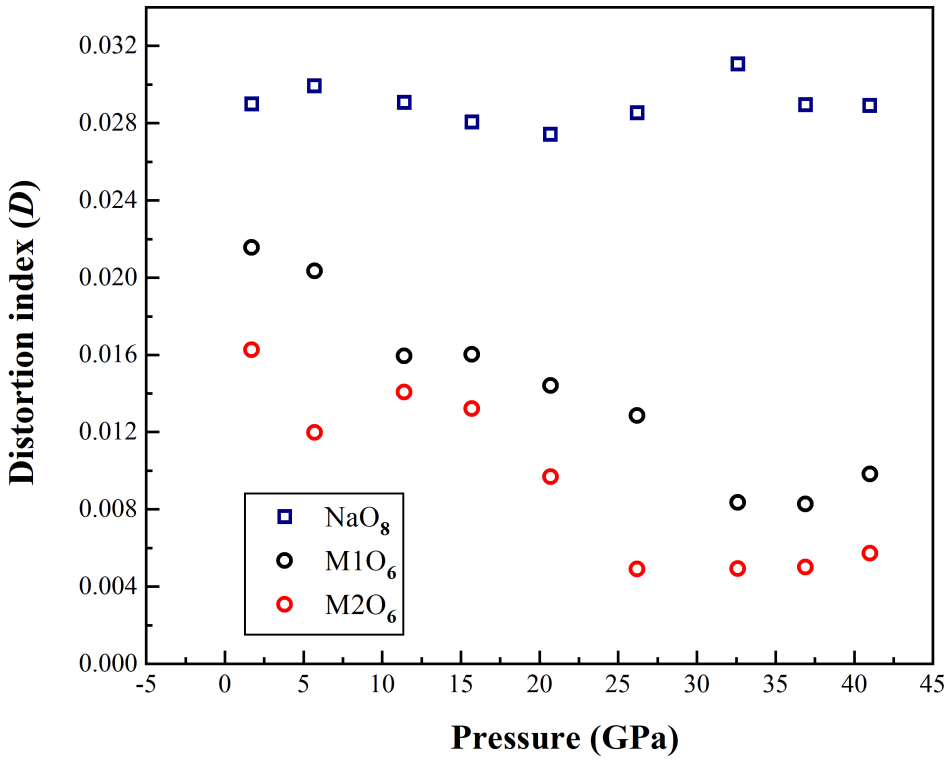

Figure S3 Several deconvoluted Raman spectra of Fe-free and Fe-bearing CF phases at selected pressures. Spectral deconvolution in the region between 680-900 cm^{-1} produces 3 main peaks assigned to the octahedral sites in CF phases.

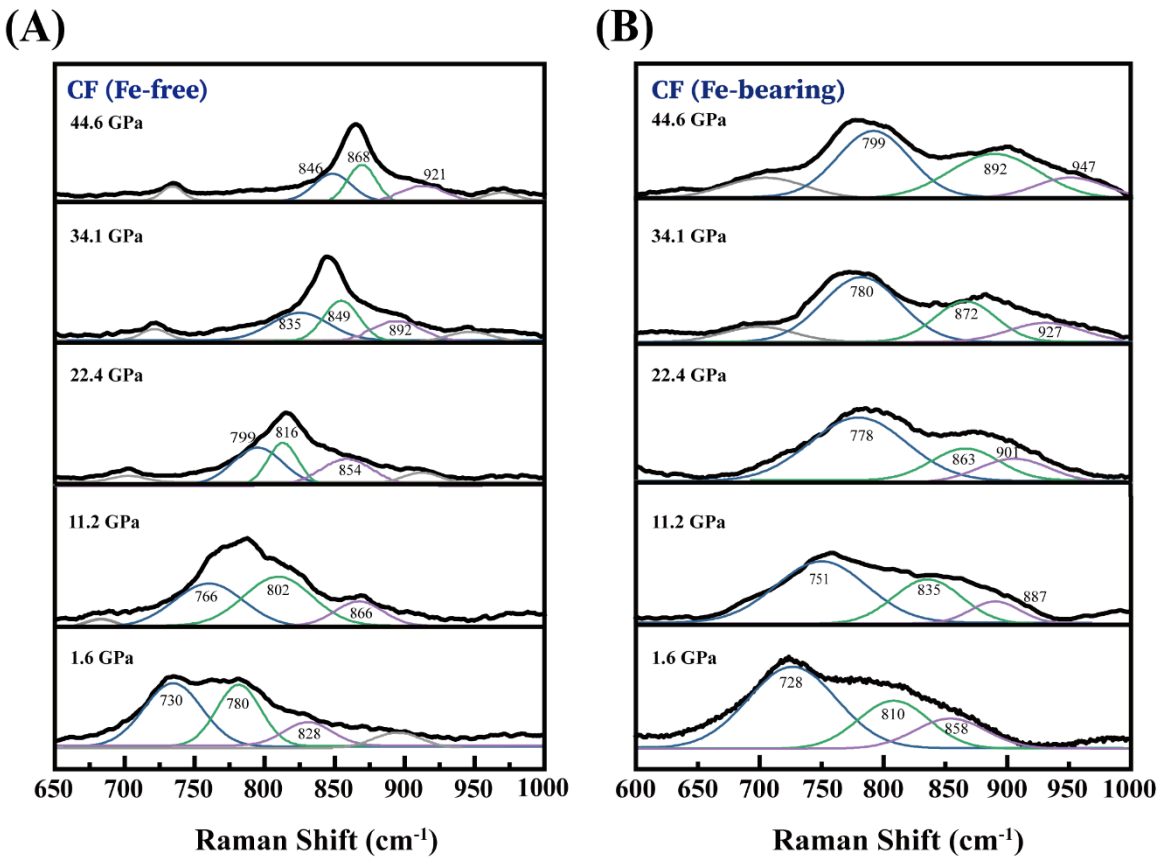

Table S1 Structure refinement details of CF phase at selected pressures up to 41.0 GPa.

Pressure (GPa)	1.7	5.7	11.4	15.7	20.7
R_{int} (%)	6.48	6.17	5.21	5.79	5.59
R_1 (all reflections, %)	4.15	4.70	4.31	3.86	4.32
R_1 (Fo > 4sig(Fo))	4.15	4.70	4.31	3.86	4.32
wR_2 (all reflections, %)	10.41	12.19	11.17	11.02	10.76
Goodness of fit	1.213	1.223	1.155	1.175	1.149
No. of total reflections	612	577	593	568	546
No. of reflections (Fo > 4sig(Fo))	108	106	107	106	103
No. of fitting parameters	22	22	22	22	22

Pressure (GPa)	26.2	32.6	36.9	41.0
R_{int} (%)	6.43	5.63	5.30	5.31
R_1 (all reflections, %)	3.02	3.96	4.15	3.58
R_1 (Fo > 4sig(Fo))	3.02	3.96	4.15	3.58
wR_2 (all reflections, %)	8.11	9.82	11.66	8.98
Goodness of fit	1.175	1.139	1.249	1.195
No. of total reflections	532	532	496	489
No. of reflections (Fo > 4sig(Fo))	94	97	92	90
No. of fitting parameters	22	22	22	22

Table S2 Fractional coordinates and displacement parameters of atoms in CF phase at selected pressures.

	P (GPa)	1.7	11.4	20.7	32.6	41.0
Na	*X*	0.6577(8)	0.6583(9)	0.6590(2)	0.6596(8)	0.6600(2)
	Y	0.7607(7)	0.7599(7)	0.7600(5)	0.7615(4)	0.7625(3)
	Z	0.75	0.75	0.75	0.75	0.75
	Uiso	0.0106(4)	0.0097(7)	0.0089(1)	0.0081(0)	0.0069(3)
Al1	*X*	0.6009(6)	0.6013(1)	0.6017(6)	0.6015(9)	0.6010(2)
	Y	1.0834(8)	1.0843(5)	1.0843(4)	1.0842(2)	1.0844(8)
	Z	0.25	0.25	0.25	0.25	0.25
	Uiso	0.0060(1)	0.0060(1)	0.0053(3)	0.0053(8)	0.0047(8)
Al2	*X*	0.3891(9)	0.3885(9)	0.3881(9)	0.3875(4)	0.3879(0)
	Y	0.5584(9)	0.5587(1)	0.5587(0)	0.5593(7)	0.5590(8)
	Z	0.25	0.25	0.25	0.25	0.25
	Uiso	0.0065(3)	0.0068(3)	0.0059(6)	0.0050(8)	0.0056(1)
Si1	*X*	0.6009(6)	0.6013(1)	0.6017(6)	0.6015(9)	0.6010(2)
	Y	1.0834(8)	1.0843(5)	1.0843(4)	1.0842(2)	1.0844(8)
	Z	0.25	0.25	0.25	0.25	0.25
	Uiso	0.0060(1)	0.0060(1)	0.0053(3)	0.0053(8)	0.0047(8)
Si2	*X*	0.3891(9)	0.3885(10)	0.3881(9)	0.3875(4)	0.3879(0)
	Y	0.5584(9)	0.5587(1)	0.5587(0)	0.5593(7)	0.5590(8)
	Z	0.25	0.25	0.25	0.25	0.25
	Uiso	0.0065(3)	0.0068(3)	0.0059(6)	0.0050(8)	0.0056(1)
O1	*X*	0.3540(3)	0.3526(5)	0.3509(9)	0.3505(7)	0.3494(2)
	Y	0.7010(9)	0.7038(8)	0.7034(5)	0.7070(9)	0.7044(2)
	Z	0.75	0.75	0.75	0.75	0.75
	Uiso	0.0093(4)	0.0093(9)	0.0092(1)	0.0076(4)	0.0070(8)
O2	*X*	0.5149(4)	0.5167(2)	0.5168(9)	0.5197(9)	0.5202(1)
	Y	0.8888(3)	0.8858(4)	0.8858(6)	0.8836(7)	0.8812(5)
	Z	0.25	0.25	0.25	0.25	0.25
	Uiso	0.0093(5)	0.0084(1)	0.0085(8)	0.0076(3)	0.0064(3)
O3	*X*	0.2111(8)	0.2128(3)	0.2133(0)	0.2133(5)	0.2130(6)
	Y	0.4714(9)	0.4719(2)	0.4715(9)	0.4727(2)	0.4747(0)
	Z	0.25	0.25	0.25	0.25	0.25
	Uiso	0.0092(9)	0.0104(3)	0.0089(4)	0.0084(3)	0.0060(7)
O4	*X*	0.5735(6)	0.5727(4)	0.5725(8)	0.5735(6)	0.5735(0)
	Y	0.5743(2)	0.5765(5)	0.5797(7)	0.5846(7)	0.5827(2)
	Z	0.25	0.25	0.25	0.25	0.25
	Uiso	0.0097(3)	0.0099(5)	0.0083(3)	0.0078(0)	0.0065(1)

Table S3 Variation of lattice parameters with pressures for Fe-free CF phase.

Pressure (GPa)	*a* (Å)	*b* (Å)	*c* (Å)	*V* (Å^3)
0.0001	10.166(1)	8.675(9)	2.7380(6)	241.5(3)
1.7[a]	10.118(1)	8.680(7)	2.7363(3)	240.3(2)
3.7	10.080(1)	8.639(7)	2.7307(3)	237.8(2)
5.7	10.040(1)	8.609(7)	2.7253(3)	235.6(2)
8.0	10.005(1)	8.578(7)	2.7199(3)	233.4(6)
9.4	9.978(2)	8.565(8)	2.7169(4)	232.2(2)
11.4	9.953(1)	8.540(7)	2.7110(3)	230.4(2)
13.7	9.925(3)	8.512(2)	2.7056(9)	228.6(5)
15.7	9.894(2)	8.479(8)	2.701(4)	226.5(2)
17.3	9.872(1)	8.450(7)	2.6963(3)	224.9(2)
19.1	9.853(1)	8.420(7)	2.6908(3)	223.2(2)
20.7	9.826(1)	8.405(8)	2.6867(3)	221.9(2)
22.1	9.809(1)	8.383(7)	2.6823(3)	220.6(2)
24.2	9.784(1)	8.359(7)	2.6764(3)	218.9(2)
26.2	9.760(1)	8.337(7)	2.6704(3)	217.3(2)
28.1	9.731(2)	8.322(8)	2.6657(4)	215.9(2)
30.2	9.714(1)	8.299(7)	2.6606(3)	214.5(2)
32.6	9.691(1)	8.278 (7)	2.6559(3)	213.1(2)
35.0	9.671(2)	8.248(7)	2.6510(3)	211.4(2)
36.9	9.656(1)	8.224(7)	2.6467(3)	210.2(2)
38.7	9.689(2)	8.212(9)	2.6412(4)	208.8(2)
41.0	9.608(1)	8.186(7)	2.6359(3)	207.3(2)

Table S4 Variation of lattice parameters with pressures for Fe-bearing CF phase.

Pressure (GPa)	*a* (Å)	*b* (Å)	*c* (Å)	*V* (Å^3)
0.0001	10.189(2)	8.686(7)	2.7571(4)	244.0(2)
1.7[a]	10.172(3)	8.666(1)	2.7511(2)	242.5(7)
10.0	10.005(1)	8.549(1)	2.7300(2)	233.5(8)
15.2	9.936(3)	8.475(1)	2.7156(2)	228.7(8)
24.0	9.838(3)	8.361(1)	2.6888(2)	221.2(8)
29.1	9.762(4)	8.296(2)	2.6715(4)	216.34(10)
33.3	9.720(3)	8.256(1)	2.6606(3)	213.5(8)
37.8	9.684(3)	8.210(1)	2.6487(3)	210.7(9)
40.8	9.651(3)	8.176(1)	2.6393(2)	208.3(8)
44.0	9.626(4)	8.161(1)	2.6327(3)	206.6(9)

Table S5 Equation of State (EoS) parameters obtained for the Fe-bearing and Fe-free CF crystals from fitting the *P*-unit-cell data using a BM3 EoS. Room pressure EoS parameters, moduli (K) and their pressure derivative (K'), volume ($V_{0\text{-measured}}$ and $V_{0\text{-fitted}}$), isothermal bulk modulus (K_{T0}) and its pressure derivative (K'_{T0}), were then obtained. EoS parameters reported in the literature are added for comparison. -, not mentioned or not measured; [a]High spin EoS; [b]Low spin EoS.

	This study	This study	Wu et al. (2017)	Wu et al. (2017)		Imada et al. (2012)	Guignot and Andrault (2004)	Dubrovinsky et al. (2002)
Composition	$Na_{0.93}Al_{1.02}SiO_4$	$Na_{0.88}Al_{0.99}Fe_{0.13}Si_{0.94}O_4$	$Na_{0.93}Al_{1.02}SiO_4$	$Na_{0.88}Al_{0.99}Fe0_{.13}Si_{0.94}O_4$		$Na_{0.4}Mg_{0.6}Al_{1.6}Si_{0.4}O_4$	$NaAlSiO_4$	$NaAlSiO_4$
P_0/GPa	10^{-4}	10^{-4}	-	-		10^{-4}	10^{-4}	-
P range/GPa	0-41.0	0-44.0	1.6-78.3	1.6-78.3		0-133.5	0-65.2	3.9-41.2
$V_{0\text{-measured}}$ /Å^3	241.5(1)	244.0(2)	-	-		239.92(367)	240.9(3)	-
$V_{0\text{-fitted}}$ /Å^3	241.6(1)	244.2(2)	241(1)	242.8(2)[a]	239(1)[b]	-	-	242.9
K_{T0}/GPa	220(4)	211(6)	201(9)	208(3)[a]	202(7)[b]	221(2)	185(5)	220(1)
K'_{T0}	2.6(3)	2.6(3)	4.2(4)	4 (fixed)	4 (fixed)	4 (fixed)	4.6(2)	4.1(1)
EoS	BM3	BM3	BM3	BM2		BM2	BM3	BM3
Pressure medium	Neon	Neon	Neon	Neon		NaCl/-	Argon	-

Table S6 Bond length (Å) and polyhedral volume (Å^3) for NaO_8, $(Al,Si)_1O_6$ and $(Al,Si)_2O_6$ in Fe-free CF phase at selected pressures.

Pressure (GPa)	0	11.4	20.7	32.6	41.0
Na–O1×2	2.4431(4)	2.382(5)	2.335(4)	2.292(4)	2.263(4)
Na–O2×2	2.2838(7)	2.232(7)	2.208(7)	2.150(7)	2.118(7)
Na–O3(A)	2.4145(18)	2.354(14)	2.318(13)	2.261(13)	2.293(11)
Na–O3(B)	2.3870(3)	2.359(12)	2.316(12)	2.297(12)	2.211(13)
Na–O4×2	2.2849(13)	2.239(9)	2.197(9)	2.146(9)	2.143(9)
(Al,Si)1–O1	1.9260(2)	1.867(13)	1.844(13)	1.790(14)	1.793(13)
(Al,Si)1–O2(C)×2	1.8222(3)	1.812(4)	1.795(4)	1.793(4)	1.781(4)
(Al,Si)1–O2(D)	1.9009(16)	1.893(10)	1.865(10)	1.840(10)	1.836(11)
(Al,Si)1–O3×2	1.8319(3)	1.816(4)	1.796(5)	1.777(5)	1.769(5)
(Al,Si)2–O1×2	1.8793(9)	1.871(9)	1.849(9)	1.840(10)	1.814(9)
(Al,Si)2–O3	1.9597(5)	1.899(6)	1.867(7)	1.834(7)	1.817(6)
(Al,Si)2–O4×2	1.8289(8)	1.823(8)	1.819(8)	1.823(8)	1.794(8)
(Al,Si)2–O4	1.8793(4)	1.840(6)	1.820(6)	1.814(6)	1.794(6)
Mean bond length					
Na–O	2.3532(6)	2.3022(8)	2.2642(8)	2.2168(8)	2.1941(8)
$(Al,Si)_1$–O	1.8558(5)	1.8360(8)	1.8155(7)	1.7951(9)	1.7882(9)
$(Al,Si)_2$–O	1.8759(7)	1.8544(7)	1.8371(7)	1.8294(7)	1.8054(7)
Volume					
NaO_8	22.4020	21.0705	20.1078	18.9229	18.3668
$(Al,Si)_1O_6$	8.3362	8.0991	7.8298	7.5963	7.5205
$(Al,Si)_2O_6$	8.6287	8.3523	8.1342	8.0639	7.7276

Table S7 Results of linear regressions to the pressure dependence of observed vibrational modes (ν_i) in epidote and clinozoisite up to ~40 GPa. The reference frequency at room pressure (ω_0) and pressure coefficients, $\alpha_i = (d\omega_i/dP)$, were used to calculate mode Grüneisen parameters (γ_i) using the fitted K_{T0} values obtained in this study from BM3-EoS fits: 220(4) GPa for Fe-free CF sample and 211(6) GPa for Fe-bearing CF.

Fe-free CF phase			**Fe-bearing CF phase**		
ω_0 (cm^{-1})	α (cm^{-1}/GPa)	γ_i	ω_0 (cm^{-1})	α (cm^{-1}/GPa)	γ_i
190	0.52(4)	0.59(2)			
348	0.61(9)	0.38(2)	324	1.39(6)	0.91(4)
384	1.64(8)	0.94(2)	384	1.08(7)	0.59(3)
457	1.12(5)	0.54(2)	459	0.92(6)	0.42(3)
460	1.44(7)	0.69(1)	464	1.17(6)	0.53(2)
549	1.95(5)	0.78(2)	534	1.17(7)	0.46(2)
653	1.84(7)	0.62(2)	630	0.90(5)	0.30(2)
730	2.26(4)	0.68(1)	718	2.06(2)	0.61(2)
770	2.12(2)	0.61(1)	804	2.87(5)	0.75(2)
820	2.31(6)	0.62(1)	814	3.90(7)	1.01(2)
936	1.57(7)	0.37(2)	918	1.99(12)	0.46(2)
988	1.73(10)	0.38(1)	982	1.08(11)	0.23(2)
1094	1.66(16)	0.33(2)	1071	1.50(15)	0.30(3)