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Revision 2

Crystal structure of calcium-ferrite type NaAlSiO₄ up to 45 GPa

Fei Qin^{1,5*}, Ye Wu², Shengchao Xue¹, Dongzhou Zhang³, Xiang Wu⁴, Steven D.
Jacobsen⁵

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

24

Abstract

25 Alkali-rich aluminous high-pressure phases including calcium-ferrite (CF) type
26 NaAlSiO₄ are thought to constitute ~20% by volume of subducted mid-ocean ridge
27 basalt (MORB) under lower mantle conditions. As a potentially significant host for
28 incompatible elements in the deep mantle, knowledge of the crystal structure and
29 physical properties of CF-type phases is therefore important to understanding the
30 crystal chemistry of alkali storage and recycling in the Earth's mantle. We determined
31 the evolution of the crystal structure of pure CF-NaAlSiO₄ and Fe-bearing CF-
32 NaAlSiO₄ at pressures up to ~45 GPa using synchrotron-based, single-crystal X-ray
33 diffraction. Using the high-pressure lattice parameters, we also determined a third-
34 order Birch-Murnaghan equation of state, with $V_0 = 241.6(1) \text{ \AA}^3$, $K_{T0} = 220(4) \text{ GPa}$
35 and $K_{T0}' = 2.6(3)$ for Fe-free CF, and $V_0 = 244.2(2) \text{ \AA}^3$, $K_{T0} = 211(6) \text{ GPa}$ and $K_{T0}' =$
36 $2.6(3)$ for Fe-bearing CF. The addition of Fe into CF-NaAlSiO₄ resulted in a $10 \pm 5\%$
37 decrease in the stiffest direction of linear compressibility along the *c*-axis, leading to
38 stronger elastic anisotropy compared with the Fe-free CF phase. The NaO₈ polyhedra
39 volume is 2.6 times larger and about 60% more compressible than the octahedral
40 (Al,Si)O₆ sites, with $K_0^{NaO_8} = 127 \text{ GPa}$ and $K_0^{(Al,Si)O_6} \sim 304 \text{ GPa}$. Raman spectra of the
41 pure CF-type NaAlSiO₄ sample shows that the pressure coefficient of the mean
42 vibrational mode, $1.60(7) \text{ cm}^{-1}/\text{GPa}$, is slightly higher than $1.36(6) \text{ cm}^{-1}/\text{GPa}$ obtained
43 for the Fe-bearing CF-NaAlSiO₄ sample. The ability of CF-type phases to contain
44 incompatible elements such as Na beyond the stability field of jadeite requires larger
45 and less compressible NaO₈ polyhedra. Detailed high-pressure crystallographic

46 information for the CF phases provides knowledge on how large alkali metals are
47 hosted in alumina framework structures with stability well into the lowermost mantle.

48

49

50 **Keywords:** CF-type NaAlSiO₄, single-crystal structure refinements, incompatible Na
51 elements, high pressures, Raman spectroscopy, lower mantle

52

53

Introduction

54 The bulk lower mantle is considered well mixed above the D'' layer, yet regional
55 heterogeneities are identified by seismology and geochemical studies (e.g. Jenkins et
56 al., 2017; Romanowicz and Wenk, 2017). Calcium-ferrite (CF) type phases and the
57 new hexagonal aluminous phase (NAL phase) may collectively account for 10-30 vol%
58 of subducted oceanic crust below ~2700 km and therefore likely play an important
59 role in the observed regional-scale seismological and geochemical heterogeneities
60 (Bina and Helffrich, 2014; French and Romanowicz, 2014; Fukao et al., 2009; Litasov
61 and Ohtani, 2005; Wu et al., 2016, 2017). However, the high-pressure behaviors (e.g.,
62 structure, stability and elasticity) of the alkali-rich aluminous high-pressure phases
63 remains poorly known compared with other lower mantle minerals such as
64 bridgmanite (Mg,Fe)SiO₃, davemaoite (CaSiO₃), and ferropericlase (Mg,Fe)O
65 (Fujino et al., 2012; Ono et al., 2004; Wentzcovitch et al., 1995). Determining the
66 structure and thermodynamic properties of the major alkali-rich phases will therefore
67 improve computational models of slab dynamics as well as our understanding of the
68 behavior of incompatible elements in the lowermost mantle.

69 Average mid-ocean ridge basalt contains 10-12 wt.% CaO and 2-3 wt.% Na₂O,
70 largely in plagioclase and clinopyroxenes in the upper mantle (Sun et al., 1979). On
71 subduction to below 50-60 km, the basalt-eclogite transition changes the mineralogy
72 of MORB where Ca-pyroxene (diopside), Na-pyroxene (jadeite) and garnet host the
73 majority of alkali metals and aluminum (Yoder Jr and Tilley, 1962; Ringwood and
74 Green, 1966). Below ~300 km, pyroxene and garnet form a solution of majoritic

75 garnet but below the transition zone (410-660 km) the breakdown of majoritic garnet
76 leads to bridgmanite, davemaoite, and stishovite, where Al, the majority of Na, and
77 some Ca are hosted in the CF-type and/or NAL-phases (depending on depth) with
78 complex chemical composition (Kesson et al., 1994; Ono et al., 2001; Ricolleau et al.,
79 2010).

80 CF phases crystallizing in the orthorhombic system (space group *Pbnm*) display
81 solid solutions with the general formula $A_3B_6O_{12}$, where A represents a large mono- or
82 divalent cations, like Na^+ , K^+ , or Ca^{2+} , and B is a six-coordinated cation site occupied
83 by Mg^{2+} and mixed-valence Fe. Incorporation of Al^{3+} or Si^{4+} into the octahedral site
84 leads to CF-type phases $CaAl_2O_4$, $MgAl_2O_4$, and $NaAlSiO_4$ (Irifune et al., 1991; Liu,
85 1977; Reid and Ringwood, 1969). Along the $NaAlSiO_4$ - $MgAl_2O_4$ join, NAL is formed
86 as a single phase up to 34 GPa, whereas above 45 GPa, $NaAlSiO_4$ and $MgAl_2O_4$ co-
87 exist as separate phases in the calcium-ferrite structure (Imada et al., 2011). Given
88 that these likely exist as separate phases over most of the depth range in lower mantle,
89 experimental determination of their physical properties is needed to properly estimate
90 the density and velocity of subducted slabs (Ricolleau et al., 2010). Furthermore, by
91 examining the influence of iron incorporation it is also possible to evaluate potential
92 impacts of iron spin-pairing transitions (e.g. Lobanov et al., 2017; Wu et al., 2017).

93 To gain insight into the elasticity and equations of state as well as alkali storage
94 mechanisms, we have undertaken high-precision, single-crystal structure
95 determinations of Fe-free and Fe-bearing CF phases up to ~45 GPa *in situ* using
96 synchrotron-based single-crystal X-ray diffraction. Vibrational properties of these

97 structures were determined by Raman spectroscopy. These results provide
98 comprehensive understanding of the crystallographic information of such alkali-
99 bearing CF phases under lower mantle conditions, thus improving our knowledge of
100 proper chemical and physical properties of these important lower mantle alkali-
101 dominated phases, and shedding new light on alkali reservoirs in the Earth's deep
102 mantle.

103

104

Materials and methods

105 Samples for the current study were synthesized in experimental runs #5K2124
106 (Fe-free) and #5K2681 (Fe-bearing) at 25 GPa and 1600 °C using a 5000-ton Kawai-
107 type multi anvil pressure apparatus (USSA-5000) at the Institute for Study of the
108 Earth's Interior (ISEI), Okayama University at Misasa, Japan. Details of the sample
109 synthesis and compositional characterization are reported in [Wu et al. \(2017\)](#). Briefly,
110 a stoichiometric mixture of high-purity Na₂CO₃, Al₂O₃, and SiO₂ were mixed with a
111 molar ratio of 1:1:2 and used as the starting material. For the Fe-bearing sample, iron
112 was added as ⁵⁷Fe₂O₃ with >95% enrichment in ⁵⁷Fe. The chemical compositions of
113 the Fe-free and Fe-bearing samples were obtained by electron microprobe analysis as
114 given by [Wu et al. \(2017\)](#) and found to be Na_{0.93}Al_{1.02}Si_{1.00}O₄ and
115 Na_{0.88}Al_{0.99}Fe_{0.13}Si_{0.94}O₄. Their crystal structure was characterized by X-ray
116 diffraction at GSECARS of the Advanced Photon Source (APS), Argonne National
117 Laboratory, beamline 13-BM-C. The results confirm that both CF samples possess
118 space group *Pbnm*, and their lattice constants are $a = 10.166(1) \text{ \AA}$, $b = 8.675(9) \text{ \AA}$, $c =$

119 2.7380(6) Å, and $V = 241.5(1) \text{ \AA}^3$ for the Fe-free CF phase, and $a = 10.189(2) \text{ \AA}$, $b =$
120 $8.686(7) \text{ \AA}$, $c = 2.7571(4) \text{ \AA}$, and $V = 244.0(2) \text{ \AA}^3$ for the Fe-bearing sample.
121 Mössbauer spectroscopy shows that 90% of the iron is ferric (Fe^{3+}) (Wu et al., 2017).
122 Crystals of the CF phases measuring $\sim 1.5 \text{ mm}$ in maximum dimension were crushed
123 into $30 \text{ \mu m} \times 40 \text{ \mu m}$ chips under an optical microscope and then polished to $\sim 10 \text{ \mu m}$
124 thickness for the high-pressure study.

125 High-pressure, single-crystal X-ray diffraction experiments were carried out at
126 GSECARS (Sector 13) of the advanced Photon Source (APS), Argonne National
127 Laboratory (ANL), beamline 13-BM-C. A monochromatic X-ray beam with a
128 wavelength of 0.434 \AA was focused to a $15 \times 15 \text{ \mu m}^2$ spot for the diamond-anvil cell
129 experiment (Zhang et al., 2017). We used a short symmetric-type diamond anvil cells,
130 fitted with Boehler-Almax diamond anvils with 300 \mu m flat culets and set into seats
131 with 76-degree opening. A Re gasket was pre-indented to $\sim 40 \text{ \mu m}$ thickness before
132 laser drilling a sample chamber of $\sim 160 \text{ \mu m}$ diameter. Polished Fe-free and Fe-bearing
133 CF samples were loaded with neon pressure medium into their respective sample
134 chambers along with Pt foil for pressure calibration (Fei et al., 2007).

135 To obtain sufficiently precise constraints on the unit-cell evolution, we obtained
136 diffraction data with multiple detector positions and for the full structure
137 determinations at least 600 reflections were used (Figure S1). The single-crystal
138 crystal structure refinements of the CF samples were carried out using ATREX/RSV,
139 SHELXL, Olex2 and VESTA software packages (Dera et al., 2013; Dolomanov et al.,
140 2009; Momma and Izumi, 2008). A crystal structure model of Yamada et al. (1983)

141 was used to initialize the refinement. We used isotropic atomic displacement
142 parameters (U_{iso}) for all atoms. Figures of merits of the refinements, atomic
143 coordinates and displacement parameters of Fe-free CF phase is presented in
144 Supplemental information [Table S1 and S2](#).

145 High-pressure Raman spectroscopy for the iron-bearing and pure CF-NaAlSiO₄
146 phases was performed up to 44.6 GPa at room temperature using Princeton-style
147 diamond-cells with 300- μ m ultra-low fluorescent diamond anvils. The diamond cells
148 for Raman spectroscopy were gas loaded with neon at HPSTAR and ruby was used as
149 the pressure calibration ([Mao et al., 1986](#)). The pressure was determined by multiple
150 measurements before and after each experimental run. Raman spectra were collected
151 on a Renishaw inVia reflex Raman spectrometer with 532 nm diode-pumped solid-
152 state laser, at Peking University. The spectrograph was calibrated using a silicon wafer,
153 and the spectra were collected in unpolarized, backscatter geometry using a charge-
154 coupled device detector with a resolution of 1 cm^{-1} . Each Raman spectrum was
155 collected with an averaged exposure time of 30 s over 5 accumulations. [The](#)
156 [deconvolution of Raman spectra and peak positions were fitted using the software](#)
157 [package PeakFit \(Systat Software, Inc.\)](#)

158

159 **Results and Discussion**

160 **Stability and compressibility of Fe-free and Fe-bearing CF phase**

161 Throughout the investigated pressure range (up to 41.3 and 44 GPa for Fe-free

162 and Fe-bearing CF, respectively), no indicators of phase transformation were
163 identified. The crystal structure of Fe-free CF-NaAlSiO₄ at 41.3 GPa is shown in
164 **Figure 1**. The CF phase consists of an alumina framework composed of double chains
165 of linked (Al,Si)₁O₆⁻ and (Al,Si)₂O₆-octahedra, while relatively large alkali Na sites
166 located in the eight-fold coordination sites in tunnels formed by the octahedral chains,
167 hereafter denoted NaO₈-polyhedra. The quality of diffraction patterns used to carry
168 out structure refinements at low (~2 GPa) and high (~40 GPa) pressures are illustrated
169 by the CCD images shown in **Figure S1**.

170 Lattice parameters of the CF phase are consistently refined to an orthorhombic
171 cell (*Pbnm* and *Z* = 4) (**Figure 2**). Volume compression and axial compression data of
172 both CF phases at different pressures are given in **Table S3 and S4**. Pressure-volume
173 data were fitted to a third-order Birch-Murnaghan equation of state (EoS) using error-
174 weighted least squares with EoSFit7c software ([Angel et al., 2014](#)). Under ambient
175 conditions, the measured *V*₀ values are 241.5(1) and 244.0(2) Å³ for the Fe-free and
176 Fe-bearing CF sample, respectively. The best-fit, third-order Birch-Murnaghan EoS
177 parameters yield *V*₀ = 241.6(1) Å³, *K*_{T0} = 220(4) GPa and *K*_{T0}' = 2.6(3) for Fe-free CF,
178 and *V*₀ = 244.2(2) Å³, *K*_{T0} = 211(6) GPa with *K*_{T0}' = 2.6(3) for Fe-bearing CF. Note
179 that at room pressure, the measured unit-cell volume and the fitted zero-pressure
180 volume in our BM3 procedure are identical within error for both Fe-free and Fe-
181 bearing phases. Although both CF phases exhibit broadly similar equation of state
182 parameters, the unit-cell volume of the Fe-bearing sample is about 1% larger and
183 about 4% more compressible than the Fe-free sample.

184 We also determined the axial compressibility of the lattice parameters using the
185 linearized third-order Birch-Murnaghan EoS (Figure 2). Details are described in
186 Supplemental Text S1. Our fitted linear moduli to a , b and c axes are 158(5), 180(8)
187 and 338(9) GPa for Fe-free CF phase, and 158(11), 181(7) and 306(16) GPa for Fe-
188 bearing CF sample, respectively, which indicate a - and b -axes exhibit similar linear
189 moduli for both CF phases. The addition of Fe into the CF phase leads to a decrease in
190 the linear compressibility of the c -axis compared with Fe-free phase. The relative
191 axial compressibility scheme is $\beta_a > \beta_b > \beta_c$ for both phases. Ratios of zero-pressure
192 axial compressibility between the three axes are 2.14:1.88:1 for Fe-free and
193 1.94:1.69:1 for Fe-bearing sample, which suggests strong elastic anisotropy on
194 compression, with the c -axis being the stiffest direction within the structure.

195 The room temperature equations of state for CF phases determined in this study
196 are shown in Figure 3, with volume normalized to measured V_0 in order to aid in
197 comparison with previous studies. The absolute difference between our equation of
198 state parameters and those from previous work (Table S5 in supporting information)
199 depends on many factors including (among others) data precision, data density, crystal
200 quality, and the experimental pressure range, resulting in the usual trade-offs between
201 V_0 , K_{T0} , and K'_{T0} fitted to different datasets, complicating a quantitative assessment of
202 the effect of Fe substitution on the compressibility of CF phase. By measuring both
203 pure-CF and Fe-bearing CF phases in the same study with high-quality single crystals,
204 we were able to tightly constrain the values of K_{T0} and K'_{T0} for both crystals under
205 similar experimental parameters, finding that $\text{Fe}_{\text{tot}} = 0.13$ pfu in the CF phase leads to

206 3.2±1.9% reduction in the bulk modulus compared with the Fe-free sample. The lower
207 bulk moduli values of $K_{T0} = 201(9)$ GPa reported for the CF-phase by Wu et al.
208 (2017), who also determined high-spin ($K_{T0} = 208(3)$ GPa) and low-spin ($K_{T0} = 202(7)$
209 GPa) bulk moduli for Fe-bearing CF phase were fitted with relatively high values of
210 K'_{T0} (fixed at 4), which are, however, poorly constrained. The derived EoS parameters
211 obtained in this study are statistically higher than that obtained by Guignot and
212 Andrault (2004) with $K_{T0} = 185(5)$ GPa but in good agreement with previously
213 reported values of $K_{T0} = 214(14)$ GPa, $K_{T0}' = 3.6(5)$ (Imada et al., 2012) and $K_{T0} =$
214 $220(1)$ GPa, $K_{T0}' = 4.1(1)$ (Dubrovinsky et al., 2002).

215 Generally, CF phases in MORB compositions exhibit complex solid solutions
216 but for simplicity can be considered along the NaAlSiO₄-MgAl₂O₄ join (Imada et al.,
217 2011). By comparison, solid solutions between NaAlSiO₄ and MgAl₂O₄ in the
218 CaFe₂O₄ structure type show roughly similar density between these two end members.
219 However, there is a very broad range of reported values for the bulk modulus of the
220 CaFe₂O₄-type MgAl₂O₄ phase in MORB composition, ranging from 184–243 GPa
221 (Funamori et al., 1998; Irifune et al., 2002; Guignot and Andrault, 2004; Ono et al.,
222 2005). The thermal equation of state of MgAl₂O₄ has also been investigated using
223 multi-anvil apparatus and DAC techniques by Sueda et al. (2009), who reported 205(6)
224 GPa for the room-temperature bulk modulus.

225

226 **High-pressure structure evolution of CF phase**

227 To better understand the compression mechanisms of CF-type NaAlSiO₄, we

228 analyzed the structure and evolution of the polyhedral elements on compression at
229 selected pressures. Here we used two parameters to characterize the compression of
230 each polyhedron: the polyhedral volume and the mean bond length. Results are given
231 in **Table S6**. More details on the high-pressure structure refinements of the Fe-free
232 sample will be discussed next.

233 The bond lengths of Na-O, (Al,Si)1-O and (Al,Si)2-O as a function of pressure
234 are shown in **Figure 4**. Average (Al,Si)-O distances related to the (Al,Si)1 and
235 (Al,Si)2 sites are 1.856 Å and 1.876 Å at room pressure, respectively. By comparing
236 with those aluminous high-pressure phases, these values are in good agreement with
237 1.929 Å in NaAlSi₂O₆ jadeite (Cameron et al., 1973) and 1.887 Å in Mg₃Al₂Si₃O₁₂
238 pyrope (Novak and Gibbs, 1971), which are typical values for the six-coordinated Al-
239 O distances. During static compression, all of the bond distances decrease linearly in
240 the range of 0.00168-0.00172 Å/GPa for (Al,Si)-O bond, while the shortening of Na-
241 O bonds are about twice than that of the (Al,Si)-site octahedral bonds. Over the whole
242 pressure range of this study, the mean bond length of Na-O shortened by 6.7%,
243 whereas the (Al,Si)-O bonds shortened by only 3.6% for (Al,Si)1-O and 3.7% for
244 (Al,Si)2-O.

245 The structural evolution of all the coordination polyhedra is presented in **Figure 5**.
246 The average (Al,Si)O₆ volume is 8.48(2) Å³ at ambient pressure and decreases to
247 7.62(2) Å³ at 41.0 GPa, while the volume of NaO₈-polyhedron is about 2.6 times
248 larger, and decreases from 22.40(3) Å³ to 18.37(2) Å³ between 0 and 41.0 GPa. The
249 average (Al,Si)O₆ volume has a much smaller value and is significantly more

250 incompressible than the NaO₈-polyhedron. In particular, the (Al,Si)O₆ octahedron is
251 much stiffer with an average bulk modulus of ~304 GPa compared with the $K_0^{NaO_8}$ of
252 127 GPa within the whole pressure range, when both K_0' fixed at 4. Our value of
253 $K_0^{SiO_6}$ for CF phase is in excellent agreement with the compressibility of SiO₆
254 octahedron in stishovite SiO₂ ($K_0^{SiO_6} = 303\text{-}346$ GPa), another important phase in the
255 lower mantle (Andrault et al., 1998).

256 The distortion index (D) describes the polyhedral distortion, defined as D
257 $= \frac{1}{n} \sum_{i=1}^n \frac{|l_i - l_{av}|}{l_{av}}$, where l_i is the distance from the central cation to the i th surrounding
258 oxygen and l_{av} is the average distance (Baur, 1974; Momma and Izumi, 2008). In this
259 study, we found that NaO₈ polyhedra have higher distortion indices than the (Al,Si)O₆
260 octahedra across the experimental pressure range. At 41 GPa, D_{NaO_8} is 0.029 while the
261 average $D_{(Al,Si)O_6}$ is 0.0078. Distortion index values of the NaO₈ did not change
262 beyond error during compression, indicating that the NaO₈ polyhedra have less
263 structural deformation compared with the (Al,Si)O₆ upon compression (Figure 6).

264

265 **Vibrational modes and Grüneisen parameters**

266 *In situ* Raman spectroscopy was conducted up to 44.6 GPa on both Fe-free and
267 Fe-bearing crystals taken from the same synthesis runs used in the XRD study.
268 Selected spectra of both crystals with increasing pressure are presented in Figure 7. As
269 the Raman active modes are 18A_g+9B_{1g}+18B_{2g}+9B_{3g}, a total of 54 Raman active
270 vibrations modes are expected. Unfortunately, the data quality is not rich enough to
271 deconvolute and assign all the peaks. The smaller number of observed modes is due to

272 weak intensity, peak overlap, and orientation dependence. In this study, around 14
273 Raman peaks were observed for the CF in the Raman shift range of 1200-150 cm^{-1} .
274 Peak positions of the major observed modes as a function of pressure are provided in
275 Figure 7 and Table S7. All observed Raman peaks shift to higher frequency with
276 increasing pressure, and some broad bands may consist of several Raman active
277 modes having very close frequencies.

278 There have been numerous investigations on MgAl_2O_4 , CaAl_2O_4 and their solid
279 solutions with Raman spectroscopy (Kojitani et al., 2007; Kojitani et al., 2013; Ono et
280 al., 2009). Yet, there is no detailed Raman spectroscopic study on Fe-free and Fe-
281 bearing CF phase. As shown in Figure 7, Raman modes located between 680-900 cm^{-1}
282 become stronger and sharper at higher pressures in both phases. At ambient conditions,
283 the peak at 190 cm^{-1} of Fe-free CF phase can be attributed to the vibrations of the Na^+
284 ions, while this peak is not observed in the Fe-bearing sample (Fei et al., 2020;
285 Kojitani et al., 2013). The vibrational modes at $\sim 348 \text{ cm}^{-1}$ and 331 cm^{-1} in Fe-free and
286 Fe-bearing CF phase, respectively, can be assigned to A_g modes with translation of
287 Al^{3+} (Kojitani et al., 2013). Mode frequencies at 374, 439, 460, 554 and 653 cm^{-1} in
288 the Fe-free sample and at 386, 453, 474, 535 and 631 cm^{-1} of Fe-bearing sample can
289 be attributed to the O–Si–O and Si–O–Si (or Al) bending, which are accordance with
290 the MgAl_2O_4 and CaAl_2O_4 in CF structure (Kojitani et al., 2013). In the frequency
291 range of 680-900 cm^{-1} , the most intense peaks at 729, 772 cm^{-1} (Fe-free CF), and 720,
292 799 cm^{-1} (Fe-bearing CF) are mainly caused by the vibrational modes related to the
293 octahedral sites. It should be noted that peak broadenings in the frequency range of

294 400-660 cm^{-1} and 680-900 cm^{-1} is generally associated with structural disorder over
295 lattice sites, i.e., Si, Al and Fe disorder over the octahedral site in the CF structure
296 (Kojitani et al., 2013). Therefore, spectral deconvolution in the region between 680-
297 900 cm^{-1} produces 3 main peaks around 720, 799, 839 cm^{-1} and 729, 772, 818 cm^{-1}
298 assigned to the (Al/Si) O_6 octahedral sites in Fe-rich and Fe-free CF phase,
299 respectively (Figure S3). It was found that the bands appearing at the 680-900 cm^{-1}
300 region in Fe-bearing CF phase tended to be broader than the pure-CF, due to presence
301 of Fe^{3+} in the octahedral sites. On this basis, the Raman bands become far apart with
302 elevated pressure, indicating less disorder in the octahedral Fe environments (Figure
303 S3). Additionally, at higher frequencies, the appearance of the peaks at 944, 985, 1099
304 cm^{-1} and 908, 980, 1080 cm^{-1} in Fe-free and Fe-rich CF sample, respectively, are
305 probably caused by Si- O_{nb} (non-bridged oxygen), Si- O_{br} (bridged oxygen) bending
306 asymmetric and symmetric stretchings (Prencipe, 2012).

307 Mode Grüneisen parameters (γ_i) were calculated using $\gamma_i = (K_0/v_i) (d_{vi}/dP)_T$, where
308 v_i is the wavenumber of the i^{th} mode and K_0 is the bulk modulus at room temperature
309 (Table S7). Here, we used the isothermal bulk modulus K_0 of 220(4) and 211(6) GPa
310 for Fe-free and Fe-bearing CF phase, respectively, which were obtained by the BM3
311 fit. The resulting mean pressure coefficient of the whole structure for pure CF-
312 NaAlSiO_4 of 1.61(7) $\text{cm}^{-1}/\text{GPa}$ is slightly higher than 1.40(6) $\text{cm}^{-1}/\text{GPa}$ found for Fe-
313 bearing sample. Correspondingly, the calculated mode Grüneisen parameters
314 determined in this study range from 0.31(2)-0.94(2) for the pure-CF, and 0.25(3)-
315 0.84(2) for the Fe-bearing CF phase, with average values from all the observed modes

316 of 0.58(1) and 0.54(2), respectively. As for the octahedral site vibrations in both
317 phases, the calculated γ values fall generally in the range of 0.57-0.84, which are
318 comparable with those experimental determined modes with AlO_6 octahedra for
319 MgAl_2O_4 in the CF-type structure (Kojitani et al., 2013). The mean pressure
320 coefficient of octahedral site-derived mode in Fe-bearing CF phase of 2.78(7)
321 $\text{cm}^{-1}/\text{GPa}$ is larger than 2.17(6) $\text{cm}^{-1}/\text{GPa}$ found in Fe-free sample, consistent with the
322 higher compressibility of the Fe-bearing phase relative to Fe-free CF phase. We
323 therefore conclude that the major difference in compressibility between the two
324 structures is related to the Al/Fe–O bonds in octahedral sites in particular along the *c*-
325 axis.

326 Implications

327 Generally, the structural compression mechanisms of the CF and NAL phases
328 can be compared with the structural shrinkage in K-hollandite. With increasing
329 pressure, a distortion of the (Al,Si) O_6 octahedral framework, which forms the tunnel
330 structure, contracts and leads to more compact tunnels. Since the $^{\text{VIII}}\text{K-O}$ bond in K-
331 hollandite is one of the most compressible bonds among the metal-oxygen pairs in
332 oxide minerals, KO_8 polyhedra are very compressible and can be compared to the
333 bulk modulus of NaO_8 in the CF phase (Mookherjee and Steinle-Neumann, 2009;
334 Zhang et al., 1993). Furthermore, in comparison to jadeite- $\text{NaAlSi}_2\text{O}_6$ (McCarthy et
335 al., 2008; Posner et al., 2014), the longer Na–O bonds and low degree of NaO_8
336 polyhedra distortion in the CF phase determined here at high pressures likely
337 contribute to its wide stability over lower mantle conditions.

338 Na-bearing majorite and Na-rich pyroxene (e.g., NaAlSi₂O₆ jadeite, NaFe³⁺Si₂O₆
339 aegirine) have similar chemical compositions and have also considered as potential
340 hosts for Na in the Earth's mantle (Bindi et al., 2011; Xu et al., 2017). Previous
341 studies have indicated that aegirine remains in the monoclinic *C2/c* structure up to 60
342 GPa, with the NaO₈ polyhedron likely controlling bulk compressibility (Xu et al.,
343 2017). However, the incorporation of Fe³⁺ to Na-pyroxene significantly increases the
344 bulk modulus as well as the transition pressure for the pyroxene to garnet transition
345 (Xu et al., 2017; Matrosova et al., 2019). Although sodium is significantly enriched in
346 continental crust compared with oceanic crust, Na is an important incompatible
347 element in the mantle because it partitions strongly into the MORB-forming melts
348 below the spreading ridges (Hofmann, 1988). Thus, subduction of MORB recycles Na
349 into the mantle where it contributes to melting in the upper-mantle wedge but is also
350 likely carried deeper into the mantle. The CF phase is regarded as the only Na-
351 dominated stable phase in the lower mantle down to ~2700 km.

352 Considering the potentially significant volume proportion of CF and NAL phases
353 in deeply-subducted MORB, the elastic properties of these minerals and their
354 compositional solid solutions are important for estimates of density and velocity of
355 MORB. In more recent studies, coupled substitutions of Al³⁺ and Mg²⁺ in the CF
356 structure by Na⁺ and Si⁴⁺ has limited influence on its elastic constants, but slightly
357 weakens the elastic wave anisotropy (Zhao et al., 2018; Wang et al., 2020). Further
358 investigations of the crystal chemistry on the CF phase at the pressure and
359 temperature relevant to the lower mantle conditions are necessary. Most importantly,

360 adopting the thermo-elastic parameters of the CF-structure end-member to estimate
361 the thermo-elastic properties of complex aluminous solid solutions would improve our
362 understanding of the role recycled oceanic crust plays in the global alkali cycle with
363 implications for the long-term evolution and internal heating of the Earth's mantle.

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552

Figure captions

553 **Figure 1** The crystal structure of the CF phase, determined at 41.3 GPa. The grey polyhedra
554 corresponded to the A sites, occupied by Na^+ or Fe^{2+} , and the smaller purple octahedra correspond
555 to the B sites, occupied by Al^{3+} and Si^{4+} .

556 **Figure 2** Normalized lattice parameters of Fe-free (filled circles) and Fe-bearing (open circles) CF
557 phases as a function of pressure at room temperature. Equations of state fits are shown by solid
558 lines for the Fe-free phase and dashed lines for the Fe-bearing CF phase.

559 **Figure 3** Pressure–volume data for the CF-phase (filled circles) and Fe-bearing CF phase (open
560 circles) from this study compared with other compositions from previous work (Guignot and
561 Andraut, 2004; Imada et al., 2012; Wu et al., 2017). Solid curves show the fitted BM3 equations
562 of state from this study.

563 **Figure 4** Pressure dependence of the mean bond lengths of the two distinct $(\text{Al,Si})\text{O}_6$ octahedra
564 and the NaO_8 polyhedra in the pure CF phase.

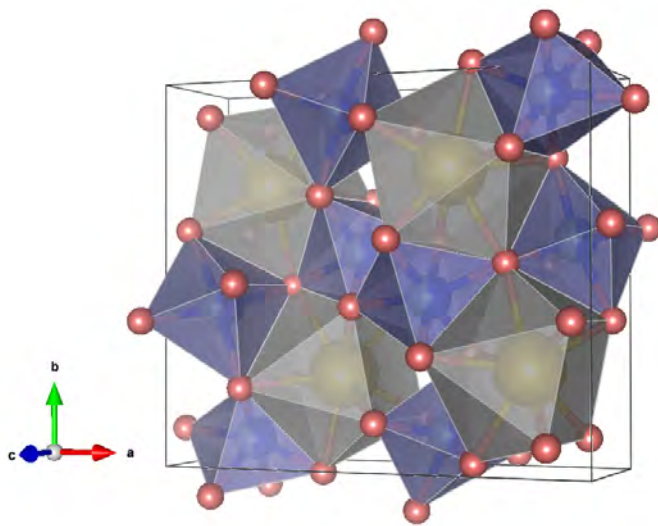
565 **Figure 5** Pressure dependence of the polyhedral volumes for the pure CF phase.

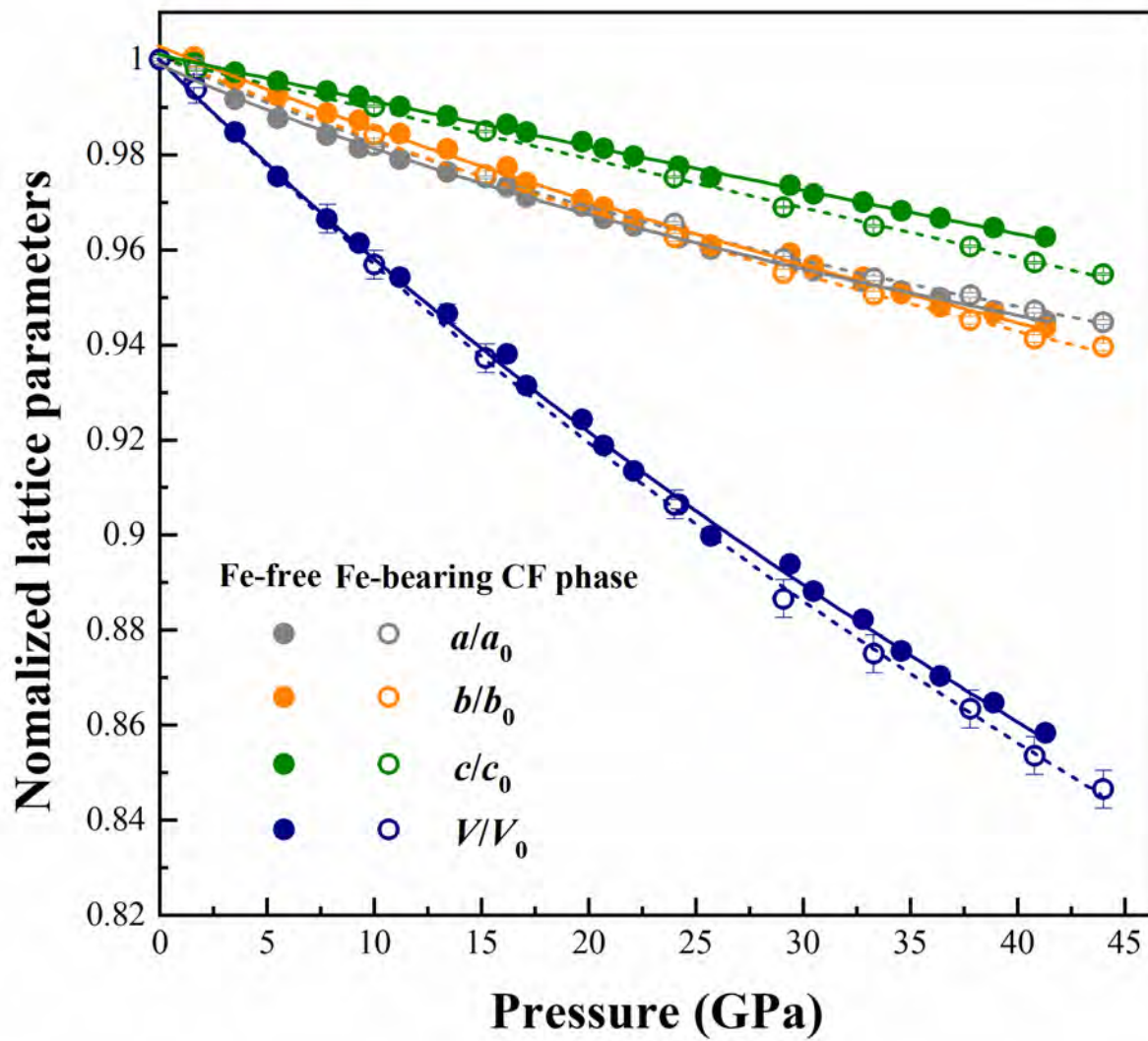
566 **Figure 6** Pressure dependence of the distortion indices of the two distinct $(\text{Al,Si})\text{O}_6$ octahedra and
567 NaO_8 polyhedra for the pure CF phase.

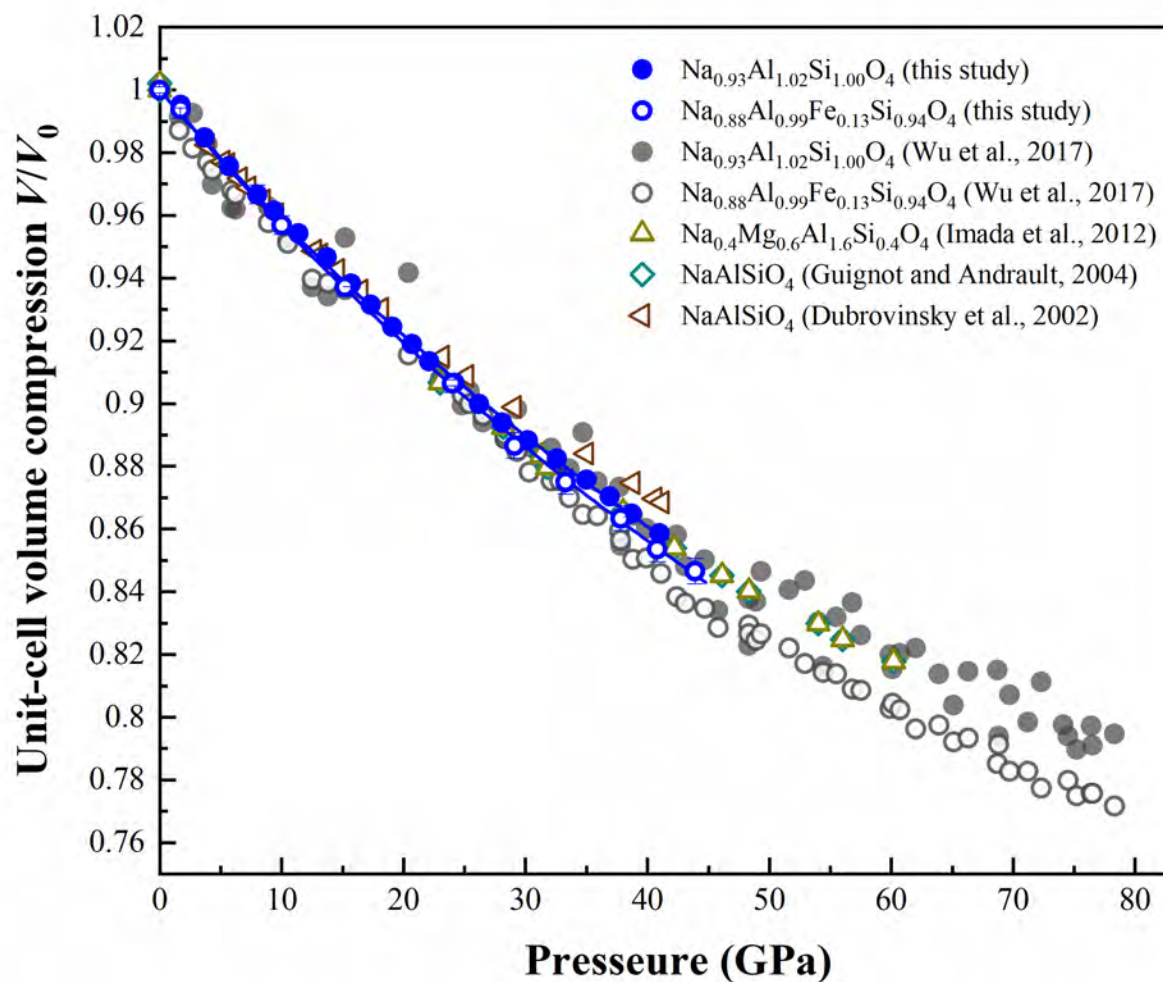
568 **Figure 7** Selected Raman spectra of Fe-free CF phase (A) and Fe-bearing CF phase (B) at various
569 pressures. [Individual plots of deconvoluted Raman spectra at ambient conditions are also shown.](#)

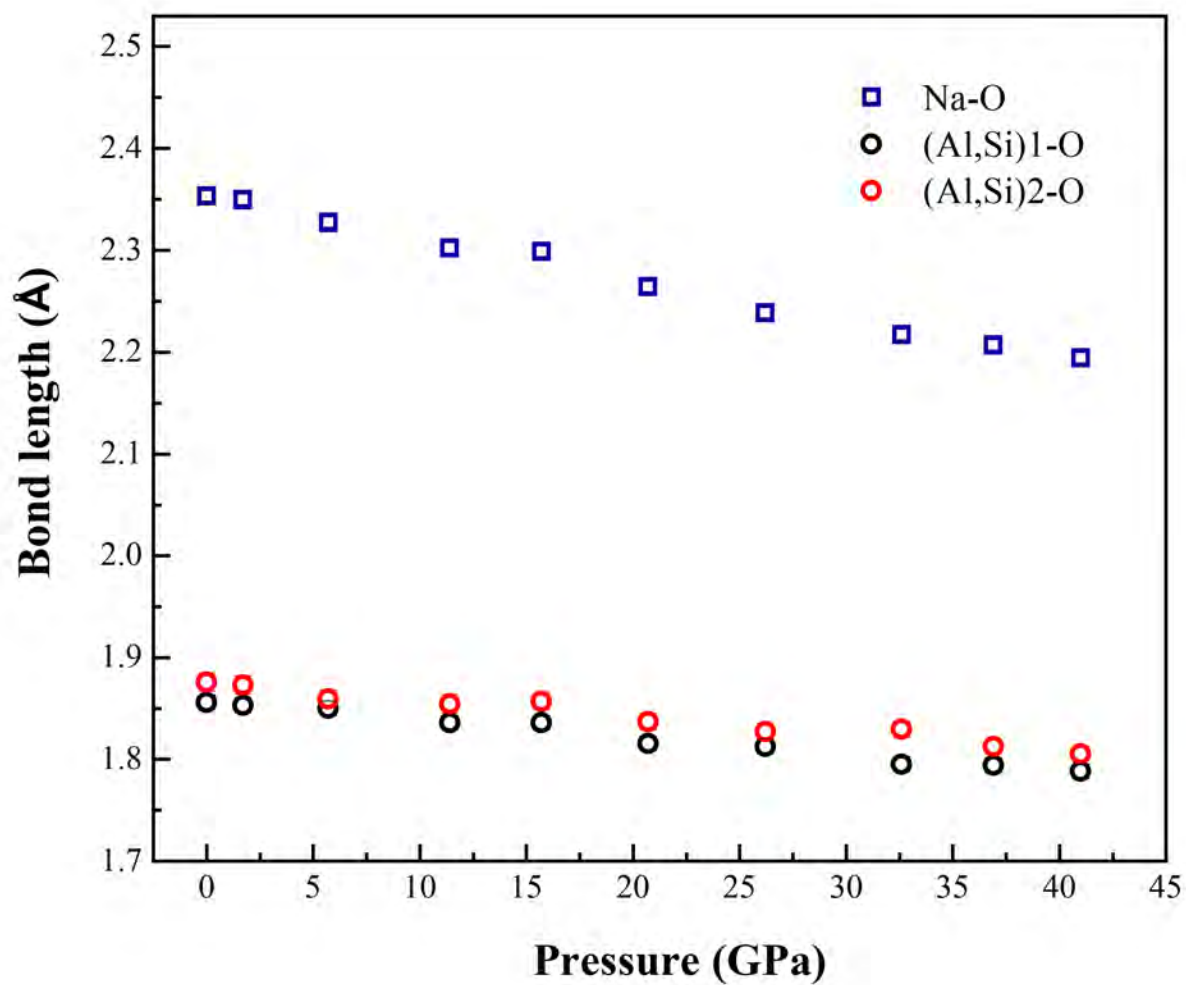
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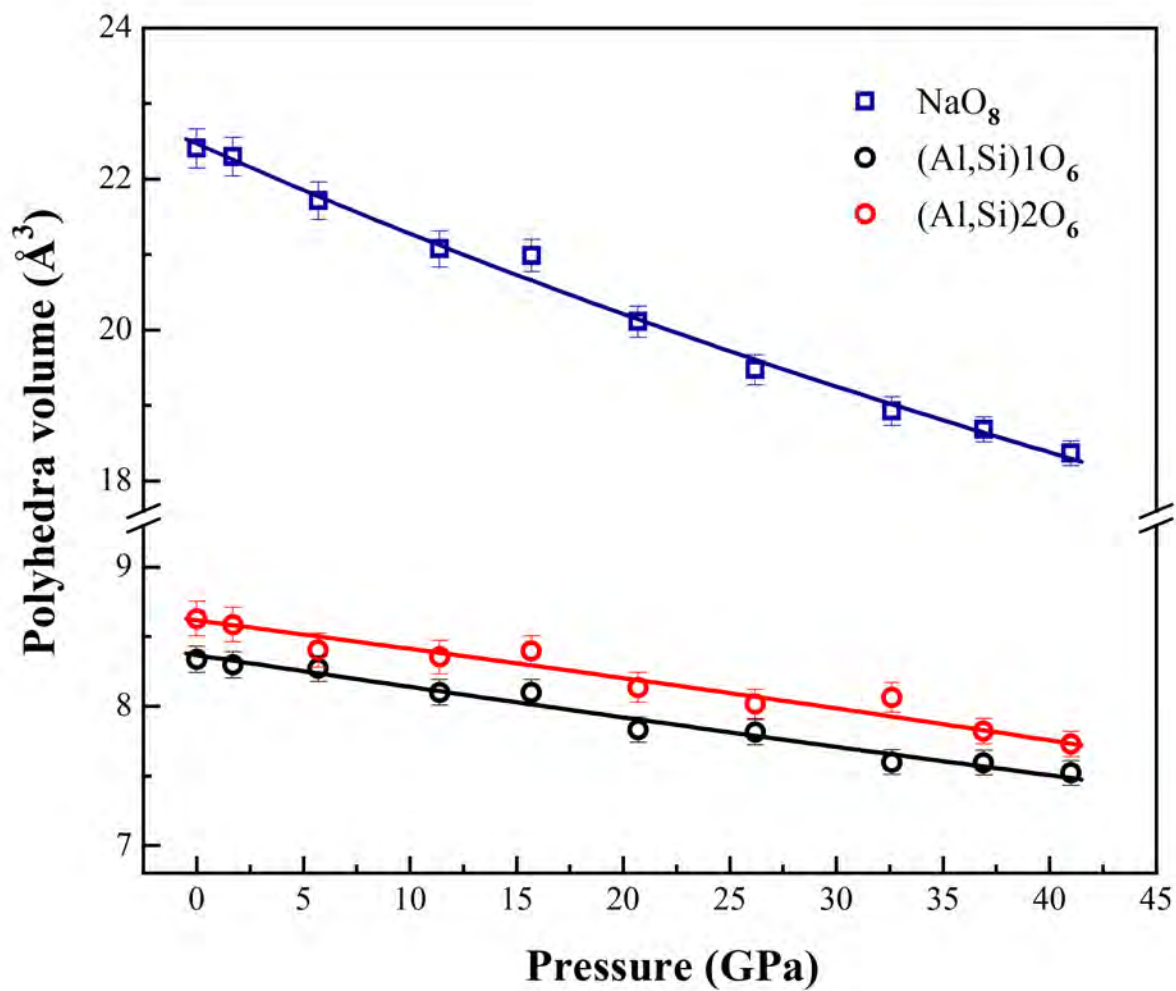
Figure 1

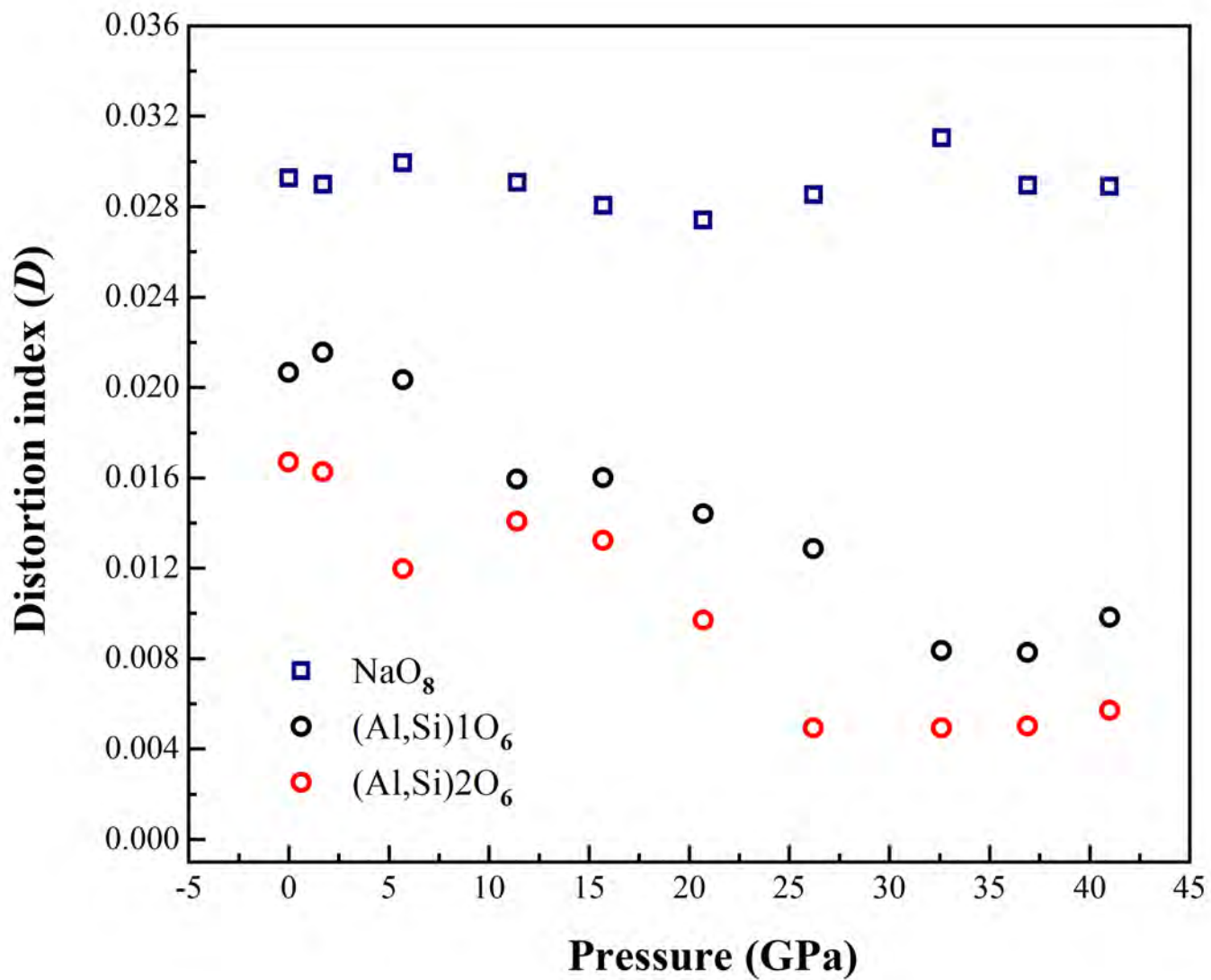




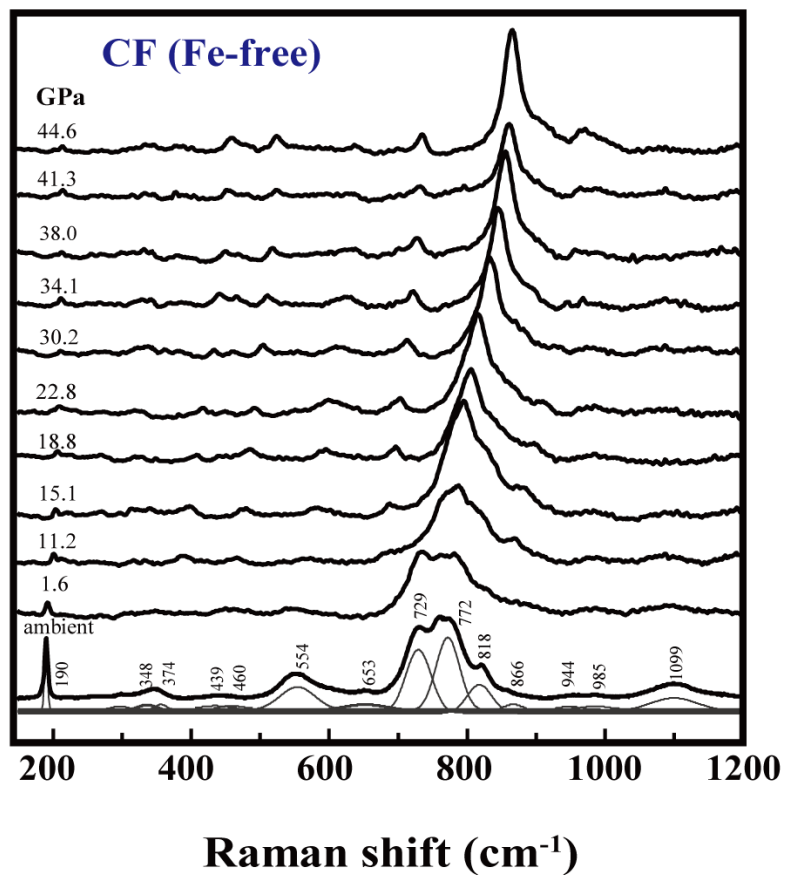








(A)



(B)

