Revision 2

Crystal structure of calcium-ferrite type NaAlSiO$_4$ up to 45 GPa

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Abstract

Alkali-rich aluminous high-pressure phases including calcium-ferrite (CF) type NaAlSiO$_4$ are thought to constitute ~20% by volume of subducted mid-ocean ridge basalt (MORB) under lower mantle conditions. As a potentially significant host for incompatible elements in the deep mantle, knowledge of the crystal structure and physical properties of CF-type phases is therefore important to understanding the crystal chemistry of alkali storage and recycling in the Earth’s mantle. We determined the evolution of the crystal structure of pure CF-NaAlSiO$_4$ and Fe-bearing CF-NaAlSiO$_4$ at pressures up to ~45 GPa using synchrotron-based, single-crystal X-ray diffraction. Using the high-pressure lattice parameters, we also determined a third-order Birch-Murnaghan equation of state, with \( V_0 = 241.6(1) \, \text{Å}^3 \), \( K_T = 220(4) \) GPa and \( K_{T0}' = 2.6(3) \) for Fe-free CF, and \( V_0 = 244.2(2) \, \text{Å}^3 \), \( K_T = 211(6) \) GPa and \( K_{T0}' = 2.6(3) \) for Fe-bearing CF. The addition of Fe into CF-NaAlSiO$_4$ resulted in a 10±5% decrease in the stiffest direction of linear compressibility along the \( c \)-axis, leading to stronger elastic anisotropy compared with the Fe-free CF phase. The NaO$_8$ polyhedra volume is 2.6 times larger and about 60% more compressible than the octahedral (Al, Si)O$_6$ sites, with \( K_{T0}^{NaO_8} = 127 \) GPa and \( K_{T0}^{(Al, Si)O_6} \approx 304 \) GPa. Raman spectra of the pure CF-type NaAlSiO$_4$ sample shows that the pressure coefficient of the mean vibrational mode, 1.60(7) cm$^{-1}$/GPa, is slightly higher than 1.36(6) cm$^{-1}$/GPa obtained for the Fe-bearing CF-NaAlSiO$_4$ sample. The ability of CF-type phases to contain incompatible elements such as Na beyond the stability field of jadeite requires larger and less compressible NaO$_8$ polyhedra. Detailed high-pressure crystallographic
information for the CF phases provides knowledge on how large alkali metals are
hosted in alumina framework structures with stability well into the lowermost mantle.

**Keywords**: CF-type NaAlSiO₄, single-crystal structure refinements, incompatible Na
elements, high pressures, Raman spectroscopy, lower mantle
The bulk lower mantle is considered well mixed above the D'' layer, yet regional heterogeneities are identified by seismology and geochemical studies (e.g., Jenkins et al., 2017; Romanowicz and Wenk, 2017). Calcium-ferrite (CF) type phases and the new hexagonal aluminous phase (NAL phase) may collectively account for 10-30 vol% of subducted oceanic crust below ~2700 km and therefore likely play an important role in the observed regional-scale seismological and geochemical heterogeneities (Bina and Helffrich, 2014; French and Romanowicz, 2014; Fukao et al., 2009; Litasov and Ohtani, 2005; Wu et al., 2016, 2017). However, the high-pressure behaviors (e.g., structure, stability and elasticity) of the alkali-rich aluminous high-pressure phases remains poorly known compared with other lower mantle minerals such as bridgmanite (Mg,Fe)SiO$_3$, dawemaoite (CaSiO$_3$), and ferropericlase (Mg,Fe)O (Fujino et al., 2012; Ono et al., 2004; Wentzcovitch et al., 1995). Determining the structure and thermodynamic properties of the major alkali-rich phases will therefore improve computational models of slab dynamics as well as our understanding of the behavior of incompatible elements in the lowermost mantle.

Average mid-ocean ridge basalt contains 10-12 wt.% CaO and 2-3 wt.% Na$_2$O, largely in plagioclase and clinopyroxenes in the upper mantle (Sun et al., 1979). On subduction to below 50-60 km, the basalt-eclogite transition changes the mineralogy of MORB where Ca-pyroxene (diopside), Na-pyroxene (jadeite) and garnet host the majority of alkali metals and aluminum (Yoder Jr and Tilley, 1962; Ringwood and Green, 1966). Below ~300 km, pyroxene and garnet form a solution of majoritic
garnet but below the transition zone (410-660 km) the breakdown of majoritic garnet leads to bridgmanite, davemaoite, and stishovite, where Al, the majority of Na, and some Ca are hosted in the CF-type and/or NAL-phases (depending on depth) with complex chemical composition (Kesson et al., 1994; Ono et al., 2001; Ricolleau et al., 2010).

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

To gain insight into the elasticity and equations of state as well as alkali storage mechanisms, we have undertaken high-precision, single-crystal structure determinations of Fe-free and Fe-bearing CF phases up to ~45 GPa \textit{in situ} using synchrotron-based single-crystal X-ray diffraction. Vibrational properties of these
structures were determined by Raman spectroscopy. These results provide comprehensive understanding of the crystallographic information of such alkali-bearing CF phases under lower mantle conditions, thus improving our knowledge of proper chemical and physical properties of these important lower mantle alkali-dominated phases, and shedding new light on alkali reservoirs in the Earth’s deep mantle.

Materials and methods

Samples for the current study were synthesized in experimental runs #5K2124 (Fe-free) and #5K2681 (Fe-bearing) at 25 GPa and 1600 °C using a 5000-ton Kawai-type multi anvil pressure apparatus (USSA-5000) at the Institute for Study of the Earth’s Interior (ISEI), Okayama University at Misasa, Japan. Details of the sample synthesis and compositional characterization are reported in Wu et al. (2017). Briefly, a stoichiometric mixture of high-purity Na₂CO₃, Al₂O₃, and SiO₂ were mixed with a molar ratio of 1:1:2 and used as the starting material. For the Fe-bearing sample, iron was added as ⁵⁷Fe₂O₃ with >95% enrichment in ⁵⁷Fe. The chemical compositions of the Fe-free and Fe-bearing samples were obtained by electron microprobe analysis as given by Wu et al. (2017) and found to be Na₀.₉₃Al₁.₀₂Si₁.₀₀O₄ and Na₀.₈₈Al₀.₉₉Fe₀.₁₃Si₀.₉₄O₄. Their crystal structure was characterized by X-ray diffraction at GSECARS of the Advanced Photon Source (APS), Argonne National Laboratory, beamline 13-BM-C. The results confirm that both CF samples possess space group $Pbnm$, and their lattice constants are $a = 10.166(1)$ Å, $b = 8.675(9)$ Å, $c =$
2.7380(6) Å, and \( V = 241.5(1) \text{ Å}^3 \) for the Fe-free CF phase, and \( a = 10.189(2) \text{ Å}, b = 8.686(7) \text{ Å}, c = 2.7571(4) \text{ Å}, \) and \( V = 244.0(2) \text{ Å}^3 \) for the Fe-bearing sample.

Mössbauer spectroscopy shows that 90% of the iron is ferric (Fe\(^{3+}\)) (Wu et al., 2017).

Crystals of the CF phases measuring ~1.5 mm in maximum dimension were crushed into 30 μm × 40 μm chips under an optical microscope and then polished to ~10 μm thickness for the high-pressure study.

High-pressure, single-crystal X-ray diffraction experiments were carried out at GSECARS (Sector 13) of the advanced Photon Source (APS), Argonne National Laboratory (ANL), beamline 13-BM-C. A monochromatic X-ray beam with a wavelength of 0.434 Å was focused to a 15×15 μm\(^2\) spot for the diamond-anvil cell experiment (Zhang et al., 2017). We used a short symmetric-type diamond anvil cells, fitted with Bohler-Almax diamond anvils with 300 μm flat culets and set into seats with 76-degree opening. A Re gasket was pre-indent to ~40 μm thickness before laser drilling a sample chamber of ~160 μm diameter. Polished Fe-free and Fe-bearing CF samples were loaded with neon pressure medium into their respective sample chambers along with Pt foil for pressure calibration (Fei et al., 2007).

To obtain sufficiently precise constraints on the unit-cell evolution, we obtained diffraction data with multiple detector positions and for the full structure determinations at least 600 reflections were used (Figure S1). The single-crystal crystal structure refinements of the CF samples were carried out using ATREX/RSV, SHELXL, Olex2 and VESTA software packages (Dera et al., 2013; Dolomanov et al., 2009; Momma and Izumi, 2008). A crystal structure model of Yamada et al. (1983)
was used to initialize the refinement. We used isotropic atomic displacement parameters \( U_{\text{iso}} \) for all atoms. Figures of merits of the refinements, atomic coordinates and displacement parameters of Fe-free CF phase is presented in Supplemental information Table S1 and S2.

High-pressure Raman spectroscopy for the iron-bearing and pure CF-NaAlSiO\(_4\) phases was performed up to 44.6 GPa at room temperature using Princeton-style diamond-cells with 300-\( \mu \)m ultra-low fluorescent diamond anvils. The diamond cells for Raman spectroscopy were gas loaded with neon at HPSTAR and ruby was used as the pressure calibration (Mao et al., 1986). The pressure was determined by multiple measurements before and after each experimental run. Raman spectra were collected on a Renishaw inVia reflex Raman spectrometer with 532 nm diode-pumped solid-state laser, at Peking University. The spectrograph was calibrated using a silicon wafer, and the spectra were collected in unpolarized, backscatter geometry using a charge-coupled device detector with a resolution of 1 cm\(^{-1}\). Each Raman spectrum was collected with an averaged exposure time of 30 s over 5 accumulations. The deconvolution of Raman spectra and peak positions were fitted using the software package PeakFit (Systat Software, Inc.)

Results and Discussion

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

Throughout the investigated pressure range (up to 41.3 and 44 GPa for Fe-free
and Fe-bearing CF, respectively), no indicators of phase transformation were identified. The crystal structure of Fe-free CF-NaAlSiO$_4$ at 41.3 GPa is shown in Figure 1. The CF phase consists of an alumina framework composed of double chains of linked (Al,Si)$_1$O$_6$- and (Al,Si)$_2$O$_6$-octahedra, while relatively large alkali Na sites located in the eight-fold coordination sites in tunnels formed by the octahedral chains, hereafter denoted NaO$_8$-polyhedra. The quality of diffraction patterns used to carry out structure refinements at low (~2 GPa) and high (~40 GPa) pressures are illustrated by the CCD images shown in Figure S1.

Lattice parameters of the CF phase are consistently refined to an orthorhombic cell (Pbnm and $Z = 4$) (Figure 2). Volume compression and axial compression data of both CF phases at different pressures are given in Table S3 and S4. Pressure-volume data were fitted to a third-order Birch-Murnaghan equation of state (EoS) using error-weighted least squares with EoSFit7c software (Angel et al., 2014). Under ambient conditions, the measured $V_0$ values are 241.5(1) and 244.0(2) Å$^3$ for the Fe-free and Fe-bearing CF sample, respectively. The best-fit, third-order Birch-Murnaghan EoS parameters yield $V_0 = 241.6(1)$ Å$^3$, $K_{T0} = 220(4)$ GPa and $K_{T0}' = 2.6(3)$ for Fe-free CF, and $V_0 = 244.2(2)$ Å$^3$, $K_{T0} = 211(6)$ GPa with $K_{T0}' = 2.6(3)$ for Fe-bearing CF. Note that at room pressure, the measured unit-cell volume and the fitted zero-pressure volume in our BM3 procedure are identical within error for both Fe-free and Fe-bearing phases. Although both CF phases exhibit broadly similar equation of state parameters, the unit-cell volume of the Fe-bearing sample is about 1% larger and about 4% more compressible than the Fe-free sample.
We also determined the axial compressibility of the lattice parameters using the linearized third-order Birch-Murnaghan EoS (Figure 2). Details are described in Supplemental Text S1. Our fitted linear moduli to $a$, $b$ and $c$ axes are 158(5), 180(8) and 338(9) GPa for Fe-free CF phase, and 158(11), 181(7) and 306(16) GPa for Fe-bearing CF sample, respectively, which indicate $a$- and $b$-axes exhibit similar linear moduli for both CF phases. The addition of Fe into the CF phase leads to a decrease in the linear compressibility of the $c$-axis compared with Fe-free phase. The relative axial compressibility scheme is $\beta_a > \beta_b > \beta_c$ for both phases. Ratios of zero-pressure axial compressibility between the three axes are 2.14:1.88:1 for Fe-free and 1.94:1.69:1 for Fe-bearing sample, which suggests strong elastic anisotropy on compression, with the $c$-axis being the stiffest direction within the structure.

The room temperature equations of state for CF phases determined in this study are shown in Figure 3, with volume normalized to measured $V_0$ in order to aid in comparison with previous studies. The absolute difference between our equation of state parameters and those from previous work (Table S5 in supporting information) depends on many factors including (among others) data precision, data density, crystal quality, and the experimental pressure range, resulting in the usual trade-offs between $V_0$, $K_{T0}$, and $K'_{T0}$ fitted to different datasets, complicating a quantitative assessment of the effect of Fe substitution on the compressibility of CF phase. By measuring both pure-CF and Fe-bearing CF phases in the same study with high-quality single crystals, we were able to tightly constrain the values of $K_{T0}$ and $K'_{T0}$ for both crystals under similar experimental parameters, finding that $Fe_{tot} = 0.13$ pfu in the CF phase leads to
3.2±1.9% reduction in the bulk modulus compared with the Fe-free sample. The lower bulk moduli values of $K_T^0 = 201(9)$ GPa reported for the CF-phase by Wu et al. (2017), who also determined high-spin ($K_T^0 = 208(3)$ GPa) and low-spin ($K_T^0 = 202(7)$ GPa) bulk moduli for Fe-bearing CF phase were fitted with relatively high values of $K_T^0$ (fixed at 4), which are, however, poorly constrained. The derived EoS parameters obtained in this study are statistically higher than that obtained by Guignot and Andrault (2004) with $K_T^0 = 185(5)$ GPa but in good agreement with previously reported values of $K_T^0 = 214(14)$ GPa, $K_T^0' = 3.6(5)$ (Imada et al., 2012) and $K_T^0 = 220(1)$ GPa, $K_T^0' = 4.1(1)$ (Dubrovinsky et al., 2002).

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

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

To better understand the compression mechanisms of CF-type NaAlSiO₄, we
analyzed the structure and evolution of the polyhedral elements on compression at
selected pressures. Here we used two parameters to characterize the compression of
each polyhedron: the polyhedral volume and the mean bond length. Results are given
in Table S6. More details on the high-pressure structure refinements of the Fe-free
sample will be discussed next.

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

The structural evolution of all the coordination polyhedra is presented in Figure 5.
The average (Al,Si)O6 volume is 8.48(2) Å³ at ambient pressure and decreases to
7.62(2) Å³ at 41.0 GPa, while the volume of NaO8-polyhedron is about 2.6 times
larger, and decreases from 22.40(3) Å³ to 18.37(2) Å³ between 0 and 41.0 GPa. The
average (Al,Si)O6 volume has a much smaller value and is significantly more
incompressible than the NaO₈-polyhedron. In particular, the (Al,Si)O₆ octahedron is
much stiffer with an average bulk modulus of ~304 GPa compared with the $K_0^{NaO_8}$ of
127 GPa within the whole pressure range, when both $K_0'$ fixed at 4. Our value of
$K_0^{SiO_6}$ for CF phase is in excellent agreement with the compressibility of SiO₆
octahedron in stishovite SiO₂ ($K_0^{SiO_6} = 303-346$ GPa), another important phase in the
lower mantle (Andrault et al., 1998).

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

**Vibrational modes and Grüneisen parameters**

*In situ* Raman spectroscopy was conducted up to 44.6 GPa on both Fe-free and
Fe-bearing crystals taken from the same synthesis runs used in the XRD study.
Selected spectra of both crystals with increasing pressure are presented in Figure 7. As
the Raman active modes are $18A_g+9B_{1g}+18B_{2g}+9B_{3g}$, a total of 54 Raman active
vibrations modes are expected. Unfortunately, the data quality is not rich enough to
deconvolute and assign all the peaks. The smaller number of observed modes is due to
weak intensity, peak overlap, and orientation dependence. In this study, around 14 Raman peaks were observed for the CF in the Raman shift range of 1200-150 cm\(^{-1}\).

Peak positions of the major observed modes as a function of pressure are provided in Figure 7 and Table S7. All observed Raman peaks shift to higher frequency with increasing pressure, and some broad bands may consist of several Raman active modes having very close frequencies.

There have been numerous investigations on MgAl\(_2\)O\(_4\), CaAl\(_2\)O\(_4\) and their solid solutions with Raman spectroscopy (Kojitani et al., 2007; Kojitani et al., 2013; Ono et al., 2009). Yet, there is no detailed Raman spectroscopic study on Fe-free and Fe-bearing CF phase. As shown in Figure 7, Raman modes located between 680-900 cm\(^{-1}\) become stronger and sharper at higher pressures in both phases. At ambient conditions, the peak at 190 cm\(^{-1}\) of Fe-free CF phase can be attributed to the vibrations of the Na\(^{+}\) ions, while this peak is not observed in the Fe-bearing sample (Fei et al., 2020; Kojitani et al., 2013). The vibrational modes at \(~348\) cm\(^{-1}\) and 331 cm\(^{-1}\) in Fe-free and Fe-bearing CF phase, respectively, can be assigned to A\(_g\) modes with translation of Al\(^{3+}\) (Kojitani et al., 2013). Mode frequencies at 374, 439, 460, 554 and 653 cm\(^{-1}\) in the Fe-free sample and at 386, 453, 474, 535 and 631 cm\(^{-1}\) of Fe-bearing sample can be attributed to the O–Si–O and Si–O–Si (or Al) bending, which are accordance with the MgAl\(_2\)O\(_4\) and CaAl\(_2\)O\(_4\) in CF structure (Kojitani et al., 2013). In the frequency range of 680-900 cm\(^{-1}\), the most intense peaks at 729, 772 cm\(^{-1}\) (Fe-free CF), and 720, 799 cm\(^{-1}\) (Fe-bearing CF) are mainly caused by the vibrational modes related to the octahedral sites. It should be noted that peak broadenings in the frequency range of...
400-660 cm\(^{-1}\) and 680-900 cm\(^{-1}\) is generally associated with structural disorder over lattice sites, i.e., Si, Al and Fe disorder over the octahedral site in the CF structure (Kojitani et al., 2013). Therefore, spectral deconvolution in the region between 680-900 cm\(^{-1}\) produces 3 main peaks around 720, 799, 839 cm\(^{-1}\) and 729, 772, 818 cm\(^{-1}\) assigned to the (Al/Si)O\(_6\) octahedral sites in Fe-rich and Fe-free CF phase, respectively (Figure S3). It was found that the bands appearing at the 680-900 cm\(^{-1}\) region in Fe-bearing CF phase tended to be broader than the pure-CF, due to presence of Fe\(^{3+}\) in the octahedral sites. On this basis, the Raman bands become far apart with elevated pressure, indicating less disorder in the octahedral Fe environments (Figure S3). Additionally, at higher frequencies, the appearance of the peaks at 944, 985, 1099 cm\(^{-1}\) and 908, 980, 1080 cm\(^{-1}\) in Fe-free and Fe-rich CF sample, respectively, are probably caused by Si–O\(_{nb}\) (non-bridged oxygen), Si–O\(_{br}\) (bridged oxygen) bending asymmetric and symmetric stretchings (Prencipe, 2012).

Mode Grüneisen parameters (\(\gamma_i\)) were calculated using \(\gamma_i = (K_0/\nu_i) \left( \frac{d\nu_i}{dP} \right)_T\), where \(\nu_i\) is the wavenumber of the \(i^{th}\) mode and \(K_0\) is the bulk modulus at room temperature (Table S7). Here, we used the isothermal bulk modulus \(K_0\) of 220(4) and 211(6) GPa for Fe-free and Fe-bearing CF phase, respectively, which were obtained by the BM3 fit. The resulting mean pressure coefficient of the whole structure for pure CF-NaAlSiO\(_4\) of 1.61(7) cm\(^{-1}\)/GPa is slightly higher than 1.40(6) cm\(^{-1}\)/GPa found for Fe-bearing sample. Correspondingly, the calculated mode Grüneisen parameters determined in this study range from 0.31(2)-0.94(2) for the pure-CF, and 0.25(3)-0.84(2) for the Fe-bearing CF phase, with average values from all the observed modes.
of 0.58(1) and 0.54(2), respectively. As for the octahedral site vibrations in both phases, the calculated \( \gamma \) values fall generally in the range of 0.57-0.84, which are comparable with those experimental determined modes with AlO\(_6\) octahedra for MgAl\(_2\)O\(_4\) in the CF-type structure (Kojitani et al., 2013). The mean pressure coefficient of octahedral site-derived mode in Fe-bearing CF phase of 2.78(7) cm\(^{-1}\)/GPa is larger than 2.17(6) cm\(^{-1}\)/GPa found in Fe-free sample, consistent with the higher compressibility of the Fe-bearing phase relative to Fe-free CF phase. We therefore conclude that the major difference in compressibility between the two structures is related to the Al/Fe–O bonds in octahedral sites in particular along the c-axis.

**Implications**

Generally, the structural compression mechanisms of the CF and NAL phases can be compared with the structural shrinkage in K-hollandite. With increasing pressure, a distortion of the (Al,Si)O\(_6\) octahedral framework, which forms the tunnel structure, contracts and leads to more compact tunnels. Since the VIII\(\text{K}-\text{O}\) bond in K-hollandite is one of the most compressible bonds among the metal-oxygen pairs in oxide minerals, KO\(_6\) polyhedra are very compressible and can be compared to the bulk modulus of NaO\(_8\) in the CF phase (Mookherjee and Steinle-Neumann, 2009; Zhang et al., 1993). Furthermore, in comparison to jadeite-NaAlSi\(_2\)O\(_6\) (McCarthy et al., 2008; Posner et al., 2014), the longer Na–O bonds and low degree of NaO\(_8\) polyhedra distortion in the CF phase determined here at high pressures likely contribute to its wide stability over lower mantle conditions.
Na-bearing majorite and Na-rich pyroxene (e.g., NaAlSi2O6 jadeite, NaFe\textsuperscript{3+}Si2O6 aegirine) have similar chemical compositions and have also considered as potential hosts for Na in the Earth’s mantle (Bindi et al., 2011; Xu et al., 2017). Previous studies have indicated that aegirine remains in the monoclinic \textit{C2/c} structure up to 60 GPa, with the NaO\textsubscript{8} polyhedron likely controlling bulk compressibility (Xu et al., 2017). However, the incorporation of Fe\textsuperscript{3+} to Na-pyroxene significantly increases the bulk modulus as well as the transition pressure for the pyroxene to garnet transition (Xu et al., 2017; Matrosova et al., 2019). Although sodium is significantly enriched in continental crust compared with oceanic crust, Na is an important incompatible element in the mantle because it partitions strongly into the MORB-forming melts below the spreading ridges (Hofmann, 1988). Thus, subduction of MORB recycles Na into the mantle where it contributes to melting in the upper-mantle wedge but is also likely carried deeper into the mantle. The CF phase is regarded as the only Na-dominated stable phase in the lower mantle down to \textasciitilde2700 km.

Considering the potentially significant volume proportion of CF and NAL phases in deeply-subduced MORB, the elastic properties of these minerals and their compositional solid solutions are important for estimates of density and velocity of MORB. In more recent studies, coupled substitutions of Al\textsuperscript{3+} and Mg\textsuperscript{2+} in the CF structure by Na\textsuperscript{+} and Si\textsuperscript{4+} has limited influence on its elastic constants, but slightly weakens the elastic wave anisotropy (Zhao et al., 2018; Wang et al., 2020). Further investigations of the crystal chemistry on the CF phase at the pressure and temperature relevant to the lower mantle conditions are necessary. Most importantly,
adopting the thermo-elastic parameters of the CF-structure end-member to estimate
the thermo-elastic properties of complex aluminous solid solutions would improve our
understanding of the role recycled oceanic crust plays in the global alkali cycle with
implications for the long-term evolution and internal heating of the Earth’s mantle.

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Figure captions

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

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

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

Figure 4 Pressure dependence of the mean bond lengths of the two distinct (Al,Si)O\(_6\) octahedra and the NaO\(_8\) polyhedra in the pure CF phase.

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

Figure 6 Pressure dependence of the distortion indices of the two distinct (Al,Si)O\(_6\) octahedra and NaO\(_8\) polyhedra for the pure CF phase.

Figure 7 Selected Raman spectra of Fe-free CF phase (A) and Fe-bearing CF phase (B) at various pressures. Individual plots of deconvoluted Raman spectra at ambient conditions are also shown.
Figure 1