Metastable high-pressure transformations of orthoferrosilite Fs$_{82}$

Przemyslaw Dera$^{a,c,*}$, Gregory J. Finkelstein$^{b}$, Thomas S. Duffy$^{b}$, Robert T. Downs$^{c}$, Vitali Prakapenka$^{a}$, Sergey Tkachev$^{d}$

$^{a}$ Center for Advanced Radiation Sources, University of Chicago, Argonne National Laboratory, 9700 S. Cass Ave., Bldg. 434, Argonne, IL 60439, USA
$^{b}$ Department of Geosciences, Princeton University, USA
$^{c}$ Geology Department, University of Arizona, USA
$^{d}$ High Pressure Collaborative Access Team, Carnegie Institution of Washington, USA
$^{*}$ Hawaii Institute of Geophysics and Planetology, School of Ocean and Earth Science and Technology, University of Hawaii at Manoa, Hawaii, USA

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High-pressure single-crystal X-ray diffraction experiments with natural ferrosilite Fs$_{82}$ (Fe$^{2+}$)$_{3.82}$Mg$_{0.16}$Al$_{0.84}$Ca$_{0.50}$Si$_{2.8}$O$_{6.07}$ reveal that at ambient temperature the sample does not transform to the clinopyroxene (cpx) structure, as reported earlier for a synthetic Fs$_{100}$ end-member (Hugh-Jones et al., 1996), but instead undergoes a series of two polymorphic transitions, first above 10.1(1) GPa, to the monoclinic P2$_1$/c phase β-opx (distinctly different from both P2$_1$/c and C2/c cpx), also observed in natural enstatite (Zhang et al., 2012), and then, above 12.3(1) GPa to a high-pressure ortho-rhombic Pbcn phase γ-opx, predicted for MgSiO$_3$ by atomistic simulations (Jahn, 2008). The structures of phases α, β, and γ have been determined from the single-crystal data at pressures of 2.3(1), 11.1(1), and 14.6(1) GPa, respectively. The two new high-pressure transitions, very similar in their character to the P2$_1$/c-C2/c transformation of cpx, make opx approximately as dense as cpx above 12.3(1) GPa and significantly change the elastic anisotropy of the crystal, with the [100] direction becoming almost twice as stiff as in the ambient α-opx phase. Both transformations involve mainly tetrahedral rotation, are reversible and are not expected to leave microstructural evidence that could be used as a geobarometric proxy. The high Fe$^{2+}$ content in Fs$_{82}$ shifts the α-β transition to slightly lower pressure, compared to MgSiO$_3$, and has a very dramatic effect on reducing the (meta) stability range of the β-phase. © 2013 Elsevier B.V. All rights reserved.

1. Introduction

Pyroxenes are among the most important minerals of the Earth’s upper mantle and account for approximately 20% of the composition of this layer by volume (Frost, 2008). The pyroxene structure is composed of close-packed layers of O atoms with alternating tetrahedral and octahedral layers that accommodate a variety of different cations ranging from the typical divalent Mg$^{2+}$, Fe$^{2+}$, Ca$^{2+}$, Mn$^{2+}$, through monovalent Na$^+$, to trivalent Al$^{3+}$, Fe$^{3+}$ and Cr$^{3+}$ without inducing major rearrangements to the topology and connectivity within the crystal. The structural and compositional flexibility is a consequence of the ability of the infinite corner-linked tetrahedral chains extending along the [001] direction to stretch or compress by rotation of the individual tetrahedra without affecting the tetrahedral bond lengths, following the rigid unit mode model (Dove et al., 1995). Because of the tetrahedral layer flexibility cations with very different ionic radii coordinated by 4 to 8 oxygen atoms can be accommodated in the M2 sites of the octahedral layers.

Four distinct ambient polymorphs of pyroxene are known, differing in crystal symmetry and layer stacking topology, including C2/c diopside-type, P2$_1$/c clinopyroxene-type (lp-cpx), Pba$_2$ ortho-enstatite-type (γ-opx), and Pbnm protoenstatite. Their structures, while easily distinguishable, are very closely related. For some compositions, e.g. in C2/c spodumene, P2$_1$/c and P2$_1$/n omphacites and P2$_1$/ca lunar orthopyroxene, small symmetry distortions are found, but their topological relations to the four basic ambient structural types are easily recognizable. Because of the distinct layer stacking patterns, transitions between the principal pyroxene polymorph types are in general reconstructive and involve significant activation barriers, which lead to metastability (Downs, 2003; Thompson and Downs, 2003).

The main geologically-relevant subset of pyroxene composition space is the MgCaSi$_2$O$_6$ (diopside)–MgSiO$_3$ (enstatite)–FeSi$_2$O$_6$ (ferrosilite)–CaFeSi$_2$O$_6$ (hedenbergite) quadrilateral. Significant (above 10%) Ca$^{2+}$ content strongly favors the monoclinic diopside-type cpx arrangement, while at low Ca$^{2+}$-content the preference between the cpx and opx structures is controlled by the pressure and
temperature of crystallization (Lindsley, 1983). The compositions richest in Ca\(^{2+}\) do not crystallize in the pyroxene structure, but instead assume a CaSiO\(_3\) wollastonite structure.

It is widely accepted that the stable high P-T phase diagram along the enstatite-ferrosilite join is composed only of the four principal pyroxene polymorphs. However, a number of recent experimental results and theoretical predictions indicate that the orthorhombic phases if compressed at ambient temperature, rather than transforming to cpx tend to undergo a different kind of structural transformations. Raman spectroscopic experiments indicate one such transition in En\(_{100}\) at a pressure of about 10 GPa (Lin, 2003, 2004; Lin et al., 2005). A similar discontinuity in the behavior of hyperfine parameters was noted in a synchrotron Mössbauer study (Zhang et al., 2011). First principles molecular dynamics simulations of the phase behavior of En\(_{100}\) starting from the opx structure, conducted at a simulation temperature of 1000 K also revealed a lack of transformation to the monoclinic cpx form, resulting from the large activation barrier for this reconstructive transition. Instead, two possible new metastable displacive polymorphs transitions to HP-OpEn2 with space group P\(_2\)/ca at 9 GPa and further, to HP-OpEn1 with space group P\(_{2\text{ca}}\) (different than the ambient structure) at 20 GPa were predicted (Jahn, 2008).\(^1\) The two metastable transformations involve gradual rotation of the tetrahedra in the O-type tetrahedral chains, characteristic of the low pressure OpEn phase to the S-type. Finally, a recent single crystal study using natural samples with OpEn\(_{7\gamma}\) composition revealed that the phase above 10 GPa is monoclinic (space group P\(_2\)/ca\(\_\text{ca}\)), but preserves the opx structure topology, with the main structural change being conversion of 25\% of the Si-chains from the O to S configuration (Zhang et al., 2012).

The two main processes limiting the geophysical occurrence of pyroxenes in the Earth lower mantle at depths below the transition zone are believed to be dissolution of pyroxene into the garnet structure and the decomposition reaction to free SiO\(_2\) and high-pressure phases of (Mg, Fe):SiO\(_4\) (Akimoto and Syono, 1970; Ming and Bassett, 1975; Liu, 1976). The boundary of the decomposition reaction coincides with the coesite-stishovite transition of SiO\(_2\), which increases the density of the SiO\(_2\) decomposition product phase by about 30\%. At about the same pressure where coesite transforms to stishovite the spinel-type Fe-ringwoodite becomes the stable form of FeSiO\(_4\), however, the volume change associated with this transition (~8\%) is smaller than in SiO\(_2\). The decomposition reaction is characterized by a significant activation barrier, and temperatures above 1000 K are needed to initiate the process. The temperature required for decomposition also increases with pressure.

Pyroxenes are abundant in the oceanic crust, which is subducted into the upper mantle at convergent margins (Poli and Schmidt, 2002). While the displacive polymorphic transformations of opx are most likely only between metastable phases, they may have some relevance for deep Earth environments that significantly depart from the standard continental geotherm, such as cold subducted slabs. Some geophysical models (e.g. Bina et al., 2001) assume that subduction can extend to depths greater than 800 km (corresponding to pressures above 30 GPa), with the coldest part of the slab remaining below 1000 K. Orthopyroxene, once stably formed in the oceanic crust, could be metastably transported within the subducting slab to these very significant depths, and experience pressures higher than 10 GPa while still at temperatures lower than the metastable boundaries of polymorphic conversion, dissolution or decomposition (e.g. Nishi et al., 2008 recently demonstrated significant kinetic inhibition of the pyroxene dissolution in garnet at cold subducted slab conditions, at depths exceeding 500 km). As a consequence, understanding of the nature and properties of the high-pressure opx polymorphs may be important in modeling the geophysical behavior of subduction zones (e.g. Bina et al., 2001; Akashi et al., 2009).

FeSiO\(_3\) ferrosilite (Fs) is an end-member of the principal pyroxene quadrilateral, and as such is very important in understanding the general crystal chemical and phase stability trends. Pure FeSiO\(_3\) has not been reported to occur in nature, but minerals with high Fe/Mg ratios are not uncommon in high-pressure rocks (Bown, 1965; Jaffe et al., 1978; Schreyer et al., 1978; Brothers and Yokoyama, 1990; Young and Cuthbertson, 1994).

Thus far only three polymorphs of synthetic Fs\(_{100}\) have been observed at ambient conditions, including opx, lp-cpx and Fs-III (Lindsley et al., 1964). Subsequent structural investigation of these polymorphs revealed that Fs-III (space group P-1) has a pyroxenoid structure (Webber, 1983). High temperature Brillouin scattering study with natural low-Fe OEn at ambient pressure revealed existence of a possible reversible displacive transition to yet unknown high temperature phase at ~1100 °C (Jackson et al., 2004). Unlike OEn, pure OFs was found to convert to cpx at about 4.2 GPa at ambient temperature through a reconstructive transition (Hugh-Jones et al., 1996). An OFs sample with intermediate composition, Fs\(_{82}\)En\(_{18}\)OpEn\(_{0.2}\) (Ts indicates Tschermak substitution), on the other hand, did not undergo the opx-cpx conversion at ambient temperature up to 9.5 GPa (Nestola et al., 2008). To understand the effect of high Fe\(^{3+}\) content on the opx-cpx and Fs-III transitions we conducted diamond anvil cell single-crystal synchrotron X-ray diffraction experiments with a natural OFs\(_{82}\) sample to 32 GPa.

### 2. Experimental methods

The natural Fs\(_{82}\) sample used in our study is from the University of Arizona RRUFF project collections (RRUFF.info/R070386) from a locality in Greenland. This sample was previously used in the thermodynamic study of Mg-Fe order–disorder in orthopyroxenes by Saxena and Ghidey (1971), and was referred to as sample XYZ in the Ramberg and DeVore (1951) study of Fe-Mg distribution between olivines and pyroxenes. Electron microprobe analysis (EMPA) indicated a composition (Fe\(^{2+}\)\_0.82Mg\(_{0.16}\)Al\(_{0.01}\)Ca\(_{0.01}\))\_\((\text{Si}_{0.39}\text{Al}_{0.01})\text{O}_3\) Unit cell parameters determined on a single crystal fragment of the sample using a Bruker D8 diffractometer at the University of Arizona were \(a = 18.383(1) \text{Å}\), \(b = 9.012(1) \text{Å}\), \(c = 5.2344(6) \text{Å}\), with a volume of 867.2(3) \text{Å}^3. This volume is approximately 1\% smaller than for pure synthetic Fs\(_{100}\) end member (Bass and Weidner, 1984). The bulk composition of the sample was close to the sample S95 of Nestola et al. (2008), \((\text{Fe}_{0.91}\text{Mg}_{0.09}\text{Ca}_{0.01})\text{Mn}_{0.02}\text{Al}_{0.08}\text{Fe}^{2+}_{0.07}\text{Si}_{0.85}\text{Al}_{0.15}\text{O}_3\), with \(a = 18.2920(3) \text{Å}\), \(b = 8.8637(4) \text{Å}\), \(c = 5.2179(3) \text{Å}\), and \(V = 845.99(6) \text{Å}^3\). However, our sample had much higher Fe\(^{3+}/\text{Mg}\) ratio, almost no ferric iron, much lower Al content (the S95 sample contained 15 mol\% of trivalent cations incorporated via Tschermak substitution), and a more uniform distribution of Fe between the M1 and M2 octahedral sites, as determined by single crystal structure refinement.

Three separate in situ single-crystal X-ray diffraction experiments were carried out at experimental stations 16IDB (experiments 1 and 2) and 13IDD (experiment 3) of the Advanced Photon Source (APS), Argonne National Laboratory. In each experiment, two crystals with different orientations were loaded into the diamond anvil cell, as shown in Supplementary Fig. 1. The same 4-pin type diamond anvil cell was used in all three experiments. Diamond anvils with culets of 0.3 mm were mounted on asymmetric backing plates (cubic boron nitride towards the X-ray source...
and Bohler/Almax with 70 deg. total opening towards the detector). A rhenium metal gasket, preindented to a thickness of approximately 0.040 mm, was used for sample containment. The DAC was placed at a sample-to-detector distance of approximately 200 mm. The data collection procedure is described in Dera et al. (2011) (rotation range was ±35°, with step size of 1° and exposure time of 0.5 s). Diffraction images were analyzed using the GSE_A-DA/RSV software package (Dera et al., 2013). Because of the high incident energy and negligible sample thickness the sample absorption was ignored. Unit cell parameters measured in all three experiments are listed in Table 1.

Refined unit cell parameters from single-crystal diffraction measurements were used for equation of state (EOS) fit. For α-opx and γ-opx the 3rd order Birch Murnaghan equation was used (Angel, 2000), with V0 of the α-phase fixed to the experimentally determined value. Statistical weights equal to 1/σ(V) were used in the fitting process. The results of EOS fitting for the two phases of opx are shown in Fig. 1, and are compared with other experimental and theoretical results for samples with compositions close to the En-Fs join in Supplementary Table 1. For the β-opx phase the two available pressure points were insufficient for estimation of the bulk moduli. To estimate the elastic anisotropy of the different phases of opx, a quadratic function was fit to the pressure dependence of each of the normalized unit cell parameters. The results of this fitting are shown in Fig. 1.

The structures of phases α-opx, β-opx and γ-opx were refined starting from atomic coordinates of the ambient α-opx Fs (Sueno et al., 1976) using the conventional least-squares crystal structure refinement approach implemented in the SHELXL program (Sheldrick, 2008). Structure refinements for the orthorhombic phases were completed with anisotropic displacement parameters for all non-oxygen atoms, whereas isotropic displacement parameters were used for all atoms in the monoclinic phase. Details of the crystal structure refinement, refined fractional coordinates for all the atoms in phases α-opx, β-opx and γ-opx, bond lengths, anisotropic atomic displacement parameters and polyhedral geometry parameters are given in Supplementary Tables 2–8.

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![Fig. 1. Pressure evolution of normalized unit cell parameters of Fs82.](image-url)
phase is 1.578, which suggests temperature of formation of 1200 K (Stimpfl et al., 1999).

3. Results

The transformation of Fs82 from the ambient α-opx to the monoclinic β-opx phase takes place between 10.1(1) and 11.1(1) GPa, which is lower than in the previously examined natural OEn87 (between 12.66 and 14.26 GPa, Zhang et al., 2012), indicating that the transition pressure is dependent on iron content. At 11.1(1) GPa, the unit cell parameters are \( a = 18.183(7) \text{ Å}, b = 8.759(3) \text{ Å}, c = 5.009(5) \text{ Å} \), and the \( \beta \) angle becomes 91.96(5), accompanied by a 1.2% volume discontinuity. As a result of the transformation, the crystal expands along the [100] and [001] directions by about 0.5%, while the [010] direction contracts by 2.2%, as shown in Fig. 1.

As a consequence of the symmetry lowering, the crystal undergoes pseudomorphedral twinning into two domains related by a mirror on (001). The changes in the single-crystal diffraction pattern are shown in Supplementary Fig. 2. The transformation is completely reversible (no signature of the twinning remains in the diffraction pattern after the reversal) and is characterized by negligible hysteresis. Because of this complete reversibility, we do not expect any microstructural evidence of the transformation to be quenchable. Because of the twinning, our initial attempts at structure refinement starting from the model of the β-opx En87 (Zhang et al., 2012) were unsuccessful. Subsequent elimination of peaks corresponding simultaneously to both twin domains produced a peak intensity dataset which yielded a very satisfactory refinement (\( R1 = 5.7\% \) for all data). Since Zhang et al. (2012) did not experience similar difficulties in their structure refinement of β-opx En87, we conclude that the extent of the problems with peaks simultaneously contributed by two twin domains depends on the orientation of the crystal in the diamond anvil cell. Similar to the case of β-opx En87, the \( \beta \)-phase of Fs82, while assuming monoclinic (clino-) symmetry, clearly preserves the topology of the opx structure.

Zhang et al. (2012) did not determine the (meta)stability range of β-opx En87; however, other, non-diffraction based studies with En100, e.g. Zhang et al. (2011), Lin (2003, 2004), Lin et al. (2005) indicate that there is no other discontinuity in the compressional behavior up to at least 25 GPa. Unlike En87, β-Fs82 transforms to orthorhombic phase \( \gamma \) only 2–3 GPa above the first change, between 12.3(1) and 13.0(1) GPa. The unit cell parameters of the \( \gamma \)-opx phase at 13.0(1) GPa are \( a = 18.188(9) \text{ Å}, b = 8.776(5) \text{ Å}, c = 4.869(1) \text{ Å} \) and the \( \beta \) angle returns to 90 again. The volume discontinuity accompanying the \( \beta \)-\( \gamma \) transition is 1.7%, with changes in individual unit cell parameters very similar to the first transition (\( a \) expands by 0.2%, \( b \) expands by 0.5%, \( c \) contracts by 2.4%). The twinning introduced in the \( \beta \)-phase disappears as the crystal assumes orthorhombic symmetry again in \( \gamma \)-opx. Similar to the first transformation, the \( \beta \)-\( \gamma \) transition is also reversible and involves only negligible hysteresis. Structure refinement using data collected at 14.6(1) GPa yielded a model consistent with the orthorhombic phase HP-OEn1 predicted by Jahn (2008) for En100 above 20 GPa.

The crystal structures of the three opx phases are compared in Figs. 2 and 3. In Fs100, at ambient condition, both tetrahedral chains have the O-configuration, however, the rotation towards the ideal O-arrangement is much more pronounced in the SiB chain, with the O3–O3–O3 tetrahedral kinking angle \( T_{\text{kB}} = 143.7(2)\degree \), whereas for the SiA chain \( T_{\text{kA}} = 169.1(3)\degree \) (Sueno et al., 1976) is much closer to the extended configuration (for E-chains \( T_k = 180\degree \)). On compression the SiB chain rotates further towards the ideal O configuration (\( T_k \) decreases), while the trend for SiA chain is less well defined (Hugh-Jones et al., 1997, Nestola et al., 2008). The tetrahedral angles obtained from our refinement for α-opx at 2.5(1) GPa are \( T_{\text{kA}} = 168.7(8)\degree \) and \( T_{\text{kB}} = 142.4(8)\degree \), which is consistent with the general trends.
In the $\alpha$-opx phase at ambient pressure the polyhedral volumes of the M1 and M2 sites are 12.81 and 13.42 Å$^3$, with the geometry of the M2 site much more distorted than M1, as indicated by the values of angle variance of 28.67, and 181.20, respectively (Sasaki et al., 1982). The octahedral geometry parameters obtained for Fs$_{82}$ at 2.5(1) GPa are 12.21 and 13.13 Å$^3$ for polyhedral volumes and 21.56 and 177.05 for angle variance, respectively. At ambient pressure, of the two SiO$_4$ tetrahedra, SiA has slightly smaller polyhedral volume (2.18 vs. 2.24 Å$^3$) and is more distorted (angle variance for the two tetrahedral sites is 30.95 and 17.08, Sasaki et al., 1982). In Fs$_{82}$ at 2.5(1) GPa the tetrahedral volumes are 2.15 and 2.21 Å$^3$, while angle variances are 32.27 and 16.78.

As expected, the main structural change involved in the $\alpha$–$\beta$ opx transition results from tetrahedral rotation. In the $\beta$-opx structure the coordination symmetry involves four independent Si chains (Fig. 3). Three of these, SiA, SiC and SiD are O-type, with $T_1A = 154(2)^\circ$, $T_1C = 139(2)^\circ$, and $T_1D = 136(2)^\circ$. The fourth chain, SiB, converts to a S-type with $T_1B = 219(2)^\circ$. The SiA and SiB sites are located within the same tetrahedral layer, and the SiA O-chain sharing the layer with the SiB S-chain is the closest to the E configuration. The change in the average polyhedral volumes of the Si tetrahedra after the $\alpha$–$\beta$ transition is negligible ($\Delta V_a = -0.2\%$), whereas both M1 and M2 sites compress by more than 4% with respect to $\alpha$-opx at 2.5(1) GPa. All of the coordination polyhedra, except for SiI become more regular in the $\beta$-opx Fs$_{82}$.

In $\gamma$-opx Fs$_{82}$, the tetrahedral layers become uniform again (contain only one type of tetrahedral chain), with SiA becoming strongly S-type ($T_1A = 223(1)^\circ$), while SiB remains strongly O-type ($T_1B = 135(1)^\circ$) (Fig. 2). The changes in polyhedral geometry after the transformation to $\gamma$-opx are similar to the first transition, with tetrahedra contracting by 0.8%, and M1 and M2 sites contracting by 2.4% and 1.3%, respectively. The angular variance for SiA, SiB, and M1 polyhedra increases to values close to the $\alpha$-opx phase, whereas the M2 octahedron becomes even more regular than in $\beta$-opx, with the variance decreasing to 42.36 at 14.6(1) GPa.

### 3.1. Equation of state and molar volume relations

In light of the new phase transitions in Fs it is important to take a closer look at the density relations between all known polymorphs with Fs composition in the context of the thermodynamics of the opx-cpx transformation and pyroxene decomposition reactions. The bulk modulus for the different pyroxene phases for compositions close to the En-Fs join are summarized in Supplementary Table 1. The bulk moduli for the different pyroxene phases for compositions close to the En-Fs join are summarized in Supplementary Table 1.

The bulk modulus does not change significantly with the Mg/Fe ratio, accompanying the En-Fs substitution and the values of the moduli obtained for our Fs$_{82}$ sample, $K_0 = 113(2)$ GPa and $K’ = 6.1(2)$ are close to those for pure end members, and are consistent with the trend. EOS fit with $K_0$ fixed to 10.0 GPa, the value obtained from Brillouin measurements on Fs$_{100}$ at ambient pressure (Bass and Weidner, 1984) gives $K’ = 9.8(4)$.

The Ip–hp clinopyroxene transition, because of its subtle displacive character is known to have a rather negligible effect on the elastic moduli, while changing $V_0$ by about 2%. We find the $\alpha$–$\gamma$ transformation in opx, very similar in the structural mechanism to its Ip–hp cpx counterpart, to also have similarly small effect on the elastic properties, with the $\gamma$-phase characterized by $K_0 = 117(8)$ GPa, $K’ = 5.1(5)$, remaining virtually unchanged (to within experimental uncertainty) and $V_0 = 849(3)$ Å$^3$ reduced by 2% with respect to the $\alpha$-opx phase.

### 3.2. Elastic anisotropy

In the application of elasticity theory to geophysical modeling, an assumption is often made that the medium is elastically isotropic. However, most rock-forming minerals exhibit some degree of elastic anisotropy, and any kind of preferred orientation of mineral grains within the rock will cause the rock to exhibit macroscopic elastic anisotropy as well (Thomsen, 1986). Orthopyroxenes are known to be elastically anisotropic. The sample S95 examined by Nestola et al. (2008) was shown to have axial compression anisotropy of $\beta_3/\beta_1 = 1.00:1.64:1.16$, whereas Bass and Weidner (1984) obtained $\beta_3/\beta_2: \beta_1 = 1.00:1.46:1.13$ for Fs$_{100}$. Results of fitting a quadratic equation to the pressure dependence of the unit cell parameters of our sample in the $\alpha$-opx phase give $\beta_3 = -0.0021(1)$ GPa$^{-1}$, $\beta_2 = -0.0039(2)$ GPa$^{-1}$, $\beta_1 = -0.0024(2)$ GPa$^{-1}$, with $\beta_3/\beta_2: \beta_1 = 1.00:1.86:1.14$. The main difference between these three results is the compressibility along the [010] direction (within the layer, perpendicular to Si-chains), most likely related to the compositional difference in Fe$^{2+}$ content and its ordering between the M1 and M2 sites. Because of the limited data for the $\beta$-opx (only two points) we could not reliably evaluate the anisotropy of compressibility of this phase. For the $\gamma$-opx phase the relations between the softest and stiffest directions remain the same with $\beta_3 = -0.0012(3)$ GPa$^{-1}$, $\beta_2 = -0.0028(3)$ GPa$^{-1}$, $\beta_1 = -0.0026(5)$ GPa$^{-1}$, but the compressibility ratio changes rather dramatically and become $\beta_3: \beta_1: \beta_2 = 1.00:2.33:2.17$. The main fact accounting for this change is significant stiffening (by almost a factor of two) of the crystal along the [100] direction (normal to the layers). Ca-poor clinopyroxenes are known to stiffen as a result of the P2$_1$/c–C2/c transition (e.g. Alvaro et al., 2011), but the direction of the largest change in compressibility in that case is [100], rather than [100].

Because of the layered character and anisotropy of the pyroxene structure the factors controlling the three linear compressibilities of the crystal differ. C$_{33}$ is the most variable of the longitudinal moduli as a function of opx composition, and is the most sensitive to structural variations, in particular to the configuration of the tetrahedral chains. Vaughan and Bass (1983) postulated that a threshold kinking angle may exist, below which the tetrahedral chain is passive and the octahedral layer becomes the dominating structural support element. C$_{11}$ is the longitudinal modulus most constant as a function of opx composition. Bass and Weidner (1984) suggested that it is linearly related to the compressibility of the smaller and stiffer M1 octahedra. Surprisingly, our linear compressibility data indicate that despite the significant discontinuous changes in the tetrahedral kinking angle across the $\alpha$–$\beta$–$\gamma$ transitions, the compressibility along [001] changes the least, whereas the drastic change in stiffness along [100] happens despite a very small, 2.4% change in the average M1–O bond length from 2.5(1) to 14.6(1) GPa, suggesting that the interplay between different structural controls of elasticity is more complex than previously assumed.

### 4. Discussion and conclusion

Elastic properties of principal mantle minerals, including orthoferrosilite and volume/density relations between their polymorphs, are fundamental parameters in geophysical modeling of the composition, properties and seismic structure of the Earth (Stixrudze and Lithgow-Bertelloni, 2005; Xu et al., 2008) and extraterrestrial bodies (e.g. Verhoeven et al., 2005). Consequently, information about significant discontinuities and new polymorphic transitions of the mantle minerals should be included in these models. The two new displacive structural transitions in Fs$_{82}$ demonstrate that after completion of the $\beta$–$\gamma$ opx transformation, at pressures above 12.3(1) GPa the density of orthopyroxene becomes comparable to that of the high-pressure clinopyroxene. While opx is still most likely to remain metastable at higher pressures, the two opx transitions are very likely to cause discontinuities in the opx–cpx phase boundary. In the low pressure range, the P2$_1$/c–C2/c phase transition in cpx has a very dramatic effect on the opx-cpx Clapeyron slope and because of the similarity be-
The estimated entropy changes $\Delta S$ for both opx-cpx and lp–hp cpx transitions are negative, which means that enthalpy, and the associated volume change work are the factors driving the transitions (Angel and Hugh-Jones, 1994). Both transitions are endothermic and have positive latent heat. In order for the Gibbs free energy of the higher-pressure polymorphs to decrease, the PAV term needs to compensate for both the entropic change and the latent heat. Similarly, for the decomposition reaction of Fe$_2$Si$_2$O$_6$ to SiO$_2$ and Fe$_2$SiO$_4$, the entropic effect of the volume change, which dramatically increases with the coesite-stishovite transformation, determines the reaction boundary in the P–T space. In Fig. 4 we compare the molar volumes of Fe$_2$SiO$_3$ in $\alpha$-opx, $\beta$-opx, $\gamma$-opx, lp-cpx, hp-cpx, SiO$_2$(coesite)+$\alpha$-Fe$_2$SiO$_4$ and SiO$_2$(stishovite)+$\gamma$-Fe$_2$SiO$_4$. Since our sample had an intermediate solid solution composition, we applied a 1% volume correction, which makes $V_0$ of Fs$_{82}$ equal to $V_{100}$. As discussed above, the possible effect of the Mg content on the bulk modulus in Fs$_{82}$ is most likely not significant. As can be seen in Fig. 4, the molar volumes of $\alpha$-opx and lp-cpx are approximately equal at ambient temperature, over the whole stability range of lp-cpx, which means that the volume work advantage of the opx-cpx conversion is negligible. As long as coesite, or lower pressure tetrahedral SiO$_2$ phases are the products of the decomposition reaction, the volume change accompanying this reaction is positive (reaction is thermodynamically unfavorable). The lp–hp cpx transition lowers the molar volume of cpx by about 2%, which makes the PAV term for opx-cpx conversion significant, and further stabilizes the pyroxene with respect to the decomposition. Above approximately 8 GPa the stishovite phase of SiO$_2$ becomes stable, and Fe$_2$SiO$_4$ transforms to the $\gamma$-phase, changing the molar volume of the decomposition products by more than 30% and strongly favoring that reaction. The $\alpha$–$\beta$ transition in opx above 10.1(1) GPa reduces the volume change for opx-cpx conversion by about half, and the further transformation to $\gamma$-opx above 12.3(1) GPa makes the volumes of opx and cpx nearly equal (at 30 GPa the cpx density remains higher by about 1%). We expect that both of the opx transitions would have a discontinuous effect on the opx-cpx conversion, shifting the phase boundary to higher pressures and extending the opx stability field, however, cpx is likely to remain the most stable pyroxene phase above 10 GPa. The increase in density in the $\gamma$-opx phase is not sufficient to fully compensate the PAV effect of the decomposition reaction above the coesite-stishovite phase boundary, and the decomposition is still going to be favored at higher pressures. Because of the molar volume relations shown in Fig. 4, it seems most likely that the metastability of $\beta$- and $\gamma$-opx phases with respect to the $\gamma$-cpx structure is kinetic in nature, caused by a high activation barrier $\Delta G^\ddagger$ of the opx-cpx conversion, rather than by a reversal of the sign of $\Delta G$.

In Fe-poor opx compositions, the pressure of the more significant $\beta$–$\gamma$ transition is shifted to much higher pressures (likely to above 25 GPa for pure En$_{100}$, Lin, 2003, 2004; Lin et al., 2005), making the iron content of natural pyroxenes a critical parameter affecting the phase equilibria.

Information about the new phase transitions in opx provides an improved understanding of the crystal chemical trends and transformation paths of opx to higher-pressure minerals with $\delta$-coordinated Si. The mechanisms of the $\alpha$–$\beta$ and $\beta$–$\gamma$ transitions, involving purely tetrahedral rotation are fully consistent with trends known for the pyroxene family, but demonstrate new possibilities for discontinuous re-arrangements of the opx structure (Downs, 2003). Recently, Plonka et al. (2012) described a new high-pressure phase of diopside, constituting an intermediate step of cpx breakdown to MgSiO$_3$ akimotoite and CaSiO$_3$ perovskite, with Si assuming octahedral coordination. The two new phase transitions in Fs$_{82}$ are a likely prelude to similar metastable conversion in orthopyroxenes.

Quenchable microstructural features resulting from polymorphic transitions at high pressures and temperatures are often used as proxies for the thermodynamic history of natural samples (Bozhilov et al., 1999; Schmitz and Brencher, 2008), however, both of the new transformations in Fs$_{82}$ are fully reversible and not expected to leave microstructural signatures usable as thermobarometry clues.

Our results indicate a significant change of the elastic anisotropy of opx across the polymorphic phase transitions. This change could have seismically detectable consequences for the subducted slabs, perhaps more significant than the subtle discontinuities in the density and bulk modulus. High-pressure rocks in collisional orogens such as Alpine eclogites, regarded as relics of subduction zones, have been demonstrated to contain pyroxenes (particularly omphacite) characterized by a significant degree of lattice preferred orientation (Bascou et al., 2001; Bascou et al., 2002), which further supports the notion of possible seismic detectability of the transformations reported here.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the
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