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Phase Stability of Iron Germanate, FeGeO₃, to 127 GPa

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Abstract

The high-pressure behavior of germanates is of interest as these compounds serve as analogs for silicates of the deep Earth. Current theoretical and experimental studies of iron germanate, FeGeO₃, are limited. Here, we have examined the behavior of FeGeO₃ to 127 GPa using the laser-heated diamond anvil cell combined with *in situ* synchrotron X-ray diffraction. Upon compression at room temperature we find that the ambient-pressure clinopyroxene phase transforms to a disordered triclinic phase (FeGeO₃ (II)) at ~ 18 GPa in agreement with earlier studies. An additional phase transition to FeGeO₃ (III) occurs above 54 GPa at room temperature. Laser-heating experiments (~1200-2200 K) were conducted at three pressures (33, 54 and 123 GPa) chosen to cover the stability regions of different GeO₂ polymorphs. In all cases, we observe that FeGeO₃ dissociates into GeO₂ + FeO at high-pressure and temperature conditions. Neither the perovskite nor the post-perovskite phase was observed up to 127 GPa at ambient or high temperatures. The results are consistent with the behavior of FeSiO₃, which also dissociates into a mixture of the oxides (FeO + SiO₂) at least up to 149 GPa.

Introduction

Bridgmanite, ((Mg,Fe)SiO₃, Pv), belongs to the family of ABO₃ oxide perovskites and crystallizes in the orthorhombic system (Space group: *Pbnm*). The structure consists of a three-dimensional network of corner-linked BO₆ octahedra surrounding distorted 8-coordinated A sites.

28 Bridgmanite is of geophysical interest as it is expected to be the most abundant phase in the
 29 Earth's lower mantle below 660-km depth. Under pressure and temperature conditions
 30 approaching those of the core-mantle boundary of the Earth (~125 GPa, >2000 K), Mg-rich
 31 bridgmanite undergoes a phase transition to the CaIrO_3 -type structure known as post-perovskite
 32 (pPv) (Murakami et al. 2004; Oganov and Ono 2004). The post-perovskite phase also crystalizes
 33 in the orthorhombic crystal system (Space group: *Cmcm*) and has the same coordination numbers
 34 as perovskite. In contrast to the corner-sharing octahedral network in the perovskite structure, the
 35 silicate octahedra share edges and corners in pPv giving rise to a structure layered along the *b*
 36 crystallographic axis.

37 The role of iron in deep Earth silicates is of key importance due to seismic evidence for
 38 possible Fe-enriched regions of the deep Earth (Lay et al. 2006). In addition, high-pressure spin
 39 transitions in Fe-bearing minerals have attracted much attention (Lin et al. 2013; Badro 2014).
 40 For the iron end-member of the (Mg,Fe)SiO₃ system, the stability of different high-pressure
 41 phases has been explored by theoretical studies at high pressures. The post-perovskite phase of
 42 FeSiO₃ is reported to be more stable than the perovskite phase above 35 GPa on the basis of
 43 density functional theory (DFT) calculations at 0 K (Stackhouse et al. 2006). Using an
 44 evolutionary algorithm together with DFT, Cohen and Lin (2014) proposed a possible high-
 45 pressure (100 GPa) structure of FeSiO₃ called PPv-II (*Cmmm*). PPv-II was predicted to be less
 46 stable than both Pv and pPv at *T* = 0 K, but could be entropically stabilized at high temperatures.
 47 Experimentally, iron-rich perovskites and post-perovskites in the (Mg,Fe)SiO₃ system

48 have been synthesized with Fe# ($\text{Fe\#} = \frac{\text{Mg} + \text{Fe}}{\text{Fe} + \text{Mg}}$) up to 0.75 (Tateno et al. 2007; Dorfman et
 49 al. 2013) and 0.8 (Mao et al. 2004). However, end-member FeSiO₃ has been shown to dissociate
 50 into the respective oxides (SiO₂ + FeO) in experiments up to 25 GPa (Ming and Bassett 1975)

66 $P1'$ designated as $\text{FeGeO}_3(\text{II})$ was observed between 13 and 20.1 GPa (Hattori et al. 2001).
67 Evidence for transformation of FeGeO_3 to the perovskite structure at room temperature has been
68 reported above 33 GPa (Nagai et al. 1998; Hattori et al. 1999). However, this result may be
69 considered inconclusive as the reported X-ray diffraction peaks are weak and broad. Upon
70 decompression to ambient conditions, the sample was found to adopt the LiNbO_3 -type structure
71 (Hattori et al. 1999), as does MgGeO_3 perovskite (Leinenweber et al. 1994).

72 Early high P-T experiments reported that FeGeO_3 decomposed into Fe_2GeO_4 (spinel) +
73 GeO_2 (rutile) at 1 GPa and 973 K (Ringwood and Seabrook 1963) and FeO (rocksalt) + GeO_2
74 (rutile) at 25 GPa and 1273 K (Liu 1977). However, at lower temperatures (638 K) Hattori et al
75 (2001) observed that $\text{FeGeO}_3(\text{II})$ transformed into the hexagonal ilmenite ($R\bar{3}$) structure at
76 21 GPa. The ilmenite phase has also been synthesized by heating clinopyroxene to 623 - 973 K
77 at 23.5 GPa (Nakatsuka et al. 2013). No high pressure-temperature experiments above 25 GPa
78 have been reported yet. To better understand this system, we have carried out studies of the high-
79 pressure, high-temperature behavior of FeGeO_3 over a wide P-T range extending beyond 1 Mbar.

80 Experimental details

81 FeGeO_3 clinopyroxene was synthesized using a stoichiometric mixture of Fe (Alfa Aesar,
82 >99.998 % purity), Fe_2O_3 (Alfa Aesar, >99.5% purity) and GeO_2 (Aldrich, >99.998% purity)
83 (Hattori et al. 1999; Redhammer et al. 2012). The sample was ground under ethanol and pressed
84 into a pellet using a hydraulic press (0.5 ton). The pellet was then transferred to vacuum sealed
85 silica tubes and heated at 1023 K for 72 hours. It was then re-ground and pressed and sealed
86 again and put back in the furnace at 1123 K for 12 days. After 12 days, it was examined using X-
87 ray diffraction and weak starting materials peaks were observed. Therefore, it was re-heated for 5

88more days. The final run products were re-examined by X-ray diffraction and confirmed to be
89C2/c clinopyroxene structure with no evidence for other phases. The calculated lattice parameters
90($a = 9.7873$ (12) Å, $b = 9.1323$ (14) Å, $c = 5.1949$ (7) Å, $\beta = 101.804^\circ$ (11)) are in good
91agreement with previous results (Hattori et al. 1999).

92   High pressure-temperature X-ray diffraction experiments on FeGeO₃ were preformed
93using laser-heated diamond anvil cells (DACs). The sample was mixed with 10% Au (by
94weight), ground to ~µm grain size, and loaded into the sample chamber of a rhenium gasket in a
95symmetric DAC. The gaskets were preindented to ~30-µm thickness and ~50 to 100-µm
96diameter holes were laser drilled to form the sample chamber. Samples were compressed in cells
97with either 100-µm or 200-µm culet diamond anvils. Experimental runs were carried out both
98with and without a neon pressure transmitting medium. Neon was loaded into the sample
99chamber using a gas-loading system at the GSECARS sector of the Advanced Photon Source
100(APS). Ruby balls were used to support the sample during loading so that Ne can flow
101underneath and around the sample. In the case of experiments without a pressure medium, the
102entire gasket hole was filled with the sample + Au mixture. Table 1 summarizes the loading
103configurations of the different samples.

104   *In situ* synchrotron X-ray diffraction was carried out at beamline 13-ID-D of the APS
105using a monochromatic X-ray beam ($\lambda = 0.3344$ Å). The incident X-rays were focused with
106Kirkpatrick-Baez mirrors to dimensions of ~3 µm x 3 µm. Diffraction patterns were collected
107using a 2D detector (MAR CCD). The detector orientation was calibrated using a lanthanum
108hexaboride (LaB₆) standard. The 2D images were integrated to produce conventional one-
109dimensional diffraction patterns using DIOPTAS (Prescher and Prakapenka 2015). High-
110temperature was achieved by heating the sample from both sides with diode pumped fiber lasers

with ~15 μm spot size (Prakapenka et al. 2008). Temperatures were measured from both sides using spectroradiometry (Jephcoat and Besedin 1996). The laser power was adjusted independently so that the temperature differences between the two sides was less than 100 K. Pressure was determined using the thermal equation of state (EOS) of gold (Fei et al. 2007). Peak positions were obtained by fitting background-subtracted Voigt line shapes to the data. Lattice parameters were calculated using least-squares refinement of the fitted peak positions (Holland and Redfern 1997).

LeBail and Rietveld refinements were carried out on selected data using GSAS/ EXPGUI (Toby 2001). The background was initially fit manually using a Chebyshev polynomial (8 terms), but refined at later stages. For each step, the parameters for all the observed phases were initially refined separately and then simultaneously. In the first step, we refined only the phase fractions and lattice parameters. For GeO_2 phases, the unit cell dimensions obtained from least squares refinement of the peak positions and atomic positions from Shiraki et al. (2003) were used as initial values. Then the profile function (Pseudo-Voigt with Finger-Cox-Jephcoat asymmetry and Stephens anisotropic strain broadening) was refined and finally the atomic positions. The isotropic displacement parameters (U_{iso}) were not refined.

Results

Room-Temperature Compression

FeGeO_3 clinopyroxene was initially compressed at room temperature to a peak pressure of 33 GPa, 54 GPa and 123 GPa in three separate experiments (Figure 1). Up to 11 GPa, the diffraction pattern can be indexed using the ambient-pressure cpx ($C2/c$) structure. Upon further compression to 18 GPa, the diffraction pattern changes indicating a structural phase transition

133(Figure 1a). The measured pattern can be fit using the triclinic unit cell of $\text{FeGeO}_3(\text{II})$ ($P\bar{1}$)
 134reported at 20.1 GPa by Hattori et al. (2001). Figure 2 shows a Le Bail refinement of our
 135diffraction pattern at 20.4 GPa. The lattice parameters obtained from our refinement ($a = 6.7831$
 136(8) Å, $b = 8.4799(11)$ Å, $c = 4.8921(5)$ Å, $\alpha = 88.717(8)^\circ$, $\beta = 89.464(8)^\circ$, $\gamma = 137.670(3)^\circ$) are in
 137good agreement with those of Hattori et al. (2001) ($a = 6.829(26)$ Å, $b = 8.490(33)$ Å, $c =$
 1384.887(3) Å, $\alpha = 88.94(13)^\circ$, $\beta = 89.40(13)^\circ$, $\gamma = 137.49(16)^\circ$). The observed pattern cannot be
 139indexed using other known high-pressure structures in pyroxenes including the HP- $P2_1/c$
 140clinopyroxene (FeSiO_3 , (Pakhomova et al. 2017) or β -diopside (Plonka et al. 2012).

141 In our initial experiment (S1), FeGeO_3 (II) was found to remain stable to 33 GPa, the
 142peak pressure reached in this sample at ambient temperature (Figure 1a). A second sample (S2)
 143was prepared and compressed directly to 41 GPa at room temperature. The diffraction pattern
 144for this sample appears to be identical with FeGeO_3 (II) although the peaks are somewhat
 145broader and there are some differences in peak intensity (Figure 1b). This may be due to
 146differing amounts of non-hydrostatic stress and preferred orientation in the two samples. The
 147 FeGeO_3 (II) phase appears to remain stable to at least 54 GPa, the maximum pressure reached on
 148this sample at 300 K.

149 A third sample (S3) was prepared and compressed at room temperature in two steps to 86
 150GPa and then 123 GPa. Changes in the diffraction pattern indicate that an additional phase
 151transformation to FeGeO_3 (III) occurs between 54 and 86 GPa and is maintained to 123 GPa
 152(Figure 1b). Determination of the structure of $\text{FeGeO}_3(\text{III})$ was not possible from the powder
 153diffraction data. Unlike the first two samples which contained a neon pressure medium, the third
 154sample was compressed without a pressure transmitting medium. The broad observed diffraction

155 peaks may therefore reflect a combination of a high degree of non-hydrostatic stress along with
156 partial disordering of the sample. Nevertheless, it appears that FeGeO₃ remains largely
157 crystalline to the highest pressure (123 GPa) at 300 K and does not undergo complete pressure-
158 induced amorphization.

159 Earlier reported the appearance of perovskite at 33-40 GPa upon room-temperature
160 compression of FeGeO₃ (Nagai et al. 1998; Hattori et al. 1999). Our diffraction data at 41 GPa (Figure 1b) cannot
161 be indexed by the perovskite unit cell ($a = 4.93(2) \text{ \AA}$, $b = 5.06(6) \text{ \AA}$, $c = 6.66(3) \text{ \AA}$ at 40 GPa)
162 reported by those authors. Table 1 compares the d -spacings for our pattern with those of Hattori
163 et al. (1999). The difference between the two are large and rules out the perovskite phase. The
164 heating runs described below also do not support the existence of the perovskite phase in this
165 system.

166 ***High-Temperature Phase Stability***

167 Laser heating experiments were carried out at pressures of 33, 54 and 123 GPa. In each
168 case, the sample was first compressed to the target pressure at room temperature and then heated.
169 Each experiment involved a fresh, previously unheated sample. The pressures were chosen to
170 cover the stability fields of high-pressure phases of germanium oxide. GeO₂ exhibits extensive
171 polymorphism under compression (Micoulaut et al. 2006). At ambient conditions, GeO₂
172 crystallizes in the rutile structure ($P4_2/mnm$). On compression to ~ 25 GPa, it transforms to the
173 CaCl₂-type structure ($Pnmm$) (Haines et al. 2000). Upon further compression to ~ 44 GPa and 70
174–90 GPa, it forms the α -PbO₂-type ($Pbcn$) and pyrite-type ($Pa\bar{3}$) structures, respectively (Ono
175 et al. 2003a; Prakapenka et al. 2004)

Sample S1 was directly compressed to 33 GPa at room temperature and then heated from 1400 K to ~2120 K in steps of ~200 K. Figure 3a shows the X-ray diffraction pattern obtained during heating to the peak temperature (*in situ* $P = 39.1$ GPa, including thermal pressure). All major peaks can be assigned to GeO_2 (rutile-type) + FeO (B1 rocksalt-type phase). The CaCl_2 -type phase of GeO_2 is a high-pressure orthorhombic distortion of the ambient-pressure tetragonal rutile-type phase (Haines et al. 2000). The phase transition can be identified from the splitting of the hkl diffraction lines ($h \neq k$). At room temperature, the rutile- CaCl_2 phase transition pressure has been reported to occur at 25-27 GPa (Haines et al. 1998, 2000; Ono et al. 2002).

(Prakapenka et al. 2004) observed the CaCl_2 -type phase at 36 GPa and 1600 ± 100 K. Ono et al. (2002) reported that the phase boundary has a positive Clapeyron slope given by:

$$P(\text{GPa}) = (34.9 \pm 1.2) + (0.0086 \pm 0.0024) \times (T - 1300)(\text{K}) \quad (1)$$

At the peak temperature of our experiment ($P, T = 39.1$ GPa, 2120 K), the splitting of the (211) and (121) peaks is not evident. The full width at half maximum (FWHM) of the (211) peak is also comparable to other peaks for which splitting is not expected ($h = k$). These observations suggest our sample remains in the rutile phase under these conditions or that we are so close to the boundary that the splitting of the CaCl_2 -type phase cannot be detected as yet. At 2120 K, the phase boundary relationship (Eqn. 2) predicts a transition pressure of 41.9 ± 3.2 GPa, which is consistent with our evidence for persistence of the rutile-type phase. The lattice parameters obtained from least squares fitting of the peaks are $a = 4.2462$ (17) Å, $c = 2.8122$ (23) Å. The calculated volume (50.707 (42) Å³) is in general agreement with that reported by Ono et al. (2002) (50.23 Å³ at 39.7 GPa and 2050 K). The lattice parameter of the B1-type FeO (4.1431 (12) Å) is about 1% larger than the predicted unit cell dimension ($a = 4.10$ Å at 39 GPa, 2120 K).

198based on the equation of state parameters reported by Fischer et al. (2011). Tables 2a and 2b
199show the observed and calculated d -spacings for the rutile-type phase of GeO_2 and B1-type FeO
200at high P-T. The differences ($\Delta d = d_{\text{obs}} - d_{\text{calc}}$) are less than 0.004 Å indicating a good fit to our
201observations. In all cases lattice parameters obtained from peak fitting were used as the starting
202guesses for whole profile Rietveld refinement. The values obtained from the two methods are in
203good agreement with each other and therefore only the Rietveld refinement results have been
204reported for the remaining experiments. The unit cell dimensions and atomic positions obtained
205from Rietveld refinement are listed in Table 3.

206 On quenching to room temperature (P, T = 33.9 GPa, 300 K), the splitting of the (211)
207and (121) peaks became distinct (inset, Figure 3b). The lattice parameters of the CaCl_2 -type
208phase (Table 3) are in good agreement with those of Prakapenka et al. (2004) ($a = 4.2617(4)$ Å, b
209= 4.1268(2) Å, $c = 2.7817(4)$ Å at 36 GPa) and Haines et al. (2000) ($a = 4.2866(6)$ Å, $b =$
2104.1742(6) Å, $c = 2.7995(2)$ Å at 32 GPa). The calculated volume (49.679 (45) Å³) is also in
211agreement with Ono et al. (2002) (50.11 Å³ at 30.7 GPa and 300 K). The rhombohedral (

212 $R\bar{3}m\bar{1}$ rB1 phase of FeO is identified from the splitting of the cubic (111) peak into the
213rhombohedral 003 and 101 peaks (Mao et al. 2002). In $\text{Fe}_{0.947}\text{O}$, the cubic-rhombohedral
214phase transition was observed at 18 GPa at room temperature using single crystal X-ray
215diffraction (Shu et al. 1998). In agreement with Wicks et al. (2015), we observe a mixture of the
216cubic and rhombohedral phases on quenching to room temperature. The c/a ratio of the
217rhombohedral phase (2.621) is consistent with Shu et al. (1998) ($\text{Fe}_{0.947}\text{O}$, 2.6362 at 30.6

218GPa) and (Jacobsen et al. 2005) ($\text{Fe}_{0.93}\text{O}$, 2.619 at 35.3 GPa). The difference between our B1

lattice parameter and that obtained from the EOS parameters of Fischer et al. (2011) is less than 1%. The atomic positions of both rutile and CaCl₂-type phases of GeO₂ are in fair agreement with existing literature (Haines et al. 2000; Shiraki et al. 2003).

As already mentioned, the pressure intervals for laser-heating were chosen such that they fall in the stability fields of different phases of GeO₂ i.e. rutile, CaCl₂-type, α -PbO₂ and pyrite-type. For the next sample (S2), we first increased the pressure up to 54 GPa at room temperature. On heating the sample to 2000 K (*in situ* P = 58.3 GPa), we observe that FeGeO₃ dissociated into a mixture of α -PbO₂-type GeO₂ and B1-type FeO within 5 minutes (Figure 4). The CaCl₂-type to α -PbO₂-type transition has been reported to occur at 44 GPa and 1600 $\pm$ 100 K (Prakapenka et al. 2004). Ono et al. 2003 found the phase boundary between CaCl₂ and α -PbO₂ also has a positive Clapeyron slope:

$$P(\text{GPa}) = (53.3 \pm 3) + (0.011 \pm 0.005) \times (T - 1800)(\text{K}) \quad (2)$$

At 2000 K, the predicted transition pressure of 55.5 $\pm$ 4 GPa supports our observation of the α -PbO₂ phase at 58 GPa. Table 3 shows the structural parameters of the oxide assemblage obtained from Rietveld refinement. The unit cell dimensions of GeO₂ are in agreement with those of (Prakapenka et al. 2003) ($a = 4.0423(8)$ Å, $b = 5.0396(8)$ Å, $c = 4.5288(0)$ at 60 GPa, 1800 K).

Finally, we compressed FeGeO₃ (S3) to a pressure of 123 GPa at room temperature and heated it from $\sim$ 1200 to $\sim$ 1700 K (Figure 5). This experiment did not have any pressure-transmitting (insulating) medium. The diffraction pattern at the peak P, T condition (127.3 GPa and 1700 K) can be indexed using GeO₂ (pyrite-type) and FeO (B1) (Table 3) again indicating the dissociation of FeGeO₃ at high-pressures. Our observation of the pyrite phase at this pressure and

temperature is consistent with previous observations that this phase can be synthesized by laser heating to 1900 K above 100 GPa (Ono et al. 2003b). The unit cell dimension and atomic positions of pyrite-type GeO_2 are in good agreement with those reported by (Shiraki et al. 2003) ($a = 4.3365(15) \text{ \AA}$ at 108 GPa).

Discussion

The behavior of FeGeO_3 under compression has been clarified by this study. FeSiO_3 has been observed in three polymorphic forms at ambient conditions: ferrosilite (orthopyroxene, $Pbca$), clinoferrosilite ($P2_1/c$) and a triclinic pyroxenoid form ($P1\bar{1}$) (Lindsley et al. 1964; Weber 1983). In room temperature single-crystal compression studies, clinoferrosilite undergoes a phase transition to the $C2/c$ clinopyroxene (cpx) structure between 1.3 and 3.0 GPa (Hugh-Jones et al. 1994; Pakhomova et al. 2017) and then into another high-pressure monoclinic phase (HP- $P2_1/c$) between 30 – 36 GPa (Pakhomova et al. 2017). In addition, single-crystal studies have investigated high-pressure phase transitions for various other compositions in the (Mg,Fe) SiO_3 system (Zhang et al. 2013; Dera et al. 2013; Finkelstein et al. 2015). In contrast, FeGeO_3 crystallizes in the high-pressure $C2/c$ cpx structure, which remains stable up to ~18 GPa. Under room temperature compression, it undergoes two phase transitions at ~ 18 GPa ($\text{FeGeO}_3(\text{II})$) and in between 54-86 GPa ($\text{FeGeO}_3(\text{III})$). $\text{FeGeO}_3(\text{III})$ was found to remain stable up to ~123 GPa.

At high temperatures, FeGeO_3 and FeSiO_3 show similar behavior. The Fe endmember compositions in these systems are distinct from intermediate iron-bearing compositions. In the (Mg,Fe) SiO_3 system, perovskites and post-perovskites have been synthesized with Fe# up to 0.8

262(Mao et al. 2004). In germanates, compositions with $Fe\# \leq 22$, single phase pv and ppv was
 263observed, while compositions with $Fe\# > 22$, evidences for partial decomposition were found
 264(Stan et al. 2017). As already mentioned, experimental studies have reported that the Pv and pPv
 265phases are not stable in $FeSiO_3$. Instead, a mixture of FeO (B1 phase) and a high-pressure SiO_2
 266phase was found in experiments covering a wide pressure range up to 149 GPa (Fujino et al.
 2672009). In this study, we have shown that $FeGeO_3$ behaves similarly and breaks down into $GeO_2 +$
 268FeO at least up to 1.27 Mbars.

269 Further understanding of the behavior of $FeGeO_3$ relative to other analogs can be obtained
 270by consideration of the Goldschmidt diagram. This type of diagram has been commonly used
 271to predict the stability of the perovskite and post-perovskite structures in ABO_3 compounds
 272(Goldschmidt 1926; Hattori et al. 1999; Fujino et al. 2009; Tateno et al. 2010) (Figure 6). The
 273Goldschmidt tolerance factor, t , can be used to assess the potential stability of the two phases. It
 274is calculated from the ionic radii of the eightfold-coordinated A cation (R_A), sixfold-
 275coordinated B (R_B) cation and the ionic radius of the oxygen anion (R_O) as given by:

$$276 \quad t = \frac{R_A + R_O}{\sqrt{2}(R_B + R_O)} \quad (3) \quad \text{Compounds with } 0.75 < t < 1.0 \text{ favor the perovskite structure (Ito}$$

277and Matsui 1979; Tateno et al. 2010). A perovskite structure has been predicted to be stable for
 278all the compounds shown in Figure 6. It is further observed that high-pressure perovskite phases
 279with $t > 0.84$ are generally quenchable and the ones with $t < 0.84$ are not (Leinenweber et al.
 2801994).

Based on Goldschmidt criteria, the Fe end-members FeSiO_3 ($t = 0.91$), FeGeO_3 ($t = 0.85$), and FeTiO_3 ($t = 0.82$) should all adopt the perovskite structure (Sato et al. 1991; Haines and Léger 1993; Wilson et al. 2005). The perovskite phase of FeTiO_3 has been synthesized from the LiNbO_3 -type structure at 16 GPa (Leinenweber et al. 1991) and from the ilmenite phase on heating at 20 GPa and 973 K (Ming et al. 2006). However, FeSiO_3 appears to be an exception to the Goldschmidt criterion as experimental studies indicate it does not transform to the perovskite structure (Fujino et al. 2009).

It has been observed that the tolerance factors of reported post-perovskites are less than 0.90 (Bremholm et al. 2011). By this criterion, FeTiO_3 should form post-perovskite. Theoretical calculations also predict both Pv and pPv to be stable (Wilson et al. 2005). However, it was found experimentally that FeTiO_3 perovskite dissociates from perovskite into $(\text{Fe}_{1-x}\text{Ti}_x\text{O}) + (\text{Fe}_{1+x}\text{Ti}_{2-x}\text{O}_5)$ at 53 GPa and 2000 K (Wu et al. 2011) or $(\text{Fe}_{1-x}\text{Ti}_{0.5x}\text{O}) + \text{FeTi}_3\text{O}_7$ at 42 GPa and 2000 K (Nishio-Hamane et al. 2010). The absence of post-perovskite in titanates (Tateno et al. 2006) has been attributed to the increase in the coordination number of Ti^{4+} to seven (compared with six in both perovskite and post-perovskite) at relatively low-pressures (Sato et al. 1991; Haines and Léger 1993).

In case of the germanate system, MgGeO_3 , MnGeO_3 and ZnGeO_3 form pPv upon heating to ~63 GPa (Hirose et al. 2005), ~60 GPa (Tateno et al. 2006) and ~115 GPa (Yusa et al. 2014) respectively. Post-perovskite has not been observed in CaGeO_3 (Nakatsuka et al. 2015) and CdGeO_3 (Tateno et al. 2006), which is also expected as $t > 0.90$ for both. In the case of FeGeO_3 , tolerance factor considerations suggest that both perovskite and post-perovskite should be stable. However, our experimental results show that, in contrast to earlier studies (Nagai et al. 1998;

Hattori et al. 1999), neither of these phases form in FeGeO_3 up to 127 GPa. Thus, the Goldschmidt criteria are not applicable to the Fe endmembers of the $(\text{Mg,Fe})\text{SiO}_3$ and $(\text{Mg,Fe})\text{GeO}_3$ systems. This can be explained by the crystal field stabilization energy (CFSE) of transition metals with unfilled 3d electrons (6 for Fe^{2+}) in the octahedral coordination of B1/rB1 structure in comparison to the dodecahedral perovskite site (Burns 1993; Fujino et al. 2009). Estimates indicate that octahedrally coordinated Fe^{2+} has a higher CFSE than 8-coordinated Fe^{2+} (e.g. CFSE of Fe^{2+} in magnesiowüstite exceeds that of Fe^{2+} in the perovskite structure by ~ 56 KJ/mole). In case of MnGeO_3 and MnSiO_3 the filled 3d electrons (5 for Mn^{2+}) lead to no CFSE, thereby making the perovskite structure stable. We also find no evidence for the formation of other phases as suggested from first-principles calculations (Cohen and Lin, 2014).

There has been interest in understanding the behavior of the $(\text{Mg,Fe})\text{SiO}_3$ system at ultrahigh pressures (Duffy et al. 2015). Theoretical studies indicate that MgSiO_3 will dissociate into CsCl-type MgO and cotunnite-type SiO_2 at 11.2 Mbar (Umemoto et al. 2006). However, no studies have examined Fe-bearing compositions in this system at ultrahigh pressures as yet. Our experiments show that FeGeO_3 dissociates into oxides across the stability fields of the $\alpha\text{-PbO}_2$ and pyrite-type phases of GeO_2 . In SiO_2 , these phases are expected to have stability ranges from 121 – 268 GPa (Murakami et al. 2003; Kuwayama et al. 2005) and 200-690 (Tsuchiya and Tsuchiya 2011) GPa, respectively. Applying our results to the silicate system suggests that the breakdown of FeSiO_3 would be expected to extend to pressures as high as 690 GPa. Theoretical studies of Fe-bearing compositions remain challenging and analog materials can provide a useful benchmark for such calculations (Shukla et al. 2015). Future studies of intermediate compositions in the $(\text{Mg,Fe})\text{GeO}_3$ system may provide further constraints on the ultrahigh pressure behavior of this system.

326Conclusions

327 FeGeO₃ clinopyroxene undergoes a pressure-induced phase transition at ~18 GPa at room
328temperature. The diffraction pattern is consistent the FeGeO₃ (II) structure. On increasing the
329pressure, the diffraction peaks broaden and there is evidence for another phase transition between
33054 and 86 GPa. This phase remains stable at room temperature up to 123 GPa, the peak pressure
331considered here. In contrast to previous studies, we did not find any evidence of formation of
332perovskite at ~ 40 GPa and 300 K. On laser heating at 33, 54 and 123 GPa, FeGeO₃ dissociated
333into a mixture of GeO₂ (rutile/ CaCl₂, α -PbO₂ and pyrite-type respectively) and FeO (B1/ B1 +
334rB1). The structural parameters of the oxide phases at different pressures were calculated using
335both least squares peak fitting and Rietveld refinement. Our calculated unit cell dimensions and
336atomic coordinates are in good agreement with existing literature. In contrast to predictions
337based on ionic ratios, the perovskite or post-perovskite phases are not formed in FeGeO₃ to
338pressures above 1 Mbar. This result is consistent with findings for FeSiO₃ and suggest that
339FeSiO₃ breakdown will persist to ~700 GPa.

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349References

- 350Badro J (2014) Spin transitions in mantle minerals. *Annu Rev Earth Planet Sci* 42:231–248.
- 351Bremholm M, Dutton SE, Stephens PW, Cava RJ (2011) NaIrO₃—A pentavalent post-
352perovskite. *J Solid State Chem* 184:601–607.
- 353Burns RG (1993) Mineralogical applications of Crystal Field Theory. Cambridge University
354Press.
- 355Cohen RE, Lin Y (2014) Prediction of a potential high-pressure structure of FeSiO₃. *Phys Rev B*
35690:140102.
- 357Dera P, Finkelstein GJ, Duffy TS, et al (2013) Metastable high-pressure transformations of
358orthoferrosilite Fe₈₂. *Phys Earth Planet Inter* 221:15–21.
- 359Dorfman SM, Meng Y, Prakapenka VB, Duffy TS (2013) Effects of Fe-enrichment on the
360equation of state and stability of (Mg,Fe)SiO₃ perovskite. *Earth Planet Sci Lett* 361:249–257.
- 361Dorfman SM, Shieh SR, Meng Y, et al (2012) Synthesis and equation of state of perovskites in
362the (Mg,Fe)₃Al₂Si₃O₁₂ system to 177 GPa. *Earth Planet Sci Lett* 357–358:194–202.
- 363Duffy T, Madhusudhan N, Lee KKM (2015) Mineralogy of super-earth planets. In: Schubert G
364(ed) *Treatise on Geophysics* (Second Edition). Elsevier, Oxford, pp 149–178
- 365Fei Y, Ricolleau A, Frank M, et al (2007) Toward an internally consistent pressure scale. *Proc*
366Natl Acad Sci 104:9182–9186.
- 367Finkelstein GJ, Dera PK, Duffy TS (2015) Phase transitions in orthopyroxene (En₉₀) to 49 GPa
368from single-crystal X-ray diffraction. *Phys Earth Planet Inter* 244:78–86.
- 369Fischer RA, Campbell AJ, Shofner GA, et al (2011) Equation of state and phase diagram of FeO.
370*Earth Planet Sci Lett* 304:496–502.
- 371Fujino K, Nishio-Hamane D, Suzuki K, et al (2009) Stability of the perovskite structure and
372possibility of the transition to the post-perovskite structure in CaSiO₃, FeSiO₃, MnSiO₃ and
373CoSiO₃. *Phys Earth Planet Inter* 177:147–151.
- 374Goldschmidt VM (1926) Die Gesetze der Krystallochemie. *Naturwissenschaften* 14:477–485.
- 375Greenblatt M, Hornreich RM, Sharon B (1974) Evidence for a spin-reorientation type phase
376transition in FeGeO₃. *Solid State Commun* 14:1177–1181.
- 377Haines J, Léger JM (1993) X-ray diffraction study of TiO₂ up to 49 GPa. *Phys B Condens Matter*
378192:233–237.
- 379Haines J, Léger JM, Chateau C, et al (1998) Ferroelastic phase transition in rutile-type
380germanium dioxide at high pressure. *Phys Rev B* 58:R2909–R2912.
- 381Haines J, Léger JM, Chateau C, Pereira AS (2000) Structural evolution of rutile-type and CaCl₂-
382type germanium dioxide at high pressure. *Phys Chem Miner* 27:575–582.

383Hattori T, Matsuda T, Tsuchiya T, et al (1999) Clinopyroxene-perovskite phase transition of
384FeGeO₃ under high pressure and room temperature. *Phys Chem Miner* 26:212–216.

385Hattori T, Nagai T, Yamanaka T, et al (2000) Single-crystal X-ray diffraction study of FeGeO₃
386high-P clinopyroxene (C2/c) up to 8.2 GPa. *Am Mineral* 85:1485–1491.

387Hattori T, Tsuchiya T, Nagai T, Yamanaka T (2001) Sequential high-pressure transformations of
388FeGeO₃ high-P clinopyroxene (C2/c) at temperatures up to 365°C. *Phys Chem Miner* 28:377–
389387.

390Hirose K, Kawamura K, Ohishi Y, et al (2005) Stability and equation of state of MgGeO₃ post-
391perovskite phase. *Am Mineral* 90:262–265.

392Holland TJB, Redfern SAT (1997) Unit cell refinement from powder diffraction data; the use of
393regression diagnostics. *Mineral Mag* 61:65–77.

394Hugh-Jones DA, Woodland AB, Angel RJ (1994) The structure of high-pressure C2/c ferrosilite
395and crystal chemistry of high-pressure C2/c pyroxenes. *Am Mineral* 79:1032–1041.

396Ito E, Matsui Y (1979) High-pressure transformations in silicates, germanates, and titanates with
397ABO₃ stoichiometry. *Phys Chem Miner* 4:265–273.

398Jacobsen SD, Lin J-F, Angel RJ, et al (2005) Single-crystal synchrotron X-ray diffraction study
399of wüstite and magnesiowüstite at lower-mantle pressures. *J Synchrotron Radiat* 12:577–583.

400Jephcoat AP, Besedin SP (1996) Temperature measurement and melting determination in the
401laser-heated diamond-anvil cell. *Philos Trans Math Phys Eng Sci* 354:1333–1360.

402Kuwayama Y, Hirose K, Sata N, Ohishi Y (2005) The pyrite-type high-pressure form of silica.
403*Science* 309:923–925.

404Lay T, Hernlund J, Garnero EJ, Thorne MS (2006) A post-perovskite lens and D'' heat flux
405beneath the central Pacific. *Science* 314:1272–1276.

406Leinenweber K, Utsumi W, Tsuchida Y, et al (1991) Unquenchable high-pressure perovskite
407polymorphs of MnSnO₃ and FeTiO₃. *Phys Chem Miner* 18:244–250.

408Leinenweber K, Wang Y, Yagi T, Yusa H (1994) An unquenchable perovskite phase of MgGeO₃
409and comparison with MgSiO₃ perovskite. *Am Mineral* 79:197–199.

410Lin J-F, Speziale S, Mao Z, Marquardt H (2013) Effects of the electronic spin transitions of iron
411in lower mantle minerals: Implications for deep mantle geophysics and geochemistry. *Rev*
412*Geophys* 51:244–275.

413Lindsley DH, Davis BTC, Macgregor ID (1964) Ferrosilite (FeSiO₃): Synthesis at high pressures
414and temperatures. *Science* 144:73–74.

415Liu L (1977) The post-spinel phases of twelve silicates and germanates. In: Manghnani MH,
416Akimoto S (eds) *High-pressure research; Applications in geophysics*. Academic Press, New York

417Mao W, Shu J, Hu J, et al (2002) Displacive transition in magnesiowüstite. *J Phys Condens*
418Matter 14:11349.

419Mao WL, Shen G, Prakapenka VB, et al (2004) Ferromagnesian postperovskite silicates in the D
420" layer of the Earth. *Proc Natl Acad Sci U S A* 101:15867–15869.

421Micoulaut M, Cormier L, Henderson GS (2006) The structure of amorphous, crystalline and
422liquid GeO₂. *J Phys Condens Matter* 18:R753.

423Ming L-C, Bassett WA (1975) High-pressure phase transformations in the system of MgSiO₃-
424FeSiO₃. *Earth Planet Sci Lett* 27:85–89.

425Ming LC, Kim Y-H, Uchida T, et al (2006) In situ X-ray diffraction study of phase transitions of
426FeTiO₃ at high pressures and temperatures using a large-volume press and synchrotron radiation.
427Am Mineral 91:120–126.

428Murakami M, Hirose K, Ono S, Ohishi Y (2003) Stability of CaCl₂-type and α-PbO₂-type SiO₂ at
429high pressure and temperature determined by in-situ X-ray measurements. *Geophys Res Lett*
43030:1207.

431Murakami M, Hirose K, Kawamura K, et al (2004) Post-perovskite phase transition in MgSiO₃.
432Science 304:855–858.

433Nagai T, Hattori T, Tsuchiya T, Yamanaka T (1998) First observation of FeGeO₃-perovskite
434under high pressure. *Solid State Commun* 107:223–225.

435Nakatsuka A, Kuribayashi S, Nakayama N, et al (2015) Temperature dependence of crystal
436structure of CaGeO₃ high-pressure perovskite phase and experimental determination of its Debye
437temperatures studied by low- and high-temperature single-crystal X-ray diffraction. *Am Mineral*
438100:1190–1202.

439Nakatsuka D, Yoshino T, Kano J, et al (2013) High-pressure synthesis, crystal structure and
440magnetic property of ilmenite-type FeGeO₃. *J Solid State Chem* 198:520–524.

441Nishio-Hamane D, Yagi T, Ohshiro M, et al (2010) Decomposition of perovskite FeTiO₃ into
442wüstite Fe_{1-x}Ti_{0.5x}O and orthorhombic FeTi₃O₇ at high pressure. *Phys Rev B* 82:092103.

443Oganov AR, Ono S (2004) Theoretical and experimental evidence for a post-perovskite phase of
444MgSiO₃ in Earth's D" layer. *Nature* 430:445–448.

445Ono S, Hirose K, Nishiyama N, Isshiki M (2002) Phase boundary between rutile-type and CaCl₂-
446type germanium dioxide determined by in situ X-ray observations. *Am Mineral* 87:99–102.

447Ono S, Tsuchiya T, Hirose K, Ohishi Y (2003a) Phase transition between the CaCl₂-type and α-
448PbO₂-type structures of germanium dioxide. *Phys Rev B* 68:134108.

449Ono S, Tsuchiya T, Hirose K, Ohishi Y (2003b) High-pressure form of pyrite-type germanium
450dioxide. *Phys Rev B* 68:014103.

451Pakhomova A, Ismailova L, Bykova E, et al (2017) A new high-pressure phase transition in
452clinoferrosilite: In situ single-crystal X-ray diffraction study. *Am Mineral* 102:666–673.

453Plonka AM, Dera P, Irmen P, et al (2012) β -diopside, a new ultrahigh-pressure polymorph of
454 $\text{CaMgSi}_2\text{O}_6$ with six-coordinated silicon. *Geophys Res Lett* 39:L24307.

455Prakapenka VB, Dubrovinsky LS, Shen G, et al (2003) α - PbO_2 -type high-pressure polymorph of
456 GeO_2 . *Phys Rev B* 67:132101.

457Prakapenka VB, Kubo A, Kuznetsov A, et al (2008) Advanced flat top laser heating system for
458high pressure research at GSECARS: application to the melting behavior of germanium. *High*
459*Press Res* 28:3 225–235.

460Prakapenka VB, Shen G, Dubrovinsky LS, et al (2004) High pressure induced phase
461transformation of SiO_2 and GeO_2 : difference and similarity. *J Phys Chem Solids* 65:8 1537–1545.

462Prescher C, Prakapenka VB (2015) DIOPTAS: a program for reduction of two-dimensional X-
463ray diffraction data and data exploration. *High Press Res* 35:3 223–230.

464Redhammer GJ, Senyshyn A, Tippelt G, et al (2012) Magnetic and low-temperature structural
465behavior of clinopyroxene-type FeGeO_3 : A neutron diffraction, magnetic susceptibility, and ^{57}Fe
466Mössbauer study. *Am Mineral* 97:694–706.

467Ringwood AE, Seabrook M (1963) High-pressure phase transformations in germanate pyroxenes
468and related compounds. *J Geophys Res* 68:4601–4609.

469Royen P, Forwerg W (1963) Darstellung und kristallographische Eigenschaften der
470Metagermanate des Mangans, Eisens und Kobalts. *Z Für Anorg Allg Chem* 326:113–126.

471Sato H, Endo S, Sugiyama M, et al (1991) Baddeleyite-type high-pressure phase of TiO_2 . *Science*
472251:786.

473Shiraki K, Tsuchiya T, Ono S (2003) Structural refinements of high-pressure phases in
474germanium dioxide. *Acta Crystallogr B* 59:701–708.

475Shu J, Mao H, Hu J, et al (1998) Single-crystal X-ray diffraction of wüstite to 30GPa hydrostatic
476pressure. *Neues Jahrb Für Mineral - Abh* 309–323.

477Shukla G, Topsakal M, Wentzcovitch RM (2015) Spin crossovers in iron-bearing MgSiO_3 and
478 MgGeO_3 : Their influence on the post-perovskite transition. *Phys Earth Planet Inter* 249:11–17.

479Stackhouse S, Brodholt JP, Price GD (2006) Elastic anisotropy of FeSiO_3 end-members of the
480perovskite and post-perovskite phases. *Geophys Res Lett* 33:L01304.

481Stan CV, Dutta R, Cava RJ, Prakapenka VB, Duffy TS (2017) High-pressure study of
482perovskites and post-perovskites in the $(\text{Mg,Fe})\text{GeO}_3$ System. *Inorg Chem* 56 (14) 8026-8035.

483Tateno S, Hirose K, Sata N, Ohishi Y (2007) Solubility of FeO in $(\text{Mg,Fe})\text{SiO}_3$ perovskite and
484the post-perovskite phase transition. *Phys Earth Planet Inter* 160:319–325.

485Tateno S, Hirose K, Sata N, Ohishi Y (2010) Structural distortion of CaSnO_3 perovskite under
486pressure and the quenchable post-perovskite phase as a low-pressure analogue to MgSiO_3 . *Phys*
487*Earth Planet Inter* 181:54–59.

488Tateno S, Hirose K, Sata N, Ohishi Y (2006) High-pressure behavior of MnGeO_3 and CdGeO_3
489perovskites and the post-perovskite phase transition. *Phys Chem Miner* 32:721.

490Toby BH (2001) EXPGUI, a graphical user interface for GSAS. *J Appl Crystallogr* 34:210–213.

491Tsuchiya T, Tsuchiya J (2011) Prediction of a hexagonal SiO_2 phase affecting stabilities of
492 MgSiO_3 and CaSiO_3 at multimegabar pressures. *Proc Natl Acad Sci* 108:1252–1255.

493Umemoto K, Wentzcovitch RM, Allen PB (2006) Dissociation of MgSiO_3 in the cores of gas
494giants and terrestrial exoplanets. *Science* 311:983–986.

495Weber H-P (1983) Ferrosilite III, the high-temperature polymorph of FeSiO_3 . *Acta Crystallogr C*
49639:1–3.

497Wicks JK, Jackson JM, Sturhahn W, et al (2015) Thermal equation of state and stability of
498 $(\text{Mg}_{0.06}\text{Fe}_{0.94})\text{O}$. *Phys Earth Planet Inter* 249:28–42.

499Wilson NC, Russo SP, Muscat J, Harrison NM (2005) High-pressure phases of FeTiO_3 from first
500principles. *Phys Rev B* 72:024110.

501Wu X, Qin S, Dubrovinsky L (2011) Investigation into high-pressure behavior of MnTiO_3 : X-ray
502diffraction and Raman spectroscopy with diamond anvil cells. *Geosci Front* 2:107–114.

503Yusa H, Tsuchiya T, Akaogi M, et al (2014) Postperovskite Phase Transition of ZnGeO_3 :
504comparative crystal chemistry of postperovskite phase transition from germanate perovskites.
505*Inorg Chem* 53:11732–11739.

506Zhang L, Meng Y, Dera P, et al (2013) Single-crystal structure determination of $(\text{Mg,Fe})\text{SiO}_3$
507postperovskite. *Proc Natl Acad Sci* 110(16): 6292–6295.

508Zhang L, Meng Y, Yang W, et al (2014) Disproportionation of $(\text{Mg,Fe})\text{SiO}_3$ perovskite in earth's
509deep lower mantle. *Science* 344:877–882.

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Figure 1. X-ray diffraction patterns of FeGeO₃ compressed at room temperature. Asterisks and solid circles indicate the main peaks of FeGeO₃ (II) and FeGeO₃ (III) respectively. (a) Diffraction data recorded up to 33 GPa. The bottom-most spectrum represents the *C2/c* clinopyroxene phase at 1 bar. The red ticks indicate the diffraction peak locations for the calculated clinopyroxene unit cell with lattice parameters $a = 9.7873$ (12) Å, $b = 9.1323$ (14) Å, $c = 5.1949$ (7) Å, $\beta = 101.804^\circ$ (11) (b) Diffraction data from 33 – 123 GPa. The red ticks indicate the observed diffraction peak positions for the perovskite unit cell reported by Hattori et al. 1999 at 40 GPa ($a = 4.93$ (2) Å, $b = 5.06$ (6) Å, $c = 6.66$ (3) Å). Diffraction peaks from gold (Au) and neon (Ne) are labeled.

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Figure 2. LeBail refinement of FeGeO₃ (II) (Space group: $P1'$) at 20 GPa ($R_p/R_{wp} = 0.0039/0.0069$).

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Figure 3a. Rietveld refinement of the diffraction pattern obtained on heating FeGeO_3 to 2120 K at 39.1 GPa. The corresponding oxide assemblage is rutile-type GeO_2 (blue sticks) and B1-type FeO (green sticks).

547 Figure 3b. Rietveld refinement of the diffraction pattern attained on quenching to room
548 temperature at 33.9 GPa. The inset shows a magnified view of the splitting of the tetragonal
549 (rutile) 211 peak into the orthorhombic (CaCl_2) 211 and 121 peaks. The blue sticks show the
550 predicted peak positions of CaCl_2 -type GeO_2 , while light and dark green represent rhombohedral

551(rB1) and cubic (B1) FeO.

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556 Figure 4. Rietveld refinement of the x-ray diffraction pattern at 58.3 GPa and 2000 K. The
 557 spectrum can be indexed by GeO_2 (α - PbO_2 -type), FeO (B1-type), Au, and Ne.

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565 Figure 5. Rietveld refinement of the diffraction pattern obtained on heating FeGeO_3 to 1700 K at
 566 127.3 GPa. The oxide assemblage consists of pyrite-type GeO_2 and B1-type FeO .

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574Figure 6. Goldschmidt diagram of $A^{2+}B^{4+}O_3$ compounds showing compositions for which the
575perovskite structure is predicted to be stable. (after Fujino et al. 2009). The dashed lines indicate
576tolerance factor values (t). The solid line ($t=0.90$) delineates the boundary above which pPv is
577generally not observed. Solid circles: compounds that adopt the post-perovskite structure; red
578crosses: compounds that have not been observed to transform to post-perovskite; open circles:
579compounds for which it is not known if post-perovskite forms.

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582 Figure S1. P-T phase diagram of FeGeO₃. The solid circles represent our room temperature data
 583 (red: cpx, blue: FeGeO₃ (II), green: FeGeO₃ (III)). The blue open circle is FeGeO₃ (II) reported by
 584 Hattori et al. (2001). The solid triangles denote the high-temperature data, the bars connect the
 585 lowest and highest temperatures reached in that run. The black plus symbols indicate literature
 586 data on different phases (Ringwood and Seabrook, 1963; Liu, 1977; Hattori et al. 2001;
 587 Nakatsuka et al. 2013). The dashed grey lines are the phase boundaries in GeO₂ (after Ono et al.

5862003). The dashed black lines are extrapolations of the data points and not an indication of the
587Clapeyron slopes.

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590Table I. Experimental conditions and observed phases.

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Sample ID	Pressure medium	P/T condition (GPa/K)	Phases present
S1	Neon	39.1 / 2120	Rutile GeO ₂ + FeO-B1
		33.9 / 300	CaCl ₂ GeO ₂ + FeO-B1 + FeO-rB1

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S2	Neon	58.3 / 2000 K	α -PbO ₂ GeO ₂ + FeO-B1
S3	N/A	127.3 / 1700	Pyrite GeO ₂ + FeO-B1

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Table 2. Comparison of the observed d -spacings of FeGeO₃ at 41 GPa with those of perovskite at 40 GPa as reported by Hattori et al. (1999).

This Study (41 GPa) d_{obs} (Å)	Perovskite, Hattori et al., 1999 (40 GPa)		
	d_{obs} (Å)	d_{calc} (Å)	(hkl)
	3.52	3.533	110
	3.333	3.333	002
2.668			
2.587			
2.504			
2.422	2.444	2.530	020
2.365	-	2.467	200
2.038	-	2.424	112
2.011			
	1.765	1.766	220
	1.665	1.667	004
1.407	1.416	1.440	132

Table 3. Calculated and observed d -spacings and their difference for rutile-type GeO₂ at 39.1 GPa and 2120 K (GeO₂: $a = 4.2462$ (17) Å, $c = 2.8122$ (23) Å, and FeO-B1 ($a = 4.1454$ (11) Å).

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611GeO₂ (rutile):

h	k	l	d_{obs} (Å)	d_{calc} (Å)	Δd (Å)
1	1	0	2.99873	3.00256	-0.00383
0	1	1	2.34516	2.34467	0.00049
0	2	0	2.12493	2.12313	0.0018
1	2	1	1.57346	1.57379	-0.00033

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614FeO (B1):

h	k	l	d_{obs} (Å)	d_{calc} (Å)	Δd (Å)
1	1	1	2.39398	2.39333	0.00065
0	0	2	2.07284	2.07268	0.00015
0	2	2	1.46541	1.46561	-0.0002

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618Table 4. Unit cell dimensions and atomic positions of GeO₂ and FeO obtained from Rietveld refinement. Numbers in parentheses
619denote the uncertainties in refinement. Z represents the number of formula units.

Pressure, Temperature	Phase	Space Group	Lattice Parameters (Å)	Site	Wyckoff Symbol	Fractional Coordinates	R _p /R _{wp} *
39.1 GPa, 2120 K	GeO ₂ (Rutile)	<i>P4₂/mnm</i> Z = 2	<i>a</i> = 4.2497 (2) <i>c</i> = 2.8192 (2)	Ge: O:	2(a) 4(f)	(0, 0, 0) (0.2874 (15), 0.2874 (15), 0)	0.0137/ 0.0202
	FeO (B1)	<i>Fm</i> $\bar{3}$ <i>m</i> Z = 4	<i>a</i> = 4.1431 (12)				
33.9 GPa, 300 K	GeO ₂ (CaCl ₂)	<i>Pnnm</i> Z = 2	<i>a</i> = 4.2831 (5) <i>b</i> = 4.1669 (4) <i>c</i> = 2.7991 (3)	Ge: O:	2(a) 4(g)	(0, 0, 0) (0.3089 (19), 0.2846 (17), 0)	0.0097/ 0.0137
	FeO (rB1)	<i>R</i> $\bar{3}m$ Z = 2	<i>a</i> = 2.8242 (49) <i>c</i> = 7.4044 (94)				
	FeO (B1)	<i>Fm</i> $\bar{3}$ <i>m</i> Z = 4	<i>a</i> = 4.1071 (5)				
58.3 GPa, 2000 K	GeO ₂ (α-PbO ₂)	<i>Pbcn</i> Z = 4	<i>a</i> = 4.1005 (10) <i>b</i> = 5.0997 (15) <i>c</i> = 4.5825 (8)	Ge: O:	4(c) 8(d)	(0, 0.1678 (7), 0.25) (0.2251 (28), 0.8744 (79), 0.4132 (46))	0.0077/ 0.0109
	FeO (B1)	<i>Fm</i> $\bar{3}$ <i>m</i> Z = 4	<i>a</i> = 4.0545 (6)				
127.3 GPa 1700 K	GeO ₂ (Pyrite)	<i>Pa</i> $\bar{3}$ Z = 4	<i>a</i> = 4.3226 (2)	Ge: O:	4(a) 8(c)	(0, 0, 0) (0.3347 (7), 0.3347 (7), 0.3347 (7))	0.0067/ 0.0095
	FeO (B1)	<i>Fm</i> $\bar{3}$	<i>a</i> = 3.7896 (17)				

		m $Z = 4$					

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621* $R_p = \sum w_i |y_i(obs) - y_i(calc)| / \sum y_i(obs)$; $R_\phi = \left\{ \sum w_i [y_i(obs) - y_i(calc)]^2 / \sum w_i [y_i(obs)]^2 \right\}^{1/2}$; where w is the weight, $y_i(obs)$

622and $y_i(calc)$ are the observed and calculated intensities after background subtraction.