Title

Stability of the perovskite structure and possibility of the transition to the post-perovskite structure in CaSiO₃, FeSiO₃, MnSiO₃ and CoSiO₃

Author(s)

Fujino, Kiyoshi; Nishio-Hamane, Daisuke; Suzuki, Keisuke; Izumi, Hiroyuki; Seto, Yusuke; Nagai, Takaya

Citation

Physics of the Earth and Planetary Interiors, 177(3-4): 147-151

Issue Date

2009-12

Doc URL

http://hdl.handle.net/2115/42494

Type

article (author version)

File Information

PEPI177-3-4_147-151.pdf
Stability of the perovskite structure and possibility of the transition to the post-perovskite structure in CaSiO$_3$, FeSiO$_3$, MnSiO$_3$ and CoSiO$_3$

Kiyoshi Fujino$^{a,b,*}$, Daisuke Nishio-Hamane$^{a,c}$, Keisuke Suzuki$^a$, Hiroyuki Izumi$^a$, Yusuke Seto$^{a,d}$, Takaya Nagai$^a$

$^a$Department of Natural History Sciences, Hokkaido University, Sapporo 060-0810, Japan
$^b$Geodynamics Research Center, Ehime University, Matsuyama 790-8577, Japan
$^c$Institute for Solid State Physics, The University of Tokyo, Kashiwa 277-8581, Japan
$^d$Department of Earth and Planetary Sciences, Kobe University, Kobe 657-8501, Japan

Abstract

High pressure and high temperature experiments on CaSiO$_3$, FeSiO$_3$, MnSiO$_3$ and CoSiO$_3$ using a laser-heated diamond anvil cell combined with synchrotron X-ray diffraction were conducted to explore the perovskite structure of these compounds and the transition to the post-perovskite structure. The experimental results revealed that MnSiO$_3$ has a perovskite structure from relatively low pressure (ca. 20 GPa) similarly to CaSiO$_3$, while the stable forms of FeSiO$_3$ and CoSiO$_3$ are mixtures of mono-oxide (NaCl structure) + high pressure polymorph of SiO$_2$ even at very high pressure and temperature (149 GPa and 1800 K for FeSiO$_3$ and 79 GPa and 2000 K for CoSiO$_3$). This strongly suggests that the crystal field stabilization energy (CFSE) of Fe$^{2+}$ with six 3d electrons and Co$^{2+}$ with seven 3d electrons at the octahedral site of mono-oxides favors a mixture of mono-oxide + SiO$_2$ over perovskite where Fe$^{2+}$ and Co$^{2+}$ would occupy the distorted dodecahedral sites having a smaller CFSE (Mn$^{2+}$ has five 3d electrons and has no CFSE). The structural characteristics that the orthorhombic distortion of MnSiO$_3$ perovskite decreases with pressure and the tolerance factor of CaSiO$_3$ perovskite (0.99) is far from the orthorhombic range suggest that both MnSiO$_3$ and CaSiO$_3$ perovskites will not transform to the CaIrO$_3$-type
post-perovskite structure even at the Earth’s core-mantle boundary conditions, although CaSiO₃ perovskite has a potentiality to transform to the CaIrO₃-type post-perovskite structure at still higher pressure as long as another type of transformation does not occur.

Keywords: silicate perovskite; CaSiO₃; MnSiO₃; FeSiO₃; CoSiO₃; crystal field stabilization energy; tolerance factor; CaIrO₃-type post-perovskite

1. Introduction

In the series of silicate compounds, MgSiO₃, CoSiO₃, FeSiO₃, MnSiO₃ and CaSiO₃, it had been known that only MgSiO₃ and CaSiO₃ have a perovskite structure at high pressure and high temperature, and very recently, MnSiO₃ was also found to have a perovskite structure (Fujino et al., 2008). However, there has been no report that CoSiO₃ and FeSiO₃ compounds have a perovskite structure at high pressure, although the tolerance factors of these compounds (0.904 for CoSiO₃ and 0.912 for FeSiO₃) are between those of MgSiO₃ (0.900) and CaSiO₃ (0.990), where the tolerance factor $t = \frac{(r_A + r_O)}{\sqrt{2 (r_B + r_O)}}$ and $r_A$, $r_B$ and $r_O$ are the ionic radii of eightfold A cation, sixfold B cation and oxygen, respectively, in ABO₃ compounds (Goldschmidt, 1926) (here the ionic radii were taken from Shannon, 1976).

The stable form of FeSiO₃ at ambient pressure, Fe₂SiO₄ (olivine) + SiO₂ (quartz), transforms to FeSiO₃ (orthopyroxene) and to FeSiO₃ (clinopyroxene) with increasing pressure (Akimoto et al., 1965). FeSiO₃ (clinopyroxene) decomposes into Fe₂SiO₄ (γ-spinel) + SiO₂ (stishovite) at 9 GPa and 1200 K (Akimoto, 1970), and it further transforms to FeO with a rock salt structure (B1 structure) + SiO₂ (stishovite) at 20 GPa and 1800 K (Ming and Bassett, 1975). However, the further phase transformation of FeSiO₃ at still higher pressure has not been reported except for the rhombohedral distortion of FeO and the polymorphic phase transition of SiO₂.

CoSiO₃ does not exist as a stable single compound at ambient pressure. The stable assemblage of Co₂SiO₄ (olivine) + SiO₂ (quartz) at ambient pressure transforms to CoSiO₃ (orthopyroxene) and to CoSiO₃ (clinopyroxene) with increasing pressure (Akimoto et al., 1965). It decomposes into Co₂SiO₄ (γ-spinel) + SiO₂ (stishovite) at 10 GPa and 1273 K (Ringwood, 1970), and further
decomposes into CoO (B1) + SiO2 (stishovite) at 17 GPa and 2000 K (Ito, 1975). So far, the phase transformation at still higher pressure has not been reported.

Meanwhile, MnSiO3 has many high pressure polymorphs at pressures up to around 20 GPa, starting from rhodonite to pyroxmangite, to clinopyroxene, and to tetragonal garnet (Akimoto and Syono, 1972; Fujino et al., 1986). Regarding the stable form of MnSiO3 at higher pressures, Liu (1976) reported that MnSiO3 garnet decomposes into MnO (B1) + SiO2 (stishovite) at 26 GPa and from 1673 to 2073 K, and Ito and Matsui (1977) also reported the stable assemblage of the same oxide mixture at 22 GPa and 1273 K. However, our recent study showed that MnSiO3 has also a perovskite structure similar to MgSiO3 and CaSiO3, at the lower temperature side of MnO (B1) + SiO2 (stishovite) (Fujino et al., 2008).

If FeSiO3 and CoSiO3 do not have a perovskite structure even at higher pressure, then, the other factor than the tolerance factor would control the stability of the perovskite structure of FeSiO3 and CoSiO3. One of the possible candidates will be the crystal field stabilization energy (CFSE) of Fe2+ and Co2+ with unfilled 3d electrons (six 3d electrons for Fe2+ and seven 3d electrons for Co2+), because Mn2+ has five 3d electrons and has no CFSE. CFSE of the octahedral site of mono-oxides is large compared to that of the dodecahedral site of perovskites (Burns, 1993), and would favor a mixture of mono-oxide + SiO2 over a perovskite structure.

Another interesting point in the above series of silicate compounds is that MgSiO3 perovskite further transforms to the CaIrO3-type post-perovskite structure at around 125 GPa and 2500 K (Murakami et al., 2004; Oganov and Ono, 2004), while there has been no report of the phase transition of the other silicate perovskites to the CaIrO3-type post-perovskite structure at very high pressure. Then, what factors control the phase transition of the perovskite structure to the CaIrO3-type post-perovskite structure? Are there any other silicate perovskites that transform to the CaIrO3-type post-perovskite structure?

To clarify the above problems, we have examined the high pressure phase relations of CaSiO3, FeSiO3, MnSiO3 and CoSiO3 using a laser-heated diamond anvil cell combined with synchrotron
X-ray diffraction. Here, the focus is laid on what factors control the stability of perovskite structure and the phase transition to the CaIrO$_3$-type post-perovskite structure in CaSiO$_3$, MnSiO$_3$, FeSiO$_3$ and CoSiO$_3$.

2. Experimental

2.1. Laser-heated diamond anvil cell experiments

The high pressure and high temperature experiments to synthesize the high pressure forms of respective compounds were carried out using an YLF or YAG laser-heated diamond anvil cell (LHDAC). The synthesis conditions were 30 - 149 GPa and 1600 - 2100 K for CaSiO$_3$-FeSiO$_3$, 15 - 85 GPa and 1200 - 2600 K for MnSiO$_3$ and 50, 79 GPa and 2000 K for Co$_2$SiO$_4$. The starting materials for the LHDAC experiments were gel (+ crystal) for CaSiO$_3$-FeSiO$_3$, synthetic MnSiO$_3$ rhodonite for MnSiO$_3$, and synthetic Co$_2$SiO$_4$ olivine for CoSiO$_3$. The reason why Co$_2$SiO$_4$ olivine was used as a starting material for CoSiO$_3$ is because the CoSiO$_3$ compound is not stable as a single phase at ambient pressure. A small amount of Au or Pt was added to some samples to determine pressure in high pressure and high temperature X-ray diffraction experiments by the equation of state (Anderson et al., 1989 for Au and Holmes et al., 1989 for Pt). Diamond anvils with a 300 or 200 μm culet were used for pressures less than 100 GPa, while beveled diamonds with an inner culet of 150 μm and an outer culet of 450 μm were used for pressures higher than 100 GPa. The samples were loaded into the hole of 50 - 100 μm diameter in a Re gasket (the original thickness was 0.25 mm) and sandwiched by NaCl pellets in a DAC. Samples in a DAC were heated from both sides with an YLF or YAG laser. Temperature was measured by the spectroradiometric method (Watanuki et al., 2001). Pressure at room temperature was measured by the ruby fluorescence technique (Mao et al., 1986), by the Raman spectral shift of diamond (Akahama and Kawamura, 2005) or by the equation of state of NaCl (Sata et al., 2002). Further details for MnSiO$_3$ are described in Fujino et al. (2008), and those for CaSiO$_3$-FeSiO$_3$ will be described elsewhere (Fujino et al., in preparation).
2.2. Synchrotron X-ray diffraction experiments

Angle-dispersive X-ray diffraction experiments of CaSiO$_3$-FeSiO$_3$, MnSiO$_3$ and Co$_2$SiO$_4$ at room temperature were performed at BL-13A (wave length of 0.42 - 0.43 Å) and BL-18C (wave length of ~ 0.61 Å) of Photon Factory, KEK, and those at high pressure and high temperature were carried out at BL-10XU (wave length of 0.41 - 0.42 Å) of SPring-8 of the Japan Synchrotron Radiation Research Institute. Monochromatic X-ray incident beams were collimated to 15 - 20 μm (BL-13A and BL-18C), and to 20 - 30 μm (BL-10XU). Diffraction patterns were recorded on an imaging plate (3000 x 3000 pixels for BL-13A and BL-10XU and 2000 x 2500 pixels for BL-18C with a pixel size of 100 μm x 100 μm) at all the beam lines. The exposure times were 10 - 60 min at BL-13A, 30 - 120 min at BL-18C and ~ 5 min at BL-10XU. Two-dimensional X-ray diffraction images on the imaging plates were integrated as a function of $2\theta$ in order to obtain the conventional one-dimensional diffraction profiles and analyzed using the software PIP (Fujisawa and Aoki, 1998) or IPA and PDI (Y. Seto, available from http://www2.kobe-u.ac.jp/~seto/). The typical diffraction patterns obtained for the compounds FeSiO$_3$, CaFeSi$_2$O$_6$, MnSiO$_3$ and Co$_2$SiO$_4$ at high pressure and high temperature or high pressure and room temperature quenched from high temperature are presented in Fig. 1.

3. High pressure phase relations

$CaSiO_3$ and $FeSiO_3$

In the system $CaSiO_3$-$FeSiO_3$ at 30 - 149 GPa and 1600 - 2100 K (Fujino et al., in the preparation), the stable assemblage of the end member $FeSiO_3$ was a mixture of $FeO$ (B1 structure) + high pressure polymorph of $SiO_2$ (stishovite, CaCl$_2$-type or $\alpha$-PbO$_2$-type with increasing pressure) up to 117 GPa and 2100 K (Fig. 1(a)). Further, the stable assemblage of the intermediate composition $CaFeSi_2O_6$ was a mixture of Fe-bearing $CaSiO_3$ perovskite + $FeO$ (B1 structure) + high-pressure polymorph of $SiO_2$ (stishovite, CaCl$_2$-type or $\alpha$-PbO$_2$-type with increasing pressure) up to 149 GPa and 1800 K (Fig. 1(b)). These results indicate that $CaSiO_3$ has a perovskite structure up to 149 GPa and it does not transform to the post-perovskite structure
even at this pressure, while the high pressure form of FeSiO$_3$ is a mixture of FeO (B1) + high pressure polymorph of SiO$_2$ and FeSiO$_3$ perovskite does not become stable up to 149 GPa. All the Fe-bearing CaSiO$_3$ perovskite phases showed cubic symmetry (space group Pm3m) at high pressure and high temperature, but showed tetragonal symmetry (exact space group could not be determined) at high pressure and room temperature. The c/a ratio (<1) of the refined cell parameters of present Fe-bearing CaSiO$_3$ perovskite at high pressure and room temperature decreases with pressure (Fujino et al., in the preparation) in the same way as pure CaSiO$_3$ perovskite (Ono et al., 2004). These results indicate that the tetragonal distortion of CaSiO$_3$ perovskite increases with pressure.

**MnSiO$_3$**

Our recent X-ray diffraction experiments at high pressure and high temperature up to 85 GPa and 2600 K (Fujino et al., 2008) revealed that at the higher temperature region MnSiO$_3$ garnet decomposes into an assemblage of MnO (B1) + SiO$_2$ (stishovite), while at the lower temperature region MnSiO$_3$ garnet directly transforms to the perovskite structure from relatively low pressure around 20 GPa as shown in Fig. 2. The triple point of the three stable regions of garnet, MnO + SiO$_2$ and perovskite is ca. 20 GPa and 1200 K. MnSiO$_3$ perovskite showed orthorhombic symmetry (space group Pbnm) both at high temperature and room temperature under high pressure (Fig. 1(c)). The refined cell parameters of MnSiO$_3$ perovskite demonstrate that the $a$ axis approaches the $b$ axis with pressure, while the $\sqrt{2a/c}$ ratio (= 1 for cubic) remains nearly constant (<1) (Fig. 4 in Fujino et al., 2008). This indicates that the orthorhombic distortion of MnSiO$_3$ perovskite decreases with pressure and MnSiO$_3$ perovskite approaches tetragonal perovskite.

**CoSiO$_3$**

The X-ray diffraction patterns of Co$_2$SiO$_4$ were all taken at room temperature quenched from high temperature. The diffraction pattern of Co$_2$SiO$_4$ at 50 GPa and room temperature quenched
from 2000 K showed the mixed peaks of CoO (B1) + SiO₂ (stishovite) (Fig. 1(d)). Its diffraction pattern at 79 GPa and room temperature quenched from 2000 K turned to be the mixed peaks of CoO (this seems to be rhombohedrally distorted from B1 as Guo et al., 2002, reports) + SiO₂ (CaCl₂-type). The variation of the diffraction peaks of CoO with increasing pressure at room temperature suggests that CoO has a B1 structure at high pressure and high temperature like FeO and MnO (Kondo et al., 2000, 2004). These results indicate that the stable form of CoSiO₃ is CoO (B1) + high pressure polymorph of SiO₂, not perovskite at high pressure and high temperature up to 79 GPa and 2000 K.

4. Stability of the perovskite structure and possibility of the phase transition to post-perovskite

4.1. Stability of the perovskite structure in FeSiO₃, MnSiO₃ and CoSiO₃

High pressure phase studies of FeSiO₃, MnSiO₃ and CoSiO₃ demonstrated that MnSiO₃ has a perovskite structure from relatively low pressure as 20 GPa, while FeSiO₃ and CoSiO₃ do not have a perovskite structure even at very high pressure. Table 1 summarizes the transformation pressures of the selected silicate compounds to the perovskite structure at 1200 K. Here, the polymorphic phase transition pressures to the perovskite structure were selected for MgSiO₃ and MnSiO₃, while the transformation pressure of Ca₂SiO₄ (larnite) + CaSi₂O₅ (titanite structure) to the perovskite structure was selected for CaSiO₃, since there is no polymorphic transition to the perovskite structure for CaSiO₃. Although the types of transformation are different among MgSiO₃, MnSiO₃ and CaSiO₃, their transformation pressures are relatively low, 13 – 25 GPa at 1200 K. On the other hand, FeSiO₃ and CoSiO₃ do not have a perovskite structure even at very high pressure beyond ~ 80 GPa. This fact is well explained by the CFSE of the transition metals with unfilled 3d electrons (≠ five) at the octahedral site of mono-oxides with a B1 structure. Fig. 3 illustrates the assumed CFSEs of Fe²⁺ and Co²⁺ at the octahedral site of mono-oxides with a B1 structure and the dodecahedral site of silicate perovskites. Compared to the CFSEs at the octahedral site of
mono-oxides, those at the distorted dodecahedral site of silicate perovskites are smaller (Burns, 1993) and further separated. Therefore, the CFSEs of both Fe$^{2+}$ and Co$^{2+}$ favor a mixture of mono-oxide + SiO$_2$ over a perovskite structure, while the mixture of MnO + SiO$_2$ is not favored because no CFSE is expected for Mn$^{2+}$ with five 3d electrons.

The above argument was discussed under the assumption that the spin states of the transition metals are high spin. When the spin states of the transition metals at the octahedral site of mono-oxides become low spin at very high pressure, the mixtures of mono-oxide + SiO$_2$ will be further stabilized by the large volume reductions induced by the high spin - low spin transitions of Fe$^{2+}$ and Co$^{2+}$ at the octahedral site of mono-oxides. Even for MnSiO$_3$ the mixture of MnO + SiO$_2$ may be favored compared to perovskite because Mn$^{2+}$ with five 3d electrons at the octahedral site also has a large volume reduction by the high spin - low spin transition.

4.2. Possibility of the transition to the CaIrO$_3$-type post-perovskite structure in CaSiO$_3$ and MnSiO$_3$

Among the silicate perovskites of MgSiO$_3$, CaSiO$_3$ and MnSiO$_3$, only MgSiO$_3$ perovskite further transforms to the CaIrO$_3$-type post-perovskite structure. How about the possibility of the post-perovskite phase of CaSiO$_3$ and MnSiO$_3$? Fig.4 shows the Goldschmidt diagram of A$^{2+}$B$^{4+}$O$_3$ compounds. All the compounds in this diagram have a perovskite structure at high pressure. Among these compounds, so far, only 4 compounds (solid circles), MgSiO$_3$, MgGeO$_3$, MnGeO$_3$ and CaIrO$_3$, transform to the CaIrO$_3$-type post-perovskite structure (Murakami et al., 2004; Oganov and Ono, 2004; Hirose and Fujita, 2005; Hirose et al., 2005; Tateno et al., 2006). In this diagram, the compounds marked by solid symbols mean that their distortions increase with pressure, while the compounds marked by open symbols mean that their distortions decrease with pressure (Tateno et al., 2006). With the above 4 compounds which transform to the CaIrO$_3$-type post-perovskite structure, 1) their tolerance factors are between 0.8 and 0.9, and 2) all their orthorhombic distortions increase with pressure. Therefore, these two criteria seem to be the
necessary conditions to transform to the CaIrO$_3$-type post-perovskite structure. However, although CaTiO$_3$, CdTiO$_3$, MnTiO$_3$ and CaSnO$_3$ marked by solid triangle satisfy these two criteria, Tateno et al. (2006) report that these compounds transform to the other structures than CaIrO$_3$-type post-perovskite. So, still the other factors may be necessary to constrain the compounds which transform to the CaIrO$_3$-type post-perovskite structure. In any case, from these criteria, we can expect that MnSiO$_3$ will not transform to the CaIrO$_3$-type post-perovskite structure even at higher pressure because its orthorhombic distortion decreases with pressure. In the case of CaSiO$_3$, we also think that this will not transform to the CaIrO$_3$-type post-perovskite structure even at the core-mantle boundary conditions because its tolerance factor (0.99) is much larger than 0.8-0.9. However, considering that its tetragonal distortion increases with pressure, CaSiO$_3$ may have a potentiality to transform to the CaIrO$_3$-type post-perovskite structure at still higher pressure, if another type of transformation does not occur.

5. Summary

In addition to MgSiO$_3$ and CaSiO$_3$, MnSiO$_3$ also has a perovskite structure from relatively low pressure, while FeSiO$_3$ and CoSiO$_3$ do not have a perovskite structure and instead, mixtures of mono-oxide + SiO$_2$ are stable up to very high pressure. This strongly suggests that the CFSEs of Fe$^{2+}$ (six 3d electrons) and Co$^{2+}$ (seven 3d electrons) at the octahedral site of mono-oxides favor mono-oxide + SiO$_2$ over perovskite. Mn$^{2+}$ has five 3d electrons and has no CFSE in the high spin state. When high spin-low spin transition occurs in these transition metals at the octahedral site of mono-oxides at high pressure, FeSiO$_3$ and CoSiO$_3$ will further, and even MnSiO$_3$ may, favor mono-oxide + SiO$_2$ by the large volume reduction induced by the high spin – low spin transition.

The orthorhombic distortion of MnSiO$_3$ perovskite decreases with pressure, while the tetragonal distortion of CaSiO$_3$ perovskite increases with pressure. However, the tolerance factor of CaSiO$_3$ (0.99) is far from 0.8-0.9 where, so far, the transition to CaIrO$_3$-type post-perovskite occurs. These characters of both MnSiO$_3$ and CaSiO$_3$ perovskites at high pressure suggest that
both of them will not transform to the CaIrO$_3$-type post-perovskite structure at the core-mantle boundary conditions, although CaSiO$_3$ perovskite has a potentiality to transform to the CaIrO$_3$-type post-perovskite structure at still higher pressure, if another type of transformation does not occur.

Acknowledgements

The X-ray diffraction experiments were carried out at SPring-8 (proposal no. 2004B0127, 2005B0283, 2006A1459 and 2006B1373) and at KEK (proposal no. 2003G206 and 2005G143). We thank Y. Ohishi and N. Sata at Spring-8, and T. Kikegawa at KEK for their help in the X-ray diffraction experiments. This work was supported in part by a 21st Century COE Program on "Neo-Science of Natural History" (Program Leader: Hisatake Okada) financed by the Ministry of Education, Culture, Sports, Science and Technology, Japan, and also by the Grant-in-Aid (no. 18340167 and 18204040) by Japan Society for the Promotion of Science (JSPS).

References


Kato, T. and Kumazawa, M., 1985. Garnet phase of MgSiO₃ filling the pyroxene-ilmenite gap at


Shannon, R.D., 1976. Revised effective ionic radii and systematic studies of interatomic distances


Table captions
Table 1. Transformation pressures of various silicate compounds to the perovskite phase at 1200 K.

Figure Captions
Fig. 1. X-ray diffraction patterns of the samples.
(a) FeSiO$_3$ at 117 GPa, 2100 K ($\lambda = 0.4170$ Å). Pressure was derived from the equation of state of Pt (Holmes et al., 1989). The phase assemblage of the sample is FeO (B1) + SiO$_2$ (CaCl$_2$-type). Lattice parameters determined from a few peaks are $a = 3.846$ Å for FeO (B1), and $a = 3.960$, $b = 3.811$, $c = 2.489$ Å for SiO$_2$ (CaCl$_2$-type). (b) CaFeSi$_2$O$_6$ at 149 GPa, 1800 K ($\lambda = 0.4170$ Å). Pressure was derived from the equation of state of Pt (Holmes et al., 1989). The phase assemblage of the sample is CaSiO$_3$ perovskite + FeO (B1) + SiO$_2$ (CaCl$_2$-type). Lattice parameters determined from a very few peaks are $a = 3.248$ Å for CaSiO$_3$ perovskite, $a = 3.782$ Å for FeO (B1), and $a = 3.889$, $b = 3.745$, $c = 2.463$ Å for SiO$_2$ (CaCl$_2$-type).
Coexistence of CaCl$_2$-type SiO$_2$ and $\alpha$-PbO$_2$-type SiO$_2$ around this pressure is often reported (Murakami et al., 2003). (c) MnSiO$_3$ at 40 GPa, 1700 K ($\lambda = 0.4177$ Å). Pressure was derived from the equation of state of Au (Anderson et al., 1989). The existing phase of the sample is MnSiO$_3$ perovskite. The refined lattice parameters of MnSiO$_3$ perovskite are $a = 4.7559(4)$, $b = 4.8073(4)$, $c = 6.7723(6)$ Å. (d) Co$_2$SiO$_4$ at 50 GPa, 300 K quenched from 2000 K ($\lambda = 0.4151$ Å). Pressure was derived from the equation of state of NaCl (B2) (Sata et al., 2002). The quenched phase assemblage of the sample is CoO (B1) + SiO$_2$ (stishovite). The refined lattice parameters are $a = 4.002(1)$ Å for CoO (B1) and $a = 3.983(1)$, $c = 2.584(1)$ Å for stishovite. SC = SiO$_2$ (CaCl$_2$-type), SP = SiO$_2$ ($\alpha$-PbO$_2$-type), FeO = FeO with a B1 structure, Ca-Pv = Ca-perovskite, MnPv = MnSiO$_3$ perovskite, CoO = CoO with a B1 structure, St = stishovite, B2 = NaCl with a B2 structure, Pt = platinum, Au = gold, Re = rhenium, Cor = corundum, ? = unknown or uncertain peak.

Fig. 2. Phase diagram of MnSiO$_3$ estimated from the product phases at high pressure and high
temperature.

Fig. 3. Schematic energy levels of 3d electrons for Fe$^{2+}$ and Co$^{2+}$ at the octahedral site of mono-oxides and at the distorted dodecahedral site of assumed perovskites. Note that the crystal field splitting at the octahedral site is larger than that at the distorted dodecahedral site (Burns, 1993). Also, the energy levels of the 3d electrons of Fe$^{2+}$ and Co$^{2+}$ at the distorted dodecahedral site of perovskites are further separated.

Fig. 4. Goldschmidt diagram of A$^{2+}$B$^{4+}$O$_3$ compounds which have a perovskite structure. This diagram was modified from Fig. 5 in Tateno et al. (2006) and the present results were added to the diagram. The horizontal axis is the ionic radius of the 6-coordinated B cation and the vertical axis is the ionic radius of the 8-coordinated A cation. The ionic radii are from Shannon (1976). The oblique lines indicate the tolerance factors (Goldschmidt, 1926). Solid circles: compounds which transform from orthorhombic perovskite to CaIrO$_3$-type post-perovskite with increasing pressure. Solid triangles: compounds which transform from perovskite to the other structure than CaIrO$_3$-type post-perovskite (Tateno et al., 2006). Compounds marked by solid symbols mean that their distortions increase with pressure, while compounds marked by open symbols mean that their distortions decrease with pressure. * (annotation: this should be replaced by the same symbol as that in the figure) = composition that does not procure perovskite in the ranges of pressure and temperature investigated.
Table 1
Transformation pressures of various silicate compounds to the perovskite phase at 1200 K

<table>
<thead>
<tr>
<th>Type of transformation</th>
<th>Transformation pressure (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgSiO$_3$ ilmenite to perovskite</td>
<td>25$^a$</td>
</tr>
<tr>
<td>MnSiO$_3$ garnet to perovskite</td>
<td>20</td>
</tr>
<tr>
<td>CaSiO$_3$ Ca$_2$SiO$_4$(larnite) + CaSi$_2$O$_5$ (titanite) to perovskite</td>
<td>13.5$^b$</td>
</tr>
<tr>
<td>FeSiO$_3$ ?</td>
<td>&gt; 149?</td>
</tr>
<tr>
<td>CoSiO$_3$ ?</td>
<td>&gt; 79?</td>
</tr>
</tbody>
</table>

$^a$Kato and Kumazawa, 1985
$^b$Akaogi et al., 2004
Fig. 2
Fig. 3
Fig. 4