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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

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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

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post-perovskite structure even at the Earth's 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 as long as another type of transformation does not occur.

Keywords: silicate perovskite; CaSiO_3 ; MnSiO_3 ; FeSiO_3 ; CoSiO_3 ; crystal field stabilization energy; tolerance factor; CaIrO_3 -type post-perovskite

1. Introduction

In the series of silicate compounds, MgSiO_3 , CoSiO_3 , FeSiO_3 , MnSiO_3 and CaSiO_3 , it had been known that only MgSiO_3 and CaSiO_3 have a perovskite structure at high pressure and high temperature, and very recently, MnSiO_3 was also found to have a perovskite structure (Fujino et al., 2008). However, there has been no report that CoSiO_3 and FeSiO_3 compounds have a perovskite structure at high pressure, although the tolerance factors of these compounds (0.904 for CoSiO_3 and 0.912 for FeSiO_3) are between those of MgSiO_3 (0.900) and CaSiO_3 (0.990), where the tolerance factor $t = (r_A + r_O) / [\sqrt{2} (r_B + r_O)]$ and r_A , r_B and r_O are the ionic radii of eightfold A cation, sixfold B cation and oxygen, respectively, in ABO_3 compounds (Goldschmidt, 1926) (here the ionic radii were taken from Shannon, 1976).

The stable form of FeSiO_3 at ambient pressure, Fe_2SiO_4 (olivine) + SiO_2 (quartz), transforms to FeSiO_3 (orthopyroxene) and to FeSiO_3 (clinopyroxene) with increasing pressure (Akimoto et al., 1965). FeSiO_3 (clinopyroxene) decomposes into Fe_2SiO_4 (γ -spinel) + SiO_2 (stishovite) at 9 GPa and 1200 K (Akimoto, 1970), and it further transforms to FeO with a rock salt structure (B1 structure) + SiO_2 (stishovite) at 20 GPa and 1800 K (Ming and Bassett, 1975). However, the further phase transformation of FeSiO_3 at still higher pressure has not been reported except for the rhombohedral distortion of FeO and the polymorphic phase transition of SiO_2 .

CoSiO_3 does not exist as a stable single compound at ambient pressure. The stable assemblage of Co_2SiO_4 (olivine) + SiO_2 (quartz) at ambient pressure transforms to CoSiO_3 (orthopyroxene) and to CoSiO_3 (clinopyroxene) with increasing pressure (Akimoto et al., 1965). It decomposes into Co_2SiO_4 (γ -spinel) + SiO_2 (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_2SiO_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_2SiO_4 olivine for CoSiO_3 . The reason why Co_2SiO_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_2SiO_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 2θ 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 , $\text{CaFeSi}_2\text{O}_6$, MnSiO_3 and Co_2SiO_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

CaSiO₃ and FeSiO₃

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 α - PbO_2 -type with increasing pressure) up to 117 GPa and 2100 K (Fig. 1(a)). Further, the stable assemblage of the intermediate composition $\text{CaFeSi}_2\text{O}_6$ was a mixture of Fe-bearing CaSiO_3 perovskite + FeO (B1 structure) + high-pressure polymorph of SiO_2 (stishovite, CaCl_2 -type or α - 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 FeSiO₃ is a mixture of FeO (B1) + high pressure polymorph of SiO₂ and FeSiO₃ perovskite does not become stable up to 149 GPa. All the Fe-bearing CaSiO₃ 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 CaSiO₃ perovskite at high pressure and room temperature decreases with pressure (Fujino et al., in the preparation) in the same way as pure CaSiO₃ perovskite (Ono et al., 2004). These results indicate that the tetragonal distortion of CaSiO₃ perovskite increases with pressure.

MnSiO₃

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 MnSiO₃ garnet decomposes into an assemblage of MnO (B1) + SiO₂ (stishovite), while at the lower temperature region MnSiO₃ 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 + SiO₂ and perovskite is ca. 20 GPa and 1200 K. MnSiO₃ 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 MnSiO₃ perovskite demonstrate that the a axis approaches the b axis with pressure, while the $\sqrt{2}a/c$ ratio (= 1 for cubic) remains nearly constant (<1) (Fig. 4 in Fujino et al., 2008). This indicates that the orthorhombic distortion of MnSiO₃ perovskite decreases with pressure and MnSiO₃ perovskite approaches tetragonal perovskite.

CoSiO₃

The X-ray diffraction patterns of Co₂SiO₄ were all taken at room temperature quenched from high temperature. The diffraction pattern of Co₂SiO₄ 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 (\neq 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 $\text{MnO} + \text{SiO}_2$ 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 $\text{MnO} + \text{SiO}_2$ 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 $\text{A}^{2+}\text{B}^{4+}\text{O}_3$ 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.

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References

- Akahama, Y. and Kawamura, H., 2005. Raman study on the stress state of [111] diamond anvils at multimegabar pressure. *J. Appl. Phys.*, 98, Art. No. 083523.
- Akaogi, M., Yano, M., Tejima, Y., Iijima, M., and Kojitani, H., 2004. High-pressure transitions of diopside and wollastonite: phase equilibria and thermochemistry of $\text{CaMgSi}_2\text{O}_6$, CaSiO_3 and CaSi_2O_5 - CaTiSiO_5 system. *Phys. Earth Planet. Inter.*, 143-144, 145-156.
- Akimoto, S., Katsura, T., Syono, Y., Fujisawa, H., and Komada, E., 1965. Polymorphic transition of pyroxenes FeSiO_3 and CoSiO_3 at high pressures and temperatures. *J. Geophys. Res.*, 70, 5269-5278.
- Akimoto, S., 1970. High-pressure synthesis of a "modified" spinel and some geophysical implications. *Phys. Earth Planet. Inter.*, 3, 189-195.
- Akimoto, S. and Syono, Y., 1972. High pressure transformations in MnSiO_3 . *Am. Mineral.*, 57,

76-84.

- Anderson, O.L., Isaak, D.G., and Yamamoto, S., 1989. Anharmonicity and the equation of state for gold. *J. Appl. Phys.*, 65, 1534-1543.
- Burns, R.G., 1993. *Mineralogical Applications of Crystal Field Theory*. Cambridge University Press, Cambridge, p. 551.
- Fujino, K., Momoi, H., Sawamoto, H., and Kumazawa, M., 1986. Crystal structure and chemistry of MnSiO₃ tetragonal garnet. *Am. Mineral.*, 71, 781-785.
- Fujino, K., Suzuki, K., Hamane, D., Seto, Y, Nagai, T., and Sata, N., 2008. High pressure phase relation of MnSiO₃ up to 85 GPa: Existence of MnSiO₃ perovskite. *Am. Mineral.*, 93, 653-657.
- Fujisawa, H. and Aoki, K., 1998. High pressure X-ray powder diffraction experiments and intensity analyses. *Rev. High Pressure Sci. Technol.*, 8, 4-9.
- Goldschmidt, 1926. Die Gesetze der Krystallochemie. *Naturwissenschaften*, 14, 477-485.
- Guo, Q., Mao, H.K., Hu, J., Shu, J., and Hemley, R.J., 2002. The phase transitions of CoO under static pressure to 104 GPa. *J. Phys. Condens. Matter*, 14, 11369-11374.
- Hirose, K. and Fujita, Y., 2005. Clapeyron slope of the post-perovskite phase transition in CaIrO₃. *Geophys. Res.Lett.*, 32, L13313, doi:10.1029/2005GL023219.
- Hirose, K., Kawamura, K., Ohishi, Y., Tateno, S., and Sata, N., 2005. Stability and equation of state of MgGeO₃ post-perovskite phase. *Am. Mineral.* 90, 262-265.
- Holmes, N.C., Moriarty, J.A., Gathers, G.R., and Nellis, W.J., 1989. The equation of state of platinum to 660 GPa (6.6 Mbar). *J. Appl. Phys.*, 66, 2962-2967.
- Ito, E., 1975. High-pressure decompositions in cobalt and nickel silicates. *Phys. Earth Planet. Inter.*, 10, 88-93.
- Ito, E. and Matsui, Y., 1977. Silicate ilmenite and the post-spinel transformations. In: Manghnani M.H. and Akimoto, S. (Eds.), *High-Pressure Research: Applications in Geophysics*. Academic Press, New York, pp. 193-208.
- Kato, T. and Kumazawa, M., 1985. Garnet phase of MgSiO₃ filling the pyroxene-ilmenite gap at

- very high temperature. *Nature*, 316, 803-805.
- Kondo, T., Yagi, T., Syono, Y., Noguchi, Y., Atou, T., Kikegawa, T., and Shimomura, O., 2000. Phase transitions of MnO to 137 GPa. *Journal of Applied Physics*, 87, 4153-4159.
- Kondo, T., Ohtani, E., Hirao, N., Yagi, T., and Kikegawa, T., 2004. Phase transitions of (Mg,Fe)O at megabar pressures. *Phys. Earth Planet. Inter.*, 143-144, 201-213.
- Liu, L., 1976. High-pressure phases of Co_2GeO_4 , Ni_2GeO_4 , Mn_2GeO_4 and MnGeO_3 : implications for the germanate-silicate modeling scheme and the Earth's mantle. *Earth Planet. Sci. Lett.*, 31, 393-396.
- Mao, H.K., Xu, J., and Bell, P.M., 1986. Calibration of the ruby pressure gauge to 800 kbar under quasi-hydrostatic conditions. *J. Geophys. Res.*, 91, 4673-4676.
- Ming, L.C. and Bassett, W.A., 1975. Decomposition of FeSiO_3 into $\text{FeO} + \text{SiO}_2$ under very high pressure and high temperature. *Earth Planet. Sci. Lett.*, 25, 68-70.
- Murakami, M., Hirose, K., Ono, S., and Ohishi, Y., 2003. Stability of CaCl_2 -type and $\alpha\text{-PbO}_2$ -type SiO_2 at high pressure and temperature determined by in-situ X-ray measurements. *Geophys. Res. Lett.*, 30, 1207, doi:10.1029/2002GL016722.
- Murakami, M., Hirose, K., Kawamura, K., Sata, N., and Ohishi, Y., 2004. Post-perovskite phase transition in MgSiO_3 . *Science*, 304, 855-858.
- Oganov, A.R. and Ono, S., 2004. Theoretical and experimental evidence for a post-perovskite phase of MgSiO_3 in Earth's D'' layer. *Nature*, 430, 445-448.
- Ono, S., Ohishi, Y., and Mibe, K., 2004. Phase transition of Ca-perovskite and stability of Al-bearing Mg-perovskite in the lower mantle. *Am. Mineral.*, 89, 1480-1485.
- Ringwood, A.E., 1970. Phase transformations and the constitution of the mantle. *Phys. Earth Planet. Inter.*, 3, 109-166.
- Sata, N., Shen, G., Rivers, M.L., and Sutton, S.R., 2002. Pressure-volume equation of state of the high-pressure B2 phase of NaCl. *Physical Review B*, 65 (10), Art. No. 104114.
- Shannon, R.D., 1976. Revised effective ionic radii and systematic studies of interatomic distances

in halides and chalcogenides. *Acta Cryst.*, A32, 751-767.

Tateno, S., Hirose, K., Sata, N., and Ohishi, Y., 2006. High-pressure behavior of MnGeO_3 and CdGeO_3 perovskites and the post-perovskite phase transition. *Phys. Chem. Miner.*, 32, 721-725.

Watanuki, T., Shimomura, O., Yagi, T., Kondo, T., and Issiki, M., 2001. Construction of laser-heated diamond anvil cell system for in situ X-ray diffraction study at SPring-8. *Review of Scientific Instruments*, 72, 1289-1292.

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 ($\lambda = 0.4170 \text{ \AA}$). 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 $a = 3.846 \text{ \AA}$ for FeO (B1), and $a = 3.960$, $b = 3.811$, $c = 2.489 \text{ \AA}$ for SiO_2 (CaCl_2 -type). (b) $\text{CaFeSi}_2\text{O}_6$ at 149 GPa, 1800 K ($\lambda = 0.4170 \text{ \AA}$). 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 $a = 3.248 \text{ \AA}$ for CaSiO_3 perovskite, $a = 3.782 \text{ \AA}$ for FeO (B1), and $a = 3.889$, $b = 3.745$, $c = 2.463 \text{ \AA}$ for SiO_2 (CaCl_2 -type). Coexistence of CaCl_2 -type SiO_2 and α - PbO_2 -type SiO_2 around this pressure is often reported (Murakami et al., 2003). (c) MnSiO_3 at 40 GPa, 1700 K ($\lambda = 0.4177 \text{ \AA}$). 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 $a = 4.7559(4)$, $b = 4.8073(4)$, $c = 6.7723(6) \text{ \AA}$. (d) Co_2SiO_4 at 50 GPa, 300 K quenched from 2000 K ($\lambda = 0.4151 \text{ \AA}$). 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 $a = 4.002(1) \text{ \AA}$ for CoO (B1) and $a = 3.983(1)$, $c = 2.584(1) \text{ \AA}$ for stishovite. SC = SiO_2 (CaCl_2 -type), SP = SiO_2 (α - 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 $\text{A}^{2+}\text{B}^{4+}\text{O}_3$ 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

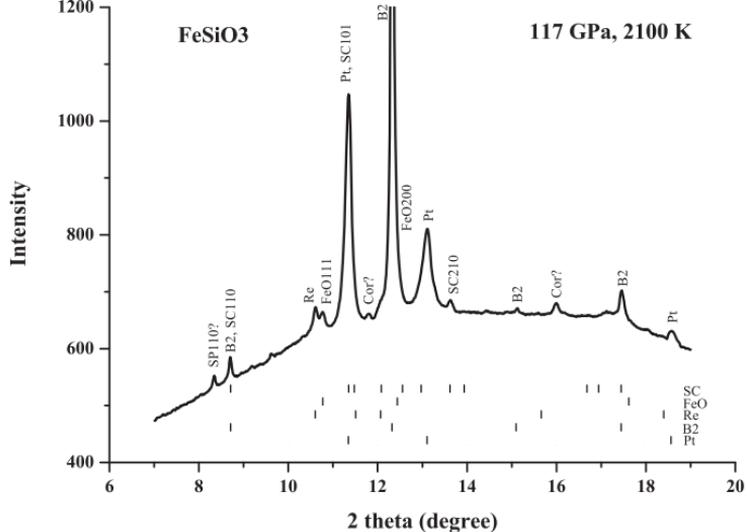
Transformation pressures of various silicate compounds to the perovskite phase at 1200 K

	Type of transformation	Transformation pressure (GPa)
MgSiO ₃	ilmenite to perovskite	25 ^a
MnSiO ₃	garnet to perovskite	20
CaSiO ₃	Ca ₂ SiO ₄ (larnite) + CaSi ₂ O ₅ (titanite) to perovskite	13.5 ^b
FeSiO ₃	?	> 149?
CoSiO ₃	?	> 79?

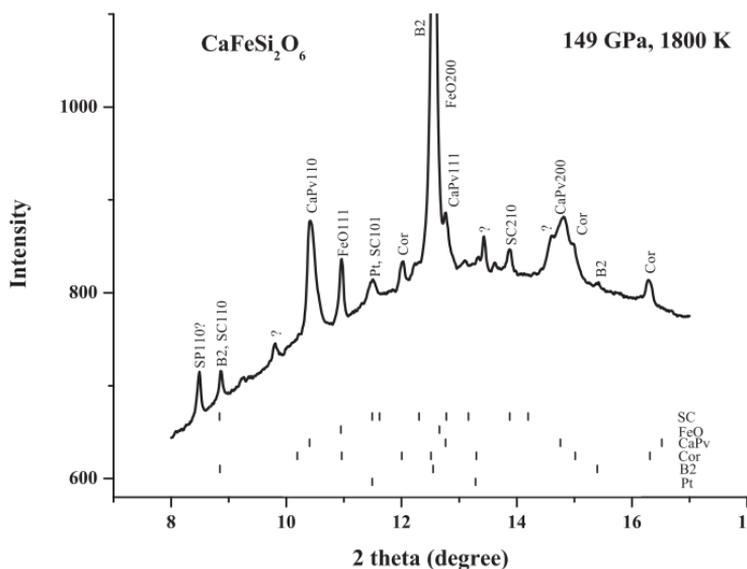
^aKato and Kumazawa, 1985

^bAkaogi et al., 2004

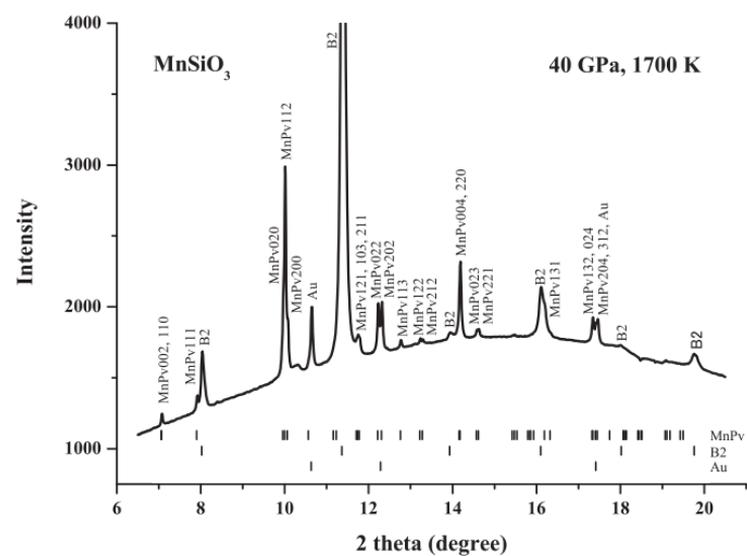
(a)



(b)



(c)



(d)

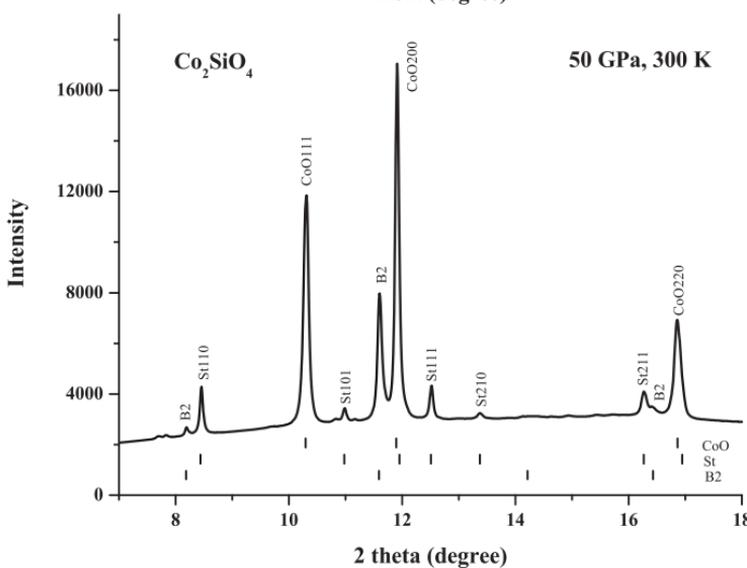


Fig. 1

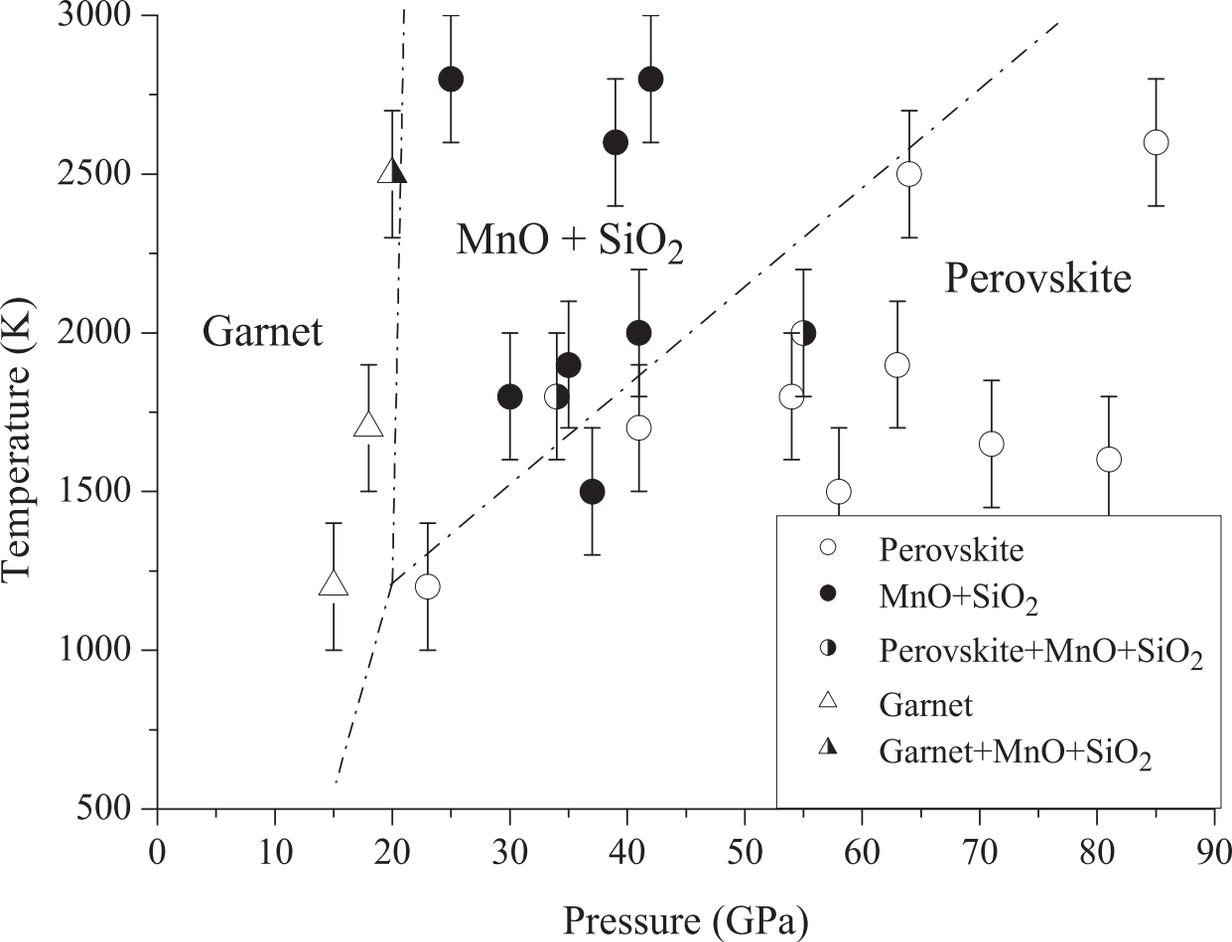


Fig. 2

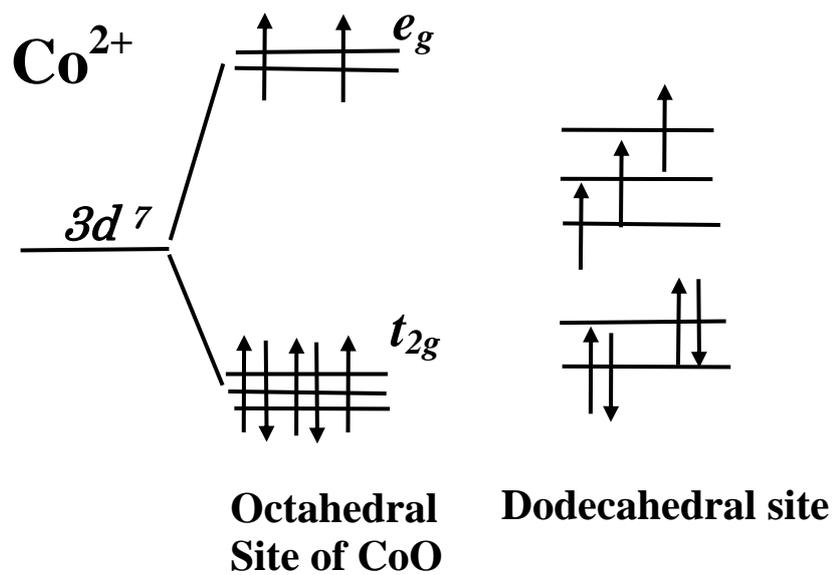
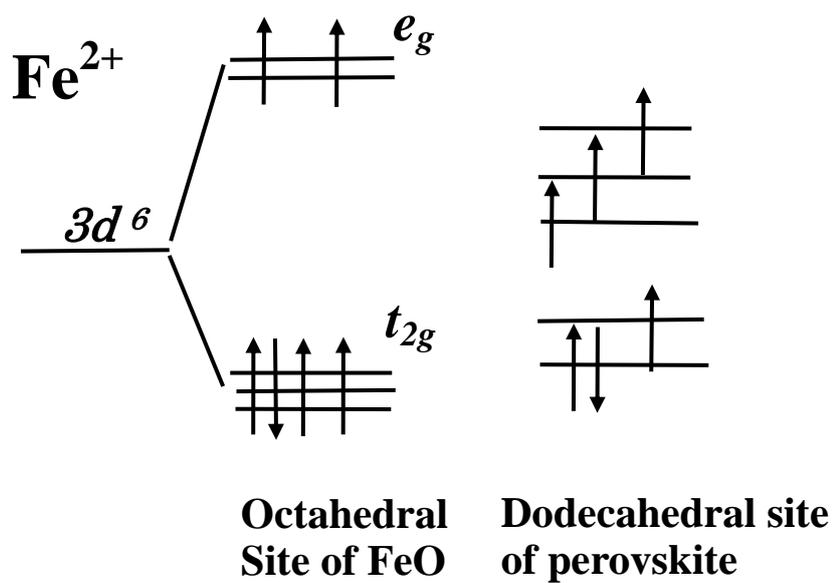


Fig. 3

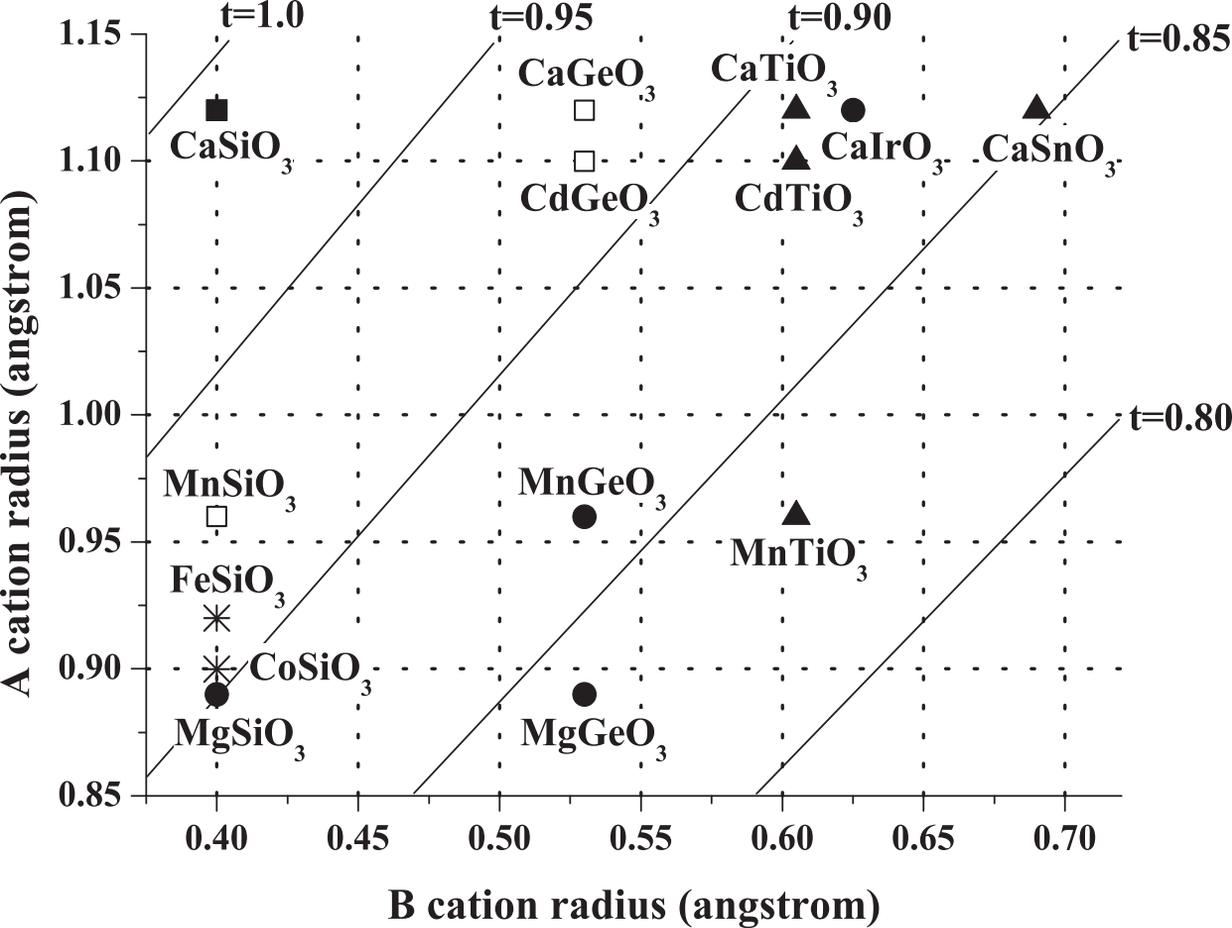


Fig. 4