

## Phase transitions, element partitioning, and density changes in a model lower mantle composition

Pyrolite is the name of a hypothetical rock, which was proposed as a model mantle material nearly 50 years ago [1]. Detailed phase relations and associated density changes in this composition have been studied using a multianvil apparatus (MA), which demonstrated that pyrolite is certainly an excellent model for the upper mantle (30-410 km), the mantle transition region (410-660 km), and the uppermost part of the lower mantle (660-2900 km) of the Earth. This kind of study, however, has been limited up to about 30 GPa, equivalent to a depth of ~800 km in the lower mantle, because of the limitation of pressures available in MA [2].

Recent developments in high-pressure generation in MA using sintered diamond (SD) anvils enabled us to extend this pressure limit toward those approaching 100 GPa, although experiments at high temperatures of the Earth's lower mantle (2000-3000 K) under such high pressures have still been quite difficult (e.g., Ref. [3]). We have firstly conducted detailed studies on phase transitions, element partitioning, and density changes in pyrolite at pressures up to 50 GPa and temperatures along an appropriate geotherm (1900-2200 K) [4] using a combination of synchrotron radiation and MA techniques with SD anvils at **BL04B1**. Mössbauer spectroscopy and electron energy-loss spectroscopy (EELS) measurements were also conducted on the recovered samples to analyze the iron valence state in the coexisting major high-pressure phases, in addition to the chemical composition measurements using a conventional scanning electron microscope with an EDX analyzer.

Figure 1 shows phase and density changes in pyrolite as a function of pressure (or depth) along the geotherm. It is seen that pyrolite consists of MgSiO<sub>3</sub>-rich orthorhombic perovskite (Mg-Pv;

75 vol%), (Mg,Fe)O ferropericlasite (Fp; 17 vol%), and CaSiO<sub>3</sub>-rich cubic perovskite (Ca-Pv; 8 vol%) in virtually constant volume proportions down to a depth of 1200 km in the lower mantle, which is consistent with earlier reconnaissance studies with a laser-heated diamond anvil cell (LHDAC). The density change of the pyrolite remarkably agrees with the model density profile (PREM) based on seismological observations, suggesting that this composition is a good model for the upper part of the lower mantle.

The partition coefficients ( $K_D$ ) of iron between Fp and Mg-Pv in pyrolite were determined as a function of pressure from the chemical composition data of these phases, which are plotted in Fig. 2, where the  $K_D$  values lower than 1 indicate that iron is preferentially partitioned in Fp. The  $K_D$  values between Fp and Mg-Pv in San Carlos olivine composition (SC olivine) are also shown in this figure for comparison. It is seen that the  $K_D$  values in pyrolite are larger than those in SC olivine, which are attributed to the presence of ferric iron in Mg-Pv in the former composition, as a result of a coupled substitution of Mg<sup>2+</sup> and Si<sup>4+</sup> by Fe<sup>3+</sup> and Al<sup>3+</sup>.

The increase in  $K_D$  in pyrolite at pressures up to ~30 GPa is due to the enrichment of Al<sup>3+</sup> and Fe<sup>3+</sup> in Mg-Pv as a result of the smeared-out phase transition of majorite garnet to Mg-Pv, which stays constant above this pressure, where the majorite-perovskite transition is completed (Fig. 1). However, we noted a sudden decrease in  $K_D$  in pyrolite at pressures above ~40 GPa. Some recent experimental and theoretical studies demonstrate that ferrous iron in Fp undergoes a high-spin to low-spin transition at pressures around 40-60 GPa. This should result in the enrichment of ferrous iron in this phase and thereby a decrease in  $K_D$ , as observed in Fig. 2. Thus, we confirmed

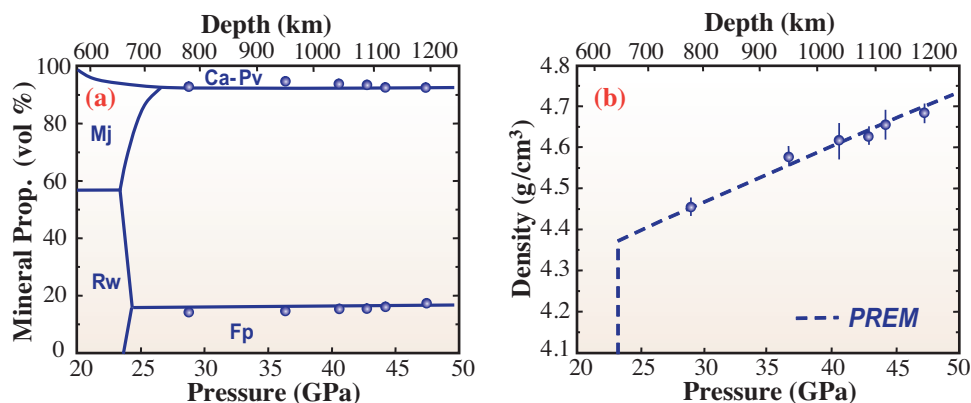


Fig. 1. Mineral proportion (a) and density (b) changes in pyrolite at pressures up to 50 GPa along a geotherm. PREM is a representative seismological model proposed by A. Dziewonski and D.L. Anderson. Mj = majorite garnet, Rw = ringwoodite, Mg-Pv = MgSiO<sub>3</sub> perovskite, Ca-Pv = CaSiO<sub>3</sub> perovskite, Fp = (Mg,Fe)O ferropericlasite.

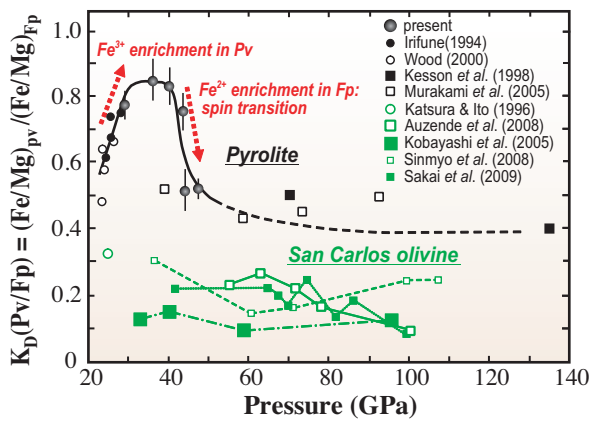


Fig. 2. Changes in iron partition coefficient ( $K_D$ ) between Mg-Pv and Fp in pyrolite and San Carlos olivine compositions as a function of pressure along a geotherm.

that the spin transition in Fp causes the enrichment of iron in Fp and a significant decrease in  $K_D$  in the realistic mantle composition, although this yields no notable anomalous changes in the density profile of pyrolite (Fig. 1).

Figure 3 shows schematic illustrations of two typical models of the compositions of the Earth's interior. It has been shown that pyrolite is a good model for the compositions of the upper mantle and the mantle transition region, except for the bottom part of the latter region, where we proposed the existence of a layer of harzburgite material on the basis of

sound velocity measurements at high pressure and temperature [5]. The chemical composition of the lower mantle, however, has not been well constrained; some believe that pyrolite is a reasonable model also in this region (Fig.3 (a)), while others claim that further Si-rich compositions, such as chondritic or perovskitite, are more feasible (Fig. 3(b)). As the lower mantle occupies more than half of the Earth's entire volume, elucidating its chemical composition is important to address the evolution and dynamics of the Earth's interior.

The present study suggests that pyrolite is a reasonably good model composition for at least the upper part of the lower mantle, in light of the density profile. However, the density profile in the Earth's interior is derived from observed seismic wave velocities with some assumptions, while the latter velocity data are more directly constrained by seismological observations. Thus, we need to compare laboratory sound velocity data of pyrolite and other compositional models with those by seismological observations. Researchers in our laboratory and those of JASRI have developed techniques to measure the sound velocities under P-T conditions of the uppermost lower mantle, which should provide important data to constrain the chemical composition of this region of the Earth's mantle in the near future.

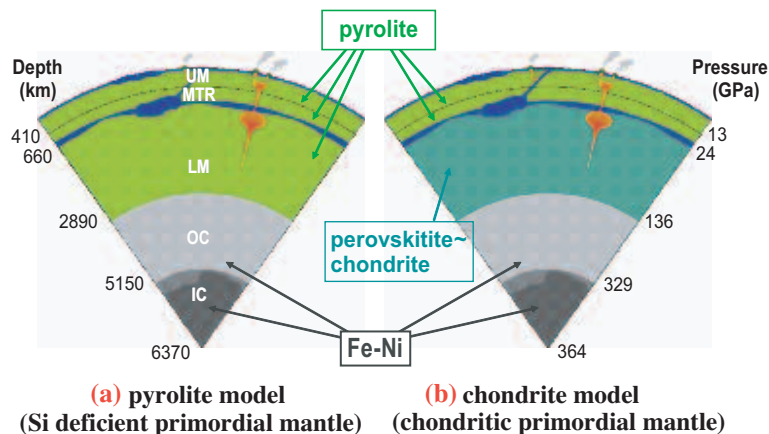


Fig. 3. Two representative models of the Earth's interior with pyrolite (a) and perovskitite/chondrite (b) compositions for the lower mantle. The core material is believed to be composed of mainly Fe-Ni alloys. UM = upper mantle, MTR = mantle transition region, LM = lower mantle, OC = outer core, IC = inner core. Illustration courtesy of Jun Tsuchiya.

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## References

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