Sound velocity of hexagonal close-packed iron up to core pressures

Measurement of sound velocities of metallic iron under extreme conditions is crucial for understanding the Earth's core. Figure 1 shows a one-dimensional seismic profile of the Earth's interior, the Preliminary Reference Earth Model, PREM [1]. The density and seismic velocities of the core-forming materials are essential in clarifying the constituent of the Earth's core. In pioneering works, Fiquet *et al.* [2] and Mao *et al.* [3] used X-ray scattering techniques to measure the velocities of metallic iron at extreme pressures in order to discuss the compositions and properties of the Earth's inner core. There are longstanding controversies regarding Birch's law, i.e., the V_p and density relation and its temperature dependence. Fiquet *et al.* [2] determined the seismic velocity of hcp-Fe to 112 GPa at room temperature by the inelastic X-ray scattering method, IXS. Their V_p-density relation overlapped with that determined by shock experiments along the Hugoniot [4]. This coincidence of the ambient temperature data with those determined by the high temperature shock compression experiment along the Hugoniot implies that there is no temperature effect on Birch's law. On the other hand, Mao *et al.* [3] determined the seismic velocity of hcp-Fe up to 153 GPa using nuclear inelastic scattering (NIS), and reported higher V_p compared with the shock compression data. The V_p-density relations of the Birch's law determined by these works are shown in Fig. 2. The discrepancy between these two works is significant. Without solving this inconsistency, it is impossible to argue the composition of the inner core using the sound velocity of hcp-Fe. In order to determine a reliable V_p-density relation for hcp-Fe at ambient temperature and at high temperatures, we measured the P-wave velocity of hcp-Fe to 174 GPa, the maximum pressure using IXS, at room temperature, and up to 1000 K in a wide pressure range up to 100 GPa [5].

Inelastic X-ray scattering spectra were taken at the high-resolution inelastic X-ray scattering beamline **BL35XU**. The energy longitudinal acoustic (LA) mode of the hcp-Fe was precisely determined by fits to the IXS spectra. All results from one set of thermodynamic (P, T) conditions, with the error bars from the spectral fits, were then fitted to a sinusoidal dependence of the LA mode energy on momentum transfer. The NaCl pressure medium was used in most runs, excepting runs made at high temperature. Pre-compressed rhenium foil was used for the gasket for confining pressure. Density was measured from the X-ray diffraction of the sample using the flat panel image plate detector before and after the IXS measurements. In some runs made in the early stage the X-ray powder diffraction of the same sample in the same DAC was taken at **BL10XU** beamline before or after the experiments. The two unit cell volumes determined by the two procedures were consistent with each other. The results of our measurements at room temperature and up to 174 GPa, and those up to 1000 K at high

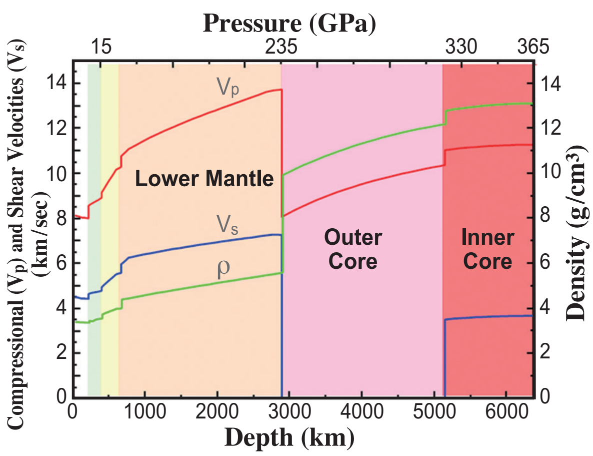

Fig. 1. Preliminary Reference Earth Model, PREM [1]. V_p is the compression and Vs is the shear velocity.

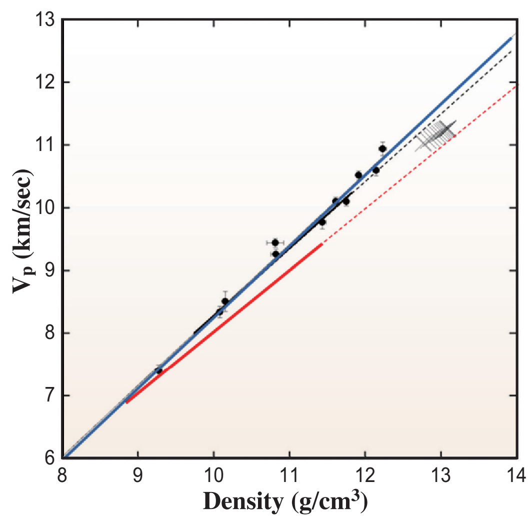

Fig. 2. Birch's law, the compressional velocity-density relation, of hcp-Fe at ambient and high temperatures determined in this study. All present data at 300 K and high temperatures up to 1000 K are shown as solid circles. Crosses, X, are V_p and density for the PREM inner core. All of the data at 300 K and high temperature determined here are fitted by the single blue line of V_p (km/s) = 1.126(±0.042) ρ (g/cm³) −2.969(±0.466) (R^2 = 0.988). The IXS [2] and NIS [3] data are shown as black and red curves, respectively.

pressures to 100 GPa are summarized in Fig. 2. Our high-temperature compressional velocities, as seen in Fig. 2, fall on the same linear velocity *vs* density line, V_p [km/s] = 1.126(±0.042)ρ [g/cm^3] – 2.969(±0.466) (R^2 = 0.988), as those at room temperature, indicating that Birch's law is valid for hcp-Fe at least up to 1000 K [5].

In previous works, two methods have been used to investigate sound velocities in hcp-Fe at high pressure: nuclear inelastic scattering (NIS) and IXS as used here [2,3]. The NIS technique [3] provides spectra from which, within a harmonic approximation, the phonon density of states may be extracted, and from this DOS, the Debye velocity, and, eventually, the sound velocity, V_p, may be isolated. Our results are in good agreement with the NIS results obtained by Mao *et al.* at pressures up to 153 GPa [3]. Thus, we solved the longstanding controversy of Birch's law of hcp-Fe in the present experiment. Although we could detect almost no temperature dependence in Birch's law for hcp-Fe, it is likely that there is a large temperature dependence at temperatures above 1000 K in Birch's law. Recent *ab initio* calculations showed that it has a negligible temperature effect below 1000 K, whereas a large effect at higher temperatures as shown in Fig. 3. A large temperature effect in Birch's law above 1000 K is consistent with the shock compression data determined along the Hugoniot [4]. The recent results on the thermal state of the outer core based on melting experiments of iron-light element systems propose that the temperature at the ICB is around 5500 K [5]. The P-wave velocity and density values at temperatures around 5500 K for the shock experiment and theoretical calculations are shown as large red circles in Fig. 3. The isothermal Birch's law at 5500 K may have a slope similar to that at 300 K obtained in the present study. Assuming the isothermal slope of Birch's law at 300 K holds even at high temperatures, we can estimate the P-wave velocity of hcp-Fe at 330 GPa and 5500 K, using the isothermal Birch's law at 5500 K and the thermal equation of state of hcp-Fe. The isothermal Birch's law at 5500 K may be expressed as follows: V_p [km/s] = 1.174ρ[g/cm^3] – 4.230(±0.032) (R^2 = 0.988) [5]. The density and P-wave velocity of hcp-Fe under the ICB condition, 330 GPa and 5500 K, are calculated to be 13.3(5) g/cm^3 and 11.4 km/s, respectively. Thus, hcp-Fe has a density about 4% higher and P-wave velocity about 3% higher than those in the seismological model, PREM, 12.76 g/cm^3 and 11.03 km/s at ICB (see Fig. 3), respectively.

On the basis of the arguments above, we can conclude that the light elements or the combination of the light elements and nickel decreases both the density and compressional velocity of hcp-Fe simultaneously under the inner core conditions, accounting for the seismic observations of the inner core. This conclusion is in striking contrast to the properties of the outer core, i.e., the outer core contains light elements, which reduces the density and increases the sound velocity of the outer core by forming molten iron alloy. The sound velocity of hcp-Fe under the inner core conditions is a key to clarifying the composition of the inner core.

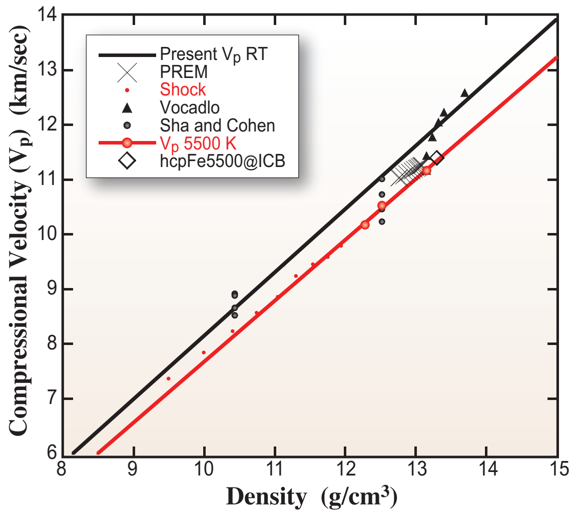

Fig. 3. Compressional velocity and density of hcp-Fe at 300 and 5500 K [5]. Small red circles, black triangles, and black circles are the shock compression data along the Hugoniot and the results of *ab initio* calculations [5]. The compressional velocity *versus* density of the PREM inner core is shown as large crosses [1]. Large red circles are V_p and density at 5500 K estimated by extrapolation of the shock compression and those calculated by the *ab initio* methods. The relation for hcp-Fe at 5500 K is V_p (km/s) = 1.174ρ (g/cm^3) –4.230(±0.032), assuming that the slope of the line is the same as that at 300 K [5]. Open diamond shows the compressional velocity and density of hcp-Fe under the inner core boundary condition, 330 GPa and 5500 K.

Eiji Ohtani

Department of Earth Science, Tohoku University

E-mail: ohtani@m.tohoku.ac.jp

References

[1] A.M. Dziewonski and D.L. Anderson: Phys. Earth Planet. Inter. **25** (1981) 297.
[2] G. Fiquet *et al.*: Science **291** (2001) 468.
[3] H.K. Mao *et al.*: Science **292** (2001) 914.
[4] J.M. Brown, R.G. McQueen: J. Geophys. Res. **91** (1986) 7485.
[5] *E. Ohtani, Y. Shibazaki, T. Sakai, K. Mibe, H. Fukui, S. Kamada, T. Sakamaki, Y. Seto, S. Tsutsui, A.Q.R. Baron: Geophys. Res. Lett.* ***40*** *(2013) 1.*