Effect of ferrous iron on elasticity of bridgmanite: Possible origin of anticorrelated seismic velocity anomaly observed in the lower mantle

A seismological study revealed that some regions show an increase in bulk sound velocity ($V_B = \sqrt{K_S/\rho}$) and a decrease in shear wave velocity ($V_S = \sqrt{G/\rho}$): $\Delta V_B > 0 > \Delta V_S$, and others show a decrease in V_B and an increase in V_S: $\Delta V_B < 0 < \Delta V_S$ (K_S, G, and ρ are the adiabatic bulk modulus, shear modulus, and density, respectively) in the deep mantle between depths of 2000 and 2891 km [1]. This feature is called an anticorrelated seismic velocity anomaly. The regions showing this anomaly, which are beneath Africa and the central Pacific, have attracted attention as large low shear velocity provinces (LLSVPs) characterized as $\Delta V_B > 0 > \Delta V_S$.

In the 200 km layer at the bottom of the lower mantle, known as the D″ layer, the anomaly can be explained by the post-perovskite (pPv) phase transition of bridgmanite, the most abundant material of the lower mantle with the perovskite structure, since V_B and V_S for the post-perovskite phase are lower and higher than those for bridgmanite, respectively [2]. However, this cannot explain the anomaly in the shallower part from 2000 to 2700 km where the pPv phase cannot exist.

There have been several proposals for the origin of the LLSVPs [3]. Thermal heterogeneity has been considered, but exclusively thermal effects are insufficient to explain the LLSVPs because usually both V_B and V_S decrease with temperature. It is thus suggested that the LLSVPs have a very different chemical composition from that of the average mantle.

Although bridgmanite is an iron-aluminum bearing magnesium silicate, the effects of cation substitution, especially Fe^{2+}, have not been well investigated. To address these issues, the elastic properties of iron-bearing bridgmanite have been investigated under ambient conditions. For this purpose, the inelastic X-ray scattering (IXS) technique was used [3]. Iron-bearing bridgmanite is a colored material. A single crystal of bridgmanite is usually tiny (< a few hundred μm). Therefore, the elastic properties of iron-bearing bridgmanite should be measured using appropriate methods. X-rays can be focused relatively easily and do not basically limit a sample. The valence state of a bridgmanite has been evaluated by synchrotron-based ^{57}Fe Mössbauer spectroscopy [3].

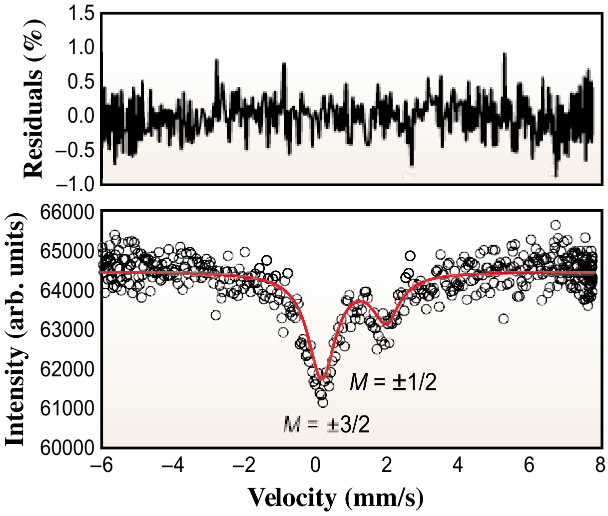

Fig. 1. Mössbauer spectrum of ^{57}Fe in FeAl-Bdg. Black circles are raw data from which the backgrounds have been subtracted. The red line indicates one doublet fitted to the data. (Top panel) Fitting residuals.

The measured samples were single crystals synthesized at 24 GPa and 1500°C using a Kawai-type multianvil apparatus. The lattice constants were refined using a four-circle diffractometer with a laboratory source. The chemical composition was analyzed using an electron microprobe and determined as $Mg_{0.943}Fe_{0.045}Al_{0.023}Si_{0.988}O_3$ (FeAl-Bdg). It is important to identify the valence state of iron in the crystal. Although the present samples were not enriched with ^{57}Fe but had iron isotopes with natural abundance, a Mössbauer spectrum was collected in the energy domain at SPring-8 **BL10XU** (Fig. 1). Taking some constraints imposed by the crystal structure into account, the absorption lines in this spectrum are interpreted as an asymmetric doublet. On the basis of this interpretation, the isomer shift and quadrupole splitting were determined to be 1.05(6) and 1.8(1) mm/s, respectively. These values indicate that the iron in this sample was in a divalent high-spin state and substituted for magnesium. The intensity

Table 1. Elastic moduli (Voigt-Reuss-Hill average of C_{ij} values) and elastic wave velocities of bridgmanites under the ambient conditions.

	Mg-Bdg	FeAl-Bdg	
K_S	236(4)	244(3)	
G	166(2)	165(1)	(GPa)
V_B	7.58(6)	7.66(5)	
V_S	6.37(4)	6.32(2)	(km/s)

asymmetry of this doublet is most probably due to the sample being a single crystal.

IXS measurements were carried out at SPring-8 **BL35XU**; $MgSiO_3$ bridgmanite (Mg-Bdg) was also measured at **BL43LXU** as well as at BL35XU as a reference. Elastic stiffness constants, C_{ij}, were determined from phonon energies and momenta obtained from the IXS spectra on the basis of the Christoffel equation. The number of phonon modes used to determine the six C_{ij} values was 461 and 319 for Mg-Bdg and FeAl-Bdg, respectively. The rather redundant data enabled us to determine the C_{ij} values precisely. Table 1 shows the determined K_S and G together with V_B and V_S. V_B for FeAl-Bdg is higher than that for Mg-Bdg, whereas V_S for FeAl-Bdg is lower than that for Mg-Bdg. Some cation substitutions in Mg-Bdg caused the anticorrelation between V_B and V_S, though the measurements were carried out under ambient conditions.

The present results have been applied to a geochemical and geothermal model assuming a perovskite mantle [4]. The seismic anomaly observed in the LLSVPs may be explained by the variation of Fe^{2+} and the temperature. When ΔT is about 226 K, the LLSVPs can be explained by only 5.4 atom% of Fe^{2+} (Fig. 2). These numbers are probably upper limits as the effect of aluminum has not been taken into account. The anticorrelated behavior of the elastic wave velocities has been successfully interpreted on the basis of the results of laboratory experiments.

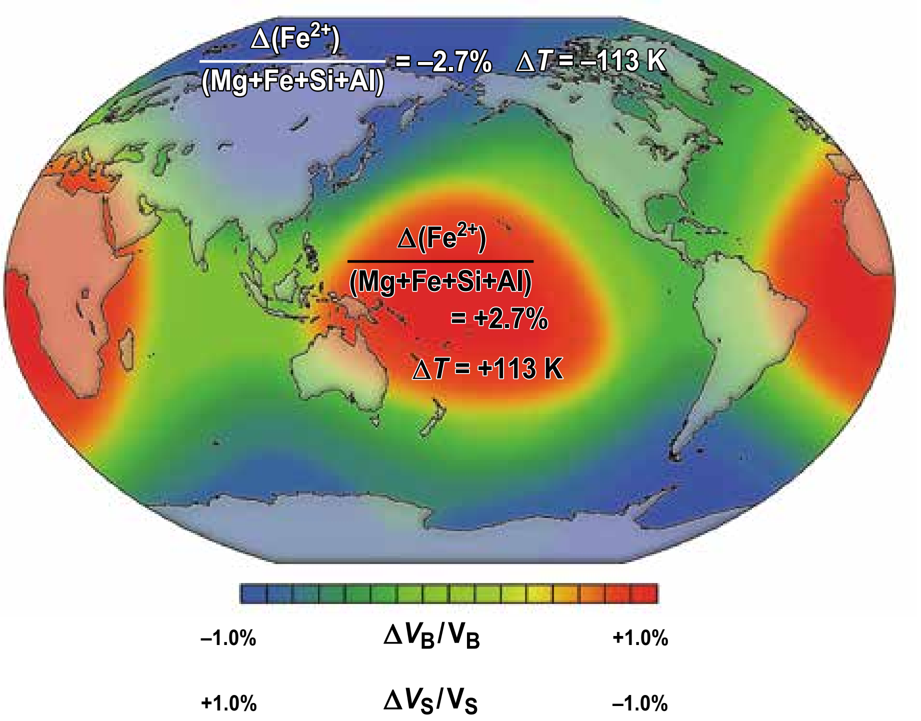

Fig. 2. Schematic image of regional variation of seismic velocities, ferrous iron composition of bridgmanite, and temperature variation at depths between 2000 and 2891 km. The map outline was made using CraftMAP *(http://www.craftmap.box-i.net/)*.

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