Elastic wave velocities and Raman shift of MORB glass at high pressures – Reply

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Kono et al. (2008) have independently measured the pressure dependence of the elastic wave velocities and the Raman shift of MORB glass at pressures up to 20 GPa at room temperature. Following are the findings of their study:

- (1) The pressure dependence of the elastic wave velocity, adiabatic bulk modulus, and density of MORB glass sample changes discontinuously at ~ 5 and ~ 10 GPa, implying local structural changes in the sample, such as an increase in the Si coordination number.
- (2) The pressure dependence of the Raman shift at ~ 1600 cm^{-1} changes discontinuously at ~ 10 GPa, which may also reflect structural modifications in the MORB glass sample.

Dr. M. Kanzaki has pointed out a misinterpretation in the second conclusion. He suggested that the Raman shift at ~ 1600 cm^{-1} may have been caused by water or carbon contamination, and not by the vibrations of the structure of the MORB glass sample.

The water content in the MORB glass sample synthesized at 1500 °C and 1 atm has been determined to be 528 wt. ppm (H_2O) by FT-IR spectroscopy by Kono et al. (2007). Dr. Kanzaki remarked that the water content in the samples should be more than a few weight percent in order to account for the observed high intensity of the 1600 cm^{-1} band (see Fig. 1 of Kono et al., 2008; Mysen and Richet, 2005). In addition, it would also be difficult for such a large amount of water to dissolve in the MORB glass sample during hot-press treatment (cf., Higo et al., 2006). Therefore, the observed 1600 cm^{-1} band is unlikely to be caused by water contamination. On the other hand, disordered graphite is known to exhibit two Raman bands

at 1580–1600 cm^{-1} (G-band) and 1350 cm^{-1} (D-band), both of which have been observed in the starting material used by Kono et al. (2008). However, Kono et al. have not used any carbon contaminant source such as graphite and carbonate in the high-pressure cell assembly used in the hot-press treatment of the sample (cf., Higo et al., 2006). In order to clarify the possibility of carbon contamination, further examinations of the MORB glass samples are carried out.

First, the amount of carbon contained in both the as-synthesized and as-hot-pressed MORB glass samples used by Kono et al. (2008) was quantified by electron probe microanalysis (EPMA). The analysis was carried out using a scanning electron microscope (SEM: JEOL, JXA-8200) equipped with a wavelength-dispersive spectrometer (WDS) at Hiroshima University. The instrument was operated at an accelerating voltage of 15 kV, and the beam current of 30 nA. The electron beam was focused to a spot size of 30 μm . Natural pure aragonite was used as a standard reference material, and the $\text{CK}\alpha$ line at 44.7 Å was analyzed for the quantification of the carbon content using an LDE1 diffractor. The samples were coated with a thin gold film of thickness ca. 15 nm. Figure 1 shows the $\text{CK}\alpha$ peaks of the as-synthesized (Fig. 1a) and as-hot-pressed (Fig. 1b) MORB glass samples. The presence of these peaks indicates that detectable amounts of carbon are present in both the samples. The amount of carbon contained in the as-synthesized and as-hot-pressed samples is calculated to be 1.1 and 1.2–1.3 wt%, respectively.

The MORB glass samples were crushed to form a powder and further examined by using a transmission electron microscope (TEM: JEOL, JEM-2010) operated at 200 kV. Figure 2 shows the bright-field images and selected area electron diffraction (SAED) patterns of the as-synthesized (Fig. 2a) and as-hot-pressed (Fig. 2b) sam-

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Figure 1. WDS spectra of MORB glass samples (a) synthesized at 1500 °C and 1 atm and (b) hot pressed at ~17 GPa and ~900 °C.

Figure 2. TEM images and SAED patterns of (a) synthesized and (b) hot-pressed MORB glass samples.

ples. A close-up examination of several particles reveals that no heterogeneous grains or contaminants are present in both the samples. However, the SAED patterns (Figs. 2a and 2b, inset) exhibit a faint broad ring with the d-spacing of approximately 3.4 Å, which is comparable to that of the d-spacing of graphite (002). Since these patterns have been obtained from the regions on the TEM grid where the carbon supporting film is not present (i.e., within a hole), the observed faint diffraction ring can be attributed to the samples, and not to the supporting film. These observations indicate that poorly crystalline graphite with short-range order is probably present in the form of randomly scattered nanodomains in the MORB glass samples.

These results indicate that the MORB glass samples used in the elastic wave velocity measurement and the Raman analysis by Kono et al. (2008) certainly contain trace amounts of carbon, as Dr. Kanzaki has pointed out. In some previous studies, it has been reported that carbon contamination occurs via diffusion from the graphite

heater in the cell assembly used in high-pressure and temperature experiments (e.g., Hemley et al., 1986). However, this is not the case in the hot-press experiment carried out by Kono et al. in which a platinum heater was used (cf., Higo et al., 2006). In addition, the detailed analyses carried out by using the SEM-WDS and TEM have shown that not only the hot-pressed sample but also the as-synthesized sample has been contaminated with trace amounts of carbon, although the Raman spectrum of the latter shows no peaks of disordered graphite (see Fig. 1 in Kono et al., 2008). Therefore, it is most likely that carbon contamination has taken place during the high-temperature synthesis of MORB glass in an electric furnace. The possible sources of the contamination may be carbonates (Na_2CO_3 and CaCO_3), which were added to adjust the composition of synthesized glass, or CO_2 gas, which was used to control the oxygen fugacity in furnaces. It is known that in a reducing atmosphere, nanocrystalline carbon such as graphite nanofibers and amorphous carbon is precipitated from carbon-containing gases such as CO

Figure 3. Temperature–time path and gas conditions in electric furnace during synthesis of MORB glass at 1500 °C and 1 atm. The sample was placed in the furnace, and a mixture of CO₂, Ar, and H₂ gases was circulated for 435 min at 600–1500 °C.

and CH₄ in the presence of catalysts (e.g., Fe, Ni, Al₂O₃, Si) (e.g., Anderson and Rodriguez, 1999; Zhou et al., 2006). In the synthesis of the MORB glass samples, similar catalytic reactions might have occurred in the furnace in which a reducing atmosphere was maintained by continuously introducing a CO₂–H₂ gas mixture (180:100) (Fig. 3), leading to the precipitation of trace amounts of nanocrystalline graphite in the samples. Fe₂SiO₄ or its reduced form (Fe) might have played a role as a catalyst in the synthesis. This result indicates that the redox state of the atmosphere inside furnaces should be controlled carefully in order to prevent such undesirable carbon contamination.

In conclusion, the Raman band at $\sim 1600\text{ cm}^{-1}$ observed in the MORB glass samples used by Kono et al. (2008) is caused by the contamination of the samples with poorly crystalline graphite, and not by the vibrations of the glass structure. The discontinuous change observed in the pressure dependence of various parameters is similar to that reported by Hanfland et al. (1989) and may be related to minor structural modifications of stacked graphene layers. However, it is assumed that carbon contamination will not affect the other conclusion drawn by Kono et al. (2008)—the observed discontinuous change in the pressure dependence of the elastic properties and density of MORB glass at $\sim 10\text{ GPa}$ is due to the local structural changes in the glass samples—since the observed carbon content of $\sim 1\text{ wt\%}$ is extremely small and cannot cause any notable changes in the elastic properties and density of the samples. In addition, the observations of this study are consistent with those of a high-pressure X-ray diffrac-

tion study on SiO₂ glass, indicating a substantial increase in the Si-coordination number in the local sample structure (Meade et al., 1992). Therefore, it is assumed that the observed discontinuous change in the pressure dependence of the elastic wave velocities and density of the MORB glass samples above $\sim 10\text{ GPa}$ reflects local structural changes in the samples, such as the densification of the tetrahedral network structure and an increase in the Si–O and/or Al–O coordination number. However, further studies on the structure of the melt have to be carried out in order to prove this assumption.

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