The post-stishovite phase transition in hydrous alumina-bearing SiO₂ in the lower mantle of the earth


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Silica is the most abundant oxide component in the Earth mantle by weight, and stishovite, the rutile-structured (P4₂/mmm) high-pressure phase with silica in six coordination by oxygen, is one of the main constituents of the basaltic layer of subducting slabs. It may also be present as a free phase in the lower mantle and at the core–mantle boundary. Pure stishovite undergoes a displacive phase transition to the CaCl₂ structure (Pnmm) at ~55 GPa. Theory suggests that this transition is associated with softening of the shear modulus that could provide a significant seismic signature, but none has ever been observed in the Earth. However, stishovite in natural rocks is expected to contain up to 5 wt % Al₂O₃ and may also be present as a free phase in the lower mantle and at the core–mantle boundary. Pure stishovite undergoes a displacive phase transition to the CaCl₂ structure (Pnmm) at ~55 GPa. Theory suggests that this transition is associated with softening of the shear modulus that could provide a significant seismic signature, but none has ever been observed in the Earth. However, stishovite in natural rocks is expected to contain up to 5 wt % Al₂O₃ and possibly water. Here we report the acoustic velocities, densities, and Raman frequencies of aluminum- and hydrogen-bearing stishovite with a composition close to that expected in the Earth. However, stishovite in natural rocks is expected to contain up to 5 wt % Al₂O₃ and possibly water. Here we report the acoustic velocities, densities, and Raman frequencies of aluminum- and hydrogen-bearing stishovite with a composition close to that expected in the Earth. However, stishovite in natural rocks is expected to contain up to 5 wt % Al₂O₃ and possibly water. Here we report the acoustic velocities, densities, and Raman frequencies of aluminum- and hydrogen-bearing stishovite with a composition close to that expected in the Earth. However, stishovite in natural rocks is expected to contain up to 5 wt % Al₂O₃ and possibly water. Here we report the acoustic velocities, densities, and Raman frequencies of aluminum- and hydrogen-bearing stishovite with a composition close to that expected in the Earth.
There have been numerous reports of seismic discontinuities and heterogeneities in the depth range of 1,000–1,500 km (8–10). Kaneshima and Helffrich (8) and Niu et al. (11) found a dipping low-velocity layers (LVL) in the vicinity of the Mariana and Izu–Bonin subduction zones, and they estimated the thickness of the LVL to be 8 km (8) to 12 km (11), with a shear velocity anomaly of 2–6%. These authors ruled out a phase transition source for the LVL because of the dipping nature of the anomaly. However, shear softening related to the rutile–CaCl₂ transition in aluminous stishovite within the mid-ocean ridge basalts (MORB) part of a subducted slab may provide a viable explanation for this feature. Similarly, LeStunff et al. (9) observed a reflector at 1,200 km in a rather different tectonic setting, under the African Rift zone. They concluded that a sharp (20–25 km thick) feature was responsible for the reflection of low-frequency P precursors. Only a few vol % of stishovite is needed to cause a visible seismic discontinuity (21), whereas stishovite may comprise up to 20 vol % of subducted MORB material.

Previously, stishovite had been considered to be an explanation of these reflectors (1, 15), but it appeared that the transition would occur too deep in the lower mantle (4). Our observations show that seismic reflectors in the depth interval of 1,000–1,500 km may be the signature of subducted MORB material not only in the regions of active subduction (8), but also in the regions where subduction became extinct in Mesozoic or even Proterozoic (9). On the other hand, some authors have argued for the existence of stishovite in “ambient” lower-mantle lithologies (22–25). Although it appears likely that the bulk of the lower mantle is dominated by magnesian silicate perovskite and ferropericlase, the possibility of stishovite (rutile or CaCl₂-structured) occurring locally in lower mantle chemical heterogeneities may explain the spatially restricted character of seismic reflectors in this depth interval.

Natural occurrences of stishovite are largely restricted to meteorites and impact craters. In studies of impacts, stishovite serves as an important pressure marker. However, sometimes, as in the case of the Shergottite meteorite, there is a mismatch between the observed phase assemblages and the pressure deduced from such markers e.g., refs. 26 and 27. Chemical analyses of stishovite from the Shergottite meteorite show that it contains 1.5 wt % impurities such as Na₂O and Al₂O₃. Our results show that aluminum and possibly hydrogen have a large effect on the stability fields of silica phases. Thus, careful chemical analysis of quenched phases and consideration of the effect of minor elements on phase boundaries are required for an accurate determination of peak pressure in shocked assemblages.

Materials and Methods

The sample studied in this work [K324, containing 6.07(5) wt % Al₂O₃ and 0.24(2) wt % H₂O synthesized at 20 GPa and 1,800°C (28)] was a single-crystal plate with the normal to the surfaces having direction cosines of (0.603 0.522 0.603). The ambient-pressure elastic properties and Raman frequencies of this and other crystals from the same batch were reported elsewhere (28).
The crystal was loaded into a symmetric piston-cylinder diamond-anvil cell along with four ruby spheres (29) and two chips of NaCl. Neon served as a pressure-transmitting medium because it provided quasi-hydrostatic conditions at pressures >60 GPa (1, 30). The choice of pressure medium was important because displacive phase transitions are sensitive to nonhydrostatic stress (15, 31).

Simultaneous Brillouin scattering and synchrotron XRD measurements were performed at 13-BMD, GeoSoilEnviroCARS, Advanced Phonon Source (Argonne, IL). We used the recently developed Brillouin scattering system (32) and angle-dispersive X-ray diffraction with an MAR-345 (Mar-USA, Evanston, IL) imaging plate detector. Pressure was increased in small (<1 GPa) increments with a typical spacing of ~5 GPa between Brillouin measurements. After each pressure increase above 20 GPa, the cell was annealed in an oven at 200–300°C for 0.5–24 h or laser-heated at ~1,500°C (CO2 laser, \( L \approx 10 \mu m \)) to relax deviatoric stresses in the sample chamber. The pressure gradient never exceeded 0.5 GPa in any experiment, as monitored by X-ray diffraction from the pressure medium (neon) and ruby fluorescence.

Raman scattering measurements obtained on decreasing pressure were performed at the University of Illinois. At pressures of 38.4(7) and 28.7(3) GPa, the pressure medium was annealed at 300°C for 30 min.

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