



Sodium-bearing phases in the transition zone and uppermost lower mantle: Experimental and natural data

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Introduction

Na is an incompatible element in the Earth's mantle and among the main hosts for sodium beneath the 410-km boundary are majoritic garnet (transition zone and upper part of the lower mantle), CaSiO₃-perovskite and NaAl-phase (NaAlSiO₄) with the Ca ferrite-type structure (lower mantle).

Na-bearing majoritic garnets (up to 5.89 wt % Na₂O; Kaminsky 2012) were discovered as inclusions in diamonds of the eclogitic assemblage in many regions worldwide including Kankan area in Guinea, West Africa, where majorite with the high sodium content (1.37 wt % Na₂O) associated with potassium-rich clinopyroxene (1.44 wt % K₂O) (Stachel 2001). As is evident from the experimental data (Akaogi 2007), majorite may be stable under pressures of up to 28 GPa (i.e., in the uppermost horizons of the lower mantle), and the concentrations of Na and Si in such garnets may be used for pressure estimation. In addition, Na-bearing majoritic garnet is compatible with sodium-rich alkaline silicate and carbonate-silicate melts produced by partial melting of the mantle material within the diamond depth facies (Bobrov et al. 2008).

Accessory lower mantle phases like CaSiO₃-perovskite or NaAl-phase can contain appreciable amounts of alkalis, but the mantle depleted from crust-extraction is expected to contain very low portions of these phases. This opens the question, how can Na be transferred back into the lower mantle. Only 'refertilization' of mantle by subduction processes can provide these elements for lower mantle phases and form high-Na phases. Recently, nyerereite (Na₂Ca(CO₃)₂) and nahcolite (NaHCO₃) have been identified in a specific lower mantle carbonatitic association (Juina area, Brazil) in association with typical lower mantle minerals, such as CaSi-perovskite and ferropericlaase (Kaminsky 2012).

Experimental techniques

To study the crystal-chemical behavior of sodium in the deep Earth, we performed experiments on a simplified chemical system involving Na-rich carbonated melt and mantle silicate at 24 GPa and 1100–1700°C, thus representing the conditions at the border between the transition zone and lower mantle.

Experiments were performed using a 2000 ton split-sphere press installed at the Ehime University (Matsuyama, Japan). A Co (17 wt%)-doped MgO octahedral pressure medium of 8 mm edge length was compressed using eight cubic tungsten carbide anvils with 3 mm truncation edge lengths. Pyrophyllite gaskets, 4 mm in width, were used to seal the compressed volume and support the anvil flanks. Heating of the sample was performed by a cylindrical LaCrO₃ heater, 3.2/2.0 mm in outer/inner diameter and 4 mm in length. Approximate sample volumes after experiments were 1.0 mm³. Starting mixtures of oxides and carbonate were dried for a few days at a temperature of 105 °C and kept in a dessicator. Temperature during the experiment was controlled by a W₉₇Re₃-W₇₅Re₂₅ thermocouple, 0.1 mm in diameter. The pressure was calibrated at room temperature using the semiconductor-metal transitions of Bi, ZnS, and GaAs (Irifune et al. 2004). The effect of temperature on pressure was further corrected using the α-β and β-γ phase transitions of olivine (Katsura and Ito 1989). The run durations were 15-60 min.

Results

In all samples, partial melting was registered: crystals of Na-bearing Al,Fe³⁺-bridgmanite occurred in microcrystalline carbonate-silicate quenched matrix; at 1300°C, grains of Na₂Mg(CO₃)₂ and (Mg,Fe)O grains were observed. With decreasing temperature melt composition evolved from silicate-carbonate to alkaline-carbonate. Bridgmanite contained Al₂O₃ (0.6-2.7 wt.%), Fe₂O₃ (1.6-3.5 wt.%), and up to 1.6 wt % Na₂O (at 1700°C). There is a positive correlation between the concentration of sodium in bridgmanite and temperature (Figure 1).

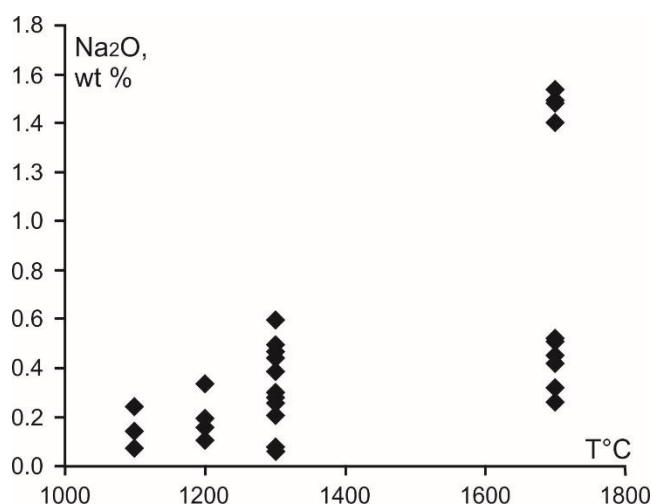


Figure 1: Na₂O concentration in synthetic bridgmanites depending on temperature.

The unit-cell volume observed for Na-bearing bridgmanite (166(1) Å³) is larger than that observed for pure MgSiO₃ (162.53(1) Å³, Dobson and Jacobsen 2004), due to the presence of the large Na cation. However, the mechanisms of Na incorporation in this structure remain unknown and require additional studies. As the chemical compositions obtained are not charge balanced, a probable solution could be a partial oxygen vacancy, as commonly observed in O-deficient perovskites (Akaogi 2007).

High-Na ringwoodite (up to 4.4 wt% Na₂O) was obtained at 24 GPa and 1700°C (Bindi et al 2016). The effect of Na in the ringwoodite structure is also apparent in the unit-cell parameter, which increases to 8.0952(3) in Na-ringwoodite with respect to 8.0816 in pure Mg₂SiO₄ (Ye et al. 2012).

Implications

Our results have implications for transport of alkalis into the lower mantle of the Earth. Although the concentration of alkalis in the Earth's transition zone and lower mantle is low and Na remains incompatible in most of the high-pressure solid phases, it is expected that some mantle phases could act as important hosts for Na, and perhaps K, in the deep transition zone and lower mantle. In the model of Walter et al. (2008), melting occurs as slabs descend and stagnate in the transition zone, and heat up to the carbonated eclogite solidus where they release a low-degree melt. Such low-degree carbonatitic melts from eclogite are expected to be mobile and rich in alkali, and so may act as effective metasomatizing agents. The presence of such melts in the deep mantle is supported by inclusions of Na-carbonates [nyerereite (Na,K)₂Ca(CO₃)₂ and eitelite Na₂Mg(CO₃)₂] in lower mantle diamonds (Kaminsky et al. 2016) and incorporation of sodium in major mantle silicates, such as majoritic garnet ringwoodite, and bridgmanite.

In contrast, proper Na–Mg silicates have not been registered as inclusions in diamonds or in mantle rocks, although they were obtained as products of experiments in many Na-rich model systems (Yang et al. 2009). This is explained by the fact that all natural lithologies are characterized by an excess of Al with respect to Na. However, the finding of an inclusion in diamond with the composition (Na_{0.16}Mg_{0.84})(Mg_{0.92}Si_{0.08})Si₂O₆ in a Chinese kimberlite (Wang and Sueno, 1996) suggests that some local areas of the Earth's deep mantle previously involved in the mantle–crust interaction may be

significantly enriched in Na. In this relation, study of Na-rich Mg-silicates will increase our knowledge on the composition and properties of the deep mantle.

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