High-pressure phase equilibria of KAlSi3O8 and NaAlSiO4 and thermodynamic properties of the high-pressure phases

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When slabs are subducted into deep mantle, basaltic oceanic crust and continentally derived sediments are entrained that contain alkali elements more abundantly than in average mantle. Therefore, host phases of K and Na in the deep mantle are a subject for current discussion. KAlSi3O8 hollandite, NaAlSiO4 calcium ferrite and hexagonal phase are possible candidates of the alkali-host phases. In this study, we examined phase transitions in KAlSi3O8 and NaAlSiO4 at high pressures and high temperatures. Enthalpies of these high-pressure phases and heat capacity of KAlSi3O8 hollandite were measured, and the high-pressure phase relations were thermodynamically calculated.

The high-pressure experiments were performed up to 27 GPa and 1600 C, using a multianvil apparatus. Starting materials were NaAlSiO4 nepheline and KAlSi3O8 sanidine. The following results were obtained. At 1000 C, NaAlSiO4 nepheline (Ne) dissociates into a mixture of NaAlSi2O6 jadeite (Jd) and beta-NaAlO2 at 4 GPa, the latter of which transforms to alpha-NaAlO2 at 7 GPa. At 19 GPa, this assemblage reacts to form NaAlSiO4 calcium ferrite (Cf). We found that Cf is stable at least 27 GPa. Enthalpies of the above transitions were measured, using a Calvet-type microcalorimeter. The obtained enthalpies of transitions at 298 K are 6.2 kJ/mol for Ne=Jd+beta, 23.6 kJ/mol for beta=alpha, and 79.6 kJ/mol for Jd+alpha=Cf. Calculated phase boundaries using the thermodynamic data are generally consistent with those by experiments, but the calculated slope of the boundary of Cf formation is smaller than that by the experiments.

Yagi et al. (1994) determined transition boundaries of KAlSi3O8 sanidine (Sa) to a mixture of K2Si4O9 wadeite(Wa), Al2SiO5 kyanite(Ky) and SiO2 coesite(Co), and further to KAlSi3O8 hollandite(Ho). The enthalpy of the former transition is 59.4 kJ/mol, and the latter 100.6 kJ/mol. The heat capacity of KAlSi3O8 hollandite was measured at 160-710 K by DSC method, and modeled on the basis of Kieffer's scheme. The calculated phase boundaries using the thermodynamic data are consistent with the boundaries by Yagi et al. (1994) and Urakawa et al. (1994). Recently, Fasshauer et al. (1998) suggested that Sa first dissociates into KAlSiO4 kalsilite(Ka) + Co and then changes to Wa+Ky+Co, using an internally consistent thermodynamic data available at that time. To examine their suggestion, we performed phase transition experiments at 5.9 and 6.6 GPa at 1100 C. The results indicated that Sa directly dissociates to Wa+Ky+Co, in contrary to Fasshauer et al's suggestion. The dissociation boundary of Sa determined in this study is about 2 GPa higher than the graphite-diamond transition boundary. This may be used as a geobarometer of kimberlitic diamonds with Sa inclusions. The present study indicated that NaAlSiO4 Cf and KAlSi3O8 Ho are stable at pressures above 19 and 9 GPa, respectively. Tutti et al. (2000, 2001) indicated that both of the phases are stable up to at least 70-95 GPa. All of these results suggest that Cf and Ho are promising candidates of alkali-host phases in the deep lower mantle.