

High-pressure phase equilibria of KAlSi_3O_8 and NaAlSiO_4 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. KAlSi_3O_8 hollandite, NaAlSiO_4 calcium ferrite and hexagonal phase are possible candidates of the alkali-host phases. In this study, we examined phase transitions in KAlSi_3O_8 and NaAlSiO_4 at high pressures and high temperatures. Enthalpies of these high-pressure phases and heat capacity of KAlSi_3O_8 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 NaAlSiO_4 nepheline and KAlSi_3O_8 sanidine. The following results were obtained. At 1000 C, NaAlSiO_4 nepheline (Ne) dissociates into a mixture of $\text{NaAlSi}_2\text{O}_6$ jadeite (Jd) and beta- NaAlO_2 at 4 GPa, the latter of which transforms to alpha- NaAlO_2 at 7 GPa. At 19 GPa, this assemblage reacts to form NaAlSiO_4 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 KAlSi_3O_8 sanidine (Sa) to a mixture of $\text{K}_2\text{Si}_4\text{O}_9$ wadeite (Wa), Al_2SiO_5 kyanite (Ky) and SiO_2 coesite (Co), and further to KAlSi_3O_8 hollandite (Ho). The enthalpy of the former transition is 59.4 kJ/mol, and the latter 100.6 kJ/mol. The heat capacity of KAlSi_3O_8 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 KAlSiO_4 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 NaAlSiO_4 Cf and KAlSi_3O_8 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.