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K in clinopyroxene at high pressure and temperature: An experimental study

GEORGE E. HARLOW

Department of Earth and Planetary Sciences, American Museum of Natural History,
New York, New York 10024-5192, U.S.A.

ABSTRACT

Clinopyroxene (Cpx) is a principal upper-mantle phase for concentrating large cations but has not been viewed as a major crystal-chemical reservoir for K because K^+ is considered too large to enter the largest site, M2, in the pyroxene structure. Accumulating data from high-pressure conditions indicate this inference is incorrect, so multianvil experiments have been performed to evaluate maximal K solubility in Cpx at high pressure. End members and mixtures of diopside, jadeite, and kosmochlor have been mixed with K_2CO_3, $KHCO_3$ or both in welded platinum capsules and heated typically for 24 h in the range of 5 to 14 GPa and 1200 to 1700 °C. These experiments produced K-rich Cpx in solid solutions by means of a fictive Kcpx component ($KCrSi_2O_6$ or $KAlSi_2O_6$). The maximum K_2O content obtained is 4.7 wt% in a Cpx ($Di_{38}Ko_{39}Kcpx_{22}En_1$) formed from a 50:50 Di + Ko mixture at 10 GPa, 1400 °C. K uptake and partitioning is dependent positively on P, complexly on Cpx composition but not demonstrably on T. ${}^{Cpx/liq}D_{K_2O}$ is in the range of 0.03–0.1 and ${}^{Cpx/liq}D_{Na_2O}$ varies from 0.5 to 5, although the variations for each with Cpx composition are different. In diopside, Kcpx increases are always accompanied by increases in Nacpx, and cooperative Nacpx solution is necessary for Kcpx solution in the compositional systems examined. K appears to be accommodated in the M2 site of the Cpx structure by two types of spatial averaging: a large average M2 site, as in the case of Di, ameliorates the fit, but local accommodation by size averaging with a smaller M2 occupant, presumably Na, appears necessary, suggesting that the polyhedral compressibility of Na and K are large in comparison with Ca. In application to Cpx inclusions in diamond, the data here imply that a chromium diopside with ~1 wt% K_2O forms in the presence of a C-rich melt with 15–28 wt% K_2O.