Potassium-bearing clinopyroxene: crystal chemical and thermodynamic model.

L. Bindi (1), O. Safonov (2), R. Downs (3), L. Perchuk (4), Yu. Litvin (2), V. Vinograd (5), G. Harlow (6)

(1) Dipartimento di Scienze della Terra, Università di Firenze, Firenze, Italy; (2) Instititute of Experimental Mineralogy, Chernogolovka, Russia; (3) Department of Geosciences, University of Arizona, Tucson, U.S.A.; (4) Department of Petrology, Moscow State University, Moscow, Russia, (5) Institut für Mineralogie, Universität Frankfurt, Frankfurt am Main, Germany, (6) Department of Earth and Planetary Sciences, American Museum of Natural History, New York, U.S.A.

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K-bearing clinopyroxene (KCpx) is considered to be a potential host for K at HP and mantle conditions. Therefore, understanding how clinopyroxene can incorporate potassium at high-pressures is important for modeling of the behavior of potassium in the deep Earth. We developed a preliminary crystal chemical and thermodynamic model for Fe-free KCpx solid solution on the basis of (1) experimental study of phase equilibria at high pressures, (2) x-ray single crystal measurements both at ambient and high pressures, and (3) static lattice energy minimization calculations.

(1) A study of the pseudo-binary system $CaMgSi_2O_6$-$KAlSi_2O_6$ (Safonov et al., 2003), modeling the isomorphism K + Al (Ca + Mg, at 7 GPa shows that KCpx solid solution is limited by composition of about 25 mol. % of $KAlSi_2O_6$, because of a critical reaction $4KAlSi_2O_6 + 3Di = Grs + Prp + 2K_2Si_4O_9$ ($KCpx_{SS} = Grt_{SS} +$ Si-wadeite).

(2) Stability of KCpx solid solution is determined by strongly different behavior of Al in the M1 site and K in the M2 site of the KCpx structure: Al induces a compaction in the clinopyroxene structure, while K shows the opposite effect. This conclusion supported by x-ray single crystal study of several KCpx crystals (e.g. Bindi et al., 2002), synthesized in the joins $CaMgSi_2O_6$-$KAlSi_2O_6$ and $CaMgSi_2O_6$-$KAlSi_3O_8$ at

7 and 6 GPa, respectively (Safonov et al., 2002, 2003).

(3) Crystal chemical parameters of synthetic KCpx $(Ca_{0.88}K_{0.12})(Mg_{0.83}Al_{0.17})(Si_{1.98}Al_{0.02})O_6$ were measured up to 9.72 GPa at ambient temperature using a four-pin diamond anvil cell (Bindi et al., 2005). Fitting the P-V data to the third-order Birch-Murnaghan equation of state yields $V_0 = 435.49(3)$ Å^3, $K_0 = 129(1)$ GPa, K$\prime$ = 2.7(3). These data allow conclusion that the substitution K + Al (Ca + Mg in diopside results in significant increase of K_0. Nevertheless, compressibility of the KCpx is mostly determined by compressibility of $M1O_6$ octahedrons, while K induces least effect.

(4) Unit cell parameters for the measured KCpx were fitted to the procedure of static lattice energy minimization (SLEM) using the GULP program (Gale, 1997). We obtained unit cell volume and bulk modulus 437.14 Å^3 and 127.64 GPa^{-1}, which closely reproduce the measured values. The calculated unit cell values for KCpx are in a good agreement with the results of diamond-cell measurements for a wide pressure interval. This allows using the SLEM method to estimate some partial thermodynamic properties of the fictive $KAlSi_2O_6$ end-member in the KCpx solid solution: $S^0 = 128.03$ J/mol/K, $_V^0 = 162.33$ J/mol/K, $V_{U.C}^0 = 442.73$ Å^3, $K_0 = 171.29$ GPa^{-1}.

(5) Effects of additional components (jadeite, Ca-Tschermack and clinoenstatite) on K-solubility in clinopyroxene are experimentally checked. All these components dramatically limit the $KAlSi_2O_6$ content in KCpx (Safonov et al., 2004, 2005), supporting an idea by Harlow (1997) about a leading role of unit cell volume in K incorporation in HP clinopyroxene.

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