



## **X-ray single-crystal study on synthetic Si and Cl-rich mica: new implications on phlogopite and celadonite miscibility at high pressure**

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Potassium-rich carbonatitic and chloride brine inclusions in diamonds from kimberlites (see Navon, 2003 for review) are associated both with eclogitic and peridotitic assemblages. Locally, products of reaction between potassic liquids and minerals are observed in single diamonds (Izraeli et al., 2004; Klein-BenDavid et al., 2006). A special attention is paid to unique high-silica micas. In diamonds from the Diavik mine (Canada), it is associated with carbonatitic inclusions (Klein-BenDavid et al., 2006), while it coexists with omphacites and chloride-rich brine in diamonds from the Koffiefontein pipe, S. Africa (Izraeli et al., 2004). The Si content in the micas reaches 7.7 a.p.f.u. at low Mg (4.7 a.p.f.u.). From IR spectra, Klein-BenDavid et al. (2006) concluded that these phases were solid solutions between phlogopite and Al-celadonite. In addition, Izraeli et al. (2004) found high Cl content in the micas from the Koffiefontein diamonds.

We produced Si-rich mica at the solidus of the join diopside-jadeite-KCl at 4 GPa and 1250-1200°C. It coexists with diopside-jadeite pyroxene, K-rich aluminosilicate glass and/or sanidine, as well as with (K,Na)Cl. Micas show negative correlation between tetrahedral Si and octahedral (Al+Mg), which corresponds to a substitution  $Al^T + (Mg+Al)^M \text{ ó } 2Si^T + \square^M$ . A hand picked single crystal of the mica  $K_{1.01}(Mg_{2.45}Al_{0.20}\square_{0.35})_{\Sigma=3}(Si_{3.52}Al_{0.48})_{\Sigma=4}O_{10}(OH_{1.66}Cl_{0.34})_{\Sigma=2}$

(measured with an electron microprobe) was used for the X-ray diffraction study. Unit-cell parameters (space group  $C2/m, 1M$  politype) are:  $a = 5.299(4) \text{ \AA}$ ,  $b = 9.167(3) \text{ \AA}$ ,  $c = 10.226(3) \text{ \AA}$ ,  $\beta = 100.06(4)^\circ$ ,  $V = 489.1(4) \text{ \AA}^3$ . The refinement of the occupancy factors of the octahedral sites shows a presence of vacancies estimated to be 15% for M1 and 6% for M2 sites. The mean electron numbers obtained from the X-ray structure refinement excellently agree with those estimated from the EMP analyses (n.  $e_{X\text{-ray}}^- = 10.72$  and n.  $e_{EMPA}^- = 10.65$ ). Chlorine was found in a split position at  $0.6 \text{ \AA}$  from O4 with partial occupancy (0.39 a.f.u). The tetrahedral rotation angle  $\alpha$  is  $2.58^\circ$ , a low value for phlogopites, meaning that the six tetrahedral ring is almost hexagonal and the interlayer cavity where K is located, is very large and likely should favour the entry of Cl instead of hydroxyl. The  $[\text{M}]^M\text{-Mg}$  substitution and the excess of Si affect the  $a$  and  $b$  parameters and the cell volume that decrease respect to a "true" phlogopite.

Our experimental and crystal structural data support an idea on better miscibility between di- and tri-octahedral micas at high pressures (Schreyer, 1965) and indicate that the OH-Cl substitution may greatly enhance it. We assume that Si-rich micas are important indicators of high potassium activity in the diamond-forming media: K extracts Al from the phlogopite to the melt, while high pressure stabilizes a phlogopite-celadonite solid solution.

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