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The incorporation of chlorine into calcium amphibole

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ABSTRACT

The exchange of halogens between fluids and solid silicates holds considerable potential to shed light on fluid-rock interactions associated with various geological processes, including seawater-ocean-crust interaction, crustal and mantle metasomatism, and economic deposit formation. This study reports on how variations in formation conditions (temperature, pressure, hydrogen fugacity), bulk composition (Na and K ratio), and choice of starting material salts affect the Cl contents of calcium amphiboles synthesized specifically from ferro-pargasite and hastingsite bulk compositions. Syntheses were attempted over the range of 600–950 °C and 0.1–0.45 GPa at logf_{H_2} of 1.4 to 2.4 (equivalent to –0.9 to –2.1 logf_{O_2} below the fayalite-magnetite-β-quartz oxygen buffer, or ΔFMβQ) for durations of 111–672 h. Amphiboles were characterized by powder X-ray diffraction and electron microprobe, with cation proportions calculated on the basis of an assumed 18% ferric iron content. Amphiboles formed from the ferro-chloro-pargasite bulk composition [$NaCa_2(Fe_{4.0}Al)(Al_2Si_6)O_{22}Cl_2$] had Cl contents of only about 0.5 atoms per formula unit (apfu), compared to the intended 2.0, and whose stabilities were about 70 °C lower at 0.1–0.2 GPa than reported in a previous study of Cl-free (OH-bearing) ferro-pargasite. Syntheses on the ferro-pargasite bulk composition in the presence of a brine with a nominal mole fraction of Cl (X_{Cl}) of 0.3 over the range of 700–950 °C at 0.2 GPa showed that temperature had less effect on the Cl content of the amphibole than small variations in the brine concentration assessed after treatment. For the chloro-hastingsite bulk composition [$NaCa_2(Fe_{4.0}Fe^{3+})(Al_2Si_6)O_{22}Cl_2$], the Cl content of the product amphibole was unaffected by the specific choice of chloride salt or salt combinations (NaCl, $CaCl_2$, $FeCl_2$), but showed a direct correlation with the substitution of K for Na. Experiments done over the range of 0.10–0.45 GPa at 700 °C and at –1.3 logf_{O_2} ΔFMβQ showed an increased rate of nucleation of amphibole with increasing pressure for a hastingsite bulk composition with 40% substitution of K for Na, but no variation in the Cl content of the amphibole. Classification of the amphiboles formed in this study showed that several were well outside their intended field, with some of those formed from the ferro-pargasite bulk composition straddling the boundary between hastingsite and ferro-pargasite, while several formed from the hastingsite bulk composition were actually ferro-ferri-hornblendes. These results confirm that K more so than Na is important for the incorporation of Cl into calcium amphiboles, and that Cl-bearing ferro-ferri-hornblende, with low A-site Na + K, can form even from mixtures with abundant Na + K. Combining these observations with the strong correlation between Cl content and Fe# [= $Fe^{2+}/(Fe^{2+}+Mg)$] noted in previous studies, a general correlation was found to exist between the Cl content and the FeAlK index, defined as Fe#·(^{T}Al + K), which combines the effects of Fe#, tetrahedrally coordinated Al (^{T}Al), and K content. A linear trend is observed once a minimum value of about 0.34 in the FeAlK index is reached. The implication is that the crystal-chemical controls for Cl incorporation in calcium amphiboles are dominated by substitution of Fe^{2+} for Mg, ^{T}Al for Si, and K for Na into the crystallographic A site with a linear dependence at the rate of 0.45 Cl per FeAlK index above a minimum value of about 0.34.

Keywords: Ferro-pargasite, hastingsite, chlorine, chloro-amphibole, synthesis, ferro-ferri-hornblende