

Effect of chlorine substitution on the thermal stability of ferro-pargasite and thermochemical properties of ferro-chloro-hornblende

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ABSTRACT

Substitution of chlorine for hydroxyls in calcium amphiboles has been widely documented, but the effect of this substitution on thermal stability is not known. Experimental reversal data are presented here comparing the upper-thermal stability of amphiboles formed in the ferro-pargasite and ferro-chloro-pargasite bulk compositions. Experiments were made over the range of 550–900 °C and 0.5–3 kbar at oxygen fugacities of $\log(f_{O_2})$ of -0.3 to $+0.5$ relative to Co-CoO. Electron microprobe analysis of amphiboles made from the ferro-pargasite bulk composition were found to be ferro-pargasite, while those made from the ferro-chloro-pargasite bulk composition were low in A-site Na and Cl and were better classified as Cl-bearing ferro-ferri-hornblende. Although the differences between desired and observed amphibole compositions complicate the comparison of their thermal stabilities, it can be deduced that the Cl-bearing amphibole has a steeper dP/dT slope and, above 1 kbar, a lower thermal stability than ferro-pargasite. Thermodynamic analysis of the Cl-bearing amphibole was also done to extract thermochemical data for the Cl end-member amphibole ferro-chloro-hornblende [$Ca_2(Fe_4Al)(AlSi_7)O_{22}Cl_2 = Fe\text{-Cl-Horn}$] that are consistent with the thermodynamic database of Holland and Powell (2011). Using an ideal-activity expression and estimated values for the heat capacity ($C_p = 1.106 + 8.9156 \times 10^{-3}(T, K) - 11\,218.3/T^2 - 5.9548/T^{0.5}$; kJ/K·mol) and volume (283.0 ± 1.5 cm³/mol) for Fe-Cl-Horn, the derived values for ΔH_f° and S° are $-10\,842.6 \pm 10.3$ kJ/mol and 618.8 ± 11.1 J/K·mol, respectively. The implication of this work is that (1) chlorine appears to lower the thermal stability of a given calcium amphibole in contrast to the marked increase in thermal stabilities caused by fluorine, and (2) thermochemical data such as those derived in this study allow absolute concentrations of chloride salts to be calculated in metasomatic paleobrine, as illustrated for the Bamble sector of southern Norway reported in the literature.

Keywords: Mineral stability, ferro-pargasite, ferro-chloro-hornblende, chlorine amphibole, thermochemistry, metasomatic paleobrine, mineral synthesis