Effect of Cl Substitution on the Thermal Stability of Ferro-pargasite

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John Holloway published one of the earliest studies on the increased thermal stability of pargasite, a good approximation to natural hornblende, resulting from the substitution of F for OH [1]. Enhanced thermal stability arising from the substitution of F^- (radius = 1.33 Å) for OH^- (1.37 Å) in Mg-rich amphibole (amph) and biotite is well documented; however, the effect of Cl^- (1.81Å) substitution is hard to deduce from field studies because of the complex interplay between fluid composition, amph composition, and imprecise knowledge of the thermal history of a given field locality. Recent experimental work at this university has helped to address this question.

Synthetic ferro-pargasite (FePg) close to the ideal composition $NaCa_2(Fe_4Al)(Al_2Si_6)O_{22}(OH,Cl)_2$ was made as the OH end-member by hydrothermal treatment of reagent oxides and metallic Fe in a Holloway-style gas vessel at 800°C, 2.4 kb, 93 h, and an Ar-H_2 pressure medium with H_2 partial pressure equivalent to $\log f_{O2}$ = -0.3ΔCoCoO. Synthetic FePg with 0.50±0.07 Cl apfu (1.7 wt% Cl) was made by dry synthesis from reagent oxides, Fe°, and $FeCl_2$ as the source of Cl at 600°C, 2 kb, 365h, and $\log f_{O2}$ = -0.2 ΔCoCoO. These amphiboles were mixed in with the equivalent high-temperature (non-amph) assemblages to make two reaction reversal mixtures: (1) OH-FePg = 1.66plag(An_{40}) + 0.33hed + 0.33gross + 1.2magnetite + H_2O, and (2) Cl-FePg = 1.54plag(An_{94}) + 0.55hed + 1.7fay + 0.9halite ± $FeCl_2$ for the Cl-amph assemblage.

Reversal of reaction (1) was obtained at 795±15°C at 2 kb and $\log f_{O2}$ = +0.5ΔCoCoO, similar to that of Gilbert [2]; while reversal of (2) was obtained at 600±40°C at 2 kb and $\log f_{O2}$ = -0.3ΔCoCoO. This is a reduction of 195°C in the stability of FePg with 0.5 Cl afpu, despite the higher f_{O2} used for the OH-FePg (limited by gas-vessel tolerance to H_2). These results indicate that Cl incorporation into (K-free) ferro-pargasite reduces its thermal stability, implying that any increase in Cl content with temperature for ferro-pargasitic amphibole arises from increasing Cl in the ambient fluid, not from increased thermal stability of Cl-bearing amphibole.

[1] Holloway, J.R. and Ford, C.E. (1975), *Earth and Planetary Science Letters*, **25**, 44-48. [2] Gilbert, M.C. (1966) *American Journal of Science*, **264**, 698-742.