Abstract

The importance of potassium in forming Cl-rich amphiboles has long been documented in multiple studies of naturally occurring amphiboles. Many of the most Cl-rich amphiboles reported tend to have $^{A}K > ^{A}Na$, though there are some studies that contradict this. Some have interpreted this as the incorporation of the much larger K ion on the A-site causes the amphibole’s lattice to expand, giving way to an increased potential for the much larger Cl to replace OH anions on the O(3) site. We report here results on synthetic hastingsites ($(Na,K)Ca_2(Fe_4^{2+},Fe^{3+})(Al_2Si_6)O_{22}(OH,Cl)_2$) that contests this interpretation.

Amphiboles were synthesized from reagent grade materials at a constant pressure, temperature, and fO_2, being 3kbar, 700°C, and Ni-NiO respectively. Five bulk compositions were explored with K#s (K# = $^{A}K/(^{A}Na+^{A}K)$) ranging from 0 to 1 in the presence of a series of different initial $FeCl_2$ brines ranging from 1 – 100 molal. The synthetic amphiboles were analyzed by electron microprobe (WDS) and Mossbauer spectroscopy.

Analysis showed a positive trend between the concentration of $FeCl_2$ brines and the amphibole Cl-content, with amphibole Cl increasing rapidly at low brine concentrations and slowing as the brine becomes more Cl-rich. Interestingly, each bulk composition showed nearly identical trends between [Cl] in the brine and Cl in the amphibole over the entire range of concentrations explored, indicating that occupant of the amphibole’s A-site does not influence its ability to incorporate Cl. The trend between A_{total} and amphibole Cl is “V”-shaped with A_{total} decreasing with increasing Cl up until a Cl-content of around 0.4 apfu and A_{total} of around 0.5 apfu, then increasing until the maximum Cl recorded of around 1.05 apfu and A_{total} of about 0.75. It is in no way affected by the K#. Mossbauer spectroscopy revealed a steady increase in the amount of Fe^{3+} in the amphibole from brine concentrations of 1-24m $FeCl_2$ which coincides with the samples that showed a negative A_{total} - Cl relationship. Between 24 and 50m $FeCl_2$, the amount of Fe^{3+} in the amphibole shows a dramatic decrease, from around 0.31 to about 0.13 ferric iron fraction which marks the beginning of the positive A_{total} – Cl trend. This suggests that the amphibole responds to changes in redox conditions by the $Fe^{2+} + A_{cation} \leftrightarrow Fe^{3+} + Avac$ exchange reaction.

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