Chlorine incorporation into amphibole and biotite in high-grade iron-formation: Interplay between crystallography and metamorphic fluids

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ABSTRACT

Minor amounts of markedly Cl-rich amphibole and biotite are found in the Archean (2.8–2.9 Ga) iron-formation lithologies from the eastern Beartooth Mountains, Montana, U.S.A. These rocks are typified by mineral assemblages of quartz + magnetite + orthopyroxene + garnet ± clinopyroxene ± plagioclase having equilibrated during granulite facies conditions of ~775–800 °C and 6–8 kbar. The metamorphic Cl-rich amphibole and biotite are prograde and occur as inclusions in orthopyroxene and garnet as well as in the matrix. The high-grade Fe-rich amphiboles (mostly Cl-rich potassic-hastingsite and magnesio-ferri-hornblende) and biotites contain concentrations of Cl reaching up to 2.9 and 3.4 wt%, respectively. Biotites contain up to 10.5 wt% BaO and 6.9 wt% TiO2. Substitution of Cl into amphibole and biotite is more likely where Cl-bearing anion sites are enlarged. In amphibole threshold values of the XFe2+, XK, and XAl appear to be a precondition before significant amounts of Cl are incorporated into the structure. In biotite, in addition to XFe2+, substitution of XAl also is positively correlated with Cl. The high Cl content in the minerals is suggestive of a coexisting high salinity aqueous fluid. Based on calculations using mineral chemistry, estimations of the aqueous fluid composition indicate a Cl-rich aqueous fluid (~25 wt% NaCl) with fH2O/fHCl ratios of ~0.68–0.82. There is evidence for brine-CO2 immiscibility during peak metamorphism. In amphibole once the threshold values for significant Cl incorporation are attained, the Fe2+-Mg partitioning of the amphibole and the coexisting mafic silicates changes such that the amphibole more favorably partitions Fe2+. A feedback mechanism can be generated such that the more Cl available from a fluid the more Fe2+-rich the amphibole can become, and this produces a crystal structure that can accommodate more Cl, which makes this amphibole more favorable for Fe2+ incorporation, and the cycle continues until Cl saturation in the crystal structures is reached or aqueous Cl is fully equilibrated with the amphibole.

Keywords: Chlorine, iron-formation, amphibole, biotite, Archean

INTRODUCTION

Chlorine (Cl) enrichment in amphibole and biotite has been observed in a variety of terrestrial and extraterrestrial geological environments. Terrestrial Cl-rich amphibole and biotite are typically found in subsolidus metamorphic/metamastic petrologic settings over variable pressure and temperature conditions. Fluid systems associated with Cl-rich amphibole and biotite range from dynamic systems in which saline aqueous fluids flux through the rocks to more static environments in which aqueous fluids become more saline through loss of H2O from the system or through CO2-brine immiscibility (e.g., Manning and Aranovich 2014). Terrestrial petrologic settings include skarns, calcareous metasediments, felsic and mafic granulite-facies rocks, amphibolites, ore deposits (e.g., Au, Pb-Zn, and Ni-Cu), ductile shear zones in mafic rocks, mafic eclogites, igneous rocks with subsolidus hydrothermal interactions, and granulite-facies iron-formations (e.g., Krutov and Vinogradova 1966; Jacobson 1975; Dick and Robinson 1979; Kamieniak et al. 1982; Vanko 1986; Suwa et al. 1987; Henry 1988; Castelli 1988; Mora and Valley 1989; Morrison 1991; Tracy 1991; Enami et al. 1992; Oen and Lustenhouwer 1992; Pan and Fleet 1992; Jiang et al. 1994; Kullerud 1995, 1996, 2000; Léger et al. 1996; Markl and Piazolo 1998; Kullerud and Erambert 1999, McCormick and McDonald 1999; Xiao et al. 2005; Liu et al. 2009; Uher et al. 2014; Bonin and Tatu 2016). Cl concentration levels of terrestrial minerals can be high with amphibole containing up to 6.51 wt% Cl and biotite containing up to 7.45 wt% Cl (Jacobson 1975; Uher et al. 2014, respectively). The extraterrestrial occurrence of amphibole with very high Cl (up to 7.0 wt%) has been documented in the nakhlite class of martian meteorites in which extreme Cl enrichment is found in amphibole associated with a late-forming melt inclusions and melt-exsolved saline aqueous fluids (e.g., Giesting and Filiberto 2016). Variations in the Cl contents of amphibole and biotite in these settings are considered to be a function of temperature, pressure, crystallographic factors, and fluid composition (e.g., Volfinger et al. 1985; Henry 1988; Morrison 1991; Zhu and Sverjensky 1991, 1992; Manning and Aranovich 2014; Daigle 2015). Of particular interest for this paper is that under high-grade metamorphic conditions, amphibole and biotite tend to either break down to anhydrous minerals (e.g., pyroxene, garnet, and feldspar), deprotonate the hydroxyl-anion to an oxy-anion and/or incorporate halogens such as Cl− and F− into the O(3) and O(4) anion sites of amphibole.

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