Experimental investigation of F and Cl partitioning between apatite and Fe-rich basaltic melt at 0 GPa and 950–1050 °C: Evidence for steric controls on apatite-melt exchange equilibria in OH-poor apatite

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ABSTRACT

Apatite-melt partitioning experiments were conducted in a Deltech vertical-quench 1-bar furnace at 0 GPa and 950–1050 °C using an Fe-rich basaltic starting composition. Each experiment had a unique F:Cl ratio to assess the partitioning of F and Cl between apatite and melt, and the oxygen fugacity of all experiments was between IW and IW-1. Apatite-melt partitioning of F and Cl along the F-Cl binary join is investigated in particular to assess the effect of non-ideal mixing of apatite X-site components. The quenched melt and apatite from each experiment were analyzed by electron probe microanalysis. Several of our experiments exhibited evidence of silicate liquid immiscibility (SLI), so we also evaluated the effect of SLI on the partitioning of F and Cl between apatite and melt in those experiments. The F-Cl exchange equilibria between apatite and melt were variable with $K_{\text{Ap}}^{\text{Ap}-\text{melt}}$ values in the range of 0.08–0.21 across the F-Cl join. The $K_{\text{Ap}}^{\text{Ap}-\text{melt}}$ values decreased with decreasing F in apatite and melt. Notably, we did not observe evidence that SLI has a first-order effect on the behavior of F and Cl partitioning between apatite and melt. The observed drop in $K_{\text{Ap}}^{\text{Ap}-\text{melt}}$ values with decreasing F abundance in melt and apatite indicate that F becomes more compatible in apatite than Cl as there is less F in the system under nominally anhydrous conditions. This behavior can be explained by the presence of an off-mirror F site in F-Cl apatite that only F can occupy, and this F site is required to stabilize the apatite structure in OH-poor systems. These results demonstrate a link between atomic arrangements of apatite X-site components, the thermodynamic mixing properties of apatite X-site components, and the values of apatite-melt exchange equilibria for apatite X-site components. These results also indicate that Cl-rich apatites [i.e., Cl > 0.1 structural formula units (sfu) of apatite X-site] with compositions near the F-Cl binary join (i.e., <0.12 sfu from the F-Cl binary join), even if formed from H2O-bearing natural systems, should not be used for apatite-based melt-hygrometry.

Keywords: Hygrometry, Moon, Mars, water, phosphate, silicate liquid immiscibility, merrillite, electron microprobe

INTRODUCTION

Apatite [Ca$_3$(PO$_4$)$_3$(F,Cl,OH)] is present in a wide range of rock types on the Earth (Harlov 2015; Harrison and Watson 1984; Patiño Douce et al. 2011; Piccoli and Candela 2002; Shemesh 1990), and it is also the primary mineralogical host of P in the silicate portion of the planet (Hughes and Rakovan 2002). Along with the nominally volatile-free phosphate mineral merrillite [Ca$_9$Na$_2$Mg$_2$(PO$_4$)$_4$], apatite constitutes one of the primary hosts of P in extraterrestrial rocks (McCubbin and Jones 2015). The ubiquity of apatite in planetary materials, coupled with the presence of volatiles (i.e., F, Cl, and OH) in its crystal structure (X-site), has motivated numerous studies to estimate the H$_2$O abundances of magmas and magmatic source regions in various planetary systems from apatite (Piccoli and Candela 1994; Patiño Douce and Roden 2006; Boyce et al. 2010; McCubbin et al. 2010a, 2012, 2015a, 2016; Patiño Douce et al. 2011; Gross et al. 2013; Tartèse et al. 2013, 2014; Filiberto et al. 2016), a practice referred to as apatite-based melt hygrometry (e.g., Boyce et al. 2014; McCubbin et al. 2015b). However, to use the volatile contents of apatite to accurately determine the abundances of volatiles in coexisting silicate melt or fluids, thermodynamic models for the apatite solid solution and for the apatite components in multi-component silicate melts and fluids are required. Although some thermodynamic models for apatite-bearing systems have been developed (i.e., Candela 1986; Tacker and Stormer 1989, 1993; Zhu and Sverjensky 1991; Hovis and Harlov 2010; Hovis et al. 2014a, 2014b; Li and Hermann 2017), they are incomplete and cannot be broadly applied to the full range of geologic conditions under which apatite has formed. Consequently, studies conducting apatite-based melt hygrometry have relied heavily on the results of individual experimental studies into apatite-melt and/or apatite-fluid partitioning behavior of F, Cl, and OH, which have limited applicability to natural systems.

Numerous modeling and experimental studies have reported apatite-melt or apatite-fluid partitioning relationships for F, Cl, and OH (i.e., Korzhinskiy 1981; Zhu and Sverjensky 1991; Brenan 1993; Mathez and Webster 2005; Webster et al. 2009, 2010; Hovis et al. 2014a, 2014b; Li and Hermann 2017), but they are incomplete and cannot be broadly applied to the full range of geologic conditions under which apatite has formed. Consequently, studies conducting apatite-based melt hygrometry have relied heavily on the results of individual experimental studies into apatite-melt and/or apatite-fluid partitioning behavior of F, Cl, and OH, which have limited applicability to natural systems.

These results also indicate that Cl-rich apatites [i.e., Cl > 0.1 structural formula units (sfu) of apatite X-site] with compositions near the F-Cl binary join (i.e., <0.12 sfu from the F-Cl binary join), even if formed from H2O-bearing natural systems, should not be used for apatite-based melt-hygrometry.