Chlorine and fluorine partitioning between apatite and sediment melt at 2.5 GPa, 800 °C: A new experimentally derived thermodynamic model

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ABSTRACT

The partitioning behavior of Cl and F between apatite and sediment melt has been investigated by performing piston-cylinder experiments at 2.5 GPa, 800 °C using a hydrous experimental pelite starting material (EPSM) with ~7 wt% H2O and variable Cl (~0, 500, 1000, 2000, or 3000 ppm) and F (~0, 700, or 1500 ppm) contents, relevant for subduction zone conditions. Cl and F partitioning between apatite and melt is non-Nernstian, with $D_{Cl-melt}$ varying from 1.9–10.6 and $D_{F-melt}$ varying from 16–72. In contrast, Cl and F partition coefficients between phengite/biotite and melt ($D_{Cl-melt}^{Phen}$, $D_{F-melt}^{Cl}$, $D_{F-melt}^{Bi}$, and $D_{F-melt}^{OH}$) were determined to be $0.24 \pm 0.01$, $0.86 \pm 0.05$, $1.4 \pm 0.1$, and $3.7 \pm 0.4$, respectively. The Nernstian partitioning of Cl and F between phengite/biotite and melt suggests ideal mixing of F, Cl, and OH in phengite, biotite, and melt.

Exchange coefficients for F, Cl, and OH partitioning between apatite and melt were determined, with $K_{Cl-OH}^{Ap-melt} = 19–49$, $K_{F-OH}^{Ap-melt} = 164–512$, and $K_{F-OH}^{Cl} = 7–21$. The evident variation of $K_a$ values was attributed to non-ideal mixing of F, Cl, and OH in apatite. A regular ternary solution model for apatite was developed by modeling the variation of $K_a$ values for experiments from this study and those from Webster et al. (2009) and Doherty et al. (2014). Positive values (~15 to ~25 kJ/mol) obtained for Margules parameters $W_{Cl}^{Ap-melt}$, $W_{F}^{Ap}$, and $W_{F-OH}^{Ap}$ at low-pressure conditions (0.2 GPa, 0.05 GPa, and 900 °C) are in contrast to zero or negative values at 2.5 GPa, 800 °C. Based on a thermodynamic framework for F, Cl, and OH exchange between apatite and melt, using values for $-\Delta G_{Cl-OH}^{Ap-melt}(P,T)$, $-\Delta G_{F-OH}^{Ap-melt}(P,T)$, $-\Delta G_{F-Cl}^{Ap}(P,T)$, $W_{Cl}^{Ap-melt}$, $W_{F}^{Ap}$, $W_{F-OH}^{Ap}$, and $W_{F-Cl}^{Ap}$ obtained through regression, F and Cl contents in melt can be derived from apatite compositions.

Keywords: Apatite, chlorine, exchange coefficient, fluorine, melt, partitioning, piston-cylinder experiments, regular solution model, subduction

INTRODUCTION

Apatite [referring to fluorapatite, chlorapatite, hydroxylapatite, and solid solutions among them with the general formula, Ca$_5$(PO$_4$)$_3$(OH,F,Cl)], is the most abundant phosphate mineral on Earth and a ubiquitous accessory mineral in igneous, metamorphic, and sedimentary rocks (Piccoli and Candela 2002; Spear and Pyle 2002; Hughes and Rakovan 2015). Apatite is also commonly found in extraterrestrial samples (e.g., Patiño Douce and Roden 2006; Jones et al. 2014). Apatite composition has been utilized as an indicator of volatile concentrations in ore-forming hydrothermal fluids (e.g., Boudreau and McCallum 1989), mantle metasomatic agents (e.g., O’Reilly and Griffin 1989), and subduction zone fluids (e.g., Li and Hermann 2015; McCubbin et al. 2012; Gross et al. 2013; Howarth et al. 2015). Although the interpretation of volatile concentrations in fluid phases has been mainly qualitative or based on experimentally determined partition coefficients (Drs) (Brenan 1993; Mathez and Webster 2005; Webster et al. 2009; Doherty et al. 2014; Kusebauch et al. 2015), many researchers have recognized the non-Nernstian partitioning behavior of F, Cl, and OH between apatite and fluids and the necessity to use a thermodynamic formulism describing the F, Cl, and OH exchange reaction between apatite and fluid (e.g., $K_{Cl-OH}^{Ap-melt}$) for the purpose of quantifying volatile contents in fluid phases (Khorzhinskiy 1981; Zhu and Sverjensky 1991; Piccoli and Candela 1994, 2002; Patiño Douce et al. 2011; Boyce et al. 2014; Li and Hermann 2015; McCubbin et al. 2015).