



## Distribution of halogens between fluid and apatite during fluid-mediated replacement processes

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### Abstract

Apatite ( $\text{Ca}_5(\text{PO}_4)_3(\text{OH}, \text{F}, \text{Cl})$ ) is one of the main host of halogens in magmatic and metamorphic rocks and plays a unique role during fluid–rock interaction as it incorporates halogens (i.e. F, Cl, Br, I) and OH from hydrothermal fluids to form a ternary solid solution of the endmembers F-apatite, Cl-apatite and OH-apatite. Here, we present an experimental study to investigate the processes during interaction of Cl-apatite with different aqueous solutions (KOH, NaCl, NaF of different concentration also doped with NaBr, NaI) at crustal conditions (400–700 °C and 0.2 GPa) leading to the formation of new apatite. We use the experimental results to calculate partition coefficients of halogens between apatite and fluid. Due to a coupled dissolution–reprecipitation mechanism new apatite is always formed as a pseudomorphic replacement of Cl-apatite. Additionally, some experiments produce new apatite also as an epitaxial overgrowth. The composition of new apatite is mainly governed by complex characteristics of the fluid phase from which it is precipitating and depends on composition of the fluid, temperature and fluid to mineral ratio. Furthermore, replaced apatite shows a compositional zonation, which is attributed to a compositional evolution of the coexisting fluid in local equilibrium with the newly formed apatite. Apatite/fluid partition coefficients for F depend on the concentration of F in the fluid and increase from 75 at high concentrations (460  $\mu\text{g/g}$  F) to 300 at low concentrations (46  $\mu\text{g/g}$  F) indicating a high compatibility of F in apatite. A correlation of Cl-concentration in apatite with  $\text{Cl}^-$  concentration of fluid is not observed for experiments with highly saline solutions, composition of new apatite is rather governed by  $\text{OH}^-$  concentration of the hydrothermal fluid. Low partition coefficients were measured for the larger halogens Br and I and vary between  $0.7 * 10^{-3}$ – $152 * 10^{-3}$  for Br and  $0.3 * 10^{-3}$ – $17 * 10^{-3}$  for I, respectively. Br seems to have  $D$  values of about one order of magnitude higher than I. These data allow an estimation of the  $D$  values for the other halogens based on a lattice strain model which displays a sequence with  $D_{\text{F}}$  of  $\sim 120$ ,  $D_{\text{OH}}$  of  $\sim 100$ ,  $D_{\text{Cl}}$  of  $\sim 2.3$ ,  $D_{\text{Br}}$   $\sim 0.045$ , and  $D_{\text{I}}$   $\sim 0.0025$ . Results from this experimental study help to better understand fluid–rock interaction of an evolving fluid, as it enables the composition of hydrothermally derived apatite to be used as a fluid probe for halogens at crustal conditions. It further shows the importance of mineral replacement as one of the key reactions to generate apatite of different composition.

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## 1. INTRODUCTION

Apatite [ $\text{Ca}_5(\text{PO}_4)_3(\text{F}, \text{OH}, \text{Cl})$ ] is one of the most abundant accessory minerals occurring in many different rock types. It is often found to be one of the major hosts of mineral-bound halogens, especially for F, on Earth (Piccoli and Candela, 2002; Spear and Pyle, 2002; Douce et al., 2011; Teiber et al., 2014, 2015) as well as in extraterrestrial bodies (Boyce et al., 2010; McCubbin et al., 2011; Sarafian et al., 2013). Natural apatite is in most cases a ternary solid solution in which either F, OH or Cl occupy a 6-fold coordinated position between a triangular plane of Ca cations. The incorporation of many different elements (Pan and Fleet, 2002) makes apatite a useful tool for geochemical and isotopic studies, including conventional and fission track dating (Gleadow et al., 2002; Harrison et al., 2002; Li et al., 2012b); deciphering of magma evolution (Webster, 2004; Boyce and Hervig, 2009; Miles et al., 2014) and ore generation. Besides the rare earth elements (REE) (Harlov and Forster, 2002; Prowatke and Klemme, 2006; John et al., 2008) distribution of halogen group elements (mainly F and Cl) between apatite and melt have been the focus of many studies and has been used to calculate halogen concentrations of terrestrial magmas (Mathez and Webster, 2005; Webster et al., 2009; McCubbin et al., 2011; Marks et al., 2012; Sarafian et al., 2013). Furthermore, halogens in apatite allow estimation of water and halogen contents as well as isotopic features of extraterrestrial bodies, e.g., Moon, Mars or meteorites (McCubbin et al., 2010; Sarafian et al., 2013). Although, F and Cl concentrations of apatite are commonly measured and widely used, Br and I data of apatite are extremely scarce (O'Reilly and Griffin, 2000; Dong, 2005; Kendrick, 2012; Teiber et al., 2014, 2015) but allow to decipher the chemical behavior of halogens in geological processes due to their trace-element character, especially when using spatially resolved analytical techniques.

Halogens influence many geological processes due to their great impact on the petro-physical properties and stabilities of solid and liquid phases (Foley et al., 1986; Dingwell and Hess, 1998; Motoyoshi and Hensen, 2001; Douce et al., 2011; Bartels et al., 2013). They play an important role in the mobilization of otherwise rather immobile trace elements such as high-field-strength elements (HFSE) and REE and are generally regarded as the major player in the formation of ore deposits as the transport and mobility of ore forming elements in hydrothermal fluids are strongly dependent on their complexation by halogens (Williams-Jones et al., 2012). Halogen ratios (i.e. Br/Cl, I/Cl, F/Cl) differ for fluids derived from different geological settings and are used as a fluid tracer to distinguish between different fluid sources (John et al., 2011; Kendrick et al., 2011). Therefore, a quantification of the amount of all halogens in hydrothermal fluids is needed. Apatite formed in equilibrium with these fluids might provide an easy to use tool for measuring halogen contents of hydrothermal fluids if the distribution of halogens between fluid and apatite is understood.

In addition to the incorporation of halogens into the apatite structure, apatite reacts rather sensitively to changes

in the halogen environment in equilibrium with apatite via a coupled dissolution–precipitation process (Yanagisawa et al., 1999; Rendon-Angeles et al., 2000b,c; Putnis, 2002; Jonas et al., 2013). During mineral replacement reactions a parent mineral phase is dissolved into either a thin fluid film or larger fluid filled pore and a more thermodynamically stable mineral phase precipitates from this fluid (Fig. 1) (Pollok et al., 2011; Raufaste et al., 2011). A complex mineral zoning can be formed during replacement as a result of ultra-local equilibrium at the reaction interface (Borg et al., 2014). Natural examples showing a replacement of one phosphate, e.g., Cl-rich apatite or monazite by an apatite of, for instance, OH-rich composition are very common and can be found in almost all rocks undergoing fluid–rock interaction at crustal conditions (Harlov et al., 2002; Engvik et al., 2009; Ondrejka et al., 2012; Upadhyay and Pruseth, 2012).

Herein we present an experimental study performed at 0.2 GPa and temperatures between 400 and 700 °C, to further our understanding of the behavior of halogens during metamorphic replacement reactions. We use the experiments to determine partitioning of F between fluid and apatite at crustal conditions. Furthermore, this paper provides first partitioning data for Br and I, and expands the existing partitioning data for F between apatite and low concentration fluid.

## 2. EXPERIMENTAL

### 2.1. Cold-seal pressure vessel (CSPV) experiments

To obtain replacement reactions we conducted hydrothermal experiments using the cold-seal-pressure-vessel apparatus (CSVP) at the University of Muenster. For all experiments, end member chlor-apatite (Cl-Ap), synthesized following the procedure of Klemme et al.

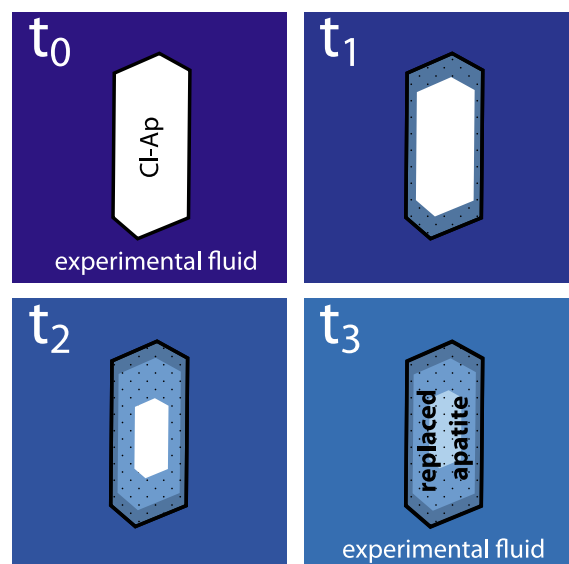


Fig. 1. General schematic illustration of apatite replacement at different times during experiment.

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