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The effect of fluorine and chlorine on trace element partitioning between apatite and sediment melt at subduction zone conditions

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ABSTRACT

The effect of F and Cl on trace element recycling during subduction-related sediment melting has been investigated by performing piston-cylinder experiments with a hydrous experimental pelite starting material (EPSM) with variable Cl (~0, 500, 1000, 2000, or 3000 ppm) and F (~0, 700, or 1500 ppm) concentrations, at 2.5 GPa, 800 °C. The variations of trace element concentrations in melt are systematically correlated with the variation of F (0.07–0.39 wt%) and Cl (0.07–0.39 wt%) contents. Trace elements Zn, V and Pb, and major elements Fe, Mg and Ca, show positive correlations with each other, and also with the Cl content in melt. The concentrations of light and medium rare earth elements (LMREE) increase with the Cl content in melt, whereas both F and Cl cause a decrease in the concentrations of high field strength elements (HFSE, such as Nb, Ta, Zr and Hf). Trace element (REE, Y, Sr, Th, U) concentrations in apatite are found to increase with the mole fraction of chlorapatite (ClAp). The preference for ClAp is stronger for cations with higher charge (e.g., Th^{4+}, U^{4+} > REE^{3+}) and larger ionic radii (e.g., LREE > HREE).

Trace element partition coefficients between apatite and melt show up to 4 times variation between experiments, e.g., $D_{La}^{Ap\text{-}melt}$ = 77–281; $D_{Sm}^{Ap\text{-}melt}$ = 176–519; $D_{Sr}^{Ap\text{-}melt}$ = 4–12 and $D_{Th,U}^{Ap\text{-}melt}$ = 4–19. The REE partition coefficients between apatite and melt ($D_{REE}^{Ap\text{-}melt}$) display a concave pattern with the peak at Sm/Nd and a negative Eu anomaly, and are significantly higher than previously reported values for partitioning experiments conducted at lower pressures and higher temperatures. The high values of $D_{LREE}^{Ap\text{-}melt}$ demonstrate the importance of apatite in terms of LREE partitioning during sediment melting, while allanite/monazite still dominates the partitioning of Th. In the absence of allanite/monazite, apatite-buffered melt is characterized by a significant enrichment of Th relative to La. Because of the contrasting behavior of LREE and HFSE in melt with the addition of Cl and F, the fractionation of these elements in slab-derived sediment melts will be enhanced by the presence of halogens.

1. Introduction

Arc basalts display distinctive trace element signatures that include marked enrichment of Pb, large ion lithophile elements (LILE) and light rare earth elements (LREE) relative to high field strength elements (HFSE) and heavy rare earth elements (HREE). Many of these elements are not significantly fractionated from each other during mantle melting and subsequent differentiation. Therefore, their variable enrichment in arcs has been taken to reflect the addition of a subduction component (Hawkesworth et al., 1993; Stolper and Newman, 1994). The $^{10}Be/Be$ ratio, Nd, Sr, Pb isotopic compositions of arc magmas (Hawkesworth et al., 1993) and correlations between the chemical characteristics of subducted sediment and arc volcanics (Plank and Langmuir, 1993), all provide definitive evidence of a sediment contribution to arc volcanism. There is increasing evidence that the aqueous fluids formed by dehydration of subducted slab are dilute in both major and trace elements (Green and Adam, 2003; Kessel et al., 2005; Manning, 2004; Spandler et al., 2007), therefore sediment melt may act as the primary agent for transporting incompatible elements from the slab to the mantle wedge (Hermann and Rubatto, 2009; Hermann and Spandler, 2008; Klimm et al., 2008; Plank et al., 2009).

A considerable number of experimental studies have investigated sediment melting at subduction zone conditions (Auzanneau et al., 2006; Hermann and Rubatto, 2009; Hermann and Spandler, 2008; Li and Hermann, 2015; Mann and Schmidt, 2015; Nichols et al., 1994; Schmidt, 2015; Schmidt et al., 2004; Skora and Blundy, 2010; Skora et al., 2015; Spandler et al., 2010; Thomsen and Schmidt, 2008; Tsuno and Dasgupta, 2011, 2012). However, only a few previous studies (Li

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and Hermann, 2015, 2017; Nichols et al., 1994) involved sediment compositions containing F and Cl. The addition of F and Cl has been shown to enhance trace element partitioning into aqueous fluids (Antignano and Manning, 2008; Bali et al., 2011, 2012; Bernini et al., 2013; Brenan et al., 1995; Keppler, 1996; Rapp et al., 2010; Schmidt et al., 2007; Tanis et al., 2016; Tropper et al., 2011, 2013; Tsay et al., 2014, 2017). However, to date, there have been no experimental investigations into the F and Cl effect on trace element uptake in sediment melt.

To address this question, we have examined the trace element compositions of melt produced by F, Cl-doped sediment melting at fixed *PT* conditions of 2.5 GPa, 800 °C. We also report the F and Cl effect on both trace element compositions of apatite and the resultant partition coefficients between apatite and melt. Implications in regard to the role of apatite during trace element recycling within subduction zones are also discussed. Apatite has been recognized as the major host for Phosphorous; however, discussions regarding LREE and Th recycling have focused primarily on the role of monazite (Hermann and Rubatto, 2009; Plank, 2005; Skora and Blundy, 2012; Stepanov et al., 2012) and allanite (Hermann and Rubatto, 2009; Hermann, 2002; Klimm et al., 2008). Apatite can also contain a significant amount of LREE, moreover, it is a ubiquitous accessory mineral in subducted lithologies (e.g., Spandler et al., 2003), and stable over a wide range of *PT* conditions (up to 7.5 GPa in subduction zones, Konzett and Frost, 2009). Therefore, knowledge of LREE partitioning between apatite and fluid/melt in subduction zone settings provides additional constraints on LREE recycling.

2. Methods

The set of experiments selected for this study has been previously reported in Li and Hermann (2015, 2017), in regards to F and Cl partitioning between apatite and melt. F, Cl and major element compositions for melt and apatite are listed in Tables A.1 and A.2 for easy reference. For details of major element analytical methods, please refer to the two publications mentioned above, whereas the experimental, analytical and theoretical methods outlined below focus primarily on the study of trace elements in melt and apatite.

2.1. Starting material

A synthetic experimental pelite starting material (EPSM, Table 1), which has a composition similar to both the average composition of "Global Subducting Sediment" (GLOSS, Plank and Langmuir, 1998) and upper continental crust (Rudnick and Gao, 2003), was used to produce sediment melts at 2.5 GPa, 800 °C. The staring compositions (EPSM-1–10, Table 2) have the same major element and H_2O contents, but variable Cl (~0, 500, 1000, 2000, or 3000 ppm) and F (~0, 700, or 1500 ppm) concentrations. The lower end of the bulk Cl range (~1.6% NaCleq for EPSM-4, 6) is comparable to the salinity of fluid produced by high-pressure antigorite breakdown (0.4–2 wt% NaCleq, Scambelluri et al., 2004), while lower bulk F contents (~700 ppm) are similar to those of the upper continental crust (e.g., 557 ppm, Rudnick and Gao, 2003). The high end for bulk Cl (~6.4% NaCleq for EPSM-8) is well within the range reported for arc magmas, e.g., 1–10% NaCleq (Wallace, 2005).

The "sol-gel" method was used to produce a trace element-doped SiO_2 gel by mixing trace elements in the form of nitrate solutions into tetraethyl orthosilicate [$Si(C_2H_5O)_4$]. The SiO_2 gel was then combined with reagent grade oxides, carbonates and phosphates, and the mixture was devolatilized at 1000 °C. F, Cl and H_2O-bearing intermediate starting compositions were prepared by adding synthetic fayalite, $Al(OH)_3$, NaCl and CaF_2 to the sintered mixture as the source of Fe, H_2O, Cl and F, respectively. EPSM-1–10 with variable F and Cl contents, were produced by blending F, Cl and H_2O-bearing intermediate starting compositions at various ratios. The actual trace element concentrations in EPSM were determined by analyzing a sintered mixture prepared for one of the intermediate starting compositions. This sintered mixture does not contain Al, Fe or volatiles and has a SiO_2 content of 81.4 wt%. It was fused at 1500 °C in a box furnace for a few minutes and quenched to glass, then analyzed for trace element contents by LA-ICPMS. As trace elements were added to the silica gel, the ratio of trace element concentration to SiO_2 content is constant among all starting compositions. The trace element compositions of EPSM were subsequently calculated based on the SiO_2 content of 64 wt% (Table 1). The resultant bulk Pb content (18 ± 9.7 ppm) is significantly lower than expected, which may be due to Pb loss during the fusion process. The actual bulk Pb content is estimated to be 50 ± 10 ppm based on the Pb concentrations in melt and the assumption that Pb and Sr have similar incompatibility.

Table 1
Major and trace element compositions of EPSM and their comparison to GLOSS (Plank and Langmuir, 1998) and upper continental crust (Rudnick and Gao, 2003).

	EPSM		GLOSS		UCC
wt%			(P & L98)		(R & G03)
SiO_2	63.56		58.57		66.62
TiO_2	0.62		0.62		0.64
Al_2O_3	13.57		11.91		15.4
FeO	4.31		5.21		5.04
MnO	0.10		0.32		0.1
MgO	2.32		2.48		2.48
CaO	2.26		5.95		3.59
Na_2O	2.42		2.43		3.27
K_2O	2.71		2.04		2.8
P_2O_5	0.92		0.19		0.15
H_2O	7.20		7.29		
F (ppm)					557
Tot.	100		97.01		100.09
ppm		*σ*		*σ*	
Li	37	*1.0*			21
Be	6	*0.2*			2.1
B	166	*3.3*			17
Sc	39	*2.1*	13.1	*1.03*	14
Ti	3833	*135*			
V	95	*4.5*	110	*10.7*	97
Mn	1228	*38.6*			
Zn	76	*13*	86.4	*8.88*	67
Rb	64	*0.9*	57.2	*6.66*	84
Sr	471	*33*	327	*53.8*	320
Y	32	*1.8*	29.8	*9.92*	21
Zr	117	*8*	130	*8.5*	193
Nb	72	*4.2*	8.94	*0.94*	12
Cs	56	*1.0*	3.48	*0.5*	4.9
Ba	867	*66*	776	*137.1*	624
La	63	*3.4*	28.8	*6.8*	31
Ce	98	*5.9*	57.3	*10.3*	63
Pr	57	*3.7*			7.1
Nd	63	*3.9*	27	*8.3*	27
Sm	61	*3.7*	5.78	*1.83*	4.7
Eu	58	*3.6*	1.31	*0.44*	1
Gd	59	*3.5*	5.26	*2.04*	4
Dy	63	*3.7*	4.99	*1.86*	3.9
Er	31	*1.8*	2.92	*1.06*	2.3
Yb	32	*1.8*	2.76	*0.88*	2
Lu	31	*1.9*	0.413	*0.133*	0.31
Hf	34	*2.8*	4.06	*0.3*	5.3
Ta	27	*1.9*	0.63	*0.06*	0.9
Pb	50	*10*	19.9	*5.4*	17
Th	31	*2.3*	6.91	*0.8*	10.5
U	35	*2.0*	1.68	*0.18*	2.7

Italic format is used for the standard deviation, in contrast to the regular font for the data. Such a choice is purely for the ease of distinguishing between the data and standard deviation.

2.2. Experimental techniques

All experiments were performed using a piston-cylinder apparatus