Chemical Geology 312–313 (2012) 118–126

Contents lists available at SciVerse ScienceDirect

Chemical Geology

journal homepage: www.elsevier.com/locate/chemgeo

Research paper

Effect of fluorine on near-liquidus phase equilibria of an Fe–Mg rich basalt

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ARTICLE INFO

Article history:
Received 17 December 2011
Received in revised form 9 April 2012
Accepted 17 April 2012
Available online 25 April 2012

Editor: D.B. Dingwell

Keywords:
Halogens
Martian meteorites
Alkali basalts
Basalt crystallization
Phase equilibria
Fluorine

ABSTRACT

Volatile species (H_2O, CO_2, F, Cl, etc.) have important effects on the formation and crystallization history of basaltic magmas. Here, we have experimentally investigated the effects of F on phase equilibria of Fe–Mg-rich basalt. Our results show that fluorine has large effects on the liquidus temperature and the chemistry of crystallizing minerals. Compared to the F-free system, addition of ~2 wt.% F moves the olivine-pigeonite liquidus point down ~2 kbar and 95 °C (from 12 kbar, 1375 °C to 10 kbar, 1280 °C). With increasing fluorine concentrations, $Kd^{Fe-Mg}_{Mineral\text{-}Melt}$ dramatically increases for both pyroxene and olivine, suggesting that fluorine in basaltic magmas complexes primarily with MgO. Complexing with MgO in the melt decreases its MgO activity, and forces the crystallizing minerals to greater Fe/Mg, and so increases $Kd^{Fe-Mg}_{Mineral\text{-}Melt}$. Models of basalt generation, where the magma is fluorine-rich, need to include the effect of not only water but fluorine on liquidus depression and minerals crystallizing/melting. Our results suggest that fluorine may significantly aid in the petrogenesis of silica-poor, alkali-rich magmas in the Earth and Mars.

1. Introduction

Volatile species (H_2O, CO_2, F, Cl, etc.) are important in basalt genesis and mantle melting in arc, plume, ridge, and other planetary tectono-magmatic settings. Previous experimental work has mainly focused on the effects of water and carbon dioxide on liquidus temperature, phase relations, and compositions of basalts produced in these systems (e.g., Green, 1970; Mysen, 1975; Gaetani and Grove, 1998; Danyushevsky, 2001; Grove et al., 2002; Nekvasil et al., 2004; Feig et al., 2006; Grove et al., 2006; Dasgupta et al., 2007; Médard and Grove, 2008; Feig et al., 2010; Gerbode and Dasgupta, 2010). The effects of halogens in general, and those of fluorine in particular, have received far less attention (e.g., Foley et al., 1986; Brey et al., 2009; Filiberto and Treiman, 2009a, 2009b). However, melts in planetary interiors can have non-negligible halogen concentrations, and the importance of chlorine and fluorine in basalt petrogenesis has been emphasized in recent literature both for Earth (Aoki et al., 1981; Brey et al., 2009) and Mars (Filiberto and Treiman, 2009a,b). Here, we explore the effects of fluorine on near-liquidus phase equilibria of a basalt.

1.1. Fluorine concentrations in terrestrial magmas

Evolved magmas (rhyolites and phonolites) can contain more than 5 wt.% F (e.g., Carroll and Webster, 1994; Webster et al., 1997; Harms and Schmincke, 2000; Giordano et al., 2004); basaltic magmas typically contain less F than their evolved counter parts as summarized by Aoki et al. (1981) and Stecher (1998) for continental and oceanic basaltic rocks. They found that the abundance of F typically correlates with that of K_2O for most basaltic magmas, although this correlation breaks down at high K_2O concentrations. In tholeiites, F concentrations range from 30 to 1000 ppm (Yoshida et al., 1971; Aoki et al., 1981; Stecher, 1998); higher primitive fluorine concentrations are seen in alkali rich rocks: nephelinites and kimberlites have concentrations up to 2000 ppm; and some lamproites contain up to 20,000 ppm (2 wt.%) F (Aoki et al., 1981). This suggests that fluorine may be especially important for alkali-rich basaltic magmas. For example, primitive mantle of the Earth is estimated to have 25 ppm F (McDonough and Sun, 1995), thus with bulk partition coefficient of ~0.08 during mantle melting (Dalou et al., 2012), 0.1 to 2 wt.% partial melts will have F concentration of ~300 ppm (Fig. 1).

1.2. Fluorine concentrations in Martian magmas

Less is known about the fluorine concentrations of Martian magmas. Bulk fluorine contents of the Martian basalts (meteorites)

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doi:10.1016/j.chemgeo.2012.04.015

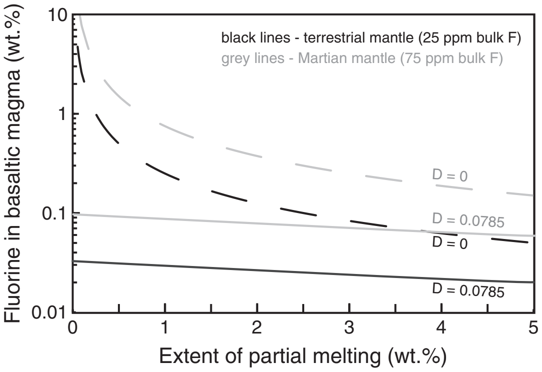

Fig. 1. Plausible concentration of fluorine in near-solidus partial melts of garnet peridotite as a function of melting degree for Earth (bulk F concentration from McDonough and Sun, 1995) and Mars (assuming that Martian mantle contains three times F than that in the Earth's mantle). Bulk partition coefficient, D_F (peridotite-basalt), of 0.0785 is used based on olivine-melt D_F of 0.1164, opx-melt D_F of 0.0158, cpx-melt D_F of 0.0428, and garnet-melt D_F of 0.0123 from the study of Dalou et al. (2012). Garnet melt, opx-melt, and cpx-melt D_F values are taken from the experiment C4p#25kb and that of olivine-melt D_F from the experiment CC01#8kb4 of Dalou et al. (2012). Peridotite mineral modes used for the calculations are 60% olivine, 20% opx, and 10% each of cpx and garnet. Because of the uncertainties in D_F (mineral-melt) for Martian mantle phase compositions, melt compositional trends for $D_F = 0$ are also shown for reference.

are similar to those of terrestrial tholeiites (29–41 ppm, Dreibus and Wänke, 1985). But based on the F to Ti ratio, Martian basalts and the bulk Martian mantle are thought to be 2–3 times richer in F (and other halogens) than terrestrial basalts and mantle (Treiman et al., 1986; Dreibus and Wänke, 1987). If the F content of the Martian mantle were three times greater than that of the Earth, similar low degree partial melting (as in the example above, 0.1–2 wt.%) should yield magmas with 950 to 750 ppm F (Fig. 1). Further, alkalic basalts (typically rich in fluorine on Earth) have been suggested to occur, and maybe significant, on Mars (McSween et al., 2006; Dunn et al., 2007; Nekvasil et al., 2007). All of this, and the chemistry of volatile-bearing minerals in Martian meteorites (amphiboles and apatite) suggests that fluorine, like chlorine (Patiño Douce and Roden, 2006; Filiberto and Treiman, 2009a, 2009b; Patiño Douce et al., 2011), may be an important factor controlling basalt genesis in Mars (possibly to the extent of replacing water as the dominant volatile species).

1.3. Previous work on fluorine in igneous systems

Previous studies on fluorine in magmatic systems have mainly focused on the solubility mechanisms of F in aluminosilicate (±Na) melt and its effect on melt viscosity (Schaller et al., 1992; Zeng et al., 1999; Liu and Nekvasil, 2002; Liu and Tossell, 2003; Mysen et al., 2004). Nuclear magnetic resonance (NMR) studies of aluminosilicate glasses have shown that fluorine preferentially complexes with Al and possibly Si (Schaller et al., 1992; Zeng et al., 1999; Liu and Nekvasil, 2002; Liu and Tossell, 2003). For Na-aluminosilicate glasses four predominant complexes have been identified: Na–F, Na–Al–F (with Al in 4-fold coordination), Na–Al–F (with Al in 6-fold coordination), and Al–F (with Al in 6-fold coordination) (Zeng and Stebbins, 2000; Mysen et al., 2004). By complexing predominantly with Al in silica-rich magmas, F decreases their viscosity by depolymerizing the melt (Dingwell et al., 1985; Dingwell, 1989; Dingwell and Hess, 1998; Giordano et al., 2004; Zimova and Webb, 2007). This is a similar effect on melt structure and viscosity as dissolved water (e.g., Giordano et al., 2004).

Similar to NMR studies, most experiments on phase equilibria in F-bearing magmas have been on granitic or simplified systems (e.g., Manning, 1981; Foley et al., 1986; Weidner and Martin, 1987; Xiao-lin et al., 1999; Scaillet and MacDonald, 2001; Xiong et al., 2002; Scaillet and MacDonald, 2003, 2006; Dolejs and Baker, 2007a, 2007b; Lukkari and Holtz, 2007). Fluorine has dramatic effects on crystallizing phases (e.g., Manning, 1981; Foley et al., 1986; Dolejs and Baker, 2007a, 2007b). At 1 bar, in the Qz–Ab–Or–H_2O system, addition of fluorine shifts the boundary of the quartz-alkali feldspar liquidus field away from the quartz apex; addition of 4%wt F shifts the minimum melting compositions from $Qz_{37}Ab_{34}Or_{29}$ to $Qz_{15}Ab_{58}Or_{27}$ (Manning, 1981). In the $NaAlSiO_4$–$CaMgSi_2O_6$–SiO_2 system, also at 1 bar, fluorine reduces the liquidus temperature and changes the compositions of the liquids produced (Luth, 1988a). For example, the liquid in equilibrium with diopside at 1250° C in the F-bearing experiments is $Di_{56}Ab_{44}$ compared with $Di_{33}Ab_{67}$ in the F-free experiments. The results suggests that F is complexing with Ca and Mg in the liquid in a $NaAlSiO_4$–$CaMgSi_2O_6$–SiO_2 simplified system (Luth, 1988a). At higher pressure (28 kbar) in the $KAlSiO_4$–Mg_2SiO_4–SiO_2 system, fluorine expands the field of enstatite stability with respect to that of forsterite by complexing with Mg, K, and Al in the melt (Foley et al., 1986).

However, the solution mechanism for F in natural basaltic melts maybe more complicated than in the simple systems. Recent NMR work has shown that a significant proportion (>30%) of dissolved fluorine complexes with Mg (Kiczenski et al., 2004); while experimental results combined with NMR and Raman spectroscopy studies have suggested that F may complex with Ca (Luth, 1988b; Zeng and Stebbins, 2000). Fluorine complexation with cations other than Al will not only lower the liquidus and affect the viscosity, but also change the phase relations of crystallizing magmas. However, these complexations are presumably bulk composition dependent.

In order to understand how fluorine behaves in a Si-poor, Mg, Fe-rich basaltic system we have experimentally determined near liquidus phase relations of a synthetic basalt doped with F. The results of these experiments can be directly compared with our previous work on the same synthetic basalt conducted nominally volatile-free (Filiberto et al., 2008) and doped with chlorine (Filiberto and Treiman, 2009a).

2. Methods

2.1. Experimental approach

2.1.1. Starting composition

We have conducted nominally anhydrous piston cylinder experiments on an Fe-rich model basalt composition synthetic starting material (Table 1). The choice of the basalt composition was motivated by the fact that the same composition had previously been used to study the effect of chlorine on near-liquidus phase equilibria (Filiberto and Treiman, 2009a). The synthetic starting material was made from reagent grade oxides and carbonates ground together under acetone in an automatic mortar and pestle for 15 min to ensure

Table 1
Starting composition. Average composition of experiments containing all glass.

wt.%		+/–
SiO_2	45.97	0.35
TiO_2	0.55	0.01
Al_2O_3	10.40	0.07
FeO_T	19.30	0.10
MnO	0.42	0.01
MgO	10.63	0.10
CaO	7.79	0.04
Na_2O	2.44	0.05
K_2O	0.10	0.01
P_2O_5	0.44	0.02
F	2.17	0.36
Total	100.21	

FeO_T = total iron (Fe_2O_3 + FeO).