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Experimentally determined distribution of fluorine and chlorine upon hydrous slab melting, and implications for F–Cl cycling through subduction zones

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Abstract

Fluorine and chlorine are volatile elements known to be enriched in primitive arc magmas, and variations of F/Cl ratios can carry information about slab devolatilization processes. Recent experiments on the fractionations of these elements suggest that aqueous fluid has limited capacity to enrich the magma source region in F. Hence, it is difficult to explain observations of primitive arc magmas particularly rich in F. To complement previous experimental studies, we examined the fractionation of fluorine and chlorine during hydrous partial melting of subducting slab. Element-doped phase equilibria experiments were carried out in a complex chemical system at conditions equivalent to potential slab melting temperatures (750–1000 °C) across the amphibolite to eclogite facies transition (1.3–3 GPa). Partition coefficients of F and Cl between hydrous silicic melts and minerals were determined by electron microprobe and/or ion probe. Fluorine is compatible in amphibole ($D_F^{amp/glass} = 1.18$–1.85), and incompatible in garnet (0.034–0.140), clinopyroxene (0.059–0.505), and allanite (0.205–0.504). Hence, amphibole is an important F host, and can retain significant quantities of F in the solid residue of partial melting. On the contrary, Cl is incompatible, with $D_{Cl}^{mineral/glass}$ generally decreasing from amphibole (0.079–0.625; one outlier at 1.87) to allanite (0.163), clinopyroxene (0.066–0.158), and garnet (0.031–0.153; outlier at 0.492). As a result, Cl is easily mobilized during partial melting. Fluorine and chlorine release during slab melting have been quantified by applying our partition coefficients to a non-modal batch melting model. The model shows that amphibole plays a key role in F/Cl fractionation during partial melting, while F/Cl is close to that of source for the melting of amphibole free eclogite. Moreover, the results from a flux-melting model employing several source compositions are compared to F and Cl abundances in primitive arc magmas. The observed variations are best described by variable additions of slab-derived aqueous fluids and hydrous melts to the mantle wedge melting region.

1. INTRODUCTION

Devolatilization of subducting slab is a cornerstone of arc magmatism (e.g. Schmidt and Poli, 2014 for a recent review). Volatile elements can enhance melting, facilitate mass transfers from the slab to the mantle wedge, lower rock and melt viscosity, and influence magma crystallization and volcanic eruption dynamics. Hence, volatiles such as H, C, S, Cl and F potentially hold crucial information on generation, transport and evolution of arc magma. Their study in volcanic rocks and melt inclusions, often in combination with non-volatile trace elements, has benefited significantly from the ongoing advances of microanalytical techniques. It has been unequivocally demonstrated that arc magmas are richer in volatile elements than other

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mantle derived melts, such as MORB and OIB (e.g. Anderson, 1974; Perfit et al., 1980; Arculus and Johnson, 1981; Sisson and Layne, 1993; Saal et al., 2002; Straub and Layne, 2003). However, there remain unknowns such as exact provenance, quantity, and pressure–temperature conditions of volatile transport.

Volatile budgets of arc magmas have been estimated through melt inclusion studies. Early crystallizing phases, such as olivine, can isolate tiny batches of magma as inclusions in the deep crust, possibly retaining undegassed volatile contents. Through interpretation of H_2O–CO_2 data, it is possible to exclude modified magmatic compositions, and the filtered data is generally thought to show that primary arc magmas contain around 4–6 wt% H_2O (Plank et al., 2013). However, recent studies have identified further complications. Several experimental data sets have shown olivine to be a leaky H_2O container (Chen et al., 2011; Gaetani et al., 2012), hence many of the earlier conclusions based on H_2O concentrations of melt/fluid inclusions require re-examination. Furthermore, because CO_2 degassing likely starts prior to melt entrapment (Saal et al., 2002), it is clear now that H_2O–CO_2 abundances of primary magmas cannot be directly measured in natural samples.

Fluorine and chlorine are volatile elements that are to variable extents enriched in primitive arc magmas. For example, Straub and Layne (2003) report enriched F and Cl contents in melt inclusions from the Izu-Bonin arc. They showed nearly complete transfer of Cl, and limited transfer of F, out from the slab to arc magma. Since these elements only start to degas at lower pressures than other volatile elements (Spilliaert et al., 2006), it is possible to find primitive F and Cl abundances in arc melt inclusions (e.g. Le Voyer et al., 2010; Bouvier et al., 2010a,b). Fig. 1 illustrates that arc basalts have systematically higher Cl concentrations than MORB, mirroring the systematics displayed by H_2O. In contrast, F concentrations of several arc magmas are on the same level as MORB, while other arc magmas are significantly enriched (Fig. 1). For example, F contents of some magmas from the Japan and Izu arcs are identical to those of MORB data, indicating nearly no enrichment

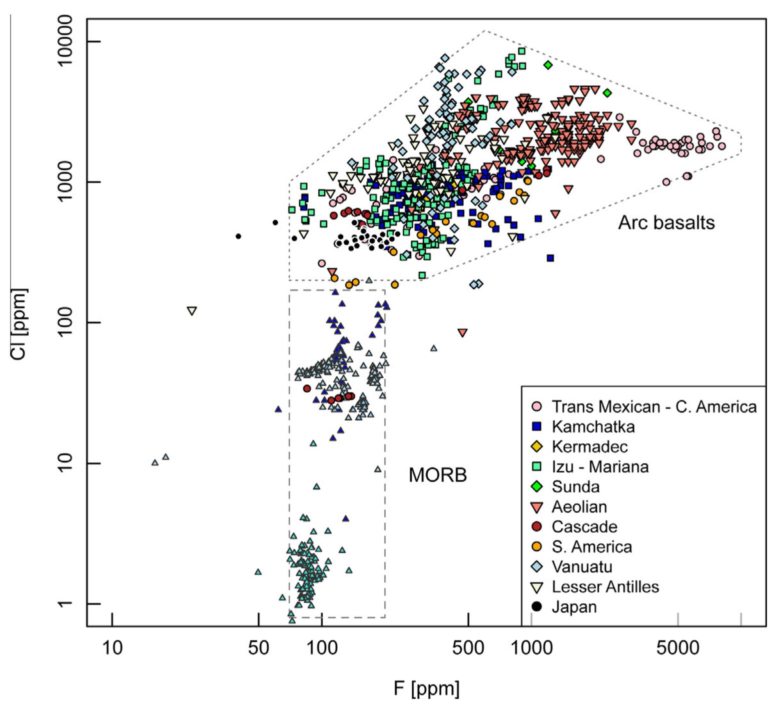

Fig. 1. F and Cl concentrations of mid-ocean ridge basalt (MORB) and basaltic arc magmas that are sampled in olivine hosted melt inclusions. Arc magmas are systematically higher in Cl concentration, while F concentrations of some arc magma are on the same order as MORB magma. Upwards pointing triangles represent MORB olivine-hosted melt inclusion samples from Gakkel Ridge (Shaw et al., 2010), Juan de Fuca Ridge (Wanless and Shaw, 2012), East Pacific Rise (Wanless and Shaw, 2012), and Siqueiros Transform Zone (Saal et al., 2002). Nearly all MORB inclusion data plot within the area indicated by the dashed gray line, excluding some outliers. Similarly, the majority of primitive arc magmas plot in the area delimited by the dotted gray line. Data from all currently available olivine-hosted magmatic inclusions for which both F and Cl was reported, are plotted on this figure. Exceptions are the data of Straub and Layne (2003), which reports cpx- and plagioclase-hosted inclusion data, with 24 out of 41 inclusion compositions more evolved than basaltic andesite. Since this is a well-cited pioneering study reporting F and Cl contents of arc magma inclusions, they are included. A second exception is the Kermadec data (Wysoczanski et al., 2006), which reports compositions of glasses from a deep submarine eruption. The following references are used to construct the figure: Trans Mexican – Central America arcs (Sadofsky et al., 2008; Vigouroux et al., 2008), Kamchatka arc (Churikova et al., 2007; Portnyagin et al., 2007), Izu – Mariana arc (Straub and Layne, 2003; Shaw et al., 2008; Kelley et al., 2010), Sunda (Elburg et al., 2007; Sorbadere et al., 2013), Aeolian arc (Métrich et al., 1993, 2004; Vaggelli et al., 1993; Clocchiatti et al., 1994; Schiano et al., 2004; Spilliaert et al., 2006; Collins et al., 2009; Rose-Koga et al., 2012; Sorbadere et al., 2013), Cascades (Le Voyer et al., 2010), South America (Le Voyer et al., 2008), Vanuatu (Sorbadere et al., 2011, 2013), Lesser Antilles (Bouvier et al., 2008, 2010a,b), Japan (Rose-Koga et al., 2014).