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The fluorine dichotomy: Amphibole control on fluorine availability during magmatic differentiation

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Abstract

Experimental and observational evidence suggests that water and fluorine (F) are incompatible in silicate minerals and originate from similar sources in the mantle. This, in turn, suggests that F and water should coevolve in magmatic systems. However, hydrous subduction zone ("arc") magmas are depleted in F relative to anhydrous magmas. We explore this apparent dichotomy in fluorine's behavior by examining amphibole, which preferentially incorporates F into its crystal structure. By developing a parametrized fluorine amphibole/silicate melt partition coefficient for F, we show that F concentrations in calculated equilibrium melts in arc systems do not increase with differentiation. This indicates that F behaves compatibly in hydrous arc magmas due to sequestration in amphibole-bearing arc cumulates. In dry magmatic systems, where amphibole does not crystallize, we show that F behaves incompatibly during differentiation, resulting in F enrichment in evolved magmas. These results have implications for the formation of ore deposits associated with elements that complex with F, such as rare-earth elements.

Keywords: Ore deposit; Delamination; Halogens; Deep volatile cycling; Magmatic differentiation.

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1 Introduction

Volatiles play an important role in magmatism, particularly in arc settings. In subduction zones, volatiles decrease the solidus temperature, facilitating melting at lower temperatures. At lower pressures, volatiles can help drive volcanic eruptions and transport metals from magmas to ore deposits [Hedenquist and Lowenstern 1994; Gonnermann and Manga 2007; Grove et al. 2012]. Understanding how different volatiles behave in magmatic settings is thus relevant to understanding the spatial distribution of magmatism on Earth, the nature of volcanic hazards, and the formation of mineral deposits critical for society.

Fluorine (F) is of special interest because it may behave differently compared to water and chlorine (Cl). Experimental and observational evidence suggests that water and fluorine are incompatible in most silicate minerals and originate from similar sources in the mantle [Straub and Layne 2003; Kendrick et al. 2017; Barnes et al. 2018; Urann et al. 2020]. Fluorine is thus thought to behave like water or Cl, which are incompatible and hence become progressively enriched in residual magmas with progressive differentiation before fluid saturation [Moore 1970; Straub and Layne 2003; Workman et al. 2006; Kendrick et al. 2017; Borchardt and Lee 2024]. However, arc magmas, which are water-rich, do not exhibit high F concentrations [Barnes et al. 2018]. Meanwhile, igneous intrusions formed in extensional or post-orogenic settings, generally away from the immediate influences of subduction zone volcanism, are frequently enriched in F, but relatively poor in water [Christiansen et al. 1986; Taylor and Fallick 1997; Christiansen et al. 2007].

These observations are also mirrored in fluorine's behavior in ore systems. In subduction zones, porphyry copper deposits form through the shallow degassing of a magma body, and ore deposits appear to be associated with Cl-bearing fluids [Dilles 1987; Seedorff et al. 2005; Sillitoe 2010]. Despite the large amount of water and Cl fluxed through these subduction zone related deposits, porphyry copper systems show little to no F alteration, and economic deposits of F are absent [Seedorff et al. 2005; Sillitoe 2010]. Meanwhile, dry rift-related magmatic environments often form economic deposits related to F, with the F sourced from magmas [Van Alstine 1976; Partey et al. 2009]. These first order observations lead to an apparent paradox. Whereas Cl seems to follow water, this is not the case for F [Moore 1970; Borchardt and Lee 2024].

Any insights into what controls F behavior could enhance understanding of how magmas differentiate in different tectonic settings. A better understanding of fluorine's behavior in different magmatic environments could also shed light on continent formation and lithosphere recycling [Han et al. 2023]. There are also implications for the formation of certain ore deposits. For example, F complexes with rare earth elements (REEs) and may play a role in controlling the REE mobility during magmatic differentiation [Agangi et al. 2010; Vasyukova and Williams-Jones 2016; Xue et al. 2024]. Coincidentally, REE deposits can be found in anorogenic, alkaline magmas, which are often associated with elevated levels of F and F-bearing minerals, such as topaz or fluorite [Burt et al. 1982; Siegel et al. 2018]. In contrast, REE deposits and F-bearing minerals (apart from apatite) are generally rare in arc magmas. Thus, understanding how F evolves in magmatic systems may provide an important clue to the spatiotemporal distribution of silicate magma-hosted REE deposits.

As a step towards understanding F systematics in magmatic systems, we explore here the behavior of F during the differentiation of arc and rift magmas. Much of our understanding of F in these systems is based on mineral-hosted melt inclusions [Straub and Layne 2003; Barnes et al. 2018]. These studies, however, tend to focus on primitive melt inclusions hosted in

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olivines and therefore were not designed to capture the entire differentiation process. Here, we turn to amphibole to reconstruct magma F contents during differentiation. Amphibole incorporates F into its crystal structure, thereby preserving a record of magma F contents [Oberti et al. 2007]. Amphibole also crystallizes from both primitive and evolved arc magmas, providing insights into a broad window of magmatic differentiation.

2 Methods

From the precompiled GEOROC database of amphiboles, we select mineral grains from extrusive and intrusive igneous rocks in convergent margins and rifts [DIGIS Team 2021]. Our treatment of data follows that of Borchardt and Lee [2024]. The dataset is first filtered to only include amphiboles with dry weight totals between 95.5 and 98.5 wt.%, resulting in 1793 samples. To remove the effect of extreme outliers, we exclude samples (n = 28) with F contents greater than 5 standard deviations above the mean F value of the dataset. Amphiboles with CaO and MgO contents 3 standard deviations below the mean CaO and MgO of the total amphibole population are also removed (n = 73). The low CaO samples are dominantly from the Mg-Fe-Mn amphibole group, which are atypical of arc igneous amphiboles. Low MgO samples are from one study focusing on unusual A-type magmas and are not typical arc amphiboles [Molina et al. 2020]. The remaining arc amphiboles represent arc magmas from a wide variety of locations and different arc settings [Borchardt and Lee 2024]. Rift-related amphiboles are primarily from continental rift settings with most of the data collected from the Rio Grande Rift or the Basin and Range.

To examine how F evolves in arc magmas, we need to quantify the extent of magmatic differentiation. Mg# (molar (Mg/(Mg+Fe^{2+})×100) is traditionally used as a differentiation index for mafic systems [Asimow 2021], but it does not effectively differentiate between amphiboles in mafic and felsic systems. Mg# as a differentiation index in amphiboles likely fails because the iron content of amphiboles does not directly correlate with melt composition [Ridolfi and Renzulli 2012; Borchardt and Lee 2024]. However, Ridolfi and Renzulli [2012] showed that Si and Al contents of amphibole evolve with melt evolution. In a global compilation of arc amphiboles, Borchardt and Lee [2024] demonstrated that Al_T/Si_T (where Al_T and Si_T are cation proportions associated with the tetrahedral site) distinguishes between mafic and felsic magmas. Al_T/Si_T decreases with increasing differentiation or increasing silica content of the host magma. Low Al_T/Si_T ratio (~0.1) amphiboles are from felsic magmas, while high Al_T/Si_T (~0.3) represents amphiboles from mafic magmas.

We divide amphiboles into mafic and felsic groups using rock name metadata attached to each amphibole from the GEOROC database to examine how Al_T/Si_T works as a differentiation index. Amphiboles that were sampled from host rocks identified as basalt, hawaiite, picrite, basaltic andesite, basaltic trachyandesite, trachytic basalt, trachyandesite, trachybasalt, andesite, gabbro, alkaline gabbro, diorite, hornblendite, tonalite, shoshonite, mugearite, foidite, and monzodiorite were considered mafic. Amphiboles from rocks identified as rhyolite, dacite, trachyte, rhyodacite, trachydacite, phonolite, granodiorite, monzodiorite, monzogranite, granite, and syenite were considered felsic. These categorizations are not perfect as igneous rocks and their associated minerals fall on a continuous compositional spectrum, but it is still informative about the overall behavior of later differentiation indices and chemometric equations.

3 Results

We classify amphiboles using the scheme of Hawthorne et al. [2012], as implemented by Locock [2014]. To observe trends in the data, we examine binned means of amphibole F concentration, with each bin being 0.02 Al_T/Si_T units wide. Error bars represent the standard error. For arc amphiboles, the Al_T/Si_T ratio increases from 0.015 to 0.41, ranging from basaltic to rhyolitic compositions. F concentrations range from 0.0001 to 2.5 wt.%. Interestingly, mean arc amphibole F concentrations are relatively constant, around 0.25 wt.%. F, and show no systematic variation with the Al_T/Si_T differentiation index (Figure 1A). This contrasts with the behavior of Cl in amphibole, which Borchardt and Lee [2024] reported to increase by a factor of 5 from mafic amphiboles with high Al_T/Si_T to felsic amphiboles with low Al_T/Si_T. Rift amphiboles cover a similar range of Al_T/Si_T values and come from compositions ranging basalt to rhyolite. Even though rift amphiboles cover similar compositions, the behavior of F is notably different from that in arc amphiboles, with mean rift amphibole F concentrations increasing from ~0.3 to 1.2 wt.% F with increasingly evolved amphibole compositions (Figure 1B).

As noted in the Methods section, Al_T/Si_T decreases with increasing differentiation, so the observation that F does not increase with decreasing Al_T/Si_T is unexpected if F behaves like a perfectly incompatible element, as is thought to be the case for most of the major crystallizing phases found in arc magmas [Moore 1970; Straub and Layne 2003; Urann et al. 2020; Flemetakis et al. 2021]. However, the lack of increase in F suggests that F is not behaving incompatibly during the differentiation of arc magmas. For comparison, the Cl concentration in arc amphiboles over a similar range of Al_T/Si_T increases 5 times from the mafic to felsic endmember [Borchardt and Lee 2024]. In contrast, the observed increase of F with decreasing Al_T/Si_T suggests that F behaves incompatibly in rift settings, roughly showing a four-fold increase.

4 Discussion

4.1 Reconstructing the magmatic evolution of F

To gain insight into what crystallizing phase controls the evolution of F, we use the amphiboles to reconstruct equilibrium melt compositions. This requires an estimate of the amphibole/melt partition coefficient, D_F^{Amp}. We compile all available experimental constraints on amphibole/silicate melt partition coefficients [Scaillet 2003; Hauri et al. 2006; Dalou et al. 2014; Iveson et al. 2017; Flemetakis et al. 2021; Dawson et al. 2025]. The compiled experiments range in composition from basalt to rhyodacite, in temperature from 660 to 1200 °C, and in pressure from 0.05 to 1.5 GPa.

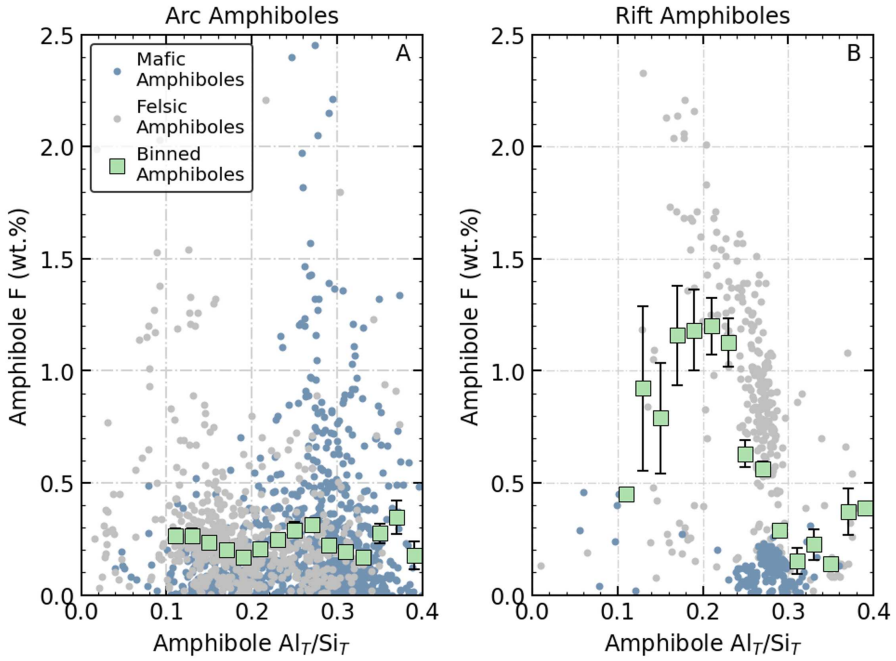


Figure 1: [A] Fluorine concentrations in arc amphiboles show no change with increasing magmatic evolution (as inferred by a decrease in the ratio of tetrahedral Al to Si), suggesting that F is behaving compatibly during magmatic differentiation. Error bars in both panels represent 2 sigma standard errors (standard deviation divided by the square root of the number of samples). Where error bars are not visible, standard errors are smaller than the symbol. [B] Rift amphiboles, in contrast, show increasing F concentrations with increasing magmatic evolution.

The compiled experiments show that the D_F^{Amp} is primarily controlled by the amount of Na and K on the A site of the amphibole, the amount of Cl present on the W site, and the Mn^{2+} present on the B site (Figure 2). Increasing amounts of Mn^{2+} on the B site and Cl on the W site lead to higher compatibility of F in the amphibole (Figures 2A and 2B). In contrast, as Na and K increase on the A site, compatibility decreases (Figures 2C and 2D). These compositional variables scale with amphibole differentiation. With decreasing Al_T/Si_T, the Na and K concentrations on the A site decrease, while Mn^{2+} on the B site and Cl on the W site increase. In practice, this means that the more evolved felsic amphiboles have higher D_F^{Amp} than more mafic amphiboles. Importantly, like Dawson et al. [2025], we do not observe a strong correlation between Mg# or Fe concentration and F partitioning behavior, inconsistent with control by Fe avoidance in amphiboles [Rosenberg and Foit 1977; Zhang et al. 2012]. We speculate that studies that previously identified such correlations were instead capturing the effect of Cl. The Mg/Fe ratio of an amphibole controls the incorporation of Cl in the amphibole structure, which in turn affects F incorporation into the lattice [Iveson et al. 2017; Borchardt and Lee 2024].

In our dataset we find that no single variable controls D_F^{Amp}. Previous attempts to fit D_F^{Amp} using amphibole and glass compositions had limited success, with calibrations that worked only on limited datasets and could not be extended to other experiments [Dawson et al. 2025]. To parametrize the distribution coefficient for complex data, we turn to recent advances in machine learning. Recently, Zhou et al. [2025] were able to greatly improve correlations between magma chemistry and crustal thickness using categorical booster regressions. Inspired by their work, we follow their workflow to fit D_F^{Amp} to the chemical data of experimental amphiboles. We use the `CatBoost` regressor, a machine learning algorithm that uses multiple rounds of gradient-boosted decision trees to identify optimal parameters [Prokhorenkova et al. 2018]. Before fitting all compositional variables of the amphibole, we scale the data using the "`StandardScaler`" routine from the `Python` package `scikit-learn` to prevent high-variance parameters from dominating the model and to simplify subsequent cross-validation [Bishop 2006; Pedregosa et al. 2011]. We use a decision tree with a depth of 2, 1000 iterations, and a learning rate of 0.1 [Prokhorenkova et al. 2018]. To validate model performance, we use the `KFold` method from `scikit-learn`, which randomly splits the data into ten groups, using each in turn as a test set while the remaining nine groups train the model [Bishop 2006; Pedregosa et al. 2011]. Differences in fit between test and training groups yield an R^2 of 0.737 and RMSE of 1.83 across all available datasets (Figure 3). With the current data, a global regression and understanding of halogen partitioning is possible. The reader can access the model and instructions on how to run the code in the supplementary section of this paper. We apply this model to calculate D_F^{Amp} for each amphibole grain, dividing the measured F concentration by the modeled D_F^{Amp} to determine the equilibrium melt F concentration.

To examine how F changes with magmatic differentiation in melts, we use the methods of Zhang et al. [2017] to calcu-

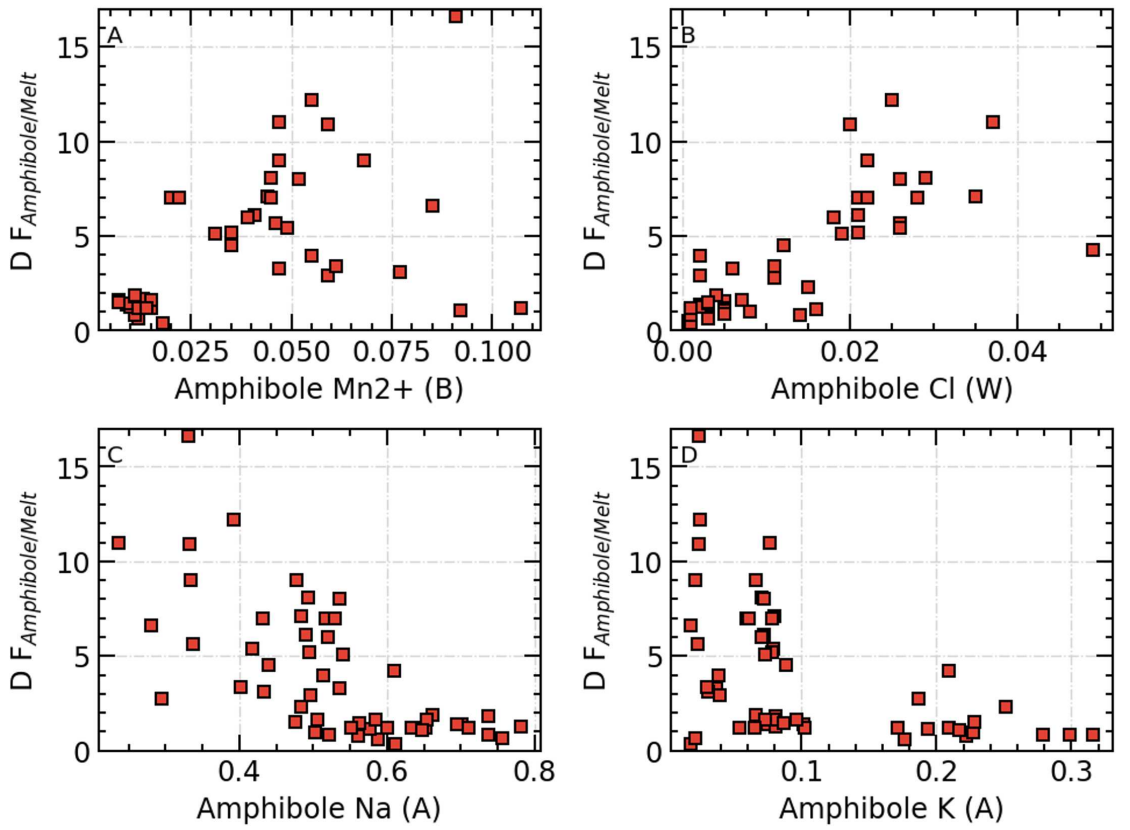


Figure 2: Experimental partition coefficients of F between amphibole and silicate melt plotted as a function of atoms per formula unit of amphibole. Data from the these studies can be found in the supplementary data [Scaillet 2003; Hauri et al. 2006; Dalou et al. 2014; Iveson et al. 2017; Flemetakis et al. 2021; Dawson et al. 2025].

late the SiO_2 content of the melt in equilibrium with amphibole. This method relies on an empirical correlation between the amount of Si in the tetrahedral site of an amphibole and the SiO_2 content of its equilibrium melt. Amphiboles with anomalously high Ti contents substitute Al for Si in the T site, potentially compromising the empirical relationship between tetrahedral Si in amphibole and SiO_2 in the melt. Applying Zhang's models on Ti-rich amphiboles returns unreallistically low SiO_2 contents for their equilibrium melts. To screen out these amphiboles, we remove 43 samples with Si/Ti ratios less than 20, leaving 1511 samples in the database for estimating F and SiO_2 contents of the magma. The calibration of Zhang et al. [2017] reports a standard error of roughly 4 SiO_2 units, not accounting for potential Si loss.

4.2 Fluorine in Arc Magmas

Calculated F and SiO_2 contents of melts in equilibrium with amphibole for arcs and rifts are shown in Figure 4. Mean F contents calculated in 2 wt.% SiO_2 bins are also shown to illustrate general trends. We first discuss F systematics in arcs before comparing them with rifts. For arc amphiboles, mean equilibrium melt F concentrations decrease systematically from 0.29 to 0.02 wt.% with increasing SiO_2, indicating that F behaves compatibly during differentiation (Figure 4A). For comparison, we show how F would behave if its partitioning behavior were like that of Cl, that is, perfectly incompatible (Cl behavior in magmas was estimated from amphibole Cl content; Borchardt and Lee [2024]). Incompatible behavior would result in a ~five-fold enrichment of F from magmatic SiO_2 contents of 50 wt.% to >70 wt.%. However, F contents show a roughly ten-fold decrease over this range of SiO_2.

Our new results agree well with the melt inclusion record of F in arc systems. Comparing our calculated equilibrium melts to a global record of melt inclusions from arcs shows broadly similar trends between the melt inclusion and amphibole records of F, with binned melt inclusions showing an overall decrease in F concentrations from 0.33 to 0.07 wt.% (Figure 5A). This small discrepancy is unsurprising, considering that the distribution coefficient between a fluid exsolving from a magma, and a silicate melt for F is usually less than ten and can be less than one [Cassidy et al. 2022]. If melt inclusions lost water, as suggested by Cl systematics, their F concentrations could increase [Cassidy et al. 2022; Borchardt and Lee 2024]. Our results differ from Urann et al. [2022], who calculated F concentrations from arc cumulates from the Kohistan arc and showed incompatible behavior, with F increasing from 0.0026 to 0.1404 wt.%. We speculate that the difference between their results and ours arises because the initial fractional crystallization sequence at Kohistan is controlled by olivine and clinopyroxene, while the amphiboles we examine crystallized under amphibole- or garnet-dominated fractionation [Jagoutz et al. 2007; Chen et al. 2023].

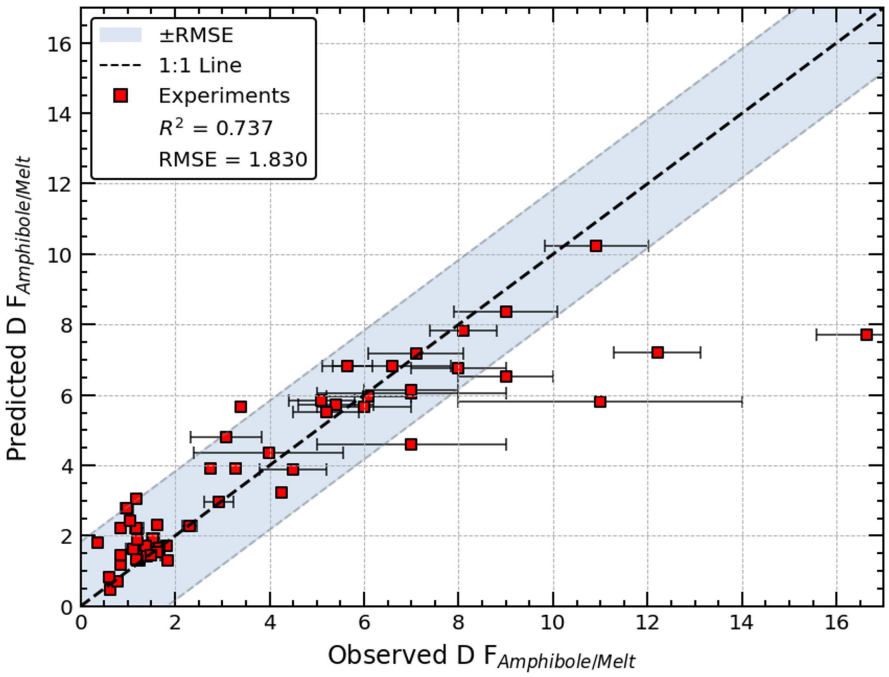


Figure 3: Observed versus model-predicted D_F^{Amp} from the `CatBoost` regression. Experimental data are from Scaillet [2003], Hauri et al. [2006], Dalou et al. [2014], Iveson et al. [2017], Flemetakis et al. [2021], and Dawson et al. [2025]. Error bars represent 1 standard deviation. Where error bars are absent, the reported error is smaller than the symbol or only one measurement was reported (n = 1).

The systematic decrease in F with increasing SiO_2 suggests compatible behavior, but the degree of compatibility and the magnitude of F depletion remain to be quantified. Because Cl behaves perfectly incompatibly, we can use Cl to track the degree of magmatic differentiation by estimating residual melt fractions, dividing magma Cl content by the Cl content of the parental magma [Borchardt and Lee 2024]. Then, using a simple mass balance model of Rayleigh fractionation, we can calculate how magmatic F evolves for a range of possible bulk partition coefficients. The observed degree of F depletion in our equilibrium magmas is similar to a modeled differentiation trend for an assumed bulk distribution coefficient for fluorine of 3, consistent with compatible behavior (Figure 4A). Independent of these forward crystallization models, the observed depletion in F, with concentration decreasing from an estimated parental composition of 0.29 to 0.02 wt.%, suggests that 0.27 wt.% of F (more than 90 % of the original F) is "missing" from evolved arc magmas. In other words, the F content of evolved arc magmas represents less than 10 % of the original F prior to differentiation.

4.3 Amphibole-bearing cumulates as the missing reservoir of F in arc magmas

We now explore where the missing F lies. Arc cumulates or arclogites are frequently used as a petrologic complement to explain the observed depletion or enrichment of elements in arc magmas. For example, compatible elements like Mg, Ni, and Fe, which are depleted in evolved arc magmas and average continental crust, are preferentially enriched in arc cumulates [Rudnick 1995; Lee 2014]. On the other hand, incompatible elements, like potassium, are depleted in the cumulates but enriched in evolved magmas. Having shown that F is compatible in arc magmas, we hypothesize that it should be enriched in arc cumulates. What phases in arc cumulates control the F budget?

Of the common major and accessory crystallizing phases in arc magmas, only apatite and amphibole are possibilities for sequestering F. Fluorine is far more compatible in apatite than in amphibole, but apatite occurs only in trace quantities (<1 %) in arc cumulates [Cai et al. 2023]. Although fluorine's compatibility in amphibole is not as high as in apatite, amphibole occurs in proportions greater than 10 % [Davidson et al. 2007]. We thus hypothesize that amphibole is the primary repository of F in arc cumulates. We can use a mass balance approach to test this hypothesis. The mass fraction of amphibole (X^{Amp}) in arc cumulates needed to balance the F deficit in the crust is given by

$$X^{Amp} = \frac{C_F^p - C_F^{bcc} \times M - X^{Ap} \times C_F^{Ap} \times (1 - M)}{D_F^{Amp} \times C_F^p \times (1 - M)} \quad (1)$$

where we have accounted for the contribution from apatite X^{Ap} (mass fraction of apatite in the cumulate). In Equation 1, C_F^p is the concentration of F in a primary arc magma, C_F^{bcc} is the concentration of F in the bulk continental or arc crust (which assumes that the complementary mafic cumulates are missing), C_F^{Ap} is the concentration of F in apatite (from stoichiometry), M is the mass fraction of the total mafic parent that differentiates to become the crust ($1 - M$ is the comple-

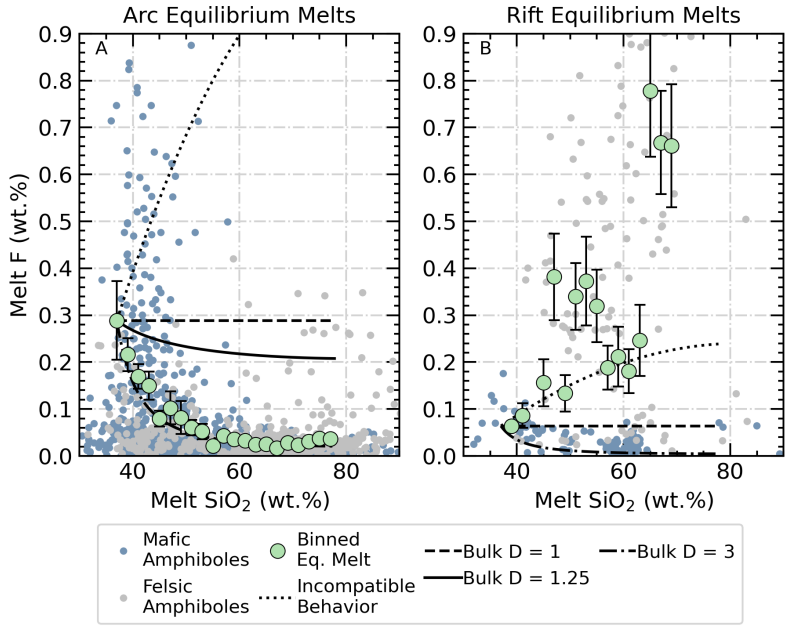


Figure 4: [A] Calculated equilibrium melt F and SiO_2 concentrations from arc amphiboles. Individual points are shown as small blue and grey circles. Binned equilibrium melts are shown as large green circles. Error bars on binned equilibrium melts with the 2-sigma standard error. Equilibrium melt concentrations decrease with increasing SiO_2 concentrations, implying compatible behavior despite fluorine's incompatibility in most major silicate phases. For comparison, the rising dotted black line represents the predicted behavior of F if it were perfectly incompatible, as is the case for Cl. The horizontal dashed line shows the predicted evolution of arc F concentrations if the bulk partition coefficient of F were 1. The solid and dash-dot lines show fluorine's behavior if its bulk D was 2 and 3, respectively. [B] Calculated equilibrium melt F and SiO_2 concentrations for rift amphiboles. Same symbols as [A]. In contrast to arc amphiboles, rift amphiboles record increasing F concentrations with increasing SiO_2.

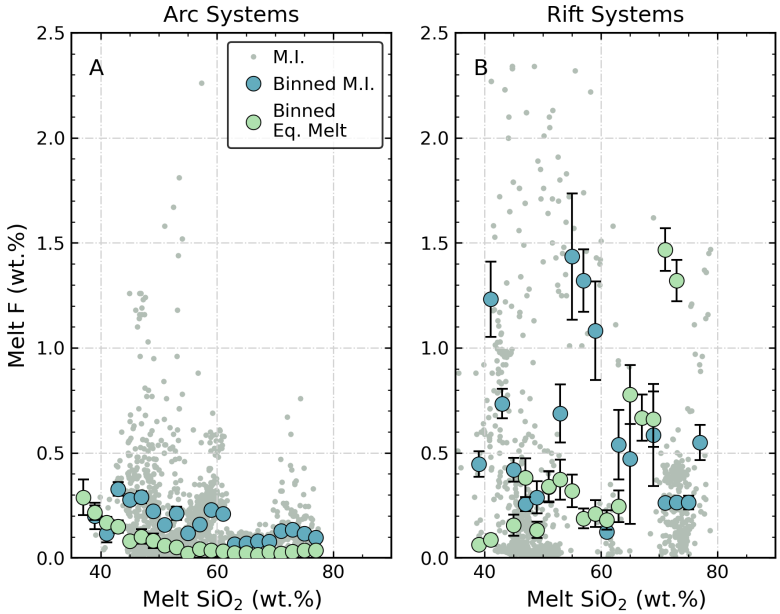


Figure 5: [A] Comparison of mean F concentrations calculated from amphibole with a global compilation of arc melt inclusions. Grey dots represent individual melt inclusion analyses while blue circles are binned means. Error bars represent the standard error. Green circles represent the binned means of calculated equilibrium melts from Figure 4. [B] Same symbols as for panel [A], but for rift melt inclusions and amphiboles. Melt inclusions data is sourced from GEOROC [DIGIS Team 2023].

mentary mass fraction of the missing cumulates), and D_F^{Amp} is the partition coefficient between amphibole and melt. Fluorine is assumed to be perfectly incompatible ($D = 0$) for all other crystallizing phases.

We take the concentration of F in a primary arc magma (C_F^p) to be 0.29 wt.%, corresponding to the value at the lowest SiO_2 as inferred from the arc amphiboles in this study. We do not know the average F chemical composition of evolved arc crust, but we can apply our calculation to that of bulk continental crust. We use an estimate of 0.0553 wt.% F for the bulk continental crust from Rudnick and Gao [2003]. For M, we use a maximum bound of 0.5 and a minimum bound of 0.2, based on independent major-element constraints [Lee 2014].

D_F^{Amp} is the most important free variable in the equation and poses unique challenges. Unlike D_F^{Amp} for individual grains, D_F^{Amp} in Equation 1 is the average distribution coefficient of all amphiboles crystallized in the assumed arc cumulates and therefore requires assumptions about their compositional range. We assume that because the bulk continental crust has a SiO_2 composition of ~60 wt.%, only amphiboles that formed from melts with 60 wt.% SiO_2 or less are retained as cumulates [Rudnick and Gao 2003]. For arc amphiboles from our compilation, lower SiO_2 amphiboles have a median D_F^{Amp} of 3.5, a mean D_F^{Amp} of 3.9, and a standard deviation of 1.67. We use the mean D_F^{Amp} of the lower silica amphiboles as our preferred value, but also plot model results for integrated D_F^{Amp} values of 2 and 5. We note that because D_F^{Amp} scales with amphibole differentiation, assuming more mafic cumulate amphibole compositions drives D_F^{Amp} lower, while assuming more evolved compositions drives it higher.

Our mass balance model results are shown in Figure 6. We first consider the case in which no apatite exists, such that amphibole is the only F-bearing phase (red lines, Figure 6). These models establish an upper bound on the amphibole fraction in arc cumulates. We also consider the case in which apatite is an accessory phase (black lines, Figure 6). A maximum bound on the F budget controlled by apatite can be estimated by assuming an apatite mode of 1 % (in reality, the value is likely much lower) and that F fully occupies the volatile site in apatite, corresponding to ~3.7 wt.% F based on stoichiometry [Cai et al. 2023]. With these assumptions on apatite chemistry and abundance, our apatite-bearing models represent lower bounds on the mass fraction of amphibole in arc cumulates.

Our calculated values of amphibole fraction in the cumulate for a D_F^{Amp} of 3.7 range from 0.25 to 0.35 (Figure 6). Our mass balance shows that large amounts of amphibole crystallization are necessary to sequester F (even in the presence of apatite). If we assume that the amphiboles in the cumulate are more mafic, with a lower D_F^{Amp} of 2, more amphibole crystallization is required to sequester F, with the amphibole fraction ranging from 0.5 to 0.8 in the cumulate. More felsic amphiboles in the cumulate with a higher D_F^{Amp} requires less amphibole crystallization to explain the compatible behavior of F. Assuming a bulk D_F^{Amp} of 5, only 0.12 to 0.20 of the crystallized cumulates need to be amphibole to explain the F depletion. The presence of apatite in our model decrease the mass fraction of amphibole necessary in the cumulate by roughly 0.08. This is likely a maximum bound on the effect of apatite, as we assume both a high mass fraction of apatite in the cumulate and maximum value of F incorporated into the apatite crystal. These results suggest that the primary reason arc magmas are F-poor is that amphibole crystallizes during differentiation, sequestering F. Although amphiboles contain structurally bound water, water is still relatively incompatible in amphiboles. Thus, as arc magmas differentiate, residual magmas still become richer in water, promoting more amphibole crystallization, which in turn depletes the residual magma of F. Fluorine's behavior thus differs fundamentally from that of Cl, which behaves incompatibly like water. Cl follows water, but F does not. Our observations and analyses thus explain why arc magmas are enriched in water but depleted in F.

4.4 Fluorine enrichment in dry magmas and the Fluorine dichotomy

If amphibole sequesters F, how does F behave in relatively dry magmas that do not crystallize amphibole? Water-poor magmas or magmas with low water activity (for example, due to high CO_2 activity) precipitate little to no amphibole except after extreme differentiation [Scaillet 2003; Krawczynski et al. 2012]. If our interpretations above are correct, dry magmas are predicted to become enriched in F. Indeed, highly silicic magmas formed at mid-ocean ridges, continental rifts, and intraplate environments are generally dry, do not precipitate amphibole, and are often enriched in F, as evidenced by the presence of topaz and fluorite [Christiansen et al. 1986; 2007]. Specific examples include the F-bearing rhyolites associated with bimodal volcanism of the Cenozoic Basin and Range extension [Burt et al. 1982]. These rhyolites likely formed from extreme differentiation of dry basaltic parents or re-melting of underplated basalt. Dry and hot granites are generally absent from the main volcanic front in subduction zone environments, but in ocean-continent subduction zones, they can be found far inboard of the arc front. Such magmas are also often enriched in F. Examples include the Cretaceous F-bearing granites associated with the continental back-arc region of a paleo-Pacific subduction zone in southern China [Wang et al. 2018] and the Paleogene F-bearing granites of the Texas Trans-Pecos associated with the termination of Farallon plate subduction [O'Neill et al. 2017; Elliott 2018].

Dry magmas thus follow a fundamentally different path in terms of F than wet magmas. In wet, subduction zone magmas, F is depleted. In dry, intraplate or back-arc magmas, F becomes enriched. To test this hypothesis, we use the compiled rift amphiboles (Figure 1B) and calculate equilibrium melts for each sample. The results are displayed in Figure 4B. In contrast to arc amphiboles, the binned mean F concentrations of rift amphiboles increase from 0.1 to 1.2 wt.%, with decreasing Al_T/Si_T. F concentrations in the estimated equilibrium melts also increase from 0.06 to 0.7 wt.% suggesting that in drier settings F is incompatible, in contrast to its compatible behavior in arcs. We refer to this divergence of F behavior as the fluorine dichotomy.

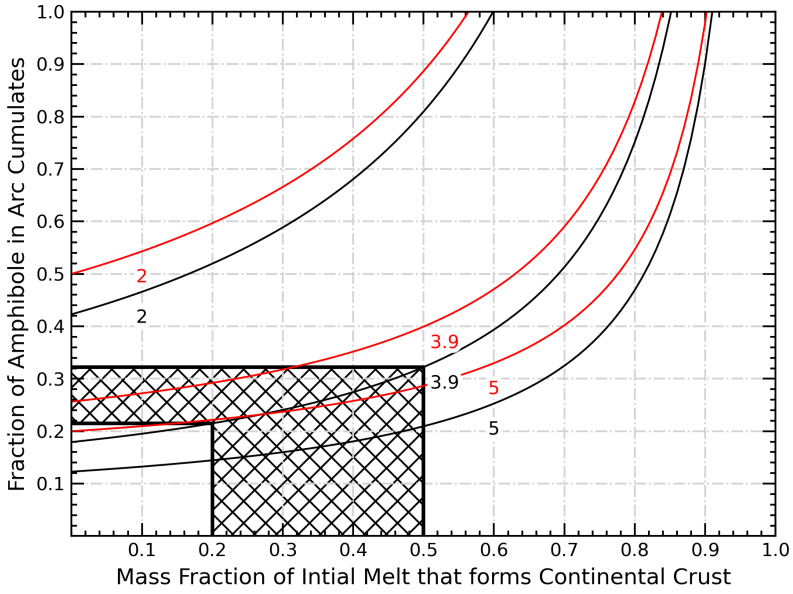


Figure 6: Calculated fraction of amphibole in arc cumulates as a function of mass fraction of evolved crust (e.g., continental crust) derived from a primary arc melt, for different values of D_F^{Amp} (2, 3.9, and 5). Black lines represent models in which apatite makes up 1 % of the arc cumulates and has a F concentration of 3.9 wt.%. Red lines represent models in which apatite is absent from the arc cumulates and amphibole is the only phase that retains F. The hatched area represents estimates of the mass fraction of evolved crust (or continental crust) relative to the original parental magma, with the remainder represented by lower crustal cumulates that may have delaminated. The fraction of amphibole in arc cumulates needed to mass balance the F deficit in evolved arc magmas is read from the intersection of the hatched area with the apatite-bearing model curve for the mean D_F^{Amp} of compiled mafic arc amphiboles.

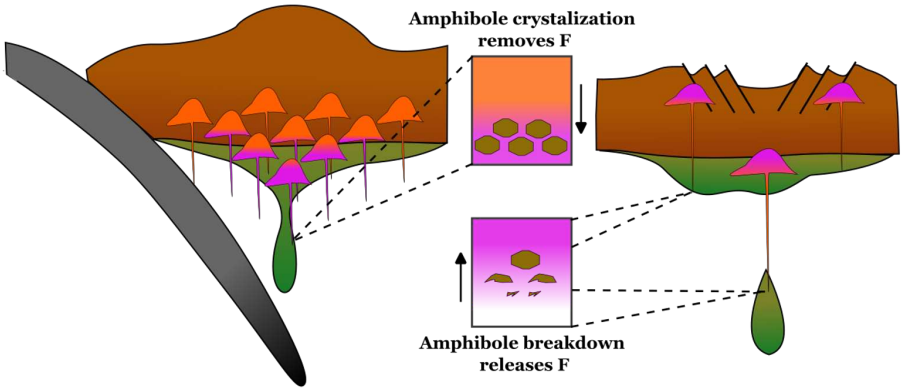


Figure 7: Schematic diagram of F cycling by amphibole in subduction zone settings. F is first introduced into the mantle wedge by the breakdown of hydrous phases in the subducting slab. F is then incorporated into melts formed by the addition of hydrous fluids or by flux melting, only to be later sequestered by fractional crystallization of amphibole, generating F-rich amphibole-bearing cumulates in the lower crust. F becomes entombed in arc cumulates. However, if the amphibole-bearing cumulates delaminate, the resulting increase in pressure causes amphiboles to break down and release their stored F into the overlying continental crust in the form of fluids or evolved felsic magmas.

4.5 The fate of amphibole cumulates

If arc cumulates are the missing reservoirs of F in the formation of arc crust, what is the fate of these arc cumulates and their F? Is the sequestered F forever entombed in these cumulates, or can it be remobilized? We hypothesize that these F-rich amphibole-bearing cumulates, which formed during arc magmatism, can subsequently be reactivated and remelted. Such remelting could readily happen during the waning of an orogeny or during later lithospheric extension. Lithospheric thinning (by extension or delamination) at the end of an orogeny could emplace hot asthenosphere against an amphibole-rich lower crust. Given the lower melting point

of amphibole-bearing lithologies, these amphibole-rich cumulates might undergo high degrees of melting, generating intermediate magmas that are enriched in F from the outset. In particular, high-degree melts of amphibole-rich lithologies would be relatively dry. Amphiboles have ~4 wt.% H_2O, but if amphiboles make up <50 % of the cumulate, the bulk rock would contain <2 wt.% H_2O. High-degree melting of such a lithology, such as by 50 % or to the point of amphibole exhaustion, would produce intermediate magmas with <4 wt.% H_2O, far lower than an intermediate magma derived from a primary arc basalt, which themselves may have already originated with high water concentrations [Gavrilenko et al. 2019; Goltz et al. 2020; Urann et al. 2020].

Rosera et al. [2023] observed F-rich amphiboles in the State Line lower crustal xenolith suite in Colorado (USA) and suggested that they could play a role in the formation of topaz-bearing rhyolites associated with Mo-porphyries in the Colorado Mineral Belt (37 to 20 Ma). They hypothesized that F-rich amphiboles could originate from high temperature metasomatism or represent former arc cumulates, the latter interpretation suggested by Chin et al. [2020]. We speculate that these xenoliths may well have been amphibole-bearing arclogites formed during prior episodes of arc magmatism. If remelting of amphibole-bearing cumulates can generate F-rich rhyolites, the same process might explain the relationship between mineral belts and Precambrian terrains [Tweto and Sims 1963; Karlstrom and Humphreys 1998; Lang and Titley 1998]. The Colorado Mineral Belt in the United States follows Precambrian boundaries defined by sutured island and continental arc terranes [Tweto and Sims 1963; Karlstrom and Humphreys 1998; Hillenbrand et al. 2024]. We speculate that this spatial relationship with ancient structural trends reflects reactivation of ancient arc cumulates in the lower crust.

Not all arc cumulates remain indefinitely in the crust to be reactivated. Mafic cumulates at high enough pressure transform into garnet-bearing lithologies and become denser than the mantle [Sosa et al. 2024]. If the formation and recycling of cumulates are intrinsic crust-forming processes, the average continental crust might be expected to become progressively enriched in incompatible elements and depleted in compatible elements through time. The chemical composition of glacial sediments through time seems consistent with this predicted progression of continental crust composition [Gaschnig et al. 2014; Tang et al. 2016].

Within this framework, however, F displays unusual behavior. Over time, the concentration of F in average continental crust has increased. Han et al. [2023] showed that from 2.9 Ga to 0.3 Ga, the F concentrations of average continental crust increased from 36–219 ppm to 349–506 ppm. If these differences are statistically significant, this behavior is at odds with our observation that F is broadly compatible in arc magmas. We are left with a conundrum. Fluorine is compatible during arc magma differentiation, but the increase of F in the continental crust over time suggests F behaves bulk incompatibly on geological timescales. However, this incompatible behavior may be the expected outcome of foundering or delamination (Figure 7). Amphiboles in arc cumulates remain stable up to 3 GPa, beyond which they become unstable, breaking down and releasing their stored F [Niida and Green 1999; Bowman et al. 2024; Sosa et al. 2024]. We suggest that foundering of arc lower crust would eventually destabilize amphibole, causing it to break down and release its stored F [Niida and Green 1999; Bowman et al. 2024]. We speculate that the released F is then incorporated into the overlying continental crust through metasomatism or through the emplacement of F rich magmas as discussed above. Thus, F exhibits a unique elemental behavior. As a compatible element stored in amphibole, it cannot be recycled back into the mantle because amphibole breaks down eventually at high pressure. Instead, it is continually reintegrated into the continental crust, concentrating towards the surface with time. This unique behavior of F hints at a previously undescribed part of the deep global volatile cycle, which is controlled by the crystallization and subsequent delamination of amphibole cumulates in arc settings [Davidson et al. 2007].

5 Conclusions

F concentrations do not increase with increasing differentiation in arc magmas, suggesting broadly compatible behavior of F. Partitioning data and mass balance models suggest that amphibole crystallization and sequestration in arc cumulates could explain why there is "missing" F in evolved arc magmas. Subduction zone magmas are water-rich but F-poor due to loss of F to amphibole-bearing cumulates. Magmas in post-orogenic, extensional, or intraplate settings are water-poor but become enriched in F because amphibole does not saturate until late. Amphibole-bearing arc cumulates may provide a future source of F-enriched magmas if conditions for melting the lower crust are met.

Author Contributions

Jackson Borchardt and Cin-Ty Lee conceived the original project idea. JSB did the data curation, analysis, visualization, and wrote the original draft. CTL procured funding for the project, helped with the analysis, and edited the original draft.

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Data Availability

The unfiltered amphibole compilation used to create these figures is available from the GEOROC repository at https://doi.org/10.25625/SGFTFN. The melt inclusion database used to create Figure 5 is available from GEOROC at https://doi.org/10.25625/7JW6XU. The subset of the amphibole data culled from the GEOROC database, a script to recreate all calculations figures in the paper, and a easy to use script to calculate D_F^{Amp} for igneous amphiboles is at https://doi.org/10.5066/P14HHQKK.

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