Eruptive styles of subduction-zone volcanoes : investigation of magmatic volatile budgets and ascent rates using apatite

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**NANYANG
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UNIVERSITY**

SINGAPORE

**ERUPTIVE STYLES OF SUBDUCTION-
ZONE VOLCANOES: INVESTIGATION
OF MAGMATIC VOLATILE BUDGETS
AND ASCENT RATES USING APATITE**

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**INTERDISCIPLINARY GRADUATE SCHOOL
EARTH OBSERVATORY OF SINGAPORE**

2019

**Eruptive styles of subduction-zone
volcanoes: investigation of magmatic volatile
budgets and ascent rates using apatite**

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Earth Observatory of Singapore**

A thesis submitted to the Nanyang Technological University
in partial fulfillment of the requirement for the degree of
Doctor of Philosophy

2019

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Statement of Originality

I hereby certify that the work embodied in this thesis is the result of original research, is free of plagiarised materials, and has not been submitted for a higher degree to any other University or Institution.

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I have reviewed the content and presentation style of this thesis and declare it is free of plagiarism and of sufficient grammatical clarity to be examined. To the best of my knowledge, the research and writing are those of the candidate except as acknowledged in the Author Attribution Statement. I confirm that the investigations were conducted in accord with the ethics policies and integrity standards of Nanyang Technological University and that the research data are presented honestly and without prejudice.

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Authorship Attribution Statement

This thesis contains material from one paper published in the following peer-reviewed journal, where I was the first and corresponding author.

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The contributions of the co-authors are as follows:

- I prepared the manuscript drafts, compiled the literature data, established the thermodynamic model, and applied it to the natural systems.
- Assoc. Prof. Fidel Costa provided the initial project direction, edited the manuscript drafts, and discussed with the first author on the calculation methods and applications to natural systems.

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Summary

The most explosive and dangerous volcanoes around the world are located at subduction zones. Understanding the changes in their eruption dynamics has great significance for mitigating volcanic hazards. In this thesis I investigate the role of volatiles on volcanic eruptions using a combination of thermodynamic, experimental, and observational approaches. First, I propose a new thermodynamic model of the partition behavior of F-Cl-OH between apatite and melt to estimate the melt water contents. This model includes a treatment of the thermodynamically non-ideal properties of the ternary apatite at magmatic temperatures, and it has been developed as a free web-based calculator. Second, I use the thermodynamic model and various crystal chemistry data to calculate the melt volatile budgets of two eruptions of distinct styles at Merapi volcano (Indonesia). I characterize for the first time the CO₂, H₂O, S, Cl and F contents of the deep melts (near the Moho) below this volcano. Fluxing of these deep volatiles to the shallower magmatic system is likely the cause of the large and explosive 2010 eruption. Third, I report new experimental results for the diffusion coefficients of F, Cl, OH and S in apatite at magmatic temperatures. I find that these volatiles re-equilibrate via a multicomponent diffusion mechanism. Application of the new diffusion data to zoning of volatiles in natural apatite allows determination of the timescales of magma ascent. I believe that the results from this Ph.D. thesis provide new insights into the plumbing system, magmatic volatile budgets and magma ascent rates of subduction-zone volcanoes, and also help to improve the interpretation of volcanic monitoring data that is critical for eruption forecasting.

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Chapter 1. Introduction

Eruptions from subduction-zone volcanoes can abruptly shift from small and effusive events with volcanic explosivity index (VEI; Newhall and Self, 1982) of 1-2, to much larger and explosive eruptions ($\text{VEI} \geq 4$) with severe hazards to the local communities and global-scale impacts (e.g. Sigurdsson et al., 1999; Oppenheimer, 2011; Cashman et al., 2013; Pyle, 2017; Cassidy et al., 2018). To mitigate the hazards of such events, volcanologists have traditionally used geophysical, geochemical, and geodetic signals recorded by volcano monitoring networks, combined with forecasting models to anticipate the size and explosivity of the eruptions (e.g. Voight, 1988; Sparks, 2003; Marzocchi et al., 2008; Cashman et al., 2013; Cassidy et al., 2018; Edmonds et al., 2019). However, proper interpretation of the monitoring data is difficult. This might be due to partly the complex nature of the volcanic system that involves many interacting parameters (e.g. Sparks, 2003), and partly the poor knowledge of the architecture of the plumbing systems of various volcanoes, and the time-evolution aspects of the pre-eruptive magmatic processes (e.g. Blundy and Cashman, 2008; Cashman and Sparks, 2013; Bachmann and Huber, 2016; Sparks and Cashman, 2017).

Changes in eruptive styles appear to be mainly controlled by two factors: (i) the abundance and composition of magmatic volatiles, and (ii) the magma ascent rate towards the surface (e.g. Sparks, 2003; Cashman and Sparks, 2013; Cassidy et al., 2018; Edmonds et al., 2019). However, the two factors usually have complex relations. For example, a large explosive eruption may be driven by the exsolution of volatiles from an ascending magma which increases its buoyancy and thus a fast ascent, which then

gives little time for magma outgassing, and further increases the magma buoyancy and accelerates the ascent (e.g. Cassidy et al., 2018). The correlation of the two factors brings up the question of their relative roles in controlling the eruptive styles. Moreover, the presence of an exsolved volatile phase at pre-eruptive conditions, or/and the role of volatile fluxing from the deep to the shallow parts of the magmatic system (e.g. Metrich et al., 2010; Degruyter et al., 2016; Moretti et al., 2018) can be also part of the complex relation between the volatile and magma dynamics that lead to a variety of eruptive styles.

This Ph.D. thesis takes a new perspective of the unsolved problems related to the eruptive styles by using the mineral apatite. A combination of the thermodynamic model and new observational and experimental data for apatite provides new constraints on (i) the amounts of magmatic volatiles and their variations from deep to shallow parts of the plumbing system, and (ii) the timescale of magma ascent to the groundmass surface, and the ascent velocity. The results and multiple apatite-based approaches in this thesis pave the way for a better understanding of the plumbing system and the eruptive styles of volcanoes around the world.

1.1. Volatiles abundances in magmatic systems

The most abundant volatiles in magmatic systems are water (H_2O) and carbon dioxide (CO_2), whose concentrations in the melt can reach a few weight percent and significantly affect the physical and chemical properties of the magmas (e.g. Sparks, 2003; Cashman, 2004; Giordano et al., 2008; Cashman and Sparks, 2013). In addition, volatiles that are

less abundant in melts, such as sulfur (S), chlorine (Cl) and fluorine (F), can also affect magmatic processes (e.g. Lowenstern, 2000; Aiuppa, 2009), and those that can be measured from volcanic plumes (e.g. CO₂, SO₂, H₂O) are informative for the impending eruption (e.g. Aiuppa et al., 2007; Allard, 2010; Kahl et al. 2013; Chiodini et al., 2016). Magmatic volatiles can be either dissolved in the melt, or exsolved as fluids/vapor (e.g. Wallace et al., 2005). The composition and abundance of dissolved volatiles in the melt (see discussion below) are usually constrained from petrological and mineralogical approaches (e.g. Lowenstern, 2003; Wallace, 2005; Metrich and Wallace, 2008), whereas those of the exsolved volatiles are more difficult to investigate with limited insights provided by the petrological, satellite, and ice-core data (e.g. Westrich and Gerlach, 1992; Costa et al., 2003; Burton et al., 2007).

The most common approach to constraining the abundances of dissolved volatiles in melts is based on measurements of the melt inclusions (MIs) hosted by minerals from igneous rocks (e.g. Lowenstern, 2003; Metrich and Wallace, 2008). However, it has become more and more apparent that melt inclusions do not necessarily record the melt volatile compositions, due to a variety of post-entrapment processes including their crystallization, the sequestration of CO₂ into the bubble, and diffusive loss/gain of H⁺ from the host crystal especially during slow magma ascent/cooling (e.g. Qin et al. 1992; Danyushevsky et al. 2000; Gaetani and Watson 2000; Cottrell et al. 2001; Portnyagin et al. 2008; Lloyd et al. 2013). In addition, investigation of MIs is faced with other problems including that MIs (i) are not always available in the investigated minerals, (ii) are sometimes too small to be analyzed (e.g. Kent et al., 2008), and (iii) are usually found in minerals that crystallized at shallow depths, and thus rarely record the volatile-rich magmas seated at deeper parts of the plumbing system (Fig. 1.1).

The compositions of exsolved volatiles can be inferred from the volcanic gas emitted before/during the eruption (e.g. Edmonds et al., 2014), and used as a potential eruption precursor (e.g. Aiuppa et al., 2007; Aiuppa et al., 2009; Allard, 2010; Kahl et al. 2013; Chiodini et al., 2016). However, to link the pre-eruptive gas composition with the composition and abundances of the dissolved/exsolved volatiles within the magmatic system is still a big challenge (e.g. Scaillet and Pichavant, 2005), which is related to (i) the complex kinetic and thermodynamic processes during magma evolution and transport (e.g. Burgisser and Scaillet, 2007), and (ii) poor constraints on the abundances and compositions of the “initial” volatiles in the deep magmas.

Fig. 1.1. Schematic view of volatile fluxes (in red arrows) and magma migration and ascent (in grey arrows) at subduction-zone volcanoes (adapted from Zellmer et al., 2015). The relationship between the dissolved volatiles in melts, the exsolved vapor/fluids, the glass inclusions, and the mineral apatite is shown in two boxes marked in black solid lines.

1.2. Magma ascent rates

Magma ascent rates of the large and explosive Plinian-style eruptions have been found to be typically higher (i.e. up to >10 m/s) than those of the small and effusive events (i.e. <0.01 - 0.1 m/s) (Cassidy et al., 2018). However, it is a big challenge to quantitatively determine magma ascent rates based on observation and/or analyses (in opposition to “pure” modeling; e.g. de’ Michieli Vitturi et al., 2010). For example, studies on the microlite crystallinity and textures can provide information of whether the magma ascent is relatively fast or slow (Preece et al., 2016), but cannot give us the absolute value of the ascent velocity. Constraints from this method are usually based on the assumption of constant crystallization and growth rates of microlites, which however can have significant variations during magma ascent (e.g. Hammer and Rutherford, 2002). Studies on bubble number densities can provide constraints on the magma decompression rates (Klug and Cashman, 1996; Toramaru, 2006; Giachetti et al., 2010), but not on the ascent rates. Although magma decompression rates can be determined from experiments (Hammer et al., 1999; Scarlato et al., 2017), their values can be different in natural systems under other P - T - X conditions. From the observational perspective, magma ascent rates can be inferred from the magma extrusion rates (e.g. Pallister et al., 2013) if the geometry of the conduit and vent is known (e.g. Thomas and Neuberg, 2014), but this has been rarely constrained in reality and can be changed by the eruption activities (e.g. magma flows through the conduit, summit collapse; de’ Michieli Vitturi et al., 2008; de’ Michieli Vitturi et al., 2010). Another way to constrain magma ascent rates is to use chemical diffusion in minerals and/or melts to obtain time constraints on the magma ascent. This method has to rely on investigation of specific components that (i) diffuse fast enough to capture the relatively short duration of magma

ascent (within hours to days), and (ii) start diffusing *just* before/during the magma ascent. These requirements are potentially met by magmatic volatile species (e.g. H₂O, CO₂, F, Cl, S), and previous studies have used the diffusive loss of H₂O-CO₂ in the melt inclusions to obtain time constraints related to magma ascent (e.g. Liu et al., 2007; Humphreys et al., 2008; Lloyd et al., 2014; Myers et al., 2016). However, the timescales obtained from these diffusion models are controlled by the initial and boundary conditions (i.e. H₂O-CO₂ concentrations) that are usually unknown, and thus can be largely biased from the real magma-ascent durations. Limitations in the existing methods discussed above indicate that there is a necessity to establish new observational-data-based approaches for determining magma ascent rates.

1.3. Why apatite?

Apatite is an ubiquitous mineral in volcanic and plutonic rocks (Scott et al., 2015; Stock et al., 2016; Stock et al., 2018). It can incorporate several volatile species (e.g. F, Cl, H₂O, S, CO₂) into its crystal structure (Webster and Piccoli, 2015; McCubbin et al., 2015; Riker et al., 2018), and thus it has been exploited to constrain volatile compositions of fluids/melt of terrestrial and extraterrestrial origins (e.g. Piccoli and Candela, 1994; Peng et al., 1997; Boyce and Hervig, 2008; Boyce and Hervig, 2009; Van Hoose et al., 2013; Scott et al., 2015; Webster and Piccoli, 2015; Stock et al., 2016; Stock et al., 2018). The most abundant magmatic volatile, i.e. H₂O, is present as hydroxide (OH⁻) at the anion site of apatite structure, together with F and Cl, i.e. [Ca₁₀(PO₄)₆(F,Cl,OH)₂] (Piccoli and Candela, 2002; Hughes, 2015). Other magmatic volatile species, such as CO₂ (as CO₃²⁻; e.g. Piccoli and Candela, 2002) and S (of

multiple valences, e.g. S^{6+} , S^{4+} , and S^{2-} ; e.g. Kim et al., 2017; Konecke et al. 2017) can be also incorporated into apatite, indicating its capability of reflecting CO_2 and S information of the melt. In addition, apatite is stable at a wide range of magmatic pressure-temperature conditions (e.g. Boudreau, 1995; O'Reilly and Griffin, 2000; Piccoli and Candela, 2002; Patiño Douce and Roden, 2006; Zhang et al., 2012; Webster and Piccoli, 2015), and thus it can potentially provide us more insights into magmatic volatile budgets from the mantle to near the ground surface (Fig. 1.1).

In addition to the capability of recording magmatic volatile information, apatite crystals in contact with the melt during magma ascent (i.e. the groundmass apatite) can provide time constraints on this process that can be used to determine the ascent velocity. Therefore, by investigating apatite we might be able to simultaneously constrain the two key parameters that control eruptive styles, i.e. the melt volatile budgets, and the magma ascent rates, and thus to evaluate the contribution of each parameter to a given eruption. However, to achieve these goals using apatite, there are still two main problems: (1) poor constraints on the partitioning relations of volatile components between apatite and melt, and (2) limited knowledge of the rates and mechanisms of volatile diffusion in apatite, which are the main subjects in this thesis.

In addition, I wish to make progress towards some other critical but unsolved questions related to the eruptive styles of subduction-zone volcanoes, such as (1) how do the magmatic volatiles evolve before eruption?; (2) what is the relationship between large amounts of volatile fluxing from depth and the explosive eruptions?; and (3) what is the trigger of the rapid magma ascent, and how different could the magma ascent rates between effusive and explosive eruptions be? In this thesis I present results that allow

unraveling the volatile records in apatite, based on thermodynamic calculations, diffusion experiments, and analyses of natural volcanic crystals/rocks. The findings from this thesis give new insights into the origins of a variety of eruptive styles of subduction-zone volcanoes, and thus contribute to better interpretation of the volcanic monitoring data and potentially improve the accuracy of eruption forecasting.

The thesis consists of five chapters and covers the findings from three projects that I carried out during my Ph.D. studies. The *first chapter* is this introduction. In the *second chapter*, I present a new thermodynamic model for constraining the partition behavior of F-Cl-OH between apatite and the melt, and for estimating the water contents in the melt. This model includes the non-ideality of F-Cl-OH mixing in ternary apatite that was determined from regression of the experimental data from the literature. I apply this model to several natural volcanic systems with apatite compositions reported in the literature and compare the results with the existing melt inclusion data. In the *third chapter*, I present the mineralogical and petrological data for the rocks collected from two eruptions with distinct styles at Merapi volcano. I combine these data with the thermodynamic model in Chapter Two to calculate the melt volatile budgets for the two events, and then propose a hypothesis for the processes that led to the most explosive eruption of 2010. In the *fourth chapter*, I present new experimental data and a theoretical model for the multicomponent F-Cl-OH diffusion in apatite at magmatic temperatures. I combine these results with natural observations of apatite from Merapi volcano to calculate the magma ascent rates. In the *fifth chapter*, I conclude what are the most significant findings from this thesis and propose possible future work.

Chapter 2

A thermodynamic model for F-Cl-OH partitioning between silicate melts and apatite including non-ideal mixing with application to constraining melt volatile budgets

A thermodynamic model for F-Cl-OH partitioning between silicate melts and apatite including non-ideal mixing with application to constraining melt volatile budgets

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Abstract

The abundance and composition of volatiles in subvolcanic melts play a key role in controlling eruptive styles of volcanoes, but they are difficult to determine directly due to volatile loss during magma transport to the surface and eruption. Most constraints on volatile abundances are obtained by studying melt inclusions in minerals, but not all samples contain suitable inclusions, and they can be modified by a range of post-entrapment and re-equilibration processes. Apatite incorporates several volatile elements such as F, Cl, H, C and S into its structure, and thus has been proposed as an alternative tool for tracking the melt volatile contents. However, application of the apatite approach relies on the partitioning of volatiles between apatite and silicate melts, which has been found to show non-Nernstian behaviour but yet to be quantified. Here we propose a thermodynamic model that considers the non-ideal mixing in apatite solution, and includes the interaction parameters (W^G) and Gibbs free energy properties calculated by regressing experimental data from the literature. We find that W^G for the Cl-F binary join is larger than those for the Cl-OH, and F-OH joins, indicating a stronger

non-ideality. We propose two equations for calculating the exchange coefficients (K_D) between apatite (Ap) and silicate melts as:

$$\ln(K_{D_{OH-F}}^{Ap-melt}) = -\frac{1}{RT} \times \{94600 (\pm 5600) - 40 (\pm 0.1) \times T - 1000 \times [7 (\pm 4) \times (X_F^{Ap} - X_{OH}^{Ap}) - 11 (\pm 7) \times X_{Cl}^{Ap}]\}$$

and

$$\ln(K_{D_{OH-Cl}}^{Ap-melt}) = -\frac{1}{RT} \times \{72900 (\pm 2900) - 34 (\pm 0.3) \times T - 1000 \times [5 (\pm 2) \times (X_{Cl}^{Ap} - X_{OH}^{Ap}) - 10 (\pm 8) \times X_F^{Ap}]\}$$

where temperature (T) is in kelvins, apatite compositions are expressed in mole fractions (X_i^{Ap}), and R is the universal gas constant. With the two equations above, we established a calculation procedure for estimating the water concentrations in the melt, and have developed it into an online calculator (<https://apthermo.wovodat.org/>). Application of this method to volcanic apatite from the literature (e.g. from Pinatubo, Campi Flegrei, Santiaguito and Augustine) gives melt water concentrations that are equivalent or higher than those measured from melt inclusions. Our new calibrations of the exchange coefficients allow us to obtain more robust estimates of melt volatile budgets, which provide more insights into the effects of volatiles on a variety of volcanic and plutonic phenomena.

Contributions

Weiran Li: Compiling literature data, establishing the thermodynamic model based on regression calculation.

Fidel Costa: Discussion on thermodynamic calculation and the applications to natural system.

2.1. Introduction

Volatile abundances in melts are very important in controlling the eruptive styles of volcanoes (e.g. Blake, 1984; Roggensack et al., 1997; Cashman, 2004; Cashman and Sparks, 2013; Cassidy et al., 2018). Specifically, water dissolved and exsolved from the melt has a significant influence on melt viscosity and density, which in turn affect magma transport, ascent, and eruption dynamics (e.g. Lange, 1994; Giordano et al., 2008). Volatile exsolution from saturated melts due to decompression can cause large overpressures in the reservoir/conduit and increase the potential of explosive eruption (e.g. Blake, 1984; Wallace, 2005; Degruyter et al., 2017). Magmatic volatiles such as H₂O, CO₂, S, F, and Cl are usually investigated using melt inclusions (MIs) in crystals, which however can be absent in some deposits or not large enough (in size) for volatile analyses (e.g. Metrich and Wallace, 2008; Kent et al., 2008). Moreover, several factors have been recognized to affect the MIs volatile information, including: (i) post-eruptive crystallization, (ii) the sequestration of CO₂ into the bubble in the inclusions, and (iii) the H⁺ loss/gain from the host crystal via diffusion during magma storage/ascent/cooling (e.g. Qin et al. 1992; Danyushevsky et al. 2000; Gaetani and Watson 2000; Cottrell et al. 2001; Portnyagin et al. 2008; Lloyd et al. 2013).

An alternative indicator of melt volatile contents and their variation with magma evolution is the composition of apatite. Apatite can incorporate several volatile elements/molecules (e.g. F, Cl, H₂O, S, and CO₂) into its crystal structure (e.g. Webster and Piccoli, 2015; McCubbin et al., 2015; Riker et al., 2018), and has been exploited in recent decades to constrain volatile compositions in fluids/melt of plutonic and volcanic systems (e.g. Piccoli and Candela, 1994; Boudreau, 1995; Peng et al., 1997; Boyce and

Hervig, 2008; Boyce and Hervig, 2009; Van Hoose et al, 2013; Scott et al., 2015; Webster and Piccoli, 2015; Stock et al., 2016; Stock et al., 2018). Igneous apatite commonly contains volatile species including F, Cl and OH, and smaller amounts of other species, such as CO₂ (as CO₃²⁻; e.g. Piccoli and Candela, 2002), S (of multiple valences, e.g. S⁶⁺, S⁴⁺, and S²⁻; e.g. Kim et al., 2017; Konecke et al. 2017), and Br (e.g. Piccoli and Candela, 2002). Given our interest in constraining melt H₂O contents, here we focus on OH and the other two high-abundance species in apatite, i.e. F and Cl. Their concentrations can be determined using various techniques, e.g. electron microprobe (EPMA) and secondary ion mass spectrometry (SIMS), and expressed as mole fractions (X_i^{Ap} , i =F, Cl, OH) by considering the three endmembers, i.e. fluorapatite (FAP), chlorapatite (ClAp) and hydroxyapatite (HAp) (Fig. 2.1).

Igneous apatite has been found in a wide variety of rocks formed under a range of pressures and temperatures: from the upper mantle (e.g. O'Reilly and Griffin, 2000; Patiño Douce and Roden, 2006) to near the earth's surface, and from about 1200 °C to down to less than 650 °C (Fig. 2.1; e.g. Boudreau, 1995; Piccoli and Candela, 2002; Zhang et al., 2012; Webster and Piccoli, 2015). Apatite can occur in a variety of textural positions even within a single rock sample: as phenocrysts/microphenocrysts/microlites in the groundmass (e.g. Boyce and Hervig, 2008), or as inclusions in other minerals such as amphibole (Dietterich and de Silva, 2010), plagioclase (Humphreys et al., 2006), clinopyroxene (e.g. Scott et al., 2015), biotite (e.g. Zhang et al., 2012; Stock et al., 2016; Stock et al., 2018), and quartz (e.g. Borisova et al., 2005). Such range of textural positions provides an opportunity to comprehensively understand the variation of volatile concentrations during magma evolution and crystallization (e.g. Scott et al., 2015; Stock et al., 2016; Stock et al., 2018).

Fig. 2.1. F-Cl-OH ternary diagram showing the compositional ranges of apatite from (a) plutonic, metasomatic and carbonatitic rocks, and (b) volcanic rocks reported in literature. Apatite from mafic plutonic rocks include those of the Bushveld (B) and Stillwater (S) mafic intrusions (e.g. Boudreau and McCallum 1989; Boudreau and Kruger 1990; Boudreau et al. 1993; Boudreau, 1995; Meurer and Boudreau, 1996; Meurer et al., 2004; Meurer and Meurer, 2006), from felsic plutonic rocks (FP; e.g. granite) and felsic ore deposits (FO) (Piccoli and Candela, 2002; Sha and Chappell, 1999; Zhang et al., 2012). The metasomatic apatite (Meta) is close to the OH-Cl join (Kusebauch et al., 2015) or F-Cl join (Harlov et al., 2006), and carbonatitic ones are close to the OH-F join (Piccoli and Candela, 2002). Volcanic apatite shows similar range of F-Cl to the mafic plutons, and similar OH range to the felsic plutonic. Data in solid outlines were obtained using SIMS (from Campi Flegrei¹, in green; Cerro Galan² in blue; Irazu³ in red), whereas the rest using EPMA (with H₂O calculated from apatite stoichiometry). Data in shaded areas are from Huaynaputina⁴ (in blue), Santiaguito⁵ (in pink), Shiveluch Volcano⁶ (in grey) and Pinatubo 1991 eruption⁷ (in yellow). Data shown as solid squares were compiled by Webster et al. (2009) and are from: Augustine (in red), Mt. St. Helens 1980 (in purple), Tambora 1815 (in orange), Santorini (in blue), bishop tuff (in green) and Krakatau 1883 (in black). Data sources: ¹ Stock et al., (2018); ² Boyce and Hervig, (2008); ³ Boyce and Hervig, (2009); ⁴ Dietterich and de Silva, (2010); ⁵ Scott et al., (2015); ⁶ Humphreys et al., (2006); ⁷ Van Hoose et al. (2013).

To be able to use the F-Cl-OH concentrations in apatite and quantify the volatile abundances in melts requires a good understanding of volatile partitioning between apatite and melt. A simple way to describe the partitioning of one volatile species is to use the distribution coefficient, i.e. $D_i^{Ap-melt} = \frac{c_i^{Ap}}{c_i^{melt}}$, where c_i^{Ap} and c_i^{melt} are weight concentrations of component i in apatite and the melt ($i = \text{F, Cl, H}_2\text{O}$; e.g. Mathez and Webster, 2005; Webster et al., 2009; Doherty et al., 2014). However, previous studies reported that the distribution coefficients of F and Cl (i.e. $D_F^{Ap-melt}$, $D_{Cl}^{Ap-melt}$) can show large variations of up to two orders of magnitude for a given pressure (P) and temperature (T) condition (e.g. Mathez and Webster, 2005; Webster et al., 2009; Doherty et al., 2014), indicating that the partitioning of F and Cl do not follow Nernstian behavior, but instead vary with apatite and/or melt composition (e.g. McCubbin et al., 2015; Li and Hermann, 2017; McCubbin and Ustunisik, 2018; Riker et al., 2018). To mitigate the compositional effects, exchange coefficients (K_{DS}) have been proposed using the ratio of two anions (e.g. Li and Hermann, 2015; McCubbin et al., 2015; Li and Hermann, 2017; McCubbin and Ustunisik, 2018; Riker et al., 2018). Thus using the mole fractions of two anions (e.g. A, B) in apatite (i.e. X_A^{Ap} , X_B^{Ap}) and melt (i.e. X_A^{melt} , X_B^{melt}) we have:

$$K_{D_{A-B}}^{Ap-melt} = \frac{X_A^{Ap} \cdot X_B^{melt}}{X_A^{melt} \cdot X_B^{Ap}} \quad (1)$$

Eq. 1 is derived from the exchange reaction of components A and B between apatite and melt:

where its equilibrium constant $K_{P,T}$ is expressed as:

$$K_{P,T} = \frac{a_A^{Ap} \cdot a_B^{melt}}{a_A^{melt} \cdot a_B^{Ap}} \quad (3)$$

where a_i^α is the activity of component i in phase α , and $a_i^\alpha = X_i^\alpha \cdot \gamma_i^\alpha$ (X_i^α is the mole fraction, and γ_i^α is the activity coefficient). Eq. 3 can be re-written to include both $K_{P,T}$ and $K_{D_{A-B}}^{Ap-melt}$ as:

$$\begin{aligned} K_{P,T} &= \frac{(X_A^{Ap} \cdot \gamma_A^{Ap})(X_B^{melt} \cdot \gamma_B^{melt})}{(X_B^{Ap} \cdot \gamma_B^{Ap})(X_A^{melt} \cdot \gamma_A^{melt})} = \left(\frac{X_A^{Ap} \cdot X_B^{melt}}{X_B^{Ap} \cdot X_A^{melt}} \right) \cdot \left(\frac{\gamma_A^{Ap} \cdot \gamma_B^{melt}}{\gamma_B^{Ap} \cdot \gamma_A^{melt}} \right) \\ &= K_{D_{A-B}}^{Ap-melt} \cdot \left(\frac{\gamma_A^{Ap} \cdot \gamma_B^{melt}}{\gamma_B^{Ap} \cdot \gamma_A^{melt}} \right) \end{aligned} \quad (4)$$

For ideal behavior of A and B in apatite and melt, $\frac{\gamma_A^{Ap}}{\gamma_B^{Ap}}$ and $\frac{\gamma_A^{melt}}{\gamma_B^{melt}}$ are of fixed values, so that the exchange coefficient $K_{D_{A-B}}^{Ap-melt}$ is proportional to $K_{P,T}$, and thus only dependent on pressure and temperature. However, large variations of $K_{D_{OH-F}}^{Ap-melt}$ and $K_{D_{OH-Cl}}^{Ap-melt}$ were observed from experiments at single pressure-temperature, whose values vary by factors of up to 10-30 (especially at low temperature of 850 to 900 °C; Table 2.1; Fig. 2.2). Such variation is most likely caused by the non-ideality of F-Cl-OH mixing in apatite solid solution (e.g. McCubbin et al., 2015), which needs to be constrained for better interpreting the partitioning behavior of these volatiles. Non-ideal mixing in apatite could be anticipated given the difference in ionic radii of F, Cl and OH that occupy the same tunnel site (i.e. F⁻: 1.33 Å, OH⁻: 1.34 Å, Cl⁻: 1.81 Å; e.g. Shannon and Prewitt, 1969; White et al., 2005), so that their interactions with the neighboring

atoms (e.g. Ca and O) are likely different, especially between F (or OH) and Cl (e.g. Hughes and Rakovan, 2015; Hughes et al., 2014; Hughes et al., 2016). Non-ideal mixing has been studied in various multicomponent minerals (e.g. Saxena, 1973), such as feldspars (e.g. Thompson and Hovis, 1979; Ghiorso, 1984; Holland and Powell, 2003) and garnet (e.g. Ganguly and Saxena, 1984; Ganguly, 1996), but not yet for apatite at magmatic temperatures (e.g. > 700 °C).

In this study, we propose a new thermodynamic model that considers the non-ideal mixing properties in apatite solutions to investigate the partitioning behavior of F-Cl-OH between apatite and melt. Specifically, we have calculated the values of activity coefficients γ_i^{Ap} using the interaction parameters (Section 2.2), which are obtained by regression of the experimental data from the literature (Section 2.3). After this, we use the calculated values of thermodynamic properties (i.e. interaction parameters and Gibbs free energies) to establish new equations for K_{DS} (Section 2.4), and we explore the presence of solvus in the ternary apatite (Section 2.5). Using the new equations for K_{DS} , we propose a calculation procedure of estimating melt volatile budgets (Section 2.6). By applying the procedure to several volcanic systems, we found that the melt H₂O contents constrained by apatite are equivalent with (considering error) or higher than those measured from melt inclusions (Section 2.7). This thermodynamic model and calculation approach has been developed as a free online tool for calculating the exchange coefficients and melt H₂O concentrations (<https://apthermo.wovodat.org/>).

Table 2.1. Summary of data from F-Cl-OH partition experiments in literature.

	T (°C)	P (MPa)	Melt composition	H ₂ O in Ap by	H ₂ O in melt by	Melt H ₂ O (wt. %)	K _D (OH-Cl)			K _D (OH-F)			K _D (Cl-F)		
							Range	N*	Error† (%)	Range	N	Error (%)	Range	N	Error (%)
M15	990-1000	1000	Fe-rich basalt	SIMS	SIMS	2.7-3.6	0.04-0.11	8	19-33	0.016-0.02	7	23-36	0.15-0.30	7	32-42
	950-1000	1200		SIMS	SIMS	3.0-3.4	0.07-0.09	2		0.01-0.03	2		0.17-0.28	2	
R18	1250	1000	Haplo-basaltic andesite	SIMS	SIMS	0.6-7	0.08-0.14	2		0.05-0.11	7		0.2-0.5	2	
	1250	1000	Trachyte	SIMS	SIMS	2	-	0	62-84	0.029	1	30-116	-	0	75-92
	1250	500	Trachyte	SIMS	SIMS	~2.6	~0.09	2		0.025	2		0.12	2	
	844	50		Sto ¹	FTIR	2.5-2.8	0.02-0.05	6		0.003-0.06	6		0.05-2.7	6	
W17	850	50	Rhyolite	Sto	FTIR	2.2-3.7	0.02-0.16	8	11-50	0.01-0.04	7	23-200	0.09-2.0	7	18-200
	862	50		Sto	FTIR	2.4-3.1	0.02-0.04	4		0.01-0.02	4		0.3-0.5	4	
L&H17	800	2500	Pelite	Sto	Mb ²	~11-12	0.02-0.05	8	7-45	0.002-0.006	6	9-100	0.05-0.14	5	11-112
D14	900	50	Rhyodacite	Sto	FTIR	~1.9-2.3	0.04-0.15	3	46-59	0.009-0.04	3	55-104	0.08-1.1	3	32-93
	900-918	50		Sto	Mb	~2-6	0.02-0.04	10	21-102	0.002-0.03	13	37-200	0.07-1.5	10	11-200
W09	900-924	~200	Rhyodacite	Sto	Mb	~3-7	0.02-0.09	7	20-85	0.001-0.02	7	29-100	0.05-0.7	7	23-100
M&W05	~1100	200	Basalt	Sto	Mb	~4-8	0.09-0.23	7	22-94	0.009-0.06	7	23-90	0.07-0.5	7	13-73
L&H15	690-850	2500- 4500	Pelite	Sto	Mb	~11-39	0.02-0.77	10 [§]	19-77	-	0	-	-	0	-

¹ H₂O in apatite from stoichiometry calculation based on data from electron microprobe analyses (EPMA).

² H₂O in melt calculated from mass balance.

* N: number of K_D data from each experiment.

† Error: relative error in %. Numbers in italic represent minimal error, given multiple error sources of the stoichiometry and mass balance calculation.

§ includes data from multiple pressure-temperatures, where the number of data is ≤3 at single temperatures.

Data sources: **L&H17**: Li and Hermann, 2017; **M15**: McCubbin et al., 2015; **R18**: Riker et al., 2018; **W17**: Webster et al., 2017; **D14**: Doherty et al., 2014; **W09**: Webster et al., 2009; **M&W05**: Mathez and Webster, 2005.

Fig. 2.2. Experimental data for F-Cl-OH partitioning between apatite-melt. Most of the experimental apatite crystals are F- or Cl-rich, and poor in OH (panel a). For the exchange coefficients K_{DS} (shown in log units in panels b-d), $K_{D_{OH-F}}^{Ap-melt}$ (panel b) and $K_{D_{OH-Cl}}^{Ap-melt}$ (panel c) show positive correlation with temperature, whereas $K_{D_{Cl-F}}^{Ap-melt}$ (panel d) shows less T dependence. Data with smaller errors (Table 2.1; in solid symbols) were used for calculation in this study: **L&H17** = Li and Hermann (2017), in black stars; **M15** = McCubbin et al. (2015), in pink stars; **R18** = Riker et al. (2018), in red stars; **W17** = Webster et al. (2017), in blue diamonds. The rest of data not used for calculation include: D14 = Doherty et al. (2014), in blue circles; W09 = Webster et al. (2009), in blue dashed-line signs; M&W05 = Mathez and Webster (2005), in pink circles; L&H15 = Li and Hermann (2015), in green crosses; W09 = Webster et al. (2009), in blue dashed-line circles are from Potts et al., (2015) with un-reported Cl contents, thus they are not plotted in panel a nor used in our calculation.

2.2. Thermodynamic background

The exchange coefficients for OH-F, OH-Cl and Cl-F are derived from reactions that involve the exchange of two anions between apatite and melt (Eq. 2), where the equilibrium constant $K_{P,T}$ (Eq. 3) can be expressed using the standard Gibbs free energy of the reaction as

$$\Delta_r G_{A-B}^0(P, T) = -RT \ln K_{P,T} \quad (5)$$

By substituting Eq. 4 into Eq. 5, we obtain the relation between $\Delta_r G_{A-B}^0(P, T)$ and $K_{D_{A-B}}^{Ap-melt}$.

$$\begin{aligned} \Delta_r G_{A-B}^0(P, T) &= -RT \ln \left(K_{D_{A-B}}^{Ap-melt} \cdot \frac{\gamma_A^{Ap} \cdot \gamma_B^{melt}}{\gamma_B^{Ap} \cdot \gamma_A^{melt}} \right) \\ &= -RT \ln(K_{D_{A-B}}^{Ap-melt}) - RT \ln \left(\frac{\gamma_A^{Ap} \cdot \gamma_B^{melt}}{\gamma_B^{Ap} \cdot \gamma_A^{melt}} \right) \end{aligned} \quad (6)$$

which can be re-arranged as:

$$\begin{aligned} RT \ln(K_{D_{A-B}}^{Ap-melt}) &= -\Delta_r G_{A-B}^0(P, T) - RT \ln \left(\frac{\gamma_A^{Ap} \cdot \gamma_B^{melt}}{\gamma_B^{Ap} \cdot \gamma_A^{melt}} \right) \\ &= -\Delta_r G_{A-B}^0(P, T) - RT \ln \left(\frac{\gamma_B^{melt}}{\gamma_A^{melt}} \right) - RT \ln \left(\frac{\gamma_A^{Ap}}{\gamma_B^{Ap}} \right) \end{aligned} \quad (7)$$

Eq. 7 shows that $K_{D_{A-B}}^{Ap-melt}$ is determined by $\Delta_r G_{A-B}^0(P, T)$ which depends on P-T, as well as the activity coefficients ratios of two anions in melt ($\frac{\gamma_B^{melt}}{\gamma_A^{melt}}$) and in apatite ($\frac{\gamma_A^{Ap}}{\gamma_B^{Ap}}$), which we discuss in turn below.

The behavior of OH in silicate melts has been found to be nearly ideal (Zhang, 1999), whereas those of F and Cl are more complex, and their activity-composition relations have not been quantitatively determined. Previous studies showed that the behavior of F in the melt is likely more ideal than that of Cl (Carroll and Webster, 1994), therefore the activity coefficient ratio of F and OH (i.e., $\frac{\gamma_F^{melt}}{\gamma_{OH}^{melt}}$) is likely to have a small variation with changes in P - T - X conditions. Thus, we assume that $\frac{\gamma_F^{melt}}{\gamma_{OH}^{melt}}$ has an (unknown) fixed value in the calculation hereafter. Moreover, previous studies showed that the Cl solubility depends on melt composition more than pressure (Webster et al., 2015), whereas the H₂O solubility depends on pressure more than melt composition (Baker et al., 2012). Using the H₂O-Cl solubility data from the literature, we found that the effects of melt composition and pressure on the $\frac{\gamma_{Cl}^{melt}}{\gamma_{OH}^{melt}}$ values partially compensate each other, and the range of $\frac{\gamma_{Cl}^{melt}}{\gamma_{OH}^{melt}}$ at the experimental P - T - X conditions concerned in this study only cause variations in K_{DS} that are numerically similar to/less than the errors propagated from the experimental data (*Appendix A*). This means that $\frac{\gamma_{Cl}^{melt}}{\gamma_{OH}^{melt}}$ can be assumed to have a fixed value, and this assumption should not introduce large error to the K_D values within the specific datasets used for the calibration of our model (although $\frac{\gamma_{Cl}^{melt}}{\gamma_{OH}^{melt}}$ may have a different value if a brine is present; Webster et al., 1999; Mathez and Webster, 2005). Overall, we suggest that our formulations for K_{DS} can be applied to (i) rhyolitic

melts at 800-900 °C, 50-200 MPa, (ii) dacitic melts at 900-950 °C, 200-500 MPa, and (iii) basaltic to andesitic melts at 950-1050 °C, 200-1000 MPa.

Based on the assumptions that $\frac{\gamma_F^{melt}}{\gamma_{OH}^{melt}}$ and $\frac{\gamma_{Cl}^{melt}}{\gamma_{OH}^{melt}}$ have fixed values, and the fact that $\Delta_r G_{A-B}^0(P, T)$ also has a fixed value at a given P-T, we define a new term $\Delta_r G_{A-B}^*(P, T)$:

$$-\Delta_r G_{A-B}^*(P, T) = -\Delta_r G_{A-B}^0(P, T) - RT \ln \left(\frac{\gamma_B^{melt}}{\gamma_A^{melt}} \right) \quad (8)$$

which should also have a fixed value at a given P-T. By substituting Eq. 8 into Eq. 7, we simplified Eq. 7 as:

$$RT \ln (K_{D_{A-B}}^{Ap-melt}) = -\Delta_r G_{A-B}^*(P, T) - RT \ln \left(\frac{\gamma_A^{Ap}}{\gamma_B^{Ap}} \right) \quad (9)$$

which shows that the value of $K_{D_{A-B}}^{Ap-melt}$ is determined by $\Delta_r G_{A-B}^*(P, T)$ and $\left(\frac{\gamma_A^{Ap}}{\gamma_B^{Ap}} \right)$, which are to be solved from this study, and are discussed below based on the constraints on their values from the literature.

2.2.1. Activity coefficients of anions in apatite (γ_i^{Ap})

The activity coefficients of components in binary/ternary solutions can be expressed using the Gibbs free-energy interaction parameters W^G (e.g. Hildebrand, 1929; Wohl, 1946). The simplest model is to assume a simple symmetric mixture, where for a A-B binary solution, the W^G s of A-B and B-A are equal to each and expressed as $W_{A,B}^G$ (e.g.

Saxena, 1973; Anderson and Crerar, 1993). Similarly, for the ternary solution of A-B-C, the three W^G s are expressed as $W_{A,B}^G$, $W_{A,C}^G$, and $W_{B,C}^G$ respectively. In the ternary apatite, the activity coefficients γ_{Cl}^{Ap} , γ_{OH}^{Ap} and γ_F^{Ap} can be then expressed as the three equations below (Li and Hermann, 2017):

$$RT \ln(\gamma_{Cl}^{Ap}) = X_{OH}^{Ap} (1 - X_{Cl}^{Ap}) W_{Cl,OH}^G + X_F^{Ap} (1 - X_{Cl}^{Ap}) W_{F,Cl}^G - X_{OH}^{Ap} X_F^{Ap} W_{F,OH}^G \quad (10)$$

$$RT \ln(\gamma_{OH}^{Ap}) = X_{Cl}^{Ap} (1 - X_{OH}^{Ap}) W_{Cl,OH}^G + X_F^{Ap} (1 - X_{OH}^{Ap}) W_{F,OH}^G - X_{Cl}^{Ap} X_F^{Ap} W_{F,Cl}^G \quad (11)$$

$$RT \ln(\gamma_F^{Ap}) = X_{Cl}^{Ap} (1 - X_F^{Ap}) W_{F,Cl}^G + X_{OH}^{Ap} (1 - X_F^{Ap}) W_{F,OH}^G - X_{Cl}^{Ap} X_{OH}^{Ap} W_{Cl,OH}^G \quad (12)$$

which can be used to obtain the ratios of any two activity coefficients. For example, by subtracting Eq. 10 from Eq. 11, we obtain the equation for $\frac{\gamma_{OH}^{Ap}}{\gamma_{Cl}^{Ap}}$ as:

$$RT \ln\left(\frac{\gamma_{OH}^{Ap}}{\gamma_{Cl}^{Ap}}\right) = (X_{Cl}^{Ap} - X_{OH}^{Ap}) W_{Cl,OH}^G + X_F^{Ap} (W_{F,OH}^G - W_{F,Cl}^G) \quad (13)$$

By substituting Eq. 13 into Eq. 9 (where we define A and B as OH and Cl, respectively), the equation for $K_{D_{OH-Cl}}^{Ap-melt}$ can be written to include W^G s as:

$$RT \ln(K_{D_{OH-Cl}}^{Ap-melt}) = -\Delta_r G_{OH-Cl}^*(P, T) - [(X_{Cl}^{Ap} - X_{OH}^{Ap}) W_{Cl,OH}^G + X_F^{Ap} (W_{F,OH}^G - W_{F,Cl}^G)] \quad (14)$$

Similar relations can be written for $K_{D_{OH-F}}^{Ap-melt}$ and $K_{D_{Cl-F}}^{Ap-melt}$:

$$RT \ln(K_{D_{OH-F}}^{Ap-melt}) = -\Delta_r G_{OH-F}^*(P, T) - [(X_F^{Ap} - X_{OH}^{Ap}) W_{F,OH}^G + X_{Cl}^{Ap} (W_{Cl,OH}^G - W_{F,Cl}^G)] \quad (15)$$

and

$$RT \ln(K_{D_{Cl-F}}^{Ap-melt}) = -\Delta_r G_{Cl-F}^*(P, T) - [(X_F^{Ap} - X_{Cl}^{Ap}) W_{F,Cl}^G + X_{OH}^{Ap} (W_{Cl,OH}^G - W_{F,OH}^G)] \quad (16)$$

Eqs. 14-16 show that the K_D values are determined by $\Delta_r G_{A-B}^*(P, T)$, the three W^G s (i.e. $W_{Cl,OH}^G$, $W_{F,OH}^G$, $W_{F,Cl}^G$), and apatite composition (i.e. X_F^{Ap} , X_{Cl}^{Ap} , X_{OH}^{Ap}), where the apatite compositions can be measured, but the values of $\Delta_r G_{A-B}^*(P, T)$ and W^G s have been poorly constrained (Sections 2.2.2 and 2.2.3). Therefore, we have calculated them by regression of experimental data from the literature (see Section 2.3).

2.2.2. Existing data for interaction parameters $W_{A,B}^G$ in apatite solutions

The $W_{A,B}^G$ in a simple symmetric mixture can be expressed using the excess mixing Gibbs free energy ($\Delta_m G_{A,B}^{ex} = W_{A,B}^G X_A X_B$; Guggenheim, 1967), where the values of $\Delta_m G_{A,B}^{ex}$ are usually derived from calorimetric measurements of the excess mixing enthalpies and entropies (e.g. Haselton et al., 1983). For an ideal solution, $\Delta_m G_{A,B}^{ex} = 0$ so that $W_{A,B}^G = 0$, whereas for non-ideal solutions, both $\Delta_m G_{A,B}^{ex}$ and $W_{A,B}^G$ differ from zero (e.g. Saxena, 1973). In addition, $W_{A,B}^G$ can also be expressed using the enthalpic,

entropic, and volumetric terms of the interaction parameters, i.e. $W_{A,B}^H$, $W_{A,B}^S$, and $W_{A,B}^V$, (Ganguly, 2001) as:

$$W_{A,B}^G = W_{A,B}^H - T \cdot W_{A,B}^S + P \cdot W_{A,B}^V \quad (17)$$

where $W_{A,B}^H$ and $W_{A,B}^S$ have non-negative values, and $W_{A,B}^V$ is typically of small positive value in solid solutions, indicating small pressure effects for $W_{A,B}^G$ (Ganguly et al., 1996; Ganguly, 2008).

The few calorimetric data have been reported for apatite binaries show larger ideality of F-OH mixing ($W_{OH,F}^G$ close to 0; Hovis et al., 2014) than F-Cl (Hovis and Harlov, 2010). For the F-Cl binary, the value of the interaction parameter of the enthalpic term ($W_{F,Cl}^H$) is large (23 to 43 $\text{kJ} \cdot \text{mol}^{-1}$; Hovis and Harlov, 2010), whereas those of the entropic and volumetric parameters are small ($W_{F,Cl}^S \cong 7.7 \pm 10.1 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$, Dachs et al., 2010; $W_{F,Cl}^V \cong 0$, Hovis et al., 2015). Based on Eq. 17, $W_{F,Cl}^G$ at magmatic temperatures should be positive (e.g. between 3 and 43 $\text{kJ} \cdot \text{mol}^{-1}$ at 700-1000 °C), indicating non-ideal mixing in F-Cl binary apatite. Although there is no calorimetric data for the Cl-OH binary, $W_{Cl,OH}^G$ has been proposed to vary from -20 to 15 $\text{kJ} \cdot \text{mol}^{-1}$ at 300-700 °C based on experimental data for Cl-OH partitioning between apatite and fluids (Tacker and Stormer, 1989). Most of the interaction parameters mentioned above have large variations and errors, which result in a wide range of calculated K_{DS} , thus here they are only considered as a first order of magnitude guidance. To better quantify the W^G values, we have used another method by regression of experimental data for apatite-melt partitioning (i.e. K_D) reported in literature (Section 2.3).

2.2.3. Difficulties in direct calculation of $\Delta_r G_{A-B}^*(P, T)$

To calculate K_D , we need to constrain $\Delta_r G_{A-B}^*(P, T)$, which is not straightforward. $\Delta_r G_{A-B}^*(P, T)$ as defined in Eq. 8 involves two parameters, i.e. (1) the ratio of the activity coefficients of two components in melt ($\frac{\gamma_B^{melt}}{\gamma_A^{melt}}$), which we assume as constant, and (2) the standard Gibbs free energy of the exchange reaction (see Eq. 2), i.e. $\Delta_r G_{A-B}^0(P, T)$, which is P- and T-dependent. The standard Gibbs free energy of the reaction is usually calculated using the thermodynamic properties of reactants and products, which in our case are the end-member apatite and the two volatile species in melts. Although the thermodynamic properties of apatite are relatively well constrained (e.g. Zhu and Sverjensky, 1992; Piccoli and Candela, 1994; Drouet, 2015), the properties of the volatile species of interest in melts are poorly known. This is probably due to the complex interaction between the halogen-bearing species in melt (present as multiple components such as NaCl, KCl and MgCl₂; Aiuppa, 2009), and the potentially more complex interaction between the volatile species and oxides in melt (e.g. SiO₂, Al₂O₃; e.g. Ghiorso and Sack, 1995). Considering these complexities, we derived the values of $\Delta_r G_{A-B}^0(P, T)$ using the same method as for calculating $W_{A,B}^G$ by regression of experimental data from literature.

2.3. An approach for determining $W_{A,B}^G$ and $\Delta_r G_{A-B}^*(P, T)$ by regression of the experimental data from the literature

Exchange coefficients (K_{DS}) reported in literature were calculated using apatite and melt compositions using: (1) the weight concentrations of F, Cl and H₂O (e.g. McCubbin et

al. 2015), or (2) the mole fractions of F, Cl, and OH, where that of OH in melt needs to be calculated using H₂O speciation models according to the reaction: $(H_2O)_{molecular} (melt) + Oxygen (melt) = 2OH (melt)$ (e.g. Burnham, 1975; Stolper, 1982; Zhang, 1999). The two methods give equal values of $K_D^{Ap-melt}_{Cl-F}$ (*Appendix B*), but not for $K_D^{Ap-melt}_{OH-F}$ or $K_D^{Ap-melt}_{OH-Cl}$, as the mole fraction of OH in melt varies with temperature, the total water concentration, and to some extent the melt composition (e.g. Zhang, 1999; Botcharnikov et al. 2006). We have used the mole fractions to calculate the values of K_D s from experiments, and the water speciation models were selected according to the melt composition as explained in *Appendix B*. Specifically, we use the water speciation model from Zhang et al. (1997) for rhyolite, from Botcharnikov et al. (2006) for basaltic-andesite, and from Lesne et al. (2010) for basalt. The calculated K_D s based on mole fractions are shown in Figs. 2.2-2.3 and their values are reported in *Appendix C*. As K_D is determined by all the three X_i^{Ap} s (Eqs. 14-16), one could not estimate the values of unknowns by simply plotting K_D with any single X_i^{Ap} (Fig. 2.3). We have used a generalized-least-squares-regression procedure to calculate the values of $W_{A,B}^G$ and $\Delta_r G_{A-B}^*(P, T)$ and their errors as described below.

Fig. 2.3. Values of $RT\ln(K_d^{Ap-melt})$ (in J/mol), plotted against apatite compositions, expressed as mole fractions of one component (panels *a*, *c*, *e*), or the differences between two components (panels *b*, *d*, *f*) (referring to Eqs. 14-16). Data symbols, abbreviations and sources as in Fig. 2.2.

2.3.1. Solution of equations

To explain our calculation approach, we take $K_{D_{OH-Cl}}^{Ap-melt}$ as an example. For an experimental dataset that contains N values of $K_{D_{OH-Cl}}^{Ap-melt}$ (each data point identified using subscript $k, k = 1, 2, 3 \dots N$), we substituted $(K_{D_{OH-Cl}}^{Ap-melt})_k$ and $(X_i^{Ap})_k$ into Eq. 14 and obtained:

$$RT \ln \left[(K_{D_{OH-Cl}}^{Ap-melt})_k \right] = -\Delta_r G_{OH-Cl}^*(P, T) - \left\{ \left[(X_{Cl}^{Ap})_k - (X_{OH}^{Ap})_k \right] \cdot W_{Cl,OH}^G + (X_F^{Ap})_k \cdot \{W_{F,OH}^G - W_{F,Cl}^G\} \right\} \quad (18)$$

The N equations in the form of Eq. 18 can be expressed in matrix form as:

$$\mathbf{Y} = \mathbf{M}\mathbf{x} \quad (19)$$

where

$$\mathbf{Y} = \begin{pmatrix} RT \ln \left[(K_{D_{OH-Cl}}^{Ap-melt})_1 \right] \\ RT \ln \left[(K_{D_{OH-Cl}}^{Ap-melt})_2 \right] \\ \vdots \\ RT \ln \left[(K_{D_{OH-Cl}}^{Ap-melt})_N \right] \end{pmatrix}$$

$$\mathbf{M} = \begin{pmatrix} -1 & -\left[(X_{Cl}^{Ap})_1 - (X_{OH}^{Ap})_1 \right] & -(X_F^{Ap})_1 \\ -1 & -\left[(X_{Cl}^{Ap})_2 - (X_{OH}^{Ap})_2 \right] & -(X_F^{Ap})_2 \\ \vdots & \vdots & \vdots \\ -1 & -\left[(X_{Cl}^{Ap})_N - (X_{OH}^{Ap})_N \right] & -(X_F^{Ap})_N \end{pmatrix}$$

and

$$\mathbf{x} = \begin{pmatrix} \Delta_r G_{OH-Cl}^*(P, T) \\ W_{Cl,OH}^G \\ \{W_{F,OH}^G - W_{F,Cl}^G\} \end{pmatrix}$$

where $\mathbf{x}$ contains the unknown parameters to be determined. Similar equations can be derived from the known values of $K_{D_{OH-F}}^{Ap-melt}$ and $K_{D_{Cl-F}}^{Ap-melt}$ for the determination of

$$\begin{pmatrix} \Delta_r G_{OH-F}^*(P, T) \\ W_{F,OH}^G \\ \{W_{Cl,OH}^G - W_{F,Cl}^G\} \end{pmatrix} \text{ and } \begin{pmatrix} \Delta_r G_{Cl-F}^*(P, T) \\ W_{F,Cl}^G \\ \{W_{Cl,OH}^G - W_{F,OH}^G\} \end{pmatrix}.$$

The parameters in curly brackets are the difference between two W^G s (e.g. $\{W_{F,OH}^G - W_{F,Cl}^G\}$), which is taken as one unknown parameter, given that from the above equations we can only determine their difference, but not the individual values of the two W^G s. Under such conditions, $\mathbf{x}$ contains three unknown parameters, which requires at least three relations in the form of Eq. 18, i.e. $N \geq 3$. Considering the errors of values in $\mathbf{M}$ (i.e. mole fractions of anions in apatite derived from measurements; *Appendices B* and *C*), we can express the weight of each data point (w_k) using its standard error (σ_k) as: $w_k = \frac{1}{\sigma_k^2}$, so that the data with smaller variance have a bigger weight in the regression (and vice versa). Using a weighted least-squares expression (e.g. Ghilani and Wolf, 2006), we can write the solution of Eq. 19 as:

$$\mathbf{x} = \begin{cases} (\mathbf{WM})^{-1}\mathbf{Y} & (N = 3) \\ (\mathbf{M}^T \mathbf{WM})^{-1} \cdot \mathbf{M}^T \cdot \mathbf{Y} & (N > 3) \end{cases} \quad (20)$$

where $\mathbf{W}$ is a diagonal matrix made up of w_k values that weight the data (see above), and $\mathbf{M}^T$ is the transpose of $\mathbf{M}$.

The solution above only considers the errors of apatite compositions, but not the error of K_D , which is still not sufficient to derive robust values of $W_{A,B}^G$ and $\Delta_r G_{A-B}^*(P, T)$. Thus, we decided to use a generalized-least-squares-regression procedure that considers the errors in all the parameter values in $\mathbf{M}$ (i.e. apatite compositions and K_D ; details of the procedure in *Appendix D*). Given the importance of the experimental data for our regression, we first provide a summary of the experimental data quality, including their errors and the total numbers of data points available for regression.

2.3.2. Availability and screening of experimental data from the literature

Experimental data of K_D for the apatite-melt partitioning have been reported for a wide range of P-T conditions (i.e. 800 to 1250 °C, 50 MPa to 2.5 GPa), and cover a spread of apatite and melt compositions (Table 2.1; Figs. 2.2-2.3; Mathez and Webster, 2005: M&W05; Webster et al., 2009: W09; Doherty et al., 2014: D14; McCubbin et al., 2015: M15; Li and Hermann, 2017: L&H17; Webster et al., 2017: W17; Riker et al., 2018: R18). The errors of K_D s differ between studies, depending on the analytical techniques and the abundances of volatiles in apatite and melts. The relative errors in the F and Cl contents (*Appendix C*) in apatite (~ 1-12% relative) are lower than those for the melts (~ 10-40%, up to >100%), due to typically lower F and Cl abundances in the melt than in apatite. This translates to relative errors of ~ 10-50% (up to 200%) in $K_D^{Ap-melt}_{Cl-F}$.

Compared to $K_D^{Ap-melt}_{Cl-F}$, the errors in $K_D^{Ap-melt}_{OH-F}$ and $K_D^{Ap-melt}_{OH-Cl}$ can be either larger or smaller, depending on how the concentrations of H₂O were determined. In some experiments, water was not directly measured but calculated with the “by difference”

method for apatite, and from “mass balance” in the melt (e.g. Piccoli and Candela, 2002). The calculated H₂O contents likely have large errors, including the analytical errors of other elements, and the assumption of full occupancy of F, Cl, OH at the anion site of apatite, which is not always true (e.g. Piccoli and Candela, 2002). Given that our regressed results are sensitive to the error of experimental data, we have mainly used K_{DS} where H₂O contents were measured (i.e. M15 and R18 in Table 2.1). Those without direct H₂O determinations (i.e. W17 and L&H17) were only used to explore the variation of the thermodynamic properties at P-T conditions not covered by other studies, and when they are consistent with the datasets with direct water determinations (i.e. M15 and R18). Some experiments were not used (Table 2.1) due to either the large uncertainties of the data, or the unavailability of melt H₂O contents. In summary, the relative errors of $K_{D_{OH-F}}^{Ap-melt}$ and $K_{D_{OH-Cl}}^{Ap-melt}$ used for regression are about 9-200% and 7-84%, respectively. The generally larger error of $K_{D_{OH-F}}^{Ap-melt}$ than $K_{D_{OH-Cl}}^{Ap-melt}$ is related to larger analytical error in F, due to the generally lower F contents (than Cl) in the experimental melts.

Another source of error is the total number of K_{DS} for each experiment: more data yield more precise solutions based on the principle of weighted-least-squares regression. When limited data are available for a given pressure-temperature, we used those from the same experiment at slightly different P-T conditions (e.g. from M15 at 1-1.2 GPa and 990-1000 °C; from W17 at 844-862 °C and 50 MPa). This does not significantly affect the results given the small temperature differences (< 20 °C) and the small P-T dependence of W^G (see Section 2.2.2). In addition, different numbers of data are sometimes reported from the same experiment for the three different K_{DS} , which is related to the compositions of the experimental apatite. For example, the experiments

by R18 used seven apatite crystals that contain only F and OH thus provide seven values for $K_{D_{OH-F}}^{Ap-melt}$, whereas only two were reported for $K_{D_{OH-Cl}}^{Ap-melt}$ and $K_{D_{Cl-F}}^{Ap-melt}$ (Table 2.1), which are insufficient for regression. We did not combine the data of R18 at different pressures for the regression of $K_{D_{OH-Cl}}^{Ap-melt}$ nor $K_{D_{Cl-F}}^{Ap-melt}$ (Table 2.1), because the melts have very different compositions (i.e. trachyte at 0.5 GPa, and haplobasaltic-andesite at 1 GPa).

In summary, the interaction parameters and Gibbs free energy reported below were calculated using the data of $K_{D_{OH-Cl}}^{Ap-melt}$ and $K_{D_{Cl-F}}^{Ap-melt}$ from three datasets (M15, W17, L&H17) and $K_{D_{OH-F}}^{Ap-melt}$ from four datasets (M15, W17, L&H17, R18; see data in *Appendix C*).

2.4. Calculated values of $\Delta_r G_{A-B}^*(P, T)$ and $W_{A,B}^G$

2.4.1 Gibbs free energy $\Delta_r G_{A-B}^*(P, T)$

The values of the $\Delta_r G_{A-B}^*(P, T)$ calculated for 800 to 1250 °C and 50 MPa to 1 GPa are: $\Delta_r G_{OH-F}^*(P, T) = 33 (\pm 1)$ to $55 (\pm 3)$ kJ/mol, $\Delta_r G_{OH-Cl}^*(P, T) = 30 (\pm 2)$ to $37 (\pm 4)$ kJ/mol, and $\Delta_r G_{Cl-F}^*(P, T) = 7 (\pm 3)$ to $34 (\pm 17)$ kJ/mol (Table 2.2). $\Delta_r G_{OH-Cl}^*(P, T)$ and $\Delta_r G_{OH-F}^*(P, T)$ show negative correlation with T (Fig. 2.4), and can be expressed (ignoring pressure effect) as:

$$\Delta_r G_{OH-F}^*(P, T) = 94600 (\pm 5600) - 40 (\pm 0.1) \times T \quad (R^2=0.90) \quad (21)$$

$$\Delta_r G_{OH-Cl}^*(P, T) = 72900 (\pm 2900) - 34 (\pm 0.3) \times T \quad (R^2=0.88) \quad (22)$$

where $\Delta_r G_{OH-Cl}^*(P, T)$ and $\Delta_r G_{OH-F}^*(P, T)$ are in J/mol, and T is in kelvins.

The pressure effects on $\Delta_r G_{OH-Cl}^*(P, T)$ and $\Delta_r G_{OH-F}^*(P, T)$ could not be constrained from the limited numbers of data that are available (i.e. $N \leq 4$) (Table 2.2), nonetheless the influence seem to be very small, considering the good linearity between the temperature and Gibbs free energy parameters, as shown in Eqs. 21-22 ($R^2=0.88-0.90$). $\Delta_r G_{Cl-F}^*(P, T)$ does not show any linear correlation with T ($R^2=0.056$; Fig. 2.4), which might be related to the large errors of $\Delta_r G_{Cl-F}^*(P, T)$ (up to ~ 17 kJ/mol) propagated from the experimental data for $K_D^{Ap-melt}$.

Fig. 2.4. The relation between temperature and the Gibbs free energies of exchange reactions calculated from regression of K_D : (a) $\Delta_r G_{OH-F}^*(P, T)$, (b) $\Delta_r G_{OH-Cl}^*(P, T)$, (c) $\Delta_r G_{Cl-F}^*(P, T)$. $\Delta_r G_{OH-F}^*(P, T)$ and $\Delta_r G_{OH-Cl}^*(P, T)$ show good linear correlation with temperature ($R^2=0.90$ and 0.88), but this is not the case for $\Delta_r G_{Cl-F}^*(P, T)$. The best-fit relations (in red solid lines) were obtained from a least-squares regression by considering the errors propagated from the experimental data.

2.4.2 Interaction parameters $W_{A,B}^G$

The W^G values are about an order of magnitude smaller than those of the Gibbs free energies (Table 2.2). Except the data from L&H17 at 2.5 GPa and 800 °C, those reported from other experiments give $W_{Cl,OH}^G = 2$ to 4 kJ/mol, $W_{F,OH}^G = -2$ to -5 kJ/mol, and $W_{F,Cl}^G = -1$ to -14 kJ/mol, with uncertainties of ± 3 to 5 kJ/mol (up to ± 7 kJ/mol). These values are within the range of data derived from calorimetric determination (i.e. $W_{F,OH}^G \approx 0$, and $W_{F,Cl}^G \leq 43$ kJ/mol; Hovis et al., 2014, Hovis et al., 2015; Section 2.2.2). The small W^G values calculated for L&H17 is unexpected, since W^G is usually larger at such low temperature and high pressure (see Eq. 17). The reason for such discrepancy is unclear but might be related to the effects of high melt H₂O contents (of 11-12 wt.%) used in those experiments on the activity of melt OH and/or Cl.

Given the small value of the entropic interaction parameters $W_{A,B}^S$ (e.g. $W_{F,Cl}^S = 7.7 \pm 10.1 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$; Dachs et al., 2010), the variation in the W^G values with temperature is small, and thus can be expressed using the mean values. With such simplification we can combine K_D data from four experiments (M15, W17, R18, L&H17) and increase the number of K_D ($N = 33 \sim 40$), to calibrate $W_{Cl,OH}^G$ and $W_{F,OH}^G$ (Appendix D). This gives smaller errors to the calculated W^G s, i.e. $W_{Cl,OH}^G = 5 (\pm 2)$ kJ/mol, and $W_{F,OH}^G = 7 (\pm 4)$ kJ/mol (Table 2.3). Given the poorly constrained values of $\Delta_r G_{Cl-F}^*(P, T)$ (see Section 4.1), we did not apply this approach to $W_{F,Cl}^G$, but instead calculated it from the other two binaries: $W_{F,Cl}^G = W_{Cl,OH}^G - \{W_{Cl,OH}^G - W_{F,Cl}^G\}$ and $W_{F,Cl}^G = W_{F,OH}^G - \{W_{F,OH}^G - W_{F,Cl}^G\}$. The two calculated $W_{F,Cl}^G$ values are consistent

within uncertainty, and thus we have taken their mean for calculations hereafter, i.e.

$$\overline{W_{F,Cl}^G} = 16 (\pm 6) \text{ kJ/mol (Table 2.3).}$$

Table 2.2. Values of $W_{A,B}^G$ (in J/mol) and $\Delta_r G_{A-B}^*$ (in J/mol) calculated by regression of data from individual experimental studies.

	L&H17	M15	R18	W17
T (°C)	800	~1000	1250	~850
P (MPa)	2500	1000	1000	50
Calculated using $K_D^{Ap-melt}_{OH-Cl}$				
N	8	11	2*	16
$W_{Cl,OH}^G$	101	3770	n.d.	3610
Error †	3950	4270	n.d.	3490
$\{W_{F,OH}^G - W_{F,Cl}^G\}$	-10100	-6440	n.d.	-8450
Error	3010	4710	n.d.	3970
$\Delta_r G_{OH-Cl}^*$	35700	29700	n.d.	36500
Error	2120	2580	n.d.	1510
Calculated using $K_D^{Ap-melt}_{OH-F}$				
N	6	10	7	17
$W_{F,OH}^G$	-22800	-2260	5410	2520
Error	7210	4280	8400	4550
$\{W_{Cl,OH}^G - W_{F,Cl}^G\}$	11500	4110	9490	-12200
Error	17300	7810	23900	6360
$\Delta_r G_{OH-F}^*$	55000	43000	33400	46400
Error	2320	2840	3410	2150
Calculated using $K_D^{Ap-melt}_{Cl-F}$				
N	5	10	2*	16
$W_{F,Cl}^G$	-20700	-1430	n.d.	13900
Error	13400	2630	n.d.	3360
$\{W_{Cl,OH}^G - W_{F,OH}^G\}$	-198	-6350	n.d.	10200
Error	33700	13200	n.d.	9990
$\Delta_r G_{Cl-F}^*$	33600	20300	n.d.	6840
Error	17100	3690	n.d.	3160

† Errors (of 1σ) are propagated from the uncertainties of experimental data (*Appendix C*). Data sources and labels in Table 2.1.

* Insufficient numbers of data for regression.

Table 2.3. Interaction parameter $W_{A,B}^G$ (in J/mol), calculated by regression of all the experimental data in Table 2.2 ($N=33-40$).

	Value	Error (1σ)
$W_{Cl,OH}^G$	4934 [†]	2088
$\{W_{F,OH}^G - W_{F,Cl}^G\}$	-4526	2692
$W_{F,OH}^G$	6618	4370
$\{W_{Cl,OH}^G - W_{F,Cl}^G\}$	-16527	6984
calc $W_{F,Cl}^G$, by difference ¹	21461	7289
calc $W_{F,Cl}^G$, by difference ²	11144	5133
Mean, $W_{F,Cl}^G$	16303	6211

[†] Values marked in bold were used for deriving equations for $K_{D_{A-B}}^{Ap-melt}$ in Section 2.4.3.

¹ Calculated by $W_{F,Cl}^G = W_{Cl,OH}^G - \{W_{Cl,OH}^G - W_{F,Cl}^G\}$.

² Calculated by $W_{F,Cl}^G = W_{F,OH}^G - \{W_{F,OH}^G - W_{F,Cl}^G\}$.

2.4.3. Formulations for the exchange coefficients K_D s

Using the calculated $W_{A,B}^G$ values (Table 2.3) and Eqs. 21-22 for $\Delta_r G_{A-B}^*(P, T)$, the new equations for $K_{D_{OH-F}}^{Ap-melt}$ and $K_{D_{OH-Cl}}^{Ap-melt}$ that include non-ideal mixing in apatite are expressed as:

$$\ln(K_{D_{OH-F}}^{Ap-melt}) = -\frac{1}{RT} \times \{94600 (\pm 5600) - 40 (\pm 0.1) \times T - 1000 \times [7 (\pm 4) \times (X_F^{Ap} - X_{OH}^{Ap}) - 11 (\pm 7) \times X_{Cl}^{Ap}]\} \quad (23)$$

and

$$\ln(K_{D_{OH-Cl}}^{Ap-melt}) = -\frac{1}{RT} \times \{72900 (\pm 2900) - 34 (\pm 0.3) \times T - 1000 \times [5 (\pm 2) \times (X_{Cl}^{Ap} - X_{OH}^{Ap}) - 10 (\pm 8) \times X_F^{Ap}]\} \quad (24)$$

where T is in kelvins, apatite composition is expressed in mole fractions (X_i^{Ap}), and R is the universal gas constant.

Given the large uncertainty in the calculated values of $\Delta_r G_{Cl-F}^*(P, T)$ (Section 2.4.1), we did not use them for calculating $K_{D_{Cl-F}}^{Ap-melt}$. Instead we derived the equation for $K_{D_{Cl-F}}^{Ap-melt}$ from the relation of $K_{D_{Cl-F}}^{Ap-melt} = K_{D_{OH-F}}^{Ap-melt} / K_{D_{OH-Cl}}^{Ap-melt}$ and Eqs. 23-24 above, and we obtained:

$$\ln(K_{D_{Cl-F}}^{Ap-melt}) = -\frac{1}{R \cdot T} \times \{21700 (\pm 6300) - 6 (\pm 0.3) \times T - 1000 \times [16 (\pm 6) \times (X_F^{Ap} - X_{Cl}^{Ap}) - 2 (\pm 5) \times X_{OH}^{Ap}]\} \quad (25)$$

The K_D values calculated from Eqs. 23-25 and those measured from experiments show good match, especially for $K_{D_{OH-Cl}}^{Ap-melt}$ (Fig. 2.5). By comparing the 37 values of $K_{D_{OH-Cl}}^{Ap-melt}$ determined from experiments with those calculated using Eq. 24, we find that 30 values from our calculation are equivalent to those reported from experiments considering errors (Fig. 2.5b).

Fig. 2.5. Exchange coefficients $K_{D_{A-B}}^{Ap-melt}$ s (in base ten logarithms) modelled from this study vs. measured from experiments: (a) $\log(K_{D_{OH-F}}^{Ap-melt})$, (b) $\log(K_{D_{OH-Cl}}^{Ap-melt})$ and (c) $\log(K_{D_{Cl-F}}^{Ap-melt})$. The modelled and measured values follow a general 1-by-1 relation (marked in dashed lines) considering the uncertainties. Symbols and data sources as in Fig. 2.2.

2.4.4. Effects of temperature, pressure, and apatite composition on K_D s

The relation between the K_D values for the three binaries at a given temperature is generally: $K_{D_{Cl-F}}^{Ap-melt} > K_{D_{OH-Cl}}^{Ap-melt} > K_{D_{OH-F}}^{Ap-melt}$ (Fig. 2.6). Both $K_{D_{OH-Cl}}^{Ap-melt}$ and $K_{D_{OH-F}}^{Ap-melt}$ decrease with decreasing temperature (by factor of ~ 1.4 with a decrease of 50°C in temperature). The value of $K_{D_{Cl-F}}^{Ap-melt}$ depends less on T (e.g. $< 10\%$ decrease with a T decrease of 50°C) than on the apatite composition (see below). The pressure

effects have not been calibrated but are likely to be small, given the strong correlation of T and $\Delta_r G_{A-B}^*(P, T)$ as shown in Eqs. 21-22 ($R^2=0.88-0.90$; Fig. 2.4). The three K_D s show larger dependence on apatite composition than on T (Fig. 2.6). At 950 °C, the maxima of $K_D^{Ap-melt}_{OH-F}$ and $K_D^{Ap-melt}_{OH-Cl}$ (of ~ 0.03 and 0.11, respectively) are near the ClAp and the FAp endmembers respectively in the ternary diagram (Fig. 2.6a-b), whereas the largest value of $K_D^{Ap-melt}_{Cl-F}$ (of ~ 1.1) is near the ClAp endmember (Fig. 2.6c). The variation of $K_D^{Ap-melt}_{Cl-F}$ across the ternary (by factor of ~ 20) is much larger than those of $K_D^{Ap-melt}_{OH-F}$ and $K_D^{Ap-melt}_{OH-Cl}$ (by factors of 4 to 6). The large compositional effects on $K_D^{Ap-melt}_{Cl-F}$ are related to less ideality of F-Cl mixing in apatite compared to that of F-OH and Cl-OH (Section 2.4.2).

Fig. 2.6. Variations in the exchange coefficients $K_D^{Ap-melt}_{OH-F}$, $K_D^{Ap-melt}_{OH-Cl}$ and $K_D^{Ap-melt}_{Cl-F}$ across the F-Cl-OH ternary at 950 °C (panels a-c), and 1000 °C (panels d-f). At a given temperature, there is a larger variation in the $K_D^{Ap-melt}_{Cl-F}$ values across the ternary than those of $K_D^{Ap-melt}_{OH-F}$ and $K_D^{Ap-melt}_{OH-Cl}$. K_D s show generally higher values at higher Ts. $K_D^{Ap-melt}_{OH-F}$ and $K_D^{Ap-melt}_{OH-Cl}$ show larger T-dependence than $K_D^{Ap-melt}_{Cl-F}$ does.

2.4.5. Activity coefficient γ_i^{Ap} calculated using $W_{A,B}^G$ s

The relationship between the activity coefficients γ_i^{Ap} and temperature (T, in kelvins) can be derived from Eqs. 10-12 using the calculated values of $W_{A,B}^G$ s (Table 2.3) as:

$$RT \ln(\gamma_F^{Ap}) = 1000 \times \{X_{Cl}^{Ap} (1 - X_F^{Ap}) \times 16 (\pm 6) + X_{OH}^{Ap} (1 - X_F^{Ap}) \times 7 (\pm 4) - X_{Cl}^{Ap} X_{OH}^{Ap} \times 5 (\pm 2)\} \quad (26)$$

$$RT \ln(\gamma_{Cl}^{Ap}) = 1000 \times \{X_{OH}^{Ap} (1 - X_{Cl}^{Ap}) \times 5 (\pm 2) + X_F^{Ap} (1 - X_{Cl}^{Ap}) \times 16 (\pm 6) - X_{OH}^{Ap} X_F^{Ap} \times 7 (\pm 4)\} \quad (27)$$

and

$$RT \ln(\gamma_{OH}^{Ap}) = 1000 \times \{X_{Cl}^{Ap} (1 - X_{OH}^{Ap}) \times 5 (\pm 2) + X_F^{Ap} (1 - X_{OH}^{Ap}) \times 7 (\pm 4) - X_{Cl}^{Ap} X_F^{Ap} \times 16 (\pm 6)\} \quad (28)$$

The values of γ_i^{Ap} s show negative correlation with T, but the T-dependence is quite small, especially for γ_{OH}^{Ap} (Fig. 2.7). The γ_i^{Ap} value is approximately equal to 1 near its endmember but can increase dramatically towards other endmembers. Compared to γ_{OH}^{Ap} , γ_F^{Ap} and γ_{Cl}^{Ap} show 2-3 times' larger variations across the ternary reflecting their larger compositional dependence.

Fig. 2.7. Variations in the activity coefficients of F, Cl, OH in apatite (γ_F^{Ap} , γ_{Cl}^{Ap} , γ_{OH}^{Ap}) across the F-Cl-OH ternary at 800 °C (panels a-c), and 1000 °C (panels d-f). The values of γ_i^{Ap} s decrease with increasing temperature. At given temperature, γ_i^{Ap} near the endmember of i (e.g. γ_F^{Ap} near the endmember FAp in panel a) is approximately equal to unity, and show increasing trend away from the endmember (e.g. $\gamma_F^{Ap} \approx 6$, near the endmember ClAp). The values of γ_i^{Ap} s show the largest variation along the F-Cl binary, due to greater extent of non-ideality in the F-Cl binary join.

2.4.6. Uncertainties of the calculated parameters

We report 1σ errors in $W_{A,B}^G$ and $\Delta_r G_{A-B}^*(P, T)$ propagated from errors in the experimental data, i.e. $\pm (2-6)$ kJ/mol for $W_{A,B}^G$, ± 2.9 kJ/mol for $\Delta_r G_{OH-Cl}^*(P, T)$, and ± 5.6 kJ/mol for $\Delta_r G_{OH-F}^*(P, T)$. This translates to smaller errors in $K_{D_{OH-Cl}}^{Ap-melt}$ than in $K_{D_{OH-F}}^{Ap-melt}$. Errors in the measured volatile concentration in apatite (e.g. $\leq 20\%$ relative) made small contributions to the errors in K_D s ($< 1\%$ relative). The relative errors in the calculated K_D values are $\sim 30-40\%$ for $K_{D_{OH-Cl}}^{Ap-melt}$, and $\sim 40-50\%$ for $K_{D_{OH-F}}^{Ap-melt}$ and $K_{D_{Cl-F}}^{Ap-melt}$, mostly propagated from the errors in $\Delta_r G_{A-B}^*(P, T)$ and $W_{A,B}^G$.

2.5 Calculation of a miscibility gap in apatite ternary

The topology of a miscibility gap in a simple symmetric ternary solution can be modelled using $W_{A,B}^G$ s and the equation below (Saxena, 1973):

$$1 - \lambda \cdot X_F^{Ap} \cdot X_{Cl}^{Ap} \cdot X_{OH}^{Ap} = 2 (\alpha \cdot X_{OH}^{Ap} \cdot X_{Cl}^{Ap} + \beta \cdot X_F^{Ap} \cdot X_{OH}^{Ap} + \theta \cdot X_F^{Ap} \cdot X_{Cl}^{Ap}) \quad (29)$$

where $\alpha = \frac{W_{Cl,OH}^G}{RT}$, $\beta = \frac{W_{F,OH}^G}{RT}$, $\theta = \frac{W_{F,Cl}^G}{RT}$, $\lambda = (W_{Cl,OH}^G + W_{F,OH}^G - W_{F,Cl}^G)^2 - 4W_{Cl,OH}^G W_{F,OH}^G$.

Using W^G values calculated from this study, i.e. $W_{Cl,OH}^G \approx 5$ kJ/mol, $W_{F,OH}^G \approx 7$ kJ/mol, and $W_{Cl,F}^G \approx 16$ kJ/mol (Table 2.3), we did not find a miscibility gap in apatite ternary at 800 to 1250 °C, consistent with the wide compositional range of the natural apatite from the literature (Fig. 2.1), and experimental apatite concerned in this study (Fig. 2.2). Using Eq. 29, we find the threshold values of $W_{A,B}^G$ (i.e. the minima) for producing miscibility gap along the A-B binary would be about 18.0, 19.7 and 21.4 kJ/mol, at 800, 900, and 1000 °C respectively (Fig. 2.8), which are greater than the W^G values calculated from this study.

Fig. 2.8. Modelled threshold values of W^G (in J/mol) required to form a miscibility gap in F-Cl-OH apatite ternary at 800-1000 °C, calculated using Eq. 29. The modelled threshold values are ~18,000 J/mol at 800 °C (panel *a*), ~19,700 J/mol at 900 °C (panel *b*), and ~21,400 J/mol at 1000 °C (panel *c*). If the three types of W^G values all exceed the threshold at a given *T* (e.g. at 800 °C in panel *d*), there could be a miscibility gap at each binary. All the above threshold W^G values are greater than those calculated from this study (Table 2.3), such that there is no miscibility gap in apatite ternary at 800-1000 °C.

2.6. Approach for calculating the water concentrations in the melt using apatite

We propose the following procedure to calculate the melt H₂O concentrations using the calibrated equations for $K_{D_{OH-Cl}}^{Ap-melt}$ and $K_{D_{OH-F}}^{Ap-melt}$, and the compositions of natural volcanic apatite as:

- (1) measurement of apatite compositions. Direct determinations of H₂O are preferred rather than calculated from stoichiometry, due to potentially larger errors in the calculated H₂O contents (see Section 2.3.2). Apatite crystals that occur in different textural positions (i.e. hosted by other minerals, or in the groundmass) possibly reflect melt H₂O contents at various stages of evolution;
- (2) estimation of temperatures. Temperatures for the apatite inclusions can be constrained from the host minerals (e.g. amphibole, pyroxene, Fe-Ti oxides; Putirka 2008), whereas temperatures for the groundmass apatite can be calculated using the liquidus of the groundmass, or by other means;
- (3) using apatite composition (from #1) and temperature (from #2) to calculate

$K_{D_{OH-Cl}}^{Ap-melt}$ and $K_{D_{OH-F}}^{Ap-melt}$ (Eqs. 23-24), and then use these values to calculate the mole fraction ratios of two volatiles in the melt, i.e. $\frac{x_{OH}^{melt}}{x_{Cl}^{melt}}$, $\frac{x_{OH}^{melt}}{x_F^{melt}}$, and $\frac{x_{Cl}^{melt}}{x_F^{melt}}$;

- (4) using $\frac{x_{OH}^{melt}}{x_F^{melt}}$ or/and $\frac{x_{OH}^{melt}}{x_{Cl}^{melt}}$ (from #3) and the known concentrations of F or/and Cl in melt to calculate the mole fraction of OH in the melt (x_{OH}^{melt}). The F and Cl contents in melt can be constrained by direct measurements on the rock samples, i.e. of the matrix glass, bulk rock, and melt inclusions. If both the Cl and F contents in the melt are known, we could obtain two independent estimates of H₂O contents in the melt;

(5) using X_{OH}^{melt} (from #4) and a water speciation model to calculate H₂O concentration in melt. The water speciation model should be selected according to the melt composition (summarized in *Appendix B*).

In addition, this calculation procedure can be revised to calculate F and Cl concentrations in melts, if the melt water contents are known. We have provided an online program (<https://apthermo.wovodat.org/>) for calculating the relevant thermodynamic properties and the melt water contents.

2.7. Melt H₂O concentrations calculated using apatite from natural volcanic systems with comparison to the melt inclusion data

We have used our new K_D equations and the procedure above to calculate the melt H₂O concentrations of several eruptions (Table 2.4), i.e. Mt. Pinatubo 1991, Santiaguito 1922-2002, Augustine 1986, and several eruptions at Campi Flegrei volcano (Minopoli 1, Astroni 1, Pomici Principali), which span a wide range of temperatures (about 780 to 1100 °C) and melt compositions (basaltic andesite, andesite, dacite, and phonolite).

2.7.1. Volcanic apatite compositions

The most OH-rich apatite crystals are inclusions in other minerals from Santiaguito (maximal $X_{OH}^{Ap} \approx 0.49$; Scott et al., 2015) and Pinatubo (maximal $X_{OH}^{Ap} \approx 0.43$; Borisova et al., 2005; Van Hoose et al. 2013), whereas the most Cl-rich ones are inclusions from

Augustine 1986 eruption ($X_{Cl}^{Ap} \approx 0.34$; Webster et al., 2009). Compared to the apatite inclusions, apatite in the groundmass typically shows higher abundances of F and lower Cl and OH (e.g. Stock et al., 2018), which is likely related to magma cooling, and/or increasing halogen/H₂O ratio in melt due to water degassing. For systems where multiple apatite compositions were reported (e.g. Campi Flegrei, Santiaguito), we have used the maximal and minimal values of X_{OH}^{Ap} to estimate a range of melt water contents. For some systems, only the average composition of apatite was reported (e.g. Pinatubo, Augustine), and thus we provide a single value of melt water (Table 2.4). Apatite compositions were mostly measured using EPMA with OH calculated from stoichiometry, except for Campi Flegrei where it was directly measured using SIMS (Stock et al., 2018) which it gives more precise estimates of the melt H₂O contents.

2.7.2. Calculated melt water abundances

We used the water speciation model by Liu et al. (2004) for dacites to calculate H₂O contents in andesitic-dacitic magmas from the Pinatubo 1991, Augustine 1986 and Santiaguito 1922-2002 eruptions. Melt water contents calculated using F and Cl are consistent within uncertainty (Table 2.4; Fig. 2.9): ~ 2.5 -7.6 wt.% H₂O for Pinatubo 1991, and lower for the smaller eruptions in 1986 at Augustine (~ 0.7 -1.8 wt.% H₂O) and in 1922-2002 at Santiaguito (~ 0.4 -1.7 wt.% H₂O). Relative errors in the melt H₂O contents calculated using Cl and F are ~ 30 -50% and 40-50%, respectively. Melt H₂O estimates from apatite are mostly within the range of H₂O in MIs considering the uncertainties (Fig. 2.9). It is worth noting that melt H₂O reflected by apatite in groundmass shows generally lower values than those reflected by apatite inclusions (e.g.

hosted by clinopyroxene from Santiaguito, and by quartz from Pinatubo volcano). This is likely related to H₂O loss from the melt due to volatile saturation that can be induced by either decompression during magma ascent, or fractional crystallization, or both.

For the phonolitic magmas from Campi Flegrei, we have used the water speciation model for basalt (Lesne et al., 2011) as an approximation (e.g. Carroll and Blank, 1997; *Appendix B*). The clinopyroxene-hosted apatite from three eruption deposits at Campi Flegrei (Minopoli 1, Astroni 1, Pomici Principali) indicates > 3-7 wt.% H₂O in melts, overlapping but are typically higher than those measured from MIs (Stock et al., 2018). These apatite inclusions recorded a wide range of melt H₂O with the highest value of ~9 wt.% (calculated from the OH-richest apatite from Astroni 1 and Pomici Principali), which might exceed the solubility of H₂O in these melts (e.g. ~ 7.5 wt.% at 200 MPa; Stock et al., 2018). This indicates a possible over-estimation of melt H₂O contents from these apatite crystals, which could be due to (1) over-estimation of OH in apatite, given the most OH-rich crystal from Pomici Principali shows ~ 40% higher OH than the rest from the same eruption, and/or (2) that the water speciation model for basalt used in the calculation above is not applicable to a phonolitic melt, and/or (3) poor calibration of our model to phonolitic melts due to limited partition experimental data for such melts.

Fig. 2.9. Melt H₂O contents (in wt.%) calculated using natural apatite reported in literature (see values and data sources in Table 2.4). H₂O estimates from melt Cl (in black symbols) and F contents (in colorful symbols) are consistent within uncertainty (error bar in black solid line), and mostly overlap with H₂O measured from melt inclusions (in dashed-line boxes). The ranges of some water estimates (vertically distributed marked in same symbols) were produced by the variations of apatite compositions and temperatures reported in literature. Results calculated using apatite at different textural positions are marked in different symbols, i.e. crystals in clinopyroxene (in triangles), plagioclase (in squares), quartz (in circles), in the groundmass (in diamonds), and at a mixture of textural positions (in stars).

Table 2.4. Melt H₂O concentrations (in wt.%) calculated using apatite from several volcanoes.

Deposits	Pinatubo 1991 ^a				Augustine 1986 ^b		Santiaguito (1922-2002) ^c		Campi Flegrei ^d				
	Dacite (white pumice)				Andesite to dacite		Dacite		Tephri-phonolite to Phonolite				
	by EPMA				by EPMA		by EPMA		by SIMS				
Bulk rock	in Qtz		in Pl		in Pl, Cpx		in GM		in Cpx				
Apatite	Mean	Mean	Mean	Mean	Mean	Mean	Min.X _{OH}	Max.X _{OH}	N=1	Min.X _{OH}	Max.X _{OH}	Min.X _{OH}	Max.X _{OH}
Textural position													
Mole fractions													
X _F , Ap	0.445	0.514	0.477	0.401	0.40	0.805	0.345	0.581	0.709	0.632	0.6	0.496	
X _{Cl} , Ap	0.132	0.198	0.166	0.173	0.34	0.105	0.170	0.122	0.147	0.152	0.14	0.129	
X _{OH} , Ap	0.423	0.288	0.357	0.426	0.26	0.090	0.485	0.297	0.144	0.216	0.26	0.375	
X _{OH} /X _{Cl}	3.20	1.45	2.15	2.46	2.46	0.86	2.85	2.44	0.98	1.42	1.86	2.91	
Measured volatile contents (in wt.%) of matrix glass and melt inclusions													
F in matrix glass	n.d.				n.d.	0.02~0.035		0.29~0.34	0.09~0.29		0.14~0.27		
Cl in matrix glass	~0.12				n.d.	0.08~0.13		0.5~0.73	0.85~0.94		0.69~0.75		
F in MIs	n.d.				0.03 (+/-0.04)	0.01~0.03		0.22~0.44	0.19~0.31		0.22~0.28		
Cl in MIs	0.09~0.15				0.29 (+/-0.07)	0.07~0.16		0.55~0.77	0.73~1.03		0.67~0.86		
H ₂ O in MIs	1~7	0.5~2.2	~0.7	n.d.	0.6~5.7	0~1.9 [†]		1.3~3.1	2~2.7		1.3~3.8		
Parameters used for calculation													
F in glass (mean)	0.02 [†]				0.03	0.03		0.31	0.23		0.23		
Cl in glass (mean)	0.12				0.29	0.11		0.61	0.93		0.71		
Cl/F in melt	6				9.7	3.7		2.0	4.0		3.1		
Temperature (°C)	780				947	877	870	950	989		1015		

(Continued on next page)

Deposits	Pinatubo 1991 ^a				Augustine 1986 ^b	Santiago (1922-2002) ^c	Campi Flegrei ^d					
	Calculated K _D and melt H ₂ O contents (in wt.%)						Minopoli 1	Astroni 1	Pomice Principali			
K _D (OH-Cl)	0.026	0.025	0.026	0.025	0.061	0.040	0.058	0.163	0.103	0.100	0.114	0.110
K _D (OH-F)	0.0028	0.0026	0.0027	0.0031	0.014	0.008	0.004	0.015	0.012	0.013	0.016	0.019
calc melt Cl/F	5.2	6.9	6.1	6.4	6.8	7.8	3.7	4.5	3.4	3.4	3.0	2.9
calc melt H ₂ O (using Cl)	7.6	2.5	4.2	5.5	1.1	1.8	0.44	1.3	4.3	8.7	6.6	19
Error	3.0	1.0	1.7	2.1	0.4	0.6	0.22	0.4	1.8	3.5	2.6	7
calc melt H ₂ O (using F)	5.9	3.0	4.3	6.1	0.7	1.4	0.45	1.7	3.3	6.4	6.4	16
Error	2.8	1.5	2.1	2.9	0.3	0.6	0.22	0.7	1.4	2.8	2.7	6

^a Average composition of crystals as inclusions in plagioclase, hornblende, Fe-Ti oxides and in groundmass (GM).

^b H₂O contents in glass, as those of MIs were not reported.

^c F content in bulk rock, as F in glass was not reported.

^d Compositions of quartz-hosted apatite and melt inclusions (MIs) are from the same rocks reported by Borisova et al. (2005). Apatite inclusion in plagioclase and in groundmass are from Imai et al. (1996). Average composition of apatite (N=401) occurring in a variety of textural position ("Mixed") is from Van Hooose et al. (2013). Other MI data are from Gerlach et al. (1996), and bulk rock data are from Pallister et al. (1996). Temperature is from Rutherford and Devine (1996).

^e Apatite compositions are from Webster et al. (2009), MI and glass compositions are from Roman et al. (2006) and Webster et al. (2010), and temperatures are from Webster et al. (2010).

^f Apatite and glass from the same rocks were reported by Scott et al. (2015). MI compositions from the 1902-1929 eruption deposits reported by Balcone-Boissard et al. (2010) are used as a reference. Temperatures are from Scott et al. (2015) and Singer et al. (2014).

^g Apatite inclusions, MIs and the matrix glass are from the same rocks reported by Stock et al. (2018). Temperatures from the same eruption deposits were reported by Forni et al. (2018).

2.8. Conclusions

We report a new thermodynamic model for F-Cl-OH partitioning between apatite and the melt (K_{DS}) that considers the non-ideality of apatite solid solution. Using experimental data from the literature, we have calculated the values of interaction parameters (W^G s) of the ternary apatite and found that W^G for the F-Cl binary join is about 2 to 3 times' larger than those for Cl-OH and F-OH indicating stronger non-ideality of F-Cl mixing. The W^G values are not large enough to form a miscibility gap in apatite ternary at 800 to 1250 °C, consistent with the wide compositional spread of igneous apatite from the literature. With the new equations for K_{DS} , we propose a calculation procedure for estimating melt water contents. The H₂O concentrations in melts calculated using our model show equivalent or higher values compared to those measured from the melt inclusions from the literature. We have developed an online tool that provides calculations for the exchange coefficients (K_D), the activity coefficients (γ_i^{Ap}), and the melt H₂O concentrations (<https://apthermo.wovodat.org/>). Applications of this model to natural apatite crystals can bring new insights into the magma storage depth and degassing, and thus help to evaluate the influence of melt volatile budgets on the eruptive styles at a variety of volcanoes.

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Summary of supplementary materials

Appendix A: Variations in the ratio of the activity coefficients of Cl and OH ($\frac{\gamma_{Cl}^{melt}}{\gamma_{OH}^{melt}}$)

with melt composition and pressure, and the influence on the value of $\Delta_r G_{OH-Cl}^*(P, T)$ (Tables A1-A2; Fig. A1).

Appendix B: Calculation of exchange coefficients K_{DS} using mole fractions of F, Cl and OH in apatite and melt (Table B1; Fig. B1).

Appendix C: Experimental data of apatite-melt partitioning from the literature used for regression in this study (Tables C1-C4).

Appendix D: Regression approaches used for the calculation of $W_{A,B}^G$ and $\Delta_r G_{A-B}^*(P, T)$ values.

Appendix A: Variations in the ratio of the activity coefficients of Cl and OH

$\left(\frac{\gamma_{Cl}^{melt}}{\gamma_{OH}^{melt}}\right)$ with melt composition and pressure, and the influence on the values of

$$\Delta_r G_{OH-Cl}^*(P, T)$$

Chlorine solubilities in silicate melts have been found to be not sensitive to temperature, but mainly determined by pressure and melt composition (Webster et al., 2015), where the latter parameter can be expressed using the molar [(Al+Na+Ca+Mg)/Si] in the melt (referred to as ANCM/S hereafter; Webster et al., 1999). Based on Cl solubilities determined at 200 MPa for a variety of silicate melts by Webster et al. (1999), the melts with ANCM/S values equivalent to those investigated in this study, i.e. between 0.30-0.73 (Table A1), could have maximal mole fractions of chloride between 0.005 - 0.04. These values are higher than those in the experimental melts that we used in this study (see *Appendix C*), indicating that Cl contents in the high-P experimental melts are below saturation, i.e. at 1 GPa and 2.5 GPa of M15 and L&H17, respectively. In addition, Cl contents in experimental melt of W17 at 50 MPa are below/close to saturation, according to Cl solubility calculated by these authors (Table A1). Considering this, experiments investigated in this study unlikely involve a brine phase, which excludes the complexity of considering its effects on the activity of Cl in the melt (see detail in Webster et al., 1999).

Given that the activity coefficient of Cl in silicate melts has not been determined, we have investigated its variation in different P - T - X conditions based on solubility data from the literature (Table A2). Below we show some preliminary estimates of the variation in the ratio of the activity coefficients between Cl and OH (i.e. $\frac{\gamma_{Cl}^{melt}}{\gamma_{OH}^{melt}}$) in the

experimental melts, and effects on the gibbs free energy terms and formulations for K_{DS} proposed in this study.

1. H₂O-Cl solubility in silicate melts and the variation in $\frac{\gamma_{Cl}^{melt}}{\gamma_{OH}^{melt}}$

The solubility of a two component H₂O-Cl fluid in silicate melts can be expressed using similar formulations as those proposed by Papale (1999) for H₂O-CO₂ in melts as:

$$\varphi_{H_2O} y_{H_2O} P = \gamma_{H_2O} x_{H_2O} f_{H_2O}^{o,l} \quad (A.1)$$

$$\varphi_{Cl} y_{Cl} P = \gamma_{Cl} x_{Cl} f_{Cl}^{o,l} \quad (A.2)$$

where y and x are the mole fractions in the fluid and liquid phase, respectively, P is pressure, φ is fugacity coefficient in the fluid phase, γ is the activity coefficient in the liquid phase (that is of interested here), and $f_i^{o,l}$ is the reference state fugacity for component i ($i = \text{H}_2\text{O}$ or Cl) in the liquid.

Dividing Eq. A.2 by Eq. A.1, we obtained (at a given pressure):

$$\frac{\varphi_{Cl} y_{Cl}}{\varphi_{H_2O} y_{H_2O}} = \frac{\gamma_{Cl} x_{Cl} f_{Cl}^{o,L}}{\gamma_{H_2O} x_{H_2O} f_{H_2O}^{o,L}} \quad , \quad (A.3)$$

which can be re-arranged as:

$$\frac{\gamma_{Cl}}{\gamma_{H_2O}} = \frac{\varphi_{Cl}\gamma_{Cl}}{\varphi_{H_2O}\gamma_{H_2O}} \times \frac{x_{H_2O}f_{H_2O}^{oL}}{x_{Cl}f_{Cl}^{oL}} . \quad (A.4)$$

Theoretically the values of γ_{Cl} and γ_{H_2O} can be calculated using an excess Gibbs free energy parameter that could be expressed (by considering the simplest regular solution) using $w_{i,j}$ which denotes the binary interaction coefficients between each pair of molecules (i.e. of volatile and non-volatile components) in the melt. However, the interaction coefficients for Cl and the non-volatile components in the melt (e.g. $w_{Cl,j}$) have not been determined. The values of these interaction coefficients can be calculated using a large amount of experimental data, as has been done for $w_{H_2O,j}$ and $w_{CO_2,j}$ in H₂O-CO₂ solubility model (Papale, 1999; Papale et al., 2006). However, such calculation is quite complex and out of the scope of this study. Without knowing the absolute values of γ_{Cl} or γ_{H_2O} , we can estimate their ratio (i.e. $\frac{\gamma_{Cl}}{\gamma_{H_2O}}$), using Eq. A.4 and the solubilities of H₂O-Cl in the melt with different compositions at a variety of pressures reported in the literature (Table A2).

Table A1. Pressure, temperature and melt compositions of the partition experiments used for calculating $K_{D_{OH-Cl}}^{Ap-melt}$ in this study.

	T (°C)	P (MPa)	Melt composition	H ₂ O (wt.%)	Cl (wt.%)	F (wt.%)	ANCM/S (calc)*	Cl solubility (wt.%)
W17	844-862	50	Rhyolite	2.2-3.7	0.03-0.36	0.01-0.19	0.30-0.32	0.27-0.4 [†]
L&H17	800	2500	Pelite	~11-12	0.11-0.62	0.04-0.14	0.34-0.39	>1.1 [‡]
M15	990-1000	1000-1200	Fe-rich basalt	2.7-3.6	0.27-2.4	0.005-0.44	0.57-0.73	>2.7 [‡]

*Calculated using the molar concentrations of Al (A), Na (N), Ca (C), Mg (M) and Si (S) in the melt.

[†]Reported by these authors, calculated using Cl solubility model of Webster et al. (2015).

[‡]Minimal solubilities referring to experimental data for the melt with equivalent compositions but at lower P, i.e. 200 MPa (see data source in Table A2).

Table A2. Solubilities of two-component (H₂O + Cl) fluid and single-component (H₂O or Cl) fluid in silicate melts from the literature.

	T (°C)	P (MPa)	Melt composition	ANCM/S	H ₂ O-Cl solubilities (wt.%)	H ₂ O or Cl solubility (wt.%)	Analog for experiments
Webster, 1997a	800-860	50	Haplogranite	0.30-0.33	H ₂ O	Cl	W17
Webster, 1997a	800-860	200	Haplogranite	0.30-0.33	5.2	0.29	
Webster, 1997a, b	825-1075	200	Latite	0.43-0.57	5.2	0.98-1.3	
Webster et al., 2015	1058	500	Latite	-	n.a.	8 [†]	1.15
<i>Estimated</i> §	800	2500	Pelite	0.34-0.39	n.a.	≥20 [§]	1.15 [§]
Webster et al., 1999	1080-1210	200	Basalt	0.77-0.98	5.7	6.5 [†]	L&H17
Webster et al., 2015	1000	1000	Basalt	-	n.a.	19 [†]	M15

[†]Values marked in bold were used in the calculation for activity coefficients.

[‡]Calculated using the H₂O solubility model of Papale et al. (2006) and the melt compositions used in experiments.

[§] Estimated according to that determined at 200 MPa, considering small P-dependence of Cl solubility (Webster et al., 2015).

§ H₂O solubility estimated based on the difference in H₂O solubility at 200 and 500 MPa in latite shown in this table, and Cl solubility estimated according to that determined at 500 MPa for latite, considering small P-dependence of Cl solubility (Webster et al., 2015).

2. Estimation of $\frac{\gamma_{Cl}^{melt}}{\gamma_{OH}^{melt}}$ for the experimental melts and effects on $\Delta_r G_{OH-Cl}^*(P, T)$

For the silicate melt with a given composition at a given P-T condition, according to Eq. A.4., $\frac{\gamma_{Cl}}{\gamma_{H_2O}}$ should be proportional to $\frac{x_{H_2O}}{x_{Cl}}$, i.e. $\frac{\gamma_{Cl}}{\gamma_{H_2O}} \propto \frac{x_{H_2O}}{x_{Cl}}$, where x_i represents maximal molar fraction of component i in the melt (i.e. solubility). Considering nearly ideal behavior of OH and molecular H₂O in the melt (Zhang, 1999), it is likely that $\frac{\gamma_{Cl}}{\gamma_{H_2O}}$ is approximately equal or proportional to $\frac{\gamma_{Cl}^{melt}}{\gamma_{OH}^{melt}}$. Considering the P-dependence of the solubility of H₂O and Cl as mentioned above, pressure could also affect the value of $\frac{\gamma_{Cl}^{melt}}{\gamma_{OH}^{melt}}$. Below we assess the effects of melt compositions and pressures on $\frac{\gamma_{Cl}^{melt}}{\gamma_{OH}^{melt}}$, using solubility data reported in literature. In addition, given that $-\Delta_r G_{OH-Cl}^*(P, T) = -\Delta_r G_{OH-Cl}^0(P, T) - RT \cdot \ln\left(\frac{\gamma_{Cl}^{melt}}{\gamma_{OH}^{melt}}\right)$, the variation in $RT \cdot \ln\left(\frac{\gamma_{Cl}^{melt}}{\gamma_{OH}^{melt}}\right)$ would affect the value of $\Delta_r G_{OH-Cl}^*(P, T)$, and thus we have also estimated the difference in $RT \cdot \ln\left(\frac{\gamma_{Cl}^{melt}}{\gamma_{OH}^{melt}}\right)$ between the three experiments that we used in our model to assess the changes in $\Delta_r G_{OH-Cl}^*(P, T)$.

2.1. Effects of melt compositions and pressures on $\frac{\gamma_{Cl}^{melt}}{\gamma_{OH}^{melt}}$

The solubility of H₂O-Cl (two-component fluid) in silicate melts were determined at very limited range of pressures (i.e. at 0.1, 50, 200 MPa) for basaltic, andesitic, latitic and haplogranitic melts (Webster, 1997a, b; Webster et al. 1999). Webster et al. (1999) showed that both H₂O and Cl are more soluble in basalt/andesite than in latite/haplogranite, implying that

the activity coefficients of Cl and H₂O in the melt should vary in the same trend with varying melt SiO₂ contents. Moreover, there is a larger compositional effect on the solubility of Cl than on H₂O (Webster et al., 1999). Take the H₂O-Cl solubility in haplogranite and basalt at 200 MPa (Webster, 1997a; Webster et al., 1999) as an example: at 200 MPa, the solubilities of H₂O and Cl are ~ 5.2 wt.% and ~ 0.29 wt.% in haplogranite (ANCM/S = 0.30-0.33), and are ~ 5.7 wt.% and ~ 2.7 wt.%, respectively in basalt (ANCM/S=0.77-0.98) (Table A1). Based on Eq. A.4, the value of $\frac{\gamma_{Cl}^{melt}}{\gamma_{OH}^{melt}}$ in haplogranite could be about 8 times' greater than that in basalt at 200 MPa. In addition, given the stronger P effect on the solubility of H₂O than on Cl, $\frac{\gamma_{Cl}^{melt}}{\gamma_{OH}^{melt}}$ increases with increasing pressure, e.g. $\frac{\gamma_{Cl}^{melt}}{\gamma_{OH}^{melt}}$ in haplogranitic melt at 200 MPa is ~ 1.6 times' greater than that at 50 MPa. The effects of melt SiO₂ contents and pressure on the value of $\frac{\gamma_{Cl}^{melt}}{\gamma_{OH}^{melt}}$ seem to compensate to each other, i.e. $\frac{\gamma_{Cl}^{melt}}{\gamma_{OH}^{melt}}$ in mafic melts at high pressure might be close to that in felsic melts at low pressure. Below we show the estimation of the variations in $\frac{\gamma_{Cl}^{melt}}{\gamma_{OH}^{melt}}$ in the experimental melts that we used for establishing our model in this study, with consideration of their pressures and melt compositions.

2.2. Variations in $\frac{\gamma_{Cl}^{melt}}{\gamma_{OH}^{melt}}$ in the experimental melts and effects on $\Delta_r G_{OH-Cl}^*(P, T)$

Among the three experimental studies used for extracting the formulation of $\Delta_r G_{OH-Cl}^*(P, T)$ (Table A1), two studies (i.e. L&H17, W17) used felsic melts (with similarly low ANCM/S) at similarly low T but different P, i.e. pelitic melts with ANCM/S $\approx$ 0.34-0.39 at 800 °C and 2.5 GPa by L&H17, and rhyolitic melts with ANCM/S $\approx$ 0.30-0.32 at 844-862 °C and 50 MPa by W17, whereas the other one (M15) used basaltic melts that have higher ANCM/S ($\approx$ 0.57-0.73)

at higher T and P (990-1000 °C, 1 GPa). Compared to the melts used for determining H₂O-Cl solubilities from the literature, the experimental melts concerned in this study have ANCM/S of 0.30-0.73, that are almost covered by those with H₂O-Cl solubilities reported (Table A2). The pressure used by W17 (of 50 MPa) is similar to the experiments used for solubility determinations, whereas there is no data for Cl solubilities at 1 GPa (M15) and 2.5 GPa (L&H17), nor for H₂O solubilities at 2.5 GPa. Considering this, we have to estimate H₂O-Cl solubilities at such high pressures, based on solubilities of H₂O or Cl determined at lower pressure, i.e. H₂O solubility from Papale et al. (2006) between 0.1 MPa and 1 GPa, and Cl solubility from Webster et al. (2015) between 0.1-700 MPa (Table A2). Below we compare the values of $\frac{\gamma_{Cl}^{melt}}{\gamma_{OH}^{melt}}$ and $RT \cdot \ln \left(\frac{\gamma_{Cl}^{melt}}{\gamma_{OH}^{melt}} \right)$ that we calculated for the three experimental melts of W17, L&H17 and M15.

(1) Comparison between W17 and L&H17

The rhyolitic melts of W17 and the pelitic melts of L&H17 (Table A1) have similar ANCM/S values, but are at very different pressures, i.e. 50 MPa for W17, and 2.5 GPa for L&H17. To estimate their difference in $\frac{\gamma_{Cl}^{melt}}{\gamma_{OH}^{melt}}$, we have used the solubility data determined for latitic melt (Webster, 1997a; Webster et al., 2015) that has similar SiO₂ content (of ~ 63 wt.%) to L&H17 as an analog for the case of L&H17, and used solubility data determined for rhyolite at 50 MPa for the case of W17.

Using solubilities of 2.5 wt.% H₂O and 0.23 wt.% Cl determined from experiments for W17, and estimated minimal solubilities of ~ 20 wt.% H₂O and ~ 1.15 wt.% Cl for L&H17, we find

that $\frac{\gamma_{Cl}^{melt}}{\gamma_{OH}^{melt}}$ for L&H17 is larger than that for W17 by a factor of ~ 1.6 . As the absolute value of

$\frac{\gamma_{Cl}^{melt}}{\gamma_{OH}^{melt}}$ is unknown, we assume that of W17 (expressed as $\frac{\gamma_{Cl}^{melt2}}{\gamma_{OH}^{melt2}}$) equal to b ($T_2=850$ °C), such

that $\frac{\gamma_{Cl}^{melt}}{\gamma_{OH}^{melt}}$ of L&H17 (expressed as $\frac{\gamma_{Cl}^{melt1}}{\gamma_{OH}^{melt1}}$, at $T_1=800$ °C) should be equal to $1.6b$. The

difference in $RT \cdot \ln\left(\frac{\gamma_{Cl}^{melt}}{\gamma_{OH}^{melt}}\right)$ between L&H17 and W17 can be expressed as: $\Delta_{1-2} = RT_1 \cdot$

$$\ln\left(\frac{\gamma_{Cl}^{melt1}}{\gamma_{OH}^{melt1}}\right) - RT_2 \cdot \ln\left(\frac{\gamma_{Cl}^{melt2}}{\gamma_{OH}^{melt2}}\right) = 8.314 \times (800+273.15) \times \ln(1.6b) - 8.314 \times (850+273.15)$$

$\times \ln(b)$ J/ mol $\approx 4200 - 416 \times \ln(b)$ J/mol, whose value is determined by the value of b . If

we consider a wide range of b between 1-10 ($b=1$ means that the activity coefficient of Cl and

OH is equal to unity), then the value of Δ_{1-2} should be between 3-4 kJ/mol, which is equivalent

to the errors in the formulation for $\Delta_r G_{OH-Cl}^*(P, T)$ (Eq. 22 in the main text). The positive value

of Δ_{1-2} means that the value of $\Delta_r G_{OH-Cl}^o(P, T)$ for L&H17 might be over-estimated, however

such change is still within the uncertainty range of the regression line (Fig. A1).

(2) Comparison between W17 and M15

The experimental conditions of W17 and M15 show large difference in both the melt compositions and pressures, i.e. rhyolitic melts at 50 MPa by W17, and basaltic melts at 1 GPa by M15 (Table A1). Cl solubility has not been determined at the pressure condition by M15 (i.e. 1 GPa), but considering its small P-dependence (e.g. nearly equivalent at 100 and 500 MPa; Webster et al. 2015), we take Cl solubility in basalt determined at 200 MPa (i.e. ~ 2.7 wt.%) for M15, and use H₂O solubility calculated from the solubility model of Papale et al., (2006), i.e. ~ 19 wt.% H₂O (Table A2). The H₂O-Cl solubility has been determined from previous studies in similar condition (rhyolite at 50 MPa; Webster, 1997a) as that of W17 as mentioned

above, i.e. ~ 2.5 wt.% H₂O and ~ 0.23 wt.% Cl. Comparison of the solubilities in the melts between W17 and M15 indicates that $\frac{\gamma_{Cl}^{melt}}{\gamma_{OH}^{melt}}$ of W17 is greater than that of M15 by a factor of ~ 1.5 . Again, if we take $\frac{\gamma_{Cl}^{melt2}}{\gamma_{OH}^{melt2}} = b$ ($T_2=850$ °C) for W17 (as mentioned above), then the value of $\frac{\gamma_{Cl}^{melt}}{\gamma_{OH}^{melt}}$ for M15 (expressed as $\frac{\gamma_{Cl}^{melt3}}{\gamma_{OH}^{melt3}}$, at $T_3=1000$ °C) should be equal to $\left(\frac{1}{1.5}\right) \cdot b = 0.65b$. Then, $RT_2 \cdot \ln\left(\frac{\gamma_{Cl}^{melt2}}{\gamma_{OH}^{melt2}}\right) = 8.314 \times (850+273.15) \times \ln(b)$ J/ mol, and $RT_3 \cdot \ln\left(\frac{\gamma_{Cl}^{melt3}}{\gamma_{OH}^{melt3}}\right) = 8.314 \times (1000+273.15) \times \ln(0.65b)$ J/ mol. The difference between the two values (referred to as Δ_{3-2}) can be expressed as: $\Delta_{3-2} = RT_3 \cdot \ln\left(\frac{\gamma_{Cl}^{melt3}}{\gamma_{OH}^{melt3}}\right) - RT_2 \cdot \ln\left(\frac{\gamma_{Cl}^{melt2}}{\gamma_{OH}^{melt2}}\right) = -4600 + 1250 \times \ln(b)$ J/mol. Again, if we consider a wide range of b between 1-10, then Δ_{3-2} should be between -1.5 and -4.5 kJ/mol (Fig. A1), which is close to the uncertainty range of the formulation for $\Delta_r G_{OH-Cl}^*(P, T)$ (Eq. 22 in the main text). The negative value of Δ_{3-2} indicates possible underestimation of the value of $\Delta_r G_{OH-Cl}^o(P, T)$ for M15 (Fig. A1), however this change is within the uncertainty range of the regression line.

Overall, the discussion above shows that the variation in $\frac{\gamma_{Cl}^{melt}}{\gamma_{OH}^{melt}}$ in the three experimental melts has an effect on the value of $\Delta_r G_{OH-Cl}^*(P, T)$, where the estimated variations are mostly within the uncertainty range of the formulation for $\Delta_r G_{OH-Cl}^*(P, T)$ proposed in this study. Due to a lack of solubility data at pressures >1 GPa, the estimated values in this section may involve some extent of uncertainty, thus we decided not to use them to calibrate the current formulation for $\Delta_r G_{OH-Cl}^*(P, T)$, unless there are more precise determinations of $\frac{\gamma_{Cl}^{melt}}{\gamma_{OH}^{melt}}$ in future studies. In the following section, we discuss the application of our model to natural systems with P - T - X conditions different from the three experimental melts.

Fig. A1. Differences in $RT \cdot \ln \left(\frac{\gamma_{Cl}^{melt}}{\gamma_{OH}^{melt}} \right)$ between W17 and L&H17 (red dots), and between W17 and M15 (black dots), plotted against a range of $\frac{\gamma_{Cl}^{melt}}{\gamma_{OH}^{melt}}$ values (between 1-10) considered for the melt of W17.

Fig. A2. Possible changes in $\Delta_r G_{OH-Cl}^*(P, T)$ (marked with arrows) with consideration of the variations in $RT \cdot \ln \left(\frac{\gamma_{Cl}^{melt}}{\gamma_{OH}^{melt}} \right)$ in different experimental melts (see Fig. 2.4b in the main text). Symbols: L&H17 – *black star*; W17 – *blue diamond*; M15 – *pink star*.

3. Evaluations on the application of our model to natural volcanic systems

We have shown that the value of $\frac{\gamma_{Cl}^{melt}}{\gamma_{OH}^{melt}}$ is affected by P and melt composition, and is likely greater in more felsic melts at higher P . Moreover, $\Delta_r G_{OH-Cl}^*(P, T)$, which determines the value of K_D , is affected by $RT \cdot \ln \left(\frac{\gamma_{Cl}^{melt}}{\gamma_{OH}^{melt}} \right)$, meaning that T also needs to be considered. Below we evaluate the possible variation in $\frac{\gamma_{Cl}^{melt}}{\gamma_{OH}^{melt}}$ at a range of P - T - X conditions for natural volcanic systems, by referring to calculations for the three experiments in previous section.

For rhyolitic melt with composition similar to W17 but at different T (e.g. 900 °C) and P (e.g. 200 MPa), the value of $\frac{\gamma_{Cl}^{melt}}{\gamma_{OH}^{melt}}$ could be greater than that of W17 by a factor of ~ 1.6 (calculated using solubility data in Table A2), which would cause an increase in $\Delta_r G_{OH-Cl}^*(P, T)$ of ~ 5 kJ/mol, and a decrease in $K_D^{Ap-melt}$ of $\sim 40\%$ (relative). Such change in $K_D^{Ap-melt}$ is equivalent to the uncertainty range of the formulation for $K_D^{Ap-melt}$ proposed in this study, i.e. the modelled value of $K_D^{Ap-melt}$ would still overlap with the real value. Hence, our formulations for $\Delta_r G_{OH-Cl}^*(P, T)$ and $K_D^{Ap-melt}$ can be applied to rhyolitic melts at 800-900 °C, and 50-200 MPa (possibly extending to <50 MPa).

According to solubilities determined at 200 MPa and 500 MPa (Table A2), the values of $\frac{\gamma_{Cl}^{melt}}{\gamma_{OH}^{melt}}$ in less felsic melts (e.g. latite with 63 wt.% SiO₂) between the two pressures should vary within a factor of ~ 1.25 . Thus, compared to L&H17, the variations in

$RT \ln \left(\frac{\gamma_{Cl}^{melt}}{\gamma_{OH}^{melt}} \right)$ in the melt with similar composition to L&H17 at higher T (e.g. 900-950 °C) and lower P (e.g. 200-500 MPa), i.e. of $\sim 2-3$ kJ/mol, are not beyond the uncertainty range of our model. Thus, our model can be also applied to andesitic-dacitic melts at 900-950 °C and 200-500 MPa.

We have noticed a large P effect on the value of $\frac{\gamma_{Cl}^{melt}}{\gamma_{OH}^{melt}}$ in basalt, as Cl solubility shows nearly equivalent values at different P, whereas H₂O solubility increase significantly with P. Therefore, more caution needs to be taken when applying our model to natural basaltic systems at pressures different from that of M15 (i.e. 1 GPa). Comparing solubility data at 500 MPa and 1 GPa for basalt, $\frac{\gamma_{Cl}^{melt}}{\gamma_{OH}^{melt}}$ at 500 MPa is likely about half of that at 1 GPa, which could differ the value in $RT \ln \left(\frac{\gamma_{Cl}^{melt}}{\gamma_{OH}^{melt}} \right)$ of ~ 7 kJ/mol (at 1000 °C), and change $\sim 30\%$ (relative) change in $\Delta_r G_{OH-Cl}^*(P, T)$ and $\sim 50\%$ (relative) change in $K_{D_{OH-Cl}}^{Ap-melt}$. The changes would be less at P higher than 500 MPa, e.g. $\sim 25\%$ change in $K_{D_{OH-Cl}}^{Ap-melt}$ at 800 MPa (T=950-1050 °C), which is within the uncertainty range of our model. Thus, our model is also valid for basaltic melts at 950-1050 °C, and 800 MPa to 1 GPa.

Overall, by considering the effects of P - T - X conditions on $RT \cdot \ln \left(\frac{\gamma_{Cl}^{melt}}{\gamma_{OH}^{melt}} \right)$, $\Delta_r G_{OH-Cl}^*(P, T)$ and $K_{D_{OH-Cl}}^{Ap-melt}$, we suggest that the formulations for $\Delta_r G_{OH-Cl}^*(P, T)$ and $K_{D_{OH-Cl}}^{Ap-melt}$ proposed in this study can be applied to (i) rhyolitic melts at 800-900 °C, 50-200 MPa, (ii) andesitic-dacitic melts at 900-950 °C, 200-500 MPa, and (iii) basaltic melts at 950-1050 °C, 800-1000 MPa.

Appendix B. Calculation of the exchange coefficients K_{DS} based on mole fractions of F, Cl and OH in apatite and the melt.

To calculate the exchange coefficient $K_{D_{A-B}^{Ap-melt}}$ ($= \frac{X_A^{Ap} \cdot X_B^{melt}}{X_A^{melt} \cdot X_B^{Ap}}$) requires the mole fractions of OH, F, and Cl in apatite and melt, which need to be calculated based on the measured mass concentrations (see Sections 1-2 below). Error propagation to $K_{D_{A-B}^{Ap-melt}}$ is shown below in Section 3.

1. Calculating mole fractions of OH, F, and Cl in apatite

1.1 Direct measurements of H₂O in apatite

Using the weight concentrations of F, Cl and H₂O in apatite, we calculated the molar fractions of F, Cl and OH using the equations below:

$$X_F^{Ap} = \frac{\frac{C_F^{Ap}}{19}}{\frac{C_F^{Ap}}{19} + \frac{C_{Cl}^{Ap}}{35.45} + \left(\frac{C_{H_2O}^{Ap}}{18} \times 2\right)} \quad (B.1)$$

$$X_{Cl}^{Ap} = \frac{\frac{C_{Cl}^{Ap}}{35.45}}{\frac{C_F^{Ap}}{19} + \frac{C_{Cl}^{Ap}}{35.45} + \left(\frac{C_{H_2O}^{Ap}}{18} \times 2\right)} \quad (B.2)$$

and

$$X_{OH}^{Ap} = \frac{\frac{C_{H_2O}^{Ap}}{18} \times 2}{\frac{C_F^{Ap}}{19} + \frac{C_{Cl}^{Ap}}{35.45} + (\frac{C_{H_2O}^{Ap}}{18} \times 2)} \quad (B.3)$$

where c_F^{Ap} , c_{Cl}^{Ap} , $c_{H_2O}^{Ap}$ are the mass concentrations in apatite (in wt.%), and the factor of 2 multiplied to $c_{H_2O}^{Ap}$ is based on the assumption that H₂O in apatite is fully present as OH (e.g. Piccoli and Candela, 2002). The error of the mole fraction is propagated from the analytical error of F, Cl, and H₂O in apatite, and can be calculated based on the standard error (of 1σ) reported from experimental studies (written as σ_F , σ_{Cl} , σ_{H_2O}):

$$\frac{\sigma_{X_F^{Ap}}}{X_F^{Ap}} = \sqrt{\left(\frac{\sigma_F}{C_F^{Ap}}\right)^2 + \left\{ \frac{\sqrt{\left(\frac{\sigma_F}{19}\right)^2 + \left(\frac{\sigma_{Cl}}{35.45}\right)^2 + \left(\frac{\sigma_{H_2O}}{18} \times 2\right)^2}}{\left[\frac{C_F^{Ap}}{19} + \frac{C_{Cl}^{Ap}}{35.45} + \left(\frac{C_{H_2O}^{Ap}}{18} \times 2\right)\right]} \right\}^2} \quad (B.4)$$

$$\frac{\sigma_{X_{Cl}^{Ap}}}{X_{Cl}^{Ap}} = \sqrt{\left(\frac{\sigma_{Cl}}{C_{Cl}^{Ap}}\right)^2 + \left\{ \frac{\sqrt{\left(\frac{\sigma_F}{19}\right)^2 + \left(\frac{\sigma_{Cl}}{35.45}\right)^2 + \left(\frac{\sigma_{H_2O}}{18} \times 2\right)^2}}{\left[\frac{C_F^{Ap}}{19} + \frac{C_{Cl}^{Ap}}{35.45} + \left(\frac{C_{H_2O}^{Ap}}{18} \times 2\right)\right]} \right\}^2} \quad (B.5)$$

$$\frac{\sigma_{X_{OH}^{Ap}}}{X_{OH}^{Ap}} = \sqrt{\left(\frac{\sigma_{H_2O}}{C_{H_2O}^{Ap}}\right)^2 + \left\{ \frac{\sqrt{\left(\frac{\sigma_F}{19}\right)^2 + \left(\frac{\sigma_{Cl}}{35.45}\right)^2 + \left(\frac{\sigma_{H_2O}}{18} \times 2\right)^2}}{\left[\frac{C_F^{Ap}}{19} + \frac{C_{Cl}^{Ap}}{35.45} + \left(\frac{C_{H_2O}^{Ap}}{18} \times 2\right)\right]} \right\}^2} \quad (B.6)$$

1.2. H₂O in apatite calculated from stoichiometry

If the H₂O contents are not directly measured, we can calculate the mole fractions using the “by difference” method assuming stoichiometry and full occupancy of F, Cl and OH at the anion site of apatite (e.g. Piccoli and Candela, 2002). Two methods have been proposed in the literature by using different oxygen numbers for normalization, i.e. the conventional method of 26 O (Deer et al., 1992) and the newer one of (26 O – [OH]/2) (Ketcham, 2015). Following the stoichiometry calculation approach from Ketcham (2015), one should use 26 O in the calculation for OH-free apatite, and 25 O in the calculation for the endmember hydroxyapatite. Although X_{OH}^{Ap} calculated from this method is theoretically more accurate, the computation is quite complex, and only gives slight difference of X_{OH}^{Ap} (of < 4%) from the conventional method (Ketcham, 2015). Considering this, we have used 26 O for calculating X_{OH}^{Ap} in the apatite from L&H17 and W17. The error of X_{OH}^{Ap} from stoichiometry includes error from not only the measurements for F and Cl in apatite, but also that from the assumption that only F, Cl, and OH occupy the anion site, which is difficult to validate. Thus, the error of X_{OH}^{Ap} calculated from the analytical error of F and Cl ($\sigma_{OH} = \sqrt{\sigma_F^2 + \sigma_{Cl}^2}$; Ketcham, 2015) likely represents the minimum.

2. Calculating mole fractions of OH, F, and Cl in melt

2.1 Mole fraction of OH in melt

The calculation of the mole fractions for melt is more complicated as we have to consider the speciation of water in melts, i.e. mainly of two species: molecular H₂O (H₂O_m) and hydroxyl groups (OH) (e.g. Burnham, 1975; Stolper, 1982; Zhang, 1999). Hereafter we use square brackets to express the mole fractions of species in water. First, we can calculate the mole fraction of total water in melt using (e.g. Zhang et al., 2012; Li and Hermann, 2015):

$$\left[H_2O_t \right] = \frac{\frac{C_{H_2O}^{melt}}{18}}{\frac{C_{H_2O}^{melt}}{18} + \frac{1 - C_{H_2O}^{melt}}{W}} \quad (B.7)$$

where $C_{H_2O}^{melt}$ is the mass fraction of total H₂O in melt, and W is the molar mass of dry silicate melt, whose value varies with melt compositions (i.e. equals to ~ 32.5 g/mol for rhyolite and 36.6 g/mol for basalt; e.g. Zhang, 1999; Lesne et al., 2011). For consistency, we take $W = 33$ g/mol for all calculation hereafter.

After this, we convert $\left[H_2O_t \right]$ into the mole fraction of OH (expressed as [OH]), based on the reaction: H₂O_m (melt) + O (melt) $\rightleftharpoons$ 2OH (melt), where its equilibrium constant K_2 can be expressed as:

$$K_2 = \frac{[OH]^2}{[H_2O_m][O]} \quad (B.8)$$

which shows large dependence on temperature and to some extent on melt composition, but little on pressure (e.g. Zhang, 1999; Botcharnikov et al., 2006; Hui et al., 2008; see below text).

Based on the relation between the mole fractions of total H₂O, molecular H₂O, OH and O, i.e. $[H_2O_t] = [H_2O_m] + [OH]/2, [O] + [H_2O_m] + [OH] = 1$, we can solve Eq. B.8 and express [OH] using only K_2 and $[H_2O_t]$ (following Li and Hermann, 2015):

$$X_{OH}^{melt} = [OH] = \frac{\frac{1}{2} - \sqrt{\frac{1}{4} - \left\{ \left(\frac{K_2 - 4}{K_2} \right) \left([H_2O_t] - [H_2O_t]^2 \right) \right\}}}{\left(\frac{K_2 - 4}{2K_2} \right)} \quad (B.9)$$

The equilibrium constant K_2 is usually determined from experiments, expressed as $\ln K_2 = a + b/T$ (Table A1). At a given temperature (e.g. 950 °C), the K_2 values for dacitic to rhyolitic magmas (0.44~0.52; Zhang et al., 1997; Liu et al., 2004; Hui et al., 2009) are lower than that of andesite (~0.63-1; Nowak and Behrens, 2001; Ni et al., 2009; Botcharnikov et al., 2006); K_2 for basalt (~0.2) is even lower (Lesne et al., 2011; Fig. B1), but still higher than that of phonolites (e.g. Carrol and Blank, 1997). Thus, OH contents in basaltic magmas are much lower than those of more silicic ones, which has effects on the overall partitioning of OH. We have thus used four equations of K_2 for calculating K_D from the experiments, according to the melt composition (Table B1).

The error propagation between $[OH]$ and $[H_2O_t]$ is difficult to compute due to the complex formalism of Eq. B.9. Here we assume that the relative error of $[OH]$ and $[H_2O_t]$ is approximately equal (ignoring the uncertainty of K_2):

$$\frac{\sigma_{[OH]}}{[OH]} \approx \frac{\sigma_{[H_2O_t]}}{[H_2O_t]} \quad (B.10)$$

where $\sigma_{[H_2O_t]}$ can be calculated from the error of total H₂O contents in melt ($\sigma_{C_{H_2O}^{melt}}$, in wt.%) as:

$$\frac{\sigma_{[H_2O_t]}}{[H_2O_t]} = \sqrt{2} \times \frac{\sigma_{C_{H_2O}^{melt}}}{C_{H_2O}^{melt}} \quad (B.11)$$

The error of total water contents from direct measurements is likely smaller than that calculated from mass balance, as the calculation includes errors propagated from the measurements of other elements.

2.2 Mole fractions of F and Cl in melt

The mole fractions of F and Cl in melt are calculated using the mass fractions of F, Cl and H₂O (i.e. c_F^{melt} , c_{Cl}^{melt} , $c_{H_2O}^{melt}$) in similar formalism as Eq. B.7:

$$X_F^{melt} = \frac{\frac{C_F^{melt}}{19}}{\frac{C_{H_2O}^{melt}}{18} + \frac{1 - C_{H_2O}^{melt}}{W}} \quad (B.12)$$

And

$$X_{Cl}^{melt} = \frac{\frac{C_{Cl}^{melt}}{35.45}}{\frac{C_{H_2O}^{melt}}{18} + \frac{1 - C_{H_2O}^{melt}}{W}} \quad (B.13)$$

The standard errors in X_F^{melt} and X_{Cl}^{melt} can be calculated using equations below:

$$\frac{\sigma_{X_F^{melt}}}{X_F^{melt}} = \sqrt{\left(\frac{\sigma_{C_F^{melt}}}{C_F^{melt}}\right)^2 + \left(\frac{\sigma_{C_{H_2O}^{melt}}}{C_{H_2O}^{melt}}\right)^2} \quad (B.14)$$

and

$$\frac{\sigma_{X_{Cl}^{melt}}}{X_{Cl}^{melt}} = \sqrt{\left(\frac{\sigma_{C_{Cl}^{melt}}}{C_{Cl}^{melt}}\right)^2 + \left(\frac{\sigma_{C_{H_2O}^{melt}}}{C_{H_2O}^{melt}}\right)^2} \quad (B.15)$$

Eqs. B.12-13 show that X_F^{melt} and X_{Cl}^{melt} are related to the total water contents in melt but not the mole fraction of OH. Their ratio is then expressed as:

$$\frac{X_{Cl}^{melt}}{X_F^{melt}} = \frac{\frac{C_{Cl}^{melt}}{35.45}}{\frac{C_F^{melt}}{19}} = 0.536 \times \frac{C_{Cl}^{melt}}{C_F^{melt}} \quad (B.16)$$

where the parameter $C_{H_2O}^{melt}$ is cancelled from the division, meaning that the determination of $K_{D_{Cl-F}}^{Ap-melt}$ does not require the knowledge of the water contents in melt (nor in apatite).

3. Error propagation from mole fractions to $K_{D_{A-B}}^{Ap-melt}$

Based on the definition of $K_{D_{A-B}}^{Ap-melt} = \frac{X_A^{Ap} \cdot X_B^{melt}}{X_A^{melt} \cdot X_B^{Ap}}$, the standard deviation error (σ_{K_D})

can be calculated based on error-propagation principles:

$$\left(\frac{\sigma_{K_D}}{K_D}\right)^2 = \left(\frac{\sigma_{X_A^{Ap}}}{X_A^{Ap}}\right)^2 + \left(\frac{\sigma_{X_B^{Ap}}}{X_B^{Ap}}\right)^2 + \left(\frac{\sigma_{X_B^{melt}}}{X_B^{melt}}\right)^2 + \left(\frac{\sigma_{X_A^{melt}}}{X_A^{melt}}\right)^2 \quad (B.17)$$

where σ represents the standard error of the parameters in subscript that were calculated using Eqs. B.4-B.6 for apatite (see Section 1 above), and Eqs. B.10-B.11 and B.14-B.15 for the melt (see Section 2 above). The calculated errors are shown in *Appendix C* (see below), and have been considered in the generalized least squares regression as explained in *Appendix D*.

Table B1. Equilibrium constant K_2 for magmas of different compositions. The reference marked in bold was used for calculation in this study.

Ref. [§]	Experimental condition				ln $K_2 = a + b/T$		Used for K_D calculation
	Melt composition	Temperature (°C)	Pressure (GPa)	Total H ₂ O (wt.%)	a	b	
H08	Rhyolite	400-603	2.83	0.8-4	1.003	-2226	L&H17
H08	Rhyolite	350-654	0.94	0.8-4	1.804	-3090	
Z97	Rhyolite	400-600	-	≤2.4	1.876	-3110	W17
N&B01	Haplo-granite	500-800	0.1-0.3	1.27-5.15	3.331	-4210	
L04 *	Dacite	480-590	0.3-0.5	1.4-2.6	1.49	-2634	
N09	Haplo-andesite	470-500	0.1	2-2.5	1.547	-2453	
B06	Andesite	1100-1300	0.2-0.5	0.8-8	2.99	-3650	R18
L11	Basalt &Tephrite	1200	0.01-0.38	0.9-9	0.641	-2704.4	M15
D95	Fe-rich basalt	1200	0.02-0.098	0.11-8.55	-	-	
B09	Phono-tephrite	1200-1250	0.05-0.5	1-12	-	-	
C&B97	Phonolite	850-973	0.019-0.15	1.2-6.3	-	-	

[§] Data sources: H08: Hui et al., 2008; Z97: Zhang et al., 1997; N&B01: Nowak and Behrens; L04: Liu et al., 2004; N09: Ni et al., 2009; B06: Botcharnikov et al., 2006; L11: Lesne et al., 2011; D95: Dixon et al., 1995; B09: Behrens et al., 2009 C&B97: Carrol and Blank, 1997.

* Equation for K_2 from TT method by Liu et al., (2004).

Fig. B1. Total H₂O (in wt.%) vs. OH (in wt.%) in the melt at 950 °C, calculated using different equations for the equilibrium constant K_2 reported from the literature. With a fixed total H₂O in melt, the calculated OH contents of dacitic-rhyolitic magmas are similar, which are lower than those of andesite (in light blue lines), and higher than those of basalt (in red solid line and red symbols) and phonolite (in black symbols). The temperature- K_2 relation used for calculating K_D from experiments are solid lines. Data sources are the same as in Table B1.

Table C1. Experimental data reported by McCubbin et al., 2015 (H₂O in apatite and the melt measured by SIMS; error: 1 s.d.).

Run No.	Q1.007	Q1.010	Q1.012	Q1.013	Q1.016	Q1.017	Q1.018	Q1.020*	Q1.057	Q1.061	Q1.062
P (MPa)	1000	1000	1000	1000	1000	1000	1000	1000	1200	1200	1200
T (°C)	1000	1000	1000	1000	990	990	990	995	1000	1000	950
X _F ,Ap	0.410	0.400	0.741	0.766	0.536	0.476	0.667	0*	0.420	0.068	0.170
Error	0.048	0.057	0.073	0.044	0.027	0.066	0.063	0	0.158	0.068	0.121
X _{Cl} ,Ap	0.240	0.371	0.083	0.072	0.173	0.257	0.090	0.854	0.440	0.761	0.660
Error	0.045	0.026	0.016	0.005	0.019	0.012	0.010	0.069	0.132	0.013	0.123
X _{OH} ,Ap	0.350	0.229	0.176	0.162	0.291	0.267	0.243	0.146	0.140	0.170	0.170
Error	0.066	0.010	0.013	0.003	0.013	0.012	0.020	0.027	0.032	0.033	0.045
X _F ,melt	0.0014	0.0026	0.0052	0.0058	0.0021	0.0022	0.0027	0	0.0051	0.0003	0.0020
Error	0.0007	0.0003	0.0003	0.0001	0.0001	0.0001	0.0001	0	0.0015	0.0002	0.0013
X _{Cl} ,melt	0.0027	0.0107	0.0029	0.0024	0.0036	0.0067	0.0025	0.017	0.019	0.022	0.029
Error	0.0009	0.0003	0.0003	0.0001	0.0002	0.0001	0.0001	0.0004	0.0045	0.0004	0.0002
X _{OH} ,melt	0.0595	0.0736	0.0613	0.0636	0.0642	0.0660	0.0625	0.072	0.067	0.071	0.069
Error	0.0028	0.0014	0.0009	0.0005	0.0006	0.0008	0.0011	0.0043	0.0018	0.0042	0.0010
$K_{D_{OH-Cl}}^{Ap-melt}$	0.066	0.089	0.100	0.085	0.094	0.105	0.108	0.040	0.090	0.069	0.109
Error	0.028	0.008	0.023	0.008	0.013	0.007	0.016	0.008	0.040	0.014	0.036
$K_{D_{OH-F}}^{Ap-melt}$	0.020	0.020	0.020	0.019	0.018	0.019	0.016	n.d.	0.025	0.012	0.029
Error	0.011	0.004	0.003	0.001	0.002	0.003	0.002	n.d.	0.014	0.013	0.029
$K_{D_{Cl-F}}^{Ap-melt}$	0.304	0.226	0.202	0.227	0.188	0.177	0.146	n.d.	0.281	0.171	0.266
Error	0.188	0.043	0.051	0.025	0.028	0.028	0.024	n.d.	0.173	0.192	0.264

* Data marked in bold were measured from ternary apatite, whereas the rest were measured from binary apatite (with zero concentration of some volatiles).

† n.d.: “not determined” values of K_D, due to binary apatite used in experiment, or those of large uncertainty due to bad measurements on melt halogen contents.

Table C2. Experimental data reported by Riker et al., 2018 (H₂O in apatite and the melt measured by SIMS; error: 1 s.d.).

Run No.	BA3	BA6	BA9	BA10	BA11	BA12	BA14	Bm13	Bm14	Bm16
P (MPa)	1000	1000	1000	1000	1000	1000	1000	1000	500	500
T (°C)	1250	1250	1250	1250	1250	1250	1250	1250	1250	1250
X _F ,Ap	0.550	0.801	0.638	0.770	0.826	0.586	0.551	0.874	0.748	0.785
Error	0.060	0.190	0.075	0.086	0.096	0.074	0.062	0.180	0.115	0.178
X _{Cl} ,Ap	0.000	0.000	0.000	0.000	0.000	0.246	0.094	0.000	0.152	0.124
Error	0.000	0.000	0.000	0.000	0.000	0.013	0.009	0.000	0.080	0.015
X _{OH} ,Ap	0.442	0.174	0.354	0.204	0.156	0.149	0.353	0.117	0.092	0.087
Error	0.021	0.022	0.056	0.048	0.055	0.061	0.066	0.022	0.023	0.023
X _F ,melt	0.0169	0.0139	0.0252	0.0175	0.0267	0.0156	0.0153	0.0150	0.0145	0.0165
Error	0.0025	0.0024	0.0024	0.0021	0.0026	0.0021	0.0018	0.0024	0.0024	0.0024
X _{Cl} ,melt	0	0	0	0	0	0.0072	0.0073	0	0.0113	0.0115
Error	0	0	0	0	0	0.001	0.001	0	0.001	0.001
X _{OH} ,melt	0.1698	0.0399	0.1300	0.0903	0.0616	0.0534	0.1921	0.0822	0.0796	0.0869
Error	0.015	0.015	0.014	0.014	0.014	0.014	0.013	0.021	0.020	0.020
$K_{D}^{Ap-melt}$ K_{D}^{OH-Cl}	n.d.	n.d.	n.d.	n.d.	n.d.	0.081	0.142	n.d.	0.086	0.093
Error	n.d.	n.d.	n.d.	n.d.	n.d.	0.040	0.033	n.d.	0.055	0.035
$K_{D}^{Ap-melt}$ K_{D}^{OH-F}	0.080	0.076	0.107	0.051	0.082	0.074	0.051	0.024	0.022	0.021
Error	0.017	0.038	0.026	0.017	0.037	0.038	0.013	0.010	0.009	0.009
$K_{D}^{Ap-melt}$ K_{D}^{Cl-F}	n.d.	n.d.	n.d.	n.d.	n.d.	0.915	0.357	n.d.	0.260	0.227
Error	n.d.	n.d.	n.d.	n.d.	n.d.	0.186	0.073	n.d.	0.151	0.069

Table C3. Experimental data reported by Li and Hermann, 2017 (H₂O in apatite and the melt from stoichiometry and mass-balance calculation, respectively; error: 1 s.d.).

Run No.	EPSM-1	EPSM-2	EPSM-6	EPSM-8	EPSM-3	EPSM-5	EPSM-4	EPSM-9	EPSM-10
P (MPa)	2500	2500	2500	2500	2500	2500	2500	2500	2500
T (°C)	800	800	800	800	800	800	800	800	800
X _F ,Ap	0.000	0.000	0.000	0.417	0.537	0.453	0.545	0.631	0.661
Error	0.000	0.000	0.000	0.043	0.036	0.028	0.022	0.039	0.043
X _{Cl} ,Ap	0.176	0.392	0.133	0.195	0	0.129	0.048	0.075	0.050
Error	0.011	0.008	0.005	0.005	0	0.003	0.004	0.002	0.003
X _{OH} ,Ap	0.824	0.608	0.867	0.387	0.463	0.419	0.407	0.294	0.289
Error	0.011	0.008	0.005	0.044	0.036	0.028	0.023	0.039	0.043
X _F ,melt	0	0	0	0	0.001	0.001	0.001	0.002	0.002
Error	0	0	0	0	0.0001	0.0001	0.0001	0.0001	0.0002
X _{Cl} ,melt	0.001	0.002	0.001	0.003	0	0.002	0.001	0.002	0.001
Error	0.000	0.000	0.000	0.000	0	0.000	0.000	0.000	0.000
X _{OH} ,melt	0.160	0.160	0.170	0.160	0.170	0.160	0.170	0.170	0.170
Error	0.030	0.030	0.030	0.020	0.030	0.030	0.030	0.030	0.030
$K_{D_{OH-Cl}}^{Ap-melt}$	0.021	0.020	0.024	0.040	n.d.	0.037	0.043	0.053	0.042
Error	0.004	0.004	0.006	0.008	n.d.	0.008	0.013	0.014	0.014
$K_{D_{OH-F}}^{Ap-melt}$	n.d.	n.d.	n.d.	0.002	0.003	0.003	0.004	0.006	0.006
Error	n.d.	n.d.	n.d.	0.001	0.001	0.0007	0.0009	0.001	0.001
$K_{D_{Cl-F}}^{Ap-melt}$	n.d.	n.d.	n.d.	0.049	n.d.	0.079	0.090	0.116	0.139
Error	n.d.	n.d.	n.d.	0.020	n.d.	0.025	0.035	0.041	0.058

Table C4. Experimental data from Webster et al, 2017 (H₂O in the melt measured by FTIR, and H₂O in apatite from stoichiometry calculation; error: 1 s.d.).

Run No.	CS- 15- 04A	CS- 15-03	CS- 15-07	CS- 15-02	CS- 15- 04B	CS- 15- 04C	CS- 14- 18A	CS- 14- 18B	CS- 14- 18D	CS- 15- 16A	CS- 15-06	CS- 15- 09B	CS- 15- 09A	CS14- 18C	CS- 15- 05C	CS- 15- 05A	CS- 15- 05D	CS- 15- 05B
P (MPa)	50	49	50	50	50	50	49	49	49	50	50	49	49	49	51	51	51	51
T (°C)	843	844	844	843	844	844	850	850	850	853	850	850	850	850	862	862	862	862
X _F ,Ap	0.370	0.380	0.430	0.370	0.150	0.080	0.390	0.420	0.510	0.590	0.180	0.240	0.280	0.420	0.270	0.480	0.480	0.500
Error	0.115	0.078	0.011	0.077	0.026	0.013	0.075	0.025	0.092	0.029	0.033	0.035	0.041	0.051	0.052	0.047	0.133	0.040
X _{Cl} ,Ap	0.300	0.260	0.300	0.300	0.470	0.560	0.270	0.340	0.220	0.090	0.530	0.060	0.020	0.310	0.360	0.190	0.190	0.200
Error	0.039	0.037	0.016	0.083	0.061	0.048	0.039	0.032	0.051	0.013	0.013	0.011	0.004	0.033	0.058	0.040	0.044	0.024
X _{OH} ,Ap	0.330	0.360	0.270	0.330	0.380	0.360	0.340	0.240	0.270	0.320	0.290	0.700	0.700	0.270	0.360	0.320	0.330	0.300
Error	0.121	0.086	0.019	0.113	0.066	0.050	0.085	0.041	0.106	0.032	0.035	0.037	0.041	0.061	0.078	0.062	0.140	0.047
X _F ,melt	0.0003	0.0002	0.0015	0.0007	0.0002	0.0008	0.0014	0.0025	0.0027	0.0032	0.0019	0.0007	0.0005	n.d.	0.0008	0.0022	0.0010	0.0012
Error	0.0003	0.0004	0.0003	0.0003	0.0002	0.0005	0.0002	0.0003	0.0003	0.0012	0.0003	0.0004	0.0007	n.d.	0.0002	0.0007	0.0005	0.0005
X _{Cl} ,melt	0.0025	0.0026	0.0028	0.0022	0.0022	0.0022	0.0033	0.0028	0.0028	0.0010	0.0027	0.0003	0.0004	0.0027	0.0026	0.0017	0.0009	0.0015
Error	0.0001	0.0001	0.0001	0.0001	0.0002	0.0002	0.0001	0.0001	0.0001	0.0001	0.0002	0.0001	0.0001	0.0001	0.0001	0.0002	0.0001	0.0001
X _{OH} ,melt	0.0665	0.0726	0.0687	0.0671	0.0679	0.0687	0.0607	0.0726	0.0728	0.0745	0.0713	0.0799	0.0887	0.0709	0.0733	0.0788	0.0657	0.0766
Error	0.0033	0.0036	0.0034	0.0034	0.0034	0.0034	0.0030	0.0036	0.0036	0.0037	0.0036	0.0040	0.0044	0.0035	0.0037	0.0039	0.0033	0.0038
$K_{D_{OH-Cl}}^{Ap-melt}$	0.041	0.050	0.037	0.036	0.026	0.020	0.068	0.027	0.047	0.048	0.021	0.044	0.158	0.034	0.035	0.036	0.024	0.029
Error	0.016	0.014	0.004	0.016	0.006	0.004	0.020	0.006	0.022	0.010	0.003	0.017	0.050	0.009	0.010	0.011	0.012	0.006
$K_{D_{OH-F}}^{Ap-melt}$	0.004	0.003	0.014	0.009	0.007	0.056	0.020	0.020	0.020	0.023	0.042	0.026	0.014	n.d.	0.015	0.019	0.010	0.009
Error	0.004	0.005	0.003	0.006	0.008	0.035	0.007	0.005	0.009	0.009	0.012	0.013	0.019	n.d.	0.005	0.007	0.007	0.004
$K_{D_{Cl-F}}^{Ap-melt}$	0.097	0.053	0.374	0.252	0.285	2.725	0.294	0.723	0.416	0.492	2.017	0.583	0.089	n.d.	0.410	0.512	0.440	0.320
Error	0.103	0.106	0.087	0.154	0.292	1.721	0.080	0.128	0.134	0.201	0.538	0.375	0.571	n.d.	0.133	0.205	0.275	0.146

Appendix D: Regression approaches used for the calculation of $W_{A,B}^G$ and $\Delta_r G_{A-B}^*(P, T)$ values.

Here we present the linear-squares regression approach (e.g. Ghilani and Wolf, 2006) used in this study for the determination of $W_{A,B}^G$ and $\Delta_r G_{A-B}^*(P, T)$, which are described in three sections below for different conditions.

1. Generalized least squares regression for determining $W_{A,B}^G$ and $\Delta_r G_{A-B}^*(P, T)$ at single P-T condition.

To determine the values of $W_{A,B}^G$ and $\Delta_r G_{A-B}^*(P, T)$ (A and B are two volatile species among F, Cl, and OH), we can use a weighted least squares regression to obtain a preliminary estimation of the solution for Eq. 19 in main text (Section 2.1). When the total number of data points is larger than 3, the solution is obtained using:

$$X_1 = (M^T W M)^{-1} \cdot M^T \cdot Y \quad (D.1)$$

where Y involves the known values of $K_{D_{A-B}}^{Ap-melt}$ (as defined in *Appendix A*), M contains the data of apatite compositions from experiments (M^T is its transpose matrix), and W is the diagonal matrix that contain the reciprocal of the variance of each data point in M , derived from errors of experimental data (*Appendix C*).

The weighted least squares regression above only considers the uncertainties of apatite compositions (in M) but not those of K_D (in Y), where the errors of K_D are typically

larger and should play a larger role in the determination of the unknown parameters. Considering this, we use a generalized least squares regression procedure for a better approximation of the results by considering the errors of apatite compositions and K_D simultaneously as shown below.

Let us take the exchange coefficient K_D for OH-Cl as an example. In Eq. 18,

$$RT \ln \left[\left(K_{D_{OH-Cl}}^{Ap-melt} \right)_k \right] = - \Delta_r G_{OH-Cl}^* (P, T) - \left\{ \left[\left(X_{Cl}^{Ap} \right)_k - \left(X_{OH}^{Ap} \right)_k \right] \cdot W_{Cl,OH}^G + \left(X_F^{Ap} \right)_k \cdot \left\{ W_{F,OH}^G - W_{F,Cl}^G \right\} \right\}$$

where $k= 1, 2, 3 \dots N$, and N is the total number of data from one experiment. First, we write this equation in a general form as:

$$y = c + ax + bz \tag{D.2}$$

where y , x and z are the variables determined from experiments, and c , a , and b are the unknown parameters to be solved. By considering the residuals to y , x and z (expressed using v), we can expand Eq. D.2 as:

$$(y + v_y) = c + a (x + v_x) + b (z + v_z) \tag{D.3}$$

Due to the multiplication of a and v_x (similar for b and v_z) in Eq. D.3, the relation between y and x (or z) is **nonlinear**, indicating the necessity of using a generalized least squares regression. By re-arranging Eq. D.2 without considering the errors at this moment, we obtain an equation as:

$$f(x, y, z) = ax + bz + c - y = 0 \tag{D.4}$$

The first-order Taylor expansion for Eq. C.4 at $x = x_1, y = y_1, z = z_1$ is written as:

$$\begin{aligned} f(x, y, z) = & f(x_1, y_1, z_1) + \left(\frac{\partial f}{\partial x}\right)v_{x_1} + \left(\frac{\partial f}{\partial y}\right)v_{y_1} + \left(\frac{\partial f}{\partial z}\right)v_{z_1} \\ & + \left(\frac{\partial f}{\partial a}\right)d_a + \left(\frac{\partial f}{\partial b}\right)d_b + \left(\frac{\partial f}{\partial c}\right)d_c = 0 \end{aligned} \quad (\text{D.5})$$

where d_a, d_b , and d_c are the corrections to the approximation values of parameters a, b , and c .

Substituting the partial derivatives where $\frac{\partial f}{\partial x} = a, \frac{\partial f}{\partial z} = b, \frac{\partial f}{\partial y} = -1, \frac{\partial f}{\partial a} = x_1,$

$\frac{\partial f}{\partial b} = z_1, \frac{\partial f}{\partial c} = 1$, Eq. D.5 can be re-written as:

$$-(ax_1 + bz_1 + c - y_1) = av_{x_1} + bv_{z_1} - v_{y_1} + x_1d_a + z_1d_b + d_c \quad (\text{D.6})$$

For N sets of (x, y, z) when $N \geq 3$, we can expand Eq. C.6 into:

$$\begin{aligned} -(ax_2 + bz_2 + c - y_2) &= av_{x_2} + bv_{z_2} - v_{y_2} + x_2d_a + z_2d_b + d_c \\ -(ax_3 + bz_3 + c - y_3) &= av_{x_3} + bv_{z_3} - v_{y_3} + x_3d_a + z_3d_b + d_c \\ &\vdots \\ -(ax_N + bz_N + c - y_N) &= av_{x_N} + bv_{z_N} - v_{y_N} + x_Nd_a + z_Nd_b + d_c \end{aligned} \quad (\text{D.7})$$

which can be written in matrix form as:

$$\mathbf{K} = \mathbf{B}\mathbf{V} + \mathbf{J}\mathbf{X} \quad (\text{D.8})$$

where

$$\mathbf{K} = \begin{bmatrix} -(ax_1 + bz_1 + c - y_1) \\ -(ax_2 + bz_2 + c - y_2) \\ \vdots \\ -(ax_N + bz_N + c - y_N) \end{bmatrix}$$

$$\mathbf{B} = \begin{bmatrix} a & b & -1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & a & b & -1 & 0 & \dots & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & \dots & \dots & 0 \\ \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & a & b & -1 \end{bmatrix}$$

$$\mathbf{V} = \begin{bmatrix} v_{x_1} \\ v_{z_1} \\ v_{y_1} \\ v_{x_2} \\ v_{z_2} \\ v_{y_2} \\ \vdots \\ v_{x_N} \\ v_{z_N} \\ v_{y_N} \end{bmatrix}$$

$$\text{the Jacobian matrix } \mathbf{J} = \begin{bmatrix} x_1 & z_1 & 1 \\ x_2 & z_2 & 1 \\ x_3 & z_3 & 1 \\ \vdots & \vdots & \vdots \\ x_N & z_N & 1 \end{bmatrix}$$

and

$$\mathbf{X} = \begin{bmatrix} d_a \\ d_b \\ d_c \end{bmatrix}$$

Considering the error of all the data for x , y , and z , we can calculate the weighting matrix W_0 using equations below:

$$W_0 = (BQB^T)^{-1} \quad (D.9)$$

where Q is the diagonal matrix made up of the variance (i.e. the square of standard error) of each data point reported from experiments:

$$Q = \begin{bmatrix} \sigma_{x_1}^2 & 0 & 0 & 0 & 0 & 0 & \dots & 0 & 0 & 0 \\ 0 & \sigma_{z_1}^2 & 0 & 0 & 0 & 0 & \dots & 0 & 0 & 0 \\ 0 & 0 & \sigma_{y_1}^2 & 0 & 0 & 0 & \dots & 0 & 0 & 0 \\ 0 & 0 & 0 & \sigma_{x_2}^2 & 0 & 0 & \dots & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & \sigma_{z_2}^2 & 0 & \dots & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & \sigma_{y_2}^2 & \dots & 0 & 0 & 0 \\ \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \ddots & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & \sigma_{x_N}^2 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \sigma_{y_N}^2 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \sigma_{z_N}^2 \end{bmatrix} \quad (D.10)$$

Using Eqs. D.8-D.10, we can obtain a correction matrix X :

$$X = (J^T W_0 J)^{-1} J^T W_0 K \quad (D.11)$$

which is added to the initial guess of the solution (i.e. X_1 in Eq. C.1) using an iteration computing procedure till the solution converges, which yields the values of a , b and c .

Their standard errors (1σ) are then calculated using equation $\begin{bmatrix} \sigma_a \\ \sigma_b \\ \sigma_c \end{bmatrix} = (J^T W_0 J)^{-1}$.

2. Regression for the temperature dependence of $\Delta_r G_{A-B}^*(P, T)$

The relation of temperature and $\Delta_r G_{A-B}^*(P, T)$ values obtained from above were obtained using a standard least squares regression. In the equation of $\Delta_r G_{A-B}^*(P, T) = kT + b$, the error of the slope (k) was obtained by an iteration computation approach (e.g. for 1000 times) by assuming all values within the error range are of same weight. The error range of the intercept to the y-axis (i.e. b) was constrained by letting the fitted line cover the minima and maxima of all data points of $\Delta_r G_{A-B}^*(P, T)$ (Fig. 2.4 in main text).

3. Refining the values of $W_{A,B}^G$ by computing the data from experiments at various pressure-temperature conditions

$W_{A,B}^G$ obtained using the data of single pressure-temperature condition shows wide ranges (Table 2.2). Considering likely small P and T dependence of $W_{A,B}^G$ (Section 2.2 in main text), we are able to use all the data from the four experiments to obtain the mean values of $W_{A,B}^G$ within the P-T range of interest. Using the obtained values of $\Delta_r G_{A-B}^*(P, T)$ (from Section 2.2), the total number of unknowns to be solved from regression is one less compared to the unknowns shown in first section. For example, Eq. D.2 now becomes:

$$y = c_0 + ax + bz \quad (\text{D.12})$$

where c_0 is $\Delta_r G_{A-B}^*(P, T)$ whose values are known from the regression before, and a and b that involve the W^G values that need to be determined. We used the generalized least squares regression in Section 2.1 to calibrate W^G s by using data from all experiments, which give us W^G values with smaller errors than those calculated using individual datasets.

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Chapter 3

Apatite reveals melt volatile budgets and magma storage depths: insights into the 2006 effusive and 2010 explosive eruptions at Merapi volcano (Indonesia)

**Apatite reveals melt volatile budgets and magma storage depths:
insights into the 2006 effusive and 2010 explosive eruptions
at Merapi volcano (Indonesia)**

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Abstract

The abundances of volatiles in magmas and their storage depths play a large role in controlling the eruptive styles of volcanoes. The melt volatiles' concentrations are usually constrained with analysis of melt inclusions, but these are not always available in the investigated rocks and may have experienced various post-entrapment processes that can modify their volatile compositions. Here we provide another perspective for investigating melt volatile budgets and their variations before eruption using apatite, which is an ubiquitous mineral in igneous rocks and incorporates several volatile species into its structure. We used SIMS and EPMA to measure in situ H₂O, CO₂, Cl, F and S concentrations in 50 apatite crystals that occur in several textural positions of the erupted products from the 2006 (effusive) and 2010 (explosive) eruptions at Merapi volcano.

The CO₂ contents measured using SIMS are likely the first ones for natural volcanic apatite.

We find that the volatile compositions of apatite from the two deposits are very similar, and show a bimodal distribution of F-H₂O-CO₂ concentrations: apatite inclusions in amphibole are F-poor but rich in H₂O (0.9-1.0 wt.%) and CO₂ ($\geq$ 2400 ppm), compared to crystals hosted by plagioclase and clinopyroxene, and those in the groundmass (H₂O: 0.4-0.7 wt.%; CO₂: 40-900 ppm). Using the apatite-melt partitioning relations from literature, we find that the melts in equilibria with apatite in amphibole have about 3-10 wt.% H₂O, 1-3 wt.% CO₂, and in average $\sim$ 800 ppm S, whereas those in equilibria with the rest of apatite have much lower volatile concentrations ($\sim$ 1-3 wt.% H₂O, $\sim$ 50-2100 ppm CO₂). Combination of these data with geothermobarometry calculations for the minerals that host the apatite (including a new Al/Si partitioning calibration in amphibole) allows us to propose a coupled magma plumbing system and volatile concentrations for Merapi volcano that provide insights into volcanic degassing and magma ascent rates. Apatite included in anhydrous minerals and those in the groundmass record melt volatile budgets similar to those in melt inclusions from literature, indicating magma storage at depths of $\sim$ 1-16 km (most at 2 to 5 km below the summit). This agrees with the depths estimated from geodetic and geophysical observations as well as seismic tomography studies. In contrast, apatite included in amphibole grew in a magma storage zone at depths of $>$ 30 km, partially overlapping with the amphibole-liquid geobarometry calculations, and the deep magma storage zones proposed by seismic tomography studies.

Combination of our new data and the fumarole gas measurements before eruption indicates that the CO₂-richest gas released just before the 2010 eruption requires a much larger proportion of volatiles exsolved from the deep C-rich melts, compared to 2006. This implies volatile CO₂ percolation and fluxing of the magma column before the 2010 eruption, which led to a larger magma buoyancy, and thus faster magma ascent rate, which in turn caused the larger explosion in 2010 than 2006. Finally, we estimate the relative magma ascent rates of the two eruptions using a diffusion model of Cl zoning in apatite. We find that the magma ascent rate in 2010 is faster by factors of > 10 than that in 2006, and this difference is on the same order of magnitude with the difference in the magma extrusion rates reported in literature. Using volatile abundances and distributions in apatite appears to be a powerful means to obtain constraints on the melt volatile contents, magma storage zones, and magma ascent rates, especially when combined with geothermobarometric methods. The calculation approaches used in this study based on apatite could be applied to a variety of volcanoes for better understanding of their eruption behaviour, and to be combined with monitoring data for better forecasting.

Contributions

Weiran Li: Majority of work on sample preparation, analyses, and calculations.

Fidel Costa: Discussion on data interpretation and implications for future work.

Kazuhide Nagashima: Assistance in SIMS analyses.

3.1. Introduction

The magmatic volatile abundances play a large role in controlling the eruptive styles of volcanoes, as they have large influence on the melt viscosity and thus can affect magma transport, ascent and the eruption dynamics (e.g. Blake, 1984; Roggensack et al., 1997; Cashman, 2004; Giordano et al., 2008; Cashman and Sparks, 2013; Cassidy et al., 2018). H₂O and CO₂ are the major components of volcanic volatiles, and their abundances in the melt are affected by multiple factors, such as the amounts of volatiles in the initial melts, the extent of magma fractionation, and the volatile solubilities that are mainly dependent on pressure, temperature and the compositions of melt/fluids (referred to as *P-T-X* condition hereafter). The amounts of dissolved volatiles in the melt before eruption cannot be measured directly, but can be inferred from petrological methods, such as mineral-melt hygrometers (e.g. of plagioclase; Lange et al., 2009) and melt inclusions (e.g. Wallace et al., 2005; Kent et al., 2008), which have various limitations. For example, the application of the mineral-based hygrometers requires the equilibrium between crystal and the melt, whereas the melt inclusions may not always represent the original melt compositions, if they have experienced post-entrapment modifications, and interaction with host minerals and/or external melt through diffusive exchange (Qin et al. 1992; Danyushevsky et al. 2000; Gaetani and Watson 2000; Cottrell et al. 2001; Portnyagin et al. 2008; Lloyd et al. 2013). In addition, melt inclusions may appear only in phenocrysts that crystallized from a rather differentiated melt (e.g. plagioclase and clinopyroxene), and thus could not reflect volatile information for the primitive melts. Considering this, here we propose an additional approach based on apatite to constrain the compositions and abundances of the dissolved volatiles in the melts.

Another important factor that affects the explosivities of eruptions is the exsolved volatiles present as fluids/vapor phases (e.g. Degruyter et al., 2017; Cassidy et al., 2018). The abundances of exsolved volatiles are difficult to measure/estimate, but it is possible to gain some insights based on the volatiles emitted as volcanic gases (e.g. Edmonds et al., 2014). For example, the CO_2/SO_2 and $\text{CO}_2/\text{H}_2\text{O}$ values in the emitted gas have been found to increase proceeding to eruption, which likely indicates magma degassing from deeper locations, and thus can be used as eruption precursor (e.g. Aiuppa et al., 2007; Aiuppa et al., 2009; Allard, 2010; Kahl et al. 2013; Chiodini et al., 2016). Nonetheless, the complex relations between the dissolved volatiles in the melt, exsolved volatiles in fluids, and those emitted as volcanic gas are still being explored. In this study we provide another perspective of the magmatic volatile budgets by investigating volatile compositions of natural volcanic apatite. By applying this method to apatite crystals in the rocks from two eruptions of different explosivities at Merapi volcano, we calculated the melt volatile budgets before the two eruptions and linked them with the compositions of the fumarolic gas.

3.1.1. The Merapi 2006 and 2010 eruptions

Merapi Volcano in central Java (Indonesia) is one of the most active volcanoes in the world. It has erupted about 27 times in the last century (e.g. Voight et al., 2000), and most of the time produced dome-forming events with VEIs of 1-3 (Volcanic Explosivity Index; Newhall and Self, 1982). Surprisingly in 2010, Merapi did not erupt in its typical style (e.g. the dome-forming eruption in 2006), but instead produced the most explosive event (VEI4) in the last hundred years, which caused a large impact to the local

community (e.g. Surono et al., 2012). Previous studies have shown that the rocks collected from the 2006 and 2010 deposits do not have significant differences in their petrological or geochemical properties, including their bulk-rock composition (basaltic andesite; Costa et al., 2013; Erdmann et al., 2016), mineral assemblage, and phenocrysts compositions (Costa et al., 2013; Preece et al., 2014). This brings up the question of what caused the change in the eruptive styles within four years, and more importantly what is the key parameter that caused the larger and more hazardous explosion in 2010.

Eruptive styles of volcanoes can be affected by multiple factors, among which the most important two are the pre-eruptive melt volatile budget, and the magma ascent rate (e.g. Kent, 2008; Cashman and Sparks, 2013; Cassidy et al., 2018). Previous studies have shown that volatile abundances in melt inclusions from the 2006 and 2010 rocks show similar ranges (Nadeau et al., 2013; Preece et al., 2014), whereas the magma ascent rates in 2010 might be faster than in 2006, given that the 2010 magma extrusion rates are about an order of magnitude faster than 2006 (e.g. Pallister et al., 2013), and the microlites of 2006 and 2010 show some differences in texture, compositions and abundances (Costa et al., 2013; Preece et al., 2016). Despite the observations mentioned above, there are still many unsolved problems about the triggers of the shifted eruptive styles from 2006 to 2010. For example, we have very little clue of the melt volatile budgets at depths, as the clinopyroxene-hosted melt inclusions reported in literature (Nadeau et al., 2013; Preece et al. 2014) likely stabilized at shallow depths, and have experienced some extent of re-equilibration, according to observation of their textures (Costa et al., 2013). Considering this, we have used apatite to provide more constraints on the melt volatile abundances and their variations before the two eruptions.

3.1.2. Using apatite to study melt volatile contents

Apatite has become a popular tool for investigating melt volatile budgets in the past decade (e.g. Boyce and Hervig, 2008; Boyce and Hervig, 2009; Van Hoose et al, 2013; Scott et al., 2015; Stock et al., 2016; Stock et al., 2018). Compared to melt inclusions, apatite has the advantages of being a common mineral in volcanic rocks (especially within andesitic-rhyolitic systems), and of being able to incorporate various volatile species (e.g. F, Cl, H₂O, S, and CO₂) into its crystal structure (e.g. Piccoli and Candela, 2002; Webster and Piccoli, 2015). To use apatite to estimate melt volatile budgets, we need to know the partition relation of volatile elements between apatite and the melt, which has been recently investigated from experiments (e.g. McCubbin et al., 2015; Li and Hermann et al. 2017; Riker et al., 2018), and thermodynamic calculations (Li and Costa, 2020).

Previous experimental studies have shown that the partitioning of F, Cl, and OH between apatite and the melt do not follow a Nernstian distribution relation (e.g. McCubbin et al., 2015; Li and Hermann, 2017). Instead this can be better described using the exchange coefficients that is derived from the exchange reaction of two components between the two phases, i.e. $K_{D_{A-B}^{Ap-melt}} = \frac{x_A^{Ap} \cdot x_B^{melt}}{x_A^{melt} \cdot x_B^{Ap}}$, where A and B are two components among F, Cl, and OH, and X represents the mole fractions of A or B in apatite or in the melt. Given our interests in constraining the H₂O contents in melts, we have focused on the exchange coefficients for OH-Cl and OH-F, referred to as $K_{D_{OH-x}^{Ap-melt}}$ ($x=F, Cl$) hereafter. The values of $K_{D_{OH-x}^{Ap-melt}}$ depend on temperature (T) and F-Cl-OH composition in apatite due to their non-ideal mixing in ternary apatite (Li and Hermann, 2017; McCubbin et al., 2018; Li and Costa, 2020). The non-ideal properties

of ternary apatite have been constrained by Li and Costa (2020) from thermodynamic calculation of experimental data from the literature, and was used in this study for estimating the melt H₂O contents.

In this chapter we report the volatile concentrations (of H₂O, CO₂, F, Cl and S) in apatite crystals that occur at various textural positions from Merapi 2006 and 2010 rocks (Section 3.4). CO₂ concentrations reported here are probably the first published CO₂ data for natural volcanic apatite (see analytical conditions in Section 3.2). For calculations of the melt water budgets following Li and Costa (2020), we have used multiple methods for constraining the melt halogen contents and temperatures (Sections 3.5-3.6). The calculated melt water contents (Section 3.7) were then used for estimating the CO₂ concentrations in the melt, based on the exchange of H₂O-CO₂ between apatite and the melt constrained by previous experimental study (Section 3.8).

3.2. Analytical techniques and calculation approaches

Juvenile bread-crust bombs from the 2006 and 2010 eruptions were collected shortly after each event in June, 2006 and November, 2010 respectively; sample localities can be found in Costa et al. (2013). The 2010 samples are from Eruption Stage 4-6 according to the chronology study by Komorowski et al., (2013), i.e. the most explosive phases on November 5-6 of 2010. Compositions of apatite, matrix glass, and amphibole from six samples (i.e. three samples from each eruption) were measured using electron microprobe (EPMA), and F, Cl, OH, S and CO₂ concentrations of apatite from the same rocks were analysed using secondary ion mass spectrometry (SIMS). Bulk rock

composition of four rocks from the 2010 deposits were analysed at Actlabs (Canada), using the fusion XRF for major elements, using Instrumental Neutron Activation Analysis (INAA) for Cl, and using the Ion Selective Electrode (ISE) method for F. The detection limits for F and Cl are 0.01 wt.%.

3.2.1. Electron microprobe analyses of apatite, amphibole, and the matrix glass

Apatite

EPMA analyses were performed on in total 42 apatite crystals from the 2006 and 2010 rocks, using a JEOL JXA 8530F field emission gun electron microprobe at the Facility for Analysis Characterization Testing and Simulation at Nanyang Technological University (Singapore). For investigating the compositional homogeneity within single crystals, X-ray maps (of Cl, F, and S) and cathodoluminescence (CL) images were obtained simultaneously, using an accelerating voltage of 15 kV, and beam current of 25 nA. The dwell times for X-ray mapping and the CL imaging are about 70 ms and 40 ms, respectively. Single-point compositions and profiles of 1- μ m spacing were obtained using accelerating voltage of 15 kV, and a focused beam of 10-nA current. We analyzed Si, Mg, Fe, Ce, Ca, Na, P, S, F and Cl, where F was measured using LDE1 crystal, and the PETJ crystal for Cl. The on-peak acquisition times were 80 s for F, Cl, S and Mg, 60 s for Ce and Fe, 40 s for Si, and 20 s for Na, Ca, and P. The standards used for calibrations are the natural minerals from Astimex Ltd., i.e. apatite standard used for calibration of F, P, Ca; tugtupite for Cl, Na; anhydrite for S; almandine for Si, Mg; and monazite for Ce. A time-dependent intensity (TDI) correction was applied to F, Cl, S,

and Na to mathematically correct signal variation. Element concentrations were quantified using a modified ZAF matrix correction procedure (Armstrong, 1988). Background intensity was calibrated based on mean atomic number of analytical volume and continuum absorption was corrected after Donovan and Tingle (1996). Stoichiometric oxygen was calculated by cation abundance and included in the matrix correction. An absorption correction was applied for carbon coating to both the standard and sample for electrical conductivity. The detection limits for F, Cl, and S are ~ 300 ppm, ~ 85 ppm, and ~ 30 ppm, respectively. Relative errors are < 1% for major elements (Ca, P), < 2-3% for F and Cl, and < 10% for the minor elements (S, Si, Ce, Na, Mg). To minimize the interference from possible F migration due to exposure of the crystal under electron beam (particularly when the beam is parallel to the c-axis of the crystal; Stormer et al., 1993; Goldoff et al., 2012; Stock et al., 2015), we have performed quantitative analyses mostly on crystals whose c-axes are not parallel to the electron beam (i.e. the elongated directions of the crystals can be observed from the thin section), and used a low-energy beam (current of 10 nA). As a result, the counts of F during each analysis did not show obvious fluctuation. Structural formula of apatite was calculated from stoichiometry following Ketcham (2015), i.e. using 25 oxygen for calculation of OH-rich apatite (hosted by amphibole), and 26 oxygen for the OH-poor apatite (at other textural positions). The OH values calculated using 25 O and 26 O only have <4% difference (Ketcham, 2015).

Amphibole

Single point analyses and compositional traverses were measured from two amphibole crystals from 2010 and one from 2006, using voltage of 15 kV and beam current of 25

nA. The on-peak acquisition times were 20 s for major elements, and 80 s for trace elements. The standards used for calibration are natural minerals from P&H Ltd. (i.e. almandine, wollastonite, rutile, diopside, albite, specularite, rhodonite, orthoclase, halite, and fluorite). TDI, ZAF matrix corrections and backgrounds calibrations are the same as used for apatite (see above). Relative errors are < 1% for major elements. Structural formula was calculated on the basis of 23-oxygen using the excel spreadsheet from Putirka (2016).

Interstitial glass

Single point analyses of the interstitial glass were measured from one sample from each eruption, using accelerating voltage of 15 kV, and a defocused beam (10 μm in diameter) of 10-nA current. Na and K were measured in the first round to minimize possible migrations. Counting times are set to be 10 s for Na and K, 20-40 s for major elements, and 60 s for minor elements (e.g. F, Cl, S). TDI and ZAF matrix corrections and backgrounds calibrations are the same as for apatite. Relative errors from analyses are < 1-2% for major elements, and ~ 5-10% for minor elements.

3.2.2. SIMS analyses of apatite

In total 50 apatite crystals in six rocks from the 2006 and 2010 deposits were analyzed using secondary ion mass spectrometer (Cameca ims-1280) in Hawai'i Institute of Geophysics and Planetology (HIGP) at the University of Hawai'i at Mānoa. Two analytical sessions were performed in 2015 and 2016, using the same instrument and

similar analytical conditions, to measure the concentrations of H₂O, F, Cl, and S of 25 crystals in 2015, and 29 crystals in 2016. CO₂ data were also obtained from the 29 crystals analyzed in 2016. Maps of secondary ions (¹⁶O¹H, ³²S, ¹⁹F¹⁶O, ³⁷Cl) with high resolution of ~100 nm were obtained from 13 crystals. Sample preparations and instrument settings for the analyses with and without CO₂ are described separately below.

F, Cl, H₂O, S

The standard-size petrographic thin sections were cut into smaller sections in square shape (of 23×23 mm² in size) to fit the sample holder. Samples were cleaned with ethanol, and coated with gold, before being loaded in the sample chamber from at least 24 hours before the analyses. A vacuum of $\sim 1 \times 10^{-9}$ torr was maintained through the analyses. Each crystal was pre-sputtered for about 8 minutes at its core area (of 35 x 35 μm^2 in size), using a primary Cs⁺ beam with current of 500 pA and accelerating voltage of -9 kV. For mapping of the secondary ions of ¹⁶O¹H, ³²S, ¹⁹F¹⁶O, and ³⁷Cl, an area of 25 × 25 μm^2 on each crystal was scanned for 50-70 cycles using a beam current of 20 pA. The mass resolving power (MRP) is ~ 6000 , which is sufficiently large to separate the targeted ions from interference. For the quantitative analyses, we selected the crack-free crystals to mitigate interference from ion migration (especially H that was observed from mapping results; Fig. 3.2). Considering the Cl or F zoning at some crystal rims (Fig. 3.3), the quantitative analyses were obtained from the more homogeneous core areas. The samples were pre-sputtered for three minutes on an area of 25 x 25 μm^2 in size, using a primary Cs⁺ beam of 3 nA, accelerating voltage of -9 kV, and field aperture size of 2500. Secondary ions of ¹⁶O¹H, ³⁴S, ¹⁹F¹⁶O, and ³⁷Cl were collected from the

central area (of $15 \times 15 \mu\text{m}^2$ in size) for 20 cycles, using electron multiplier. An electronic gating of 50% was used to reduce the noise from the edge of the analysis pits. Eventually only the signals from the most central area (of $\sim 7.5 \times 7.5 \mu\text{m}^2$) were used for determining the concentrations. Secondary ions were normalized to ^{18}O to calibrate H_2O , F, Cl and S concentrations using four apatite standards reported by McCubbin et al. (2012), which show good linear correlation between the intensity and concentrations (*Appendix A*). The volatile-poor San Carlos Olivine (SC olivine) was measured at the beginning and the end of each analytical session, reflecting low analytical backgrounds (H_2O : ~ 7 ppm; S, Cl, F: < 1 ppm). Relative errors are ~ 2 -5% for F and H_2O , and ~ 5 -20% for Cl and S due to their lower abundances.

CO_2

CO_2 was measured together with other volatile species (in 2016) from apatite crystals within the thin sections prepared from three rocks from each eruption: two thin sections were analyzed in 2015, and the other four without analyses nor carbon coating. Samples were carefully polished using silk cloth, and cleaned using ethanol, then coated with gold. Each sample was loaded in the sample chamber of SIMS overnight to minimize air contamination. The crystals were pre-sputtered for about 5 mins to remove possible residual carbon on the surface. After pre-sputtering, $^{12}\text{C}^-$ was collected simultaneously with other secondary ions ($^{16}\text{O}^{1}\text{H}$, ^{34}S , $^{19}\text{F}^{16}\text{O}$, ^{37}Cl), using the same analytical conditions as used in 2015 (including the voltage, current, analyzed area, e-gate). The only difference is that to reduce the CO_2 backgrounds, we used a smaller field aperture (of 1202) than that used before (of 2500) (see below). The CO_2 concentrations were

calibrated using a natural apatite standard that contains 0.142 (± 0.034) wt.% CO₂ (Clark et al., 2016; *Appendix A*).

Analytical conditions for CO₂ were optimized by trial analyses on the San Carlos olivine, silicon wafer, and some C-poor crystals in our samples (e.g. clinopyroxene and Fe-Ti oxide). Using the field aperture of 2500 as was used for analyzing other volatile species before, we found unexpectedly high CO₂ (of ~ 100 ppm) from the San Carlos olivine, implying some extents of external C from analyses. By using a variety of field-aperture sizes (of 8005, 2500, 1202) to analyze a carbon-free gold-coated silicon wafer, we find that there is a decrease in the obtained CO₂ concentration (from ~ 500 to 100 to 50 ppm) with aperture size, whereas the concentrations of other volatile species do not show obvious difference (*Appendix A*). This observation indicates the extra C measured using large apertures is likely due to the presence of positive ion $^{12}\text{C}^+$, whereas the positive ions of volatiles (F, Cl, OH, S) do not exist. The positive ion of $^{12}\text{C}^+$ was likely ejected from the crystal surface during pre-sputtering, and re-deposited in/around the analysis pits (due to the negative charge of the stage), and then collected together with the anion of $^{12}\text{C}^-$, which leads to higher C concentrations when using a larger aperture size. The small aperture of 1202 yields ~ 37 ppm CO₂ in the San Carlos Olivine and ~ 20 ppm CO₂ in clinopyroxenes and Fe-Ti oxides from our thin sections, indicating a low CO₂ background (of ~ 20 ppm), possibly due to residual C within the instrument. Relative errors of the measured CO₂ concentrations are ~ 10 -30 %.

After SIMS analyses, the pit locations were double checked using a scanning electron microscope for excluding the suspicious results, e.g. SIMS pits partially out of the targets crystals, and over the cracks (*Appendix B*). Three extremely high CO₂ values (of

about 4-11 wt.%) exceed the maximal CO₂ that can be preserved within these crystals given the total of the analysed components of > 98 wt.% (*Appendix B*). These abnormally high values might be caused by local C contamination (e.g. C-bearing inclusions within the crystals), thus have been excluded from calculations hereafter.

3.2.3. Symbols, abbreviations and formulations of the exchange coefficients

Abbreviations used in this chapter are: Apatite –Ap; Amph – amphibole; Cpx – clinopyroxene; Opx – orthopyroxene; Pl – plagioclase; Olivine – Ol; Biotite – Biot; Gm – groundmass; MI – melt inclusion. Symbols that express mineral compositions are:

$An = \frac{Ca}{Ca+K+Na} \times 100$; $Mg\# = \frac{Mg}{Mg+Fe^*} \times 100$ (Fe* as Fe²⁺); FeO*: Total iron as Fe²⁺. Mole fractions of F, Cl, and OH in apatite were calculated following Li and Costa (2020), i.e.

$$X_i^{Ap} = \frac{\frac{C_i^{Ap}}{M_i}}{\frac{C_F^{Ap}}{19} + \frac{C_{Cl}^{Ap}}{35.45} + (\frac{C_{H_2O}^{Ap}}{18} \times 2)}, \text{ where } M_i \text{ is the atomic mass of component } i (= F, Cl, OH),$$

and C_i^{Ap} is the mass concentration of i from SIMS analyses.

Formulations for the exchange coefficients $K_D^{Ap-melt}$ s ($x = F, Cl$) were taken from Li and Costa (2020), expressed using temperature (T , in kelvins) and apatite composition (X_i^{Ap}) as:

$$\ln(K_D^{Ap-melt}) = -\frac{1}{RT} \times \{94600 (\pm 5600) - 40 (\pm 0.1) \times T - 1000 \times [7 (\pm 4) \times (X_F^{Ap} - X_{OH}^{Ap}) - 11 (\pm 7) \times X_{Cl}^{Ap}]\} \quad (1)$$

$$\ln(K_D^{Ap-melt}) = -\frac{1}{RT} \times \{ 72900 (\pm 2900) - 34 (\pm 0.3) \times T - 1000 \times [5 (\pm 2) \times (X_{Cl}^{Ap} - X_{OH}^{Ap}) - 10 (\pm 8) \times X_F^{Ap}] \} \quad (2)$$

The exchange coefficient for H₂O-CO₂ between apatite and the melt, $K_D^{Ap-melt}_{H_2O-CO_2}$, is defined as (Riker et al., 2018):

$$K_D^{Ap-melt}_{H_2O-CO_2} = \frac{c_{H_2O}^{Ap} \cdot c_{CO_2}^{melt}}{c_{CO_2}^{Ap} \cdot c_{H_2O}^{melt}} \quad (3)$$

where c represents the weight concentrations of H₂O or CO₂ (expressed in subscript) in apatite or in the melt (expressed in superscript). We use $K_D^{Ap-melt}_{H_2O-CO_2} = 0.629 \pm 0.08$ determined from experiments at 1250 °C and 1 GPa for basaltic-andesitic melts (Riker et al., 2018) for estimating the CO₂ contents in melts (Section 3.8).

The exchange coefficients for Cl-OH and Al-Si between amphibole and the melt are

expressed in mole fractions as: $K_D^{Amph-melt}_{Cl-OH} = \frac{X_{Cl}^{Amph} \cdot X_{OH}^{melt}}{X_{Cl}^{melt} \cdot X_{OH}^{Amph}}$, and $K_D^{Amph-melt}_{Al-Si} =$

$\frac{X_{Al}^{Amph} \cdot X_{Si}^{melt}}{X_{Al}^{melt} \cdot X_{Si}^{Amph}}$. The $K_D^{Amph-melt}_{Al-Si}$ value is determined from this study by regression of a

large number of experimental data from the literature (*Appendix D*). The equation for

$K_D^{Amph-melt}_{Cl-OH}$ was taken from Humphreys et al. (2009) based on regression of experimental data reported by Sato et al. (2005) as:

$$K_D^{Amph-melt}_{Cl-OH} = \exp(8.62 - 3.46 \times Mg\# - 0.0062 \times T) \quad (4)$$

where Mg# is the Mg number of amphibole, and T is temperature in kelvins.

3.3. Observations of the Merapi 2006 and 2010 rocks

The samples investigated in this study are the same as those reported from Costa et al. (2013). The 2006 and 2010 rocks show similar basaltic-andesite composition for the bulk rocks, and similar mineral assemblages of Pl + Cpx + Opx + Amph + Fe-Ti oxide + Ap $\pm$ Ol $\pm$ Biot (see abbreviations in methods). The phenocrysts (defined as $> 500 \mu\text{m}$ in length) occupy about 30-40% in volume (vol.%) out of the whole rocks (vesicle-free normalization; Costa et al., 2013). The most abundant mineral is plagioclase (of ~ 20 -30 vol.%), followed by Cpx (of ~ 5 -7 vol. %), Amph (of ≤ 0.5 vol. %), Opx (of ≤ 0.5 vol. %), and very minor Ol and Biot (of ≤ 0.1 vol. %). Most Fe-Ti oxide and apatite crystals are present as microphenocrysts (of ~ 100 -500 μm in length), or microlites (of $< 100 \mu\text{m}$ in length).

Plagioclase phenocrysts from both 2006 and 2010 rocks show a wide range of texture and zoning patterns, and varied An compositions (An 40-90; Costa et al., 2013; Cheng and Costa, 2019). Cpx phenocrysts from 2010 rocks show oscillatory/sectoral zoning, and sometimes have narrow well-defined rims surrounding the resorbed interiors. Modelling of Fe-Mg diffusion zoning in Cpx suggests magma intrusions that occurred < 2 -3 years before 2010, and < 2 -5 years before 2006 (Costa et al., 2013). The complex zoning patterns in Pl and Cpx from both eruption deposits indicate the open-system magma evolution, where the more mafic magmas at depths migrated to the shallower

reservoir(s), and interacted with the crystal-rich and more evolved shallow magmas (Costa et al., 2013; Preece et al., 2014; Erdmann et al., 2016).

The most significant petrological differences between 2006 and 2010 are the texture/composition of the amphibole phenocrysts and the plagioclase microlites. Amphibole from 2006 rocks commonly shows reaction rims made up of fine-grained Pl + Opx + Fe-Ti oxides of tens of microns in thickness, which was rarely observed from 2010 samples (Costa et al., 2013; Preece et al. 2014), indicating a probably slower magma ascent in 2006 than 2010 (Costa et al., 2013). Some amphibole crystals from 2010 rocks show complex zoning of Al_2O_3 and Mg#, where those from 2006 rocks are more homogeneous (of 11-12 wt. % Al_2O_3 , Mg# = 68-69) (Table 3.5). Microlites (< 100 μm in length) from the two deposits are made up of Pl, Cpx, Fe-Ti oxide and trace amounts of apatite. The larger abundances of microlites in 2006 rocks (than 2010) are likely related to larger extent of degassing-induced crystallization during slower magma ascent in 2006 (Costa et al., 2013; Preece et al., 2016).

3.4. Textural positions and compositions of apatite

Apatite crystals are only about 0.2-0.6 volume percent in Merapi 2006 and 2010 rocks, but have been observed from various textural positions, i.e. some are in contact with the interstitial glass as microlites (~ 30-100 μm in length) or microphenocrysts (~ 100-180 μm in length; referred to as groundmass apatite below), whereas the others are included in phenocrysts of Amph, Cpx, Pl and Opx (Fig. 3.1). According to the textures and size of the apatite inclusions, they likely crystallised under two different conditions (named

as Type-1 and Type-2): Type-1 is the anhedral or needle-shape tiny inclusions ($< 10\ \mu\text{m}$ in length), which likely crystallised due to local saturation of apatite-forming elements (e.g. phosphorus) at the boundary layer between the silicate host mineral and the melt (Harrison and Watson, 1984; Bacon, 1989); whereas Type-2 is the larger ($\sim 20\text{-}80\ \mu\text{m}$ in length), subhedral-euhedral, hexagonal or tabular-shape inclusions, which more likely record the “global” composition of the melts. Hence in this study, we have only analysed the Type-2 inclusions and the subhedral-euhedral groundmass apatite, for estimation of the melt volatile budgets.

H₂O and CO₂ concentrations in apatite were measured by SIMS, whereas F, Cl and S concentrations were measured by both SIMS and EPMA (Table 3.1; completed EPMA data in *Appendix C*). The results from SIMS and EPMA likely represent different perspectives of apatite compositions, i.e. the SIMS data show average compositions of the analyzed areas (of $\sim 7.5 \times 7.5\ \mu\text{m}^2$ in size) at the core of each crystal, whereas the EPMA data show the “local” compositions (given the small electron beam of $< 1\ \mu\text{m}$ in diameter) at the rim/mantle/core of the analyzed crystals. Below we report the data from both techniques for comparison.

(1) 2006

(2) 2010

Fig. 3.1. BSE images of apatite crystals from the Merapi (1) 2006 and (2) 2010 eruption deposits, that occur in various textural positions (Ap: apatite; Amph: amphibole; Cpx: clinopyroxene; Opx: orthopyroxene; Pl: plagioclase; Gm: groundmass). The inclusions show two types of morphology: anhedral and tiny Type-1 inclusions (“Ap1”), and euhedral-subhedral larger Type-2 inclusions (“Ap2”). Scale bars are 10 μm for the images in panel 1e, 1f and 2f, and 100 μm for the rest.

3.4.1. F, Cl, H₂O in apatite

Apatite crystals from 2006 and 2010 analysed by SIMS show similar ranges of fluorine (F), chlorine (Cl), and H₂O concentrations (F: ~ 1.1-2.2 wt.%; Cl: ~ 0.4-1.2 wt.%; H₂O: ~ 0.5-1.0 wt.%) (Table 3.1). The inclusions in amphibole have about twice amounts of H₂O (~ 0.9-1.0 wt.%) and about half amounts of F (~ 1.1-1.3 wt.%) than the crystals in clinopyroxene, plagioclase, and the groundmass (mean: ~ 0.5 wt.% H₂O, ~ 2.0 wt.% F). Comparison of the SIMS and EPMA data show similar F and Cl contents, but up to 25% difference between H₂O measured using SIMS (H₂O_M) and calculated from EPMA based on apatite stoichiometry (H₂O_{Calc}) (Table 3.1, *Appendix C*). This is likely due to the large uncertainty of H₂O_{Calc} from the stoichiometry calculation, which has included the analytical errors of EPMA, and the (unknown extent of) uncertainty from the assumption of full occupancy of F, Cl and OH at the anion site of apatite, which ignores the possible existence of other components (e.g. O²⁻, vacancy; Piccoli and Candela, 2002). Considering this, we only use the H₂O concentrations from direct measurements of SIMS (H₂O_M) for calculation of melt H₂O contents hereafter.

The weight concentrations of F, Cl, and H₂O (by SIMS) were converted into mole fractions (X_F^{Ap} , X_{Cl}^{Ap} , X_{OH}^{Ap} ; see methods), and shown in the F-Cl-OH ternary diagram (Fig. 3.2). The crystals from 2006 and 2010 lie in similar fields in the ternary diagram, and show a bimodal distribution: those in Amph are OH-rich and F-poorer ($X_{OH}^{Ap} = 55-63\%$, $X_F^{Ap} = 30-38\%$, $X_{Cl}^{Ap} = 7-9\%$), similar to apatite from mafic plutonic rocks (e.g. Boudreau, 1995), whereas the crystals in Cpx/Pl/Gm are poorer in OH and richer in F ($X_{OH}^{Ap} = 26-40\%$, $X_F^{Ap} = 50-60\%$, $X_{Cl}^{Ap} = 12-16\%$), similar to the typical volcanic apatite from the literature (e.g. Peng et al., 1997; Webster, 2009; Van Hoose et al., 2013; Scott

et al., 2015; Stock et al., 2016; Stock et al., 2018). Such different F-Cl-OH compositions observed from crystals at different textural positions are likely caused by crystallisation/growth under different P - T - X conditions (e.g. Stock et al., 2018). Considering the multiple magma storage-crystallization zones at Merapi and the likely stability fields of the host minerals (e.g. Costa et al., 2013, Preece et al., 2014), the OH-rich crystals in Amph likely grew from H₂O-rich melts at greater depths than the OH-poor crystals in Cpx/Pl/Gm, where the calculations for the water contents in the melts are shown in the following sections.

Fig. 3.2. F-Cl-OH ternary diagrams of apatite from 2010 (red solid symbols, $N=29$) and 2006 deposits (open symbols, $N=23$). Mole fractions were calculated using F-Cl-H₂O concentrations from SIMS analyses (error bars of ± 1 s.d.; Table 3.1). Panels *b-e* show compositions of crystals according to their textural positions. The crystals from 2006 and 2010 have similar compositional ranges, and bimodal distribution of F-Cl-OH: the crystals in Amph (*diamonds*) are OH-rich but F- and Cl-poorer, within the range of apatite from mafic plutonic rocks (*pink field*; Boudreau, 1995; Piccoli and Candela, 2002); in contrast to the OH-poor and F-rich crystals in Cpx/Pl/groundmass, which are similar to other volcanic apatite (*grey field*; Boyce and Hervig, 2009; Webster et al., 2009; Scott et al., 2015; Stock et al. 2018), and less enriched in F than felsic plutonic apatite (*green field*; Sha and Chappell, 1999; Zhang et al., 2012).

Table 3.1. Volatile compositions of apatite crystals from Merapi 2006 and 2010 eruption deposits (from SIMS analyses).

Eruption	Textural positions	Label	Concentrations (in wt.%)					Mole fraction			
			CO ₂	H ₂ O	F	Cl	S	X F	X Cl	X OH	
2006	Apatite in Amphibole	061506L_1, Amph5	n.d.	0.90 (4)*	0.94 (3)	0.37 (2)	0.15 (1)	0.309	0.065	0.626	
	Apatite in Clinopyroxene	061406, Cpx3	0.09 (2)	0.52 (5)	1.95 (5)	1.08 (4)	0.06 (2)	0.538	0.160	0.302	
		061406, Cpx1	0.031 (6)	0.52 (5)	1.96 (5)	1.08 (4)	0.05 (2)	0.536	0.159	0.305	
		061406, Cpx_v	0.022 (5)	0.56 (6)	1.83 (5)	1.07 (4)	0.04 (1)	0.511	0.160	0.328	
		061506L_2, Cpx2	0.014 (4)	0.51 (2)	2.06 (5)	1.01 (4)	0.033 (3)	0.561	0.148	0.291	
		061506L_2, Cpx6	0.005 (2)	0.52 (2)	1.83 (5)	0.97 (4)	0.032 (2)	0.532	0.151	0.317	
		061406, Cpx6	0.004 (2)	0.55 (4)	2.00 (4)	1.0 (2)	0.031 (4)	0.541	0.145	0.314	
		061506L_2, Cpx1	0.002 (2)	0.58 (2)	1.92 (3)	0.90 (4)	0.040 (3)	0.531	0.133	0.336	
		061506L_1, Cpx4	n.d.	0.61 (3)	1.94 (6)	0.97 (3)	0.026 (2)	0.517	0.139	0.344	
		061506L_1, Cpx7	n.d.	0.61 (3)	1.94 (6)	0.93 (3)	0.024 (2)	0.522	0.133	0.345	
		061506L_1, Cpx3, Ap3	n.d.	0.59 (3)	1.85 (6)	0.79 (3)	0.026 (2)	0.527	0.120	0.354	
		061506L_1, Cpx3, Ap4	n.d.	0.55 (3)	1.72 (5)	0.92 (4)	0.022 (2)	0.508	0.146	0.346	
2006	Apatite in Groundmass	061506L_1, Cpx3, Ap5	n.d.	0.56 (3)	1.79 (6)	0.92 (4)	0.037 (4)	0.516	0.141	0.342	
		061506L_2, Ox3Ap	0.08 (2)	0.48 (2)	2.13 (5)	0.94 (4)	0.13 (1)	0.585	0.138	0.277	
		061406, GmAp8	0.047 (8)	0.67 (3)	1.55 (3)	1.0 (2)	0.039 (6)	0.443	0.153	0.404	
		061406, GmAp4	0.035 (5)	0.51 (2)	2.30 (4)	1.0 (2)	0.029 (4)	0.587	0.138	0.275	
		061406, GmAp7	0.014 (2)	0.50 (2)	2.25 (4)	1.1 (2)	0.11 (1)	0.578	0.151	0.271	
		061506L_2, GmAp3	0.009 (3)	0.52 (2)	2.08 (6)	0.83 (3)	0.038 (3)	0.576	0.122	0.301	
		061506L_2, Gm_v	0.004 (2)	0.42 (2)	2.29 (4)	0.93 (4)	0.057 (5)	0.623	0.136	0.241	
		061506L_1, GmAp3-2-1	n.d.	0.58 (3)	1.74 (7)	0.96 (4)	0.027 (2)	0.500	0.148	0.352	
		061506L_1, GmAp3-1	n.d.	0.60 (3)	1.84 (6)	1.00 (4)	0.024 (2)	0.505	0.147	0.348	
		061506L_1, Apl	n.d.	0.53 (3)	2.12 (8)	0.88 (4)	0.019 (2)	0.571	0.127	0.302	

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Eruption	Textural positions	Label	Concentrations (in wt.%)					Mole fraction		
			CO ₂	H ₂ O	F	Cl	S	XF	XCl	XOH
2006	Apatite in Groundmass	061506L_1, GmAp5	n.d.	0.46 (3)	2.30 (8)	0.90 (4)	0.027 (4)	0.613	0.128	0.259
2010	Apatite in Amphibole	1011211A, Amph1	1.6 (2)	0.90 (4)	1.37 (2)	0.55 (3)	0.31 (5)	0.384	0.082	0.533
		10111123, Amph4-1 #1 †	0.24 (5)	0.91 (4)	1.17 (2)	0.55 (2)	0.090 (1)	0.345	0.087	0.569
		10111123, Amph4-1 #2 †	n.d.	0.98 (3)	1.24 (4)	0.54 (2)	0.19 (2)	0.346	0.081	0.573
		10111123, Amph4-2	n.d.	0.93 (4)	1.12 (5)	0.41 (2)	0.18 (2)	0.339	0.066	0.595
2010	Apatite in Clinopyroxene	1011211A, Cpx5-1	0.03 (2)	0.59 (2)	1.99 (4)	1.18 (4)	0.041 (6)	0.515	0.163	0.322
		11051903, Cpx8, Ap1	0.017 (3)	0.55 (2)	2.06 (4)	1.05 (4)	0.11 (2)	0.546	0.149	0.305
		11051903, Cpx8, Ap2	0.012 (2)	0.55 (2)	2.07 (4)	1.03 (4)	0.030 (5)	0.549	0.146	0.305
		11051903, Cpx8, Ap3	0.017 (3)	0.55 (2)	2.10 (4)	1.04 (4)	0.037 (5)	0.551	0.146	0.303
		11051903, Cpx6	0.014 (2)	0.55 (3)	1.99 (3)	1.08 (4)	0.029 (4)	0.533	0.154	0.313
		1011211A, Cpx6	0.007 (2)	0.54 (2)	2.22 (4)	1.03 (4)	0.046 (7)	0.566	0.141	0.293
		1011211A, Cpx4	0.006 (2)	0.51 (2)	2.13 (2)	1.11 (4)	0.058 (9)	0.560	0.156	0.284
		1011211A, Cpx5-2	0.005 (2)	0.59 (2)	1.87 (5)	1.08 (4)	0.039 (6)	0.507	0.157	0.337
2010	Apatite in Plagioclase	10111123, Cpx5	n.d.	0.57 (2)	1.79 (6)	0.96 (3)	0.023 (2)	0.509	0.147	0.344
		10111123, Cpx6, Ap2	n.d.	0.57 (2)	2.00 (5)	1.01 (3)	0.028 (2)	0.535	0.144	0.321
		10111123, Cpx6, Ap3	n.d.	0.54 (2)	1.93 (5)	1.01 (3)	0.026 (2)	0.534	0.149	0.317
		1011211A, Pl4	0.017 (5)	0.54 (2)	2.19 (6)	1.12 (4)	0.037 (6)	0.560	0.152	0.288
		10111123, Pl3	n.d.	0.55 (2)	1.84 (6)	0.93 (3)	0.037 (4)	0.527	0.142	0.330
		10111123, Pl1, Ap1	n.d.	0.44 (2)	1.24 (4)	0.75 (2)	0.15 (2)	0.482	0.157	0.361
		10111123, Pl1, Ap2	n.d.	0.53 (2)	1.80 (7)	0.97 (4)	0.18 (2)	0.525	0.151	0.325
		1011211A, GmAp8	0.07 (1)	0.55 (2)	2.09 (4)	1.07 (4)	0.047 (7)	0.548	0.150	0.302

(Continued on next page)

Eruption	Textural positions	Label	Concentrations (in wt.%)					Mole fraction		
			CO ₂	H ₂ O	F	Cl	S	XF	XCl	XOH
	1011211A, GmAp7		0.039 (5)	0.54 (2)	2.12 (4)	1.04 (4)	0.07 (1)	0.556	0.145	0.298
	11051903, GmAp6 #1		0.018 (3)	0.55 (2)	2.07 (4)	1.08 (4)	0.037 (5)	0.544	0.152	0.304
	11051903, GmAp6 #2		0.012 (2)	0.55 (3)	2.05 (4)	1.09 (4)	0.12 (2)	0.542	0.154	0.304
	10111123, GmAp3 #1		n.d.	0.57 (2)	1.97 (6)	1.03 (3)	0.022 (2)	0.528	0.148	0.324
	10111123, GmAp3 #2		n.d.	0.57 (2)	1.95 (6)	1.01 (3)	0.017 (2)	0.527	0.147	0.326
	10111123, GmAp8		n.d.	0.62 (2)	1.98 (6)	0.99 (3)	0.025 (2)	0.520	0.139	0.341
	10111123, GmAp9		n.d.	0.60 (2)	1.96 (5)	1.00 (3)	0.13 (1)	0.523	0.142	0.335
	10111123, GmAp6		n.d.	0.60 (2)	1.90 (6)	0.97 (3)	0.14 (2)	0.516	0.141	0.343

n.d.: not determined.

* Values in parenthesis represent the 2 σ standard deviation of analyses on F, Cl, H₂O and S, and 1 σ standard deviation of CO₂.

† #1 and #2 were measured from the same apatite crystal at different pit locations.

A striking feature of the apatite microlites from 2006 rocks is Cl-rich zones at crystal rims (Fig. 3.3; sample labels as in Table 3.1), which were not observed from the 2010 apatite (Fig. 3.4). The Cl zones in 2006 apatite show distances of $\sim 3\text{-}7\text{ }\mu\text{m}$, and are anisotropic, i.e. appearing only along the elongated direction of the crystal (nearly parallel to the c-axis, //c), but not on other directions. Such anisotropic Cl zoning could be formed by either anisotropic growth, or anisotropic diffusion, or both. If it is caused by anisotropic growth, we would expect the Cl-zoned crystals to show some zonation of trace elements (e.g. REE), however, this is not observed from the cathodoluminescence (CL) images (Fig. 3.3). Therefore, the anisotropic Cl zoning is more likely formed by diffusion, in agreement with the anisotropic Cl diffusion observed from experimental studies, i.e. Cl diffusion parallel to the c-axis of apatite structure is about two orders of magnitudes' faster than parallel to the a-axis (Brenan,1994).

We have observed F zoning from one apatite microlite from 2006 (Fig. 3.3), but did not observe any OH zoning, except some abnormal signals at the cracks or previous EPMA pits shown in the secondary ion maps from SIMS analyses, which are unlikely real and could be related to H migration on the crystal surface during the analyses (Figs. 3.3, 3.4).

Fig. 3.3. Compositional maps of F, Cl, OH and S in the groundmass apatite from Merapi 2006 rocks, shown in X-ray maps (by EPMA) and secondary ion maps (by SIMS) (labels as in Table 3.1). Most crystals show oscillatory S zoning (panels *a*, *c*), and anisotropic Cl zoning at crystal rims (panels *a-c*, higher contents shown as warmer colour), which is only along the elongated directions of the crystals (i.e. nearly parallel to c-axis). One crystal show F zoning (panel *c*). All maps for OH⁻ and some for other volatiles (e.g. Cl, F, S) show locally abnormal signals at the cracks, or the pits of previous EPMA analyses, likely related to ion migration during SIMS analyses due to microtopography on the crystal surface. The cathodoluminescence (CL) image (panel *a*) does not show zoning, but has some artefacts of low signals at the cracks, or along the traverses where compositional profiles were obtained before mapping.

Fig. 3.4. Compositional maps of F, Cl, OH, and S in apatite crystals at various textural positions from Merapi 2010 rocks, shown in X-ray and secondary ion maps (labels as in Table 3.1). Most crystals show oscillatory S zones (panels *b-d*). The S-rich zones sometimes correspond to the low-signal areas in the cathodoluminescence (CL) images that reflect abundances of REEs (panels *a-c*). Only the inclusion in Amph (panel *a*) shows normal zoning of S. None of the crystals from 2010 rocks is zoned of Cl nor F. Some maps from SIMS analyses show locally abnormal signals at the cracks and the pits of previous EPMA analyses, due to the same reason shown in the caption of Fig. 3.3.

3.4.2. CO₂ in apatite

CO₂ concentrations in apatite in Cpx/Pl/groundmass from 2006 and 2010 show similar ranges between 40-900 ppm, although the mean concentrations of 2010 are higher (~400 ppm; $N=14$) than 2006 (~270 ppm; $N=13$) (Table 3.1). The highest CO₂ concentrations (of ~2,400-16,000 ppm) were obtained from two inclusions in Amph from 2010 rocks (Fig. 3.5a). Unfortunately it was not possible to obtain CO₂ data from the apatite inclusions in 2006 Amph, thus we cannot compare their CO₂ concentrations with those of the apatite inclusions in Amph from 2010.

3.4.3. Sulfur in apatite

Sulfur (S) concentrations in apatite in Cpx/Pl/groundmass from 2010 measured by SIMS show large variations between ~170-1750 ppm with a mean value of ~600 ppm, slightly higher than those in the crystals from 2006 (~190-1300 ppm S; Mean: ~420 ppm S) (Table 3.1; Fig. 3.5b). The H₂O- and CO₂-rich inclusions in Amph from 2006 and 2010 are S-rich (2006: ~1510 ppm; 2010: ~900-3120 ppm), showing normal zoning in the X-ray maps from EPMA analyses (Figs. 3.3-3.4). Most crystals show oscillatory zoning with very narrow S-rich bands (< 1-5 μm in width) at crystal mantles or rims. S concentrations of the S-rich bands (~500-1000 ppm) and their surrounding areas ($\leq$ 200 ppm) show large variation by factors of ~3-10.

The incorporation of S into apatite is related to its oxidation state, i.e. S²⁻, S⁴⁺ and S⁶⁺, which is determined by the oxidation conditions of magmas (Kim et al., 2017;

Konecke et al., 2017). Previous studies have shown that at oxygen fugacity (fO_2) $\geq FMQ+1.2$, S^{6+} occupies $> 95\%$ of total S in apatite (Konecke et al., 2017), such that for arc magmas with $fO_2 \geq NNO+1$ (e.g. Luhr, 1990) as concerned in this study, we have considered all S in the Merapi apatite as S^{6+} . The incorporation of S^{6+} into apatite can occur via a variety of exchange reactions for replacing P^{5+} at the tetrahedral site (e.g. Pan and Fleet, 2002). EPMA analyses of apatite investigated in this study show strong positive correlation between S-Na and between S-Si, indicating a dominate substitution mechanism that follows the exchange reaction: $S^{6+} + Na^+ + Si^{4+} + 2Ce^{3+} \Leftrightarrow 3P^{5+} + Ca^{2+}$ (Parat et al., 2011) (*Appendix C*). Based on this reaction, the S-rich crystals are expected to show high Ce, however the opposite was observed, i.e. the single-point analyses from a large number of crystals show negative correlation between S and Ce (Fig. 3.5), and the S-rich zones within some crystals show lower signals in the CL images (reflecting the abundances of REEs) (Fig. 3.4). This means that the substitution of Ce into our apatite is unlikely controlled by S, and may follow more complex mechanisms (e.g. Pan and Fleet, 2002).

Fig. 3.5. Ternary diagrams of (a) C-F-OH and (b) S-F-OH for apatite crystals from the Merapi 2006 and 2010 deposits (Table 3.1). C and S concentrations were multiplied by 10 for ease of comparison. Two crystals in Amph from 2010 (*red diamonds in red dashed-line areas*) are much richer in OH, C and S than the crystals in Cpx/Pl/groundmass. No CO₂ data was obtained from apatite inclusions in Amph or in Pl from 2006 rocks, due to limited numbers of crystals.

3.4.4. Non-volatile elements in apatite

The H₂O-, CO₂- and S-rich apatite inclusions in Amph are much poorer in Ce (Ce₂O₃: 0.01-0.03 wt.%) than the crystals included in anhydrous minerals and in the groundmass (Ce₂O₃: 0.1-0.3 wt.%) (Fig. 3.6; Table 3.1). Such large difference in Ce contents could be related to Ce enrichment in the melts with fractionation (as Ce is incompatible), and/or the changes in the partition behavior of Ce between apatite-melt (i.e. distribution coefficient $D_{Ce}^{Ap-melt}$). Given the increasing $D_{Ce}^{Ap-melt}$ with decreasing T and increasing SiO₂ in the melt (Watson and Green, 1981), apatite crystals in equilibria with more silicic melts and at lower T are likely Ce-richer. Considering this, the Ce-rich crystals in Cpx/Pl/Gm from our samples likely grew from more evolved melts than the Ce-poor crystals in amphibole, which is consistent with the observation of bimodal volatile compositions (of F, H₂O, CO₂) as described above.

Fig. 3.6. Concentrations (in wt.%) of Ce vs. (a) CO₂, (b) H₂O, (c) S, (d) F and (e) Cl in apatite from Merapi 2006 and 2010 rocks (Table 3.1; *Appendix C*; symbols as in Fig. 3.5). CO₂ contents (panel *a*) are shown in log unit. The CO₂-, H₂O- and S-rich apatite crystals in Amph (shown in dashed-line areas) show less Ce than the rest of crystals. H₂O, F, Cl and S contents from SIMS analyses (symbols in red colour) are within the ranges of those by EPMA (apatite in Amph: *black circles*; other crystals: *grey cross*; see data in *Appendix C*). Error bars show ± 2 s.d. of concentrations of H₂O, F, Cl and S, and ± 1 s.d. of the CO₂ concentrations.

3.5. Liquid compositions

The mineral and textural features of the 2010 and 2006 rocks show significant evidence of being the result of open-system processes and crystallization under multiple pressure-temperature and melt compositions (i.e. P - T - X conditions). The existing data for the bulk-rock and glass compositions do not provide enough information of the range of liquids from which apatite grew, which are needed for calculating the melt H_2O - CO_2 concentrations. Below we show a series of calculations for constraining the compositional range of the liquids in equilibria with apatite (Tables 3.2-3.4).

3.5.1. Major/minor elements

The range of SiO_2 concentration of the melts that were involved in the 2006 and 2010 magmas are unknown, but likely vary from ~ 54 - 55 wt.% of bulk rocks (Costa et al., 2013), through ~ 62 - 73 wt.% of the Cpx-hosted MIs (Nadeau et al., 2013; Preece et al., 2014), to ~ 68 - 72 wt.% of the interstitial glass (Table 3.2). The liquid composition of the groundmass (before microlites crystallisation) was calculated using the bulk-rock composition, and the modal abundances and compositions of the phenocrysts (Table 3.2). By subtracting the phenocrysts from the 2010 bulk rocks, we obtain an andesitic groundmass (~ 58 wt.% SiO_2) that falls on the linear trend between the bulk rocks and the interstitial glass in Harker diagrams (Fig. 3.7). Most MIs from the 2006 and 2010 rocks (Nadeau et al., 2013; Preece et al., 2014) are somewhat more evolved than the interstitial glass, and have lower Ti and P but higher Na; whether this is due to post-entrapment crystallisation or the analytical bias is unclear. Besides the major elements, P_2O_5 concentration calculated for the groundmass can have large uncertainties, whose

value is largely dependent on the extent of apatite crystallisation from the melts. Therefore, we did not use P_2O_5 in the groundmass to calculate the apatite saturation temperatures (AST; e.g. Piccoli and Candela, 1994).

Fig. 3.7. Harker diagrams showing compositions (in wt.%) of matrix glass (GL: triangles), melt inclusions (open circles; ³Preece et al., 2014; ⁴Nadeau et al. 2013), and the bulk rocks (WR) from the eruption deposits of 2010 (red solid squares), 2006 (blue open squares) (¹Costa et al, 2013) and historical times (grey open squares; ²Gertisser and Keller, 2003). The groundmass composition of 2010 (*red star*) calculated from mass balance falls on the linear trend between the bulk rock and the matrix glass.

Table 3.2. Representative compositions (in wt.%) of the bulk rock, matrix glass, and minerals from Merapi rocks, and the groundmass composition from mass balance calculation.

	Data source	SiO ₂	TiO ₂	Al ₂ O ₃	FeO*	MnO	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	Total	Modal abundance (in vol.) ‡
2006, Glass (N=5)	This study	71.33	0.52	13.74	2.43	0.10	0.19	0.59	3.57	5.84	0.11	98.4	
2010, Glass (N=3)	This study	67.99	0.56	15.80	3.07	0.12	0.36	1.68	3.73	5.38	0.23	98.9	
2010, Bulk rock	[1]	54.43	0.77	19.10	8.30	0.20	2.56	8.60	3.71	2.02	0.32	100	
Minerals from 2010 rocks													
Pl [†]	[2]	53.93	0.00	28.83	0.51	0.00	0.00	11.35	4.61	0.34	0.00	99.6	25%
Cpx	[3]	51.90	0.36	2.09	8.83	0.64	14.73	20.83	0.35	0.01	0.00	99.7	5.9%
Mgt	[1]	0.10	9.28	2.93	78.01	0.90	2.66	0.00	0.00	0.00	0.00	93.9	2.0%
Opx	[3]	53.87	0.15	0.75	18.40	1.34	24.23	1.45	0.02	0.01	0.00	100.2	0.5%
Amph	[1]	39.46	2.68	12.44	12.89	0.27	12.81	11.60	3.08	0.95	0.00	96.2	0.4%
Ap	This study	0.20	0.00	0.00	0.00	0.00	0.35	54.50	0.08	0.00	41.40	96.5	0.4%
Ol	[1]	37.81	0.00	0.00	25.97	1.16	34.06	0.12	0.00	0.00	0.00	99.1	<0.1%
Biot	[1]	36.99	5.22	14.36	15.24	0.25	14.45	0.00	0.84	8.79	0.00	96.1	<0.1%
Calc, groundmass (2010)		58.28	0.57	18.40	6.90	0.19	2.18	6.39	3.96	2.94	0.20	100	65.6%

*Total Fe as Fe²⁺.

† All the mineral and bulk-rock compositions were normalized to 100% (anhydrous) for calculation of the groundmass.

‡ For calculation of groundmass composition, modal abundances in volume (Costa et al., 2013) were converted into mass, based on the densities of minerals and the bulk rock.

Data sources: [1] Costa et al., 2013; [2] Cheng and Costa, 2019, submitted; [3] Erdmann et al., 2016.

3.5.2. F and Cl

The fluorine (F) concentrations in the 2010 bulk rocks are < 0.01 wt.%, i.e. below the detection limit of the technique we used (see methods above), thus they were excluded from the discussion hereafter. The F contents of the interstitial glass (~ 700 -900 ppm) from 2006 and 2010 rocks are similar, and within the wide range of concentrations from the literature (2010 glass: ~ 180 -2640 ppm; 2006 glass: < 2350 ppm; Preece et al., 2014). The F contents in melt inclusions also vary in a broad range (2010 MI: 140-2390 ppm; 2006 MI: 40-2050 ppm; Preece et al., 2014), and do not show obvious increasing/decreasing trend with melt differentiation (Fig. 3.8b).

The chlorine (Cl) concentrations in the bulk rocks from 2010 are between 500-700 ppm, overlapping with those measured from the ash samples from 2010 eruption (of ~ 550 -1120 ppm; Borisova et al., 2013). The Cl concentrations of the interstitial glass (~ 1500 -1700 ppm) from 2006 and 2010 rocks are similar, and within the range of literature data (2010 glass: 900-3550 ppm, 2006 glass: 1000-2920 ppm; Preece et al., 2014). They are however much lower than those of the melt inclusions (2010 MI: 2060-5130 ppm, 2006 MI: 2330-3720 ppm; Nadeau et al., 2013; Preece et al., 2014), which could be due to Cl degassing at low pressures (e.g. Allard et al., 2010), and/or due to Cl partitioning into some hydro-saline liquids (HSL; Webster et al., 2009). Considering the Cl solubility of > 4500 ppm at ambient pressure calculated using the model from Webster et al. (2015), the latter process is more likely. Nadeau et al. (2013) proposed a model of possible brine-vapor exsolution at ~ 5 km depths, in agreement with the hydrothermal system at ≥ 2 km depths constrained by electrical resistivity tomography study (Byrdina et al., 2016). Considering that Cl has outgassed from our rocks, we

cannot use the measured Cl contents of the matrix glass nor the bulk rocks for any calculation. Alternatively, we have taken the mean Cl (and F) concentrations of the dacitic-rhyolitic MIs ($\text{SiO}_2: \geq 67 \text{ wt.}\%$) reported by Preece et al. (2014) as the representatives of the halogen contents of the differentiated melts, i.e. 3050 ppm Cl and 900 ppm F (Table 3.4). With these values we calculated the halogen concentrations of the less differentiated melts (C_i^o), using a *Rayleigh* fractionation model (e.g. Philpotts and Ague, 2009):

$$C_i^l = C_i^o \cdot \varphi^{\bar{D}_i - 1} \quad (5)$$

where C_i^l is the concentration of i ($i = \text{F, Cl}$) of the residual liquid, φ is the mass fraction of the residual liquid, and $\bar{D}_i$ is the bulk distribution coefficient of i defined as:

$$\bar{D}_i = \sum D_i^{c/m} \cdot w_i^c \quad (6)$$

where $D_i^{c/m}$ is the crystal-melt distribution coefficient of i , and w_i^c is the modal abundance of each mineral normalized to the total abundances of crystals.

Based on the mean Cl and F contents in the dacitic-rhyolitic MIs, i.e. $C_{Cl}^l = 3050 \text{ ppm}$, and $C_F^l = 900 \text{ ppm}$, and using $D_i^{c/m}$ reported in literature (Table 3.3) and the modal abundances of minerals in 2010 rocks (Costa et al., 2013; Table 3.4), we obtained $\bar{D}_F \cong 0.38$ and $\bar{D}_{Cl} \cong 0.05$. Then we calculated the fractionation of the residual liquid (φ) using the K_2O concentration (Table 3.4), assuming that potassium is perfectly incompatible ($\bar{D}_K \approx 0$). Given that biotite is very rare in our samples (e.g. volume

abundance: $< 0.1\%$), it should not bring much change to the K concentrations calculated for the melt. The φ values calculated for the glass and the groundmass are $\sim 0.38 (\pm 0.02)$, and $0.69 (\pm 0.02)$ respectively. The difference in φ between the glass and groundmass (of ~ 0.3) reflects the proportion of microlite crystallization, which matches with the total abundances of microlites observed from the 2010 rocks (Preece et al., 2016).

We find that the hypothetically crystal-free basaltic-andesite melt could have $1200 (\pm 250)$ ppm Cl, and $500 (\pm 200)$ ppm F (mole Cl/F: 1.3 ± 0.2), whereas the andesitic groundmass could have $1700 (\pm 350)$ ppm Cl, and $620 (\pm 270)$ ppm F (mole Cl/F: 1.5 ± 0.3) (Table 3.4; Fig 3.8). The increase in Cl/F in the melt with differentiation is due to that Cl is less compatible than F (i.e. $\bar{D}_{Cl} < \bar{D}_F$; Table 3.4). The range of Cl/F calculated using the fractionation model above is consistent with that calculated using apatite compositions, which can be used to test the equilibrium between apatite and the melt (Section 3.7).

Table 3.3. Distribution coefficients of F and Cl for crystal-melt from literature.

Mineral	w [†]	$D_F^{c/m}$	$D_{Cl}^{c/m}$	$D_{Cl}^{c/m} / D_F^{c/m}$ [‡]	Data sources
Pl	0.774	0.098	0.0014	0.014	[1]
Cpx	0.183	0.114	0.011	0.096	[2]
Opx	0.015	0.056	0.02	0.357	[2]
Amph	0.012	0.635	0.378	0.595	[2]
Ol	0.003	0.0026	0.0003	0.115	[3]
Ap*	0.012	22	3.3	0.150	[4]

*Distribution coefficients of apatite-melt estimated using halogens content of the melt and the crystals in Cpx/Pl/Gm.

[†] modal abundances of each mineral normalized to that of the total crystals.

[‡] The ratios of $D_{Cl}^{c/m}$ and $D_F^{c/m}$ show values of <1.

Data sources: [1] Dalou et al., 2012; [2] Dalou et al., 2014; [3] Hauri et al., 2006; [4] This study.

Table 3.4. Halogen concentrations in the melts, calculated using the Rayleigh fractionation model, and bulk distribution coefficients of $\bar{D}_F=0.382$, and $\bar{D}_{Cl}=0.050$ (calculated using Eq. 6 and literature data in Table 3.3).

Liquid	K ₂ O (wt.%)	φ * (calc)	F (ppm)	Cl (ppm)	mole Cl/F
Differentiated liquid [†]	5.38 (±0.21) [§]	0.36-0.40	900 (±400)	3050 (±620)	1.8 (±0.3)
Bulk rock (initial liquid)	2.04 (±0.02)	1	500 (±200)	1200 (±250)	1.3 (±0.2)
Groundmass	2.7-3.1 [¶]	0.66-0.72	620 (±270)	1700 (±350)	1.5 (±0.3)
A liquid of 62 wt.% SiO ₂ [‡]	3.6-4.0 [¶]	0.43-0.47	800 (±360)	2600 (±500)	1.7 (±0.3)

* Fraction of differentiated liquid (φ) calculated using Rayleigh fractionation model (Eq. 5) and K₂O concentrations in liquid, assuming $\varphi=1$ for bulk rock.

[§] Values in bold are from measurements; the rest calculated using the fractionation model.

[†] K₂O concentration measured from the glass; F and Cl taken from the mean concentrations of the dacitic-rhyolitic melt inclusions from 2010 (Preece et al., 2014).

[‡] The most primitive melt inclusion from 2010 rocks reported by Preece et al. (2014).

[¶] Concentration calculated assuming linear correlation between K₂O and SiO₂ with melt evolution (Table 3.2).

Fig. 3.8. Halogen contents in the melts with evolution: (a) chlorine, (b) fluorine, and (c) mole Cl/F (Table 3.4). The matrix glass (2010: *solid triangles*; 2006: *empty triangles*) shows lower Cl and F contents than most melt inclusions (2010: *red circles*; 2006: *blue circles*; Nadeau et al., 2013; Preece et al., 2014), likely due to Cl exsolution at late melt evolution stage. Mean F and Cl contents of MIs from 2010 (*circles in grey colour*) were used to calculate halogen contents in more primitive liquids, i.e. the phenocryst-free primitive melt (“PM”, *squares in grey colour*) and the groundmass (“GM”, *stars in grey colour*), using the Rayleigh fractionation model (see Section 3.5). Mole Cl/F in the melts (panel *c*) increase with differentiation, as Cl is less compatible than F.

3.6. Temperatures calculated using amphibole thermometry

To calculate the exchange coefficients $K_{D_{OH-x}}^{Ap-melt}$ (Eqs. 1-2) for melt H₂O and CO₂ estimates, we need to know the temperature of apatite-melt equilibrium. This is difficult to determine only from the apatite chemistry, given that the calculation of apatite saturation temperature (AST; e.g. Piccoli and Candela, 1994) strongly depends on the SiO₂ and P₂O₅ concentrations in melts that were in equilibria with apatite, i.e. $AST = \frac{26400 \cdot C_{SiO_2}^l - 4800}{12.4 \cdot C_{SiO_2}^l - \ln(C_{P_2O_5}^l) - 3.97}$, where $C_{SiO_2}^l$ and $C_{P_2O_5}^l$ are the weight fractions of SiO₂ and P₂O₅ in the melt at the temperature at which apatite started to crystallize. The values of $C_{SiO_2}^l$ and $C_{P_2O_5}^l$ are rarely known, and they can vary significantly with apatite crystallization and growth (see Section 3.7), and thus would bring large uncertainties to the calculated ASTs. Hence, to obtain T estimates for the calculation of $K_{D_{OH-x}}^{Ap-melt}$, we have referred to the Ts constrained by the minerals that host apatite inclusions, such as amphibole as described below.

Amphibole has been widely used for constraining the magmatic temperatures and pressures (e.g. Hammarstrom and Zen 1986; Hollister et al. 1987; Johnson and Rutherford 1989; Blundy and Holland 1990; Schmidt 1992; Holland and Blundy 1994; Anderson and Smith 1995; Anderson 1996; Ridolfi et al. 2010; Ridolfi and Renzulli, 2012; Putirka, 2016). Here we have used the amphibole-liquid thermometer of Putirka (2016) and the amphibole-only thermometer of Ridolfi and Renzulli (2012) for T estimates, and only used the same amphibole-liquid thermometer for P estimates, considering that it likely gives more reliable results than the amphibole-only method. To apply the amphibole-liquid thermometer, we need to know the composition of the

melt in equilibria with amphibole. Putirka (2016) has proposed an equilibrium test, i.e. $K_{D_{Fe-Mg}}^{Amph-melt} = 0.27 \pm 0.11$, which however appears to be an ambiguous test, given its large variation of ~ 0.16 - 0.38 (considering error). To improve the constraints on the liquids in equilibria with amphibole, we have used the Al-Si partitioning between amphibole-melt ($K_{D_{Al-Si}}^{Amph-melt}$; see methods) to test the equilibrium (Sisson and Grove, 1993). We have performed a least-squares regression for the data from Sisson and Grove (1993), combined with those from more recent experiments (Scaillet and Evans, 1999; Pichavant et al., 2002; Grove et al., 2003; Rutherford and Devine, 2003; Costa et al., 2004; Sato et al., 2005). The regression results show $K_{D_{Al-Si}}^{Amph-melt} = 0.96 (\pm 0.04)$, which is independent on P, T and the melt composition (*Appendix D*).

The amphiboles from our rocks that have mole Al/Si of ~ 0.34 - 0.41 (Table 3.5). Using $K_{D_{Al-Si}}^{Amph-melt} = 0.96 (\pm 0.04)$, they should be in equilibria with the melts that have mole Al/Si of ~ 0.36 - 0.43 . Considering the linear correlation between SiO₂ and mole Al/Si (Fig. 3.9), the melts in equilibria with amphibole should have ~ 54 - $60 (\pm 2)$ wt.% SiO₂, i.e. between the basaltic-andesitic bulk rock and the andesitic groundmass, and more mafic than the Cpx-hosted MIs (Nadeau et al., 2013; Preece et al., 2014).

Fig. 3.9. (a) Mole Al/Si measured from amphibole and calculated for the melt, based on $K_D^{Amp-melt} = 0.96$ (i.e. the slope of the dashed line), and (b) SiO₂ contents and the mole Al/Si of the bulk rocks (*squares*), the matrix glass (*triangles*), and the calculated groundmass (*star*). The melts that equilibrated with amphibole have mole Al/Si of ~ 0.36 - 0.43 , which corresponds to SiO₂ of ~ 54 - 60 (± 2) wt.%, calculated using the equation in panel *b* (assuming linear correlation between SiO₂ and mole Al/Si of the melt; *Appendix D*). These melts in equilibria with amphibole are more mafic than melt inclusions from Merapi 2006 and 2010 rocks. Data sources as in Fig. 3.7.

Using the amphibole-liquid pairs constrained above and the recommended formulations of Putirka (2016) (i.e. Eqs. 7a, 7b), we obtained $T \approx 950\text{-}1000\text{ }^{\circ}\text{C}$ for the 2010 amphiboles, and $T \approx 960\text{-}980\text{ }^{\circ}\text{C}$ for 2006 (Table 3.5). The calculation of Putirka (2016) requires an input value of H_2O in liquids, the input values have very small effects on the calculated temperatures, e.g. using 6 wt.% H_2O for calculation would give only $\sim 3\text{ }^{\circ}\text{C}$ higher T than our results calculated from 5 wt.% H_2O . The T estimates above are equivalent within error with those calculated using the amphibole-only thermometry of Ridolfi and Renzulli (2012), i.e. $T \approx 950\text{-}1020\text{ }^{\circ}\text{C}$ (Table 3.5). Given the difficulty of deciding which of the two thermometers gives more accurate results, we take the mean values yielded by the two methods as the temperature, along with the volatile compositions of the apatite crystals in amphibole, to calculate $K_D^{Ap-melt}_{OH-x}$ (see Section 3.7.1).

Table 3.5. Representative compositions of amphibole from Merapi 2006 and 2010 rocks, and the calculated temperatures and pressures.

and the calculated temperatures and pressures.						
Eruption deposits	2010				2006	
Sample Label	1011123, Amph4		1011211A, Amph1		061506L_1, Amph5	
(EPMA, wt.%)	Max [§]	Min [§]	Max	Min	Max	Min
SiO ₂	40.79	40.23	38.86	38.60	40.40	40.55
TiO ₂	2.42	2.22	2.68	2.66	2.58	2.53
Al ₂ O ₃	11.90	13.13	12.73	12.95	12.00	12.08
FeO *	12.95	13.45	12.69	12.87	10.98	10.95
MnO	0.23	0.22	0.25	0.26	0.22	0.25
MgO	12.65	12.8	12.82	12.63	13.41	13.02
CaO	11.75	11.62	11.63	11.80	11.43	11.32
Na ₂ O	2.35	2.37	3.41	3.39	2.28	2.35
K ₂ O	1.03	1.02	0.84	0.92	0.95	0.96
F	0.19	0.06	0.13	0.15	0.02	0.10
Cl	0.04	0.01	0.03	0.03	0.02	0.03
Calc H ₂ O [✧]	1.77	1.85	1.79	1.78	1.84	1.79
Sum (hydrous)	98.07	98.98	97.85	98.05	96.14	95.93
Mg#	64	63	64	64	69	68
Mole Al/Si	0.34	0.38	0.39	0.39	0.35	0.35
Mole OH/Cl	179	562	241	233	362	272
Results of amphibole-liquid thermobarometry of Putirka (2016)						
SiO ₂ in melt (wt. %) [†]	60	56	55	54	59	59
K _D (Fe-Mg) [‡]	0.31	0.33	0.31	0.31	0.26	0.26
T (°C), using Eq. 4a [based on D(Na)]	953	963	1001	1004	962	965
T (°C), using Eq. 4b [based on D(Ti)]	954	965	977	976	981	980
P (MPa), using Eq. 7a	580	720	840	850	560	590
P (MPa), using Eq. 7b	366	462	470	466	380	390
Results of the amphibole-only thermobarometry from R&R (2012)						
T, using Eq. 2 (°C)	945	957	1013	1012	963	961
P, using Eq1b (MPa)	340	439	418	432	391	403
P, using Eq1c (MPa)	408	484	493	505	444	449
Mean values and variation of P-T estimates						
T (°C)	959 (± 6)		990 (± 15)		972 (± 10)	
P (MPa)	530 (± 150)		660 (± 220)		480 (± 110)	
OH-Cl partition between Amph-melt (Eq. from Humphreys et al., 2006)						
K _D (Cl-OH)	0.281	0.290	0.220	0.224	0.240	0.244
Melt OH/Cl	50	163	53	52	87	67

[§] Min & Max refer to SiO₂ concentrations in the melts in equilibria with amphibole.

* Total Fe as Fe²⁺. * Calculated based on stoichiometry, following Ridolfi et al (2010).

† Liquid composition determined based on K_D(Al-Si) = 0.96. The calculated SiO₂ in the melt has relative error of ~ 4%.

‡ K_D(Fe-Mg) = 0.28 ± 0.11, when amphibole and the liquid are in equilibrium (Putirka, 2016).

3.7. Parameter values used for estimating melt water contents

In the previous sections, we have shown the ranges of parameter values required for calculating the exchange coefficients $K_{D_{OH-x}}^{Ap-melt}$ (Eqs. 1-2) and the melt water contents, i.e. apatite compositions (from SIMS analyses), halogen concentrations in the melts, and temperature. Given that apatite included in amphibole and those in clinopyroxene, plagioclase, and groundmass show different volatiles and Ce concentrations, they likely grew from different P - T - X conditions. Thus, the calculations for the two groups of apatite crystals require the melt halogen contents and temperatures to be determined correspondingly, as is discussed in detail below. Errors in the parameter values used for calculation were translated to those of the $K_{D_{OH-x}}^{Ap-melt}$ and the melt H₂O-CO₂ estimates, shown at the end of this section.

3.7.1. Parameter values for apatite in amphibole

From calculation of the amphibole-liquid thermometer (see Section 3.6 above), we have found that the core of the 2006 amphibole equilibrated with a melt similar to the groundmass (of ~59 (±2) wt.% SiO₂) at $T = 972 (\pm 10) ^\circ\text{C}$, whereas the cores of the 2010 amphiboles indicate a wider T range between $959 (\pm 6)$ and $990 (\pm 15) ^\circ\text{C}$, and the melt compositions similar to either the bulk rock or the groundmass, i.e. of 54 to 60 (± 2) wt.% SiO₂ (Table 3.5). The halogen concentrations of the melts in equilibria with amphibole were calculated using the *Rayleigh* fractionation model described above (Section 3.5.2; Table 3.4). Eventually we have used $T \approx 959$ - $990 ^\circ\text{C}$, ~500-620 ppm F and ~1200-1700 ppm Cl in the calculation for apatite in amphibole (Table 3.6).

3.7.2. Parameter values for apatite in Cpx, Pl, and the groundmass

The melt halogen concentrations used in the calculation for apatite in Cpx can be inferred from those measured from the glass inclusions in Cpx (Nadeau et al., 2013; Preece et al., 2014), whereas the temperature can be estimated from the crystallization temperature of Cpx (Costa et al., 2013). We have shown that the 2010 groundmass is more mafic (SiO_2 : ~ 58 wt.%) than the MIs (SiO_2 : 62-73 wt.%), indicating that the MIs in Cpx might be entrapped at rather late evolution stage, and/or have some extents of post-entrapment crystallization, as was observed from their textures (Costa et al., 2013). Considering this, we have taken the most primitive Cpx-hosted MI in literature (of ~ 62 wt.% SiO_2) as the representative liquids in equilibria with apatite in Cpx. Based on the linear trends between the bulk rock and the matrix glass shown in Harker diagrams (Fig. 3.7), a liquid with ~ 62 wt.% SiO_2 should have ~ 3.6-4.0 wt.% K_2O , using which and the Rayleigh fractionation model (Section 3.5.2) yield melt halogen concentrations of about 800 (± 360) ppm F, and 2600 (± 500) ppm Cl (Table 3.4). Considering that the low-Al Cpx phenocrysts that host apatite likely crystallized at ~ 1000 °C from MELTS modelling (Costa et al., 2013), we have taken $T \approx 1000$ °C in the calculation for apatite in Cpx (Table 3.6). The crystallization T of Cpx used here might be larger than the T of apatite-melt equilibria, which might lead to some extent of over-estimated $K_{D_{OH-x}}^{Ap-melt}$ (due to positive correlation of $T-K_{D_{OH-x}}^{Ap-melt}$), and thus under-estimated water contents in the melt.

The plagioclase phenocrysts in equilibrium with Amph (at ~ 950-1000 °C) have An values of > 60 (Costa et al., 2013), implying that the plagioclase phenocrysts with An values of < 60 that contain apatite inclusions likely grew from cooler and more evolved

melts, where the phase equilibrium experiments on Merapi 2010 rocks suggest temperatures of 925-950 (± 25) °C and melt compositions of dacitic-rhyolite (Erdmann et al., 2016). Considering this, in the calculation for apatite in Pl we have taken $T \approx 950$ °C, and the mean F and Cl concentrations in the dacitic-rhyolitic MIs, i.e. 900 (± 400) ppm F, and 3050 (± 620) ppm Cl.

The groundmass apatite shows basically the same compositions of F-Cl-OH and Ce as the apatite inclusions in Pl, thus they likely grew from the melts under similar conditions. Using the equation for apatite saturation temperature (AST) from Piccoli and Candela (1994) (see above) and the compositions measured for the matrix glass of 2010, we found $AST \approx 945$ °C for the groundmass apatite. Considering this, in the calculation for the groundmass apatite, we have used $T \approx 945$ °C, and the melt F-Cl concentrations same as those used for calculation of apatite in Pl as shown above (Table 3.6).

3.7.3. Error propagation

To constrain the uncertainties of the melt H₂O and CO₂ estimates following Li and Costa (2020), we have considered the errors of parameter values used in our calculation: i.e. the analytical errors of apatite compositions (from SIMS), the uncertainties of the calculated temperatures, and Cl (or F) concentrations in the melts, and the uncertainties of the formulations for $K_{D_{OH-Cl}}^{Ap-melt}$ (or $K_{D_{OH-F}}^{Ap-melt}$). Given the smaller uncertainties of $K_{D_{OH-Cl}}^{Ap-melt}$ (relative error: ~30-40 %) than $K_{D_{OH-F}}^{Ap-melt}$ (relative error: ~40-50%), as well as the smaller uncertainties in the estimated Cl contents in the melt than F, the “Cl approach” that we mainly rely on in this study (i.e. based on $K_{D_{OH-Cl}}^{Ap-melt}$ and Cl contents

in the melt) propagates less error to the melt H₂O estimates, than the “F approach” (i.e. using $K_D^{Ap-melt}_{OH-F}$ and F contents in the melt). The melt H₂O contents calculated using the “Cl approach” have relative error of ~ 36-45%. Considering the additional uncertainty from $K_D^{Ap-melt}_{H_2O-CO_2}$ (relative error: ~13%; Riker et al., 2018), the melt CO₂ estimates have relative error of ~ 40-50% (Table 3.6).

3.8. Results

3.8.1. Calculated exchange coefficients, and OH/Cl and OH/F in the melt

The values of the partitioning relations for the apatite crystals included amphibole from the two deposits are $K_D^{Ap-melt}_{OH-Cl} = 0.08-0.11$, and $K_D^{Ap-melt}_{OH-F} = 0.015-0.020$, which overlap with those calculated from apatite in Cpx/Pl/groundmass ($K_D^{Ap-melt}_{OH-Cl} = 0.08-0.11$, $K_D^{Ap-melt}_{OH-F} = 0.010-0.017$) (Table 3.6). With these values and the apatite compositions, we find that the melts in equilibria with apatite in Amph have $\frac{x_{OH}^{melt}}{x_{Cl}^{melt}}$ of ~ 62-111, $\frac{x_{OH}^{melt}}{x_F^{melt}}$ of ~ 71-121, and $\frac{x_{Cl}^{melt}}{x_F^{melt}}$ of ~ 1.1-1.4. In contrast, the melts in equilibria with apatite crystals in Cpx/Pl/groundmass have lower $\frac{x_{OH}^{melt}}{x_{Cl}^{melt}}$ (of ~ 17-30) and $\frac{x_{OH}^{melt}}{x_F^{melt}}$ (of ~ 33-71), but higher $\frac{x_{Cl}^{melt}}{x_F^{melt}}$ (~ 1.5-2.1) (Table 3.6; Fig. 3.10). Using mole Cl/F values calculated from apatite and those obtained from the Rayleigh fractionation model (Table 3.4), we find the melts that equilibrated with apatite in Amph as andesitic, whereas the

melts in equilibria with apatite in Cpx/Pl/Gm are more similar to the interstitial glass (Table 3.4).

Comparison of $\frac{x_{OH}^{melt}}{x_{Cl}^{melt}}$ calculated from apatite with those estimated using OH-Cl compositions of the amphibole hosts also show overlapping ranges. Taking the equation for calculating $K_D^{Amph-melt}$ from Humphreys et al., (2009) (see Eq. 4 in methods), $K_D^{Amph-melt}$ values calculated using amphibole from the 2006 and 2010 rocks lie in similar ranges between ~ 0.22 - 0.29 , which give OH/Cl in the melt between ~ 50 - 163 (Table 3.5; large variation due to varied Cl contents in Amph), which include those calculated from apatite inclusions in amphibole ($\frac{x_{OH}^{melt}}{x_{Cl}^{melt}}$ of ~ 63 - 109) (Fig. 3.10). The good agreements of results from multiple methods above further validates our choice of parameter values (e.g. T and melt halogen contents) for calculating the melt water contents below.

Fig. 3.10. Mole OH/Cl and OH/F of the melt calculated using apatite. The melts in equilibria with apatite in Amph show higher values than those in equilibria with crystals in Cpx/Pl/Gm (Table 3.6). Melt OH/Cl calculated from apatite in Amph overlap with those calculated from their host Amph crystals (ranges on the top; Table 3.5). The slope equals to mole Cl/F in the melt. Error bars show ± 2 s.d. for the calculated mole OH/F and OH/Cl in the melt.

3.8.2. Calculated H₂O and CO₂ concentrations in the melt

The melt H₂O contents can be calculated using either the “Cl approach” (based on $K_{D_{OH-Cl}}^{Ap-melt}$ and Cl contents in the melt), or the “F approach” (based on $K_{D_{OH-F}}^{Ap-melt}$ and F contents in the melt (Li and Costa, 2020). Here we have taken the “Cl approach”, as it propagates less error to the melt H₂O estimates (Section 3.7.3). With the calculated melt water contents, we have calculated the melt CO₂ concentrations, using the CO₂-H₂O concentrations in apatite, and $K_{D_{H_2O-CO_2}}^{Ap-melt} = 0.629 \pm 0.08$ determined from experiments (Riker et al., 2018; Section 3.2).

We find that the melts of 2006 and 2010 in equilibria with apatite in Cpx/Pl/Gm show similar abundances of H₂O and CO₂, i.e. about 1.4 (± 0.7) to 3 (± 1) wt.% H₂O, and ~ 50-2100 ppm CO₂ (Fig. 3.11; Table 3.6), within the range of those measured from MIs (of ~ 0.2-4 wt.% H₂O, ~ 10-3000 ppm CO₂; Preece et al., 2014). The melts in equilibria with apatite in amphibole from 2010 have higher abundances of H₂O (between 3 ± 1 and 10 ± 4 wt.%) and CO₂ (~ 1-3 wt.%). Using the H₂O-CO₂ solubility model of Papale et al. (2006), we find that the volatile saturation pressures for the shallow melts of 2010 and 2006 are respectively about 20-400 MPa and 20-360 MPa (most at ~ 40-100 MPa), whereas the volatile saturation pressures for the deeper 2010 melts are > 800 MPa (Fig. 3.11). The higher range of pressures are higher than those reflected by the amphibole from the two eruptions, i.e. 480-660 MPa (± 100 to 200 MPa) (Table 3.5), and are discussed below (Section 3.9.1).

Fig. 3.11. Melt H₂O and CO₂ concentrations calculated using apatite from Merapi 2006 and 2010 deposits (panel *b* as zoomed-in view of the grey field in panel *a*). Symbols as in Fig. 3.10. The melts in equilibria with apatite in Amph (Ap-Amph in panel *a*) show much higher CO₂ contents than the melts in equilibria with other apatite crystals, where these lower values show overlap range with melt inclusion data (empty circles; Preece et al. 2014). Isobars and isopleths (of given mole fraction of CO₂ in fluids) were calculated using the H₂O-CO₂ solubility model from Papale et al. (2006). Decompression paths were modelled using initial volatile compositions of the two CO₂-richest melts calculated from apatite in Amph (#1, #2), showing the trends of closed-system (solid line) and open-system (dashed line) degassing. Error bars show ± 2 s.d. of calculated H₂O and CO₂ concentrations in the melts (Table 3.6).

3.8.3. Calculated S concentration in the melt

The sulfur concentrations in the melt (c_S^{melt}) were calculated using S in apatite (c_S^{Ap}), and the distribution coefficient defined as $D_S^{Ap-melt} = \frac{c_S^{Ap}}{c_S^{melt}}$. The values of $D_S^{Ap-melt}$ depend on temperature, and S concentration in the melt and apatite (Peng et al., 1997; Parat and Holtz, 2004, 2005). Given the large variation of S contents in our apatite (of ~ 200 -3000 ppm), we have used different $D_S^{Ap-melt}$ values in the calculation for the S-rich and S-poor crystals.

For the S-rich crystals in amphibole (of > 1500 ppm S) which likely grew from the S-rich mafic melts, we take the T - $D_S^{Ap-melt}$ relation from Peng et al. (1997) for trachyandesitic melts, i.e. $\ln D_S^{Ap-melt} = \frac{21130}{T} - 16.2$ (T in kelvin). Using $T \approx 950$ -1000 °C from amphibole thermometry calculation (Table 3.5), we find $D_S^{Ap-melt} \approx 2$ -3, using which the melts in equilibria with apatite in Amph from 2006 and 2010 should have about 670 (± 100) ppm S, and 340 (± 40) to 2000 (± 300) ppm S, respectively (considering analytical error of S contents in apatite). It is worth noting that the highest S content in the 2010 melt (of ~ 2000 ppm) was calculated using the S-richest apatite inclusion in amphibole, which contains the highest CO₂ and reflects ~ 3 wt.% CO₂ in the melts at depths near Moho (see above; Table 3.6).

For the crystals in Cpx/Pl/Gm that are S-poorer (of < 1500 ppm) and likely grew from S-poorer and more felsic melts, we have calculated $D_S^{Ap-melt}$ using an empirical equation for rhyolitic melts (Parat and Holtz, 2005), i.e. $\ln(D_S^{Ap-melt}) = -0.0025 \times c_S^{melt} \text{ (in ppm)} + 2.9178$. Considering the definition of $D_S^{Ap-melt} (= \frac{c_S^{Ap}}{c_S^{melt}})$, both sides

of this equation involve the unknown parameter c_S^{melt} . To solve this equation, we combined it with $D_S^{Ap-melt} = \frac{c_S^{Ap}}{c_S^{melt}}$, and obtained the equation below

$$c_S^{Ap} (in ppm) = \exp(-0.0025 \times c_S^{melt} + 2.9178) * c_S^{melt} \quad (7)$$

using which we can obtain c_S^{melt} , based on c_S^{Ap} from SIMS analyses and inputting different guessed values of c_S^{melt} till the left- and right-hand sides of Eq. 7 equal to each other. We find that the melts in equilibria with apatite in Cpx/Pl/Gm from 2006 and 2010 have similar S concentrations of about 10-130 ppm (relative error: 7-16%; $D_S^{Ap-melt} \approx 12-18$) (Table 3.6), within the range of those measured from MIs (of $\sim 5-760$ ppm; Costa et al., 2013; Nadeau et al., 2013; Preece et al., 2014). We have noticed that there is a large range of melt H₂O/S values calculated from apatite in Amph (Fig. 3.12), and it is unclear what process(es) should be responsible for such a range.

Fig. 3.12. H₂O and S concentrations (in wt.%) in the melts of 2006 and 2010, calculated using apatite (symbols as in Fig. 3.10), with comparison to the melt inclusion data (*empty circles*; Preece et al. 2014). The melts in equilibria apatite in Amph (diamonds) show higher H₂O and S concentrations than the melts in equilibria with apatite in Cpx/Pl/Gm, and most melt inclusions. Error bars show the representative error (±1 s.d.) of the calculated melt H₂O and S contents (the error for S covered by symbols; Table 3.6).

Table 3.6. Calculated H₂O, CO₂ and S concentrations in Merapi 2006 and 2010 melts (error: ± 2 s.d. for melt H₂O, and ± 1 s.d. for melt CO₂).

Textural position*	T	F in melt	Cl in melt	$K_{D_{OH-Cl}}^{Ap-melt}$	$K_{D_{OH-F}}^{Ap-melt}$	mole OH/Cl in melt	mole OH/F in melt	mole Cl/F in melt	Calc melt H ₂ O	$\pm$	Calc melt CO ₂	$\pm$	Calc melt S [†]
	°C	ppm	ppm						wt. %	wt. %	ppm	ppm	ppm
2006 Ap in Amph	972	620	1700	0.087	0.017	111	121	1.1	9.79	3.62	n.d.	n.d.	665
2006 Ap in Cpx	1000	800	2600	0.103	0.016	18	34	1.9	1.43	0.60	1522	667	37
	1000	800	2600	0.103	0.016	19	35	1.9	1.45	0.61	531	233	31
	1000	800	2600	0.102	0.017	20	38	1.9	1.59	0.65	391	169	22
	1000	800	2600	0.105	0.016	19	33	1.8	1.46	0.62	264	117	19
	1000	800	2600	0.104	0.016	20	36	1.8	1.61	0.67	95	41	18
	1000	800	2600	0.105	0.016	21	36	1.7	1.65	0.69	79	35	18
	1000	800	2600	0.105	0.016	24	39	1.6	1.96	0.82	51	22	23
	1000	800	2600	0.104	0.017	24	40	1.7	1.94	0.80	n.d.	n.d.	14
	1000	800	2600	0.105	0.016	25	40	1.6	2.03	0.84	n.d.	n.d.	13
	1000	800	2600	0.107	0.016	28	41	1.5	2.35	0.98	n.d.	n.d.	15
	1000	800	2600	0.103	0.017	23	40	1.8	1.87	0.77	n.d.	n.d.	12
	1000	800	2600	0.104	0.017	23	40	1.7	1.90	0.78	n.d.	n.d.	21
	1000	800	2600	0.107	0.015	19	31	1.7	1.47	0.64	1476	667	87
2006 Ap in Gm	945	900	3050	0.077	0.013	34	71	2.1	3.92	1.58	1729	729	22
	945	900	3050	0.083	0.010	24	45	1.8	2.46	1.10	1047	485	16
	945	900	3050	0.081	0.011	22	44	2.0	2.20	0.97	377	173	74

(continued on next page)

Textural position*	T	F in melt	Cl in melt	$K_{D_{OH-Cl}}^{Ap-melt}$	$K_{D_{OH-F}}^{Ap-melt}$	mole OH/Cl in melt	mole OH/F in melt	mole Cl/F in melt	Calc melt H ₂ O wt. %	±	Calc melt CO ₂ ppm	±	Calc melt S ^{II} ppm
	°C	ppm	ppm						wt. %	wt. %	ppm	ppm	ppm
2006	Ap in Gm	945	900	3050	0.084	0.011	29	49	1.7	3.19	1.41	351	161
		945	900	3050	0.084	0.010	21	39	1.8	2.08	0.95	119	56
		945	900	3050	0.079	0.012	30	59	2.0	3.27	1.37	n.d.	n.d.
		945	900	3050	0.079	0.012	30	58	2.0	3.24	1.36	n.d.	n.d.
		945	900	3050	0.083	0.011	29	49	1.7	3.06	1.35	n.d.	n.d.
		945	900	3050	0.084	0.010	24	42	1.8	2.43	1.10	n.d.	n.d.
2010	Ap in Amph	990	500	1200	0.105	0.020	62	71	1.2	2.43	0.92	27,179	10,885
		959	620	1700	0.082	0.015	80	109	1.4	5.71	2.16	9515	3795
		959	620	1700	0.083	0.015	86	110	1.3	6.39	2.42	n.d.	n.d.
		959	620	1700	0.084	0.015	108	116	1.1	9.36	3.54	n.d.	n.d.
2010	Ap in Cpx	1000	800	2600	0.102	0.017	19	37	1.9	1.53	0.63	544	235
		1000	800	2600	0.104	0.016	20	35	1.8	1.55	0.65	307	135
		1000	800	2600	0.105	0.016	20	35	1.7	1.57	0.66	213	94
		1000	800	2600	0.105	0.016	20	34	1.7	1.56	0.66	299	132
		1000	800	2600	0.103	0.016	20	36	1.8	1.55	0.65	244	107
		1000	800	2600	0.106	0.016	20	33	1.7	1.54	0.66	118	53
		1000	800	2600	0.104	0.016	17	32	1.8	1.35	0.57	98	44
		1000	800	2600	0.102	0.017	21	39	1.9	1.68	0.69	98	42

(continued on next page)

Textural position*	T	F in melt	Cl in melt	$K_{D_{OH-Cl}}^{Ap-melt}$	$K_{D_{OH-F}}^{Ap-melt}$	mole OH/Cl in melt	mole OH/F in melt	mole Cl/F in melt	Calc melt H ₂ O	±	Calc melt CO ₂	±	Calc melt S [†]
	°C	ppm	ppm						wt. %	wt. %	ppm	ppm	ppm
2010	Ap in Cpx	1000	800	2600	0.103	0.017	23	40	1.8	1.84	0.76	n.d.	13
		1000	800	2600	0.104	0.016	21	37	1.7	1.71	0.71	n.d.	16
		1000	800	2600	0.104	0.016	20	36	1.8	1.62	0.68	n.d.	14
2010	Ap in Pl	950	900	3050	0.081	0.011	23	47	2.0	2.37	1.03	478	21
		950	900	3050	0.080	0.011	29	55	1.9	3.10	1.32	n.d.	21
		950	900	3050	0.078	0.012	30	61	2.1	3.21	1.32	n.d.	110
		950	900	3050	0.080	0.011	27	54	2.0	2.85	1.21	n.d.	131
2010	Ap in Gm	945	900	3050	0.080	0.011	25	50	2.0	2.57	1.11	2103	27
		945	900	3050	0.081	0.011	25	49	1.9	2.61	1.14	1194	40
		945	900	3050	0.080	0.011	25	50	2.0	2.55	1.10	533	21
		945	900	3050	0.080	0.011	25	50	2.0	2.52	1.09	345	76
		945	900	3050	0.080	0.011	27	54	2.0	2.90	1.24	n.d.	12
		945	900	3050	0.080	0.011	28	54	2.0	2.93	1.25	n.d.	10
		945	900	3050	0.081	0.012	31	57	1.9	3.35	1.42	n.d.	14
		945	900	3050	0.080	0.011	29	56	1.9	3.17	1.35	n.d.	91
		945	900	3050	0.080	0.012	30	57	1.9	3.32	1.41	n.d.	93

*Apatite crystals used in the calculation of melt volatile concentrations are listed in the same order as in Table 3.1 (showing apatite compositions and labels).

†Relative errors in calculated melt S contents are 7-16%, propagated from the analytical errors of S in apatite.

3.9. Discussion

3.9.1. The multi-reservoir plumbing system of Merapi

Constraining the architecture of the volcano plumbing system helps to understand the eruption dynamics and better interpret the monitoring data for forecasting (e.g. Blundy and Cashman, 2008; Cashman and Sparks, 2013; Bachmann and Huber, 2016; Sparks and Cashman, 2017). However, determining where melts are stored below the volcano is fraught with difficulty. Existing petrological, geophysical, and geodesic approaches are still not able to constrain the locations of magma storage with the high spatial resolution and precision required for anticipating the sizes and frequency of future eruptions. For example, seismic tomography in continental areas is rarely capable of identifying small magma bodies (e.g. of $< 5 \text{ km}^3$; Lowenstern et al., 2017), nor distinguishing a bulk mush containing a small fraction of melt in its pore space, from several isolated melt lens in a rock matrix (e.g. Magee et al., 2018). In deformation modelling, a simple spherical cavity ‘Mogi source’ is commonly used (e.g. Segall, 2010), which is inappropriate to be applied to plumbing systems that consist of multiple reservoir at various depths (e.g. Amoroso and Crescentini, 2009; Segall, 2019). Petrological studies based on mineral (with or without coexisting melt) compositions to obtain pressure (e.g. amphibole, pyroxenes) usually show a broad range of pressure-depths of mineral crystallisation/growth, and have large uncertainties (of 5-10 km; e.g. Putirka, 2008; Preece et al., 2014). The large calibration errors of mineral barometers is related to their small pressure dependence (specially within depths of $< 50 \text{ km}$), which is related to the small values of the partial molar volumes of solid solutions (e.g. Putirka, 2008). In addition, it is very difficult to constrain the composition of the melt in equilibria with

the chemically-zoned crystals that were commonly observed from the intermediate-felsic magmatic systems (e.g. Pichavant et al., 2007), and the crystals could be even out of equilibrium with the interstitial melts (e.g. of the Unzen 1991-1995 eruptions; Nakada and Motomura, 1999), which further widens the range of pressures estimated using mineral barometry. The pressures estimated from volatile contents in melt inclusions based on the assumption of magmatic volatile saturation also have large uncertainties, considering that the melt inclusions would not reflect the original volatile concentrations in the melt if they have experienced some extent of re-equilibration and/or post-entrapment crystallisation (Qin et al. 1992; Danyushevsky et al. 2000; Gaetani and Watson 2000; Cottrell et al. 2001; Portnyagin et al. 2008; Lloyd et al. 2013).

Despite the limitations of the existing approaches, our current knowledge of the plumbing systems of various volcanoes mostly concentrates at quite shallow depths (e.g. < 10 km), whereas the deeper part of the plumbing system is still poorly constrained (e.g. Cashman et al., 2017; Edmonds et al., 2019). Another challenge is to link the magma storage zones proposed by different techniques that use materials/data of distinct spatial scales, e.g. the relatively small minerals/rocks (of a few micrometres) used in petrology studies, versus the deformation/tomography data on a much broader scale (of a few meters to kilometres).

The plumbing system of Merapi volcano has been studied using a variety of methods, suggesting that there are multiple magma reservoirs spanning a wide range of depths from 1 to 45 km (e.g. Beauducel and Cornet, 1999; Ratdomopurbo and Poupinet, 2000; Gertisser, 2001; Chadwick et al. 2007; Chadwick et al., 2013; Costa et al., 2013; Preece et al., 2014; Erdmann et al., 2016; Widiyantoro et al., 2018). In the following paragraphs

we review the literature data, and compare them with our results calculated using apatite (Fig. 3.13). We have converted the pressures proposed by previous petrological studies into depths, using average crustal densities proposed by Widiyantoro et al. (2018), i.e. average densities of 2242 kg/m³ at depths of ≤ 10 km (Tiede et al. 2005), and of 2900 kg/m³ below 10 km (Rudnick and Fountain. 1995).

Previous monitoring and geodetic data at Merapi have suggested magma storage depths in the upper crust (Fig. 3.13). A reservoir at ~ 1.5 -2.5 km below the summit has been constrained by seismic and deformation studies of several past eruptions, including those in 2006 and 2010 (Ratdomopurbo and Poupinet, 2000; Budi-santoso et al., 2013; Saepuloh et al., 2013; Aisyah et al., 2018). Shallow magma ponding at ~ 0.8 -1.8 km has also been identified by gravity anomalies (Saepuloh et al., 2010). Magma storage < 4 km below the summit has also been proposed by a seismic tomography study (Widiyantoro et al., 2018). A deeper magma storage area at $\sim 8.5 (\pm 0.4)$ km has been revealed by the GPS and tiltmeter data obtained during the quiescence (Beauducel and Cornet, 1999). In summary, the geodetic and geophysical data in literature have mainly recognized magma storage zones at depths of < 10 km, with probably two main storage depths of < 4 km, and ~ 9 km respectively.

The depths of the magma crystallisation/volatile-saturation found by most petrological and experimental studies overlap at 1-15 km, i.e. in the mid-upper crust (Nadeau et al., 2013; Preece et al., 2014; Erdmann et al., 2016), whereas a few studies suggested larger crystallisation depths of ~ 23 -30 km (Costa et al., 2013; Nadeau et al., 2013), or even to the Moho (maximum: ~ 45 km; Chadwick et al., 2013) (Fig. 3.13). Melt inclusions from 2006 and 2010 rocks (Nadeau et al., 2013; Preece et al., 2014) record magma volatile-

saturation depths between 1-12 km, which could reflect magma storage and/or magma degassing during transport towards the surface, and partially overlap with the crystallisation depths of 4.5-12 km, constrained by phase equilibria experiments on 2010 rocks (Erdmann et al., 2016). The crystallisation pressures, transformed into depths as noted above, from various mineral barometry calculations indicate a much broader range of depths: (1) of 2-45 km, calculated using the clinopyroxene-only barometer of Nimis (1999) for the magmas from 1994 and 1998 eruptions (Chadwick et al., 2013); (2) a concentrated range of 4-13 km, calculated using the clinopyroxene-liquid barometer of Putirka (2008) for the magmas from 2006 and 2010 eruptions (Preece et al., 2014); (3) of about 13 (± 2) km to 30 (± 2) km, calculated using the amphibole-only barometer of Ridolfi and Renzulli (2012) for amphibole phenocrysts from 2006 and 2010 eruptions (Costa et al., 2013), and of ~ 23 -28 (± 3) km calculated using the amphibole-only barometer of Ridolfi et al. (2012) for amphibole megacrysts from previous eruptions (Nadeau et al., 2013) (Fig. 3.13). It is worth noting that these mineral barometry calculations have large uncertainties, which translate to the error of ± 5 to 10 km in depths. In addition, the pressure-depths yielded by the mineral barometers could suffer from the difficulty of identifying the composition of a liquid in equilibrium with a given crystal. As has been discussed in several parts of this chapter and highlighted by other authors, the emitted rocks from Merapi are the products of the open-system magmatic processes with mixtures of crystals and melts from different origins. Therefore, it is unrealistic to know whether the investigated crystals are in equilibrium with the erupted melts, and difficult to assess which of the barometric calculations above could better reflect the real situations. Some more evidence for the magma storage zones at the mid-lower crust have been found from seismic tomography study (Widiyantoro et al., 2018), suggesting two distinct depths of ~ 10 -20 km and > 25 km, with

uncertainties of about ~ 5 km (Fig. 3.13). Combination of the results from the tomographic and mineral barometry studies in literature, there seems to be a deep magma reservoir at > 25 km depth below Merapi. However, given the large uncertainties of these data, it is unclear at this moment whether the depths of 10-20 km for the intermediate magma storage zone(s) were properly determined, and whether these storage areas are isolated or interconnected with those at shallower/deeper locations still needs to be explored in the future.

Our results calculated using the volatile compositions of apatite and the amphibole-liquid barometry indicate mainly two magma storage depths (Fig. 3.13): a shallow zone with a range of depths from ~ 1 to 16 km but mostly between ~ 2 -5 km, reflected by apatite in Cpx/Pl/groundmass, and a deeper zone at > 30 km depths, reflected by apatite inclusions in amphibole. The main depths of the shallow magma storage (< 5 km) found in this study match with most determinations from the studies of geophysical and geodetic unrest, seismic tomography, and melt inclusions, which suggest that this shallow magma storage zone is mainly located within the volcanic conduit, where the magma degassing and crystallization occurred before eruption and during the quiescence. Given that only a few data from our calculation indicate the depths between 5-16 km, we are unable to obtain good constraints on the structure of the plumbing system at this depth. Nonetheless, a magma reservoir at about 9 km depths has been quite well determined from previous study on the GPS and tilt data, and also with some supports from the barometric calculations in literature. The presence of magmas at depths of 10-20 km was revealed by seismic anomalies but with uncertainties of about 5 km, and also proposed by the flurry of mineral barometric data, which however is fraught with problems as discussed above. It is more confident to point out a deeper

magma storage zone at depths of > 30 km, as supported by our apatite data and amphibole-liquid barometry calculation, as well as previous seismic tomography study.

In summary, our preferred interpretation for the plumbing system of Merapi is that there are two main magma storage areas, one at < 10 km depths which comprises the volcanic conduit and upper reservoir, and the other at depths of > 30 km (Fig. 3.14). It is unclear at this moment whether there are large amounts of magmas or significant extents of crystallization occurring between these two main magma reservoirs, considering that the wide ranges of barometric data in literature may reflect the mixing of melts and crystals from these two regions. Additional constraints on the magma storage zones could be obtained by studying the brittle to ductile transition and the buoyancy of the magma, but precise determinations on these parameters are still facing some problems, given the influence of the high thermal flux on the crustal properties and densities at active volcanoes, such as Merapi. The structure of the plumbing system of Merapi propose here is different from the trans-crustal mush system (TCMS; Sparks and Cashman, 2017; Cashman et al., 2017) at Soufriere hills volcano (SHV), where the multiple magma storages zones continuously extend from the shallow to the deep crust. The difference between the two models is reflected by the different eruption frequencies and magma fluxes at the two volcanoes, although we emphasize that the TCMS model proposed for SHV is mainly based on the mineral barometric data, which have been noticed of large uncertainties and hard to evaluate, and would tend to give a blurred picture of the magma storage areas due to mixing and mingling of melts and crystals from various origins.

Fig. 3.13. Pressures and depths of magma storage zones at Merapi constrained in this study for 2006 and 2010, and those reported in literature (different eruptions marked in different colors; see legend). Abbreviations and data sources: Grav – Gravity anomalies; Seism – seismicity; EDM – Electronic Distance Measurements; SAR – Synthetic Aperture Radar; Tomo – Seismic tomography; PhaExp – Phase equilibria experiments; MI – melt inclusions (in clinopyroxene or amphibole megacrysts); Cpx-liq – clinopyroxene-liquid barometer of Putirka (2008): #1 – Eq. 32b, #2 – Eq. 32c; Cpx-only – clinopyroxene-only barometer of Nimis (1999); Amph-only – amphibole-only barometer of Ridolfi et al. (2010) on megacrysts, and of Ridolfi et al. (2010) and Ridolfi and Renzulli (2012) on phenocrysts; Amph-liq – amphibole-liquid barometer of Putirka (2016); Pl-liq – plagioclase-liquid hygrometer of Waters and Lange (2015) on plagioclase microlites. Data sources: ¹ Saepuloh et al., 2010; ² Budi-santoso et al., 2013; ³ Aisyah et al., 2018; ⁴ Saepuloh et al., 2013; ⁵ Beauducel and Cornet, 1999; ⁶ Widiyantoro et al., 2018; ⁷ Erdmann et al., 2016; ⁸ Nadeau et al., 2013; ⁹ Preece et al., 2014; ¹⁰ Chadwick et al. (2013); ¹¹ Erdmann et al. (2014); ¹² Costa et al. (2013); ¹³ Preece et al., 2016.

3.9.2. Links between magmatic volatiles and pre-eruptive gas emission

The magma storage depths and magmatic volatile compositions in the Merapi system can be used to gain insights into the change of the pre-eruptive gas emission, which could be a potential eruption precursor (e.g. at Etna and Stromboli volcanoes; Aiuppa et al., 2009; Aiuppa et al., 2010; Kahl et al., 2013). The gas emissions from Merapi have been traditionally monitored by sampling the high-temperature fumaroles from the summit Woro-field (e.g. Humaida et al., 2007; Surono et al., 2012). During periods of quiescence and passive degassing before the 2006 and 2010 eruptions, the fumarole gas had CO_2/SO_2 of $\sim 5\text{--}9$, whereas as the system was closer to eruption, the CO_2/SO_2 in the fumarole gas increased to up to ~ 37 in July 2005, and ~ 118 on October 20th, i.e. one week before the first explosion (Humaida et al., 2007; Surono et al., 2012). These changes in the gas composition likely indicate outgassing of C-rich magmas that are stored significantly deeper and move to the shallower part of the plumbing system (Surono et al., 2012).

Another possible source of CO_2 could be the decarbonation of the limestone units that commonly exist in the upper crust in Java (e.g. Allard, 1983; Chadwick et al., 2007; Deegan et al., 2010; Troll et al., 2012; Troll et al., 2013; Carr et al., 2018). Based on the results from this study, we cannot comment on the extents of carbonate assimilation before the two eruptions, given that the CO_2 gas from decarbonation (e.g. Troll et al., 2013) tends to exist as vapor rather than being dissolved in the melt, and thus was unlikely recorded by apatite nor melt inclusions (Preece et al., 2014). Despite that, the apatite inclusions in amphibole provide the first evidence of the CO_2 -rich Merapi melts (CO_2 : > 1 wt.%) at depths of > 30 km, which should be responsible for the fumarole gas with a striking mantle isotopic signature proposed in literature (e.g. Allard, et al., 2011).

Our data can also help to explain the changes of gas composition before eruption due to movement from deep magma to shallower depths. A SO₂ flux of ~ 150-200 tons/day was recorded on October 20th, 2010 by ground-based DOAS (Surono et al., 2012), which is on the same order of magnitude to that during the quiescence (of ~100 tons/day; Le Cloarec and Gauthier, 2003). Based on the CO₂/SO₂ in the fumarole gas, we find that the fumarolic CO₂ flux during the quiescence should be < 500 tons/day, but as high as ~ 12,000-16,000 tons/day on October 20th, 2010. This means that the major change in the pre-eruptive gas emission was an increase in the CO₂ flux, whereas the SO₂ flux remained similar to quiescence times. This can be explained by the movement of a deep CO₂-rich magma (as inferred from our apatite data) from > 25 km to about 10 km (the base of the upper part of the magmatic system), followed by CO₂ exsolution that flushed the shallow part of the magmatic system. The depths where the intruded magma stalled should be deep enough to prevent significant amounts of S exsolution to the fluid phase (according to the gas data). These depths could be better constrained from the C-H-S melt solubility model (Moretti et al., 2003; Scaillet and Pichavant, 2005), using which the amounts of magma intrusion could be estimated, however this is beyond the scope of this chapter.

In summary, we propose that the similarity in H₂O-CO₂ concentrations in the pre-eruptive melts of 2006 and 2010 requires a larger amounts of magma intrusion from depths before 2010 eruption, which supplied more volatiles to the magmas in the shallow system, which were the leftover from 2006 eruption (Fig. 3.14). The exsolved volatiles could have produced larger magma buoyancy and faster ascent rate, which eventually caused the large explosion in 2010. We have been able to constrain the

difference in the magma ascent rates between the 2006 and 2010 eruptions, based on the Cl diffusion in apatite crystals in touch to the matrix glass shown in the discussion below.

Fig. 3.14. Sketch of the plumbing system of Merapi Volcano, showing a deep magma reservoir at depths of ≥ 26 -30 km (near Moho), and multiple vertically distributed magma storage zones at ~ 1 -16 km below the summit (most at ~ 2 -5 km; calculated using apatite). The volatile-rich deep magmas supplied large amounts of volatiles to shallower magmas, which produced large magma buoyancy and faster magma ascent, thus causing the larger explosive eruption in 2010.

3.9.3. Faster magma ascent in 2010 than 2006 revealed by Cl zoning in apatite

Magma ascent rate has been proposed as a key parameter for controlling the eruptive styles (e.g. Cashman and Sparks, 2013; Cassidy et al., 2018). However, the quantification of the magma ascent rates and their effects on the eruptive styles are still poorly supported by data. In the case of Merapi, previous studies have shown much larger magma extrusion rates in 2010 (of $\sim 25\text{-}35\text{ m}^3/\text{s}$) than in 2006 (of $\leq 1\text{-}4\text{ m}^3/\text{s}$) (Surono et al., 2012; Pallister et al., 2013; Ratdomopurbo et al., 2013), which likely indicates faster magma ascent in 2010, assuming similar geometry of the conduit during the two eruptions. Petrological studies on the texture of amphibole (with or without the breakdown reaction rims) and abundances of microlites (Costa et al., 2013; Preece et al., 2016) both indicate faster magma ascent in 2010. However, these data could not provide precise constraints on the difference in magma ascent rates between the two eruptions. Below we provide another perspective of magma ascent rate based on chlorine diffusion in apatite microlites, which can be potentially applied to study other volcanic systems.

We have shown that a main mineralogical difference between the 2006 and 2010 rocks is that apatite microlites from the 2006 rocks show anisotropic Cl zoning, but this zoning is absent in 2010 apatite crystals (Figs. 3.3-3.4). We believe that the Cl zoning is resulted from Cl diffusion (Section 3.4), whose driving force could be the enrichment of Cl in the melt due to anhydrous microlite crystallization during magma ascent. To perform appropriate calculation for the diffusion timescales requires (1) well-determined diffusion rates (see Chapter 4), and (2) a proper diffusion model with consideration of the varying melt Cl concentrations with time, which is a complex function of the magma ascent and degassing, and the associated microlite crystallization. The complex computation that is to be involved in this diffusion model is beyond the scope of this

chapter. Below we report a preliminary estimate on the difference in the magma ascent rates between the two eruptions.

Here we consider the proportional relation between the diffusion time (t) and the square of diffusion distance (x^2), i.e. $(Dt) \propto x^2$ (Crank et al., 1975), and assume (approximately) equivalent diffusivities (D) of Cl in apatite crystals from 2006 and 2010. Given the lengths of Cl zoning of $\sim 3\text{-}7\text{ }\mu\text{m}$ in 2006 apatite and $< 1\text{ }\mu\text{m}$ in 2010 apatite, the difference in the diffusion times between 2006 and 2010 would be about 10-50. Using the same storage depths for the 2006 and 2010 magmas, the average ascent rate in 2010 would be at least 10 times' faster than that in 2006. Such difference in ascent rate is of the same order of magnitude as the difference in magma extrusion rates (Surono et al., 2012; Pallister et al., 2013; Ratdomopurbo et al., 2013), which indicates that our preliminary estimation using apatite is within realistic bounds. Incorporation of a changing boundary composition and a thermal history during magma ascent would lead to even slower magma ascent rates in 2006 than in 2010, and it seems likely that our magma ascent rates will be significantly higher than magma extrusion rates. The faster magma ascent in 2010 was likely caused by a larger magma buoyancy produced by a larger amounts of exsolved volatiles before the 2010 explosion.

3.10. Conclusions

The volatile compositions (H_2O , CO_2 , F, Cl, S) of apatite from Merapi 2006 and 2010 rocks have been combined with multiple calculation approaches for estimating the melt volatile budgets, from which we find similar volatile abundances within the shallow magma column before the 2006 and 2010 eruptions, despite their different explosivities. Apatite crystals that occur in different textural positions are able to preserve melt volatile information at different depths: those in amphibole indicate the volatile-rich melts of about 3-10 wt.% H_2O , 1-3 wt.% CO_2 , and 340-2000 ppm S, which are not recorded by melt inclusions in literature. We propose that the plumbing system at Merapi is likely made up of a deep magma reservoir at depths of ≥ 26 -30 km (near the Moho), and a major shallow magma storage zone at about 1.5 to 5 km below summit. Analyses of a larger number of apatite crystals especially those hosted by amphibole would potentially lead to better constraints on the structure of the plumbing system, and on the range of magmatic volatile abundances at deep locations.

The CO_2 -richer fumarolic gas in 2010 than 2006 indicate percolation of CO_2 -rich volatiles that were released from the deep magma and fluxed the pre-existing magma column in 2010, and thus produced higher magma buoyancy, faster magma ascent rates, and larger explosivity, compared to the dome-forming eruption in 2006. Our estimation using Cl zoning in apatite indicates that the average magma ascent rate in 2010 is at least one order of magnitude faster than that in 2006. The calculation procedure for apatite used in this study has wide application of determining the volatile budgets of the pre-eruptive melts and the magma storage zones, which could contribute to better

interpretation of the pre-eruptive gas and monitoring data for more accurate forecast in the future.

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Summary of supplementary materials

Appendix A: Analytical conditions and apatite standards used for SIMS analyses, and the calibration curves used for volatile determination.

Table A1. Volatile compositions of apatite standards used for SIMS analyses.

Fig. A1. Calibration curves used for CO₂ determination.

Fig. A2. Calibration curves used for H₂O, F, Cl and S determination.

Appendix B: Validation of CO₂ data from SIMS analyses.

Fig. B1. SEM observation of apatite crystals before and after SIMS analyses

Table B1. Examples of major element compositions measured by EPMA from crystals with CO₂ determined by SIMS.

Appendix C: EPMA data for apatite crystals from Merapi 2006 (**Table C1**) and 2010 (**Table C2**) rocks.

Appendix D: Regression of experimental data from the literature for determining

$K_{D_{Al-Si}}^{Amp-melt}$, and the amphibole-liquid thermobarometry calculation (**Fig. D1**).

Appendix A. Analytical conditions and apatite standards used for SIMS analyses, and the calibration curves used for volatile determination.

To determine the volatile concentrations in our apatite crystals, we normalized the secondary ions of ^{12}C , $^{17}[\text{OH}]$, $^{19}\text{F}^{16}\text{O}$, ^{37}Cl and ^{34}S to ^{18}O , and calibrated them with apatite standards measured using same analytical settings on the same days (Table A1). Two field apertures sizes have been used for analyses in 2016, where we used a regular large aperture (of 8005) for the first measurement, and then changed to a smaller aperture (of 1202) from which we obtain more precise results for CO_2 . The smaller aperture used for analyses minimizes the interference from the extra $^{12}\text{C}^+$ that was deposited on sample surface during pre-sputtering (see method in text). Considering the ion signals acquired using different field apertures are different (especially for CO_2), we calibrated these signals separately using the calibration curves obtained under corresponding conditions (Figs. A1, A2). The CO_2 signals acquired from the C-poor apatite standard (“Cerro”) fall out of the calibration curve (Fig. A1), likely because the CO_2 concentration reported for this standard was estimated using the absorbance from infrared method and could have large uncertainty (Clark et al., 2016; Table A1). Compared to “Cerro”, the other apatite standard used in our analyses (i.e. “HAM”) has more CO_2 (of 0.142 ± 0.034 wt.%) with lower uncertainty, whose absolute concentration was directly determined by Nuclear Reaction Analysis (NRA). Considering this, we have used only the standard ‘HAM’ for determining CO_2 in our apatite crystals.

For determination of H_2O , F, Cl, and S concentrations, we have used four apatite standards, i.e. two from Clark et al (2016), and two from McCubbin et al. (2012) (Table. A1). The calibrate curves show generally good linearity, and equivalent slopes (within

error) of those measured using field aperture sizes of 1202 and 8005 (Fig. A2). This is likely related to negligible interference from cation depositions of OH, F, Cl and S (due to their chemistry property) on the sample surface during the pre-sputtering, where such interference is more significant for C due to the presence of $^{12}\text{C}^+$ (see Section 3.2 in text).

Table A1. Volatile concentrations (in wt.%) in apatite standards used for SIMS analyses.

	H ₂ O	2 σ^*	F	2 σ	Cl	2 σ	S	2 σ	CO ₂	1 σ
Durango (Ap003) ¹	0.06	0.04	3.44	0.22	0.45	0.12	0.13	0.02	n.d.	n.d.
Morocco (Ap004) ¹	0.55	0.05	2.39	0.24	0.41	0.04	0.10	0.01	n.d.	n.d.
Crystal Lode (Ap005) ¹	0.37	0.03	2.45	0.22	0.95	0.06	0.04	0.01	n.d.	n.d.
Russia (Ap018) ¹	0.2	0.04	3.28	0.38	0.13	0.04	0.36	0.05	n.d.	n.d.
HAM ²	0.44	0.01	2.51	0.08	0.33	0.02	0.18	0.02	0.142 [†]	0.034
Cerro ²	0.085	0.014	3.4	0.09	0.46	0.02	0.18	0.02	0.028 [‡]	0.012

*Values in parentheses represent the standard deviation of analyses on the standards, reported by ¹

McCubbin et al. (2012) from SIMS analyses, and ² Clark et al. (2016) from NRA analyses.

[†] Absolute concentration determined by NRA.

[‡] Estimated from FTIR absorbance with potentially larger uncertainty than reported.

Fig. A1. Calibration curves for CO₂ determination obtained by measuring apatite standard (“HAM”) using two field aperture sizes from SIMS. The regression lines (black line) were forced to the origin (solid squares), and their ranges (dashed line) were determined by considering the uncertainties of the standards (Table A1). The C signals obtained from the standard “Cerro” fall out of the linear trend, due to the large uncertainty in its CO₂ content (Table A1), thus “Cerro” was not used for calibration. Error bars show 2 σ standard deviation of analyses on the standards (Table A1).

Fig. A2. Calibration curves for H₂O, F, Cl, and S, measured from four apatite standards using SIMS (Table A1). Considering the detection limits of our analyses close to 0 (~7 ppm for H₂O, <1 ppm for F, Cl and S), the regression lines (black line) were forced to the origin (solid squares). The range of the regression lines (dashed line) was determined by considering the uncertainties of the standards (Table A1). Error bars show 2σ standard deviation of analyses on the standards (Table A1).

Appendix B: Validation of CO₂ data from SIMS analyses

The pits of SIMS analyses were observed using a scanning electron microscope (SEM) at Nanyang Technological University. Most pits are located within the apatite crystals (Fig. B1 a-c); a few pits were found to partially cover the surrounding phases or above the cracks, which might yield results biased from the real volatile concentrations. For example, one crystal hosted by amphibole was found to contain about 11 wt.% CO₂, 0.66 wt.% H₂O, 1.6 wt.% F and 1.0 wt.% Cl, which obviously had C contamination, likely related to the crack beneath the crystal surface which could not be noticed before analyses (Fig. B1d). The higher F and Cl but lower H₂O contents obtained from this crystal (than other crystals in amphibole; Table 3.1) indicate that the contamination might come from the epoxy resin left in the crack, given that the epoxy resin could contain large amounts of C, and some Cl and F.

CO₂ in apatite is present as CO₃²⁻, which could be preserved at two sites of apatite structure, i.e. A-type at the anion site (e.g. LeGeros et al. 1969; Bonel 1972; Fleet and Liu, 2003), and B-type at the tetrahedral site (e.g. Pan and Fleet, 2002). To determine which type(s) of carbonate are preserved in our crystal would require direct analyses of the crystal structure, which is not available in this study. Nonetheless, we could perform a first-order test for the acquired CO₂ data by considering that the total weight concentrations of major/minor components measured by EPMA and the volatiles measured by SIMS should be < 100 wt.%. We find the sum (hydrous) of weight concentrations in our apatite crystals are > 97.8 wt.%, meaning that the maximal CO₂ should be < 2.2 wt.% (trace elements such as REEs were not measured; see examples in Table B1). Therefore we have excluded three extremely high CO₂ data (of >4 wt.%) from further consideration nor calculation of melt CO₂ budgets in this study.

Fig. B1. Apatite crystals shown in BSE images obtained before SIMS analyses (left-hand side), and in SE images obtained after SIMS analyses (right-hand side). Only the signals acquired from the most central areas ($\sim 1/4$) of the total sputtered areas (in red boxes) were used for determining volatile concentrations (panels *a-c*). The pit location shown in panel *d* is over a crack, which could contain additional C (e.g. from the epoxy resin), so that CO_2 measured from this crystal is abnormally high (of ~ 11 wt.%), and thus was excluded from consideration in the study.

Table B1. Representative EPMA data for apatite crystals from Merapi 2010 rocks, with CO₂ concentrations determined by SIMS.

(wt.%)	1011211A, Amph1	10111123, Amph4-1 #1	10111123, Amph4-1 #1	10111123, Amph4-1 #1	1011211A, GmAp7
P ₂ O ₅	39.85	40.31	40.34	40.09	41.20
SiO ₂	0.36	0.40	0.33	0.26	0.17
Ce ₂ O ₃	0.01	0.02	0.01	0.01	0.25
MgO	0.15	0.20	0.17	0.17	0.27
CaO	54.69	54.57	54.11	54.30	54.36
Na ₂ O	0.10	0.13	0.13	0.10	0.01
SO ₃	0.61	0.70	0.60	0.52	0.08
F	1.48	1.42	1.59	1.48	2.00
Cl	0.56	0.51	0.51	0.52	0.89
O=F	0.62	0.60	0.67	0.62	0.84
O=Cl	0.13	0.12	0.11	0.12	0.20
Sum (anhydrous)	97.07	97.53	97.01	96.71	98.18
H ₂ O (SIMS)	0.90 (4)	0.98 (3) *	0.98 (3)	0.98 (3)	0.54 (2)
CO ₂ (SIMS)	1.6 (2)	0.24 (5)	0.24 (5)	0.24 (5)	0.039 (5)
Total (including H ₂ O, CO ₂)	99.57	98.68	98.16	97.86	98.76
<i>Atom per formula unit: Ca₁₀(PO₄)₆(X)₂</i>					
P	5.692	5.716	5.741	5.738	6.029
Si	0.061	0.066	0.055	0.043	0.029
Ce	0.001	0.001	0.000	0.001	0.016
Mg	0.039	0.050	0.044	0.044	0.070
Ca	9.885	9.793	9.747	9.837	10.07
Na	0.033	0.042	0.043	0.033	0.003
S	0.155	0.175	0.152	0.133	0.019
F	0.790	0.751	0.847	0.789	1.093
Cl	0.160	0.145	0.145	0.149	0.261
2-F-Cl	1.050	1.104	1.008	1.062	0.646

* Values in parentheses represent error of 2σ from SIMS analyses. The other H₂O content of 0.91 (± 0.04) wt.% (Table 3.1 in text) was measured from this crystal at different pit location.

Table C1. EPMA data for apatite crystals from Merapi 2006 deposits (crystals with labels in bold were also analysed by SIMS shown in Table 3.1 in text).

Label	P ₂ O ₅	SiO ₂	Ce ₂ O ₃	MgO	CaO	Na ₂ O	SO ₃	F	Cl	O=F	O=Cl	Sum (anhydrous)	Calc H ₂ O	S
061506L_1, Amph5	43.16	0.29	0.02	0.30	53.30	0.07	0.37	1.22	0.57	0.51	0.13	98.66	1.11	0.148
061406, Cpx3	41.55	0.34	0.20	0.30	53.43	0.02	0.09	1.95	1.05	0.82	0.24	97.88	0.55	0.038
061406, Cpx6	41.16	0.26	0.20	0.33	53.68	0.01	0.08	2.50	0.89	1.05	0.20	97.85	0.33	0.031
061506L_1, Cpx4	40.96	0.20	0.19	0.35	53.80	0.08	0.08	2.50	0.85	1.05	0.19	97.76	0.33	0.030
061506L_1, Cpx4	41.08	0.26	0.24	0.35	53.51	0.07	0.11	2.04	0.96	0.86	0.22	97.55	0.51	0.045
061506L_1, Cpx3, Ap3	41.24	0.25	0.21	0.36	53.36	0.10	0.05	2.05	1.03	0.86	0.23	97.55	0.50	0.019
061506L_1, Cpx3, Ap4	41.52	0.22	0.20	0.37	53.17	0.10	0.07	2.18	1.10	0.92	0.25	97.75	0.43	0.027
061506L_1, Cpx3, Ap5	40.98	0.20	0.18	0.35	53.22	0.09	0.07	2.10	0.98	0.88	0.22	97.05	0.48	0.027
061406, GmAp8	42.84	0.16	0.30	0.32	54.61	0.01	0.06	1.90	0.79	0.80	0.18	100.01	0.67	0.024
061406, GmAp7	42.96	0.30	0.26	0.29	53.92	0.02	0.06	2.30	0.89	0.97	0.20	99.83	0.46	0.025
061506L_1, GmAp3-2-1	42.34	0.49	0.19	0.32	51.47	0.03	0.07	1.70	1.12	0.72	0.25	96.76	0.64	0.029
061506L_1, GmAp3-2-1	41.66	0.24	0.17	0.34	52.54	0.08	0.09	1.64	0.81	0.69	0.18	96.69	0.74	0.035
061506L_1, GmAp3-2-1	42.03	0.16	0.20	0.31	52.48	0.09	0.07	1.67	0.80	0.70	0.18	96.93	0.73	0.028
061506L_1, GmAp3-2-1	42.14	0.16	0.16	0.29	52.49	0.11	0.05	1.42	0.87	0.60	0.20	96.89	0.83	0.020
061506L_1, GmAp3-2-1	42.14	0.20	0.18	0.29	52.44	0.10	0.06	1.62	0.85	0.68	0.19	97.02	0.74	0.024
061506L_1, GmAp3-2-1	42.62	0.12	0.20	0.30	52.49	0.05	0.05	1.66	0.91	0.70	0.20	97.51	0.72	0.021
061506L_1, GmAp3-2-1	42.33	0.20	0.19	0.28	52.32	0.04	0.06	1.56	0.78	0.66	0.18	96.93	0.79	0.023
061506L_1, GmAp3-2-1	42.05	0.26	0.18	0.30	52.09	0.08	0.09	1.67	1.01	0.70	0.23	96.80	0.68	0.037
061506L_1, GmAp3-2-1	42.01	0.24	0.18	0.29	51.91	0.15	0.09	1.89	1.17	0.80	0.26	96.86	0.53	0.037
061506L_1, GmAp3-2-1	41.88	0.20	0.16	0.31	51.44	0.10	0.08	2.09	1.25	0.88	0.28	96.35	0.41	0.032
061506L_1, GmAp3-2-1	41.63	0.15	0.17	0.34	51.79	0.08	0.07	2.08	1.52	0.88	0.34	96.62	0.35	0.028

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Label	P ₂ O ₅	SiO ₂	Ce ₂ O ₃	MgO	CaO	Na ₂ O	SO ₃	F	Cl	O=F	O=Cl	Sum (anhydrous)	Calc H ₂ O	S
061506L_1, GmAp3-2-1	41.91	0.28	0.16	0.36	51.48	0.15	0.08	2.08	1.78	0.87	0.40	97.00	0.29	0.031
061506L_1, GmAp3-2-1	41.64	0.34	0.21	0.36	51.68	0.16	0.04	2.00	1.63	0.84	0.37	96.84	0.36	0.015
061506L_1, GmAp3-2-1	42.61	0.24	0.15	0.35	51.70	0.11	0.05	1.96	1.38	0.83	0.31	97.40	0.46	0.020
061506L_1, GmAp3-2-1	42.14	0.17	0.13	0.33	51.76	0.08	0.07	1.90	1.26	0.80	0.28	96.75	0.51	0.029
061506L_1, GmAp3-2-1	41.87	0.22	0.14	0.31	51.89	0.06	0.08	1.95	1.11	0.82	0.25	96.56	0.52	0.032
061506L_1, GmAp3-2-1	42.19	0.20	0.17	0.29	52.34	0.05	0.09	1.87	1.04	0.79	0.23	97.21	0.58	0.036
061506L_1, GmAp3-2-1	41.79	0.20	0.14	0.30	52.15	0.05	0.07	1.90	0.97	0.80	0.22	96.55	0.57	0.026
061506L_1, GmAp3-2-1	41.85	0.21	0.14	0.30	52.25	0.05	0.08	1.99	0.93	0.84	0.21	96.75	0.55	0.030
061506L_1, GmAp3-2-1	42.43	0.18	0.18	0.30	52.54	0.05	0.09	1.92	0.89	0.81	0.20	97.58	0.60	0.036
061506L_1, GmAp3-2-1	42.42	0.20	0.22	0.29	51.65	0.05	0.11	1.79	0.88	0.76	0.20	96.66	0.65	0.045
061506L_1, GmAp3-2-1	41.81	0.18	0.15	0.29	52.13	0.16	0.07	1.40	0.97	0.59	0.22	96.34	0.80	0.029
061506L_1, GmAp3-2-1	41.85	0.08	0.18	0.30	52.69	0.13	0.08	1.34	1.01	0.57	0.23	96.86	0.83	0.032
061506L_1, GmAp3-2-1	42.46	0.18	0.18	0.29	52.18	0.07	0.10	1.48	1.02	0.62	0.23	97.10	0.77	0.041
061506L_1, GmAp3-2-1	42.24	0.13	0.18	0.30	52.25	0.05	0.08	1.53	1.04	0.64	0.23	96.93	0.74	0.032
061506L_1, GmAp3-2-1	41.80	0.17	0.20	0.30	52.37	0.08	0.15	1.48	1.02	0.62	0.23	96.71	0.76	0.059
061506L_1, GmAp3-2-1	41.95	0.11	0.15	0.28	52.97	0.10	0.09	1.53	1.04	0.64	0.23	97.34	0.74	0.035
061506L_1, GmAp3-2-1	42.47	0.19	0.18	0.31	52.14	0.14	0.29	1.47	1.06	0.62	0.24	97.39	0.77	0.116
061506L_1, GmAp3-2-1	41.86	0.20	0.21	0.29	51.98	0.21	0.26	1.52	1.07	0.64	0.24	96.71	0.73	0.106
061506L_1, GmAp3-2-1	42.03	0.18	0.10	0.31	51.91	0.12	0.22	1.54	1.09	0.65	0.25	96.60	0.72	0.086
061506L_1, GmAp3-1	41.11	0.09	0.17	0.35	53.89	0.03	0.10	1.80	1.00	0.76	0.23	97.55	0.62	0.040
061506L_1, GmAp3-1	41.50	0.13	0.17	0.35	52.95	0.09	0.09	1.79	1.09	0.75	0.25	97.16	0.60	0.037
061506L_1, GmAp3-1	41.33	0.16	0.16	0.34	53.31	0.05	0.09	1.83	1.07	0.77	0.24	97.31	0.58	0.037
061506L_1, GmAp3-1	41.43	0.14	0.20	0.36	53.55	0.06	0.10	1.82	1.00	0.77	0.23	97.68	0.61	0.038

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Label	P ₂ O ₅	SiO ₂	Ce ₂ O ₃	MgO	CaO	Na ₂ O	SO ₃	F	Cl	O=F	O=Cl	Sum (anhydrous)	Calc H ₂ O	S
061506L_1, GmAp3-1	41.00	0.11	0.18	0.36	53.24	0.11	0.06	1.88	1.01	0.79	0.23	96.93	0.57	0.024
061506L_1, GmAp3-1	41.00	0.17	0.13	0.35	53.23	0.02	0.09	1.84	1.01	0.78	0.23	96.85	0.58	0.035
061506L_1, GmAp3-1	41.45	0.11	0.16	0.36	53.47	0.08	0.08	1.93	1.09	0.81	0.24	97.68	0.54	0.031
061506L_1, GmAp3-1	41.15	0.12	0.13	0.36	53.79	0.11	0.08	1.82	1.02	0.76	0.23	97.59	0.61	0.033
061506L_1, GmAp3-1	41.03	0.15	0.16	0.36	53.75	0.08	0.09	1.83	1.04	0.77	0.23	97.48	0.59	0.034
061506L_1, GmAp3-1	40.93	0.15	0.17	0.37	53.44	0.05	0.07	1.79	1.01	0.75	0.23	97.01	0.61	0.030
061506L_1, GmAp3-1	40.74	0.13	0.17	0.38	53.13	0.05	0.05	1.99	0.97	0.84	0.22	96.56	0.52	0.021
061506L_1, GmAp3-1	41.40	0.20	0.19	0.36	52.81	0.08	0.09	1.83	0.98	0.77	0.22	96.94	0.60	0.035
061506L_1, GmAp3-1	41.23	0.17	0.18	0.36	53.36	0.10	0.05	1.78	1.00	0.75	0.23	97.26	0.62	0.019
061506L_1, GmAp3-1	40.73	0.37	0.19	0.37	53.12	0.09	0.11	1.93	0.93	0.81	0.21	96.81	0.56	0.043
061506L_1, GmAp3-1	41.31	0.12	0.16	0.35	53.74	0.10	0.08	1.74	1.02	0.73	0.23	97.64	0.64	0.030
061506L_1, GmAp3-1	41.31	0.17	0.20	0.35	53.33	0.10	0.06	1.84	1.02	0.77	0.23	97.37	0.59	0.025
061506L_1, GmAp3-1	41.55	0.08	0.18	0.35	53.51	0.06	0.07	1.95	1.04	0.82	0.23	97.73	0.54	0.027
061506L_1, GmAp3-1	41.79	0.12	0.17	0.35	53.07	0.03	0.06	1.80	0.99	0.76	0.22	97.42	0.62	0.025
061506L_1, Ap1	42.23	0.40	0.24	0.29	51.69	0.05	0.05	2.37	1.06	1.00	0.24	97.14	0.35	0.020
061506L_1, Ap1	42.37	0.28	0.23	0.29	52.02	0.08	0.05	2.44	0.96	1.03	0.22	97.48	0.35	0.020
061506L_1, Ap1	42.57	0.26	0.17	0.28	51.56	0.07	0.07	2.52	0.83	1.06	0.19	97.08	0.34	0.026
061506L_1, Ap1	42.40	0.26	0.21	0.28	51.54	0.06	0.03	2.51	0.85	1.06	0.19	96.91	0.33	0.014
061506L_1, Ap1	42.46	0.24	0.20	0.28	51.20	0.04	0.06	2.37	0.88	1.00	0.20	96.54	0.39	0.023
061506L_1, Ap1	42.51	0.19	0.19	0.27	51.54	0.12	0.04	2.57	0.86	1.08	0.20	97.02	0.30	0.018
061506L_1, Ap1	42.18	0.21	0.17	0.29	51.68	0.10	0.05	2.51	0.83	1.06	0.19	96.78	0.33	0.020
061506L_1, Ap1	42.20	0.31	0.21	0.26	51.87	0.06	0.05	2.33	0.85	0.98	0.19	96.96	0.42	0.018
061506L_1, Ap1	42.77	0.17	0.18	0.28	51.78	0.05	0.07	2.23	0.96	0.94	0.22	97.33	0.45	0.027

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Label	P ₂ O ₅	SiO ₂	Ce ₂ O ₃	MgO	CaO	Na ₂ O	SO ₃	F	Cl	O=F	O=Cl	Sum (anhydrous)	Calc H ₂ O	S
061506L_1, Ap1	42.76	0.21	0.18	0.28	52.08	0.04	0.04	1.94	0.86	0.82	0.19	97.39	0.60	0.017
061506L_1, Ap1	42.19	0.17	0.20	0.29	51.63	0.11	0.05	2.02	0.95	0.85	0.22	96.56	0.52	0.022
061506L_1, Ap1	42.68	0.18	0.21	0.29	52.05	0.15	0.05	2.05	0.96	0.86	0.22	97.53	0.53	0.021
061506L_1, Ap1	42.45	0.17	0.20	0.27	52.26	0.02	0.05	2.05	0.94	0.86	0.21	97.33	0.53	0.018
061506L_1, Ap1	42.18	0.20	0.23	0.27	51.87	0.02	0.08	2.16	1.11	0.91	0.25	96.95	0.43	0.030
061506L_1, Ap1	42.05	0.19	0.24	0.29	51.90	0.12	0.20	2.23	1.26	0.94	0.28	97.26	0.36	0.080
061506L_1, Ap1	41.99	0.22	0.16	0.30	51.58	0.11	0.20	2.29	1.37	0.96	0.31	96.94	0.30	0.079
061506L_1, Ap1	41.98	0.18	0.17	0.31	52.17	0.08	0.16	2.17	1.40	0.91	0.32	97.40	0.35	0.065
No SIMS data for crystals below														
061506L_1, Cpx2	41.09	0.17	0.20	0.34	53.82	0.05	0.08	1.97	1.03	0.83	0.23	97.68	0.53	0.030
061506L_1, Cpx2	40.63	0.34	0.19	0.36	53.24	0.07	0.07	2.20	0.88	0.93	0.20	96.86	0.45	0.029
061506L_1, Cpx2	41.47	0.22	0.16	0.33	53.29	0.08	0.08	1.87	0.96	0.79	0.22	97.47	0.60	0.031
061506L_1, Cpx2	41.29	0.25	0.16	0.35	53.35	0.08	0.07	1.97	0.90	0.83	0.20	97.39	0.57	0.028
061506L_1, Cpx2	41.41	0.30	0.18	0.35	53.42	0.08	0.09	2.45	0.85	1.03	0.19	97.91	0.36	0.036
061506L_1, Cpx5-1	41.14	0.20	0.16	0.36	53.03	0.06	0.08	2.01	0.98	0.85	0.22	96.94	0.52	0.032
061506L_1, Cpx5-1	40.98	0.21	0.22	0.37	53.91	0.13	0.11	2.03	1.01	0.85	0.23	97.89	0.51	0.042
061506L_1, Cpx5-1	41.41	0.19	0.18	0.37	53.57	0.09	0.12	1.87	0.98	0.79	0.22	97.77	0.60	0.047
061506L_1, Cpx5-2	41.15	0.13	0.15	0.36	53.27	0.06	0.09	1.95	1.01	0.82	0.23	97.13	0.54	0.036
061506L_1, Cpx5-2	41.28	0.08	0.15	0.36	53.12	0.05	0.10	1.94	1.08	0.81	0.24	97.10	0.53	0.040
061506L_1, Cpx5-2	41.09	0.14	0.20	0.35	53.27	0.12	0.10	1.94	1.12	0.82	0.25	97.26	0.52	0.040
061506L_1, Cpx5-2	41.34	0.12	0.18	0.35	52.87	0.09	0.13	1.95	0.97	0.82	0.22	96.96	0.55	0.051
061506L_1, Cpx5-2	41.05	0.16	0.19	0.35	53.85	0.17	0.11	1.86	1.01	0.78	0.23	97.73	0.59	0.042

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Label	P ₂ O ₅	SiO ₂	Ce ₂ O ₃	MgO	CaO	Na ₂ O	SO ₃	F	Cl	O=F	O=Cl	Sum (anhydrous)	Calc H ₂ O	S
061506L_1, Cpx5-2	41.54	0.15	0.22	0.35	53.30	0.15	0.15	1.86	1.03	0.78	0.23	97.73	0.59	0.059
061506L_1, Cpx5-2	40.82	0.17	0.24	0.33	53.00	0.10	0.18	1.93	1.15	0.81	0.26	96.85	0.51	0.070
061506L_1, Cpx5-2	41.10	0.14	0.18	0.35	52.93	0.16	0.17	1.98	1.02	0.83	0.23	96.96	0.52	0.067
061506L_1, Cpx5-2	41.33	0.11	0.19	0.35	53.04	0.05	0.14	1.86	1.05	0.78	0.24	97.09	0.57	0.055
061506L_1, Cpx5-2	40.87	0.17	0.17	0.35	53.84	0.13	0.08	1.89	1.07	0.80	0.24	97.55	0.55	0.033
061506L_1, Cpx5-2	41.00	0.14	0.14	0.35	52.66	0.09	0.10	1.91	1.04	0.81	0.24	96.38	0.54	0.038
061506L_1, Cpx5-2	41.05	0.16	0.17	0.36	53.03	0.12	0.08	1.93	0.96	0.81	0.22	96.83	0.56	0.033
061506L_1, Cpx5-2	41.16	0.33	0.17	0.36	53.63	0.09	0.09	2.14	0.91	0.90	0.20	97.77	0.49	0.036
061506L_1, Cpx5-2	40.97	0.19	0.16	0.34	53.22	0.07	0.12	1.93	0.93	0.81	0.21	96.89	0.57	0.048
061506L_1, Cpx5-2	41.04	0.10	0.16	0.34	52.74	0.05	0.08	1.87	1.09	0.79	0.25	96.43	0.54	0.032
061506L_1, Cpx5-2	41.32	0.22	0.19	0.36	53.78	0.10	0.11	2.50	0.77	1.05	0.17	98.12	0.36	0.043
061506L_1, Cpx5-2	41.06	0.20	0.15	0.35	52.66	0.07	0.09	2.50	0.78	1.05	0.18	96.63	0.34	0.038
061506L_1, Cpx5-2	41.59	0.15	0.20	0.35	53.21	0.04	0.07	2.23	0.97	0.94	0.22	97.64	0.43	0.027
061506L_1, Cpx5-2	41.50	0.17	0.22	0.33	53.57	0.05	0.08	1.87	0.99	0.79	0.22	97.76	0.60	0.031
061506L_1, Cpx5-2	40.15	0.14	0.18	0.39	53.26	0.08	0.08	2.15	1.06	0.91	0.24	96.35	0.41	0.030
061506L_1, Cpx5-2	41.56	0.27	0.13	0.35	53.01	0.07	0.12	2.43	0.82	1.02	0.18	97.54	0.38	0.048
061506L_1, Cpx5-3	41.23	0.14	0.19	0.36	53.70	0.09	0.12	1.87	0.96	0.79	0.22	97.66	0.60	0.050
061506L_1, Cpx5-3	41.08	0.24	0.18	0.36	53.15	0.05	0.09	2.29	0.90	0.97	0.20	97.18	0.41	0.037
061506L_1, Cpx5-3	41.12	0.19	0.20	0.37	52.88	0.15	0.06	1.86	1.05	0.78	0.24	96.84	0.57	0.025
061506L_1, Cpx5-3	41.06	0.19	0.19	0.36	51.22	0.12	0.07	1.86	1.00	0.78	0.23	95.06	0.56	0.027
061506L_1, Cpx5-3	41.21	0.13	0.14	0.37	52.83	0.01	0.14	1.91	1.02	0.80	0.23	96.74	0.55	0.056
061506L_1, Cpx6-1	41.05	0.17	0.12	0.40	52.96	0.04	0.08	1.85	0.85	0.78	0.19	96.56	0.62	0.033

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Label	P ₂ O ₅	SiO ₂	Ce ₂ O ₃	MgO	CaO	Na ₂ O	SO ₃	F	Cl	O=F	O=Cl	Sum (anhydrous)	Calc H ₂ O	S
061506L_1, Cpx6-1	41.59	0.14	0.13	0.38	52.86	0.03	0.07	1.93	0.83	0.81	0.19	96.96	0.60	0.029
061506L_1, Cpx6-1	41.45	0.18	0.12	0.39	53.21	0.09	0.12	1.82	0.79	0.77	0.18	97.22	0.66	0.046
061506L_1, Cpx6-1	41.02	0.18	0.11	0.39	52.74	0.04	0.08	1.78	0.86	0.75	0.19	96.26	0.64	0.031
061506L_1, Cpx6-2	40.84	0.18	0.11	0.38	52.49	0.11	0.10	1.88	0.91	0.79	0.21	96.02	0.58	0.041
061506L_1, Cpx6-2	41.41	0.19	0.13	0.37	53.20	0.06	0.09	1.88	0.93	0.79	0.21	97.25	0.60	0.036
061506L_1, Cpx6-2	41.04	0.31	0.19	0.39	52.88	0.02	0.08	1.87	0.91	0.79	0.21	96.70	0.60	0.031
061506L_1, Cpx6-2	41.00	0.17	0.16	0.37	53.14	0.08	0.10	1.82	0.95	0.77	0.21	96.80	0.61	0.042

Table C2. EPMA data for apatite crystals from Merapi 2010 deposits (crystals with labels in bold were also analyzed by SIMS in Table 3.1).

Label	P ₂ O ₅	SiO ₂	Ce ₂ O ₃	MgO	CaO	Na ₂ O	SO ₃	F	Cl	O=F	O=Cl	Sum (anhydrous)	Calc H ₂ O	S
1011211A, Amph1	39.85	0.36	0.01	0.15	54.69	0.10	0.61	1.48	0.56	0.62	0.13	97.07	0.93	0.244
10111123, Amph4-1 #1	40.31	0.40	0.02	0.20	54.57	0.13	0.70	1.42	0.51	0.60	0.12	97.53	0.99	0.279
10111123, Amph4-1 #1	40.34	0.33	0.01	0.17	54.11	0.13	0.60	1.59	0.51	0.67	0.11	97.01	0.90	0.241
10111123, Amph4-1 #1	40.09	0.26	0.01	0.17	54.30	0.10	0.52	1.48	0.52	0.62	0.12	96.71	0.94	0.209
10111123, Amph4-2	40.68	0.19	0.03	0.17	53.99	0.07	0.32	1.47	0.55	0.62	0.12	96.72	0.94	0.127
11051903, Cpx8, Ap1	41.27	0.42	0.21	0.27	53.07	0.11	0.40	2.19	1.10	0.92	0.25	97.87	0.42	0.160
11051903, Cpx8, Ap3	42.54	0.22	0.27	0.26	53.09	0.02	0.08	2.15	0.98	0.91	0.22	98.48	0.49	0.031
1011211A, Cpx6	41.28	0.29	0.22	0.24	54.34	0.04	0.09	1.81	1.03	0.76	0.23	98.35	0.62	0.036
1011211A, Cpx5-1	42.41	0.28	0.20	0.28	54.68	0.01	0.09	1.92	1.06	0.81	0.24	99.88	0.59	0.036
10111123, Cpx5	41.20	0.26	0.18	0.40	55.08	0.06	0.05	2.03	0.92	0.85	0.21	99.11	0.55	0.021
10111123, Cpx5	41.29	0.15	0.19	0.37	54.44	0.08	0.03	1.91	0.89	0.81	0.20	98.34	0.60	0.013
10111123, Cpx5	40.89	0.13	0.18	0.36	54.72	0.05	0.04	2.01	0.91	0.85	0.20	98.24	0.55	0.015
10111123, Cpx5	40.93	0.15	0.17	0.36	54.11	0.12	0.15	1.89	0.92	0.80	0.21	97.80	0.59	0.061
10111123, Cpx5	41.16	0.16	0.15	0.37	54.91	0.09	0.20	1.98	0.93	0.84	0.21	98.91	0.57	0.080
10111123, Cpx5	40.94	0.11	0.14	0.36	54.70	0.07	0.04	1.91	0.89	0.80	0.20	98.16	0.60	0.018
10111123, Cpx5	41.03	0.22	0.20	0.38	54.34	0.06	0.06	1.87	0.95	0.79	0.21	98.11	0.60	0.024
10111123, Cpx5	41.22	0.18	0.21	0.37	54.28	0.06	0.05	1.98	0.89	0.83	0.20	98.20	0.57	0.019
1011211A, Pl4	42.40	0.24	0.29	0.32	54.20	0.06	0.08	1.96	0.99	0.83	0.22	99.49	0.58	0.033
10111123, Pl3	40.95	0.20	0.21	0.32	54.68	0.07	0.05	1.63	0.74	0.69	0.17	97.98	0.77	0.019
10111123, Pl3	40.24	0.26	0.15	0.31	54.60	0.19	0.32	1.58	0.77	0.66	0.17	97.58	0.77	0.126
10111123, Pl1, Ap1	40.84	0.11	0.13	0.39	55.08	0.08	0.24	1.80	0.87	0.76	0.20	98.60	0.66	0.097
10111123, Pl1, Ap1	41.04	0.30	0.14	0.41	54.93	0.10	0.23	1.94	0.84	0.82	0.19	98.92	0.61	0.093

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Label	P ₂ O ₅	SiO ₂	Ce ₂ O ₃	MgO	CaO	Na ₂ O	SO ₃	F	Cl	O=F	O=Cl	Sum (anhydrous)	Calc H ₂ O	S
1011211a, GmAp7	41.20	0.17	0.25	0.27	54.36	0.01	0.08	2.00	0.89	0.84	0.20	98.18	0.56	0.030
11051903, GmAp6	41.17	0.22	0.29	0.28	54.43	0.03	0.07	1.82	1.06	0.77	0.24	98.36	0.60	0.028
10111123, GmAp3	41.37	0.22	0.19	0.35	54.48	0.08	0.12	2.13	1.02	0.90	0.23	98.84	0.48	0.049
10111123, GmAp3	41.58	0.20	0.23	0.34	54.19	0.07	0.02	2.11	0.99	0.89	0.22	98.62	0.49	0.009
10111123, GmAp3	41.39	0.14	0.19	0.34	53.70	0.07	0.04	2.11	1.02	0.89	0.23	97.88	0.48	0.016
10111123, GmAp3	41.33	0.13	0.19	0.35	54.04	0.06	0.13	2.23	0.96	0.94	0.22	98.26	0.44	0.053
10111123, GmAp3	41.28	0.13	0.18	0.35	54.16	0.07	0.06	2.24	1.02	0.94	0.23	98.31	0.42	0.024
10111123, GmAp3	41.64	0.15	0.18	0.34	54.61	0.08	0.06	1.89	1.00	0.80	0.22	98.92	0.60	0.025
10111123, GmAp3	41.40	0.14	0.15	0.35	54.37	0.08	0.06	2.27	0.99	0.96	0.22	98.65	0.42	0.026
10111123, GmAp3	41.53	0.15	0.21	0.34	53.58	0.06	0.06	2.22	0.92	0.93	0.21	97.93	0.45	0.026
10111123, GmAp3	41.54	0.15	0.18	0.34	54.50	0.08	0.09	2.14	0.96	0.90	0.22	98.86	0.49	0.035
10111123, GmAp3	41.13	0.13	0.22	0.34	54.35	0.07	0.05	2.27	1.04	0.96	0.23	98.41	0.40	0.021
10111123, GmAp3	41.78	0.09	0.21	0.35	54.25	0.08	0.03	2.09	0.94	0.88	0.21	98.73	0.52	0.012
10111123, GmAp3	41.21	0.17	0.22	0.34	54.23	0.06	0.05	2.16	0.91	0.91	0.21	98.24	0.48	0.019
10111123, GmAp3	41.24	0.15	0.24	0.34	54.16	0.06	0.04	2.19	0.96	0.92	0.22	98.24	0.46	0.017
10111123, GmAp3	41.21	0.17	0.21	0.34	54.18	0.08	0.06	2.42	0.91	1.02	0.20	98.34	0.36	0.024
10111123, GmAp3	41.16	0.23	0.21	0.33	53.65	0.13	0.09	2.22	0.97	0.94	0.22	97.83	0.43	0.036
10111123, GmAp3	41.24	0.18	0.19	0.34	54.11	0.11	0.25	2.46	0.99	1.03	0.22	98.60	0.33	0.100
10111123, GmAp3	41.35	0.14	0.22	0.35	54.74	0.07	0.08	2.08	0.93	0.88	0.21	98.88	0.53	0.032
10111123, GmAp3	41.33	0.17	0.19	0.34	54.65	0.08	0.08	2.58	0.95	1.09	0.22	99.09	0.29	0.033
No SIMS data for crystals below														
10111123, Cpx4	40.62	0.17	0.17	0.30	54.22	0.07	0.06	2.24	1.03	0.95	0.23	97.73	0.40	0.026

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Label	P ₂ O ₅	SiO ₂	Ce ₂ O ₃	MgO	CaO	Na ₂ O	SO ₃	F	Cl	O=F	O=Cl	Sum (anhydrous)	Calc H ₂ O	S
10111123, Cpx4	40.75	0.19	0.14	0.29	54.14	0.06	0.08	2.41	1.11	1.01	0.25	97.92	0.31	0.034
10111123, Cpx3	41.32	0.17	0.19	0.35	55.87	0.05	0.07	2.00	0.87	0.84	0.20	99.85	0.59	0.027
10111123, Cpx3	41.22	0.19	0.23	0.37	55.03	0.10	0.13	2.83	0.90	1.19	0.20	99.60	0.19	0.052
10111123, Cpx3	40.26	0.43	0.17	0.39	54.69	0.18	0.58	1.91	0.90	0.80	0.20	98.52	0.60	0.232
10111123, Cpx2	40.64	0.18	0.16	0.36	54.19	0.07	0.07	2.40	1.12	1.01	0.25	97.92	0.31	0.030
10111123, Cpx2	40.60	0.16	0.18	0.37	54.20	0.10	0.08	2.41	1.11	1.02	0.25	97.95	0.30	0.031
10111123, Cpx2	40.41	0.20	0.19	0.36	53.93	0.12	0.06	2.30	1.11	0.97	0.25	97.45	0.35	0.022
10111123, Pl2	40.38	0.29	0.13	0.38	54.75	0.16	0.44	2.13	1.08	0.89	0.24	98.59	0.46	0.174
10111123, Pl2	40.93	0.25	0.14	0.38	53.86	0.16	0.39	2.16	1.03	0.91	0.23	98.15	0.45	0.157
10111123, OxAp1	40.81	0.30	0.19	0.33	53.78	0.07	0.08	2.28	0.99	0.96	0.22	97.65	0.40	0.032
10111123, OxAp1	40.84	0.11	0.16	0.32	53.75	0.07	0.07	2.24	0.96	0.94	0.22	97.37	0.41	0.029
10111123, OxAp1	40.75	0.15	0.17	0.31	53.70	0.00	0.06	2.29	0.97	0.96	0.22	97.22	0.39	0.024
10111123, GmAp4	40.87	0.16	0.18	0.35	53.74	0.08	0.07	2.39	1.10	1.01	0.25	97.68	0.32	0.027
10111123, GmAp4	41.08	0.19	0.19	0.35	53.95	0.11	0.04	2.39	1.10	1.01	0.25	98.13	0.33	0.016
10111123, OxAp2-1	42.27	0.10	0.17	0.38	52.58	0.09	0.07	2.64	1.05	1.11	0.24	98.01	0.23	0.026
10111123, OxAp2-1	40.81	0.14	0.19	0.36	54.07	0.09	0.06	2.77	1.08	1.17	0.24	98.17	0.15	0.026
10111123, OxAp2-2	41.30	0.22	0.22	0.36	53.74	0.09	0.07	2.83	1.18	1.19	0.27	98.55	0.11	0.029
10111123, OxAp2-2	40.86	0.18	0.21	0.38	54.63	0.12	0.12	2.15	1.06	0.90	0.24	98.56	0.45	0.048
10111123, OxAp2-3	40.46	0.15	0.17	0.37	53.49	0.05	0.06	1.99	1.11	0.84	0.25	96.76	0.48	0.023
10111123, OxAp2-3	42.15	0.15	0.16	0.36	52.97	0.11	0.09	1.51	1.06	0.63	0.24	97.68	0.75	0.037
10111123, OxAp2-3	40.44	0.07	0.18	0.36	54.01	0.07	0.10	2.06	1.10	0.87	0.25	97.26	0.46	0.038
10111123, Pl4	39.57	0.32	0.15	0.34	53.25	0.14	0.53	2.91	1.20	1.22	0.27	96.92	0.03	0.213

Appendix D: Regression of experimental data from the literature for determining

$K_{D_{Al-Si}}^{Amp-melt}$ and the amphibole-liquid thermobarometry calculation

We have used the amphibole-liquid barometer from Putirka (2016), which requires the known compositions of the liquids in equilibria with given amphibole crystal. To determine the equilibria liquids, we have used an equilibrium-test parameter based on Al-Si exchange between amphibole and the melt, i.e. $K_{D_{Al-Si}}^{Amp-melt} = \frac{x_{Al}^{Amp} \cdot x_{Si}^{melt}}{x_{Si}^{Amp} \cdot x_{Al}^{melt}}$, whose value has been found to be quite T-independent (Sisson and Grove, 1993). To constrain the variation of $K_{D_{Al-Si}}^{Amp-melt}$ with T and melt compositions, we have compiled a large number of experimental data from literature ($N=34$) determined at 800-1000 °C, 200-400 MPa for the melts of basaltic to rhyolitic compositions (Sisson and Grove, 1993; Scaillet and Evans, 1999; Pichavant et al., 2002; Grove et al., 2003; Rutherford and Devine, 2003; Costa et al., 2004; Sato et al., 2005). Using a least-squares regression method, the calculated value of $K_{D_{Al-Si}}^{Amp-melt}$ is 0.96 ± 0.04 (Fig. D1). This value can be used to calculate the mole Al/Si of the equilibria melt, using mole Al/Si measured from amphiboles.

Based on the linear correlation of SiO₂ and Al/Si in the melt with evolution (between the bulk rocks and the matrix glass; see Fig. 3.9 in text), the mole Al/Si in the melt, i.e. $\frac{x_{Al}^{melt}}{x_{Si}^{melt}}$, can be converted into absolute SiO₂ concentrations using: $\frac{x_{Al}^{melt}}{x_{Si}^{melt}} = -0.97 \times c_{SiO_2} + 0.94$, where c_{SiO_2} is the mass fraction of SiO₂ in the melt. Using the determined SiO₂ concentrations in the melt, we can obtain the compositions of other major elements by mixing different proportions of the bulk rocks with the matrix glass, based on the

linear correlation between SiO₂ and major elements shown in the Harker diagrams (see Fig. 3.7 in text).

Fig. D1. Mole Al/Si in amphibole and the equilibria melts, reported in literature for experiments that cover P-T range of 800-1000 °C and 200-400 MPa, and melt compositions from basalt to rhyolite (basalt: red; andesite: green; dacite: blue; rhyolite: black). The regression line is forced to the origin, and its slope equals to $K_D^{Amp-melt}_{Al-Si}$ (best fit marked in dark solid line, and the uncertainty range marked in blue dashed lines). Data sources: S&G93 = Sisson and Grove, 1993; G03 = Grove et al., 2003; P02 = Pichavant et al., 2002; C04 = Costa et al., 2004; S05 = Sato et al., 2005; R&D03 = Rutherford and Devine, 2003; S&E99 = Scaillet and Evans, 1999.

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Chapter 4

Multicomponent diffusion of F, Cl and OH in apatite with application to magma ascent rates

Multicomponent diffusion of F, Cl and OH in apatite with application to magma ascent rates

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Abstract

Chemical zoning in igneous minerals is a potential record of the time, processes, and thermal evolution that were in operation during the lifetime of a given magma reservoir. The volatile contents (Cl, F, OH) of apatite in terrestrial and extraterrestrial plutonic and volcanic rocks has been used to understand a variety of magmatic processes, but their diffusivities are still poorly constrained. Here we report new experimental results on Cl, F and OH diffusion in apatite and apply them to constrain magma ascent rates. Diffusion in oriented natural Durango fluorapatite crystals was investigated at 800-1100 °C, 1-atm, and oxygen fugacity (f_{O_2}) of Wüstite-Magnetite (WM) buffer. The experimental charges and chemical profiles were investigated with a range of methods including scanning electron microscopy (SEM), transmission electron microscopy (TEM), electron probe microanalyses (EPMA), secondary ion mass spectrometry (SIMS), and nuclear reaction analyses (NRA).

We find that the Cl profiles show evidence of uphill diffusion that is likely related to the co-existence of three monovalent anions (Cl, F, OH) at the same site of apatite structure. We have modelled the chemical gradients of F, Cl, and OH using a multicomponent diffusion model from which the tracer diffusion coefficients D_i^* of each component were extracted. The calculated values of D_i^* ($\parallel \mathbf{c}$) show a general relation of $D_F^* > D_{Cl}^* > 7 \times D_{OH}^*$, and define the following Arrhenius relations (parallel to the c-axis at 1-atm) as:

$$D_{Cl}^* = 5.1 \left(\begin{smallmatrix} +17 \\ -4.0 \end{smallmatrix} \right) \times 10^{-5} \times \left[\exp \left(\frac{-290 (\pm 19) \text{ kJ} \cdot \text{mol}^{-1}}{RT} \right) \right] \text{ m}^2 \cdot \text{s}^{-1}$$

$$D_F^* = 9 \left(\begin{smallmatrix} +88 \\ -8 \end{smallmatrix} \right) \times 10^{-5} \times \left[\exp \left(\frac{-288 (\pm 73) \text{ kJ} \cdot \text{mol}^{-1}}{RT} \right) \right] \text{ m}^2 \cdot \text{s}^{-1}$$

$$D_{OH}^* = 1.7 \left(\begin{smallmatrix} +22 \\ -1.6 \end{smallmatrix} \right) \times 10^{-2} \times \left[\exp \left(\frac{-397 (\pm 60) \text{ kJ} \cdot \text{mol}^{-1}}{RT} \right) \right] \text{ m}^2 \cdot \text{s}^{-1}$$

The activation energy $E_a = 290 (\pm 19) \text{ kJ} \cdot \text{mol}^{-1}$ for Cl is equivalent (considering error) to that reported by Brenan (1994), but D_0 from this study is about 5-time smaller. D_{Cl}^* and D_{OH}^* parallel to the a-axis ($\parallel \mathbf{a}$) are 1-2 orders of magnitude slower than those parallel to the c-axis ($\parallel \mathbf{c}$), indicating anisotropic diffusion of Cl and OH in apatite. Preliminary data for the S diffusivities at 800 and 900 °C show values between the diffusivities of Cl and OH.

The diffusion coefficients and model can be used to estimate the timescales of re-equilibration of volatiles in apatite in a variety of contexts, from plutonic rocks and layered intrusions, to volcanic rocks and meteorites. We show that for example, the magma ascent rates may be determined by the Cl zoning in natural volcanic apatite,

which could contribute to better understanding of the eruption styles of a variety of volcanoes with large significance for the volcanic hazards assessment.

Contributions

Weiran Li: Sample preparation, performing diffusion experiments, analyzing diffusion profiles, and establishing the program for the diffusion modelling.

Fidel Costa: Discussion on experiment design, sample preparation and data interpretation.

Sumit Chakraborty: Discussion on performing the experiments and modelling on diffusion profiles.

Kazuhide Nagashima: Assistance in the SIMS analyses.

4.1. Introduction

Apatite is a common mineral in terrestrial igneous, metamorphic, and sedimentary rocks on Earth (e.g. Piccoli and Candela, 1994; Boudreau, 1995; Peng et al., 1997; Boyce and Hervig, 2008; Boyce and Hervig, 2009; Van Hoose et al, 2013; Kusebauch et al., 2015; Scott et al., 2015; Webster and Piccoli, 2015; Stock et al., 2016; Stock et al., 2018), as well as in rocks from the Moon (e.g. McCubbin et al., 2010; Greenwood et al., 2011; Boyce et al., 2014; Ustunisik et al., 2015; Brounce et al., 2019; Wang et al., 2019), and in the Martian meteorites (Greenwood et al., 2008; McCubbin and Nekvasil, 2008; Filiberto and Treiman, 2009). Apatite ($[\text{Ca}_{10}\text{P}_6\text{X}_2]$, where $\text{X} = \text{F}, \text{Cl}, \text{OH}$) can incorporate various volatile species (e.g. fluorine, chlorine, hydroxyl, oxygen, sulfur, carbonate) into its structure (e.g. Piccoli and Candela, 2002; Hughes, 2015), thus it is a powerful tool of investigating volatile concentrations in the melt/fluids from which it crystallized/grew. Previous experimental and thermodynamic studies have proposed a range of apatite-melt equilibrium partitioning relations for estimating the melt volatile budgets (see Chapter 2). Successful application of such relations to understanding magmatic processes requires a good knowledge of the diffusivities of volatiles in apatite. If the diffusion rates are too fast, then the apatite crystals may re-equilibrate under changing temperature, pressure, or/and composition, and their compositions would not reflect those of the original melts from which they crystallised. Evidence of partial re-equilibration of apatite has been found in the zoning of Cl and OH (or F) at the rim of apatite crystals (of $< 80 \mu\text{m}$ to $> 300 \mu\text{m}$ in lengths) from volcanic rocks (Boyce and Hervig, 2008; Scott et al., 2015; see Chapter 3 of this thesis), and from the plutonic rocks (Cornejo and Mahood, 1997).

There have been quite a few experimental studies on diffusion rates of cations (e.g. Sr, Pb, U, Th, REEs) and noble gas element (e.g. He) in apatite (see review in Cherniak et al., 2010). However, diffusivity data for volatiles (i.e. F, Cl) in apatite were only reported by Brenan (1994), who found that the diffusion rates of Cl parallel to the c-axis are much faster than that parallel to the a-axis (by at least 2 orders of magnitudes), which could explain the anisotropic Cl zoning observed from the natural volcanic apatite (Boyce and Hervig, 2008; see Chapter 3 of this thesis). Such anisotropic Cl diffusion is likely due to the anion column parallel to the c-axis in the apatite structure, which allows faster migration of Cl along this direction (e.g. Piccoli and Candela, 2002; Hughes, 2015) and may also explain the anisotropic OH zoning in some apatite phenocrysts (Boyce and Hervig, 2008). Moreover, the Cl diffusivities determined from experiments at given temperature have been found to show a 6-fold variation, affected by the abundances of OH in apatite. This implies some compositional effects on Cl diffusion, likely indicating a quite complex mechanism of Cl diffusion, which requires more experimental investigation. In addition, S in natural apatite has a variety of zoning patterns (Van Hoose et al., 2013; Scott et al., 2015; see Chapter 3 of this thesis) that have been interpreted used to understand sulfur and volatile fluxes of magmas, but S diffusion rates have not been yet determined.

In this study we reported new data for the diffusion rates of F, Cl, OH and S in apatite determined at 800-1100 °C, 1-atm, and oxygen fugacity of Wüstite-Magnetite buffer. Experimental conditions and multiple analytical approaches used for investigation of the run products are described in Section 4.2. With the diffusion profiles obtained from the run products (Sections 4.3 and 4.4), we calculated the diffusion rates of F-Cl-OH using a multicomponent diffusion model (Section 4.5), and applied this model to natural

apatite from the Merapi 2006 rocks to constrain the timescales of the magma ascent before this eruption (Section 4.6).

4.2. Experimental and analytical approaches

4.2.1. Starting materials and diffusion couples

Gem-quality apatite crystals from Durango (Mexico) and Morocco were purchased from Excalibur Mineral Corp (USA), and used as starting materials. The two types of apatite have different volatile compositions, which were determined using a Cameca ims-1280 secondary ion mass spectrometry (SIMS) at University of Hawai‘i at Mānoa, USA (see analytical conditions in Section 3.2, Chapter 3). The Durango crystals are close to the end-member fluorapatite (mole fractions calculated based on F, Cl and OH compositions: $X_F \approx 92\%$, $X_{Cl} \approx 5\%$ and $X_{OH} \approx 3\%$), whereas the Morocco crystals have higher Cl and OH ($X_F \approx 66\%$, $X_{Cl} \approx 11\%$, $X_{OH} \approx 23\%$) (Fig. 4.1; Table 4.1). Both starting materials have low CO₂ contents (< 34 ppm). The Durango crystals have much higher S (of ~ 1600 ppm) than the Morocco crystals (≤ 15 ppm). Analytical errors are ~ 2-5 % (relative) for F and H₂O, and ~ 5-20% for Cl and S, and ~10-30% for CO₂ (due to lower abundance).

Fig. 4.1. F-Cl-OH ternary diagram showing the compositions of the natural Durango fluorapatite (marked in *circles*), and the OH and Cl-rich natural apatite from Morocco (marked in *triangle*; measured by SIMS). Error bars show 2σ standard deviation of the mean from all analyses on the same crystals ($N=8$; Table 4.1).

Table 4.1. Compositions of the two types of apatite used as starting materials, measured by SIMS and EPMA.

SIMS	Durango (N=8)		Morocco (N=8)	
wt. %	Value	2 σ	Value	2 σ
F	4.11	0.35	2.78	0.15
Cl	0.44	0.05	0.84	0.07
S	0.158	0.057	0.0012	0.0001
H ₂ O	0.048	0.011	0.46	0.02
CO ₂	0.0016	0.0007	0.0028	0.0003
Mole fraction				
X _F	0.924	0.079	0.662	0.036
X _{Cl}	0.053	0.006	0.107	0.009
X _{OH}	0.023	0.079	0.231	0.037
EPMA	Durango (N=19)			
CaO	54.0	0.2		
P ₂ O ₅	41.8	0.6		
SiO ₂	0.36	0.03		
Na ₂ O	0.19	0.03		
Ce ₂ O ₃	0.59	0.07		
S	0.12	0.01		
F	3.51	0.08		
Cl	0.405	0.007		
Calc, H ₂ O	0.08	0.04		
<i>Structural formula: Ca₁₀(PO₄)(X)₂, calculated using 26 O following Ketcham, 2015</i>				
Ca	9.37			
P	5.73			
Si	0.06			
Na	0.06			
Ce	0.03			
S	0.04			
F	1.80			
Cl	0.11			
Calc, OH	0.09			

The Durango crystals were orientated either parallel or normal to the long direction of the crystals (i.e. the c-axis). Orientations of three crystals (4d, 6d#1, 6d#2) that were analyzed in this study were determined a posteriori using the EBSD technique (electron backscatter diffraction) on a scanning electron microscope, which show less than three-degree tilts from the expected orientations. These orientated Durango crystals were then cut into slices of ~ 2 mm in thickness using a wire saw. The crystal slices were mounted in epoxy, and polished using diamond compounds (to $0.25\ \mu\text{m}$) and a highly alkaline colloidal silica solution (OPS). Then the slices were cut into cuboids (of $5\times 5\times 2\ \text{mm}^3$) or cubes (of $2\times 2\times 2\ \text{mm}^3$). Crystals of Morocco apatite were grinded into fine powders (of $\sim 5\text{-}100\ \mu\text{m}$ in length) using an agate mortar.

The two types of apatite crystals of different volatile compositions were made into diffusion couples in two forms: (1) the Durango cubes embedded in Morocco powders, referred to as crystal-powder couple hereafter, and (2) the Durango cuboids with the polished sides deposited with thin film that is expected to have the composition of Morocco apatite, referred to as substrate-thin film couple. The thin films were made using the pulse laser deposition technique (PLD; c.f. Dohmen et al., 2002) at Ruhr Universität Bochum, Germany, where the Morocco powders were compressed into a pellet and ablated with a 10-Hz pulsed laser for deposition. The deposition times were 15 mins for DAp7 using laser power of $\sim 212\ \text{mJ}$, 5 mins for DAp9 and DAp11 using laser power of $\sim 192\ \text{mJ}$, and 7 mins for DAp15 and DAp16 using laser power of $\sim 96\ \text{mJ}$. The thin films were $\sim 100\text{-}200\ \text{nm}$ thick, estimated from their birefringence color on a clean Si wafer (refractive indices of apatite: ~ 1.63), and later observed using transmission electron microscope, and determined with Nuclear Reaction Analysis (see below).

The diffusion couples were loaded in small alumina crucibles (~ 8 mm in diameter). In the crystal-powder couple experiments, the polished side of the crystal was placed facing the bottom of the crucible for good contact with the powders (Fig. 4.2a), whereas the substrate-thin film couples were placed with the thin film facing upward (Fig. 4.2b). The small crucible was placed into a larger alumina crucible (of ~ 2 cm in diameter), which was then tied to an alumina rod using platinum wires (Fig. 4.2c) to be loaded into the furnace. The crucibles have an opening on top, so that the samples were exposed to the furnace atmosphere during experiments.

(a) Durango crystals

(b) Crystal-Powder couple

(c) Substrate-Thin film couple

Fig. 4.2. (a) Durango apatite crystals cut into small cubes ($2 \times 2 \times 2$ mm³) or cuboids ($5 \times 5 \times 2$ mm³), shown in a view parallel to the c-axis. (b) A diffusion couple made up of a F-rich Durango cube (D) with its polished side facing downward, embedded in powders made from Cl- and OH-rich Morocco apatite crystals (M). (c) A Diffusion couple made up of a Durango cuboid (D) and a laser deposited thin film (TF) made from Morocco apatite powders.

4.2.2. Experimental conditions

All diffusion anneals were performed in a vertical gas-mixing furnace at atmospheric pressure. Temperatures were monitored with a B-type thermocouple placed within 2 cm of the sample container and remained within ± 2 °C of the desired temperature during experiments. Oxygen fugacity (fO_2) was maintained at the Wüstite-Magnetite (WM) buffer (e.g. $fO_2 = 5.0 \times 10^{-12}$ bars at 1100 °C), using a continuous CO-CO₂ gas flow. The furnace was equilibrated to the run conditions (of T and fO_2) for at least 30 mins, after which the crystals were loaded into the furnace close to the thermocouple. The crystal-powder couples (for diffusion $\parallel$ c) were run at 1100 °C for 67-161 hours, whereas the substrate-thin film couples were run at 800-1000 °C for 40-220 mins for the investigation of diffusion $\parallel$ c, and at 950 °C for ~ 21 hours for diffusion $\parallel$ a. The experiments were terminated by quickly removing the samples from the surface for annealing in the air, where the temperatures quickly dropped down to < 100 °C within 2-3 mins. The experimental conditions for the samples used for diffusion modelling are summarized in Table 4.2. The crystal-powder couples annealed for shorter times of 1-17 hours show diffusion distances that are too short (e.g. of < 20 μm for F) for precise determination of the diffusivities, thus they are not reported in this manuscript.

Table 4.2. Experimental conditions (1-atm).

Crystal-powder couples					
Sample Label	Orientation	T (°C)	Time (hrs)	logfO ₂ (WM buffer)	
4d	c	1104	66	-11.30	
6d#1	c	1100	161	-11.02	
6d#2	c	1100	161	-11.02	
Thin film samples					
Sample Label	Orientation	T (°C)	Time (hrs)	logfO ₂ (WM buffer)	Thin film label Thin film thickness (nm)
DAp7	c	998	2.00	-12.64	TF2 ~ 210
DAp9	c	804	3.67	-15.44	TF4 ~ 130
DAp11	c	900	0.67	-14.78	TF4 ~ 130
DAp15	c	900	2.00	-14.76	TF7 ~ 170
DAp16	a	950	21.12	-13.57	TF7 ~ 170

4.2.3. EPMA analyses of crystal-powder couples

The Durango apatite crystals were taken out from the powders and mounted in epoxy with their polished sides oriented perpendicular to the epoxy surface (Fig. 4.3). One crystal (4d) was kept within the powder and sectioned together with the whole alumina crucible for investigation of the contact at the interface.

X-ray maps and compositional profiles were acquired, using a JEOL JXA 8530F field emission gun electron microprobe (EPMA), at the Facility for Analysis Characterization Testing and Simulation at Nanyang Technological University (Singapore). X-ray maps for F, Cl and S (of $\sim 100 \times 100 \mu\text{m}^2$) were acquired from the corner of the crystals, using an accelerating voltage of 15 kV, beam current of 25 nA, and dwell time of ~ 70 ms (see methods in Chapter 3). Compositional profiles (of 1- μm spacing) were acquired perpendicular to the crystal boundary, using a voltage of 15 kV and a focused beam with low current (of 10 nA), in order to minimize the migration of F during analyses. Given the orientation of our samples (i.e. with the c-axis perpendicular to the electron beam, the interference of F migration, that was mostly found parallel to the c-axis, should be negligible (e.g. Stormer et al., 1993; Goldoff et al., 2012; Stock et al., 2015). The counting times for analyses of different elements, the standards used for calibration, and the procedures used for data correction were referred to Li et al., 2019 (submitted), except for acquiring more precise Cl concentrations, here we used longer on-peak counting time (of ~ 120 s for Cl). Relative errors of our data are $\sim 1.5\%$ for F, $\sim 1\%$ for Cl, $\sim 7\text{-}10\%$ for S (due to its low abundance), and $< 1\%$ for the major elements (e.g. Ca, P).

4.2.4. TEM observation of thin films

We observed the thin-film samples using transmission electron microscopy (TEM), for which a cross section of an annealed sample (DAP11) was sectioned using a focused ion beam (FIB; Wirth, 2009), and using a FEI Nova 600 Nanolab Dual Beam at the Microelectronics Reliability and Characterization Laboratory, School of Materials Science and Engineering, Nanyang Technological University (Singapore). To expose the interface between the thin film and the substrate, the sample was cut perpendicular to its surface using ion beam of 30 kV and 2.8-6.5 nA, for obtaining thin foil of $\sim 10\ \mu\text{m}$ in length and $\sim 1\ \mu\text{m}$ in thickness. The cut foil was transferred to a copper half grid, and then thinned till reaching electron transparency, using a decreasing ion beam current from 93 to 28 pA. After this, the foil was cleaned from both sides, using a broad milling of 0.5 kV and ion beam current of 82 pA, down to $<100\ \text{nm}$ in thickness. Eventually the clean foil was observed using TEM (JEOL 2010-UHR) operating at a voltage of 200kV, and oriented till the electron beam is parallel to the interface for good image contrast. Images were taken using TEM bright-field mode, which usually gives stronger signals and causes less sample damage than using the dark-field mode (Wirth, 2017).

4.2.5. SIMS analyses of depth profiles

Compositional profiles of OH, F, Cl, S, and P were measured from the substrate-thin film couples, using a Cameca ims-1280 secondary ion mass spectrometry (SIMS) at University of Hawai'i at Mānoa (USA), where six profiles were obtained from the annealed samples, and two from the unannealed samples for comparison. Samples were coated with gold (of $\sim 30\ \text{nm}$ in thickness), and then loaded into the sample chamber for

at least 20 hours before analyses to reduce air contamination. The vacuum of the system was maintained at $< 10^{-9}$ torr during the analyses. The central areas (of about $50 \times 50 \mu\text{m}^2$ in size) of each sample was pre-sputtered for 2-5 mins, using a primary Cs^+ beam with current of 600 pA, and an accelerating voltage of -5 kV. After that, the secondary ions of ^{16}OH , ^{18}O , ^{31}P , ^{34}S , $^{19}\text{F}^{16}\text{O}$, ^{37}Cl were collected for 180-350 cycles, using an electron multiplier. The mass resolving power (MRP) was ~ 6000 , which is high enough for separation between the targeted and interferential ions. Scanning ion images (SIIs) were obtained from each cycle, where each image contains 64×64 pixels, i.e. with spatial resolution of $50 \mu\text{m}/64 \approx 0.78 \mu\text{m}$. The depth profiles were obtained by carefully selecting the areas that show nearly homogeneous ion distributions in the SIIs (of ~ 40 - $150 \mu\text{m}^2$ in size), using a region of interest (ROI) function of the L'IMAGE software package (*Appendix A*). As a result, the depth profiles reported in this study should reflect the mean abundances of each component within the selected areas.

The depths of the profiles obtained from SIMS were measured using the Atomic Force Microscopy (AFM) at the WinTech Nano-Technology Services Pte Ltd. (Singapore). Each SIMS pit was measured to produce a three-dimension depth map (of $80 \times 80 \mu\text{m}^2$ in size; *Appendix B*). The total depths of the pits were calculated using the height differences between the sample surface and the central areas at the bottom of the pits, which gives the spacing of depths between two scanning cycles (of ~ 2.5 - 3.1 nm). Surface roughness was obtained by measuring from an $\sim 90 \times 90 \mu\text{m}^2$ area on the surface of annealed and un-annealed samples for comparison (*Appendix B*).

4.2.6. NRA of depth profiles for fluorine

Concentration profiles of F were measured from the annealed thin-film sample (DAp11), using nuclear reaction analysis (NRA) at RUBION, Central Unit for Ion Beams and Radioisotopes, Ruhr Universität Bochum (Germany). The resonance nuclear reaction between the fluorine atom and the injected ion beam can be expressed as: $^{19}\text{F} + \text{p} \rightarrow ^{16}\text{O} + \gamma + \alpha + Q_R$ (Gavrilov et al., 2003). By increasing the injection beam energy during analyses, the resonance that follows the reaction above can be “shifted” from the sample surface to deeper layers within the sample, which emits γ rays that can be used for determining element concentrations (Becker and Rogalla, 2016). Here we used an ion beam current of ~ 200 nA with $\sim 2 \times 2$ mm² size, and increasing voltages from 340 kV to 420 kV, with a step of 5 kV (i.e. the spacing of the acquired depth profile is ~ 50 nm). The atom concentrations of F were converted into weight concentrations based on the structure formula of apatite, and then calibrated using an in-lab CaF₂ standard. Considering the possible F migration during the analyses due to the high-energy injection beam exposed on/into the sample (Becker and Rogalla, 2016), we did not use the NRA profile for any quantitative calculation, and only compared it with the SIMS profile to check the consistency.

4.2.7. Calculating the mole fractions of F, Cl and OH

Given that H₂O contents cannot be measured using EPMA, we estimated the H₂O concentrations following the stoichiometry calculation method of Ketcham (2015), i.e. assuming 26 oxygen in the OH-poor fluorapatite used in our experiments. Using the known values of F, Cl, and H₂O (in wt.%), we calculated the mole fractions of F, Cl,

and OH, following Li and Costa (2020), i.e. $X_i^{Ap} = \frac{\frac{C_i^{Ap}}{M_i}}{\frac{C_F^{Ap}}{19} + \frac{C_{Cl}^{Ap}}{35.45} + (\frac{C_{H_2O}^{Ap}}{18} \times 2)}$, where M_i is the

atomic mass of component i (= F, Cl, OH), and C_i^{Ap} is in weight percent. The mole fractions of F, Cl and OH in the crystals measured by SIMS were calculated using the same equation above (H₂O was directly measured).

4.3. Observation of run products

4.3.1. Crystal-powder couples

The annealed apatite crystals show a smooth boundary of the polished faces without apparent re-crystallization at the crystal rims during/after annealing, as can be seen in optical microscope and SEM images of the crystal boundary and the powders (Fig. 4.3b-c). Thus, we believe that the powers provided an effective infinite diffusion source of constant composition of the concerned components during experiments, as has been revealed by the equivalent compositions between the powders near interface and the crystal rim measured using EPMA (see Section 4.3.2).

Fig. 4.3. A crystal-powder diffusion couple (4d) annealed at 1100 °C for 66 hours. The apatite crystal was fully embedded in powders (panel *a*), and with its smooth polished face (at bottom) in good contact with powders, shown in reflected-light image in panel *b*, and BSE image in panel *c*. Empty spaces between powders and the crystal were filled in epoxy for making the mounts. X-ray maps were obtained from the corner of the crystal (marked in white box in panel *b*) to investigate diffusion anisotropy, whereas the concentration profiles were obtained from the central bottom area of the crystal (marked in black box in panel *b*; see concentration profile in Fig. 4.6) to minimize potential contribution of diffusion from multiple directions.

4.3.2. Substrate-thin film couples

The cross sections of an annealed sample (DAp11) and two un-annealed samples were sectioned using focused ion beam and observed using SEM and TEM (see methods). The thin films show similar greyscales as the substrate in secondary electron images (Fig. 4.4 a, f, g). The apatite substrates are quite homogeneous, whereas the thin film after annealing shows heterogenous structures with some nuclei (of ~10-50 nm in diameter; Fig. 4.4 b-e), which were not observed from the un-annealed thin films (Fig. 4.4 f, g). This indicates that the nuclei within the thin film were likely formed by recrystallization during/after the annealing. This heterogenous thin-film structure was also observed from the secondary ion images (SIIs) obtained from SIMS analyses (*Appendix A*), and also supported by the larger surface roughness of the annealed samples than the un-annealed ones, according to AFM analyses (*Appendix B*). To minimize the effect of the thin-film structure on determinations of the diffusion rates, we only used the signals collected from the nearly homogeneous areas from the SIMS analyses (see methods in Section 4.2.5; see SIIs in *Appendix A*) for determination of the depth profiles and the modelling on the diffusion rates.

Annealed sample (*D*Ap11)

(f) Un-annealed sample (*D*Ap11r)

(g) Thin film on Si wafer

Fig. 4.4. Cross section of a thin film-substrate (apatite) sample (*D*Ap11, annealed at 900 °C for 0.67 hours) shown in SEM (panel *a*) and TEM bright-field images (panels *b-e*); and cross sections of un-annealed thin films on apatite substrate (*D*Ap11r, panel *f*), and on silicon wafer (panel *g*), shown in SEM images. The thin film of *D*Ap11 is about 100- to 200-nm thick and shows some heterogenous structures with perhaps a few nuclei (panels *c-e*) formed by re-crystallization during/after the annealing. The unannealed thin films seem to be more homogenous. Voids between the several platinum layers above the thin film of *D*Ap11 (dark areas in panel *a*, and bright areas in panels *b-d*) are artifacts produced by multiple-time deposition of Pt on this sample, before it was sectioned using FIB for the TEM observation (see methods). Scale bars are 200 nm in panel *b*, 100 nm in panels *c-d*, and 10 nm in panel *e*.

4.4. Measured compositions and diffusion profiles of the run products

We have used a variety of techniques to obtain compositional profiles from the two types of diffusion couples due to different scales of diffusion distances within, i.e. EPMA for the crystal-powder couples, and SIMS and NRA for the substrate-thin film couples, which are described below.

4.4.1. Crystal-powder couples

X-ray maps of F, Cl and S were obtained from the corners of two crystals, annealed at the same T (i.e. 1100 °C) but different durations. The crystal annealed for 161 hours (6d#1) shows longer diffusion distances of F, Cl, and S (Fig. 4.5a), compared to that annealed for shorter times (of ~66 hours for 4d) (Fig. 4.5b). In both crystals F shows normal zoning (lower concentration at the rim) of similar distances parallel or normal to the c-axis, indicating nearly isotropic diffusion. The zoning pattern of Cl is more complex, where the Cl-rich zones within the crystals show longer distances parallel to the c-axis ($\parallel c$) than normal to it (Fig. 4.5). S shows normal zoning, with distances shorter than those of F and Cl in the same crystals, likely indicating the slower diffusion of S.

Fig. 4.5. Compositional distribution of F, Cl, and S in two crystals annealed at 1100 °C for 66 hours (4d in panel *a*), and 161 hours (6d#1 in panel *b*). The directions of arrows show the c-axis perpendicular to the polished face of the crystal, and their lengths show diffusion distances. Scale bar is 20 μm .

Concentrations profiles ($> 200\ \mu\text{m}$ in length) were measured perpendicular to the crystal boundary, i.e. parallel to the c-axis ($\parallel c$) of the crystals. Concentration profiles of the crystals annealed at $1100\ ^\circ\text{C}$ for 66 hours (4d) and 161 hours (6d#1, #2) show similar trends, whereas the diffusion distances vary by a factor of about 2. The F concentrations decrease towards the crystal rims (Fig. 4.6a), consistent with the observation of normal zoning in the X-ray maps. H_2O concentrations (calculated from stoichiometry) increase towards the crystal rims within similar distances to F (Fig. 4.6c). It is worth noting that the Cl profiles do not show a simple increasing or decreasing trend as do F and H_2O , but instead show a more complex pattern with a high-Cl peak at some distance from the crystal rims, i.e. the so-called uphill diffusion (Fig. 4.6b). The Cl peaks appear at $\sim 8\text{-}10\ \mu\text{m}$ from the rim for the crystal annealed for 66 hours (4d), and at $\sim 20\text{-}30\ \mu\text{m}$ from the rims of the two crystals annealed for 161 hours (6d#1, #2).

The F and H_2O concentrations of areas away from the diffusion zones (i.e. at $>100\ \mu\text{m}$ from the crystal rims) are within error in the three crystals (Fig. 4.6a, c). The Cl contents show larger variation (Fig. 4.6b), likely caused by the original variation in the starting materials (i.e. the natural Durango apatite). Thus, for modelling the diffusivity shown below, we have taken the composition acquired from the area out of the diffusion zone of each crystal as the initial condition.

The powders closest to the crystal rim of 4d show similar F and H_2O contents to those of the crystal rim, but higher Cl that approximately equals to the maximal Cl contents in the crystal (i.e. at the peak of the “hill”) (Fig. 4.7). Comparison of the compositions between the annealed powders ($> 150\text{-}\mu\text{m}$ far away from the crystal) and the starting

material of Morocco crystals shows that they have equivalent F and H₂O concentrations within error (Fig. 4.7; Table 4.2). However, the Cl contents of the powders (i.e. ~ 0.6 wt.%) are lower than those of the Morocco apatite (i.e. ~ 0.8 wt.%), which was also observed from the un-annealed thin films made by the same batch of powder (Table 4.2; see below). It is likely that the lower Cl contents in the powders are caused by the heterogeneous Cl distribution in the starting material, i.e. the large Morocco crystal, rather than due to the Cl loss during experiment. Considering possibly different compositions in the powders and the crystal, we have used the compositions of the crystal rims as the boundary condition for the diffusion modelling below.

Fig. 4.6. Concentration profiles ($\parallel$ c) of F and Cl measured using EPMA and of H₂O calculated from stoichiometry, for three apatite crystals annealed at 1100 °C for 66 hours (4d), and 161 hours (6d #1 and #2 are from the same run). Cl profiles show uphill diffusion. Concentrations at the boundary of the two crystals from the same run (6d #1, #2) are similar, but different from that from the other run (4d), reflecting different compositions of the powders in contact with the crystals. F and H₂O contents of the crystal cores show similar values, whereas Cl contents show larger difference. Error bars show 1 s.d. of F and Cl concentrations measured using EPMA, and H₂O calculated from stoichiometry.

Fig. 4.7. Comparison of F, Cl, and H₂O concentrations across the crystal (|| c) and surrounding powder interface (at position zero) for sample 4d annealed at 1100 °C for 66 hours. H₂O concentrations were calculated from apatite stoichiometry (see methods). The powder (Distance < 0) and the crystal (Distance > 0; measured from a traverse parallel to the c-axis; see Fig. 4.3c) show equivalent F and H₂O concentrations at the interface (Distance = 0), whereas Cl contents in the powders next to the crystal are higher than that of the crystal rim, and approximately equals to the maximal Cl in the crystal (i.e. the peak of the “uphill” profile). Compositions measured from the areas far from the diffusion zones in the annealed sample show equivalent values (within error) to those of the starting materials, except that Cl contents in the powders are much lower than in the un-annealed Morocco crystal. Error bars show 1 s.d. of F and Cl concentrations measured using EPMA, and H₂O calculated from stoichiometry, and the compositional variation in the starting materials measured using SIMS (Table 4.1).

4.4.2. Substrate-thin film couples

We have obtained secondary ion profiles of F, Cl, S, OH, O and P from the un-annealed and annealed samples using SIMS. The collected ion signals from SIMS were normalized to ^{31}P to be converted into weight concentrations with calibration from the un-annealed Durango crystal, whereas the distances of the profiles were measured using atomic force microscopy (AFM) (see methods). The profiles of F from SIMS analyses show good agreement with those obtained from NRA (see below).

Un-annealed sample

The depth profiles from the un-annealed sample show lower F, and higher Cl and OH in the thin film than in the substrate (Fig. 4.8), as expected from the compositions of the starting materials (Table 4.1). However, the $^{31}\text{P}/^{18}\text{O}$ of the thin film (≈ 7) is only about half of that of the substrate (≈ 14), meaning that the thin film could have a different structural formula from the substrate. Considering this and that the profile of P shows the sharpest change at the interface (i.e. convolution lengths of ~ 20 nm), we have used the variation in P to identify the interface locations, i.e. at depths of ~ 130 nm from thin-film surface of this sample. The similar S abundances in the thin film and substrate, and the high-S peak at the interface are difficult to explain but may be related to contamination on the crystal surface before the thin-film deposition.

According to the length of the transition of the thin film-substrate interface, the convolution lengths are about ~ 30 nm for OH, ~ 35 nm for F, and ~ 50 nm for Cl. These lengths are likely caused by mixing effect during the SIMS analyses, or/and some surface topography effect of the thin films (i.e. roughness of ~ 9 nm measured by AFM;

Appendix B). Nonetheless, these convolution lengths are much smaller than the diffusion distances within the annealed crystals (e.g. of $\sim 400\text{-}800\text{ nm}$ for Cl, and $\sim 100\text{-}400\text{ nm}$ for F and OH), which may cause maximal overestimation of diffusion rates of $\sim 10\%$ for Cl, and $\sim 30\%$ for F and OH (Ganguly et al., 1988).

Fig. 4.8. Depth profiles of (a) F, (b) OH, (c) Cl, (d) S, and (e) P (expressed as secondary ions normalized to ^{18}O), measured using SIMS from an un-annealed thin film sample ($\parallel$ c). The interface between the thin film and the substrate is shown as a dashed line. The differences in F, Cl and OH concentrations between the thin film and the substrate are as expected from the two starting apatite crystals. The abundances of P in the thin film are about half of those in the substrate, indicating that the deposited thin film has different composition from the Morocco apatite. The P profile shows the sharpest change at the interface, which serves as a good indicator for determining interface location of the annealed samples.

Annealed samples

Depth profiles were measured from five samples annealed between 800-1000 °C (Table 4.2), among which four crystals were oriented parallel to the c-axis and annealed at 800 °C-900 °C, and one crystal was oriented parallel to the a-axis and annealed at 950 °C. The depths of the profiles measured from AFM are between 830-1250 nm (Fig. 4.9). The diffusion distances in the substrates are ~ 400-800 nm for Cl, and ~ 100-400 nm for F and OH. Based on the variations in P abundances with depth, we find that the thickness of the three thin films deposited with different time durations (of 5-15 mins) and laser powers are ~ 210 nm (for TF2), ~ 130 nm (for TF4) and ~ 180 nm (for TF7) (see methods; Table 4.2).

Three profiles (two $\parallel$ c, and one $\parallel$ a) show uphill diffusion of Cl in the thin films, which has also been observed in the crystal-powder samples as mentioned above, indicating a multicomponent diffusion mechanism. For the crystals oriented parallel to the c-axis (i.e. DAp7, DAp9, DAp11, DAp15), the profiles of OH show the larger difference between the thin film and the substrate compared to F and Cl, due to the high OH abundances in the thin film. The two crystals annealed at 900 °C for 0.67 hours (DAp11) and 2 hours (DAp15) show diffusion distances of Cl of ~ 500 nm and ~ 650 nm, respectively (Fig. 4.10). The crystal annealed at lower temperature (800 °C) shows the shortest diffusion distance of Cl (~ 300 nm). The crystal oriented parallel to the a-axis (DAp16) that was annealed at 950 °C for 21 hours shows shorter diffusion distances of about 300-400 nm along this axis (Fig. 4.10).

(a) DAp3r (un-annealed)

(b) DAp11 #2 (annealed)

Fig. 4.9. Three-dimensional maps of the surface and pits from SIMS analysis obtained using AFM (a) un-annealed (b) annealed thin film-substrate samples. The different depths were produced by different scanning cycles. The surface and bottom of pit of the annealed sample (panel b) are rougher than those of the un-annealed sample (panel a), likely reflecting re-crystallization of the thin film during/after annealing.

Fig. 4.10. Depth profiles of (a) F, (b) OH, (c) Cl, (d) S and (e) P in four annealed thin-film samples measured using SIMS, showing diffusion parallel to the a-axis (// a; *pink dots*), or parallel to the c-axis (// c; marked in other symbols). The interface between thin film-substrate was determined from the kink of the P profile (panel e; in *dashed lines*). The two thin films deposited for different durations during PLD show different thickness (TF4: ~130 nm; TF7: ~180 nm). P and S signals in the thin films increase towards the substrate (panels d-e), probably caused by some extent of diffusion during the annealing.

To compare the depth profiles measured from SIMS and NRA, and further modelling on the diffusivities based on the mole fractions of F, Cl and OH, we need to convert the relative abundances of anions from SIMS analyses into absolute concentrations. To avoid effects from oxygen diffusion within the crystal and assuming nearly constant P contents in apatite, we have calculated the concentrations of F, Cl and OH, using the relative abundances of each anion (normalized to $^{31}\text{P}^-$) calibrated by the absolute concentrations measured from the un-annealed crystals (Table 4.1). The F profiles measured by SIMS and NRA show good agreement (Fig. 4.11). The slightly smaller slope of the NRA profile within the thin film compared to those by SIMS is likely caused by the larger convolution lengths of NRA, given the possible F migration during NRA due to the high-energy ion beam used for the analyses (see methods). In addition, the F concentrations measured from NRA show variations of up to ~ 0.7 wt.% at the same depths within the substrate apatite crystal, which might be related to the F migration. Considering this, the F profiles obtained with NRA were not used for the extraction of the diffusion coefficients. Nonetheless, the absolute concentrations of F and the distances from NRA and their general agreement with the SIMS data further validate our determination for the profile lengths using AFM and our calculation methods for the absolute concentrations.

Fig. 4.11. Concentration profiles of F measured from an annealed thin-film sample (DAp11), using NRA (solid circles in red color), and SIMS (empty symbols; #1, #2 measured from two locations). The location of the interface between thin film and substrate was determined from the P profiles obtained from SIMS analyses (Fig. 4.9). The F concentrations within the substrate (~ 350 - 550 nm away from the thin film surface) determined from NRA overlap with those in the un-annealed Durango crystals (from SIMS). Their variations are likely related to F migration as the sample was exposed under the high-energy ion beam of NRA for a long time. The F contents of the surface layer of the thin film (from NRA) show equivalent values to F in the un-annealed Morocco apatite, indicating little F loss during/after the annealing.

4.5. Multicomponent diffusion modelling used for calculating the diffusion rates

We have observed from the crystal-powder couples and the thin film samples that the diffusion of Cl occurs against its concentration gradient, i.e. namely “uphill” diffusion. This has been found in other multicomponent solid solutions, e.g. Ca diffusion in the Ca-Fe-Mg-Mn garnet (see review in Ganguly, 2010), and is related to the coupling between the different component where flux of one component affected by those who have similar chemical properties and occupy the same site of the crystal structure (Chakraborty and Ganguly, 1991; Ganguly, 2002). Thus, the “uphill” Cl diffusion in apatite may be related to the coupling with F, OH and the need of mass conservation at the anion site (Piccoli and Candela, 2002; Hughes, 2015). In this section, we briefly introduce the theories of multicomponent diffusion in solid solutions, and then describe the modelling approach that we have used for extracting the diffusion coefficients.

4.5.1. Background of multicomponent diffusion

In an n -component system ($n \geq 3$), the diffusion of each component can be treated using a simplified binary diffusion, where the diffusing component is considered as the solute, and the other $(n-1)$ components are considered as the solvent (e.g. Chakraborty and Ganguly, 1991; Ganguly, 2002). Under this condition, there are $(n-1)$ independent components, where the flux of the n -th component is fixed by those of the other components because of stoichiometric constraint ($\sum X_i = 1$). Considering one-

dimensional diffusion, the diffusivity of component i can be expressed following the Fick-Onsager relation (Onsager, 1945) as:

$$\frac{\partial C_i}{\partial t} = \sum_{j=1}^{n-1} \frac{\partial}{\partial x} \left(D_{ij} \frac{\partial C_j}{\partial x} \right) \quad (1)$$

where the diffusion coefficient D_{ij} is related to the self-diffusion coefficients of i and j , and the thermodynamic mixing properties of the solution. Following Ganguly (2002), the $(n-1)$ equations in the form of Eq. 1 can be written as:

$$\frac{\partial \mathbf{C}}{\partial t} = \frac{\partial}{\partial x} \left(\mathbf{D} \frac{\partial \mathbf{C}}{\partial x} \right) \quad (2)$$

where $\mathbf{C}$ is a concentration vector of $(n-1)$ independent components, and $\mathbf{D}$ is an $(n-1)$ by $(n-1)$ matrix (referred to as $\mathbf{D}$ -matrix) that contains the diffusion coefficients D_{ij} s. As the components of interests (i.e. F, Cl, OH) have the same charge, D_{ij} can be calculated using a simplified formulation following Lasaga (1979):

$$D_{ij} = \left[D_i^* \delta_{ij} - \frac{X_i D_i^*}{\sum_{k=1}^n X_k D_k^*} (D_j^* - D_n^*) \right] (TF) \quad (3)$$

where δ_{ij} is the Kronecker delta, i.e. $\delta_{ij}=1$ when $i = j$, and $\delta_{ij}=0$, when $i \neq j$, and X_i is the mole fraction of i , and D_i^* is the tracer diffusion coefficients of i (equivalent to its diffusion rates when in the absence of other components; see definition in Zhang and Cherniak, 2010). TF represents the thermodynamic factor of the solid solution, which equals to unity for an ideal solution. The mixing of F-Cl-OH in apatite has been found to be non-ideal, especially for the Cl-rich apatite and low temperatures (see Chapter 2).

However, this is not the case for the Cl-poor fluorapatite ($X_{Cl} < 0.08$) used in our experiments. Using the formulations of the activities coefficients (γ_i^{Ap}) in Chapter 2, we have calculated γ_i^{Ap} using the F-Cl-OH compositions in apatite from EPMA and SIMS analyses, and the experimental temperatures. We find small variations in γ_i^{Ap} s across the analysed locations of the crystals, e.g. the ratios of γ_F^{Ap} , γ_{Cl}^{Ap} , and γ_{OH}^{Ap} at the rim and the un-zoned areas of DAp11 (at 900 °C) are about 0.96-1.25. Considering this, we take the crystals used in our experiments as nearly ideal solutions so that $TF \approx 1$. Under this condition, we have calculated the diffusion coefficients by simulation of the profiles, using Eqs. 1-3 and the modelling approach below.

4.5.2. Simulation of the measured diffusion profiles

We converted the concentrations from EPMA and SIMS analyses into mole fractions of F, Cl and OH (see methods). The initial and boundary conditions were determined according to the compositions at the profile plateaus (i.e. at the un-zoned areas), and the rims (or surface) of the crystals (or the substrates) (Figs. 4.12-4.13). Following the modelling approach described by Chakraborty and Ganguly (1991), we have developed a MATLAB-based program for simulation of the diffusion profiles. By inputting some guessed values for $\{D_F^*, D_{Cl}^*, D_{OH}^*\}$, the elements of the $\mathbf{D}$ matrix (i.e. D_{ij} in Eq. 3) were calculated at each grid point for every time step using a finite difference algorithm (see the script in *Appendix C*). By running this program for many times using different input values of D_i^* s, we eventually obtained the group of D_i^* s which reproduces the diffusion profiles of all the three components (as judged by visual inspection) (see examples in Figs. 4.12-4.13; all the profiles shown in *Appendix C*).

4.5.3. Uncertainties in the determined diffusivities

The maximal and minimal diffusion rates obtained from each sample were determined by fitting the diffusion models to the measured ones with consideration of the analytical errors from EPMA or SIMS (*Appendix C*). For the modelling on the multicomponent diffusion of F, Cl, and OH, we have considered the errors propagated from the analytical errors of the three components in the calculation of mole fractions (X_i), which eventually show errors of less than ± 0.01 . The profiles of S from SIMS analyses are expressed as the relative abundances of S (i.e. $^{34}\text{S}/^{31}\text{P}$), which have smaller uncertainties (depending on the analytical error of S), and thus propagate smaller errors to the calculated S diffusivities (Table 4.3).

Fig. 4.12. Example of diffusion profiles measured using SIMS for 6d#1 after annealing at 1100 °C for 161 hours (*black dots*), and the best-fit diffusion profiles from modelling (*red solid lines*). The initial and boundary conditions (*blue dashed lines*) were determined by the compositions at the un-zoned areas and the crystal rim. Error bars show 1 s.d. of analyses from EPMA.

Fig. 4.13. Example of depth profiles measured using SIMS from DAP11 annealed at 900 °C for 0.67 hours (*black dots*), and the best-fit diffusion profiles from modelling (*red solid lines*). The initial and boundary conditions (*blue dashed lines*) were determined by the compositions of the un-zoned areas and the surface of the crystal (substrate). Error bars show 1 s.d. of analyses from SIMS.

4.5.4. Calculated diffusion coefficients

The D_{OH}^* is the smallest tracer diffusion coefficient, and there is a general relation of $D_F^* > D_{Cl}^* > 7 \times D_{OH}^*$ (all parallel to the c-axis; Table 4.3). The D_{Cl}^* we have obtained are in general smaller than those reported by Brenan (1994). For example, at 1100 °C we find $D_{Cl}^* = 5 (\pm 1) \times 10^{-16} \text{ m}^2/\text{s}$, which is about 2-8 times' smaller. The values of D_F^* and D_{OH}^* from our calculation show larger variations than those of D_{Cl}^* ; the wide ranges of D_F^* s cover those reported by Brenan (1994). The calculated best-fit D_F^* values are about twice smaller than those reported by Brenan (1994). The tracer diffusion coefficients calculated from this study define the following Arrhenius relations (Fig. 4.14):

$$D_{Cl}^* = 5.1 \left(\begin{smallmatrix} +17 \\ -4.0 \end{smallmatrix} \right) \times 10^{-5} \times \left[\exp \left(\frac{-290(\pm 19) \text{ kJ} \cdot \text{mol}^{-1}}{RT} \right) \right] \text{ m}^2 \cdot \text{s}^{-1} \quad (4)$$

$$D_F^* = 9.0 \left(\begin{smallmatrix} +88 \\ -8.0 \end{smallmatrix} \right) \times 10^{-5} \times \exp \left(\frac{-288 (\pm 73) \text{ kJ} \cdot \text{mol}^{-1}}{RT} \right) \text{ m}^2 \cdot \text{s}^{-1} \quad (5)$$

$$D_{OH}^* = 1.7 \left(\begin{smallmatrix} +22 \\ -1.6 \end{smallmatrix} \right) \times 10^{-2} \times \left[\exp \left(\frac{-397 (\pm 60) \text{ kJ} \cdot \text{mol}^{-1}}{RT} \right) \right] \text{ m}^2 \cdot \text{s}^{-1} \quad (6)$$

The activation energy E_a for Cl is within error to Brenan (1994), whereas the pre-exponential factor is ~ 5 times' smaller than Brenan (1994). With regards to diffusion anisotropy we find that at 950 °C, D_{Cl}^* ($\parallel c$) is about 90-400 times' faster than D_{Cl}^* ($\parallel a$), and D_{OH}^* ($\parallel c$) is about 1 to 2 orders of magnitude faster than D_{OH}^* ($\parallel a$), in agreement with the anisotropic diffusion of Cl and O found in previous studies (Farver and Giletti, 1989; Brenan, 1994). The diffusion rate of F seems to be slower $\parallel a$ than $\parallel c$ (Fig. 4.14),

however, given the large uncertainties of the calculated values of D_F^* , our data could not provide good constraints on the anisotropic properties of the F diffusion in apatite.

The S in Durango apatite has been found to be mostly S^{6+} (i.e. >95 % of total S in the crystal; from XANES study by Konecke et al., 2017), which should be present at the tetrahedral site of apatite (by substituting phosphorus). Given the reduced condition (fO_2 of WM buffer) used in our experiments, it is unclear whether S in the Durango apatite was reduced to S^{2-} . We have treated S as a single component and separately from the multicomponent diffusion of F, Cl and OH. We used a finite-difference algorithm to model the single-component diffusion of S (see model fits and the Matlab script in *Appendix D*), from which we find D_S ($\parallel c$) of $1.5 (\pm 0.5) \times 10^{-19} \text{ m}^2/\text{s}$ at 800 °C, and $1.0 (\pm 0.1) - 2.5 (\pm 0.5) \times 10^{-18} \text{ m}^2/\text{s}$ at 900 °C, where the latter values overlap with the calculated D_{Cl}^* ($\parallel c$) at the same temperature, and are greater than D_{OH}^* ($\parallel c$) (Fig. 4.14; Table 4.3). We have not attempted to define the activation energy for D_S given that we have only data for two temperatures, but it seems that D_S parallel to the c-axis could be at least two orders of magnitude greater than parallel to the a-axis (Fig. 4.14), indicating possibly anisotropic S diffusion.

The diffusion rates of F, Cl and S ($\parallel c$) calculated from this study are greater than those of the trace elements (e.g. Pb, Sr, Mn, LREE) reported in literature (Watson et al., 1985; Cherniak, 2000; Cherniak, 2005; Cherniak, 2010), whereas the diffusivities of OH ($\parallel c$) from our calculation overlap with those of Pb, Sr and Mn, but are greater than LREE (Fig. 4.14). The diffusivity of S ($\parallel a$) at 950 °C is between those of Mn and LREE (e.g. La), which should be considered for investigation of the coupled substitution and zonings of S and REE found in natural apatite (see Figs. 3.3-3.4 in Chapter 3).

Fig. 4.14. Calculated diffusion coefficients of Cl, F, OH and S in this study, compared with literature data for the diffusivities of F, Cl, O (in colorful/grey fields) and trace elements (in dotted lines). The diffusion rates of La are shown as the representative of LREE, which were found to be of similar values. Data sources: [1] Brenan, 1994; [2] Farver and Giletti, 1989; [3] Cherniak, 2010; [4] Cherniak, 2005; [5] Cherniak, 2000.

Table 4.3. Calculated tracer diffusion coefficients of F, Cl, OH and S in apatite.

Label	T (°C)	10000/T (K ⁻¹)	D_F^* (m ² /s)		D_{Cl}^* (m ² /s)		D_{OH}^* (m ² /s)		D_S (m ² /s)
			Best fit	Range	Best fit	Range	Best fit	Range	Range
6d (ll c)	1100	7.283	1×10 ⁻¹⁵	6×10 ⁻¹⁶ – 1×10 ⁻¹⁴	5×10 ⁻¹⁶	3×10 ⁻¹⁶ – 8×10 ⁻¹⁴	2×10 ⁻¹⁷	1×10 ⁻¹⁷ – 5×10 ⁻¹⁷	n.a.
DAp7 (ll c)	998	7.868	n.a.	n.a.	7×10 ⁻¹⁷	4×10 ⁻¹⁷ – 1.5×10 ⁻¹⁶	4×10 ⁻¹⁹	1×10 ⁻¹⁹ – 2×10 ⁻¹⁸	n.a.
DAp11#1 (ll c)	900	8.525	1×10 ⁻¹⁷	8×10 ⁻¹⁹ – 1×10 ⁻¹⁶	7×10 ⁻¹⁸	5×10 ⁻¹⁸ – 1×10 ⁻¹⁷	5×10 ⁻²⁰	1×10 ⁻²¹ – 1×10 ⁻¹⁹	2.5 (±0.5) ×10 ⁻¹⁸
DAp15 (ll c)	900	8.525	1.8×10 ⁻¹⁷	n.a.	3×10 ⁻¹⁸	1.5×10 ⁻¹⁸ – 4.5×10 ⁻¹⁸	4×10 ⁻²⁰	1×10 ⁻²⁰ – 7×10 ⁻²⁰	1.0 (±0.1) ×10 ⁻¹⁸
DAp9 (ll c)	800	9.320	n.a.	n.a.	5×10 ⁻¹⁹	2.5×10 ⁻¹⁹ – 8×10 ⁻¹⁹	n.a.	n.a.	1.5 (±0.5) ×10 ⁻¹⁹
DAp16 (ll a)	950	8.177	2×10 ⁻¹⁸	1×10 ⁻¹⁹ – 5×10 ⁻¹⁷	1.2×10 ⁻¹⁹	5×10 ⁻²⁰ – 2×10 ⁻¹⁹	6.0×10 ⁻²¹	2×10 ⁻²¹ – 2×10 ⁻²⁰	3.8 (±1.3) ×10 ⁻²⁰

4.6. Discussion

4.6.1. Effects of apatite compositions, pressures and oxygen fugacities on the determined diffusivities

We have shown that the tracer diffusion coefficients of Cl calculated in this study are generally slower than those reported by Brenan (1994) with difference by factors of ~2-8. Such differences might be related to different compositions of the diffusion sources, where the diffusion source (of powders/thin films) used in this study is Cl-poorer and OH-rich ($X_{\text{Cl}} < 0.08$, $X_{\text{OH}} > 0.2$) than the powder-source used by Brenan (1994) (i.e. $X_{\text{Cl}} > 0.5$ and $X_{\text{OH}} < 0.02$, calculated using the volatile concentrations reported by Brenan). This is consistent with the findings from Brenan (1994) that the Cl diffusion is slower in the OH-rich crystals than OH-poorer ones, likely because the flux of Cl is affected by OH due to the multicomponent diffusion. Hence, we suggest that for diffusion modelling on experimental/natural apatite that contains more than one component among F, Cl and OH, it is necessary to apply a two- or three-component diffusion model (see Matlab script for the three-component diffusion model in *Appendix C*).

All experiments in this study were performed at fixed pressure (1-atm) and oxygen fugacity ($f\text{O}_2 = \text{WM buffer}$), thus we cannot use our results to comment on the effects of pressure and $f\text{O}_2$ on the diffusion rates of F-Cl-OH in apatite. Brenan (1994) found that the Cl diffusivities at high pressure of 1 GPa are about 1-2 orders of magnitude faster than those at 1-atm, indicating some extent of water-pressure effect on the diffusivity (likely related to the activity of OH in apatite). Future experiments between 1-atm and 1 GPa are needed to quantify the pressure effects on the F-Cl-OH diffusivities.

Given that the oxygen fugacities used in the experiments by Brennan (1994) were not reported, we cannot compare the diffusivities determined from their experiments with those determined at WM buffer from this study for evaluation of the fO_2 effect. Nonetheless, given the single valence of F, Cl and OH (as monovalent anions) in apatite, there is unlikely an effect of fO_2 on the F-Cl-OH diffusivities. But this might not be true for the diffusion rates of S, given that S can exist as $S^{2-}/S^{4+}/S^{6+}$ in apatite depending on the fO_2 condition of the system. Hence, future experiments at other fO_2 conditions are needed for investigation of the effect of fO_2 on the S diffusivities in apatite.

4.6.2. Applications to natural volcanic apatite and magma ascent rates

Using the Arrhenius relations in Eqs. 4-6, we can calculate the diffusivities of F, Cl, and OH at given temperature, and apply these values to estimate the timescales of volatile diffusion in natural apatite crystals. We have shown in Section 3.9.3 of Chapter 3 that the Cl diffusion in apatite microlites was likely triggered by the increase in the Cl contents in the melt due to de-compression crystallization of anhydrous minerals (e.g. plagioclase) during the ascent. Thus, the timescales of Cl diffusion in these apatite crystals likely represents that of the magma ascent, which can be used to estimate the ascent velocity, if the depth of the start of magma ascent is known. Below we show two examples of applications of the new diffusivity data and diffusion models reported in this study to be able to (1) calculate the magma ascent times and velocities, by modelling the diffusion profiles measured from the volatile-zoned crystals (Fig. 4.15), and (2) estimate the minimal magma ascent rates, based on natural apatite that lacks a Cl zone (Fig. 4.16).

We have used one apatite crystal in the groundmass from Merapi 2006 rocks that is chemically zoned (e.g, Cl zoning of $\sim 6 \mu\text{m}$) to illustrate an approach to determine magma ascent rates. Concentration profiles with $1 \mu\text{m}$ in spacing of F and Cl were measured using EPMA, and that of H_2O was calculated from stoichiometry (see analytical conditions in Section 4.2.3). The concentrations were converted into the mole fractions of F, Cl and OH for modelling the diffusion timescales (Fig. 4.15c; see calculation method in Section 4.2.6). Considering the anisotropic diffusion of Cl and OH found in this study, we have measured the orientation of the c-axis of this crystal using EBSD (see methods), and then calculated the diffusivities of each component i (= F, Cl, OH) along the direction of the traverse (D_i^{traverse}) using the equation below from Costa et al. (2008):

$$D_i^{\text{traverse}} = D_i^a(\cos\alpha)^2 + D_i^b(\cos\beta)^2 + D_i^c(\cos\gamma)^2 \quad (7)$$

where D_i^a , D_i^b and D_i^c are the diffusion rates parallel to the a-, b-, c-axis of crystal, and α , β , and γ are the angles between the traverse and each axis, respectively.

Given the hexagonal structure of apatite, the values of D_i^a and D_i^b should be approximately equal to each other, i.e. D_i^* ($\parallel$ a) as defined in this study, thus the values of α and β should be equal to the angle between the traverse and the a-b plane. We find that the angle between the traverse and the c-axis of the crystal investigated here (γ) is about 18 degrees, and α and β equal to 82 degrees. Using the diffusion rates $\parallel$ a and $\parallel$ c at 950 °C determined from our experiments, we find the values of D_i^{traverse} calculated from Eq.7 and those calculated from only considering the angle between the traverse and the c-axis show very small differences (of $\sim 2\text{-}3\%$ relative for F and Cl, and $\sim 6\%$ relative for OH), which is due to the much greater diffusion rates $\parallel$ c than $\parallel$ a. Given

that D_i^a was only determined at 950 °C in this study, we can use $D_i^{traverse} \approx D_i^c (\cos\gamma)^2$ as an approximation of Eq. 7 to calculate $D_i^{traverse}$ at other temperatures (between 800-1100 °C). Taking the temperature of 900 °C for the dacitic-rhyolitic magmas of the Merapi 2006 eruption, we obtain the diffusion rates along the traverse as $D_{Cl}^{traverse} \approx 5.9 \times 10^{-18} \text{ m}^2/\text{s}$, $D_F^{traverse} \approx 1.4 \times 10^{-17} \text{ m}^2/\text{s}$, and $D_{OH}^{traverse} \approx 3.6 \times 10^{-20} \text{ m}^2/\text{s}$.

With the diffusivities above and a multicomponent diffusion model where we assume the initial condition to be compositionally homogeneous across the crystal with F-Cl-OH concentrations equivalent to those at the crystal core, and the boundary condition to be fixed with volatile concentrations measured from the crystal rim. Running the diffusion program using different values of diffusion times, we obtained profiles that show good match with the measured profiles for the three components (Fig. 4.15c). The modelled diffusion times (at 900 °C) are between 280-340 hours, i.e. ~ 12-14 days, slightly shorter but overlap with the duration of volcanic unrest before the 2006 eruption (i.e. ~ 14-20 days) suggested by previous deformation and seismic studies (Ratdomopurbo et al., 2013; Aisyah et al., 2018).

The caveats from this simple diffusion model include the fixed boundary condition (according to the composition at crystal rim) and temperature used in the diffusion modelling, which might not be true considering the complex processes of fractional crystallization, magma degassing and cooling during the ascent. For example, during magma ascent, the melt Cl concentrations can either increase due to de-compression microlite crystallization or decrease due to Cl exsolution into a vapor/fluid phase. The possible decrease in temperature and water pressure during the ascent would likely lead to variations in diffusivities and thus affecting the timescale estimates. Considering this,

the diffusion model above can be improved in the future by combining with other models that incorporate the variations in temperature and Cl behavior in melts during magma ascent, and with new experimental data for the F-Cl-OH diffusivities at pressures higher than 1-atm.

Fig. 4.15. X-ray maps for Cl (panel *a*) and F (panel *b*) obtained using EPMA from the groundmass apatite from the Merapi 2006 rocks. Concentration profiles were obtained using EPMA nearly parallel to the *c*-axis of this crystal (traverse shown in panel *a*). Mole fractions of F, Cl, and OH (panel *c*) were modelled using diffusion rates determined at 900 °C. The modelled profiles (*red solid lines*) show good fits with the measured ones (*black dots*), indicating diffusion times of 280-340 hours (initial and boundary conditions shown in blue dashed lines). Error bars show 1 s.d. of the mole fractions propagated from the analytical errors in the EPMA data.²

Application of the diffusion model described above requires that the natural apatite crystals have F/Cl/OH zones that are long enough for modelling (e.g. of $> 3 \mu\text{m}$ in distance). For example, the apatite crystals from Merapi 2010 rocks (see Chapter 3 of this thesis) do not show any zoning, which we interpreted as being related to the much faster magma ascent in 2010 than 2006. Although these un-zoned crystals from 2010 cannot provide diffusion profiles for us to precisely determine the timescales, they can be used to estimate the maximal times for the magma ascent which prevent any obvious zoning to be formed. Below we show the timescales required to produce a zoning of ≤ 3 micrometers in length at a variety of temperatures, where we take 3 micrometer as the minimum profile length that can be used for diffusion modelling (Fig 4.16).

Considering the time as that of magma ascent and the knowledge of magma pre-eruptive depth, we obtained a range of magma ascent rates (Fig. 4.16) which represent the maximal ascent velocities that can produce a 3- μm Cl zone in apatite crystals (e.g. at 900°C), with given starting locations of magma ascent (e.g. between 0.5 and 5 km). For example, considering the depths of 2.5-5 km as the starting locations for the ascending magmas before the Merapi 2010 eruption, and temperatures between $900\text{-}925^\circ\text{C}$, the ascending magma that could produce Cl zoning for diffusion modelling should have velocity less than 0.01-0.04 m/s (Fig. 4.16). Since no Cl zoning was observed from the apatite from the Merapi 2010 rocks (see Fig. 3.4 in Chapter 3), the magma ascent rates in 2010 have to be larger than 0.01-0.04 m/s, i.e. at least 5-8 times faster than the ascent rates of 0.002-0.005 m/s in 2006 (assuming the ascent from depths of 2.5-5 km and temperature of 900°C). Again, the velocities mentioned above likely represent the average magma ascent rates before each eruption, given the assumption of fixed temperature and chlorine content at the crystal-melt boundary used in our model.

Nonetheless, this simple diffusion model can provide us a preliminary estimate of the lower limits of magma ascent rates of a variety of eruptions, if no obvious Cl zone was observed from the groundmass apatite in the emitted rocks.

Fig. 4.16. Magma ascent rates modelled using the diffusion distance of 3 μm of Cl in apatite for a range of temperatures, and pre-eruptive magma storage depths. The length of 3 μm is assumed as the minimum for Cl zoning in apatite that can be used for diffusion modelling to determine the timescale and magma ascent rates. For example, for a system at 900 °C, and magma storage depth of 5000 m, the apatite crystal with Cl zoning of < 3 μm would imply magma ascent rates of > 0.02 m/s (marked in black dashed line with arrows).

4.7. Conclusions

We report new experimental data for the diffusion rates of F, Cl and OH in apatite at 800-1100 °C and 1-atm, and possibly the first determination of the diffusivities of S. We find a “uphill” diffusion for Cl, which is likely caused by the multicomponent diffusion of F, Cl and OH in apatite, as they are present in the same anion column of apatite crystallographic structure. We have developed a multicomponent diffusion model to calculate the diffusivities from the experimental run products, from which we find smaller tracer diffusion rates of Cl than those reported in literature (which assumed that Cl follows a single-component diffusion mechanism). We have applied the new diffusivities and a multicomponent diffusion model to calculate the diffusion time of a Cl-zoned groundmass apatite from the Merapi 2006 eruption. The obtained timescale of ~ 2 weeks likely represents the duration of the magma ascent in 2006, which agrees with the starting time of volcanic unrest before eruption. This diffusion model can be improved by considering the time-space variations in temperatures and the melt Cl concentrations during magma ascent. Future experimental data on the diffusion rates of F-Cl-OH in apatite at higher pressures (e.g. 200 MPa) can be combined with our results to improve the precision of this diffusion model. We propose that natural apatite crystals in contact with the melt/glass with or without volatile zoning can help us to gain some insights of the magma ascent rates during a variety of eruptions, and thus contribute to better understanding of the eruption activities. The findings from this study can be also applied to constrain the history of volatile fluxing in plutonic systems, and the volatile information recorded by apatite from the meteorites.

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Summary of supplementary materials

Appendix A: Secondary ion images (SIIs) obtained from SIMS analyses and the signals used for yielding the depth profiles (**Figs. A1, A2**).

Appendix B: The surface roughness of the un-annealed and annealed thin films shown in three-dimensional maps obtained using Atomic Force Microscope (**Fig. B1**).

Appendix C: Model fits for the diffusion profiles of F, Cl and OH, and the Matlab script for modelling the multicomponent diffusion.

Appendix D: Model fits for the diffusion profiles of S, and the Matlab script for modelling the single-component diffusion.

Appendix A: Secondary ion images (SIIs) obtained from SIMS analyses and the signals used for yielding the depth profiles.

Fig. A1. Secondary ion images (SIIs) of $^{16}\text{O}^1\text{H}$, ^{18}O , ^{31}P , ^{34}S , $^{19}\text{F}^{16}\text{O}$, and ^{37}Cl (the order marked in panel a), obtained from different scanning cycles of the SIMS analyses on a thin film-substrate sample (DAP7). The substrate (panels d-e) shows lower OH and S (in darker color), but higher F and Cl (in brighter color) than the thin film (panels a-c). The ion distributions in the substrate (panels d-e) are in general more homogenous than those within the thin film (panels a-c). The interface between the substrate and thin film was scanned at about the 70th cycle for this sample.

Fig. A2. Diffusion profiles of chlorine obtained using SIMS for a thin film-substrate sample (DAP7). Panels *a-d* show profiles yielded from different areas (ROI, marked in white lines) from the secondary ion image (SII) for ^{37}Cl (normalized to ^{18}O) after scanning for 350 cycles. The four profiles show similar results, but the profile in panel *d* yielded by signals collected from larger “ROI” areas is less scattered with smaller uncertainties, and thus was taken for diffusion modelling.

Appendix B: The surface roughness of the un-annealed and annealed thin films shown in three-dimensional maps obtained using Atomic Force Microscope (AFM).

(a) Un-annealed Si wafer with thin film deposition

(b) Annealed sample (DAp11)

Fig. B1. Three-dimensional maps obtained using AFM from the surface of (a) the apatite thin film deposited on a silicon wafer (without annealing), and (b) a thin film-substrate couple after annealing. The surface roughness shown in panel *a* is likely over-estimated due to the presence of some scratches on the Si wafer. The surface roughness of the annealed sample (panel *b*) is rougher, likely resulted from the roughness of the thin film superimposed with that of the substrate.

Appendix C: Model fits for the diffusion profiles of F, Cl and OH, and the Matlab script for modelling the multicomponent diffusion.

Below are the diffusion profiles modelled using the diffusion rates (“good fits”) reported in Table 4.3 in text, and some bad-fit profiles (“bad fits”) out of the uncertainty range of those measured using EPMA or SIMS considering the analytical error.

(1) 6d#1 (analyzed using EPMA)

Good fits considering analytical errors:

(a) Best-fit

(b) Min. D

(c) Max. D

Bad fits:

(2) DAp11 (analyzed using SIMS)

Good fits considering analytical errors

(a) Best-fit

(b) Min. D

(c) Max. D

(3) DAp7 (analyzed using SIMS): Good fits for Cl but not for F or OH.

(4) DAp9 (analyzed using SIMS): Good fits considering analytical error

(5) DAp15 (analyzed using SIMS): Good fits considering analytical error

(6) DAp16, ||a (analyzed using SIMS):

Fits for the substrate

Fits for the substrate and thin film

Below are the Matlab scripts used for modelling the multicomponent diffusion of F-Cl-OH in apatite, shown in three parts.

(1) MCD.m

```
%% Multi-Component Diffusion (MCD) in Apatite
% By Weiran Li. Updated on 21/06/2019.
clear all; close all; format compact; format longe
fprintf('\n          Apatite F-Cl-OH diffusion  \n');
fprintf('_____ \n');

%% USER DEFINED PARAMETERS
% Defining PARAMETERS
gamma    = 0;    % 0-Linear,1-Cyl,2-Sph.
dx       = 1;    % 'xstep'(in nm)
dt0      = 0.03; % 'tstep'(in hours)
Intf_pos = 0;    % 'Intf_pos' (in nm)
C_Mode   = 1;    % Interpolation for initial composition
R_gas    = 8.3144; % Universal gas constant (J/mol/K)
num_tol  = 1e-18; % Numerical tolerance limit
% measured profile: column 1-4: Distance, Cl, F, OH (in mole fractions)
fname_meas = 'Apa_Durango.txt';

% GEOMETRY of Domain; var.-'gamma'-0-Linear,1-Cylindrical,2-Spherical
if gamma == 0;geom = 'Linear';end
if gamma == 1;geom = 'Cylindrical';end
if gamma == 2;geom = 'Spherical';end

%% Proceeding towards MAIN CALCULATION
% Load initial profiles: recall MC_SETUP.m
MC_SETUP
press=input(' Proceed with computation?[y-YES;n-NO] : ','s'); %input "y" to continue the
running
if strcmpi(press,'y')== 1
    fprintf(' Computation starts..!\n\n');
    % variables storing evolution of parameters
    C_f      = zeros(component,xnum); % final concentration matrix
    time_evo(1) = 0;                % time evolution record
    T_evo(1)   = temp(1);            % Temp evolution record

    % converting 'phi0' from row to column vector so as to match
    % with dimensions of 'phin' for ease of programming
    % size (phi0/phin) = matrix (xnum,component)
    phi0     = C_i';
    phin     = zeros(size(phi0));
```

```

timesum = 0; % total real time elapsed
t = 0; % iteration/time-step index

%% Main Computation starts
while timesum < t_length
    t = t+1; % increasing the iteration index
    if rem(t,50) == 0
        fprintf(' ... %d iterations ... \n',t);
    end
    %% Calculating Temperature
    for i = 2:length(time)
        if timesum >= (time(i-1)-num_tol) && timesum <= (time(i)+num_tol)
            Tslope = (temp(i)-temp(i-1))/(time(i)-time(i-1));
            Tintercept = temp(i-1)-(Tslope*time(i-1));
            T_rock = Tslope*timesum+ Tintercept;
        end
    end

    %% Calculating the TIME-STEP (dt)
    dt = min(dt0,t_length-timesum); % given time-step is dt0
    timesum = timesum + dt; % increasing the total time

    %% Tracer_D as f(Pressure-Temperature)
    DLft = zeros(component,1); DRgt = zeros(component,1);
    for kl=1:component
        DLft(kl) = D0_L(kl);%*exp((-Ea_L(kl)-P_rock*Va_L(kl))/(R_gas*T_rock));
        DRgt(kl) = D0_R(kl);%*exp((-Ea_R(kl)-P_rock*Va_R(kl))/(R_gas*T_rock));
    end

    %% Tracer_D as f(composition)
    % creating Tracer_D vector of each componenet at each cell
    % centers to account for compositional dependence of D*
    % calculating D at each cell-centre acc. to composition
    D_xcp = zeros(component,xnum);
    for l = 1:component
        for j = 1:length(x)
            if j<=Intf_ind-1
                D_xcp(l,j) = DLft(l);
            else
                D_xcp(l,j) = DRgt(l);
            end
        end
    end

    %% CALCUALTION FOR NUMERICAL SOLUTION BEGINS
    for gg = 1:component-1

        %% MC_D-coeff terms for appro. component from D_matrix

```

```

% calculating terms from D_matrix for a component

% D11   D12   D13   D14   ..... D1(n-1)
% D21   D22   D23   D24   ..... D2(n-1)
% .
% D(n-1)1 D(n-1)2 D(n-1)3 D(n-1)4.....D(n-1)(n-1)

% e.g; for component 1; D11, D12, D13,..., D1(n-1) will be calculated at
% new time step, i.e. implicit time
% component index should be used to identify the component

MC_D = zeros(component-1,xnum);
for i=1:xnum
    %Sig_DX
    sig_DX = 0;
    for k=1:component
        sig_DX = sig_DX + D_xcp(k,i)*phi0(i,k);
    end
    for hh=1:component-1
        % Kronecker delta
        Kro_del = 0; if gg==hh; Kro_del = 1; end
        term1= D_xcp(gg,i)*Kro_del;
        term2= ((D_xcp(gg,i)*phi0(i,gg))/sig_DX)*...
            (D_xcp(hh,i)-D_xcp(component,i));
        % by default last component will be taken as dependent component
        MC_D(hh,i)= term1-term2;
    end
end

%% interpolating D at cell-interfaces from surrounding cell-centres
D_xip_0 = zeros(component-1,length(xip));
for m = 1:component-1
    for j = 2:length(xip)-1
        D_xip_0(m,j) = (2*MC_D(m,j-1)*MC_D(m,j))/...
            (MC_D(m,j-1)+MC_D(m,j));
    end
    % putting the immediate next D values for domain boundaries
    D_xip_0(m,1) = D_xip_0(m,2);
    D_xip_0(m,end) = D_xip_0(m,xnum);
end
% storing D_xip_0 in to the working variable
D_xip = D_xip_0;

%      AAA=D_xip(:,5)./(1e12*hr2sec);
%      Array(gg,:)=D_xip(:,5)';
%      if gg==2
%          t
%          DLft(1)/(1e12*hr2sec);

```



```

%      DLft(2)/(1e12*hr2sec);
%      DLft(3)/(1e12*hr2sec);
%      Array./(1e12*hr2sec);
%      end

%% Assigning boundary,flux & interface cond. for each componenet
% input in 'Boundary.txt':
BC_left = Bound_left(gg); flux_left = F_left(gg);
BC_right = Bound_right(gg); flux_right = F_right(gg);

%% Numerical solution
L = zeros(xnum,xnum); % matrix of the coefficients
R = zeros(xnum,1); % right hand side vector
% Space Loop starts
for i = 1:xnum
    %% Defining the boundaries by FVM EQUATIONS
    if i == 1 % LEFT BOUNDARY CONDITION

        if BC_left == 1 % fixed concentration
            A3 = 0; rRri = 0; off_D_term = 0;

        elseif BC_left == 2 % zero flux
            % diagonal D_terms for L Matrix
            Dr = D_xip(gg,i+1); A3 = Dr*dt/(dx*dx);
            rRri = ((x(i)+0.5*dx)/x(i)).^gamma;

            % off diagonal D_terms for RHS coefficients
            off_D_term = 0;
            for hh=1:component-1
                if hh==gg
                    off_D_term = 0;
                else
                    B3 = D_xip(hh,i+1)*dt/(dx*dx);
                    % adding all off-diagonal terms
                    off_D_term = off_D_term + ...
                        ((B3*rRri*phi0(i+1,hh)) - ...
                        (B3*rRri*phi0(i,hh)));
                end
            end
        end

        % MATRIX
        L(i,i) = 1+(A3*rRri); L(i,i+1) = -A3*rRri;
        % RHS coefficients
        R(i,1) = phi0(i,gg) + off_D_term;

    elseif i == xnum % RIGHT BOUNDARY CONDITION

```

```

if BC_right == 1 % Fixed concentration
    A1 = 0; rLri = 0; off_D_term = 0;

elseif BC_right == 2 % Varying concentration
    % diagonal D_terms for L Matrix
    D1 = D_xip(gg,i); A1 = D1*dt/(dx*dx);
    rLri = ((x(i)-0.5*dx)/x(i)).^gamma;

    % off diagonal D_terms for RHS coefficients
    off_D_term = 0;
    for hh=1:component-1
        if hh==gg
            off_D_term = 0;
        else
            B1 = D_xip(hh,i)*dt/(dx*dx);
            % adding all off-diagonal terms
            off_D_term = off_D_term + ...
                ((B1*rLri*phi0(i-1,hh)) - ...
                (B1*rLri*phi0(i,hh)));
        end
    end
end

% MATRIX
L(i,i-1) = -A1*rLri; L(i,i) = 1+(A1*rLri);
% RHS coefficients
R(i,1) = phi0(i,gg) + off_D_term;

else % INTERNAL NODES
    %diagonal D_terms
    D1 = D_xip(gg,i); Dr = D_xip(gg,i+1);
    A1 = D1*dt/(dx*dx); A3 = Dr*dt/(dx*dx);
    % radius_terms
    rLri = ((x(i)-0.5*dx)/x(i)).^gamma;
    rRri = ((x(i)+0.5*dx)/x(i)).^gamma;

    % MATRIX coefficients
    L(i,i-1) = -A1*rLri;
    L(i,i) = 1+ (A1*rLri) + (A3*rRri);
    L(i,i+1) = -A3*rRri;

    % RHS VECTOR
    % off diagonal D_terms
    off_D_term = 0;
    for hh=1:component-1
        if hh==gg
            off_D_term = 0;
        else

```

```

        B1 = D_xip(hh,i)*dt/(dx*dx);
        B3 = D_xip(hh,i+1)*dt/(dx*dx);
        % adding all off-diagonal terms
        off_D_term = off_D_term + ...
            ((B1*rLri*phi0(i-1,hh))-...
            ((B1*rLri+B3*rRri)*phi0(i,hh))+...
            (B3*rRri*phi0(i+1,hh)));
    end
end
R(i,1) = phi0(i,gg) + off_D_term;
end

end % SPACE LOOP ENDS

% computing the matrix
phin(:,gg) = L\R;

end % COMPONENT LOOP ENDS

%% calculating the concentration of the dependent component
for i=1:xnum
    sum_IndComp = 0;
    for hh=1:component-1
        sum_IndComp = sum_IndComp+phin(i,hh);
    end
    phin(i,component) = 1.0-sum_IndComp;
end
% saving to initial profile
phi0 = phin;
% plotting:
C_plot = phin;
MC_PLOT % recall MC_PLOT.m
time_evo(t) = timesum;
T_evo(t) = T_rock;

end %(end of time loop)
fprintf('\n Computation ends..!\n');

%% Storing the last profile & Mass-balance check
for kk = 1:component
    for i=1:length(phin)
        C_f(kk,i)= phin(i,kk);
    end
end
% mass-balance check
massf = zeros(1,component); mass_error=zeros(1,component);
Hesse_error = zeros(1,component);
for kk=1:component

```

```

    massf(kk)    = x(1:xnum).^gamma*phin(1:xnum,kk)*dx;
    Hesse_error(kk) = abs(massf(kk)-mass0(kk))/xnum;
    mass_error(kk) = (abs(massf(kk)-mass0(kk))/mass0(kk))*1e2;
end

fprintf(' Total No. of iterations :  %d\n',t-1);
fprintf(' Total time lapsed (hrs) :  %5.4e\n\n',timesum);
fprintf(' Mass balance...\n');
fprintf(' Component   Error[%%]      Error[Hesse]\n');
for kk = 1:component
    fprintf(' C-%d      %6.3e      %6.3e \n',...
            kk,mass_error(kk),Hesse_error(kk));
end

end

fprintf('\n Program finished..!\n');
fprintf('_____!\n\n');
%% End of script

```

(2) MC_SETUP.m

```
%% SEQUENTIAL STEPS PERFORMED IN SETUP.m routine
% 1. Defining filenames to be read
% 2. Reading all 4 files and assigning variables
% 3. Unit conversion
% 4. Checking of data reading
% 5. Executing various Initial setups

%% Filenames
fname_xC = 'initial_boundary.txt';
fname_tTPV = 'tTPV.txt';
fname_DC = 'Diffusion coeff.txt';
fname_BC = 'Boundary.txt';

%% Reading DIFFUSION COEFFICIENT data
fid = fopen(fname_DC,'rt');
if fid==-1
    fprintf('\n >>ERROR: problem in opening D_Left file\n');
    read_DCL = 0; % conditional statement to go for profile setting
else
    heading = fscanf(fid,'%s',6); % headings of the file
    data1 = fscanf(fid,'%f',[6 inf]); fclose(fid);
    % Storing the input data of Diffusion coeff. in column vectors
    data1_inp = data1';

    % for LHS medium
    D0_L = data1_inp(:,1); % [in m2/sec]
    Ea_L = data1_inp(:,2); % [in J/mol]
    Va_L = data1_inp(:,3); % [in m3/mol]
    % for RHS medium
    D0_R = data1_inp(:,4); % [in m2/sec]
    Ea_R = data1_inp(:,5); % [in J/mol]
    Va_R = data1_inp(:,6); % [in m3/mol]
    read_DC = 1;
end

%% Reading Boundary & Interface conditions for each component
fid=fopen(fname_BC,'rt');
if fid==-1
    fprintf('\n >>ERROR: problem in opening Boundary cond. file\n');
    read_BC = 0;
else
    heading = fscanf(fid,'%s',4); % headings of the file
    data2 = fscanf(fid,'%f',[4 inf]); fclose(fid);
    % Storing the input data of Diffusion coeff. in column vectors
    data2_inp = data2';
    Bound_left = data2_inp(:,1); F_left = data2_inp(:,2);
```

```

    Bound_right = data2_inp(:,3); F_right = data2_inp(:,4);
    read_BC = 1;
end

%% Determining no. of componenets given by user
if length(D0_L)==length(D0_R) && length(D0_L)==length(Ea_R)
    if length(D0_R)==length(F_left) && length(D0_L)== length(Bound_right)
        component = length(D0_L);
    end
end

%% Reading INITIAL initial_boundary data
fid = fopen(fname_xC,'rt');
if fid == -1
    fprintf(' >>ERROR: problem in opening initial_boundary file\n');
    read_xc = 0; % conditional statement to go for profile setting
else
    heading = fscanf(fid,'%s',component+1); % headings of the file
    data3 = fscanf(fid,'%f',[component+1 inf]); % data as matrix;
    fclose(fid);
    % sorting the data initial concentration profiles
    % each column in input file is a row vector in 'data'
    % input data as column vectors
    data3_inp = data3';
    a = data3_inp(:,1); % [in nm]; space data
    conc_i = zeros(component,length(a));
    for k=1:component
        conc_i(k,:) = data3_inp(:,k+1); % [in given units]
    end
    read_xc = 1;
end
Intf_pos=a(2,1);
%% Reading time-Temperature-Interface velocity data
fid=fopen(fname_tTPV,'rt');
if fid==-1
    fprintf("\n >>ERROR: problem in opening t-T-P-Intf_V file\n");
    read_tTPV = 0;
else
    heading = fscanf(fid,'%s',2); % headings of the file
    data4 = fscanf(fid,'%f',[2 inf]); % data as matrix
    fclose(fid);
    % Storing the input data on time, Temp., Press. and Dissolution rate
    % in column vectors
    data4_inp = data4';
    time = data4_inp(:,1); % [in years]
    temp = data4_inp(:,2); % [in Celsius]
    read_tTPV = 1;
end

```

```

%% Reading MEASURED PROFILE
fid = fopen(fname_meas,'rt');
if fid == -1
    fprintf("\n >>ERROR: problem in reading parameters\n");
else
    heading = fscanf(fid,'%s',component+1); % headings of the file
    % data as matrix; each column in input file is a row vector in 'data'
    data5 = fscanf(fid,'%f',[component+1 inf]); fclose(fid);
    % input data as column vectors
    data5_inp = data5';
    % sorting the data
    meas_dis = data5_inp(:,1); % [in  $\mu\text{m}$ ] ; space data
    meas_profile = zeros(component,length(meas_dis));
    for k=1:component
        meas_profile(k,:) = data5_inp(:,k+1); % [in given units]
    end
end

%% CHECKING of reading status of files
read_status = 0; % invalid reading
if read_DC == 1 && read_BC == 1
    if read_xc == 1 && read_tTPV == 1
        read_status = 1;
        fprintf(' Reading input files completed! \n');
    end
end

% READING OF FILES ENDED
% -----

if read_status == 1
    %% CONVERSION OF UNITS
    % space variables in  $\mu\text{m}$  / time in hours / Temp in Kelvin
    % / Energy in Joules

    % converting unit of D
    hr2sec = 60*60;
    % converting D into  $\text{nm}^2/\text{hours}$ 
    D0_L = D0_L.*(1e+18*hr2sec); D0_R = D0_R.*(1e+18*hr2sec);
    % converting 'Celsius' to 'Kelvin'
    temp = temp + 273.15;

    %% Setting space gridding(s)
    % position of cell-walls
    xip = a(1):dx:a(end);

    % position of INTERFACE
    Intf_ind = find(xip==Intf_pos);

```

```

% Checking the position of Interface; xip(1) < Intf_ind < xip(end)
if Intf_ind<2; Intf_ind = 2; end;
if Intf_ind>(length(xip)-1); Intf_ind = length(xip)-1; end;
Intf_ind0 = Intf_ind; % to store the initial interface pos.

% position of cell-centres
xcp = zeros(1,length(xip)-1);
for k=1:length(xip)-1
    xcp(k) = xip(k)+dx/2.0;
end

% checking space values for sph./cyl. geometry;
if gamma>0
    % setting the first element to zero value for sph./cyl. geometry;
    if xip(1)<=0
        %xip(1) = 0;
        read_status = 0;
        fprintf(' >> Msg: Geometry is non-linear!\n');
        fprintf(' >> Don't give negative distance \n');
    end
    % resetting Intf_pos for sph./cyl. geom with given value at 0
    if Intf_pos <= 0
        %Intf_pos = xip(1);
        read_status = 0;
    end
end
end

if read_status == 1
    % storing in appro. variables
    x = xcp; xnum = length(x); xsize = xip(end)-xip(1);
    % total time-period for computation
    t_length = time(end)-time(1);

    %% Setting initial concentraion profile(s)
    % pre-allocating the vectors
    C_i = zeros(component,xnum);
    % setting initial profile
    if C_Mode == 1
        % Flat homogenous initial concentration in each medium
        for j = 1:component
            for i= 1:xnum
                if i<Intf_ind
                    C_i(j,i)= conc_i(j,1);
                elseif i>=Intf_ind
                    C_i(j,i)= conc_i(j,end);
                end
            end
        end
    end
end

```



```

end

else
    % Linearly interpolated concentration for each component
    % interpolating at cell-faces
    C_intf = zeros(component,length(xip));
    for k = 1:component
        for y = 1:length(xip)
            for i = 2:length(a)
                if xip(y)>=a(i-1) && xip(y)<=a(i)
                    cslope = (conc_i(k,i)-conc_i(k,i-1))/...
                        (a(i)-a(i-1));
                    cintercept = conc_i(k,i-1)-(cslope*a(i-1));
                    C_intf(k,y) = cslope*xip(y)+ cintercept;
                end
            end
        end
    end
    % interpolating at cell-centres
    for l = 1:component
        for k=1:xnum
            slope = (C_intf(l,k+1)-C_intf(l,k))/(xip(k+1)-xip(k));
            C_i(l,k)= slope*x(k)+ C_intf(l,k)-(slope*xip(k));
        end
    end
end

%% Total initial concentration for mass-balance check
x_mb=x'; mass0 = zeros(component,1);
for kk = 1:component
    mass0(kk,1) = C_i(kk,1:xnum)*x_mb(1:xnum).^gamma*dx;
end

%% Plotting initial profile and printing certain details
C_plot = C_i'; timesum = 0; MC_PLOT

fprintf(' Solving for...\n');
fprintf([' MC Diffusion (',num2str(component),' component)\n\n']);
fprintf(' Space grid-size : %3.2e μm \n',dx);
fprintf(' Number of grids : %d \n',xnum);
fprintf(' No. of Interf. Pos. : %d \n',length(xip));
fprintf('\n');

else
    fprintf('\n >> ERR: Error in input files! \n');
end
%% End of script

```

(3) MC_PLOT.m

```
%% Plotting Concentration Evolution for each time step
set(0,'DefaultAxesFontName','Arial');
set(0,'DefaultAxesFontSize',16);
formatSpec = '%7.3f\n';

% forming handles for each component for plotting
h = zeros(1,component);
% forming string arrays for components' conc.
C_legend{1} = 'Cl'; C_legend{2} = 'F'; C_legend{3} = 'OH';
pq = Intf_ind; % for shortening the variable name
figure(2)
D_Cl= data1_inp(1,4);D_F= data1_inp(2,4);D_OH= data1_inp(3,4);
% x limit, symbols and line properties
xmax=800;symbol='ko';msize=5;width=3;

%% Plotting Cl
set(gcf,'unit','centimeters','position',[2 10 50 15]);
subplot(1,3,1);
for kk = 1:l
    h(kk)=errorbar(meas_dis,meas_profile(kk,:),0.1*meas_profile(kk,:),'-','color',[0.5 0.5
0.5]);hold on;
    h(kk)=plot(meas_dis,meas_profile(kk,:),symbol,'markerfacecolor','k','markersize',msize);
hold on;
    if pq>1
        h(kk)= plot([xip(1),xcp(1:pq-1),xip(pq),xip(pq),xcp(pq:xnum),xip(end)],...
[C_plot(1,kk),C_plot(1:pq-1,kk)',C_plot(pq-1,kk),...
C_plot(pq,kk),C_plot(pq:xnum,kk)',C_plot(xnum,kk)],...
'r-','LineWidth',width); hold on;
    else
        h(kk)= plot([xip(1),xcp,xip(end)],[C_plot(1,kk),C_plot(:,kk)',C_plot(xnum,kk)],...
'r-','LineWidth',width); hold on;
    end
    if pq>1
        plot(xcp(pq-1),C_plot(pq-1,kk),'ro','MarkerSize',2.5,...
'MarkerFaceColor','r'); hold on
        plot(xcp(pq),C_plot(pq,kk),'r','MarkerSize',2.5,...
'MarkerFaceColor','r'); hold on;
    end
    hold on;
    h(kk)=plot(x,C_i(kk,:),'--b','LineWidth',1.5); hold on;
end
xlabel('Distance (nm)'); ylabel('X_C_l');
xlim([0 xmax]);
D_Cl_str=streat('D(Cl) =', num2str(D_Cl), ' m^2/s');
text(200,0.03,D_Cl_str);
set(gca,'fontsize',16);
```

```

hold off;
fig = gcf; set(findall(fig,'-property','fontWeight'),'fontWeight','bold');
drawnow

%% Plotting F
subplot(1,3,2);
for kk = 2:2
    h(kk)=errorbar(meas_dis,meas_profile(kk,:),0.005*meas_profile(kk,:),'-','color',[0.5 0.5
0.5]);hold on;
    h(kk)=plot(meas_dis,meas_profile(kk,:),symbol,'markerfacecolor','k','markersize',msize);
hold on;
    if pq>1
        h(kk)= plot([xip(1),xcp(1:pq-1),xip(pq),xip(pq),xcp(pq:xnum),xip(end)],...
[C_plot(1,kk),C_plot(1:pq-1,kk)',C_plot(pq-1,kk),...
C_plot(pq,kk),C_plot(pq:xnum,kk)',C_plot(xnum,kk)],...
'r-','LineWidth',width); hold on;
    else
        h(kk)= plot([xip(1),xcp,xip(end)],[C_plot(1,kk),C_plot(:,kk)',C_plot(xnum,kk)],...
'r-','LineWidth',width); hold on;
    end
    if pq>1
        plot(xcp(pq-1),C_plot(pq-1,kk),'ro','MarkerSize',2.5,...
'MarkerFaceColor','r'); hold on;
        plot(xcp(pq),C_plot(pq,kk),'b','MarkerSize',2.5,...
'MarkerFaceColor','b'); hold on;
    end

    hold on;
    h(kk)=plot(x,C_i(kk,:),'--b','LineWidth',1.5); hold on;
end
xlabel('Distance (nm)'); ylabel('X_F');
xlim([0 xmax]);
D_F_str=strcat('D(F) =', num2str(D_F), ' m^2/s');
text(200,0.82,D_F_str);
hold off;
fig = gcf; set(findall(fig,'-property','fontWeight'),'fontWeight','bold');
drawnow

```

```

%% Plotting OH
subplot(1,3,3);
for kk = 3:3    h(kk)=errorbar(meas_dis,meas_profile(kk,:),0.15*meas_profile(kk,:),'-
','color',[0.5 0.5 0.5]);hold on;
    h(kk)=plot(meas_dis,meas_profile(kk,:),symbol,'markerfacecolor','k','markersize',msize);
hold on;
    if pq>1
        h(kk)= plot([xip(1),xcp(1:pq-1),xip(pq),xip(pq),xcp(pq:xnum),xip(end)],...
[C_plot(1,kk),C_plot(1:pq-1,kk)',C_plot(pq-1,kk),...
C_plot(pq,kk),C_plot(pq:xnum,kk)',C_plot(xnum,kk)],...

```

```

        'r-', 'LineWidth', width); hold on;
    else
        h(kk)= plot([xip(1),xcp,xip(end)], [C_plot(1,kk),C_plot(:,kk)',C_plot(xnum,kk)],...
            'r-', 'LineWidth', width); hold on;
    end
    if pq>1
        plot(xcp(pq-1),C_plot(pq-1,kk),'ro', 'MarkerSize',2.5,...
            'MarkerFaceColor','r'); hold on;
        plot(xcp(pq),C_plot(pq,kk),'b.', 'MarkerSize',2.5,...
            'MarkerFaceColor','b'); hold on;
    end
    hold on;
    h(kk)=plot(x,C_i(kk,:),'--b', 'LineWidth',1.5); hold on;
end
xlabel('Distance (nm)'); ylabel('X_O_H');
xlim([0 xmax]);
D_OH_str=strcat('D(OH) =', num2str(D_OH), ' m^2/s');
text(200,0.12,D_OH_str);
hold off;
fig = gcf; set(findall(fig,'-property','fontWeight'),'fontWeight','bold');
drawnow
%% End of script

```

Appendix D: Model fits for the diffusion profiles of S, and the Matlab script for single-component diffusion modelling.

Below are the modelled profiles showing the best fit with the diffusion profiles of S measured from four crystals.

(1) DAP11 ($\parallel$ c): Annealed at 900 °C for 0.67 hours.

(2) DAP15 ($\parallel$ c): Annealed at 900 °C for 2 hours.

(3) DAp9 (|| c): Annealed at 804 °C for 3.67 hours.

(4) DAp16 (|| a): Annealed at 950 °C for 21.12 hours.

Below is the script for modelling the single-component diffusion of S in apatite.

```

%% By Weiran Li. Updated on 21/06/2019.
Close all; clear all;
%% measured profile
A = load('S_Exp.txt');      %column1: distance; column2: concentration
B = A';
x_nat= B(1,:);             %Distance
c_nat = B(2,:);            %concentration
Length_nat= B(1,end);      %Total length of the measured profile
Measure_i=length(x_nat);    %Total data points in measured profile
relativeErr = 0.02;         %Relative error from analyses
err = relativeErr*c_nat;    %Error of concentration

%% Set variables
D_c  = 3.8E-20*(10^18);     %Diffusion rate parallel to c-axis, in nm2/s
D_tra = D_c;               %Diffusion rate along the traverse, in nm2/s
delta_x= 5;                %distance step, in nanometer
Exp_t = 21.12*3600;        %Experimental duration, in seconds
max_dt = 0.5*((delta_x)^2)/D_tra;%maximum delta t to sustain stability (<=0.5)
delta_t = 100;             %time step, in seconds;
t_itr = (Exp_t/delta_t)+1;  %time iteration for modelling

%% Check stability
Stability = D_tra*delta_t/((delta_x)^2) %Stability should be <=0.5
if Stability > 0.5
    x=['Stability =',num2str(Stability),'Check!'];
    disp(x)
else

%% Initial & Boundary conditions (j=1 represents time series)
x_model = [1:delta_x:Length_nat]; %Distance of model
x_i = length(x_model);            %Total data points in model
c_ini = mean(c_nat(1,end-30:end)); %Set initial concentration
c_bl = min(c_nat);                %left-side boundary: comp at the rim
c_br = c_ini;                    %right-side boundary: comp at the core

kink=delta_x;                    %kink point in initial profile
c_ini_arr =[c_bl*ones(1,(kink)/delta_x - 1),c_ini*ones(1,(B(1,end)-kink)/delta_x - 1)];

%% Modelling & plot
hfig = figure(1);
set(hfig, 'Position', [20, 10, 1000, 800]);
box on
for j=1:t_itr
    for i=2:x_i-1

```

```

c(2:x_i,1)= [c_bl*ones(1,(kink)/delta_x - 1) c_ini*ones(1,(B(1,end)-kink)/delta_x)];
c(1,j)= c_bl; %fixed comp at left-side boundary
c(x_i,j)= c_br; %fixed comp at right-side boundary
% calculate c at location i of next time-step
c(i,j+1) = Stability *(c(i-1,j)+c(i+1,j)-2*c(i,j))+ c(i,j);
end
Ans = c(1:x_i,j); %profile at time j

% plot initial, measured, and modelled profiles (and error)
ini_x=[1:delta_x:Length_nat]; %initial+boundary condition: x
ini_y=[c_bl c_ini_arr c_br]; %initial+boundary condition: y
plot(ini_x,ini_y,'b--',x_nat,c_nat,'ko',x_model,Ans,'r-','linewidth',2,'markerfacecolor','k');
errorbar(x_nat,c_nat,err,'k-');
% set x-, y-axis
xlabel('Distance (nm)');ylabel('^3^4S/^3^1P'); set(gca,'fontsize',16);
xlim([0 Length_nat]);
t = delta_t*(j-1); % modelling time
text(100,0.112,['Time=',num2str(t),' s'],'Fontweight','bold','fontsize',14);
text(100,0.087,['D=',num2str(D_tra*10^(-18)), 'm^2/s'],...
'Fontweight','bold','fontsize',12)
pause(0.01);
end
end
legend('Initial+Boundary','Measured','Modelled','Location','southeast');
%% End of script

```


Chapter 5. Conclusions and future work

Many subduction-zone volcanoes are located at densely populated areas and have caused severe hazards to the local communities and even impacts of a planetary scale. Understanding and anticipating the eruption dynamics of these volcanoes is a major scientific and societal endeavor, yet a big challenge for volcanologists. In this thesis, I have focused on understanding the role of magmatic volatiles in controlling the eruption styles, and introduced several novel approaches based on the mineral apatite that have wide applications to a variety of volcanic and plutonic systems.

First, I have developed a new thermodynamic model for constraining the partition behavior of F-Cl-OH between apatite and the melt, with the final goal of estimating the melt water budgets. This model points out the non-ideality of F-Cl-OH mixing in the ternary apatite, especially the mixing between F-Cl. With this model, I propose to use apatite as a new hygrometer applicable for a variety of melts and magmatic pressure-temperatures. I have developed this hygrometer as a user-friendly free online calculator (<https://apthermo.wovodat.org/>). Improvements on this model for more precise estimation of melt water budgets require additional phase equilibria experiments and theoretical analyses of the activity-composition relations of volatile species (especially F and Cl) in the melt. Experimental determinations on the volatile partitioning of other hydrous minerals than apatite (e.g. biotite, amphibole) and the melt at a variety of P - T - X conditions would also benefit the determination of melt volatile budgets.

Second, I have performed petrological analyses using a variety of techniques of the rocks from two eruptions at Merapi volcano (Indonesia) in 2006 and 2010 which had

different explosivities and erupted magma volumes. I have used the measured CO₂, H₂O, Cl, F, S in apatite and combined it with various geothermometers to calculate magmatic volatile budgets of the two eruptions. I show that apatite crystals at a variety of textural positions can be used to track the variations of volatile concentrations in the melts at different magma storage depths. Specifically, I characterize for the first time the concentrations of H₂O, CO₂ and S of the deep melts (near the Moho) below Merapi. The results show that melt volatile budgets were similar before the two eruptions, but the fluxing of CO₂-rich volatiles from the deep reservoir to the pre-existing shallower magma column led to a higher magma buoyancy and faster magma ascent in 2010. Similar models have been found at more mafic volcanoes (e.g. Etna and Stromboli). These findings triggered new questions, such as at what depth did the volatile exsolution occur, and how it is related to the volcanic gas emitted *prior to* the eruption to monitor the deep magma intrusion that could initiate the eruption. A better use of apatite for estimating the melt CO₂ budgets will require additional experimental determination of CO₂ partitioning between apatite and the melt at a variety of magmatic temperature-pressures, with combination of direct measurements on the site occupancy of carbonate in the crystal structure of the experimental and natural apatite.

Third, I report new experimental data for the diffusion rates of F, Cl, OH and S (the latter two were not determined before this work) in apatite at magmatic temperatures. I show that F, Cl, and OH re-equilibrate via a multicomponent diffusion mechanism, where the Cl profiles in particular show evidence of uphill diffusion. With this in mind, I have developed a multicomponent diffusion model that can be applied to natural volcanic/plutonic apatite to estimate the timescales of magmatic processes. With application of this model to the Cl-zoned apatite from the Merapi 2006 eruption,

I find a timescale in agreement with those inferred by the volcanic unrest and magma extrusion. The new diffusion data should also be applicable to study the processes of the terrestrial and extraterrestrial plutonic systems. Future work will be to develop a web-based calculator for modelling volatile diffusion in apatite and extraction of magma ascent rates. Such model could be coupled with the existing numerical magma-ascent models that track the changes in vesicularity, crystallinity, temperature and other physical properties with time.

The work presented in this thesis expands the current knowledge of the multiple roles that volatiles can play in the eruptive styles of volcanoes, which helps to better interpret the volcanic monitoring data, and thus improves the probability of accurate forecasting on the styles and sizes of eruptions from the most dangerous volcanoes around the world. Future work on better understanding of volatiles in subduction-zone magmatism will be to investigate (i) the inputs of volatiles from the subducting slab to the magmas in the deep parts of the system; (ii) volatile budgets and degassing rates of the deep magmas and their influences on magma intrusion and the eruption cycles; (iii) the gain/loss of volatiles at shallower depths from the decarbonation of the crustal materials and/or the interaction between the melt and hydrothermal fluids; (iv) the fingerprints of volatiles exsolved at different depths on the emitted gases; and (v) the thermodynamic and kinetic properties of various volatile species in the melt and in hydrous minerals from experimental and theoretical perspectives.

Supplementary materials

S.1. “ApThermo” online calculator

The “ApThermo” online calculator (<https://apthermo.wovodat.org/>) is developed based on the apatite-melt thermodynamic model described in Chapter 2 of this thesis for calculating the chemical formula of apatite (based on the major/minor elements and volatile concentrations from measurements), the exchange coefficients K_D s for the volatiles (of OH, F, Cl) partitioning between apatite-melt, the activity coefficients of OH, F, Cl in binary/ternary apatite solutions, and eventually the water concentrations of the melts in equilibria with apatite. The user interface is shown in the figures below.

**APATITE THERMODYNAMIC MODEL
FOR CALCULATING VOLATILE ABUNDANCES IN MAGMAS**

Instruction:

This thermodynamic model aims to calculate volatile abundances in magmas using volatile compositions of apatite (F, Cl, H₂O), and the equations of exchange coefficient (K_D) from the paper below.

Li W and Costa F (2019)...GCA...
[doi:10.1016/j.gca.2019.04.011](#)

Input 1 **1. Calculating chemical formula of apatite:**

Enter the measured apatite compositions
Boxes marked as "required" need to be filled in for calculation, whereas those marked as "optional" can be left as empty if the values are unknown.

Required:		Optional:	
CaO	<input type="text" value="54.57"/> wt. %	SiO ₂	<input type="text" value="0.4"/> wt. %
P ₂ O ₅	<input type="text" value="40.31"/> wt. %	Na ₂ O	<input type="text" value="0.13"/> wt. %
F	<input type="text" value="1.17"/> wt. %	MgO	<input type="text" value="0.2"/> wt. %
Cl	<input type="text" value="0.55"/> wt. %	Al ₂ O ₃	<input type="text" value="0"/> wt. %
		MnO	<input type="text" value="0"/> wt. %
		FeO	<input type="text" value="0"/> wt. %
Optional:		Ce ₂ O ₃	<input type="text" value="0.02"/> wt. %
H ₂ O*	<input type="text" value="0.91"/> wt. %	SrO	<input type="text" value="0"/> wt. %
CO ₂	<input type="text" value="0.24"/> wt. %	BaO	<input type="text" value="0"/> wt. %
SO ₃	<input type="text" value="0.225"/> wt. %		

*If H₂O in apatite was not directly measured, leave this box empty, so that our model will calculate it based on stoichiometry, assuming that only F, Cl and OH occupy the anion site.

Calculate chemical formula

Chemical formula: $\text{Ca}_{10}(\text{PO}_4)_6\text{X}_2$
(Using 26 Oxygen)

Output 1

Ca (a.p.f.u) 10.237
P (a.p.f.u) 5.975
F (a.p.f.u) 0.648
Cl (a.p.f.u) 0.163

Mole Fraction ☒

X_F 0.346
 X_{Cl} 0.087
 X_{OH} 0.567
 $X_{OH}(\text{calc})^{**}$ 0.567

**Calculated based on stoichiometry (e.g. Deer et al., 1992)

Data sources shown in Fig. 1 from Li and Costa (2019) (link as above).

2. Calculating exchange coefficients and volatile ratios in melt using known temperature

Temperature °C ← **Input 2**

Compute!

Exchange coefficients

$K_D(\text{OH-Cl})$ 0.083
 $K_D(\text{OH-F})$ 0.0153
 $K_D(\text{Cl-F})$ 0.185

Activity coefficients

$\gamma(\text{OH})_{Ap}$ 1.08
 $\gamma(\text{F})_{Ap}$ 1.38
 $\gamma(\text{Cl})_{Ap}$ 1.84

Output 2

Calculated volatile ratios in melt using apatite:

Mole OH/Cl 78.47
Mole OH/F 107.11
Mole Cl/F 1.36

3. Calculating H_2O in melt using known melt Cl and/or F concentrations

Fill in at least one box below:

Cl in melt ppm
F in melt ppm

Input 3

Compute!

- ☒ Dacitic-rhyolitic magma[†]
☐ Basaltic magma^{††}

H_2O calculated using Cl wt. % (Error: $\pm 30\text{-}40\%$)
 H_2O calculated using F wt. % (Error: $\pm 30\text{-}40\%$)

Output 3

Water speciation models from Lesne et al. (2010)[†] and Zhang et al. (1997)^{††}

S.2. Abstracts and presentations at international conferences

Below are the abstracts presented at Goldschmidt 2016, IAVCEI 2017, EMPG 2018, AGU 2018.

(1) Goldschmidt 2016 in Yokohama, Japan (Poster presentation)

Goldschmidt Conference Abstracts 1773

Same initial volatile budget but different ascent paths led to contrasting eruptive styles at Merapi Volcano in 2006 and 2010

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Eruptions at Merapi Volcano (Indonesia) flipped from effusive in 2006 to explosive in 2010, without significant change in magma composition or mineralogy. In such case, the contrasting eruptive styles are controlled by two principal parameters: pre-eruptive volatile budget and/or magma ascent rate. It is often difficult, however, to constrain the two parameters or to establish which plays a larger role in an eruption. For example, it is difficult to apply the “melt inclusion” approach, if the deposits cooled slowly and inclusions are not quickly quenched into glass. Here we show that volatiles in apatite can preserve a temporal and evolutionary record on magma, and thus used to address this problem. We determined the pre-eruptive volatile budgets and magma ascent rates of the 2006 and 2010 eruptions at Merapi, to better understand what controls the eruptive styles.

F, Cl, OH and S concentrations in apatite were measured using secondary ion mass spectrometry and electron microprobe. Point analyses and chemical maps were obtained for apatite crystals in different textural context. We found that amphibole-hosted apatite inclusions in 2006 and 2010 deposits have similarly high volatile contents, indicating similar initial volatile budgets in magmas of the two events, despite the difference in their eruptive styles. Besides, apatite inclusions in clinopyroxene and plagioclase and apatite in the matrix have distinctly low volatile contents. Thus we propose at least two reservoirs in the plumbing system of Merapi: a deep reservoir where amphibole crystallized from volatile-rich magma, and a shallower one where magma was more degassed and crystallized clinopyroxene and plagioclase.

In addition, the 2006 apatite crystals in the matrix show increasing Cl content towards the rim, possibly resulting from an increase in partition coefficient with decreasing pressure, and/or increasing Cl concentration in the residual melt due to microlite growth during slow ascent. In contrast, Cl zoning is not observed in apatite of 2010 deposits. Diffusion modelling of Cl concentrations indicate that the ascent rate of 2010 magma was >25 times faster than that of 2006, consistent with extrusion rates obtained from monitoring data. We propose that the faster magma ascent rate in 2010 is responsible for the greater explosivity of this event, rather than higher pre-eruptive volatile budget, compared to 2006.

Weiran Li, Fidel Costa, Jason S Herrin, Kazuhide Nagashima

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Contrasting eruption styles of Merapi volcano but similar magma pre-eruptive volatile compositions (CO₂, H₂O, S, Cl, F) and contents

Eruption styles of subduction-zone volcanoes may abruptly change. For example, Merapi Volcano (Indonesia) erupted effusively (VEI 2) in 2006, but explosively (VEI 4) in the following event in 2010. What caused this change in eruption style within such short period is still unclear, especially when considering that bulk rock compositions and major mineral assemblages of the 2006 and 2010 deposits are virtually indistinguishable. Here we address this question, by investigating the pre-eruptive volatile compositions and contents using apatite crystals located in various textural positions and hosted by different crystals.

All the major magmatic volatile species including CO₂, OH, S, Cl and F were measured in apatite using Cameca ims-1280 ion microprobe at the University of Hawai'i at Mānoa. We used apatite standards with known concentrations of volatile species. We find that volatile abundances in apatite fall into two groups: clinopyroxene-hosted crystals and microphenocrysts in the groundmass are depleted in CO₂ (~50-800 ppm) and H₂O (~0.5-0.6 wt. %), whereas crystals included in amphibole show distinctly higher CO₂ (>2400 ppm) and H₂O contents (~1 wt. %). Such differences in volatile concentrations indicate at least two magma reservoirs at different depths beneath Merapi, consistent with previous studies. Similar bimodality of apatite volatile content was observed in both the 2006 and 2010 deposits. We used thermodynamic models and exchange coefficients $\{Kd_{\{Cl-OH\}}^{Ap-melt}\}$ from the literature to estimate melt volatile contents. We find that both 2006 and 2010 magmas had ~4-6 wt. % water and ~1000-2000 ppm Cl in the deep reservoir, and ~1-2 wt. % water and ~1500-5000 ppm Cl in the shallower one. These results overlap with the range of volatile contents in melt inclusions and measured gases found in previous studies. Moreover, we find that CO₂ concentrations are at least 3 times higher in the deep reservoir(s) than in the shallower ones. These results show that the main magma plumbing architecture (e.g. two main reservoirs) and the initial volatile abundances in the magmas of 2006 and 2010 were very similar. Thus, magma ascent rates, pre-eruptive accumulation and transfer of volatiles from depth, and/or rapid decompression after dome explosion are likely to be responsible for the contrasting eruption styles of the two events.

- (3) The 16th International Conference on Experimental Mineralogy, Petrology and Geochemistry (EPMG, 2018) in Clermont-Ferrand, France
(Oral presentation; awarded as the “Best student presentation”)

EMPG XVI – Conference Abstracts

**A new experimental study on
multicomponent diffusion of F, Cl and OH
in apatite and implications for magma ascent
rate determinations**

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Chemical zonings in minerals from volcanic rocks have been used to constrain timescales of pre-eruptive magmatic processes, such as magma mixing, yet rarely for those occur within short times but may control eruption styles, such as magma ascent. Recent studies show that Cl zoning in volcanic apatite varies with eruptive styles and thus may be related to ascent rate [1]. Halogen diffusivities in apatite, however, have not been thoroughly studied given only one dataset from literature. Here we report new experimental results for diffusivities of F, Cl and OH in apatite at 800-1100 °C, 1-atm and f_{O_2} of WM buffer. Diffusion couples consist of two types of apatite showing distinct F-Cl-OH compositions. Two types of diffusion sources are used: powders, and thin films deposited using pulsed laser deposition method. Diffusion couples were annealed in a furnace at constant P, T and f_{O_2} for a series of run durations. Concentration profiles of F and Cl were measured using electron microprobe, and OH was calculated assuming stoichiometry. Depth profiles will be measured from thin film samples using SIMS. We find that Cl profiles show uphill diffusion, indicating multicomponent diffusion of F, Cl, and OH. By using a finite difference algorithm to calculate diffusion matrix, we obtain diffusivities of F and OH at 1100 °C as $\sim 3 (\pm 1) 10^{-15} \text{ m}^2/\text{s}$ and $\sim 2 (\pm 1) 10^{-16} \text{ m}^2/\text{s}$, respectively, consistent with those from literature. Despite that F and OH show isotropic diffusion, Cl diffusion is anisotropic, where its diffusivity parallel to c-axis at 1100 °C is $\sim 6 (\pm 2) 10^{-16} \text{ m}^2/\text{s}$, >25 times faster than that parallel to a-axis. D_{Cl} parallel to c-axis obtained here is ~ 5 -10 times slower than that from [2]. Using the new diffusivities, Cl zoning in apatite from Merapi deposits would give timescales of ~ 2 -4 weeks, implying similar time periods of magma ascent before the eruption in 2006, consistent with ground deformation data from literature.

[1] Li et al., 2018, in prep

[2] Brennan, 1994.

(4) 2018 AGU Fall Meeting in Washington D. C., USA (poster presentation).

Title: F, Cl, OH and S diffusion in apatite and applications to constrain magma ascent rates
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Abstract

Chemical zonings in minerals from volcanic rocks have been widely used to constrain timescales of magmatic processes, but rarely exploited to study shorter processes that occur just before eruptions and could control eruptive styles, such as magma ascent. Recent studies show that the appearance of chlorine zoning in groundmass apatite from volcanic rocks varies with eruptive styles and may be related to ascent rates. However, the timescales are difficult to constrain, due to limited studies on the diffusivities of volatile species in apatite, given only one dataset from literature. Here we report new experimental results for F, Cl, OH and S diffusivities in apatite at 800-1100 °C, 1-atm and fO₂ of WM buffer. Diffusion couples are made up of two types of apatite showing distinct volatile compositions. Two types of diffusion sources are used: powders, and thin films deposited using laser pulse deposition method. Diffusion couples were annealed in a furnace at constant P, T and fO₂ for a series of experimental run durations (0.67-161 hours). Concentration profiles of F and Cl from crystal-powder samples were measured using EPMA, whereas depth profiles of F, Cl, OH and S were measured using SIMS.

Uphill diffusion profiles of Cl were observed using both EPMA and SIMS, indicating a complex multicomponent diffusion in apatite, which makes sense given that F, Cl and OH occupy the same channel site. Using a finite difference algorithm, we calculate the effective binary diffusion coefficients (EBDC) of F, Cl and OH. At 800-1100 °C, F and OH show nearly isotropic diffusion whereas Cl diffusion is anisotropic, e.g. 2-3 orders of magnitude faster parallel to c-axis (*//c*) than a-axis (*//a*) at 950 °C. Parallel to c-axis, the diffusivities of F, Cl and OH are: $D_F > D_{Cl} > D_{OH}$. Using preliminary constraints on depths and ignoring convolution effects, the calculated D_F is consistent with Brennan (1994) whereas D_{Cl} (*//c*) from their study is 3-10 times faster than our results, e.g. $1 (\pm 0.1) \times 10^{-17} \text{ m}^2/\text{s}$ at 900 °C. S diffusion is likely anisotropic, and D_S (*//c*) is 5-10 times slower than D_{Cl} (*//c*) at the same T. Using the new diffusivities, the Cl zoning in apatite from Merapi 2006 deposits would give diffusion times of 2-4 weeks, indicating equivalent timescales of magma ascent before the eruption in 2006, consistent with ground deformation data from literature.