



The isotope mass effect on chlorine diffusion in dacite melt, with implications for fractionation during bubble growth



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ARTICLE INFO

Article history:

Received 5 June 2017

Received in revised form 22 September 2017

Accepted 23 September 2017

Available online xxx

Editor: F. Moynier

Keywords:

diffusion in magmas
chlorine isotopes
isotope fractionation
bubble growth

ABSTRACT

Previous experimental studies have revealed that the difference in diffusivity of two isotopes can be significant in some media and can lead to an observable fractionation effect in silicate melts based on isotope mass. Here, we report the first characterization of the difference in diffusivities of stable isotopes of Cl (³⁵Cl and ³⁷Cl). Using a piston–cylinder apparatus, we generated quenched melts of dacitic composition enriched in Cl; from these we fabricated diffusion couples in which Cl atoms were induced to diffuse in a chemical gradient at 1200 to 1350 °C and 1 GPa. We analyzed the run products by secondary ion mass spectrometry (SIMS) for their isotopic compositions along the diffusion profiles, and we report a diffusivity ratio for ³⁷Cl/³⁵Cl of 0.995 ± 0.001 ($\beta = 0.09 \pm 0.02$). No significant effect of temperature on the diffusivity ratio was discernable over the 150 °C range covered by our experiments. The observed 0.5% difference in diffusivity of the two isotopes could affect our interpretation of isotopic measurements of Cl isotopes in bubble-bearing or degassed magmas, because bubble growth is regulated in part by the diffusive supply of volatiles to the bubble from the surrounding melt. Through numerical simulations, we constrain the extent of Cl isotopic fractionation between bubble and host melt during this process. Bubble growth rates vary widely in nature—which implies a substantial range in the expected magnitude of isotopic fractionation—but plausible growth scenarios lead to Cl isotopic fractionations up to about 5‰ enrichment of ³⁵Cl relative to ³⁷Cl in the bubble. This effect should be considered when interpreting Cl isotopic measurements of systems that have experienced vapor exsolution.

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1. Introduction

Volatile elements have an important impact on a wide range of geochemical processes throughout the Earth system. For example, in shallow volcanic systems, exsolved fluids play a fundamental role in controlling crystallization, magma differentiation, hydrothermal mineralization and alteration, and volcanic eruptions (e.g., Carroll and Holloway, 1994, and references therein). Analyses of trapped volatiles and melt inclusions have led to important developments in understanding the geochemistry of light elements, isotopic tracers, and more broadly, in shedding light on the complex recycling processes and pathways between the Earth's different reservoirs of volatiles (e.g., Jambon, 1994; Humphreys et al., 2009).

In terms of both abundance and geochemical usefulness, Cl could be considered the most important halogen. In basaltic melt inclusions, for example, Cl abundances range up to ~2000 ppm

(e.g., Michael and Cornell, 1998; Métrich et al., 1999), and Cl has been shown to play an important role in the evolution volcanic systems (see Aiuppa et al., 2009, and references therein), where it also serves as a valuable tracer of processes leading to eruption (e.g., Humphreys et al., 2009). Stable isotopes of chlorine, ³⁵Cl and ³⁷Cl, have proven to be an effective tool in various geological studies (e.g., Barnes et al., 2014; Boyce et al., 2015; Manzini et al., 2017). In water, Cl isotopes are known to experience diffusive fractionation (e.g., Desaulniers et al., 1986; Eggenkamp and Coleman, 2009; Barnes and Sharp, 2017). Eggenkamp et al. (1994) attributed the light Cl isotopic signature of saline sediments in Kau Bay, Halmahera, Indonesia to diffusive fractionation. This phenomenon has also been investigated for Cl in hydrothermal fluids (e.g., Eastoe et al., 1989), but it remains uncharacterized for Cl in magmatic systems. The potential importance of diffusive isotopic fractionation in magmatic systems has been recognized previously (e.g., Richter et al., 2003; de Moor et al., 2013; Watkins et al., 2009, 2011, 2017), but the magnitude of the effect has not been documented for Cl—or for any other component that diffuses as an anion or behaves as a volatile species under all magmatic conditions. Lithium partitions into the vapor phase under some cir-

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cumstances (Webster et al., 1989; Vlastélic et al., 2011)—and the $^7\text{Li}/^6\text{Li}$ diffusivity ratio has been measured previously by Richter et al. (2003)—but Cl's strong volatile behavior directly lends itself to fractionation effects during bubble growth.

The development of diffusive boundary layers against growing crystals has the potential to fractionate any two species having different diffusivities in the melt, including both elements (e.g., Albarède and Bottinga, 1972; Baker, 2008) and isotopes (Jambon, 1980; Watson and Müller, 2009). Key experimental data needed to model diffusive fractionation during crystal growth and other magmatic phenomena (e.g., magma mixing) have been provided by Richter et al. (1999, 2003, 2008, 2009a, 2009b). The broad conclusion from these studies is that small differences in diffusivity in basaltic melts exist for isotopes of most elements characterized to date, including Li, Mg, Ca, and Fe (Ge and Si are exceptions; see summary in Richter et al., 2009b). Of the four elements showing an isotope mass dependence of diffusion, the effect is largest for Li and smallest for Fe, but the overall (inverse) correlation with atomic number is not very good, and Mg and Ca violate the overall trend. Because of the proportionately larger mass differences among isotopes of light elements, the isotope effect on diffusion is expected to be largest for light elements, as is the case for equilibrium fractionations. A significant isotope mass effect on diffusion of ^{56}Fe and ^{54}Fe (mass difference $\sim 4\%$) was measured by Richter et al. (2009b), so it is not unreasonable to anticipate a potentially larger effect for diffusion of ^{37}Cl and ^{35}Cl , which have a mass difference of $\sim 6\%$.

For low-density gases in which the molecules have mainly translational energy and a large mean free path, the diffusivity ratio of two molecules of different mass is given by:

$$\frac{D_1}{D_2} = \left(\frac{m_2}{m_1}\right)^{\frac{1}{2}} \quad (1)$$

(Chapman and Cowling, 1970), where D is the diffusivity of the subscripted isotope (1 or 2), and m is its mass. The relation is appealing for its simplicity, but of limited value for condensed materials. In metals and other crystalline solids, isotopic diffusivity differences have been related to the vibrational characteristics of bonds and neighboring atoms (e.g., Vineyard, 1957; Peterson, 1975; Glicksman, 1999); however, similar approaches cannot be readily invoked for complex silicate melts of geological relevance because the species of interest do not occupy fixed sites and their neighbor atoms and bonding characteristics are largely unknown (see Richter et al., 2009a and Watkins et al., 2017 for further discussion). For this reason, researchers working on diffusion in silicate melts have taken a practical approach to characterizing the isotope mass effect, specifically:

$$\frac{D_1}{D_2} = \left(\frac{m_2}{m_1}\right)^{\beta} \quad (2)$$

where the isotope diffusivities (D_1 and D_2) are related to one another using an expression of the same form as eqn. (1) but in which the exponent of $1/2$ is replaced by an empirical constant β , obtained by experiment (Richter et al., 1999, 2003, 2008, 2009a, 2009b). For chemical diffusion in silicate melts, Richter et al. (2003) found that β for Ca isotopes is 0.06 ($D_{44\text{Ca}}/D_{40\text{Ca}} = 0.994$), and β for Li isotopes is 0.215 ($D_{7\text{Li}}/D_{6\text{Li}} = 0.967$). Richter et al. (2008, 2009a) later determined the value of β to be 0.05 for Mg ($D_{26\text{Mg}}/D_{24\text{Mg}} = 0.996$) and 0.03 for Fe ($D_{56\text{Fe}}/D_{54\text{Fe}} = 0.999$). The diffusivity differences between isotopes of a single element are small, but under favorable circumstances these differences can lead to readily measurable isotopic fractionations in (for example) a layered magma chamber in which melt domains of different composition interact (Richter et al., 1999). Richter et al. (2009a) and

others have suggested that β should be independent of temperature for diffusion in a specific medium, but this has not been confirmed for diffusion of any species in silicate melts.

In a study focusing on melt composition effects on β in simple systems, Watkins et al. (2011) characterized diffusive fractionation of Ca and Mg isotopes in albite–anorthite and albite–diopside melts and found β to be strongly dependent on melt composition. The data of Watkins et al. (2011) cannot be directly applied to natural systems because of the compositional simplicity of the melts they investigated, but these researchers provided vital insight into the fact that atomic structural changes in silicate melts can alter the magnitude of the isotope mass effect on diffusion. This finding means that melt compositions similar to those of direct interest in nature should be used in studies targeting practical applications, as we have done here.

Given the above observations, it seems likely that the isotopes (isotopologues) of magmatic volatiles (like other melt components) will fractionate diffusively under circumstances that involve chemical diffusion of the volatile of interest. Magmatic scenarios leading to chemical diffusion include boundary layer effects against rapidly growing crystals (Watson and Müller, 2009) and bubble growth, among other phenomena. Because mass addition to bubbles occurs by diffusive supply to the bubble/melt interface (e.g., Sparks et al., 1994), bubble growth is a particularly interesting case in which a kinetic effect occurring at the millimeter scale might influence much larger-scale interpretations of the evolution of a magmatic system. Here, we extend existing studies of diffusive isotope fractionation in silicate melts to ^{35}Cl and ^{37}Cl in a synthetic dacitic melt modeled after natural compositions. Further, because of the low solubility of Cl into silicate melts (e.g., Webster and De Vivo, 2002; Botcharnikov et al., 2007), and its strong partitioning into the gaseous phase (e.g., Webster, 1992; Webster et al., 2009; Alletti et al., 2009), we apply our findings to bubble growth through numerical simulations. Our hope is that the data and models will help in the interpretation of Cl isotopic measurements on natural glasses and vesicles, for which—as with other volatile elements—diffusive fractionation is rarely considered.

2. Experimental and analytical techniques

2.1. Overview

To characterize β for Cl isotopes, we use the piston–cylinder apparatus at Rensselaer Polytechnic Institute to achieve geologically-relevant high-temperature, high-pressure conditions. Because the diffusivities of ^{37}Cl and ^{35}Cl are expected to be too similar to distinguish on the basis of separate measurements, we employ the approach of Richter et al. (1999), which involves measurement of the isotopic ratio rather than the absolute, individual concentrations of each isotope. We conducted diffusion–couple experiments in which chemical diffusion of Cl atoms was induced by juxtaposition of two melts having the same major element and Cl isotopic compositions, but with different total Cl concentrations. In this setup, Cl diffuses down the chemical gradient, but the lighter of the two isotopes, ^{35}Cl , diffuses slightly farther on average than its heavier counterpart within the same timeframe. In $^{37}\text{Cl}/^{35}\text{Cl}$ -space, and in our diffusion couples, this creates a small region of enrichment in ^{35}Cl relative to ^{37}Cl in the low-concentration half just “downstream” of the original interface. Conversely, another region near the initial edge of the high-concentration domain is slightly enriched in ^{37}Cl relative to ^{35}Cl (see Fig. 1). As the duration of the experiment increases, these enrichment features become progressively longer and widen in $^{37}\text{Cl}/^{35}\text{Cl}$ -space, as illustrated in Fig. 1a. The degree of enrichment, or the depth of those features in $^{37}\text{Cl}/^{35}\text{Cl}$ -space, is directly related to the diffusivity ratio, and thus also the β -factor (see Fig. 1b). By characterizing the extent of these

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