



Isotope fractionation of Li and K in silicate liquids by Soret diffusion

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Abstract

Laboratory experiments were used to determine the thermal (Soret) isotopic fractionation of lithium and potassium in a basalt melt, which adds elements with ionic charge +1 to the list of elements for which thermal isotopic fractionations in silicate liquids have been previously reported (i.e., Ca, Mg, Fe, Si, O, Sr, Hf, and U). The new experiments were run at a moderate pressure of about 1.5 GPa in a piston cylinder apparatus in order to avoid gas bubbles once the sample was melted. The samples were displaced slightly below the hot spot of the piston cylinder assembly graphite furnace so that there would be a temperature difference of about 125° C across the samples while molten. The thermal isotopic fractionation factor Ω (per mil fractionation per 100° C per one atomic mass unit difference) was found to be 6.0 for lithium isotopes and 1.1 for potassium isotopes. The isotopic fractionation in both cases resulted in the heavy isotopes becoming enriched at the cold end. The expanded data set of thermal isotopic fractionation in silicate liquids is used to evaluate the degree to which recently proposed parameterizations are able to reproduce the experimental data.

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1. INTRODUCTION

Kinetic separation of elements and isotopes by diffusion (i.e. mass flux driven by chemical potential gradients) is a well-known process, which in gases can be understood in terms of kinetic theory (see Chapman and Cowling, 1970). In the simplest case of a rarefied mono-atomic gas the equality of kinetic energy results in the relative mobility D of isotopes being inversely proportional to the square root of their atomic mass m (i.e., $D_i/D_j = (m_j/m_i)^{1/2}$). In condensed

systems, the relative mobility of isotopes can be similarly parameterized in terms of the inverse ratio of the isotope masses to some empirically determined exponent β (i.e., $D_i/D_j = (m_j/m_i)^\beta$), but there is as yet no theoretical framework comparable to the kinetic theory of gases for specifying the value of the exponent β in the condensed systems. A number of recent laboratory experiments have determined the value of β in systems such as water (Richter et al., 2006), silicate melts (Richter et al., 1999, 2003, 2008, 2009a; Watkins et al., 2009, 2011), minerals (Richter et al., 2013), and in metal alloys (see references in Richter et al., 2009b and Müller et al., 2013). Molecular dynamics calculations can provide important insights into the processes leading to isotope separation in condensed systems, a recent example was given by Bourg et al. (2010) who reported

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calculations that reproduced the experimental data on the isotopic fractionation of salts dissolved in water.

Kinetic fractionations of elements and isotopes also arise in gases and liquids due to mass fluxes driven by differences in temperature. In the case of gases the phenomenon is referred to as thermal diffusion and in liquids as Soret diffusion. The existence of this phenomenon in gases was first described theoretically in 1911 by Enskog (1911a,b) and confirmed by the experiments of Chapman and Dootson (1917). The Enskog–Chapman theory, while mathematically complex, provides many useful general insights such as how the intra-atomic force law determines the sign and degree of thermal fractionation. The interested reader is referred to Cowling (1970) to appreciate the degree of complexity involved in even an approximate theory of thermal diffusion in gases. In the case of liquids, thermal diffusion appears to have been first discovered by Ludwig (1856) and described more quantitatively by Soret (1879) for the steady state separation of ionic salts dissolved in water. Given sufficient time, a steady state arises from a balance between the elemental and isotopic fluxes driven by ordinary chemical diffusion and that due to the temperature difference. Here we address the specific issue of what progress has been made in documenting and theoretically understanding isotope fractionation by the Soret effect in silicate liquids. Such a reassessment is timely given numerous recent experiments documenting surprisingly large thermal isotope fractionations of all the major elements of silicate liquids (Kyser et al., 1998; Richter et al., 2008, 2009a; Huang et al., 2010; Lacks et al., 2012a) and associated efforts to account for these experimental results by theoretically-motivated considerations by Huang et al. (2010), Dominguez et al. (2011), and Lacks et al. (2012a).

2. EXPERIMENTAL METHODS

Two new experiments were run to determine the thermal isotopic fractionation of lithium (SRT1B) and potassium (SRT22) in the same basalt liquid (SUNY MORB) used previously by Richter et al. (2008, 2009a) in their experimental study of the thermal isotope fractionation of all the major elements of basalt. The lithium fractionation experiment (SRT1B) used a liquid composed of 7.5 wt.% spodumene in SUNY MORB that was run for 24 h in a piston cylinder apparatus at 1.4 GPa and with 1440 °C at the hot end and 1320 °C at the cold end of the molten sample. The potassium fractionation experiment (SRT22) used a liquid consisting of 14.3 wt.% Wards microcline plus 2.4 wt.% spodumene in SUNY MORB that was run in a piston cylinder apparatus for 50 h with 1540 °C at the hot end and 1360 °C at the cold end, and a pressure of 1.6 GPa. Table 1 gives the bulk composition of SUNY MORB and the new compositions used in experiments SRT1B and SRT22. The experiments

were run in a piston cylinder apparatus so that a moderate pressure could be applied ensuring that gas trapped along with the starting material dissolves in the melt thus avoiding bubbles that would distort the diffusion profile. Fig. 1 shows a typical piston cylinder assembly used for this study. Fig. 2 shows the sample recovered from experiment SRT1B and the temperature distribution in the piston cylinder assembly as determined by the method of Watson et al. (2002) that uses the thickness of the spinel (MgAl_2O_4) layer that develops where MgO and Al_2O_3 were intentionally juxtaposed as a monitor of the local temperature. The thermal profile in the melt at run conditions is reconstructed by interpolating the measured temperatures into that part of the assembly containing the molten sample. The thermal profile in the sample at run conditions is especially important in the case of Soret experiments because the quantity one seeks is the degree of element or isotope separation as a function of the temperature differences. The largest source of error in determining the thermal separation parameters is the uncertainty in the temperature distribution in the molten sample, not the precision of the elemental or isotopic measurements made on recovered samples.

The recovered thermal diffusion samples were first cut in half along their long axes with one half reserved for measuring the major element concentration profiles, and in the case of the SRT1B sample, for lithium isotope measurements using a 1280 ion microprobe. The other half of the sample was sectioned into wafers 350–500 μm thick using a blade with a nominal thickness of 165 μm .

3. ANALYTICAL METHODS

3.1. Concentration measurements

The major element and potassium concentrations in the samples recovered from the thermal fractionation experiments were measured using a JEOL JSM-5800LV scanning electron microscope equipped with an Oxford Link ISIS-300 energy dispersive X-ray microanalysis system (EDS). When operated at 15 kV with a primary beam current of 8 nA a precision of better than 1% relative is routinely achieved. The lithium concentration of sample SRT1B was measured in solutions made by dissolving thin slabs cut perpendicular to the long axis of the sample using the Nu Instruments multi-collector inductively coupled plasma mass spectrometer (MC-ICPMS) at the University of Maryland.

3.2. Lithium isotopic measurements

The lithium isotopic measurements of sample SRT1B were made both with the CAMECA 1280 ion microprobe at the Centre de Recherches Pétrographiques et Géochimiques (CRPG) in Nancy France and by MC-ICPMS at the

Table 1
Bulk composition of SUNY MORB (from Richter et al., 2003) and that used for experiments SRT1B and SRT22.

Wt.%	Na_2O	MgO	Al_2O_3	SiO_2	K_2O	CaO	TiO_2	FeO	Li ppm
MORB	3.1	8.5	15.8	50.2	0.2	10.9	1.6	9.4	~20
SRT1B	3.4	9.1	16.3	50.2	0.2	10.1	1.5	9.4	280
SRT22	2.5	7.3	16.4	53.1	2.1	9.6	1.2	7.8	<100

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