Multicomponent Diffusion in Silicate Melts:
SiO₂-TiO₂-Al₂O₃-MgO-CaO-Na₂O-K₂O System

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Abstract

Nine successful diffusion couple experiments were carried out in a 7-component haplobasaltic silicate melt $\text{SiO}_2\text{-TiO}_2\text{-Al}_2\text{O}_3\text{-MgO-CaO-Na}_2\text{O-K}_2\text{O}$ system to study multicomponent diffusion at $\sim 1500^\circ\text{C}$ and 1 GPa, typically with compositional gradients in only two components in each experiment. At least two concentration traverses were measured for each experiment. Effective binary diffusion coefficients (EBDC) for monotonic profiles were obtained by an error function fit, and the EBDC of a given component is dependent on its counter diffusing component, especially for SiO_2 . The EBDC's of SiO_2 vary from $15.7 \mu\text{m}^2/\text{s}$ when diffusing against Al_2O_3 , to $102.9 \mu\text{m}^2/\text{s}$ when diffusing against K_2O . Furthermore, the multicomponent diffusion matrix was obtained by simultaneously fitting profiles of all oxides in all experiments. Most features in the diffusion profiles, for example uphill diffusion, are captured well by this 6×6 diffusion matrix. The slowest diffusing eigenvector is largely due to the exchange between Si and Al, and the fastest diffusing eigenvector is the exchange of Na with all other components. An anorthite dissolution experiment was also conducted to test whether the diffusion matrix can be applied to mineral dissolution experiments. The calculated diffusion profiles in the melt during anorthite dissolution roughly match the measured profiles, demonstrating the validity and utility of the diffusion matrix in this FeO-free aluminosilicate melt system.

1. Introduction

Silicate melt consists of numerous components and diffusion in it is always multicomponent in nature. Hence, multicomponent diffusion in silicate melts is a

fundamental process for mass transport in natural systems, such as mixing and contamination of magmas (Sato, 1975; Watson, 1982; Koyaguchi, 1985, 1989; Oldenburg et al., 1989), double-diffusive convection of magmas (Turner, 1985), and growth or dissolution of minerals in magma (Watson, 1982; Zhang, 1989). The often-observed uphill diffusion profiles in natural systems and experiments (Sato, 1975; Watson, 1982; Zhang et al., 1989) require multicomponent diffusion treatment, which has not been fully understood yet. Instead, effective binary diffusion approximation (Cooper, 1968) has been widely used to treat chemical diffusion of components without uphill diffusion, it has difficulty to account for uphill diffusion profiles, as well as the variability of effective binary diffusivity of a given component on other components (Zhang et al., 1989; Chen and Zhang, 2008, 2009). Empirical treatments of uphill diffusion have been developed (Cooper, 1968; Lasaga, 1979; Richter, 1993; Zhang, 1993; Liang et al., 1997).

Great efforts have been made in studying multicomponent diffusion in synthetic and natural silicate melts (including $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-CaO}$, $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-MgO}$, $\text{SiO}_2\text{-CaO-Na}_2\text{O}$, $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-MgO-CaO}$, $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-Na}_2\text{O-K}_2\text{O-H}_2\text{O}$ and $\text{SiO}_2\text{-TiO}_2\text{-Al}_2\text{O}_3\text{-FeO-MgO-CaO}$) (Sugawara et al., 1977; Oishi et al., 1982; Kress and Ghiorso, 1993, 1995; Chakraborty et al., 1995; Liang et al. 1996; Mungall et al., 1998; Richter et al., 1998; Liang and Davis, 2002; Lundstrom, 2000, 2003; Liang, 2010; Watkins et al., 2014). Chemical diffusion in silicate melts $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-CaO-MgO}$ and simpler systems shows the degree of diffusive coupling among components depends strongly on compositions (Sugawara et al., 1977; Oishi et al., 1982; Trial and Spera, 1994; Liang et al., 1996; Richter et al., 1998; Liang and Davis, 2002). Furthermore, diffusion of Na_2O and H_2O in Na_2O - and K_2O -bearing silicate melts was found to be strongly coupled to the diffusion

of SiO₂ (Chakraborty et al. 1995; Mungall et al., 1998; Lundstrom, 2000 and 2003). Although diffusion matrices for a limited number of components in melts have been obtained (e.g., Kress and Ghiorso, 1995; Mungall et al., 1998; Lundstrom, 2000, 2003; Morgan et al., 2006), full diffusion matrices for major oxide components in natural silicate melts have not been reported yet. Several empirical models to calculate diffusion matrix in a multicomponent system have been proposed (Lasaga, 1979; Richter 1993; Liang, 1997), with which diffusive dissolution profiles were calculated (Alexander, 2011). However, limited success is achieved in natural silicate melts using these empirical models (e.g., comparison in Fig. 1 and 2), although this doesn't mean that empirical models wouldn't work.

To better understand the diffusion behavior of a multicomponent silicate system, and as part of a program to obtain diffusion matrix in natural silicate melts, we investigated multicomponent diffusion in a 7-component haplobasaltic melt SiO₂-TiO₂-Al₂O₃-MgO-CaO-Na₂O-K₂O system at 1500°C and 1 GPa. This FeO-free system is chosen to avoid complexities associated with FeO in the melt, such as ferric/ferrous ratio variation and iron loss during the experiments. The concentration profiles in all experiments were simultaneously fit to obtain the 6×6 diffusion matrix. In addition, we tested the validity of the extracted diffusion matrix by carrying out an anorthite dissolution experiment in the same melt, and using the extracted diffusion matrix to predict the diffusion behavior during anorthite dissolution.

2. Experimental Strategy and Analytical Methods

The 7-component haplobasaltic melt $\text{SiO}_2\text{-TiO}_2\text{-Al}_2\text{O}_3\text{-MgO-CaO-Na}_2\text{O-K}_2\text{O}$ has an average composition (or interface composition) of 50% SiO_2 , 1.5% TiO_2 , 15% Al_2O_3 , 10% MgO , 19% CaO , 3% Na_2O , and 1.5% K_2O (in wt%). Chemical diffusion couple experiments were conducted in a $\frac{1}{2}$ piston-cylinder apparatus at the University of Michigan, at $\sim 1500^\circ\text{C}$ and ~ 1 GPa. The experimental temperature of 1500°C is chosen because an initial experiment at 1400°C resulted in partial crystallization although the calculated liquidus temperature from the MELTS program (Ghiorso and Sack, 1995; Asimow and Ghiorso, 1998) is less than 1380°C . The average composition will be referred to as the “base composition”. A diffusion couple is made of two halves, typically with one half deviating from the base composition by about +1.5 wt% in one oxide and – 1.5 wt% in another oxide, and the other half deviating by –1.5 wt% and +1.5 wt%. Diffusion couples with other types of compositional differences were also made. The compositional variation is chosen to be large enough for significant diffusion profiles to be obtained, and small enough so that the dependence of the diffusion matrix on the melt composition along a profile can be ignored as a first approximation.

The starting glass for each half of a diffusion couple was synthesized in a Deltech furnace at the University of Michigan. Oxide and carbonate powders were weighed, mixed in ethanol, dried, placed in a graphite crucible, heated up to 1500°C in a 1-atm Deltech furnace, kept there under N_2 flow for 3 hours to homogenize, and quenched in air into glass. The compositions and calculated liquidus of the starting glasses are listed in Table 1.

Nine successful diffusion couple experiments were carried out. The name of each diffusion couple indicates the two halves of the diffusion couple, e.g., HB7&8B means

that one half is HB7, and the other half is HB8, and the last letter “A” means the first experiment for this couple and “B” means the second experiment for this couple (often because the first experiment failed). The interface (average) composition of each diffusion couple is listed in Table 2. The 1σ standard deviation of the interface composition of the 9 diffusion couple experiments is 1.1 wt% for SiO_2 and < 0.5 wt% for all other oxides.

Glasses were cut and ground into cylinders with ~ 2.0 -mm diameter, sliced into discs with ~ 1.5 -mm thickness, and then one-side polished. Densities of melts were estimated using Lange and Carmichael (1990), and the less dense melt was placed on top of the denser melt to suppress convection. Sample discs were placed into the graphite capsule. The graphite capsule was placed into MgO rod. The MgO rod was placed into a graphite heater, and then the graphite heater was placed into BaCO_3 pressure medium. To maintain consistency in the actual temperature among different experiments, the same experimental design was used for all experiments.

Experimental procedures are as follows. The experimental assembly is first brought to a pressure that is 10-15% higher than the target pressure and then relaxed to the target pressure (piston-out procedure). Then the assembly is relaxed at 200°C for ~ 6 hours. After relaxation, the pressure is brought back to the target pressure and the assembly is heated up to the target temperature at a programmed rate in less than 1 minute. The assembly is kept at target temperature and pressure for a planned duration (~ 5 min), and then quenched down by turning off the power.

Temperature is controlled by an S-type thermocouple with its tip covered by alumina cement and separated by a ~ 0.5 -mm thick MgO disc from the graphite capsule.

Temperature and pressure history is recorded. The temperature fluctuation is within 1°C, and the pressure is adjusted manually with a fluctuation within ~10 MPa.

The temperature at the center (also the interface) of the diffusion couple is corrected based on the distance from the thermocouple tip to the interface and the thermal gradient calibrated by Hui et al. (2008). The temperature uncertainty is estimated to be ~20°C at 1500°C. Pressure correction is applied by dividing the nominal pressure by 1.06 (Hui et al., 2008; Ni and Zhang, 2008).

After experiments, sample assembly was embedded in epoxy, grounded, polished and prepared for electron microprobe analysis. Concentration profiles were measured at 15 kV using a 10 nA focused beam by a Cameca SX100 electron microprobe at Electron Microbeam Analysis Laboratory of the University of Michigan.

3. Experimental Results

Table 3 shows experimental conditions and effective binary diffusion coefficients (EBDC) of all 9 successful experiments. The first 6 experiments listed in Table 3 have initial concentration gradients in SiO₂ and oxide *i*, where *i* = TiO₂, Al₂O₃, MgO, CaO, Na₂O and K₂O. These 6 experiments are the minimum for obtaining the 6×6 diffusivity matrix (Tieck and Spera, 1994) unless the analytical accuracy is much higher than regular electron microprobe analyses (Liang, 2010). Three additional and successful experiments with initial gradients in TiO₂-MgO, MgO-CaO, and CaO-Na₂O were carried out to further constrain the diffusion matrix. Experimental durations are corrected following Zhang and Behrens (2000) with $t_{\text{exp}} = \int_0^t D dt / D(T_{\text{exp}}) = \int_0^t e^{-E/(RT)} dt / e^{-E/(RT_{\text{exp}})}$ where $D(T_{\text{exp}})$ is D at the experimental temperature. Fig. 3 shows a microscopic image of a

polished experimental charge. Quench crystals are not observed, and cracks are present in 6 out of 9 experiments. Interface between the two halves is not visible in the glass, but the physical interface can be seen near the graphite capsule (Fig. 3).

Two or more traverses were measured to obtain concentration profiles for each experimental charge. Profiles across cracks were re-connected smoothly using different traverses. Profiles for one experiment (HB7&8B) are shown in Fig. 4. Other profiles as well as the digital electron microprobe data of the concentration profiles can be found in the supplementary file. Uphill diffusion is observed for most components if the initial concentration difference between the two halves is negligible.

4. Fitting the diffusion profiles

Far-field melt compositions were determined by taking the average of the data in the far-field, and used as boundary conditions for fitting. They may be slightly different from the starting glass compositions listed in Table 1, due to small variability in composition in a large chunk of synthesized glass. Standard errors at 1σ level were determined from the numerous points in the far-field melt, and the errors were used in fitting the corresponding profiles to obtain the multicomponent diffusion matrix.

Interface positions x_0 for each experiment were determined by fitting the best diffusion profile (the oxide with a significant initial concentration difference) using the equation:

$$w = \frac{w_{-\infty} + w_{+\infty}}{2} + \frac{w_{+\infty} - w_{-\infty}}{2} \times \text{erf}\left(\frac{x - x_0}{2\sqrt{Dt}}\right), \quad (1)$$

where w is the concentration (in mass fraction or wt%) of the component, $w_{-\infty}$ and $w_{+\infty}$ are the concentrations in the far-field melts on the left and right sides respectively, x_0 is the

interface position from effective binary fitting of the best constrained diffusive component, t is the experimental duration and D is the effective binary diffusivity. The new distance x in each experiment was determined by subtracting the interface position x_0 $x_{new} = x - x_0$, so that the new interface position would be at $x = 0$.

The corrected experimental temperatures vary from 1484 to 1520°C, which means moderate variations of the elements in the diffusion matrix. In order to reduce the errors in fitting the diffusion matrix, the experimental temperatures are “normalized” to 1500°C, with an assumption of activation energy of 230 kJ/mol (Zhang et al., 1989). That is, the corresponding experimental durations are “normalized” to the temperature of $T = 1773$ K, with relation $t_{1773K} = D(T_{exp}) \times t_{exp} / D(1773) = e^{-E/(RT_{exp})} \times t_{exp} / e^{-E/(1773R)}$ (Zhang and Behrens, 2000).

For fitting concentration profiles to obtain the diffusion matrix, SiO₂ is used as the dependent component. Because the dependent component makes the total concentrations of all components to be 100%, it means that we are actually using SiO₂^{*} = SiO₂ – (total – 100) as the dependent component. For effective binary fitting of SiO₂ concentrations, we found that the SiO₂^{*} profile shows less scatter than the SiO₂ profile, and hence SiO₂^{*} is used in the fitting. This means, we attribute the difference between the total and 100% to analytical errors in the SiO₂ concentration (note that these are synthetic melts containing essentially no trace elements).

4.1 Effective binary diffusivity

Effective binary diffusivities or effective binary diffusion coefficients (EBDC) were fit by equation (1) for components with monotonic profiles (Table 3). Note that

these diffusion couples have a similar bulk (or interface) composition, but the opposing concentration gradients are in different components. Because of our experimental design, most of the effective binary diffusivities may be regarded as inter-diffusivities between two components.

One observation is that the effective binary diffusivities are strongly dependent on the counter-diffusing component. That is especially significant for SiO₂, partially because more interdiffusion coupling experiments have been run for SiO₂. The effective binary diffusivity of SiO₂ varies from 15.7 $\mu\text{m}^2/\text{s}$ when the counter-diffusing component is Al₂O₃, to 28.7 $\mu\text{m}^2/\text{s}$ for SiO₂-CaO, to 44.2 $\mu\text{m}^2/\text{s}$ for SiO₂-Na₂O, and to 102.9 $\mu\text{m}^2/\text{s}$ when the counter-diffusing component is K₂O, with total variation by a factor of almost 7. This clearly shows that effective binary diffusivities depend not only on the bulk composition (all the experiments in this study have a similar bulk composition), but also on the compositional gradients. The effective binary diffusivities of other components seem to depend less on the counter-diffusing component. The effective binary diffusivity of CaO varies by a factor of about 2, from 60.5 $\mu\text{m}^2/\text{s}$ for SiO₂-CaO, to 70.4 $\mu\text{m}^2/\text{s}$ for CaO-Na₂O, and to 115.7 $\mu\text{m}^2/\text{s}$ for MgO-CaO.

4.2 Multicomponent diffusion matrix

Mass fraction (wt%) rather than mole fraction are used for fitting concentration profiles to obtain the diffusion matrix. The concentration profiles in all experiments were simultaneously fit using the Levenberg-Marquardt-Fletcher method (LFM method) (Fletcher, 1971). To obtain the 6×6 diffusion matrix, we minimized χ^2 :

$$C^2 = \frac{1}{2} \sum_{k=1}^{Nd} \sum_{j=1}^{Np_k} \sum_{i=1}^{Nc} \left(\frac{w_{ijk}^{meas} - w_{ijk}^{calc}}{S_{ik}} \right)^2, \quad (2)$$

where w_{ijk}^{meas} and w_{ijk}^{calc} are the respectively measured and calculated concentrations of component i at location j in diffusion couple k , S_{ik} is 1σ error of w_{ijk}^{meas} , N_d is the number of diffusion couples fit, $N_c = 6$ is the number of independent components ($N_c = n - 1$), and N_p is the number of data points in each diffusion couple. The solution to the multicomponent diffusion equation for diffusion couple is given by Equation (A5) in Appendix A1. Errors on the fitting parameters D_{ij} are estimated by error propagation (Clifford, 1973).

We carried out the fitting for two cases. One fit uses all the 9 diffusion couple experiments, and the obtained diffusion matrix is referred to as matrix A, which is shown in Table 4, together with the eigenvalues and eigenvectors. The other fit uses 6 experiments with initial gradients in SiO_2 and i , where i varies from TiO_2 , Al_2O_3 , MgO , CaO , Na_2O and K_2O (the first 6 experiments in Table 3), and the obtained diffusion matrix is referred to as matrix B (Table 5). An example of the fits (HB7&8B) using Matrix A is shown in Fig. 4. The fit curves by matrix A for all experiments are shown in Fig. S1 to S9 in the supplementary file; the fit curves for the first 6 experiments and the calculated curves for the rest three experiments by matrix B are shown in Fig. S10 to S18 in the supplementary file. The purpose of reporting matrix B is to check how different the diffusion matrix B obtained from 6 experiments is from the better constrained matrix A. In other words, the purpose of carrying out more than 6 experiments to determine matrix A is to check whether significant improvement of the diffusion matrix can be obtained by extra experiments.

All features in the profiles of 7 oxide components of all experiments are well reproduced by diffusion matrix A (Fig. 4, where the black solid curves are fit curves). Furthermore, matrix B successfully fits the profiles from the first 6 experiments (which are used in fitting) and predicts most features in the rest three experiments, which means 6 independent experiments are sufficient to obtain the diffusion matrix, but 9 experiments are better. Eigenvalues of matrix A and matrix B are close to each other (Table 4 and 5), with relative differences of about 10%. We tested whether matrices A and B are significantly different by calculating $T_{ij} = (A_{ij} - B_{ij}) / \sqrt{\sigma_{A,ij}^2 + \sigma_{B,ij}^2}$. If A and B agree with each other within error, then absolute values of T_{ij} should be less than 2 at 95% probability assuming normal distribution. About 40% of the T_{ij} values are outside the range [-2, 2]. That is, A and B are statistically different. Therefore, the improvement by extra experiments is significant even though it is small.

4.3 Diffusion matrix when another component is used as the dependent component

Diffusion matrix when another component is treated as the dependent component can be derived. Assuming k is the new dependent component and denoting SiO₂ as n ($k \neq n$), the new diffusion matrix is (see Appendix A3 for derivation):

$$D_{ij}^k = D_{ij}^n - D_{ik}^n, \quad \text{if } i \neq n \text{ and } j \neq n \quad (3a)$$

$$D_{in}^k = -D_{ik}^n, \quad \text{if } i \neq n \quad (3b)$$

$$D_{nj}^k = \sum_{i=1}^{n-1} (D_{ik}^n - D_{ij}^n), \quad \text{if } j \neq n \quad (3c)$$

$$D_{nn}^k = \sum_{i=1}^{n-1} D_{ik}^n. \quad (3d)$$

Equation (3b) is the same as that in Kirkaldy et al. (1963). In ternary systems, the above relations reduce to the relations in Kirkaldy and Young (1987, p.157). Using equations (3a-d), the diffusion matrix A has been transformed into diffusion matrices using different components as the dependent component: A_1 (Table S1) with TiO_2 , A_2 (Table S2) with Al_2O_3 , A_3 (Table S3) with MgO , A_4 (Table S4) with CaO , A_5 (Table S5) with Na_2O and A_6 (Table S6) with K_2O as the dependent component, in the supplementary file. These results are needed for discussion below.

4.4 Eigenvalues and eigenvectors of the diffusion matrix

Eigenvalues and eigenvectors of diffusion matrix A are calculated and shown in Table 4. Each column is one eigenvector, in the vector space of oxide components TiO_2 - Al_2O_3 - MgO - CaO - Na_2O - K_2O . The largest eigenvalue (λ_5) is 21.5 times the smallest eigenvalue (λ_2) in this system. The value of each eigenvalue is fairly close to the corresponding diagonal term in the diffusion matrix. For example, the first eigenvalue $\lambda_1 = 19.56$ is very close to the first diagonal term 18.12. The largest difference between an eigenvalue and a corresponding diagonal term in matrix A is about 41% relative between $D_{\text{Al-Al}}$ and λ_2 .

The eigenvectors are related to the diffusion mechanism and species, and are often difficult to interpret. To better interpret the eigenvectors, we calculated the associated eigenvectors using the transformed diffusion matrices (A_1 to A_6), in which a different component is used as the dependent component. The eigenvectors associated with each eigenvalues are listed in Tables S1 to S6 in the supplementary file. Note that the eigenvalues of these transformed matrices are the same as those of matrix A , because

they are derived from elementary transformation, during which the eigenvalues are invariant.

By examining the eigenvectors when different components are treated as the dependent component, eigenvector 2 (v_2 , the eigenvector associated with the smallest eigenvalue λ_2 , meaning the slowest diffusing eigenvector) is largely due to Si-Al exchange: when SiO_2 is used as the dependent component, v_2 has essentially only one component (Al_2O_3), meaning that this component is exchanging with the dependent component (SiO_2); when Al_2O_3 is used as the dependent component, v_2 contains essentially only the SiO_2 component, meaning that SiO_2 is exchanging with the dependent component Al_2O_3 ; when TiO_2 , MgO , CaO , Na_2O and K_2O are used as the dependent component, v_2 contains mostly SiO_2 and Al_2O_3 components in opposite sign, meaning the exchange of Al_2O_3 with mostly SiO_2 . It is reasonable that the slowest eigenvector is largely due to Al-Si exchange, because both Al and Si are network-formers.

In a similar fashion, eigenvector 1 (v_1 , the eigenvector associated with the second smallest eigenvalue λ_1) is largely due to the Si-Ti exchange (with minor Mg and Ca). Eigenvector 3 (the third smallest eigenvector) is largely due to the exchange between Mg+Ca and Si+Al. Eigenvector 4 is mostly due to the Mg-Ca exchange. Eigenvector 5 is associated with the largest eigenvalue λ_5 , and is due to Na exchanging with all other components (Si, Mg, Al, etc.): note that the sign for the Na_2O term is opposite to that of all other components in eigenvector v_5 . It is also reasonable that the eigenvalue associated with Na exchange with all other components is the largest, because Na self-diffusivity is the highest among the 7 components studied (see diffusivity sequence in Zhang et al.,

2010). Eigenvector 6 (v_6) is the second fastest diffusing eigenvector and is due to the exchange between Ca+K and all the other components (Al, Mg, Na, ...).

In summary, the slowest diffusing eigenvector (v_2) is largely the exchange between two network-formers Al and Si, the second slowest (v_1) is largely the exchange between Si and Ti, and the third slowest (v_3) is the exchange between Si+Al (network-formers) and Mg+Ca. The third fastest (v_4) is largely the exchange between Ca and Mg, the second fastest (v_6) is the exchange between Ca+K and all the others, and the fastest diffusing eigenvector (v_5) is the exchange between Na and all the others.

One may also divide multicomponent diffusion eigenvectors into two groups: (1) relatively simple diffusion exchange along v_2 (SiO_2 - Al_2O_3 exchange), v_1 (SiO_2 - TiO_2 exchange), v_4 (MgO-CaO exchange) and v_5 (Na_2O exchange with all the others); (2) more complex exchange as a combination of two or more simple diffusion exchange along v_3 (MgO+CaO exchange with all the others) and v_6 (CaO+ K_2O exchange with all the others) (Table 6). This classification is approximate because no eigenvector is purely due to the exchange of two components.

5. Prediction of diffusion profiles during anorthite dissolution

In order to test the validity and utility of the diffusion matrix that we obtained, we conducted an experiment on anorthite dissolution in this haplobasaltic melt (49.63% SiO_2 , 1.52% TiO_2 , 16.02% Al_2O_3 , 9.87% MgO, 18.80% CaO, 2.88% Na_2O , and 1.28% K_2O , in wt%) at 1500°C and 1 GPa for ~2.5 min. The composition of the starting anorthite (Waythomas et al., 2010; Yu et al., 2016) used is $44.77\pm0.15\%$ SiO_2 , $35.07\pm0.24\%$ Al_2O_3 , $0.50\pm0.03\%$ FeO, $18.96\pm0.16\%$ CaO, and $0.66\pm0.02\%$ Na_2O (in

wt%). Anorthite is chosen because it is almost FeO-free and because its dissolution kinetics is fairly well known (Yu et al., 2016). The experimental procedure follows that of Yu et al. (2016). Fig. 5 shows microscopic and back-scattered electron (BSE) image of the polished experimental charge. Cracks are present in the glass and sub-parallel to the interface, but no quench crystal is observed. The part of anorthite in contact with melt is dissolved and indented, while the corner part not in contact with the melt remains intact, allowing an independent estimation of the anorthite dissolution distance.

Three concentration traverses were measured. Profiles across cracks were reconnected smoothly. The three traverses (Fig. 6) are highly consistent with each other, and the Al_2O_3 concentration profile could be fit very well (dotted curve in Fig. 6) by the dissolution-diffusion equation (equations 13-14 in Zhang et al., 1989), yielding an effective binary diffusivity for Al_2O_3 of $17.9 \mu\text{m}^2/\text{s}$. Strong uphill diffusion is observed in CaO, Na_2O and K_2O profiles, which requires a multicomponent diffusion treatment. Dissolution distance was estimated by three different ways: (1) direct measurement under optical microscope ($L_1 = 65.5 \mu\text{m}$), (2) measurement from mass balance ($L_2 = 71.6 \mu\text{m}$) and (3) measurement from the profile with largest concentration gradient ($L_3 = 2ar_m\sqrt{D_{\text{Al}_2\text{O}_3}t} / r_c = 74.5 \mu\text{m}$).

Fig. 6 also shows predicted diffusion profiles during anorthite dissolution using equation (A14) in Appendix A2 with diffusion matrix A from all the 9 diffusion couple experiments, compared with the measured data points. For the solid curves, the interface melt composition based on extrapolation of actual data points is used. For the dashed curves, the calculated interface melt composition as summarized in Appendix A2, with Al_2O_3 concentration in the interface melt estimated from Yu et al. (2016), is used. The

parameter α is determined by equation (A19) in Appendix A2. The calculated anorthite dissolution distance is 69.4 μm , close to $L_2 = 71.6 \mu\text{m}$.

It can be seen that all the major features of the concentration profiles are fairly well produced. The experimental and calculated diffusion profile lengths match well. SiO_2 , TiO_2 , Al_2O_3 , MgO , CaO and Na_2O profiles show good agreement between calculation and experimental data. However, K_2O profile couldn't be predicted well. The K_2O profile is also somewhat strange (different traverses agree well, meaning that the strange features are likely real). The disagreement may be partially due to the inaccuracy of the $[D]$ matrix, especially the matrix elements related to K_2O diffusion, or due to the compositional dependence of the diffusion matrix. For the diffusion couple experiments from which the diffusion matrix is extracted, the compositional variation is small (± 1.5 wt%). Hence, the compositional dependence of the diffusion matrix is likely negligible. However, during anorthite dissolution, the Al_2O_3 concentration varies from 16 to 31 wt%, SiO_2 from 50 to 43 wt%, and MgO from 10 to 3 wt%. These variations may be large enough to cause significant variation in the values of the elements in the diffusion matrix, and hence cause the mismatch between the predicted K_2O concentration profile and the measured K_2O profile. The overall χ^2/n (n is the number of points multiplied by the number of oxides) for the prediction of oxide concentration profiles for anorthite dissolution in our Fe-free melt is 3.6 (Fig. 6), much smaller than the value (8.6) obtained from the calculation of Alexander (2011) for olivine dissolution in andesitic melt (Fig. 2), and the value (250.5) from the calculation of Kress and Ghiorso (1995) for olivine dissolution in andesitic melt (Fig. 1).

6. Summary and Conclusions

Chemical diffusion profiles in silicate melts in a haplobasaltic $\text{SiO}_2\text{-TiO}_2\text{-Al}_2\text{O}_3\text{-MgO-CaO-Na}_2\text{O-K}_2\text{O}$ system have been determined at 1500°C and 1 GPa. Effective binary diffusion coefficients (EBDC) of monotonic diffusion profiles in each experiment are extracted, and show strong dependence on the compositional gradients, specifically the counter-diffusing component, especially for SiO_2 . More importantly, multicomponent diffusion matrix in this system is extracted from 9 diffusion couple experiments, and all features in the diffusion profiles have been captured by this diffusion matrix. The resulting diffusion eigenvectors are intuitively reasonable. The extracted multicomponent diffusion matrix has been applied to calculate diffusion profiles during anorthite dissolution in the haplobasaltic melt at 1500°C and 1 GPa, and the diffusion distances and most features in concentration profiles are well reproduced, but with some mismatch for the K_2O profile. It is necessary to experimentally determine the effect of FeO to multicomponent diffusion and to evaluate the compositional effect for reliable applications to natural melts.

We have verified that with the electron microprobe precision, when the number of diffusion couple experiments is the same as the number of independent components and when every experiment is an “interdiffusion” couple between the dependent component and an independent component, the diffusion matrix can be roughly obtained, consistent with Trial and Spera (1994). More experiments of other “interdiffusion” couples will significantly improve the accuracy of the diffusion matrix.

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APPENDIX A

A1. Analytical Solution to Multicomponent Diffusion for Diffusion Couple

Diffusion in an n -component system can be described by a diffusion matrix $[D]$. In a mass-fixed frame of reference, when the melt density variation is negligible, without sink or generation, the non-convective multicomponent diffusion equation (e.g. Onsager, 1945; de Groot and Mazur, 1962) is:

$$\frac{\partial w_i}{\partial t} = \sum_{j=1}^{n-1} \nabla (D_{ij} \nabla w_j) \quad (\text{A1})$$

where t is the time, w_i is the concentration (in mass fraction or wt%) of component i , and D_{ij} are elements of a $(n-1) \times (n-1)$ diffusivity matrix $[D]$ with component n treated as the dependent component.

With the assumption that the elements of the diffusion matrix do not change within the composition range, for infinite diffusion couple in one dimension, defining the interface as $x = 0$, diffusion equation (A1) can be simplified to:

$$\frac{\partial w}{\partial t} = [D] \frac{\partial^2 w}{\partial x^2}. \quad (\text{A2})$$

with the initial condition of

$$w|_{t=0, x<0} = w_{-} \text{ and } w|_{t=0, x>0} = w_{+}, \quad (\text{A3})$$

and the boundary conditions of

$$w|_{x=-\infty} = w_{-\infty} \text{ and } w|_{x=+\infty} = w_{+\infty} \text{ at } t > 0, \quad (\text{A4})$$

where x is the distance from the interface $x = 0$, w is a column vector of concentrations (in mass fraction wt%), $w_{-\infty}$ and $w_{+\infty}$ are column vectors representing far-field concentrations on the left and right sides respectively.

The analytical solution to diffusion equations (A2-A4) is (Trials and Spera, 1994; Liang, 2010):

$$w = \frac{w_{-\infty} + w_{+\infty}}{2} + [P][\Lambda][P^{-1}] \cdot \frac{w_{+\infty} - w_{-\infty}}{2}, \quad (\text{A5})$$

where $[\Lambda]$ is a diagonal matrix with diagonal elements $L_{ii} = \text{erf}\left(x / \sqrt{4 / \lambda_i t}\right)$ and $L_{ij} = 0$

when $i \neq j$, λ_i 's are the eigenvalues of $[D]$, and columns of $[P]$ are the eigenvectors of $[D]$.

The solution is used to fit experimental concentration profiles.

A2. Analytical Solution for Multicomponent Diffusion during Mineral Dissolution

Denote the crystal dissolution rate as u_c , and the melt growth rate is $u = (r_c / r_m) \times u_c$, where ρ_c and ρ_m are crystal and melt density (Zhang, 2008). Diffusion in the melt is a moving boundary problem.

Assume that the melt density and elements of the diffusion matrix do not vary within the compositional range. For one-dimensional crystal dissolution in a semi-infinite melt medium, defining crystal-melt interface as $x = 0$ (i.e., using a crystal-melt interface-fixed frame of reference for this moving boundary diffusion problem), multicomponent diffusion in the melt can be described as (Zhang et al., 1989; Liang, 1999, 2000)

$$\frac{\partial w}{\partial t} = [D] \frac{\partial^2 w}{\partial x^2} - u \frac{\partial w}{\partial x}, \quad (\text{A6})$$

with initial condition of

$$w|_{t=0, x>0} = w_{\infty}, \quad (\text{A7})$$

and boundary condition of

$$w|_{x=\infty} = w_{\infty} \text{ at } t > 0, \quad (\text{A8})$$

$$\left([D] \frac{\partial w}{\partial x} \right) \bigg|_{x=0} = u(w_0 - w_c), \quad (\text{A9})$$

where t is time, x is distance from the crystal-melt interface in the melt, w is a column vector of concentrations (in mass fraction wt%) in the melt, w_0 is a column vector of concentrations at the interface in the melt, w_c is a column vector of concentrations at the interface in the crystal, and w_{∞} is a column vector of concentrations in the melt at the far-field.

If the interface reaction is rapid, the transition stage can be ignored and the interface melt composition w_0 is practically a constant (Zhang et al., 1989; Chen and Zhang, 2008; Yu et al., 2016). Then the dissolution can be treated as purely diffusion controlled, and the melt growth rate (Crank, 1975; Zhang et al., 1989) is

$$u = a / \sqrt{t}. \quad (\text{A10})$$

Equations (A6) to (A10) form the mathematical description of the diffusion problem, in which w_0 and α are unknowns to be solved. Note that u , α , t and x are scalars, w , w_0 , w_c and w_{∞} are column vectors, and $[D]$ is a square matrix.

Decompose $[D] = [P][\lambda][P^{-1}]$, where $[\lambda]$ is a diagonal matrix of eigenvalues, and $[P]$ is the associated eigenvector matrix. Define $C = [P^{-1}]w$, in which the diffusion of C_i is described by a single diffusion coefficient (eigenvalue) λ_i . Because w_0 (and therefore C_0) is constant, the problem can be solved as:

$$C_i = C_{i,\infty} + (C_{i,0} - C_{i,\infty}) \cdot \operatorname{erfc}\left(\frac{x}{\sqrt{4l_i t}} - \frac{a}{\sqrt{l_i}}\right) / \operatorname{erfc}\left(-\frac{a}{\sqrt{l_i}}\right), \quad (\text{A11})$$

or in matrix form:

$$C = C_{\infty} + [E](C_0 - C_{\infty}), \quad (\text{A12})$$

where $[E]$ is a diagonal matrix with:

$$E_{ii} = \operatorname{erfc}\left(\frac{x}{\sqrt{4l_i t}} - \frac{a}{\sqrt{l_i}}\right) / \operatorname{erfc}\left(-\frac{a}{\sqrt{l_i}}\right), \quad (\text{A13})$$

Replacing C in (A12) by $C = [P^{-1}]w$, leads to:

$$w = w_{\infty} + [P][E][P^{-1}](w_0 - w_{\infty}), \quad (\text{A14})$$

which is the solution once α (appearing in $[E]$) and w_0 are known.

To obtain the full solution, we also need to solve α and w_0 . For an n -component system, there are $(n-1)$ unknowns in w_0 plus one unknown α , with a total of n unknowns. Combining (A9) and (A10) leads to:

$$\left([D] \frac{\partial w}{\partial x}\right)_{x=0} = \frac{a}{\sqrt{t}}(w_0 - w_c). \quad (\text{A15})$$

Use solution (A14) to obtain $(\partial w / \partial x)_{x=0}$, (A15) can be written as:

$$[P][I] \left[\frac{\partial E}{\partial x} \right]_{x=0} [P^{-1}](w_0 - w_{\infty}) = \frac{a}{\sqrt{t}}(w_0 - w_c). \quad (\text{A16})$$

where $(\partial E / \partial x)_{x=0}$ is a diagonal matrix with:

$$\left[\frac{\partial E_{ii}}{\partial x} \right]_{x=0} = - \frac{e^{-a^2/l_i}}{\sqrt{\rho l_i t} \times \operatorname{erfc}\left(-a/\sqrt{l_i}\right)}. \quad (\text{A17})$$

Define $[F]$ as a diagonal matrix with F_{ii} :

$$F_{ii} = \sqrt{t} \left[\frac{\partial E_{ii}}{\partial x} \right]_{x=0} = - \frac{e^{-a^2/l_i}}{\sqrt{\rho l_i} \times \operatorname{erfc}\left(-a/\sqrt{l_i}\right)}. \quad (\text{A18})$$

Therefore, (A16) is simplified as:

$$[P][I][F][P^{-1}](w_0 - w_{\infty}) = a(w_0 - w_c), \quad (\text{A19})$$

or,

$$w_0 = \left([P][I][F][P^{-1}] - \alpha[I] \right)^{-1} \times \left([P][I][F][P^{-1}]w_{\neq} - \alpha w_c \right), \quad (\text{A20})$$

if $[P][I][F][P^{-1}] - \alpha[I]$ is invertible. Therefore, from (A20), w_0 is an explicit function of α . Equation (A20) provides $n-1$ equations, with only one unknown α left.

We need one additional equation to solve α . This additional equation is the thermodynamic constraint. For example, for quartz dissolution, the additional equation can be in general written as: $m_{\text{SiO}_2}^{\text{melt},0} = m_{\text{SiO}_2}^{\text{qtz}}$. For the dissolution of a mineral that is a solid solution with k components, there would be k equations such as,

$$m_i^{\text{melt},0} = m_i^{\text{mineral},0}, \text{ where } i = 1, \dots, k. \quad (\text{A21})$$

Note that the composition of a mineral that is a solid solution is not fixed, and hence the interface mineral composition, which contains $k-1$ unknowns, is not necessarily the initial mineral composition and must also be solved (e.g., Fig. 4-18 in Zhang, 2008). Therefore, the total number of unknowns is $n+k-1$ ($n-1$ for w_0 , 1 for α , and $k-1$ for the interface mineral composition), which equals to the total number of equations in (A20) and (A21).

The chemical potential of a component in the melt cannot be easily expressed as a function of composition. Models such as MELTS (Ghiorso and Sack, 1995; Asimow and Ghiorso, 1998) are available, but they do not lead to simple algebraic equations for chemical potentials. Hence, solving the set of equations for the interface melt composition is not straightforward. Furthermore, there are unknown and possibly large uncertainties in the thermodynamic models. Hence, if the interface melt composition w_0 can be obtained from experimental data, it would remove much uncertainty in diffusion treatment.

A rough approach is when the interface melt concentration of one component can be roughly estimated, such as SiO_2 concentration during quartz dissolution in rhyolitic or basaltic melts, Al_2O_3 concentration during anorthite dissolution in basaltic melts (Yu et al., 2016), and MgO concentration during olivine dissolution in basaltic melts (Chen and Zhang, 2008). Once this condition is given, α can be solved by (A20) and therefore w_0 .

A3. Derivation of transformation of diffusion matrices when a different component is used as the dependent components

For an n -component system, with component n chosen as the dependent component, in a mass-fixed frame of reference, diffusion flux equals to:

$$\begin{aligned}
\mathbf{J}_i &= -r \left(\sum_{j=1}^{n-1} D_{ij}^n \nabla w_j \right) \\
&= -r \left(\sum_{j \neq k}^{n-1} D_{ij}^n \nabla w_j + D_{ik}^n \nabla w_k \right) \left(\text{use identity } \nabla w_k = - \sum_{j \neq k}^n \nabla w_j \right) \\
&= -r \left(\sum_{j \neq k}^{n-1} D_{ij}^n \nabla w_j - D_{ik}^n \sum_{j \neq k}^n \nabla w_j \right) \\
&= -r \left(\sum_{j \neq k}^{n-1} (D_{ij}^n - D_{ik}^n) \nabla w_j + (-D_{ik}^n) \nabla w_n \right), \text{ for all } i \neq n.
\end{aligned}$$

$$\begin{aligned}
\mathbf{J}_n &= - \sum_{i=1}^{n-1} \mathbf{J}_i \\
&= r \left(\sum_{i=1}^{n-1} \sum_{j \neq k}^{n-1} (D_{ij}^n - D_{ik}^n) \nabla w_j - \sum_{i=1}^{n-1} D_{ik}^n \nabla w_n \right) \\
&= -r \left(\sum_{j \neq k}^{n-1} \sum_{i=1}^{n-1} (D_{ik}^n - D_{ij}^n) \nabla w_j + \sum_{i=1}^{n-1} D_{ik}^n \nabla w_n \right).
\end{aligned}$$

The equations above express all diffusion flux $\mathbf{J}_i$'s with all components but k , which is identical to choose component k as the dependent component:

$$\mathbf{J}_i = -r \sum_{j \neq k}^n D_{ij}^k \nabla w_j.$$

Therefore,

$$D_{ij}^k = D_{ij}^n - D_{ik}^n, \quad \text{if } i \neq n \text{ and } j \neq n \quad (\text{A22})$$

$$D_{in}^k = -D_{ik}^n, \quad \text{if } i \neq n \quad (\text{A23})$$

$$D_{nj}^k = \mathring{a}_{i=1}^{n-1} (D_{ik}^n - D_{ij}^n), \quad \text{if } j \neq n \quad (\text{A24})$$

$$D_{nn}^k = \mathring{a}_{i=1}^{n-1} D_{ik}^n. \quad (\text{A25})$$

A4. Supplementary figures, tables and data

Supplementary figures, tables and data associated with this article can be found as online supplements.

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Fig. 1. Comparison between the experimental profiles of exp. 227 in Zhang et al. (1989) and the calculated profiles using diffusion matrix of Kress and Ghiorso (1995) of multicomponent diffusion during forsterite dissolution in an andesitic melt at 1300°C and 5 kbar. Kress and Ghiorso (1995) ignored Na₂O and K₂O and other minor components, so SiO₂, Na₂O and K₂O are not shown here. The interface and far-field concentrations are determined from experiments. It can be seen that the calculated profiles are much longer than the experimental profiles, and the shape match is not close either. χ^2/n is calculated and shown for those five components.

Fig. 2. Comparison between the experimental profiles of exp. 26 in [Chen and Zhang \(2008\)](#) and the calculated profiles using diffusion matrix of [Alexander \(2011\)](#) for multicomponent diffusion during forsterite dissolution in an basaltic melt at 1372°C and 4.7 kbar. It can be seen that the lengths of the calculated profiles roughly match the data, but the shape match is not so good. χ^2/n is calculated and shown for each component.

Fig. 3. Microscopic image of polished experimental charge HB7&8B. Three traverses (L1, L2 and L3) were measured. Physical interface position is preserved after experiment.

Fig. 4. Fitting results of HB7&8B. All the points are measured data. The different symbols indicate different traverses, and the black solid curves are fit curves to obtain diffusion matrix A. Other profiles and fits are shown in the [supplementary file](#).

Fig. 5. Optical and BSE image of the polished sample charge of anorthite dissolution in the haplobasaltic melt. Three traverses (L1, L2, and L3) were measured on the right side, because the left side was affected by a piece of graphite in the melt. A flat glass-anorthite interface could be observed in both microscopic and BSE images. Note that the BSE image only shows the right side of the sample.

Fig. 6. Predictions of diffusion profiles during anorthite dissolution by diffusion matrix A in [table 3](#), with the calculated interface melt composition (dashed curves) and the experimentally determined interface composition (solid curves), respectively. Al_2O_3 concentration profile fit by a dissolution equation (equation 13-14 in [Zhang et al., 1989](#)) is also shown in Al_2O_3 panel (dotted curves) for comparison. FeO profile is shown for information, but is not calculated because our diffusion matrix does not include the FeO component. χ^2/n is calculated and shown for each component.