

Diffusion of Major and Trace Elements in Dry and Hydrous Natural Silicate Melts: Insights from Diffusion Couple Experiments

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INTRODUCTION

Exchange of chemical elements by diffusion plays a key role in several magmatic processes, (e.g. crystal growth and dissolution, bubble nucleation and growth), and among them, it has a major role in mass transfer occurring in magma mixing events. Magma mixing, particularly, is currently regarded as a trigger mechanism of highly explosive volcanic eruptions (Leonard et al., 2002). Since diffusion is a time-dependent process, it has the potential to shed light into the timescales involved in pre-eruptive magma mixing, and thus providing a volcanic geochronometer (Perugini et al., 2015).

A detailed knowledge of the diffusive behaviour of major and trace elements is crucial to achieve this goal. However, the available database of diffusivities, though extensive, is not systematic and data for natural melts is scarce. We present here an experimental study of the diffusion of major and trace elements between two dry and hydrous natural melts at high pressure and temperature.

MATERIALS AND METHODS

Two natural volcanic products from Vulcano (Aeolian Islands, Italy) were chosen as end-members for the diffusion couple experiments. The mafic end-member is a shoshonite from the Vulcanello lava platform (A.D. 1000-1250), and the felsic end-member is a rhyolite sampled at the A.D. 1736 Pietre Cotte obsidian flow (La Fossa cone). Evidence of magma mixing is widespread in the Vulcano system.

Powders of the starting materials were melted and crushed twice at 1600 °C to achieve homogeneity. Then, both nominally dry (ND) and hydrous glasses (1 wt.% and 2 wt.% added H₂O)

were synthesized at high pressure and temperature in an Au₈₀Pd₂₀ capsule using an Internally Heated Pressure Vessel (IHPV) (Institute of Mineralogy, University of Hannover). The resulting glass cylinders (5 mm diameter) of each end-member were cut and polished in one end.

Experiments were performed using the diffusion couple technique. Pairs of shoshonite and rhyolite glass cylinders with the same nominal water content are placed inside Au₈₀Pd₂₀ capsules and run in the IHPV at 1200 °C for 1 to 4 hours (plus one zero-time experiment). Pressure varies from 50 to 500 MPa. Experiments are finished by a rapid quench device (Berndt et al., 2002), avoiding the formation of crystals.

Analyses were performed on doubly polished glass sections (100 to 200 µm thick) from the experimental products. Water contents were characterized by Fourier Transform Infrared (FTIR) spectroscopy in the near infrared region of the spectrum. Major element concentration-distance profiles were acquired by electron microprobe (Cameca SX-100 at the University of Hannover), and trace element profiles were measured by LA-ICP-MS (Teledyne Photon Machine G2 / Thermo Fisher iCap q, University of Perugia). The analytical profiles are centered in the interface and extend 1 mm into each half of the couple (2 mm total length), and when possible, a second, offset profile was acquired.

RESULTS

All experiments, including nominally dry experiments, are crystal free glasses. Water contents measured by FTIR are close to the intended nominal values, except for the ND experiments, which show an H₂O content of 0.3 wt.%. This observation can be explained by

hydrogen permeation through the capsule wall and reaction with ferric iron. The 300 and 500 MPa experiments are bubble-free, but the experiments performed at 50 and 100 MPa show a variable amount of bubbles of very small size.

Concentration-distance profiles

The major element concentration-distance profiles (Fig. 1) show a Fickian behaviour with an asymmetric shape, extending deeper into the shoshonite half than into the rhyolite. This is a consequence of the different diffusion rates occurring in melts of differing composition, meaning a different degree of polymerization. A particular case is Al, which shows a prominent minimum in the rhyolite side next to the interface, related to an uphill diffusion process (diffusion against concentration gradient). Na shows hints of uphill diffusion, but analytical scatter prevents full resolution of the diffusion profiles.

Most trace elements show Fickian diffusion profiles, with some notable exceptions. Uphill diffusion is observed in Ga, Zr, Nb, Pb, Y and especially, in the trivalent REE (La to Sm and Gd to Lu), which display a very strong minimum in their composition-distance profiles around the interface of the couples (Fig. 1). The apparent effect of uphill diffusion is greatest in the LREE and diminishes gradually towards the HREE.

Diffusion coefficients

Due to the variable diffusivity along the profiles, a simple error function approach (assuming constant diffusivity) cannot be used. Diffusion coefficients are calculated using the modified Boltzmann-Matano method of Sauer and Freise (1962) in a three-step procedure: (1) polynomial fitting of the composition data, (2) normalization of the

palabras clave: Difusión, Mezcla de Magmas, Shoshonita, Riolita, Vulcano.

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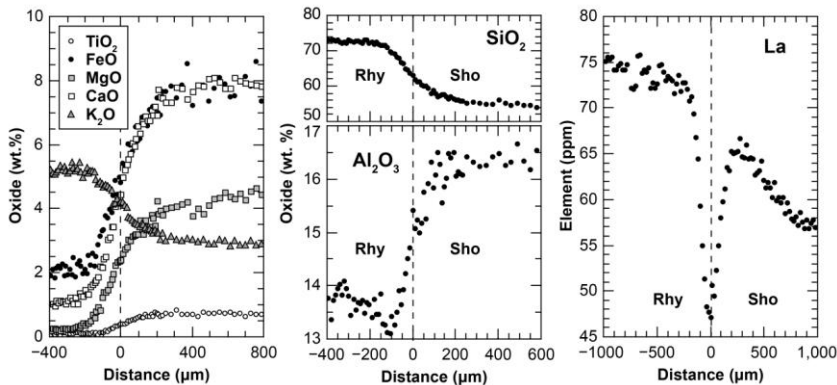


fig 1. Examples of concentration-distance profiles. Dashed line is the position of the interface between rhyolitic (left) and shoshonitic (right) melts. Conditions: 1200 °C, 300 MPa, 2 wt.% H₂O and 1h run time.

compositional range of the fit, and (3) application of the analytical solution of Sauer and Freise (1962) for one-dimension, molar volume independent diffusion. Diffusivities are extracted along the profiles at four compositional terms spanning from 20% to 80% of the compositional range, corresponding to a latite (Lt₅₈), trachytes (Tr₆₂ and Tr₆₆) and a rhyolite (Rh₇₀). Subscripts denote SiO₂ content.

Results (Fig. 2) show that H₂O content in the melt is the most important factor influencing the diffusion of major and trace elements through our experimental setup. Diffusivities with 2 wt.% H₂O are up to 1.5 orders of magnitude faster than in the ND melts, although some variations are observed in different elements. Compositional variability is also notable, with diffusivities being up to 0.8 log units faster in the mafic end member. On the

other hand, no systematic pressure influence could be resolved in our data.

Among major elements, data show the occurrence of strong coupling among components. Ti is the slowest diffusing component through all experimental conditions, followed by Si. The remaining components show a very similar diffusivity at the same conditions and falling within error, hinting at complex elemental interactions in natural melts. The presence of strong coupling is further supported by the occurrence of uphill diffusion in Al and possibly Na. Coupled and uphill diffusion has been observed both in synthetic melts (Liang, 2010) and in natural basalt-rhyolite couples (e.g., Koyaguchi, 1989).

Trace element diffusion shows variability between elemental groups. LIL elements display a moderate (Rb, Cs) to non-existent (Ba, Sr) compositional

dependence and are notably enhanced by water. In contrast, transition elements (Ni, Co) have moderate water and compositional dependence, and HFS (Eu, U, Th) show a strong compositional dependence but mild water dependence.

IMPLICATIONS

Our experimental results highlight that even low water contents can produce a notable enhancement in diffusivities. Since natural magmas are rarely dry, these data have implications in the rate of homogenization of chemical variability in magma mixing events and are essential to evaluate mass transfer processes during such process, subsequently producing the wide compositional spectrum observed in mixed rocks. However, this study hints at the complexity of the diffusion mechanism in multicomponent natural melts, making evident that further systematic studies are needed to generate consistent datasets for different end-member magmas.

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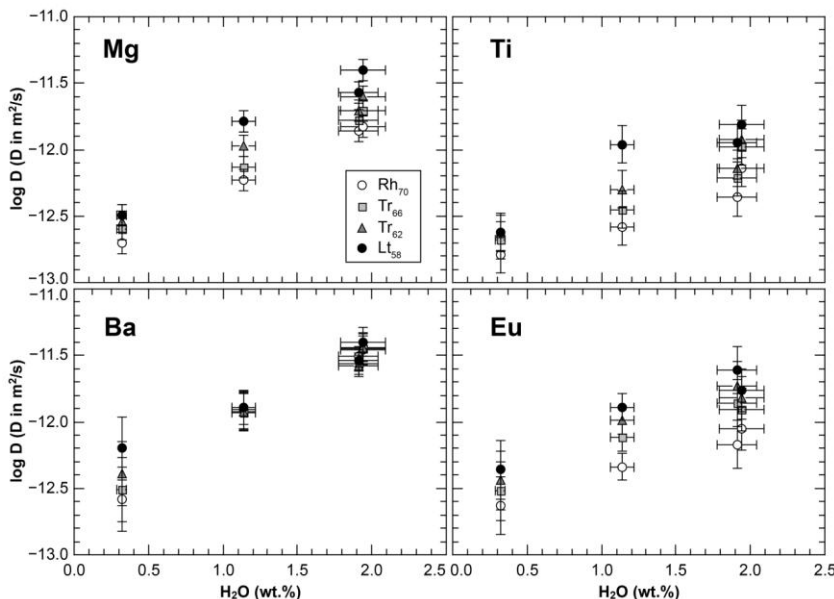


fig 2. Diffusivities (expressed as log D) of Mg, Ti, Ba and Eu versus water content at 1200 °C and 300 MPa in all four intermediate compositional terms (Lt₅₈, Tr₆₂, Tr₆₆ and Rh₇₀). Subscripts indicate SiO₂ content.