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Water-enhanced interdiffusion of major elements between natural shoshonite and high-K rhyolite melts

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ABSTRACT

The interdiffusion of six major elements (Si, Ti, Fe, Mg, Ca, K) between natural shoshonite and a high-K rhyolite (Vulcano island, Aeolian archipelago, Italy) has been experimentally measured by the diffusion couple technique at 1200 °C, pressures from 50 to 500 MPa and water contents from 0.3 ('nominally dry') to 2 wt%. The experiments were carried out in an internally heated pressure vessel, and major element profiles were later acquired by electron probe microanalysis. The concentration-distance profiles are evaluated using a concentration-dependent diffusivity approach. Effective binary diffusion coefficients for four intermediate silica contents are obtained by the Sauer-Freise modified Boltzmann-Matano method. At the experimental temperature and pressures, the diffusivity of all studied elements notably increases with dissolved H_2O content. Particularly, diffusion is up to 1.4 orders of magnitude faster in a melt containing 2 wt% H_2O than in nominally dry melts. This effect is slightly enhanced in the more mafic compositions. Uphill diffusion was observed for Al, while all other elements can be described by the concept of effective binary interdiffusion. Ti is the slowest diffusing element through all experimental conditions and compositions, followed by Si. Fe, Mg, Ca and K diffuse at similar rates but always more rapidly than Si and Ti. This trend suggests a strong coupling between melt components. Since effects of composition (including water content) are dominant, a pressure effect on diffusion cannot be clearly resolved in the experimental pressure range.

1. Introduction

Diffusive exchange of chemical elements plays a key role in many magmatic processes. As an example, it governs crystal growth and dissolution, bubble nucleation and growth and the compositional modulation during magma mixing processes. In particular, magma mixing is widely considered as one of the basic processes responsible for the generation of the wide compositional variety of igneous rocks on the Earth, within both plutonic and volcanic environments (Anderson, 1976). In addition, it has been recognized as a major trigger mechanism for some highly explosive volcanic eruptions (Sparks et al., 1977; Leonard et al., 2002). The time and space evolution of magma mixing between two chemically distinct magmas is controlled by both physical and chemical processes where diffusion plays a significant role (Perugini et al., 2006; Perugini et al., 2008). Hence, as a time-dependent process, diffusion has the potential to be used as a chronometer of such magma mixing processes (e.g. Perugini et al., 2015). However, in order to fully achieve this goal, a detailed understanding of the diffusion process in natural melts is mandatory.

Although a large number of diffusion data in silicate melts has been published in recent years (for a review of published data, see Zhang et al., 2010), the dataset is not systematic and data for natural systems are scarce. Furthermore, specific literature on the effect of water in diffusivity of major and trace elements is limited (Baker, 1991; Baker and Bossányi, 1994; Mungall et al., 1998; Behrens and Hahn, 2009).

The aim of the present work is to systematically fill this gap by gathering a consistent dataset of diffusion data and relative diffusion coefficients that are applicable to geologically relevant scenarios. We use melts of rhyolitic and shoshonitic composition sampled at Vulcano Island (Aeolian archipelago, Italy) to probe timescales and compositional signatures of diffusion. In detail, we aim at determining the effective binary diffusion coefficients (EBDC hereafter) of six major elements (Si, Ti, Fe, Mg, Ca, K) between the two natural end-members at 1200 °C and at pressures of 50, 100, 300 and 500 MPa, relevant to relatively shallow magmatic systems. The influence of water in the enhancement of the diffusion processes is also considered in detail.

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A problem in the use of EBDCs is that they are not generally transferable to other compositions and other conditions. Additionally, non-Fickian effects such as uphill diffusion cannot be described. Complete description of multi-component diffusion in silicate melts requires the determination of the diffusion matrix, which considers the interaction of all melt components (Liang, 2010). In practice, such diffusion matrix can only be determined for melts containing a few components, but not in complex natural systems where the number of components is far larger. In such cases the concept of effective binary diffusion coefficients, when being critically applied, is a suitable approach to get insights into the fundamental mechanisms driving the diffusion process.

2. Materials and methods

2.1. Starting materials and glass synthesis

Rocks out-cropping on the island of Vulcano range in composition from mafic to silicic with high-K calc-alkaline to shoshonitic and potassic alkaline affinities (Peccerillo, 2005; Keller, 1980; Gioncada et al., 2003). Two natural end-member compositions, sampled during a field campaign (Oct. 2014), have been selected for the present study (Fig. 1). The least evolved end-member is a shoshonite sampled at the Vulcanello lava platform (Vetere et al., 2007; Davì et al., 2009). The most evolved is a high-K rhyolitic obsidian from the Pietre Cotte lava flow, belonging to the La Fossa cone (Vetere et al., 2015; De Astis et al., 1997; Clocchiatti et al., 1994; Piochi et al., 2009). Both end-members are products of historic activity within the island. The Vulcanello platform was formed during a long-lasting eruptive period between 1000 CE and 1250 CE (Arrighi et al., 2006; Vetere et al., 2007). The Pietre Cotte lava flow was emplaced during the 1736 eruption of the La Fossa cone (Keller, 1980; Frazzetta et al., 1983); evidence of magma mixing has been recognized in both systems (Clocchiatti et al., 1994; Aparicio and Frazzetta, 2008; Vetere et al., 2015). Water content in the magmas from Vulcano was found to be lower than 2 wt%, and usually between 1.0 and 1.5 wt% (Clocchiatti et al., 1994).

Alteration-free rock samples have been selected and, after a deep cleaning with distilled water, they were crushed in an agate mortar to obtain a fine-grained powder. End-member powders were subsequently homogenized through two cycles of melting at 1600 °C for 4 h in a high temperature furnace (Nabertherm® HT 04/17) at ambient pressure using a platinum crucible, followed by crushing and fine powdering in the agate mortar. During this process, the material loses most volatiles that were originally present. Alkali loss was also checked by comparing the re-melted material with literature data on the same rocks (Vetere et al., 2007; Davì et al., 2009) and results indicated that it can be considered negligible. Measured compositions of end-member glasses are reported in Table 1 and Fig. 1. In agreement with Peccerillo and Taylor (1976), the studied compositions define a shoshonitic trend.

Glass with defined water contents were synthesized using $Au_{80}Pd_{20}$ alloy tubes with 5 mm diameter and 4 to 5 cm length. The tubes were welded at one end and filled step by step with rock powder and compacting by a metal rod after each filling step; when necessary, distilled water was added. Welding was carried out with a Lampert PUK04 pulse arc welder in Ar atmosphere. In the wet experiments, added water was introduced by using a micrometric syringe and checked with a balance with precision of 0.1 μg. Added water contents were 1 wt% and 2 wt%, chosen to possibly match that of magmas erupted at Vulcano. Moreover, a water-free ('nominally dry', hereafter ND) capsule for each end-member was prepared. Capsules were filled and weighed before and after the welding procedure. Finally, the capsule was tested for leakage by annealing at 100 °C for 12 to 24 h.

Glass syntheses were performed in an internally heated pressure vessel (IHPV) (Holloway, 1971; Berndt et al., 2002) at 1200 °C and 300 MPa for 24 h and isobarically quenched to room temperature by switching off the heating power of the furnace. During experimental

runs, the temperature variation within the capsule was less than 10 °C. Initial quench rates were in the order of 200 °C per minute. Subsequent lower quenching rates (100 °C/min at the glass transition range) avoided formation of internal stresses within the glasses during cooling. Glass chips from the end tips of the hydrous glass cylinders were analyzed for water content by pyrolysis and subsequent Karl-Fischer titration (Behrens, 1995; Behrens et al., 1996) to provide a quality control for synthesis procedure. Finally, synthesized glass cylinders were cut with a diamond saw to obtain pieces with length of 3 to 4 mm, and one end of each cylinder was polished.

In addition, the Fe^{2+}/Fe^{3+} ratio was measured by a wet-chemical method in synthesized glasses at high-pressure in the IHPV as described by Schuessler et al. (2008). An advantage of this method is that ferrous iron content and total iron content are determined on the same base solution so that the Fe^{2+}/Fe^{3+} ratio can be determined with high precision using a Shimadzu UV 1800 spectrometer. From each quenched sample, two pieces of glass from the top and bottom of the capsule were analyzed. Table 2 shows the measured iron oxidation state in both dry and hydrous starting glasses. A relationship between water content of the melt and the oxidation state of iron is evident: higher water contents result in lower the Fe^{2+} due to the dependence of oxygen fugacity on water fugacity (Vetere et al., 2014).

2.2. Diffusion couple experiments

Diffusion experiments were performed using the diffusion couple technique (Baker, 1989; Baker, 1990; Nowak and Behrens, 1997). Couples of rhyolite and shoshonite glass cylinders with the same nominal water content (dry, 1 wt% and 2 wt%) were placed in contact through their polished end inside a 5 mm diameter $Au_{80}Pd_{20}$ capsule, which was sealed as previously described. The higher density shoshonite glass was located in the bottom side of the capsule in order to avoid gravitationally induced mixing. Tightness of the sealed capsule was checked by weighing it before and after compression in a Cold Seal Pressure Vessel (CSPV) and observing the adaptation of the capsule to the sample shape.

Experiments were run in an IHPV using heating ramps of 30/50/ 20 °C/min from ambient temperature to 100, 1150 and 1200 °C, respectively. Temperature was kept constant at 1200 ± 5 °C for all experiments, and run pressures were 50 MPa, 100 MPa and 300 MPa. Experimental times were 1 h and 4 h in the 300 MPa experiments, and 4 h in the 50 and 100 MPa experiments. An additional experiment was run at 500 MPa, 2 wt% H_2O with a duration of 4 h. After each run was completed, a rapid quench was applied by letting the capsule fall from the hot region of the vessel to the cold part (Berndt et al., 2002). A zero-time experiment (i.e. an experiment rapidly quenched soon after reaching 1200 °C) was performed at 300 MPa to quantify the effect of heating/cooling on diffusion profiles and to demonstrate that quench phases, which might form after synthesis in the shoshonitic glass, were absent when reaching the target temperature. Table 3 summarizes experimental conditions.

The IHPV vessel used for syntheses and diffusion couple experiments was pressurized with argon, and experiments were performed at the intrinsic hydrogen fugacity of the vessel. The oxygen fugacity within the capsules was controlled by the fugacity of H_2 and H_2O through the equilibrium reaction $H_2 + 1/2\ O_2 = H_2O$. Under intrinsic conditions in the IHPV, the oxygen fugacity in capsules containing H_2O-saturated melts (pure H_2O fluid) was found to be close to the $MnO–Mn_3O_4$ buffer (i.e. 3.7 log units higher than the Ni/NiO buffer; Berndt et al., 2002).

2.3. Analytical procedure

2.3.1. Sample preparation for analyses

Analyses were carried out on doubly polished glass sections (with thickness of ca. 200 μm) from each of the experimental products.