



Titanium diffusion in olivine

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Abstract

Diffusion of Ti has been characterized in natural olivine and synthetic forsterite. Experiments on the natural olivines were run under buffered conditions (IW and NNO), and those on synthetic forsterite were run in air. Titanium diffusion appears relatively insensitive to crystallographic orientation and oxygen fugacity under the range of investigated conditions, and diffusivities are similar for Fe-bearing olivine and forsterite. For Ti diffusion in synthetic forsterite, we obtain the following Arrhenius relation for diffusion over the temperature range 900–1400 °C:

$$D_{\text{Forst}} = 5.97 \times 10^{-14} \exp(-203 \pm 19 \text{ kJ mol}^{-1}/RT) \text{ m}^2 \text{ s}^{-1}.$$

For Ti diffusion in San Carlos olivine, we obtain the following “global” fit to all diffusion data (incorporating diffusion parallel to *b* and *c*-axes, and experiments run under IW and NNO buffers), over the temperature range 1050–1254 °C:

$$D_{\text{ol-SC}} = 2.11 \times 10^{-14} \exp(-195 \pm 32 \text{ kJ mol}^{-1}/RT) \text{ m}^2 \text{ s}^{-1}.$$

Titanium diffusivities in olivine are similar to those of the trivalent REEs, but considerably slower than those of Cr, Ca, and Fe–Mg in olivine. Titanium diffusivities in olivine, diopside and orthopyroxene are comparable over investigated temperature ranges, differing by about half a log unit at 900 °C, but have increasing variance at lower temperatures given the higher activation energies (by 40–70 kJ mol⁻¹) for Ti diffusion in pyroxene compared with olivine. These large differences in cation mobility among Ti, Cr, Ca, Fe–Mg and the REE in pyroxene and olivine may allow us to distinguish dominant processes that give rise to the chemical disequilibria in olivine and pyroxene. With decreasing temperature, Ti is preferentially partitioned from olivine to pyroxene in ultramafic rocks, giving rise to characteristic reversed zoning in olivine and orthopyroxene and normal zoning in clinopyroxene. Diffusive exchange models with temperature-dependent diffusion and partition coefficients have been developed for the olivine–pyroxene bi-mineralic and tri-mineralic systems, allowing us to assess cooling rates and closure temperatures of the ultramafic and mafic rocks.

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1. INTRODUCTION

Titanium is a trace element in olivine, which is the first mineral to crystallize from mantle-derived silicate melts at pressures below multiple saturation depth. Olivine coexists with at least one pyroxene in mafic and ultramafic rocks such as lherzolite, harzburgite, wehrlite, websterite, and dunite, are major constituents of the Earth's upper mantle and lower crust. There is considerable interest in the

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geochemistry of Ti and other trace elements in olivine in mantle rocks and mantle derived igneous rocks (e.g., Milman-Barris et al., 2008; De Hoog et al., 2010; Foley et al., 2011, 2013). Under typical upper mantle and lower crust conditions, titanium is tetravalent (Ti^{4+}) and has an ionic radius of 0.605 Å, which is smaller than that of Mg^{2+} (0.72 Å) or Fe^{2+} (0.78 Å) at the M1 site (sixfold coordination), but larger than Si in fourfold coordination (0.26 vs. 0.42 Å for Si and Ti, respectively) (Shannon, 1976). Under very reducing conditions, such as the lunar interior, a portion of titanium may be trivalent, although the proportion of Ti^{4+} and Ti^{3+} is still not well quantified. Titanium has been found to energetically favor the Si site in anhydrous forsterite, but under hydrous conditions may also be incorporated on the M1 site in substitution for Mg, with the most stable configuration involving edge sharing with a vacant Si site and OH groups formed to stabilize the underbonded O around the Si site (Berry et al., 2007). Schmädicke et al. (2013) have demonstrated that the coupled substitution $\text{Ti}^{4+} + 2\text{H}^+ \rightarrow \text{Mg}^{2+} + \text{Si}^{4+}$ is the most important means of incorporating water in olivine in upper mantle rocks, and thus a dominant means of water storage in the shallow upper mantle. Hence measurements of Ti contents of olivine can be a useful way to estimate the maximum amount of water incorporated in olivine through this coupled substitution and may also provide a means to approximate the extent of water loss, since water will be more mobile than Ti. Quantification of the diffusivity of Ti in olivine will provide additional constraints on these determinations.

According to Foley et al. (2013), titanium abundances in olivine in kimberlites and basaltic rocks (up to 340 ppm) are typically higher than those in olivine in peridotites (typically <70 ppm) that have not been affected by mantle metasomatism. These authors also suggested that differences in Ti and other trace element (Al, Ca, and Ni) abundances in olivine can be used to discriminate between igneous and mantle olivine. One possible explanation of this dichotomy in Ti abundances in olivine in mantle rocks and mantle derived igneous rocks is subsolidus redistribution of Ti among olivine and pyroxenes. Titanium is incompatible in olivine relative to pyroxene, and its olivine–pyroxene partition coefficients decrease with decreasing temperature (e.g., Witt-Eickschen and O'Neill, 2005; Sun, 2014). Hence, during subsolidus re-equilibration, titanium diffuses out of olivine (and orthopyroxene) and into adjacent clinopyroxene. The extent of Ti redistribution depends on cooling rate and Ti diffusion rates in olivine and pyroxene, as well as the temperature-dependent olivine–pyroxene Ti partition coefficient.

In a recent study, we measured tracer diffusion coefficients of Ti in natural orthopyroxene and clinopyroxene over a range of temperatures (900–1250 °C) and oxygen fugacity (IW, NNO, QFM, and air, Cherniak and Liang, 2012). We showed that the rates of Ti diffusion in pyroxene are comparable to the rates of REE diffusion in orthopyroxene and the rates of Al and middle REE diffusion in diopside at magmatic temperatures, but 1–3 orders of magnitude smaller than the rates of Fe and Mg diffusion in pyroxenes. During subsolidus re-equilibration, titanium dif-

fuses out of orthopyroxene and into coexisting clinopyroxene, producing characteristic “bell shaped” reversed Ti zoning in the former but “U shaped” normal Ti zoning in the latter. Such contrasting zoning patterns can be readily distinguished from simple normal or reversed zoning in coexisting pyroxenes produced by crystal–melt fractionation processes, and can be used to infer cooling rates of two-pyroxene bearing mafic and ultramafic rocks.

In this study, we report results from an experimental investigation of Ti diffusion in natural olivine and synthetic forsterite over a range of temperatures (900–1400 °C), oxygen fugacity (IW, NNO, and in air) and major element compositions ($\text{Fo}_{88.5}$ – Fo_{100}). Based on consideration of ionic charge and size, we would expect Ti^{4+} diffusion in olivine to be slower than those of divalent cations Ca and Ni, as well as Fe–Mg interdiffusion and Cr^{3+} diffusion, and perhaps comparable to Si, given that Ti may substitute on tetrahedral sites in olivine. However, other studies (Spandler et al., 2007; Spandler and O'Neill, 2010; Jollands et al., 2013) suggest that Ti diffusivities are comparable to those of Fe–Mg and Ni in olivine. Given the paucity of Ti diffusion data in olivine, we first focus our effort on anhydrous systems and at 1 bar. In a companion study, we will examine the effects of pressure and water content on Ti diffusion in olivine. Our measured Ti diffusion data for olivine complement earlier diffusion measurements of Ti in orthopyroxene and clinopyroxene, and permit us to assess the potential for diffusive fractionation of Ti among olivine and pyroxenes during magmatic and metamorphic processes under upper mantle and lower crust conditions.

2. EXPERIMENTAL PROCEDURE

Titanium diffusion experiments were conducted with synthetic forsterite and natural olivine from two localities. The synthetic forsterite was from the Morion Corporation, and natural olivines from Kilbourne Hole, New Mexico (designated as KBH), and San Carlos, Arizona (SCO). Compositions of the olivines are presented in Table 1, which shows analyses for these materials originally reported by Thomas et al. (2008) and Morgan and Liang (2005). Samples selected for experiments were optically clear and free of inclusions.

The synthetic forsterite samples were oriented to measure diffusion parallel to the *c*-axis, and to the *a*-axis, while the San Carlos olivine was oriented to measure diffusion parallel to the *c*- and *b*-axes. The Kilbourne Hole olivine, which was in small crystal fragments of a few mm in size, was not oriented prior to experiments given the size of the grains, but instead the largest faces of grains were polished. All specimens were polished with SiC paper, followed by polishing with 1.0 μm and 0.3 μm alumina powders, and finished with a chemical polish using a colloidal silica suspension. Following polishing, samples were cleaned ultrasonically in distilled water and ethanol.

The source of diffusant for the experiments on the synthetic forsterite was a mixture of dried MgO , SiO_2 and TiO_2 powders (in molar ratio 20:9:1), combined and heated at 1250 °C overnight, then thoroughly mixed with synthetic forsterite powder (Alfa-Aesar, 99% purity) in 1:2 proportions

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