Diffusion of phosphorus in olivine and molten basalt†

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ABSTRACT

The diffusivity of phosphorus in San Carlos olivine (SCO) was measured at near-atmospheric pressure and 650–850 °C by in-diffusion of P from a surface powder source consisting of pre-reacted SCO and AlPO4. The experiments were conducted in evacuated silica-glass ampoules at oxygen fugacities fixed by solid-state buffers, generally Ni-NiO but also including two experiments buffered at wüstite-magnetite. Phosphorus uptake profiles were characterized by Rutherford backscattering spectroscopy (RBS) and nuclear reaction analysis (NRA). The temperature dependence of P diffusion in SCO conforms to the expected Arrhenius relation \( D = D_0 \exp(-E_a/RT) \), where the constants are as follows: \( \log(D_0, \text{m}^2/\text{s}) = -10.06 \pm 0.80 \) and \( E_a = 229 \pm 16 \text{ kJ/mol} \). These values characterize P as a relatively slow diffuser in olivine—slower by about an order of magnitude than Cr and Ca at basalt near-liquidus temperatures—but substantially faster than Si.

With a view toward modeling P uptake during rapid growth of natural olivines, P diffusion was also characterized in dry MORB basalt melt over the temperature range 1250–1500 °C at 1 GPa, using traditional diffusion couples contained in graphite. Phosphorus diffusion profiles in the quenched and depressurized samples were quantified by laser-ablation ICP/MS. Phosphorus diffusion in basaltic melt is similar to that of Si, with \( \log(D_0, \text{m}^2/\text{s}) = -6.30 \pm 0.7 \) and \( E_a = 147 \pm 22 \text{ kJ/mol} \).

The new data for P diffusion in olivine and basalt melt can be used to explore the acquisition of fine-scale zoning in natural olivine phenocrysts through kinetic models, as well as the survival of P zoning in olivine with time spent at elevated temperature. Models of growth entrapment of a P-enriched near-surface layer in the olivine lattice indicate that crystal growth at plausible sustained rates is indeed likely to result in regions of anomalously high P content in the resulting crystal. Phosphorus concentrations above the equilibrium partitioning value can also result from development of a diffusive boundary layer in the melt against a rapidly growing crystal, but this mechanism is ineffective at typical sustained olivine growth rates, requiring dendrite-forming growth speeds. Preservation of P zoning on the scale of a few micrometers apparently requires cooling within a few months of formation of the zoning.

Keywords: Diffusion, phosphorus, olivine, basaltic melt, growth kinetics, basalt thermal history

INTRODUCTION

Because of its abundance in Earth’s mantle and crust and in some meteorites, magnesian olivine has been the subject of numerous diffusion studies, targeting both major components (Mg, Fe, Si, O) and trace elements (H, Li, Be, Al, Ca, Ti, Cr, Mn, Co, Ni, Sr, REE; see summary by Chakraborty 2010 and references therein; Spandler et al. 2007; Spandler and O’Neill 2010; Cherniak 2010). Conspicuously missing from the group of elements whose diffusion properties have been characterized is phosphorus. The lack of P diffusion data is a significant shortcoming given the complex P-zoning patterns noted in some terrestrial and meteorite olivines (Milman-Barris et al. 2008; Mallman et al. 2009; Tschegg et al. 2010; Sakyi et al. 2012; McKibbin et al. 2013; Welsch et al. 2013, 2014): the formation and persistence of this sometimes delicate zoning may be related in some way to ineffective P diffusion. Here we address this gap in diffusion information by measuring the diffusivity of P in San Carlos olivine (Fo90) at near-atmospheric pressure, 650–850 °C and oxygen fugacities buffered at Ni-NiO and FeO-Fe2O3.

A second goal of this effort was to incorporate the new diffusion measurements into numerical models of olivine crystal growth that might shed light on the remarkable P-zoning patterns observed in some natural and synthetic olivines. Some of these models require knowledge of diffusion in the growth medium, so we also characterized chemical diffusion of P in basaltic melt as a function of temperature over the range 1250–1500 °C. To our knowledge, P diffusion in basaltic melt has not been characterized thoroughly at temperatures directly relevant to natural systems. Four data points spanning ~1250–1450 °C are available in the combined studies of Lundstrom (2003) and Baker (2008), but one of these studies involved complex diffusion phenomena—e.g., co-diffusion of Ca and P away from dissolving apatite in the study of Baker (2008). The previous results are not in good agreement, which complicates the choice of diffusivities for modeling purposes.

EXPERIMENTS AND ANALYSES

Materials and preparation

The P diffusion experiments on olivine were conducted using oriented slabs (~1 × 2 × 3 mm) of San Carlos olivine (SCO) cut from ~centimeter-sized pieces. The slabs were ground and polished on one face, beginning with SiC grit (down