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## SPECIAL COLLECTION: MECHANISMS, RATES, AND TIMESCALES OF GEOCHEMICAL TRANSPORT PROCESSES IN THE CRUST AND MANTLE Experimental study of phlogopite reaction rim formation on olivine in phonolite melts: Kinetics, reaction rates, and residence times<sup>†</sup>

## THOMAS BARTHOLOMEW GRANT<sup>1,2,\*</sup>, RALF MILKE<sup>1</sup>, BERND WUNDER<sup>2</sup>, RICHARD WIRTH<sup>2</sup> AND DIETER RHEDE<sup>2</sup>

<sup>1</sup>Institut für Geologische Wissenschaften, Freie Universität Berlin, Malteserstrasse 74-100, 12249 Berlin, Germany <sup>2</sup>GeoForschungsZentrum Potsdam, Telegrafenberg, 14473 Potsdam, Germany

## ABSTRACT

Experiments were conducted to reproduce reaction rims of phlogopite  $\pm$  diopside around olivine that have been observed within a wide range of potassic melts, including phonolite. Phlogopite is also a common secondary phase formed at the expense of olivine during metasomatic events involving K<sub>2</sub>Oand H<sub>2</sub>O-rich fluids or melts. Piston-cylinder experiments where olivine single crystals were reacted with synthetic phonolite melt at 10.7–14.7 kbar and 950–1000 °C recreate the mineralogy and textures documented in natural samples. Rim growth is parabolic with time, indicating a diffusion-controlled reaction. Fast diffusion in the melt and varying compositions across the phlogopite reaction rims suggest that diffusion through the rims, along grain boundaries is rate limiting. Reaction rates dramatically increase with temperature as well as the bulk water content of the sample charge. This is because of increasing amounts of atomically bound hydrous species along the grain boundaries that increase the rates of diffusion and thereby the rates of rim growth. Atomically bound hydrous species increase the rates of rim growth by lowering the activation energy for diffusion and by increasing the solubility of diffusing species in the grain boundary region. Transmission electron microscopy shows the presence of isolated pores and open grain boundaries. Most of these may have opened during quenching, but there is some evidence to suggest that a free fluid phase may have been locally present in experiments with high melt water contents (>8 wt%). The measured rim growth rates at different conditions are used to estimate residence times of reacting olivine crystals in natural systems.

Keywords: Phlogopite, olivine, reaction rims, grain boundary diffusion, metasomatism