Experimental study of phlogopite reaction rim formation on olivine in phonolite melts: Kinetics, reaction rates, and residence times†

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ABSTRACT

Experiments were conducted to reproduce reaction rims of phlogopite ± 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 K2O- and H2O-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

INTRODUCTION

Phlogopite-bearing peridotite rocks have been identified in several locations; the Ivrea Zone, Southern Alps (Zanetti et al. 1999; Grieco et al. 2001); the Horoman peridotite complex (Arai and Takahashi 1989); and Lherz (Bodinier et al. 2004). Additionally, phlogopite-bearing peridotite xenoliths are observed (Aoki 1975; Lloyd et al. 1991; Wulff-Pedersen et al. 1996; Stiefenhofer et al. 1997). The phlogopite, along with other phases, is often secondary and forms at the expense of primary peridotite phases such as olivine during metasomatic events involving K2O- and H2O-rich melts or fluids. Clear evidence of replacement of olivine by phlogopite was described in the Horoman peridotite complex (Arai and Takahashi 1989). The origin and composition of the fluids or melts involved in these reactions are not always well constrained. Slab derived melts or fluids (Sudo and Tatsumi 1990; Zanetti et al. 1999; Prouteau et al. 2001; Wunder and Melzer 2003), partial melting of pre-metasomatized mantle (Grieco et al. 2001; Thibault et al. 1992) and fluids released from fractionating alkaline basalts (Arai and Takahashi 1989) have been suggested as potential sources. The range in pressures and temperatures of phlogopite formation are also potentially very large. Xenolith samples from Bultfontein Floors (Aoki 1975) are thought to originate from 170–100 km compared with much shallower conditions in the Horoman peridotite complex (Arai and Takahashi 1989) and the Ivrea Zone (Grieco et al. 2001). The stability field of phlogopite has been shown to extend deep into the mantle (Trønnes 2002) making it an important reservoir for volatiles, alkalis, and trace elements. Phlogopite, may also be an important phase in the genesis and alkali budget of arc magmas (Sudo and Tatsumi 1990), intraplate magmas (Pilet et al. 2011), and ultrapotassic melts (Foley 1992) during partial melting of metasomatized mantle. Therefore, the mechanisms by which phlogopite forms at the expense of upper mantle minerals is of particular interest.

In addition, there are numerous examples of olivine xenocrysts that have reacted to form phlogopite ± diopside reaction rims when in contact with K2O- and H2O-rich melts such as: lamprophyre (Foley et al. 2002; Semiz et al. 2012), lamproite (Carmichael 1967; Çoban and Flower 2006), kimberlite (Neal and Taylor 1989), minettes (Davis and Smith 1993), nepheline–leucitite (Lloyd et al. 2002) as well as phonolite (Henderson et al. 2012; Grant et al. 2013). These are very small-scale analogs of metasomatic reactions and in all these cases olivine cores...