Experimental determination of quartz solubility in H$_2$O-CaCl$_2$ solutions at 600–900 °C and 0.6–1.4 GPa

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ABSTRACT

Fluid-mediated calcium metasomatism is often associated with strong silica mobility and the presence of chlorides in solution. To help quantify mass transfer at lower crustal and upper mantle conditions, we measured quartz solubility in H$_2$O-CaCl$_2$ solutions at 0.6–1.4 GPa, 600–900 °C, and salt concentrations to 50 mol%. Solubility was determined by weight loss of single-crystals using hydrothermal piston-cylinder methods. All experiments were conducted at salinity lower than salt saturation. Quartz solubility declines exponentially with added CaCl$_2$ at all conditions investigated, with no evidence for complexing between silica and Ca. The decline in solubility is similar to that in H$_2$O-CO$_2$ but substantially greater than that in H$_2$O-NaCl at the same pressure and temperature. At each temperature, quartz solubility at low salinity ($X_{CaCl_2} < 0.1$) depends strongly on pressure, whereas at higher $X_{CaCl_2}$ it is nearly pressure independent. This behavior is consistent with a transition from an aqueous solvent to a molten salt near $X_{CaCl_2} \sim 0.1$. The solubility data were used to develop a thermodynamic model of H$_2$O-CaCl$_2$ fluids. Assuming ideal molten-salt behavior and utilizing previous models for polymerization of hydrous silica, we derived values for the activity of H$_2$O (a$_{H2O}$), and for the CaCl$_2$ dissociation factor (α), which may vary from 0 (fully associated) to 2 (fully dissociated). The model accurately reproduces our data along with those of previous work and implies that, at conditions of this study, CaCl$_2$ is largely associated (<2) at H$_2$O density <0.85 g/cm$^3$. Dissociation rises isothermally with increasing density, reaching ~1.4 at 600 °C, 1.4 GPa. The variation in silica mobility with a$_{H2O}$ in H$_2$O-CaCl$_2$ is nearly identical to that in H$_2$O-CO$_2$ solutions at 800 °C and 1.0 GPa, consistent with the absence of Ca-silicate complexing. The results suggest that the ionization state of the salt solution is an important determinant of a$_{H2O}$ and that H$_2$O-CaCl$_2$ fluids exhibit nearly ideal molecular mixing over a wider range of conditions than implied by previous modeling. The new data help interpret natural examples of large-scale Ca-metasomatism in a wide range of lower crustal and upper mantle settings.

Keywords: Metasomatism, quartz, silica, experimental, brines, fluids, halogens, solubility; Experimental Halogens in Honor of James Webster

INTRODUCTION

Fluid-mediated replacement of rock bodies with calcium silicate and/or carbonate assemblages (Ca-metasomatism) is an important process in the Earth’s crust and upper mantle. Ca-metasomatized metamorphic rocks are found in various lithologies and grades, from surficial to deep-crustal and upper mantle parageneses. Examples include “epidosites” and prehnite-pumpellyite rocks after intermediate and mafic lithologies (Harper 1995), lawsonite-replaced blueschists and eclogites (Vitale Brovarone and Beyssac 2014), rodingite alteration of ultramafic rocks after intermediate and mafic lithologies (Harper 1995), scapolite-rich rocks after granites, metasediments and sodic anorthosites (Oliver et al. 1994; Moecher et al. 1992), and fluid-induced formation of calcic clinopyroxene in low-Ca diamondiferous peridotites (Schulze 1995). Carbonated “megashear” terranes such as the Late Precambrian Attur Valley of southern India (Wickham et al. 1994) show replacement of up to 20% of the dominantly quartzofeldspathic country rocks by calcite or dolomite. Of considerable interest to economic geology is the conspicuous involvement of Ca-metasomatism in the genesis of major Au, Cu, and rare-earth element deposits, as in the Cloncurry District of Queensland, Australia (Mark et al. 2006), the Zambian “Copperbelt” (Eglinger et al. 2014), and the porphyry Cu ore body at Yerington, Nevada (Carten 1986). The presence of Ca$^{2+}$ ions in ore-forming fluids can facilitate disproportionation of an SO$_2$-bearing fluid to form anhydrite and sulfides (Mavrogenes and Blundy 2017).

Mobilization and transport of Ca is facilitated by chloride in aqueous solutions, as shown by fluid-inclusion studies of metasomatized rocks (De Jong and Williams 1995). These fluids promote high mobility of alkalies and alkaline earths in exchange processes involving feldspar, and pervasive replacement, consonant with the high “wetting” ability of chloride solutions (Holness 1992). However, little is known about the actual nature of the solutions: their concentrations, acid-base relations, accompanying cations and anions such as carbonate and sulfate, specific interaction with mineral assemblages, or mode of origin, whether magmatic (Mark 1998), diagenetic (Kendrick et al. 2008), or evaporitic (Oliver et al. 1994).

Ca metasomatism is commonly associated with substantial silica mobility. The combination of Ca and Si mobility with