

Carbon dioxide in granitic magma under lower crustal conditions Carbon dioxide in granitic magma under lower crustal conditions

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<Introduction>

Carbon dioxide is a major volatile component in the crust and mantle. Its solubility and speciation in silicate melts are important in understanding of mechanisms of magmatism and volcanism. However, they are not well constrained under lower-crustal conditions, especially in granitic magma, which is common in the crustal magmatism. In this study, we carried out equilibrium experiments in the CO₂-H₂O-granitic melt system to investigate the solubility and speciation of CO₂.

<Experimental procedure>

High-PT experiments were performed using a piston cylinder apparatus and a cold-seal pressure vessel. Obsidian flakes of a granitic composition and oxalic acid dehydrate (fluid source) were put in a gold or platinum capsule and run at 1123 and 1473 K and 0.1-1.5 GPa. Oxygen fugacity was estimated to be close to NNO. After quench, volatiles dissolved in the glass were analysed with FTIR spectroscopy. The composition of the coexisting fluid was quantified either by manometric analysis or based on the low-pressure solubility law and volatile contents of the glass.

<Results>

FTIR spectra showed that both CO₂ molecules (CO_{2mol}) and carbonate anions (CO₃²⁻) were present in all of the glass samples. The concentrations of CO_{2mol}, CO₃²⁻ and total H₂O increased generally with increasing pressure; they were 9200 ppm, 2100 ppm and 6.1 wt%, respectively, at 1.5 GPa and 1473 K. Here, we used new molar absorption coefficients of 2350 cm⁻¹ (1192 ± 130 L cm⁻¹ mol⁻¹; CO_{2mol}) and 1410 cm⁻¹ (91 ± 28 L cm⁻¹ mol⁻¹; CO₃²⁻) determined in this study. The fraction of CO₃²⁻ to total CO₂ in the granitic melt increased with increasing total CO₂ content, from 0.09 (total CO₂ = 260 ppm) to 0.19 (11300 ppm). The molar fractions of CO₂ in the fluids (X_{CO₂^{fluid}}) were 0.25-0.48 for the cold-seal experiments and 0.73-0.79 for the piston cylinder experiments.

<Discussion>

We formulated the solubility law of CO_{2mol} based on a vapour-liquid equilibrium equation. On the basis of the reaction CO₂ (vapour) ⇌ CO_{2mol} (melt), we calculated the partial molar volume of CO_{2mol} in the granitic melt and the reaction enthalpy to be 24.9 ± 2.0 cm³/mol and -22.2 ± 6.3 kJ/mol, respectively. These values are similar to those in previous experiments carried out at <6.6 kbar (Fogel and Rutherford, 1989; Behrens et al., 2004), indicating that the low-pressure solubility law can be extrapolated to 1.5 GPa. As for the formation of CO₃²⁻, we assumed a reaction CO_{2mol} + O²⁻ (non-bridging oxygen) ⇌ CO₃²⁻. Possible factors shifting the equilibrium to the right-hand side include the total pressure (e.g., Fine and Stolper, 1985; Guillot and Sator, 2011) and water content (King and Holloway, 1992; Behrens et al., 2004). In this study, it was difficult to evaluate these parameters separately, since the water content increased simultaneously with total pressure. If we assume that the effect of water is small enough to be neglected, the change of the partial molar volume of CO₂ in the melt and the reaction enthalpy can be calculated to be -8.6 ± 6.0 cm³/mol and -0.4 ± 3.1 kJ/mol, respectively.

<Application>

Recently, unusually CO₂-rich rhyolitic melt inclusions (up to 1.7 wt% total CO₂) were reported by Blundy et al. (2010). The saturation pressure of this CO₂ content is estimated to be 1.4 GPa when CO₂ dissolved only as CO_{2mol} (X_{CO₂^{fluid}} = 1; T=1173 K). If we consider the formation of CO₃²⁻, the saturation pressure is estimated to 1.2 GPa.

キーワード: CO₂, H₂O, solubility, granitic melt
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