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Raman spectroscopic study of the quartz solubility and the CO_3^{2-}-HCO_3^- equilibrium in H_2O + 3 molal $NaHCO_3$ fluids to 600°C and 1.74 GPa

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Alkali hydrogencarbonate and carbonate in aqueous fluids may play an important role in the mobilization of the REE and other elements at crustal conditions [1] and in subduction zones [2]. The CO_3^{2-}–HCO_3^- equilibrium in aqueous $KHCO_3$ and K_2CO_3 solutions has been studied at elevated temperature and pressure by Raman spectroscopy, e.g. to 219 °C [3] and to 550 °C and 200 MPa [4]. Here, this equilibrium and the quartz solubility were investigated on the assemblage H_2O + 3.0 molal $NaHCO_3$ solution and quartz to 600 °C and 1.74 GPa using a hydrothermal diamond-anvil cell [5]. Pressure was determined from the calibrated wavenumber shift of the most intense Raman line of quartz [6].

The equilibrium concentrations of the species HCO_3^-(aq) and CO_3^{2-}(aq) were obtained from the integrated intensities of the HCO_3^- mode at ~1016 cm^{-1} and the CO_3^{2-} mode at ~1066 cm^{-1} and the relative molar scattering factors of the two Raman bands (J-values) assuming that their ratio J_{1000}/J_{1060}=0.1667/0.2434 [3] is independent of pressure and temperature. Along all studied isotherms from 24 to 600 °C, the fraction of the species CO_3^{2-}(aq) generally decreased nonlinearly with pressure along an isotherm, e.g. at 500 °C from 0.162 at 0.22 GPa to 0.071 at 0.72 GPa to 0.054 at 1.5 GPa. Consequently, the isobaric increase in this fraction with temperature was much stronger at low pressures. The concentration of CO_2 in the aqueous liquid was below or just above the Raman spectroscopic detection limit.

The only detectable Raman band from dissolved silica was at ~770 cm^{-1}, which indicates a predominantly monomeric silica speciation. This allowed for use of the normalized and calibrated integrated intensity of this band to determine the SiO_2(aq) molality as described in ref. [7] as a function of pressure along four isotherms between 300 and 600 °C. As expected for an alkaline solution, the quartz solubility in 3.0 molal $NaHCO_3$ obtained from Raman spectroscopy was at low pressures significantly higher compared to the solubility of quartz in water at the same P-T conditions [8]. With increasing pressure, however, both solubilities converged along all studied isotherms. This is because the solubility of quartz in water shows an isothermal increase with pressure, whereas the quartz solubility in 3.0 molal $NaHCO_3$ decreases with pressure along the 500 and 600 °C isotherms and is, within error, approximately constant at 300 and 400 °C. The latter implies that there is a sharp drop in the isobaric solubility of quartz in the aqueous $NaHCO_3$ solution at lower pressures, as the temperature falls from 500 to 400 °C.

References:

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