

SHOCK13-2013-000506

Abstract for an Invited Paper
for the SHOCK13 Meeting of
the American Physical Society

Solubility and speciation of carbonate in aqueous fluids at HP-HT¹

ISABELLE DANIEL², Universite Lyon1 - Laboratoire de Geologie de Lyon

We report an integrated experimental and theoretical study of the equilibration of CaCO_3 minerals with aqueous solutions (pure H_2O or NaCl solutions) at HP-HT (0.5 to 8 GPa, 250 to 500° C). The fluid speciation was studied using in situ Raman spectroscopy in an externally heated membrane-type diamond anvil cell. The aqueous fluid and a calcite crystal were loaded in a rhenium gasket. P was determined from the calibrated shift of the carbonate ν_1 symmetric stretching mode of aragonite and the T measured with a K-type thermocouple. Spectra were recorded using a LabRam HR800 Raman spectrometer (Horiba Jobin-Yvon) coupled to a Spectra Physics Ar^+ laser. At equilibrium with an aragonite crystal, the Raman data show that bicarbonate is the most abundant species in low-pressure fluids below 4 GPa whereas carbonate becomes progressively dominant at higher pressure. After correction from their Raman cross-sections, the relative amounts of dissolved carbonate and bicarbonate were estimated from the areas of the ν_1 and ν_5 symmetric stretching Raman modes of the carbonate and bicarbonate ions, respectively. The presence of sodium chloride extends the pressure range of predominance for bicarbonate species in the fluid. The Raman data were also used to constrain a theoretical thermodynamic model of the fluid speciation in equilibrium with CaCO_3 . Revised thermodynamic properties of aqueous CO_2 and HCO_3^- , data for the aqueous CaHCO_3^+ complex from 4 to 90° C, and estimated dielectric constants of water, enabled an equation of state characterization of the standard Gibbs free energy of CaHCO_3^+ at the conditions of the Raman study. At 300-400° C, the Raman speciation results were used to constrain equilibrium constants involving the carbonate ion. The results indicate that CO_2 is a minor species in fluids in equilibrium with aragonite at 300-500° C and $P > 1$ GPa. Instead, the CaHCO_3^+ species becomes important at high pressures until carbonate ion becomes the dominant C-species.

¹The authors gratefully acknowledge the support of the Deep Carbon Observatory

²co-authors: Sebastien Facq (Universite Lyon1 - Laboratoire de Geologie de Lyon); Dimitri Sverjensky (The John Hopkins University, Carnegie Institution of Washington)