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Experimental determination of calcite solubility in H_2O-NaCl solutions at deep crust/upper mantle pressures and temperatures: Implications for metasomatic processes in shear zones

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ABSTRACT

The solubility of calcite in NaCl-H_2O solutions was measured at 600–900 °C, 10 kbar, at NaCl concentrations ranging from dilute to near halite saturation, and at 6–14 kbar, 700 °C, in 30 mol% NaCl solutions. Solubility was determined from the weight loss of cleavage rhombs of a pure natural calcite after experiments of 1/2 to 6 days in a piston-cylinder apparatus with NaCl-graphite furnaces. $CaCO_3$ molality (m_{CaCO_3}) increases greatly with NaCl mole fraction (X_{NaCl}): at 800 °C and 10 kbar, m_{CaCO_3} increases from ~0.1 in pure H_2O to near 4.0 at halite saturation ($X_{NaCl} \sim 0.6$). There is also a large temperature effect at 10 kbar, with m_{CaCO_3} increasing from 0.25 at 600 °C to 3.0 at 900 °C at $X_{NaCl} = 0.3$. There is only a 20% increase with increasing pressure between 6 and 14 kbar at 700 °C and $X_{NaCl} = 0.3$. Melting to a carbonate-rich liquid was inferred at 900 °C, 10 kbar, from X_{NaCl} of 0 to 0.2. The composition, temperature, and pressure dependence of m_{CaCO_3} are described by:

$$m_{\mathbf{CaCO_3}} = [-0.051 + 1.65 \times 10^{-4}\ T + X^2_{NaCl}\exp(-3.071 + 4.749 \times 10^{-6}T^2)]\ (0.76 + 0.024P)$$

with T in Kelvins and P in kbar. The predicted increase of calcite solubility with salinity and temperature is so great that critical mixing of NaCl-rich hydrous carbonate liquid and $CaCO_3$-rich saline solution is probable at 10 kbar near 1000 °C and $X_{NaCl} \sim 0.4$.

The experimental results suggest a genetic mechanism for the enigmatic carbonated shear zones, such as the Attur Valley of southern India, where crustal rocks have been replaced by up to 20% by calcite and ankerite with mantle-like stable-isotope signatures. The high $CaCO_3$ carrying capacity of concentrated alkali-chloride solutions, together with the drastic decrease in solubility between 1000 and 700 °C, plausibly account for large-scale emplacement of mantle-derived carbonate from concentrated chloride-carbonate solutions (or hydrosaline magmas) formed as immiscible fluids in the late stages of alkalic magmatism. Such solutions may also mobilize sulfate and phosphate minerals, which would have important consequences for redistribution of incompatible and heat-producing elements in the crust.