

# The Solubility of Quartz and Calcite in H<sub>2</sub>O-NaCl Solutions at High Pressure: Constraints on Mass Transfer in the Deep Crust

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Recognition of the presence of saline brines during upper amphibolite and granulite facies metamorphism raises the possibility that such fluids may cause significant mass transfer in the middle and lower crust. We investigated this by measuring quartz and calcite solubility in H<sub>2</sub>O-NaCl fluids at high pressures and temperatures. Solubilities were determined by weight-loss using externally heated cold-seal and piston-cylinder devices.

The solubility of quartz in H<sub>2</sub>O-NaCl solutions was measured at 2, 4.35, 10 and 15 kbar, 500-900 °C, and NaCl concentrations up to halite saturation. Below 4 kbar, silica concentration in equilibrium with quartz increases (salts in) with increasing X(NaCl). At 2 kbar and 700 °C, this behavior persists to ~70 wt% NaCl before quartz solubility again becomes as low as in pure H<sub>2</sub>O. The maximum solubility occurs at X(H<sub>2</sub>O)~0.9 and is 50% higher than in pure H<sub>2</sub>O. By contrast, quartz solubility decreases slightly from 0 to 45 wt% NaCl at 4.35 kbar and 700°C, but then begins to drop rapidly at higher salinity. At 10 and 15 kbar silica molality decreases steeply at low NaCl concentration, but then levels off at higher salinity at all temperatures from 500 to 900 °C. There is thus a pronounced change in solution behavior with pressure, from initial salting-in below 4 kbar to monotonic salting-out above 5 kbar. Because this pressure-induced change in silica solubility parallels the sharp decrease in H<sub>2</sub>O activity in NaCl solutions in the same pressure range (Aranovich and Newton, 1996), we infer that the change in silica solubility behavior is caused by the dissociation of NaCl<sup>0</sup> to Na<sup>+</sup> and Cl<sup>-</sup> with increasing solution density.

Calcite solubility in H<sub>2</sub>O-NaCl solutions was determined at 600-800°C, 10 kbar. At 10 kbar, the behavior of calcite is opposite to that of quartz (fig. 1), in that solubility increases exponentially with increasing salinity. For example, as X(NaCl) increases from 0 to 0.54 at 800°C, calcite solubility increases from 0.10 to 3.35 ± 0.20 molal. Similar behavior is suggested by our more limited data set at 600 and 700°C.

The experimental results provide a crude guide to the solubility behavior of different classes of rock-forming minerals. Quartz solubility at 10 kbar shows exponential decline with increasing salinity at all temperatures in the range 500 to 900°C. This is the expected behavior of a two-component solvent, in which the solute is sparingly soluble in one component. Similar behavior should be expected for minerals with oxide components that have low solubility in chloride-rich solutions (e.g. Mg silicates). By contrast, calcite solubility increases linearly with the square of X(NaCl), consistent with the strong interaction between calcite and the NaCl component of the solvent via the

reaction  $\text{calcite} + 2\text{NaCl} = \text{CaCl}_2(\text{aq}) + 2\text{NaCO}_3(\text{aq})$ . Such behavior should be typical of soluble salt and oxysalt minerals, such as apatite and anhydrite.

The solubility of quartz in CO<sub>2</sub>-H<sub>2</sub>O fluids at 800°C and 10 kbar is much smaller than in NaCl solutions at the same P,T and H<sub>2</sub>O activity (Newton and Manning, 2000). When combined with our observation of strong calcite solubility at high X(NaCl), it is evident that soluble constituents will strongly partition into concentrated salt solutions in deep crust-upper mantle metamorphic and metasomatic processes, in preference to a coexisting immiscible CO<sub>2</sub>-rich fluid. The much greater permeability of silicate rocks for salt solutions than for CO<sub>2</sub>-rich solutions, together with the much higher solubility of quartz and calcite in the former, suggests that the saline component of deep fluids is the dominant agent for the redistribution of elements during high-grade metamorphism in the lower crust.

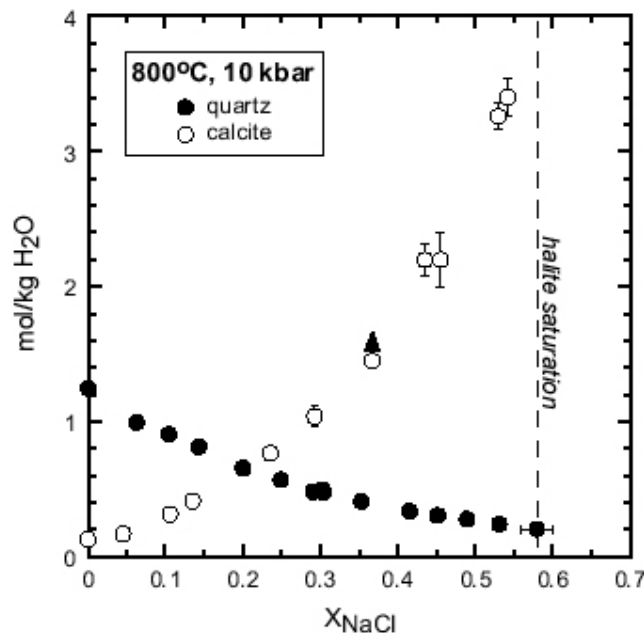


Figure 1. Solubility of quartz and calcite in H<sub>2</sub>O-NaCl solutions at 800 C and 10 kbar. Quartz solubility decreases with increasing salinity, whereas calcite increases.

Aranovich LY & Newton RC, *Contrib.Mineral.Petrol.*, **125**, 200-212, (1996).  
Newton RC & Manning CE, *Geochim.Cosmochim.Acta*, **in press**, (2000).