Influence of the liquid-liquid transition in water on the solvent-solute properties in carbonate solutions at high pressure

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Pure water and aqueous fluids undergo a structural transformation during compression from a low-density form (LDW) to a high-density form (HDW). Given the ubiquity of hydrous fluids in Earth and planetary interiors and their unique role in geochemical and biological processes, the mutual influence of such a structural phase transition on both the solutes and the water solvent shall be addressed.

Here we investigate the high-pressure behavior of pure water and carbonate-bearing fluids by *in situ* Raman spectroscopy at 25°C, from ambient pressure to 2 GPa at the highest concentrations through the LDW-HDW transition with unprecedented spectral and pressure resolution.

Our results show that the compression of liquid water induces a progressive transfer of water molecules from the intermediate water population, i.e. molecules engaged in two hydrogen bonds, mostly to the network of tetrahedrally coordinated water molecules. This gradual evolution is broken by a steady distribution in a virtually incompressible liquid that preceeds the LDW-HDW transition. Adding solutes such as Na_2CO_3 stabilizes the structure of the low-density form of water enlarging its stability domain and deferring the occurrence of the LDW-HDW transition towards higher pressures. The LDW-HDW transition in water decreases the compressibility of the carbonate solute by a factor of 2 in the high-pressure regime. Increasing the Na_2CO_3 concentration up to 2 $mol.kg^{-1}$ leads to a structural ordering of water molecules towards a stable and fully bonded water network constituted of relaxed H bonds, likely due to the strong kosmotropic character of carbonate ions and water then behaves as a normal liquid.