

PVT properties of D₂O from acoustic measurements in the diamond-anvil cell by Brillouin scattering

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The thermodynamic properties of heavy water (D₂O) have important applications in various technologies and are of interest to a range of scientific communities, from chemistry to engineering and earth sciences. For instance, D₂O is used in nuclear reactor engineering for its excellent nuclear and thermal properties. In geochemistry, a quantitative understanding of the isotopic properties of water are required to interpret H/D isotopic exchange between minerals and fluids at high temperatures and pressures [1,2].

Because of its primary importance, a number of equations of state (EoS) of D₂O have been developed to predict its thermodynamical properties up to 0.1 GPa and 525°C [3,4]. While this P-T range largely covers the conditions encountered in most technological processes, the lack of PVT properties of D₂O at higher P-T seriously limits the quantitative interpretation of isotopic behavior in deep geological settings (e.g., subduction zones).

In this contribution we present an extension of the experimental EoS of D₂O up to 5 GPa at 300°C, determined from acoustic velocity measurements in externally heated diamond-anvil cells using Brillouin scattering spectroscopy. Acoustic velocities measured at low pressure (< 0.1 GPa) at various temperatures are in excellent agreement with literature data, showing the reliability of the method. The newly determined PVT data is combined with previous high temperature data to generate an extended EoS that predict the thermodynamic properties of D₂O up to 525°C and 5 GPa.

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The influence of ethanol adsorption on the {10 $\bar{1}$ 4} calcite surface

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Previous studies have demonstrated that water is ordered by the calcite surface and that OH is bonded to Ca [1]. Theoretical work on polysaccharides shows sorption through OH [2]. To increase understanding about the fundamental controls on biomineralisation, we investigated the interaction between calcite and the OH of ethanol, and bonding strength relative to that of water. Ethanol is known to stabilize vaterite [3] and may stabilize calcite [4] but the mechanism is not known. Molecular simulations show that ethanol orders itself on the {10 $\bar{1}$ 4} calcite surface with the OH group near Ca and the CH₃ group oriented away from the surface. The next layer is semi-ordered so the OH end faces solution. Ethanol attachment to calcite is stronger than that of water, meaning that once ethanol is adsorbed, energy is needed for water to detach it.

We used atomic force microscopy (AFM) to watch calcite surface behaviour during exposure to air after cleavage under ethanol or water. Behaviour was considerably different. Ostward ripening was much slower and the pattern and placement of the recrystallised areas were controlled by terrace edges on the ethanol-exposed sample. Modelling combined with imaging under a variety of conditions suggests that growth is controlled by differences between water and ethanol bonding at step edges.

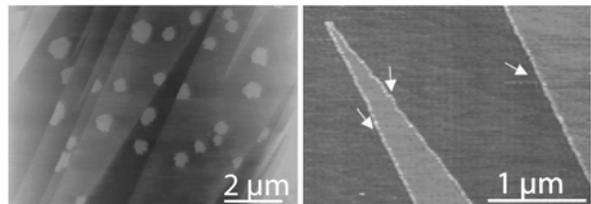


Figure 1: (left) Calcite after 4 h in air, (right) Calcite after 4 h in ethanol. Note recrystallizing along step edges (arrow).

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