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Forces and ionic transport between clays: Implications for 'pressure solution'

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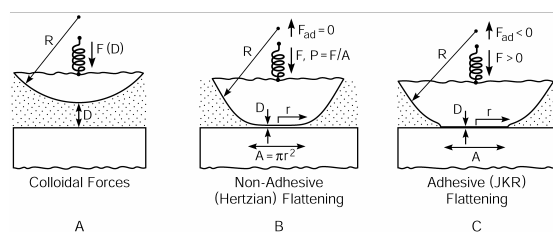
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Using a Surface Forces Apparatus (SFA), we have studied the interactions between mica surfaces in pure and mixed NaCl and CaCl₂ solutions at relevant geological conditions of pressure and electrolyte composition. Our results show that the short-range (0-50 Å) colloidal forces, including attractive van der Waals and ion-correlation forces, repulsive electrostatic forces, and oscillatory or monotonically repulsive hydration (surface-induced water structure-dependent) forces are involved in different stages of pressure solution. These forces depend on the type (Na⁺, Ca²⁺ and H⁺) and concentration (6-600 mM) of the cations present in the solution. Equilibrium water film thicknesses were measured as a function of the applied (normal) pressure up to 50 MPa (500 atm) and ranged from 30 to 0 Å at pressures above 10 MPa (100 atm). Measurements were also made of the rates of diffusion and exchange of ions into and out of such ultra-thin films, and on the nucleation and growth of ionic crystallites on and between the surfaces, which occurred only in the presence of calcium ions. Diffusion of ions into and out of structured water films as thin as one to five water molecules (3 to 15 Å) were found to be surprisingly rapid and never less than two orders of magnitude below the diffusion in bulk water. In contrast, the rates of binding and exchange of ions to the surfaces were found to be the rate-limiting steps to adsorption and crystal formation.

Implications for pressure solution mechanisms

Our findings imply that, for certain systems or conditions, pressure solution rates could be limited by surface reactions rather than by ion diffusion in thin fluid films.



Schematic of SFA, showing parameters that can be directly measured and surface profiles that can be visualized when used with the FECO optical technique. (B) For 'non-adhering' surfaces, adhesion force is zero. (C) For 'adhering' surfaces, F_{ad} is finite.

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Molecular Dynamics simulations of crystallisation under confinement conditions

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Molecular Dynamics computer simulations of crystallisation of a Lennard-Jones system under confinement conditions in the vicinity of the triple point are reported. We calculate the force exerted on a crystal by a melt when it crystallises. The force due to crystallisation is reflected in the disjoining pressure isotherms as a characteristic peak. We find that at conditions of high confinement, i.e., pore thicknesses of ~ 1 nm, the disjoining pressure can rise up to $\sim 10^8$ Pascals. We also analyse the dependence of the crystallisation under confinement as a function of temperature and pore shape. Confinement can stabilise the crystal phase at temperatures significantly higher than the melting temperature. For the systems studied in this work, a pore of 1 nm thickness stabilises the crystal phase at temperatures up to 45 % higher than the normal melting temperature. Otherwise it is shown that the interplay between the pore shape and the pore epitaxy induces crystal formation in specific patterns.

Reference

[1] L.G. Camara and F. Bresme (2003) *J. Chem. Phys.*, **119**, 2792.