Interfacial processes at dissimilarly charged mineral surfaces in contact – a surface forces apparatus (SFA) study

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When two mineral surfaces are in close contact, nanometers to microns apart, the proximity of another surface can significantly influence the pathways of chemical reactions happening in the interfacial region. Apart from affecting the kinetics of dissolution and nucleation reactions in spatial confinement, the proximity of charged surfaces can lead to electrochemically induced recrystallization processes. The latter may happen in an asymmetric system, in which two surfaces have a dissimilar surface charge.

The charge and mass transferred during electrochemical reactions can induce dissolution or growth of solids and can significantly affect the local topography of surfaces, causing them to smooth out or to roughen. Electrochemical reactions can play a major role in pressure solution – one of the most common deformation processes in rocks.

EXPERIMENTAL METHOD

In this work, we used electrochemical surface forces apparatus (EC-SFA), in order to study the interactions between dissimilarly charged surfaces. EC-SFA setup consists of one mineral surface and one gold surface (working electrode), the surface charge of which is controlled by applying an electrical potential. EC-SFA can, therefore, monitor electrochemically induced surface recrystallization processes. As the SFA technique is based on white light interferometry measurements, the changes in mineral thickness during recrystallization can be determined with an accuracy better than a nanometer over micrometer-large contact regions.

RESULTS

Electrochemically-induced growth of CaCO3 in confinement

 Electrochemically-induced growth and dissolution of minerals

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Electrochemically-induced precipitation of CaCO3 in confinement reveals nucleation of submicron-size precipitate within the contact area and regular, large crystals outside the confinement zone. This process is related to kinetic trapping of thermodynamically unstable CaCO3 phases. Such precipitate significantly influences the interactions between two mineral surfaces. Although it is composed of submicron-sized particles, the precipitate can also give rise to substantial repulsive force of crystallization.

Nucleation in confinement generates long-range repulsive forces between surfaces

Nucleation of CaCO3 in confinement gives rise to long-range repulsion between two solid surfaces. Nucleation was significantly postponed in the presence of Mg²⁺.

This repulsive force cannot be explained by changes in surface roughness, or by electrostatic (EDL) or hydration repulsion, but it is correlated with the precipitation events which started at µm-thick separations. The submicron-sized precipitate that formed in the confined solution was liquid-like and viscous and did not undergo any spontaneous ripening into larger crystals, which was prevented by spatial confinement.

Such non-classical crystalization pathway in confinement can have crucial impact on deformation processes in porous and fractured rocks.

Read more here: Dziadkowiec et al., 2019, Scientific Reports 9, 8948