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Potential sequestration of toxic elements: the specific example of cadmium and carbonates

Maude Julia¹, Christine V. Putnis^{1,2}, François Renard^{3,4}, and Oliver Plümper⁵

¹Institute für Mineralogie, Universität Münster, Münster, Germany (mjulia@uni-muenster.de)

²School of Molecular and Life Sciences, Curtin University, Perth, Australia

³The Njord Centre, Departments of Geosciences and Physics, University of Oslo, Blindern, Oslo, Norway

⁴ISTerre, Université Grenoble Alpes, Université Savoie Mont Blanc, CNRS, IRD, Université Gustave Eiffel, Grenoble, France

⁵Department of Earth Sciences, Utrecht University, Utrecht, The Netherlands

Coupled dissolution-precipitation reactions have been studied extensively recently for their ability to retain elements of interest into a stable solid form that can sequester potentially toxic elements. This is achieved through the initial dissolution of a substrate mineral in a fluid containing the target (often toxic) element. The dissolution leads to the supersaturation of a boundary layer at the mineral surface with respect to another solid phase containing the element of interest¹. When the relative solubilities of the different minerals (in the aqueous fluid at the reaction interface) and their molar volume difference allow it, a coupled dissolution-precipitation can lead to the pseudomorphic replacement of the original substrate². We tested this reaction for CaCO₃ and cadmium (Cd) containing solutions as calcite (CaCO₃) and otavite (CdCO₃) form an almost perfect solid solution. We compared the reaction in similar solutions with different types of CaCO₃: calcite single crystal, Carrara marble (polycrystalline calcite) and aragonite single crystals. For single calcite crystals, the reaction in a Cd-solution passivates the crystal's surface due to the epitaxial growth of a (Ca,Cd)CO₃ solid solution layer of low solubility. However, the random orientation of the grains in the Carrara marble samples and the change of crystal structure for the aragonite crystals modified the mechanism and allow the replacement of CaCO₃ by (Ca,Cd)CO₃ to take place³. Hydrothermal experiments and in situ fluid-cell atomic force microscopy (AFM) were used to observe the reaction both at room temperature and high pressure and temperature (200°C). In addition to SEM, BSE and EDX observations, synchrotron X-ray microtomography images were acquired on Carrara marble and aragonite samples at different stages of the reaction in order to gather more information about the replacement mechanism and the extent of Cd-uptake achievable through this process. The extent of the reaction was shown to be similar for the different solution concentrations used and limited in the case of Carrara marble. The porosity closes fast after the start of the reaction blocking the fluid pathways necessary for the reaction to proceed. The reaction in the aragonite samples seems to progress mainly through a reaction-induced fracture network probably created by the stress caused by the crystallographic structural differences between parent and product phases. Overall, these results demonstrate the capacity of CaCO₃ to trap and store cadmium into a solid phase by a mechanism of coupled dissolution-precipitation.

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