

## Using ToF-SIMS isotope mapping to constrain dissolution/reprecipitation and redox reactions in experimental CO<sub>2</sub>-sequestration studies

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The sequestration of CO<sub>2</sub> gas streams of different origins into e.g. deep saline aquifers opened a major area for geochemical research on gas-fluid-rock interaction at elevated, *in situ* pressures and temperatures. Besides the inherent problems of experimental approaches to constrain the kinetic parameters of the slow dissolution processes of silicates in highly saline brines, the often coincident dissolution and precipitation reactions hamper the determination of precise dissolution or precipitation rates in more complex experimental approaches, e.g. flow-through experiments.

To facilitate the precise determination of the amount of dissolved ions incorporated into newly formed precipitates within the reaction chambers, a spatial analysis of incorporation of isotopically-labelled elements/ions (e.g. <sup>18</sup>O) into mineral precipitates is being developed by using high resolution ToF-SIMS techniques. With this technique it is possible to simultaneously image the elemental, isotopic, and molecular composition in rocks with high spatial resolution. Also, the elemental and isotopic distribution as a function of depth can be monitored.

To set up a database of a variety of rock-forming minerals, ToF-SIMS spectra were recorded in different measurement modes - either on individual crystal grains of less than 500 μm diameter or in thin sections from rocks envisaged as potential storage formations in Germany.

Furthermore, a calibration of the isotopic scale has been performed by measuring artificially prepared minerals with different percentages of isotope labels incorporated. Thereby, the distinction of the incorporation of ions from dissolution (e.g. 99% <sup>16</sup>O) in contrast to those from the synthetic brine (e.g. 99% <sup>18</sup>O) is possible. In addition, using e.g. <sup>18</sup>O labels as atomic oxygen ions, the isotopic composition in larger molecules such as CO<sub>3</sub> could be used to unambiguously identify the mineral, into the labeled oxygen has been incorporated (e.g. clay minerals or carbonates).

## Extracellular electron transport coupling biogeochemical processes centimeters apart

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Recent observations in marine sediment have revealed conductive networks transmitting electrons from oxidation processes in the anoxic zone to oxygen reduction in the oxic zone [1]. The electrochemical processes and conductors seem to be biologically controlled and may account for more than half of the oxygen uptake in laboratory incubations of initially homogenized and stabilized sediment.

Using microsensors and process rate measurements we further investigated the effect of the electric currents on sediment biogeochemistry. Dissolved sulfide readily donated electrons to the networks and could be depleted below detection limit in a several cm thick layer below the oxic zone. Subsequent dissolution of iron sulfide was indicated by mobilization of ferrous iron being precipitated again as ferric iron at the oxic-anoxic interface. Lowered sulfate reduction rates in the upper centimeters of the sediment confirmed the depth range of the electric communication and indicated donation of electrons directly from organotrophic bacteria. The separation of oxidation and reduction processes created steep pH gradients eventually causing carbonate precipitation at the surface.

The results indicate that electron exchanging organisms have major biogeochemical importance as they allow widely separated electron donors and acceptors to react with one another.

[1] Nielsen *et al* (2010) *Nature* **463**, DOI 10.1038/nature08790