## Cell permeability/senescence controls the reduction rate of iodate to iodide in marine phytoplankton

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The role of marine organisms in the redox cycling of iodine in the ocean is not well understood presently. Previous studies have suggested that phytoplankton play an important role in the biogeochemical cycling of iodine, and were responsible for the appearance of the non thermodynamically favoured species iodide in the euphotic zone. A key question that arises however is how this reduction occurs; Is it driven by primary production, via direct biologically mediated uptake, or alternatively is it driven chemically by redox reactions related to the passive release of reduced substances from the decay of biological materials?

To directly address this question we have recently performed laboratory experiments and field measurements (Tropical Atlantic and Pacific, Southern Ocean) for this purpose. In culture experiments, including a variety of phytoplankton taxa (diatoms, dinoflagellates and prymnesiophytes), we observed changes in the speciation of iodine over the course of an experiment indicating the apparent ability to reduce iodate to iodide. Production rates were found to be species specific and not related to biomass. In all but one species tested the iodide production commenced in the stationary growth phase and peaked in the senescent phase of the algae. This indicates that iodide production is connected to cell senescence and suggests that iodate reduction results from increased cell permeability. We hypothesize that this is due to subsequent reactions of iodate with reduced sulphur species exuded from the cell. Combined with our field observations we suggest that cell senescence and other related processes that cause cell breakage (e.g. grazing, viral lysis) are responsible for the production of iodide.

Our data additionally suggest that the iodine redox cycle is completed via biological processes also. We observed that an experimentally induced shift from senescence back to the exponential growth phase resulted in a decline in the iodide concentrations, suggesting reoxidation back to iodate. Our new data help to provide a more complete picture of iodine cycling in the ocean.

## Fault zone stability in cap rocks affected by CO<sub>2</sub>

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A safe geological storage of  $CO_2$  requires a better understanding of alteration processes in cap rock formations as a function of temperature, pressure, fluid and cap rock mineralogical composition. Alterations in the cap rock can influence the tightness and the stability of a storage site. With regard to fault zones it may lead to increases or decreases of permeability due to solution with widening of flow paths or precipitation with self-healing effects. Increased permeability and consequently leakage might also change the stress field and the rock mechanical properties.

To investigate these relationships, an experimental setup was designed within the BMBF-funded GEOTECHNO-LOGIEN joint project  $CO_2SEALS$ , to study experiment-related shear planes in natural rock samples, the changes in the mineralogical and rock mechanical properties and their interactions.

Annular shear planes were produced within samples of several pelictic reference rocks by a punching process. The punched samples were installed in newly developed reaction vessels, in which they were continuously percolated with a  $CO_2$ -saturated NaCl-brine at a constant pressure (5 bar) and different constant temperatures (45 to 100°C). By varing temperature and reaction time (up to 24 months) it was expected to extract reaction rates from the experiments and also study the extent of alteration.

Results of the experiments with duration up to 6 months show that interactions between  $CO_2$ -saturated brine and cap rock are most visible at temperatures >75°C. Changes in the chemical composition of the effluent and in the solid phase show, that beside carbonate dissolution and precipitation, which is the dominant short term process, silicate alteration must have occured also. Thin-layer shear tests at high pressures up to 40 MPa normal stress on powder samples (before and after reaction with  $CO_2$ ) will be carried out to characterise the change of the geomechanical properties due to alterations.

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