## The biogeochemistry of phytosiderophores in the rhizosphere in relation to Fe uptake

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Phytosiderophores (PS) are naturally occuring chelators, which are exuded by graminaceous plant species for the sake of iron acquisition (Strategy II) [1]. PS are highly efficient in mobilizing Fe from soil [2], and upregulation of PS exudation is the key iron deficiency stress response mechanism for graminaceous plants [1].

Despite the extensive research on the mechanism of action of PS, the understanding of the biogeochemistry of PS in the rhizosphere is still limited. The vast majority of studies have been carried out under conditions quite remote from those present in the rhizosphere (e.g. with hydroponic systems).

A lack of adequate analysis and sampling techniques, the complicated acquisition of PS from root exudates and the biodegradation of PS by rhizosphere microorganism are among the principal problems, prohibiting a more detailed study of PS in relation to soil-grown plants.

Our research project addresses several of these issues, amongst others through synthesis of PS ligands, development of new analytical methods suitable for measuring PS and metal-PS complexes in soil solution, and application of novel rhizosphere sampling techniques with rootboxes and microsuction cups.

The overall aim of the projects is an integral quantification of the source and sink terms determining PS concentrations in the rhizosphere. Both reaction kinetics and thermodynamic equilibrium aspects will be considered. Processes that will be examined include adsorption, desorption, mobilization of iron and other metals from the soil, biodegradation, PS exudation and PS-facilitated iron uptake.

[1] Marschner *et al.* (1986) *J. Plant Nutr.* 9, 695–713.
[2] Krämer *et al.* (2006) *Adv. Agron.* 91, 1–46.

## Hydrothermally induced changes of electrical rock conductivity and permeability in porous feldspar-rich materials

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Due to the extraction of heat during geothermal energy production from deep sedimentary reservoirs, dissolution and/or precipitation reactions may be induced which potentially alter the pore space properties of the reservoir rocks. In this study hydrothermal batch and flow-through experiments were conducted with feldspar-rich porous materials at temperatures up to ~160°C, under hydrostatic pressure conditions, and durations up to 4 months to investigate the influence of such reactions on electrical rock conductivity ( $\sigma_r$ ) and permeability (k).

Sample materials were feldspar-rich Rotliegend sandstone samples and granular analogue materials composed of quartz, K-feldspar, and plagioclase grains. The temperature range applied in the experiments pertains to a low enthalpy geothermal energy production scenario. The starting fluids ranged from deionised H<sub>2</sub>O to 2 mol/L NaCl<sub>aq</sub> solutions.  $\sigma_r$  was continuously monitored while k was measured at irregular intervals throughout the flow-through experiments. In the batch experiments electrical fluid conductivity ( $\sigma_r$ ) was measured at irregular intervals.

Chemical fluid analyses were performed on the resulting fluids with respect to the major ions of the system H<sup>+</sup>, Na<sup>+</sup>, Al<sup>3+</sup>, Si<sup>4+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, OH<sup>-</sup>, Cl<sup>-</sup>, and SO<sub>4</sub><sup>2-</sup>. Aliquots of the solid materials were characterised prior and after the experiments with XRD, BET, Hg-porosimetry, SEM, and EMPA. Sub  $\mu$ m sized structures on altered grains were also investigated with TEM. One sandstone sample was analysed with X-ray CT with a resolution of ~2  $\mu$ m prior and after a flow-through experiment to image the pore space *in situ*.

Dissolution features were common on the altered solid materials while precipitates were rarely observed. Precipitates were sub  $\mu$ m sized amorphous particles occurring mainly on plagioclase surfaces. The transient increases of concentrations of dissolved ionic species, of  $\sigma_r$ , and  $\sigma_r$  indicate a kinetically controlled dissolution process. Concurrently k decreases in the course of the flow-through experiments. The k decrease is mainly due to thermo-mechanical effects but may also result from the observed dissolution and precipitation reactions which lead to an alteration of the geometrical properties of the pore space.

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