

Adsorption of desferrioxamine-B and oxalate on Al-goethite: implications for microbial dissolution processes

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Our study examines the effect of i) Al substitution in goethite on its steady-state dissolution by DFO and oxalate at pH 5, ii) adsorption of oxalate and DFO on the electrophoretic mobility (EM) of Al-goethite. Low concentrations of oxalate (36 μM) brought about decreases in DFO-B adsorption, whereas DFO-B even at 100 μM did not affect oxalate adsorption. Adsorption of oxalate lowered EM and, therefore, the positive surface charge of goethite with mol% Al < 4 (e.g., 4.1 ± 0.4 to $2.7 \pm 0.5 \times 10^{-8} \text{ m}^2 \text{ v}^{-1} \text{ s}^{-1}$ for mol% Al = 4), but did not affect the surface charge of samples with mol% Al > 4. The greatly enhanced dissolution of goethite by DFO and oxalate together can be explained by the ability of oxalate to adsorb strongly at the goethite surface, and by the high selectivity of DFO-B for Fe(III) in solution, thus promoting Fe release. Ferric oxalate complexes formed during dissolution will lose Fe by ligand substitution with DFO-B, leading to the production of Fe(HDFO-B)⁺ and uncomplexed oxalate, the latter of which, in turn, can adsorb to the goethite surface again. For Al-goethites with mol% Al > 4, this however, synergism was not apparent, possibly because of a decreased surface density of Fe-OH sites.

Variations in EM of goethite following the addition of MES (pKa= 6.19), a zwitterionic buffer, strongly suggest MES surface complexation *via* i) sulphonate induced-dipole or ii) N and O lone-pair dipole-dipole interactions with structural Fe (Figure 1). Multiple coordination sites available in MES for structural Fe complexation, including ring chelation, and the higher electrophilicity of structural Fe(III) relative to Fe³⁺_(aq) may facilitate MES complexation to the goethite surface.

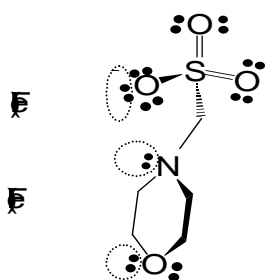


Figure 1: Possible modes of MES surface complexation.

U-Sr isotopic tracing of water-rocks interactions in aquifer: Example of the pollution of the Rhine water table by salty waters

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Rhine aquifer waters are polluted by infiltration of salty waters coming from the leaching or dissolving of the mine dumps of Alsacian potash mines. Propagation of this chloride pollution follows the flow lines of the aquifer and results in the formation of salty water encroachment into the groundwaters. Major and trace elements, Sr isotopic ratios and U series disequilibrium have been analysed in water collected at different depths along two pollution sheets.

The results highlight that waters during their transfer within the alluvial aquifer are chemically and isotopically modified by interactions with the surrounding rocks. An exchange takes place between Na of water and Ca of the rocks. The waters lose their initial Sr isotopic ratio (Pit waters of Figure) and acquire a Sr signature close to that of the surrounding rocks (deep waters end-member of Figure). U series disequilibria are also modified during the water transfer. These modifications do not result from the water ageing, and are not correlated with the ⁸⁷Sr/⁸⁶Sr variations. U series disequilibria would depend on the nature of the water-rock interactions (dissolution/leaching) within the aquifer.

These data point out the importance and the rapidity of the water-rocks interactions in ground waters, and could suggest that a large part of the chemical and isotopic characteristics of waters acquired into the vadoze zone are erased by water-rocks interactions in aquifers and groundwaters.

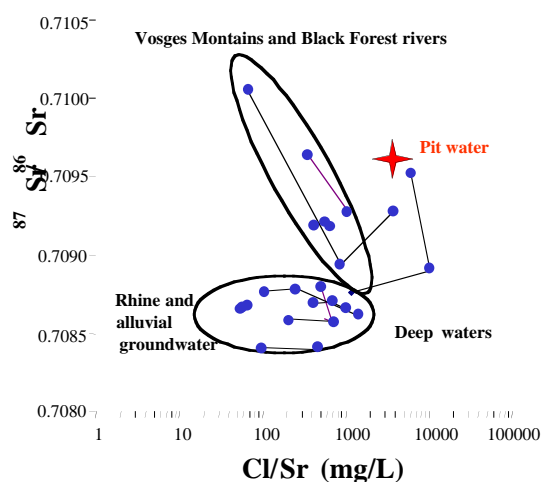


Figure: ⁸⁷Sr/⁸⁶Sr and Cl/Sr variations in salt pollution encroachment samples.