

Iron catalysed thermal and photochemical oxidation of arsenic(III)

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Arsenic redox reactions and mobility

The mobility of arsenic, one the most prevalent natural pollutants in groundwater systems, is largely determined by its redox state. As(III) is generally more mobile in the aqueous environment than As(V). Due to the slow redox kinetics, arsenic is often not in redox equilibrium with the environment. Despite of their importance, the rather complex redox kinetics are poorly understood. We have investigated the role of dissolved iron and of Fe(III)(hydr)oxides in the oxidation of As(III) in the dark and in sunlit waters with kinetic and spectroscopic methods.

Results and Discussion

When reduced groundwater containing Fe(II) and As(III) comes into contact with air or aerated water, dissolved O₂ leads to partial oxidation of As(III) in parallel to the oxidation of Fe(II). The As(III) is apparently oxidised by reactive oxygen species (•O₂⁻, H₂O₂, •OH) and/or by higher-valent iron species, which are formed as intermediates during the oxidation of Fe(II). The forming Fe(III)(hydr)oxide colloids influence the reaction by adsorbing As(V) and As(III) and by catalysing the decomposition of H₂O₂. In water exposed to sunlight, UV-A radiation leads to photochemical oxidation of As(III) by photolysis of Fe(III) complexes, which produces Fe(II) and reactive oxygen species. Naturally occurring or added organic ligands, such as citrate, form Fe(III)-complexes which are photolysed efficiently, with quantum yields of 0.1-1.0. With light, As(III) can be readily oxidized even in the presence of only catalytic amounts of iron, with iron cycled between Fe(II) and Fe(III) by photoreduction and by oxidation with O₂.

Conclusions

Redox reactions of arsenic are closely tied to the redox reactions of iron. The importance of the different reaction pathways can be estimated with kinetic models based on detailed reaction schemes.

References

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Lithium isotopes as a probe of weathering processes: Hawaiian soil climosequence

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Over geologic time scales, continental weathering of silicates is a major sink of atmospheric CO₂ and thus is an important factor to consider in determining past variations in atmospheric CO₂ and therefore climate. Because of the large relative mass difference between the two stable isotopes, the magnitude of Li isotope fractionation as manifested in rivers may be linked to silicate weathering *processes*, whereas Sr and Os isotope ratios mainly reflect the *sources* (Huh et al., 2001). To understand the behaviour of this relatively new isotopic system during weathering, a soil climosequence in Hawaii is under study.

A soil transect across the Kohala Peninsula provides several powerful constraints that make it a simplified system for studies of Li isotope fractionation during soil evolution—good control on the precipitation gradient, constant substrate, and an extensive data set of geochemical and mineralogical properties from previous work (Chadwick and Chorover, 2001).

The depth profile of Li in soils show enrichment in the upper horizons (~30 ppm), whereas Li concentrations in weathered rock behaves relatively conservatively (~10 ppm). For all depths the concentrations are higher than the estimated basalt bedrock value (~5 ppm). Similar upward enrichment is seen for K, Na, Ca and Si.

Li isotope ratios show a large variation for soils (-10 to -3‰) and less for weathered rocks. The two lowermost horizons have δ⁶Li that are comparable with lava values (~5‰). According to the current state of knowledge, light Li is preferentially taken up in alteration minerals and heavy Li is lost to solution. However, upper soil horizons are heavier than estimated bedrock values and indicate input of heavy Li, possibly atmospheric.

References

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