Interaction of selenite with iron sulphide minerals: a new perspective

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The geochemistry of selenium, exhibiting valence states from +VI to –II, is of key importance due to its role as a highly toxic essential micronutrient and as a significant component of high level radioactive waste (HLRW). XAS studies conducted at circum-neutral pH have shown that pyrite (FeS_2), the most relevant redox-active mineral in Boom clay, reduces selenite to a solid-state Se(0) phase. This observation raises several questions. First, why does an Fe-free Se(0) phase form in presence of pyrite, while selenite is reduced to $FeSe_x$ by troilite and mackinawite (FeS)?[1-4]. What is the exact identity of this Se(0) phase, which has been observed by several authors? Why is a dissolved, low oxidation-state selenium species encountered in association with the Se(0) phase; and what is its identity? Correlating selenium redox chemistry with sulphide mineral oxidation pathways allowed to link these observations to the different oxidation behaviour of acid-soluble and acid-insoluble metal sulphides [5].

Acid insoluble metal sulphides such as pyrite, molybdenite or tungstenite exhibit oxidative dissolution only. Upon six consequent one-electron oxidation steps, a thiosulphate anion is liberated (thiosulphate pathway). In contrast, acid soluble metal sulphides (troilite, mackinawite, sphalerite, etc.) exhibit also non-oxidative dissolution thereby liberating sulphide species (H_2S, HS^-,S^{2-}). Under oxidative dissolution in presence of Fe^{III}, they release sulphide cations (e.g. H_2S^+). The latter can spontaneously dimerize into disulphide species, which may further react to polysulphide (polysulphide pathway) and finally elemental sulphur.

The end products of Se(IV) reduction by acid-soluble iron sulphur minerals are fairly well known, but the solid and liquid phase species present during interaction of SeO_3^{2-} with pyrite are poorly characterized. The solid phase reaction product could not yet be assigned as a specific phase, but clearly identified as a Se^0 compound. Trigonal (grey) selenium could be excluded as a canditate.[4]

The presence of an unexpected high concentration of reduced, dissolved species in presence of pyrite, led to a new pyrite-centered reduction mechanism. Based on this mechanism, a hypothesis about the identity of the unknown dissolved species was put forward. In addition, the new mechanism explains all current experimental observations, especially the presence of the currently non-identified dissolved species and the unexpected relation between Se(IV) reduction and pH.[6]

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Numerical modelling of nano-scale mineral dissolution and simulation of mycelial growth dynamics to couple observations of mycorrhizal weathering at single-hypha and whole-plant scales

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Soil mycorrhizal fungi act through biochemical interactions at nanometre scale to dissolve minerals and transport weathering products to plant symbionts through metre-scale mycelial networks. This symbiosis has profound consequences for rates of carbon sequestration from the atmosphere to soil, and rates of nutrient mobilisation from soils, that are apparent on global and geological time scales [1]. Previous research within our consortium has shown convincingly the nanoscale weathering of minerals by hyphae in direct contact with minerals [2], and at the same time the transport and redistribution of mineral- and plant-derived nutrients (carbon, phosphorus) within the rhizosphere and the plant itself [3].

A key factor in this biologically-driven weathering system is the relationship between the energy supplied from the plant to the mycorrhiza, and the rate of weathering of minerals. Critically, what is the nature of the feedback between the plant root and the distal hyphae that controls allocation of photosynthate within the mycelial network in response to nutrient uptake? Here, we present the results of numerical modelling and simulation of hypha-mineral weathering and hyphal network growth which couples a mechanistic model of element release from minerals with fluxes of carbon and mineral nutrients between the plant root and the whole mycelium. Our models indicate that the efficiency of mycorrhizal weathering is sensitive to both geochemical and biological parameters and is time-dependent. We hypothesize that pore-scale variations in weathering efficiency as mycorrhizae progressively spread through soil provide a mechanism to drive hyphal growth behaviour (e.g., exploratory vs. exploitative) and direct photosynthate demand.

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