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How biogenic ligands promote redox transformations in soil phoshate minerals

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Highly insoluble lanthanide phosphate minerals form as the result of weathering of apatite [$Ca_5(PO_4)_3$.(OH,F,Cl)] and are important phosphorous repositories in some soils. Although these phases can be dissolved via biologically-mediated pathways, the dissolution mechanisms are poorly understood. Here in we show that biogenic ligands (1mM) including ascorbate, citrate, oxalate, humic acids, and to a lesser extent phtalate and glutamate, facilitate the dissolution of lanthanide phosphate minerals, $CePO_4$ ($3 < pH < 8$). Batch dissolution experiments for 400 h show that, on a molar basis, oxalate ([P]=450 ± 50 μM) is the most effective biogenic ligand in releasing P, followed by citrate (([P] =250 ± 20 μM), and humic acids ([P]=100 ± 15 μM) and ascorbate ([P]= 87 ± 8 μM). The extent of P release by oxalate and citrate surpasses the extent of P release by EDTA ([P]= 220 ± 15 μM). For selected ligands, electron transfer with structural Ce limits mineral dissolution. Evidence of non-congruent dissolution, and micro x-ray/fluorescence and ATR-FTIR analyses of weathered phosphate minerals samples provides evidence to indicate that, under oxic conditions, catecholate, ascorbate, and humic acids facilitate the oxidation of Ce^{3+} ions at phosphate mineral surfaces, and the formation of CeO_2, a stronger oxidant than manganese oxides. As confirmed by organic carbon and mass spectrometry, CeO_2 promotes the oxidative polymerization of ascorbate and catecholate. Particularly, catecholate undergoes decarboxylation to CO_2 and soluble organic acids [1]. The organic byproducts can then promote dissolution of secondary lanthanide phosphate minerals by complexing with dissolved lanthanide ions. As CeO_2 can be regenerated by re-oxidation [1], small quantities of cerium can play a disproportionately large role in abiotic degradation of organics. These previously unrecognized-coupled processes may exert key controls on phosphate and organic carbon cycles in soils.

Reference

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Microbially mediated mobilisation and precipitation of gold in Australian soil and regolith

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Isolates of various microorganisms have been shown to dissolve and precipitate gold [1,2]. However, for the development of successful exploration strategies it is vital to understand the effect of a complex microflora on gold dispersion and concentration in a natural environment, such as soil or regolith. In this study we used microcosms, which simulate natural systems, to monitor the microbially mediated mobilisation of gold. Soil and regolith samples were taken, and gold flakes panned from soils and sediments in and around gold mines at a temperate (Tomakin Park), a semi-arid (Peak Hill) and a tropical (Palmer River) site in Australia.

In microcosms incubated under oxic or anoxic conditions with live microflorae, dissolved gold concentrations of up to 3 ppm were measured after 20 to 40 days. After 40 to 60 days gold disappeared from solution and was readsorbed to the solid. Liberated gold and added $AuCl_4^-$ predominantely adsorbed to the organic matter. Community structure analysis during the incubation of the organic soils using BIOLOG-Ecoplates, suggested that changes in the community structure of heterotrophic microflora during the incubation could be responsible for the gold liberalisation and readsorption. In sterile control experiments little or no dissolved gold was detected even after 90 days. To assess the microbially mediated gold precipitation, gold colloids and $AuCl_4^-$ were added to bacterial and fungal isolates. Both bacteria and fungi isolated from the soil above the Tomakin Park mine were able to accumulate gold on their cell walls. Samples of fungal hyphaea obtained from soil above the mineralisation at Tomakin Park showed 5 times higher gold concentrations indicating microbial gold accumulation occurring in the field.

Authigenic gold mineralisation was studied using gold flakes from Tomakin Park and Palmer River. Pure gold flakes indicated secondary origin. On untreated flakes, spheroidal forms, budding cellular structures with apparent cell walls were visible with scanning electron microscopy (SEM). Parts of these structures were covered with a fine seemingly organic film. DNA-staining indicates the presence of biofilms on these grains. Biofilms were also detected on industrial gold pellets incubated in soil and their structures resembled those from natural gold flakes. These results indicate an immediate involvement and a netto effect of the natural microflora on gold solubilisation and precipitation and the formation of authigenic gold in soil and regolith in Australia.

References

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