

Nanoparticle remediation through porous media

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The use of engineered nanoparticles continues to expand rapidly. As this intensifies, so does the environmental risk posed if they are released into the environment. This is of particular concern due to the potential toxicity of some nanoparticles. As it stands, we are poorly prepared to deal with nanoparticle pollution and thus remediation strategies must be developed. Here, ureolysis-driven calcium carbonate precipitation by the urease positive bacterium *Sporosarcina pasteurii* is investigated as a means of removing nanoparticles from aquatic systems. This technology has been investigated for the solid phase capture of radionuclide and trace element contaminants in groundwater systems [1]. However its potential to capture nanoparticles has yet to be examined.

Batch experiments show the successful removal of highly stable organo-metallic nanoparticles at concentrations up to 10mg/l (the highest concentration tested thus far). Over 90% of nanoparticles were captured within 24 hours and capture efficiency appeared to be inversely proportional to calcite precipitation rate. As calcite precipitates, the nanoparticles become trapped within the growing calcite crystal. As the calcite-nanoparticle composite continues to grow, it adheres to surfaces (such as the edge of the reaction flask, or the edge of a pore space), immobilizing the nanoparticles from solution.

Following this an experiment was devised to determine the capture efficiency of nanoparticles through saturated porous media. It has been demonstrated that nanoparticles act as nucleation sites to the precipitating calcite, it is now imperative to determine whether nanoparticles are preferentially incorporated into the precipitating calcite when multiple nucleation sites are available, that is the sand grains. Breakthrough curves obtained determine the capture efficiency of nanoparticles in saturated porous media.

This technology has the potential for application in contaminated groundwater and soil as an in-situ remediation technique for nanoparticle pollutants.

[1] Warren, L.A Maurice, P.A Ferris, N, P, F, G. (2011) *Geomicrobiology Journal* **18**, 93-115.

Bottom water redox conditions and sea level changes during Zn-Pb and phosphate mineralization, Howards Pass district, Yukon Territory

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Stratabound Zn-Pb sulphide deposits of the Howards Pass district occur in the Middle Ordovician-Early Silurian Duo Lake Formation (DLF). From base to top, the DLF in the district comprises four principal members: pyritic mudstone, calcareous mudstone, active (Zn-Pb), and upper siliceous mudstone. Sulphide lenses in the active member consist of layered, laminated, and massive sphalerite ± galena. Pyrite forms thin laminae of fine-grained framboids. The upper calcareous mudstone and the base of the active member locally contain apatite-rich units; the upper siliceous member has abundant apatite laminae 0.1-1.5 cm thick.

Whole-rock analyses for Zn- and Pb-poor DLF mudstones ($n = 58$) from three drill cores in relatively undeformed parts of the XYC and HCW deposits contain variable silica (to 90 wt % SiO₂), phosphate (to 24.7 wt % P₂O₅), and carbonaceous material (to 16.5 wt % Corg). V concentrations are highest in the calcareous mudstone member (to 3000 ppm), implying sedimentation near the suboxic-anoxic boundary; large variations in marine V/Mo ratios (0.74-209) reflect fluctuating bottom-water redox over time [1]. Re/Mo ratios [2], considered the best paleoredox proxy, record sulphidic or anoxic conditions (Re/Mo <0.001) in bottom waters during deposition of the pyritic mudstone, most of the calcareous mudstone, and active members; these conditions predominated in the basin prior to and during Zn-Pb mineralization, aiding accumulation and preservation of sulphides. In the upper siliceous member, Re/Mo ratios are mostly higher (0.004-0.013), indicating suboxic (<5 μM O₂) bottom waters. Suboxic conditions within the upper part of the calcareous mudstone and the base of the active member, and especially in the upper siliceous member, promoted deposition of abundant phosphate and correlate temporally with two periods of global sea level rise [3]; falling sea level may have facilitated the development of crucial anoxic to sulphidic bottom waters during Zn-Pb mineralization. Lithologic similarity to part of the Monterey Formation (Miocene) of coastal California suggests that the DLF and its contained Zn-Pb deposits formed in a restricted basin near a continental margin, accompanied by high productivity required for the accumulation of abundant phosphate, biogenic silica, and organic matter.

[1] Piper, D.Z., Calvert, S.E. (2009) *Earth-Sci. Reviews* **95**, 63-96.

[2] Ross, D.J.K., Bustin, R.M. (2009) *Chem. Geol.* **260**, 1-19.

[3] Munnecke, A., et al. (2010) *Palaeogeogr. Palaeoclimatol. Palaeoecol.* **296**, 389-413.