## Importance of colloidal iron in mine waters revealed by differential pulse voltammetry

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Whilst polluted mine waters are of course enriched in iron, we are remarkably ignorant of the iron's physical state and chemical speciation. This is a problem since the physical and chemical state of iron is central to understanding a range of processes relevant to mine water geochemistry and remediation. Examples include the hydrolysis of dissolved Fe(III) to release protons, the adsorption of trace metals onto iron colloids and the bioavailability of iron within wetlands designed to remediate acidic mine waters.

In this work we have developed Differential Pulse Voltammetry (DPV) as a rapid and robust method of determining the concentration of truly dissolved iron and colloidal iron in 0.45  $\mu$ m filtered waters from a series of mine water discharges and remediation sites in NE England. The waters have a pH range of 3 to 5 and concentrations of <0.45 $\mu$ m iron between 30 and 800mg/L across the sites.

The good agreement between the iron concentrations measured in acidified samples electrochemically and by ICP-OES validates the accuracy of DPV as an analytical method for iron. Since DPV measures uniquely dissolved iron, particulate (>0.45 $\mu$ m) and/or colloidal (<0.45 $\mu$ m) iron can then be estimated as the difference between the voltammetric responses of natural samples and samples in which the solid phase iron has been dissolved by the addition of HCl.

Percentage dissolved Fe ranged from 60-90% (in most cases) in unfiltered samples while percentage colloidal iron varied widely across the sites and ranged from 25-45% in unfiltered samples and 50-75% and 35-85% for dissolved and colloidal Fe in the  $0.45\mu$ m filtered samples. The proportion of colloidal Fe increases with pH.

Atomic Force Microscopy shows that the colloids range in size from nm to  $\mu$ m for lower pH mine waters; at higher pH, particles are mainly aggregates on the  $\mu$ m to mm scale. FT-IR, XRD and TEM show that the most common colloidal phase is poorly crystalline Fe oxi-hydroxide.

## Revisiting the oxygen isotopic composition of the Archean ocean

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Recent studies as diverse as of evolution of temperature tolerant proteins, silicon isotope ratios in cherts and climate modeling, have all reinvigorated the 40 year old controversy regarding the  $\delta^{18}$ O value of the Archean ocean. All cherts of Archean age have  $\delta^{18}$ O at least 10 to 15% lower than from the Cenozoic. If not reset, the chert data imply substantially higher seawater temperature or proportionately lower  $\delta^{18}$ O seawater. Either alternative has profound implications to evolution, tectonics, metalogeny and climatology.

All early Archean sub aqueous basaltic rocks from South Africa, W. Australia and Isua, Greenland reflect interaction with the Archean ocean and have  $\delta^{18}$ O values within the range (6 - 17%) now observed on the ocean floor and young ophiolites. The  $\delta^{18}$ O of the water had to have had a  $\delta^{18}$ O similar to today's. The alternatively suggested and modeled -13% ocean would have left a low-<sup>18</sup>O imprint on any crust. The magnitude of the imprint can be estimated from what is now seen on Iceland at Krafla, in the northern rift zone where geothermal steam is produced from hydrothermal systems fed by low-<sup>18</sup>O glacial melt waters (ca. -13%). Several km of basalt recovered by deep drilling are all pervasively altered to  $\delta^{18}$ O of -3 to -11% $_{0}(1)$ . The data from Iceland show that were the  $\delta^{18}$ O of the Archean ocean -13%, then the hydrothermally altered Archean crust would be similarly depleted of <sup>18</sup>O irrespective of the elevation of the Archean seafloor.

[1] Hattori & Muehlenbachs (1982) JGR 87, 6559.