Formation of acidic micro-environments during pyrite framboid oxidation in pH-neutral sediments

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Due to increases in salinity and water regulation, environmentally significant sulfide deposits have recently become ubiquitous throughout saline wetlands of the Murray River floodplains, Australia [1]. At the wetland scale these sulfidic sediments largely have excess buffering capacity in the form of carbonate but localised unbuffered sediments form acidic (pH 3.4) 'hot spots' upon oxidation. Laboratory oxidation of unbuffered sediments produced low pH (2.8) and high amounts of sulfide oxidation whilst buffered sediments remain pH-neutral (6.8) with only small amounts of pyrite oxidation. However, oxidation of sediments under both acidic and pH-neutral conditions in the field produce high amounts of sulfide oxidation suggesting an acceleration of pyrite oxidation under field pH-neutral conditions.

Under oxidising field conditions pyrite framboids in pH-neutral sediments are distinct from acidic sediments forming coatings and halos of iron oxides and bacteria (SEM-EDX, DAPI, 16s PCR, DGGE). Additionally, pH-neutral sediments form jarosite 'honeycombs' within pyrite framboids not associated with iron oxide coatings (SEM-EDX).

Iron oxide and bacterial coatings indicate initial pyrite oxidation occurs in acidic nano-environments at the pyrite surface. As jarosite forms only at pH <3, the discovery of jarosite 'honeycombs' demonstrate accelerated acid production between pyrite crystals resulting in acidic micro-environments. Bacterial halos and the absence of iron oxide coatings around jarosite 'honeycombs' indicate an expanding acid front outward into the sediment matrix. These results characterise the formation and expansion of acidic micro-environments during pyrite framboid oxidation within pH-neutral sediments.

[1] Lamontagne *et al.* (2006) *Marine & Freshwater Research* **57**, 775-788.

The genesis of the Gayna River carbonate-hosted Zn-Pb deposit, Northwest Territories

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The Gayna River deposit is located in the Mackenzie Mountains of NW Canada and is hosted by the platform carbonates of the Neoproterozoic Little Dal Group. The mineralization occurs as a series of sphalerite cemented breccias and veins which have a clear structural control. The deposits at Gayna have the following main paragenetic components: pre-ore (pyrite, limestone, dolostone, calcite cement and early sphalerite), ore-related (dolospar, quartz, sphalerite, and galena) and post-ore (quartz, pyrite, calcite, and pyrobitumen).

In total the $\delta^{34}S$ composition of sulphides at Gayna River range from -4.4 to 25.7‰ (CDT). The pre-ore phase pyrite and sphalerite samples have the lower $\delta^{34}S$ values (-4.4 to 2.4‰ and 1.5 to 5.2‰ respectively). Carbon and oxygen isotope results for the host dolomite were $\delta^{13}C = 1.8$ to 4.6‰ (PDB) and $\delta^{18}O = 22.1$ to 25.2‰ (SMOW).

The ore-phase sphalerite has $\delta^{34}S$ values from 12.2 to 25.7‰ and the galena ranges from $\delta^{34}S = 14.9$ to 23.2‰. The dolospar phase has $\delta^{13}C$ values of 0.7 to 2.5‰ (PDB) and $\delta^{18}O$ values of 20.0 to 26.6‰ (SMOW). Primary fluid inclusion data in sphalerite suggest the main phase of mineralization was formed by fluids that ranged in homogenization temperature (Th) from 107 to 227°C (mean 204°C) and 23.0 to 34.4 wt.% NaCl equiv.

Pyrites from the post-ore phase have $\delta^{34}S$ values of 11.5 to 21.2‰. The late calcite phase had $\delta^{13}C$ values of -3.0 to 3.0‰ (PDB) and $\delta^{18}O$ values of 16.6 to 20.3‰ (SMOW). Inclusions in late quartz and calcite have Th values that range from 99 to 233°C and 59 to 159°C respectively and corresponding salinities of 13.7 to 32.9 wt % NaCl equiv. for quartz, and 13.6 to 23.7 % NaCl equiv for calcite.

The data suggests that the Gayna River deposit likely was formed by mixing of at least two fluids and one of those fluids originated as seawater. The sulphur for the deposit was derived from the evaporite sequences found in the Little Dal Group possibly by thermochemical sulphate reduction. Post-mineralization fluids are cooler and less saline, possibly due to the mixing of the mineralizing brine with a more dilute fluid.