Earth System Evolution in the Proterozoic – the Story from Marine Pyrite

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Marine pyrite, formed in the top few mm of organic-rich muds, concentrates many trace elements derived dominantly from seawater (>90%) with a minor pore fluid component (<10%). LA-ICP-MS analyses of modern framboidal pyrite, indicate that nutrient trace elements are concentrated in the pyrite in approximately the same order as their mean concentration in modern seawater. Analyses of over 5,000 marine pyrites from black shales over the past 3.5 billion years enables a record of first order nutrient trace element trends in the global ocean. This approach suggests that the Meso- to Neoarchean oceans were enriched above mean levels in Fe, Co, Ni and Cr. By comparison the Paleo- to Mesoproterozoic oceans were depleted in all nutrients except V and K, whereas the Neoproterozoic oceans were very nutrient rich with Cu, Zn, Mn, P, V and K all above mean levels. The most nutrient-rich intervals are 3000-2800 Ma (Ni, Co, Fe, Cu Cr), 1200-1000 Ma (Se, Zn, Co) and 600-400 Ma (Mo, Cd, Se, Zn, Cu, Mn, P, V). The most nutrient-poor intervals are 2800-2600 and 2000-1400 Ma. Oxygenation of the Proterozoic atmosphere has been mapped out by the Se/Co ratio in marine pyrite, which suggests that pO_2 rose from the Archean to a peak of roughly 17 wt. % O_2 at 2000-1800 Ma and then declined to roughly 5 wt. % at 1200-1000 Ma, before rising again to around 19 wt % at 600-400 Ma. These estimates differ substantially from previous suggestions based on Cr isotopes (Planavsky et al. 2014; Cole et al., 2016).

Cole et al., 2016, Geology 44, DOI: 10.1130/G37787;
Planavsky et al., 2014, Science. 31;346(6209):635-8. doi: 10.1126/science.1258410.

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