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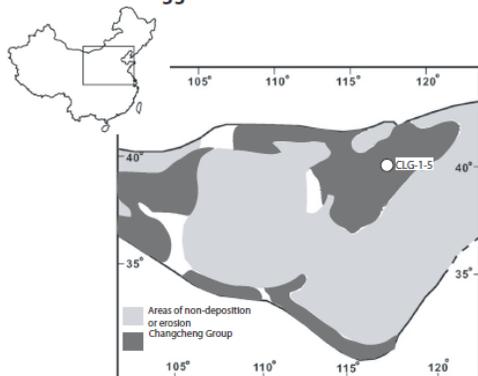
Sulfur isotopes in Paleoproterozoic carbonates: The key to understanding post oxygenation chemical oceanography?

PROJECT REPORT:

The chemical composition of the ocean changed markedly with the oxidation of the Earth's surface, and this process has profoundly influenced the evolutionary and ecological history of life. The early Earth was characterized by a reducing ocean-atmosphere system, whereas the Phanerozoic eon (less than 542 million years ago) is known for a stable and oxygenated biosphere conducive to the radiation of animals. The redox characteristics of surface environments during Earth's middle age (2.4 – 0.55 billion years ago) are less well known. I conducted fieldwork in 2009 funded by the Lewis and Clark Fund for Exploration and Field Research in Astrobiology in North China with the goal of collecting a suite of samples for geochemical work to better constrain the history of surface oxygenation.

Specifically, I explored the Liaohe and Changchang Groups in North China, with the goal of collecting carbonates and shales for sulfur isotope and for iron speciation work. Exposure of the Liaohe Group was poorer than indicated in initial reports and I was not able to sample a stratigraphic section for geochemical work. In contrast, I was able to sample several sections from the Changchang Group. Foremost, I was able to collect 4 sections from the Chuanlinggou Formation. The Chuanlinggou Formation, part of the lower Changcheng Group, was deposited approximately 1700 million years before present (Ma). Fresh outcrop samples come from recent excavation sites in the Jixian region (see map). These samples lie stratigraphically near (within 200 meters) the contact with the overlying Tuanshanzi Formation. I found there is a significant amount reduced biogeochemically reactive iron (carbonate-bound iron) in fresh outcrop samples, but low amount of iron oxides, confirming that our samples were not significantly affected by surface oxidation and that dissolved iron was high at the time of deposition. I also sampled from the ca. 1.4 Ga Gaoyuzhuang formation, but found the samples to have been heavily influenced by recent oxidative continental weathering. All collected samples will be archived at repositories in the Department of Geology and Geophysics at Yale University.

ca. 1.7 Ga Chuanlinggou Formation



Location of field work in North China. Samples from four sections of the ca. 1.7 Ga Chuanlinggou Formation were collected for coupled iron-carbon-sulfur geochemical work with the goal of improving our understanding of Proterozoic redox conditions.

Sulfur isotope and iron speciation data from the Chuanlinggou Formation, contrary to the popular model, suggest that ferruginous (anoxic and iron-rich) conditions were both spatially and temporally extensive in the mid-Proterozoic ocean. Previously mid-Proterozoic oceans were suggested to be oxic or sulphidic. Further, an integrated view of Chuanlinggou Formation shale geochemistry suggests that organic matter delivery control on the distribution of sulphidic marine conditions. The analyzed samples contain substantially less organic carbon than do typical Precambrian and Phanerozoic shales that have geochemical evidence for sulphidic conditions. Samples in our study contain on average less than 1% organic carbon, which is several fold lower than concentrations common in sulfidic shales. Low levels of organic matter in ferruginous shales suggest relatively low productivity in the overlying water column. In addition, there is a sulfur isotope signal consistent with bacterial sulfate reduction occurring predominately in the porewaters. Pyrite in our samples has $\delta^{34}\text{S}$ values that are slightly lower than or equivalent to coeval sulfate. A simple explanation for these results is that bacterial sulfate reduction is occurring largely in sediments where potentially high isotopic fractionations are muted by limited sulfate availability. Sulfate supplies in the sediments would be controlled by rates of diffusional replenishment, and associated deficiencies would be exacerbated by the comparatively small amount of sulfate in mid-Proterozoic seawater. In other words, limited availability of organic matter probably caused the onset of appreciable bacterial sulfate reduction to be restricted to the sediments. However, these sulfur isotope results do not completely exclude water column sulfur cycling.

Broadly speaking, the data generated from the Chuanlinggou Formation with similar work from other Proterozoic sedimentary successions now provides the foundation for a unified model for the chemical evolution of the Proterozoic oceans. The emerging view is redox conditions were much more spatially and temporally heterogeneous than initially expected in a dynamic early ocean. Specifically work on the Chuanlinggou Formation funded by the Lewis and Clark Fund is part of foundation for the model that there was almost continuous coexistence of sulphide-rich and iron-rich conditions for billions of years beneath oxic surface waters in the Proterozoic oceans. These geochemical conditions were the backdrop for Precambrian biological evolution and specifically the protracted radiation of eukaryotes and the ultimate rise of animals.