Spatial and temporal trends of iron and iron isotope cycling in the Peruvian oxygen minimum zone

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Iron (Fe) is a key element in the global ocean's biogeochemical framework because of its essential role in numerous biological processes. A poorly studied link in the oceanic Fe cycle is the reductive release of Fe from sediments in oxygen depleted ocean regions - the oxygen minimum zones (OMZs). Changing rates of Fe release from OMZ sediments may have the potential to modulate ocean fertility which has far-reaching implications considering the high amplitude oxygen fluctuations throughout earth history as well as the ongoing ocean deoxygenation projected for the near future. In order to explore spatial and temporal trends of Fe cycling in OMZs, we present here Fe isotope and speciation data for surface sediments from a transect across the Peruvian upwelling area, one of the most pronounced OMZs of the modern ocean.

Because of continuous dissimilatory Fe reduction and diffusive loss across the benthic boundary, sediments within the OMZ are strongly depleted in reactive Fe components, and the little reactive Fe left behind has a heavy isotope composition. In contrast, surface sediments below the OMZ are enriched in reactive Fe, with the majority being present as Fe oxides with comparably light isotope composition. This lateral pattern of Fe depletion and enrichment indicates that Fe released from sediments within the OMZ is reoxidized and precipitated at the oxycline. First-order calculations suggest that the amount of Fe mobilized within the OMZ and that accumulated at the boundaries are largely balanced. Therefore, benthic Fe fluxes in OMZs should be carefully evaluated prior to incorporation into global models, as much of the initially released Fe may be reprecipitated prior to vertical or offshore transport.

First XRF core scanning results for partly laminated piston cores from the OMZ boundaries reveal downcore oscillations in the content of reactive Fe and redox-sensitive trace metals that are attributed to past changes in OMZ extension. Ongoing work on these cores will focus on their dating and the downcore investigation of Fe and trace metal records in order to better understand past Fe cycling within the Peruvian OMZ and potential interactions with climate variability.

Lung Fluid-Mineral Interaction: Experimental Challenges and Outcomes

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Introduction

The inhalation of mineral dust can potentially lead to lung disease. Perhaps the best-known examples are exposure to asbestos, quartz, and coal, which can lead to mesothelioma, silicosis, and coal workers' pneumoconiosis, respectively. Despite clear causal evidence, the mechanisms by which mineral particles induce these diseases remain, in part, unknown. Geochemists are in a position to contribute to a better understanding of the mechanisms by which particles induce disease by conducting experimental studies to determine mineral biodurability and their ability to generate reactive oxygen species (ROS). Biodurability is an important factor as it expresses how long a particle is expected to remain in the lung after inhalation on the basis of its solubility in lung fluid. ROS are intermediate species in the reduction of molecular oxygen. Hydrogen peroxide and hydroxyl radical are the two most important ROS. Recent work shows that minerals, such as pyrite and olivine, produce hydrogen peroxide and hydroxyl radical when dispersed in water. Hydroxyl radical is particularly detrimental to human health.

While there is a wealth of data on the dissolution of minerals in water and some data is available on ROS formation in mineral slurries, few experiments have been conducted in a lung fluid proxy. A promising avenue of research is to conduct mineral dissolution experiments in Simulated Lung Fluid (SLF). There is, however, no single, standard recipe for SLF. One approach is to create a "simple" SLF solution that contains a phosphate buffer and several inorganic salts and organic acids. This formulation captures the essentials in terms of pH and ionic strength, but lacks complexity due to the absence of proteins, lipids and other macromolecules.

A comparison of pyrite dissolution rate in water and a simple SLF showed a drastic decrease in rate of dissolution in SLF. Addition of Survanta™, a bovine pulmonary surfactant, showed little or no change in rate, suggesting that the addition of the natural mixture of lipids, proteins and other biomolecules had no effect on dissolution rate. On the other hand, the addition of Survanta™ did lead to a rapid decrease of hydrogen peroxide in the slurry.

Conclusion

It is possible for Geochemists to contribute to a better understanding of lung diseases triggered by inhalation of mineral dust by conducting experiments with well-characterized minerals in SLF. While the addition of complex biomacromolecules is likely to affect the stability of hydrogen peroxide and possibly hydroxyl radical, dissolution rate data obtained in simple SLF are probably good biodurability indicators. The speciation of ROS is affected by the presence of complex biomolecules. It is possible that their presence promotes reactions that consume hydrogen peroxide and/or hydroxyl radicals.