Sediment biogeochemistry in low-oxygen settings

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Low-oxygen conditions are becoming increasingly common in open-ocean and coastal environments due to global warming and cultural eutrophication. There are multiple effects on sediment biogeochemistry and benthic ecology, including changes in benthic community structure and functioning, diagenetic pathways and direction and magnitude of sediment-water exchange fluxes. The direct and indirect (via benthic animals) effects of reduced bottom-water oxygen levels on sediment biogeochemistry will be discussed. Low-oxygen conditions have also a strong effect on organic matter preservation and burial. However, the mechanisms involved are poorly known. Here we present and summarize experimental research on processing of organic carbon in oxygen minimum zone (OMZ) settings. A series of ^{13}C tracer studies involving addition of phytodetritus to sediments in the Arabian Sea area including the OMZ revealed that labile organic matter is rapidly processed by all benthic community members (bacteria, foraminifera, animals), although their relative share may depend on oxygen levels. Organic matter bioavailability assessments based on various approaches (enzymatically available amino acids, carbon dioxide production per unit organic carbon) indicate that organic matter availability in sediment underlying OMZ may be lower than that in other settings because of extensive predepositional processing. Organic matter quality assessments based on chemical approaches (amino acids, pigment, lipid spectra and concentrations) provide alternative, though not always, conclusive evidence for an oxygen effect on organic matter preservation.

An experimental study of the stability of hydrosulfide species of Co(II) at hydrothermal conditions

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Cobalt can be actively involved in processes of hydrothermal alteration and mineralization, up to the level of formation of ore deposits such as that, for example, at Bou Azzer, Morocco. However, our knowledge of the speciation of this metal at elevated temperatures is surprisingly limited. The stability of cobalt species in high-temperature aqueous fluids is relatively well known for cobalt hydroxide complexes (e.g. Ziemniak *et al.* [1]), but experimental information is sparse for cobalt chloride species; the only study (Pan & Susak [2]) was restricted to temperatures ≤90 °C). There are no data at all for cobalt hydrosulphide species, which have been ignored in models that evaluate Co mobility in natural systems. The goal of our study was therefore to derive experimentally stability constants of hydrosulfide complexes of cobalt at temperatures up to 350 °C, and to refine the stability of chloride species of this metal.

Experiments involved investigation of the solubility of Co-pentlandite (Co_9S_8) in acidic solutions (pH<3) containing various concentrations of H_2S, HCl and $HClO_4$ (the latter constituent was used for experiments at T≤250 °C). Experiments were performed in titanium autoclaves under H_2S pressures of 15 to 80 bar. After equilibrium was attained, the autoclaves were quenched, Co_9S_8 was removed, any Co precipitated was dissolved by hot HNO_3. The concentrations of Co and Cl were analysed using NAA, and concentrations of dissolved H_2S were calculated from partial pressures. The first data obtained at 150 and 200 °C have demonstrated that under experimental conditions cobalt is predominantly transported as $CoHS^+$ species. Logarithms of formation constants derived from the experimental data for the reaction

$$Co^{2+} + H_2S_{aq} = CoHS^+ + H^+$$

are 0.41 and 0.26 for 150 and 200 °C, respectively. These values suggest that hydrosulfide species should play a major role in the transport and concentration of Co in H_2S-rich hydrothermal systems.

[1] Ziemniak, S. E., Goyette, M. A., Combs, K. E. (1999). *Journal of Solution Chemistry*, *28* (7), 809-836. [2] Pan, P., Susak, N. J. (1989). *Geochimica et Cosmochimica Acta*, *53*, 327-341.