

The redox chemistry of antimony in lakes

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Approximately 100'000 tons of the annually mined Sb is coming into use in ever increasing quantities in products (in alloys, as a fining agent in glass and plastics, as a flame retardant in plastics, textiles and brake pads) and waste streams. It is entering the environment through various paths, its toxicity is similar to that of As, yet still very little is known of its behaviour in environmental systems.

The key to understanding the factors that control solubility and thus the mobility of Sb is its redox chemistry. The predominant and more soluble form of Sb in aqueous environmental systems under ambient conditions is Sb(V). Under reducing conditions Sb(III) predominates, either in association with organic ligands, sulphides or sorbed to particle surfaces and rarely making up more than a few percent of total dissolved Sb. Dissolved Sb(III) appears to slowly oxidised by O₂, but there is information to suggest that it is rapidly oxidised to Sb(V) by Mn(III;IV) and possibly by Fe(III) (hydr)oxides. Preliminary experiments show that Sb(III) is oxidised by H₂O₂ and by intermediate species produced during the oxidation of Fe(II). The oxidation is pH dependent, the rate increasing with pH. The indirect oxidation of Sb(III) by Fe(II) is complete after a few hours at neutral pH. Preliminary experiments also show that Sb(V) can be reduced by Fe(II) under alkaline conditions and it is known from the literature that S(-II) reduces Sb(V).

Lakes are ideal systems for the study of geochemical processes. Though we have a rudimentary understanding of the redox processes that control Sb solubility, few studies have been made of the cycling of Sb in environmental systems. Measurements made by Fabian (EAWAG) in the eutrophic lake Baldeggersee, Switzerland, suggest that 60% of Sb deposited into the sediment is released into lakewater. Since Sb(V) is the more mobile than Sb(III), it is possible that Sb is being oxidised in the sediment and is subsequently released to the lakewater. In order to confirm that a) Sb is rapidly recycled in lake systems and b) to elucidate the processes that lead to the release of Sb from sediments, an artificial lake system (7 L) containing sediments from Lake Zug, Switzerland and artificial lake water was constructed. The system was spiked with Sb(V) (8 µM) and repeatedly subjected to anoxic and oxygenated cycles. The results confirm the findings of the field data and showing that the reduction of Sb(V) occurred in the presence of S(-II), but that this process was not very efficient and that the release is highest during the reoxygenation of the system.

Fractionation of Fe isotopes by anaerobic phototrophic bacteria.

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In biological systems, iron has a wide range of functions. It can be used either as an electron acceptor in anaerobic environments or as an electron donor in aerobic and anaerobic environments. Transport and metabolic reactions catalysed by enzymes are a likely source of kinetic fractionation of iron. This is why iron isotope fractionation has initially been considered as a potential tracer for biological activity.

Studies have shown fractionation of iron by bacteria through reduction or during hydrolysis of iron at mineral surfaces (1,2). However it has also been shown that significant abiotic fractionation of aqueous ferrous iron to ferric iron was also possible showing that Fe isotopes can provide ambiguous results (3). All these studies concern aerobic environments. But Fe was certainly very important for early life in the anoxic Archean. This is why we have investigated the fractionation of Fe by *Chlorobium ferrooxidans*, a phototrophic anaerobic bacterium (4) that uses Fe(II) as an electron donor for carbon fixation.

Batch experiments have been done at different temperatures (15 to 25°C) with Fe(II) as sole electron donor. In some experiments fulvic and humic acids were added and this can play a role of mediator in the electron transfer.

Our first results show a large enrichment in heavy isotopes of the ferric iron formed. The evolution of the isotopic composition can be modelled as a Rayleigh fractionation process with a fractionation factor α as high as 1.003. This enrichment in heavy isotopes shows that the fractionation is probably not controlled kinetically by transport proteins or enzymes in the cell membrane favouring lighter isotopes. Considering that iron oxides separate rapidly from the reacting system, the results show that reasonably large fractionations (+10 to +20‰ in $\epsilon_{57/54}$) could easily be preserved during the formation of iron oxides in natural anoxic environments.

References

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