

Hg accumulation in reducing sediments of the Mediterranean Sea: Trace metal and Hg isotope evidence

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Mercury (Hg) has a complex biogeochemical cycle involving multiple oxidation states with gaseous, dissolved, and particle-associated species. We investigated the effects of different redox conditions on Hg partitioning in the marine environment. We analyzed Hg concentration and isotopic composition, as well as concentrations of a suite of trace metals that are widely used as indicators of productivity and redox conditions, in sediments from a mid-Pleistocene sapropel sequence in the Tyrrhenian Basin of the Mediterranean Sea. During episodes of sapropel formation, high productivity and reducing conditions produce organic-rich sediments, with characteristic trace metal patterns.

Concentrations of Hg and other metals covary with total organic carbon (TOC) content, with a Hg enrichment factor of 3.9 in high TOC sapropels versus low TOC non-sapropels. Enrichment factors determined for other elements are 1.3-2.1 for Cr, Cu and Zn; 3.0-4.9 for V, Co, Ni and U; 5.0-8.0 for Mo and Cd; and 13 for Re. Hg concentrations in these sediments are highly correlated with trace elements normally associated with organic matter delivery (Co, Ni, Cu, Zn and Cd) as well as with elements associated with enrichment in reducing sediments by mineral precipitation and adsorption occurring below the sediment-water interface (V, Cr, Mo, Re and U) (Tribovillard *et al.*, 2006). The strong correlation between Hg and both suites of trace metals suggests that particulate scavenging and/or in situ precipitation contributes to Hg accumulation in marine sediments. If we specifically look at the variation in metal concentrations in only those samples with low TOC content deposited under oxic conditions (non-sapropel layers), we find that Hg does not covary with V, Cr, Ni, Mo, Cd, Re or U, but does covary with Co, Cu, and Zn. These patterns may be related to variations in terrigenous sediment sources or preservation of these metals in sediments.

We also explored whether Hg isotope values could provide insight into changes in Hg deposition between sapropel and non-sapropel layers. Preliminary isotopic analyses show that sapropels have lower $\delta^{202}\text{Hg}$ values (Blum and Bergquist, 2007) than non-sapropel layers (-1.1‰ vs -0.7‰). This likely reflects either a change in Hg sources or isotopic fractionation during redox transformations.

References

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Mobilisation and speciation of depleted uranium in water and soils

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Depleted uranium (DU) from penetrating ammunition was exposed to several environmental conditions in order to determine the binding forms of uranium as well as in its dissolved and solid forms.

In a first series fresh disks of DU were treated with a calcium phosphate solution. The results from time-resolved laser-induced fluorescence spectroscopy clearly show that metaautunite $\text{Ca}(\text{UO}_2)_2(\text{PO}_4)_2 \times 2-6(\text{H}_2\text{O})$ has formed during alteration [1].

In a second experiment the corrosion and leaching of used up DU was investigated for three years in a column with a soil core. The columns were irrigated with synthetic rainwater.

The luminescence spectrum of a yellow material, which was crystallized at the soil surface was assigned clearly to be the mineral sabugalite $\text{AlH}(\text{UO}_2)(\text{PO}_4)_4 \times 16(\text{H}_2\text{O})$.

In contrast to the luminescence spectra of the solid material the spectra of the uranium species in the dissolved samples could only be obtained at temperatures below 220 K. From the shape of the spectrum and the emission maxima of the luminescence of seepage water samples it could be clearly concluded that the solution species are mostly uranyl carbonate species $\text{UO}_2(\text{CO}_3)_3^{4-}$ [2].

References:

- [1] Baumann, N., Arnold, T., Geipel, G., Trueman, E.R., Black, S. and Read D., (2006), *Science of the Total Environment* **366**, 905-909.
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