

Microbially-catalyzed cementation of modern gypsum-dominated thrombolites

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Large gypsum-dominated microbialites coated by well developed and stratified microbial mats have been found growing in the shallow waters of a restricted hypersaline lagoon on the Archipelago Los Roques, Venezuela. The overlying hypersaline water is characterized by temperatures in excess of 30°C and elevated total alkalinity (164 meq/L as CaCO₃), pH (~9.1), and Mg/Ca ratio (6.1). In the organic mud- and gypsum-dominated basin the environmental conditions promotes bacterial growth and abundant production of EPS matrix forming a microbial mat which in the shallow areas (to a depth < 1 m) can be linked to the development of unusual subaqueous microbialites, cemented by Mg-carbonates. These microbialites have a crudely laminated to clotted internal fabric and thus can be morphologically regarded as thrombolites [1]. Results from various analytical approaches, including standard and fine-scale petrography, C and O stable isotope analysis, and laser-ablation ICP-MS, suggest that carbonate cementation of these thrombolites is an early diagenetic process, catalyzed by the breakdown of gypsum by SRB. The thrombolites no longer occur at water depths > ~1 m, and in deeper parts of the lagoon (max. depth = 1.6 m), sedimentation consist of gypsum nodules growing in a gelatinous organic matrix without any carbonate cementation. The carbon and oxygen isotopic composition of the carbonate phases within the thrombolitic fabric reflect the timing of precipitation and the interplay of organic and inorganic carbon reservoirs; early-diagenetic carbonate cements ($\delta^{13}\text{C}_{\text{PDB}} \approx -2\text{‰}$) are close to equilibrium with respect to inorganic carbon, while deeper in the thrombolites, gypsum-replacing carbonates are relatively enriched in ¹²C ($\delta^{13}\text{C}_{\text{PDB}} \approx -5\text{‰}$), likely incorporating carbon released by SRB heterotrophy of organic matter. The oxygen isotopic composition ($\delta^{18}\text{O}_{\text{PDB}} \approx -0.6$ to -0.1‰) results from equilibrium mineral precipitation from evaporated seawater ($\delta^{18}\text{O}_{\text{SMOW}} = +2.0$ to $+4.0\text{‰}$); the uniformity of the $\delta^{18}\text{O}$ values, as compared with allochemical grains in the basin (aeolian-transported *Halimeda* flakes, $\delta^{18}\text{O}_{\text{SMOW}} = -3.0\text{‰}$) suggests that authigenic precipitation exceeds trapping and neomorphism within the microbial mat. This thrombolite-rich lagoon thus serves as an unparalleled field site for the study of chemical and isotopic processes influencing early diagenetic gypsum microbialite formation.

[1] Aitken (1967) *J. of Sed. Petrol.* **37**, 1163-1178.

Mercury in contaminated soils from the Zlatna mining district (Apuseni Mountains, Romania)

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In the Apuseni Mountains (Romania) Hg ores were mined at Ampoiului Source. The historical mine is situated on the left side of Dosului Valley Creek. The Hg ore at Ampoiului Source is mainly cinnabar and is found in sedimentary bedrock of Cretaceous sandstones and limestone. The speciation of Hg is a critical determinant of its mobility, reactivity, and potential bioavailability in mine impacted regions. This is the first attempt to identify the contaminant fractionation of Hg in soil in this area. Information of major Hg fractions in soil is required in order to predict the effect of future changes in the environment

Total mercury was determined by a CV-AAS Hg analyzer AMA 254. A sequential extraction technique produced data on the following fractions of Hg in soil: organomercury species, water soluble, acid soluble, associated with humic matter and residual. The clear solutions were analyzed for Hg using a HORIBA Jobin Yvon ICP-OES system. Quality control was ensured using certified materials SRM 2711 and SRM 2709.

Total mercury concentrations in the mine waste samples (n=32) were highly variable. Hg concentrations in soils ranged from 3.70 to 27.85 mg·g⁻¹ with a mean value of 14.03 mg·g⁻¹ (dry wt.). The fraction contributing the most to the total Hg concentration in the soils was residual 82.4%. The organically-bound fraction also contributed highly, with 10.8 % of total mercury. The fractions that contributed least to the total mercury content were water-soluble (contributing 0.8%) and organomercury compounds (contributing 1.4%).

In general, mine waste materials are reported to be very heterogeneous. From our data, over 80% of the total Hg content of soils was highly refractory to the extractors used and only 17.6% of total Hg is weakly adsorbed to the mineral components. This suggests that the only possible form of Hg would be either Hg present in silicates or Hg sulphides. Hg could appear also as Hg (II) bound to mineral or organic components. Our samples containing mostly Hg in phases which are relatively stable in subsurface environment of mine waste dumps and are not subject to any significant methylation that results in the formation of highly toxic methyl-Hg. Only Hg associated with mineral surfaces may undergo methylation processes, and thus, may represent a potential long-term environmental risk.