Discovery of a "vital" bacterial effect in the formation of biogenic carbonates

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Carbon and oxygen stable isotope compositions of carbonates are widely used to provide information on their conditions of precipitation. However, most carbonates result from a biological activity, which in the case of some skeleton-forming eukaryotic organisms has been shown to lead to isotopic characteristics that differ from those expected for isotope equilibrium. The origin of this difference remains poorly understood and is referred to as the “vital effect”. So far, potential microbial vital effects have been overlooked and microbial carbonation is considered from an oxygen isotope perspective as occurring at equilibrium with water. We revisit this assumption by performing an isotope study of carbonates precipitation by the strain *Sporosarcina pasteurii*, a bacterial model of carbonatogen metabolisms. Its ureolytic activity produces ammonia (thus increasing the pH) and dissolved inorganic carbon (DIC) that precipitates as solid carbonates. $\delta^{18}O_{CaCO3}$ results show values up to 20‰ lower than what was expected for carbonate precipitation in equilibrium with water. This demonstrates for the first time that bacteria may precipitate carbonates with a vital effect. The addition of carbonic anhydrase, an enzyme able to equilibrate the oxygen isotopes between DIC and water, yields equilibrium values. This result demonstrates that the vital effect observed in solid carbonates results from disequilibrium between DIC and water, a mechanism also strongly suspected to account for vital effects in skeleton-forming organisms.

X-Ray Spectroscopy and Spectromicroscopy Study of Sulfur Speciation in Urban Soils

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This study shows the applicability of sulfur x-ray spectroscopy and spectromicroscopy to analytical problems in urban soils.

A combination of x-ray microscopy, elemental mapping and XANES spectroscopy at the K-absorption edge of sulfur was used to analyze the elemental and particulate composition of an urban soil loaded with debris from WWII, exemplarily from Berlin, Germany. The goal was to specify and analyze the sulfur pool of soils with major anthropogenic impact, i.e. the dumping of war debris. This impact obviously influences soil composition and soil formation processes, but may, due to sulfate leaching, also be a substantial risk to urban water quality. The sulfur load of different debris components was studied and the sulfur content of different soil samples was evaluated and correlated to different parameters, such as position of the respective soil horizon within the soil profile or location of the soil profile in the surrounding terrain. With XANES spectroscopy, the averaged sulfur pool of whole soil horizons as well as of single debris components was studied. With X-ray fluorescence imaging and spectromicroscopy, soil aggregates, debris particles, and soil solution were analyzed on the micrometer and sub-micrometer scale. Different soil and debris constituents could be assigned to elemental distribution patterns within collected fluorescence maps, allowing for a detailed analysis of the sulfur pool and release from war debris in subsequent studies. These measurements show highly heterogeneous sample composition and clear gradients in sulfur speciation and oxidation state within single particles. The weathering of the anthropogenic material is therefore directly observable. A detailed understanding of this sulfur lixiviation is central to preserve urban water quality.

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