Zinc isotopes of particulate matter from the combustion of coal and a coal+tire-derived fuel blend

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Emissions from coal- and tire-derived fuel (TDF)-burning power plants are potential contributors to atmospheric Zn pollution. Tracing these Zn sources using stable isotopes could be a valuable tool. We evaluated the Zn isotopes (reported as δ^{66}Zn relative to a JMC standard) of coal, a mixture of 95wt% coal + 5wt% TDF, and the particulate matter (PM) derived from their combustion in a power generating plant. The average Zn concentrations and δ^{66}Zn values were 36 mg/kg and 183 mg/kg and +0.24‰ and +0.13‰ for the coal and coal+TDF, respectively. Samples of PM were collected from the bottom ash, cyclone-type mechanical separator, electrostatic precipitator, and the stack outlet. The δ^{66}Zn in the ash from the mechanical separator was the lightest measured, -0.48‰ for coal and -0.81‰ for coal+TDF. The δ^{66}Zn in the ash from the electrostatic precipitator showed a slight enrichment (relative to the starting material) in the heavier Zn isotopes, +0.36‰ and +0.20‰ for the coal and coal+TDF, respectively. The PM from the stack had the heaviest δ^{66}Zn in the system, +0.63‰ and +0.50‰ for the coal and coal+TDF, respectively. Initial fractionation during the generation of a Zn-rich vapor is followed by temperature-dependent fractionation as Zn condenses onto the PM. The isotopic changes of the two fuel types are remarkably similar, suggesting that their inherent chemical differences have only a secondary impact on the fractionation process.

Quantitative and qualitative morphological signatures of photosynthesis on early Earth

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Stromatolites may be Earth's oldest macroscopic fossils, however, it remains controversial what, if any, biological processes are recorded in their morphology. Although the biological interpretation of many stromatolite morphologies is confounded by the influence of sedimentation, conical stromatolites form in the absence of sedimentation and are, therefore, considered to be the most robust records of biophysical processes. We develop quantitative and qualitative models of the formation of vertical structures in modern photosynthetic mats that can be used to evaluate fossil stromatolites as records of biological and environmental evolution on early Earth.

We note that all modern conical stromatolites and many that formed in the last 2.8 billion years display a characteristic centimeter-scale spacing between neighboring structures. To understand this prominent organization, we consider the role of diffusion in mediating competition between stromatolites. Having confirmed this model through laboratory experiments and field observation, we find that organization of a field of stromatolites is set by a diffusive time scale over which individual stromatolites compete for nutrients, thus linking form to physiology. The centimeter-scale spacing between modern and ancient stromatolites corresponds to a rhythmically fluctuating metabolism with a period of approximately 20 hours. The correspondence between the observed spacing and the day length provides quantitative support for the photosynthetic origin of conical stromatolites throughout geologic time. Diffusion limitation also likely governs the growth of individual vertical structures in modern conical stromatolites in Yellowstone National Park. Their thick, porous laminae accumulate by faster growth of thin filamentous cyanobacteria within the upper ~ 0.5 mm region of the tips. The importance of diffusion in the growth of large Proterozoic conical stromatolites remains to be evaluated against the alternative hypothesis: light limitation. Regardless of the cone size, sub-mm and mm-scale morphological signatures of oxygenic photosynthesis may also be present in some Proterozoic and Archean conical stromatolites as old as 2.7 Ga. Quantitative and qualitative signatures of processes that build modern stromatolites thus strengthen the case for stromatolites as records of widespread photosynthesis on early Earth.