

The isotopic composition and controls on modern seawater sulfate

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The isotopic composition of seawater sulfate carries great utility for informing rates of modern biogeochemical cycling and tracking changes in oxidant budgets on geological timescales. These applications, and numerous others, lean on the analysis of modern seawater sulfate. Through decades of great work, it is broadly understood that the sulfate reservoir carries a long residence time (~ tens of millions of years), with the oxygen in sulfate turning over much more quickly (~ one million years). With this context, the modern ocean should carry a homogeneous isotopic composition. However, recent and quite provocative work suggests that oxygen minimum zones host a cryptic sulfur cycle (implicating potential effects on the isotope composition of both S and O in sulfate), while in parallel, experimental work on oxygen isotope exchange with S-bearing intermediates suggests that interpretations of ¹⁸O/¹⁶O in sulfate may also may also require updating.

To address these questions, we present ~ 200 measurements of modern seawater sulfate (³⁴S/³²S via SO₂ and ¹⁸O/¹⁶O via CO) through 10 vertical, 1-D profiles in different ocean basins with variable nutrient regimes. To complement these measurements, we targeted 4 of the profiles (BATS, SAFE and 2 profiles through oxygen minimum zones) for high precision ³³S and ³⁶S measurements generated via SF₆. With this, we first revisit decades of work on ¹⁸O and ³⁴S to place these data on a common scale (V-CDT and relative to SF₆), alleviating small but important differences in inferred compositions. The resultant isotopic composition of seawater sulfate (³⁴S/³²S, ³³S/³²S, ³⁶S/³²S, ¹⁸O/¹⁶O) allows for a series of major questions to be revisited. Of particular interest are: 1) Does the cryptic S cycle exist at a measurable scale? 2) What biogeochemical information is locked within the ¹⁸O/¹⁶O of sulfate? 3) What are the implications for the state of the marine sulfur cycle as a whole (is the modern cycle in steady-state or imbalanced)? We thank K. Casciotti, D. Capone, W. Homoky and A. Knapp for assistance in sample collection.

Iron geochemistry in redox-dynamic coastal wetlands: Consequences for trace element cycling in the environment

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Many acidic coastal wetlands in eastern Australia contain abundant reactive iron species within their sediments due to oxidation of bioauthigenic pyrite. Redox fluctuations occur periodically within these wetlands due to changes in hydrology that are driven by natural climate variations, anthropogenic drainage and wetland remediation practices. These redox fluctuations drive complex iron geochemical cycling in the environment, influencing the bio-mineralisation, mobilisation and redistribution of iron species and co-associated trace elements. Here, we employ case-studies to explore iron redox transformations and trace element cycling within these wetlands at a variety of spatial and temporal scales. We examine the consequences for sediments, surface water and groundwater quality.

Remediation of acidic, Fe-rich wetlands via inundation with seawater can lead to mobilisation and redistribution of As and extreme enrichment of poorly crystalline Fe(III) (hydr)oxides (~40% Fe w/w) in redox-interfacial sediments. This results from a complex interplay between tidally controlled hydrology, landscape topography, sediment geochemistry and macroporosity. Highly heterogenous intertidal sediments also contain organic-rich micro-niches, where sulfate reduction occurs alongside As-bearing, pedogenic jarosite. We examine this spatial pairing of thermodynamic opposites by reacting S(-II) with As-bearing jarosite under a range of pH conditions. We quantify the corresponding iron mineral transformations and co-associated arsenic mobilisation, re-partitioning and speciation.

Anthropogenic drainage of Fe-rich acidic wetlands can also cause off-site impacts on estuarine sediments and receiving waters. Impacts include; tidally modulated discharge of low pH (~3) and metal-rich waters; elevated reactive-Fe, trace elements and REE's in downstream sediments and porewaters; drastically altered sedimentary sulfur geochemistry and; enhanced trace elements in some estuarine plant species.

We also explore how large, seasonal flood events in Fe-rich coastal wetlands can drive landscape-scale reductive mobilisation of Fe into floodplain surface waters. Anthropogenic drainage of these anoxic, C and Fe²⁺-rich waters influences the subsequent magnitude and intensity of large-scale (>40 km) riverine hypoxic events.