

New applications of dissolved gallium in the oceans: Promoting increasingly routine measurement

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Dissolved gallium (Ga) is present in the oceans at picomolar concentrations, consistent with more routinely measured dissolved trace metals such as iron and aluminum, yet Ga exhibits comparatively less contamination risk, therefore easing sample collection and analysis. Shown here are three applications utilizing dissolved Ga concentrations in the ocean to study carbon dynamics, climate change, and mechanisms controlling sources and sinks of trace elements and isotopes (TEIs) in the ocean. Dissolved Ga is applied to 1) development of a model utilizing dissolved Ga profiles to estimate particulate abundance, 2) utilization of dissolved Ga as a new parameter differentiating Pacific and Atlantic source waters to the western Arctic Ocean, and 3) identification of differentially sourced plume waters of the Columbia River. Particulate abundance is vital to estimates of carbon flux and drawdown of CO₂ from the atmosphere. Dissolved Ga profiles are utilized here to model relative particulate abundance of CaCO₃ and opal, complimenting established sediment trap and U-Th methods, and providing potential for particulate abundance to be estimated on an increasingly routine basis. Arctic inputs from the Atlantic, identified by a strong dissolved Ga gradient, represent comparatively warm waters that threaten sea ice melt and CO₂ release if able to permeate Pacific source water stratification via upwelling over the extensive shelf area of the Arctic Ocean. Finally, the Columbia River plume provides a spatially and temporally unique environment, combining the plume induced salinity gradient with dynamic winds resulting in upwelling and downwelling conditions oscillating on the order of days. A plume endmember mixing model developed here utilizes dissolved Ga to identify offshore waters associated with formation under divergent wind conditions, influencing scavenging reactions and therefore concentrations of dissolved TEIs. Oceanographic study of complex multiparameter problems such as climate change requires a broad suite of variables including trace elements and isotopes. Results of this work encourage increasingly routine measurement of dissolved Ga concentrations and application to oceanographic research, including future GEOTRACES cruises.

Experimental dissolution of FeCO₃ under controlled sulfidic conditions

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In modern sedimentary environments, reduced Fe minerals (e.g. siderite; FeCO₃) tend only to precipitate under anoxic conditions in environments where high Fe(II)_{aq} pore water concentrations are accompanied by low rates of sulfide fixation. In contrast, siderite-rich sediments are extensively observed throughout the Precambrian rock record, both in marine shales and banded iron formations. However, rising atmospheric oxygen and the gradual rise in oceanic sulfate concentrations through time ultimately led to the increased sulfidation of reactive Fe minerals, and hence less preservation of siderite in marine sediments. Nevertheless, high concentrations of siderite, particularly during the Precambrian, persist in sediments that contain pyrite, likely due to sulfate limited conditions during diagenesis. However, the reactivity of siderite towards dissolved sulfide is currently unknown.

We investigate the kinetics of siderite dissolution in the presence of sulfide under varying conditions. The rate of Fe(II) carbonate dissolution was measured experimentally on samples of synthetic and natural FeCO₃, under controlled initial sulfide concentrations, mineral surface area and pH. We propose a reaction mechanism where carbonate species undergo direct substitution with dissolved sulfide on the mineral surface, ultimately producing FeS as a major reaction product. The rate constant (k_{Fe}) determined by the sulfidation of siderite is similar to other highly reactive Fe minerals, such as ferrihydrite, but up to 5 orders of magnitude faster than more crystalline Fe(III) oxides; with complete siderite dissolution occurring over just tens of minutes.

Our data suggest siderite in marine sediments is highly reactive towards dissolved sulfide, even in the presence of low sulfide concentrations. FeS formation is limited by sulfide (and hence, initial sulfate) availability, with experimental results explaining the stability of co-precipitating FeS and FeCO₃ species observed within some sedimentary environments. We therefore conclude that the remobilization of reduced Fe(II) minerals by sulfide may have contributed greatly to Fe cycling in both modern and ancient anoxic environments.