POTENTIAL ENVIRONMENTAL FATE AND BEHAVIOUR OF INORGANIC MANUFACTURED NANOPARTICLES IN THE AQUATIC ENVIRONMENT

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Introduction

Manufactured nanoparticles are usually defined as materials between 1 and 100 nm. They are widely used industrially and in consumer products because of their novel properties and ease of use; metals (e.g. Ag, Au, Fe) and their oxides (e.g. Ti, Zn and Fe) are of particular ubiquity and are produced in high volumes. It is certain that these nanoparticles are entering the aquatic environment in large volumes and are present in low but increasing concentrations. Once in the environment, these nanoparticles are subject to transformations due to alterations in the physical and chemical environment. Potentially the nanoparticles are subject to interactions with salts, natural organic macromolecules (NOM) such as humic substances and polysaccharides and are potentially altered by pH variation. Changes include surface alterations such as oxidation followed by dissolution and possibly regrowth and sulfidation followed by reduced dissolution especially for Ag, shape changes and coating or corona formation often leading to reduced aggregation or even diaggregation. Microbiological effects are also observed.

This paper will discuss these changes in relation to NP properties such as core material type, capping agent and size with particular examples drawn form ceria and silver. Both natural aquatic and toxicological media will be considered.

The sulfur isotope fractionation of dissimilatory sulfite reductase (Dsr)

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The sedimentary sulfur isotope record is an integrator of biochemical processes, among the most quantitatively important of which is microbial sulfate reduction (MSR). Interpretations of the sedimentary sulfur isotope record rely largely on our understanding of the fractionation associated with MSR. This has been empirically determined by numerous cellular-scale studies [1, 2]. Still, a mechanistic understanding of the controls on this fractionation has proven elusive. Here, through whole-cell (*in vivo*) and pure-enzyme (*in vitro*) experiments, we provide the next generation of quantitative constraints on the fractionation capacity of a key reductive step in the MSR metabolic network. We present data from experimental work with purified dissimilatory sulfite reductase (Dsr) protein, from which we can extract enzyme-specific isotope fractionation factors. These data represent the first enzyme level constraints on isotope fractionation during MSR, and serve as a template for evaluating the other prominent enzymatic reduction steps within this metabolic process. Akin to the early carbon isotope work on RuBisCO and its importance to the carbon cycle [3], the work presented herein will help to unlock the secrets of the sulfur cycle and ultimately allow for the full isotopic interpretation of Earth's sulfur isotope records.

Metabolic isotope models of MSR are at the heart of interpreting modern and ancient sulfur isotope records [2], but models require a quantitative understanding of the magnitude of fractionation at each node within the metabolic network. To provide fundamental boundary conditions for the metabolic fractionation models of MSR [2, 4], we measured the enzyme-specific (*in vitro*) isotope fractionation factors for the key enzyme Dsr ($^{34}\alpha_{Dsr}$) which catalyzes sulfite reduction. Our pure Dsr enzyme fractions are from the model bacterial sulfate reducer *Desulfovibrio vulgaris* Hildenborough (DvH). In replicate closed-bottle experiments, Dsr catalyzed sulfite reduction at the expense of molecular hydrogen. After freeze-quenching the reaction, products and residual reactant were collected and quantified. In all cases, elemental and isotopic mass balance was satisfied. Individual sulfur pools were isolated from the bulk solution by sequential precipitation. To support the novel *in vitro* experiments, we also performed a set of continuous culture controls and classical *in vivo* closed bottle growth experiments. During closed bottle experiments, MSRs were grown first utilizing sulfate, then sulfite or thiosulfate. These later experiments represent an attempt to get whole-cell quantification of the same reductive process that the pure enzyme experiments facilitated.

Taking an enzyme-level approach to understanding isotopic fractionation in MSR provide the most fundamental constraints on the biogeochemical sulfur cycle. It is through coupled biochemical and physiological observations that we are able to better quantify the key fractionations during MSR. As a result, we gain insight into the physicochemical controls on the directionality of sulfur flow through a bacterium and resulting net sulfur isotope fractionation signatures.

[1] Kaplan & Rittenberg (1964) *J. Gen. Micrbio.* 34, 195-212. [2] Johnston *et al.* (2007) *GCA* **71**, 3929–47. [3] Park & Epstein (1960) *GCA* **21**, 110–26. [1141-62. [4] Bradley *et al.* (2011) *Geobio.* 9, 446-57.