Biogeosciences Discuss.,
https://doi.org/10.5194/bg-2019-471-RC3, 2020

Biogeosciences Discussions

Interactive comment on "Cryptic role of tetrathionate in the sulfur cycle: A study from Arabian Sea sediments" *by* Subhrangshu Mandal et al.

Anonymous Referee #3

Received and published: 17 March 2020

Mandal and co-authors correctly point out tetrathionate, although seldom detected, may be an important intermediate in sulfur cycling in marine sediments. This is especially born out by the number of organisms that carry enzymes capable of reducing, oxidizing or even disproportionating tetrathionate. To examine potential tetrathionate sampling in marine sediments, the authors examined sulfur speciation in two long gravity cores, performed sediment slurry experiments, enriched tetrathionate reducing organisms, and performed an extensive metagenomic analysis on the two cores.

My expertise does not lie in the field of metagenomic analysis, so I will limit my comments to the sulfur analyses and experimental set-ups.

The authors took care to avoid oxidation artefacts by blowing inert dinitrogen gas over the cores and sample tubes. Was this done in a laminar flow hood? My experience is that blowing dinitrogen gas over samples in an open environment tends to entrain oxygen from the air and actually increases the flux of oxygen to surfaces. If the samples are taken out quickly and placed into vials containing inert atmospheres, this may not be much of a problem. However, the thiosulfate/sulfide data presented in Figure 3 shows that thiosulfate concentrations track those of sulfide with a 1:100 ratio. Could this be simply oxidation during sample handling?

The method for determining tetrathionate is highly unspecific. The thiocyanate resulting from the cyanolysis will include zerovalent sulfur contained not only in tetrathionate and polythionates, but also zerovalent sulfur contained in polysulfides and colloidal sulfur (See for instance Kamyshny et al., 2009, Geostandards and Geoanalytical Research, or Kamyshny, 2010, Marine Chemistry). The thiocyanate analysis is also problematic in saline solutions. There are far more compound specific methods for determining thiocyanate and tetrathionate (See for instance, Rong et al., 2005, Chromatographia; Bak et al., 1993, FEMS Microbiology Ecology).

In the slurry experiments, the authors used thioglycolate to reduce the media. Thioglycolate is a thiolic reducing agent that will reduce disulfide bonds. Did the authors test this on tetrathionate? I suspect that it may also react with zerovalent sulfur in colloidal sulfur, polysulfides and polythionates to release thiosulfate.

While the genomic approach may be adequate to describe the distribution of potential organisms involved in S cycling, given the non-specificity of the analytical methods employed, I am afraid that the authors cannot draw any conclusions at all about the sulfur intermediate oxidation state cycling in the cores or in the experiments.

The experiments also lead to rates of tetrathionate reduction and oxidation that are spectacularly high (nearly a thousand fold greater than rates that one would expect for sulfate reduction in these deep sediments). Also something is wrong with the units in

Figure 3 (umol/L*day*g?)

Finally, the authors have missed key earlier work on this topic that addresses specifically the distribution and cycling of tetrathionate, thiosulfate and sulfite in marine sediments: Bak et al., 1993; and in particular Zopfi et al., 2004, Distribution and fate of sulfur intermediates – sulfite, thiosulfate, tetrathionate and elemental sulfur – in marine sediments. Geol Soc America Sp. Paper 379, and more recently, Findlay, A. J., & Kamyshny, A. (2017) Turnover Rates of Intermediate Sulfur Species (Sx2-, S0, S2O32-, S4O62-, SO32-) in Anoxic Freshwater and Sediments. Frontiers in Microbiology, 8. https://doi.org/10.3389/fmicb.2017.02551

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