

# The enigmatic polythionate $S_4O_6^{2-}$ as a key junction in the sulfur cycle of continental slope sediments

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Benthic and sedimentary sulfur cycling has been studied extensively across the global ocean. Focus has typically been on the biogeochemical transformations of the redox end-members sulfide and sulfate, and also thiosulfate, a key junction in the network of sulfur species transformations in marine sediments. Tetrathionate or other polythionates, however, are seldom appreciated for their potential role(s) in marine sedimentary sulfur cycle, apparently because these sulfur species are highly reactive, and so do not accumulate in the environment to detectable quantities. Our investigation of ~300 cm sediment cores, drawn from across the Western Indian continental margin, underlying the perennially hypoxic waters of the Arabian Sea, revealed metabolically active communities of tetrathionate-forming, oxidizing, and respiring/reducing bacteria. Metagenome analysis along the sediment depths revealed (i) widespread occurrence of bacterial genes for all the three modes of tetrathionate transformation mentioned above, plus (ii) copious diversity of bacteria that are already known to render tetrathionate formation/oxidation/reduction *in vitro*. Phenotypes of slurry cultures in thiosulfate-/tetrathionate-containing media, alongside those of pure culture isolates, corroborated the *in situ* activities of tetrathionate forming, oxidizing, and reducing bacteria in conjunction with metatranscriptomic data. Albeit up to 11.1  $\mu$ M thiosulfate was detected in the sediment pore-waters using ion chromatography, tetrathionate was not measureable via spectroscopy involving cyanolysis. We concluded that thiosulfate oxidation by native chemolithotrophic bacteria could be the main source of cryptic tetrathionate in this ecosystem, even as abiotic origin of the polythionate could neither be ruled out nor confirmed from the geochemical data available. While the chemolithotrophs present *in situ* could further oxidize tetrathionate to sulfate, native sulfate-respiring microorganisms might convert it back to thiosulfate (and sulfide); sulfide (present up to 2.01 mM across the cores) may also reduce tetrathionate abiotically to thiosulfate and elemental sulfur. There being no possibility of photosynthetic production, or physical influx, of  $O_2$  in this sediment system, feasibility of the oxidative half of the tetrathionate cycle rests on the potential cryptic presence of bacteriogenic  $O_2$ . In that direction, metagenome analyses provided important clues which, via future investigations of geomicrobiology, may well resolve the oxidant conundrum of sulfur cycling in highly sulfidic (apparently anoxic) environments.