



Abiotic sulfide oxidation via manganese fuels the deep biosphere: Stable isotope evidence

S.H. Bottrell (1), M.E. Böttcher (2, 3), A. Schippers (2, 4), R.J. Parkes (5) and B.B. Jørgensen (2), R. Raiswell (1), J. Telling (5) and M. Gehre (6)

(1) University of Leeds, UK, (2) Max Planck Institute for Marine Microbiology, Bremen, Germany, (3) present address: Leibniz Institute for Baltic Sea Research, Warnemünde, Germany, (4) present address: Bundesanstalt für Geowissenschaften und Rohstoffe, Hannover, Germany, (5) Cardiff University, UK, (6) Helmholtz Center for Environmental Research, Leipzig, Germany (michael.boettcher@io-warnemuende.de, s.bottrell@see.leeds.ac.uk, a.schippers@bgr.de)

The deep biosphere in marine sediments consists of large populations of metabolically active, mainly not described Bacteria and Archaea (1, 2). Buried organic carbon as the main energy source for the deep biosphere is anaerobically oxidized via sulphate-, carbonate-, nitrate-, Fe(III)- or Mn(IV)-reduction (3, 4), however the overall microbial activity is limited by the availability of organic carbon and oxidants. Sulfate reduction has been identified as the most important of these processes (3, 4), yet sulphate is typically quantitatively removed in the upper few meters of marine sediments. Stable sulphur isotope fractionation of sulphur and oxygen are particular useful to characterize biogeochemical processes upon sediment-pore fluid interactions (5, 6). Here we used stable oxygen and sulphur isotope analysis to demonstrate that the oxidant sulphate is generated by anoxic sulphide oxidation in deeply buried sediments of the Cascadia margin and the Blake ridge, as well as in near-surface marine sediments. Experiments confirmed that Mn(IV)-containing oxide minerals abiotically oxidize iron sulfides such as pyrite and thereby producing ^{18}O depleted sulphate (with respect to water) in contrast to pyrite oxidation at low pH values. Oxidized manganese stored within the mineral fraction of marine sediments drives abiotic anaerobic sulphide oxidation, which together with microbial sulphate reduction, forms a closed sulphur cycle feeding the deep biosphere in marine sediments.

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- (2) Schippers et al. (2005) Prokaryotic cells of the deep sub-seafloor biosphere identified as living bacteria. *Nature* 433: 861
- (3) D'Hondt et al. (2002) Metabolic activity of the subsurface biosphere in deep-sea sediments. *Science* 295: 2067
- (4) D'Hondt et al. (2004) Distributions of microbial activities in deep subseafloor sediments. *Science* 306: 2216
- (5) Bottrell et al. (2000) Isotopic evidence for deep anoxic pyrite oxidation and stimulation of bacterial sulphate reduction. *Journal of the Geological Society* 157: 711
- (6) Böttcher et al. (2006) Sulfur isotope fractionation by the deep biosphere within sediments of the Eastern Equatorial Pacific and Peru Margin. *Proc. ODP, Sci. Res.* 201-109, 1