

Abiotic Carbon Fixation Promoted by Transition Metal Sulfides Under Hydrothermal Conditions

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Methanogens and acetogens utilize a broad array of metalloenzymes to autotrophically fix carbon under anaerobic conditions. Enzyme complexes such as acetyl-CoA synthase, hydrogenase, and pyruvate ferredoxin oxidoreductase, utilize predominantly iron-sulfur clusters, as well as nickel and cobalt to synthesise energy rich acetyl-CoA from the reduction of CO₂ by H₂ for both ATP synthesis and biosynthetic purposes.

Natural environments where transition metal sulfides exist in contact with fluids containing CO₂ and H₂ include the spectacular mineral sulfide dominant chimneys associated with deep-sea hydrothermal vents. We have been exploring the capacity of a broad range of pure transition metal sulfides to promote potentially biochemically useful carbon fixation. The sulfides include NiS, Ni₃S₂, CoS, FeS, FeS₂, (Ni,Fe)₉S₈, Cu₂S, Cu₃FeS₄, CuFeS₂, and ZnS.

The initial experiments set out to assay the catalytic qualities of these sulfides benchmarked against a model fixation reaction; the hydrocarboxylation of nonane thiol over a given catalyst in the presence of CO₂ and H₂. In order to ensure conditions that would allow valid comparison, high pressures (200 MPa, to enhance adsorption) and high substrate concentrations were employed. Somewhat surprisingly, all of the transition metals studied (excluding CuS) promoted the hydrocarboxylation reaction to some extent.

In the case of reactions run over NiS, a linear relationship between product yield and surface area is observed suggesting that the reactions are surface catalyzed. In the case of FeS, however, there is clear evidence of reaction of the mineral with nonane thiol and CO to produce carbonylated iron-sulfur organometallic complexes in solution (Cody et al. 2000). None of the other transition metal sulfides exhibited evidence of similar reactions, although such reactions cannot be discounted.

Subsequent experiments using methacrylic acid and itaconic acid over nickel yield di and tri-carboxylated products, respectively (Cody et al. 2001). These results point to a potential primordial carbon fixation pathway superficially similar that used by extant anaerobic autotrophs.

References

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Isotopic and geochemical evidence for changes in global weathering during the Toarcian OAE

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The widespread deposition of organic-rich mudrocks across N. W. Europe during the Toarcian ca. 183 Ma ago has been attributed to the influence of an oceanic anoxic event (OAE)¹. The precise cause(s) of the OAE, which is characterised by a sudden $\delta^{13}\text{C}$ excursion of -6‰ in marine organic matter and carbonate coincident with high levels of organic carbon, remain unclear; suggestions include expansion of an oxygen minimum zone, recycling of isotopically light CO₂ within a stratified basin², and massive dissociation of methane hydrates³. If it was the result of methane hydrate dissociation, a further expected outcome of the OAE would have been a substantial perturbation of weathering patterns and a sudden change (most likely an increase) in mean global temperature.

We investigate the relative timing and nature of these changes using high-resolution isotopic and geochemical profiles across the OAE and adjacent units from the Jet Rock (Yorkshire, U.K.) and the Posidonia Shale (Germany). Although the precise timescale of the $\delta^{13}\text{C}$ excursion remains unknown, its magnitude, onset and duration are similar to those of the Palaeocene/Eocene event. Previous work on samples from the Toarcian OAE⁴ has shown that the ¹⁸⁷Os/¹⁸⁸Os ratio of seawater was unusually radiogenic (≈ 0.80) at that time. Preliminary data from Yorkshire suggest that the seawater ¹⁸⁷Os/¹⁸⁸Os ratio fell suddenly after the end of OAE to values of ≈ 0.4 . These results are consistent with high levels of continental weathering during the OAE resulting in the enhanced release of radiogenic Os to the oceans, followed by less continental weathering and lower seawater ¹⁸⁷Os/¹⁸⁸Os ratios afterwards. The Os isotope changes are similar in nature to, but greater in size than, those reported for the Palaeocene/Eocene event⁵. The present study will establish the precise timing and magnitude of the changes in the ¹⁸⁷Os/¹⁸⁸Os ratio of seawater with respect to the deposition of high levels of organic carbon and other isotopic and geochemical excursions associated with the Toarcian OAE.

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