

Synchrotron X-ray fluorescence reveals the colourful chemistry of fossils

N.P. EDWARDS^{1*}, P.L. MANNING¹, H. BARDEN¹,
W.I. SELLERS², U. BERGMANN³ AND R.A. WOGELIUS¹

¹University of Manchester, SEAES, Williamson Research
Centre for Molecular Environmental Science, Manchester,
M13 9PL, UK (correspondance:
nicholas.edwards@manchester.ac.uk)

²University of Manchester, Faculty of Life Science,
Manchester, M13 9PT

³SLAC National Accelerator Laboratory, Linac Coherent
Light Source, Menlo Park, CA, 94025, USA

Despite the widely accepted biogenic origin and composition of sedimentary organic matter, identification of endogenous chemical signals within intact fossil organisms is often met with scepticism. Fossilisation processes (both biological and geochemical) are widely believed to eradicate any original biochemical information, but many studies have identified endogenous chemistry within fossils. However, these studies have predominantly focused on biological structures composed of relatively geo-stable molecules (e.g., lignin and chitin) and have used techniques that have limitations with regards to maintaining sample integrity that preclude many fossils from analysis and provide only small scale or no spatial information. Synchrotron Rapid Scanning X-ray Fluorescence (SRS-XRF) is an advance in XRF imaging that provides decimeter scale, 2D maps of elements in ppm concentrations in large (100x100x30cm) fossils at rapid acquisition rates (~30 s/cm² at 100 micron resolution). This allows the non-destructive visualisation of chemical variation of entire fossil organisms and their enclosing matrices *in-situ*, allowing the identification of biologically and geologically derived phases. This technique has shown that certain elements correlate with, and can reveal, discrete biological structures in a range of fossil and extant organisms. Additionally, X-ray absorption spectroscopy shows that the chemical inventory of fossil tissues commonly consists of organo-metallic and organo-sulfur compounds coordinated in a manner similar to comparable extant organisms. These findings support an endogenous origin for the observed fossil chemistry and thus fossil tissues may retain useful biochemical information. For example, previously unknown remnant tooth chemistry (phosphorus) within a 50 Mya fossil reptile has been revealed, and elements (e.g., copper) associated with dark eumelanin pigmentation have been identified and mapped within feathers of an exceptionally preserved 120 Mya Chinese bird.

Coupled Fe-S-P cycling in sediments of an oligotrophic coastal basin and the role of anaerobic oxidation of methane

MATTHIAS EGGER, TOM JILBERT
AND CAROLINE P. SLOMP

Department of Earth Sciences, Utrecht University, The
Netherlands

Studies of phosphorus (P) dynamics in coastal marine sediments typically emphasize the role of coupled iron (Fe), sulfur (S) and P cycling for sedimentary P burial and release. Here, we present field results suggesting that this model may have to be extended to include interactions of reactive Fe(III) phases with methane (CH₄).

Using pore water and solid phase analyses for sediments from an oligotrophic coastal basin (Bothnian Sea) we provide evidence for the formation of Fe-bound P, possibly vivianite (Fe₃(PO₄)₂·8H₂O), below the sulfate/methane transition zone (SMTZ). Solid phase Fe and S profiles indicate that the SMTZ in these sediments has recently shifted upwards to its current position close to the sediment-water interface (< 10 cm). This upward shift is attributed to an enhanced rate of methanogenesis driven by an increased eutrophication over the past decades. Below the SMTZ, extremely high Fe²⁺ concentrations (> 2 mM) are observed, and supersaturation with respect to vivianite is reached. We suggest that the exceptionally high dissolved Fe²⁺ concentrations in this non-sulfidic zone may be explained by anaerobic oxidation of methane (AOM) coupled to the reduction of Fe-oxides. Dissimilatory iron reduction appears to be unlikely due to the presence of relatively refractory organic matter. Instead, the concurrent presence of both abundant CH₄ and reactive ferric Fe rather suggests Fe reduction coupled to AOM. The resulting release of Fe²⁺ into the pore water and subsequent formation of Fe(II)-P provides an important sink for P released during reductive dissolution of Fe-oxides within and below the SMTZ. If this P sink below the SMTZ would be absent this would likely lower the P burial capacity and enhance the diffusive P flux out of the sediment back into the overlying water column.

Thus, while AOM coupled to Fe reduction likely accounts for only a relatively small percentage of CH₄ removal, our study suggests that the impact on the sedimentary P cycle could be large.