Iron: Potential Fuel of the Deep Biosphere?

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It is usually assumed that iron weathered at the Earth's surface and deposited into sedimentary environments occurs as Fe(III), mainly as oxides and silicates. Here, we are interested in the extent to which Fe(III) survives early diagenesis and remains available as a terminal electron acceptor for use by microbes inhabiting deeply buried sediments. We have studied the distribution and valence of iron within rapidly deposited upper slope mudstones (0.5-1% TOC) from the foot of the Mississippi Delta. Sample well depths range from 1500-6900 metres, corresponding to a temperature range of 33–145°C. Wet chemical, XRD and electron beam approaches have been integrated to determine the location of iron and the stability of its valency during diagenesis.

Total Fe concentrations average 4.2 ± 1%, the majority of which is Fe(III) , with only a small fraction present as pyrite and carbonate. Iron oxides persist throughout the section and comprise around 10% of the total Fe. Around 90% of the total Fe is bound within silicates. Wet chemical analysis of the silicate fraction shows that at temperatures below ~115ºC, most silicate Fe occurs as Fe(III), mainly within smectite and partly within detrital chlorite and mica. XRD and AEM data indicate that the conversion of smectite to illite (temperatures between 115-130ºC) results in the loss of Fe from the illite-smectite phase and its partial relocation into Fe-rich chlorite. The bulk silicate data are supported by data from EELS, here used for the first time to track changes in the valence of silicate Fe during burial diagenesis.

What are the implications of these data for the deep biosphere? Firstly, they show that sufficient Fe(III) is buried into deep mudstones to convert every atom of organic carbon to carbonate. However, the extent to which this potential energy source is actually tapped remains uncertain. Most Fe-reduction in these sediments occurs during the recrystallisation of smectite, at temperatures in excess of those normally associated with the base of the biosphere. Furthermore, iron oxide, the most reactive Fe phase buried below the early diagenetic zone, is present in similar amounts throughout the sediment pile. If Fe(III) is acting as a terminal electron acceptor in these deeply buried muds, either its influence is small and/or the rates of metabolism are extremely low.

Carbon isotope composition of bioturbation infills as indication of the macrobenthic-colonization timing across the Cretaceous-Tertiary boundary (Agost section, SE Spain)

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The Cretaceous-Tertiary (K-T) boundary section of Agost (SE Spain) is one of the most complete K-T boundary sections. Here, the K-T boundary is marked by a 2 mm-thick rust-red layer containing the impact evidence and representing the distal ejecta of the Chicxulub impact. A relatively abundant trace-fossil assemblage is observed in the *Plummerita hantkeninoides* Biozone (Late Maastrichtian). The trace-fossil assemblage is mainly composed of traces filled by dark-colored sediment (*Chondrites*, *Zoophycos*, *Thalassinoides* and *Planolites*), and secondarily structures filled by light sediment (*Chondrites*, *Zoophycos*, *Planolites*, and some unident-ified structures). Difficulties in recognizing trace fossils affecting the K-T boundary layer, as well as obtaining a biostratigraphic characterization of these traces avoided a conclusive interpretation on the timing of this macro-benthic colonization at the Agost section. Since the carbon isotope composition of uppermost cretaceous and lowermost tertiary sediments is clearly different as con-sequence of the sudden decrease in ocean productivity, we determined the $\delta^{13}C$ of the carbonate fraction of dark and light filling materials from passively filled bioturbations to discriminate between traces fossils generated at different moments during the K-T boundary transition. The data obtained revealed a clear differentiation related to the type of analyzed material: (a) Most of the $\delta^{13}C$ values are in a range between 0.21 to 1.22‰; all of them corresponding to samples from dark filling material. (b) Few samples show a $\delta^{13}C$ higher than 1.6‰, corresponding to light colored sediment filling bioturbation. These data evidence a significant discrimination between light-filled traces, with $\delta^{13}C$ values higher than 1.6‰ PDB, coherent with those obtained from uppermost cretaceous sediments, and dark-filled bioturbations with $\delta^{13}C$ values between 0.21 and 1.2‰ PDB, in accordance with those obtained from lowermost tertiary materials. Thus, the obtained data evidence that the macrobenthic colonization occurred at different phases across the K-T boundary interval, pre- and post- impact event corresponding to light and dark-colored traces, respectively.