Revealing the signature of ancient biochemistry with Soft X-rays

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The preservation of organic fossils extends back to the dawn of the Cambrian. Notwithstanding such an extent of preservation, the preservation of intact or molecularly identifiable biological molecules extends only a much shorter interval of time, 10's of millions of years. The preservation potential of organic fossils is related to the emergence of recalcitrant biopolymers, e.g. polysaccharides and in the case of vascular plants, lignin. The disappearance of a molecular signal of discrete biopolymers results from diagenetic molecular transformation, either through thermogenic and/or microbial processes. Over the past decade we have been developing the use of Scanning Transmission X-ray microscopy (STXM) and micro-spectroscopy utilizing the fine absorption fine structure on carbon's, nitrogen, and oxygen K-edges, i.e. X-ray Absorption Near Edge Structure (XANES) spectroscopy. Exploiting the high-energy resolution of the STXM monochromator (5000 $\Delta E/E$) and the spatially resolving power of the soft X-ray optics (25 nm) has allowed us to explore sub-micron biochemical complexity that is preserved in ancient organic fossils. Our goal has been to use the signature of sub-micron chemical differentiation to address issues related to biochemical evolution; e.g. searching for the evolutionary emergence of lignin by studying the fossil record of extinct plants near the phylogenetic root of plants [1]. Most organic fossils, either derived from arthropod cuticle or vascular plant tissue have been subjected to considerable molecular modification, yet with a judicious choice of absorption energy, remnant chemical differentiation can be still observed. Chemical differentiation is a hallmark of tissue that was originally composed of two or more biopolymeric material. For example, lignin and cellulose in the case of vascular plant tissue. Traditionally, the loss of characteristic spectroscopic and/or molecular features associated with polysaccharide was interpreted to suggest that all carbon associated with polysaccharide had been removed from the organic fossil. Thus, distorting understanding of the nature of the actual molecular transformation chemistry. Studies employing STXM and micro-XANES now reveal a more complex story in which the presence and retention of a substantial amount of polysaccharide derived carbon is an essential aspect of organic matter preservation in ancient organic fossils [2].

[1] Boyce K. C., et al *Geology* 30, 1039-1042.
[2] Cody G. D., et al (2011) *Geology* 39, 255-258.

Objective mapping of the geographical distribution of εNd in seawater and outlook for past and present Nd budget in the oceans

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Neodymium (Nd) isotope composition (expressed in εNd notation, in per 10 000) in sediment cores are commonly used in paleoceanography and paleoclimatology to reconstruct changes in ocean circulation and/or continental weathering over the last thousands to tens of millions of years. A good understanding of the present processes affecting the transport of Nd in the oceans, the different sources and their relative influence is a prerequisite for its use in paleoceanography.

We compiled all the present data available for direct seawater measurements and authigenic fractions of core-top sediments in order to plot up-to-date interpolated maps displaying a depth averaged as well as a the deep distributions of present seawater εNd, using optimization methods. We observe clear patterns of Nd injections in the different basins, especially the clearly distinct isotopic signature of the different basins, the deep Atlantic circulation, the deep circum Antarctic water masses penetrating Pacific ocean, the Indonesian througflow into the Indian ocean, the Iceland local influence, the Himalayan rivers discharge, the East Pacific Rise local contribution… We also compared this distribution to an interpolated map of detrital εNd data, which show similar patterns. The misfits obtained help us to discuss what both types of data (sediments and seawater measurements) really tell us in such an approach.

All these observations lead us to distinguish different geographical groups consistent with εNd distribution, and to conclude on the major role of the rivers as source of Nd in seawater, the important vertical transfer in the water column from the superficial layers to the bottom and the limited exchange of Nd between the different ocean basins, due to a short residence time. These conclusions lead to conceptualize a model on Nd cycling in the oceans that will be presented in a joint paper by C.J. Allègre. Simulations on a coarse box model and on a matricial form of the MIT GCM are still in progress and will be helpful to put this model to the test.