Imaging traces of life in metamorphic rocks using Raman, STXM and NanoSIMS

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Detecting traces of life in the geological record can be challenging, especially in ancient rocks, as most of them can completely lose their original biochemical structure. Recently, we observed Triassic metasedimentary rocks from the french Alps[1], which contain organic fossils of lycophyte megaspores displaying a well preserved morphology although they experienced high-grade metamorphism (~360°C, ~14kbars, i.e. 40 km depth). By combining Raman Microspectroscopy (RM), Scanning Transmission X-ray Microscopy (STXM) and X-ray Absorption Near Edge Structure (XANES) spectroscopy, we have observedchemical and structural heterogeneities of organic matter (OM) composing the spore walls at a submicrometer scale, which we interpreted as remnants of original biochemical heterogeneities. Moreover, we also evidenced the systematic occurrence of a (Fe-Mg)-rich calcium carbonate corona (ankerite) along the spore walls, chemically different from the pure calcium carbonate matrix (calcite) [1, 2].

Here we present maps of the carbon isotopic composition (δ^{13}C) of OM and carbonates at high-spatial resolution (200nm), collected by NanoSIMS N50 ion microprobe. These maps reveal that (1) the δ^{13}C of metamorphic OM is comparable to the original isotopic signature of a non-metamorphosed spore wall (δ^{13}C=-35‰), and (2) the ankerite (δ^{13}C=-10‰) has significantly lighter carbon than the calcite (δ^{13}C=0‰), supporting the hypothesis that this ankerite corona might result from the diagenetic replacement of an original cellulose inner layer composing the spore walls. This study illustrates the capabilities of RM, STXM and NanoSIMS to provide *in situ* observations indicative of biogenicity, even for metamorphic fossils.

[1] Bernard *et al*. (2007) *EPSL.* **262**, 257-272. [2] Bernard *et al*. (2008) *Appl. Spec.* **62**, 1180-1188.

CO_2 pulses and carbonate and biotic crises in the Mesozoic

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The Mesozoic is characterized by a number of rapid changes in the mode of global carbon cycling documented as positive excursions in the marine and terrestrial carbon isotope record. Several of these large perturbations are preceeded by a negative carbon isotope spike and they are accompanied by major biotic crises and/or extinction events. Many of these events have been related to massive CO_2 inputs to the ocean and atmosphere related to the emplacement of Large Igneous Provinces. The biosphere was affected by massive C-cycle perturbations to a variable degree.

Contrasting response of the biosphere is observed if two of the most extreme C-cycle perturbations in the Mesozoic, the Triassic-Jurassic (T-J) Boundary Event and the Oceanic Anoxic Event 1a (OAE1a) in the Cretaceous are compared. The Triassic-Jurassic boundary C-isotope anomaly is coupled with a major biotic extinction event while the Early Aptian C-isotope excursion coincides with widespread biocalcification crises in neritic and pelagic environments but with no major extinction. New stratigraphic data at high resolution (10^4 years) from a pelagic T-J boundary section from the Budva Basin in Montenegro allow for the first time to document the sudden termination of carbonate deposition in a pelagic environment, coinciding with the T-J extinction event. A very high-resolution study of OAE1a indicates that the short-lived negative carbon isotope excursion coincides with a biocalcification crisis in nannoconids, which is synchronous to the increase in volcanism-induced pCO_2 as revealed by compound-specifc carbon isotope analyses. We propose that ocean acidification following a massive carbon release to the atmosphere and ocean triggered both observed carbonate crises. Differing oceanographic boundary conditions and tempo of perturbation may explain contrasting response of end-Triassic and of Aptian biota to volcanic CO_2 pulses.