Nutrient replenishment in late Palaeozoic oceans

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During the last decade a number of researchers put forward the hypothesis that land plant evolution during the Devonian and Carboniferous had enhanced nutrient fluxes to the marine realm and hence ultimately caused many of the extinction events concurrent with widespread marine anoxia. But there is no indication whether the anoxic conditions were caused and sustained by marine productivity fuelled by enhanced riverine nutrient input or by effective recycling of nutrients within the oceanic basins.

In modern oceans the two situations could be distinguished regarding the use of nitrogen compounds and hence the resulting nitrogen isotopic composition of the organic material: Effective recycling of nitrogen or even additional fixation of dinitrogen is reflected in low $\delta^{15}N$ values – productivity enabled by nutrient replenishment via upwelling or additional riverine input is reflected in elevated $\delta^{15}N$ values.

The question, whether a primary $\delta^{15}N$ signal of late Palaeozoic sediments could had been preserved, several investigations have been carried out. The influence of temperature on the nitrogen isotopic composition of sediments hitherto has been neglected or not been taken into account in the literature. But a detailed study of a maturity trend of Toarcian sediments of the Hils syncline revealed significant changes of the $\delta^{15}N$ values with the onset of oil generation.

Therefore 212 immature late Palaeozoic rock samples have been investigated regarding their nitrogen isotopic composition. The predominant marine origin of the organic matter was confirmed by biomarker analysis. Interestingly, more than 95% of the Devonian and Early Carboniferous samples have $\delta^{15}N$ values between –2 and +2‰, whereas the Late Carboniferous and Permian samples exhibit $\delta^{15}N$ values between +5 and +15‰. This could point to a long term influence of increased riverine nutrient input.

But at the time of extinction events there is a superimposed trend to lower $\delta^{15}N$ values. At the Frasnian-Famennian boundary event at two different localities a shift of -2‰ is evident. This would imply that enhanced riverine nutrient inputs could not have been responsible for the extinction events, but on the long term may have moved the ecosystem to a vulnerable state – until its communities had adopted to the new nutrient fluxes.

The primary nature of the preserved $\delta^{15}N$ signal of the rocks is corroborated by first nitrogen isotopic analysis of isolated porphyrin fractions and single porphyrins. These may enable to differentiate different nitrogen sources for the primary producer community in the past ocean and shed light on possible explanations for the very low $\delta^{15}N$ values in the Devonian and Lower Carboniferous.

Field evidence for abiotic syntheses of organic matter in hydrothermal conditions

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Fluid inclusion volatile and aqueous phase species confined to 72 vein quartz collected from Hishikari mine, an epithermal gold deposit in Japan were recovered by crush and analyzed by gas and ion chromatography. Temperature (T) and oxygen fugacity (fo_2) involved in chemical reactions for $CO/CO_2/CH_4$ system were estimated. The temperature ranges from 400°C to 600°C, which is higher than homogenization temperatures of fluid inclusions (ca. 200°C). This shows that the equilibration is quenched at higher temperatures than the deposition temperatures of host minerals, owing to the low kinetic rate in the carbon gas system. On fo_2 vs. T plots, data points cluster thickly along NNO buffer curve. This trend is similar to that for fumarole gases around felsic lava volcanoes, and this suggests that the hydrothermal fluids under consideration were genetically related to felsic magama at depth, as inferred from geological evidence. Formic acids and acetic acids ubiquitously occur in the samples. Assuming that the equilibrium temperature for the two organic acids is the same as that for $CO/CO_2/CH_4$ system in each sample, we calculated fo_2 involved in the relation; this fo_2 is consistent to that for $CO/CO_2/CH_4$. Thus, both volatiles and organic ions belong to a common thermodynamic condition prevailing in the hydrothermal system. Even if the original materials of the detected organics, particularly carbon, have been derived from the host sediments of quartz veins and hence they had been biogenic, they have undergone chemical evolution at high temperatures and have been reorganized into new species during the formation of the ore deposits. This process is equivalent to abiotic genesis of organic species.