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Ammonium in Neoproterozoic and Palaeozoic sediment records a tracer for climate changes?

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Focus of our studies was to light up the fate of nitrogen in ancient sediments, where NH_4^+ is the dominating nitrogen species. The ammonium nitrogen in sediments is derived from organic matter. The nitrogen isotopic signature of organic matter depends on the metabolism and is related to the kind of nutrient and its availability as well as the biological production rate. During diagenesis, coupled organic-inorganic geochemical processes result in the mineralization of nitrogen. The formed ammonium may be incorporated in clay minerals. The fixed structurally bonded NH_4^+ is not easily released or exchanged and records the chemistry of the diagenetic environment in the sediments (e.g. Williams et al., 1989, 1991, 1995; Compton et al., 1992; Lindgreen, 1994).

Devolatilization processes of NH_4^+ during regional and/or contact metamorphism decrease the ammonium content and enrich ^{15}N in metasediments (e.g. Haendel et al. 1986; Bräuer et. al. 1990; Bebout and Fogel 1992; Bebout 1997 and Mingram and Bräuer 2001). There has been little work on the distribution of ammonium and its $\delta^{15}N$ values in ancient low metamorphic sediments. Therefore, this study wants to bridge the gap between investigations on nitrogen of early diagenetic sediments and studies of NH_4^+ in metamorphic rocks.

For this reason, the concentration and isotopic composition of NH_4^+-nitrogen and organic carbon have been determined in anchimetamorphic sedimentary sequences from different regions of Central Europe. The pelitic rocks and black shales stem from the Saxothuringian (Thuringia, signed as TH), the NE German Basin (East Avalonia) and from an offshore-borehole in the Baltic Sea (Baltica, signed as G 14).

The stratigraphic units span from Neoproterozoic to Triassic age. Correlations between NH_4^+ and ^{15}N as well as TOC and $^{13}C_{TOC}$ will be presented. About 240 samples were analyzed. The TOC contents range from 0.05 to 24 wt. % and the $\delta^{13}C$ values from -35 to -22 ‰ PDB. The fixed N contents (NH_4^+) range from 50 to 4000 ppm and the $\delta^{15}N$ values vary between -2.4 and 6.6 ‰. NH_4^+- and TOC contents are positively correlated. This correlation does not hold for the black shales. $\delta^{15}N$ and NH_4^+ are inverse correlated due to the relationship between nutrient supply and utilization. The higher the nutrient supply, the lower the $\delta^{15}N$ values.

A clear inverse correlation was found between $\delta^{15}N$ and $\delta^{13}C_{TOC}$ of the G 14 samples deposited under strictly marine conditions. A similar trend can be seen in the TH sediments if the Neoproterozoic samples are excluded.

Finally, it should be proved whether sedimentary $\delta^{15}N$ has the potential to track early changes in nitrogen cycle and past climate changes. The high TOC contents of the Cambro-Ordovician and Silurian black shales are more caused by the extremely low redox potential than by unusually high biological production. In contrast to that the Lower Carboniferous TOC rich sediments were a consequence of a high biological production rate and evolution of live forms.

The ^{15}N isotopic signature of the mineralized organic matter could be preserved by the NH_4^+-incorporation in clay minerals, but only if the supplied clay minerals are able to recrystallize. Detrial clay minerals deposited under arid climate conditions offer little possibility for K/NH_4^+ exchange.

Nitrogen isotopes provide a useful tool to evaluate the nitrogen consumption in relation to its biogeochemical cycle and the palaeoclimatical situation.

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