

Nitrogen Isotope Systematics of Modern and Ancient Immature Sediments: Isotopic Composition and Percentage of Different Nitrogen Forms

Christine Ostertag-Henning (costerta@geol.uni-erlangen.de) & Christian Ostertag-Henning

Department of Geology, Schlossgarten 5, D - 91054 Erlangen, Germany

Inspired by the applications of nitrogen isotopes in modern ecological and oceanographic studies over the last decade a number of articles dealing with nitrogen isotopes in Mesozoic and Paleozoic rocks have been published. As the absolute $\delta^{15}\text{N}$ values of the bulk sediment or the kerogen often were suspiciously low (often negative) the interpretations were mainly based on the relative shifts within sets of samples. Because of these compared to nowadays marine sediments depleted values one author has argued for a completely different importance of parts of the nitrogen cycle (nitrogen fixation vs. changed ratios of denitrification or nitrification) during the earlier history of the earth. This study attempted to clarify means to detect altered nitrogen isotopic signals in immature ancient sediments and to point to the nitrogen forms most probably retaining a primary isotopic signal. In addition, the transformations of different N forms during diagenesis should be unravelled by quantifying inorganic and organic compounds released in a sequential extraction scheme. As model sediments (ages in brackets) one lacustrine (20 yrs), one marine (28 ka), and two Paleozoic immature rocks (345 Ma, 367 Ma) with similar TOC (1.9 to 2.6%) and TN (0.11 to 0.29%) contents but differing bulk $\delta^{15}\text{N}$ (-0.4 to +6.4 per mil) values have been chosen. In triplicate extractions and analyses free nitrate and ammonium, adsorbed ammonium, adsorbed amino acids and sugars, with organic solvents extractable N-compounds (EOM), hydrolysable amino acids and other N-compounds, and the kerogen were quantified and isotopically characterized. Both Paleozoic samples were classified as immature according to pyrolysis and biomarker maturity indices. First results indicate

that in the Paleozoic rocks the kerogen accounts for 61 to 68% of total nitrogen, with the hydrolysable amino acids fraction being second in importance. The modern sediments are characterized by higher amounts of not yet quantified nitrogen contained probably in amino sugars. The EOM accounts for 3 to 7% of the total N, with highest values in one porphyrin-rich Paleozoic sample. Adsorbed ammonium and free nitrate only contribute negligible amounts compared to the total nitrogen content. The two modern samples contain substantial concentrations of labile chlorophyll-degradation products, which are absent in the Paleozoic rocks. In the EOM of the 367 Ma sample a series of carbazoles and benzo[b]carbazole were present. The porphyrin concentrations differ markedly between the two Paleozoic samples. The nitrogen isotopic composition of different fractions in the two modern samples exhibit a consistent pattern with the bulk sediment enriched by ca. 1 per mil to the kerogen, and the EOM depleted ca. 2 per mil to the kerogen. This is contrasted by an enrichment of 0.6 per mil of the kerogen compared to the bulk sediment in the 345 Ma sample with the EOM being depleted by 4.6 per mil. This is interpreted as result of generation of light ammonium and N-compounds and concomitant enrichment of the kerogen during late diagenesis, therefore the bulk isotopic signal of this sample should not be used for paleoecological reconstructions. The 367 Ma sample exhibits nearly identical $\delta^{15}\text{N}$ values for kerogen and bulk sediment, the EOM is depleted by 0.7 per mil. An explanation for this pattern has to await the isotopic measurements of the adsorbed ammonium, the amino acids and the porphyrins.