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NITROGEN IN PALAEOZOIC SHALES OF THE CENTRAL EUROPEAN BASIN - CONCEPTS FOR N_2-RICH NATURAL GAS RESERVOIRS

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Carboniferous, Permian, and Triassic natural gas reservoirs in the Central European Basin (CEB) regionally contain high percentages of molecular nitrogen (N_2). The major gas source rocks are Carboniferous coal-bearing strata of Westphalian age and marine black shales of Namurian and Viséan age. Palaeozoic sedimentary sequences are also considered the most likely sources of the molecular nitrogen. The highest nitrogen contents are found within Rotliegend reservoirs of the North East German Basin (NEGB) where thick, highly mature Palaeozoic sedimentary sequences are present.

The nitrogen geochemistry of Carboniferous shales from the CEB has been studied by elemental analysis, stable isotope mass spectrometry and non-isothermal open-system pyrolysis. The principal goal was to explore the contents, isotopic composition ($\delta^{15}N$) and the speciation of nitrogen in organic and inorganic constituents of these sequences. Current concepts consider both sedimentary organic matter and ammonium-bearing minerals as primary nitrogen sources (Krooss *et al.*, 2005; Mingram *et al.*, 2005).

Total nitrogen contents of Namurian shales from four deep wells (4400 - 7000 m) in NE Germany ranged from ~500 to ~2700 ppm. Between 50 and 100 % of this nitrogen is inorganic and fixed as ammonium. Although there is a clear facies trend from marine sediments in the lower part to paralic and terrestrial sediments in the upper part of the Carboniferous sequence, the corresponding $\delta^{15}N_{fix}$ values are within a narrow range (+1 to +3.5‰) along the entire profile while the isotopic composition of the thermally liberated nitrogen was consistently lighter by 3-5‰. Low nitrogen contents (as low as 460 ppm) and high $\delta^{15}N$ values (up to +5.6‰) in one well in the basin centre suggest a significant release of nitrogen (as NH_3 and/or N_2) associated with ^{15}N enrichment in the residual nitrogen.

Open-system non-isothermal pyrolysis of shales and isolated kerogen has revealed the presence of inorganic nitrogen species with relatively low thermal stability (decomposition of nitrogen-containing minerals between 450 and 700°C) in marine Namurian A shales (Figure 1, left). Inorganic nitrogen components in the paralic Namurian B facies (Figure 1, right) show a higher thermal stability range (decomposition range 600 – 800°C) while nitrogen in

kerogen and coals is fixed in very refractory compounds decomposing in the 700 – 1200°C temperature range. The presence of significant amounts of inorganic nitrogen is also reflected in the high N/C_{org} (atomic) ratios of the Palaeozoic shales ranging between 0.035 – 0.108. Thus the on-line isotope analysis indicates the presence of precursor pools with different thermal stability and nitrogen isotopic composition.

While pyrolysis is being used in this study as an experimental/analytical tool to screen the N_2-liberating entities in terms of their thermal stability, the nature of the N_2 generation processes in deep sedimentary systems on a geologic time scale is still not understood. These processes appear to be both thermally and chemically controlled. N_2 liberation can be envisaged as a single-step process or as multi-step process involving intermediate products such as ammonium. The combination of laboratory data, field data and numerical simulations is expected to further constrain the time, temperature and fluid flow conditions and result in an improved understanding of this complex issue.

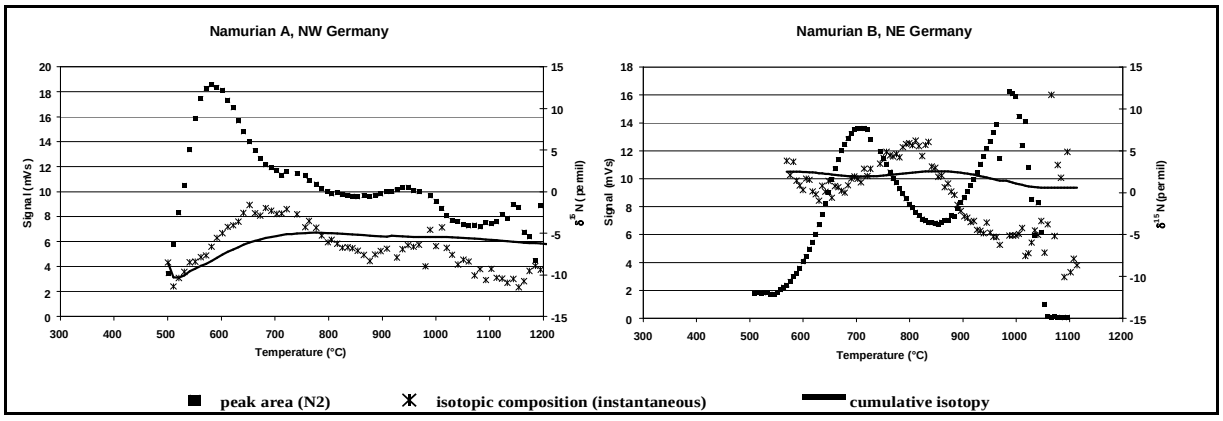

Figure 1. N_2 pyrograms and corresponding $\delta^{15}N$-values from Namurian A and B shales

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