



0.1 The generation and migration of nitrogen in the North-German Basin

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Comparative studies on the fixation and release processes of nitrogen in Palaeozoic sediments from different parts of the Central European Basin (CEB) show that, especially the eastern part of the North German Basin represents a key area for the investigation of nitrogen accumulation in natural gas reservoirs. In this part of the basin, very nitrogen-rich natural gases are preferentially stored in Rotliegend reservoirs.

The principal source of nitrogen in sediments is the decomposition of organic material during diagenesis that results in inorganic nitrogen compounds such as ammonium. This NH_4^+ can be adsorbed on mineral surfaces or substituted for K^+ on the interlayer sites in clay-minerals. Preliminary studies show that Palaeozoic sediments have a high potential to fix nitrogen in the form of NH_4^+ . The studied Palaeozoic shales of the CEB show total nitrogen contents up to 3000 ppm with an ammonium portion up to 90 % mainly fixed in illites. This indicates that illites and micas act as efficient nitrogen storage sites during burial.

Ammonium either can be released from silicates by thermal decomposition, by cation exchange reaction or oxidation. Namurian shales from a well in the eastern part of the North German Basin show a significant decrease in ammonium coupled with a shift in $\delta^{15}\text{N}$ suggesting a large scale nitrogen release. Calculations of nitrogen loss and isotopic fractionation in comparison to relative unaffected Namurian shales reveal that more than 30 % of nitrogen was released as ammonium. Carbonate displacement, chloritization, Sr and NH_4^+ depletion, and K enrichment implies brine-induced cation

exchange reactions as a potential ammonium release process.

Intensive interaction of brines with Palaeozoic shales is further evidenced by fluid inclusion data of fissure minerals and sulfur isotopic compositions of abundant anhydrite from fissures. Preliminary results of K-Ar dating on NH_4^+ -bearing illites indicate that illite was formed not only during burial diagenesis but also during brine migration events. The characterization of all these processes will contribute to a detailed p-T, geochemical, and chronological description of nitrogen generation and migration during stages of subsidence and inversion in the NGB.