Nitrogen isotope geochemistry of ammonium during diagenesis and brine events in sedimentary basins

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The isotopic composition of ammonium fixed in minerals or availabel in fluids is a sensitive monitor for the thermal history and hydrothermal alteration events in sedimentary basins. Our studies focus on the processes and relative timing of NH_4 fixation, its behaviour during deep burial, and the release and migration of nitrogen in the North German Basin (NGB), Central Europe. NH_4 content and isotopic composition were measured in Palaeozoic sedimentary, metamorphic and magmatic rocks, and in formation waters.

The primary source of nitrogen in sediments is the breakdown of organic material that results in inorganic nitrogen compounds such as ammonium. NH_4^+ may be adsorbed on mineral surfaces or substituted for K^+ on the interlayer sites in clay-minerals. In this form, ammonium may be deeply buried into the sedimentary basin. The studied Cambrian to Carboniferous sediments of the NGB show a high storage potential for nitrogen in form of NH_4 mainly fixed in illites or micas.

Ammonium either can be released from silicates by thermal decomposition, cation exchange reaction or oxidation. Studies on Variscan Ordovician metasediments display a continuous loss of nitrogen (N₂ or NH₃) at temperatures higher than 400°C. This process can be postulated for all sediments buried deeper than 15 km in the NGB. Furthermore, a significant shift in δ^{15} N and depletion in fixed-NH₄ found in Namurian shales indicates a nitrogen loss under diagenetic conditions. Carbonate displacement and chloritization in these shales as well as Sr and NH₄ depletion coupled with K enrichment in illites suggest brine-induced K-NH₄ exchange reactions. Intensive interaction of brines with the shales is further evidenced by fluid inclusion data from fissure minerals.

Preliminary results of K-Ar dating on NH_4 -bearing illites imply that illite was formed not only during burial diagenesis but also during brine migration events associated with NH_4^+ or K⁺ exchange processes. The characterization of all these processes will contribute to a detailed p-T, geochemical, and chronological description of nitrogen generation and migration during subsidence and inversion events in the NGB.