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Conversion of ammonium to organic nitrogen in maturing kerogen

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Thermally maturing kerogen (i.e., the insoluble fraction of sedimentary organic matter) loses most of its organic nitrogen with time and increasing temperature. Surprisingly, this large-scale elimination of organic nitrogen is not associated with strong isotopic fractionation of the shrinking pool of organic nitrogen. Hydrous pyrolysis experiments of various source rocks containing kerogen types I, II and III in the presence of regular and ¹⁵N-enriched ammonium chloride at temperatures of 330°C for up to 144 hours demonstrated that ammonium can be partly converted to organic nitrogen in kerogen. New hydrous heating experiments of the same types of source rocks for 5 years at temperatures of 100, 144 and 196°C confirm that ammonium is not only produced during heating of sedimentary organic matter, but ammonium can also backreact with kerogen and form organic nitrogen abiogenically at temperatures that are realistic for naturally maturing sediments. Ammonium ions are an ubiquitous component of formation fluids, especially in organic-rich sediments. Ammonium ions' mobility and ability to isotopically interact with kerogen makes them an effective isotopic buffer for organic nitrogen. The absence of strong nitrogen isotopic fractionation during the net diagenetic loss of organic nitrogen is therefore in part a result of isotopic exchange between ammonium nitrogen and organic nitrogen. This exchange limits the paleoenvironmental value of organic $\delta^{15}N$ values to thermally immature substrates.