

Nitrogen Isotopic Composition of Fixed Ammonium in Rocks: Evidence for a Possible Ammonia Stability in Fluids?

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Introduction

Daniels and Altaner (1990) and Sucha et al. (1994) showed that ammonium-bearing illite/muscovite is formed, at temperature above 200 °C, by reaction of kaolinite with ammonium derived from the thermal degradation of organic nitrogen. We have shown that in low grade metamorphic rocks of Eastern Pennsylvania (anthracites, meta-anthracites and shales) 1) with increasing maturity of the organic matter, the organic N content decreases while its $\delta^{15}\text{N}$ remains unchanged (Ader et al., 1998a), and 2) the $\delta^{15}\text{N}$ of fixed ammonium varies between 3 and 13‰, showing no change either with nitrogen content in minerals or with coal maturation (Ader et al, 1998b), but showing for the first time a positive correlation with the amount of ammonium substituted for potassium in illite/muscovite.

We performed ammonium-illite/muscovite formation by co-transformation of kaolinite and organic nitrogen (using isothermal heating under hydrostatic pressure in sealed gold cell) to identify the process responsible for the $\delta^{15}\text{N}$ values of fixed ammonium.

Experiments and analysis

One anthracite sample containing no clay, and carbazole (taken as a model compound for nitrogen in mature kerogen) were mixed with various amounts of kaolinite (10 to 80%) and heated in sealed gold cell at 460–600 °C, 0.2 Gpa for 7 days. For each experiment, the $\delta^{15}\text{N}$ of the organic matter, of the fixed ammonium, and, for some of them of the free/exchangeable ammonium, were determined. The kerogen was separated by HF attack. The free/exchangeable ammonium was separated from another fraction of the sample by agitation in a 2 M KCl solution for two hours. The solution containing this ammonium was recovered by filtration, and the residual solid agitated for 12 hours in HF solution to free the fixed ammonium. The ammonium of both solutions was steam distilled, and precipitated as ammonium-sulphate. Molecular nitrogen was prepared from the nitrogen of ammonium sulphate or kerogen by combustion with copper oxide in a sealed tube (Ader et al., 1998a), and analysed for $\delta^{15}\text{N}$ using a Finnigan

Delta E mass spectrometer. Results, reported relative to atmospheric nitrogen, give $\delta^{15}\text{N}$ with $\pm 0.15\%$ reproducibility.

Results and discussion

In our experiments: 1) the organic N content decreases while the $\delta^{15}\text{N}$ of the organic matter remains unchanged; 2) ammonium-illite/muscovite is readily synthesised by reaction of kaolinite and ammonium derived from organic matter (evidenced by XRD, Ader et al, 1998) and 3) the $\delta^{15}\text{N}$ of the ammonium-illite/muscovite was equal to or higher than that of the organic matter. These experiments reproduce exactly the observations made on natural samples. In such a closed experimental system, the isotopic variations observed could result either from the process of fixation of ammonium, or from isotopic fractionation between ammonium and gaseous nitrogen species. The $\delta^{15}\text{N}$ of free/exchangeable ammonium being the same as that of the fixed ammonium, the hypothesis of isotopic fractionation linked to the process of fixation of the ammonium can be eliminated. The hypothesis of equilibrium fractionation between ammonium and another species of nitrogen can be tested by plotting $\delta^{15}\text{N}$ ammonium versus F the remaining fraction of nitrogen in the gaz. $F = \text{N-lost} / \text{N-produced}$, N-produced being the nitrogen yielded from organic matter during the experiment, and comprising free/exchangeable nitrogen, fixed nitrogen and N-lost (ammonia or molecular nitrogen). In fact, the values define a line with $\delta^{15}\text{N}$ ammonium $\delta^{15}\text{N}$ organic for $F=0$. $\delta^{15}\text{N}$ ammonium for $F=1$ gives a fractionation factor of $8\pm 1\%$, which for the temperature range of the experiments (500–600 °C) corresponds exactly to the theoretical equilibrium fractionation between ammonium and ammonia. Therefore, $\delta^{15}\text{N}$ ammonium of Eastern Pennsylvania samples can also be explained by an isotopic equilibrium between ammonium and a gaseous species of nitrogen. It is not yet possible to define which species (ammonia or molecular nitrogen), since the isotopic equilibrium between ammonium and molecular nitrogen is still poorly defined. However, if its determination by Hanschman (1981) is the closest to reality (as supposed by Bebout and Fogel, 1992), then ammonia was a major component of the fluid during metamorphism of the anthracite field of Pennsylvania. This would be the first evidence for the stability of ammonia in crustal fluids.

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