

Nitrogen isotopic composition of ammonium-rich illite in anthracites and organic-rich shales from Eastern Pennsylvania

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Previous studies (Daniels and Altaner 1990; Sucha *et al.*, 1994) have shown that ammonium-bearing illite/muscovite can be formed, at temperature above 200°C, by reaction of kaolinite with ammonia, derived from the thermal degradation of organic nitrogen. In the particular case of Eastern Pennsylvania, the present work reports, for the first time, the isotopic composition of nitrogen in ammonium - rich illite from low grade metamorphic rocks associated with anthracites ranking above Rmax: 4%.

Methods

Pennsylvanian anthracite and shale samples were collected from outcrops and strip mines. Ammonium could easily be evidenced *in situ* in meta-anthracite

samples by means of electron microprobe (Cameca SX 50) and of nuclear microprobe using the $^{14}\text{N}(\text{d},\text{p}_0)^{15}\text{N}$, $^{14}\text{N}(\text{d}, \alpha_0)^{12}\text{C}$ nuclear reactions. It was either isolated by low temperature ashing (Daniels and Altaner, 1990), or selectively extracted by HCl/HF attack using a microwave digester.

Isotopic analyses were made using a Finnigan DeltaE mass spectrometer. Nitrogen samples were prepared by combustion in quartz tubes (Kendall and Grin, 1990). Quartz tube and reactants were degassed for 4 hours at 600°C, then the powdered sample was added and conditioned at 300°C under vacuum for 2 hours. The loaded quartz tube was flame sealed and heated at 950°C for 4 hours. Isotopic composition was reported in the 'delta' notation: per mil, relative to the atmospheric nitrogen ($\delta^{15}\text{N}$). Precision for nitrogen content was $\pm 0.15\%$, and $\pm 0.05\%$ for $\delta^{15}\text{N}$.

TABLE 1. Isotopic composition of minerals isolated by low temperature ashing of anthracites and of coaly shales showing very high vitrinite reflectance

Sample reference	Vitrinite reflectance Rmax, %	N, wt.% minerals	Mole % NH ₄ substitution in illite	$\delta^{15}\text{N}\%$ in minerals
20L	4.32	0.90	70	9.70
16I	5.56	0.64	n.d.	11.40
17F	5.61	2.38	90	12.00
2A	5.64	0.90	77	8.55
16H	5.66	1.50	70	9.70
19A	5.97	1.65	76	9.10
31D	6.03	2.13	70	6.30
19J	6.30	1.82	76	13.00
Average	5.54	1.44	76	9.54

Results

As shown in Table 1, for vitrinite maximum reflectance between 4.3 and 6.3 %, the average N content in minerals (low temperature ash) of the studied samples is 14 400 ppm. Mole % NH_4 substitution in ammonium-bearing illite is high (average 76%) and relatively constant. The total N content is positively correlated with the ammonium-illite content in the LTA ash. Sample 16I, where ammonium-illite is undetectable by XRD analysis, contains the smallest amount of N in LTA ash, and LTA samples 17F, 31D and 19J, which display the highest ammonium-illite content, have the highest N content. The mean $\delta^{15}\text{N}$ of ammonium in minerals is + 9.5‰. This value is much higher than the mean $\delta^{15}\text{N}$ of organic matter which is + 4.6‰ (Ader *et al.*, 1997). The ammonium $\delta^{15}\text{N}$ shows no change either with the nitrogen content in minerals, or with the molar ammonium fraction in illite, or with coal maturation.

Discussion

The absence of correlation between the isotopic composition or content of nitrogen in minerals with vitrinite reflectance indicates that ammonium-illite genesis is not simply temperature controlled, but depends also on other factors such as the initial mineralogy, fluid composition and time. The high $\delta^{15}\text{N}$ in minerals, with respect to $\delta^{15}\text{N}$ in organic matter, can be explained by a net isotopic fractionation due to several possible elemental reactions occurring during primary/secondary co-genesis of heavy ammonium and light molecular

nitrogen, during expulsion/ primary migration out of the rock, and during ion intercalation between the clay layers. In order to assess these supposed reactions, gold cell experimental simulations have been performed. Anthracite samples were heated in sealed gold cell at 450 or 600°C, 0.2 GPa during 7 or 15 days. The simulation showed that, in gold cell experiments, organic N content decreases while $\delta^{15}\text{N}$ of the organic matter remains unchanged, as in nature (Ader *et al.*, 1997). ^{15}N rich ammonium ($\delta^{15}\text{N}$ c. +10 ‰) was co-generated with fluids of lower $\delta^{15}\text{N}$ ($\delta^{15}\text{N}$ c. +2 ‰). As shown by XRD, ammonium-illite was readily synthesized under the same conditions by heating, with or without any water, pure kaolinite or illite with ammonium chloride or carbazole – taken as a model of organic nitrogen. Ammonium becomes enriched in ^{15}N as a result of isotope fractionation due to the genesis of N_2 with low $\delta^{15}\text{N}$, as observed, for instance, in gas reservoir of North Germany (Gerling *et al.*, 1997).

References

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