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Isotope study on organic nitrogen of Westphalian anthracites from the Western Middle field of Pennsylvania (U.S.A.) and from the Bramsche Massif (Germany)

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Abstract—The objective of this study was to examine an aspect of the thermal cycling of organic nitrogen in sediments and metasediments. The cycling of organic nitrogen is important because sedimentary organic matter is a shuttle of nitrogen from the atmosphere to the lower crust and thermal decomposition of organic matter is a critical step in the recycling of nitrogen between the different nitrogen pools. Abundance and isotopic composition of organic nitrogen were determined in the particular case of two low sulfur Westphalian anthracites series from Pennsylvania and Bramsche Massif. They represent good examples of Euramerica coals spanning the whole range of anthracitization in single fields. Gold cell experimental simulation of the denitrogenation process was conducted at moderate pressure to show that both suites make ideal metamorphic profiles without any shift due to change of facies or to hydrothermal disturbance. During anthracitization, organic nitrogen content decreases rapidly while organic nitrogen isotopic composition does not change with rank increase. The preservation of the isotopic signature implies that organic nitrogen isotopes could be used as indicators for the paleoecological and paleodepositional history reconstruction of the basins. The striking contrast between the rapid and sharp decrease of nitrogen organic content and the invariance of its isotopic composition during the whole anthracitization suggests that ammonia is an important product of the denitrogenation process.

Key words nitrogen, isotope, anthracite, Pennsylvania, North Germany, metamorphism, coal, kerogen, gold cell

INTRODUCTION

Thermal nitrogen cycling in sediments and metasediments has received little attention. Variations of organic nitrogen content and of its isotopic composition with maturation remain largely unknown. However, since highly metamorphosed organic matter is supposed to contain only trace amounts of nitrogen, one can predict that nitrogen is released by sedimentary organic matter during diagenesis and metamorphism. Improvements of our knowledge about the fate of organic nitrogen in natural and experimental maturation series should lead to a better understanding of the process of denitrogenation and may help in using organic nitrogen isotopes to establish the distribution of nitrogen among various reservoirs in earth (Javoy et al., 1986; Zhang and Zindler, 1993; Bebout, 1995; Javoy, 1997).

The present study reports organic nitrogen abundance and isotopic composition during anthracitization. The objective is to investigate ideal metamorphic profiles of organic nitrogen from low vascular plants in two Westphalian anthracite suites.

MATERIAL AND METHODS

The samples are listed in Table 1. The Western Middle anthracite field of Pennsylvania (U.S.A.) and the Bramsche Massif (Germany), paleobotanically dated as Westphalian (Middle Pennsylvanian), were chosen because the coals represent a wide range of rank from anthracite to meta-anthracite. Hence, the whole anthracitization could be easily observed in the same field. A second reason was that there is an abundance of background material available for the region, including geological, petrophysical, geochemical syntheses and experimental simulation of coal anthracitization and graphitiza-
Table I. Samples, rank, organic N abundance and isotopic composition

<table>
<thead>
<tr>
<th>Sample No</th>
<th>Source*</th>
<th>Field</th>
<th>Stratigraphy</th>
<th>Rvana (%)</th>
<th>100 N/Ct</th>
<th>15N (%))</th>
<th>613C (‰)</th>
</tr>
</thead>
<tbody>
<tr>
<td>WM-GP-M8-CH</td>
<td>JL</td>
<td>Mammoth8</td>
<td>Mid. Penn.</td>
<td>2.68</td>
<td>1.34</td>
<td>4.45</td>
<td>-24.30</td>
</tr>
<tr>
<td>WM-ED-M9-CH</td>
<td>JL</td>
<td>Mammoth9</td>
<td>Mid. Penn.</td>
<td>2.97</td>
<td>1.43</td>
<td>4.65</td>
<td>-23.50</td>
</tr>
<tr>
<td>WM-SH-M8-GR</td>
<td>JL</td>
<td>Mammoth8</td>
<td>Mid. Penn.</td>
<td>3.45</td>
<td>1.29</td>
<td>4.35</td>
<td>-24.30</td>
</tr>
<tr>
<td>WM-RN-LO-CH</td>
<td>JL</td>
<td>Little Orch.</td>
<td>Mid. Penn.</td>
<td>3.78</td>
<td>1.22</td>
<td>5.05</td>
<td>-25.80</td>
</tr>
<tr>
<td>WM-CR-LY-CH</td>
<td>JL</td>
<td>Lykens</td>
<td>Mid. Penn.</td>
<td>5.30</td>
<td>0.66</td>
<td>4.05</td>
<td>-24.20</td>
</tr>
<tr>
<td>PSOC 1468</td>
<td>PSOC</td>
<td>Buck Mtn</td>
<td>Mid. Penn.</td>
<td>5.45</td>
<td>0.61</td>
<td>4.95</td>
<td>-24.15</td>
</tr>
<tr>
<td>PSOC 870</td>
<td>PSOC</td>
<td>Primrose</td>
<td>Mid. Penn.</td>
<td>5.57</td>
<td>0.62</td>
<td>4.85</td>
<td>-23.95</td>
</tr>
<tr>
<td>I6H</td>
<td>ED</td>
<td>Mammoth</td>
<td>Mid. Penn.</td>
<td>5.66</td>
<td>0.67</td>
<td>4.75</td>
<td>-24.40</td>
</tr>
<tr>
<td>17A</td>
<td>ED</td>
<td>Buck Mtn</td>
<td>Mid. Penn.</td>
<td>5.74</td>
<td>0.69</td>
<td>5.35</td>
<td>-23.50</td>
</tr>
<tr>
<td>2C</td>
<td>ED</td>
<td>Buck Mtn</td>
<td>Mid. Penn.</td>
<td>6.30</td>
<td>0.66</td>
<td>4.15</td>
<td>-23.50</td>
</tr>
<tr>
<td>U150-7723</td>
<td>AVR</td>
<td>Ibbenburen</td>
<td>Westfal. C</td>
<td>2.91</td>
<td>1.00</td>
<td>2.80</td>
<td>-24.10</td>
</tr>
<tr>
<td>U150-7796</td>
<td>AVR</td>
<td>Ibbenburen</td>
<td>Westfal. B</td>
<td>3.51</td>
<td>1.01</td>
<td>3.72</td>
<td>-25.40</td>
</tr>
<tr>
<td>IB-115229</td>
<td>BGR</td>
<td>Ibbenburen</td>
<td>Westfal. B</td>
<td>4.22</td>
<td>0.92</td>
<td>3.05</td>
<td>-23.70</td>
</tr>
<tr>
<td>IBW1-13493</td>
<td>AVR</td>
<td>Ibbenburen</td>
<td>Westfal. B</td>
<td>4.27</td>
<td>0.92</td>
<td>2.70</td>
<td>-24.00</td>
</tr>
<tr>
<td>IBW2-14488</td>
<td>AVR</td>
<td>Ibbenburen</td>
<td>Westfal. B</td>
<td>4.72</td>
<td>0.98</td>
<td>3.00</td>
<td>-23.30</td>
</tr>
<tr>
<td>PIES-751</td>
<td>AVR</td>
<td>Piesberg</td>
<td>Westfal. D</td>
<td>6.00</td>
<td>0.50</td>
<td>3.70</td>
<td>-24.15</td>
</tr>
<tr>
<td>PIES-693</td>
<td>BGR</td>
<td>Piesberg</td>
<td>Westfal. D</td>
<td>7.00</td>
<td>0.40</td>
<td>3.60</td>
<td>-24.05</td>
</tr>
<tr>
<td>PIES-6770</td>
<td>AVR</td>
<td>Piesberg</td>
<td>Westfal. D</td>
<td>7.14</td>
<td>0.41</td>
<td>3.45</td>
<td>-24.92</td>
</tr>
</tbody>
</table>


Organic N/organic C, atomic ratio x 100.

Pennsylvania

Results and Discussion

Variation of organic nitrogen content with maturation

In Fig. 1, the atomic N/C ratio of organic matter is expressed with respect to vitrinite reflectance between R0 = 2.5 and 7.5%. The organic N/C ratio...
(x100) for the Pennsylvanian coals decreases from —1.4 to 0.6 (at $R_{\text{max}}$ 6%) whereas for Bramsche coals N/C (x100) the range is lower and decreases from —1.0 to 0.4 (at $R_{\text{max}}$ 7%). The decreasing organic N/C with rank for the Ibbenbiren/Piesberg series is here reported for the first time. Similar rapid organic N/C decrease above $R_{\text{max}}$ 4.5% was also reported, but not commented on, by Volkova and Bogdanova (1989) in the Donetz anthracite and meta-anthracite suite. A few authors, who claim that total nitrogen is an acceptable substitute for organic nitrogen, also reported a decreasing trend in the late stages of coalification: Suggate (1959) on New-Zealand coals (who wrote that "further information is clearly required" to provide an adequate justification of the observed trends), Shapiro and Gray (1966) on Antarctic coals, Drechsler and Stiehl (1977) on German anthracites, Paxton (1983) on the Pennsylvania anthracite field and Burchill and Welch (1989) on the British coals. More recently, Litke et al. (1995) showed a very weak decrease of the total N content in a series of 3 anthracites and 2 meta-anthracites from several origins. These repeated observations tend to support the validity of a general interpretative scheme where the main loss of organic nitrogen occurs in the very late stage of coalification (Boudou et al., 1984; Boudou and Espitalie, 1995).

**Organic nitrogen isotopic composition as a tracer of origin**

Previous works (Peters et al., 1978; Mariotti, 1982; Rigby and Batts, 1986; Scholten, 1991) have assessed the potential of $^{15}N/^{14}N$ ratio as indicator of sedimentary environment. In the Pennsylvania and Bramsche Massif suites, $^{15}N$ as well as $^{13}C$ do not change systematically with rank (Table 1), but anthracites display two narrow ranges of $^{15}N$ values: Pennsylvanian $^{15}N$ values range from 4.1 to 5.4‰ and Bramsche values range from 2.7 to 3.7‰ (Fig. 2). As expected, there is no $^{13}C$ shift during maturation (Galimov, 1980; Lewan, 1986). The present paper shows, for the first time, that in the particular case of sedimentary organic matter from lower vascular plants, organic nitrogen isotopic composition does not change during metamorphism (until $R_{\text{max}}$ 7%), from anthracite (PPennsylvania facies) to meta-anthracite rank (greenschist facies, Kish, 1987). In the case of Northern Germany, Gerling et al. (1997), studying the total nitrogen, presented similar results to ours for the anthracite stage (until $R_{\text{max}}$ 4%), it means for the less important stage of coal denitrogenation where inorganic nitrogen content is still very low (Daniels and Altaner, 1990, 1993). Our results add substance to the argument of Haendel et al. (1986) who had...
assumed that a leveling of the nitrogen isotope composition would take place during diagenesis up to the boundary of greenschist facies.

Slight differences of organic N content and \( \delta^{15}N \) in both anthracite suites (Pennsylvania and Bramsche) are thought to reflect the similarities and slight differences of the paleophytogeography and the paleoclimate of the two basins, at a time of maximum assembly of Pangaea drifting northward (Scotese et al., 1979). These facts would be in conformity with the paleobotanical results of Philips et al. (1985) who wrote that regional differences in tectonic setting, historical aspects of the vegetation and local environmental differences may make the patterns of vegetational change somewhat different in each coal region. The drastic changes in coal-swamp vegetation are transitional across the Middle-Upper Pennsylvanian boundary and are very similar in each of the major coal regions of the United States and Europe. However, an important difference between the vegetation on either side of the Appalachians is the continued presence of some Lycospora-bearing Lycopsids in Europe. This is possibly the result of a more asymmetric change in the drying of the climate there (Hedemann and Teichmüller, 1971). The slight differentiation of the Pennsylvanian and of the Bramsche anthracite suites on the basis of organic nitrogen isotopes shows that nitrogen isotope data may be a significant indicator of the precursor flora, the environment of deposition and the type and degree of alteration of the plant substances. This differentiation should be explained by further studies on the paleoecology of both coal-bearing depositional systems following the approach of Altebdumer (1983), Wnuk (1985, 1989), Wnuk and Pfefferkorn (1987) and Diessel (1992).

**Experimental simulation**

Since there is no valid method to experimentally simulate the natural metamorphism starting with an immature coal (Wilks et al., 1993), the simulation was done with an anthracite sample taken at the onset of the denitrogenation window (anthracitization and further graphitization). The simulation was conducted under hydrostatic pressure because the role of tectonic shearing on anthracitization has not yet been put in evidence (Levine, 1993). Moderate hydrostatic pressure (0.2 GPa) was chosen because high pressure may have a suppressing effect on maturation (Goffe and Villey, 1984; Domine, 1987; Dalla Torre et al., 1997). The anthracite sample, the temperature and pressure conditions were chosen according to our previous work on open system pyrolysis (Boudou and Espitalie, 1995), gold cell experiments previously performed by Hryckowian et
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Table 2. Analysis of anthracite sample WM-GP-M8-CH

<table>
<thead>
<tr>
<th></th>
<th>As received</th>
<th>% Dry</th>
<th>% Dry ash free</th>
</tr>
</thead>
<tbody>
<tr>
<td>H2O</td>
<td>1.47</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Volatile matter</td>
<td>9.97</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fixed carbon</td>
<td>74.82</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ash</td>
<td>15.21</td>
<td></td>
<td></td>
</tr>
<tr>
<td>BTU*</td>
<td>12869</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>92.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H</td>
<td>3.74</td>
<td></td>
<td></td>
</tr>
<tr>
<td>N</td>
<td>1.42</td>
<td></td>
<td></td>
</tr>
<tr>
<td>O (by difference)</td>
<td>0.98</td>
<td></td>
<td>2.94</td>
</tr>
</tbody>
</table>

*British Thermal Unit per pound.

... and some preliminary experiments using isostatic pressure by means of an anvil press (Boudou et al., 1997). Being the least mature anthracite of the Pennsylvanian series, anthracite sample WM-GP-M8-CH from the Middle Mammoth seam (Hryckowian et al., 1967; Levine and Davis, 1983) was chosen for the gold cell experiment. Its main characteristics, given by Levine and Davis (1983), are presented in Table 2. The sample was heated at 600°C, 0.2 GPa for 15 days, in a sealed gold cell (Domine, 1987). Hryckowian et al. (1967), who performed gold cell experiments with an anthracite sample from the same coal seam as WM-GP-M8-CH, had observed that 600°C is critical in reactions producing a rapid increase of reflectance and a fusion of the material to form a hard compact mass that we effectively observed in our experiments. The gold cell simulation, performed in our laboratory, showed that organic N content decreases while $^{15}$N and $^{13}$C of the organic matter remain unchanged (Fig. 3 and Table 3). These changes are similar to those observed in the natural series (Figs 1 and 2, Table 1). The constancy of the $^{15}$N suggests that denitrogenation, in confined system, as well as in nature, involves other reactions than in open system pyrolysis, where $^{15}$N increases (Drechsler and Steihl, 1977). The experimental work of Katritzky et al. (1995), Everlien (1997) and Gerling et al. (1997) suggests that pressured water, which, in our study, may result from anthracite degradation as well as from clay paragenesis, might play a denitrogenating role. Water, in a sealed capsule, as well as in hydrous pyrolysis experiments, would have an hydrogenating role (Huang, 1996; Everlien, 1997; Lewan, 1997). Wintsch et al. (1981) propose coal hydrogenation by pressured neo-formed molecular hydrogen as an important step in the mechanism of graphitization, consequently of denitrogenation.

Organic nitrogen isotopes as tracers of the mechanism of denitrogenation

Because it takes less energy to break $^{14}$N-$^{12}$C bonds than $^{15}$N-$^{12}$C bonds, thermocracking of N-C bonds should produce a preferential release of $^{14}$N (Bigeleisen, 1965; Melander and Saunders, 1980). As a result, if denitrogenation involved thermal breaking of a high energy bond, it should lead to a strong enrichment of the heavier nitrogen isotope (Drechsler and Steihl, 1977; Haendel et al., 1986; Bebout and Fogel, 1992). The present study
shows that 615N of organic nitrogen does not change with rank despite the N/C ratio falling to half of its original value. Assuming that ammonia has been produced by irreversible reactions without any isotopic fractionation (Williams et al., 1995; Shearer and Kohl, 1993) and that molecular nitrogen derived from organic matter has a low 815N (Boigk et al., 1976; Prasalov et al., 1990), it comes that molecular nitrogen would not be an important primary product of the anthracite denitrogenation. After Sohns et al. (1994), the Boigk et al. (1976) data show systematic deviation from the true values, as a result of air contamination for a sample with very low nitrogen concentration, of incomplete combustion of hydrocarbons, of fluctuation amounts of oxygen in the ion source due to contamination with air, etc. However, new stable nitrogen isotope ratio by GC/IRMS (Sohns et al., 1994; Gerling et al., 1997) still show that light nitrogen predominates (615N ranging from −9 to +3‰) in the area adjacent to the intrusive of the Bramsche massif, where the rocks reach maturity above 12%, 4%. Therefore, ammonia with higher 615N should be an important primary product of the denitrogenation process. This interpretation does not preclude a direct co-genesis of molecular nitrogen from coal (Krooss et al., 1995), a generation of molecular nitrogen from a secondary decomposition of ammonium (Rohrbach et al., 1983) or a mixing of N, from several sources (Muller et al., 1973; Gerling et al., 1997). In deep sedimentary basins, where the redox potential is low, NH4+, which would find its way in the illite/muscovite interlayers, is the most stable form of aqueous nitrogen, unless an oxidizing catalytic agent is encountered along the path that produces N2 (Getz, 1976, 1981; Hallam and Eugster, 1976; Everlien and Hoffmann, 1991). In fact, Daniels and Altaner (1990, 1993), showed, in the case of the Pennsylvanian anthracite field, that the organic matter dispersed in the shale and concentrated in nearby coal seams releases nitrogen in connate brine in the form of aqueous ammonium. Authigenic NH4-rich illite forms by high temperature reaction of ammonia, derived from maturation of locally abundant organic matter, with kaolinite Cluster et al., 1987). The postulated hydrothermal fluids that flowed through some joints in the anthracite appear to have been enriched in Mg, Fe and other transition elements. They are responsible for forming some unusual ordered mixed-layer clay minerals, such as tosudite, sudoite and rectorite. These brines do not appear to have carried ammonium into authigenic minerals, such as NH4—illite and pyrophyllite. Rather, these minerals occur in closed, low permeability environments in the shale and coal matrix and sporadically in some joints sets. All elements in NH4—illite and pyrophyllite are easily derived from the rock matrix itself.

CONCLUSIONS

The study of organic nitrogen abundance and isotopic composition in Upper Carboniferous anthracite suites of Pennsylvania (U.S.A.) and of the Bramsche Massif (Germany) brings the following results:

1. The data presented confirm earlier reports that the organic nitrogen content decreases rapidly from anthracite to higher rank.

2. Contrarily to nitrogen content, the organic nitrogen isotopic composition does not change with rank and hence could not be used as indicator of metamorphism.

3. Slight differences of 815N in both anthracite suites may reveal differences of the paleophytogeography and the paleoclimate of the two basins.

4. Sealed gold cell experimentation reproduces the behavior of organic nitrogen with rank increase: rapid decrease of N content and persistence of nitrogen isotope composition as well as carbon isotope composition.

5. The rapid denitrogenation and the invariance of N isotope composition in both anthracite suites suggest that ammonia might be an important product of the denitrogenation process in the late stages of coalification.

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REFERENCES


Wnuk, C. (1989) Ontogeny and paleoecology of the Middle Pennsylvanian arborescent *lycopod* *Bothrodendron punctatum*, Bothrodendraceae (Western...