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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, petrographical, geochemical syntheses and experimental simulation of coal anthracitization and graphitiza-

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Table I. Samples, rank, organic N abundance and isotopic composition

Sample No	Source*	Field	Stratigraphy	R _{org} , (%)	100 N/Ct	$\delta^{15}\text{N}$ (‰)	$\delta^{13}\text{C}$ (‰)
Pennsylvania							
WM-GP-M8-CH	JL	Mammoth#8	Mid. Penn.	2.68	1.34	4.45	-24.30
WM-ED-M9-CH	JL	Mammoth#9	Mid. Penn.	2.97	1.43	4.65	-23.50
WM-SH-M8-GR	JL	Mammoth#8	Mid. Penn.	3.45	1.29	4.35	-24.30
WM-RN-LO-CH	JL	Little Orch.	Mid. Penn.	3.78	1.22	5.05	-25.80
WM-CR-LY-CH	JL	Lykens	Mid. Penn.	5.30	0.66	4.05	-24.20
PSOC 1468	PSOC	Buck Mtn	Mid. Penn.	5.45	0.61	4.95	-24.15
PSOC 870	PSOC	Primrose	Mid. Penn.	5.57	0.62	4.85	-23.95
16H	ED	Mammoth	Mid. Penn.	5.66	0.67	4.75	-24.40
17A	ED	Buck Mtn	Mid. Penn.	5.74	0.69	5.35	-23.50
2C	ED	Buck Mtn	Mid. Penn.	6.30	0.66	4.15	-23.50
Bramsche							
U150-7723	AVR	Ibbenburen	Westfal. C	2.91	1.00	2.80	-24.10
U150-7796	AVR	Ibbenburen	Westfal. B	3.51	1.01	3.72	-25.40
IB-115229	BGR	Ibbenburen	Westfal. B	4.22	0.92	3.05	-23.70
IBW1-13493	AVR	Ibbenburen	Westfal. B	4.27	0.92	2.70	-24.00
IBW2-14488	AVR	Ibbenburen	Westfal. B	4.72	0.98	3.00	-23.30
PIES-751	AVR	Piesberg	Westfal. D	6.00	0.50	3.70	-24.15
PIES-693	BGR	Piesberg	Westfal. D	7.00	0.40	3.60	-24.05
PIES-6770	AVR	Piesberg	Westfal. D	7.14	0.41	3.45	-24.92

*JL: J. Levine, PSOC: Penn State Office of Coal Research, ED: E. Daniels, AVR: A. Vieth-Redemann (Geologisches Landesamt NRW), BGR: Bundesanstalt für Geowissenschaften und Rohstoffe.

*Organic N/organic C, atomic ratio x 100.

tion (Teichmiüller and Teichmüller, 1950; Hryckowian *et al.*, 1967; Mundry, 1971; Stadler and Teichmüller, 1971; Bunterbarth and Teichmiüller, 1979; Edmunds *et al.*, 1979; Oleksyshyn, 1982; Levine and Davis, 1983, 1989; Philips *et al.*, 1985; Daniels and Altaner, 1990, 1993; Levine and Eggleston, 1992; Wilks *et al.*, 1993; Daniels *et al.*, 1994; Bustin *et al.*, 1995).

Pennsylvanian coal samples were collected from outcrops and strip mines. Bramsche Massif samples were collected from the coal mines of Ibbenburen and Piesberg. In order to avoid any change of paleodepositional facies along the anthracitization sequence, only samples with low sulfur content (< 1%) were selected for the study. Low-sulfur coal indicates particular paleogeographical-sedimentological origin and non-marine post-depositional geochemistry. Acid conditions during the peat stage of coal formation should result in leaching of acid-soluble elements, as well as inhibiting sulfur fixation and microbial degradation of organic matter (Westgate and Anderson, 1984; Cecil *et al.*, 1985).

Vitrinite reflectance measurements and elemental analysis of crude samples were performed according to Stach *et al.* (1982), Levine and Davis (1983), Daniels and Altaner (1990, 1993) and Daniels (1992). Organic matter was isolated using HF/HCl digestion of the mineral matter in a Prolabo microwave digester (Microdigest 301). Isotopic analyses of the organic matter were made using a Finnigan DeltaE mass spectrometer and were reported in the "delta" notation: per mil, relative to the Pee Dee Belemnite Standard ($\delta^{13}\text{C}$) and relative to the atmospheric nitrogen ($\delta^{15}\text{N}$). Nitrogen samples were

prepared using combustion in quartz tubes with CuO, Cu and CaO in order to trap CO₂ and H₂O (Kendall and Grim, 1990; Boyd *et al.*, 1994; Boyd *et al.*, 1995). Evacuation on a vacuum line proceeded as follows: CuO, Cu and CaO were degassed for 4 h at 600°C, then powdered sample was added and conditioned at 300°C for 2 h. The loaded and pretreated tube was then flame sealed, combusted at 950°C for 4 h, cooled at 600°C for 3 h to allow (i) residual oxygen to recombine with cupric oxide, (ii) nitrous oxide to be reduced by copper and (iii) carbon dioxide to be trapped by CaO. Then the tubes were slowly cooled to ambient temperature allowing water to combine with CaO. The quartz tube was opened on a vacuum line with a tube cracker. The combustion gases were cooled to liquid nitrogen temperature. Using a Toepler pump, the purified nitrogen was concentrated in a calibrated volume allowing quantification. Possible contamination was checked by scanning of m/z 12, 15, 16, 30, 32 and 40 (Ar). Samples for $\delta^{13}\text{C}$ determination were prepared in a similar but simpler way: no CaO was added to the combustion tube and the CO₂ was separated cryogenically using a liquid nitrogen trap. Precision for $\delta^{15}\text{N}$ was +0.15‰ and for $\delta^{13}\text{C}$ +0.05‰.

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 R_{org} 2.5 and 7.5%. The organic N/C

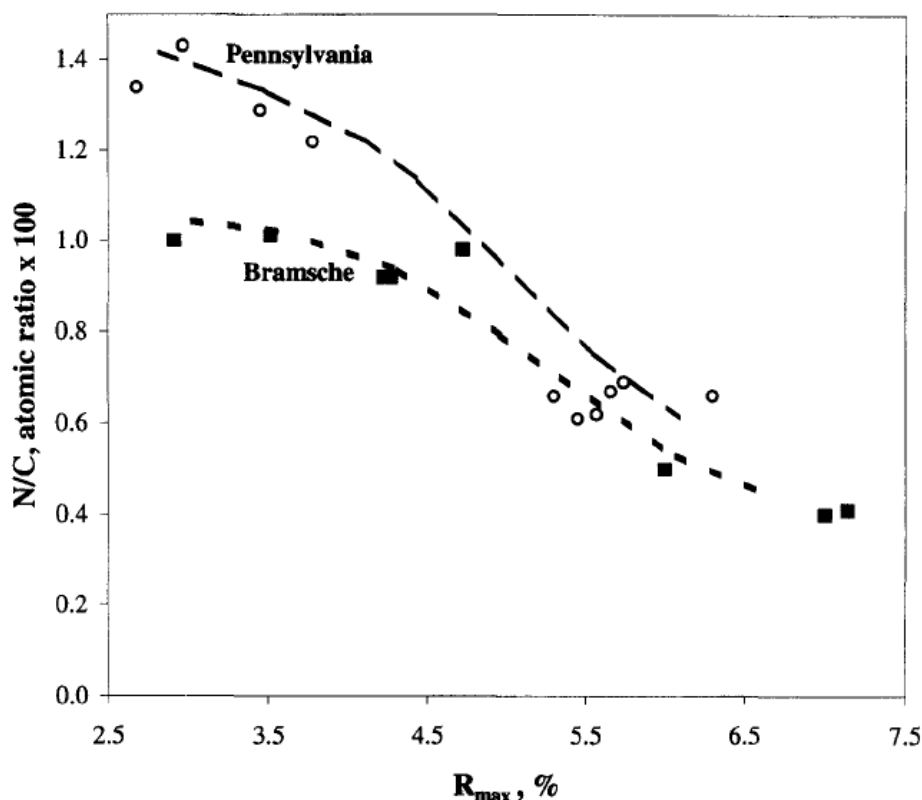


Fig. 1. Organic nitrogen abundance vs R_{max} for Pennsylvania and Bramsche natural samples.

(x100) for the Pennsylvanian coals decreases from 1.4 to 0.6 (at R_{max} 6%) whereas for Bramsche coals N/C (x100) the range is lower and decreases from 1.0 to 0.4 (at R_{max} 7%). The decreasing organic N/C with rank for the Ibbenbüren/Piesberg series is here reported for the first time. Similar rapid organic N/C decrease above R_{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 Pennsylvanian anthracite field and Burchill and Welch (1989) on the British coals. More recently, Littke *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 $^{15}\text{N}/^{14}\text{N}$ ratio as indicator of sedimentary environment. In the Pennsylvania and Bramsche Massif suites, (^{15}N as well as $\delta^{13}\text{C}$) do not change systematically with rank (Table 1), but anthracites display two narrow ranges of ($\delta^{15}\text{N}$ 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 $\delta^{13}\text{C}$ 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_{ma} , 7%), from anthracite (PP 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_{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

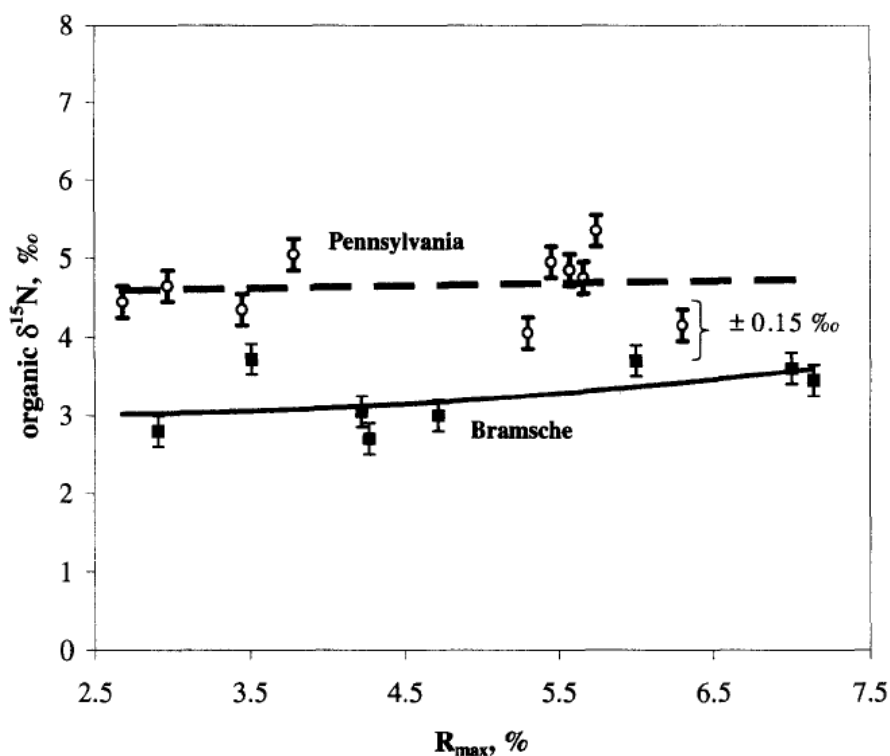


Fig. 2. $\delta^{15}N$ of organic nitrogen vs R_{max} for Pennsylvania and Bramsche natural samples.

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 *Lycopods* 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*

Table 2. Analysis of anthracite sample WM-GP-M8-CH

	% As received	% Dry	% Dry ash free
H ₂ O	1.47		
Volatile matter		9.97	
Fixed carbon		74.82	
Ash		15.21	
BTU*		12869	
C			90.9
H			3.74
N			1.42
			0.98
0 (by difference)			2.94

*British Thermal Unit per pound.

al. (1967) 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 $\delta^{15}\text{N}$ and $S^{\delta}\text{N}$ 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

Table 3. Effect of the gold cell experimental simulation on the organic atomic N/C ratio, $\delta^{15}\text{N}$ and $\delta^{13}\text{C}$ of the WM-GP-M8-CH anthracite

Experimental conditions	N/C	$\delta^{15}\text{N}$ (‰)	$\delta^{13}\text{C}$ (‰)
Initial sample	1.34	4.45	-24.30
Gold cell, 600°C, 0.2 GPa, 360 h	0.77	4.40	-24.35

$\delta^{15}\text{N}$ suggests that denitrogenation, in confined system, as well as in nature, involves other reactions than in open system pyrolysis, where $\delta^{15}\text{N}$ increases (Drechsler and Stiehl, 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 neoformed 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 $^{14}\text{N}-^{12}\text{C}$ bonds than $^{15}\text{N}-^{12}\text{C}$ 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 Stiehl, 1977; Haendel *et al.*, 1986; Bebout and Fogel, 1992). The present study

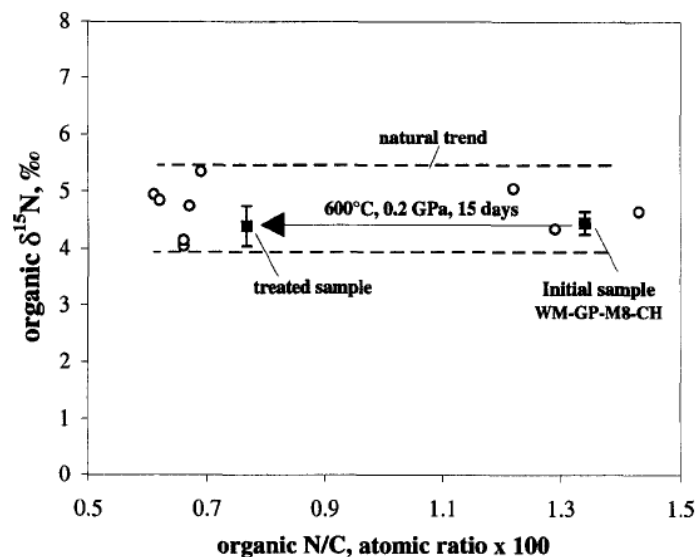


Fig. 3. Results of gold cell experimental simulation with the Pennsylvania WM-GP-M8-CH sample at 600°C and 0.2 GPa during 15 days (average of 2 runs). ○: natural Pennsylvania samples (Table 1).

shows that ^{15}N 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 $\delta^{15}\text{N}$ (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 ($\delta^{15}\text{N}$ ranging from -9 to $+3$ ‰) in the area adjacent to the intrusives of the Bramsche massif, where the rocks reach maturity above 12,000°C, 4%. Therefore, ammonia with higher $\delta^{15}\text{N}$ 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 ammonia (Rohrback *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, NH_4^+ , 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 N_2 (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 NH_4 -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 NH_4 -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 NH_4 -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 $\delta^{15}\text{N}$ in both anthracite suites may reveal differences of the paleogeography 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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