Comparison of solid state ^{13}C NMR of algal coals/anthracite and charcoal-like fusinites: further evidence for graphitic domains

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Abstract: Carbon distribution in coals and coal macerals was studied by ^{13}C NMR cross-polarization (CP)/ magic angle spinning (MAS) spectrometry. We examined two charcoal-like fusinites from Serbia: the Jerma (Jerma mine) and Miroč (mine 'Aliksar') seams. This examination revealed that atomic H/C ratios calculated (on the basis of the CP/MAS parameters) for fusinites studied are higher by 68% (Jerma) and by 64% (Miroč) than the H/C values which are determined by elemental analysis. Calculated H/C values infer that either more carbon or less hydrogen is required for the fusinite structures than is contained in the samples. We conclude that the differences in the estimation of H/C for bituminous charcoal-like fusinites between solid state ^{13}C NMR and elemental analysis can be explained by graphitic domains within the maceral 'invisible' in the CP/MAS experiment.

Coals have been subjected to many magnetic resonance studies, and many parameters have been measured to obtain information about coal molecular structure. During the last decade researchers have focused their attention on solid state ^{13}C NMR spectroscopy with CP/MAS because in principle this technique provides a non-destructive way to measure the aromatic/alkenic carbon fraction of coals f_a (the ratio of aromatic/alkenic carbon C_{ar} to total carbon C), one of the key parameters which characterize the coal structure (Wilson & Vasallo 1985). Usually in ^{13}C NMR spectra of most coals two broad lines can be distinguished belonging to the aromatic/alkenic and aliphatic carbon atoms respectively: f_a of coal is defined as the ratio of the integrated line intensity for aromatic/alkenic carbon atoms to the total integrated line intensity (Speight 1994).

In addition to aromaticity f_a, dipolar dephasing (DD) experiments provide estimates of other structural parameters of coals including the aliphatic (s) and the aromatic/alkenic (p) fraction which are protonated (Wilson & Vasallo 1985). Yet major problems exist concerning the use of solid state ^{13}C NMR spectrometry in coal research. One such problem is that the ^{13}C NMR experiment gives inadequate quantitative estimation of carbon distribution in coal which strongly contradicts other geochemical data (Premović et al. 1992). This contributes to the difficulty in the unequivocal interpretation of the NMR data. The purpose of this report is to show that the estimation of H/C for fusinite (maceral of the inertinite group) with solid state ^{13}C NMR is not in agreement with elemental data. For the sake of clarity, we will consider only two fusinite materials from two Serbian

seams: Jerma (the Jerma mine) and Miroč (the Aliksar mine) with high maceral purity (>90%). For comparison, two fresh-water algal coals (torbanites) (Scotland and S. Africa) and, marine algal coal tasmanite (Australia) and the Vrška Čuka anthracite (Serbia) were also examined.

The earliest spectroscopic work of which we are aware which discusses chemical structure of algal coal-torbanites is that of Millais & Murchison (1969). These authors investigated five torbanite samples from: S. Africa, France and Scotland. Their petrographic examination indicates that these freshwater coals contain alginite (maceral of the exinite group) in excess of 90% by volume. Cane & Albion (1971) have proposed that alginite is an oxidative polymer of straight-chain alkadiens of molecular formula: $CH_2 = CH(CH_2)_nCH = CH(CH_2)_4CH_3$ ($n = 15$, 17 and 19). Allan et al. (1979) analyzed three torbanites (S. Africa, Australia and Scotland) using various geochemical and optical techniques. They concluded that the torbanites are composed of polymeric materials which contain relatively high proportion of aliphatic structures. According to Allan et al. (1979) the evidence for aromaticity is conflicting but the total C_{ar} is suggested to be small on the basis of the elemental analysis and infrared (IR) spectra.

For a number of years, this laboratory has been engaged in the structural elucidation of coals and kerogens. Premović et al. (1987) studied two torbanites from Scotland and S. Africa by both ^{13}C NMR CP/MAS technique combined with DD experiments and ^{1}H NMR MAS technique. This examination has shown that these coals have predominantly both aliphatic carbon and protons (>95% of total

organic carbon and hydrogen) incorporated into polymethylene ($-CH_2-$) skeleton structures.

Experimental procedure

The isolation procedure was similar to that used by Premović (1984) and Premović *et al.* (1986). Powdered rock (50 g) was extracted with benzene methanol (3:1 v/v) for 96 h in a Soxlet apparatus. The residue remaining in the Soxlet thimble was treated with boiling hydrochloric acid (HCl, 4 M) to remove most of the carbonates. Carbonate removal was checked by IR analysis. The insoluble residue was further demineralized by repeated treatment with boiling hydrofluoric/hydrochloric acids (HF/HCl, 22 M and 0.25 M, respectively). This acid mixture removes silicates and the removal was checked by IR analysis. The final residue is the coal sample. It contained only small traces of inorganic minerals, including pyrite, as confirmed by the electron microprobe analysis.

Algal coals (Table 1) are of Permian age (about 250 Ma). The Vrška Čuka antracite and the maceral concentrates from Serbian seams (Table 1b) are of Jurassic age (about 200 Ma).

All ^{13}C NMR spectra of the coal samples were recorded at 25.15 MHz on a Bruker CXP-100 as previously described (Premović *et al.* 1986). The

1 K FIDS, acquired with a 3 ms contact time, 0.35 second recycle time and a rotor frequency of *c*. 4 kHz, were zero filled to 8 K before Fourier transformation. The pulse sequence employed for obtaining the dipolar dephasing (DD) spectra is described elsewhere (Premović *et al.* 1987).

Proton NMR spectrum of tasmanite was taken at 270 MHz with MAS and BR-24 at room temperature on an NMR pulse spectrometer constructed in the laboratories of the Friedrich Schiller University, Jena (Germany) (Premović *et al.* 1987).

For FTIR analysis, the sample was mixed with anhydrous potassium bromide and pressed into the disc (2.5 mg/150 mg KBr) with a load of 200 MPa. The spectra were recorded at room temperature on a Bruker ISF 113 V FTIR spectrometer.

Results and discussions

In addition to torbanites, we have studied by ^{13}C CP MAS marine algal coal: tasmanite containing more than 90% by volume sporinite (maceral of the exinite group). Figure 1 shows typical ^{13}C and ^{1}H NMR spectrum of tasmanite which indicate a presence of a strong aliphatic carbon (Fig. 1a) and proton (Fig. 1b) bands

Table 1. *Geochemical data on the coals: (a) algal coals; (b) bituminous coal macerals (Serbian seams)*[b]

(a)

Location	Maceral	C	H	(O,N)[a]	f_a	s	$\dfrac{H}{C}$	$\dfrac{H}{C}$
			(mol/kg)					
South Africa	alginite	67	111	5	0.09	0.89	1.66*	1.61†
Scotland	alginite	69	108	4	0.12	0.92	1.57*	1.62†
Tasmanite	sporinite	60	92	1	0.10	0.90	1.53*	1.62†

(b)

Location	Maceral[c]	C	H	(O,N)[a]	f_a	s	p	$\dfrac{H}{C}$	$\dfrac{H}{C}$
			(mol/kg)						
Vrškačuka	vitrinite	76	19	0.7	1.00	0.00	0.25	0.25*	0.25‡
Jerma	inertinite	78	32	2	0.90	0.80	0.55	0.40*	0.66‡
Miroč	inertinite	76	38	3	0.80	0.80	0.65	0.50*	0.85‡

* Experimental.
† Calculated using expression 2.
‡ Calculated using expression 1.
[a] Dry, ash-free corrected maceral data.
[b] Separated by sink-and-float procedures by heavy liquids starting with hand-picked lithotypes that were rich in the desired maceral.
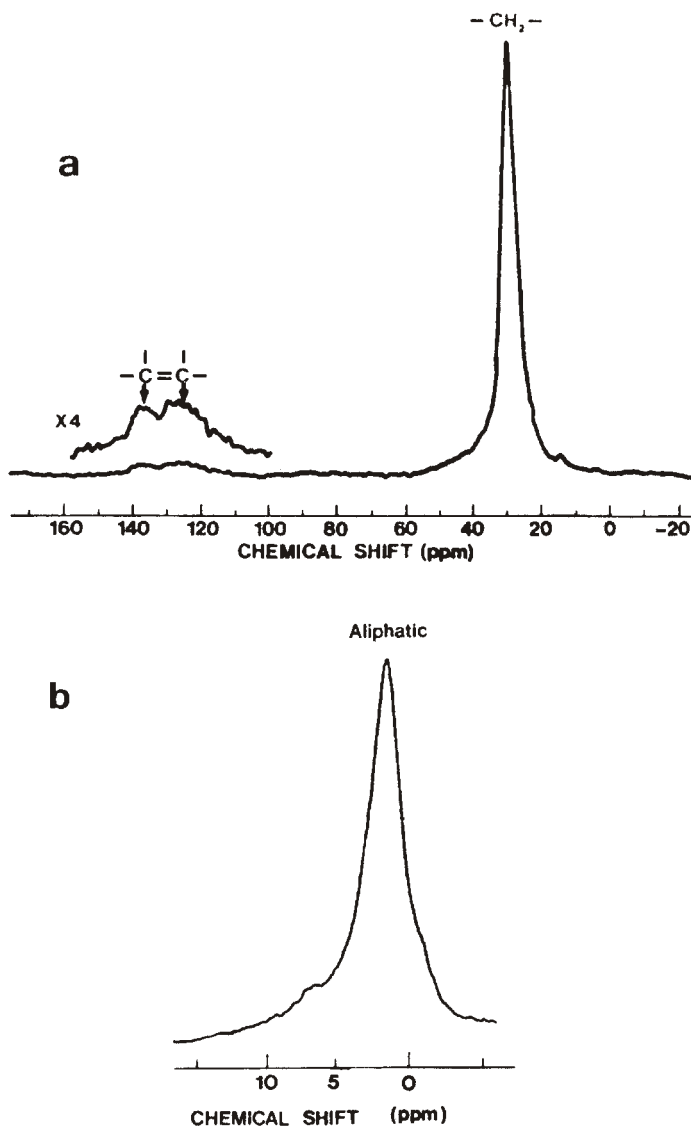[c] Predominant maceral (>95%) component.

Fig. 1. ^{13}C (a) and ^{1}H NMR (b) spectra of the powdered sample of the Vrška Čuka anthracite.

inferring that more than 95% of both organic carbons and protons are aliphatic. Thus these results suggest that the tasmanite is an aliphatic material which also contains a relatively high proportion of polymethylene chains and rather low amount of aromatic/alkenic groups in the structures. It is likely that the best estimated f_a value for these materials is close to 0.10 (Premović et al. 1987).

If total coal carbon is apportioned to both aliphatic (C_{al}) and aromatic/alkenic carbons C_{ar}, then $C = C_{al} + C_{ar}$ assuming an overall H/C

value of: 2 for aliphatic portion and 1 for aromatic/alkenic part, we may write

$$H = 2sC_{al} + pC_{ar}$$

were H is the total hydrogen of coal.

Combining these two equations we obtain

$$\frac{H}{C} = 2s(1 - f_a) + pf_a. \quad (1)$$

As NMR study indicates that f_a values for the algal coals in question is small ($c. 0.1$) and that

most of aromatic/alkenic carbons are non-protonated (Premović *et al.* 1987) then the product pf_a is small and can be neglected. In this case, formula (1) is simplified into the form:

$$\frac{H}{C} = 2s(1 - f_a). \qquad (2)$$

The H/C values (calculated using the expression 2) of algal coals studied are listed in Table 1a. Unless the calculations are more seriously in error (than the stated uncertainly

in elemental data tend to imply) there is a good correspondence between experimental (obtained by elemental analysis) and calculated (through NMR data) H/C ratios for algal coals considered here.

We have also studied the Vrška Čuka anthracite using both the ^{13}C NMR CP/MAS (Fig. 2a), ^{1}H NMR MAS (Fig. 2b). The results show that this coal has predominantly polyaromatic structures with $f_a = 1.0$ and consists chiefly of the vitrinite maceral (>90%). It has been suggested that all ^{13}C atoms in these structures

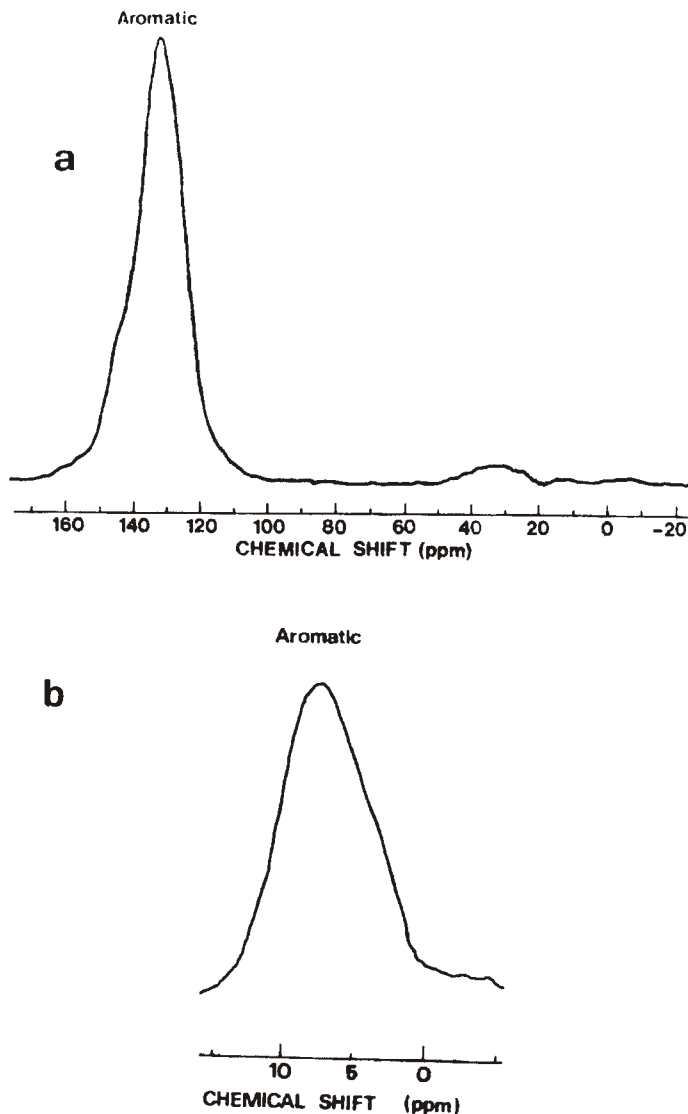Fig. 2. ^{13}C (a) and ^{1}H NMR (b) spectra of the powdered sample of tasmanite.

are not equally cross polarized with ^{1}H nuclear spins. Most researchers of the subject now agree, however, that the number of ^{13}C atoms in these coal structures that are not observed by ^{13}C NMR is small (Speight 1994).

Since the anthracite is wholly polyaromatic, the total carbon can be expressed as $C = C_{ar}$. If this is correct then the total hydrogen is given by

$$H = pC_{ar} = pC.$$

Hence $p = H/C$. The calculated value of $H/C(=p)$ shown in Table 1b is in excellent agreement with the experiment. Table 1b lists atomic H/C ratios of Serbian (Jerma and Miroč) fusinite samples computed using expression (1). An examination of this table reveals that calculated H/C values for the fusinite samples are higher by 68% (Jerma) and by 64% (Miroč) than those experimentally determined values. Thus, the H/C values calculated on the basis of the CP/MAS parameters suggest that either more carbon or less hydrogen is required for the fusinite structures than it is contained in the sample. If this notion is valid then there are only two reasonable explanations for the contradiction (between experimental and calculated H/C value given in Table 1b): (1) the fusinite carbons are extensively substituted e.g. by O or N for which there is, however, no persuasive geochemical evidence; and, (2) in the fusinite structures there are carbon atoms which do not show their resonancies in the ^{13}C NMR CP/MAS spectrum.

In general, the CP/MAS experiment relies on the presence of organic structures abundant in protons in order to observe the ^{13}C NMR resonancies. Consequently, the ^{13}C NMR spectra do not show signals from carbon atoms in structural domains within coal lacking protons, such as graphite. On the other hand, physical, chemical and other studies indicate that the coal fusinites are similar to natural charcoals which is consistent with the view that these macerals had been exposed to elevated temperatures and charred before incorporation in the sediment (Pantić and Nikolić 1973). If this concept is true then fusinites as natural charcoal materials would undoubtedly contain a high amount of graphitic components which are inactive for the CP/MAS approach.

Thus, we suggest that the differences in the estimation of H/C for charcoal-like fusinites (Serbian seams) between solid state ^{13}C NMR and elemental analysis can be explained by graphitic domains* within these macerals invisible in the CP/MAS NMR experiment.

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* Consists chiefly of amorphous charcoal.