

Aspects of solid state ^{13}C CPMAS NMR spectroscopy in coals from the Balkan peninsula

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Abstract: The cross-polarized magic-angle-spinning NMR (CPMAS-NMR) technique was used in this work to assess the carbon distribution in coals of different rank (peat, lignite, xylite, sub-bituminous coal) from important deposits in Greece and Bulgaria. The technique is assumed to be only semiquantitative, due to a number of interferences, such as spinning side bands (SSB) in the spectra, paramagnetic species in the samples, and low or remote protonation of aromatic carbons. The Bulgarian sub-bituminous coal shows the greatest amounts of aromatic structures. The lignite sample from the Drama basin, Northern Greece, is relatively unaltered and largely unweathered, and shows the greatest amounts of aliphatic groups. The ^{13}C -NMR spectra of Pliocene lignites from endemic areas in Serbia and Montenegro and Bosnia, taken from published papers, show significantly more intense resonances for methoxyl, phenolic, and polysaccharide moieties compared to the Drama lignite NMR spectrum. Xylite reveals high contents of carbohydrates.

Keywords: Balkan endemic nephropathy, ^{13}C CPMAS-NMR, Greece, lignite, peat, sub-bituminous coal, xylite.

INTRODUCTION

The transfer of magnetization from abundant ^1H spins to dilute rare spins such as ^{13}C (abundance 1.1 % of all naturally occurring carbon) or ^{15}N by means of cross polarization (CP) is the initial step in most solid state magic angle spinning (MAS)-NMR pulse sequences. The gain in sensitivity afforded by CP usually outweighs the drawbacks associated with the technique.¹ However, there are cases where the CP spectra exhibit problems related to interference such as spinning sidebands (SSB) in the spectra, the presence of para- and/or ferromagnetic centers in the sample, and low or remote protonation of the aromatic carbons.^{2–4} Solid state ^{13}C nuclear magnetic resonance (NMR) spectroscopy is a very powerful tool for determining the chemical structure of complex organic substrates such as lignins, humic substances, coals of various rank, fossil fuels and marine sediment organics.^{3,5–24} Potentially this technique is an attractive, non-destructive alternative for the study of lignocellulose²⁵ or for determining the concentration of charcoal or black carbon

in environmental samples.²⁶ Orem *et al.*²⁷ have investigated by ¹³C-NMR spectroscopy the possible link between Balkan endemic nephropathy (BEN) and the leaching of toxic organic compounds from Pliocene lignites from known endemic areas in Serbia and Montenegro and Bosnia by groundwater. Chemical analyses using ¹³C nuclear magnetic resonance spectroscopy indicated a high degree of organic functionality in the Pliocene lignite from the Balkans, and suggested that groundwater can readily leach organic matter from the coal beds.²⁷ The present work is concerned with Greek and Bulgarian coals of increasing rank from peat to the sub-bituminous stage. The evolution of the major organic structural units in the samples was identified by using high-resolution, solid-state ¹³C nuclear magnetic resonance spectroscopy (NMR), using a spectrometer with cross-polarization and magic-angle spinning.

EXPERIMENTAL

Materials

Four coal samples from well-studied coal basins in Greece and Bulgaria were selected for the purposes of the present study. The samples were obtained from mines, outcrops or drill cores. Samples P1 (peat) and Dra3 (lignite) were collected in the large intramontane basin of Drama, Eastern Macedonia and the Thrace District, Northern Greece. The central part of the Drama basin comprises an important lignite deposit consisting of three lignite seams (A, B, and C), and including proven reserves of 570 million tons of lignite (on a dry basis). Sample Dra3 was collected from a drill core and belongs to the deepest, thickest and best developed lignite seam A. In the southern part of the Drama basin, which constitutes the Philippi sub-basin, the peat continued accumulating from the Cromerian period up to drainage of the area for agricultural use between 1931–1944. The Philippi peatland is considered today to be the thickest known peatland in the world (190 m thick) and the largest fossil fuel deposit in the Balkans.²⁸ The Holocene peat sample P1 was obtained from a drill core in the central part of the Philippi peatland, which is classified as *Rheotrophic* peat.²⁸ The xylite sample Ach3 was collected in the active mine of Achlada, which belongs to the northern part of a number of fault bounded lignite/xylite-bearing basins developed in northwestern Greece as a result of intense tectonic activity during the upper Miocene period. Finally, the higher rank sample Bul7 is a sub-bituminous coal from the Pernik basin, Bulgaria. All coal samples were ground to <60 mesh and were packed in 7-mm diameter cylindrical zirconia rotors with Kel-F end-caps for the NMR analysis.

Methods

A Bruker AMX300 spectrometer operating at 75.48 MHz on the ¹³C and ¹H resonance frequency of 300.136 MHz was used for the CPMAS ¹³C NMR experiments. Cross-polarisation with magic angle spinning (CPMAS) was applied at 5 kHz. A contact time of 1 ms was used, while a pulse delay of 1 s was chosen. A rotor filled with sample was allowed to spin before each experiment in order to stabilize the sample packing and improve the field homogenization. Chemical shifts, given in parts per million (ppm), were referred to the resonance signal of tetramethylsilane (TMS). More than 6000 scans were needed to obtain acceptable S/N (signal/noise) ratios for these coal samples. The spectrometer was calibrated before and during the NMR spectra acquisition with glycine (H₂NCH₂COOH, Merck standard). A line broadening (LB) of 100 Hz was applied to transform all the free induction decays (FIDs). Usually, in a typical NMR study, the spectra of the analyzed samples are integrated by the available spectrometer software for resonance intervals 220–190 ppm (ketones, quinones, and aldehydes), 190–162 ppm (carboxyls), 162–145 ppm (phenolic carbons), 145–120 ppm (quaternary aromatic carbons), 120–108 ppm (protonated aromatic carbons), 108–96 ppm (anomeric carbons), 96–60 ppm (oxidized carbons), 65–50 ppm (nitrogenated carbons), 50–35 ppm (complex aliphatic carbons), 35–25 ppm (methylene carbons), and 25–0 ppm (methyl carbons).

To investigate a possible influence of paramagnetic species on the CPMAS-NMR spectra of the coals used in the present study, EPR (Electron Paramagnetic Resonance) experiments were performed. EPR studies provide great information on the nature and dispersion of mineral matter in coal, identification of organic matter and of interactions between mineral and organic matter. A Bruker ESP 300E apparatus was used. Typical

operating parameters were as follows: microwave frequency of 9.63 GHz, microwave power 2.6 mW, modulation frequency 100 kHz, and sweep time 42 s. The sweep width was of 5000 G, while the value of the center field was 3444 G. The EPR spectrum of the glass holder was subtracted from the EPR spectra of the coal samples in order noise provoked by the resonance of the glass to be avoided.

RESULTS, DISCUSSION AND CONCLUSION

The ^{13}C NMR spectra of the whole coal samples are shown in Fig. 1. The positions of the peaks in NMR spectra (ppm scale) are determined by the electronic environments of the carbon atoms in different types of chemical structural moieties.²⁷ Major peaks observed in the spectra of the coals under study represent aliphatic carbons (0–50 ppm region), methoxyl carbons (peak at 56 ppm), O-bonded aliphatic carbons, usually polysaccharide structural units in coal (72 and 106 ppm), aromatic carbons (110–150 ppm region), phenolic carbons (150–160 ppm region), and carboxyl/amide carbons (175 ppm).⁵ It is likely that the aliphatic carbons represent refractory cuticular waxes from vascular plants, microbial lipids, long chain hydrocarbons and fatty acids, and other compounds.

The lowest rank peat sample P1 provides a CPMAS-NMR spectrum (Fig. 1-P1) containing a sharp peak for aliphatic moieties (0–50 ppm) from cuticular waxes, resins, and other sources, as mentioned before. A sharp peak presenting a slight hump on the downfield side is also present between 50–60 ppm. This peak is attributed to methoxy ($\text{CH}_3\text{O}-$), methyne (CH , $\text{CH}-\text{NH}$), and aliphatic quaternary carbons. The carbon nuclei of

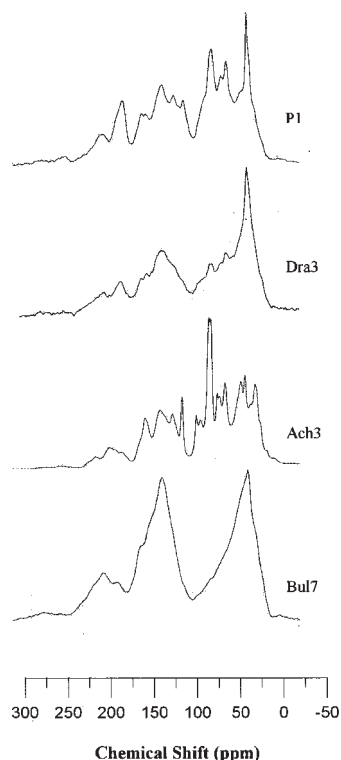


Fig. 1. ^{13}C NMR spectra of peat (P1), lignite (Dra3) and xylite (Ach3) from Northern Greece and a sub-bituminous coal (Bul7) from Bulgaria.

the peat sample P1 also resonate at 72 ppm (polysaccharides), and in the 100–160 ppm interval (aromatic carbons). The intense peak area at 72 ppm indicates that most of the cellulose and other carbohydrates in the original plant material have not been biodegraded and have not been lost during peatification. The aromatic region can be separated into three intervals: (1) the 145–162 ppm interval that is assigned to C–O– and C–OH [O-substituted aromatic (phenolic) moieties indicators of lignin]; (2) the 120–145 ppm range that is attributed to unprotonated aromatic carbons to which only one carbon atom is ascribed; and, (3) the 108–120 ppm region that is attributed to protonated aromatic carbons. The carboxylic region (162–190 ppm) contains signals assigned to both COOH and COO–R systems. Finally, the 190–200 ppm interval was attributed to both ketonic (C=O) and aldehydic (HC=O) carbonyls.

During coalification, the effects of increasing heat and pressure result first in the loss of methoxyl and later in the loss of phenolic functional groups from lignin, followed by an increase in the condensation of the aromatic structures to form more polycyclic structures.^{27, 29,30} The presence of large peaks for methoxyl (50–60 ppm) and phenolic (150–160 ppm) carbons in the spectra of a coal sample shows that this sample is not highly altered from the peat stage. Another feature indicative of the unaltered nature of a coal is the presence of a large peak for structural polysaccharides (72 ppm). Polysaccharides are largely degraded by microbial processes during the peat stage,^{27,31,32} and residual polysaccharides are typically lost during the earliest stages of coalification.³³ Thus, the presence of a significant polysaccharide peak in the spectra of a coal also attests to its largely unaltered character.

The ¹³C NMR spectrum of sample Dra3 (lignite) is typical of many lignites, with peaks for aliphatic (0–50 ppm), methoxyl (50–60 ppm), polysaccharide (72 ppm), aromatic (110–150 ppm), phenolic (150–160 ppm), and carboxyl/amide carbons (175 ppm) present. This lignite sample is relatively unaltered as indicated by the presence in the spectrum of methoxyl, phenolic, and residual polysaccharides. The peak for carboxyl/amide carbons (175 ppm) is small, indicating that this lignite is largely unweathered. Compared to the Pliocene lignite samples from endemic areas of the former Yugoslavia,²⁷ the Drama lignite sample does appear to have undergone a greater degree of thermal alteration. This is indicated by the significantly more intense resonances for methoxyl, phenolic, and polysaccharide moieties in the ¹³C-NMR spectra of the Pliocene lignites from the endemic areas in former Yugoslavia.²⁷

The xylite sample (Ach3) from near the FYROM border appears to have a better preservation of functional groups (methoxyl and phenolic) compared to the lignite sample Dra3. The ¹³C-NMR spectrum of sample Ach3 more closely resembles the lignite samples from the endemic areas of former Yugoslavia.²⁷ The NMR spectrum of this sample is mainly characterized by the presence of a large peak for structural polysaccharides (\approx 75 ppm).

The great variations observed in the organic structural characteristics of coal samples of the same age from the Balkans are probably due to variations in the thermal regime of this tectonically very active region.

The Bulgarian sub-bituminous coal sample (Bul7) has a distinctive NMR spectrum due to its highly aromatic nature (Fig. 1-Bul7). The spectrum for this sample is quite differ-

ent from the coal samples from Greece. It presents three major peaks. The first very pronounced signal in the 0–70 ppm interval is attributed to methyl carbons ($-\text{CH}_3$, 0–25 ppm), methylene carbons ($-\text{CH}_2-$, 25–35 ppm), complex aliphatic carbons (35–50 ppm) and nitrogenated carbons (50–65 ppm). The second signal is attributed to aromatic carbons (110–165 ppm), and carboxyl/amide carbons (175–250 ppm). The sharp aromatic peak has a slight hump on the downfield side, indicating the presence of a small amount of phenolic carbon (150–160 ppm) in this coal, but this coal sample has lost most of its oxygen functionality during the coalification process.

Solid state ^{13}C CP/MAS NMR spectroscopy, being a solid state technique, offers the advantage that spectra can be acquired on whole coal samples with little or no pretreatment. Secondly, it offers the possibility of quantitation, that is, the relative amounts of carbons in different environments can be determined.³⁴ These potential advantages are both limited by the presence of paramagnetic materials, in particular iron (III) compounds. The presence of paramagnetic material (Mn^{2+} , Fe^{3+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Pr^{3+} , Eu^{3+}) results in broadened resonances and decreases in signal intensity, increasing the time required to obtain a reasonable spectrum. This is especially important in obtaining spectra of whole coals of low rank since relatively low concentrations of carbon and the isotopic rarity of the ^{13}C nucleus (naturally about 1 % of all carbon nuclei) already put limitations on the signal to noise (S/N) ratio.³⁴ Nevertheless, in the present study reasonable and useful ^{13}C CP/MAS NMR spectra were obtained on whole coal samples and the EPR study revealed that signal loss and broadening were not so severe. This is probably due to a C:Fe ratio >1 . Apart from causing problems with quantitation of ^{13}C CP/MAS NMR spectra, the selective interaction of paramagnetic materials, particularly paramagnetic cations, with certain functional groups in the heterogeneous organic material in coal provides an opportunity to probe its structure.³⁴

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ИЗВОД

НЕКИ АСПЕКТИ ПРИМЕНЕ ^{13}C CP/MAS NMR СПЕКТРОСКОПИЈЕ НА УГЉЕВЕ БАЛКАНСКОГ ПОЛУОСТРВА

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NMR (CPMAS-NMR) техника је искоришћена да се утврди расподела угљеника у угљевима различитог квалитета (тресет, лигнит, ксилит, ниско-битуминозни угаљ) из важнијих лежишта у Грчкој и Бугарској. Прихваћено је да је ова техника само полу-квантитативна због низа интерференција као што су сателити који потичу од модулације сигнала услед ротације кивете (spinning side bands, SSB) у спектрима, парамагнетне компоненте у узорцима као и ниска протонација ароматичних угљеника. Бугарски ниско-битуминозни угаљ има највећи садржај ароматичних структура. Узорци угља из басена Драма (северна Грчка) релативно су

неизмењени и највећим делом нематурисан, и имају највећу количину алифатичних група. ^{13}C -NMR спектри плиоценских лигнита из ендемских области Србије и Црне Горе и Босне, преузети из публикованих радова, показују значајно интензивније резонанције за метоксилне, фенолне и полисахаридне врсте него спектри лигнита из Дrame. Ксилити имају висок садржај угљоводоника.

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