ELSEVIER

0016-2361(95)00205-7

Fuel Vol. 75 No. 1, pp. 71-77, 1996

0016-2361/96/$15.00 + 0.00

^{13}C Solid-state n.m.r. spectra of Shanxi coals

Huaying Huai, Christopher J. Groombridge*, Andrew C. Scott† and Alec F. Gaines‡
Center for Micro Analysis and Reaction Chemistry, University of Utah, Salt Lake City, UT 84112, USA
** Department of Chemistry, Royal Holloway, University of London, Egham, Surrey TW20 0EX, UK*
† Department of Geology, Royal Holloway, University of London, Egham, Surrey TW20 0EX, UK
‡ Middle East Technical University, Institute of Marine Sciences, PO Box 28, Erdemli 33731, Içel, Turkey
(Received 20 July 1994; Revised 3 April 1995)

^{13}C solid-state n.m.r. spectra of samples of 14 coals and their pyridine residues representative of the three depositions in the Shanxi province of the People's Republic of China are described in detail. The results confirm those of previous infrared spectroscopy in showing these vitrinite–inertinite coals to have similar chemical structures and aromaticities to coals of the same rank from Euramerica and Gondwana.

(Keywords: coal; China; ^{13}C n.m.r.)

The province of Shanxi, on the North China Plate, is the present source of about a fifth of China's production of coal. An introduction to the geochemistry of Shanxi coals has already been published[1] and maceral group compositions, vitrinite reflectances and infrared spectra of the coals have been discussed. Three depositional episodes are known, which have embraced tropical, subtropical and temperate conditions, and the subsequent geological history has been complicated by the intrusion of magma into the seams[1]; nevertheless, Shanxi coals appear to possess a consistent chemistry not markedly different from that of other coals. None of the samples examined contained significant quantities of liptinite and it is therefore sensible to compare their chemistry with that of coals deposited in Gondwana rather than in Euramerica. It should be added that the recent description of the plate tectonics of the Altaid[2] appears to have resolved the dichotomy between the palaeobotany and the palaeomagnetism of the (Shanxi) North China Plate[1]: it was the north eastern corner of the North China Plate which first impinged on the Altaid Plates and Shanxi subsequently rotated anticlockwise into its present position (A. M. C. Sengör, personal communication, 1994). Thus, by the late Carboniferous and the Taiyuan coal deposition, much of Shanxi was around a latitude of 60°N as shown by palaeomagnetism[3] but the land bridge at the north east corner was sufficient to permit the subsequent entry of a European flora[4].

The present paper extends the understanding of Shanxi coals by reporting their characterization by solid-phase ^{13}C n.m.r., a well-established[5–7] but everdeveloping technique[8–13] for describing the chemical structure of coals in terms of the specification and organization of their carbon atoms, thereby improving the interpretation of the previous infrared spectral measurements[1].

EXPERIMENTAL

The elemental analysis of the Shanxi and other coal samples is shown in *Table 1*. Residues of coals were prepared by extracting powdered samples with pyridine in a Soxhlet apparatus under a blanket of nitrogen until the extract was colourless (24–40 h). The residues were freed from pyridine in a rotary evaporator, washed with dilute hydrochloric acid, distilled water and a small amount of acetone, and dried under vacuum at 70°C.

^{13}C cross-polarization magic-angle spinning (CP–MAS) Fourier transform n.m.r. spectra were recorded using a 7 mm diameter, double-bearing, magic-angle spinning probe at room temperature. The aluminium oxide rotor was spun at ~4.5 kHz. The range of parametric values in ^{13}C CP–MAS experiments was: proton pulse width 5.4 μs; contact time 1–2 ms; acquisition time 24 ms; pulse repetition time 100 ms; total accumulation 6000–150 000 scans.

The contact, acquisition and repetition times were optimized for each sample from preliminary measurements of proton T_1 and $T_{1\rho}$ relaxation times obtained from wide-line proton n.m.r. spectra. Proton n.m.r. spectra were recorded using a Bruker 5 mm transverse solenoid probe. Spin–lattice relaxation times, T_1, were obtained by measuring the intensity of the proton n.m.r.

Table 1 Elemental analysis of coals (wt% daf)[a]

		C	H
1	Datong Wuhougou	78.5	5.1
2	Pinglu Erpu	80.5	4.9
3	Datong Emao Kou	81.7	5.2
4	Markham Dull (UK)	83.5	5.2
5	Datong Jueqiang Buxiang	83.9	5.1
6	Xuangang Jiaojia Zhai	86.2	5.2
7	Xishangujiao	86.9	5.0
8	Jucaita	89.0	4.4
9	Bulli (Australia)	89.3	4.9
10	Jishuigou	89.6	4.8
11	Jiajiagou	89.6	4.7
12	Fenxi	89.9	5.1
13	Zaiyandi	90.1	4.8
14	Fenghuang Shan	94.2	2.9

[a] See *Table 1* of Ref. 1 for full analysis; and country of origin is indicated for non-Shanxi coals

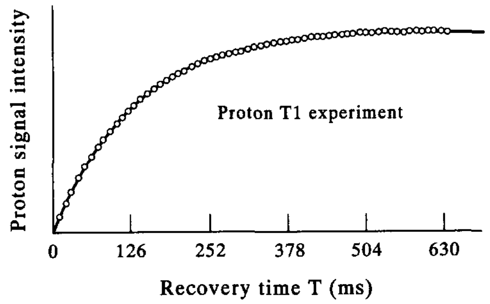

Figure 1 Proton signal intensity versus recovery time, showing the single T_1 relaxation time of Datong Jueqiang Buxiang coal

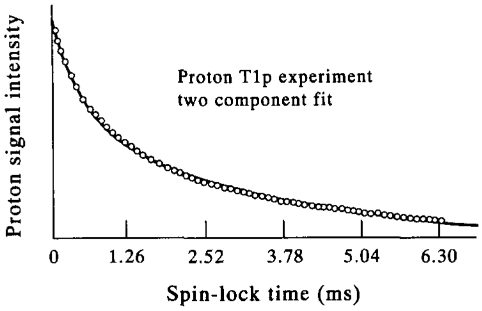

Figure 2 Proton signal intensity versus spin lock time, showing the two-component fit for $T_{1\rho}$ relaxation times of the pyridine residue of Datong Jueqiang Buxiang coal

signal as a fuction of the recovery time after a saturating burst of pulses; $T_{1\rho}$ was determined by measuring the proton signal as a function of the spin–lock time.

Sets of three spectra—^{13}C CP–MAS, ^{13}C CP–MAS TOSS and NQS TOSS—were obtained for each coal and its pyridine residue. Resolution-enhanced spectra were also produced from the CP–MAS data using a Lorentzian-to-Gaussian function[14]. The TOSS (total suppression of sidebands) sequence with 180° carbon pulses of ~8.7 μs width was used when aromaticities were determined quantitatively[15]. In NQS (non-quaternary suppression) TOSS experiments for studying the proportion of non-protonated aromatic carbon atoms and methyl groups, proton decoupling was switched off for 40 μs at the beginning of the last four

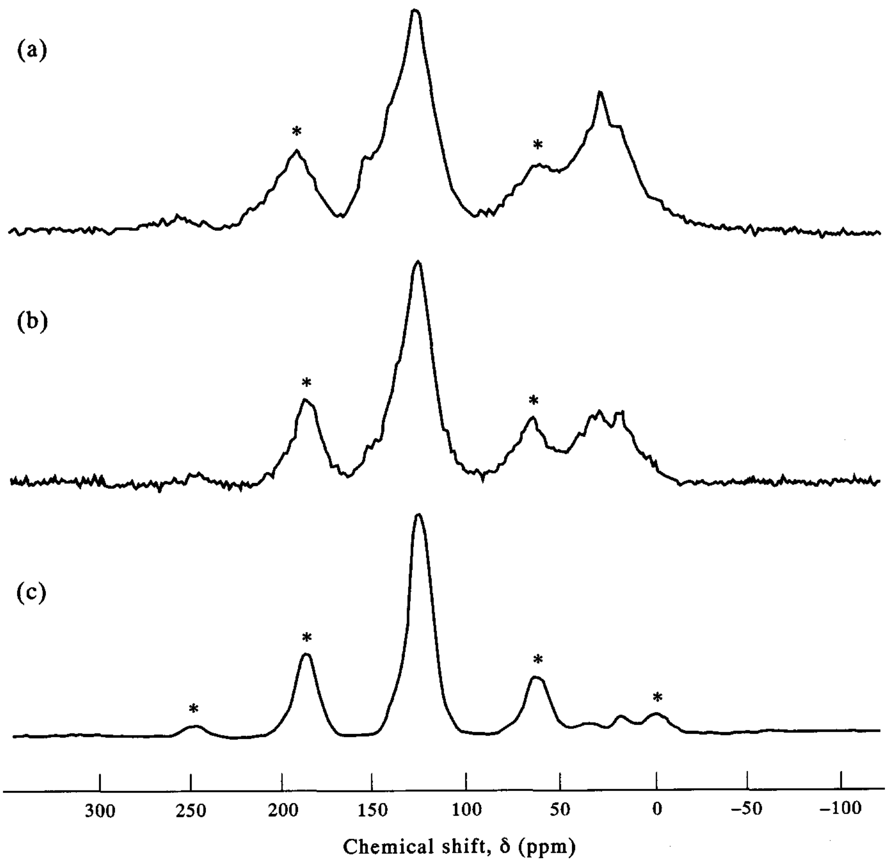

Figure 3 ^{13}C CP–MAS n.m.r. spectra of Shanxi coals: a, Datong Wuhougou; b, Xuangang Jiaojia Zhai; c, Fenghuang Shan (*denotes spinning sideband)

Table 2 Proton relaxation times (ms)

		T_1	$T_{1\rho}$
3	Datong Emao Kou	213	0.483 (42%) 3.77 (58%)
3*	Datong Emao Kou, pyridine residue	36.7	0.419 (45%) 2.85 (55%)
5	Datong Jueqiang Buxiang	136	0.328 (46%) 3.12 (54%)
5*	Datong Jueqiang Buxiang, pyridine residue	141	0.46 (46%) 3.3 (54%)
6	Xuangang Jiaojia Zhai	217	0.657 (46%) 4.54 (54%)
6*	Xuangang Jiaojia Zhai, pyridine residue	48.7	0.466 (48%) 2.96 (52%)
14	Fenghuang Shan	57.4	1.37 (29%) 11.5 (71%)
14*	Fenghuang Shan, pyridine residue	62.5	2.24 (35%) 9.88 (65%)

180° TOSS pulses to alleviate problems which otherwise occur in phasing the spectra.

RESULTS AND DISCUSSION

To obtain ^{13}C n.m.r. spectra as quantitative as possible, the operating parameters were optimized for each coal individually. Further details of these studies are available[16]. The choice of contact time was determined by the proton T_1 and $T_{1\rho}$ relaxation times, which determine the relaxation times in coal experiments[7]. Proton relaxation times of four coals—two of low rank, one of medium rank and one of high rank—were studied in detail. The proton line-shape showed various sets of protons to have been present, each set having a characteristic T_2 relaxation time. As previous workers have found[5,17], the shape of the peaks was consistent with there being two sets of protons in each coal and in each residue remaining after pyridine extraction, and it has become customary to speak of 'mobile' and 'immobile' protons. Because T_1 spin diffusion is very rapid, transmitting relaxation over distances of the order of 10 nm even if this distance is not chemically uniform, a single proton T_1 is observed for each sample[18]. Typical results are plotted in *Figure 1*. Proton spin diffusion with respect to the rotating frame of axes is relatively slow, affecting distances of $\sim$1 nm[18]. Two component $T_{1\rho}$ were observed, typical results, fitted by two exponential decays, being shown in *Figure 2*. The measured relaxation times are summarized in *Table 2*. It will be seen that $\sim$46% of the protons in the low- and medium-rank coals and 29% of the protons in the high-rank anthracite were mobile. It has been stated that the whole of the mobile hydrogen cannot be extracted by pyridine[6]. This is consistent with the results in *Table 2*, showing residues after pyridine extraction to contain a similar proportion of mobile hydrogen to the parent (demineralized) coal. The Fenghuan Shan anthracite was an extreme case; it gave no significant yield of pyridine extract; nevertheless $\sim$29% of its hydrogen was mobile.

The relaxation times shown in *Table 2* are similar to those reported previously[7] and the consequent contact times, 1–2 ms, are also similar to those used by most other workers.

Figures 3–5 show ^{13}C n.m.r. spectra typical of those obtained from each sample of demineralized Shanxi coal and its residue after pyridine extraction. As expected, the spectra of the residues after pyridine extraction were closely similar to those of the parent coals. In virtually all the samples, absorption by methyl groups, resolved in the resolution-enhanced spectra and clearly distinguished by the ^{13}C NQS TOSS spectra, gave maxima in the range 18–22.5 ppm together with a shoulder close to or below 15 ppm, showing most of the methyl groups in Shanxi coals to be in ethyl groups or alpha to aromatic rings[19].

The major absorption due to methylene and methine groups gave structured absorption between 24 and 50 ppm which was readily distinguished by elimination of the (methyl) aliphatic absorption in ^{13}C NQS TOSS spectra from either resolution-enhanced spectra or ^{13}C CP–MAS TOSS spectra (*Figures 4, 5*). Consistent with the observation that none of the samples of Shanxi coal contained liptinite[1], the spectra in this region resembled those of telocollinite and not those of sporinite (compare *Figure 4* in ref. 20). In particular, the peak at 29–30 ppm, dominant and sharp when it is in methylene groups in alkyl chains, was less pronounced in the Shanxi samples. Clearly the proportion of alkyl chains in these vitrinite–inertinite coals—as in Bulli coal—is limited and at least part of the absorption at 29–30 ppm was due to hydroaromatic structures such as 9, 10-dihydrophenanthrene[19,21]. Further

Table 3 Synthesis of NQS and CP–MAS TOSS spectra[a]

		H/C	f_a	f_h	CH$_n$	m_1	m_2	m_2*	f_0	f'_a
1	Datong Wuhougou	0.77	0.68	0.26	1.59	0.31	0.36	0.30	0.14–0.30	0.72–0.77
2	Pinglu Erpu	0.73	0.72	0.34	1.39	0.24	0.36	0.35	0.19–0.32	0.77–0.81
3	Datong Emao Kou	0.75	0.70	0.26	1.63	0.41	0.38	0.30	0.13–0.28	0.74–0.78
9	Bulli	0.65	0.76	0.28	1.54	0.31	0.34	0.42	0.15–0.23	0.79–0.815
12	Fenxi	0.68	0.77	0.25	1.87	0.34	0.29	0.38	0.04–0.13	0.78–0.80

[a] Sample numbers as in *Table 1*
f_a = aromaticity
f_h = fraction of carbon atoms which are protonated and aromatic
CH$_n$ = aliphatic hydrogen atoms per aliphatic carbon atom
m_1 = fraction of aliphatic carbon atoms in methyl groups
m_2 = fraction of aliphatic carbon atoms with chemical shifts in the range 0–24 ppm
m_2* = as m_2 but for pyridine residues
f_0 = fraction of unobserved (non-protonated) aromatic carbon atoms required to make CH$_n$ equal to 2–2.2 (ranged values depend on CH$_n$ and the correction for hydroxyl groups)
f'_a = consequent aromaticity allowing for unobserved aromatic carbon atoms

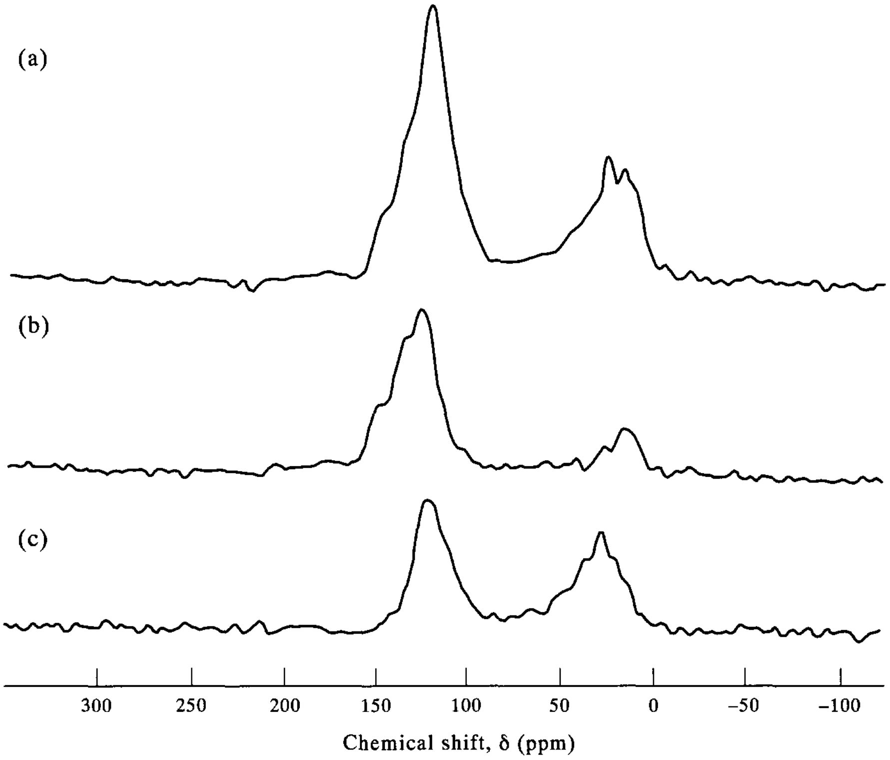

Figure 4 ^{13}C CP–MAS n.m.r. spectra of Datong Wuhougou coal: a, spinning sideband suppressed (TOSS); b, with non-quaternary suppression (NQS TOSS); c, difference a–b

work to distinguish methine from methylene would be valuable; methine groups alpha to aromatic rings and absorbing between 40–50 ppm are important in coal liquefaction[22]. Absorption observable between 50–63 ppm may be assigned to alkyl groups in alkyl–aryl ethers, but 'spinning sidebands' usually occurring in this region may not have been removed completely in the TOSS experiments.

Three usual characteristics of the envelope of aromatic absorption[20] were readily distinguished, especially in resolution-enhanced spectra (*Figure 5*): a pronounced maximum at 126–129 ppm sometimes showing more than one peak, a shoulder near 137 ppm and a second shoulder or peak at about ~154 ppm. The aromatic region having chemical shifts of <126 ppm is due to aromatic carbon atoms bonded to carbon and either ortho and para to phenolic hydroxyl groups or beta to the oxygen atom in benzofuran, furan and indole structures[19], these being the only possibilities consistent both with the infrared spectra of the coals[1,23] and with spectra obtained for solid fluorescein, dibenzofuran, 4-phenoxyphenol and 2-phenoxybiphenyl. Comparison of CP–MAS TOSS and NQS TOSS experiments (see *Figure 4*) shows that <126 ppm there was also significant absorption by protonated aromatic carbon atoms. Most protonated aromatic carbon atoms however absorbed in the normal benzene region close to 128 ppm, but some absorption between 129 and 137 ppm may be ascribed to polynuclear aromatic structures[19]. A small proportion of the protonated aromatic carbon atoms absorbed between 135 and 150 ppm, confirming the presence of small quantities of furans and benzofurans. The NQS TOSS spectra also showed (*Figure 4*) aromatic carbon atoms attached to carbon absorbing not only in the expected region between 137 and 154 ppm but also, as has been described, <126 and between 126 and 137 ppm. This is a more precise interpretation of the aromatic region than that given previously[20,22]. The regions 137–148 and 150–171 ppm were due to aromatic carbon atoms bound to carbon and to oxygen (either as phenols or as diaryl ethers, few alkyl aromatic ethers being present) atoms respectively.

In considering the extent to which the spectra are quantitative, it can be observed that many, though not all, of the different spectra were repeated on several subsamples of the same powdered coal and, generally, absorption was reproducible to ~5% whether the intensities were measured as peak heights or as integrated areas. Most of the variance arose in the n.m.r. experiment. In the following discussion of *Tables 3–5* such ratios of intensities as aromaticities are accordingly accurate to ~10%.

CP–MAS TOSS spectra give the aromaticities of the coals. NQS TOSS spectra provide the ratios of the numbers of carbon atoms in methyl groups to those which are aromatic but not protonated. For five coals the NQS TOSS and CP–MAS TOSS spectra were obtained under similar conditions, so that subtraction of the two spectra gave the proportion of aromatic carbon atoms that were not protonated (*Figure 4*). The fraction of aromatic hydrogen atoms in the coals is seen to be larger

Table 4 Percentage of aliphatic carbons in methyl groups

	Coal	Pyridine residue
1 Datong Wuhougou	36	30
2 Pinglu Erpu	36	35
3 Datong Emao Kou	38	30
4 Markham Dull	31	31
5 Datong Jueqiang Buxiang	24	24
6 Xuangang Jiaojia Zhai	33	37
7 Xishangujiao	44	37
8 Jucaita	42	44
9 Bulli	34	42
10 Jishuigou	44	–
11 Jiajiagou	41	39
12 Fenxi	29	38
13 Zaiyandi	49	50
14 Fenghuang Shan	70	57

than the value originally assessed from infrared spectra[23]. From the fraction of protonated aromatic carbon atoms, the aromaticity of the coal and its hydrogen/carbon atomic ratio (and a correction for the number of hydrogen atoms in hydroxyl groups), the number of hydrogen atoms, CH_n, in an average aliphatic group is obtained. The results are shown in *Table 3*, which also provides a comparison of the proportion of methyl groups, m_1, and of aliphatic carbon atoms absorbing between 0–24 ppm, m_2, the usual range for methyl groups both in coals and in their pyridine residues. The results are in reasonable agreement with the exception of those for Pinglu Erpu coal (coal 2), which in this respect must have something slightly unusual about its chemical structure.

Table 5 Average aromatic structure of Shanxi coals (percentage of total carbon)

		Region			
	f_a	a	b	c	d
1 Datong Wuhougou	68	7	13	20	28
1* pyridine residue	72	6	11	25	30
2 Pinglu Erpu	72	4	14	24	30
2* pyridine residue	74	6	14	22	32
3 Datong Emao Kou	70	4	15	21	30
3* pyridine residue	73	7	15	19	32
4 Markham Dull	67	4	14	22	27
4* pyridine residue	68	8	10	18	32
5 Datong Jueqiang Buxiang	67	4	11	20	32
5* pyridine residue	73	6	15	23	29
6 Xuangang Jiaojia Zhia	77	6	12	23	35
6* pyridine residue	80	5	14	20	41
7 Xishangujiao	69	3	11	26	29
7* pyridine residue	79	5	12	32	31
8 Jucaita	80	4	14	28	34
8* pyridine residue	86	5	9	37	34
9 Bulli	76	4	13	25	34
9* pyridine residue	80	2	15	30	32
10 Jishuigou	75	4	15	27	30
11 Jiajiagou	77	2	8	35	33
11* pyridine residue	83	2	14	33	32
12 Fenxi	77	3	16	22	36
12* pyridine residue	80	3	19	22	36
13 Zaiyandi	78	2	11	31	34
13* pyridine residue	82	4	13	29	35
14 Fenghuang Shan	95	0.6	13	38	43

Table 4 gives the percentages of aliphatic carbon atoms in methyl groups for all the samples studied; these percentages are in fact those of carbon atoms absorbing in the 0–24 ppm region and should be accepted cautiously. The values of CH_n in *Table 3* are very similar to those found in previous n.m.r. studies for American

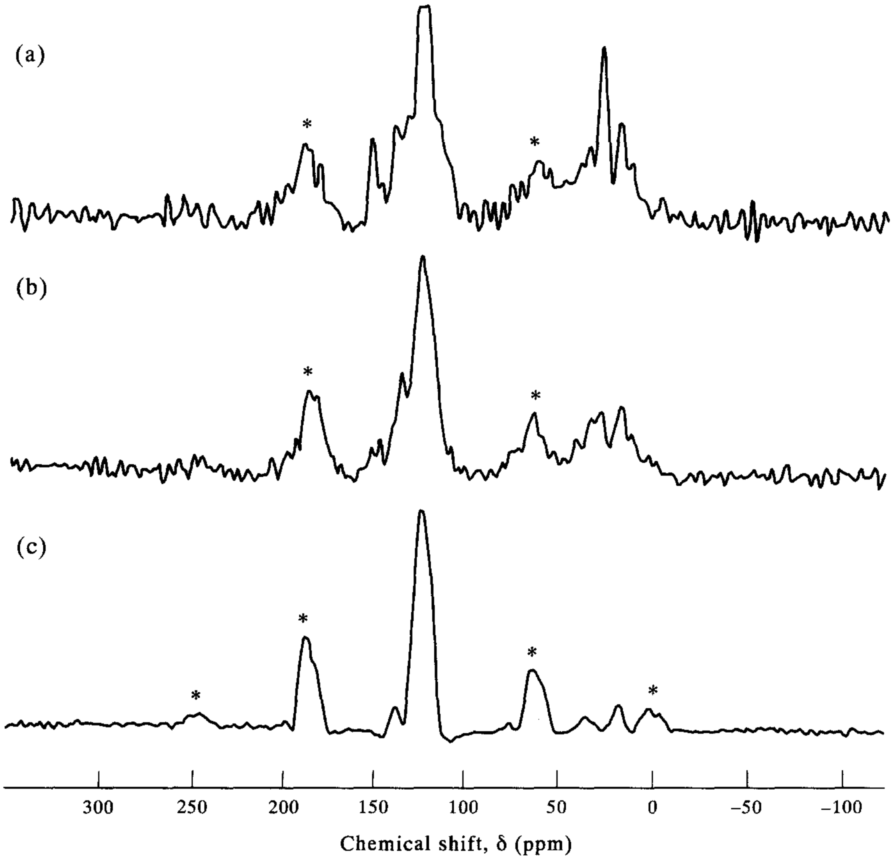

Figure 5 Resolution-enhanced ^{13}C CP–MAS n.m.r. spectra of Shanxi coals: a, Datong Wuhougou; b, Xuangang Jiaojia Zhai; c, Fenghuang Shan (* denotes spinning sideband)

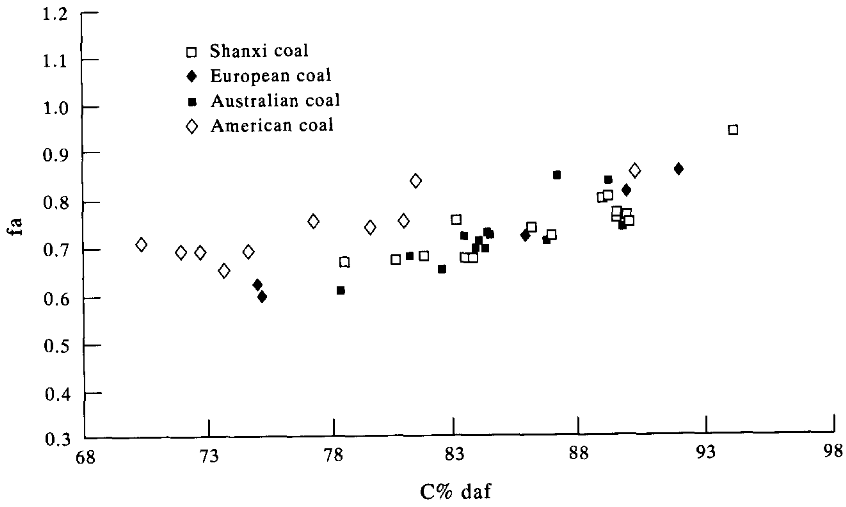

Figure 6 Variation of aromaticity from ^{13}C n.m.r. spectra with carbon content of American, European, Australian and Shanxi coals

coals[24]. This is further important evidence of the similarities to be found in coal structures despite the wide range of conditions under which deposition and diagenesis occur. Nevertheless, the values of CH_n must be regarded sceptically. Work suggests that CP–MAS n.m.r. spectra fail to observe a significant proportion of the carbon atoms, particularly non-protonated aromatic carbon atoms[8,9]. Moreover, with the exception of Fenghuan Shan coal (coal 14), the calculated values of CH_n are lower than those obtained by supposing the proportions of methyl groups to have been determined correctly and all the other aliphatic carbon atoms to have been methines (i.e. supposing methylene groups to have been absent), which is unlikely. The number of non-protonated aromatic carbon atoms (expressed as a proportion of the total number of observed carbon atoms) which would appear to have been 'missed' had the real value of CH_n been 2–2.2[23] has been calculated. The calculation assumes both the hydrogen/carbon atomic ratios and the n.m.r. absorption protonated carbon atoms to have been determined correctly. This calculation suggests that as much as 30% of the carbon atoms in the coal present as non-protonated aromatic carbons may not have been observed (even more carbon atoms would not have been observed if aliphatic carbons had also been missed). However, the increase in aromaticity that the missing non-protonated aromatic carbon atoms would cause, though significant, is probably within the experimental error. Quantification of the n.m.r. spectroscopy of coals would be aided if the proportions of methylene and methine groups could be determined. With the number of methyl groups already reasonably well established, CH_n could be calculated from the aliphatic region of the spectra and this, together with the hydrogen/carbon atomic ratios, would provide a check on the proportions of protonated aromatic carbon atoms. Relatively few methines (alpha to aromatic rings) can be observed absorbing at chemical shifts of 40–50 ppm. However, overlapping methylene and methine absorption between chemical shifts of 24 and 40 ppm can be distinguished only by chemical tests or studies of relaxation times.

Table 5 shows the aromaticities, f_a, of the coals and their residues after pyridine extraction. *Figure 6* provides a comparison with values obtained for European, American and Australian coals[25–28]. Shanxi coals possess aromaticities of the expected order of magnitude which increase straightforwardly with rank. It is readily shown that the H/C atomic ratio is equal to $[n - (n - x)f_a]$, where x is the ratio of f_h to f_a and the other symbols have already been defined. It is found that, at least between aromaticities of 0.65 and 0.80, H/C appears to be a linear function of aromaticity, suggesting n and x to be roughly constant over this range of rank. Also shown in *Table 5* are the proportions of the total numbers of aromatic carbon atoms which absorb in the regions (a) 170–154 ppm, (b) 154–137 ppm, (c) 137–126 ppm and (d) < 126 ppm, assignments discussed in the previous section (the order a,b,c,d, is the reverse of that used in Ref 20). *Table 5* shows that, as would be expected, residues from pyridine extraction have essentially the same aromatic structure as the parent coals, though they appear to be slightly more aromatic, confirming that pyridine extracts are slightly rich in aliphatic material. The property (a) of aromatic carbon atoms attached to oxygen diminished normally as the rank of the coals increased. The fraction of carbon atoms in region (b) consisting of aromatic carbon atoms attached to carbon (though, as the discussion of NQS spectra has shown, this is not precise) showed little variation with rank. Thus, 13.7 ± 0.8% of the carbon atoms in pyridine residues were in region (b). This may be misleading; it probably conceals how the proportion of aliphatic to aromatic carbon atoms substituting aromatic rings decreases with increase in rank. *Table 5* reveals that the proportions of aromatic carbon atoms in regions (b), (c) and (d) show little variation. The ratio of carbon atoms in regions (b) and (d) was usually 2–3 : 1 and the ratio of carbon atoms in regions (d) and (c) was 1.5–1.2 : 1 (there were exceptions). this suggests clearly that the mix of aromatic structures in all these coal samples was rather similar. This is consistent with their infrared spectra[1], which showed that, with the exception of the lowest (Datong Wuhugou) and highest (Fenghuan Sahn) coals, all these samples possessed similar patters of aromatic ring substitution, the aromatic out-of-plane CH deformation vibrations giving infrared absorption dominated by peaks at 755, 810 and 873 cm^{-1}. An effort to determine the aromatic structures involved would be rewarding.

CONCLUSIONS

^{13}C CP–MAS n.m.r. studies have confirmed that the chemical structures of the three vitrinite-rich sequences of Shanxi coals are very similar to those of Gondwanan coals. Their aromaticities vary with rank in very nearly the same was as those of Gondwanan coals, irrespective of the details of their deposition and diagenesis. Comparison of CP–MAS TOSS and NQS TOSS spectra has permitted reasonably accurate determinations of the percentages of carbon atoms in the coals that are present as methyl groups, but it is not yet possible to distinguish methylene from methine groups.

The fraction of aromatic carbon atoms attached to aliphatic substituents remains uncertain; nevertheless, the aromatic structures present in Shanxi coals appear rather similar throughout most of the range of rank. This is consistent with the similarity in patterns of aromatic substitution previously revealed by infrared spectra[1]. As in other coals, both n.m.r.-mobile and -immobile protons are present in Shanxi coals, even in pyridine residues and in anthracite.

ACKNOWLEDGEMENTS

Much of the work was conducted at Birkbeck College, University of London, and was generously supported by Taiyuan University of Technology and the SERC (UK). All spectra were run on the University of London Intercollegiate Research Service (ULIRS) instrument with the assistance of David Butler. The authors are sincerely grateful to Professor Colin Flint for his encouragement. Dr Colin Snape has been kind enough to read the manuscript and make several constructive suggestions for its improvement.

REFERENCES

1 Huai, H., Gaines, A. F. and Scott, A. C. *Fuel* 1994, **73**, 1322

2 Sengor, A. M. C., Natalin, B. A. and Burtman, V.A. *Nature* 1993, **364**, 299

3 Donovan, S. K. *Nature* 1987, **327**, 139

4 Zhao, X. and Coe, R. S. *Nature* 1987, **327**, 141

5 Sullivan, M. J. and Maciel, G. E. *Anal. Chem.* 1982, **54**, 1606 and 1615

6 Davidson, R. M. 'Nuclear Magnetic Resonance Studies of Coal', Report ICTIS/TR32, IEA Coal Research, London, 1986

7 Axelson, D. E., 'Solid State Nuclear Magnetic Resonance of Fossil Fuels', Multiscience Publications CANMET and Canadian Government Publishing Centre, Ottawa, 1985

8 Franz, J. A., Garcia, R., Linehan, J. C., Love, G. D. and Snape, C. E. *Energy Fuels* 1992, **6**, 598

9 Love, G. D., Law, R. V. and Snape, C. E. *Energy Fuels* 1993, **7**, 639

10 Chen Peng, Chen Mingxiu and Tao Yuling. *Ranliao Huaxue Xuebao (J. Fuel Chem. Technol.)* 1988, **16**, 260

11 Ye Chaohui, Wind, R. A. and Maciel, G. E. *Sci. Sin. A (Engl. Ed.)* 1988, **31**, 968

12 Wilson, M. A., Vassallo, A. M., Liu, Y. L. and Pan, L. S. K. *Fuel* 1990, **69**, 931

13 Li Fan, Zhang Yongfa and Xie Kechang. *Fuel Sci. Technol. Int.* 1993, **11**, 931

14 Ferrige, A. G. and Lindon, J. C. *J. Magn. Reson.* 1978, **31**, 337

15 Dixon, W. T., Schaefer, J., Sefcik, M. D., Stejskal, E. O. and Mackay, R. A. *J. Magn. Reson.* 1982, **49**, 341

16 Huai, H. Ph.D. Thesis, University of London, 1989

17 Pugmire, R. J., Soderquist, A., Burton, D. J., Beeler, A. L. and Grant, D. M. In '1985 International Conference on Coal Science', Pergamon Press, Sydney, 1985, p. 28

18 McBrierty, V. J. and Douglass, D. C. *Phys. Rep.* 1980, **63**, 61

19 Snape, C. E., Ladner, W. R. and Bartle, K. D. *Anal. Chem.* 1979, **51**, 2189

20 Davies, M. R., Abbott, J. M., Cudby, M. and Gaines, A. F. *Fuel* 1988, **67**, 960

21 Retcofsky, H. L. and Friedel, R. A. In 'Spectrometry of Fuels' (Ed. R. A. Friedel), Plenum Press, New York, 1970, p. 90

22 Gaines, A. F. In 'Clean Utilization of Coal' (Ed. Y. Yurum), Kluwer Academic, Dordrecht, 1992, p. 1531

23 Brown, J. K. *J. Chem. Soc.* 1955, 744

24 Solum, M. S., Pugmire, R. J. and Grant, D. M. *Energy Fuels* 1989, **3**, 187

25 Sfihi, H., Quinton, M. F., Legrand, A., Pregermain, S. and Chiche, P. *Fuel* 1986, **65**, 1006

26 Miknis, F. P., Sullivan, M. and Maciel, G. E. *Org. Geochem.* 1981, **3**, 19

27 Russel, J. N., Wilson, M. A., Pugmire, R. J. and Grant, D. M. *Fuel* 1983, **62**, 601

28 Lynch, L. J., Webster, D. S., Sakurovs, R., Barton, W. A. and Maher, T. P. *Fuel* 1988, **67**, 579