ESTONIAN DICTYONEMA SHALE AND SWEDISH ALUM SHALE. ESTIMATION OF AROMATICITIES BY ^{13}C NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY

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The percentages of aromatic carbon in several Lower Paleozoic black alum shales of the Baltoscandian region have been determined by solid state high resolution nuclear magnetic resonance spectroscopy. In marked contrast to the Estonian Middle Ordovician shale kukersite, the black shales have a much higher rank of maturation, and carbon aromaticity in the Cambrian shales exceeds 50 %. The overall structure of the organic matter is similar to that found in typical samples of major US shales.

The Lower Paleozoic sedimentary sequence in Southeastern Baltoscandia rests upon a gneissic basement and reaches in Northern Estonia up into the Lower Silurian. These sediments comprise several formations starting with basal sandstone and followed by Cambrian and Early Ordovician black alum shales. The latter are covered by a thick Middle Ordovician layer of limestones, interlaced with layers of brown kukersite shale. Swedish alum shale deposits at Hynneberg (Närke), Ranstad (Billingen, Västergötland) and Bårstad (Östergötland), Fig. 1, are Late Cambrian and thus the oldest in Baltoscandia [1]. The Estonian Early Ordovician (Tremadoc) graptolite argillites are younger and cover a wide area along the shoreline of Northern Estonia. These black laminated clay rocks are known as Dictyonema shales. The distinctive black colour of alum shales is caused by the highly disperse and homogeneously distributed organic matter or kerogen. It is of considerable interest to follow shale maturation in the Baltoscandian sedimentary sequence. In particular, chemical compositions and carbon aromaticity factors were determined for the Dictyonema alum shale samples from single boreholes at Maardu and Toolse in Northern Estonia as well as for the alum shales from Hynneberg, Ranstad and Bårstad.
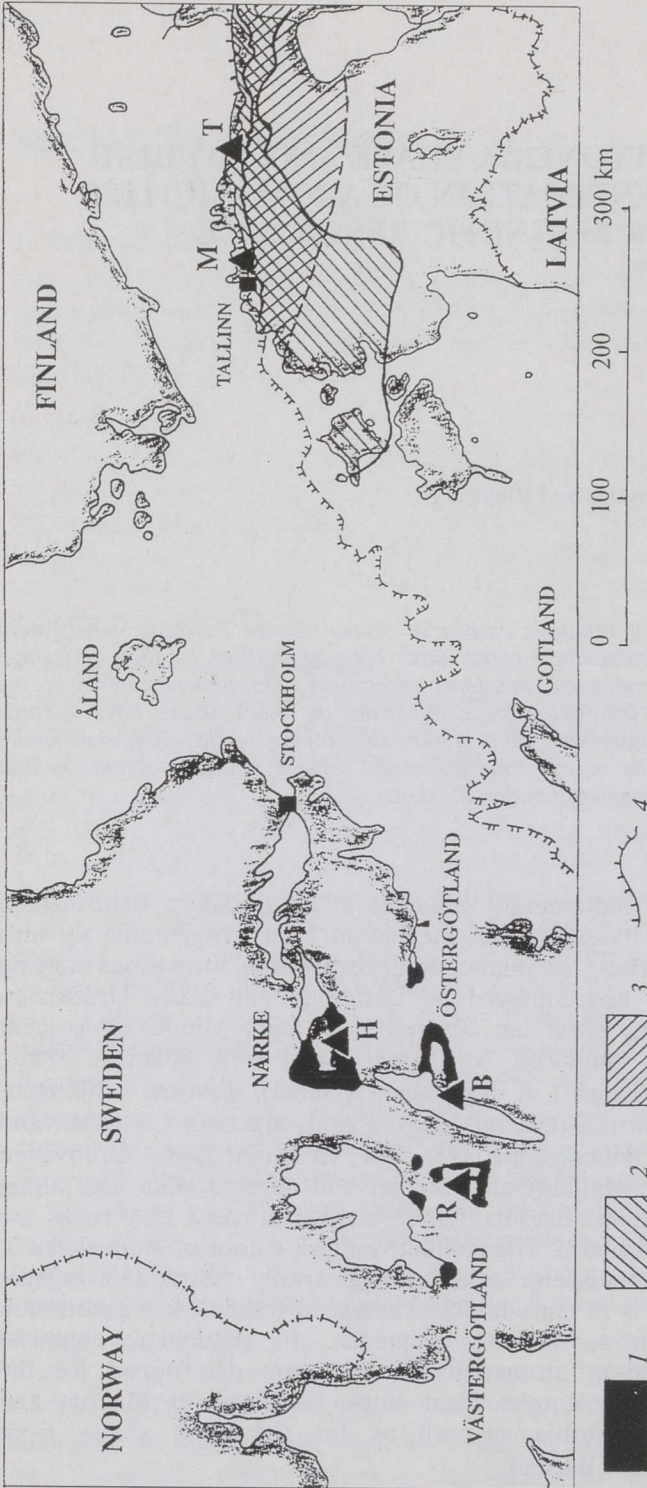
Fig. 1. Cambrian and Ordovician deposits of Southeastern Baltoscandia. *1* - Cambrian alum shale, *2* - Early Ordovician Dictyonema shale, *3* - Middle Ordovician oil shale (kukersite), *4* - clint, H - Hynneberg, B - Bårstad, M - Maardu, R - Ranstad, T - Toolse

Experimental

The samples were prepared by grinding the shales in an agate mortar to a < 0.2 mm grain size. In some cases argon atmosphere was used to avoid oxidation during grinding.

The solid state high resolution ^{13}C MAS-NMR spectra were obtained at 50.3 MHz using a Bruker Physik CXP 200 NMR spectrometer and a MAS probe equipped with 7 mm and 4.5 mm O.D. cylindrical rotors for fast (5 or 8 kHz) sample rotation under the magic angle. Magic angle spinning MAS permits to remove linebroadenings due to chemical shift anisotropy and particle susceptibility effects, and is thus the prerequisite for successful quantitative solid state NMR. Rotation sideband formation is a complicating factor which can be held within tolerable limits only by choosing spinning speeds close to or exceeding the chemical shift anisotropy values of the carbons actually measured. In practical terms this means the easily achievable 5 kHz spinning rates in a 4.7 Tesla magnetic field used by us. Sideband suppression through the use of special pulse sequences (PASS, TOSS) can be successfully applied if the main emphasis is upon chemical shift determination, but in alum shale samples they lead to severe signal intensity distortions in the spectra so registered.

The most serious problem in quantitative ^{13}C MAS-NMR spectroscopy of shales and other fuels low in organic matter is sensitivity. MAS together with direct excitation of the carbons with a strong 90° *rf* pulse and a sequence recycle time much longer than T_{1C} can provide quantitatively accurate data, but the sensitivity is very low because the carbon spin-lattice relaxation times T_{1C} can be very long and widely different for various chemical structures in the sample. Inadequate sensitivity leads to very long measurement times and baseline distortions due to the finite dead time of the NMR probe and input circuitry. Faster pulsing shortens the measurement time, but this can lead to underestimation of the more highly condensed carbon clusters with large T_{1C} values. The shortest allowable sequence recycle time can be found through estimation of the longest significant T_{1C} value in the sample. In practice this is best done from the aromaticity factor vs pulse delay time plot. Direct excitation ^{13}C NMR spectra can provide reliable benchmark values for further evaluation of the results obtained by the much more sensitive cross-polarization (CP) technique.

The cross-polarization technique as developed by Pines et al. [2] uses resonant, spin-locked polarization transfer from the dipolar-decoupled abundant (^1H) to the rare (^{13}C) spins and it can be easily combined with MAS [3, 4]. The sensitivity gain is much larger than the direct $\gamma_{1H}/\gamma_{13C} = 4$ carbon polarization enhancement, because polarization of the proton spin system occurs much faster than polarization of the carbon spin system ($T_{1H}^{-1} > T_{1C}^{-1}$). The quantitative accuracy depends upon four relaxation processes. These are the proton polarization buildup rate T_{1H}^{-1}, the cross-polarization rates T_{CH}^{-1} and finally the polarization decay rates in the rotating frame $T_{1\rho H}^{-1}$ and $T_{1\rho C}^{-1}$. All these time constants have significant and generally unknown distributions over the various chemical structures and components present in the shale sample.

The cross-polarization time T_{CH} depends upon carbon-hydrogen dipolar interactions and is much longer for unprotonated aromatic carbons than for the alicyclic or aliphatic ones. In the usually assumed simplest case $T_{CH} \ll T_{1\rho H} \ll T_{1\rho C}$, the carbon magnetization both increases (T_{CH}) and decreases ($T_{1\rho H}$) exponentially with cross-polarization contact time, and peaks in coals and shales at around 1 ms. The CP-MAS NMR spectra are quantitatively reasonably accurate only in case of proton-rich polymers or shales like Estonian kukersite, which is younger than local alum shale and where the aromatic structures are still phenolic and well protonated [3].

Aromaticity Factors

The percentages of aromatic carbon, or aromaticity factors of the shales can be directly obtained from integrated line intensities in the MAS-NMR spectra. We have taken the integrated intensity between 170 and 100 ppm to represent aromatic carbons and that between 100 and −20 ppm to represent the alicyclic and aliphatic ones. In case of relatively slow sample spinning at 5 kHz, the aromatic carbon resonances form sidebands. The total intensity of the lower and higher sidebands must be added to that of the aromatic carbon centerband at 130 ppm. In this, both sidebands are considered to have equal intensities, including the higher sideband which always overlaps with the line of aliphatic and alicyclic carbons at 30 ppm.

Results

The percentages of organic aromatic carbon in eight Baltoscandian alum shale samples are given in Table 1.

Table 1. **The Apparent Percentages of Aromatic Carbon Found**

Sample	Aromaticity in per cent			
	Direct excitation[1]	Cross-polarization[2]		Calculated[3]
		5 kHz spinning	8 kHz spinning	
Ranstad 1	59	57	47	58
Ranstad 2	52	52		58
Hynneberg[4]		52		42
Bårstad 1[5]		48		54
Bårstad 2[6]		48		54
Toolse 1		48	39	42
Toolse 2		50	39	42
Maardu		39		39

[1] 45° pulse excitation, 10 s delay time.

[2] Cross-polarization time 1 ms, recycle delay 1 s.

[3] Calculated from the ultimate analysis data.

[4] Drillcore at 5.5 to 6.5 m depth

[5] Drillcore at 3 to 4 m depth.

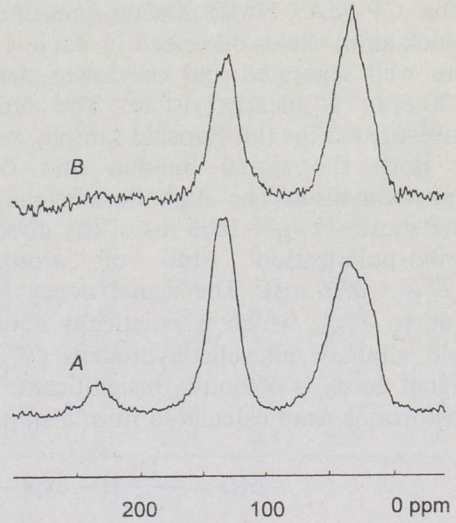[6] Drillcore at 10 to 11 m depth.

Fig. 2. ^{13}C CP MAS spectra of Ranstad 1 (*A*) and Toolse 1 (*B*) samples. 5 kHz spinning

The first (Ranstad 1) sample was used for calibration. The two direct excitation experiments took 46 hours and 23 hours, involving 16 500 free induction decays with 10 s and 5 s delays between pulses, respectively. The apparent percentages of aromatic carbon found were 59 % and 55 %. Assuming a single T_{1C} value, this leads to the limiting value of 59.5 %. The measurement error is consequently less than 1 % in case of a 10 s delay time, which gives $T_{1C} \ll 10$ s. The carbon spin-lattice relaxation time did not change with acid extraction, which makes the presence of organic free radicals rather likely.
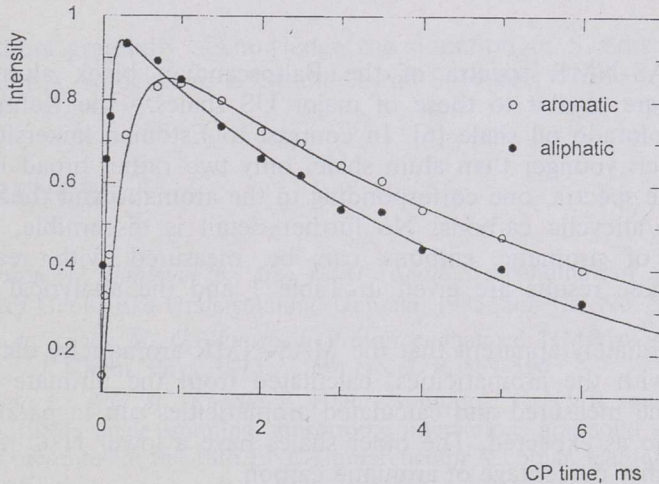

Fig. 3. ^{13}C signal buildup and decay in CP MAS experiment, normalized curves. Ranstad 1 sample

The CP-MAS-NMR spectra presented in Fig. 2 are typical for all the black alum shales described in Table 1. The aliphatic and aromatic carbons are well separated and the lower field sideband of the aromatic line at 130 ppm is clearly visible. The cross-polarization dynamics was also investigated for the Ranstad sample, see Fig. 3.

Both the signal buildup and decay are exponential in a good approximation. The aliphatic/alicyclic signal growth is much faster due to the shorter $T_{CH} = 0.05$ ms of the directly protonated carbons. The average cross-polarization time of aromatic carbons is much longer ($T_{CH} = 0.25$ ms). The signal decay at longer cross-polarization times is due to $T_{1\rho H}$, which is practically equal for the aromatic ($T_{1\rho H} = 6.7$ ms) and aliphatic/alicyclic hydrogens ($T_{1\rho H} = 5.1$ ms). The role of $T_{1\rho C}$ in signal decay is obviously insignificant. The possible ^{13}C CP signal intensity distortions were calculated from a spin temperature $\beta(t)$ equation

$$\beta(t) = \frac{1}{1-\lambda}\left[1 - \exp\left[-\frac{1-\lambda}{T_{CH}}t\right]\right]\exp\frac{-t}{T_{1\rho H}},$$

where $\lambda = \frac{T_{CH}}{T_{1\rho H}}$

derived from Ref. 5, and assuming the found T_{CH} and $T_{1\rho}$ values and 1 ms contact time. In case of sample aromacity $f_a = 0.5$, the error caused by cross polarization dynamics differences of aromatic and aliphatic carbons while using 1 ms CP time is 0.007, i.e. practically it remains below the experimental error level. For further experiments the cross-polarization time was taken to be 1 ms and the pulse sequence recycle time 1 s.

These conditions are quite similar to these generally applied in NMR-investigations of solid fossil fuels such as oil shales [6] or coals [7].

Discussion

The CP-MAS-NMR spectra of the Baltoscandian black alum shales investigated are similar to those of major US shales - the Kentucky oil shale and Colorado oil shale [6]. In contrast to Estonian kukersite shale, which is much younger than alum shale, only two rather broad lines are present in the spectra, one corresponding to the aromatic and the other to the aliphatic/alicyclic carbons. No further detail is discernible, but the percentages of aromatic carbons can be measured with reasonable accuracy. These results are given in Table 1 and the analytical data in Table 2.

It is immediately apparent that the MAS-NMR aromaticity data are in correlation with the aromaticities, calculated from the ultimate analysis data. Both the measured and calculated aromaticities run in parallel with the H/C ratio as expected. The older shales have a lower H/C ratio and contain a higher percentage of aromatic carbon.

All the shales investigated in this study belong to the class of sapropelites. It is well known that sapropelites are generally less aromatic than the humic coals at the same brown coal stage of coalification. This general tendency is well borne out in this study.

Table 2. **Analysis of the Dictyonema and Alum Shale Samples**

Sample	Proximate analysis			Ultimate analysis [*1]					
	Mois-ture	Ash (dry basis)	Organic matter	C	H	O[*2]	N	S	H/C
Ranstad 1	5.5	72.8	19.8	14.65	1.25	3.24	0.3	0.36	1.02
Ranstad 2	1.2	71.0	19.0	13.54	1.17	3.64	0.3	0.32	1.03
Hynneberg	1.9	72.1	23.8	18.12	1.81	2.84	0.3	0.69	1.19
Bårstad 1	1.2	74.4	21.5	17.78	1.73	1.26	0.3	0.39	1.16
Bårstad 2	1.2	69.8	23.3	19.00	1.90	1.32	0.4	0.68	1.19
Toolse 1	2.7	79.5	16.5	11.71	0.96	3.06	0.4	0.35	0.98
Toolse 2	3.2	80.0	17.9	12.86	1.21	3.05	0.4	0.38	1.12
Maardu	1.6	81.8	15.8	11.13	1.21	2.48	0.4	0.57	1.29

[*1] Dry basis, acid treated.
[*2] From difference.

Conclusions

Both the sapropelites and humic coals undergo roughly similar chemical changes during the coalification process, which leads to an increasing content of aromatic carbon, from 39 % to 59 % in this study. These changes in aromaticity accompany the process of coalification of the sapropelites in the following order: Maardu < Toolse ≅ Bårstad < < Hynneberg < Ranstad.

Acknowledgements

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