

MULTINUCLEAR NMR CHARACTERIZATION OF THE LAYER SILICATES IN ARGONNE PREMIUM COALS AND MODEL SYSTEMS

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INTRODUCTION

A variety of pulse sequences have been used to obtain solid-state aluminum-27 and silicon-29 nuclear magnetic resonance (NMR) spectra on the mineral matter in Argonne Premium Coals. The aim of this research investigation is two-fold; to improve our knowledge of minerals found in coals and to elucidate the possible roles of layer silicates in coal formation. To facilitate the latter objective, layer silicates that are intimate with the carbonaceous portion and present during coalification must be identified. Nuclear magnetic resonance should provide valuable information because it is sensitive to all mineral particles independent of their size and it is a direct characterization method, thus does not require any modification of the coals.

In the present study, NMR has been applied to the entire suite of Argonne Premium Coals before and after separation of the detrital mineral particles by sink-float separation (1). Preliminary results are presented for the direct characterization of the minerals more intimately associated with the organic portion of these coals.

EXPERIMENTAL

NMR Spectroscopy. The silicon-29 cross-polarization (CP) (2) and spin-echo (3) spectra employing magic-angle sample-spinning (MAS) (4) were recorded at 19.89 MHz on a Bruker Instruments spectrometer, model CXP-100. The CP/MAS spectra were recorded with contact times varying from .1 to 20 ms, a 2-second repetition time and with proton-decoupling during acquisition. The Hartman-Hahn matching condition was set with pure kaolinite spinning at about 3.5 kHz; all CP/MAS spectra were recorded at the same speed as the standard. The spin-echo spectra were recorded with and without proton decoupling during acquisition and with a repetition time of .2 to 2 seconds depending on T_1 . The total time required to obtain the silicon-29 spectra varied from an hour to 15 hours for CP/MAS spectra and 2 to 50 hours for spin-echo spectra. The aluminum-27 MAS, variable angle sample spinning (VAS) (5) and static spectra were recorded with a 45° pulse (2.5 μ s pulse width) at 52.2 MHz on a Nicolet Magnetics spectrometer, model NTC-200. The aluminum-27 spectra required an hour to 15 hours for data acquisition. Chemical shifts are referenced to TMS for silicon-29 and a 1 M aqueous solution of $AlCl_3$ for aluminum-27.

Preparation of Mineral Concentrates by Sink-Float Separation. A typical procedure to obtain concentrates of minerals was to suspend -100 mesh Argonne Premium Coal in a 1.42 g/cm solution (1 g coal/10 mLs) by ultrasonification. The coal slurries were centrifuged for 30 to 90 minutes to allow for the density separation. The raw coal was clearly separated into a black,

carbonaceous upper portion (low density) and a grayish mineral portion on the bottom. These two portions could be readily separated with minimal mixing by decantation. The two portions were separately washed with water and ethanol to remove the CsCl and Brij-35 and were subsequently dried in a vacuum oven at room temperature.

RESULTS AND DISCUSSION

Several commercially available layer silicates and their chemically modified variants were analyzed to determine the optimum spectral parameters required for their observation. Methods were also developed to distinguish between the layer silicates present and to find ways to overcome the problems of poor sensitivity. In silicon-29 NMR experiments, cross-polarization can be used to take advantage of the dipolar coupling to protons thereby enhancing the signal of the dilute nuclear spin system. The appropriate mix time depends on the rate of polarization transfer, or the effective silicon-proton internuclear distance, and the lifetime of the proton magnetization. The results of these experiments on all Argonne Premium coals showed that using a mix time of approximately 5 ms selectively enhances the sharp kaolinite resonance at -92.5 ppm (compare Figs 1a and 1b). This was a surprising result since other silicates are expected to have structures with silicon-proton distances similar to kaolinite. However, it allowed the unambiguous identification of kaolinite in all of the Argonne Premium Coals even when a small amount of kaolinite was found in the presence of a large number of other minerals. The silicon-29 spin-echo NMR spectrum, in addition to having a resonance from kaolinite (see Fig. 1a) also exhibits a resonance at -108 ppm from quartz, as well as resonances from several other silicon sites (some minerals may have several resonances due to crystallographic inequivalence) in the region from -75 to -95 ppm. Silicon-29 resonances in the latter region are typical of montmorillonite or illite clays having SiO_4 structures with two or three of their next nearest neighbors as silicon and the remaining next nearest neighbors as aluminum and/or hydrogen. The kaolinite resonance at -92.5 ppm was narrowed from 3 ppm to 1 ppm when proton decoupling was employed. However, no significant change in linewidth was observed for the other resonances which prevented further identification of other layer silicates. A proton decoupling field of 48 kHz was employed and should have been of sufficient magnitude to decouple all protons from silicon. Thus, other line-broadening mechanisms, for example, bulk susceptibility anisotropy effects arising from noncrystallinity, must dominate the resonances of the other minerals. It should be pointed out that the silicon-29 NMR spectral parameters were selected to discriminate against quartz-like minerals (although quartz resonances do appear in some spectra at -108 ppm, Figs. 1a and 1c) in order to maximize conditions for observation of the layer silicates.

The solid-state aluminum-27 NMR spectra of the Argonne Premium Coals show that a greater proportion of their aluminum is found in octahedral environments (Table 1), some of which is due to kaolinite, and differing amounts of tetrahedral aluminum. The aluminum-27 spectrum of Illinois #6 bituminous coal (APCS #3) shown in Fig. 2a exhibits tetrahedral resonances in the region centered at 65 ppm and octahedral resonances in the region at 0 ppm. The Utah bituminous coal (APCS #6) was found to have the most tetrahedral aluminum, about one-third the area of the total aluminum signal (see Table 1 and

Fig. 2c). The values in Table 1 were determined from the MAS spectra. Static and VAS spectra were also run to confirm that the octahedral resonances were devoid of spinning sidebands that would influence the relative intensities of the tetrahedral and octahedral aluminum centerbands.

In addition to the spectra of the raw coals, NMR measurements were performed on density separated materials. The predominantly carbonaceous portion of the Argonne Premium Coals was separated from the heavier, mineral-rich material to provide information on the distribution of the different layer silicates closely associated with the organic matter. Minerals that are finely dispersed within the organic matrix were found to float in a solution of density 1.42 g/cm^3 (aqueous solution of CsCl and Brij-35), while the larger, mineral-rich material sank after centrifugation. We chose APCS #6 as one of the first coals to separate because it had the most favorable tetrahedral to octahedral aluminum ratio. The aluminum-27 NMR spectrum (Fig. 2d) of the mineral concentrate obtained from density separated APCS #6 shows at least a two-fold increase in intensity of the tetrahedral resonance over that observed for the raw coal (Fig. 2c). Moreover, this treatment apparently does not alter the structure of the minerals. The aluminum-27 or silicon-29 NMR spectra of raw APCS #3 (Illinois #6) are essentially the same as the corresponding spectra of its mineral concentrate obtained by sink-float, Figs. 1a and 1c, 2a and 2b. The effect of concentrating the mineral matter is apparent from the reduction in time needed to acquire the spectra; the raw coal required approximately 15 hours of total acquisition (Fig. 2c) while the mineral concentrate required less than 2 hours (Fig. 2d). In addition, the silicon-29 spectrum of the carbonaceous upper portion of the same coal (Fig. 1d) (50 hours total accumulation time) shows substantial differences in mineral composition compared with spectra of the raw coal or mineral concentrate.

These spectra of the density separated fractions clearly demonstrate that a different mix of minerals is intimately dispersed in the organic matrix compared to that found for the detrital material. We are currently pursuing additional density separations in order to see whether spectral differences can be observed with mesh size or whether other Argonne Premium Coals show interesting behavior. We feel these initial results demonstrate that NMR can yield valuable information about the type of mineral matter present in coal and that the technique has the potential to resolve mineral matter intimately associated with the organic portion of coals from epigenetic minerals that are present.

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TABLE 1. Distribution of Tetrahedral and Octahedral Aluminum Found in the Argonne Premium Coal Samples (APCS) by Solid-State Aluminum-27 NMR.^a

Coal	Number	% Tetrahedral	% Octahedral
Upper Freeport mv bituminous	(APCS #1)	25	75
Wyodak subbituminous	(APCS #2)	8	92
Illinois No. 6 hvC bituminous	(APCS #3)	10	90
Pittsburgh No. 8 hvA bituminous	(APCS #4)	13	87
Pocahontas lv bituminous	(APCS #5)	32	68
Utah bituminous	(APCS #6)	33	67
Stockton hvA bituminous	(APCS #7)	10	90
North Dakota lignite	(APCS #8)	5	95

^aEstimated error is $\pm 5\%$.

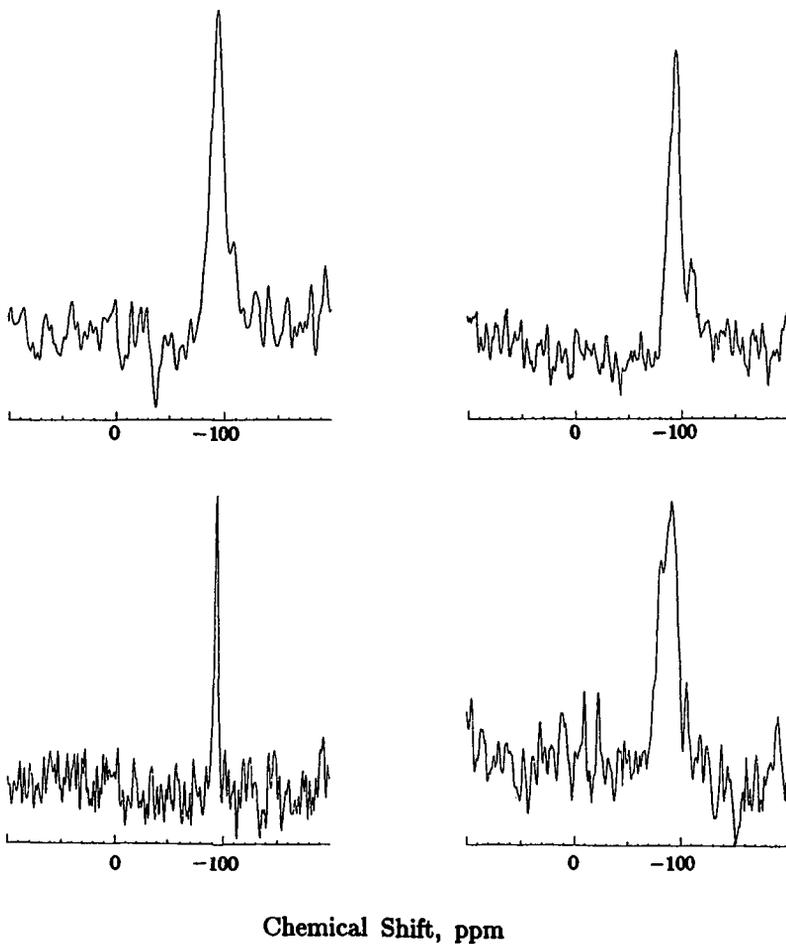
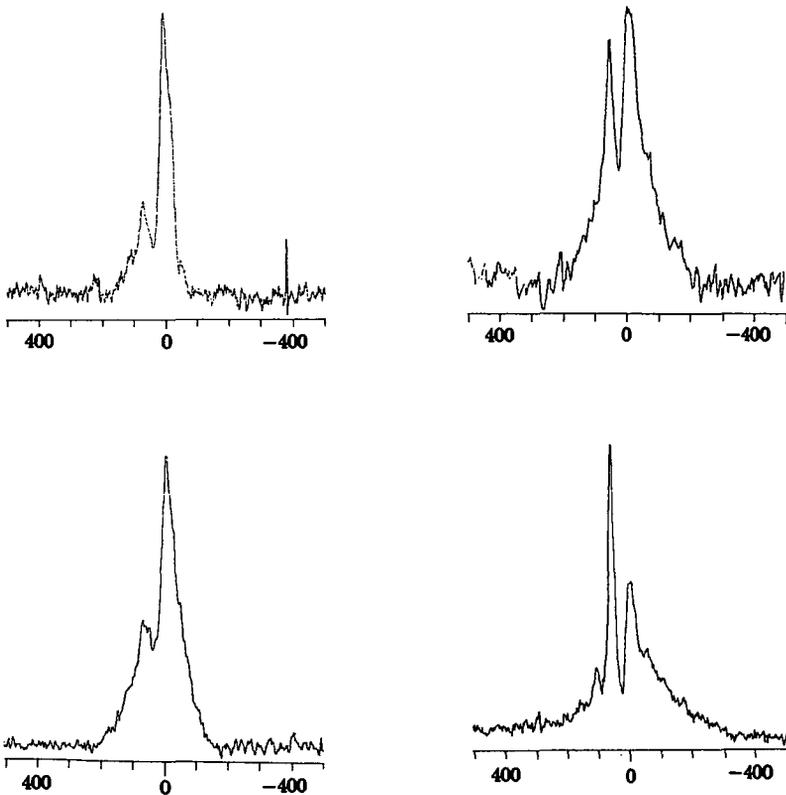


Figure 1. Silicon-29 MAS NMR spectra of raw APCS #3: (a) spin-echo and (b) CP; and spin-echo spectra of its density separated (c) sink (mineral-rich) and (d) float (organic-rich) material.



Chemical Shift, ppm

Figure 2. Aluminum-27 MAS NMR spectra of (a) raw APCS #3 (b) sink of APCS #3 (c) raw APCS #6 and (d) sink of APCS #6.