

PROTON NUCLEAR MAGNETIC RESONANCE STUDIES OF "ONE-LAYER" HYDRATES OF ORIENTED HECTORITE

Key Words—Hectorite, Hydrate, Nuclear magnetic resonance.

The "two-layer" hydrate of Na-vermiculite with low iron content (1700 ppm) was investigated by continuous-wave nuclear magnetic resonance (NMR) of H^1 and H^2 nuclei (Hougardy *et al.*, 1976). The NMR absorption spectra consist of a doublet whose splitting obeys Pake's law and of a central line which does not depend on the angle δ between the C_2^z crystallographic axis and the steady magnetic field. This central line was attributed to proton exchange between water molecules.

Hectorite, having an exchange capacity of 91 meq/100 g (value determined for the calcined mineral) can reach a "one-layer" and a "two-layer" state by hydration. These hydrated states correspond to 3- and 6-Å intervals along the C_2^z crystallographic axis, respectively; the elementary spacing between hectorite sheets becoming 12.6 and 15.6 Å, respectively. According to the isotherms established by Prost (1975) for hectorite saturated with Li, only the "one-layer" state is well defined, with 12.6 Å for the elementary spacing.

In this note, continuous-wave proton NMR studies of the "one-layer" hydrate of hectorite from Hector, California, with very low iron content (≈ 80 ppm) are presented. The spectra of this hectorite also consist of a doublet and a central line. However, a careful analysis of these spectra suggests that, in addition to proton exchange, other effects related to poor orientation of the clay may contribute to the central line.

"One-layer" hydrates of hectorite were saturated with Li and Ba. The samples used for these experiments have a pseudo-single crystal shape. Oriented hectorite films with dimensions of $10 \times 8 \times 0.04$ mm were superimposed to form a block with dimensions of $10 \times 8 \times 7$ mm. Continuous-wave proton NMR measurements were made using a Varian wide-line NMR spectrometer operating at 14 MHz, with a field homogeneity of approximately 10 mG. The spectra obtained at

295°K for the "one-layer" hydrate of Li-hectorite are characterized by a doublet and a central line (Figure 1). The line separation for the doublet, h , is equal to 3.8 G for $\delta = 0^\circ$, where δ is the angle between the C_2^z crystallographic axis and the steady magnetic field. It can be noted that for $\delta = 0^\circ$, a broad, weak signal is present instead of the central line between the doublet components. The spectra obtained at the same temperature for the "one-layer" hydrate of Ba-hectorite also consist of a doublet with a line separation h of 2.15 G for $\delta = 0^\circ$, and a central line which, in contrast to the previous case, is present for all δ values (Figure 2).

For an oriented sample, a doublet with a line separation larger than 10.8 G corresponds to fixed water molecules (Gutowsky and Pake, 1950). When the line separation is smaller than 10.8 G, the water molecules rotate rapidly about an axis (Andrew and Newing, 1958). In the present case, the line separation of the doublet is 3.8 G and 2.15 G for Li-hectorite and Ba-hectorite, respectively; therefore, the water molecules rotate about an axis, which will be chosen parallel to C_2^z for simplicity. Hectorite has a turbostratic structure, i.e., the elementary layers are shifted with respect to each other by translations and rotations. Following the general expression for the line separation (Gutowsky and Pake, 1950), and taking into account this turbostratic structure, h can be expressed as:

$$h = \frac{1}{2}\alpha(3 \cos^2\gamma - 1)(3 \cos^2\psi - 1)(3 \cos^2\delta - 1)$$

where $\alpha = 3/2 \mu r^{-3}$, r is the interproton distance, μ is the nuclear magnetic moment, γ is the angle between the interproton vector and the symmetry axis C_2^z of the H_2O molecule, and ψ is the angle between the axis C_2^z and C_3^z . Only one doublet was observed for D_2O -hydrated hectorite; therefore, each OD bond must be tilted by the same angle

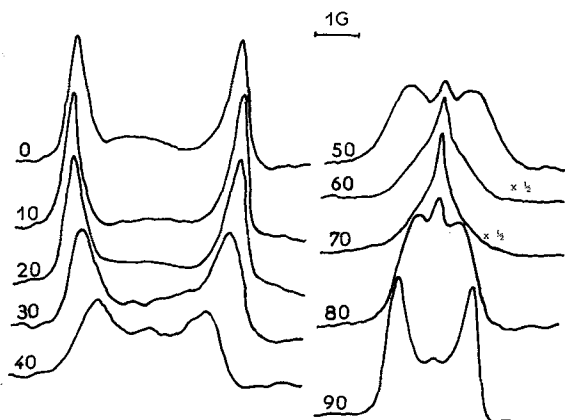


Figure 1. NMR absorption spectra at 295°K for the "one-layer" hydrate of Li-hectorite for different values of the angle δ (angle between C_2^z and the steady magnetic field); for $\delta = 60$ and 70° , the ordinate scale is multiplied by $1/2$.

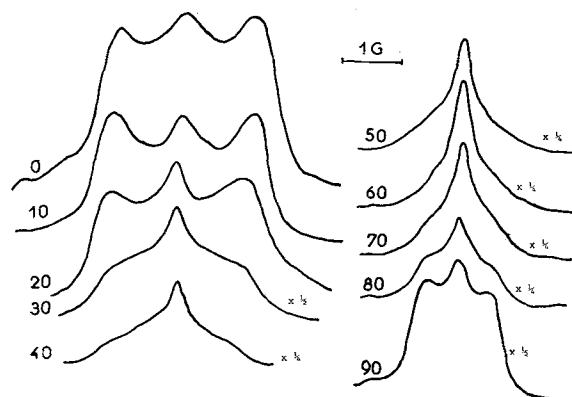


Figure 2. NMR absorption spectra at 295°K for the "one-layer" hydrate of Ba-hectorite for different values of the angle δ ; the ordinate scale is multiplied by $1/2$ for $\delta = 30$ and 90° , by $1/4$ for $\delta = 40, 50, 60, 70,$ and 80° .

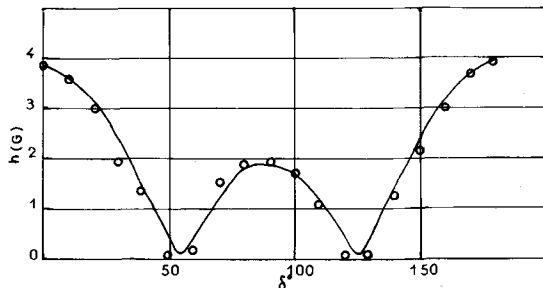


Figure 3. Angular dependence of the line separation of the doublet, h , versus δ for the "one-layer" hydrate of Li-hectorite; the circles represent the experimental points, the continuous line the theoretical curve with ψ and γ constant (see text).

with respect to the symmetry axis of the water molecule. This implies that $\gamma = 90^\circ$. With this value and where $\delta = 0^\circ$, $\psi = 71^\circ$ for Li-hectorite, and $\psi = 63^\circ$ for Ba-hectorite. If ψ and γ are constant, the line separation for the doublet must be proportional to $(3 \cos^2 \delta - 1)$; this was verified experimentally (Figures 3 and 4).

The central line observed for a synthetic fluoromontmorillonite by Hecht (1971) was attributed either to a H_3O^+ triplet, or to proton exchange between water molecules. The latter interpretation was also proposed by Hougardy *et al.* (1976) for Na-vermiculite "two-layer" hydrate. Proton exchange between water molecules may in the same way contribute to the central line which was observed for hectorite hydrates. Here, however, additional contributions can be invoked. If there is in fact a distribution of elementary doublets which coalesce at different angles, some of these doublets may coalesce and form a central line, while the others still show a splitting. Such an effect has been observed in powdered hectorite hydrated at 5% RH (Conard, 1975). For oriented hectorite, the different doublets may originate from the poor orientation of the layers. For Ba-hectorite, which does not orient as well as Li-hectorite, the central line was always observable. The presence of outer-sphere water molecules, which have more freedom than those directly bound to the exchangeable cations, would give a central line without angular dependence. A similar suggestion was made by Khaganov and Gabuda (1969), who attributed the central line to capillary water. These two contributions could add to the contribution of proton exchange in forming the central line; it is not possible, however, to determine the relative importance of these contributions.

In conclusion, proton exchange between water molecules is very probable in "one-layer" hydrates of Li- and Ba-hectorite. However, from the analysis of the NMR absorption spectra, it is possible that several doublets, poor orientation, and capillary water may contribute to the observed central line.

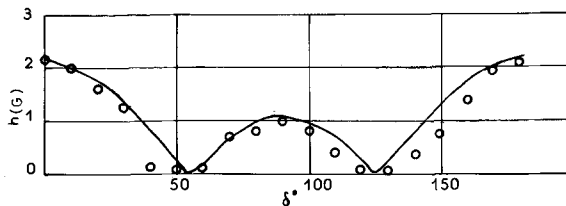


Figure 4. Angular dependence of the line separation of the doublet, h , versus δ for the "one-layer" hydrate of Ba-hectorite; the circles represent the experimental points, the continuous line the theoretical curve with ψ and γ constant (see text).

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