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ON THE HYDROGEN ATOM POSITIONS IN A KAOLINITE: FORMAMIDE INTERCALATE

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For some time it has been known that the kaolin minerals kaolinite and, to a lesser extent, its two layer monoclinic modification, dickite, form intercalation compounds (Wada, 1961; Weiss *et al.*, 1963) with small polar molecules. The rate of insertion of the guest species and the stability of the product vary widely and have been studied in some detail (Weiss *et al.*, 1966; Olejnik *et al.*, 1970) by X-ray diffraction. The kaolinite-formamide intercalate is stable under ambient conditions and a good model of the structure is available by analogy with the dickite-formamide intercalate studied by Adams and Jefferson (1976). The full 3-D crystallographic structure of this system (Figure 1) was determined and the coordinates of all of the non-hydrogen atoms were refined to reasonably low estimated standard deviations.

A neutron powder diffraction study of an oriented aggregate of a kaolinite-formamide intercalate was undertaken to determine the positions (along a direction perpendicular to the clay layers) of the hydrogen atoms of both the formamide molecules and the clay hydroxyl groups. Previous work on neutron diffraction by clays has been limited to an exploratory study of kaolinite itself (Sanders *et al.*, 1970) and also an investigation of the sodium montmorillonite–pyridine system (Adams *et al.*, 1975).

The intercalate was prepared by immersion of the kaolinite (Greensplatt pit, Cornwall, containing <0.6% Fe) in formamide for 100 hr and subsequently a relatively large sample (*ca.* 7 × 3 × 0.3 cm) was used on the Badger 2-circle neutron diffractometer at Harwell. All calculations were performed using the *X-Ray System* of programmes

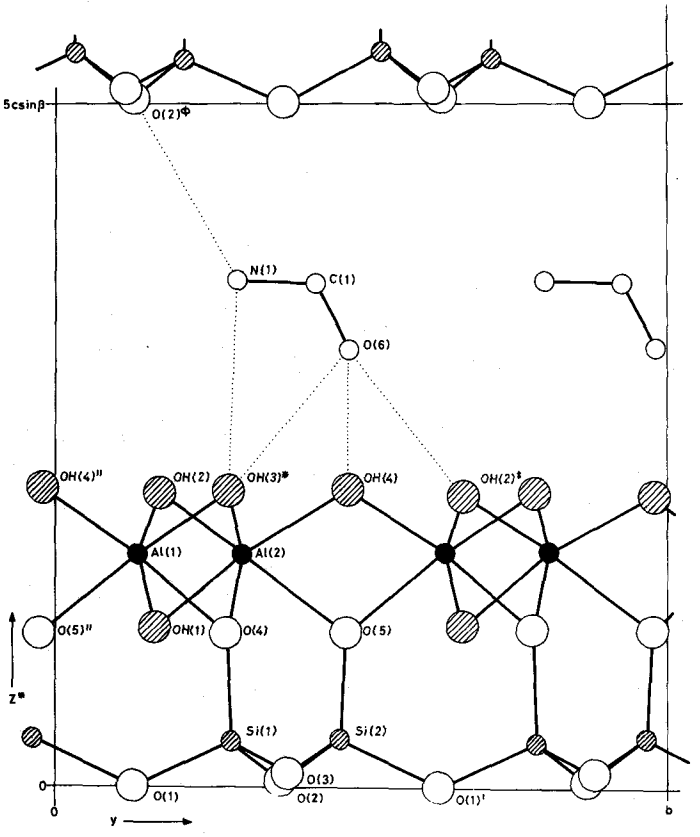


Fig. 1. Projection of the dickite-formamide structure ($Al_2Si_2O_5(OH)_4 \cdot HCONH_2$) down the a axis. The superscripts on the atom labels denote equivalent atoms generated by symmetry. (′) $x + \frac{1}{2}$, $y + \frac{1}{2}$, z; (″) $x - \frac{1}{2}$, $y - \frac{1}{2}$, z; (*) $x - 1$, y, z; (‡) $x - \frac{1}{2}$, $y + \frac{1}{2}$, z; (Ø) $x + \frac{1}{2}$, $-y + \frac{1}{2}$, $z + \frac{1}{2}$. (After Adams and Jefferson, 1976).

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Table 1. Atomic parameters

		z/d_{001}	(d_{001} = 10.2 Å)
O	(1)	0.000	All these parameters have been derived from the single-crystal X-ray study of the dickite-formamide intercalate.
O	(2)	0.002	
O	(3)	0.018	
O	(4)	0.217	
O	(5)	0.221	
O	(7)	0.227	
O	(8)	0.423	
O	(9)	0.425	
O	(10)	0.428	
Si	(1)	0.060	
Si	(2)	0.070	
Al	(1)	0.333	
Al	(2)	0.333	
O	(6)	0.634	
C	(1)	0.739	
N	(1)	0.739	
H	(1), H(2)	0.807	Hydrogen atoms of the formamide molecule
H	(3)	0.655	
H	(4)	0.180	Hydrogen atom of the 'inner' hydroxyl
H	(5), H(6)	0.520	Hydrogen atoms of the 'outer' hydroxyl
H	(7)		

N.B. (i) Overall temperature factor = 4.2Å^2 (ii) Final reliability index, $R = 0.16$. (iii) O(7), O(8), O(9), O(10) are the oxygen atoms of the OH(1), OH(2), OH(3), OH(4) groups in Fig. 1.

(Stewart *et al.*, 1972) with coherent scattering lengths taken from the *International Tables for X-Ray Crystallography*, Vol. IV.

Approximate phases for the different orders of diffraction were calculated using the *z*-coordinates obtained for the dickite intercalate by Adams and Jefferson (1976) (adjusted for the halving of the basal spacing). This procedure was considered admissible since the clay layers are identical in the two cases—the only difference is in the stacking pattern of the layers—and there seems no obvious reason why the position of the hydrogen atoms should be altered. The atomic *z*-coordinates therefore correspond with those obtained by Weiss *et al.*, (1966) but are much more precise. Projection along the layer normal, using as coefficients for the Fourier series both the observed structure factors and also the differences ($F_o - F_c$) between the observed and calculated structure factors gave 'dips' which corresponded to the positions of the hydrogen atoms (hydrogen has a negative coherent scattering length). The positions of the hydrogen atoms were refined slightly as was an overall thermal parameter for the atoms, since it was considered that the necessarily limited amount of data prohibited use of individual temperature factors.

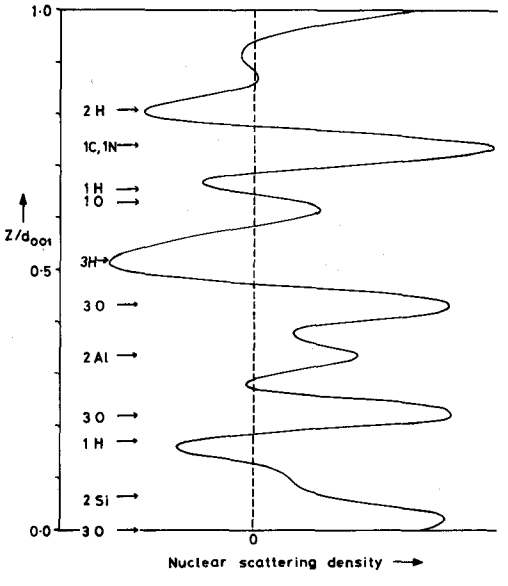


Fig. 2. Projection of nuclear scattering density for the intercalate onto a line normal to the clay basal planes.

While the coordinates for the hydrogen atoms of the formamide (Fig. 2 and Table 1) are close to the values postulated for a planar molecule with 'normal' bond lengths, the positions of the hydrogen atoms of the clay structure are more revealing since the orientation of the hydroxyl group cannot be predicted on simple geometric grounds. Some work has been carried out on defining hydrogen positions in micas, notably muscovite, by neutron diffraction (Rothbauer, 1971) and by i.r. spectroscopy (e.g. Vedder and McDonald, 1963; Farmer and Russell, 1964) which have shown that in dioctahedral micas the O—H bond makes a small angle (12–16°) with the basal layers. It is interesting to observe that the analogous hydroxyl (O7–H4, corresponding to OH(1) in Fig. 1) in this study is at approx. 25° to the layers, indicating that the same structural feature is present in both classes of layer silicate. This observation agrees with the i.r. data of Farmer and Russell (1964), who found, in the kaolin minerals, one absorption at 3620 cm^{-1} which was independent of whether the sample was oriented or a random powder—a fact interpretable on the assumption that the hydroxyl is at a small angle to the basal surfaces. The remaining hydrogen of the "outer surface" hydroxyls have been found to have approximately the same *z*-coordinate and the data would, therefore, appear to support the previous conclusion that all three of the hydroxyl hydrogen atoms are involved in hydrogen bonding to the formamide oxygen. The dickite-formamide study has shown O—H...O hydrogen bond lengths to be 2.91, 2.93 and 2.95 Å.

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Edward Davies Chemical Laboratories, University of Wales, Aberystwyth SY23 1NE

John M. Adams
Paul I. Reid
John M. Thomas
Michael J. Walters

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