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ONE-DIMENSIONAL NEUTRON DIFFRACTION STUDY OF A VERMICULITE

Key Words—Atomic coordinates, Hydrogen, Neutron diffraction, Vermiculite.

As part of a project on neutron scattering from layered silicates the basal reflexions from a Co(II)-exchanged vermiculite from St. Olalla, Spain, (kindly provided by Professor G. Lagaly), have been studied. The sample was prepared by refluxing flakes of the natural vermiculite (~3 mm × 3 mm × 0.1 mm) in $CoCl_2$ solution for 1 week, after which the flakes were washed carefully with deionized water to remove excess salt. The diffractometer data (13 orders) were collected on the high flux diffractometer D8 at the Institut Laue-Langevin in Genoble using a θ, 2θ scan. The basal spacing of the sample was 14.25 Å.

Norrish (1972) analyzed fully two samples of vermiculite from St. Olalla and partitioned cations among octahedral, tetrahedral, and interlayer sites (Table 1). The mean of his two analyses has been used here, together with his allocation of cations to tetrahedral and octahedral sites. The water content of the actual vermiculite flake used for the neutron experiments (3.6 H_2O per $(SiAl)_4$) was determined from the sample weight loss up to 120°C using a Stanton-Redcroft TG-770 thermobalance.

The z-coordinates of the non-hydrogen atoms in the clay layer were taken from previous X-ray diffraction studies on single crystals of vermiculites, as were the coordinates of the water oxygen atoms and the exchangeable cations (e.g., Mathieson and Walker, 1954; Mathieson, 1958; Shirozu and Bailey, 1966). An initial one-dimensional F_{obs} Fourier map showed large dips due to the hydrogen atoms of the 'inner' hydroxyls and the interlayer water molecules. When these atoms were included, a difference ($F_{obs} - F_{calc}$) nuclear scattering density map showed that slight adjustments were needed to the z-coordinates of some of the atoms. The final one-dimensional projections are given in Figure 1.

The position of the H atoms of the inner hydroxyls shows that the O–H bond is essentially perpendicular to the silicate sheets. This fact is consistent with previous work on trioctahedral layer silicates (e.g., Farmer and Russell, 1964) and is distinctly different from dioctahedral clay minerals where the O–H bond makes an angle of ~25° with the clay sheets (e.g., Adams *et al.*, 1976).

The hydrogen atoms of the interlayer water molecules are split equally between two different z-coordinates (0.353 and 0.420), which corresponds to one hydrogen per water molecule lying roughly in the plane of the water oxygen atoms and the other hydrogen per water molecule making a large angle (80–90°) with this plane. This type of orientation for the water molecule was postulated some time ago (Mathieson and Walker, 1954) from X-ray diffraction work (although the H atoms could not be located directly) and was thought to arise from the following bonding scheme: one hydrogen atom of every water molecule is involved in a hydrogen bond to another water oxygen in the same sheet (z = 0.420); the remaining hydrogen atom forms a hydrogen bond to an oxygen of one of the silica tetrahedra on the nearby aluminosilicate layer. This latter bond is analogous to that found between the interlayer OH groups and the silicate layers in chlorite (e.g., Brown and Bailey, 1963). This scheme is consistent with that used recently by Giese and Fripiat (1979) in their studies of interlayer cation and water arrangement in vermiculites.

One interesting feature in Figure 1b is the low level of the fluctuations on the difference nuclear scattering density map. Since this map is very sensitive to the allocation of cations to different sites, the lack of large deviations tends to support the cation distribution made for this material by Norrish (1972). Foster (1963) pointed out that because there are few complete

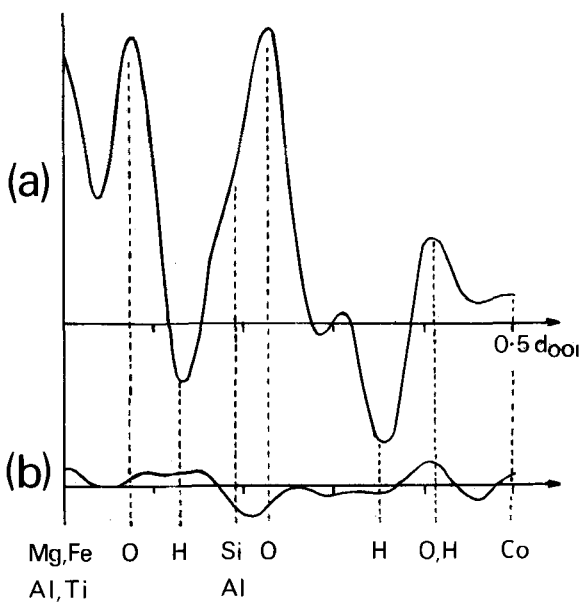


Figure 1. (a) Variation of neutron scattering density along the perpendicular to the vermiculite sheets. (b) Difference ($F_{obs} - F_{calc}$) neutron scattering density. Scale = same as in (a).

Table 1. Distribution of cations between different sites in St. Olalla vermiculite (Norrish, 1972).

Site \ Ion	Mg	Ti	Mn	Fe^{2+}	Fe^{3+}	Al	Si	Ca
Octahedral	5.17	0.03	0.02	0.04	0.44	0.29		
	5.05	0.03	0.03	—	0.58	0.28		
Tetrahedral						2.62	5.38	
						2.52	5.48	
Interlayer								0.93
								0.85

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Table 2. Atomic parameters in St. Olalla vermiculite.

Atom	Population	Z/d(001)	
Mg(1)	5.11	0.000	Parameters for the aluminosilicate layer are derived from single crystal X-ray diffraction data (Mathieson, 1958).
Fe(1)	0.53	0.000	
Al(1)	0.28	0.000	
Ti(1)	0.03	0.000	
Mn(1)	0.01	0.000	
O(1)	6.00	0.074	
Al(2)	1.29	0.192	
Si(1)	2.71	0.192	
O(2)	6.00	0.228	
O(3)	3.60	0.420	Parameters for the interlayer water oxygen atom and interlayer cation are from single crystal X-ray diffraction data (Mathieson, 1958).
Co(1)	0.89	0.500	
H(1)	2.00	0.130	Hydrogen atoms of the 'inner' hydroxyls.
H(2)	3.60	0.353	Hydrogen atoms of the interlamellar water.
H(3)	3.60	0.420	

Final reliability index, R, = 0.12. Overall temperature factor is 5.5 Å^2. The non-hydrogen atoms have been refined slightly from Mathieson's original values to give the best fit to the data. The maximum shift in Z/d(001) is 0.006 for O(3). The e.s.d.s. in the positions of the H atoms are ~0.005.

chemical analyses of vermiculites and hydrobiotites, which also give cation-exchange capacity data, the structural formulae calculated from the majority of analyses are unreliable as there is uncertainty in partitioning ions between octahedral and interlayer positions. One-dimensional X-ray diffraction has been used in the past (Bradley and Grim, 1961) to give information about such site occupancy. A combination of neutron and X-ray experiments would make this procedure much more reliable since the scattering factors for different species are very different for X-rays and neutrons: two separate but consistent conditions must therefore be satisfied concurrently. The experimental time required for this double determination is relatively short.

All calculations were performed using the *X-ray System* of programs (Stewart *et al.*, 1972) with coherent scattering lengths taken from the *International Tables for X-ray Crystallography*, Vol. IV (1974).

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