X-RAY AND DTA CHARACTERISATION OF SOME VERMICULITES

by PURNIMA SINHA, *Central Glass and Ceramic Research Institute, Calcutta-700032*

Five Indian vermiculite samples were studied both in their natural form and after saturation with K^+, H^+, Mg^{2+} to observe the variation in the samples and to examine if all the samples exhibit similar properties through similar cation saturation when subjected to X-ray analysis. In all the samples, while the X-ray spacings remain constant for a particular cation, the differential thermal characteristics change unpredictably although saturated in the same manner with the same cation. However, Mg^{2+} saturated vermiculites have common differential thermal characteristics and X-ray spacings. Thus it seems that for characterisation of vermiculites, Mg^{2+} saturation plays a role similar to that of glycerol solvation in case of montmorillonite.

INTRODUCTION

Naturally occurring vermiculites usually have Mg^{2+} and Ca^{2+} as exchangeable interlayer cation and have a basal spacing of 14Å. After heating vermiculite to 700° the spacing collapses to 9.3Å (Gruner 1934). With H^+ saturation the spacing changes to 12Å and with K^+ saturation to 10Å (Barshad 1948). When vermiculite is heated to 110° the basal spacing changes to 11.8Å which becomes 14Å with rehydration (Walker 1951).

In natural vermiculites two sharp endothermic peaks appear in the DTA pattern in the range 150° to 250°. Lattice hydroxyl is gradually lost from 500° to 850° and an endothermic peak occurs between 700° and 800°. Some vermiculites (Barshad 1948) gave an exothermic peak, which showed considerable variation depending on the interlayer cation. Exothermic peak is absent in some vermiculites. Thus it is difficult to characterise vermiculite on the basis of exothermic peak (Sinha 1962). Barshad observed that the initial double peak of natural vermiculites changes to a single peak on saturation with Ba, Li and Na. In K-, NH_4- and Rb- saturated vermiculites almost no initial endothermic peak was observed.

Hydrobioties, which have mixed layers of mica and vermiculites, always have smaller basal spacing than natural vermiculite. But vermiculites with interlayer Na^+, Cs^+, NH_4^+ have a basal spacing close to that of hydrobiotite. Thus if vermiculite with monovalent interlayer cation occurs in nature, it would be difficult to distinguish them from hydrobiotite. In that case determination of interlayer cation would be necessary along with X-ray and differential thermal analysis.

The ion-exchange properties of some Indian vermiculites have been studied with the object of resolving the observed variation among them and also to find whether vermiculites acquire similar characteristics on being saturated with any particular cation.

EXPERIMENTAL

The following vermiculite samples were studied by X-ray and DTA in the raw form and also after saturating with H^+, K^+, and Mg^{2+} :—

	Name and description	*Locality*
(1)	Bagespura Vermiculite : Light brown laminated soft mass	Bagespura (Mysore)
(2)	Malavanghatta Vermiculite : Dark brown laminated mass comparatively harder than sample 1.	Malavanghatta (Mysore)
(3)	Hazaribagh Vermiculite : Soft light brown laminated mass	Hazaribagh (Bihar)
(4)	Ranchi Vermiculite : Light brown laminated mass	Ranchi (Bihar)
(5)	Salem Vermiculite : Dark brown flakes much softer than mica.	Salem (Madras)

Note : Samples 1 and 2 were received from Mysore Geological Survey. Samples 3, 4 and 5 were received from the Geological Survey of India. All the samples exfoliate on heating.

X-ray and DTA pattern of the natural samples were taken after being ground and sieved through 200 mesh, and packed in thin walled celluloid tubes. For X-ray analysis of vermiculites, heated to 110° and 250°, the sample packed in Lindemann glass capillary was heated in a furnace up to the required temperature and the mouth of the capillary was sealed inside the furnace by passing electric current through a coil of thin copper wire wound round the mouth of the capillary.

For preparing K^+ and Mg^{2+} vermiculite the powdered samples were repeatedly leached with normal solutions of respective chlorides at 70°. For H^+ saturation, the samples were leached with 2N hydrochloric acid. Cation exchange capacity was measured by the method described by Ganguly (1951).

X-ray analysis—A Machlette sealed tube with cu-target and an adjustable plate camera were used for taking X-ray photograph.

Differential thermal analysis—The DTA curves were taken with an analyser set up at the Khaira laboratory of Physics, Calcutta University (Sinha 1969) and also with the unit described by Atma Ram *et al.* (1955).

RESULTS AND DISCUSSION

On the basis of the X-ray patterns (Tables I to VI) the vermiculite samples studied may be divided into two broad groups as follows :

Group I	Group II
1. Bagespura	4. Ranchi
2. Malavanghatta	5. Salem
3. Hazaribagh	

TABLE I

d-spacings and C.E.C. of Sample I

Natural powder		Heated 750°		Heated 110°		Heated 250°		Sealed end broken		After five days		H-saturated		K-saturated		K-Mg-saturated		C.E.C.
d	I	d	I	d	I	d	I	d	I	d	I	d	I	d	I	d	I	
14.5	v.s.	9.65	v.s.	11.8	v.s.	10.2	v.s.	14.69	v.s.	14.69	v.s.	12	vs	10.5	vs	14.76	vs	100 meq/100 g
7.69	m							10.02	m	10.02	vvw	9.52	w	9.32	w	9.25	w	
4.65	m	4.58	m	4.69	m	4.68	m	4.64	m	4.69	m					7.09	w	
3.77	m	3.3	m									4.64	m	4.61	m	4.67	m	
2.98	m	3.05	m											3.34	m	3.56	m	
		2.63	m											2.89	m	2.86	m	
		2.33	m															

The common characteristics of Group I, which also correspond to those of true vermiculites according to Barshad (1948) are the following :

(*i*) A basal spacing of about 14Å, changing to 10Å with K^+ saturation and 12Å with H^+ saturation, and to 9.6Å on being heated to 750° (Tables I, II and III).

(*ii*) Two sharp water-loss peaks at about 150° and 250° and an OH-loss peak at about 850° (Fig. 1). C.E.C. and d-spacings at 110° and 250° also correspond to that of true vermiculites as observed in case of sample 1.

Samples 4 and 5 may be placed in the same group on the basis of the common basal spacing of 10Å (Tables IV and V). Corresponding to that of mica. The samples may be either mica hydrobiotite or K^+ -vermiculite.

Sample 5 seems to be a natural K^+ Vermiculite for the following reasons :

(*i*) The sample is softer than mica and exfoliates on heating.

(*ii*) There is no interlayer Mg or Ca in the lattice, and the sample contains 7.8 per cent potassium.

(*iii*) The double water loss peak characteristic of (Mg.Ca) vermiculite is absent, and the single water loss peak is similar to that of artificial K^+ vermiculite (Barshad 1948).

(*iv*) On leaching with $MgCl_2$ the basal spacing changes to 14Å from 10Å and double water-loss peak appears in the DTA pattern.

TABLE II

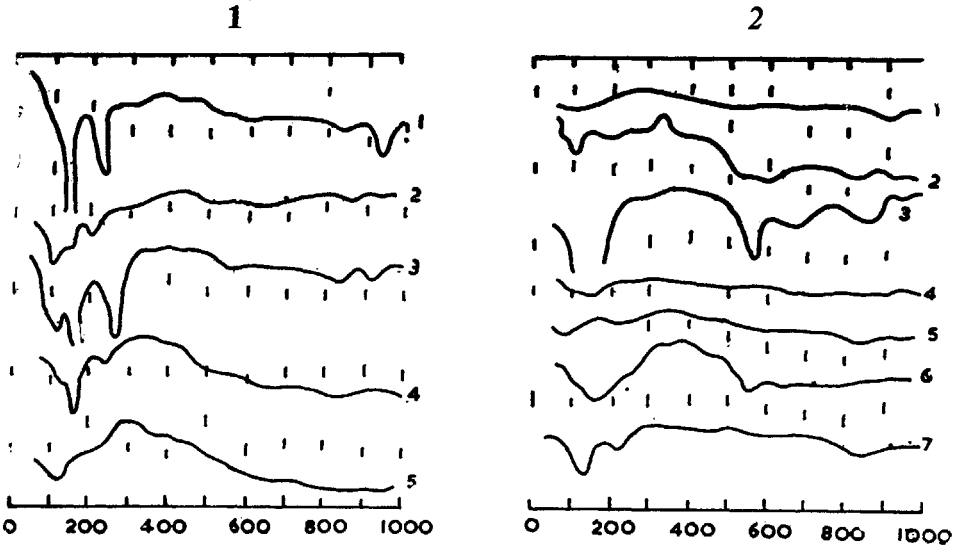
d-spacings of Sample 2

Natural powder		Heated 750°		H-saturated		K-saturated	
d	I	d	I	d	I	d	I
14.44	s	9.65	s	12.65	s	10.2	s
4.54	m	4.58	s				
		3.3	s				
2.63	w	2.63	w				

TABLE III

d-spacings of Sample 3

Natural powder		Heated 750°		H-saturated		K-saturated	
d	I	d	I	d	I	d	I
14.15	s	9.68	s	12.47	s	9.90	s
7.21	vw						
4.69	m	4.64	m			4.55	m
3.79	m						
2.95	m						



FIGS. 1–2. 1, Differential thermal curves of natural vermiculites. Nos. 1, 2, 3, 4, 5 represent the respective Sample No. 2, Differential thermal curves of heat-treated and cation-satured vermiculite. 1, Sample 1 : heated to 750°; 2, Sample 1 : K saturated; 3, Sample 1 : H saturated; 4, Sample 3 : H saturated; 5, Sample 3 : K saturated; 6, Sample 2 : H saturated; 7, Sample 5 : Mg saturated.

TABLE IV

d-spacings and C.E.C. of Sample 4

Natural powder		Mg-saturated		Heated 750°		C.E.C.
d	I	d	I	d	I	
10.3	vs	10.5	vs	10.3	vs	26 meq/100g. Both
4.55	m	4.60	m			Mg and K are
3.4	m	3.36	m			present as inter-
2.95	m	2.93	m			layer cation.

TABLE V

d-spacings and chemical analysis data of Sample 5

natural powder		Heated 750°		Mg-saturated		
d	I	d	I	d	I	
10.5	vs	10.5	vs	14.5	s	The sample contains
4.35	w			4.54	m	7.8% potassium. No
						Mg is present as
						interlayer cation.

Sample 4 gives the characteristic DTA peak of vermiculite and hydrobiotite. But the presence of both Mg^{2+} and K^+ as interlayer cation and the low value of C.E.C. (26 meq) inidcates that the sample is a hydrobiotite. Also the basal spacing does not change to 14Å by leaching with $MgCl_2$.

Behaviour on saturation with different cations

K^+ saturation—Although samples 1, 2, 3 attain the same basal spacing with K^+ saturation, there is considerable variation in their DTA curves. Sample 2 does not give any peak with K^+ Saturation, but sample 1 gives a flat initial single peak, the 900° endothothermic peak disappears and a peak appears at 600°. Thus the curve became more like that of montmonllonite than that of biotite.

H^+ saturation—With the same basal spacing of 12Å of the H^+ saturated vermiculites the DTA peaks change in different way for different samples. With initial single peak at 150° and new peaks at 500° and 700° the curve of sample 1 becomes like that of a mixture of two kinds of montmorllonites (Sinha 1969). In Sample 2, the peaks at 150° and 500° correspond to those of sample 1 but other peaks are absent. In sample 3 the single peak at 150° is present but peak at 550° is absent.

Sample 5 on Mg^{2+} saturation attains all the characteristics of natural samples 1, 2 and 3, in the X-ray and DTA pattern.

From analysis of the X-ray and DTA data of natural and different cation saturated vermiculites it becomes clear that the properties of the samples are not sufficiently closely related for them to be classified in the same group. Thus there is a need for determining the basis on which such a grouping is possible.

Bases of classification

Samples 1, 2, and 3 have many properties in common with the true vermiculites but if sample 5 is to be included in the group then the basal spacings of the group would range from 10 to 14Å and no definite DTA characteristics can be attributed to the group. But on saturating sample 5 with Mg^{2+} the X-ray spacing and DTA pattern shows features common to those of samples 1, 2 and 3. Thus Mg-saturation plays a role in case of vermiculite, similar to that of glycerol solvation in case of montmonllonite in identification of the group. Hydrobiotite may be distinguished from vermiculite by analysing for K^+ in $MgCl_2$ leachate.

References

Atma Ram, Banerjee, J. C, and Mandy, D. N. (1955). *Trans. Indian Ceram. Soc.*, **14**, 169–188.

Barshad, I. (1948). *Amer. Min.*, **33**, 655.

Ganguly, A. K. (1951). *J. Phys. Coll. Chem.*, **55**, 1417.

Gruner (1934). *Amer. Min.*, **19**, 557.

Sinha, Purnima (1962). *Nature*, **196**, 765.

——— (1969). *Bull. Cent. Glass. Ceram. Res. Inst.*, **16** (1), 22–29.

Walker, G. F. (1951). X-ray Identification and Crystal Structure of Clay Minerals *ed. by* G. W. Brindley. Mineralogical Society, London. Chap. VIII.

——— (1961). X-ray Identification and Crystal Structure of Clay Minerals *ed. by* G. Brown. Mineralogical Society, London. Chap. Vermiculite Minerals.