

Table 1. CALCULATED VALUES OF E AND ρ FOR INTEGRAL $x \leq 10$

x	E	ρ	x	E	ρ
1	0	0	6	4.2332	0.70553
2	1	0.5	7	4.9808	0.71154
3	2	0.66667	8	5.7284	0.71604
4	2.7425	0.68561	9	6.4759	0.71955
5	3.4851	0.69701	10	7.2235	0.72235

a region of length x . Then by considering the position after placing one sphere, we find:

$$F(x) = E(x-1) + 1$$

and hence the limiting density is the same as for the model discussed in the present communication. Using equation (4) we find the approximate relation $F(x) = \lambda x$. Smalley finds the two "observed values" of $x^{-1}F(x)$ of 0.78 and 0.75 for $x=10$ and 50 respectively, in fair agreement with our calculated λ .

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¹Smalley, I. J., *Nature*, **194**, 1271 (1962).

MINERALOGY

Appearance of Exothermic Peak in the Differential Thermal Curves of Vermiculites

THE following three Indian vermiculite samples: (i) Bagespura, (ii) Malavanghatta and (iii) Hazaribagh have been examined by X-ray and differential thermal analysis. The samples are of flaky habit and exfoliate on heating. All the samples give a basal reflexion of 14 Å, which collapses to 9.6 Å on heating to 750° C. In the differential thermal analysis curves (Fig. 1) there are two sharp water-loss peaks at 150° and 250° C, similar to true vermiculites. In each of the samples (i) and (ii) there is an additional endothermic peak at about 100° C, perhaps due to absorbed water. In all the samples there is an endothermic peak near 900° C.

The high-temperature exothermic peak present in Barshad's¹ samples 1 and 2 is absent in all these samples. Barshad's sample 4, which has been classed as hydrobiotite by Gruner² on the basis of X-ray analysis, has a differential thermal analysis curve more like that of (i), (ii) and (iii). As biotite is not responsive to differential thermal analysis, it seems that the vermiculite part of sample 4 is similar to (i), (ii) and (iii) in so far as the exothermic peak is concerned. Among the five samples examined by Barshad¹ samples 1 and 2 (natural) give an endothermic peak followed immediately by an exo-peak. However, when saturated with NH^+ and Na^+ , the exo-peak becomes so small that only two endothermic peaks seem to be present, side by side, at 800° and 850° C respectively. Sample 2, when saturated with Ca^{2+} , Na^+ and Li^+ , shows a similar effect. Sample 3 (natural) gives small endothermic peaks at 800°, 850° and 900° C, but no well-defined exothermic peak. It may be noted that an exothermic peak similar to that of sample 1 and 2 is present in chlorite. In the case of sample 5, this peak is attributed to chlorite, which, present as impurity, is characterized by a 600° C endothermic peak.

Thus it is observed that the exothermic peak of some of the vermiculites appears when saturated with certain cations but disappears when saturated with others. But since the different vermiculites saturated with the same cation do not behave alike, so far as

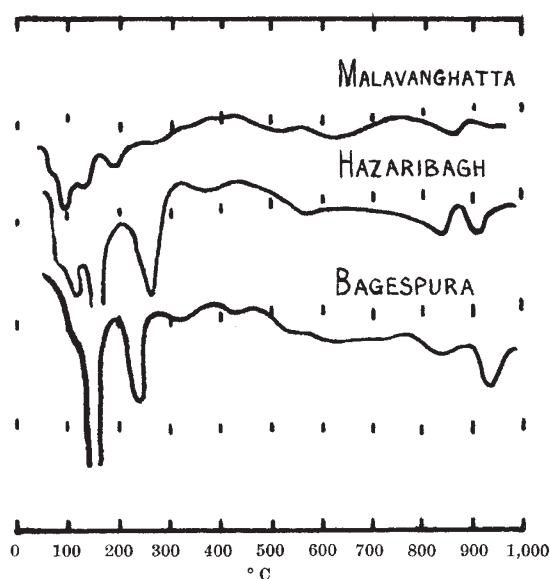


Fig. 1

the exothermic peak is concerned, the exchangeable cation does not seem to be a decisive factor in this regard. Barshad¹ suggests that the exothermic peak corresponds to the contraction of the lattice from the basal spacing 10.2 Å of moderately heated vermiculite to 9.4 Å on ignition. This suggestion does not appear tenable, since this contraction also occurs in samples in which the exothermic peak is altogether lacking. In view of the fact that the contraction occurs below the temperature of the exothermic peak, near about the region of the removal of the hydroxyl groups, the suggestion seems all the more unacceptable.

From the results so far obtained, no conclusion can be drawn as to whether the exothermic peak is an essential feature of vermiculite or not. Three possibilities may be argued as follows:

(1) The exo-peak is not a characteristic feature of vermiculite but occurs due to an impurity (for example, chlorite) in the sample. Hence the absence of the peak would mean that the impurity is absent, so that the sample showing the other characteristic features of vermiculite is pure.

(2) The peak is really a feature of vermiculite. It may then be ascribed to a rearrangement of the lattice after the OH loss is complete (as in montmorillonite). If the peak is absent, it is possible to suppose that it is neutralized by an opposing reaction proceeding at the same temperature in an associated impurity.

(3) The two types may represent two polymorphic variations of the vermiculite group. Depending on the nature of substitution in the lattice, the exothermic reaction may be retarded.

It thus appears difficult to draw, on the basis of the data obtained so far, a valid conclusion regarding the true characteristic of the vermiculites in so far as the appearance of the exothermic peak is concerned.

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¹ Barshad, I., *Amer. Min.*, **33**, 665 (1948).

² Gruner, J. W., *Amer. Min.*, **19**, 557 (1934).