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Hydrobiotite, a regular 1:1 interstratification of biotite and vermiculite layers

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Abstract

Well-ordered hydrobiotites consist of a regular alternation of biotite and vermiculite layers. Current requirements for use of a special name for an interstratified mineral specify that the coefficient of variation, CV, of the basal spacings obtained from ten or more reflections should be less than 0.75. Data for three hydrobiotites from different sources give mean basal spacings of 24.51Å measured to 0.0.31 for individual flakes and 0.0.22 for oriented powder layers. The CV values for these samples are 1.25, 0.35, and 0.98 when equal weight is given to all reflections. The large values for the first and third samples arise primarily from the first-order diffractions which are least accurately measurable; when these are omitted, the CV values are 0.67, 0.29, and 0.20. Observed and calculated structure factors for 00*l* diffractions up to *l* = 31 vary similarly with the index *l*. Values of *d*(00*l*), calculated by Reynolds' method and by a modified Mering method for ordered mixed-layer sequences from 40–60% biotite layers, show that the three samples studied have 45%, 53%, and 49% biotite layers. The calculations also show that if the percentage of biotite layers falls outside the range 45–55% biotite, variable basal spacings with CV > 0.75 will be obtained.

Introduction

The name hydrobiotite has been in the mineralogical literature for at least a century. It was used by Schrauf (1882, p. 381–383) for a mineral from Kremze resembling biotite in its chemical composition but containing considerably more water. It was mentioned by Dana (1892, p. 632). Gruner (1934) recognized that the X-ray diffraction data of hydrobiotites "show clearly that [they] are made up of interstratified single or double layers of mica and vermiculite." He considered an alternating 1:1 sequence with a 24Å basal spacing and also more complex sequences. He found two samples in which "the sequence of layers . . . may approach a definite ratio of 1:1 biotite: vermiculite units." Boettcher (1966, p. 284), discussing the origin of vermiculites and hydrobiotites, stated that "the name hydrobiotite has been used in a variety of ways and should be defined wherever used"; he specifically defined hydrobiotite as "a regular 1:1 heteropolytypic (mixed-layer) biotite:vermiculite" and (p. 286) stated that "the sharp X-ray peak at 25.5Å and the high order of rational basal peaks obtainable in the X-ray patterns of hydrobiotite attest to the regularity of spacing."

Foster (1963) made a critical review of the available chemical data for vermiculites and hydrobiotites and, despite inherent difficulties in arriving at structural formulae in the absence of cation exchange data, showed

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that the formulae of hydrobiotites are intermediate between those of biotite (or ferruginous phlogopite) and vermiculite, and therefore, are consistent with an interstratification of layers. Hey (1962) recognized hydrobiotite as "a mixed-layer mineral, an interstratification of vermiculite and biotite," but did not mention regularity of the mixed layering.

Despite these studies, the name hydrobiotite seems not to have been fully accepted as a valid mineral species. The name is not included by Fleischer (1980) in his "Glossary of Mineral Species" among a long series of hydro-minerals. In a critical review of interstratified layer silicates, Bailey *et al.* (1982) made no mention of hydrobiotite. They specified the following requirements for the use of special names. An interstratification of two layer types, A and B, should have sufficient regularity to give a well-defined series of at least ten essentially integral orders of reflection from the summation spacing, $d_{AB} = d_A + d_B$, and the coefficient of variation of d_{AB} should be less than 0.75 to demonstrate adequate regularity of layer alternation. The diffraction breadths of odd and even order reflections should be closely similar. If odd orders are absent, their absence should be shown to be consistent with calculated intensities.

The present study was undertaken to establish whether interstratified biotite/vermiculites exist that satisfy these requirements for use of the name hydrobiotite.

Materials and methods

Vermiculite ores from the Enoree area of S. Carolina, made available many years ago to one of us (G.W.B.) by the Zonolite division of W. R. Grace & Company, showed a varied mineralogy that included vermiculite, biotite, and variously ordered mica/vermiculites. From material described as a Cooper concentrate, small blackish flakes were selected under a binocular microscope. They were lightly ground in water with a small pestle and mortar. The dispersed material was allowed to dry slowly in air to form thin layers on glass slides. Only basal diffractions appeared in the recorded patterns. X-ray data for this material are presented in section 3 of Table 1.

A number of samples were made available by Dr. S. W. Bailey and from among these, a well-developed flaky material from north-western Transvaal provided thin flakes up to about 8 × 8 mm size, which could be examined directly without reduction to powder. Many of the flakes were contaminated with apatite and, to a lesser extent, with zircon. Uncontaminated flakes were selected under a microscope and were mounted directly on glass slides with a trace of adhesive. A sample supplied by Wards Natural Science Establishment, labelled vermiculite from north-eastern Transvaal, proved to be a regularly interstratified biotite/vermiculite. Golden yellow and pinkish flakes were selected for study but were smaller than those from north-western Transvaal and were less suitable for X-ray intensity measurements.

Optical properties of the north-western Transvaal material were as follows: $\beta = 1.560–1.562$, $\gamma = 1.565–1.567$, a biaxial negative interference figure, $2V_\alpha \simeq 10°$.

X-ray diffraction data were obtained using a Philips diffractometer with Ni-filtered Cu$K\alpha$ radiation and were recorded at 1° 2θ/min and with chart recording on a scale of 2° 2θ/inch. When samples in the form of single flakes were used, the incident X-ray beam divergence was choosen so that the radiation was confined to the surface of the flake but this condition was not wholly satisfied at $2\theta < 10°$. To record diffracted intensities, it was necessary to make changes in the silt system, the X-ray tube operating conditions, and the recording conditions. Several diffractions were recorded before and after each change of experimental conditions so that all recorded intensities could be placed on a common basis. The diffractometer was calibrated with respect to a silicon standard and a secondary tetradecanol standard (Brindley, 1981).

Attention has been given particularly to the evaluation of basal X-ray diffractions. Imperfectly interstratified layer sequences give diffraction peaks which do not follow precisely the Bragg reflection equation. The apparent spacings $d(00l)$ multiplied by the apparent order l give a variable product $ld(00l) = d_l$ and the degree of order in the layer sequence is evaluated by a statistical treatment of values of d_l. If $\bar{d}$ is the arithmetical mean value, the mean deviation, $\Delta\bar{d}$, is $(\Sigma_n|d_l-\bar{d}|)/n$, and the coefficient of variation, CV, is $[\Sigma_n(d_l-\bar{d})^2/(n-1)]^{1/2} \times 100/\bar{d}$, where n is the number of terms in the summations.

Results

Basal spacing measurements

Table 1 summarizes the results for two samples examined in flake form and one sample as a thin oriented powder layer. The two samples examined as flakes yielded diffractions up to 0.0.31 and the powder data were measured as far as 0.0.22. The mean basal spacings are respectively 24.46±0.17, 24.51±0.05 and 24.45±0.13Å where the ± values are mean deviations. The CV values are respectively 1.25, 0.35 and 0.95 when equal weight is given to all reflections. The second sample easily satisfies the condition CV < 0.75 to justify the acceptance of a specific mineral name.

The large CV values for the first and third samples arise largely from the first order diffractions which are the least accurately measurable because of the small 2θ angles, 3.6–3.8°, at which they occur. When the first order diffraction data are omitted, the mean spacings (as given in Table 1) are respectively 24.51±0.10, 24.51±0.04, and 24.51±0.04Å and the CV values are 0.67,0.29, and 0.20, all of which satisfy the condition of CV < 0.75. Although we cannot give an unequivocal explanation for the low values of the first order spacings for the first and third samples, the balance of evidence appears in favor of retaining hydrobiotite as a specific mineral name.

Table 1. X-ray diffraction data for basal reflections from hydrobiotites

ℓ	(1) Flake, North-western Transvaal. d(00ℓ)	d(001)	I(peak)	(2) Flake, North-eastern Transvaal. d(00ℓ)	d(001)	I(peak)	(3) Oriented powder, South Carolina d(00ℓ)	d(001)	I(peak)
1	23.3	23.3	10	24.3	24.3	7	23.6	23.6	20
2	12.30	24.60	80	12.23	24.46	60	12.26	24.52	>100
3	7.99	23.97	3	8.27	24.81	2	8.18	24.54	5
4	--	--	--	--	--	--	6.146	24.58	1
5	4.880	24.40	30	4.909	24.55	30	4.880	24.40	15
6	--	--	--	--	--	--	--	--	--
7	3.504	24.53	50	3.493	24.45	50	3.500	24.50	50
8	3.035	24.28	14	3.071	24.57	15	3.051	24.41	20
9	2.742	24.68	12	2.725	24.52	20	2.733	24.60	10
10	--	--	--	--	--	--	--	--	--
11	2.261	24.87	0.5	--	--	--	--	--	--
12	2.045	24.54	16	2.041	24.49	16	2.043	24.52	15
13	1.881	24.45	1.0	1.889	24.56	1	1.881	24.45	1
14	--	--	--	--	--	--	--	--	--
15	1.630	24.45	1.5	1.633	24.50	2	1.633	24.50	1.5
16	--	--	--	--	--	--	--	--	--
17	1.442	24.51	8	1.441	24.50	8	1.443	24.53	5
18	--	--	--	--	--	--	--	--	--
19	1.293	24.57	1.8	1.290	24.51	4	1.292	24.55	0.5
20	1.224	24.48	1.2	1.224	24.48	1	1.227	24.54	1
21	1.173	24.63	0.2	--	--	--	--	--	--
22	1.115	24.53	0.3	1.114	24.51	0.4	1.115	24.53	0.5
23	--	--	--	--	--	--	--	--	--
24	1.023	24.55	1.0	1.021	24.50	2			
25	0.9795	24.49	0.2	0.9773	24.43	0.2			
26	0.9455	24.58	0.3	0.9433	24.52	0.4			
27	0.9080	24.52	1.4	0.9069	24.49	2			
28	--	--	--	--	--	--			
29	0.8480	24.59	1.0	0.8445	24.49	2			
30	--	--	--	--	--	--			
31	0.7921	24.56	0.1	0.7900	24.49	0.2			
$\bar{d}$ (001)		24.51			24.51			24.51	
$\overline{\Delta d}$		0.10			0.04			0.04	

Two flakes treated with ethylene glycol yielded the following results: mean basal spacings 24.45±0.11Å and 24.50±0.05Å, CV values 0.60 and 0.30 based on 20 and 16 diffractions with $d(00l)$ omitted. The negligible change of basal spacing with glycolation is consistent with vermiculite rather than smectite layers.

Diffraction intensities

The peak intensities recorded in Table 1 take account of the various conditions of divergence and receiving slits, X-ray tube operating conditions and recording conditions. Most attention will be given to the data in section 1 of Table 1 for material from north-western Transvaal, because these were obtained with a flake of the largest surface area, about 8 × 8 mm. The least satisfactory intensities are those for $l = 1,2,3$ for which an uncertain allowance was made for the incident beam not falling entirely on the flake surface. Relative values of F^2_{obs} (F = structure factor) were calculated from observed relative intensities, taken as (peak intensities) × (breadths at half-maximum intensity), by the relation

$$I_{\text{obs}} = F^2_{\text{obs}}\,(1 + \cos^2 2\theta)/\sin 2\theta$$

Calculated values of F^2 have been derived using z parameters in Å, for the hydrobiotite layer structure taken as follows:

1 K at 0.00, 3 O at ±1.67, 2(Si,Al) at ±2.28, 3 O at ±3.94, 3(Mg,Fe) at ±5.00, 3 O at ±6.06, 2(Si,Al) at ±7.72, 3 O at ±8.33, 3 H_2O at ±11.07, 0.22 Mg at ±12.24.

These parameters are based on data tabulated by Bailey (1980, p. 56–7) for trioctahedral micas and given by Shirozu and Bailey (1966) for Mg-vermiculite. Calculations were made for trioctahedral cations ranging from Mg_3 to $Mg_{1.5}Fe_{1.5}$ and all octahedral sheets were assumed to have the same cation compositions. No attempt has

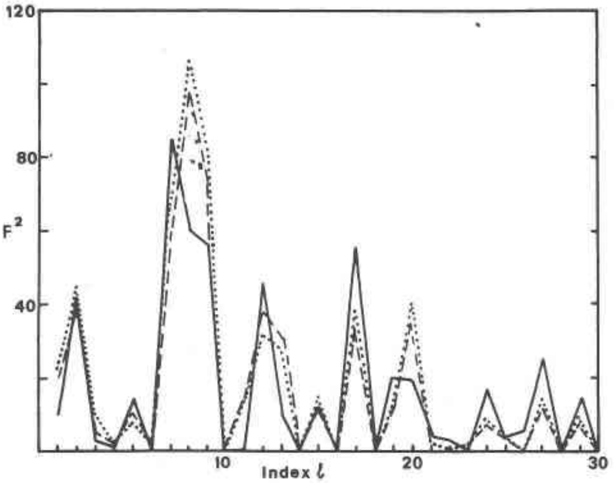

Fig. 1. Comparison of F^2 values derived from experimental data (full line) and calculated from theoretical compositions based on Mg_3 and($Mg_{2.75}$ $Fe_{0.25}$) in octahedral positions (dashed line, dotted line).

been made to obtain an optimum agreement between observed and calculated F^2 values. The principal objective has been to show that unobserved basal reflections are consistent with the assumed structure of hydrobiotite and this is clearly established by the comparison shown in Figure 1. The observed F^2 values have been placed on a scale to make them generally comparable with the calculated values, which are shown for two octahedral cation compositions, Mg_3 and $Mg_{2.75}$ $Fe_{0.25}$. There is a good general concordance between strong, medium, weak and absent reflections.

The results support the second main requirement for the use of hydrobiotite as a valid species name.

Calculated diffraction patterns

Reynolds (1980) has shown that computer generated diffraction patterns can be used to study the statistics of mixed-layer systems. Table 2 summarizes data used for computing such patterns for hydrobiotite with biotite/vermiculite ratios ranging from 60/40 to 40/60. Values of $\bar{d}(00l)$, $\Delta\bar{d}$, and CV have been calculated from the result-

Table 2. Numerical data for biotite/vermiculite mixed-layer sequences

A. Statistical data used in computing biotite-vermiculite diffraction patterns

Ratio of Layers		Junction Probabilities						
% B	% V	$P_{B.B}$	$P_{B.V}$	$P_{V.B}$	$P_{V.V}$	$\bar{d}(001)$	$\Delta\bar{d}$	CV
60	40	0.333	0.667	1.000	0.000	24.57	± 0.29	1.84
55	45	0.183	0.818	1.000	0.000	24.48	0.12	0.73
50	50	0.000	1.000	1.000	0.000	24.43	0.07	0.35
45	55	0.000	1.000	0.818	0.182	24.44	0.14	0.85
40	60	0.000	1.000	0.667	0.333	24.43	0.26	1.62

B. Peak migration data from calculated patterns

% B	% V	Calculated peak positions, °(2θ) for CuKα						
		l = 2	3	7	8	9	12	13
60	40	7.46	10.66	25.66	28.97	33.10	44.55	48.07
55	45	7.36	10.80	25.55	29.08	33.03	44.47	48.25
50	50	7.26	10.92	25.45	29.20	32.94	44.40	48.35
45	55	7.14	11.06	25.38	29.34	32.80	44.34	48.45
40	60	7.00	11.15	25.28	29.48	32.62	44.28	48.58

C. Peak migration data by a modified Mering method

% B	% V	Calculated values of 2θ, with (00l) in parentheses						
67	33	7.72 (003)	10.28 (004)	25.90 (00,10)	28.54 (00,11)	33.88 (00,13)	44.80 (00,17)	47.58 (00,18)
50	50	7.24 (002)	10.88 (003)	25.55 (007)	29.28 (008)	33.04 (009)	44.56 (00,12)	48.50 (00,13)
33	67	6.83 (003)	11.40 (005)	25.30 (00,11)	29.93 (00,13)	32.31 (00,14)	44.35 (00,19)	49.33 (00,21)

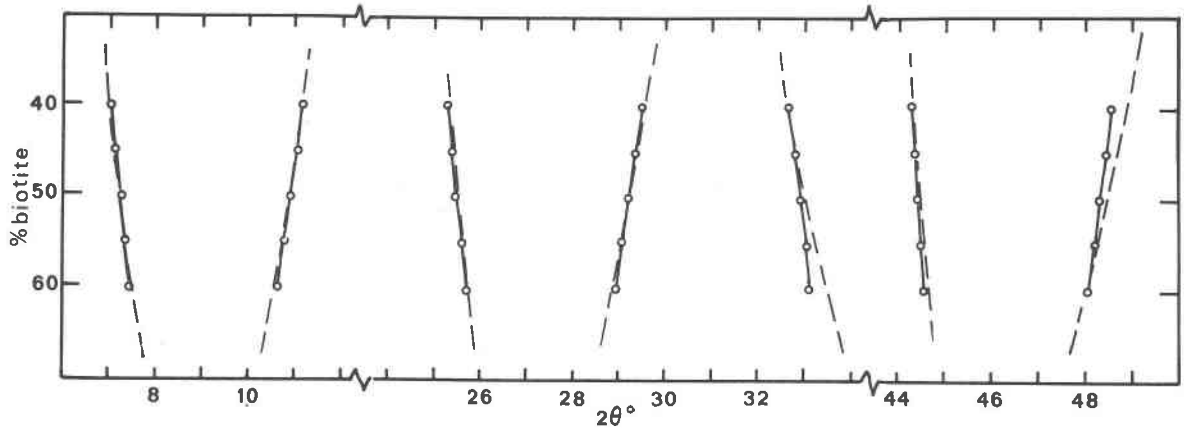

Fig. 2. Migration curves for diffraction peaks from hydrobiotites, calculated by Reynolds' method (full line) and by a modified Mering method (dashed line). Small circles show calculated values for 40–60% biotite layers by Reynolds' method.

ing patterns for direct comparison with the experimental data. Values for $l = 1$ have been included, for although these values may be influenced by the Lorentz-polarization and structure factor variations, they will not be subject to experimental errors. In these calculations, the same z parameters for the layer structures have been employed as were used earlier for the calculation of F^2 values.

As expected, the calculated values of $\Delta\bar{d}$ and CV are smallest for the 50/50 biotite/vermiculite ratio, and they increase more or less symmetrically as the ratio is changed to 40/60 and 60/40. It appears that within a biotite/vermiculite range about 55/45 and 45/55, the CV satisfies the requirement of being less than 0.75 to merit the use of the name hydrobiotite. Conversely we may conclude that a biotite/vermiculite will satisfy the criterion of $\mathrm{CV} < 0.75$ provided the ratio of the components lies within 5% of the 50%/50% ratio.

The theoretical patterns show that the basal diffraction maxima migrate to higher or lower 2θ values as the B/V ratio changes (Fig. 2). Values of 2θ for diffraction peaks which will be useful in estimating the B/V ratios of hydrobiotites and of less regular interstratifications are listed in part B of Table 2. The calculated data can be used in two ways. First, one can match observed 2θ values against the migration curves, and second, one can take differences $\Delta(2\theta)$ between adjacent pairs of reflections. Figure 3 illustrates this second method; $\Delta(2\theta)$ is plotted against percentage of biotite layers. Experimental values of $\Delta(2\theta)$ for the three samples used in Table 1 are located on the curves and the percentage values of biotite layers are read directly. For each sample, four estimates are obtained, and the average values are: sample 1, 45% biotite; sample 2, 53% biotite; sample 3, 49% biotite. The order in which these values depart from 50% biotite corresponds to the sequence of CV values given earlier.

Possible application of a modified Mering procedure for interpreting diffraction by mixed-layer systems

It was shown by Mering (1949) that in a system of mixed spacings d_1 and d_2, regions of strong diffraction tend to occur when integral values of $1/d_1$ and $1/d_2$ are closely similar. In mixed systems ranging from entirely d_1 spacings to entirely d_2 spacings, a migration from order n_1 of d_1 to order n_2 of d_2 would be expected when $n_1/d_1 \simeq n_2/d_2$. The modified system to be considered visualizes migration of diffractions between adjacent ordered systems with simple ratios. For example, if we wish to consider the effect of deviations from a 50/50 B/V system, *i.e.*, a 1:1 ratio, we could consider ordered 33/67 and 67/33 systems, *i.e.*, 1:2 and 2:1 systems. A system with 60% biotite layers could be considered as falling between the ordered systems with 50% and 67% biotite layers. Physically, this model presupposes that a 60% biotite system would have a sequence of either one biotite layer,

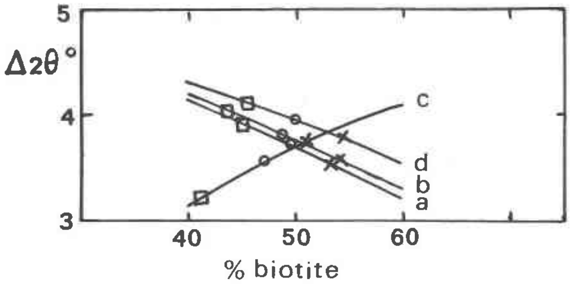

Fig. 3. Values of $\Delta(2\theta)$ between adjacent basal reflections, obtained from Reynolds'-type calculations, *vs.* % biotite layers, (a) 002–003, (b) 007–008, (c) 008–009, (d) 0.0.12–0.0.13. Samples 1, 2 and 3 of Table 1 gives data points shown by □, x, and o.

or two biotite layers between each consecutive pair of vermiculite layers; the proportion of B or BB units would be governed by the overall B/V ratio.

Figure 2 compares the migration curves calculated by the Reynolds method and by the modified Mering procedure. Four and perhaps five of the peak migrations derived by the two methods agree very closely and only two show appreciable differences. Here we wish to point only to the potential applicability of the very simple modified Mering method. Table 2C shows values of 2θ calculated for regular 2:1, 1:1, and 1:2 B/V ratios and the $00l$ values used. These data were used in plotting the modified Mering migration curves in Figure 2. In those cases where the curves calculated by the two methods show appreciable differences, these differences might be explained by an interaction of diffraction peaks of different intensities or of rapidly changing values of F^2.

Relation of hydrobiotite to biotite

It is relevant to the discussion of hydrobiotite to draw attention to conclusions reached by Boettcher (1966). Discussing particularly the vermiculite and hydrobiotite found near Libby, Montana, he stated that "A comparison of chemical analyses of the hydrobiotite and biotite suggests no simple compositional relationship as might be expected if the hydrobiotite is a simple weathering product." Furthermore, "the regular stacking sequence exhibited by the hydrobiotite is not inherited from the parent biotite. Consequently, the hydrobiotite is considered to be a high-temperature alteration product in which the 1:1 stacking sequence represents the attainment of homogeneous equilibrium at the time of alteration." (The description "regular stacking sequence" relates only to the alternation of layer types and carries no implication of space group symmetry.)

There are therefore good reasons for regarding hydrobiotite as a valid mineral species besides the evidence that the component layers are organized in a manner sufficiently regular to meet the requirements set out for allocation of names to interstratified layer minerals.

Acknowledgments

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