90. Thermal and Chemical Studies of Lepidomelane from Ishikawa.

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The locality of the lepidomelane under present consideration is Ishikawa, Fukushima Prefecture, Japan. The thermal and chemical studies were made from the fresh part which was carefully separated from a large fragment of the mineral.

Chemical composition:—The chemical analysis was made by two different methods. The first method is the usual one decomposing the mineral material by a fusing mixture, and in the second the analysis was made from the two separated parts, soluble and insoluble treated by HCl. The results are given in Table I. In Table I, the weight loss of the charge, heated at 105° C until the weight became constant, was taken as hygroscopic water (H_2O-). For the crystallization water (H_2O+), the weight-change was taken, which was obtained from the total weight-loss on ignition to which was added the weight of oxygen (0.88%) corresponding to the change of FeO into Fe_2O_3 by heating and subtracting the hygroscopic water (H_2O-). A further discussion with regard to hygroscopic and crystallization waters will be given later.

TABLE I.

	I	Mol. prop. of I with $SiO_2=300$.	II
SiO_2	33.32	300.0	34.03...
Al_2O_3	17.44	92.4	17.46
Fe_2O_3	19.15	64.7	19.14
FeO	7.89	59.2	7.89
MgO	3.86	52.1	3.78
CaO	0.05	0.5	0.06
Na_2O	0.42	3.7	0.14
K_2O	7.19	41.3	7.20
H_2O+	5.19	155.8	—
H_2O-	3.99	—	—
TiO_2	1.27	8.6	0.45
P_2O_5	tr	—	tr
MnO	0.34	2.6	0.35
F	0.03	0.9	—
Total	100.14		90.50

Insoluble
part.
Soluble
part.

It will be seen from Table I, the present mica may be classified as lepidomelane in containing a high amount of $Fe_2O_3 + FeO$ and comparatively low amounts of SiO_2 and MgO.

A remarkable feature is that the mica contains a specially high amount of Fe_2O_3 . Examining the charge under the microscope, it was found difficult to obtain perfectly fresh material from the mineral. Though the greater part of the charge was fresh, with dark green colour by transmitted light, but there were smaller parts distributed

sporadically in the fresh part which had changed to a dark brownish green colour. Hence the some amounts of Fe_2O_3 detected by the chemical analysis must be attributed to the altered composition. However a fairly large amount of Fe_2O_3 must be expected in the mica. The facility of the alteration of FeO to Fe_2O_3 by heating is also remarkable. By heating for one hour in air, FeO in the mineral entirely alters to Fe_2O_3 at 500°C .

Chemical formula :—To facilitate comparison, the analysis of the mica given in Table I was recalculated to molecular proportions with $\text{SiO}_2 = 300$. The results are also given in Table I. If we indicate from these figures the type-formula of biotite proposed by Machatschki,¹⁾ we have

With fairly large approximation, the above formula may be simplified as

This formula differs from any type-formulae of the mica group in containing $(\text{OH})_3$ instead of $(\text{OH})_2$. In order to make more clearly this question, the following experiments were made.

Change in weight of the mica during heating :—The change in weight of the mineral during heating was measured by a thermo-balance in the range of temperature from 25°C to 1000°C . The rate of raising of temperature was 10°C per 3 minutes. The change of weight was read by the deflection of a mirror attached to the thermo-balance. The results are given under No. 1 in Table II and Fig. 1. In Fig. 1, we can see 3 breaks at 260°C , 510°C and 630°C on the thermal curve. Further, three more experiments were repeated in the different ranges of temperature, the results being also given under Nos. 2–4 in Table II and Fig. 2. From these four experiments, we must

TABLE II.

Temp. in $^\circ\text{C}$.	Defl. of mirror in mm.			
	No. 1	No. 2	No. 3	No. 4
25	0.0	0.0	0.0	0.0
40	0.0	0.0	0.0	0.0
50	0.5	0.6	0.5	0.5
100	6.5	6.8	6.5	6.6
140	11.5	12.4	12.5	12.2
150	12.5	13.5	13.5	13.1
200	16.5	18.2	17.5	16.5
250	20.0	21.0	21.0	19.3
260	20.5	21.0	21.0	19.3
270	21.5	22.2	22.0	20.7
300	24.5	25.0	25.0	24.5
340	28.5	28.4	28.0	—
350	29.0	29.0	28.5	—
380	31.0	30.7	30.5	—
400	32.0	32.4	32.0	—
440	34.0	35.2	34.5	—
500	37.0	38.1	37.5	—
510	37.0	38.1	37.5	—
520	38.0	39.2	38.5	—
540	40.0	40.4	40.0	—
550	41.0	40.9	41.0	—
560	41.5	42.1	41.5	—
600	44.5	44.9	—	—
620	45.5	46.6	—	—
630	46.0	46.6	—	—
640	47.5	48.3	—	—
650	48.5	49.5	—	—
700	54.0	54.0	—	—
750	59.5	—	—	—
800	64.0	—	—	—
850	67.0	—	—	—
900	68.5	—	—	—
950	69.5	—	—	—
1000	70.5	—	—	—

Fig. 1. The curve shows the change in weight of lepidomelane during heating from 25°C to 1000°C and during cooling from 1000°C to 300°C.

certainly recognise that these 3 breaks are characteristics of the mineral.

To know the essential cause producing these three breaks, the following experiments were made.

1. The amount of change in weight by oxidation of FeO into Fe_2O_3 , heated at 260°C for one hour, was 0.10%. 2. The temperature at which FeO completely changes into Fe_2O_3 is 500°C, heated for one hour. 3. The weight change of the mineral was measured for the charges heated at desired temperatures in air and then cooled in the furnace until they reached room-temperature. The results are seen in Table III. In this case, the hygroscopic water was 2.10% which was obtained by heating between 105°–135°C until the weight became practically constant. The crystallization water was 5.15% which was obtained by calculation from the ignition-loss (6.37%) minus hygroscopic water (2.10%) plus the weight of oxygen required for alteration of FeO into Fe_2O_3 (0.88%). 4. To know the relation between the loss of weight and the amount of expelled water by heating, the charge was heated in dry air-current at desired temperatures, and the

Fig. 2. The curves show the change in weight of lepidomelane during heating in the ranges 25°–300°C, 25°–560°C and 25°–700°C and during cooling 300°–100°C, 560°–100°C and 700°–200°C respectively.

TABLE III.

Temp. in °C.	Loss of weight by heating
105	1.85%
135	2.10
260	2.46
510	3.64
630	4.27
1000	6.01
Loss on ignition	6.37

weight of the expelled water absorbed in CaCl_2 in a U-tube and of the heated material which remained in the furnace were measured respectively. The results are seen in Table IV.

From the Table, we see that the crystallization water is about 5.42% which is obtainable by a calculation as $5.42 - 2.10 + (6.37 - 4.27)$. 5. The determination of H_2O expelled from the mineral was also made by Jakob's method,²⁾ using $\text{Na}_2\text{B}_4\text{O}_7$, and the results were 7.28, 7.16, 7.22 and 7.25 in percentage for four different cases, the mean value being 7.23%. The crystallization water is 5.13% in this case.

TABLE IV.

Temp. in °C.	Change in weight of charge by heating	Expelled water by heating
260	2.69%	2.77%
510	3.78	4.63
630	4.55	5.42
750	5.04	5.84

The crystallization water obtained from the different experiments stated above are 5.19, 5.15, 5.42 and 5.13 in percentage. These results clearly indicate that $(\text{OH}, \text{F})_3$ must reasonably exist in the chemical composition of the lepidomelane instead of $(\text{OH}, \text{F})_2$. We also see from the above experiments that the three breaks at 260°, 510° and 630°C are essentially due to the different escaping velocities of OH from the mineral material.

In conclusion the writer wishes to offer his hearty thanks to Prof. S. Kôzu, under whose guidance the present study was carried out.

References.

- 1) F. Machatschki, CBl. 1932, pp. 65-68.
- 2) J. Jakob, Z. X., 64, 1932, p. 451.