

## On the Weathering of Allanite found in South Manchuria ( I )

By

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Allanite is one of the unstable silicate minerals, so we can occasionally find it covered with yellowish-to-reddish brown crust produced by the weathering. To investigate the process of this weathering, the authors have recently made up a special apparatus in which artificial weathering is constantly going on. This experiment is now progressing. Its results will be reported in adjoining papers.

The crust of allanite produced by natural weathering has formerly been studied by J. W. Mallet<sup>(1)</sup> on a specimen from Amherst County, Virginia; by E. P. Valentin<sup>(2)</sup> on a specimen from Nelson County, Virginia, and by S. Hata<sup>(3)</sup> on a specimen from Fukushima Prefecture, Japan. By these investigators the alteration of chemical composition has, to some extent, been made clear, but they did not employ X-ray analysis in their studies. First of all, we have studied not only the chemical composition but also the structure of this crust by X-ray analysis.

### Experimental results

The specimen used for this experiment was collected by one of the authors (Takubo) in the pegmatite dyke at Hsiayuhkou in Haicheng district, South Manchuria. The crust of this specimen is about 2mm in thickness and had almost changed into limonite-like substance. This altered part can be easily scraped off from the harder interior of the mineral.

To examine what effect the natural weathering inflicted upon each constituent, chemical analysis of the crust as well as the hard interior was carried out. The results are shown in Table I:

Table I

Constituents	Interior part	Crust
	%	%
FeO	6.31	0.00
MnO	4.51	0.00
CaO	18.53	4.56
MgO	0.39	0.00
Fe <sub>2</sub> O <sub>3</sub>	9.51	20.51
Al <sub>2</sub> O <sub>3</sub>	12.37	11.05
(Ce, Y) <sub>2</sub> O <sub>3</sub>	10.16	2.08
SiO <sub>2</sub>	33.01	28.49
TiO <sub>2</sub>	0.30	0.43
ThO <sub>2</sub>	3.29	4.20
CO <sub>2</sub>	—	4.32
H <sub>2</sub> O(+)	2.16	7.33
H <sub>2</sub> O(-)	0.34	17.12
Total	100.88	100.09

From these results it is evident that manganese and magnesium are entirely lost, calcium and rare earths are remarkably decreased, ferrous iron is wholly changed to a ferric state; silicon, aluminium, titanium, thorium and total iron probably remain in constant. Besides these alterations, carbon dioxide and water are added. These facts quite agree with the previous studies carried out by the foregoing workers.

Effects of the natural weathering upon the structure were examined by means of X-ray powder method using copper *K $\alpha$*  radiations for 8 hours, under the condition of about 24,000V. and 8 ~ 12 mA. The distance from sample to camera plate is 33.0mm. The X-ray diffraction rings thus obtained were somewhat indistinct, but they were clear enough to measure their radii. The spacing of each atomic plane (*d*) will be seen in Table II:

Table II

Interior part		Crust	
<i>d</i> (Å)	Intensity	<i>d</i> (Å)	Intensity
4.53	s	3.62	m
3.67	m	2.89	s
2.95	s	2.58	m
2.60	m	2.37	m
2.37	w	2.08	w
		1.85	v.w

From these results, we can conclude that the lattice structures are to some extent still kept after such severe decomposition. Considering that allanite is a silicate mineral, it is thought that silicon-oxygen bonds, which are the strongest in all the structures and whose arrangements are considered as the frame-work of the silicate structure, hold their original positions after the replacement of certain elements. (The spacings corresponding to 2.08 and 1.85 are considered due to calcite crystals).

Under the microscope, in the portion that is in contact with the crust, many cracks were observed filled up by minor but abundant calcite crystals. In the crust, two sorts of minute but crystalline grains could be observed. One is abundant, the other is much less and extremely minute. Under the crossed nicol, either of these two sorts of grains is proved to be anisotropic, but they could not be identified on account of their extreme minuteness. These few and minute crystal grains, however, are inferred to be calcite from the results of chemical analysis and from the fact of their being in the portion in contact with the crust.

Taking the results of microscopical and X-ray investigations into consideration, we believe that the crust consists of calcite and a sort of complex compound whose structure bears a close resemblance to the original mineral, and whose chemical formula is to be derived from the molecular ratios of constituents. In Table III, the molecular ratios of each constituent, calculated from the results of chemical analysis, are shown:

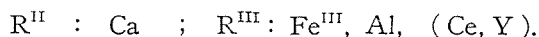
Table III

Constituents	Molecular ratio	Constituents	Molecular ratio
FeO	0	(Ce, Y) <sub>2</sub> O <sub>3</sub>	6
MnO	0	SiO <sub>2</sub>	475
CaO	81	TiO <sub>2</sub>	5
MgO	0	ThO <sub>2</sub>	16
Fe <sub>2</sub> O <sub>3</sub>	128	CO <sub>2</sub>	98
Al <sub>2</sub> O <sub>3</sub>	108	H <sub>2</sub> O(+)	407

Then,

$$\begin{aligned}
 & R^{II}O : R_2^{III}O_3 : (Si, Ti, Th)O_2 : CO_2 : H_2O \\
 & = 81 : 242 : 496 : 98 : 407 \\
 & = 1 : 2.99 : 6.12 : 1.21 : 5.02 \\
 & = 1 : 3 : 6 : 1 : 5
 \end{aligned}$$

Where



Now we can determine that the crust consists of two crystalline substances, that is  $\text{CaCO}_3$  and  $\text{H}_5\text{R}_2^{\text{III}}\text{R}^{\text{III}}\text{O} [(\text{Si}, \text{Ti}, \text{Th})\text{O}_4]_3$ .  $\text{CaCO}_3$  is, of course, calcite and  $\text{H}_5\text{R}_2^{\text{III}}\text{R}^{\text{III}}\text{O} [(\text{Si}, \text{Ti}, \text{Th})\text{O}_4]_3$  is one of the orthosilicates which hold allanite-like structure.

### Conclusion

As mentioned above, at the portion in contact with the crust, there are abundant calcite crystals in the cracks, while in the crust itself they are very scarce. From these facts we can say that at the earlier stage of the natural weathering of allanite calcite and a sort of orthosilicate are produced whose chemical formula is represented by  $\text{H}_5\text{R}_2^{\text{III}}\text{R}^{\text{III}}\text{O} [(\text{Si}, \text{Ti}, \text{Th})\text{O}_4]_3$  and whose structure bears a close resemblance to allanite; at the later stage calcite is remarkably decreased on account of further weathering. In fact, the crust must be in this later stage.

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(1). J. W. Mallet: *Z. Kryst.*, 6 (1883), 96.

(2). E. P. Valentin: *Am. Chem. J.*, 7 (1885), 172.

(3). S. Hata: *Sc. Pap. I. P. C. R.*, 36 (1939), 301.