Pseudomorphs after olivine in Markle basalt.

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Summary. Pseudomorphs after olivine in Markle basalt from Holyrood Park, Edinburgh, consist of an intimate mixture of hematite and chlorite, along with a small percentage of quartz. A definite relationship exists between the orientations of the two main constituents and is dependent upon their structures.

THE Markle basalt, which forms part of the Whinny Hill Series of lavas in Holyrood Park, Edinburgh, is hydrothermally altered in that the original olivine phenocrysts are completely replaced. In the weathered rock, the resultant pseudomorphs are very conspicuous since they consist of a glittering red platy product which has at least one excellent cleavage or rather 'pseudocleavage'. In the past, material like this would probably have been described as a single mineral termed iddingsite. This name was originally applied by Lawson in 1893 following earlier descriptions of the material (from Carmelo, California) by Iddings in 1892. From the many chemical analyses of 'iddingsite' carried out by Ross and Shannon (1926) and Tomkeieff (1934), ten were selected by Wilshire (1958) to express a range of composition for this material. An average composition was calculated, and these results are compared with the analysis of the Markle basalt material in table I. The Markle sample differs, however, in having a comparatively high content of alumina and ferrous oxide.

Variations in chemical composition are not surprising, since recent X-ray investigations have revealed that the name 'iddingsite' has been used for at least two different mixtures. Sun (1957) identified 'iddingsite' from Carrizozo, New Mexico, and from Paton Peak, Colorado, as a mixture of goethite and amorphous material, and Wilshire (1958) identified material from various localities in California, including the type locality Carmelo Bay, also New South Wales and Hawaii, as mixed-layer montmorillonite–chlorite and goethite. The Markle basalt pseudomorphs after olivine were likewise found to contain more than one mineral, viz. hematite, chlorite, and a small quantity of quartz.

An attempt to determine the percentages of hematite and quartz by

X-ray powder methods with corundum as an internal standard was not very satisfactory, owing to the small quantity of material available for making specimens. Six results ranged from 33 to 42 % hematite, against 32·39 % total Fe_2O_3 by chemical analysis of the air-dried sample. By the dithionite method of determining free iron oxide (Mitchell and Mackenzie, 1954) it appeared that all the ferric oxide in the sample was in the free state and therefore the quantity of hematite was taken to be 32·39 % of the air-dried sample. Quartz was determined by X-ray methods as approx. 2 % of the mixture, whence the remainder of the sample was found to have the composition of a chlorite with formula $0{\cdot}22\ M^+[Si_{3\cdot27}Al_{0\cdot73}][Al_{1\cdot85}Mg_{2\cdot94}Fe^{2+}_{0\cdot55}]O_{10}(OH)_8$. The calculation of this formula was based on the assumption that each structural unit contained 10 oxygen and 8 hydroxyl ions. Since there was no shift in the 14·5 Å. basal spacing of this mineral after heat treatment at 600° C., it is considered to be a true chlorite and of the pennine species according to the classification proposed by Hey (1954). Its cation-exchange capacity is 24 m.e. per 100 g. with calcium as the exchangeable cation.

TABLE I. Chemical analyses of 'iddingsite' and of the pseudomorphs from the Markle basalt.

	*Iddingsite**		*Material from Markle Basalt*
	Range	*Average*	
SiO_2	22·08–48·36	41·20	24·77
TiO_2	0·12–0·26	0·14	—
Al_2O_3	0·00–5·09	3·81	14·77
Fe_2O_3	25·48–60·13	35·42	34·09
FeO	0·00–1·97	0·38	4·50
MnO	0·00–0·11	0·05	—
MgO	0·60–12·71	6·85	13·27
CaO	1·72–3·26	2·35	0·73
Na_2O	0·12–0·13	0·12	—
K_2O	0·09–0·10	0·10	—
H_2O+	5·74–11·00	9·30	8·26
		99·72	100·39
H_2O- (300° C.)			5·04

* Analyses of ten iddingsite samples are represented and are quoted from Wilshire (1958). All analyses were recalculated to 100 % excluding H_2O- before averages were computed.

The *optical properties* of the combined product, as seen in thin section, tend to be similar to those of biotite, especially the pleochroic effect with strong absorption of the rays vibrating parallel to the main cleavage. The colour ranges from a pale straw yellow to a dark reddish brown, as in biotite. An electron-micrograph of crushed fragments of this material shows transparent chlorite coated with iron oxide as pigment (fig. 1). The platy form of the chlorite and hematite and the manner in which these minerals aggregate result in a well-developed cleavage within the pseudomorphs (fig. 2). Where it is possible to obtain an interference figure along the normal to the cleavage planes, the material is always biaxial negative with 2V varying from 0° to 20°.

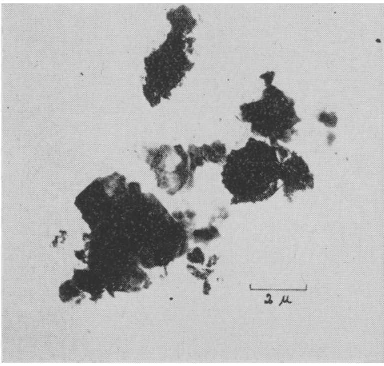

FIG. 1

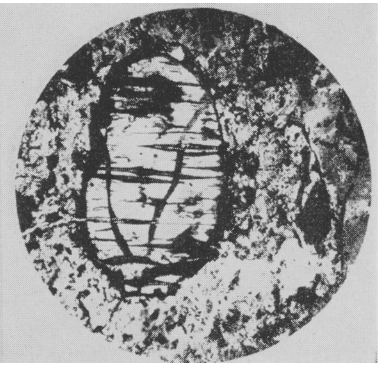

FIG. 2

FIG. 1. Electron-micrograph of crushed fragments of pseudomorphs after olivine.

FIG. 2. Photomicrograph of thin section of rock showing well-developed cleavage of pseudomorph. ×43.

Orientation relationships. The hematite and chlorite exist as intimately mixed aggregates of very small crystals, as shown by the smoothness of the reflections in an X-ray diffraction photograph obtained from a stationary cleavage flake. The same photograph also shows that the crystals exist in a preferred orientation. The quartz occurs as very small mosaic-like patches within the pseudomorphs, as seen in thin sections using polarized light. The X-ray evidence shows that the individual crystals of quartz are in random orientation.

The orientation relationship between the hematite and the layer-silicate was studied by taking a series of X-ray rotation photographs. For convenience, the hematite is referred to hexagonal crystallographic axes x, y, u, and z while the monoclinic chlorite is assigned the axes a, b, and c. When the specimen was rotated about a vertical axis normal to the cleavage plane, the c-axes of the layer-silicate particles and the z-axes of the hematite particles were simultaneously vertical (fig. 3).

With the *a*-axes of the chlorite crystals vertical, the zero layer line contained the general 060 reflection and orders of the basal 00*l* reflection, while at the same time one of the three short axes of the hematite was vertical (fig. 4).

From the rotation photographs, the unit cell dimensions of the two components were calculated and a definite epitaxial relationship was established: *a* (5·20 Å.) of chlorite approx. parallel to *x* (4·97 Å.) of hematite, *c* (14·50 Å.) of chlorite approx. parallel to *z* (13·76 Å.) of hematite. The chlorite has *b* 9·18 Å., *β* approx. 97°.

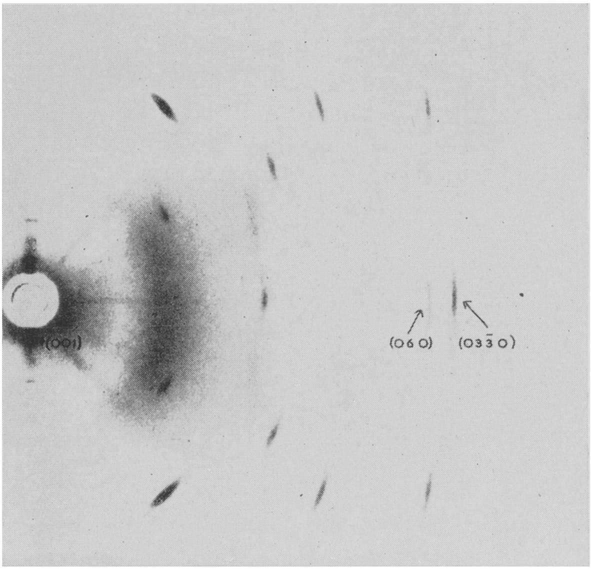

FIG. 3. Rotation photograph about the *z*-axis of the hematite (= *c*-axis of the chlorite).

The *a* and *b* unit-cell dimensions of the chlorite were also calculated from an electron diffraction pattern taken along the *c*-axis direction and these agreed well with the X-ray data.

Disorientation effects. Both the hematite and the chlorite gave some sharply defined spots and some elongated streaks in the rotation photographs.

When a cleavage flake of the pseudomorph was rotated with the *x*-axis of the hematite vertical the $03\bar{3}0$ hematite and 060 chlorite reflections, which appeared on the zero layer line, were sharp and short, whereas when the flake was rotated with the z-axis of the hematite vertical the same reflections, again on the zero layer line, were elongated (figs. 4 and 3). The streaking of the reflections must be due to slight disorientation of the crystals about a direction normal to their z- or c-axis, as this type of displacement would have almost no lengthening effect upon the $03\bar{3}0$ and 060 reflections with the flake adjusted for rotation about the x-axis. For the same setting, however, the $00l$ reflections of the chlorite are elongated as one would expect (fig. 4). Similarly, when the crystals were set up for rotation about their y^*- or b-axes the reflections $2\bar{1}\bar{1}0$ and $4\bar{2}\bar{2}0$ were sharp and short compared with the $2h\bar{h}\bar{h}l$ and $00l$ reflections (fig. 5).

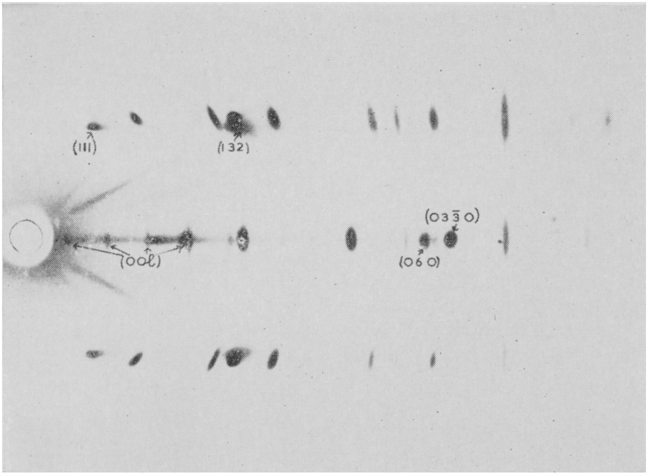

FIG. 4. Rotation photograph about the x-axis of the hematite ($=$ a-axis of the chlorite).

The conclusion that disorientation takes place in a direction normal to the c- or z-axis is confirmed by the radial streaking of all reflections in a Laue photograph taken with the X-ray beam parallel to the c- or z-axis. The fact that the streaking effect is of uniform length in all directions indicates that the disorientation occurs as a tilting of the crystal plates about any axis in the ab or xyu plane. In comparison, very little disorientation of the crystal plates occurs about the direction of the c- or z-axis. This has already been mentioned in connexion with the short reflections in the rotation photographs and is also demonstrated by the absence of any marked circular spread of reflections in the Laue photograph.

An attempt was made to measure the extent of disorientation by taking Weissenberg photographs of the material rotated about each of the three principal chlorite axes. Most of the reflections appeared as straight lines on these photographs, their length depending on the amount of angular disorientation about the direction of the rotation axis. Intensity distribution for each spot was calculated using calibration curves which had been prepared from measurements of the optical density of films exposed to X-rays by a step sector arrangement. Optical density measurements were made in every case by a photometer with photo-electric cell and galvanometer. The curves shown in fig. 6 were drawn from average measurements of six reflections in each case, taking the maximum calculated intensity of each reflection to be 100 % and the film background intensity to be 0 %. The intensity profile of reflections from a quartz crystal (similar in size to the cleavage flake of the pseudomorph) is included in fig. 6, to show the angular

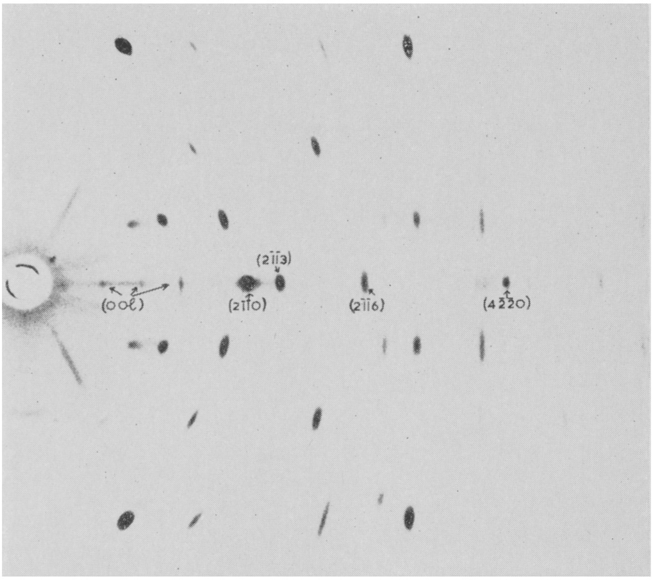

FIG. 5. Rotation photograph about the y^*-axis of the hematite (= b-axis of the chlorite).

spread of intensity one would expect from a perfectly oriented aggregate of crystals.

In the Weissenberg photographs some chlorite reflections were represented by rods in reciprocal space passing through (ha^*,kb^*,0) parallel to c^*, indicating that the crystals of chlorite are extremely thin along the c-axis direction.

Discussion. Comparison of curves *B* and *C* in fig. 6 shows that disorientation of the crystals of hematite is less about the z-axis than about any normal to this axis. The chlorite crystals behave in the same way.

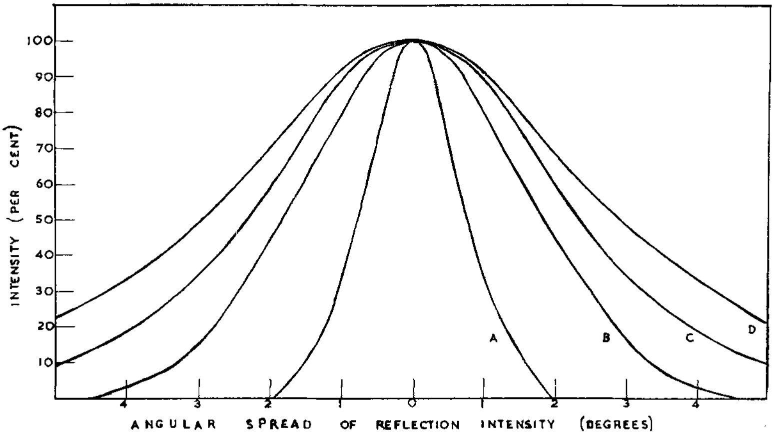

Fig. 6. Intensity profiles of Weissenberg zero-layer reflections. A, Quartz crystal rotated about the z-axis. B, Hematite crystals rotated about the z-axis. C, Hematite crystals rotated about the x- and y^*-axes. D, Chlorite crystals rotated about the b-axis.

Both minerals have sheets of oxygen atoms in hexagonal close packing, parallel to the (00l) and (000l) planes of chlorite and hematite respectively. These are the cleavage planes and are most likely to be the contact surfaces between the crystals. The superposition of the sheets of oxygen atoms brings the a- and x-axes into alignment with almost no disorientation about the z-axis direction. In the electron-micrograph, thin films of hematite are seen formed on the surfaces of chlorite plates.

The disorientation normal to the z- or c-axis direction may be due to bending of the chlorite plates, since they are extremely thin in the c-axis direction. Also, the thinness of the chlorite plates and the fact that the chlorite is twice as abundant as the hematite suggest that the basal surface area of the chlorite is much greater than that of the hematite. The extent of hematite disorientation in comparison with chlorite (cf. curves *C* and *D*, fig. 6) may depend on the positioning of the hematite crystals upon the chlorite, e.g. they may be restricted to the flatter portions of the chlorite plates.

Some of the hematite reflections do not satisfy the conditions limiting possible reflections in the space-group $R\bar{3}c$ to which hematite belongs. Twinning could account for these reflections but a more obvious explanation is that the hematite may have more than one orientation on the chlorite plates. The apparent hexagonal symmetry of the hematite is probably due to the hexagonal symmetry inherent in the chlorite tetrahedral layer enabling the x-axis of the hematite to take up any one of six possible positions at 60° intervals of rotation about z.

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