

## A STRUCTURAL STUDY OF IDDINGSITE FROM NEW SOUTH WALES, AUSTRALIA

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### ABSTRACT

Iddingsite from New South Wales, Australia, is polycrystalline and consists of goethite and a layer lattice silicate. In the alteration of olivine to iddingsite the original lattice of close-packed oxygens appears not to have been greatly disturbed and the changes have occurred by the movement of cations within small regions to form microcrystals of the alteration products. The parallel alignment of the components explains why it behaves optically as a single crystal.

### INTRODUCTION

Iddingsite is the name generally given to the deep reddish brown to ruby red lamellar minerals commonly found in basaltic and allied rocks as an alteration product of olivine (Winchell, 1951). The origin, occurrence, composition, and physical properties of iddingsite were first described in detail by Ross and Shannon (1926), and subsequent studies include those by Tomkiewf (1934), Edwards (1938), and Bogue and Hodge (1940). Since this investigation was begun Ming-Shan Sun (1957) published the results of  $x$ -ray powder examinations of iddingsites, and concluded that goethite was the only substance present in the crystalline state, and that other substances whose presence was shown by chemical analysis were largely amorphous. Wilshire (1958), using a similar technique, found that iddingsites were largely smectite-chlorites with goethite always present; quartz and calcite are common and talc and mica rare constituents.

The present study was undertaken to investigate iddingsite more adequately, and in particular to find the reason for its optical homogeneity, and also to obtain information on a naturally occurring alteration process. The material used was obtained from an olivine-basalt of Tertiary age from near Lismore in northern New South Wales, Australia (Norrish, 1952), and grains were isolated that were favourable for study by optical and single crystal  $x$ -ray diffraction techniques.

### PETROGRAPHY

The rock is a porphyritic olivine-basalt with phenocrysts of labradorite and olivine in a medium-fine grained groundmass of abundant laths of a less basic plagioclase, augite, ilmenite, nontronite and apatite. The phenocrysts of labradorite range up to 1 cm. in size, while those of the olivine attain a length of about 2 mm. Some of the olivine grains are completely transformed to iddingsite, but usually unaltered cores of oli-

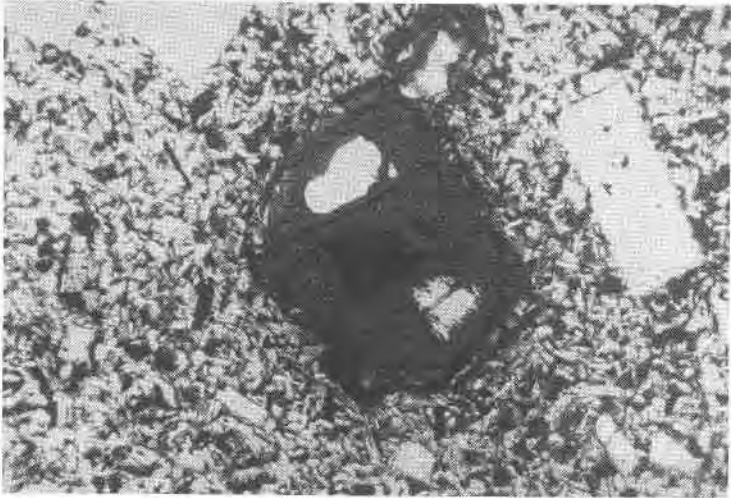


FIG. 1. Olivine-basalt, Lismore, N.S.W., Australia, showing an iddingsite pseudomorph with cores of remnant olivine. Magnification:  $\times 25$ .

vine are preserved within the iddingsite with a fairly sharp boundary, which, in places, may be somewhat ragged, suggesting reaction (Fig. 1). The pseudomorphs are normally rimmed by a thin zone of yellowish brown or greenish cryptocrystalline material. It is probable that the iddingsite is of deuteritic origin, as the associated minerals show little signs of weathering, and, in particular, the labradorite phenocrysts are very clear and unaltered.

#### OPTICAL PROPERTIES

In thin section the iddingsite shows a lamellar habit, with one well developed cleavage, and two subsidiary cleavages at right angles to each other and to the principal cleavage direction: extinction is parallel to the cleavage traces and to the extinction directions of the remnant olivine. Pleochroism is distinct with Y and Z deep orange brown to reddish brown and X light orange brown to yellowish brown.\* The majority of the individual grains isolated after crushing the rock are tabular in habit due to the presence of the well developed cleavage. These cleavage fragments are deep reddish brown and are essentially non-pleochroic. The refractive indices vary slightly but most of the grains have  $\alpha = 1.67-1.68$  and  $\gamma = 1.71-1.72$ , with the birefringence approximately 0.04. The optic

\* A few of the olivine grains show an alteration product having olive green tints in its pleochroic scheme in addition to shades of brown: morphologically the material is similar to iddingsite, but this variant has not been studied.

TABLE 1.  $\zeta$  VALUES (CuK  $\alpha$ ) AND DESCRIPTION OF LAYER LINES ON PHOTOGRAPH OF IDDINGSITE ROTATED ABOUT Y OPTIC VIBRATION DIRECTION

$\zeta$	Axial repeat in Å	Nature of reflections	
		Broad	Sharp
0.0	—	Many, strong	present
.075	20.6	Few, weak	
.15	10.3	Many, strong	present*
.23	6.7	Few, weak	
.29	5.3	Few, strong	
.31	5.0	Many, strong	present*
.38	4.1	Few, weak	
.46	3.35	Few, medium	present*
.52	2.98	Few, weak	
.58	2.68	Few, weak	
.62	2.50	Few, weak	present*
.76	2.00	Few, weak	present*

\* These sharp spots do not lie precisely on the same layer lines as the broad spots, but are close to them.

sign is negative with moderate optic axial angle ( $2V$  30–40°): the dispersion is distinct,  $r < v$ .

The grains selected for  $x$ -ray analysis were optically homogeneous, showing the emergence of the acute bisectrix normal to the plates, and giving a centred biaxial interference figure from which the directions of the optical constants could readily be determined.

#### X-RAY ANALYSIS

A preliminary single crystal rotation photograph of a grain (0.25  $\times$  0.25  $\times$  0.05 mm.) rotated about the Y optic vibration direction showed well developed layer lines, but the pattern was complex. Table 1 summarizes the  $\zeta$  (CuK  $\alpha$ ) values, the corresponding axial repeat distance, and the nature of the layer lines. The majority of the reflections were broad, but on or near a number of layer lines were very small sharply defined spots: comparison with an olivine  $b$ -axis rotation photograph showed that the sharp spots could be attributed to olivine.

The layer lines of broad spots with  $\zeta = n(.075)$  were provisionally attributed to one mineral, and those with  $\zeta = n(.29)$  from the axial repeat distance and hexagonal arrangement of the inner reflections were attributed to a layer lattice mineral rotated about the  $a = 5.35$  Å axis. A powder photograph of a few crushed grains suggested that goethite was present, and also showed a reflection  $d = 15.6$  Å which could be the basal reflection of the layer lattice silicate.

The powder pattern was poor, and to obtain further information, Weissenberg and oscillation photographs were taken with the Y optic direction as the rotation axis. As many of the reflections were weak and broad the Weissenberg photographs showed only the stronger spots, which were insufficient for complete characterization. From a complete set of 5° oscillation photographs reciprocal lattice nets were obtained for each of the twelve levels of the broad spot pattern, and also for the zero, first and second levels of the material giving the sharp spots: these were constructed by plotting the co-ordinates of the reflections, which were 5° arcs rather than points. The reciprocal nets showed that the symmetry of the entire diffraction pattern is *mmm*. Complete sets of oscillation photographs were also taken about the two other orthorhombic axes, corresponding to the X and Z vibration directions, and the reciprocal nets were constructed for all broad spot levels.

All the applied criteria indicate that the olivine is being transformed into a material comprising goethite in three orientations and a layer lattice silicate with layer stacking disorder.

#### *Olivine*

The cell dimensions  $a=4.8$ ,  $b=10.3$ ,  $c=6.0$  Å and space group *Pbnm* of the material giving the sharp spots confirmed its identification as olivine. Bragg and Brown (1926) gave  $a=4.755$ ,  $b=10.21$ ,  $c=5.985$  Å and space group  $V_h^{16}$  ( $\equiv Pbnm$ ) for olivine. Powder photographs of crushed iddingsite grains with included olivine gave for the latter  $d(130)=2.779$  Å corresponding to the composition Fo (80%) determined by the method of Yoder and Sahama (1957). The olivine axes are oriented with  $a\parallel X$ ,  $b\parallel Y$  and  $c\parallel Z$  of the iddingsite.

#### *Goethite*

The goethite was identified from the cell dimensions  $a=4.6$ ,  $b=10.0$ ,  $c=3.0$  Å, determined from the layer line separations and the reciprocal nets, and the systematic absences,  $h0l$  absent for  $(h+l)$  odd,  $0kl$  absent for  $k$  odd, which are consistent with the space group *Pbnm*. Goldsztaub (1931) gave  $a=4.64$ ,  $b=10.0$ ,  $c=3.03$  Å and the space group *Pbnm* for goethite. The absences were derived from rather limited data, reflections with  $2\theta > 90^\circ$  being too diffuse to index with certainty. The observed intensities, however, gave additional evidence, for 110 the strongest reflection is the strongest goethite reflection and all the strong observed intensities correspond to strong goethite reflections.

Most of the goethite is aligned parallel to the original olivine with

$$a_G\parallel a_F; \quad b_G\parallel b_F; \quad c_G\parallel c_F^\dagger$$

† The subscripts G, F and L refer to goethite, olivine and the layer lattice silicate respectively.

The goethite in this orientation accounts for the reflections occurring on the  $\zeta = n$  (.15) layer lines (Table 1). When account was taken of the reflections due to the layer lattice silicate it was found that those remaining could be attributed to goethite oriented so that

$$a_G \parallel a_F; \quad b_G \parallel [0\bar{1}3] \text{ and } [0\bar{1}3]_F; \quad c_G \parallel [0\bar{1}1] \text{ and } [0\bar{1}1]_F$$

In these orientations only a few medium or weak reflections could be observed, and these correspond to the strong goethite reflections. Fig. 2 illustrates the three orientations of the goethite cells in relation to the original olivine. From the intensities of the 110 reflection from goethite in the three orientations about 80 per cent appeared to be in parallel orientation with the olivine and only 10 per cent in each of the other two orientations. From the width of the reflections the size of the individual goethite crystals is estimated to be 200–300 Å.

#### *Layer lattice silicate*

This component accounts for the layer lines  $\zeta = n$  (.29) (Table 1). The reciprocal lattice consists of a single row of reciprocal lattice points passing through the origin, and reciprocal lattice rods parallel to the point row arranged in a hexagonal pattern around the central row. The repeat period along the point row corresponds to a spacing of 15.6 Å and the cell side of the hexagonal array is 5.35 Å. The stacking of the layers is highly disordered, the only observable regularity in addition to the parallel and equidistant stacking of the silicate layers being the parallel alignment of the *a*-axes of the  $(\text{Si}_2\text{O}_5)^{2-}$  layers which make up the half layers of the mineral. Table 2 gives  $\xi$  values, derived values of  $h^2 + hk + k^2$  and  $hk$  indices for the rods which are continuous except  $11l^*$  and  $22l^*$  which have zero intensity at  $l^* = 0$ . The values of  $h^2 + hk + k^2$  confirm the hexagonal nature of the array.

The *a* dimension corresponds closely to the value found for trioctahedral layer lattice silicates, e.g. chlorite  $a = 5.33\text{--}5.37$  Å (Steinfink, 1958) and vermiculite  $a = 5.33$  Å (Mathieson and Walker, 1954). The repeat distance along the point row corresponds to the layer thickness of smectites in the air-dry condition when saturated with divalent cations. Unlike most smectites, however, the basal spacing could not be increased by treatment with water, ethylene glycol or glycerol. The layer thickness is reduced to 10 Å by heating at 500° C. for one hour. These properties appear sufficient to identify the material as a mineral of the vermiculite or smectite group, but obviously a more detailed examination is desirable. The layer lattice mineral of iddingsite has been identified by Wilshire as a smectite-chlorite. However, the collapse to a layer thickness of 10 Å on heating, both of the majority of the specimens studied by Wilshire and of those examined in the present study, does not fully support his con-

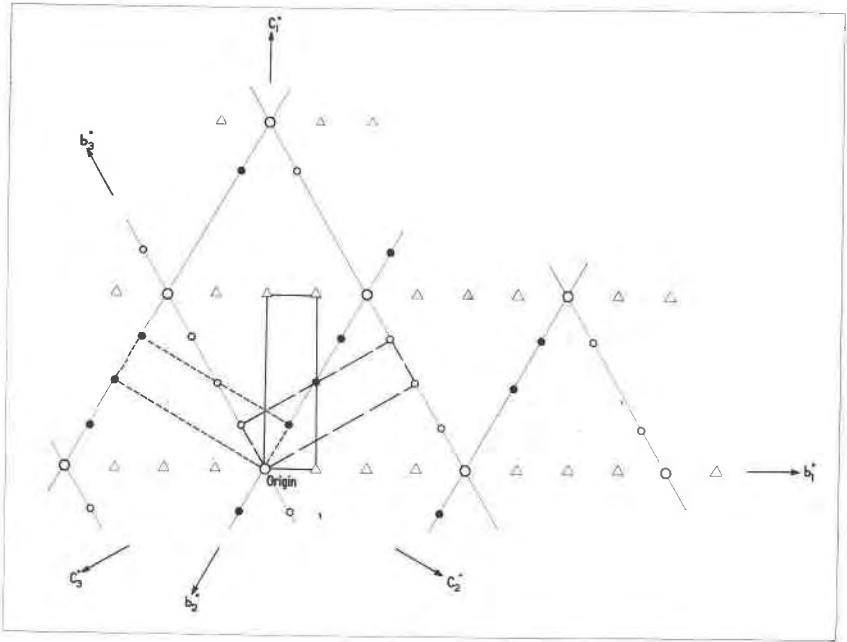


FIG. 2. Projection along  $a^*$  of reciprocal lattice of goethite showing its three orientations. Heavy continuous line shows goethite cell in same orientation as olivine, axes  $b_1^*$  and  $c_1^*$ .

Dotted line and broken line show goethite cells in subsidiary orientations with axes  $b_2^*c_2^*$  and  $b_3^*c_3^*$  respectively

$\Delta$   $\bullet$  and  $\circ$  denote observed reciprocal lattice points for orientations 1, 2 and 3.

$\circ$  are reciprocal lattice points where corners of the differently oriented cells coincide, and thin continuous lines show large reciprocal cell of the close packed oxygens.

TABLE 2.  $\xi$  VALUES (CuK  $\alpha$ ) AND  $hk$  INDICES (HEXAGONAL) OF RECIPROCAL LATTICE RODS OF LAYER LATTICE MINERAL; IDDINGSITE ROTATED ABOUT X OPTIC VIBRATION DIRECTION

$\xi$	$\xi^2$	$h^2+hk+k^2$	$hk$
.33	.11	1	10
.58	.33	3	11
.65	.42	4	20
.88	.77	7	21
1.00	1.00	9	30
1.14	1.30	12	22
1.19	1.42	13	31
1.44	2.07	19	32
1.53	2.34	21	41

clusions. Although slight atomic re-arrangement takes place, the basal spacing of chlorite layers remains near 14 Å until recrystallization takes place (Brindley and Ali, 1950), and interstratified smectite-chlorite would be expected to give intensity maxima between 10 and 14 Å after heating.

The orientational relationships between olivine and the layer lattice silicate are as follows:

$$a_L \parallel [010], [0\bar{1}3] \text{ and } [0\bar{1}\bar{3}]_F; \quad c_L \parallel [100]_F$$

The use of  $a$  and  $c$  here is not intended to imply a true unit cell, but only to denote a structural unit.

#### DISCUSSION

It has been shown that the transformation of olivine into iddingsite involves the production of new crystalline phases, and it is pertinent here to consider more closely the relationships of these new materials to the parent olivine.

Olivine and goethite belong to the same space group  $Pbnm$  and the cell dimensions have the following relations:

$$a_F \simeq a_G; \quad b_F \simeq b_G; \quad c_F \simeq 2c_G$$

Both structures are based on sheets of oxygen in hexagonal close-packing parallel to (100), which, considering oxygens only, leads to the equivalence of the directions  $[010]$ ,  $[0\bar{1}3]$  and  $[0\bar{1}\bar{3}]_F$  at angles of  $120^\circ$ ; similarly  $[001]$ ,  $[0\bar{1}\bar{1}]$ , and  $[0\bar{1}\bar{1}]_F$  are equivalent. Structurally only slight adjustments of the oxygen framework are required in the change from olivine to goethite; the cation replacements and rearrangements could easily take place by ionic diffusion. The three observed orientations of goethite are explained by the equivalence of the three directions mentioned above. The preponderance of goethite in parallel orientation to olivine suggests, however, that the three directions are not exactly equivalent and that the cation arrangement in olivine exerts considerable control over that of the derived goethite. It is interesting to note that the triple points, where the corners of the differently oriented goethite cells coincide, outline a hexagonal cell  $a = 2.9 \text{ \AA}$ ,  $c = 4.6 \text{ \AA}$ , which corresponds to the unit cell of hexagonal close-packed oxygens (Fig. 2).

The alteration of olivine to a layer lattice silicate involves some breaking up of the close-packed oxygen framework of the olivine. Nevertheless in a study of what is in effect the reverse reaction, the alteration on heating of layer lattice silicates (chlorite and serpentine) to olivine, Brindley and Ali (1950) and Brindley and Zussman (1957) have shown that the majority of the Si—O bonds remain unbroken, only slight rotations of

tetrahedra and migrations of Si being required to effect the alterations. In these studies the following dimensional and orientational relations were established between the layer lattice mineral and the resultant olivine.

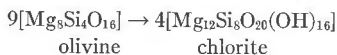
$$2a_L \simeq b_F \text{ and } 2b_L \simeq 3c_F \ddagger$$

$$[100]_L \parallel [010] \text{ and } [013]_F; \quad [010]_L \parallel [001] \text{ and } [011]_F$$

The same mechanism is proposed for both mineral groups, the transformation being visualised as occurring layer by layer, one layer of chlorite giving two layers of olivine and one layer of serpentine yielding one layer of olivine. The same dimensional and orientational relations are found in the present study if the transformation from hexagonal to face-centred orthorhombic axes for the layer lattice silicate is made, and it appears that alteration takes place by a mechanism similar to that postulated above.

It is difficult to make any statements about the chemical changes involved in the absence of knowledge of the proportions of goethite and the layer lattice silicate in the iddingsite. Although the iddingsite occupies the same volume as did the olivine, its density (ca. 2.8) is considerably less than that of olivine (3.4–3.5) determined for Fo (80%) from the graph given by Winchell (1951, p. 500). Material has obviously been lost in the change, but as the system is not a closed one the overall loss is the resultant of both gains and losses. If the change is considered to occur layer by layer, one olivine layer is equivalent to one goethite layer, but the alteration to the layer lattice silicate is more complicated.

From the relationship  $4(ab)_L \simeq 3(bc)_F$  and  $c_L \simeq 3c_F$ , an alteration without volume change involves nine cells of olivine giving four cells of the layer lattice silicate. If the silicate is considered as being a chlorite (this having the densest packing in the inter-layer region and therefore requiring most material), and ignoring isomorphous substitution, the equivalence in volume is found to be such that



From these approximations it is evident that large amounts of Mg are expelled from the regions which alter to the layer lattice silicate, and from the regions which alter to goethite all the Mg and Si are lost while Fe and H are added. These conclusions, loss of Mg and addition of Fe and H are similar to those arrived at by Ross and Shannon on the basis

‡ The  $a=5.3 \text{ \AA}$  and  $b=9.2 \text{ \AA}$  axes of layer lattice minerals lie in the plane of the layers;  $b=a\sqrt{3}$  due to the pseudo-hexagonal or hexagonal nature of the layers.



of chemical analysis. The suggestion by Ming-Shan Sun that the ratio of  $\text{Fe}_2\text{O}_3$  to  $\text{H}_2\text{O}+$  represents the composition of goethite in iddingsite seems unlikely. Obviously the layer lattice silicate will contain considerable amounts of  $\text{H}_2\text{O}+$  and it is improbable that it would accept  $\text{Mg}^{2+}$  and entirely reject  $\text{Fe}^{3+}$ .

The most unusual feature of iddingsite is that, although polycrystalline and consisting of two components, grains exhibit the optical properties of a single crystal. Describing the rocks of the Eureka district, Nevada, Iddings (1892) discussed the alteration product of olivine (later named iddingsite) and stated that "the resultant mineral from its optical properties is evidently not a confused aggregate, but a crystallographic individual, with parallel orientation of all its parts, for the extinction of light is the same throughout and the interference figure that of a doubly refracting crystal." As has been shown by the present investigation, this homogeneity in optical properties occurs because the small crystals of both components are strictly oriented throughout a single grain. The parallel alignment arises from the nature of the alteration, the products of which inherit, goethite completely and the layer lattice silicate partly, the oxygen framework of the original olivine. The same alignments of the major components probably holds for all iddingsites which show coherent optical properties.

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