

SOME OBSERVATIONS ON "IDDINGSITE"

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ABSTRACT

Specimens of "iddingsite" for many localities have been examined by x-ray, chemical, and optical methods in a study of the alteration of olivine to "iddingsite." This proves to be a continuous transformation, and although at any stage it is possible to recognize embryonic structures, the pseudomorph is throughout a disordered atomic arrangement, and at no stage can it be assigned a definite structure or chemical composition or be regarded as a simple submicroscopic mineral intergrowth. The mechanism of the alteration appears to be one of cationic diffusion and replacement, the anion framework suffering little change; the presence of a high proportion of mobile hydrogen ions is probably an important factor. Some speculations are offered regarding the physical and chemical conditions under which alteration takes place.

INTRODUCTION

The name "iddingsite" was proposed by Lawson (1893) for certain phenocrysts occurring in the eruptive, basaltic rocks of Carmelo Bay, California. In thin section they were described as ranging in color from deep chestnut-brown to citron-yellow and occasionally clear yellowish-green, with marked pleochroism in sections transverse to the cleavage; in hand specimen "iddingsite" is described as soft but brittle, with a very well developed cleavage. Lawson was not convinced that the phenocrysts had altered from olivine, as he thought that the absence of residual olivine, and the presence of appreciable amounts of lime and soda were difficult to explain on the basis of alteration. Ross and Shannon (1925) in a detailed study give optical data for a considerable number of specimens and several chemical analyses; they deduce the formula of "iddingsite" to be $\text{MgO} \cdot \text{Fe}_2\text{O}_3 \cdot 3\text{SiO}_2 \cdot 4\text{H}_2\text{O}$ with MgO replaced by CaO in the ratio $\text{CaO}:\text{MgO}=1:4$. They also point out that "iddingsite" is confined almost entirely to extrusive or hypabyssal rocks and is practically absent from deep-seated rocks. They conclude that "iddingsite is most probably a deuteric mineral formed in the presence of heat, water and gases after the magma has reached a horizon near enough the surface to give oxidizing conditions." Later Edwards (1938) described three lines of evidence that "iddingsite" formed during consolidation of the magma. Firstly, rims of augite commonly surround "iddingsitized" olivine crystals; secondly, zones of fresh olivine can be seen enclosing embayed and "iddingsitized" olivine phenocrysts; and finally, a boulder from a "boulder tuff," Victoria, Australia, contained fresh olivine in the tachylitic outer

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zone, and an "iddingsitized" olivine in the crystalline core. Unlike Ross and Shannon, Edwards does not consider that the formation of "iddingsite" is dependent on the original composition of the olivine. He concludes that the formation of "iddingsite" is a process of oxidation and hydration and that the magma should not only be rich in water vapor, but should also have differentiated to give an iron-rich liquid.

The first x-ray data on "iddingsite" were published by Ming-Shan Sun (1957). Using powder methods only, he concluded that "iddingsite" consisted of cryptocrystalline goethite and amorphous material and gives a new chemical analysis and optical data. With regard to the conditions of formation, he states that "the alteration of olivine to iddingsite occurs most likely in a highly oxidizing solution containing HCl, at high temperatures and under high pressure." Further x-ray powder data on the alteration of olivine are given by Wilshire (1958). Unfortunately he does not clearly distinguish the various types of alteration. He concludes that "iddingsite" consists mainly of "mixed layer smectite-chlorite with a variety of accessory minerals"; among the accessory minerals are feldspar, quartz and calcite which strongly suggest that the material was contaminated. Recently Brown and Stephen (1959) have presented structural observations on an "iddingsite" from New South Wales, Australia, examined by single-crystal x-ray methods. Their results are in good agreement with those for some specimens examined during the present study, and will be referred to in more detail at the appropriate point. Smith (1959) has recently described the single crystal examination of pseudomorphs after olivine in the Markle basalt.

The object of the present study was to obtain more information on the structural arrangements in "iddingsites," so as to examine the process of alteration and to attempt to define the conditions under which "iddingsitization" takes place. To do this, a large number of specimens of "iddingsite" were examined from many different localities by single-crystal x-ray methods; chemical analyses, together with the optical properties, were obtained for several of the specimens. The results are now presented in this paper.

DESCRIPTION OF SPECIMENS

The selection of specimens of "iddingsite" for examination is difficult owing to the complexity of the possible alterations of olivine e.g. to serpentine, bowlingite and "iddingsite," and to the uncertainty of the exact physical and chemical conditions required for these alterations. Further the optical characterization of "iddingsite" is not well defined. The specimens available from many different localities were divided into two groups. In the first group, the "iddingsites" conformed to the following

conditions:—(a) they were optically homogeneous in plane polarized light, and crystalline; (b) they ranged from orange-red to red-brown in thin section; (c) they were obviously pseudomorphing olivine and unaccompanied by any other obvious alteration product of olivine and (d) they occurred in basic or intermediate, volcanic or hypabyssal rocks. Six different specimens satisfying these conditions have been examined in some detail; *x*-ray, optical and, where possible, chemical data have been obtained. In the second group of seven specimens, the examination has not been so full, and has usually only consisted of single crystal *x*-ray studies. Some of these specimens, although described as "iddingsite," show deviations which suggest that they may not be the product of an identical alteration process as the others. Their relationship to specimens of the first group will be commented on after the results have been described.

The six specimens of the first group will now be described with brief petrographic comments on the rocks in which they occur.

"Iddingsite," G.133 from a picrite basalt: Gough Island:

In thin section the rock is strongly porphyritic with phenocrysts of diopsidic augite and olivine set in a groundmass of pyroxene, plagioclase, ilmenite, magnetite and alkali feldspar. The "iddingsite" occurs as thin shells to the otherwise perfectly fresh olivine phenocrysts. It is a red-brown to orange-brown in color and is only very slightly pleochroic. No new cleavage is developed.

"Iddingsite," V. 3, from a nepheline-bearing basalt: Vogelsberg, Hesse, Germany:

In thin section (see Fig. 5), the rock is micro-porphyritic with abundant microphenocrysts of euhedral to subhedral "iddingsitized" olivine, up to 1 mm. long, and a few highly zoned, titaniferous augites. In the smaller crystals the original olivine has been completely altered to an orange-brown slightly pleochroic "iddingsite," which in plane polarized light appears to be perfectly homogeneous. Between crossed nicols, however, it often shows a patchy extinction and in places has a slightly fibrous appearance. In the larger crystals where there is still some olivine present in the core, the junction between olivine and "iddingsite" is very gradational and consists of numerous, exceedingly minute hair-like fingers of "iddingsite" penetrating into the olivine. This border zone is usually about 0.02 mm. wide. Closely associated with the "iddingsitized" olivine are equidimensional grains of iron ore up to 0.2 mm. across.

The groundmass consists of abundant, euhedral to subhedral crystals of highly zoned titaniferous augite poikilitically enclosed in large clear crystals of plagioclase and nepheline. Iron ore is absent from the groundmass.

"Iddingsite," 57303, from an olivine basalt: Tahiti:

In thin section this rock is very similar to V.3 except that the nepheline is absent and the plagioclase occurs as laths. It is a microporphyritic rock with abundant microphenocrysts of "iddingsitized" olivine, up to 1 mm. across, and euhedral to skeletal iron ore, up to 0.5 mm. across. The "iddingsite" is identical to that described for V.3 except that the junction between the olivine and the "iddingsite" is often perfectly gradational with no sign of the penetrating hair-like growth of the "iddingsite."

The groundmass consists of abundant small euhedral to subhedral crystals of titaniferous augite, and basic plagioclase laths.

"Iddingsite," G. 50 from a trachybasalt: Gough Island:

In thin section, the rock is porphyritic, with phenocrysts of plagioclase, "iddingsite" and titanaugite. The plagioclase is irregularly veined with an isotropic material, which is probably analcite, but the titanaugite is perfectly fresh. The "iddingsite" occurs as pseudomorphs after euhedral to subhedral olivine, although very few remnants of the original olivine are present. It is an orange-brown in color, and under crossed nicols it has a rather patchy and fibrous extinction.

The groundmass consists of plagioclase, pyroxene, "iddingsite" and iron ore.

"Iddingsite," 11537, from an olivine basalt: Dunchideock, nr. Exeter, Devon:

A general petrographic description of this rock has been given by Tidmarsh (1932). The "iddingsite" is a very rich ruby-red to orange-red color and is moderately pleochroic in these colors; maximum absorption occurs when the light vibrates parallel to the micaceous cleavage, which is fairly well developed. Some of the grains are so dark as to be almost opaque, and in some of the crystals there is a central rounded core of almost opaque, amorphous material.

"Iddingsite," FEAE No. 124 from a pyroxene trachyte, Mount Moroto, Uganda:

In thin section the rock is porphyritic with phenocrysts of strongly zoned titanaugite-up to 3 mm. across, and "iddingsite," up to 1 mm. across, and iron ore. The "iddingsite" is a deep orange-red and is moderately pleochroic. In plane polarised light it appears homogeneous, but between crossed nicols it has a patchy extinction. No remnants of the original olivine are present and no micaceous cleavage is developed.

The groundmass consists of titanaugite, iron ore, plagioclase, and interstitial zeolitic material, probably analcite.

The specimens of the second group are described much more briefly in Table 1.

TABLE I. DESCRIPTIONS OF "IDDINGSITES" OF THE SECOND GROUP

Reference No.	Locality	Rock type	Comments on "iddingsite"
X11 A	Gough Island	Gabbroic xenolith in tuff	Dark red brown, weak pleochroism. Occurs in thin films and hair-like rods. (See Fig. 6)
87366	Juan Fernandez Island (Quensel 1952)	Olivine basalt	Reddish-brown to greenish-yellow
303-I-15	Carmelo Bay, Calif., U.S.A.	Carmeloite (olivine basalt)	Medium to dark orange-brown. Moderately pleochroic with new cleavage slightly developed
303-I-17	Carmelo Bay, Calif., U.S.A.	Carmeloite (olivine basalt)	As above but no new cleavage.
X18 C	Gough Island	Gabbroic xenolith in lava flow	Bright ruby-red. Moderately pleochroic but no new cleavage developed
DH 1378	Rungwe, Southern Province, Tanganyika	Olivine basalt	Orange-brown, only very slightly pleochroic

X-RAY METHODS

The optical homogeneity of many "iddingsites" suggests that, even if the material is not to be regarded as a definite compound with relatively fixed chemical constitution, there is some structural control over the alteration process. It appears, therefore, that the identification of the alteration products and the structural character of the "iddingsite" are advantageously studied by single-crystal, rather than powder x -ray methods. Similar methods for the identification of oriented intergrowths have been applied previously to pyroxenes by Bown and Gay (1959).

Oscillation photographs taken about the x - or z -crystallographic directions of the original olivine with $\text{FeK}\alpha$ radiation have been mainly used; the oscillation ranges were usually selected to be symmetrically across diad directions. The single crystals examined were carefully chosen from the most optically homogeneous part of the specimen; as far as possible, it was ensured that no unaltered olivine was present. It was also found necessary to examine a number of crystals from the same specimen for the alteration process in some specimens had proceeded to a different extent in different local areas. For such specimens, the results to be described below may be regarded as representing the average state of alteration of the specimen.

CHARACTERISTICS OF DIFFRACTION PATTERNS

The original olivine from which the "iddingsite" has been derived has an orthorhombic structure (space group $Pbnm$) determined first by Bragg and Brown (1926) and later refined by Belov *et al.* (1951). The dominant feature apparently controlling the structural rearrangements of the alteration process is the hexagonal sequence of approximately close-packed oxygen sheets; these oxygen layers are perpendicular to the x -axis, with one of the close-packed directions parallel to the z -axis of the olivine cell. Whilst it is not our purpose in this paper to discuss the structural rearrangements in detail, it must be emphasised that, just as in the pyroxenes described by Bown and Gay (1959), it is the anion arrangement which controls the structural orientation of the alteration products.

The characteristic x -ray diffraction patterns of various phases which occur in "iddingsites" will now be described.

(a) Olivine-like structures

Often a pattern can be recognized which retains features of the photographs of an unaltered olivine, despite the fact that the specimen shows the strong coloration of an "iddingsite." The patterns vary from those which are barely distinguishable from true olivine patterns, through those where the diffraction maxima have become diffuse, to patterns

with very diffuse spots and obvious discrepancies in the relative intensities of various reflections when compared with the corresponding intensities from an unaltered olivine.

Structurally, these patterns must represent the stages in the breakdown of the original olivine structure with the chemical changes introduced by the alteration. The diffuse character of the reflections could be attributed to a mosaic texture or to a distorted structure; it would seem probable that the atomic replacements taking place give a very distorted atomic arrangement.

(b) *Goethite-like structures*

The occurrence of goethite (α -FeOOH) in "iddingsites" has been reported both by Ming-Shan Sun (1957) and Brown and Stephen (1959). The latter authors have presented a full analysis of the orientation of the goethite with respect to the original olivine. Goethite belongs to the same space group as olivine, and has similar cell dimensions except that the z -axis length is halved; there is a structural equivalence in that the approximately hexagonal close-packed oxygen sheets form the basis of the arrangement. The mutual orientation of goethite and olivine deduced by Brown and Stephen, and confirmed in the present investigation, is that expected if the structural control is exerted by the anion framework. The goethite grows within the olivine so that the close-packed planes are common to both structures, but with three different orientations corresponding to the effectively close-packed z -direction of the goethite being parallel to the three "close-packed" directions of the olivine oxygen sheet. Full details of the complex diffraction patterns produced by this arrangement are given by Brown and Stephen.

Often the diffraction spots due to the goethite are rather diffuse, though the material is quite well oriented; in a few specimens, however, poor orientation of the goethite seems to be linked with sharper diffraction maxima. The relative amounts of goethite in the three possible orientations vary from specimen to specimen, suggesting that the three "close-packed" directions in the olivine sheet are not exactly equivalent; the parallel orientation with the z -axis of olivine and goethite coincident seems to be preferred. The poor quality of the goethite patterns from "iddingsites" makes the comparison with patterns from single crystals of goethite difficult, but it is apparent that the relative intensities are not always correct, and the cell dimensions are slightly variable. This suggests that it would be better to call this phase of the alteration product "goethite-like" for, like the olivine, it may well be defective and distorted, and variable in chemical constitution depending on the state of the alteration process. The size of the equi-dimensional goethite-like particles can be as

small as a few hundred Ångströms when estimated from the breadth of the reflection maxima, but this must be regarded as a lower limit as it takes no account of broadening due to the probable lattice distortion.

(c) *Hematite structures*

Hematite ($\alpha\text{-Fe}_2\text{O}_3$) occurs in some specimens (see Smith, 1959), usually in place of goethite. Although trigonal, it may again be regarded as having an approximately hexagonal close-packed oxygen framework, and its orientation is that expected from its similarity to the olivine structure. It is "twinned" in accordance with the intergrowth symmetry principle (Bown and Gay, 1959) so that its orientation may be described as

$$a_{0l} \parallel c_H, \quad b_{0l} \parallel \pm [01.0]_H, \quad c_{0l} \parallel \pm [21.0]_H$$

In all specimens, the hematite is very well oriented, though the breadth of the reflections is variable from quite diffuse to relatively sharp. Comparison with standard hematite photographs show no obvious relative intensity discrepancies, nor any detectable change in cell size; it seems more probable that this phase may be identified with $\alpha\text{-Fe}_2\text{O}_3$ with little impurity. The origin of the hematite cannot be regarded as being established. It is possible that it is formed by dehydration of a goethite-like phase formed during the alteration; indeed heating experiments have been carried out in which this transformation occurred. However other experiments (to be described elsewhere) have shown that hematite can be exsolved directly from olivine under suitable oxidizing conditions. Whatever its origin, its occurrence, as with the other structures so far described, points to the high stability of the anion framework through while the cations can be made to migrate. It is important to realize that the strength of the silicon-oxygen bond is not so great as to prevent a structural reorganization in which the Si-O tetrahedra do not remain as discrete structural units.

(d) *Spinel structures*

Multiple oxide structures of this type are cubic, with the oxygen atoms in approximately cubic close packing. The orientation of such phases with respect to the original olivine is controlled by a correspondence of the close-packed sheets, with a "twinned" orientation required by the intergrowth symmetry principle; it is

$$a_{0l} \parallel (111)_{sp}, \quad b_{0l} \parallel \pm (\bar{1}\bar{1}2)_{sp}, \quad c_{0l} \parallel \pm (1\bar{1}0)_{sp}$$

These phases are rarely present in "iddingsites," but when they are, their diffraction spots are sharp, but with an appreciable range of disorientation. It is difficult from x-ray data alone to distinguish the different mixed oxides of the spinel group, but it seems likely that the phase present in

"iddingsites" is probably magnetite (Fe_3O_4) or a magnesioferrite (MgFe_2O_4); the cell dimensions and intensity relationships are roughly in agreement with these compositions. It seems probable that these phases are directly exsolved by the olivine (possibly before the alteration has begun) when it is heated in an oxidizing atmosphere. Experiments to be described elsewhere have shown that a spinel phase can be developed within an olivine crystal in this way, though spinel phases in other orientations and entirely different products can also be obtained if the oxidizing conditions are too severe.

(e) *Silicate structures*

These structures are represented on the diffraction pattern in a manner more variable than any other phase identified in the "iddingsites."

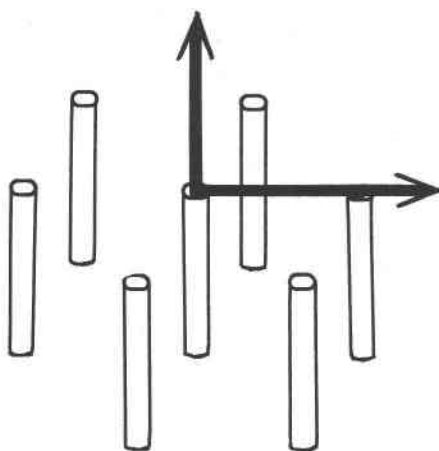


FIG. 1. Schematic representation of reciprocal space relationship between the hexagonal array of cylinders due to the silicate phase and the axes of the original olivine. (x -axis vertical, z -axis horizontal)

Brown and Stephen (1959) have described some of the characteristics of the pattern and have suggested that in their specimen a layer lattice silicate is present, probably belonging to the vermiculite or smectite group.

The diffraction effects may be considered in two parts. First, there occurs a hexagonal pattern of cylinders in reciprocal space (Fig. 1). The length of the cylinders is parallel to the x -axis of the original olivine; the side of the hexagonal "cell" marked out by these cylinders in reciprocal space is parallel to the z -axis of the original olivine. The "cell" side of the hexagonal array is slightly variable around a value of about 5.3 \AA . Along

the length of the cylinders, the intensity distribution, which is usually continuous, fades away sharply at about $\zeta=0.5$ for $\text{FeK}\alpha$ radiation. Radially the intensity falls away fairly quickly, so that rods with low ξ values are the only ones which are seen, unless fairly heavy exposures are made. The diameters of the rods in reciprocal space are variable from specimen to specimen, some even being relatively sharp. Others with relatively large diameter have a marked asymmetric intensity distribution, with a sharp cut-off on the low angle side. Diffraction effects of this general character seem to be present on most specimens containing a silicate phase; associated with them, however are low angle effects, which again show a marked degree of variability. Broadly these low angle effects fall into two categories. For the majority of specimens, there is a strong broad streak extending continuously from 70–80 Å down to about 10 Å, where it appears to tail off; the streak probably extends to even higher spacings than have been experimentally detected, for it shows no sign of diminished intensity at the limit of the present experimental observation. The streak extends in the x -direction of the olivine, and is thus parallel to the hexagonal array of cylinders. However for a few specimens, although the continuous streak still remains it appears to be considerably diminished in intensity, and fades away in the region 20–30 Å; intensity maxima, at times not very well defined, are then found at spacings of about 14–15 Å, with higher orders of this reflection also present.

The specimen described by Brown and Stephen (1959) gives a pattern showing both the hexagonal cylinders and sharp basal spacings. These authors suggest that the diffraction effects are due to the formation of a sheet silicate structure with a highly disordered stacking of the layers; the collapse of the basal spacing to ~ 10 Å by heating at 500° C. for one hour indicates that the sheet silicate may belong to the vermiculite or smectite groups. However, the variability of the diffraction patterns of this phase, identified in the present study, in which very few “iddingsites” seem to have developed a basal spacing, and the chemical evidence to be given in a later section suggest that it is highly speculative to attempt to identify this phase with any recognized sheet silicate group. The diffraction patterns showing only the continuous low angle streak could be interpreted as being due to effectively two-dimensional crystals of the silicate phase; rough calculations form the extent of the cylinders and streaks in reciprocal space show that, if the particles of this phase are perfect, they are 50–100 Å in diameter, and about 5 Å thick. At the early stages of development, they represent an embryonic silicate structure, which has not achieved any three dimensional regularity; they are probably very variable in constitution. At this stage, too, the possibility must be considered that the embryonic silicate should not be regarded as a sheet silicate

structure at all, but rather as a random local linkages of chain and band structures (the development of oriented pyroxene structures from heat treated olivines will be described in another publication). The close packed oxygen framework of the olivine does not require severe atomic rearrangement to form the oxygen arrangement of chain, band or sheet silicate, whilst the Si atoms appear to have considerable freedom of migration during the alteration process, so that local concentration of Si atoms may form embryonic linked tetrahedra structures which do not conform to the ordered arrangements recognized in silicate minerals.

The occurrence of basal spacings of 14–15 Å for some specimens containing a silicate phase indicates that some three dimensional regularity of the silicate structure can be achieved. However, it is not certain whether this can be obtained under the conditions of alteration which lead to the disordered structures of the majority of specimens. Apart from its rarity of occurrence in specimens which can be said to be "iddingsitized" olivine, the silicate pattern with sharp basal spacings seems to be characteristic of material described by other workers as bowlingite, another alteration product of olivine. It is possible that the processes which alter olivine to "iddingsite" or bowlingite cannot be sharply distinguished, and that the specimens which show basal spacings should be described as being partly "bowlingitized." The silicate phase occurring in the pseudomorphs after olivine in Markle basalt (Smith, 1959) has a basal spacing of 14.5 Å and is considered by the author to be a true chlorite of the pennine series. These pseudomorphs are unusual in that they are reported to contain quartz, which is not detected at all in the present investigation. It seems unlikely that they could have formed solely by the process of "iddingsitization" defined by the present investigation; for the Markle pseudomorphs the effects of weathering may be important.

EXPERIMENTAL RESULTS AND CLASSIFICATION OF SPECIMENS

The results of the x-ray examination are summarised in Table 2; for each specimen, the phases identified are shown together with a brief comment on the diffraction patterns. While the patterns (Figs. 2 and 3) cannot be divided into rigid categories, these data, together with the optical and chemical data on the specimens of the first group, allow some inferences as to the structural changes taking place during the alteration process.

To trace out these changes, we shall confine discussion for the moment, to the first group of selected typical "iddingsites." In the first stages of alteration, the anion framework of the original olivine remains unchanged; initially the diffusion through this framework of the cations

TABLE 2. RESULTS OF X-RAY EXAMINATION

Specimen No.	Phases Present	Comments
G.133	O _S +G _D	Relative intensities of "olivine" effectively normal; very little "goethite."
V.3	O _D	Relative intensities of "olivine" effectively normal.
57303	O _D	Relative intensities of "olivine" effectively normal.
G.50	O _D +G _D +H _D	Very little "olivine" and hematite; marked discrepancies of relative intensities of "olivine" from normal.
11537	G _D +S _L +H _D	There are also sharp powder rings of "goethite."
FEAE 124	G _D +S _L +H _D	Only a trace of hematite.
X11 A	O _S +S _L +H _D +Sp _S	Specimen may contain unaltered olivine. Very little "silicate," with low angle streak barely visible. There are also powder rings of spinel phase.
87366	O _{S-D} +C _D	"Olivine" sharp in some specimens, diffuse in others; when diffuse, relative intensities incorrect, and small amounts "goethite" present.
303-I-15	G _S +S _L	"Goethite" poorly oriented and sharp.
303-I-17	G _D +S _L	
X18C	O _{S-D} +S _L +H _D	"Olivine" showing both sharp and diffuse spots within same single crystal specimen
DH 1378	O _D +S _B	"Olivine" has relative intensity discrepancies; "silicate" has basal basing of 14.1 Å.

Key to Table:

- O indicates olivine-like phase
- G indicates goethite-like phase
- S indicates silicate phase
- H indicates hematite phase
- Sp indicates spinel phase.

The subscripts S and D give some indication of whether the diffraction spots are sharp or diffuse; the subscripts L and B after the symbol S, indicate continuous low angle streak and basal spacing respectively.

only slightly changes the structure (G.133), though as the chemical reconstitution becomes more drastic, the structure becomes more and more distorted, and less and less like true olivine (V.3 and 57303). The presence of increasing numbers of hydroxyl ions (see next section) allows the formation locally in areas effectively denuded of silicon of increasing amounts of a goethite-like structure (G. 50); this phase may appear as hematite if at any time during or after the alteration process the goethite-like structure is dehydrated. At this stage it would not appear that there is any order in the arrangement of the silicon atoms remaining within the "iddingsite." As the goethite or hematite regions increase, local silicon concentrations increase to the point where they begin to organize into a

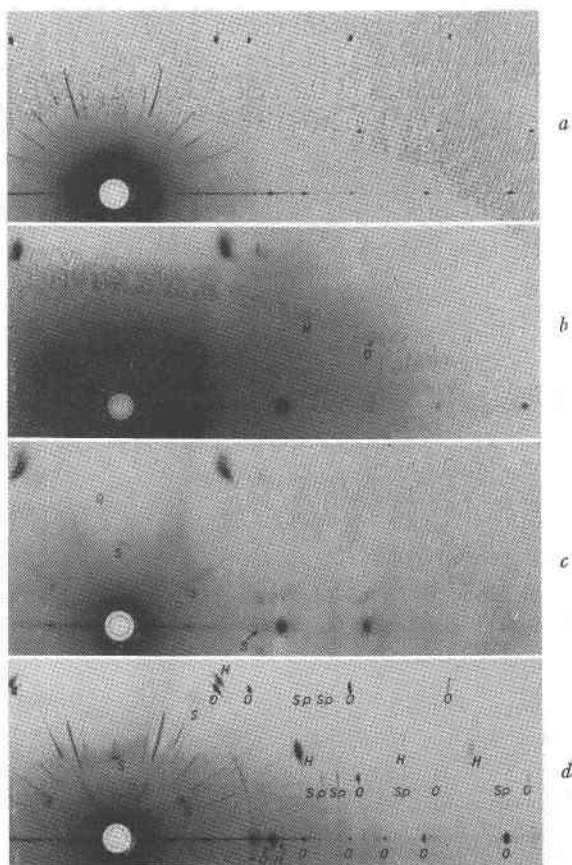


FIG. 2. X-ray diffraction photographs of "iddingsites." All the photographs are taken on a camera of 3 cm. radius with $\text{FeK}\alpha$ radiation. The oscillation axis is in all cases the z -axis of the original olivine, the 15° oscillation range is symmetrically across the x -axis of the original olivine. Only a part of the photographs is shown (magnification $\times \frac{3}{4}$).

- (a) An unaltered olivine for comparison. Skaergaard Intrusion, East Greenland. EG 4265.
- (b) Specimen G.50, Gough Island. Some of the spots of the remaining olivine-like structure is labelled O, a weak hematite spot H. The formation of the "goethite-like" structure is shown by the diffuse regions almost coincident with "olivine" spots.
- (c) Specimen FEAE 124, Mount Moroto, Uganda. All spots other than those marked are due to "goethite" structure in three orientations. Spots marked S are due to silicate phase. In this specimen, diffraction spots due to hematite are barely visible.
- (d) Specimen X11A, Gough Island. Diffraction spots are marked as O, olivine-like, S, silicate, H, hematite, Sp, spinel. All rings belong to misoriented spinel structure, except for short spotty arcs which are due to misoriented olivine fragments.

kind of local order, with consequent rearrangement of the anion framework, this marks the appearance of the silicate phase (11537 and FEAE 124). So far as the specimens of the first group are concerned, this appears to denote the end of the alteration process. We cannot be certain whether specimens in which the silicate structure has gained some kind of three-dimensional regularity (as exemplified by the formation of a definite basal spacing) represent a further development of this particular alteration process or whether they have been formed by some different

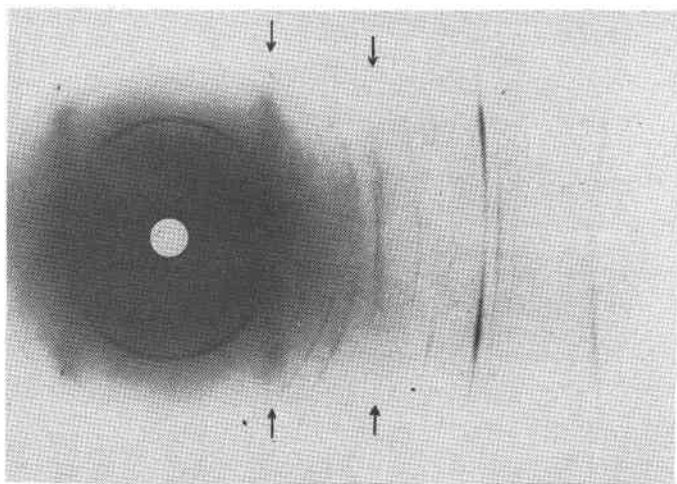


FIG. 3. Specimen 303-I-15, Carmelo Bay, Calif., Oscillation photograph, 3 cm. camera, FeK α ; oscillation axis, x -axis of original olivine, the 15° oscillation range is symmetrically across the z -axis of the original olivine. The sharp, poorly oriented preferred orientation pattern is due to "goethite." Note particularly the continuous blackened regions (arrowed) due to the silicate phase.

but related alteration; the limited chemical evidence given later can be interpreted as showing that specimens like 11537 and FEAE 124 will change little more.

Commenting briefly on the second group, it seems probable that in specimen X11A small regions of olivine have been "iddingsitized," leaving other regions of unaltered olivine. Reheating has then caused the dehydration of the "goethite" to hematite in the "iddingsitized" regions with the simultaneous precipitation of the spinel phase from the unaltered olivine regions. No. 87366 shows the early stages of alteration (like G.133 and V.3) which has been local, to give different degrees of alteration in different parts of the specimen. 303-I-15 and 303-I-17 are probably products of the same changes as the specimens of the first

group though other alteration products are also present in thin section; for 303-I-15, the structural control of the orientation of the products has been disturbed. X18C represents another example of local alteration, together with reheating of the specimen as evidenced by the hematite phase. DH 1378, in addition to the basal spacing, does not show either the "goethite" or hematite usually observed at the stage in alteration when a "silicate" phase is present, and must be regarded as anomalous.

The results can be summarized in the following manner. The structural changes involved suggest that the alteration process proceeds continuously through the various stages which are marked by the occurrence of poorly crystalline but characteristic phases. Individual specimens of "iddingsite" may differ from one another by being at different points of the structural change, though there may also be minor variations caused by different geological histories. We shall now examine chemical and optical data to see if they can be reconciled with a classification of this kind.

THE CHEMICAL COMPOSITION OF SOME OF THE "IDDINGSITES"

Two of the specimens of the first group, V.3 and G.50 were analyzed, and the analysis of a third, FEAE 124, was kindly supplied by K. Hytönen. These analyses are given in Table 3, together with the ideal composition of an olivine (Fa_{20}) approximating to the chemical composition before alteration. Qualitatively the changes involve a decrease in SiO_2 , FeO and MgO with an increase in Al_2O_3 , Fe_2O_3 and H_2O as the alteration process proceeds. It is interesting also, as first pointed out by Lawson (1893), that small quantities of CaO , Na_2O and K_2O enter the "iddingsite."

In Fig. 4 the proportions of the major constituents of the olivine and the three "iddingsites" have been plotted against their β refractive indices. It is seen that MgO , Fe_2O_3 and Al_2O_3 all show a reasonably smooth variation, whilst SiO_2 and Al_2O_3 vary rather more irregularly. If it is assumed that the chemical process is essentially one of addition of Fe_2O_3 and removal of MgO from the original olivine, the end product of the "iddingsitization" process would have a composition corresponding to the removal of all the MgO . On this assumption it is possible to derive an approximate composition for the hypothetical end product of $\text{SiO}_2 = 16\%$, $\text{Al}_2\text{O}_3 = 8\%$, $\text{Fe}_2\text{O}_3 = 62\%$ and $\text{H}_2\text{O} = 14\%$, with a corresponding β refractive index of just over 1.9. The x -ray data suggests that this bulk composition must be interpreted in terms of goethite-like and silicate structures. If the bulk composition is rewritten in terms of atoms it is

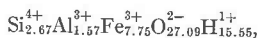


TABLE 3. CHEMICAL ANALYSES OF "IDDINGSITES"

	1	2	3	4
SiO ₂	39.3	37.9	25.59	17.52
TiO ₂	—	0.7	0.61	0.42
Al ₂ O ₃	—	5.6	6.53	8.00
Fe ₂ O ₃	—	20.7	31.44	55.09
FeO	18.9	3.3	4.64	0.00
MnO	—	n.d.	n.d.	0.45
MgO	41.8	24.0	15.83	2.73
CaO	—	3.6	1.30	1.29
Na ₂ O	—	n.d.	0.31	0.18
K ₂ O	—	n.d.	0.28	0.31
H ₂ O ⁺	—	4.2	9.09	13.74
H ₂ O ⁻	—		3.74	
Total	100.0	100.0	99.36	99.73
R.I. (β)	1.694	1.766	1.816	1.885

1. Ideal composition of olivine (Fa₂₀).
2. Specimen V.3. Nepheline bearing olivine basalt, Vogelsberg, Germany. Analyst R. W. LeMaitre. (The "iddingsite" was taken into solution with HCl from a mixture containing pyroxene. The H₂O was determined on the mixture assuming zero water content of the pyroxene.)
3. Specimen G.50. Trachybasalt, Gough Island. Analyst: R. W. LeMaitre.
4. Specimen FEAE 124. Pyroxene trachyte, Mt. Moroto, Uganda. (Hytönen, 1959). Analyst: P. Ojanperä.

it is clear that the hydrogen content is very high. The ratio of the number of hydrogen ions to the number of oxygen ions present in the silicate can be fixed between two limits. If all the Fe³⁺ ions are associated with the goethite-like phase, an upper limit of 0.67 for this ratio is derived for the

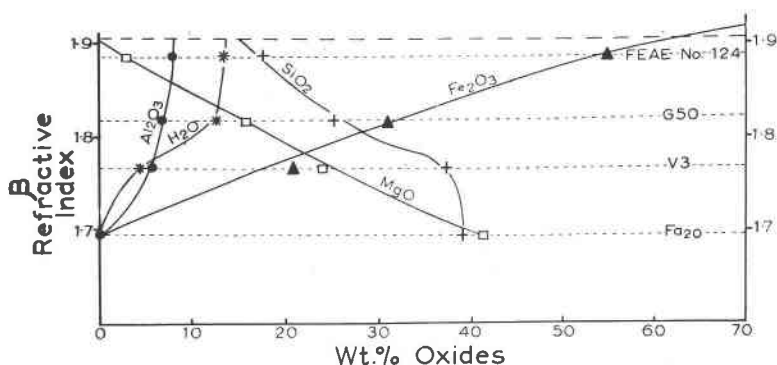


FIG. 4. The relation between the major chemical constituents of an olivine (Fa₂₀) and the three analyzed "iddingsites" and the value of the β refractive index.

silicate phase; on the other hand, if the equally unlikely assumption is made that no goethite-like phase is present, the lower limit of the H^+/O^{2-} ratio for the silicate phase is about 0.57. Now for most recognized sheet silicate minerals this ratio is usually well below 0.5; only for partially hydrated halloysite does it have the high values of the highly altered "iddingsites." While it is undoubtedly possible to express this bulk composition in terms of a recognized mineral assemblage such as goethite and a hydrated halloysite, the authors must stress that this does not mean that recognizable or even identifiable areas of a hydrated halloysite exist within the "iddingsite." All the data suggest that the silicate structure is very irregular and disordered and should not be equated, at this stage of alteration at least, with any recognized mineral species. Whether the development of a basal spacing leads to a more regular and recognizable silicate structure merits further investigation if the data of Brown and Stephen (1959) on the properties of the phase are to be resolved.

OPTICAL PROPERTIES

Some of the characteristic optical properties of the first group of typical "iddingsites," is given in Table 4. The most notable feature is the increase in the β refractive index as the alteration proceeds; this is also ac-

TABLE 4. OPTICAL PROPERTIES OF "IDDINGSITES" OF THE FIRST GROUP

Specimen No.	Depth of alteration (mm.)	Color	Pleochroism	Cleavage	Amount of alteration	Dispersion	Other alterations	R.I. (β)
G.133	0.2	Red-brown to orange-brown	Slight	None	Partial	—	None	1.76 ± 0.01
V.3	0.2	Orange-brown	Slight	None	Partial	—	None	1.766 ± 0.003
57303	0.3	Orange-brown	Slight	None	Partial	—	None	1.762 ± 0.005
G.50	0.5	Red-brown to orange brown	Slight	None	Complete	—	Feldspar analcitized	1.816 ± 0.003
11537	0.4	Deep ruby-red to orange-red	Moderate, maximum absorption parallel to cleavage	Micaceous	Complete	Strong	Calcite and chlorite present	1.86 ± 0.01
FEAE 124	0.5	Orange-red	Moderate	None	Complete	Very strong $r > v$	Amygdales and slight alteration of feldspar	1.885 ± 0.005

accompanied by an increase in the total birefringence and dispersion. The color in plane polarized light is almost the same at all stages, though there is a tendency for it to be darker in the later stages of alteration, where the pleochroism, though never marked, is stronger. Where "iddingsite" and olivine are present in the same crystal it is always found that their optic orientations are identical.

The development of the micaceous cleavage, characteristic of the material from Carmelo Bay described by Lawson (1893), does not appear to be diagnostic of the late stages of alteration. It is interesting to note that when the micaceous cleavage is developed (as in the material of Brown and Stephen (1959) and some specimens of Ross and Shannon (1925)), the refractive indices are considerably lower than would be expected; it appears that this lowering of refractive indices is to be correlated with the development of a basal spacing in the silicate. Since these "iddingsites" are often accompanied by other ill-defined alteration products of olivine, it is difficult to be certain if such effects are to be regarded as part of the process of "iddingsitization."

THE ALTERATION PROCESS

From the evidence presented, it seems clear that the mechanism for the alteration of olivine to "iddingsite" is one of ionic diffusion. As with the hydration of dicalcium silicate (personal communication, Dr. J. D. C. McConnell), under suitable conditions of temperature, pressure and chemical environment, highly mobile hydrogen ions can diffuse into the olivine structure. By temporary attachment to the oxygen ions, they are capable of releasing magnesium, ferrous and silicon ions from their sites in the olivine structure, and allowing their replacement by ferric, aluminium and calcium, etc., ions, provided that suitable concentration gradients exist across the boundary.

The structural changes involved are only slight. For some of the phases recognized, only cation changes are needed; for the others, only slight rearrangement of the essential oxygen framework is necessary. The continuity of the oxygen framework throughout the "iddingsite" and the short range order of the cations could undoubtedly account for the optical homogeneity of most of the "iddingsites" (see Brown and Stephen, (1959)). It must be emphasized again that this alteration process represents another example of the ability of silicon ions to diffuse fairly readily from their tetrahedral sites in the oxygen framework, and shows that in consideration of transformations in silicate structure, the SiO_4 tetrahedra cannot always be regarded as rigid units of structure (cf. Taylor (1957)).

The conditions under which the alteration takes place are still a matter for some speculation, except for the pressure, which can be assumed to be relatively low (see however Sun (1957)), as "iddingsite" is confined to volcanic and hypabyssal rocks. So far as the temperature of formation is concerned, considerable evidence has been accumulated which suggests that the alteration took place in the deuteric stage, before consolidation of the magma (Edwards (1938), Ross and Shannon (1925)). Rims of fresh olivine mantling "iddingsite," which have been observed by Edwards, can also be seen in some of the basaltic rocks from Gough Island and imply that the "iddingsite" formed before the olivine finished crystallizing. However it seems unlikely that a crystal with small domains of "goethite" and "silicate" structures, having a relatively high free energy, would be stable at high temperatures; it would tend to reorganize itself into a more ordered structure. It can only be concluded that "iddingsite" is formed at intermediate temperatures, below those necessary for structural reorganization, and above those at which the rock has completely solidified. The chemical environment is undoubtedly one of strong oxidizing conditions, with most of the iron in the ferric state, Fe^{3+} , but the suggestion by Edwards (1938) that the magma must differentiate to give an iron-rich liquid cannot be completely valid, for "iddingsite" occurs in many non-iron enriched basaltic rocks. The formation of "iddingsite" with a high Fe^{3+} content requires only the oxidizing conditions and does not necessarily imply the presence of an iron-rich liquid.

During the present investigation attempts to synthesize "iddingsite" from olivine in iron-rich, aqueous and acid solutions, at temperatures up to 600°C . and pressure up to 1000 atmospheres, were unsuccessful. When alteration rims were produced, x-ray examination showed they were of the serpentine type.

In conclusion, it must be made clear that "iddingsite" is not a mineral with a definite structure and chemical composition as implied by Ross and Shannon (1925); neither can it be regarded, as other workers have done, as a simple sub-microscopic intergrowth of two or more well characterized minerals. "Iddingsitization" is a continuous transformation in the solid state, during which the original olivine crystal may pass through various stages of structural and chemical change; it may be possible at any stage to recognize embryonic structural arrangements, some of which approximate to normal ordered mineral structures, but the altered olivine is at all times a disordered, irregular arrangement which cannot be described as a simple sub-microscopic mineral intergrowth. In view of these difficulties it is proposed that the term used for any member of the alteration series should be written "iddingsite."

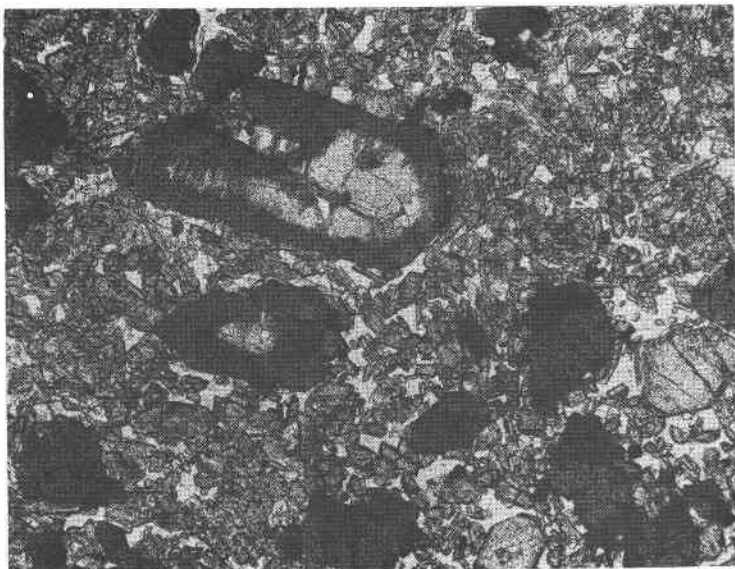


FIG. 5. Photomicrograph of a typical "iddingsite" in a basic lava. Specimen V.3, Vogelsberg, Hesse, Germany. Ordinary light, magnification $\times 65$.

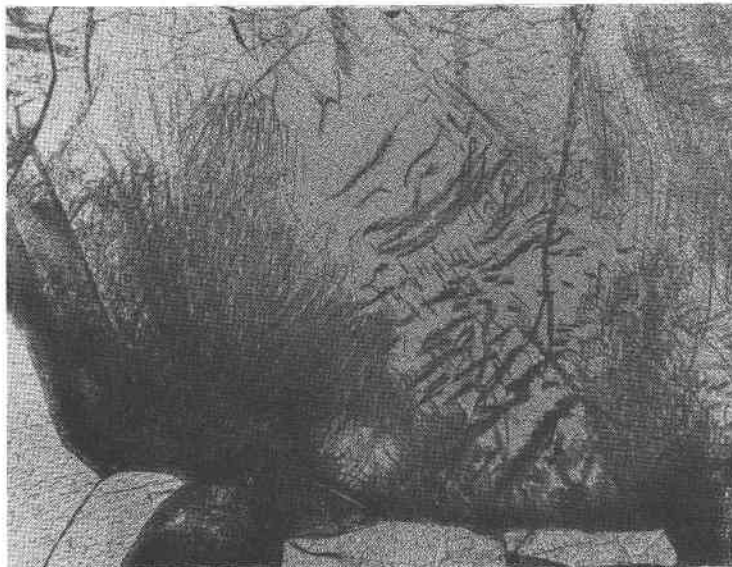


FIG. 6. Photomicrograph of an olivine exsolving iron ores. Specimen X11A, Gough Island. Note the difference in appearance between this and the "iddingsite" shown in Fig. 5. Ordinary light, magnification $\times 65$.

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