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The Alteration of Olivine in Basaltic and Associated Lavas

Part II: Intermediate and Low Temperature Alteration

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Abstract. Olivines which cool under oxidizing conditions exsolve iron oxides at high temperature, and at low temperatures break down to essentially chloritic materials. Olivines which cool under non-oxidizing conditions alter at intermediate temperatures to complex assemblages of chlorite and interstratified phyllosilicates containing a smectite. Alteration under oxidizing conditions at low temperature, probably below 140°C, produces "iddingsite", an orientated assemblage of goethite and interstratified phyllosilicates also containing a smectite.

Post-deuteric[1] alteration extends or initiates the breakdown of olivine to phyllosilicate mixtures often resulting in widespread movement of materials through the flow. Post-deuteric alteration of "iddingsite" produces strongly pleochroic, highly ordered varieties which eventually break down to green phyllosilicate assemblages.

Weathering of olivine may produce orientated assemblages similar to deuteric forms of "iddingsite". Weathering of green alteration products results in oxidation and the liberation of discrete iron hydroxides.

Alteration in all cases requires exchange of material between interstitial components and olivine. During deuteric alteration, plagioclase and pyroxene are usually unaffected.

Introduction

A survey of the literature demonstrates the conflicting views held by many geologists and mineralogists concerning the time and temperature of formation, and the composition, of the numerous alteration products after olivine in lavas. The aims of this study are to attempt to establish criteria for the recognition of the various processes which have resulted in the alteration of olivine in lava flows.

Over 500 thin sections of basaltic and associated lavas were studied. Principally the rocks were from Iceland and St. Helena, but collections of lavas from Fuertaventura, Tenerife, Morocco and the British Isles, and olivine-bearing xenoliths from Lanzarote, the Auvergne and Faial (Azores) were also examined. Many of the specimens studied in transmitted light were also examined in polished section.

X-ray diffractometer traces were made from a number of alteration products, but most data were obtained from X-ray powder photographs using an 11 cm Phillips X-ray camera.

Optical Mineralogy

a) "Iddingsite"

Many alteration products after olivine have been called "iddingsite", although the term should be restricted to orientated products in various shades of brown.

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[1] The term 'deuteric' is used throughout, in the sense of SEDERHOLM (1929), who defined deuteric alterations as: "those that have taken place in direct continuation of the consolidation of the magma of the rock itself."

The degree of alteration of the olivine ranges from traces of brown fibres at the rim to complete pseudomorphs of fibrous, strongly cleaved, or optically homogeneous material, the "iddingsite" and relic olivine exhibiting pronounced optical continuity throughout.

From a study mainly of the volcanic rocks of St. Helena, "iddingsites" could be broadly classified into four types:

I. partial or complete alteration without rims of fresh olivine,
II. complete or partial alteration of olivine surrounded by a rim of fresh olivine,
III. development in the weathering rinds of basalts,
IV. highly pleochroic varieties.

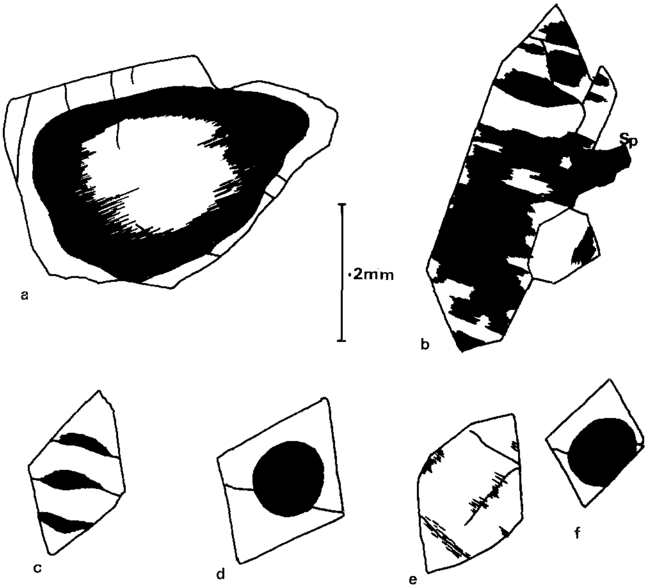

Fig. 1. Various forms of "iddingsites" of type II, developed within olivine phenocrysts or microphenocrysts in basaltic flows. Annulus variety 'a' is from Iceland, the remainder are from St. Helena. In 1b, *Sp* included spinel grain

"Iddingsites" of type I are usually orange or red-brown, with a more or less pronounced fibrous structure. Pleochroism is either absent or very weak and birefringence ranges from 0.025 to 0.034. Apparently homogeneous "iddingsites" may show a fibrous structure and up to three irregular zones of varying birefringence under crossed Nicols. In many pseudomorphs extinction is progressive from centre to rim through a rotation of 90°. There is no regular correlation between colour and optical properties, 2V varies from zero to 90°, and the optic sign may be negative or positive. Lighter coloured, golden or yellow-green, "iddingsites" are found in the more vesicular flows.

"Iddingsites" included within rims of fresh olivine (type II) have been extensively described (see especially SHEPPARD, 1962), and are common in lavas from most of the areas examined. Inside the fresh rim the olivine may be wholly or partially affected to give complete cores or partial annuli of "iddingsite" (Fig. 1). Complete cores often appear optically homogeneous, and flare and fibrous varieties may be slightly more pleochroic than "iddingsites" of type I. These "iddingsites" are optically negative or positive, with 2V close to 90° or almost zero [cf. Sheppard (1962): 2V from 20° to 74°, all optically negative].

Certain features appear to be common in flows showing alteration of this type:

a) Totally "iddingsitized" olivines may be contained in sieve-pyroxenes, altered phenocrysts may be rimmed with fresh olivine, and groundmass olivines may be unaffected.

b) The rim olivine may be more fayalitic than the core olivine, and may be closer in composition to the groundmass olivines.

c) In strongly embayed, unzoned, olivines, "iddingsite" of the annulus type closely parallels highly irregular crystal boundaries.

d) The outline of the rim olivine is usually more euhedral than that of the "iddingsite".

e) The core "iddingsite" has contact with the outside of the crystal directly, or via cracks.

f) The fresh olivine rim may show alteration to "iddingsite" as a result of weathering.

"Iddingsites" of type III are those pseudomorphs occurring in, and adjacent to, the weathering rinds of otherwise fresh basalts. The fresh olivine is replaced in the same systematic fashion as described for type I, the orientated fibrous nature being well developed throughout the whole process.

Pleochroic, 'cleaved' varieties of "iddingsite" (type IV), were very rare in the Tertiary and Recent volcanic areas studied. The relationship of the material to the original olivines is identical to that described for other varieties of "iddingsite" (annulus varieties of type II are common), and the open parting, parallel to the c-axis of the host olivine is visible at all stages of the alteration process. Although the "iddingsite"-olivine contact is often irregular the bulk of the "iddingsite" lacks the fibrous appearance common to other varieties. It is biaxial with a very low 2V, and is optically negative with a birefringence of 0.028 to 0.036. Extinction is parallel to the parting which coincides with the slow direction of the pseudomorph. Colour is evenly distributed throughout, and there is no sign of zoning, even under crossed Nicols. Sections cut at right angles to the parting, exhibit strong pleochroism in a variety of schemes:

golden — yellow-brown — brown-green
golden-orange — dark green-brown — very dark green-brown
bright orange — red-orange — very dark reddish green.

In all rocks examined containing these highly pleochroic "iddingsites" the groundmass was invariably highly altered, and in many cases the non-"iddingsitized" olivine was partially or wholly altered to green materials.

b) Green and Associated Alteration Products

Olivine phenocrysts from lavas are usually traversed by a number of irregular cracks, often arranged more or less perpendicular to the c-axis. Alteration, resulting in the formation of green materials, which are completly disordered in relation to the original olivine, commences in these cracks. Initially a fine sawtooth pattern forms along the cracks (Fig. 2a), and later, jagged "teeth", projecting into fresh olivine are developed (Fig. 2b). At this stage the rim of the olivine is almost invariably altered, and increasing alteration causes the migration of the toothed surface through the olivine (Fig. 2c) until the whole crystal is pseudomorphed. Isolated olivine relics within pseudomorphs retain completely the optical continuity of the original crystal throughout this process. [Alteration in olivines with good (010) or (100) cleavage commences along transverse cracks, not along the cleavages.]

The initial alteration product developed is a murky, medium to dark green chlorite, with birefringence usually 0.006 or less. The chlorite is biaxial with a low 2V and is usually optically negative.

The stage at which large "teeth" are developed is characterized by material to be referred to as "montmorillonite" (within inverted commas as its true structural nature is not optically discernible). It is more or less strongly pleochroic in shades of green or green to colourless, with a high birefringence (0.026 to 0.031), very low 2V, negative optic sign and straight extinction. An open parting is developed parallel to the slow direction, which is also the direction of maximum absorption (Figs. 3a and 3b). The refractive indices lie either side of that of Canada Balsam.

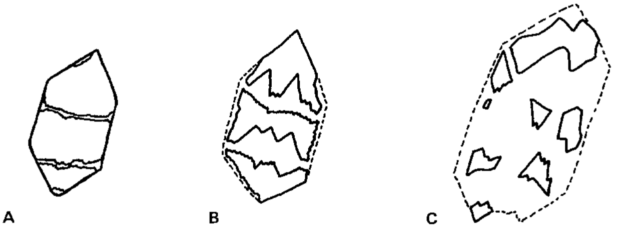

Fig. 2. Successive stages in the alteration of olivine to green phyllosilicate assemblages: migration of "teeth" in b results in isolated, orientated relics of olivine in a non-orientated pseudomorph, c, before complete breakdown of the olivine

Green materials with properties intermediate between those of chlorite and the "montmorillonite" may also be developed in the olivines (Figs. 3a and 3c). Birefringence, colour, and refractive indices of these materials show complete gradations from those of chlorite to those of "montmorillonite". In a given thin section however, the intermediate materials occur as one or two distinct forms. All are optically negative with low 2V, and varieties with a birefringence of more than .018 may exhibit an open parting.

In certain sections the "montmorillonite" is pleochroic in schemes of medium green to pale yellow-neutral, olive-green to golden, and dark olive-green to golden-pink or pale orange. The birefringence of these varieties is 0.034 or 0.036 and there is a slight increase in refractive indices. The optical properties of these varieties closely resemble forms of the pleochroic "iddingsites" described above.

The groundmass of the flows may also be replaced by green or yellow-green alteration products, with similar materials occurring in small vesicles in compact parts of the flows. Blue-green material occurs rarely in isolated interstitial patches and possibly consists largely of celadonite. Except in completely weathered or strongly hydrothermally altered rocks, the pyroxenes and feldspars are usually fresh, and in many cases late crystallizing, interstitial biotite is unaffected by alteration processes affecting olivines and groundmass material. The alteration products in

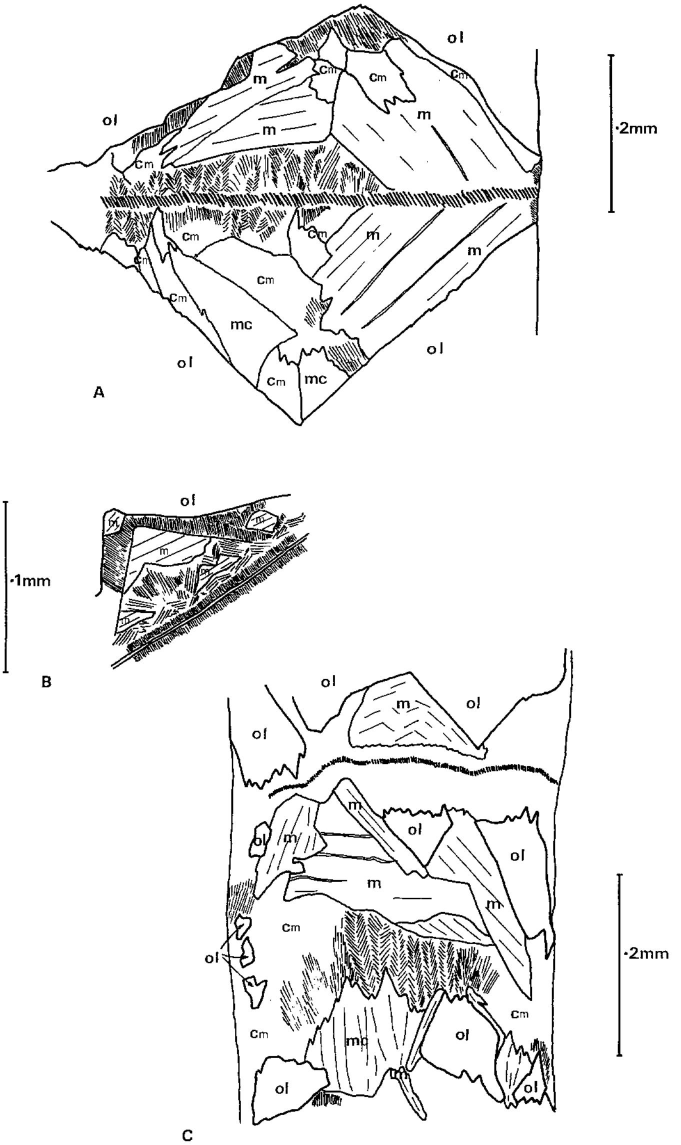

Fig. 3. Alteration of olivine phenocrysts to green phyllosilicates showing typical development of "teeth" protruding into the olivine host. (Olivine, *ol*; chlorite, unlabelled and fibrous areas; "montmorillonite", *m*; intermediate materials, *cm* (if optically closer to chlorite) and *mc* (if optically closer to "montmorillonite")

interstitial areas are identified principally as chlorites. "Montmorillonite" is very rare, occurring as a pleochroic intermediate form with a birefringence of 0.025 to 0.026, and is the latest phase developed.

Groundmass chlorites are often slightly paler in colour than those occurring within the olivines, the birefringence, rarely exceeds 0.014 and is commonly between 0.006 and zero; interference colours may be weakly anomalous. Pleochroism is usually weak, the intensity increasing slightly with increasing birefringence. The fibres are length slow, and refractive indices lie in the range 1.55—1.60.

The chlorites of interstitial areas, and small vesicles frequently exhibit a fibrous concentric structure. In several cases an isotropic band occurs within the patch, with birefringence increasing away from it, towards the rim and the centre of the area. This isotropic zone frequently coincides with the rim of the patch, and towards the centre there are gradual increases in birefringence, refractive indices and pleochroism. Between the rim and the isotropic zone the chlorite may be optically positive with low 2V. Between the isotropic zone and centre of the patch the optic sign is negative and 2V either very low or zero. These variations are consistent with increases in total iron in relation to magnesium, and in silicon with respect to aluminium in the chlorites (HEY, 1954).

In more highly altered lavas interstitial patches show textures similar to those described by FAWCETT (1965, p. 62), with an outer rim of chlorite fibres everywhere perpendicular to the abutting crystals, and a central mass of chlorite spherulites, often of paler colour.

The spherulitic fibres, may show a weak pleochroism and slightly higher birefringence. In rocks showing this type of alteration feldspars were observed with green chloritic material developed along some of the cleavage traces.

All of the green alteration products turn green-brown, yellow, or brown on weathering, and the birefringence usually increases. This colour change on weathering may be accompanied by irregular limonitic staining of the rock in general, as a result of release of iron from the phyllosilicates in the form of discrete hydroxides.

Often olivines are almost completely pseudomorphed by calcite with relic green minerals occurring at the crystal rim. Vesicles may show concentric bands of green minerals at the rim and a central infilling of carbonate. Several basaltic dykes from Saint Helena consist of fresh plagioclase laths and poikilitic titanaugite in a mesostasis largely of secondary calcite. These occurrences of carbonate can be explained by intense post-deuteric alteration of the olivine and groundmass, the products being taken partially or completely into solution and removed, the carbonate then being precipitated from solution. None of the rocks examined containing calcite, irrespective of degree of alteration, show alteration of the pyroxene (cf. FAWCETT, 1965).

Identification of the Alteration Assemblages

Alteration products after olivine consisting of complex mineral assemblages have been extensively described (see especially, WILSHIRE, 1958; BROWN and STEPHEN, 1959; GAY and LEMAITRE, 1961). Highly complex interstratified clay minerals have been identified from altered basalt (see especially, HAYASHI *et al.*, 1961). X-ray powder data, and possible interpretations, from a number of alteration products described above are presented in Table 1. Considering only the broad, strong reflections a relatively simple interpretation may be suggested, but the very numerous weaker reflections signify a highly complicated structure which cannot be adequately or accurately explained completely from this data. Only those components which we believe to be dominant have been annotated. Numerous lines with intensities less than one have largely been omitted, and a number of

Table 1. *X-ray powder photographs of alteration products after olivine*

1			2			3			4			5		
821			10/33			1a			1c			1f		
Line Å	I	$Ident^n$	Line Å	I	$Ident^n$	Line Å	I	$Ident^n$	Line Å	I	$Ident^n$	Line Å	I	$Ident^n$
12.2^b	10	SM	14.8^b	10	S, SC	5.13	4	O	14.4	6	SC	14.4^b	10	SC
5.13	1/2	SM	5.13	4	SM, O, C	3.90	6		9.5	1	SC	3.87^a	1	S
4.56^a	9	S, SM ?	4.92	2	G	3.72	4		5.14	2	O	3.72	1/2	SC
4.46	1	SM	4.60^b	8	SM, S	3.51	6		3.90	5	O	3.49	3	C
3.59	1	Mi	3.90	5	? S, ? O	3.00	4		3.73	4	O	3.35	1/2	G
3.39	8	Mi	3.76	4	? SC	2.78	9		3.50	5	SC, O	3.24	4	SC
3.26	6	SM } ?	3.40	5	(Mi)C	2.52	9		3.22	1	SC	3.00	6	O, ? S
3.20	4	SM }	3.30	4	Mi	2.46	10		3.00	5	O, ? S	2.95	6	S
2.99	6	S	3.20	3	SM	2.36	2		2.95	1		2.91	3	
2.94	6	S, Mi	3.12	2	? Mi	2.32	1		2.88	1	SC	2.78	2	O
2.72	2		3.02	4	S	2.28	4		2.78	8	O	2.57	5	S
2.69	3	Mi	2.90	1		2.26	4		2.52	9	O	2.52	5	O, G, S
2.47	5	S, SM, ? O	2.79	8	O, ? SC	2.16	4		2.47	10	O	2.45	5	G, S, O
2.36	2	Mi	2.71	4	G, Mi	2.04	1		2.32	2	O	2.31	1	? SC
2.33	3		2.58	2	Mi, G	1.88	1/2		2.27	4	O	2.26	2	G
2.27	1	? Mi	2.53^a	10	S, O	1.80	1/2		2.26	2	O, G	2.05	1	C
2.11	3	? S	2.48^a	9	S, O	1.76	8		2.16	3	O	1.75^a	5	S, G
2.10	3		2.33	2		1.68	3		1.88	1		1.71	1	G
1.97	6	Mi	2.27	4	Mi, G	1.65	4		1.75	9	O, S	1.67	1/2	O
1.91	5	Mi	2.22	2	Mi, G	1.63	4		1.68	2	O	1.63	2	O
1.80^a	3	S, SM	2.16	2	Mi	1.60	1/2		1.65	2	O	1.61	1	
1.72^a	3		2.03	1		1.58	1		1.63	2	O	1.56	1	G
1.62	3	Mi	1.97	5	SC, Mi	1.52	1		1.61	1/2		1.53	1	S
1.53	6	S	1.88	3		1.50	5		1.60	1/2	O	1.50	2	O, G
1.50	1	Mi	1.82	2	G	1.49	5		1.58	1	O	1.49	2	O
1.49	2	? O	1.73	8	G, S	1.44	2		1.56	1/2	G	1.42	1/2	
1.48	2		1.68	3		1.40	3		1.52	1	O	1.40	2	C
1.32	2	S	1.63	3	Mi, O	1.39	2		1.50	4	O			
			1.58	1	Mi				1.49	4	O			
			1.53	5	S				1.47	1/2				
			1.50	4	Mi				1.44	1/2	O			
			1.49	6	? SM, ? O									
			1.46	2	G									

Suggested interpretation: O = olivine; SC = interstratified smectite-chlorite; C = chlorite; SM = interstratified smectite-mica; S = smectite; G = goethite; Mi = mica. Only very strong lines of 143 and 604 are given.

[a] Broad reflection. [b] Very broad reflection.

Table 1. Continued

6			7			8			9			10		
1h			1i			143			604			607		
Line Å	I	Ident^{n}	Line Å	I	Ident^{n}	Line Å	I	Ident^{n}	Line Å	I	Ident^{n}	Line Å	I	Ident^{n}
14.4^{b}	4	SC	14.4^{b}	10	SC	14.5^{b}	10	SC	15.8^{a}	10	SC	15.2^{b}	10	SC
9.4	2	SC	7.4	2	SC	7.7	2	SC, C	9.4^{a}	3	SC	10.0	4	SC
4.95	1	G	4.93^{b}	3	G	6.03	4	SC ?	7.3	6	SC	7.2	3	SC
4.15	$^{1}/_{2}$	? G	4.57	10	S, SC ?	5.03	4	SC, G	5.13	6	G, SC	4.97	3	G
3.87	5	S	4.44^{b}	3	SC	4.53^{a}	8	S	4.92	6		4.75	1	SC
3.72	6	SC ?	4.21	3	G	4.20^{b}	10	G	4.42^{b}	8	S	4.48^{b}	8	S, SC
3.50	8	C, SC	4.05	2	SC ?	2.45^{b}	10	S, G	4.20^{b}	8	G	4.17^{b}	10	G
2.98	4	S	3.86	1	S	1.72^{a}	6	S	2.43^{a}	9	S, G	4.05	3	S
2.93	1		3.71	1	SC	1.51^{a}	8	S, G	2.25	6	G, SC ?	3.36	3	G
2.76	5	G, ? O	3.51	2	C				1.74	4	G, S	3.21	5	SC
2.51	5	S, G, ? O	3.33	3	G							3.01	1	S
2.46^{a}	10	S, G, ? O	3.03	2	S							2.93	2	SC ?
2.37	1		2.80	1	SC ?							2.70	6	G
2.31	3	SC	2.64	3	? G							2.60	2	SC
2.25	6	G	2.59	3	S, ? G							2.57	3	S
2.16	5	? O, G	2.54	3	S							2.52	3	S, G
2.02	1	C	2.47	2	S							2.44^{a}	8	G
1.95	1	SC	2.44	2	G							2.25	3	SC, G
1.75^{a}	8	S, G, C	2.39	2								2.22	1	
1.68	1		2.30	2	SC ?							2.19	2	G
1.63	4	? O	2.25	1	G							2.00	2	G
1.61	1		2.21	2	S							1.74	2	G
1.57	2	G	2.17	1	G							1.72	6	S
1.52	2	S	2.00	2	SC, C ?							1.64	1	
1.50	2	G	1.99	2	G							1.56	3	G
1.49	1	O	1.92	1	G							1.51	6	S
1.44	1	G	1.74	2	S, G							1.48	3	
1.40	2	C ?	1.68	1								1.45	3	G
			1.56	2	G									
			1.53	7	S									
			1.50	2	G									
			1.48	2										
			1.45	2	G									
			1.42	1	C									

821 = "Montmorillonite". 10/33 = Pleochroic "iddingsite". 1a—1i = Successive phenocrysts across a weathering rind; 1a is perfectly fresh, 1h and 1i are completely altered. 143 = "Iddingsite" produced by weathering. 604 and 607 = "Iddingsite" of type I, i.e. deuteric.

lines in the Table are not assigned to specific phases. The presence of other, either randomly or irregularly, interstratified phyllosilicates is strongly suspected from both the powder photographs, and the optical mineralogy.

Specimen 821 is of optically homogeneous "montmorillonite" as described above. The X-ray diffractometer trace and powder photographs are interpreted as resulting dominantly from two interstratified sheet silicates, believed to be a smectite and a hydromica. Some degree of ordering between the layers is suggested by very broad reflections at approximately 12.2 Å, 4.2 Å, 2.5 Å and 1.7 Å on the diffractometer trace, which may be (00*l*) repeat reflections for an interstratified structure with a total layer thickness of about 25Å. Sharper, discrete superimposed peaks however, indicate the presence of some random interstratification.

Specimen 10/33 is a strongly pleochroic "iddingsite", occurring as an annulus variety, with open partings and strong optical homogeneity. The X-ray film shows certain similarities to that of 821, with the complication of interference from goethite. The position of the low angle 14.8 Å line, and the strength of other smectite lines, strongly suggest dominance of this group. The possibility of a coexisting chlorite is not ruled out, and may account for interference bands at 5.1, 3.4 and 1.97 angstroms.

Specimens 1a, 1c, 1f, and 1i, of Table 1, show various stages in the alteration of olivine by weathering producing pseudomorphs indistinguishable from other "iddingsites". Specimens 1h and 1i are from the same pseudomorph, 1i being material from irregular cracks cutting the otherwise oriented fibrous brown materials (1h). In these weathered varieties of "iddingsite" goethite lines are subordinate and show only weak interference with the dominant phyllosilicate lines. The sheet silicates are here interpreted as consisting principally of smectite, with chlorite and possibly vermiculite, discretely or in varying degrees of interstratification.

The "iddingsites" of columns 8—10 (Table 1) are characterized by a strong, broad to diffuse reflections at about 15 Å, 9.4—10 Å and 7.2—7.3 Å, interpreted as the (002), (003), (004) reflections of a fairly regularly interstratified smectite-chlorite, or possibly smectite-vermiculite, with a basal spacing of 29—30 Å (see also Hayashi *et al.*, 1961). Distinct smectite lines occur however, at about 4.5 Å, and the dominant feature in all of these "iddingsites" is the goethite pattern.

The complexity of the green alteration products after olivine determined from optical study becomes even more apparent from the X-ray data. The pseudomorphs therefore consist of chlorites, interstratified smectite-hydromica and intermediate materials composed of variously interstratified combinations of these three phyllosilicates. It is probable also, that the materials identified optically as chlorites in fact exhibit various degrees of interstratification with other phyllosilicates, and that there are progressive variations in the degree of that interstratification. Although the individual constituent phases have been tentatively identified, the complexity of the alteration minerals cannot be sufficiently stressed.

Temperatures and Mechanism of Alteration

a) "Iddingsite"

Temperatures of formation of "iddingsite" have ranged from very high (within the magma chamber), through intermediate, deuteric alteration, to very low (weathering). One of the strongest criteria for a magmatic, or high temperature extrusive, origin of "iddingsite" has been the occurrence of "iddingsite" surrounded by rims of unaltered olivine, or contained in sieve-pyroxenes. However, certain properties associated with all of the "iddingsites" studied, including those with fresh olivine rims, suggest to us that "iddingsite" forms at a low temperature in *all* cases:

i) The hydrous smectite-bearing assemblage could not exist under the conditions allowing reprecipitation of olivine to form a rim.

ii) Xenoliths containing olivine, subjected to high temperatures and high volatile concentrations during explosive or extrusive activity, show high temperature exsolution of magnetite or hematite, not alteration to goethite and a phyllosilicate[2].

iii) Weathering produces identical structures and very similar mineral phases to other forms.

iv) Certain flows may be characterized by "iddingsitized" olivines over a very large area (see also Ross and Shannon, p. 5, 1925); and adjacent flows may contain only fresh olivine. A "boulder tuff" described by Edwards (1938), contained fresh olivine in the tachylitic rims and "iddingsite" in the more crytalline cores of the "boulders". These occurrences discount weathering as the process responsible for their formation.

v) Olivines from lava flows which show the development of high temperature oxidation zones initially exsolve discrete iron oxides, and then alter to chloritic materials; they do not alter to "iddingsite".

vi) The coexistence with "iddingsite" of maghemite in the discrete oxides, demonstrates that alteration occurred at temperatures well below those producing the high temperature oxidation assemblage pseudobrookite, titanohematite and rutile (this study, Part 1).

vii) Goethite is unstable at temperatures above approximately 140° C (Tunnel and Posnjak, 1931).

The suggestion that the orientated assemblage goethite + phyllosilicate(s) is merely a low temperature analogue of high temperature alteration products is discredited by ii, v and vi. (See also Part 1).

The reasons for "iddingsitization" to occur within olivine rims is not understood, although temperature/oxidation conditions appear to be the same as for the other deuteric varieties.

b) Green Phyllosilicates

A zonation in the oxidation state of discrete iron-titanium oxides through single lavas has been described by Watkins and Haggerty (1967). The oxidation state of chloritic alteration products after olivine closely parallels this zonation. Sato and Wright (1966) measured oxygen fugacities in cooling lava lakes and showed that oxidizing conditions persisted to low temperatures. It would therefore

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[2] The alteration of olivines to "iddingsite" in gabbroic xenoliths has been recorded by M. J. Baker, 1966. The interpretation of this alteration as a form of "iddingsite" was based on Gay and Lemaitre's 1961 paper, Fig. 6, p. 110 (M. J. Baker — personal communication). Study by us of this Faial material shows it to consist of exsolved magnetite/hematite, as a high temperature oxidation alteration feature, and is not "iddingsite".

appear that alteration producing these chloritic assemblages is a continuous process throughout cooling.

Schreyer and Yoder (1964) have shown smectite-bearing assemblages in the system Mg-cordierite — water to be stable only below 400°C at pressures below 2 kilobars. Certain chlorites however, have been shown to be stable up to 700°C at 1000 bars (Nelson and Roy, 1958). The development of sawtooth structures and the formation of smectite-bearing products are results therefore, of alteration at lower temperatures than those producing chloritic assemblages. Moreover, the alteration is a nonoxidizing process, the co-existing Fe-Ti oxides being magnetite and ilmenite. Analyses of 25 lavas from St. Helena showing variously altered olivines confirm these non-oxidizing conditions. Six lavas with completely altered olivines and oxidized Fe-Ti oxides have an average Fe_2O_3:FeO ratio of 3.10; six flows containing "iddingsite" have a ratio of 0.99; and thirteen flows showing green alteration products have a ratio of 0.39.

c) Strongly Pleochroic Varieties of "Iddingsite"

Just as at high temperature under oxidizing conditions iron oxides are exsolved by the olivine, so at low temperatures under oxidizing conditions, we believe that goethite polycrystalline 'rods' are segregated from the olivine structure. The optically ordered nature of the "iddingsite" at all stages of development, is a result of this initial segregation of goethite, the cell volume of which is one half that of olivine. Although the goethite 'rods' are everywhere perpendicular to the c-direction of the olivine host, they need not be highly ordered within this plane.

We believe that the highly pleochroic varieties of "iddingsite" represent two stages of alteration, the first being the initiation of "iddingsitization" under normal conditions of low temperature deuteric oxidation. Later hydrous alteration (i.e. post-deuteric) induced by hydrothermal reheating or deep burial, results initially in: (a) increasing the orientation, but not the further development, of the "iddingsite" assemblage within the olivine; (b) strengthening the smectite control over the phyllosilicate; (c) the production of an interstratified hydromica with the smectite; and (d) initiation of the open parting. This process may produce a more ordered goethite structure by increasing the segregation of the 'rods' during ordering of the sheet silicates, producing the increase in pleochroism. A process of this nature could explain the conflicting views upon the orientation of the pseudomorph assemblage held by Brown and Stephen (1959, p. 255-6, Fig. 2) who studied a pleochroic variety, and Gay and Lemaitre (1961, p. 109) who studied essentially non-pleochroic varieties. If the rise in temperature is sufficiently great, goethite may form hematite by dehydration — this is seen in lavas from Glencoe and Iceland, and hematite in strongly pleochroic "iddingsites" has been described by Smith (1959) and Brousse (1961). Increasing post-deuteric alteration results in the relic olivine altering to green minerals, initially along transverse cracks. "Iddingsite" relics retain their optical continuity until more intense alteration results in total breakdown of the original olivine-"iddingsite" assemblage. Highly pleochroic varieties of "iddingsite" are often associated with obviously secondary products and/or are very old geologically, i.e. Palaeozoic. Of the younger varieties examined, those of St. Helena were associated with areas of probable later hydrothermal alteration, and those from Iceland had been subjected to burial beneath nearly a thousand meters of lava flows.

Of interest in this respect are those varieties of "montmorillonite" showing pleochroism from green to gold, in olivines otherwise altered to green materials. These varieties exhibit slight increases in refractive index and birefringence which may be interpreted as an increase in the $Fe^{+3}:Fe^{+2}$ ratio (Ross and HENDRICKS, 1945); alternatively these variations could result from weak, post-deuteric oxidation producing the segregation of discrete goethite orientated within the interstratified layer-lattice silicates.

Chemistry of Alteration

Relevant analyses of alteration products associated with olivine-bearing basalts have been abstracted from the literature and are shown in Table 2. Several aspects of the chemistry of alteration are common to the formation of both "iddingsite" and green phyllosilicate assemblages:

i) Alteration of the groundmass is always visible.

ii) The nature of the alteration products necessitates the introduction of water and alumina.

iii) The change in density of the alteration products relative to the original olivine requires overall loss of material from the olivine, since there is no volume change.

Textural relationships of chloritic material occupying interstitial areas in which an outer rim of chloritic fibres is everywhere perpendicular to the surrounding crystals, strongly suggest precipitation from solution. However, in view of the composition of the late stage crystallizing fraction of alkali-basaltic lavas (WILKINSON, 1966), we cannot accept that the chloritic assemblage represents the composition of a *primary* late residuum as suggested by FAWCETT (pp. 62—65, 1965). The occurrence of chloritic mesostasis associated with the deuteric alteration of olivine in basaltic lavas indicates reaction between the late crystallizing fraction and the mafic minerals. In the case of the lavas showing high temperature oxidation, the alteration process is almost certainly continuous, i.e. the late residual fluids react with the olivine to form chloritic assemblages within the olivines and in interstitial patches. This may well be true also for the majority of cases resulting in sawtooth types of alteration. However, since smectite-bearing assemblages are ubiquitous in the lavas described, the alteration process must proceed to temperatures below 400° C.

The residual liquid of alkali olivine-basaltic lavas is characterized by a composition close to that of trachyte (WILKINSON, 1966, p. 851, analyses 1 and 2), being richer than the basalt as a whole in alumina, silica, alkalis and water, and lower in total iron, calcium, and magnesium. Reaction with olivine would result in the introduction of alumina to, and some removal of iron and magnesium from, cracks in the olivine, producing initially a chlorite and subsequently an interstratified smectite-hydromica, this latter necessitating introduction of potassium with accessory sodium for the smectite. Reactions within the bounds of the olivine crystal provide excess magnesium and iron available for reaction with the remaining interstitial fluids, also producing phyllosilicate assemblages. Much of the alteration process must take place by solid state reactions within the original olivine

Table 2. *Chemical analyses of alteration products after olivine, or from basaltic rocks*

	1	2	3	4	5	6	7	8	9	10	11	12	13
SiO_2	39.3	39.11	37.9	28.0	25.59	23.22	17.52	24.77	36.41	35.22	40.52	38.41	40.04
TiO_2	—	0.18	0.7	0.64	0.61	—	0.42	—	—	—	0.20	0.06	0.41
Al_2O_3	—	3.29	5.6	4.0	6.53	3.18	8.00	14.77	21.71	16.54	8.83	6.89	6.76
Fe_2O_3	—	31.49	20.7	42.0	31.44	53.88	55.09	34.09	2.50	4.41	5.82	3.93	9.29
FeO	18.9	0.96	3.3	0.0	4.64	0.72	0.0	4.50	6.62	6.94	5.73	9.48	2.38
MnO	—	—	nd	0.35	nd	—	0.45	—	—	—	—	0.09	—
MgO	41.8	8.05	24.0	10.0	15.83	3.01	2.73	13.27	19.51	10.98	20.81	17.96	19.13
CaO	—	2.28	3.6	1.0	1.30	2.36	1.29	0.73	1.07	4.98	0.49	3.39	2.27
Na_2O	—	—	nd	nd	0.31	—	0.18	—	—	—	—	nd	—
K_2O	—	—	nd	nd	0.28	—	0.31	—	—	—	—	nd	—
H_2O^+ H_2O^-	—	16.27	4.2	15.84	12.83	13.84	13.74	8.26	12.14	21.01	17.40	19.77	19.75
P_2O_5	—	—	—	0.32	—	—	—	—	—	—	—	—	—
CO_2	—	—	—	0.1	—	—	—	—	—	—	—	—	—
Total	100.0	101.63	100.0	102.25	99.36	100.21	99.73	100.39	99.96	100.08	99.80	99.98	100.03

1 = Olivine Fa_{20} (theoretical)
2 = "Iddingsite" (average of 5; Ross and Shannon, 1925)
3 = "Iddingsite" (Gay and Lemaitre, 1961)
4 = "Iddingsite" (Sun, 1957)
5 = "Iddingsite" (Gay and Lemaitre, 1961)
6 = "Iddingsite" (Brazos River Specimen, Ross and Shannon, 1925)
7 = "Iddingsite" (from pyroxene trachyte, Hytönen, 1959)
8 = Markle basalt pseudomorph (Smith, 1959) Recalc. H_2O^- free
9 = Col. 8 recalc. after removal of 32.39% Fe_2O_3 (hematite)
10 = Bowlingite (type specimen, Hannay, 1877)
11 = Bowlingite (average of two, Caillere and Henin, 1951)
12 = Amygdale infilling (Hayashi *et al.*, 1961)
13 = Saponite (Caillere and Henin, 1951)

framework, since totally isolated olivine relics in otherwise complete pseudomorphs completely retain their crystallographic orientation.

Since groundmass chlorites show progressive optical changes as a result of increasing iron content, it is suggested that iron is removed from the olivine in preference to magnesium, and the smectite formed is saponite. The interstratified phyllosilicate assemblage of this study ("montmorillonite"), and of HAYASHI *et al.* (1961), closely resemble, optically, material often described as "bowlingite". In spite of the identification of "bowlingite" solely as saponite by CAILLERE and HENIN (1951), it would appear that it in fact consists of an interstratified assemblage.

In the case of the deuteric formation of "iddingsite" most of the iron from the olivine is segregated as goethite, leaving magnesium and silicon as the available cations to form the coexisting phyllosilicates, migration occurring with strong anionic control. The introduction of water and alumina causes slight reorganization of the olivine lattice, forming sheet silicates, the surplus magnesium and silicon being removed, to result in the dominance of goethite (Table 2, cols 1—7). Two "iddingsites" with unusually high iron, and very low SiO_2 and MgO (Table 2, cols 6, 7) are from an andesite and a trachyte, both of which are likely to contain olivines more fayalitic than those of basalts, and the analyses are thought to reflect compositional variation of the original olivine.

In the weathering alteration of olivine the subordinate character of the goethite reflections in powder photographs has been noted; and optically in those rocks showing complete "iddingsite" pseudomorphs the brown-orange colour decreases to yellow or yellow-green, close to vesicular, porous parts of the flow. This initial retention of iron in weathering apparently does not hold for increasing alteration, when much iron may be removed with magnesium and silicon, leaving an ill-defined assemblage of largely alumina-rich end products (see also ABBOTT, 1958).

The increasing role of the phyllosilicates in highly pleochroic "iddingsites" is seen in Table 2, cols 8 and 9, which may be compared with columns 10—13.

The introduction of iron into the olivine in order to form "iddingsite" is not necessary. Table 3 shows the effect of adding 10% water and 5% alumina, and removing 80% of the original MgO and 75% of the original SiO_2, and recalculating all iron as Fe_2O_3. The chemistry of the original olivine of Fa_{20} composition changes to that of a typical "iddingsite".

Table 3

	SiO_2	Al_2O_3	Fe_2O_3	FeO	MgO	H_2O	Total
Fa_{20}	39.3			18.9	41.8		100.0
Recalc.	21.0	4.6	46.0		13.8	14.6	100.0

The two types of alteration, therefore, demonstrate essential chemical differences (Table 2): in the oxidation process producing "iddingsite", iron is retained and its valency state increased, alumina and water are introduced, and magnesium and silicon are removed. In alteration involving non-oxidizing processes Mg and Fe are in part retained, Mg more strongly, and in part removed; silicon is retained, alumina and water are both abundantly introduced, and to a lesser extent so are the alkalis.

The processes of alteration described above must be seen as continuous, intermediate to low temperature, cooling phenomena. Patches of interstitial alteration products resemble those of the pseudomorphs in that both consist of assemblages of phyllosilicates. In the initial stages of alteration compositional differences will be marked, but with increasing chemical migration these differences decrease, resulting in similar mineral groups with similar compositions in both groundmass and olivine pseudomorphs.

Conclusions

1. Olivines cooling under oxidizing conditions show high temperature exsolution of iron oxides and lower temperature deuteric alteration of the Mg-enriched host olivine and groundmass to essentially chloritic materials.
2. Intermediate and low temperature deuteric alteration results in the production, in the olivine and interstices of the rock, of very complex phyllosilicate assemblages, a smectite appearing to be a dominant constituent.
3. "Iddingsite" forms deuterically at low temperatures under oxidizing conditions, as indicated by goethite in the pseudomorph and maghemite in the discrete Fe-Ti oxides. Its optical orientation is dependent upon the initial segregation of discrete goethite.
4. "Iddingsites" subjected to post-deuteric alteration are highly pleochroic as a result of an increase in the order of the intergrowth of goethite and phyllosilicates. Increasing alteration may totally destroy the original deuteric features.
5. Weathering of olivine may produce pseudomorphs with similar composition and properties to deuteric forms of "iddingsite".
6. The principal chemical features of the intermediate and low temperature alteration are, introduction of water and alumina (and in some cases alkalis) to the olivine, and removal of iron, magnesium, and silicon, in varying proportions. Some overall loss of material from the olivine must occur.
7. Increasing alteration results in increasing similarity in the mineralogical assemblages of the olivine pseudomorphs and the altered groundmass.

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