THE AMERICAN MINERALOGIST, VOL. 46, MARCH-APRIL, 1961

SOME ASPECTS OF THE CALCIFEROUS AMPHIBOLES, OXYHORNBLENDE, KAERSUTITE AND BARKEVIKITE

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ABSTRACT

The brown calciferous amphiboles oxyhornblende, kaersutite and barkevikite have been examined briefly in terms of their chemistry, optical properties and mode of occurrence. The titaniferous amphibole kaersutite, generally considered to be a variety of oxyhornblende, often has low Fe_2O_3/FeO ratios and is therefore distinct from the latter mineral. Kaersutite and barkevikite compositions are dominated respectively by the end-member series pargasite-ferropargasite.

Optical properties of brown amphiboles assigned to the three species show considerable overlap. Birefringences greater than 0.040 characterize true oxyhornblendes.

Kaersutite and barkevikite are the brown calciferous amphiboles typically encountered in undersaturated alkaline rocks, barkevikite possessing higher Fe_2^+/Mg ratios than kaersutite, and $Mg<2$ atoms. Kaersutite occurs most commonly in analcite-bearing rocks of wide compositional range, and in nepheline-bearing basic rocks. On the other hand, barkevikite is more characteristic of the nepheline-syenites, and is an iron-enriched amphibole developed as a consequence of relatively less hydrous conditions resulting in increased Fe^{2+}/Mg ratios in the magma.

INTRODUCTION

Questions of nomenclature of oxyhornblende* kaersutite and barkevikite reflect one of the many problems arising from extensive ionic substitution in the calcium-sodium amphibole group. Apart from the problem of identification by optics, actual measurements of optical properties of the three minerals in question are rendered more difficult by their strong brown or reddish-brown absorption colours. And, as emphasized by Boyd (1955), the ways in which the composition of a particular amphibole reflects the chemical and physical environment in which it formed, as yet are not clearly understood.

Amphiboles referred to oxyhornblende, kaersutite and barkevikite have been described from a wide range of igneous rocks. Generally these minerals have been most frequently recognized in alkaline undersaturated types, particularly kaersutite and barkevikite. One feature of their chemistry, namely frequent enrichment in TiO_2, recalls a similar feature of clinopyroxenes of alkali olivine-basalt magma (Wilkinson, 1956, Table 2). In these minerals, TiO_2 contents of 2–4 per cent are not uncommon.

Basaltic hornblende, oxyhornblende (Winchell, 1932, p. 473) and

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* Throughout this paper the term oxyhornblende is used in preference to the synonymous terms basaltic hornblende and lamprobolite.

lamprobolite (Rogers, 1940) are synonymous terms to cover the dark brown amphibole with high ferric iron content, high indices of refraction and rather strong to extreme birefringence. A small extinction angle also has been cited as a diagnostic optical property. Both Winchell and Rogers have pointed out the unsatisfactory usage of the term basaltic hornblende to cover an amphibole with these properties, as this mineral is by no means confined to basalts.

The term kaersutite was proposed by Lorenzen (1884) for a highly titaniferous amphibole occurring in feldspathic veins and dikes cutting the picrite at Kaersut, Greenland. Lorenzen's original material was subsequently re-examined by Washington and Wright (1908). The term kaersutite has carried various connotations, *e.g.* a highly titaniferous oxyhornblende (Washington and Wright, 1908, p. 210; Benson, 1940, p. 285; Winchell, 1951, p. 437; Kerr, 1959, p. 330); a rare variety of barkevikite (Yagi, 1953, p. 783) and a brown hornblende with abundance of TiO_2 (Aoki, 1959, p. 278).

Barkevikite (Brögger, 1890) has been variously defined in relation to other amphiboles, e.g. as a member of the oxyhornblendes (Kunitz, 1930, p. 214; Sundius, 1946, p. 30) or the soda amphiboles (Winchell, 1951, p. 440).

Attention has been frequently directed to experiments (*e.g.* Kôzu *et al.*, 1927; Barnes, 1930) whereby green hornblende on heat treatment changes to a mineral having the appearance and optical properties of oxyhornblende. In this transformation, the principal chemical change is oxidation of the ferrous iron and loss of hydrogen. Barnes showed that the principal optical changes associated with heating green hornblende in air at about 800° C. are: increase in the indices of refraction, birefringence and dispersion; decrease in the extinction angle and change in 2V to 65°; change in colour and pleochroism from greens to browns.

CHEMISTRY AND CLASSIFICATION

In recent years the classification of the calciferous amphiboles has been discussed by Hallimond (1943), Winchell (1945), Sundius (1946), Boyd (1959) and Smith (1959). In general, four principal magnesian end-members (plus their ferriferous analogues) have been recognized (Table 1), namely tremolite (-ferrotremolite or actinolite*), edenite

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* The terminology of these two ferriferous end-members varies with different authors. In this paper the term ferropargasite is preferred for the pure ferriferous end-member equivalent of pargasite, inasmuch as the term hastingsite for many years has referred to Fe-rich amphiboles with small amounts of MgO, or else to various calciferous amphiboles with variable FeO/MgO ratios (Billings, 1928). The term ferrotremolite is preferred for the Fe-analogue of tremolite.

(-ferroedenite), tschermakite (-ferrotschermakite) and pargasite (-ferropargasite or hastingsite*). The most significant end-member series in the present discussion is the pargasite-ferropargasite series, the Mg end-member pargasite $NaCa_2Mg_4Al^{VI}Al_2^{IV}Si_6O_{22}(OH)_2$ being derived from tremolite $Ca_2Mg_5Si_8O_{22}(OH)_2$ by the double substitution AlAl for MgSi and NaAl for Si.

Boyd (1959, p. 382) has shown graphically that the two most important end-member series of the calciferous amphiboles (including the more familiar green igneous hornblendes) are $Ca_2FM_5Si_8O_{22}(OH)_2$ and $(Na, K)Ca_2FM_4(Al^{VI}, Fe^{3+})Al_2^{IV}Si_6O_{22}(OH)_2$, where $FM = Fe^{2+} + Mg$. The amphiboles considered by Boyd had Ca = 1.8–2.1 and low contents of Ti (<0.20).

TABLE 1. END-MEMBERS OF CALCIFEROUS AMPHIBOLES

tremolite $Ca_2Mg_5Si_8O_{22}(OH)_2$

$$\left.\begin{array}{l}\text{ferrotremolite}\\ \text{actinolite}\end{array}\right\} Ca_2Fe_5Si_8O_{22}(OH)_2$$

pargasite Na $Ca_2Mg_4Al^{VI}Al_2^{IV}Si_6O_{22}(OH)_2$

$$\left.\begin{array}{l}\text{ferropargasite}\\ \text{hastingsite}\end{array}\right\} \text{Na } Ca_2Fe_4^{2+}Al^{VI}Al_2^{IV}Si_6O_{22}(OH)_2$$

edenite Na $Ca_2Mg_5Al^{IV}Si_7O_{22}(OH)_2$
ferroedenite Na $Ca_2Fe_5^{2+}Al^{IV}Si_7O_{22}(OH)_2$

tschermakite $Ca_2Mg_3Al_2^{VI}Al_2^{IV}Si_6O_{22}(OH)_2$
ferrotschermakite $Ca_2Fe_3^{2+}Al_2^{VI}Al_2^{IV}Si_6O_{22}(OH)_2$

Tables 2–4 list analyses of amphiboles assigned by various workers to oxyhornblende, kaersutite and barkevikite respectively. In Table 5, these amphiboles have been recalculated on a basis of 24 (O, OH, F). Much of this latter data has been taken from Hallimond (1943, Table 1). An uncertainty in these calculations is the determination of H_2O^+, and non-determination of F, particularly in older analyses. Only analyses showing reasonably close agreement with the general calcium-sodium amphibole formula $W_{2-3}(XY)_5Z_8O_{22}(OH)_2$* have been listed. Many analyses were rejected because of significant departures of the W (where greater than 3.2) and XY (greater than 5.4) groups.

In the three amphiboles, Si is close to 6 atoms, associated with two Al atoms in four-fold co-ordination. Ca is generally 1.8–2.0. In five cases there is insufficient aluminium to satisfy the Al^{IV} requirements in the

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* W = (Na, K, Ca), X = (Mg, Fe_2^+, Mn), Y = (Al^{VI}, Fe^{3+}, Ti), Z = (Si, Al^{IV}).

TABLE 2. CHEMICAL ANALYSES AND OPTICAL PROPERTIES OF OXYHORNBLENDE

	1	2	3	4	5	6	7	8	9	10
SiO_2	40.17	39.83	39.85	39.96	42.05	39.82	41.97	39.48	40.69	45.17
TiO_2	3.78	2.56	4.25	4.05	1.80	2.42	4.20	3.10	2.98	2.11
Al_2O_3	15.09	14.98	13.07	12.83	12.59	12.34	12.59	10.97	12.09	7.68
Fe_2O_3	5.49	7.66	6.76	7.40	8.61	11.86	4.69	11.23	11.83	14.30
FeO	5.99	3.78	5.09	6.37	6.45	8.02	5.80	8.21	0.21	2.81
MnO	0.09	—	—	—	—	—	n.d.	0.53	0.70	0.41
MgO	12.48	14.44	13.58	12.92	12.40	9.78	14.20	10.30	14.34	13.44
CaO	11.21	12.39	12.42	12.07	12.28	12.26	11.99	13.65	11.85	11.18
Na_2O	2.27	2.27	2.79	2.28	2.03	2.28	3.17	0.99	2.45	1.35
K_2O	1.55	1.25	0.98	1.48	0.87	1.03	1.63	0.67	1.56	1.09
H_2O^+	2.10	0.58	0.66	0.72	0.63	0.45	0.26	1.49	1.24	0.19
H_2O^-	0.25	—	—	—	—	—	—			0.06
F	—	—	—	—	—	—	n.d.	—	—	0.35
etc.	—	—	—	—	—	—	—	0.24	0.10	—
Less O=F	100.47	99.74	99.45	100.08	99.71	100.26	100.50	100.86	100.04	100.14 0.14
Total	100.47	99.74	99.45	100.08	99.71	100.26	100.50	100.86	100.04	100.00
α	1.670	1.667	1.677	1.679	1.668	1.681	1.675	—	1.685	1.675
β	1.682	—	—	—	—	—	1.691	—	1.711	1.715
γ	1.693	1.688	1.700	1.701	1.688	1.700	1.701	—	1.731	1.735
$\gamma-\alpha$	0.023	0.021	0.023	0.022	0.020	0.019	0.026	—	0.046	0.060
$2V_\alpha$	82	—	—	—	—	—	—	—	82	large
$\gamma\wedge c$	9	3	6	—	—	0	11–12	2–10	0–2	5
Pleochroism										
X	Pale yellow with tinge of brown	—	—	—	—	—	—	—	amber yellow	pale yellow
Y	dark brown	brownish green	brown	brown	greenish brown	brown	"scarcely noticeable pleochroism"	—	yellowish brown	dark chestnut brown
Z	dark olive green with tinge of brown	—	—	—	—	—	—	—	reddish nrown	dark chestnut brown
Absorption	X<Y<Z	—	—	—	—	—	—	—	X<Y<Z	X<Y<Z

1. From tuff-breccia, L. Balaton, Hungary (Vendl, 1924, p. 238).
2. From tephrite, Grosspriessen, Bohemia (Kunitz, 1930, p. 245).
3. From trachydolerite, Madeira (Kunitz, 1930, p. 245).
4. From volcanic-bomb, "Isleta-Krater" (Kunitz, 1930, p. 245).
5. From gabbro, "S. Vincent" (Kunitz, 1930, p. 245).
6. From essexitic phonolite, "Tejedatal" (Kunitz, 1930, p. 245).
7. From sodic lava, Kilimanjaro, E. Africa (Washington and Merwin, 1922, p. 124).
8. From hypersthene-andesite, Shabō-zan, Taiwan (Ichimura, 1931, p. 564).
9. From hypersthene-andesite, Shabō-zan, Taiwan (Ichimura, 1931, p. 564. Note: this amphibole referred to brown hornblende by the author. Winchell, 1945, Table 4, treats it as an oxyhornblende).
10. From quartz-latite, San Juan region, Colorado (Larsen *et al.* 1937, p. 895. Analysis calculated to 100 per cent from material with 0.79 per cent P_2O_5).

TABLE 3. CHEMICAL ANALYSES AND OPTICAL PROPERTIES OF KAERSUTITE

	1	2	3	4	5	6	7	8	9	10	11	12
SiO_2	39.30	39.50	40.73	39.51	41.46	40.36	39.78	39.20	39.01	38.30	39.68	40.85
TiO_2	10.25	10.33	8.47	5.64	5.70	7.09	7.00	6.53	6.05	6.02	7.12	8.47
Al_2O_3	11.16	11.12	10.62	14.26	14.24	13.78	14.13	13.87	13.60	12.87	12.81	9.89
Fe_2O_3	1.21	0.06	1.39	1.75	3.32	3.39	4.61	4.03	5.25	7.98	4.04	8.85
FeO	8.76	9.44	11.91	10.92	5.70	7.91	7.31	7.33	7.42	6.96	8.79	3.96
MnO	0.06	0.10	0.25	0.09	0.08	0.14	0.12	0.11	0.14	0.12	0.16	0.12
MgO	13.24	12.90	10.46	11.36	13.68	11.08	11.01	11.96	11.73	11.79	11.22	12.47
CaO	11.29	10.91	10.40	10.12	11.62	10.82	10.75	12.37	12.05	10.47	11.06	12.16
Na_2O	2.93	3.82	2.92	2.80	2.29	2.78	2.57	1.99	2.51	3.11	3.37	2.01
K_2O	1.06	1.43	1.33	1.59	1.72	1.34	1.58	1.45	1.11	1.30	1.04	0.63
H_2O^+	0.59	0.59	1.97	1.68	0.12	0.79	0.37	0.87	0.98	1.10	0.78	0.19
H_2O^-	—	—	0.23	nil	—	0.26	0.22	0.27	0.19	0.26	0.15	—
F	—	—	—	abs.	0.42	0.37	—	—	abs.	0.05	0.33	0.28
etc.	0.32	—	—	0.09	—	—	—	—	0.09	—	—	0.10
	100.17	100.20	100.68	99.81	100.35	100.65	99.45	99.98	100.13	100.33	100.55	99.98
Less O=F					0.18	0.16				0.02	0.14	0.12
Total	100.17	100.20	100.68	99.81	100.17	100.49	99.45	99.98	100.13	100.31	100.41	99.86
α	1.676	—	α' on (110) 1.680	1.677	1.670	1.688	1.687	1.680	1.682	1.684	1.685	1.692
β	1.694	—	—	1.694	1.692	1.708	1.705	1.700	1.697	1.701	1.710–1.718	1.731
γ	1.708	—	γ' on (110) 1.703	1.707	1.701	1.720	1.718	1.709	1.717	1.720	1.736	1.760
$\gamma-\alpha$	0.032	—	—	0.030	0.031	0.032	0.032	0.029	0.035	0.036	0.051	0.068
$2V_\alpha$ meas.	81	—	77–79	82	81	78	80	75	78	—	74–66	71
$2V_\alpha$ calc.	82	—	—	81	—	—	79	—	—	—	—	80
$\gamma \wedge c$	8	—	16–19	6	8–10	4	4	—	2	3–5	4	1.5
X	—	—	brownish yellow	pale yellowish brown	light yellow brown	pale yellowish brown	pale yellowish brown	—	pale straw brown	—	pale yellowish brown	pale olivine brown
Y	—	—	reddish brown	brown	reddish brown	brown	reddish brown	—	reddish brown	—	brown	brown
Z	—	—	deep chestnut brown with violet tinge	dark brown with reddish tinge	darker reddish brown	dark brown	greenish brown	—	darker reddish brown	—	deep brown	dark brown
Absorption	—	—	X<Y<Z	X<Y<Z	X<Y<Z	X<Y<Z	X<Y<Z	—	X<Y<Z	—	X<Y<Z	X<Y<Z

1. From vein in picrite, Kaersut, Greenland (Washington and Wright, 1908, p. 198).
2. From picrite, Kaersut, Greenland (Gossner and Spielberger, 1929, p. 121).
3. From monzonite, Morotu district, Sakhalin (Yagi, 1953, p. 784).
4. From analcite-basalt, Spring Mount, west of Glen Innes, New South Wales (new analysis).
5. From camptonite, Boulder Dam, Arizona (Campbell and Schenk, 1950, p. 684).
6. From trachyandesite, Gonoura-machi, Iki Islands (Aoki, 1959, p. 279).
7. From kaersutite-basalt dyke (teschenitic), Dôgo, Oki Islands, Japan (Tomita, 1934, p. 103).
8. From volcanic ejectamenta, Uturyo Island, Korea (Harada, 1936, p. 282).
9. From trachybasalt, Leith Valley Quarry, Dunedin, N. Z. (Benson, 1940, p. 286).
10. From "andesine-basalt," Yohodo, Korea (Kawano, 1937, p. 127).
11. From cognate xenolith in trachyte, Gonoura-machi, Iki Islands (Aoki, 1959, p. 279).
12. From basic lava, Monte Rosso, Linosa (Washington and Wright, 1908, p. 192).

TABLE 4. CHEMICAL ANALYSES AND OPTICAL PROPERTIES OF BARKEVIKITE

	1	2	3	4	5
SiO_2	38.41	36.12	40.88	41.12	37.86
TiO_2	1.26	4.82	0.22	0.45	1.25
Al_2O_3	16.39	12.46	11.04	11.02	12.06
Fe_2O_3	3.75	9.60	7.56	6.54	11.47
FeO	21.75	10.43	17.41	17.73	16.23
MnO	0.15	0.28	1.32	1.03	0.82
MgO	2.54	9.09	5.92	6.14	4.03
CaO	10.52	12.01	10.46	10.42	11.43
Na_2O	2.95	2.58	3.75	3.65	2.98
K_2O	1.95	1.41	0.78	0.94	0.72
H_2O^+	0.24	1.02	1.16	1.45	1.23
Total	99.91	99.82	100.50	100.49	100.08
α	—	1.687	1.691	1.687	1.694
β	—	—	—	—	—
γ	—	1.708	1.707	1.701	1.710
γ-α	—	0.021	0.016	0.014	0.015
$2V_\alpha$	—	—	—	—	—
$\gamma \wedge c$	13	10	16	—	20
Pleochroism					
X	yellow brown	—	—	—	—
Y	dark brown	dark brown	dark brown	greenish brown	brown
Z	dark brown	—	—	—	—
Absorption	$X<Y<Z$	—	—	—	—

1. From sodalite-syenite, Square Butte, Montana (Lindgren and Melville, 1892, p. 292).
2. From essexite, Fuerteventura, Canary Isles (Kunitz, 1930, p. 245).
3. From nepheline-syenite, Skuttersundskjär (Kunitz, 1930, p. 245).
4. From nepheline-syenite, Stavarnsjö, Norway (Kunitz, 1930, p. 245).
5. From foyaite, S. Vincente, C. Verde (Kunitz, 1930, p. 245).

Z group, and Ti, apparently replacing Si, has been added to bring this group up to 8.00, as required by the amphibole formula. A comparable procedure has been found necessary in certain titaniferous clinopyroxenes.

Several analyses of kaersutite (Table 3, Analyses 1–4) are significant from the point of view of nomenclature inasmuch as they reveal low Fe_2O_3 contents relative to FeO. The mineral from the type area is included here. This feature of kaersutite chemistry immediately sets it apart from the widely accepted concept of an oxyhornblende. In terms of end members, recalculated analyses of kaersutites with low degrees of oxidation indicate a composition close to that of a titaniferous pargasite with part of the Mg replaced by Fe^{2+}. As an approximation, the composition of the type kaersutite can be written as

TABLE 5. ATOMIC RATIOS OF OXYHORNBLENDE, KAERSUTITE, AND BARKEVIKITE FOR (O, OH, F) = 2400

	Si	Al^{IV}	Al^{VI}	Ti	Fe^{3+}	Fe^{2+}	Mn	Mg	Ca	Na	K	H	F	W	X	Y	XY	Z	(OH, F, Cl)
	Z		Y			X			W										
Oxyhornblende																			
1	585	215	43	41	60	73	1	272	175	64	29	205	—	2.68	3.46	1.44	4.90	8.00	2.05
2	592	208	53	29	86	47	—	321	196	66	24	59	—	2.86	3.68	1.68	5.36	8.00	0.59
3	595	205	25	48	76	74	—	303	199	81	17	67	—	2.97	3.77	1.49	5.26	8.00	0.67
4	599	201	25	46	84	80	—	291	194	66	29	72	—	2.89	3.71	1.55	5.26	8.00	0.72
5	629	171	52	20	97	80	—	278	198	60	17	60	—	2.75	3.58	1.69	5.27	8.00	0.60
6	607	193	25	30	137	103	—	222	201	68	20	46	—	2.89	3.25	1.92	5.17	8.00	0.46
7	622	178	42	47	52	73	n.d.	315	192	92	31	20	—	3.15	3.88	1.41	5.29	8.00	0.20
8	595	195(Ti 10)	—	25	127	103	7	231	220	29	13	150	—	2.62	3.41	1.52	4.93	8.00	1.50
9	599	201	9	33	131	3	9	315	187	70	29	122	—	2.86	3.27	1.73	5.00	8.00	1.22
10	673	127	8	24	160	35	5	298	178	39	21	19	16	2.38	3.38	1.92	5.30	8.00	0.35
Kaersutite																			
1	573	227	17	112	13	107	8	287	170	83	20	57	—	2.73	4.02	1.42	5.44	8.00	0.57
2	593	196(Ti 11)	—	105	6	118	1	281	176	111	27	59	—	3.14	4.00	1.11	5.11	8.00	0.59
3	604	185(Ti 11)	—	83	16	147	4	233	166	84	25	194	—	2.75	3.84	0.99	4.83	8.00	1.94
4	589	211	39	63	19	136	1	252	162	81	30	167	—	2.73	3.89	1.21	5.10	8.00	1.67
5	612	188	60	63	37	70	1	301	184	65	32	12	20	2.81	3.72	1.60	5.32	8.00	0.32
6	601	199	43	79	38	98	2	246	173	80	25	78	17	2.78	3.46	1.60	5.06	8.00	0.95
7	600	200	51	79	52	92	2	247	174	75	30	37	—	2.79	3.41	1.82	5.23	8.00	0.37
8	587	213	32	73	45	92	1	267	198	58	28	87	—	2.84	3.60	1.50	5.10	8.00	0.87
9	584	216	24	68	59	93	2	262	193	73	21	98	—	2.87	3.57	1.51	5.08	8.00	0.98
10	575	225	2	68	90	87	1	264	168	90	25	110	5	2.83	3.52	1.60	5.12	8.00	1.15
11	594	206	20	80	45	110	2	250	177	98	20	78	16	2.95	3.62	1.45	5.07	8.00	0.94
12	610	174(Ti 16)	—	80	98	46	1	280	196	63	11	20	14	2.70	3.27	1.78	5.05	8.00	0.34
Barkevikite																			
1	614	186	123	15	45	291	2	60	180	91	40	26	—	3.11	3.53	1.83	5.36	8.00	0.26
2	560	228(Ti 12)	—	44	112	135	4	210	199	78	28	106	—	3.05	3.49	1.56	5.05	8.00	1.06
3	629	171	47	3	88	225	17	137	173	111	15	120	—	2.99	3.79	1.38	5.17	8.00	1.20
4	635	165	36	5	77	234	13	143	173	110	19	149	—	3.02	3.90	1.18	5.08	8.00	1.49
5	597	203	21	14	137	217	10	95	187	105	14	128	—	3.06	3.22	1.72	4.94	8.00	1.28

$(Na, K, Ca)_{2-3}(Mg_3, Fe^{2+})\ Ti\ Al_2^{IV}\ Si_6O_{23}(OH)$. In kaersutite the amount of Ti in the Y group is generally between 0.6 and 1. In all cases Mg is greater than 2. Despite variable degrees of oxidation, Fe^{2+} is generally greater than Fe^{3+}.

The analysis of barkevikite cited by Brögger (1890, p. 412) was incomplete. It is characterised by relatively high lime *and* soda (CaO 10.24; Na_2O 6.08 per cent), making it difficult to place in either the calciferous or alkali amphiboles (Miyashiro, 1957, Table 1). Another analysis of barkevikite from the same area (Table 4, Analysis 3) presents no abnormalities in its composition. Compared with kaersutite, barkevikite is characterised by lower contents of Ti and a higher degree of replacement of Mg by Fe^{2+} in the X group, so that Fe^{2+} is generally greater than Mg. In the barkevikite analyses, there is a tendency for the W group to closely approach its maximum value of 3.

It is clear that kaersutite and barkevikite compositions are respectively dominated in their compositions by the pargasite-ferropargasite end-members, in which may be particularly noted the replacement of Al^{VI} by both Ti and Fe^{3+}.

Billings (1928) proposed the following classification of the hastingsite group based on the ratio FeO/MgO (molecular proportions): $FeO/MgO > 2$, ferrohastingsite; $FeO/MgO < 2 > 0.5$, femaghastingsite; $FeO/MgO < 0.5$, magnesiohastingsite. A classification in this manner possesses limitations when, for any reason, oxidation of the iron has taken place. The brown titaniferous (4–7 per cent TiO_2) amphibole from the Mount Royal essexites (Bancroft and Howard, 1923, p. 20), referred to magnesiohastingsite and femaghastingsite by Billings (*op. cit.*), would be regarded as kaersutites by many workers. Sundius (1946, p. 22) has pointed out the similarity of such Mg-rich amphiboles to pargasite.

It is proposed that the chemical distinction between kaersutite and barkevikite be based on the number of Mg atoms in the formula, titaniferous amphiboles with $Mg > 2$ atoms being kaersutites. On this classification the amphibole ($Mg = 2.1$) from the Fuerteventura essexite (Table 4, Analysis 2) would be referred to kaersutite. Barkevikite is analogous in its fundamental chemistry to the TiO_2-poor green or blue-green hastingsites occurring in both acid and over- and undersaturated intermediate rocks.

The term kaersutite has carried with it the implication of a high content of TiO_2, generally greater than 5 per cent. This is perhaps unfortunate, as analogous brown amphiboles with 3–5 per cent TiO_2 are probably not uncommon, particularly in basic alkaline rocks (for example, see Mason, 1958, p. 251). The TiO_2 content of a particular brown amphibole is sensitive to the magma chemistry at the time of its formation. Viewed in this light, there appears to be no reason why brown amphiboles conforming in their essential chemistry to kaersutite but possessing slightly lower TiO_2 contents, should not be covered also by this term. In the writer's opinion, kaersutite should not be regarded as a rare mineral, and it is anticipated that the brown or reddish brown amphibole in intrusive basic alkaline rocks will be of the kaersutite type.

Of those brown amphiboles referred to oxyhornblende, only two (Table 2, Analyses 9 and 10) possess the chemistry and optical properties consistent with oxyhornblende. Of the other amphiboles listed, those types with low birefringences and moderate TiO_2 contents are more akin to kaersutites with moderate degrees of oxidation. Two amphiboles (Analyses 3 and 5) occur in rocks where there is little possibility of the oxyhornblende reaction having occurred (cf. Hallimond, 1943, p. 70). It may be noted that a graphical representation of selected oxyhornblende compositions (Winchell, 1945, p. 45) indicated a tendency for many compositions to plot closest to a $Na\,Ca_2\,(Mg, Fe^{2+})_4\,(Al, Fe^{3+})_3\,Si_6O_{22}(OH)_2$ end-member.

OPTICAL PROPERTIES

The optical properties of analyzed amphiboles referred to oxyhornblende or kaersutite (Tables 2 and 3) suggest that the high birefringences (0.05–0.09) measured on brown amphiboles produced in laboratory heating experiments are not frequently attained in natural material. In particular, the frequency with which the optical properties (particularly $\gamma - \alpha = 0.068$) of the Linosa amphibole (Table 3, Analysis 12) have been quoted, would indicate that such properties have been considered typical of kaersutite. Chemically, the Linosa mineral is atypical when compared with other kaersutites, notably because of its relatively high Fe_2O_3/FeO ratio, a feature which prompted Washington to assign it to a distinct species, linosite. It is however akin in its optics and chemistry to an oxyhornblende.

The majority of analyzed kaersutites have $(\gamma - \alpha)$ in the range 0.030–0.032. Variation in the Fe_2O_3/FeO ratios apparently has little effect on the birefringence. However a kaersutite with the abnormally high birefringence of 0.083 ($2V_\alpha = 79$–80; TiO_2 7.55, Fe_2O_3 7.11, FeO 5.05 per cent) has recently been described by Aoki (1959, p. 279). This amphibole occurs as phenocrysts in a scoria. Other kaersutites from the same area with comparable TiO_2 contents but slightly lower degrees of oxidation possess distinctly lower birefringences (Table 3, Analyses 6 and 11).

Irrespective of the contents of TiO_2 or total iron, or degree of oxidation of the iron, a large number of kaersutites have $2V_\alpha = 80 \pm 2°$.

On the assumption that kaersutite is a titaniferous variety of oxyhornblende, many workers appear to have taken an upper limit of 5 per cent TiO_2 for oxyhornblende. Despite Fe_2O_3/FeO ratios close to or greater than unity, many amphiboles designated as oxyhornblende have $(\gamma-\alpha) = 0.019-0.026$ (Table 2), particularly those described by Kunitz (1930). These values do not differ markedly from the birefringence of many green hornblendes. Comparison of oxyhornblendes and kaersutites with comparable degrees of oxidation but differing TiO_2 contents indicates that the birefringence increases slightly with increasing TiO_2.

Not a great deal of optical data on barkevikite is available (Table 4). The birefringence is comparable with many of the oxyhornblendes listed in Table 2. With a higher content of $(FeO+Fe_2O_3)$ and often containing moderate amounts of TiO_2, barkevikite might be expected to possess higher refractive indices than kaersutite. There is need for much more data, which may reveal a distinction from kaersutite based on $2V_\alpha$ (cf. Benson, 1940, p. 289).

It is clear from the data listed in Tables 2–4 that identification of any particular amphibole under discussion cannot be confidently accomplished solely on the over-generalized optical data assigned to these minerals by various workers, since amphiboles referred to these species possess similar ranges of refractive indices, extinction angles and absorption colors. Much more data is necessary in order to define any significance in 2V. The difficulties of optical identification are particularly accentuated by the variation and possible interplay of titania, and degree of iron enrichment and oxidation. The use of low extinction angles as a guide to the degree of oxidation is misleading inasmuch as several kaersutites with low Fe_2O_3/FeO ratios have $\gamma:c$ values less than 10 degrees. It may also be questioned whether the size of $2V_\alpha$ is indicative of the degree of oxidation, inasmuch as certain oxyhornblendes with high $(\gamma-\alpha)$ have $2V_\alpha \sim 80°$.

Engel (1959, p. 974) has recently emphasized the lack of obvious correlations of optics and composition of hornblende, particularly in relation to optical properties/composition diagrams. This point is again emphasized, and here attention may be particularly directed to the limitations of optical properties/composition diagrams showing relationships between various amphibole end-members which themselves are titania-free.

The experimental work of Barnes (1930) demonstrated that the increase in the birefringence depends on the iron content of the amphibole, Fe-free or Fe-poor amphiboles showing little or no increase in $(\gamma-\alpha)$ on heating. Such amphiboles however would be expected to be rare in the normal range of igneous rock compositions. In the formation of an oxyhornblende with comparatively high birefringence, the γ index frequently increases at a greater rate than either the α or β indices. In view of several natural amphiboles with high degrees of oxidation failing to show strong birefringence, it would seem desirable to investigate carefully the products of controlled heating experiments to determine: (i) Whether differing Fe_2O_3/FeO ratios affect the birefringence. (ii) The nature of the structural changes involved in the production of increased birefringence at known temperatures under controlled oxidizing conditions.

Increased birefringence (>0.040) characterizes the oxyhornblendes from Taiwan and Colorado (Table 2, Analyses 9 and 10) and Linosa (Table 3, Analysis 12). These minerals occur in lavas and have high Fe_2O_3/FeO ratios. Parsons (1930, p. 31) has listed an amphibole from Bohemia (TiO_2 5.10, Fe_2O_3 6.96, FeO 2.34 per cent; $\gamma-\alpha=0.042$) whose chemistry and optics conform to the conventional view of an oxyhornblende. The strongly birefringent amphiboles described by Aoki (1959) appear to represent distinctive types inasmuch as they show comparatively little oxidation. Such amphiboles are worthy of more detailed investigation.

In terms of available analyses and detailed descriptions, it is seen that amphiboles conforming both in chemistry and optical properties (particularly high birefringence) to oxyhornblende, are comparatively uncommon. Pending analysis, it would seem desirable to limit the term oxyhornblende to brown calciferous amphiboles with $(\gamma-\alpha)>0.040$ and occurring in lavas. These amphiboles may frequently show strong evidence of magmatic reaction and resorption.

Other brown or reddish-brown amphiboles (particularly those occurring in undersaturated alkaline rocks) with $(\gamma-\alpha)<0.040$, may be conveniently referred to brown hornblendes, unless chemical data results in more precise nomenclature. However, as will be discussed in the occurrence of those minerals, the nature of the parent rock may serve to indicate whether kaersutite or barkevikite is present.

Occurrence

Arising from the results of amphibole heating experiments has been the concept that oxyhornblende (and kaersutite) is not strictly a primary mineral, but is an alteration product of common green hornblende (cf. Hatch, Wells and Wells, 1949, p. 66; Winchell, 1951, p. 439), "probably due to hot gases at a late magmatic stage" (Rogers, 1940, p. 828). In the San Juan lavas, Larsen *et al.* (1937, p. 905) considered that "in considerable part the change from common to basaltic hornblende . . . takes place after eruption and during the crystallization of the groundmass." The latter conclusion is substantiated by chemical and optical data on amphiboles within the one volcanic horizon.

If the term oxyhornblende is to carry with it genetic implications, it is clear that this term should not be used indiscriminately to include brown calciferous amphiboles occurring in intrusive rocks (e.g. many kaersutites) and which have been demonstrated to contain low to moderate Fe_2O_3 contents. Such amphiboles represent normal magmatic crystallization products.

In the case of brown amphiboles possessing comparatively high Fe_2O_3 contents relative to FeO and occurring in intrusive rocks, it is possible that in many cases their composition indicates a response to initially high Fe_2O_3/FeO ratios in the parent melts, crystallizing under conditions of high $[P]H_2O$ or high $[P]O_2$.

Where brown amphiboles with relatively high Fe_2O_3/FeO ratios, but not possessing abnormal birefringences, are present in lavas, then it is likely that oxidation attendant on extrusion has contributed to their chemistry. In lavas where exothermic surface reactions have resulted in temperatures in excess of 750–800° C., a true oxyhornblende may be locally developed. Those lavas in which a calciferous amphibole is a common ferromagnesian constituent and where there is evidence that such temperatures may be attained (Ingerson, 1955) are represented by andesitic and dacitic types.

Under the appropriate physical conditions it is highly likely that any common calcium-sodium amphibole (including kaersutite and barkevikite) may suffer subsequent conversion to a true oxyhornblende. It may be noted that although some kaersutites occurring as cognate xenocrysts in lavas and dyke rocks (Tomita, 1934; Benson, 1940) show varying degrees of resorption and alteration, nevertheless their degree of oxidation and their birefringence are comparable with similar amphiboles present in intrusives. It is inferred that in such cases oxidation took place at only moderate temperatures.

Kaersutite and barkevikite appear to have been recorded dominantly from undersaturated rocks or those members of a differentiation series, in which the principal undersaturated felsic minerals are respectively analcite and nepheline. The latter amphibole has been most frequently noted in nepheline-syenites.

Although the parent rocks vary in composition from highly basic to intermediate, the range of composition of the kaersutites is not very marked, being mainly restricted to limited replacement in the X group of Mg by Fe^{2+}. By contrast, barkevikite reveals a much higher degree of replacement of Mg by Fe^{2+}. This feature, together with a tendency for enrichment in Mn with respect to Fe^{2+} (cf. Goldschmidt, 1954, p. 628), indicates its precipitation at a relatively advanced stage of differentiation, the magma at that time possessing high Fe^{2+}/Mg ratios. The TiO_2-poor amphibole from the Wausau (Wisconsin) quartz-syenite, referred by Weidman (1907, p. 204) to barkevikite, is associated with fayalite and hedenbergite and is thus a member of an iron-enriched assemblage.

In undersaturated rocks the development of analcite rather than the pair albite-nepheline would be facilitated by high water pressures (cf. Turner and Verhoogen, 1960, p. 124). Such hydrous magmatic conditions would not be favorable to any degree of absolute iron enrichment. Where a calciferous amphibole is precipitated in such an environment, it would be expected to show limited replacement of Mg by Fe^{2+} *i.e.* kaersutite would be developed. It is frequently stated that the dark brown amphibole in teschenites is barkevikite, although there appears to be little analytical data to substantiate this claim. It is more likely that the amphibole in question is a kaersutite.

In a nepheline-bearing differentiation series varying in composition from basic to intermediate types, and carrying a brown calciferous amphibole, it is anticipated that a kaersutite would be present in the more basic varieties (*e.g.* the Mount Royal essexites) and that with progressive fractionation, the amphibole would change in its compostion towards a barkevikite. Such a trend is analogous to the trend magnesiohastingsite→ferrohastingsite, proposed by Billings (1928, p. 293), and is similar to the trend in hornblendes from certain calc-alkaline igneous series, *e.g.* the amphiboles from the Southern California bathylith (Larsen and Draisin, 1950, Table III).

The TiO_2-rich environment from which kaersutites have crystallized is illustrated by two examples of co-existing biotites containing 6–8 per cent TiO_2 (Table 3, Analyses 3 and 4). Some confirmation of the differing magmatic conditions under which kaersutite and barkevikite are precipitated may be furnished by a study with a particular differentiation series of the associated opaque oxides. Unfortunately there appears to be little analytical data on the associated opaques.

In rocks with barkevikite, earlier relatively anhydrous conditions would tend to favor the formation early in the differentiation series of a titano-magnetite composed dominantly of a Fe_3O_4-Fe_2TiO_4 solid solution and possessing $(FeO+TiO_2) > Fe_2O_3$. In analcite-bearing rocks with kaersutite, the opaque oxides would tend to be either a TiO_2-poor magnetite with $Fe_2O_3 > FeO$, or else a magnetite of the Fe_3O_4-$FeTiO_3$ solid solution type. Concentration of TiO_2 at the stage of kaersutite precipitation would be facilitated by the early separation of a TiO_2-poor magnetite.

Ultimate clarification of many of the proposals in the present discussion obviously must await more detailed studies on possible chemistry/optical properties relationships and response by the amphibole chemistry to varying conditions of differentiation. In particular, a great deal remains to be done concerning the effects of dominant cations (particularly Ti) on optics; in addition, *x*-ray diffraction studies represent a field where considerable information is needed.

ACKNOWLEDGMENTS

The writer is indebted to Professors C. E. Tilley, A. F. Buddington and H. H. Hess and to Dr. F. R. Boyd for their criticism of the manuscript.

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Manuscript received June 2, 1960.