Kaersutite from San Carlos, Arizona, with comments on the paragenesis of this mineral

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Summary. A 230 g kaersutite xenocryst from basalt at San Carlos, Arizona, has the composition SiO_2 40·10 %, TiO_2 4·44, Al_2O_3 14·53, Fe_2O_3 3·24, FeO 10·05, MnO 0·14, MgO 11·00, CaO 11·06, Na_2O 2·99, K_2O 1·62, H_2O+ 0·73, H_2O- 0·10; $D = 3·28$; α 1·680, β 1·700, γ 1·715; a 9·858 Å, b 18·063 Å, c 5·315 Å, β 105° 14'. Kaersutite occurring as xenocrysts in basic volcanic rocks and tuffs, and as a phase in garnet–pyroxene xenoliths from such rocks, is probably of upper mantle origin, and may be the important potassium-bearing phase in this region.

LAUSEN (1927) described the occurrence of peridotite xenoliths in a basalt flow on the San Carlos Indian Reservation, about 20 miles E. of Globe, Arizona. He also mentioned the occurrence of xeno-crysts of spinel, augite, and hornblende. When collecting at this locality in 1964 my attention was drawn to these xenocrysts, and I collected several. Among them was a nodule of hornblende about 5 cm in diameter and weighing 230 g. Part of the nodule had a smooth, polished, coal-black surface and part was crusted with scoriaceous basalt.

A thin section of this nodule showed that it was a granular aggregate of anhedral brown hornblende crystals up to 6 mm long, with a little inter-granular ilmenite. The properties of the hornblende are: α 1·680, β 1·700, γ 1·715; $2V_\alpha = 80°$; strongly pleochroic, α pale yellow, β reddish-brown, γ dark chestnut brown; D 3·28. Miss Peggy Hall of the U.S. Geological Survey has determined the unit cell dimensions, with the following results (in Å): a 9·858±0·001, b 18·063±0·002, c 5·315±0·001, β 105° 14'±1', cell volume 913·1±0·2 Å³.

The chemical analysis is given in table I, together with the analysis of a similar xenocryst from a volcanic breccia at Kakanui, New Zealand. The Kakanui analysis is a revised version of the analysis of this speci-men published previously (Mason, 1966a), an error having been dis-covered in the figures for TiO_2 and Al_2O_3. The analysed San Carlos material contained small inclusions of ilmenite; microprobe analyses showed that the TiO_2 content of this hornblende was essentially identical

with that of the Kakanui material, and the analysis has been corrected
by the subtraction of 1 % of ilmenite. The San Carlos and the Kakanui
hornblendes are very similar in composition, the only significant differ-
ence being the somewhat higher FeO and lower MgO percentages in the
San Carlos specimen. When recalculated in atoms per 24(O,OH), both
analyses agree well with the accepted formula for hornblende.

<div align="center">TABLE I</div>

	Chemical analysis			*Atoms per 24(O,OH)*			*Norm*	
	1	1a	2		1a	2		1a	2
SiO_2	39·63	40·10	40·42	Si	6·04	6·02	Or	—	3·8
TiO_2	4·93	4·44	4·43	Al^{iv}	1·96	1·98	Lc	7·5	6·5
Al_2O_3	14·36	14·53	13·90	Al^{vi}	0·63	0·45	Ne	13·7	13·9
Fe_2O_3	3·20	3·24	4·84	Ti	0·51	0·50	An	21·4	18·1
FeO	10·36	10·05	6·85	Fe^{3+}	0·37	0·54	Di	26·8	25·6
MnO	0·14	0·14	0·10	Fe^{2+}	1·27	0·85	Ol	16·7	15·2
MgO	10·90	11·00	12·95	Mg	2·48	2·88	Mt	4·7	7·0
CaO	10·93	11·06	10·28	Mn	0·02	0·01	Il	8·4	8·4
Na_2O	2·96	2·99	3·04	Ca	1·79	1·64			
K_2O	1·60	1·62	2·05	Na	0·88	0·88			
H_2O^+	0·72	0·73	0·96	K	0·31	0·39			
H_2O^-	0·10	0·10	0·00						
	99·83	100·00	99·97*						

<div align="center">* Includes F, 0·15.</div>

1. Hornblende, San Carlos, Arizona (J. Nelen, analyst).
1a. Anal. 1, recalculated to 100 after deducting 1·0 % ilmenite.
2. Hornblende, Kakanui, New Zealand (H. B. Wiik, analyst).

The norms corresponding to each analysis have also been calculated,
in order to draw attention to the possible petrogenetic significance of
this kind of hornblende. The norms show that the mineral composition
corresponds to a highly undersaturated alkali-rich rock, an olivine
nephelinite. From tables of rock analyses it is possible to find olivine
nephelinites that are almost identical in composition with these minerals.
The parent magma of the Kakanui volcanic breccia is a melanephelinite
(Dickey, 1968), and nephelinites are common host rocks for peridotite
nodules. This suggests that these xenocrystal hornblendes may represent
the high-pressure solid equivalent of a nephelinite magma.

<div align="center">*Similar hornblendes from other occurrences*</div>

The remarkable similarity between the San Carlos and the Kakanui
hornblendes stimulated a search—in the literature, in museum collec-

tions, and in the field—for comparable material, with the following results:

Xenocrysts in basic volcanic rocks and tuffs. Kakanui, New Zealand; San Carlos, Arizona; Bulli, New South Wales; Sauclieres, Aveyron, France; Eifel, Germany; Kilimanjaro, East Africa; Alnö, Sweden; Linosa, Italy; Lake Balaton, Hungary; Bilin, Bohemia; Monte Somma, Italy; East Fife, Scotland; Fehring, Styria, Austria; Kosakov, Bohemia.

As a primary constituent of basic (often feldspathoidal) igneous rocks. Mt. Alarm, New Zealand, in gabbro pegmatite; Orkney Islands, in hornblende monchiquite; Skaergaard, Greenland, in camptonite; Kola, U.S.S.R., in monchiquite; Grosspriessen, Bohemia, in tephrite; Kaersut, Greenland, in gabbro pegmatite; localities in Japan, Korea, and Sakhalin, in monzonite, teschenite, trachybasalt, trachyandesite, and gabbro; Dunedin district, New Zealand, in trachybasalt and kaiwekite; Canary Islands, in essexite; near Boulder Dam, Arizona, in camptonite; Mount Royal, Montreal, Canada, in essexite; St. Pauls Rocks, in mylonitized alkaline metagabbro; Mont-Doré, Auvergne, France, in trachyandesite; Lugar, Scotland, in teschenite.

In xenoliths, associated with omphacitic or tschermakitic pyroxene and sometimes pyrope garnet, in basic igneous rocks. Delegate, New South Wales; Salt Lake Crater, Oahu, Hawaii; Kakanui, New Zealand.

Most of these occurrences are recorded, many with analyses, in Wilkinson (1961), Aoki (1963), and Deer, Howie, and Zussman (1963).

It can be difficult to tell, from published descriptions and even at times from hand specimens, whether a specific occurrence should be classed as xenocrystal or as a primary constituent. For example, the numerous localities listed by Aoki (1963) are all included as primary hornblende; most of these occurrences are described as phenocrysts, but some of these may well be xenocrysts.

Some of the specimens available in the U.S. National Museum collections were analysed with the electron-beam microprobe, using the analysed Kakanui and San Carlos hornblendes as standards. The results are given in table II. Since the microprobe does not discriminate ferrous and ferric iron, all Fe is reported as FeO, and the analysed San Carlos and Kakanui specimens have been recalculated on this basis. The most significant feature of these analyses is their remarkable uniformity. The principal variables are iron and magnesium, which as might be expected show an inverse relation.

In the literature hornblendes of this type have been variously termed oxyhornblende, kaersutite, basaltic hornblende, barkevikite, hastingsite,

pargasite, syntagmatite, and other more obscure names. Wilkinson (1961) pointed out that they can all be accommodated in a pargasite–ferropargasite series, with the general formula $NaCa_2(Mg,Fe^2)_4Al^{vi}$ $Al_2^{iv}Si_6O_{22}(OH)_2$; in pargasite $Mg > Fe^2$, in ferropargasite $Fe^2 > Mg$; Al^{vi} may be partly or completely replaced by Ti and Fe^3 (barkevikite is essentially a ferropargasite with some Fe^3); some of the OH may be replaced by O and occasionally in part by F.

TABLE II. Analyses of kaersutite (nos. 3 and 7 from table I, remainder electron-probe analyses by the author)

	1	2	3	4	5	6	7	8
SiO_2	41·9	40·0	40·42	40·0	40·6	40·6	40·10	40·6
TiO_2	4·2	4·4	4·43	4·3	5·1	3·5	4·44	5·1
Al_2O_3	13·6	14·2	13·90	13·6	14·2	13·7	14·53	13·7
FeO*	7·9	9·7	10·2	11·0	11·3	11·3	13·0	13·9
MgO	15·1	14·6	12·95	13·4	12·4	12·7	11·00	10·2
CaO	10·3	11·7	10·28	10·7	10·3	11·7	11·06	9·7
Na_2O	3·9	3·3	3·04	3·1	3·3	2·9	2·99	3·6
K_2O	1·20	1·30	2·05	1·70	1·45	1·35	1·62	1·35

* All Fe as FeO.

1. In pyroxenite xenolith, Salt Lake Crater, Oahu, Hawaii.
2. Xenocryst in basaltic rock, Bulli, N.S.W., Australia.
3. Xenocryst in tuff, Kakanui, New Zealand.
4. Xenocryst in basaltic rock, Sauclieres, Aveyron, France.
5. In eclogite xenolith, Kakanui, New Zealand.
6. In alkaline metagabbro, St. Pauls Rocks.
7. Xenocryst in basaltic rock, San Carlos, Arizona.
8. In eclogite xenolith, Kakanui, New Zealand.

The following features of the published analyses are significant: Al^{iv} is always close to the theoretical limit of 2; Al^{iv} much in excess of 2 suggests the possibility of the Al_2O_3 percentage in the analysis being erroneously high. Fe^{3+} is generally less than 1, except in specimens that have probably suffered deuteric oxidation. Mg and Fe^{2+}, as might be predicted, vary inversely; maximum MgO is about 15 %, minimum FeO* about 8 % (Salt Lake Crater); if MgO is less than about 9 %, the mineral is Fe^{2+}-dominant and is a ferropargasite; Kempe (1968) has described a titanium-rich ferropargasite (9·1 % TiO_2, 7·2 % MgO) from minverite in Cornwall. Ca is often somewhat less than 2 (CaO = 12·4 % $\approx$ Ca = 2). Na + K is often greater than 1; these amphiboles are characterized by a relatively high potassium content. OH is usually considerably less than 2, often about 1, although the difficulty in expelling combined water from these hornblendes makes the analyses somewhat uncertain on this

point. Ti ranges up to about 1 or a little more; the maximum recorded TiO_2, 10·33 %, in a Kaersut specimen, corresponds to 1·05 Ti in the formula.

The last point brings up the question of the use of the name kaersutite for these amphiboles. Aoki (1963) considered an amphibole from a trachyte with 4·36 % TiO_2 (0·49 Ti) as not a typical kaersutite, and referred to it as 'kaersutitic hornblende'; he apparently set a lower limit of titanium in kaersutite as 0·5 Ti. Wilkinson (1961) wrote: '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 hornblendes with 3–5 per cent TiO_2 are probably not uncommon, particularly in basic alkaline rocks.' The analyses in this paper confirm Wilkinson's suggestion, and it is clear that any lower limit of titanium for kaersutite must be an arbitrary one. The subcommittee on amphibole nomenclature of the International Mineralogical Association will presumably consider this problem.

Discussion

Oxburgh (1964) has cogently argued for the presence of amphibole in the upper mantle. He pointed out that none of the generally accepted upper mantle phases (olivine, spinel, orthopyroxene, clinopyroxene, pyropic garnet) contains more than trace amounts of potassium, so that to account for the potassium content of mantle-derived basalts some amount of a potassium-bearing phase must be present. He concluded that the only probable phase would be an amphibole or a phlogopitic mica, and rejected the latter because it would give an improbable K:Na ratio for a resulting basaltic melt. He therefore adopted amphibole as the significant potassium-bearing phase in the upper mantle, without, however, specifying the particular type of amphibole.

The data reported here strongly suggest that upper mantle amphibole is probably a kaersutitic hornblende. This variety of hornblende is usually richer in potassium than other amphiboles, and its mode of occurrence, as xenocrysts and as a phase in eclogitic rocks, indicates a deep-seated source. Laboratory studies have shown that the presence of sodium and aluminium in the amphibole structure greatly increases its thermal stability. Boyd (1959) made synthetic pargasite and found that it was stable up to 1040° C at 1000 bars vapour pressure, whereas under the same conditions tremolite decomposed at 835° C. The results of these studies are paralleled by the geological occurrence of the natural amphiboles discussed in this paper. They are evidently stable at the

temperatures of basaltic magmas, provided oxygen fugacity is low, and at least in some occurrences—those associated with omphacitic or tschermakitic pyroxenes and pyropic garnets—they have probably crystallized at rather high pressures.

Recently Green and Ringwood (1968) have shown experimentally that the crystalline residuum from the partial melting of a hydrous basalt at 30 to 40 km depth under conditions $P_{H_2O} < P_{load}$ consists largely of hornblende closely similar in composition to that described here.

The high titanium content of kaersutitic hornblendes may also have some significance. Recently (Mason, 1966b), in comparing the probable compositions of mantle and crust, I commented on the notable enrichment of titanium in the crust, almost as great as that shown by potassium, and remarked that there was no apparent geochemical reason for this enrichment, since titanium might be expected to remain in the mantle as $FeTiO_3$ or in substitution in the pyroxene structure. Possibly, therefore, the crystallization of kaersutitic hornblende in the upper mantle provides a mechanism for the concurrent concentration of both potassium and titanium. In this connection it is also noteworthy that titanium is enriched in oceanic versus circumoceanic basalts (Chayes, 1965); the median TiO_2 value for oceanic basalts is 2·80 %, whereas for circumoceanic basalts it is 1·05 %, with practically no overlap in the ranges of values for each group. This also suggests a source of material for the oceanic basalts that is enriched in titanium.

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