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STABILITY RELATION OF KAERSUTITE

by

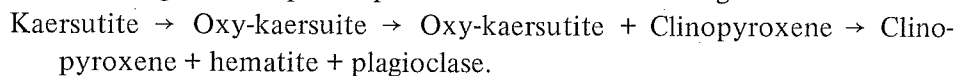
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(with 3 Tables and 2 Text-figures)

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Abstract

Thermal experiments under atmospheric and elevated pressures have been made on the samples of kaersutite obtained from mineral breccia of Kakanui, New Zealand and trachybasalts of Iki Island in order to determine its stability relation. Heating at atmospheric pressure shows the following reaction:



It is noticed that the oxy-kaersutite consists of crystal lattices of both the clino-amphibole and the clinopyroxene on the submicroscopic scale, though the crystal as the whole retains the homogeneous kaersutite outline under the microscope. High pressure experiments were carried out in the pressure range from 5 to 40 Kb, and temperature range from 600°C to 1250°C by the piston-cylinder and the tetrahedral-anvil type apparatus, and stability fields of kaersutite itself and other mineral assemblages were determined. Perovskite is separated at pressures higher than 10 Kb, and garnet appears at pressures higher than 20 Kb together with clinopyroxene and perovskite. Kaersutite has fairly wide field of stability up to 23 Kb at temperatures less than 700°C, i.e., it can be stable not only in the lower crust, but also in the upper mantle. Therefore it is possible that kaersutite in the mineral breccia of Kakanui was also derived from the upper mantle, associated with Ti-poor clinopyroxene and garnet, as indicated by the present experiments. Kaersutite should be considered as an important phase which may contain high titanium and some potassium in the upper mantle like phlogopite.

Introduction

Kaersutite is a variety of pargasite with more than 0.50 Ti in a unit formula of amphibole: $\text{NaCa}_2\text{M}_5\text{Si}_8\text{O}_{22}(\text{OH})_2$. Formerly kaersutite has been found

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mainly as a phenocrystic mineral in the alkalic basaltic rocks or related rocks. However, recent studies have indicated that the mineral is also widely present as constituent mineral of mafic or ultramafic inclusions in basaltic rocks.

In 1965 one of the authors (Yagi) visited Kakanui, New Zealand during the International Symposium on Volcanology field trip, and collected many samples of inclusions from the volcanic breccia at this celebrated locality. The mineral association of the inclusions, kaersutite-clinopyroxene-garnet-magnetite, attracted his attention for it suggests, as does the chemical composition, that they may have been derived from the upper mantle. If kaersutite is one of the original mineral constituents of the inclusions it would indicate that kaersutite is stable at pressures much higher than hitherto believed.

In the authors' experiments on titanium-bearing pyroxenes, it was noticed that titan-bearing pyroxenes are not stable at high pressure, dissociating into less titaniferous pyroxene and perovskite. Since the other major constituents of the upper mantle, olivine, garnet and spinel, do not contain appreciable amounts of titanium it may occur mainly in amphibole under such conditions.

Therefore, from these view points experiments on the stability relation of kaersutite under conditions of high temperatures and pressures have been made.

Samples of kaersutite

The sample used for the present experiments are mostly kaersutite from Kakanui. For comparison some runs were made on kaersutites from Iki Island, Japan, which were given to the authors by Prof. K. Aoki.

Kaersutite forms an important constituent of ultramafic inclusions in the mineral breccia at Kakanui, where it is associated with garnet, clinopyroxene and magnetite. According to Mason (1966) they have the following compositions:

clinopyroxene	diopside	$\text{CaMgSi}_2\text{O}_6$	62 mol%
	Mg-Tschermak's molecule		
		$\text{MgAl}_2\text{SiO}_6$	18
	hedenbergite	$\text{CaFeSi}_2\text{O}_6$	11
	acmite	$\text{NaFeSi}_2\text{O}_6$	9
garnet	pyrope		66.4 mol%
	almandine		20.0
	grossular		10.9
	andradite		2.1
	spessartine		0.6

It is worthy of note that clinopyroxene is fairly rich in Mg-Tschermak's molecule and poor in TiO_2 , as low as 0.74%, and that garnet is very high in pyrope molecule. These features indicate that these minerals were formed under high pressures.

Kaersutite usually occurs as irregular crystals enclosed in the matrix. Less commonly it forms rounded, well-polished crystals up to 5 cm in diameter due to the friction in the mineral breccia. Optical properties and unit cell dimensions determined by x-ray data are as follows (Mason, 1966):

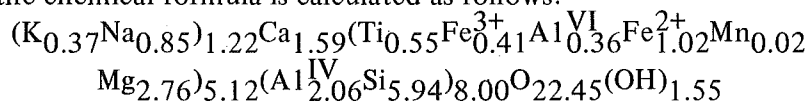
$$\begin{array}{ll} \alpha = 1.676 & \text{pleochroism very strong;} \\ \beta = 1.687 & \text{X ----- pale yellow} \\ \gamma = 1.695 & \text{Y = Z -- deep brown} \\ a = 9.870 \text{ \AA} & b = 18.058 \text{ \AA} \quad c = 5.307 \text{ \AA} \quad \beta = 105^\circ.12' \end{array}$$

Table 1. Chemical composition of kaersutite from Kakanui, New Zealand

	Wt %	Atomic ratio	
SiO_2	40.09	Si	5.94
TiO_2	4.97	Al^{IV}	2.06
Al_2O_3	13.88	Al^{VI}	0.36
Fe_2O_3	3.71	Ti	0.55
FeO	8.29	Fe^{3+}	0.41
MnO	0.11	Fe^{2+}	1.02
MgO	12.44	Mn	0.02
CaO	10.02	Mg	2.76
Na_2O	2.95	Ca	1.59
K_2O	1.94	Na	0.85
$\text{H}_2\text{O} +$	1.57	K	0.37
$\text{H}_2\text{O} -$	0.06	OH	1.55
F	n.d.	O	22.45
Total	100.03		

Analyst K. Aoki

The chemical composition is given in Table 1, together with atomic ratios from which the chemical formula is calculated as follows:



The crystals were first broken into small cleavage flakes, then selected carefully under the binocular microscope to eliminate contamination of grains of clinopyroxene. Pure samples thus obtained were used for the experiments. The Iki kaersutites were separated from the trachybasalts from Sofure, Iki Island (Aoki, 1959), and were purified in the same way as the Kakanui kaersutite.

Experiments under atmospheric pressure

Preliminary experiments showed that there was little difference in temperatures when using air or nitrogen stream. Therefore the experiments were done in a flat lying electric furnace in air from 600°C up to 1300°C. The results are given in Table 2.

Table 2. Experimental results of the runs at atmospheric pressure

Temperature (°C)	Time (Hrs)	Results	Indices of kaersutite	
			α	γ
500	48	Ka	1.678	1.697
600	48	Oxy-Ka	1.703	1.732
700	48	Oxt-Ka	1.703	1.732
800	48	Oxy-Ka+small amt Px	1.703	1.732
800	144	Oxy-Ka+small amt Px	1.703	1.732
900	24	Oxy-Ka+small amt Px	1.712	1.742
900	48	Oxy-Ka+small amt Px	1.712	1.742
940	48	Oxy-Ka+small amt Px	1.712	1.742
940	170	Oxy-Ka+Px	1.712	1.742
980	48	Oxy-Ka+Px	1.712	1.742
1000	40	Oxy-Ka+Px		
1060	30	Oxy-Ka+Px		
1060	48	Px+Hm+Pl		
1100	48	Px+Hm+Pl		
1170	48	Px+Hm+Pl		
1170	175	Px+Hm+Pl+Mt?		
1180	24	Px+Hm+Pl		
1180	175	Px+Hm? +Pl+Mt		
1190	2	Px+Mt+Gl		
1190	4	Px+Ol+Mt+Gl		
1190	144	Ol+Mt+Px+Ru+Gl		
1200	120	Ol+Mt+Ru+Gl		
1210	24	Mt+Ol+Gl		
1250	24	Mt+Ol+Gl		

Ka: kaersutite, Oxy-ka: oxy-kaersutite, Px: clinopyroxene, Ol: olivine, Pl: plagioclase, Hm: hematite, Mt: magnetite, Ru: rutile, Gl: glass

At about 600°C kaersutite becomes oxy-kaersutite, which is characterized by much stronger pleochroism and smaller extinction angle. X-ray patterns of single crystal show that the oxy-kaersutite obtained by heating at temperatures higher than 800°C consists of crystal lattices of clino-amphibole, associated with very small amounts of clinopyroxene. However, the crystals as seen under the microscope, retain apparently the characteristic kaersutite optics and outline, since they consist of submicroscopic intergrowth of clino-amphibole and clinopyroxene lattices as suggested by Yamaguchi from his thermal experiments on some hornblendes (Yamaguchi, 1969).

At 940° C oxy-kaersutite begins to decompose and a small amount of clinopyroxene is now recognized under the microscope. At 1060°C oxy-kaersutite is completely decomposed to form crystalline aggregates of clinopyroxene, hematite and plagioclase and oxy-kaersutite can no longer be detected either microscopically or by x-ray powder pattern. This change corresponds to the opacitization, commonly observed in natural hornblendes in volcanic rocks. With further increase in temperature, the aggregates begin to melt, and become aggregates of clinopyroxene, olivine, magnetite, rutile and glass at about 1190°C. The formation of magnetite instead of hematite is due to the reduction of ferric iron with increasing temperature (Yagi, 1966). Probably clinopyroxene melts incongruently to form olivine and liquid, separating titanium as rutile.

Experiments under high pressures

High pressure experiments were done by a single stage piston-cylinder apparatus in the Department of Geology and Mineralogy, Hokkaido University for runs at pressure lower than 35 Kb and by a tetrahedral anvil in the Institute of Solid State Physics, University of Tokyo for runs at pressure higher than 35 Kb. Well-ground samples were contained in Pt-capsules, which were then folded and sealed. No water was added. First the pressure was raised to desired value, and then the temperature was raised. It is estimated from the authors' experience that the sealing was complete and that the content of the capsule formed a closed system with water vapor derived from the sample. The P_{H_2O} is unknown, however, it is probably less than the load pressure.

A chromel-alumel thermocouple was used to measure temperature for runs below 1000°C and Pt-Pt 13% Rh thermocouple for runs above 1000°C. No correction was made for the effect of pressure on the e.m.f. of the thermocouples.

At the end of the runs, the samples were quenched to room temperature by cutting off the power to the furnace and then the pressure was gradually

Table 3. Experimental results of the runs at high pressures

Pressure (Kb)	Temperature (°C)	Time (Hrs)	Results
5	1120	5	Px+Ol+Mt
5	1200	3	Px+Ol+Mt+G1
8	1150	72	Px+Ol+Mt+G1
10	850	6	Ka
10	950	5	Ka+Px
10	1050	8	Ka+Px
10	1250	4.3	Px+Ol+Mt+G1
13	1100	5	Px+Ol+Pv
13	1150	5	Px+Ol+Pv+G1
13	1200	3	Px+Ol+Mt+G1
15	600	8	Ka
15	800	5	Ka
15	1000	6	Ka+Px+Pv
15	1050	3	Px+Ol? +Pv
20	650	12	Ka
20	700	153.5	Ka
20	800	10	Ka+Px+Pv
20	825	69.5	Ka+Px+Pv
20	900	5	Ka+Px+Pv
20	1000	6	Ka+Px+Pv
20	1025	47	Ka+Px+Pv
20	1100	5	Px+Ol+Pv
21	1030	47	Ka+Px+Pv
22	1125	47.5	Px+Ga+Pv+Ru
22.5	1100	4.5	Px+Ga+Pv
23	650	12	Ka
25	650	12.3	Px+Ga+Pv
25	1100	6	Px+Ga+Pv
26	1000	5	Px+Ga+Pv
28	800	10	Px+Ga+Pv
32	600	8	Px+Ga? +Pv?
35	900	1	Px+Ga+Pv
35	1000	0.5	Px+Ga+Pv
35	1050	0.7	Px+Ga+Pv
40	1000	0.5	Px+Ga+Pv
40	1100	0.5	Px+Ga+Pv
40	1200	0.3	Px+Ga+Pv

Ka: kaersutite, Px: clinopyroxene, Ol: olivine, Mt: magnetite, Pv: perovskite, Ga: garnet, Ru: rutile, Gl: glass.

lowered. The phases obtained in the run were identified by petrographic microscope or X-ray powder diffractometer, or both. The duration of the run was usually less than 10 hrs, however, much longer runs were also made in

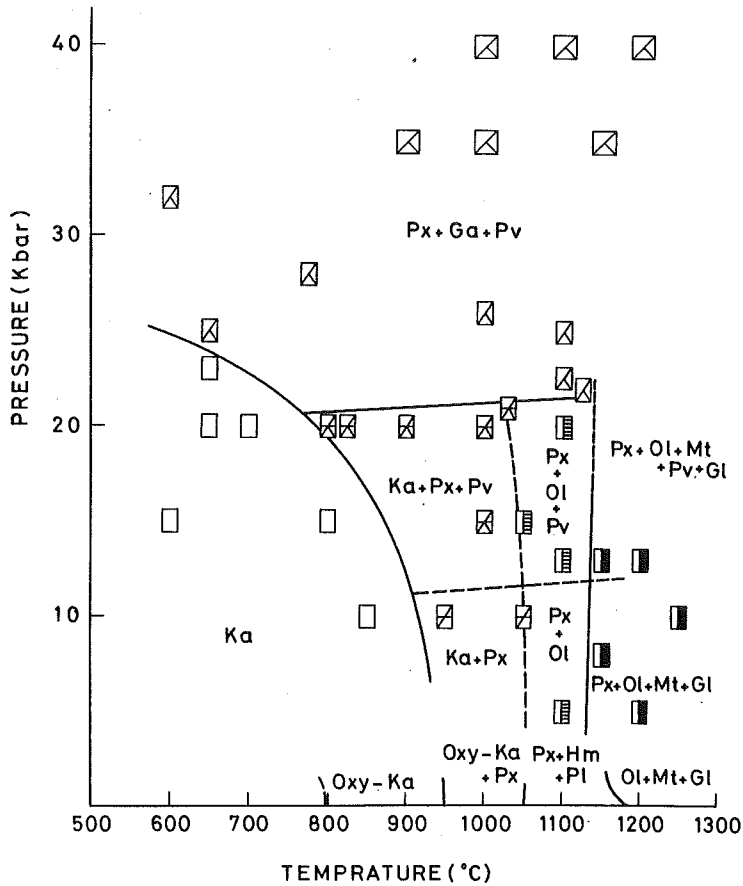


Fig. 1 The stability field of kaersutite.

Ka: kaersutite, Oxy-Ka: oxy-kaersutite, Px: clinopyroxene, Pv: perovskite, Ol: olivine, Hm: hematite, Pl: plagioclase, Mt: magnetite, Ru: rutile, Ga: garnet, Gl: glass.

order to ensure the attainment of equilibria. Nevertheless sometimes kaersutite remains as metastable phase. When the amount of kaersutite decreases markedly among the products of some runs at different temperatures, it is assumed that kaersutite is no longer stable at higher temperature. From this view point the mineral assemblage was determined. The results are given in Table 3 and are graphically shown in Fig. 1.

Experimental results

The change of kaersutite to oxy-kaersutite is very noticeable in the experiments under atmospheric pressure in air due to marked increase in both refringence and birefringence, decrease in extinction angle and also increase in the intensity of pleochroism. In the high pressure experiments, however, this change is not so distinct. There is only slight change of optical properties, as will be mentioned later, and therefore no boundary between kaersutite and oxy-kaersutite can be drawn in the higher pressure ranges. Kaersutite is stable up to 23 Kb at 650°C, and at higher temperatures the breakdown pressure of kaersutite is gradually decreased with increasing temperature: i.e. at 10 Kb, kaersutite dissociates into kaersutite + clinopyroxene at about 900°C; at 15 Kb kaersutite dissociates into kaersutite + clinopyroxene + perovskite at about 770°C. At temperatures and pressures lower than the above-mentioned values, kaersutite or oxy-kaersutite is the stable phase.

At pressures higher than 20 Kb at 770°C, or 23 Kb at 650°C, kaersutite or oxy-kaersutite is no longer stable, and is replaced by the assemblage clinopyroxene + garnet + perovskite. Garnet forms almost colorless, isotropic and rounded crystals enclosing minute grains of perovskite. Though the composition could not be measured, it is probably rich in both almandine and pyrope molecules when the composition of original kaersutite is taken into consideration. The appearance of garnet is at 22.5 Kb and 1100°C, and at 22 Kb and 1125°C. It is estimated that the lower boundary of the garnet-bearing assemblage is slightly inclined to the temperature axis.

In the previous experiments on titanium-bearing synthetic clinopyroxenes, it was noticed that perovskite is exsolved at pressures higher than 10 Kb (Yagi and Onuma, 1967). In the present experiments perovskite is also observed as extremely minute rounded grains always enclosed in clinopyroxenes, but never in oxy-kaersutite.

It should be mentioned here that kaersutite at higher temperatures and pressures is different from the original kaersutite, although the name "kaersutite" is always used here. This difference is evident from the difference in optic properties, though small, and the shift of some of the peaks in x-ray powder diffraction patterns.

The refractive indices of kaersutite decrease slightly with increase in pressure applied as shown below:

	γ
original kaersutite	1.695
13 Kb	1.688
20 Kb	1.680
23 Kb	1.687

Contrary to the experiments under atmospheric pressure in air, no increase in indices is noticed with the increase of temperature in high pressure experiments. Probably this is due to the absence of oxidation within the capsule.

Complete disappearance of kaersutite is observed at about 1050°C at both 10 Kb and 15 Kb, indicating that the reaction is not so sensitive to pressure. Above this temperature, olivine is observed together with clinopyroxene and perovskite. It forms beautiful euhedral crystals enclosed in pale brownish glass in the runs higher than 1150°C.

Kushiro in his experiment on the system forsterite-diopside-silica found that the incongruent melting of pyroxene solid solutions along the join En-Di does not exist at 20 Kb (Kushiro 1969). It is also known that enstatite ceases to melt incongruently at pressures less than 3 Kb (Boyd, *et al.* 1964). Therefore the appearance of olivine in the present experiments should be considered as the product of direct dissociation of kaersutite.

At pressure higher than 20 Kb very small amounts of a fibrous mineral are observed in the assemblage of clinopyroxene + garnet + perovskite, but it cannot be identified by either microscope or x-ray. Since the original kaersutite has fairly high potassium content, and none of the other minerals can contain this potassium, it seems likely that this mineral may be phlogopite, which has fairly wide field of stability as shown by Kushiro *et al.* (1967).

Rarely nice crystals of rutile are present in addition to perovskite, especially in the runs on kaersutite from Ike Island.

Genetic consideration

The results of the present experiments are compared in Fig. 2 with the results obtained on hornblende from tonalite by Lambert and Wyllie (1968) and on hornblende from gabbro by Nishikawa *et al.* (1971). Although there is some discrepancy in the details of the relations, fairly good agreement is observed in regards to the stability range of amphiboles and their reaction fields in general. It seems likely that the main difference may be ascribed to the difference in composition of the samples used for the experiments.

The results indicate that hornblendes can be stable up to 23–25 Kb at temperatures as low as 600°–700°C, i.e. hornblende can be stable not only in the lower crust, but also in the upper mantle. It is especially noteworthy that kaersutite is associated in the present experiments with Ti-poor clinopyroxene, garnet and perovskite.

In the natural occurrence at Kakanui, no perovskite is found, but titaniferous magnetite or ilmenite in the mineral breccia may substitute for perovskite produced in the experiments. The association of these minerals in

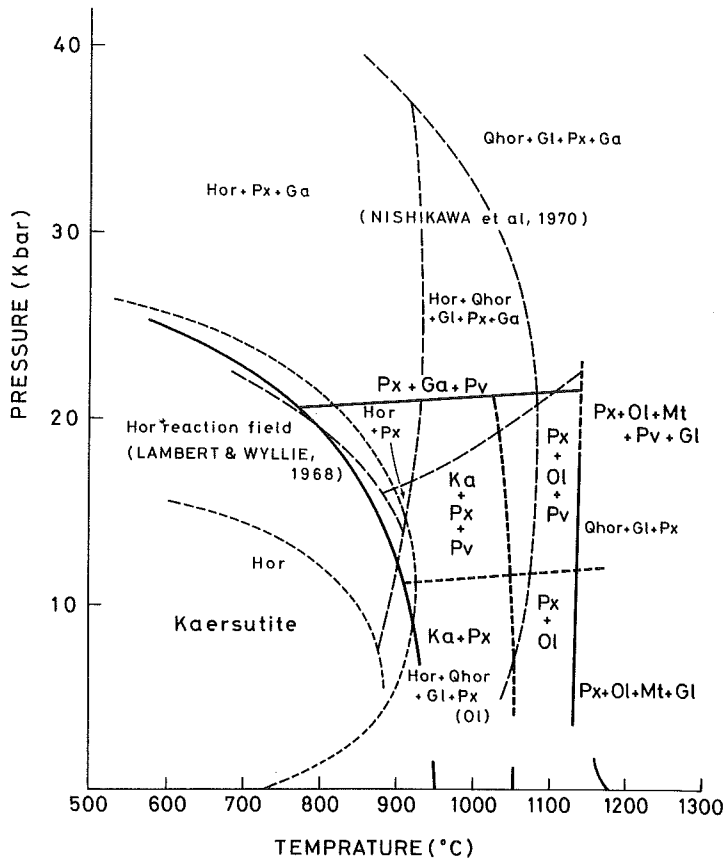


Fig. 2 Stability field of kaersutite compared with that of hornblende by Lambert and Wyllie (1968) and by Nishikawa *et al.* (1971).

Hor: hornblende, Qhor: quench hornblende. Other legends are the same as in Fig. 1.

the mineral breccia at Kakanui does not necessarily mean that they were derived from the same depth within the earth or of same origin. Nevertheless the present experiments indicate that the kaersutite may have been derived from the upper mantle. Therefore kaersutite should be considered as an important phase which may contain high titanium and some potassium in the upper mantle, as is the case with phlogopite.

Acknowledgment

Although the present work has been done mostly at Hokkaido University, some of the experiments at high pressures were also made at Institute of Solid State Physics, University of Tokyo with the kind co-operation of Prof. S. Akimoto. Chemical analysis of the kaersutite from Kakanui was made by Prof. K. Aoki of Tohoku University. He also provided the samples of kaersutites from Iki Island. The diagrams of the present paper were prepared by Mr. S. Terada of Hokkaido University. To all of them the authors' thanks are due. The authors are grateful to Dr. J.G.Souther of the Geological Survey of Canada for a critical reading of this paper.

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