

# CHEMICAL COMPOSITIONS OF HYPERSTHENE AND PIGEONITE IN EQUILIBRIUM IN MAGMA

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## ABSTRACT

Hypersthene and pigeonite occurring as microphenocrysts in the groundmass of hypersthene-olivine andesite from Hakone volcano were analyzed. They are almost identical in composition except that the pigeonite contains 4.06% CaO whereas the hypersthene contains 2.67% CaO. The mode of occurrence of these pyroxenes indicates that this difference in CaO content corresponds to the difference in composition across the inversion interval between the two pyroxenes in the magma. The unusually high CaO content of the hypersthene is discussed.

## INTRODUCTION

Microphenocrysts of hypersthene and pigeonite, both from 0.1 to 0.7 mm. long, occur in basic andesite and basalt from Izu, Hakone, and other regions of northeastern Japan. They are characteristic of rocks free from augite phenocrysts (hypersthene andesite and hypersthene-olivine andesite), and are regarded by Kuno (1950*b*) as formed in a magma from which phenocrysts of hypersthene were separated prior to those of augite. The sequence of crystallization of pyroxenic phases in these rocks is as follows:

Intratelluric stage	During or just before extrusion	Effusive stage
Hypersthene phenocrysts	→ Hypersthene and/or pigeonite micro- phenocrysts	→ Small crystals of subcalcic au- gite (pigeonitic augite of Kuno)

This sequence is seen also in pyroxenes of many dolerite and gabbro intrusions. The orthopyroxene occurring in the lower part of the dolerite sheets and the pigeonite (the early pigeonite of Walker and Poldervaart, 1949) in the upper part of the same sheets correspond respectively to the microphenocrystic hypersthene and pigeonite in the volcanic rocks. The pigeonite is interpreted as formed in place of the orthopyroxene when the magma crossed the clinopyroxene-orthopyroxene inversion curves (Hess, 1941; Edwards, 1942; Walker and Poldervaart, 1949; Kuno, 1950*b*; Poldervaart and Hess, 1951). The relation is illustrated by

Figs. 1 and 2. During the crystallization of magma, the orthopyroxene changes its composition until point *a* of both figures is attained. At this point, the orthopyroxene changes to pigeonite of the composition represented by point *b*. The distance between points *a* and *b*, namely the inversion interval, can be determined by analyzing the two pyroxenes associated in a single rock.

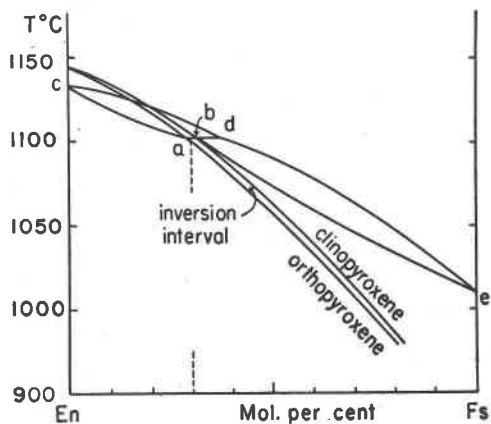


FIG. 1. Binary diagram En-Fs showing solidus (*c-a-b-e*) and liquidus (*c-d-e*) curves of crystallizing magma postulated by Kuno (1950*b*) and inversion curves given by Bowen and Schairer (1935). The inversion interval is shown schematically.

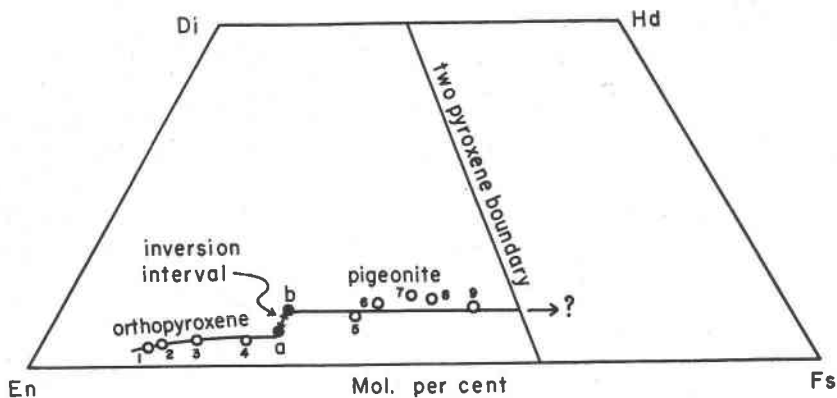


FIG. 2. The lower part of ternary diagram Wo-En-Fs showing the course of crystallization of orthopyroxene and pigeonite (after Poldervaart and Hess, 1951). Selected analyses of pyroxenes are plotted in the diagram. 1 is the orthopyroxene from Great Dike, South Africa, and 2-4 are those from Stillwater Complex, Montana (all unpublished analyses of Hess). *a* and *b* are orthopyroxene and pigeonite, respectively, described in this paper. 5 is pigeonite from Hakone (unpublished analysis of Kuno). 6, 7, 8, and 9 are pigeonites Nos. 41, 43, 42, and 44, respectively, in the table of analyses given by Hess (1949).

The separation of the two pyroxenes in dolerite and gabbro is extremely difficult, if not impossible, because part or all of the pigeonite has inverted again to orthopyroxene with exsolved blebs or plates of augite upon further cooling. However, the microphenocrystic pyroxenes can be separated from their mother rocks.

The microphenocrystic pyroxenes were separated by one of the writers (H. K.). The materials were analyzed by the other writer (K. N.). The former is responsible for the optical examination and interpretation.

#### MODE OF OCCURRENCE OF THE PYROXENES

The hypersthene and pigeonite microphenocrysts occur either independently in different rocks or side by side in the same rock. In the latter case, some of the crystals form parallel intergrowths, the pigeonite being always outside the hypersthene.

At the base of the lava flow exposed on the eastern caldera wall of Hakone volcano, just below the horizon of basalt lava and agglomerate, there are several successive flows of basaltic andesite.\* These flows are mostly scoriaceous and blocky, and are nearly identical to each other in mineral composition. The phenocrysts are plagioclase, olivine, and hypersthene. The microphenocrysts of hypersthene and/or pigeonite are set in a fine-grained groundmass consisting of plagioclase, clinopyroxene with  $2V$  about  $40^\circ$  in the  $\{010\}$  plane, magnetite, glass, and cristobalite.

Two specimens were collected from a single lava flow exposed at an elevation of 450 m. on the northeastern wall of a valley named Tengu-zawa, southeast of Hatazyuku. One of them contains microphenocrysts of hypersthene alone whose optical properties are shown in No. 1 of Table 1. The other contains microphenocrysts of both hypersthene and pigeonite with optical properties shown in No. 2*a* and No. 2*b*, respectively.

A lava exposed at an elevation of 440 m. on the southwestern wall of a small valley named Usugoya-zawa, about 900 m. west of the former locality, is probably a continuation of the same flow. A specimen from Usugoya-zawa contains microphenocrysts of pigeonite alone whose optical properties are shown in No. 3 of Table 1.

Table 1 shows almost complete agreement between the optical properties of the hypersthene Nos. 1 and 2*a* and between those of the pigeonites Nos. 2*b* and 3. This indicates the close proximity of their compositions.

It may be inferred that during the crystallization of these microphenocrysts the temperature of the magma was very near the inversion

\* Lettered  $O_2$  in the geologic map by Kuno (1950*a*).

TABLE 1. OPTICAL PROPERTIES OF THE PYROXENE MICROPHENOCRYSTS FROM HAKONE

No. 1 Hypersthene from Tengu-zawa	No. 2a Hypersthene from Tengu-zawa	No. 2b Pigeonite* from Tengu-zawa	No. 3 Pigeonite* from Usugoya-zawa
$\alpha=1.687-1.695$	$2V=62^{\circ}(-)$	$\alpha=1.693$ (min.)	$\alpha=1.693-1.698$
$\beta=1.695-1.703$		$2V=33^{\circ}-8^{\circ}(+)$	$\beta=1.696-1.701$
$\gamma=1.699-1.707$		(O.P. $\perp$ 010)	$\gamma=1.720-1.725$
$2V=64^{\circ}-62^{\circ}(-)$			$2V=27^{\circ}-0^{\circ}(+)$
$r>v$			(O.P. $\perp$ 010)
Average:			$\rightarrow 5^{\circ}$
$\alpha=1.691$			(O.P. in 010)
$\beta=1.699$			$r>v$
$\gamma=1.703$			$c\wedge Z=42^{\circ}$
$2V=63^{\circ}$			
			Average:
			$\alpha=1.695$
			$\beta=1.698$
			$\gamma=1.722$
			$2V=14^{\circ}$ (O.P. $\perp$ 010)
			Z=Y=very pale green
			X=pale brown

\* Showing zonal structure from less calcic core to more calcic margin.

temperature of hypersthene to pigeonite, and that a slight variation of temperature or composition in different parts of the magma has resulted in the difference of the pyroxenic phases. The pyroxenes Nos. 2a and 2b represent the hypersthene and pigeonite approximately in equilibrium with one another across the inversion interval. However, this interval was determined by analyzing the pyroxenes Nos. 1 and 3, instead of Nos. 2a and 2b, in view of the difficulty of separating the two pyroxenes within the same rock.

#### CHEMICAL COMPOSITIONS

Special care was taken in obtaining pure materials for chemical analysis. The olivine phenocrysts in these rocks are entirely altered to chlorite and a carbonate mineral. The porphyritic hypersthene is almost negligible in quantity. The rocks were first crushed to a powder with grain size a little larger than the microphenocrysts but smaller than the hypersthene phenocrysts. After passing through the electromagnetic separator, it was found that most of the hypersthene phenocrysts entered into the less magnetic fraction, whereas the pyroxene microphenocrysts were attracted to the more magnetic fraction owing to adhering grains of the

groundmass magnetite. Next the more magnetic fraction was crushed to a powder with grain size a little smaller than the microphenocrysts but much larger than the groundmass grains of clinopyroxene and magnetite. After the electromagnetic treatment, a mixture of plagioclase and microphenocrystic pyroxenes free from groundmass pyroxene and magnetite was obtained from which the plagioclase was entirely removed by heavy liquids.

The materials thus separated still contained minute dust of an opaque mineral, probably hematite, but no lime bearing impurity. Repeated analyses were made which gave almost the identical results. The estimated amounts of the hematite impurity were subtracted from the analyses as shown in Nos. 1 and 3 of Table 2.

TABLE 2. CHEMICAL COMPOSITIONS OF THE PYROXENES FROM HAKONE

	No. 1	No. 3		Numbers of metal atoms on the basis of 6 oxygens	
				No. 1	No. 3
SiO <sub>2</sub>	53.17	52.84	Si	1.958	1.956
Al <sub>2</sub> O <sub>3</sub>	0.45	0.44	Al	0.022	0.018
Fe <sub>2</sub> O <sub>3</sub>	1.32	1.06	Al	—	—
FeO	17.18	16.89	Ti	0.007	0.007
MgO	23.81	23.51	Fe'''	0.035	0.031
CaO	2.67	4.06	Fe''	0.528	0.522
Na <sub>2</sub> O	0.47	0.19	Mn	0.015	0.018
K <sub>2</sub> O	0.00	0.00	Mg	1.315	1.305
H <sub>2</sub> O+	n.d.	n.d.	Ca	0.104	0.160
H <sub>2</sub> O-	0.21	0.22	Na	0.031	0.013
TiO <sub>2</sub>	0.22	0.22			
P <sub>2</sub> O <sub>5</sub>	n.d.	n.d.	{ Ca	5	8
MnO	0.48	0.56	{ Mg	66	64
SrO	0.00	0.00	{ Fe''+Fe''' + Mn	29	28
Total	99.98	99.99			

No. 1. Hypersthene in hypersthene-olivine andesite (HK49032901b) from Tengu-zawa, eastern caldera wall of Hakone volcano. The analysis was corrected for 0.5% hematite impurity.

No. 3. Pigeonite in hypersthene-olivine andesite (HK47122401) from Usugoya-zawa, eastern caldera wall of Hakone volcano.

The analysis was corrected for 1% hematite impurity.

By comparing the analyses Nos. 1 and 3, it will be seen that each oxide, except CaO, varies within the limit of only 0.33%. The difference of CaO content is obviously more than the analytical error.

It may be concluded that the change from hypersthene to pigeonite during the crystallization of the magma involved an increase of CaO content of about 1.4% but no appreciable change in the contents of the other oxides, the ratio  $Mg:Fe^{+2}+Fe^{+3}+Mn$  remaining nearly constant. This ratio is 70:30, agreeing exactly with the generalization by Hess and Poldervaart (1951). However, the change takes place at more iron-rich compositions in porphyritic pyroxenes (Kuno, 1950*b*).

The analyzed hypersthene shows the highest CaO content so far known for orthopyroxenes from volcanic rocks. The CaO content of orthopyroxene phenocrysts is less than 2% (Kuno, 1941, 1947, 1950*b*; Larsen and others, 1936, 1937, 1938; Taneda, 1946). According to Hess\* the CaO content of orthopyroxenes of basic plutonic rocks is also less than 2%.

Two alternative explanations may be offered to account for the high Ca content of the hypersthene No. 1. (1) It is a metastable phenomenon caused by rapid cooling of the magma. (2) The high Ca content is normal for an orthopyroxene which is in equilibrium with pigeonite across the inversion interval. One of the writers (H. K.) prefers the second alternative. He expects that such a lime-rich orthopyroxene would be found commonly in dolerite and gabbro, if chemical analyses were made on crystals directly surrounded by the orthopyroxene with exsolved blebs or plates of augite (inverted pigeonite).

From the ratio  $Mg:Fe^{+2}+Fe^{+3}+Mn$  of the two pyroxenes given in Table 2 and the diagram Fig. 1, the temperature of the lava at the time of extrusion can be determined approximately as 1100°C.

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