

PHENOCRYSTS AND GLASS INCLUSIONS AND THEIR  
BEARING ON OXIDATION AND MIXING OF BASALTIC  
MAGMAS, KILAUEA VOLCANO, HAWAII<sup>1</sup>

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ABSTRACT

The textures and chemical compositions of phenocrysts and glasses reveal how the composition, temperature, and oxygen fugacity of three fractionated lavas of Kilauea volcano changed before, during, and after ascent of the magmas to the surface. Intratelluric crystallization of magnetite and ilmenite begins in fractionated liquids at about 1120°C,  $\log f_{O_2} = -8.1$  but with variations depending upon the nature of prior magma mixing. These conditions are consistent with initial evolution of the magmas from a submarine-type precursor in systems closed to both oxygen and water. The fractionated magmas mix together and possibly with variable amounts of less fractionated liquids prior to or during eruption. Reversely zoned oxide phenocrysts with anomalously fractionated glass inclusions result. Magma effervescence during ascent causes rapid crystallization of microphenocrysts, *rise* in temperature, and *decrease* in oxidation state. These changes are contrary to popular belief and are attested to by the compositional zoning and resorption of the oxide phenocrysts. The inferred heating and reduction (to 1180°C,  $\log f_{O_2} = -8.1$ ) are in quantitative agreement with expectations based on the effects of H<sub>2</sub>O on crystallization temperature and of SO<sub>2</sub> on oxidation state. Following eruption the inferred temperatures and oxygen fugacities fell to 1050°C and  $\log f_{O_2} = -10.2$ .

Comparison of Kilauean with other basalts and with minerals of ultramafic nodules suggests that the intratelluric redox conditions of oxide saturated basaltic magmas and mantle materials are collinear within an uncertainty of 0.5 log units  $f_{O_2}$ . Differences in redox state between various oxide saturated basalt magmas may be due to differential gas loss prior to eruption.

INTRODUCTION

Study of iron-titanium oxides can yield information regarding the oxygen fugacity-temperature history of the rocks in which they occur. If the compositions of coexisting titaniferous magnetite and ferrian ilmenite are known, and if the two minerals were equilibrated, then the oxygen fugacity and temperature of equilibration of the pair may be estimated (Buddington and Lindsley, 1964).

Kilauea Volcano is one of the most thoroughly studied volcanoes of the world and there already exist considerable data on the oxygen

<sup>1</sup> Publication authorized by the Director, U. S. Geological Survey.

fugacity-temperature relations of its lavas (Fudali, 1965), lava lakes (Sato and Wright, 1966), and gases (Heald and others, 1963). From this point of view it is well suited to a study of the iron-titanium oxide phenocrysts for the information they can give as to the conditions of intratelluric crystallization.

Fe-Ti oxide phenocrysts have been found only in some of the more chemically fractionated lavas from Kilauea. Such lavas, erupted from the rift zones, show close to a twofold enrichment in  $P_2O_5$ ,  $K_2O$ , and  $TiO_2$  compared to lavas erupted at Kilauea summit (Table 1 and Wright and Fiske, 1971). We describe the oxide phenocrysts from

Table 1. Chemical composition<sup>a</sup> of fractionated and unfractionated Kilauean lavas.

Oxide	A	B	C	D	E	F
$SiO_2$	51.10	50.60	53.50	55.38	54.54	51.11
$Al_2O_3$	13.75	13.85	13.75	13.51	13.63	13.75
$FeO^b$	12.60	12.0	12.50	10.10	10.17	11.04
$MgO$	5.40	6.40	3.90	5.63	6.59	7.62
$CaO$	9.40	10.25	7.75	7.36	7.04	10.63
$Na_2O$	2.80	2.55	3.35	2.99	2.66	2.28
$K_2O$	0.75	0.65	1.10	1.19	1.12	0.41
$TiO_2$	3.6	3.15	3.35	2.54	2.50	2.40
$P_2O_5$	0.40	0.35	.60	0.32	0.32	0.23
$MnO$	0.20	0.20	.20	0.15	0.16	

<sup>a</sup>Analyses recalculated to dry weight. The 1955 data are averages of the early and late lavas from data of Macdonald and Eaton (1964, Table 2) and Wright and Fiske (1971). All analyses by the Denver rock analysis laboratory, U. S. Geol. Survey, L. C. Peck, Project leader.

<sup>b</sup>All iron as  $FeO$ .

A: Average lava from the early vents of 1955 (vents A-S).

B: Average lava from the late vents of 1955 (vents T-Z).

C: Kamakaia lava.

D: Yellow Cone lava (Wright and Fiske, 1971).

E: Yellow Cone lava (Wright and Fiske, 1971).

F: Cone Craters lava (assumed initial, unfractionated composition of the parent of the 1955 and Kamakaia lavas, Wright and Fiske, 1971).

three sets of fractionated lavas; 1) lavas of the 1955 eruption on the east rift zone; 2) lava and cinder from the prehistoric Kamakaia cone, southwest rift zone; 3) cinders from the prehistoric Yellow Cone, southwest rift zone.

An electron microprobe was used to analyze the oxide phenocrysts; the host glass with which the phenocrysts are in contact, as well as inclusions of glass in the phenocrysts.

#### FIELD RELATIONS AND PETROGRAPHY

##### *1. Lavas of the 1955 eruption*

The 1955 eruption occurred on the lower east rift zone of Kilauea and was described by MacDonald and Eaton (1964). Their report includes a chronology of the eruption, a map showing the location of source vents, and a brief description of the petrography and chemistry of the erupted lavas. Wright and Fiske (1971) give additional chemical and petrographic data and present hypotheses to explain the origin of the 1955 magma and to explain the variations in lava composition which occurred in the course of the eruption. The lavas are subdivided by Wright and Fiske according to date of eruption. The lavas erupted from February 1 to March 25, 1955 have less than 6.0 percent MgO; those lavas erupted after March 25 are less fractionated, and have more than 6.0 percent MgO. The average compositions of the early and late lavas are given in Table 1. Evidence is given by Wright and Fiske that the composition of the later lavas was produced by mixing of magma originating from beneath Kilauea summit with the early fractionated lava stored in the rift zone.

Of the samples studied by us six are early lavas (HK1955-AP, -AG, -EG, -KG, -KI, and -QG) and two are late lavas (HK1955Z and HW3).

HK1955AP is a single, 10 cm thick slab of vesicular pahoehoe about 40 meters southeast of vent A, from which the earliest lava of the 1955 eruption was extruded.

HK1955AG is glassy spatter collected at the base of the western most spatter conelet of the A vent.

HK1955EG is glassy, ropy surface of a pahoehoe flow about 100 meters north of the road between Kapoho and Pahoia and immediately southeast of the E vent area.

HK1955KG and HK1955KI were collected where the road between Pohoiki and Kapoho crosses the Kii lava flow which was erupted from the E vent. The KI sample consists of several large blocks from the dense interior of the flow which was exposed when the road was

rebuilt following the 1955 eruption. The KG sample came from the spiny top of the flow and is glassy to microcrystalline.

HK1955QG (TLW67-60, Wright and Fiske, 1971) consists of vent spatter and glassy flow tops from the area of the Q vent.

HK1955Z was collected about 100 yards northeast of the W-Z vent cones. Ropy slabs of lava were taken from a single tongue of lava at the western margin of a lava pond which extends towards the east and south from the W-Z cinder cones.

HW3 was collected in September 1965, at the place where the Kehena lava flow originating from Vent Y is crossed by the coastal highway between Kapoho and Kalapana. Several blocks of dense lava from the interior of the flow were taken adjacent to an access ramp to the sea.

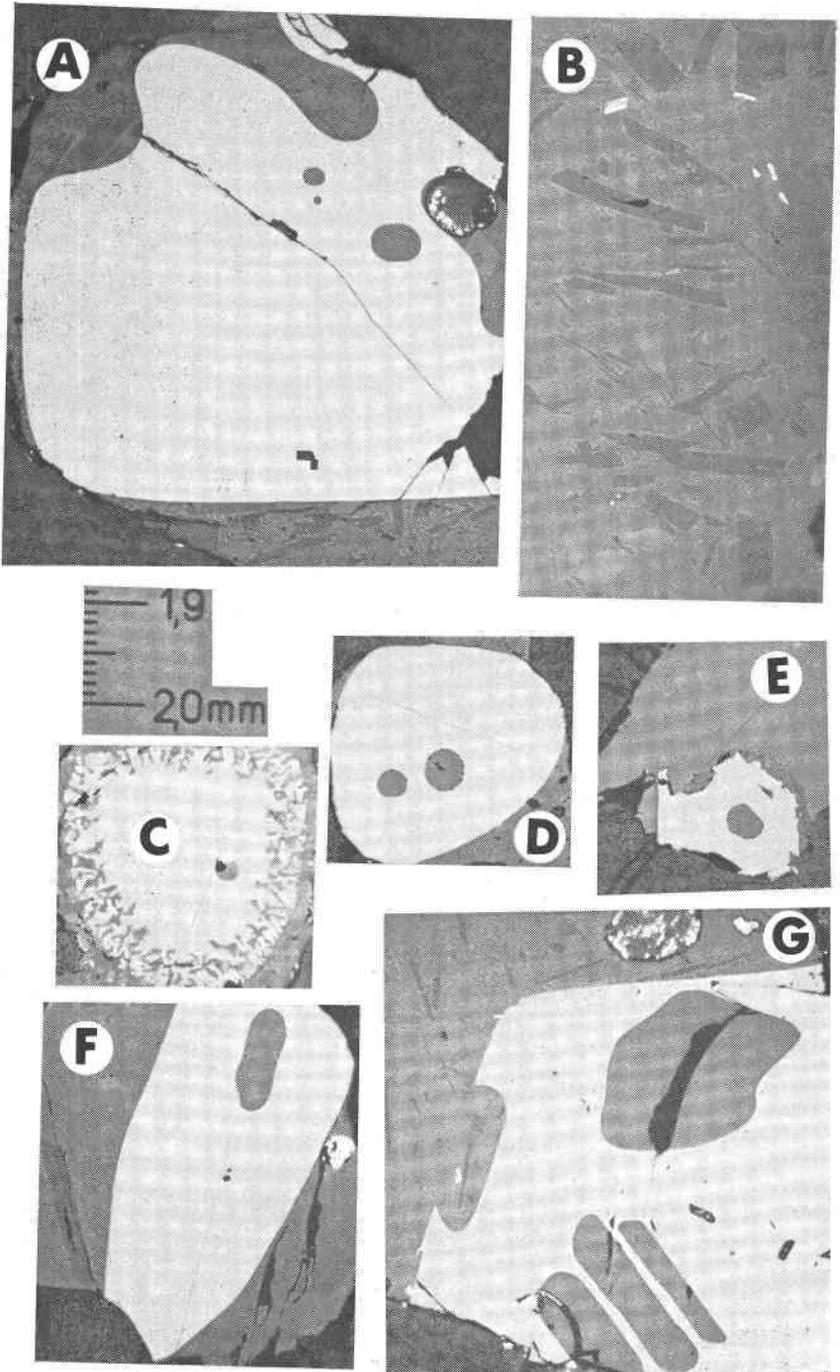
Megaphenocrysts (longest dimension greater than 0.1 mm) of plagioclase, augite, bronzite, olivine, ilmenite, and magnetite are present in all 1955 lavas studied (Table 2). With the exception of bronzite

Table 2.  
Phenocryst content of fractionated Kilauea basalts.

Specimen Number	Volume per cent phenocrysts						Total
	Ol	Opx	Cpx	Pl	Il	Mt	
HK1955AG <sup>a</sup>	tr	1	2	18	tr.	tr.	22
HK1955AP	0.45	0.40	0.85	3.40	0.3	tr.	5.4
HK1955EG	0.80	0.35	2.24	4.65	tr.	tr.	8.1
HK1955K1	0.60	2.10	2.15	2.65	--	--	7.5
HK1955QG	0.35	1.45	3.25	8.20	1.40		14.7
HK1955Z	1.45	--	2.55	3.15	--	--	7.2
HW 3	1.70	--	2.30	3.10	--	--	7.1
HK-K 4	--	tr.	tr.	tr.	tr.	tr.	1.0
HK-YC	2.0	tr.	tr.	tr.	tr.	tr.	2.0

<sup>a</sup>1955 AG was counted on the polished section used for probe analysis. All samples of 1955 lava counted in this way contain 15-25 per cent crystals (mega- and micro-phenocrysts). The rest of the 1955 data are percentage of mega-phenocrysts counted in transmitted light (data from Wright and Fiske, 1971, Table 3).

Abbreviations: Ol=olivine, Opx=orthopyroxene, Cpx=augite, Pl=plagioclase, Il=ilmenite, Mt=magnetite.



and magnetite these same minerals also occur as microphenocrysts (Fig. 1B). Bronzite phenocrysts nearly always have a thin rim of augite and no orthopyroxene occurs in the groundmass of the crystallized lavas. Phenocryst percentages vary widely in lavas erupted from different vents and even in different lava samples from the same vent. The Fe-Ti oxides have a particularly erratic distribution. There is no discernible correlation between the bulk composition of the lava and the total or relative amount of phenocrysts (see Wright and Fiske, 1971, Table 3). In comparison to most Kilauean lavas the 1955 lavas are exceptionally variable in petrography while having relatively uniform bulk chemistry.

## 2. Kamakaia lava

The Kamakaia lava and cinder cone are at the upper end of a line of vents which produced fractionated lavas and which is an extension of the Koae fracture system and slightly east of the principal southwest rift zone of Kilauea.

HK-K4 was collected from the central of three cinder cones called the Kamakaia hills which are about 13 km southwest of Kilauea summit. The Kamakaia lava flowed out of the central cone toward the



FIG. 1. Reflected light photographs of Fe-Ti oxides in fractionated Kilauean basalts. All photographs same scale.

- A) Phenocryst of ilmenite (white) with glass inclusions (dark gray) surrounded by glass and microphenocrysts (as in B) and epoxy (as in E). HK1955EG.
- B) Glassy crust showing euhedral microphenocrysts of ilmenite (white), pyroxene (medium gray), glass (medium-dark gray), plagioclase (dark gray). HK1955AG.
- C) Phenocryst of chrome-rich magnetite (light gray) with inclusion containing sulfide (white), vesicle (black), glass (medium gray). HK1955KI.
- D) Phenocryst of ilmenite (white) with devitrified, vesiculated glass inclusions (as in A). HK1955EG.
- E) Attached phenocrysts of magnetite (white) and augite (medium gray) with inclusion of glass (medium dark gray) in magnetite, some devitrified glass between magnetite and augite surrounded by epoxy plastic (mottled dark gray). HK1955AP.
- F) Phenocryst of ilmenite with glass inclusions and host glass and crystals (as in B) and sulfide droplet (white).
- G) Phenocryst of magnetite (white) with four separate inclusions of glass (medium-dark gray) surrounded by glass and microphenocrysts (as in B) and epoxy (as in E). HK1955AG.

west and southwest. The flow has a distinctively spiny and contorted top surface which is transitional between broken pahoehoe and aa. The K4 sample was taken from a single slab of ropy lava at the northern margin of the flow in the saddle between the two cinder cones.

The Kamakaia lava is nearly aphyric and is more highly fractionated than any of the lavas of the 1955 eruption (Table 1). It contains sparse mega- and microphenocrysts of augite, hypersthene, plagioclase, magnetite, and ilmenite (Table 2). Olivine phenocrysts are absent.

### 3. Yellow Cone

Yellow Cone is a small cinder cone about 15 km from the Kilauea summit which lies just east of the main trace of the southwest rift zone and is completely surrounded by younger lavas (Stearns and MacDonald, 1946). Yellow cone has a highly unusual fractionated chemical composition which has been explained as resulting from mixing of a hot olivine-rich magma with a very highly fractionated (60 percent SiO<sub>2</sub>) magma in a ratio of about 1:2 (Wright and Fiske, 1971, Tables 13 and 15, Figure 8 and accompanying discussion). Megascopically the Yellow Cone pumice (HK-YC = TLW67-126 of Wright and Fiske, 1971) contains sparse phenocrysts of olivine and resembles many unfractionated Kilauea pumices. Under the microscope the presence of rare phenocrysts of hypersthene, ilmenite, and magnetite in addition to augite and plagioclase, attest to the fractionated character of the lava.

## RESULTS

Our studies were done in an attempt to determine how and why temperature, oxygen fugacity, and magma composition change during eruption. Compositions of silicate phenocrysts (Table 3) are generally compatible with equilibrium but exotic Mg-rich olivine and Fe-rich augite indicate complexity. The compositions<sup>1</sup> and textures of Fe-Ti oxide phenocrysts (Tables 4 and 5) lead to estimates of temperature and oxygen fugacity (Table 7) and magma composition during different stages of eruption. The compositions of glasses included in phenocrysts (Table 6) reveal variations in magma composi-

<sup>1</sup> Compositions of the oxides are abbreviated in terms of familiar end members (Anderson, 1968): Usp = 100 mol % Fe<sub>2</sub>TiO<sub>4</sub>/(mol % Fe<sub>2</sub>TiO<sub>4</sub> + mol % Fe<sub>3</sub>O<sub>4</sub>), Hm = 100 mol % Fe<sub>2</sub>O<sub>3</sub>/(mol % Fe<sub>3</sub>O<sub>3</sub> + mol % FeTiO<sub>3</sub>), Fpsb = 100 mol % FeTi<sub>2</sub>O<sub>5</sub>/(mol % FeTi<sub>2</sub>O<sub>5</sub> + mol % Fe<sub>2</sub>TiO<sub>5</sub>). The Mg and Al contents of the oxide phenocrysts are appreciable and have been taken account of according to the scheme of Anderson (1968) (see also Speidel, 1970).

Table 3

MICROPROBE ANALYSES OF SILICATE PHENOCRYSTS<sup>a</sup> FROM  
FRACTIONATED BASALT, KILAUEA VOLCANO, HAWAII

	(A)	(B)	(C)	(D)	(E)	(F)	(G)
SiO <sub>2</sub>	50.8	49.8	49.8	50.3	55.1	53.0	52.6
Al <sub>2</sub> O <sub>3</sub>	4.1	1.1	2.2	2.3	1.2	0.7	1.7
FeO <sup>b</sup>	7.5	14.6	12.2	12.9	15.7	22.2	17.9
MgO	17.1	18.2	13.9	15.6	26.9	22.4	25.2
CaO	19.3	15.8	17.6	17.0	2.1	1.8	2.0
Na <sub>2</sub> O	0.4	0.2	0.3	0.3	0.07	0.0	0.06
MnO	0.12	0.3	0.25	0.3	0.22	0.40	0.3
TiO <sub>2</sub>	1.33	0.91	0.89	0.9	0.52	0.37	0.6
Cr <sub>2</sub> O <sub>3</sub>	0.3	0.00	n.d.	0.01	0.01	n.d.	0.04
Sum	101.0	100.9	97.1	99.6	101.8	100.9	100.4

(A) Augite phenocryst, HK1955AG, spot 145-12-2-2;

(B) Augite phenocryst, HK1955AG, spot 168-15-4-6, with magnetite attached;

(C) Augite phenocryst, HK-K4, interior of grain;

(D) Augite phenocryst, interior, intergrown with magnetite and ilmenite, HK-YC;

(E) Bronzite phenocryst, HK1955AG, spot 145-13-1-2;

(F) Hypersthene phenocryst, HK-K4, interior of grain;

(G) Bronzite phenocryst, interior, intergrown with olivine (FO<sub>79</sub>) and Cr-titano-magnetite, HK-YC.

n.d. No data.

a. Partial analyses of feldspar and olivine phenocrysts gave the following results (wt. percent): 1) Plagioclase: HW3-An73Or0.6, 0.06% Sr, 0.002% Ba (standards: Ca-anorthite glass, K-feldspar, Sr-Mt. Anakie feldspar, Ba-Kokomo feldspar, cf. Smith and Ribbe, 1966). 2) Olivine: HK1955AG-Fo67, 0.14% Ni, HK1955EG-Fo74, 0.16% Ni, 0.24% Mn, HK1955Z-Fo79, 0.20% Mn, HW 3-Fo78, 0.21% Mn (standards: Mg, Fe, Ni Ross 7 (YS25) olivine crystal Fo88.5, 0.32% Ni, Mn-tephroite, Cf. Smith, (1966). Analytical conditions: 15KV, 0105-02 microamp specimen current, corrected for instrument drift, background, deadtime, absorption and atomic number effects as outlined by Smith (1965). Ca, Mg, Si - CaMgSi<sub>2</sub>O<sub>6</sub> glass, Al-Mg<sub>3</sub>Al<sub>2</sub>Si<sub>3</sub>O<sub>12</sub> glass, Fe, Ti-ilmenite, Na-aegirite, K-orthoclase, Mn-tephroite, Cr-chromite, P-apatite.

b. Total iron as FeO.

tion and temperatures. The above results are presented in detail below.<sup>1</sup>

In general, our data indicate initial crystallization of Fe-Ti oxides in a relatively cool, oxidizing intratelluric magma and subsequent heat-

<sup>1</sup> Additional analyses of Fe-Ti oxide phenocrysts and glass inclusions (Tables 8-11) are available on request. To obtain a copy of this material, order NAPS Document Number 01666 from National Auxiliary Publications Service of the A.S.I.S., c/o CCM Information Corporation, 866 Third Avenue, New York, N. Y. 10022; remitting \$2.00 for microfiche or \$5.00 for photocopies, in advance, payable to CCMIC-NAPS.

ing and reduction during ascent and eruption caused by loss of  $H_2O$  and  $SO_2$  as well as magma mixing.

### 1. 1955 Eruption

(a) *Silicate phenocrysts*. Analyses of silicate phenocrysts are given in Table 3.<sup>2</sup> Large single phenocrysts of bronzite and augite are zoned toward more iron-rich rims and plagioclase is zoned toward more sodic rims. Augites intergrown with magnetite and ilmenite (Fig. 1E) are richer in iron than isolated augites, and some of these are zoned toward more magnesian margins.

Olivine phenocrysts from the early 1955 lavas are generally smaller than pyroxene and plagioclase and are of composition Fa 33–34.

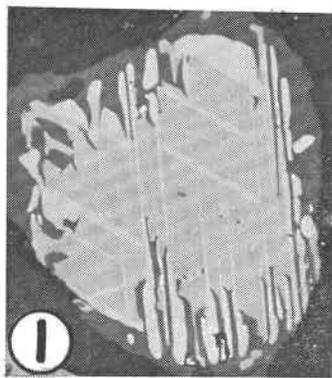
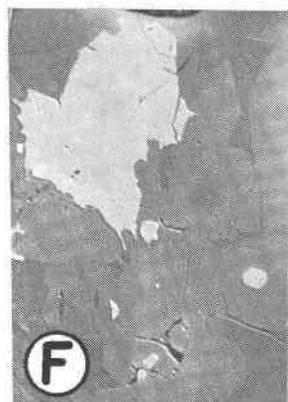
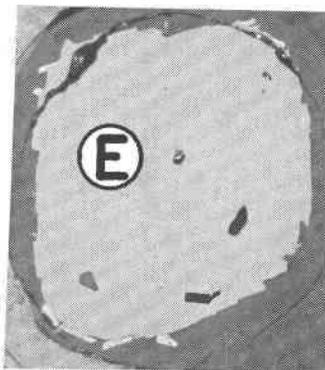
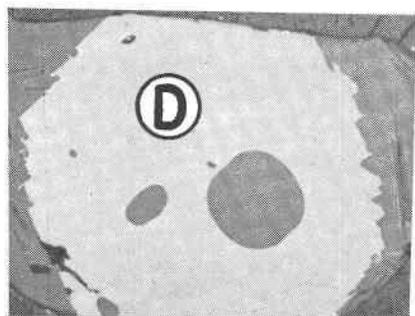
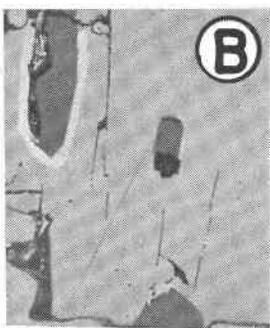
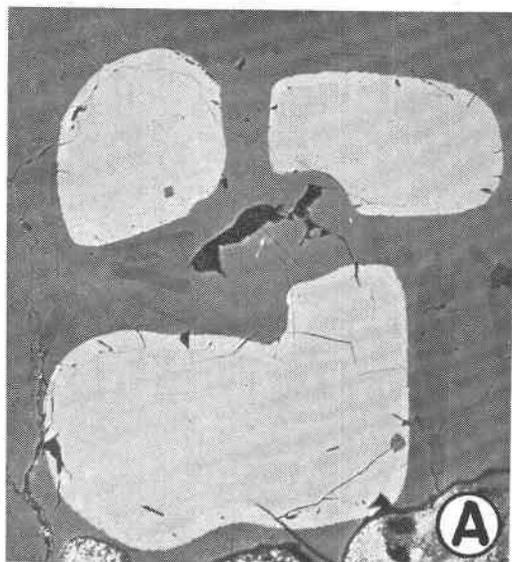
(b) *Titaniferous magnetite*. Megaphenocrysts of titaniferous magnetite in the 1955 lavas are subhedral to anhedral (Fig. 1C, 2D). They are continuously but sharply zoned with rims 10 to 50 $\mu$ m wide en-

<sup>2</sup> Additional analyses of phenocrysts from the 1955 lavas are given by Aramaki (1965; plagioclase—An62) and Murata and Richter (1966, p. A25;—augite— $Mg_{47.6}Fe_{12.3}Ca_{40.1}$ ).



FIG. 2. Reflected light photographs of Fe-Ti oxides in fractionated Kilauean basalts. Scale same as Fig. 1.

- A) Phenocrysts of ferropseudobrookite (light gray) rimmed by ilmenite (white) and intergrown with augite (medium gray) surrounded by glass and crystals (as in 1B) and carbon coated epoxy (mottled light gray). HK1955AG.
- B) Glass inclusions (medium gray) in ferropseudobrookite phenocryst (light gray) with ilmenite rims (variable, white to gray). HK1955EG.
- C) Phenocrysts of ferropseudobrookite (small light gray crystals) one with a thin ilmenite rim (white) near magnetite phenocryst (large light-gray crystal) in glass. HK1955QG.
- D) Phenocryst of magnetite (light gray) with glass inclusions (dark gray) and host glass and crystals (as in 1B) and epoxy (as in 1E). HK1955EG.
- E) Magnetite phenocryst (light gray) with attached ilmenite euhedra (white) and surrounding host lava (as in 1B) and epoxy (mottled light gray). HK1955AG.
- F) Phenocrysts of magnetite (white) with chrome-rich cores (light gray) intergrown with hypersthene and olivine (medium gray) and surrounded by glass and microphenocrysts (as in 1B). HK-YC.
- G) Adjoined phenocrysts of magnetite (light gray) and ilmenite (white) in host lava (as in 1B) and epoxy (as in 1E). HK1955EG.
- H) Same as G. HK1955EG.
- I) Ilmenite lamellae (white) in magnetite phenocryst (light gray) surrounded by host lava (as in 1B) and epoxy (as in 1E). HK1955QG.



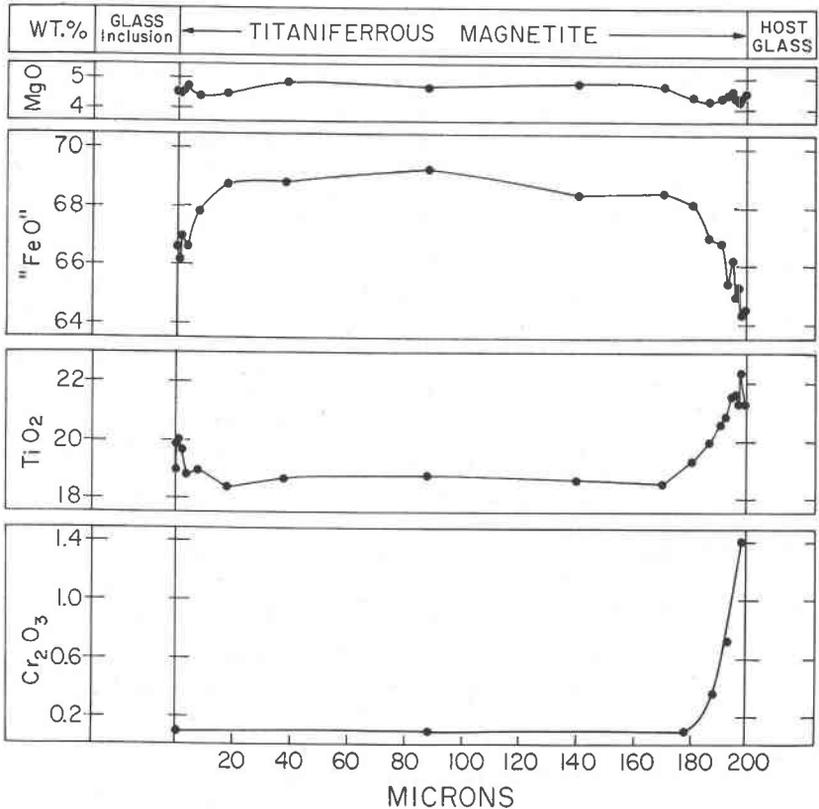


FIG. 3. Compositional zonation of titaniferous magnetite phenocryst in a fractionated Kilauean basalt, HK1955QG.

riched in Ti, Cr, and Usp and impoverished in Fe (Fig. 3). Although part of the apparent impoverishment in Fe may be the result of extension of the X-ray generating volume (about  $20\mu\text{m}^3$ ) into adjacent glass poor in Fe, most of it is not, because the sums of FeO, TiO<sub>2</sub>, and MgO remain near 96 percent for most of the distance over which Fe depletion is observed. The glass is poorer in Ti and Cr than the magnetite; therefore, marginal enrichment of the magnetite in these elements must be real. Adjacent to inclusions of glass, magnetites are enriched in Ti (but not Cr) and depleted in Fe to a lesser extent than at their margins (Fig. 3). The amounts of Ti enrichment and Fe depletion increase with lower Fe and higher Ti contents of the glass inclusions. The compositions of representative titaniferous magnetites are shown in Table 4. The composition range is summarized in Table 5 and

Table 4  
Microprobe analyses<sup>a</sup> of representative oxide phenocrysts  
from a fractionated Kilauean lava (HKL955AG)

Note <sup>b</sup>	TITANIFERROUS MAGNETITES					FERRIAN ILMENITES						FESP		
	1	2	3	4	5	6	7	8	9	10	11	12	13	14
	a	i	g	m	I	a	i	g	m	M	F	p	i	I
MgO (wt.%)	4.3	3.8	4.0	4.3	4.4	4.8	4.8	5.1	5.6	5.1	6.8	7.3	5.6	5.5
Al <sub>2</sub> O <sub>3</sub> "	2.7	3.0	3.7	2.9	3.3	0.6	0.8	0.8	0.8	1.9			1.5	1.5
TiO <sub>2</sub> "	19.5	17.5	19.8	22.5	23.4	48.0	45.0	45.7	49.0	47.7	50.0	48.0	50.6	60.2
Cr <sub>2</sub> O <sub>3</sub> "	0.10	0.34		0.85	0.20	0.05		0.30						
MnO "	0.3	0.4	0.4	0.4	0.4	0.3	0.3	0.3	0.4	0.4				
FeO "	42.4	41.3	43.1	44.6	45.4	32.8	31.7	31.5	33.8	33.6	32.8	30.2	12.6	13.3
Fe <sub>2</sub> O <sub>3</sub> <sup>c</sup>	30.2	32.9	27.8	22.5	19.9	24.8	16.0	14.4	9.3	9.6	7.5	11.3	18.3	15.2
Sum <sup>c</sup>	99.5	99.2	98.8	98.1	97.0	101.4	98.6	98.1	98.9	98.3	97.1	96.8	98.6	95.7
Usp <sup>d</sup>	51	47	55	63	66									
Hm <sup>d</sup>						17	18	17	11	11	9	14		
Fpsb <sup>d</sup>													60	66

a) Analytical conditions: 15 or 20 KV, 0.05 to 0.2 microamp-specimen current. Standards: Mg, Fe, Ti (Ilmenite K-13-131-8), Al, Cr (Chromite), Mn (Tephroite), as in Anderson (1968). Corrected for instrument drift, background, deadtime, and absorption and atomic number effects as described in Anderson (1968). Accuracy:  $\pm 2\%$  Ti,  $\pm 3\%$  Fe,  $\pm 5\%$  Mg, Al, Cr, Mn.

b) The letter abbreviations at the headings of the columns summarize the petrographic relations of the analysed spots as follows:

a = intergrown with augite phenocryst, g = adjacent to a glass inclusion, i = interior of megaphenocryst, m = margin of megaphenocryst, p = microphenocryst, F = mantle on ferropseudobrookite megaphenocryst, I = adjoining ilmenite, M = adjoining magnetite. The individual oxide analyses are calculated from data given in tables 8a, 9a and 10. Analyses 1-5 correspond to 168-15-4-1; 168-15-1-7; 168-15-1-6; 68-5-7, 6; and 168-15-5-4 of table 8a; analysis 6 is not reproduced in table 9a; analyses 7-12 correspond to 168-4-1-4; 168-4-1-7-3; 168-4-1-5; 168-15-5-5; AG-2-3-4; and AG Pol. Sectn. of table 9a; analyses 13 and 14 correspond to AG-2-3-1 and AG-2-3-3 of table 10. Slight differences in the sums of corresponding data result from rounding off through alternate paths of calculation.

c) Ferric iron and oxide sums calculated for ideal oxide stoichiometry: R<sub>2</sub>O<sub>3</sub> for magnetites, R<sub>2</sub>O<sub>3</sub> for ilmenites, R<sub>2</sub>O<sub>3</sub> for ferropseudobrookites.

d) See footnote a, table. 5.

Figure 5. The interiors of the magnetite phenocrysts have compositions ranging from Usp 42 to Usp 60 (Table 5) compared to margins ranging from Usp 49 to Usp 68. Magnetite adjacent to ilmenite (Figures 2H, 2E, 2G) ranges in composition from Usp 54 to Usp 66.

(c) *Ilmenite*. Ilmenite phenocrysts are subhedral to anhedral (Fig. 1A, D, F) with cores of composition Hm 15-22 (Tables 4 and 5, Fig. 5). Adjacent to the host glass most ilmenite is strongly zoned toward higher MgO and TiO<sub>2</sub> and lower "FeO" (Fig. 4). Rim compositions

are Hm 9-21 (Fig. 5). Zoning is also present adjacent to glass inclusions but is not as pronounced (Hm 17). Euhedral to subhedral microphenocrysts of ilmenite occur both as isolated crystals and attached to magnetite phenocrysts (Fig. 1B, 2E). An isolated euhedral crystal has a composition of Hm 14. Ilmenite compositions adjacent to attached magnetite ranges from Hm 10 for euhedral ilmenite to Hm 17 for anhedral ilmenite (Fig. 2G, H, K, L, Table 7). Ilmenite lamellae in magnetite (Fig. 2I) range in composition from Hm 17 to Hm 48

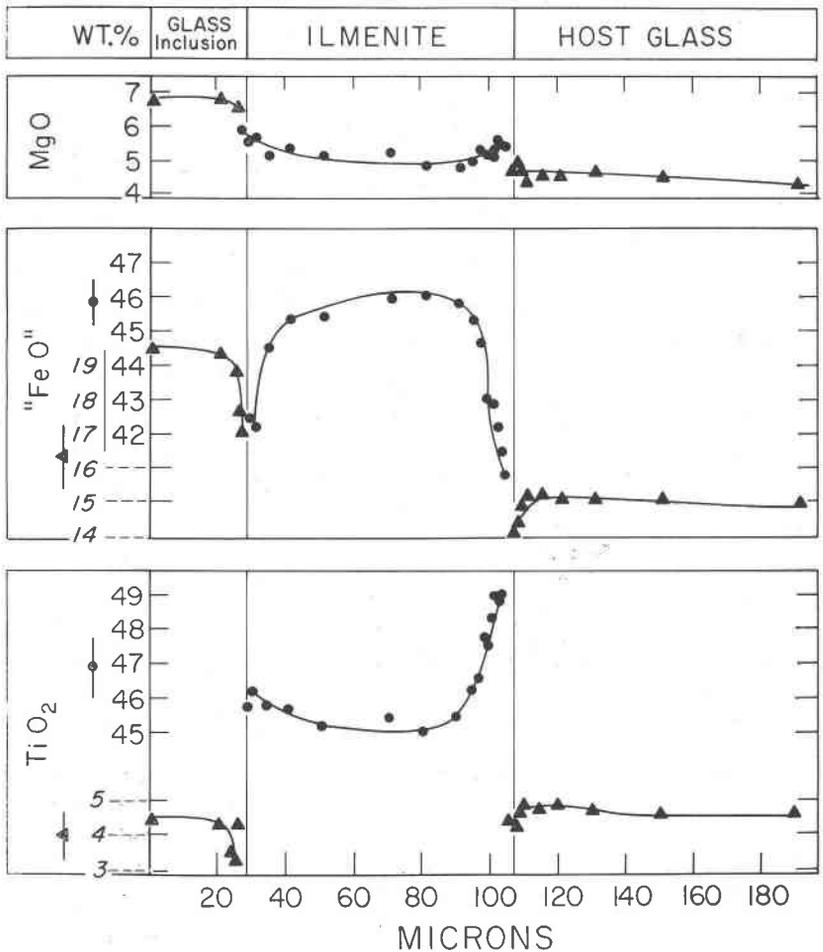


Fig. 4. Compositional zonation of ilmenite phenocryst in a fractionated Kilauean basalt, HK1955AG.

END MEMBER COMPOSITIONS OF KILAUEAN OXIDES

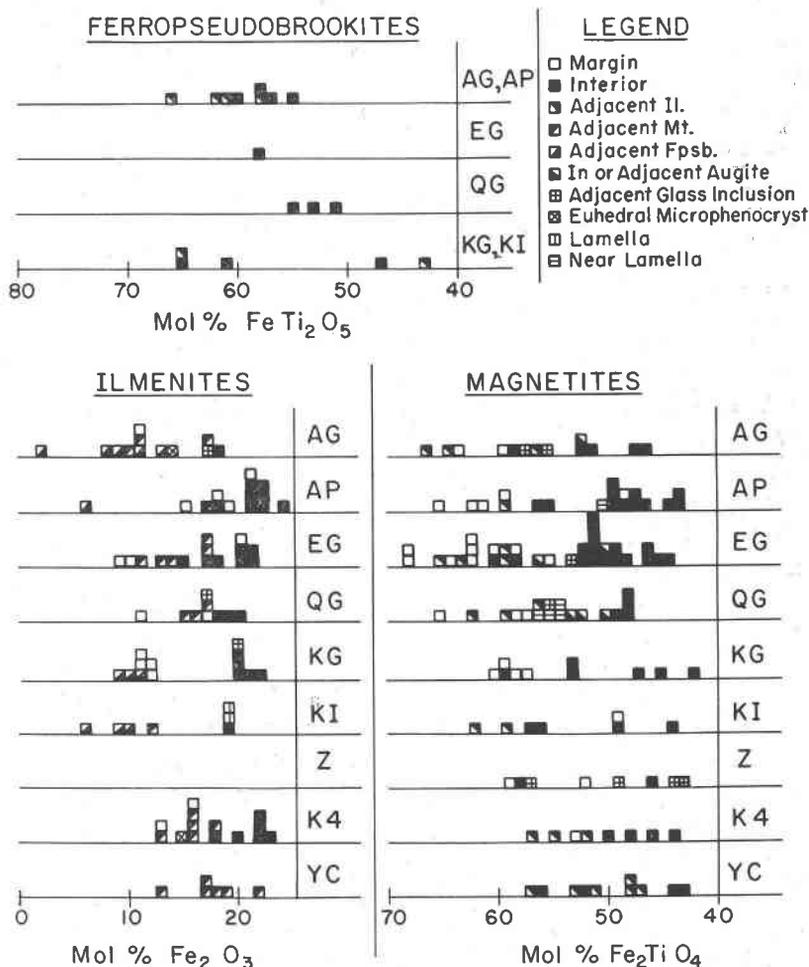


FIG. 5. End member compositional variation of oxide phenocrysts in fractionated Kilauean basalts. The sample designations are the abbreviated suffixes of HK1955AG, AP, EG, QG, KG, KI, and Z and HK-K4, HK-YC. The petrographic relations of the analysed oxides are indicated by the different symbols and explained in the legend. Each square represents a single analysed spot reported in Tables 8-10. Data for some Cr-rich magnetites and ilmenomagnetites (including ilmenite lamellae) are omitted to conserve space.

Table 5  
 Ranges of composition for magnetite (Usp<sup>a</sup>), ilmenite (Hm<sup>a</sup>)  
 and ferropseudobrookite (Fpsb<sup>a</sup>) for fractionated lavas of Kilauea volcano.

Sample	Magnetite			Ilmenite				Ferropseudobrookite		
	1	2	3	1	2	4	5	6	1	3
HK1955AG	46-56	63-66	56-66	17-18	10	10-17	14	2-13	55-60	58-66
HK1955AP	43-56	65	59	18-24	15-21	17		6	58	62
HK1955EG	46-60	58-68	63-65	15-21	9-20	14-17				
HK1955KG	42-59	57-68		20-22	11-12			9-11	61-65	65
HK1955KI	44-56	49	15-59	19		12		6-10	47	43
HK1955QG	48-53	57-65	54-62	20-18		15-17			51-55	
HK1955Z	43-54	52								
HK K4	44-50	53	52-57	18-22	13-16	13-18	15			
HK YC	43-56	47-57	47-57			13-22				

a) Usp = 100 mol %  $\text{Fe}_2\text{TlO}_4$  / (mol %  $\text{Fe}_2\text{TlO}_4$  +  $\text{Fe}_3\text{O}_4$ ), Hm = 100 mol %  $\text{Fe}_2\text{O}_3$  / (mol %  $\text{Fe}_2\text{O}_3$  +  $\text{FeTiO}_3$ ), Fpsb = 100 mol %  $\text{FeTi}_2\text{O}_5$  / (mol %  $\text{FeTi}_2\text{O}_5$  +  $\text{Fe}_2\text{TlO}_5$ ) - Anderson (1968) and Speidel (1970).

Key to column headings:

- 1 - Interior and included 2 - Rim 3 - Next to ilmenite 4 - Next to Magnetite  
 5 - Microphenocryst 6 - Next to Ferropseudobrookite.

(Tables 4 and 7). Partial rims of ilmenite on ferropseudobrookite (Fig. 2A, B, C) generally are less iron rich (Hm 2-13) than ilmenite phenocrysts.

(d) *Ferropseudobrookite*. Megaphenocrysts of ferropseudobrookite occur in the early 1955 lavas but have not been found in the later lavas.

The ferropseudobrookite phenocrysts are subhedral to euhedral tablets with partial or complete borders of ilmenite (Fig. 2A, B, C) which are wider (about 100 $\mu\text{m}$ ) in a flow collected away from the vent (HK1955KG) than in samples collected at the vent (HK1955EG) in which the rims are 5 to 30 $\mu\text{m}$  wide. In HK1955QG ferropseudobrookite microphenocrysts with incomplete ilmenite borders about 1 $\mu\text{m}$  wide are closely associated with magnetite (Fig. 2C). Centers of the ferropseudobrookites range from Fpsb 47 to 65 whereas the margins next to ilmenite range from Fpsb 43 to 66 (Tables 4 and 5, Fig. 5). The individual crystals are weakly zoned and nearly all have margins slightly richer in Fpsb than the centers.

(e) *Glasses*. Glass occurs both surrounding the phenocrysts (here called "host glass") and included within phenocrysts (Figs. 1 and 2). The host glasses of the early 1955 lavas are surprisingly uniform (Table 6) in view of the variable nature and abundance of phenocrysts (Table 2). Compared with analyses of corresponding bulk rocks the host glasses are enriched in  $\text{P}_2\text{O}_5$ ,  $\text{K}_2\text{O}$ ,  $\text{TiO}_2$ , total iron oxide, and  $\text{SiO}_2$  and depleted in  $\text{Al}_2\text{O}_3$ ,  $\text{MgO}$ ,  $\text{CaO}$  and  $\text{Na}_2\text{O}$ . Glasses surrounding oxide phenocrysts have compositions very close to the averages host glass but most are slightly richer in  $\text{TiO}_2$ ,  $\text{FeO}$ , and  $\text{MgO}$  and poorer in  $\text{Al}_2\text{O}_3$  and  $\text{SiO}_2$ .

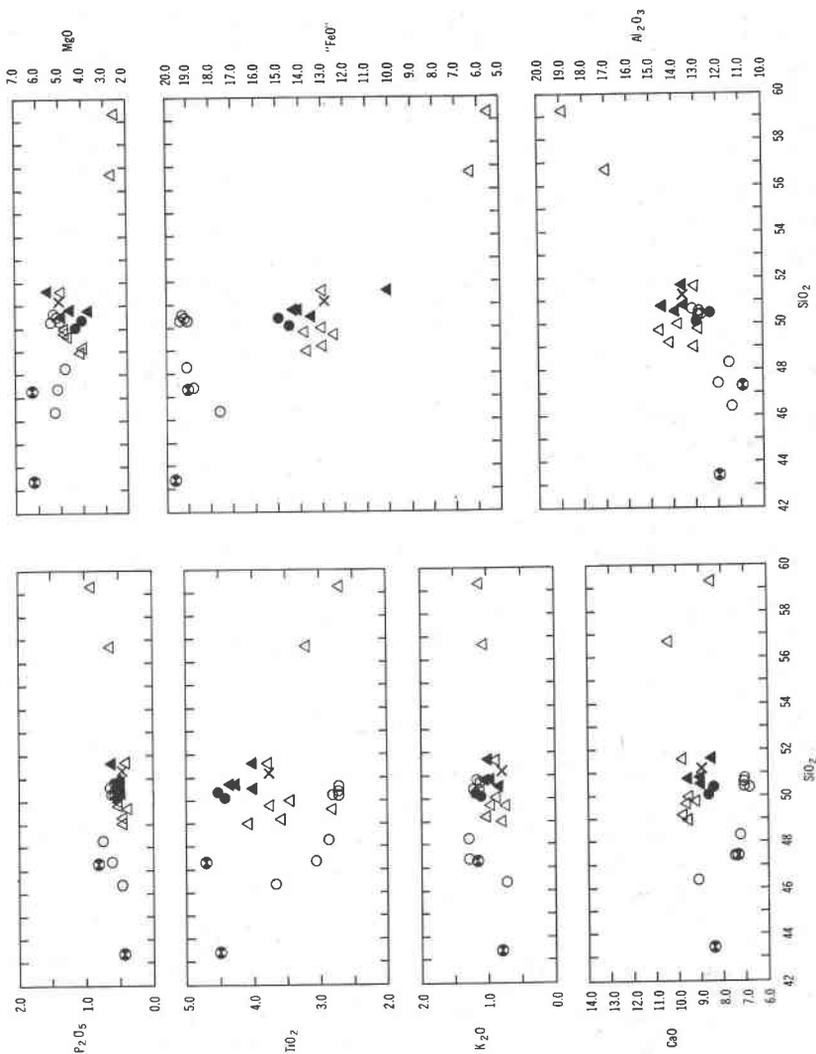


Fig. 6. Silica variation diagrams for glasses from a fractionated Kilauean basalt (HK195AG). Symbols for all glasses as follows:

- cross = bulk composition,
- solid circle = host glass,
- open circle = glass included in olivine,
- triangle = glass included in pyroxene,
- circle with two quadrants = glass included in ilmenite,
- open circle = glass included in magnetite.

Table 6  
MICROPROBE ANALYSES<sup>a</sup> OF HOST GLASSES AND REPRESENTATIVE  
GLASS INCLUSIONS IN OXIDE AND SILICATE PHENOCRYSTS  
OF FRACTIONATED KILAUEAN LAVAS

Host	Host Glasses										
	1	2	3	4	5	6	7	8	9	10	11
	CC	CC	I-1	I-87	I-85	K4	KG	QG	EG	AP	AG
SiO <sub>2</sub>	51.2	50.7 <sup>d</sup>	48.7 <sup>b</sup>	49.6 <sup>e</sup>	55.7 <sup>e</sup>	55.2 <sup>d</sup>	51.4 <sup>d</sup>	52.3 <sup>d</sup>	51.6 <sup>d</sup>	51.1 <sup>d</sup>	51.6 <sup>d</sup>
Al <sub>2</sub> O <sub>3</sub>	13.8	14.3 <sup>e</sup>	13.1 <sup>e</sup>	11.5 <sup>e</sup>	11.9 <sup>e</sup>	12.2	12.7	13.2	12.6	12.8	12.4
FeO <sup>b</sup>	11.0	10.8	11.7	13.8	13.7	13.4	14.2	13.9	14.4	14.5	14.9
MgO	7.6	6.7 <sup>d</sup>	6.2	4.7	2.5	3.5 <sup>d</sup>	3.7 <sup>d</sup>	3.9 <sup>d</sup>	4.1 <sup>d</sup>	4.4 <sup>d</sup>	3.8 <sup>d</sup>
CaO	10.7	10.7	10.5	8.7	6.3	7.5	8.6	8.0	8.5	8.6	8.4
Na <sub>2</sub> O <sup>c</sup>	2.3	2.3 <sup>d</sup>	2.3	2.4	2.1	2.6 <sup>d</sup>	2.8 <sup>d</sup>	3.0 <sup>d</sup>	2.6 <sup>d</sup>	2.7 <sup>d</sup>	2.6 <sup>d</sup>
K <sub>2</sub> O	0.41	0.43	0.62	0.87	1.65	1.21	1.23	1.07	1.05	1.03	1.04
TiO <sub>2</sub>	2.40	2.3	2.7	4.0	2.4	3.3	4.7	4.2	4.5	4.4	4.5
P <sub>2</sub> O <sub>5</sub>	0.23	0.24	0.38	0.62	0.94	0.66	0.62	0.65	0.58	0.48	0.48
Sum	99.7	98.5	96.2	96.2	97.2	99.6	99.9	100.3	99.9	100.0	99.7
F <sub>2</sub> O <sub>5</sub>	0.56	0.56	0.61	0.71	0.57	0.55	0.50	0.61	0.55	0.47	0.46
K <sub>2</sub> O											

Key to analyses by column headings.

1: Cone Craters lava—wet analysis, Denver rock analysis laboratory, U. S. Geol. Survey, L. C. Peck, Project director. 2: Glass of Cone Craters lava—the lava is 98% glass. 3-5: Host glasses of Kilauea Iki lavas: pumice of Nov. 14, 1959 (3), base of crust of lava lake (#4), ooze from 84.9' (#5), both from drill core collected in March 1967. 6-11: Host glasses of fractionated Kilauean lavas: HK-K4, HK1955KG, QG, EG, AP, and AG. 12-21: Glasses included in phenocrysts of olivine (Fa33 and Fa20), augite (CPX), bronzite (OPX), plagioclase (PL), magnetite (MT), an ilmenite (IL) from the HK1955AG lava. Analyses 12-22 are selected from tables 11a-11d. Analyses 12 and 13 are numbers 9 and 4 of table 11c. Analyses 14, 15 and 16 are numbers 1, 2 and 5 of table 11d. Analyses 17-20 are numbers 10, 2, 3, and 11 of table 11a. Analyses 21 and 22 are numbers 1 and 4 of table 11b.

a) Operating conditions: 15KV, 0.05 to 0.1 microamp specimen current, 3-4 successive 10 sec. counts per spot. Reported values are corrected for instrument drift, background, and absorption and atomic number differences (Smith, 1965) between the standards (Fe, Ti-ilmenite, Na-aegirite, Al-Mg<sub>2</sub>AlSi<sub>2</sub>O<sub>12</sub> glass, P-apatite, K-orthoclase, Ca, Mg, Si-CaMgSi<sub>2</sub>O<sub>5</sub> glass) and a basaltic glass with 50.7% SiO<sub>2</sub>, 13.8% Al<sub>2</sub>O<sub>3</sub>, 0.9% Fe<sub>2</sub>O<sub>3</sub>, 11.8% FeO 6.6% MgO, 10.3% CaO, 2.5% Na<sub>2</sub>O, 0.7% K<sub>2</sub>O, 3.1% TiO<sub>2</sub>, 0.3% P<sub>2</sub>O<sub>5</sub> and 0.2% MnO by multiplying by the following factors: Si - 1.04, Al - 0.98, Fe - 1.09, Mg - 1.066, Ca - 0.99, Na - 0.91, K - 1.00, Ti - 1.07, P - 1.22. Small variations in composition of the glasses change these factors by a few percent or less. Accuracy = ± 3% of the amount reported for SiO<sub>2</sub>, CaO, TiO<sub>2</sub> and FeO, ± 5% for MgO, Al<sub>2</sub>O<sub>3</sub>, K<sub>2</sub>O, P<sub>2</sub>O<sub>5</sub>.

b) Total iron reported as FeO. c) Most values for Na<sub>2</sub>O are too low by 10 to 100 percent due to volatilization by the electron beam and possibly other causes. d) Microprobe reference standard = Mak I basaltic glass prepared by H. R. Shaw and analysed at the Denver rock analysis laboratory, U. S. Geol. Survey, L. C. Peck, project director. e) Accuracy = ±5% for SiO<sub>2</sub>, ± 10% for Al<sub>2</sub>O<sub>3</sub>.

Table 6 (continued)

	Glasses Included in Silicates						Glass Included in Fe-Ti Oxides				
	12	13	14	15	16	17	18	19	20	21	22
Host	AG Fa33	AF Fa20	AG CPX	AF OPX	AG PL	AF MT	AI MT	AF MT	AF MT	IL	IL
SiO <sub>2</sub>	51.6	56.7	51.7	50.8	51.3	48.3	45.7	46.1	51.1	43.4	47.3
Al <sub>2</sub> O <sub>3</sub>	13.1	17.0	13.4	14.5	13.8	11.5	12.8	12.7	13.2	12.0	10.9
FeO <sup>b</sup>	13.0	6.3	10.1	14.2	13.4	19.1	20.7	19.9	16.0	19.7	19.1
MgO	4.9	2.7	5.5	4.5	5.2	4.8	4.8	4.7	2.7	6.2	6.3
CaO	9.8	10.4	8.5	8.8	8.2	7.2	9.4	9.4	9.9	8.4	7.4
Na <sub>2</sub> O <sup>c</sup>	2.5	1.9	2.6	2.8	2.2	2.6	2.2	2.1	1.9	2.4	2.7
K <sub>2</sub> O	0.88	1.05	0.96	1.02	1.2	1.28	0.70	0.79	1.04	0.81	1.16
TiO <sub>2</sub>	3.77	3.2	4.0	4.2	4.8	2.87	4.4	4.6	4.4	4.5	4.71
P <sub>2</sub> O <sub>5</sub>	0.40	0.62	0.55	0.50	0.43	0.74	0.81	0.76	0.57	0.42	0.82
Sum	99.9	99.8	97.2	101.2	100.5	98.7	101.5	101.0	100.8	97.8	100.4
P <sub>2</sub> O <sub>5</sub> K <sub>2</sub> O	0.45	0.59	0.57	0.49	0.36	0.58	1.15	0.96	0.55	0.52	0.71

Compositions of glass included in phenocrysts are summarized in Table 6 and are plotted in Figure 6. There is wide variation in glass composition most of which is real as demonstrated by close similarity in composition of multiple inclusions within individual phenocrysts (Table 6, nos. 18, 19; Fig. 1G), but a small part of the variation is caused by analytical error and the small diameter of some of the inclusions.

The composition of included glass is correlated with the nature of the host phenocryst. In silicate phenocrysts glass compositions generally fall between that of the host glass and the bulk composition of each specimen. However, some included glasses have high Al<sub>2</sub>O<sub>3</sub>. The composition of glass in the mafic silicates is consistent with entrapment of liquid before much plagioclase had crystallized from the host magma.

The compositions of glass inclusions in the magnetite and ilmenite phenocrysts are marked by very high iron oxide (up to 22 percent as FeO), low SiO<sub>2</sub> (down to 43 percent), and generally low TiO<sub>2</sub> (2–5 percent) (Table 6 and see Figure 6).<sup>1</sup> To a lesser extent the glasses are depleted in CaO and enriched in MgO, K<sub>2</sub>O, and P<sub>2</sub>O<sub>5</sub> relative to the host glasses. Although widely variable, the K<sub>2</sub>O and P<sub>2</sub>O<sub>5</sub> contents of glasses in magnetite and ilmenite phenocrysts overlap and indicate coeval crystallization.

<sup>1</sup>The few analyses that fall within the composition range of the host glass and the glass included in silicates might be of intersected embayments rather than true inclusions of entrapped glass. The TiO<sub>2</sub> contents of many glasses in the magnetite and ilmenite phenocrysts of specimen HK1955AG are high by comparison with equivalent glasses from other specimens (Table 11).

The three analyzed inclusions of glass in a ferropseudobrookite from Vent E (Fig. 2B, Table 11f) are similar in composition to the glass in pyroxene and olivine and not similar in composition to glass inclusions in the other Fe-Ti oxides.

## 2. Kamakaia cinder

(a) *Silicate phenocrysts.* Analyses of augite and bronzite are given in Table 3. They are considerably richer in iron than most of the 1955 pyroxenes, consistent with the more advanced stage of fractionation of the Kamakaia lava (Table 1).

(b) *Magnetite and ilmenite.* Phenocrysts of magnetite in the Kamakaia cinders and lava differ from those in the 1955 lavas, texturally and chemically. They are subhedral to euhedral and lack the rounded corners and edges typical of those in the 1955 lavas. As in the 1955 lavas, magnetite phenocrysts of the Kamakaia lava and cinders are richest in  $\text{Fe}_2\text{TiO}_4$  at their outer margins, but the degree of enrichment is less (Tables 4 and 5, Fig. 5). About 10 percent of the Kamakaia magnetite phenocrysts have tiny crystals of ilmenite attached to their exterior margins. The sense and range of compositional zoning of ilmenite phenocrysts in the Kamakaia lava and cinders (Tables 4, 5, and 7, and Fig. 5) are nearly the same as in the 1955 lavas.

(c) *Glass.* The host glass of the Kamakaia cinder is reasonably uniform and more fractionated than the bulk lava composition (Table 6). Glasses in ilmenite and magnetite are richer in FeO,  $\text{TiO}_2$ , and MgO, and poorer in  $\text{SiO}_2$  than the host glass. They show less extreme iron enrichment than the glass inclusions in ilmenite and magnetite from the 1955 lavas.

## 3. Yellow Cone Cinder

(a) *Silicate phenocrysts.* Analyses of augite and bronzite phenocrysts are given in Table 3. Most olivine crystals are only weakly zoned and have compositions of Fa 11–15. Some grains however have rims of bronzite and are more iron rich (Fa 20–25).

(b) *Magnetite and ilmenite.* Magnetite phenocrysts are subhedral to euhedral and several have optically distinct cores of a chromium rich oxide (Fig. 2F). The composition of the phenocrysts varies from Usp 43–56 in the interiors to Usp 47–57 at the margins and Usp 47–57 adjacent to ilmenite (Tables 4 and 5, Fig. 5). Ilmenite is intergrown with and attached to the margins of the magnetite phenocrysts and ranges in composition from Hm 13 to Hm 22 (Tables 4 and 5, Fig. 5).

(c) *Glass.* The host glass is more fractionated than the bulk rock;

glasses included in magnetite are rich in "FeO" and  $\text{TiO}_2$  and poor in  $\text{SiO}_2$ , those in olivine are high in CaO and  $\text{Al}_2\text{O}_3$  and poor in "FeO".

#### INTERPRETATIONS

##### 1. 1955 eruption

The early 1955 lavas are interpreted by Wright and Fiske (1971) as fractionated liquids derived from a magma whose composition was similar to that erupted at Kilauea Summit at least 100 years prior to 1955. The small composition variation within the early 1955 lavas was interpreted as reflecting different degrees of fractionation of the parent magma, parent magmas of slightly different composition or both. The data of the present study indicate that the evolution of the early 1955 lavas was complex and most likely involved magma mixing and gas loss as well as crystal-liquid fractionation. The principal evidence can be outlined as follows:

1. Most silicate phenocrysts are euhedral and normally zoned suggesting crystallization just prior to and during eruption. Zoning in the oxide phenocrysts is reversed (Mg- and Cr- rich margins) indicating re-resolution during heating just prior to eruption as is also suggested by their rounded shapes.

2. The composition of glass included in the silicates is intermediate between that of the bulk lava and that of the host glass surrounding the phenocrysts. This suggests that the silicates grew from a magma similar in composition to that of the lava as erupted.

The composition of glass inclusions in magnetite and ilmenite is dissimilar to that of the host glass. The more fractionated character of these glasses expressed as generally higher values of  $\text{K}_2\text{O}$  and  $\text{P}_2\text{O}_5$  and lower CaO compared to the host glass suggests that the cores of the Fe-Ti oxides grew from a more highly differentiated magma than that in which they were erupted. The higher degree of iron enrichment in the included glasses indicates that these glasses have been modified subsequent to entrapment by reaction with the enclosing magnetite and ilmenite. The zoning of the oxide phenocrysts adjacent to glass inclusions and the moderate depletion of the glasses in titania suggest preferential re-resolution of the iron-rich component of the oxide phenocrysts.

3. The compositions of cores of magnetite and ilmenite phenocrysts reflect presumed initial equilibrium conditions of about  $1120^\circ\text{C}$ ,  $\log f_{\text{O}_2} = -8.1$ . The temperature and oxygen fugacity during eruption ranged from about  $1180^\circ\text{C}$ ,  $\log f_{\text{O}_2} = -8.1$  (for anhedral crystals) to

Table 7.

Compositions of adjacent magnetite and ilmenite from fractionated Kilauean lavas and estimated temperature and oxygen fugacity.

Specimen	Hm	Usp	T° C	log $f_{O_2}$	Remarks
HK1955AG	11	66	1080	-9.7	euhedral il. adj. margin of mt.
HK1955AG	17	56	1120	-8.5	il. and mt. included in Fe rich augite euhedral.
HK1955AG	10	64	1050	-10.2	euhedral il. adj. margin of mt.
HK1955AP	17	61	1150	-8.2	large il. and small mt.
HK1955EG	17	63	1180	-8.1	large mt. and small il.
HK1955EG	14	65	1120	-8.8	large il. and small mt.
HK1955QG	16	59	1130	-8.6	small il. and large mt.
HK1955QG	17	55	1120	-8.5	ilmeno-magnetite
HK1955QG	15	52	1140	-8.6	il. near mt.
HK1955KG	12	62	1090	-9.4	veinlet of mt. in il.
HK1955KI	19	58	1180	-7.7	ilmeno-magnetite
HK1955KI	41	31			ilmeno-magnetite
HK1955KI	48	16			ilmeno-magnetite
HK-K4	16	57	1120	-8.7	small il. on large mt.
HK-K4	18	52	1120	-8.4	small il. near large mt.
1959 Iki Ooze	11	62	1060	-9.9	il. and mt. in ooze, KI67-1, 84', thermocouple temperature: 1040°C
1959 Iki Sv	11	64	1070	-9.8	il. and mt. in segregation vein, KI67-1, 79.0'.
HK-YC	18	51	1110	-8.4	euhedral il. adj. margin of mt.
HK-YC	17	53	1100	-8.7	euhedral il. adj. margin of mt.
HK-YC	17	48	1070	-9.0	subhedral il. and mt. attached to augite.
HK-YC	13	57	1050	-9.8	subhedral il. adj. margin of mt.
HK-YC	22	47	1150	-7.6	large il. and mt. anhedral.

1050°C,  $\log f_{O_2} = -10.2$  (for euhedral ilmenites mantling magnetite) assuming that the compositions of adjacent magnetite and ilmenite equilibrated with each other and with the liquid, (Table 7).

The above facts taken together support the following model: a) Crystallization of ilmenite, magnetite, and Fe-rich augite initially took place in an oxidizing, fractionated, hybrid magma, b) Significant heating, and reduction as well as reverse zoning of magnetite and ilmenite (possibly accompanied by crystallization of ferropseudobrookite) occurred in a new doubly hybrid magma prior to and/or during its ascent and eruption.

Two causes of heating and reduction prior to and during eruption are magma mixing and loss of gas. A mixture of 43 weight percent of cool, oxidizing, fractionated magma ( $T = 1120^\circ\text{C}$ ,  $f_{\text{O}_2} = 10^{-8.1}$ ,  $\text{Fe}_2\text{O}_3 = 2.0$  weight percent,  $\text{K}_2\text{O} = 1.2$  weight percent) together with 57 weight percent of hot, primitive magma ( $T = 1200^\circ\text{C}$ ,  $f_{\text{O}_2} = 10^{-8}$ ,  $\text{Fe}_2\text{O}_3 = 1.5$  weight percent,  $\text{K}_2\text{O} = 0.5$  weight percent) would yield a hybrid product with attributes ( $T = 1166^\circ\text{C}$ ,  $f_{\text{O}_2}$  near  $10^{-8}$ ,  $\text{Fe}_2\text{O}_3 = 1.7$  weight percent,  $\text{K}_2\text{O} = 0.8$  weight percent) similar to those of lava erupted from vent E ( $T \leq 1180^\circ\text{C}$ ,  $f_{\text{O}_2} = 10^{-8.1}$ ,  $\text{Fe}_2\text{O}_3 = 1.8$  weight percent,  $\text{K}_2\text{O} = 0.8$  weight percent).<sup>1</sup> Magma mixing has been demonstrated by Wright and Fiske (1971) to be a common process in the conduits of the east rift zone of Kilauea and through which the early 1955 magmas flowed. Wright and Fiske (1971) concluded that the early 1955 lavas could be derived from a prehistoric summit magma composition by variable degrees of closed system fractional crystallization and without magma mixing. The Cr-rich outer margins of some oxide phenocrysts and the variable compositions of the glass inclusions and host glasses indicate that magma mixing did affect the early 1955 lavas. The early mixing possibly involved only batches of fractionated magmas without any primitive summit-type magma which Wright and Fiske concluded did affect the *late* 1955 lavas. Although superficially consistent with some kind of magma mixing the properties of the *early* 1955 lavas are difficult to reconcile with admixture of *primitive* (0.4 percent  $\text{K}_2\text{O}$ ) magma.

Loss of gas could also have contributed to the reduction and heating of the 1955 lavas. Recent data collected by J. G. Moore and B. P. Fabbri (in preparation) reveal systematically low sulfur contents of subaerial lava compared to submarine lava. Loss of sulfur as  $\text{SO}_2$  or  $\text{S}_2$  during

<sup>1</sup> Estimates used in this calculation were arrived at as follows: a) for the fractionated magma:  $T$  and  $f_{\text{O}_2}$  from the compositions of the *interiors* of magnetite and ilmenite phenocrysts (Usp 45, Hm 20),  $\text{K}_2\text{O}$  from the  $\text{K}_2\text{O}$  content of glasses included in oxide phenocrysts,  $\text{Fe}_2\text{O}_3$  by assuming closed system subtraction of 1.4 percent olivine (0.00 percent  $\text{Fe}_2\text{O}_3$ ), 17.8 percent augite (1.5 percent  $\text{Fe}_2\text{O}_3$ ), 8.5 percent pigeonite (0.5 percent  $\text{Fe}_2\text{O}_3$ ), 21 percent plagioclase (0.3 percent  $\text{Fe}_2\text{O}_3$ ), and 0.6 percent ilmenite (20 percent  $\text{Fe}_2\text{O}_3$ ) (Wright and Fiske, 1971 and other data on mineral compositions) from the initial primitive magma (b) with  $T$  and  $f_{\text{O}_2}$  estimated from Peck *et al.* (1966) and Fudali (1965), and  $\text{K}_2\text{O}$  and  $\text{Fe}_2\text{O}_3$  from Moore (1965). The 0.4 weight percent  $\text{H}_2\text{O}$  and the lower  $\text{Fe}_2\text{O}_3$  content of glassy submarine lava suggest that  $T$  and  $f_{\text{O}_2}$  of initial primitive magma are less than observed for erupted magma by a small but uncertain amount.

The proportions of fractionated and primitive magmas are calculated from their  $\text{K}_2\text{O}$  contents assuming 0.8 weight percent  $\text{K}_2\text{O}$  in the product.  $T$  of the product assumes negligible heat of mixing. Log  $f_{\text{O}_2}$  assumed linear (increase in  $\text{Fe}_2\text{O}_3/\text{FeO}$  balanced by decrease in  $T$ ).

eruption could lead to significant reduction of the melt, if the melt is relatively depleted of hydrogen prior to eruption (Sato, oral comm. 1971). Sulfur presumably exists mostly as sulfide ( $S^{-2}$ ) anion in basaltic melt. Dissolved sulfide in intratelluric magma is indicated by the presence in glassy lavas of spherical blebs of immiscible sulfide (Skinner and Peck, 1969, Desborough *et al.*, 1968, Skinner, 1970, and Moore and Calk, 1971) and by the abundance of sulfides in diabase and gabbro. According to reactions such as  $FeS$  (in melt) +  $3 Fe_2O_3$  (in melt) =  $7 FeO$  (in melt) +  $SO_2$  (gas) release of pressure favors the production and liberation of  $SO_2$ . For every 0.1 weight percent  $SO_2$  produced 0.72 weight percent  $Fe_2O_3$  is reduced to  $FeO$ . The 1.8 weight percent of  $Fe_2O_3$  in the 1955 lavas is less than the 2.1 weight percent  $Fe_2O_3$  expected for a closed system fractionate with the same  $K_2O$  content (0.8 weight percent). Production and loss of 0.03 weight percent  $SO_2$  during eruption could account for this difference. The decrease in  $Fe_2O_3$  corresponds to a decrease in oxygen fugacity of 0.6 bar (at  $1200^\circ \log f_{O_2} = -5.5 d \log (FeO/FeO_{1.5})$ , Fudali, 1965). This difference is consistent with the changes in  $\log f_{O_2}$  from  $-8.1$  to  $-8.5$  at  $1120^\circ C$  as suggested by the compositions of the Fe-Ti oxide phenocrysts.

Gas loss can lead to an increase in the temperature of the magma because of its effect on crystallization temperature. An initial magma with 0.4 weight percent  $H_2O$  (Moore, 1965) would have about 0.8 weight percent  $H_2O$  at a stage of closed system fractionation equal to that of 1955 lava from vent E. Loss of this water during rise to the surface would raise the crystallization temperature by a few tens of degrees (Hamilton *et al.*, 1964). Crystallization of the microphenocrysts (20 weight percent) would yield 2,000 calories per 100 grams bulk and vaporization of the water and other gases would extract about 1,000 calories per 100 grams bulk lava. The net effect would be to heat the lava about  $30^\circ C$ . To this should be added a small amount of frictional heating (Shaw *et al.*, 1968). The heat loss to the walls by conduction and radiation will be initially large and probably dominant but will become minor as eruption continues through localized conduits with low ratios of surface area to volume (McBirney and Williams, 1969). We conclude that effervescence of the 1955 magmas could have raised the temperature of the erupting lava by a few tens of degrees centigrade or less. The estimated increase in temperature of presumed equilibrated magnetite and ilmenite from  $1120^\circ C$  to  $1180^\circ C$  (table 7) is possibly consistent with a rise in temperature induced by gas loss (the errors inherent in the estimate are about  $\pm 20^\circ C$ —analytical error  $\pm 1$  percent Hm and  $\pm 2$  percent Usp and uncertainty in reading the graph of  $f_{O_2}$ ,  $T$  versus composition). If the actual increase in temperature

was 60°C then a combination of heating due to magma mixing and gas loss appears necessary.

The deduced heating, reduction and reverse zoning of ilmenite and magnetite phenocrysts in the early 1955 lavas can be explained by mixing of variously fractionated magmas and by effervescence and loss of gas during eruption. Magma mixing is directly supported by the reverse zoning of the phenocrysts and the compositions of glass inclusions but can explain the heating and reduction only if primitive magma is involved, a possibility ruled out by Wright and Fiske (1971). However, sulfur and water were in fact lost during eruption and the estimated effects of these losses are in quantitative and/or qualitative agreement with the decrease in oxygen fugacity and increase in temperature which accompanied eruption as estimated from the compositions of the iron-titanium oxide phenocrysts. The agreement between the decrease in oxygen fugacity estimated from the iron-titanium oxide compositions and that predicted on the basis of change in the ratio of ferric to ferrous iron in a closed system as well as the high contents of sulfur in glass inclusions in magnetite and ilmenite phenocrysts indicates that crystallization of magnetite and ilmenite *began* in a system which had remained closed to losses of sulfur and gains of oxygen. Thus crystal-liquid fractionation, magma mixing and effervescence all played important roles in affecting the properties of the 1955 lavas of Kilauea volcano.

### 2. Kamakaia

Wright and Fiske (1971) interpret the Kamakaia lava as having formed by fractionation of a magma similar in composition to that parental to the early 1955 lavas but at a somewhat lower temperature. The zoning of magnetite and ilmenite phenocrysts and the composition difference between glass inclusions and host glass are similar to those in the 1955 lavas but are not as pronounced. These data suggest heating and reduction prior to and/or during eruption. There is no evidence of a new addition of less fractionated magma. Loss of SO<sub>2</sub> and H<sub>2</sub>O gas from the Kamakaia lava during eruption best explain the heating and reduction of the oxide phenocrysts.

### 3. Yellow Cone

Yellow Cone has an unusual and heterogeneous chemical composition. Wright and Fiske (1971) interpret Yellow Cone as a mixture of a hot picritic magma with a cool, highly fractionated magma containing about 60 percent SiO<sub>2</sub>. The heterogeneity both in the bulk composi-

tion and in the host glass suggest a less complete mixing than that postulated for the 1955 lavas. The absence of extensive reaction of either olivine or of Fe-Ti oxides suggest that the mixing took place just prior to eruption of the pumice. In general the compositions of the glass inclusions support the mixing hypothesis. Those in magnetite and ilmenite are high in  $\text{SiO}_2$  and  $\text{K}_2\text{O}$ , low in  $\text{CaO}$ . Those in olivine are lower in  $\text{SiO}_2$  and high in  $\text{CaO}$ . The low  $\text{MgO}$  of the glass inclusions in olivine indicates continued crystallization of olivine after entrapment of the liquid.

The adjoined magnetite and ilmenite phenocrysts in the Yellow Cone pumice have compositions similar to the cores of magnetites and ilmenites in the 1955 and Kamakaia lavas and imply oxidizing conditions of crystallization similar to the initial crystallization of magnetite and ilmenite in the 1955 and Kamakaia lavas.

#### SUMMARY: OXIDATION AND MIXING OF KILAUEAN AND OTHER BASALTS.

Figure 7 summarizes the  $f_{\text{O}_2} - T$  relations for Kilauean basalts as determined by: 1) equilibration under laboratory conditions (Fudali, 1965); 2) direct measurement of  $f_{\text{O}_2} - T$  in a crystallizing basalt (Sato and Wright, 1966); and 3) composition of coexisting magnetite-ilmenite pairs (Wright and Weiblen, 1968, this paper). There is a conspicuous, correlated variation in oxygen fugacity and temperature. With reduction during eruption the rims of oxides in the early 1955 lavas attained compositions that are consistent with the redox conditions of historic Kilauea lava lakes (Sato and Wright, 1966, Wright and Weiblen, 1968).

In the specific case of the early 1955 lavas and in general the case is strong for reduction of lava by means of  $\text{SO}_2$  loss. In the Yellow Cone cinders, which are the most conspicuous case of magma mixing, the zoning of the oxide phenocrysts is weak and unsystematic. Magma mixing in this instance did not result in conspicuous reduction. The early 1955 and Kamakaia magmas seem to have evolved in closed systems with magma mixing involving only fractionated batches of liquid. The lavas of Tristan da Cunha (Anderson, 1968) underwent strong reduction during eruption. Reduction of lava seems so widespread that a general mechanism related to the eruption process seems required. Loss of gas ( $\text{SO}_2$ ) is a convincing explanation.

From the data on the early 1955 lavas it is possible to estimate the oxygen fugacity of the primary magma prior to reduction, gas loss, and differentiation. Let us begin with the estimated conditions of eruption ( $T = 1120^\circ\text{C}$ ,  $f_{\text{O}_2} = 10^{-8.5}$  atm. and  $\text{Fe}_2\text{O}_3 = 1.74$ ,  $\text{FeO} = 11.32$ , vent A—Wright and Fiske 1971 table 3 col. 2). We can estimate

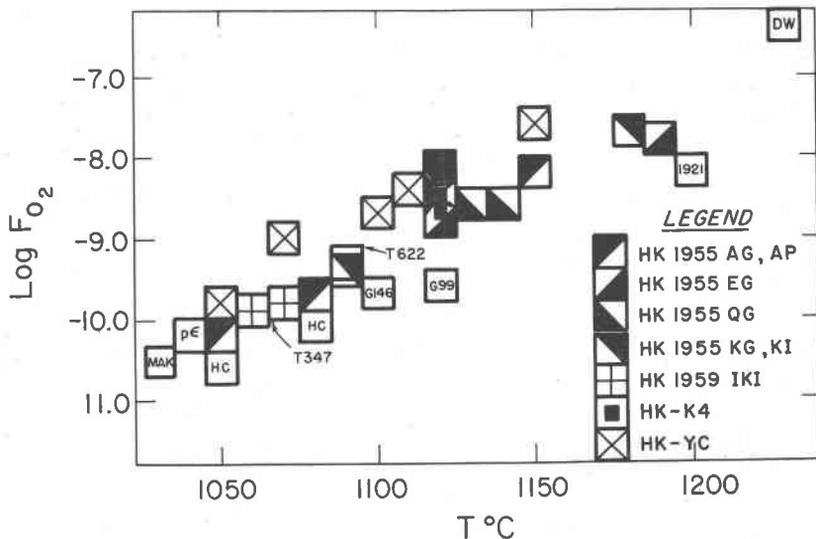
OXYGEN FUGACITY and TEMPERATURE  
 of KILAUEAN and OTHER BASALTS


Fig. 7. Estimated oxygen fugacities and temperatures of Kilauean and other selected basalts. Data for the squares keyed to the legend are given on Table 7. The black square (1120°C,  $-8.1 \log f_{O_2}$ ) is the condition suggested by the average compositions of the interiors of magnetite and ilmenite phenocrysts in the 1955 Kilauean lavas. Other points are: MAK (Makaopuhi lava lake, Kilauea—Wright and Weiblen, 1968), PC (Precambrian basalt dikes, Adirondack Mountains, New York—Anderson, 1966), HC (Hat Creek high-alumina olivine tholeiite, California—Smith and Carmichael, 1968, Anderson, unpublished data), T347, T622 (alkaline basalts, Tristan da Cunha, Anderson, 1968), G146, G99 (basalts Thingmuli volcano, Iceland, Carmichael, 1967), 1921 (summit lava, 1921, Kilauea volcano, Fudali, 1965), DW (ultramafic xenolith (E113 of Aoki) in alkaline basalt, Dreiser Weiher, Germany, Anderson, unpublished data). Except for 1921, all points are deduced from chemical analysis of magnetite and ilmenite and the experimental data of Buddington and Lindsley (1964) and Taylor (1964) including extrapolation and interpolation.

the  $FeO/Fe_2O_3$  ratio and  $Fe_2O_3$  content of the magma prior to eruption by using the Fudali relation (see footnote 1, page 209) and the estimated temperature and oxygen fugacity ( $T = 1120^\circ C$ ,  $f_{O_2} = 10^{-8.1}$ ). The result is 2.00 wt. percent  $Fe_2O_3$ . We can allow for crystallization by using the results of Wright and Fiske, 1971 (see footnote 1, page 209). This yields a parent with 1.51 wt. percent  $Fe_2O_3$  and 9.98 wt. percent  $FeO$ , in good agreement with analyses of glassy submarine lavas of Kilauea<sup>1</sup> (Moore, 1965). Slight extrapolation of Fudali's data on the 1921 Kilauea lava suggests that the primary parent had an oxygen fugacity of  $10^{-8.5}$  atm. at 1200°C. This value is slightly less than that

estimated by Fudali for the 1921 lava ( $10^{-8.2}$  atm.). The small discrepancy seems best explained by partial subaerial oxidation of the 1921 lava analysed by Fudali since it has more  $\text{Fe}_2\text{O}_3$  (1.8 wt. percent) than several recently analysed glassy lavas from Kilauea (1.2 wt. percent  $\text{Fe}_2\text{O}_3$ , Wright and Fiske, 1971, table 4a).

The estimated intratelluric conditions for crystallization of oxides in Tristan basalts are  $1040^\circ\text{C}$ ,  $\log f_{\text{O}_2} = -8.5$  compared to  $1120^\circ\text{C}$ ,  $\log f_{\text{O}_2} = -8.1$  for Kilauean basalts and  $1240^\circ\text{C}$ ,  $\log f_{\text{O}_2} = -6.4$  for an inclusion from Deiser Weiher Germany (Figure 7). These conditions of oxide crystallization are in good accord with the Hm-rich magnesian ilmenites characteristic of probable mantle rocks associated with kimberlites (Smirnov, 1959; Dawson, 1962; Nixon *et al.*, 1963). It thus appears that crystallization of oxides in basaltic magmas occurs under similar redox conditions both in near surface magma reservoirs and deep within the mantle.

The estimated redox conditions of primary, undifferentiated Kilauean magma (not saturated with oxides) are much more reduced (at  $1200^\circ\text{C}$ ,  $\log f_{\text{O}_2} = -8.5$ ) than those of a hypothetical oxide saturated magma at  $1200^\circ\text{C}$  ( $\log f_{\text{O}_2} = -6.9$ ). The existence at depth of both magma types at the same temperature would require a considerable oxygen fugacity gradient. Such a gradient may have considerable bearing on the origins of basalts and the evolution of the mantle and will be treated in a later article.

High alumina olivine tholeiite from Hat Creek, California (Smith and Carmichael, 1968, Anderson, unpublished data) and lavas of Thingmuli volcano, Iceland (Carmichael, 1967), contain more reduced oxides (Fig. 6). These differences possibly reflect a greater degree of reduction during eruption and prior to the crystallization of the groundmass oxides. An interesting alternative hypothesis is that the lower oxygen fugacities of the Hat Creek and Thingmuli basalts reflect a more reduced mantle environment where the initial magmas originated. The Hat Creek lava is chemically similar to other basalts from ocean ridges which were initially interpreted as being exceptionally reduced on account of low amounts of  $\text{Fe}_2\text{O}_3$  (Engel *et al.*, 1965). The iron-rich Tertiary basalts of Iceland such as those of Thingmuli likewise probably were produced in an ocean ridge environment. Upward

<sup>1</sup>Several of the analyses of the submarine lavas have somewhat higher  $\text{Fe}_2\text{O}_3$ . Possibly loss of  $\text{H}_2\text{S}$  during low temperature solution of the rock for analysis results in partial oxidation of the iron just as loss of  $\text{SO}_2$  at igneous temperature results in reduction of the iron. This artifact would not significantly affect subaerial lavas because they are so poor in sulfur. Alternatively loss of  $\text{H}_2$  during cooling may explain the high  $\text{Fe}_2\text{O}_3$  values (J. G. Moore, written communication, 1971).

movement beneath ocean ridges conceivably could bring deeper (? more reduced) mantle into the zone of melting. In the light of present data, however, the similarities of the redox conditions of oxide saturated basaltic magmas are more striking than are the differences.

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