Petrology of volcanic rocks from Kaula Island, Hawaii Implications for the origin of Hawaiian phonolites

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Abstract. A compositionally diverse suite of volcanic rocks, including tholeiites, phonolites, basanites and nephelinites, occurs as accidental blocks in the palagonitic tuff of Kaula Island. The Kaula phonolites are the only documented phonolites from the Hawaiian Ridge. Among the accidental blocks, only the phonolites and a plagioclase basanite were amenable to K-Ar age dating. They yielded ages of 4.0-4.2 Ma and 1.8 ± 0.2 Ma, respectively. Crystal fractionation modeling of major and trace element data indicates that the phonolites could be derived from a plagioclase basanite by subtraction of 27% clinopyroxene, 21% plagioclase, 16% anorthoclase, 14% olivine, 4% titanomagnetite and 1% apatite, leaving a 16% derivative liquid. The nephelinites contain the same phenocryst, xenocryst and xenolith assemblages as the tuff. Thus, they are probably comagmatic. The strong chemical similarity of the Kaula nephelinites and basanites to those from the post-erosional stage Honolulu Group on Oahu, the presence of garnet-bearing pyroxenites in the Kaula nephelinites (which previously, had only been reported in the Honolulu volcanic rocks) and the similar age of the Kaula basanite to post-erosional lavas from nearby volcanoes are compelling evidence that the Kaula basanites and nephelinites were formed during a "post-erosional" stage of volcanism.

Introduction

Kaula Island is a crescent shaped tuff cone remnant $(\sim 0.5 \text{ km}^2)$ 33 km west-southwest of the island of Niihau, along the Hawaiian Ridge (Fig. 1). It is located on the southeast corner of a wave-cut platform that is not part of the Niihau shield as inferred by Shaw et al. (1980). Instead, it is part of a separate and distinct volcanic edifice that together with Niihau and Kauai forms a ridge oriented nearly orthogonal to the main trend of the Hawaiian Ridge (Fig. 1). Relatively little geologic information on Kaula Island was available prior to this study, because the island has been used as a bombing target by the U.S. military since World War II. Palmer (1927) published the first geologic descriptions of Kaula Island based on observations from a boat. Palmer (1927, 1936) also provided petrographic descriptions of volcanic rocks from the island. We

visited the island by helicopter courtesy of the U.S. Navy. Abundant unexploded ordnance, bird nests (total bird population >45,000) and steep cliffs surrounding the island made sample collection hazardous.

Kaula Island consists of approximately 160 m of wellbedded, palagonitic tuff (Fig. 2). The tuff contains accidental fragments of light gray (phonolite) and dark gray (basalt) volcanic rocks, coralline material, coarse-grained ultramafic and mafic xenoliths (including spinel pyroxenites, garnet pyroxenites, spinel peridotites and dunites) and megacrysts (augite, anorthoclase, olivine, Al-spinel and titanomagnetite). The purpose of this paper is to present petrographic, geochemical and geochronological data on the distinctive, accidental volcanic blocks recovered from Kaula Island and to compare these results with data for other lavas erupted along the Hawaiian Ridge. Phonolites (differentiation index >75 and normative nepheline >10%, Coombs and Wilkinson 1969) had not been reported from the subaerial Hawaiian Ridge but were dredged from Koko Seamount, at the southern end of the Emperor Seamount chain (Clague and Greenslate 1972; Clague 1974). A rock reported as a nepheline-bearing phonolite from Pearl and Hermes Volcano (Clague et al. 1975), midway along the Hawaiian Ridge, should be classified as a trachyte as it contains only 4.5% normative nepheline (compared to 17% for the Kaula phonolites).

Petrography

The volcanic rocks of Kaula Island consist of four main groups: palagonitic tuff, light gray biotite-bearing volcanic blocks (phonolites), dark gray to black volcanic blocks (basanites and nephelinites) and a reddish volcanic block (tholeiitic basalt). The tuff consists of lapilli to ash-size fragments of altered volcanic rock, coralline debris, bird bones and blocks of volcanic rock, pyroxenite and peridotite.

The phonolites contain rare phenocrysts of biotite, up to 5 mm in length, and microphenocrysts of apatite, magnetite and very rare anorthoclase in a matrix of anorthoclase microlites, apatite, olivine, magnetite and devitrified glass (Table 1). Biotite is rare in rocks from the Hawaiian Islands, having been previously reported only as a rare groundmass phase in some trachytes (Macdonald and Abbott 1974). Nepheline was not observed in any of the phonolite thin sections even after the sections were stained with methylene blue. Biotite and feldspar are fresh, but olivine is commonly reddish, and glass is devitrified. Rare secondary minerals, zeolite and calcite, occur in fractures and vesicles.

Three types of basaltic lava were recovered. Modes for representative samples of each basalt type are in Table 1. The most

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Fig. 1. Bathymetric map of the Hawaiian Islands and nearby seamounts with 1,000 and 2,000 fathom contours. Note oblique trend of Kaula, Niihau and Kauai (NE-SW) to the trend of the Hawaiian Islands (NW-SE)



Fig. 2. Geologic map of Kaula Island. Topographic base map from Palmer (1936). Cross section shows depositional anticline exposed at the north end of Kaula Island. Kaula Island consists entirely of palagonitized tuff

common basalt is an olivine nephelinite/basanite (KA-15, 17, 19, 28, 31 and 34) which contains abundant megacrysts of olivine, clinopyroxene, anorthoclase, aluminous spinel and titaniferous magnetite and xenoliths of peridotite and pyroxenite. These rocks are devoid of plagioclase. To avoid confusion this group of samples will be referred to as nephelinites. Other basalt types are rare and include: a plagioclase (plag) basanite (KA-29) with rare anorthoclase megacrysts; and a tholeiitic basalt (KA-14) with olivine, au-

 Table 1. Modes for representative volcanic rock types from Kaula

 Island based on 500 counts. Values reported are vesicle free and

 are volume percent

Rock type sample #	Tholeiite KA-14	Plag basanite KA-29	Nephe- linite KA-31	Phonolite KA-36
Phenocrysts/				
Microphenocrysts				
Olivine	7	3	12	·
Срх	<1	<1		
Plag.	2			
Biotite				0.1 - 1
Magnetite				1
Apatite				0.1–1
Groundmass				
Olivine	1	9	5	<1
Срх	33	32	38	_
Plagioclase	32	45		
Anorthoclase				28
Apatite	<1	<1	2	5
Magnetite	21	10	14	1
Glass	3		20	65
Xenocrysts	—	<1	9	
Vesicles	17	13	4	
Texture	Sub- ophitic	Inter- granular	Inter- sertal	Hyalo- pilitic

gite and plagioclase phenocrysts in a matrix of plagioclase, augite and magnetite.

Phenocryst and groundmass minerals in these basaltic samples are unaltered (except olivine in sample KA-14). Devitrified glass is present in some of the samples. Samples with abundant glass (50–70 vol.%; KA-19, 34) commonly contain 5–10% zeolites (primarily thompsonite and chabazite).

Analytical methods

Major element contents (Table 2A) were determined at the University of Manitoba: Si, Al, Fe (total), Mg, Ca, K, Ti and Mn by X-ray fluorescence; Na by atomic absorption; and P by colorimetry. Ferrous iron analyses were made by titration with sodium diphenylamine sulfonate used as an indicator. H₂O contents were determined gravimetrically by heating samples in a stream of dry oxygen in an induction furnace at 1100° C, with collection on anhydrone. For CO₂ analyses, the sample was decomposed in warm HCl, and the evolved CO₂ was passed through a drying train and collected on ascarite. Abundances of the trace elements (Table 2B), Rb, Sr, Ba, V, Ni, Zn, Ga, Y, Zr and Nb were determined by X-ray fluorescence at the University of Massachusetts (Rhodes 1983) and abundances of Cs, Sc, Cr, Hf, Ta, Th and REE were determined by instrumental neutron activation at the Massachusetts Institute of Technology (Ila and Frey 1984). Precision and accuracy of these trace element data are indicated in Table 2B.

Mineral analyses were made with an electron microprobe operated at 15 kV and 10–20 nA sample current. Raw data were corrected for dead time of detectors, instrument current drift (0.1%/h)and spectrometer background. Mineral analyses were obtained using ZAF corrections. Accuracy is estimated to be 1–2% for major elements and 5–10% for minor elements, on the basis of replicate microprobe analyses compared with wet chemical analyses.

Conventional K-Ar age measurements were made at the Hawaii Institute of Geophysics with isotope dilution mass spectrometry methods described by Dalrymple and Lanphere (1969, 1971) and Gramlich (1970). K was determined by atomic absorption. Samples were treated in dilute nitric acid prior to analysis

	Tholeiite	Plag	Phonolites			Nephelinites ^a					Honolulu		
	14	Basanite 29	41	100E	36	37	19	15	28	31	34	17	volcanics ⁶
SiO ₂	47.60	46.65	54.55	56.50	54.40	54.25	40.75	42.35	42.05	40.95	39.20	40.60	40.93-42.63
TiO ₂	1.59	2.13	0.54	0.48	0.55	0.51	2.60	2.74	2.81	2.83	2.71	2.56	2.44- 2.92
Al ₂ Õ ₃	15.10	14.71	17.35	18.03	17.98	17.86	11.54	11.58	12.44	12.02	11.42	11.68	11.06-12.69
Fe ₂ O ₃	9.67	4.12	2.76	2.86	3.22	4.47	6.16	3.94	4.04	4.51	5.74	5.22	3.21-3.44
FeO	3.40	6.56	1.98	2.04	2.00	0.92	6,44	9.40	9.40	8.72	7.56	7.84	10.22-10.96
MnO	0.12	0.16	0.32	0.30	0.35	0.28	0.19	0.22	0.22	0.23	0.32	0.24	0.20- 0.22
MgO	5.40	8.61	1.90	1.93	2.05	1.85	12.10	13.43	10.35	12.82	11.38	12.14	11.84-13.85
CaO	11.49	9.96	2.36	1.64	1.65	1.29	10.98	10.48	10.58	10.84	12.10	11.16	10.60-12.49
Na ₂ O	2.39	3.70	6.75	7.85	8.23	7.88	1.67	3.32	3.72	3.74	2.42	3.28	2.72 - 3.68
Na ₂ O (INAA)	2.27	3.57	6.57		8.32	8.03	1.57	3.28	3.23	3.76	2.48	3.24	
K ₂ O	0.45	1.03	4.09	4.35	4.38	5.09	1.21	1.16	1.48	1.23	1.29	1.19	0.79-1.10
P_2O_5	0.44	0.62	0.63	0.64	0.66	0.63	0.66	0.70	0.73	0.86	0.83	1.11	0.61-0.82
$\tilde{H_2O^+}$	0.97	0.57	3.77	2.40	2.59	1.09	2.68	0.33	0.30	0.34	2.02	1.68	-
H_2O^-	0.79	0.41	2.57	0.80	1.53	3.43	2.63	0.23	1.26	0.49	2.83	1.23	
\dot{CO}_2	0.28	0.59	0.19	0.08	0.17	0.18	0.04	0.09	0.35	0.19	0.11	0.10	-
Total	99.69	99.82	99.76	99.90	99.76	99.73	99.65	99.96	99.73	99.77	99.93	100.03	~
100 Mg/ (Mg + Fe ⁺²) (norms ^c)	50.5	65.7	49.3	48.9	48.9	46.1	69.8	70.3	64.5	69.6	67.1	68.9	65.8 -69.5
Q	0.2	_	_	_	-	_	~	_	_	-	_	_	
Ôr	2.7	6.2	26.0	26.7	27.2	31.8	7.6	6.9	8.9	6.7	2.4	7.3	
Ab	20.9	22.3	47.2	46.4	39.1	34.8	6.6	4.3	4.2	-	_	1.9	
An	30.1	20.9	5.3	1.2	-		21.7	13.4	13.2	12.6	17.4	14.1	
Lc	_	-	_	_	-		_		_	0.5	4.4		
Ne	_	5.2	7.7	12.2	17.5	17.5	4.5	13.0	15.2	17.4	11.7	14.5	
Ac		-	-	_	1.4	2.9	_	-	_	_	_	_	

Table 2A. Major element abundances and selected components of CIPW normative mineralogy for Kaula samples and for comparison a compositional range for basanites and nephelinites from the Honolulu Volcanics, the post-erosional series on Oahu

^a Basanite samples arranged in approximate order of increasing incompatible element content

^b Honolulu volcanics (the post-erosional series on Oahu) data are for range (anhydrous) of basanites and nephelinites (5.0-16.8% normative nepheline) from vents 13, 14, 20, 21, 22, 27 and 31 (Clague and Frey 1982)

 $^{\circ}$ 100 Mg/(Mg + Fe⁺²) and normative mineralogy calculated on anhydrous basin with Fe₂O₃/FeO*=0.24

to remove or at least reduce the presence of any alteration products in the samples.

Geochronology

Conventional K-Ar age determinations were attempted on representatives from all of the Kaula volcanic rock types. The tholeiite and nephelinites were too gas-rich for Ar analyses. Two whole rock age determinations were made on Kaula phonolites yielding ages of 4.01 ± 0.09 and 4.22 ± 0.25 Ma (Table 3). A biotite separate from one of these samples yielded a nearly identical age, 3.98 ± 0.70 MA. The phonolite ages overlap with ages for the oldest, tholeiitic shield-building stage lavas on Kauai $(3.81 \pm 0.06 \text{ to } 5.14 \pm 0.20 \text{ Ma}; \text{ McDougall 1979})$, but are significantly younger than any of the shield-building lavas on Niihau ($\sim 4.7-5.5$ Ma; Clague et al. 1982). However, they are significantly older than the post-erosional lavas on Niihau and Kauai (Fig. 3).

A plag basanite sample (KA-29) yielded a K-Ar age of 1.8 ± 0.2 Ma, which is well within the age range for posterosional lavas from Niihau and Kauai (Fig. 3).

Mineral chemistry

Olivine phenocrysts (ph) and microphenocrysts (mph) are common in the Kaula basalts. In the nephelinites, the oliv-



Fig. 3. Ages in millions of years (Ma) of Hawaiian shield (solid bars) and post-erosional (stippled bars) lavas as a function of distance in kilometers from Kilauea Volcano. Modified from Clague et al. (1982). Dashed line represents projection of age trend from well-dated Koolau and Kauai post-erosional groups to Kaula Volcano

	Tholeiite	Plag	Phonol	ites		Nephe	linitesª					Honolulu
	14	29	41	36	37	19	15	28	31	34	17	- Volcanics
Rb	4.8	21.3	72	72	98	20.7	28.1	33.0	29.9	24.9	19.6	9-20
Cs	-	0.3	0.6	0.6	0.6	0.4	0.4	0.3	_	0.2	0.2	_
Sr	330	938	690	274	406	6,404	1,247	1,969	1,376	2,274	2,380	810-1.050
Ва	169	513	505	561	628	494	663	825	757	860	947	650-825
Sc	35	22	11	12	12	24	24	21	23	21	22	18–26
V	325	230	6	8	9	286	290	270	293	281	279	295
Cr	470	493	3	3	3	428	457	277	477	366	412	240-350
Ni	145	455	8	8	8	311	429	228	360	294	295	240-460
Zn	94	110	136	143	132	106	108	126	118	114	115	107-168
Ga	20	18	19	18	19	16	16	18	18	15	15	_
Y	15	21	51	51	52	18	20	21	22	21	24	
Zr	95	136	485	509	507	106	143	215	161	151	180	149–188
Nb	14.3	31.6	110	115	115	40.2	42.8	55.7	48.9	51.4	55.2	-
Hf	2.2	2.9	9.5	9.9	9.8	3.0	3.1	4.3	3.5	3.5	3.7	3.3-3.9
Та	0.65	1.7	5.9	6.1	5.8	2.5	3.7	3.5	_	2.8	3.2	2.3-3.3
Th	1.0	2.0	7.1	7.5	7.7	2.5	3.8	3.7	4.9	5.3	5.3	3.6-5.9
La	10.0	27.1	114	119	120	32.8	37.3	37.2	47.5	48.4	55.7	45-54
Ce	22.3	59	232	227	227	72	77	84	95	98	114	81-110
Nd	12.3	29.7	80	79	78	34.5	37	42	44	45	53	42-56
Sm	3.21	6.48	12.7	11.6	12.5	7.27	7.54	8.34	8.56	9.01	10.4	9.2-11.1
Eu	1.24	2.00	3.37	3.55	3.63	2.39	2.57	2.78	3.00	2.96	3.37	2.77-3.24
Tb	0.51	0.76	1.52	1.55	1.62	0.82	0.83	0.88	0.88	0.93	1.13	0.9-1.3
Yb	1.33	1.70	4.96	5.31	5.32	1.53	1.54	1.54	1.73	1.64	1.94	1.5-1.7
Lu	0.19	0.27	0.71	0.74	0.73	0.20	0.19	0.19	0.23	0.23	0.25	0.25-0.30

Table 2B. Trace element abundances (ppm on hydrous-basis) in Kaula samples and for comparison a range for basanites and nephelinites from the Honolulu volcanics

^a Precision of INAA analyses indicated by samples (17, 28, 29, 34 and 41) analyzed in duplicate and 2 samples (14 and 15) analyzed in triplicate; these multiple analyses yield mean standard deviations of 1%-3% (La, Eu, Sc, Cr), 3%-6% (Ce, Nd, Sm, Yb, Hf, Ta, Th), 6%-10% (Tb, Lu) and ~50% (Cs). Accuracy of MIT INAA data can be evaluated from standard rock data in Chen and Frey (1985)

^b Precision of XRF data indicated by standard deviations of 11 samples analyzed in duplicate; for basaltic samples these are Rb (2.6%), Sr (0.8%), Ba (1.8%). V (1%), Ni (0.8%), Zn (2.5%), Ga (4.8%), Y (1.4%), Zr (2.0%), and Nb (1.2%)

Table 3. Potassium-argon age measurements o	n phonolites an	nd a plag basanite	from Kaula Island
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Sample	K	Argon			Calculated age ^b
	(wt.%)"	Weight (grams)	⁴⁰ Ar _{RAD} . (mol/gram)	$\frac{{}^{40}\text{Ar}_{\text{RAD.}\times100}}{{}^{40}\text{Ar}_{\text{Total}}}$	- (10° yrs) Ma
Phonolites Whole rock (from Macdonald). KA-100E	3.89 ± 0.02	4.343	2.71×10^{-11}	94.2	4.01 ± 0.09
Whole rock KA-36	3.79 ± 0.04	3.007	2.77×10^{-11}	37.5	4.22 ± 0.25
Biotite (handpicked from whole rock) KA-36	5.58 ± 0.16	0.1545	3.84×10^{-11}	15.9	3.98 ± 0.70
Plag basanite whole rock KA-29	0.93 ± 0.02	5.3884	1.55×10^{-11}	18.4	1.8 ± 0.2

^a Mean and range of two measurements

^b $\lambda_{\epsilon} = 0.581 \times 10^{-10} \text{ yr}^{-1}$; $\lambda_{\beta} = 4.962 \times 10^{-10} \text{ yr}^{-1}$; ⁴⁰K/K = 1.167 × 10⁻⁴ mol/mo. Errors are estimates of standard deviations of precision

ine ph have high forsterite (Fo) and NiO contents, ranging from 86.5-88.5% and 0.25-0.34 (Table 4). Olivine in dunitic xenoliths varies from Fo 80.4-90.0, NiO 0.29-0.45. CaO contents are low (<0.20 wt.%) in the dunitic olivines in contrast to the phenocrystic olivine.

Pyroxene phenocrysts are absent in the Kaula volcanics, except in crystal clots in the tholeiitic basalt KA-14 where they are endiopsidic, with low Ti and moderate Al (Table 5). Only groundmass clinopyroxene (cpx) occurs in the other basaltic lavas. Two types are present in the plag basanite: a moderate Ti and Al salite and in segregation vesicles, a mauve-colored, high Ti and Al salite. The nephelinites have only the high Ti and Al salites. Rare, unzoned and high Al and Na augite megacrysts are also present in the nephelinites. The composition of the megacrysts is identical to augites from clinopyroxenites (some containing garnet) that are common accidental blocks in Kaula tuff (Presti 1982).

Table 4. Representative olivine analyses from Kaula nephelinite

	KA-17 Xenocryst	KA-34 PH-Core	KA-15 PH-Core	KA-28 PH-Core	KA-19 mph
SiO ₂	40.58	40.04	40.02	39.78	39.32
FeO	9.80	11.10	10.95	13.01	13.61
MnO	0.16	0.15	0.13	0.15	0.18
NiO	0.45	0.34	0.31	0.32	0.26
MgO	49.34	47.89	47.82	46.59	46.36
CaO	0.08	0.22	0.25	0.23	0.25
Total	100.41	99.74	99.48	100.08	99.98
Fo%	90.0	88.5	88.6	86.5	85.9

PH = phenocryst; mph = microphenocryst

 Table 5. Composition of clinopyroxenes in volcanic blocks from

 Kaula Island, Hawaii

	Thole	iite	Plag H	Basanite	Nephe	elinite		
	KA-1	4	KA-2	KA-29		3	KA-1	7
	Gm	Clot pH	Gm	SV ^a	Gm	Gm	Core	Rim
SiO	50.56	51.42	49.39	43.7	41.07	45.99	49.51	49.13
TiO ₂	1.02	0.60	1.74	5.15	4.85	2.82	0.97	0.97
$Al_2\bar{O}_3$	3.46	3.52	3.01	8.20	10.92	6.85	8.70	8.88
Cr_2O_3	0.03	0.85	0.04		0.02	0.01	0.03	0.03
FeO	9.79	5.82	11.58	11.10	9.30	8.60	6.37	6.48
MnO	0.21	0.17	0.26		0.11	0.13	0.12	0.16
MgO	14.50	15.73	11.28	9.25	10.08	11.86	14.02	13.88
CaO	20.00	21.41	21.78	21.6	22.49	22.62	17.94	17.81
Na ₂ O	0.32	0.30	0.61	0.65	0.60	0.53	1.89	1.79
Total	99.89	99.82	99.69	99.65	99.44	99.41	99.55	99.13
Mg	42.2	45.8	33.7	30.1	32.0	36.0	46.0	45.8
Fe	16.0	9.5	19.4	20.0	16.6	14.6	11.7	12.0
Ca	41.8	44.7	46.9	49.9	51.4	49.4	42.3	42.2

^a In segregation vesicle

Anorthoclase megacrysts are present in the basanites, nephelinites and the tuff. Very rare anorthoclase mph are present in the phonolites. Groundmass (gm) anorthoclase grains are present in the phonolites and plag basanite. The megacrysts have higher Na and lower K and Fe than the mph and gm grains (Table 6).

Labradorite composition mph and gm grains are present in the plag basanite (KA-29).

Spinel megacrysts are common in the Kaula nephelinites. There are two types: a gray-green to opaque variety with high Al_2O_3 (up to 60 wt.%) and an Al, Ti magnetite (Table 7).

The biotites in the Kaula phonolite are a high Ti, low K variety (Table 8) like those in Gough Island trachytes (le Roex 1985).

Whole rock geochemistry

Major elements

The major element composition of the twelve analyzed Kaula samples ranges widely, from tholeiite to nephelinite (Table 2A). The suite of samples include: An evolved tholeiitic basalt (KA-14); a plag basanite (sample KA-29) with 5% normative nepheline; nephelinites (samples KA-15, 17, 19, 28, 31 and 34) which range in normative nepheline from ~ 12 to 17% (except for sample KA-19, 4.5% nepheline, which has anomalously low Na₂O); and phonolites (samples KA-36, 37, 41 and 100E) with 7.7 to 17.5% normative nepheline (Table 1, Fig. 4). In an alkalies-silica diagram (Fig. 5), sample KA-14 plots in the tholeiite field. The basanites and nephelinites overlap with other Hawaiian alkalic lavas; the four phonolites are more enriched in alkalies than any other previously reported subaerial Hawaiian lava (Fig. 5).

The nephelinites are MgO-rich (10.4–13.4 wt.%) and have high Mg numbers $[100 \text{ Mg/(Mg+Fe}^{2+})]$ (64.5–70.3 with Fe₂O₃/FeO adjusted to 0.24 following Clague and Frey, 1982, to allow comparison with the Honolulu Group), which is consistent with the high forsterite content of their phenocrysts (85.9–88.5% Fo). Relative to the nephelinites,

Table 6. Composition of feldspars in volcanic blocks from Kaula Island. Total iron is calculated as FeO for plagioclases and Fe_2O_3 for anorthoclases

	Phonolites		Plag Basani	te		Nephelinite	
	KA-37	KA-36	KA-27			KA-22	
	GM	GM	Mega.	MPH	GM	Mega-Core	Mega-Rim
SiO ₂	65.47	66.38	67.55	51.81	52.11	66.82	67.00
Al_2O_3	20.20	19.80	20.74	30.25	30.04	20.82	20.69
FeO ^t				0.82	0.69		20.09
Fe ₂ O ₃ ^t	0.73	0.50	0.07			0.06	0.32
CaO	0.74	0.47	0.50	13.20	13.11	0.55	0.57
Na ₂ O	7.92	7.61	9.38	3.72	3.78	8.55	8.25
K ₂ O	4.55	5.10	1.58	0.21	0.22	3.24	3.26
Total	99.61	99.86	99.82	100.01	99.95	100.04	100.09
Ab	70.0	67.8	87.8	33.3	64.8	77 9	77.0
Or	26.4	29.9	9.7	1.2	1.3	19.4	20.0
An	3.6	2.3	2.5	65.5	33.9	2.7	3.0
Mineral name	Anortho.	Anortho.	Anortho.	Labra.	Labra.	Anortho.	Anortho.

Mega=megacryst



Fig. 4. Differentiation Index (normative quartz, albite, orthoclase and nepheline) versus normative nepheline. Fields are from Coombs and Wilkinson (1969). Symbols: *open circles* phonolites; *closed circles* nephelinites; *open square* plag basanite; *closed square* with g-plag basanite segregation vesicle glass; Kohala field (Garcia, unpubl.) is representative of Hawaiian alkalic lavas. All data plotted in this and all subsequent figures were dry normalized to 100% with Fe₂O₃/FeO = 0.24



Fig. 5. Total alkalies (Na₂O and K₂O wt.%) versus SiO₂ wt.%. Honolulu field from Clague and Frey (1982); Hawaiian shield alkali suite data from Macdonald (1968). Symbols: x tholeiite; others as in Fig. 4. Dividing line for alkalic and tholeiitic Hawaiian volcanic rocks from Macdonald (1968)

the phonolites are highly enriched in Na₂O and K₂O, moderately enriched in SiO₂ and Al₂O₃, highly depleted in FeO, MgO, CaO and TiO₂ and slightly depleted in P₂O₅ (Table 2A). Consequently, the phonolites have very low CaO/ Al₂O₃ and high K₂O/P₂O₅ ratios relative to the basalts. The phonolites are more oxidized than the basanite and nephelinites (Fe₂O₃/FeO wt.%=1.4-4.8 vs. 0.4-1.0). High Fe₂O₃/FeO ratios are common in phonolites. The unaltered, late Quaternary Laacher Sea phonolite tephra have ratios of 0.9 to 5.2, averaging about 1.6 in the upper unit (Worner and Schmincke 1984a) which is compositionally similar to the Kaula phonolites. The four Kaula phonolitic samples differ significantly in CaO and K₂O contents, with decreasing CaO and increasing K₂O correlating with de-

 Table 7. Spinel group xenocrysts in a nephelinite and a titanomagnetite phenocryst in a phonolite from Kaula Island

	Nepheli KA-19	Phonolite KA-37		
	gn-gy	Ti-n	nagt	-
SiO ₂	0.10	0.15	0.19	0.15
TiO,	0.61	13.32	14.49	6.60
$Al_2 \tilde{O}_3$	59.14	9.16	10.37	2.50
Cr_2O_3	1.53	0.03	0.06	
FeO	19.35	68.64	65.36	83.10
MnO	0.00	0.25	0.55	
MgO	18.36	4.94	5.40	2.50
Total	99.09	96.49	96.42	94.85
Recalculated FeO	13.79	37.36	37.56	34.06
Fe ₂ O ₃	6.18	34.76	30.89	54.50
Recalculated total	99.71	99.97	99.51	100.31

Table 8. Representative biotite analyses from		KA-37	
Kaula phonolites		ph-core	mph-core
	SiO ₂	38.55	38.1
	TiO ₂	6.45	5.25
	Al_2O_3	14.40	14.20
	FeO	13.40	15.0
	MgO	15.10	15.3
	CaO	0.04	0.02
	Na ₂ O	0.98	0.95
	K₂Õ	7.65	7.90
	Total	96.57	96.72

creasing Mg number (Table 2A). These phonolites have nearly twice as much MgO and P_2O_5 as do most other mafic phonolites (e.g. Kyle 1981; Worner and Schmincke 1984a).

Although olivine phenocrysts are fresh in the nephelinites, these samples have high and variable Fe₂O₃/FeO ratios and H₂O contents (Table 2A) which are indicative of low temperature alteration. Among the nephelinites, sample KA-19 has the highest Fe₂O₃/FeO ratio and H₂O content, and it has an anomalously low Na₂O content (Table 2A). The other basanite with high H₂O content (KA-34, 4.85 wt.% H₂O) also has relatively low Na₂O content (Table 2A). The low Na_2O content results in anomalously low normative nepheline in KA-19, compared with the other nephelinites (4.5 vs. 11.7-17.4%). Except for Na₂O and H₂O, the other major and minor oxide abundances of KA-19 are within the range defined by the other nephelinites (see Table 2A). These H₂O-rich, Na₂O-poor nephelinites (KA-19 and 34) contain the greatest amounts of devitrified glass (50-70%). Na2O loss from felsic glass is welldocumented (e.g., Lipman 1965; Conrad 1984; Leat et al. 1984) and we infer that the low Na₂O contents reflect Na₂O loss from the abundant glass. A microprobe analysis of black glass in KA-19 shows that it has a low Na₂O content (Table 9), which is atypical of magmatic values for nephelinites (e.g. Clague and Frey 1982).



Fig. 6a, b Correlations among incompatible trace elements. All values are dry normalized to 100%. Symbols as in Fig. 4. a Incompatible trace element versus La in ppm. Fields are for basanites and nephelinites from the Honolulu Group (Clague and Frey 1982)

the Honolulu Group (Clague and Frey 1982). **b** Incompatible trace elements ratios versus La in ppm. Error bars indicate ± 1 standard deviation

Trace element abundances

Among the nephelinite samples there are positive correlations between MgO, V, Cr, and Ni contents; however, there is no inverse correlation between MgO content and abundances of incompatible elements (Table 2A, B). There are well-defined positive correlations of incompatible element abundances, such as P, Ba, LREE, Zr, Hf, Nb, Ta and Th (Fig. 6a) among the Kaula basalts. Rb and Sr contents are not well-correlated with abundances of other incompatible elements. Although Sr and H₂O contents are not strongly correlated, among the nephelinites the three samples (KA-19, 34, and 17) with the highest H_2O contents have the highest Sr abundances (Table 2B); most notable is the 6400 ppm Sr in KA-19. Sr X-ray mapping of the zeolite-rich areas of KA-19 by microprobe revealed rare grains with high Sr. Microprobe analyses of these grains indicate that they contain virtually no SiO₂, TiO₂, Al₂O₃, FeO, Na₂O and K₂O (all <0.25 wt.%) and moderate CaO contents (1.40 wt.%). SrO contents are high (40–50 wt.%). This Sr-rich mineral apparently formed with the zeolites along fractures in the rock possibly due to seawater reaction



Fig. 7. a Chondrite-normalized REE diagrams for Kaula samples showing range for three phonolites, six nephelinites, and data for plag basanite, KA-29 (+) and tholeiitic basalt, KA-14 (x). A representative basanite from the Honolulu Group (vent 14C; Clague and Frey 1982) and the range for phonolites from Koko Seamount (Clague 1986) are plotted (Δ) for comparison. Note similarity of the Kaula nephelinites to the Honolulu Group lava. **b** REE abundances in phonolites relative to the most evolved associated basanites. Note that these phonolites have well-defined convex downwards REE patterns relative to possible mafic parental rocks. However, only phonolites from Dunedin, New Zealand have large negative Eu anomalies. Data from: Kaula (this paper); Bokkos, Nigeria (Irving and Price 1981); Dunedin, New Zealand (Price and Taylor 1973); Ross Island, Antarctica (Sun and Hanson 1976; Kyle 1981); Canary Islands (Thompson et al. 1984).

Table 9. Microprobe analyses of glasses in Kaula volcanic blocks

	Nephelir	nites	Plag Basanite K A-29			
	KA-19 Ave-5	KA-17 Ave-3	<u> </u>	В	С	
SiO ₂	40.0	41.0	54.6	56.7	55.5	
TiO ₂	3.7	3.3	3.3	1.9	1.3	
$Al_2 \tilde{O}_3$	14.4	14.4	.15.1	17.6	18.6	
FeO	12.7	12.2	9.5	6.0	5.5	
MgO	6.2	6.3	1.75	1.1	1.0	
CaO	13.8	14.0	5.8	5.1	2.3	
Na ₂ O	1.40	4.4	6.1	6.8	8.0	
K₂Ō	2.2	2.0	3.0	3.3	4.9	
Total	94.4	97.6	99.2	98.5	97.1	

with this glassy basalt. Alteration has apparently not affected the other trace elements which yield good correlations even for elements that are susceptible to alteration (e.g. Ba; see Fig. 6a).

All of the Kaula basalts have similar ratios of Ba/La and Zr/Hf, but with increasing incompatible element content Zr/Nb and La/Th decrease and La/Nb and La/Zr increase, reflecting a wider abundance range for La relative to Zr and Nb (Fig. 6b). However, because of anomalously high abundances of Zr, Hf and Nb, sample KA-28 deviates from several trends (Fig. 6b). Although all the basalts have nearly log-linear chondrite-REE patterns (Fig. 7a), there is an increase in La/Ce, La/Sm and La/Yb with increasing REE content (Fig. 6b).

Relative to the basanite and nephelinites the phonolites are: 1) strongly enriched (factors of 2 to 4) in the highly incompatible elements Rb, Zr, Hf, Nb, Ta, LREE and Y and enriched in Th and HREE; 2) strongly depleted in the ferromagnesian compatible elements, Sc, V, Cr, Co and Ni; 3) slightly enriched in Zn and Ga; and 4) moderately depleted in Sr, Ba and P. As a result, compared to the basanite and nephelinites, the phonolites have markedly lower Ba/La, Sr/Ba, Ti/Zr, and higher Rb/Sr; they also have different abundance ratios for highly incompatible elements such as higher Zr/Hf, Nb/Ta, La/Th, La/Nb and Zr/Nb (Fig. 6b). When normalized to the plag basanite, the phonolites have a distinct depletion in the middle REE compared to the heavy and light REE (Fig. 7b). Nevertheless, none of the Kaula samples have negative Eu anomalies relative to chondrites (Fig. 7a).

Discussion

Comparison of Kaula basanite and nephelinites to Hawaiian post-erosional basalts

Many Hawaiian volcanoes have a period of dormancy (0.2 to 2.5 million year long) during which erosion dissects the volcano (Clague 1986). Following this period, small volumes of moderately to strongly alkaline magma are erupted. These magmas are distinct from the underlying shield-forming lavas in having: (1) Higher concentrations of incompatible elements; and (2) generally lower ⁸⁷Sr/⁸⁶Sr and higher ¹⁴³Nd/¹⁴⁴Nd ratios (Roden et al. 1984; Chen and Frey 1985). The Honolulu Group is the best studied example of this "post-erosional" stage of volcanism in Hawaii (e.g. Clague and Frey 1982; Roden et al. 1984) and has the most diverse suite of rock types (i.e. alkali olivine basalt to melilite nephelinite).

The Kaula basanite and nephelinites are similar compositionally to basanites and nephelinites from the Honolulu Group (Table 2A, B) and are unlike any Hawaiian shield building lava. The lithological and compositional similarities between nephelinites from Kaula and the Honolulu Volcanics include: (1) occurrence of upper mantle peridotite and garnet-bearing pyroxenite xenoliths in the nephelinites (garnet-bearing pyroxenite xenoliths have only been found in the post-erosional stage lavas in Hawaii; Jackson and Wright 1970); (2) high Mg numbers, equivalent to those expected in equilibrium with olivines of $\sim Fo_{88}$; indeed, Kaula nephelinites contain olivine phenocrysts of $Fo_{86.5}$ to $Fo_{88.6}$ composition (Table 4); (3) similar abundances of major compatible and incompatible trace elements (Table 2, Fig. 6b and 7a); and (4) similar K/Ba and Zr/P₂O₅ ratios



Fig. 8. Zr versus P_2O_5 diagram for distinguishing alkalic shield building lavas from alkalic post-erosional lavas (after Clague 1986). Symbols as in Fig. 4

(Fig. 8). This last similarity is important because Clague and Beeson (1980) and Frey and Clague (1983) have shown that K/Ba and Zr/P₂O₅ ratios can be used to distinguish alkalic lavas erupted during the post-erosional stage of Hawaiian volcanism from alkalic lavas from the shield stage. Therefore, on the basis of petrography and composition, the Kaula basanite and nephelinites are equivalent to post-erosional lavas at other Hawaiian volcanoes. Of course, field relationships, e.g. a pronounced erosional unconformity, are key in defining the post-erosional stage (Macdonald and Abbott 1974). At Kaula, we lack this field control because all lava samples occur as accidental blocks in tuff. However, the wave-cut platform on which Kaula Island is built may have formed during a prolonged hiatus in volcanic activity. The nephelinites bear a strong resemblance to the tuff: they both contain the same phenocryst, megacryst and xenolith assemblages. Therefore, it is likely that the nephelinites were derived from the magmas that produced the tuff cone and that the cone formed well after the underlying shield volcano. The K-Ar age on the plag basanite accidental block of 1.8 ± 0.2 Ma is a minimum age for the tuff cone. This age is well within the age range of post-erosional volcanism on the adjacent shield volcanoes (Fig. 3).

In detail there are some minor differences between the nephelinites from Kaula and the Honolulu Volcanics. Kaula nephelinites have higher K, Rb, Sr and Ba and lower La contents (Table 2B), higher Ta and Nb at given La contents (Fig. 6a) and lower La/Yb ratios. These differences probably reflect only minor variations between the sources for these widely separated lavas.

Occurrence of phonolite during Hawaiian volcanism

During the waning stages of shield building on most Hawaiian volcanoes, evolved alkalic lavas have been erupted (exceptions are Koolau and Lanai). Compositions of these late-stage lavas range from hawaiite to trachyte and are either mildly hypersthene or nepheline normative (Fig. 4). Strongly nepheline normative (>10%), evolved lavas have not been reported from the Hawaiian Ridge, but they have been recovered from Koko Seamount near the southern end of the Emperor Seamount Chain with a suite of lavas that includes alkali basalts, hawaiites, mugearite and trachytes (Clague and Greenslate 1972; Clague 1974; Clague et al. 1975). Clague (1974) proposed a model for these phonolites, involving extensive fractional crystallization of an alkali olivine basalt to create trachyte [which is present in the alkalic caps of several Hawaiian volcanoes (e.g. Hualalai, Kohala, Haleakala, W. Maui; Macdonald 1968; Velde 1978)]. With further fractionation involving alkali feldspar, these trachytes would evolve to phonolites (Nash et al. 1969; Clague 1974). Because of the extensive feldspar fractionation the resulting phonolites have negative Eu anomalies and low Sr and Ba contents. Such features are characteristic of many phonolites (e.g. Irving and Price 1981) and in particular Koko Seamount phonolites have \leq 30 ppm Sr and Ba and pronounced negative Eu anomalies (Clague 1974, 1986). However, Kaula phonolites have relatively high Sr (274-690 ppm) and Ba (505-628 ppm) and lack negative Eu anomalies (Fig. 7a). Apparently phonolites from Kaula and Koko formed by significantly different petrogenetic processes.

Origins of the Kaula phonolites

The lack of lavas of intermediate composition between the basalts and the phonolites at Kaula presents a severe obstacle to determining the origin of the phonolites. Glasses in the basanite and nephelinites were analyzed by microprobe to determine whether they might represent suitable intermediate composition parents for the phonolites. Analyses of glasses in the nephelinites yielded low MgO (6.2-6.3 wt.%), basaltic compositions (Table 9). Crystal fractionation modeling of these glasses and of the nephelinite bulk rock compositions to produce phonolite (using observed mineral compositions from the nephelinites, Tables 4-7) yielded poor solutions (i.e. $R^2 > 1.0$). Thus, they are unlikely parents for the Kaula phonolites. In contrast, the basanites contain phonolitic glasses in segregation vesicles (Table 9, Fig. 4). Crystal fractionation modeling of the basanite as a parent for the phonolites yields low residuals ($R^2 = 0.05$) using observed mineral compositions (Table 10).

The model based on major elements (Table 10) can be tested with trace element abundances. For example, derivation of phonolites KA-36 and 37 by 19 and 15.5% fractionation from basanite KA-29 leads to maximum enrichments of 5.1 and 6.3, respectively, for highly incompatible elements, i.e., solid/melt partition coefficient = 0. The observed maximum enrichment are 4.6 for La and 4.8 for Rb which require bulk solid/melt partition coefficients of ~ 0.2 . For derivation of phonolite KA-37 from the basanite the inferred solid/melt partition coefficients are 0.87 for Ba, 1.4 for Sr and 0.26 to 0.66 for Y, Zr, Nb, Hf, Ta, REE and Th. Because trace element mineral/melt partition coefficients are not well known over the wide range of melt composition from basanite to phonolite, we can not use trace element data as a quantitative test. However, these inferred partition coefficients are qualitatively consistent with the fractionating phases required by the major element data (Table 10), particularly, alkali-rich feldspar for Rb, Sr and Ba and clinopyroxene, magnetite and apatite for the other elements. Furthermore, the REE pattern for Kaula phonolite normalized to the proposed parent (plag basanite) is

Table 10. Least squares mass balance calculation for derivation of phonolite (KA-37) from a plag basanite (KA-29). Mineral compositions are for groundmass grains coexisting with phonolitic glasses in KA-29

		SiO ₂	TiO ₂	Al_2O_3	FeO	MgO	CaO	Na ₂ O	K₂O	P ₂ O ₅		
KA-29	Obs.	47.79	2.18	15.07	10.47	8.82	10.20	3.79	1.06	0.62		
	Calc.	47.82	2.07	15.04	10.49	8.78	10.18	3.59	1.10	0.65		
	Diff.	-0.03	0.11	0.03	-0.02	0.04	0.02	0.20	-0.04	-0.03		
	ΣR^2	=0.05	·	1/F = 6.	5							
Mineral	ls	CPX	OI		Plag	A	north.	Magt	A	Apt		
SiO ₂		43.70	40	.20	52.11	63	.43	0.24		0.16		
TiO ₂		5.15	0	.00	0.00	0	.25	12.29		0.00		
Al_2O_3		8.20	0	.00	30.04	21	.40	0.22		0.00		
FeO		11.10	19	.60	0.69	0	.68	82.96		0.20		
MgO		9.35	39	.40	0.30	0	.39	2.00		0.00		
CaO		21.60	0	.23	13.11	3	.62	0.00	5	5.20		
Na ₂ O		0.65	0	.00	3.78	8	.08	0.00		0.00		
K ₂ O		0.01	0	.00	0.22	1	.36	0.00		0.20		
P_2O_5		0.00	0	.00	0.00	0	.00	0.00	4	2.20		
Total		99.76	99	.43	100.25	99	.21	97.71	9	7.96		

KA-29 = 15.5 KA-37 + 27.3 CPX + 20.8 Plag + 16.2 Anorthoclase + 14.4 Ol + 4.3 Magt + 1.3 Apt

virtually identical (see Fig. 7b) to REE patterns for well studied parent basanite-daughter phonolite pairs which had crystal fractionation schemes similar to the one proposed here.

Although our modelling suggests that basanite KA-29 is a suitable parental composition for the phonolites, their age differences (1.8 vs. 4.0 Ma; see Table 3) preclude a parent-daughter relationship. Nevertheless, the parent magma for the phonolites was probably similar in composition to the basanite KA-29. Formation of Kaula phonolites by segregation of a clinopyroxene-dominated feldspar-bearing assemblage is identical to the model proposed for some phonolites from Ross Island, Antarctica (Sun and Hanson 1976). However, there are several diverse paths which lead to phonolitic melts. We find no evidence for alternatives such as 1) segregation of amphibole- or phlogopite-bearing assemblages (e.g., Sun and Hanson 1976; Kyle 1981; Worner and Schmincke 1984b) or 2) segregation of feldspar-dominated assemblages (e.g., Nash et al. 1969; Clague 1974; Price et al. 1985). Derivation by partial melting has also been suggested (Wilkinson and Stolz 1983). We have no mineralogical or composition constraints on the source for the phonolites, so we were not able to evaluate this model.

Summary

The Kaula tuff cone contains a diversity of blocks including tholeiitic, basanitic, nephelinitic and phonolitic lavas. The same mineral, xenocryst and xenolith assemblages occur in the tuff and nephelinite blocks; thus, they are probably comagmatic. The other blocks are accidental. A 1.8 Ma K-Ar age for a basanite block provides an upper limit for the age of the cone. The similarity in age of the Kaula basanite to post-erosional lavas on adjacent volcanoes, Kauai and Niihau (0.4 to 2.6 Ma), and in composition of the Kaula nephelinites to some post-erosional lavas from the Honolulu Group leads us to conclude that the Kaula basanites and nephelinites are from a post-erosional stage of volcanism. The Kaula phonolites are the only documented phonolites from the Hawaiian Ridge. Their 4 Ma K-Ar age can not be unambiguously assigned to the shield-building or post-erosional stages of Kaula (Fig. 3). However, a much younger, ~ 1.8 Ma, Kaula basanite has a composition which could evolve to the phonolite compositions by segregation of a clinopyroxene, feldspar, olivine, magnetite and apatite assemblage.

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