Volatiles in Basaltic Glasses from Loihi Seamount, Hawaii: Evidence for a Relatively Dry Plume Component

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New H_2O, CO_2 and S concentration data for basaltic glasses from Loihi seamount, Hawaii, allow us to model degassing, assimilation, and the distribution of major volatiles within and around the Hawaiian plume. Degassing and assimilation have affected CO_2 and Cl but not H_2O concentrations in most Loihi glasses. Water concentrations relative to similarly incompatible elements in Hawaiian submarine magmas are depleted (Loihi), equivalent (Kilauea, North Arch, Kauai–Oahu), or enriched (South Arch). H_2O/Ce ratios are uncorrelated with major element composition or extent or depth of melting, but are related to position relative to the Hawaiian plume and mantle source region composition, consistent with a zoned plume model. In front of the plume core, overlying mantle is metasomatized by hydrous partial melts derived from the Hawaiian plume. Downstream from the plume core, lavas tap a depleted source region with H_2O/Ce similar to enriched Pacific mid-ocean ridge basalt. Within the plume core, mantle components, thought to represent subducted oceanic lithosphere, have water enrichments equivalent to (KEA) or less than (KOO) that of Ce. Lower H_2O/Ce in the KOO component may reflect efficient dehydration of the subducting oceanic crust and sediments during recycling into the deep mantle.

KEY WORDS: *basalt; Hawaii; mantle; plumes; volatiles*

INTRODUCTION

Most mantle convection models require the buoyancy of a mantle plume to be of thermal origin, thus the term 'hotspot', with temperature differences of 200°C or more between hotter upwelling plumes and the ambient mantle adiabat (e.g. White & McKenzie, 1989; Campbell, 1998; Davies, 1998). In contrast, it has long been known that ocean island basalts (OIB) are enriched in volatiles relative to depleted mid-oceanic ridge basalts (MORB), leading to speculation that the excess magmatism associated with plumes is related to a mantle 'wet spot' (Schilling et al., 1980) or a 'not-so-hot-spot' (Bonatti, 1990). Thus, there is still lively debate over the relative importance of 'hot' and 'wet' in the generation of mantle plumes.

The knowledge that OIB are wetter than MORB, however, does little to answer the question of the origin of volatiles in plume basalts. If the enrichments of volatile elements in OIB are proportional to those of nonvolatile incompatible elements, then their higher concentrations can be accomplished through simple mineral–melt fractionation processes. In contrast, if the volatile elements are decoupled from major and trace elements, then more complex processes must take place, including involvement and possible migration into or out of the plume of a separate C + H + O fluid phase, mixing of source regions having different volatile contents, or shallow-level processes such as assimilation or degassing. In particular, the recognition of recycled lithospheric components in plume source regions has invigorated the discussion of partitioning of water during dehydration of the subducting oceanic plate. In summary, plumes may be wet, but to answer the question of the origin of excess water and other volatiles, we need to know if they are anomalously wet relative to other trace elements.

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One approach is to measure volatile contents, along with major and trace elements, in submarine basaltic glasses or melt inclusions that have preserved the bulk of their initial volatile contents through quenching. Recent work on volatile solubilities and degassing provides the framework for separating shallow-level phenomena, such as degassing and assimilation, from the underlying variations in volatile contents of primitive magmas and mantle sources (Gerlach, 1986; Michael & Schilling, 1989; Dixon et al., 1991, 1995, 1997; Dixon & Stolper, 1995; Michael, 1995; Dixon, 1997; Michael & Cornell, 1998; Wallace & Anderson, 1998; Kent et al., 1999b; Danyushevsky et al., 2000).

Hawaii is the ideal location for investigating the role of volatiles in plume magmatism. Over a century of study has resulted in a robust geological, geophysical, and geochemical framework. Whereas a generally accepted geochemical model for Hawaiian volcanism has emerged that satisfactorily explains major element, trace element, and radiogenic isotopic compositions of the erupted lavas (e.g. Stille et al., 1986; Wyllie, 1988; Frey & Rhodes, 1993; Kurz, 1993; Kurz et al., 1995; Hauri, 1996; Lassiter & Hauri, 1998), a similarly rigorous model for the behavior of volatiles in plume magmatism has remained elusive.

In fact, almost every publication on the subject has a different hypothesis for the origin of volatile element variations in Hawaiian magmas. The range of processes proposed to control volatile element concentrations includes (1) addition of volatiles to magmas by seawater assimilation (e.g. Rison & Craig, 1983; Kyser & O'Neil, 1984; Kent et al., 1999a, 1999b); (2) loss of volatiles from magmas as a result of shallow degassing effects (e.g. Dixon et al., 1991; Clague et al., 1995; Wallace & Anderson, 1998); (3) addition of volatiles to mantle source regions through redox melting at the interface of relatively reduced ambient mantle with more oxidized subducted lithosphere (e.g. Green & Falloon, 1998); (4) depletion of volatiles from mantle source regions by progressive melting (Garcia et al., 1989). Some studies argue for decoupling of volatiles (especially He) from lithophile elements during melt generation (Poreda et al., 1993; Valbracht et al., 1996; Kurz & Geist, 1999) or during crystallization of magmas within or below the crust (Okano et al., 1987; Clague, 1988; Vance et al., 1989). In contrast, other studies (e.g. Kurz et al., 1995, 1996; Lassiter et al., 1996; Eiler et al., 1998) show rough correlations between He, Nd, and Pb isotopic ratios, and argue against decoupling of volatiles from magmatic components and for mixing of source materials.

This paper aims to resolve these apparent paradoxes. We present new H_2O, CO_2, S and Cl data for basaltic glasses from Loihi within a framework of a comprehensive model for the evolution of the degassing environments during growth and maturation of Hawaiian volcanoes.

The studied sample suites are submarine-erupted, important for the preservation of volatiles in quenched glasses. We will show that enrichments in water in Hawaiian shield magmas are less than (Loihi) or equal to (Kilauea) those of similarly incompatible trace elements. Thus, although the Hawaiian plume source is wetter than MORB, at least one component is relatively dry. In contrast to the shield lavas, water enrichments in marginal alkalic magmas are equal to (downstream from plume) or significantly higher than (upstream from plume) those of similarly incompatible elements, implying metasomatism by hydrous melts at the leading edge of the plume.

GEOLOGIC SETTING AND SAMPLE LOCATIONS

Loihi Seamount is the southernmost, youngest, and submarine Hawaiian shield volcano, rising to 950 m below sea level, on the southern flank of Mauna Loa volcano on the island of Hawaii (Fig. 1). Discovery of alkalic basalts on Loihi revolutionized our understanding of the life cycle of oceanic volcanoes as they evolve from pre-shield alkalic to shield-building tholeiitic back to post-shield alkalic volcanism (Moore et al., 1982). The most recent eruption of Loihi in 1996 was preceded by the largest swarm of seismicity ever recorded from a Hawaiian volcano (Loihi Science Team, 1997), confirming its status as an active volcano.

Loihi glasses analyzed in this study were collected by the US Geological Survey in 1978 and 1981. Locations and depths of dredges are shown in Fig. 2 (Moore et al., 1982). These samples have been the subject of comprehensive geochemical analysis for major elements (Moore et al., 1982), trace elements (Frey & Clague, 1983; Kent et al., 1999a), noble gases (Kaneoka et al., 1983; Kurz et al., 1983; Honda et al., 1991, 1993), radiogenic isotopes (Lanphere, 1983; Staudigel et al., 1984), and volatiles (Moore & Clague, 1981, 1982; Moore et al., 1982; Exley et al., 1986; Kent et al., 1999a). These studies and others on different sample suites (Hawkins & Melchior, 1983; Hiyagon et al., 1992; Garcia et al., 1993, 1995, 1998; Valbracht et al., 1996; Kent et al., 1999b; Norman & Garcia, 1999; Clague et al., 2000) provide the context for interpreting variations in major volatile contents.

Also shown in Fig. 1 are the locations of other submarine lavas representing various stages in the development of Hawaiian volcanism where volatiles may be preserved in quenched glassy rinds. These include the South Arch volcanic field (precursory alkalic stage), Kilauea (mature shield-building stage), the North Arch volcanic field (peripheral alkalic stage), and the Kauai–Oahu Channel (rejuvenated alkalic stage). Petrology and
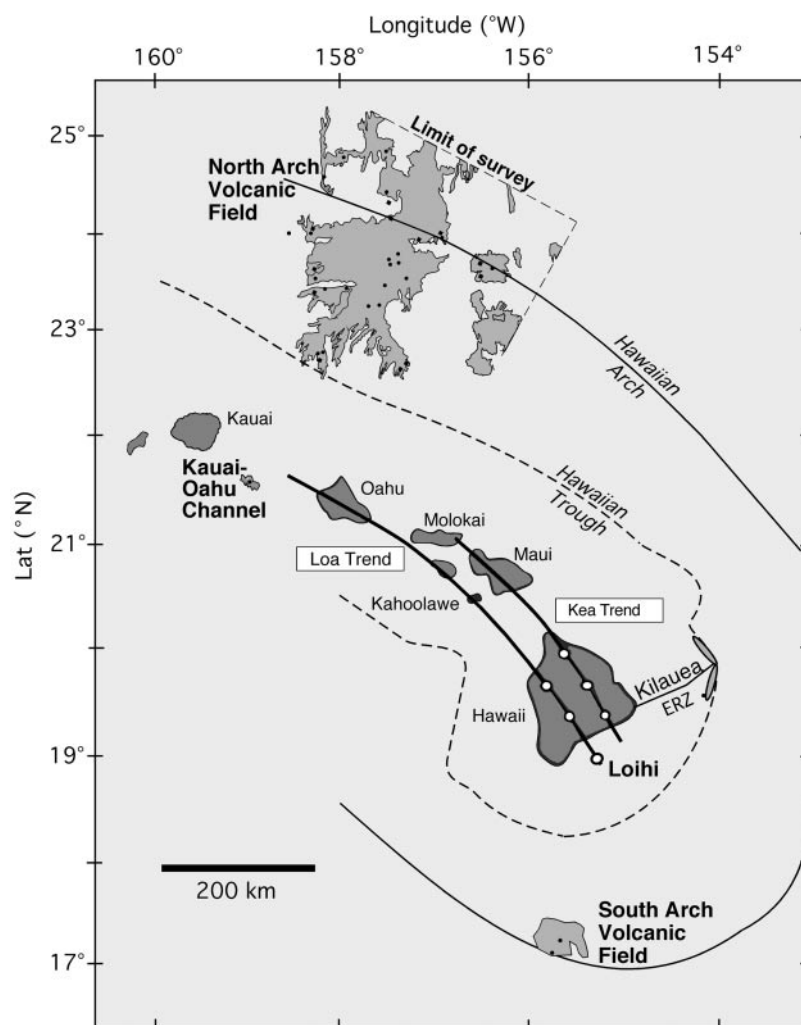
Fig. 1. Overview map of Hawaiian Islands showing location of samples discussed in this study, including the following: (1) South Arch volcanic field (precursory) lavas include basanite and alkali olivine basalt erupted at 5 km water depth on the Hawaiian Arch upstream from the plume center (USGS 1988 cruise; Lipman *et al.*, 1989). (2) Loihi (submarine preshield to early shield*)* lavas include basanite to tholeiite collected from 1–2·5 km water depth (USGS 1978 and 1982 cruises; Moore *et al.*, 1982). (3) Kilauea (subaerial shield) lavas include high-MgO tholeiitic glass sands (Clague *et al.*, 1991) and alkali olivine basalt collected at 5 km water depth within the Hawaiian Trough at the base of the Puna Ridge (KilD41; USGS 1988 cruise; Clague *et al.*, 1995). Puna Ridge glasses are not considered in this study because of variable extents of mixing between approximately subaerially degassed and undegassed lavas (Dixon *et al.*, 1991). (4) Kauai–Oahu Channel (rejuvenated stage) lavas include alkali olivine basalts (2D and 4D) collected at 3·9 km water depth between Kauai and Oahu (USGS 1988 cruise; Clague *et al.*, 1989). (5) North Arch volcanic field (peripheral) lavas include alkali olivine basalt to nephelinite erupted at 4 km water depth on the axis of the Hawaiian Arch downstream from the plume center.

petrogenesis of these lavas have been presented by Clague *et al.* (in preparation).

ANALYTICAL TECHNIQUES
Infrared spectroscopy

Concentrations of dissolved water and carbon dioxide were measured using IR spectroscopy. Glass chips were doubly polished to a thickness between about 50 and 200 µm. Transmission IR spectra in the 4000–1200 cm^{-1} (2·5–8·3 µm) range were collected using an IR microscope attachment to a Brüker IFS-66 FTIR spectrometer at the University of Miami, a Globar source, a KBr beamsplitter, a HgCdTe detector, and a mirror velocity of 1·57 cm/s. Spot sizes ranged from 60 to 150 µm. Typically, 2024 scans were collected for each spectrum. The spectrum of a decarbonated basanitic or tholeiitic glass was subtracted from the sample spectrum as a background correction. Absorbance measurements for the molecular water (1630 cm^{-1}) and carbonate (1515 and 1430 cm^{-1}) bands
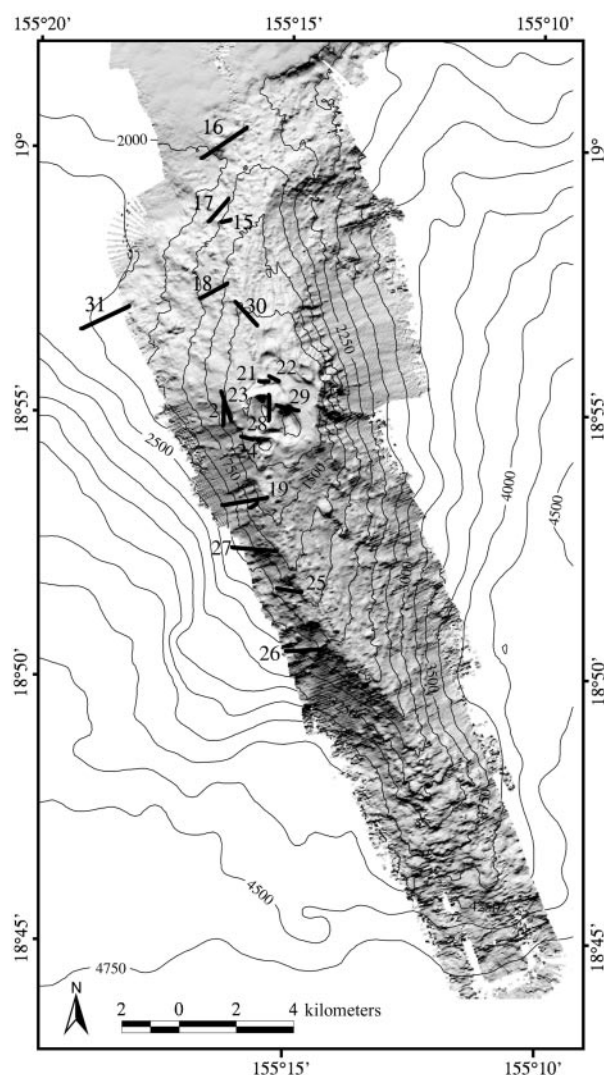
Fig. 2. Detailed bathymetric map of Loihi seamount showing 17 dredge stations during 1981 R.V. *Kana Keoki* cruise and a single dredge station during 1978 R.V. *S. P. Lee* cruise (Moore *et al.*, 1982) superimposed on new bathymetric data produced by the SIMRAD system (D. Clague, unpublished data, 1988).

were made on reference subtracted spectra using an interactive curve-fitting routine as described in the caption to Table 1. Concentrations were determined through Beer–Lambert law calibration [see review by Ihinger *et al.* (1994)]. The thickness, or path length, is measured by a digital micrometer with a precision of ± 1–$2 \, \mu m$. Glass density was calculated for each sample using the Gladstone–Dale rule and the Church–Johnson equation as described by Silver *et al.* (1990).

The molar absorptivity for total dissolved water using the fundamental OH stretching band at $3535 \, cm^{-1}$ is not strongly compositionally dependent for basaltic compositions and we use a value of $63 \pm 5 \, l/mol \, cm$ (P.

Dobson, S. Newman, S. Epstein & E. Stolper, unpublished data, 1988). Other molar absorptivities used are $330 \pm 20 \, l/mol \, cm$ for the carbonate bands, and $20 \pm 5 \, l/mol \, cm$ for the molecular water band at $1630 \, cm^{-1}$ (Dixon *et al.*, 1997).

Precision of the analyses is about $\pm 2\%$ for total water and ± 7–10% for molecular water and carbonate. The accuracy of the total water analyses is the same as reported by Dixon *et al.* (1991) (about $\pm 10\%$). Because of the larger uncertainty in the compositional dependence of the molar absorptivity for carbon dissolved as carbonate and water dissolved as molecular water in silicate glasses, the accuracy of the CO_2 and molecular water analyses are estimated to be about $\pm 20\%$.

Electron microprobe

Concentrations of sulfur and chlorine were determined on a nine-spectrometer ARL electron microprobe using natural and synthetic standards and instrumental parameters described by Clague *et al.* (1995). Mean-atomic-number calculations, based on the backgrounds measured on high and low mean-atomic-number standards, were used to obtain the background counts. Sulfur analyses determined by these procedures are consistent with those measured by electron probe in MORB and seamount glasses (Wallace & Carmichael, 1992) based on interlaboratory comparison of glasses from Loihi seamount (D. Clague, unpublished data, 1988). Error in the S analyses is estimated to be $\pm 6\%$ based on analysis of a standard with comparable S content (mean of 14 analyses on standard VG-2 is 0.127 ± 0.008 wt %, $\pm 6\%$ relative). Error in the Cl analyses is estimated to be $\pm 8\%$ based on analysis of standards A-99 (mean of 17 analyses is 0.024 ± 0.002 wt %, $\pm 8\%$ relative) and VG-2 (mean of 12 analyses is 0.031 ± 0.002 wt %, $\pm 7\%$ relative).

Secondary ion mass spectrometry

Trace element concentrations of glasses were measured using the Cameca IMS 6f ion microprobe at the Department of Terrestrial Magnetism following procedures of Shimizu & Hart (1982). Analytical uncertainties are estimated to be ± 5–10% (Shimizu & Hart, 1982).

RESULTS

Major and volatile element concentrations are listed in Table 1. For completeness, we have included electron microprobe analyses of the samples analyzed for volatiles to supplement the representative analyses published by Moore *et al.* (1982). Trace element data are listed in

Table 1: Major and volatile element compositions

Sample:	L78-2A	KK15-1	KK15-4	KK15-5	KK16-1	KK17-2
Flow unit/type:	/Thol.	A/Trans.	B/Basanite	C/AOB	A/Thol.	A/AOB
Depth (m):		1534 (44)	1534 (44)	1534 (44)	1950 (77)	1617 (45)
SiO_2	49·6	48·8	46·8	47·1	50·1	47·2
Al_2O_3	13·4	14·1	15·4	13·4	13·7	14·1
FeO	11·6	11·8	11·7	11·4	11·1	12·0
MnO	0·17	0·18	0·19	0·17	0·17	0·19
MgO	7·25	6·03	4·37	6·39	7·91	5·86
CaO	11·1	10·9	9·7	11·8	11·0	11·2
Na_2O	2·42	2·72	4·44	3·10	2·35	3·18
K_2O	0·39	0·65	1·56	0·84	0·32	0·85
P_2O_5	0·23	0·33	0·66	0·37	0·19	0·38
TiO_2	2·50	3·28	3·61	3·05	2·10	3·27
S	0·151	0·195	0·178	0·105	0·130	0·203
Total	98·8	99·0	98·7	97·7	99·1	98·4
Cl (ppm)	310	930	1240	650	240	690
H_2O (wt %)		0·76 (8)	1·01 (1)	0·78 (5)	0·50 (2)	0·85 (4)
H_2Omol (wt %)*		0·093 (14)		0·074 (11)	0·031 (5)	0·113 (17)
CO_2 (ppm)*		29 (4)		92 (18)	45 (2)	52 (4)
P_{equil}†		111	108	169	120	136
$(X_{CO_2})^v$†		0·52	0·00	0·64	0·81	0·46
Vesicles (vol. %)	1·4	6·2	16·4	27·9	2·0	5·1
Bulk CO_2 (ppm)‡		596		6279	340	548
Bulk H_2O (wt %)‡		0·78	1·14	0·92	0·50	0·87
Bulk vol. (wt %)‡		0·84		1·55	0·54	0·93
Sample:	KK17-17	KK18-8	KK18-6	KK19-1	KK19E	KK19-10
Flow unit/type:	B/Basanite	A/Trans	B/AOB	A/Thol	/Trans	F/AOB
Depth (m):	1617 (45)	1451 (155)	1451 (155)	1509 (144)	1509 (144)	1509 (144)
SiO_2	43·9	48·1	46·9	49·0	48·7	47·9
Al_2O_3	12·5	12·6	13·5	12·8	13·6	13·7
FeO	12·9	11·7	12·0	11·6	11·5	11·7
MnO	0·18	0·18	0·17	0·18	0·17	0·17
MgO	6·19	7·60	6·24	7·42	6·43	5·84
CaO	12·7	12·3	11·5	12·0	11·5	11·1
Na_2O	3·89	2·47	3·11	2·43	2·83	3·17
K_2O	1·35	0·50	0·82	0·48	0·59	0·80
P_2O_5	0·55	0·27	0·36	0·22	0·29	0·33
TiO_2	3·46	2·79	3·22	2·41	2·68	3·02
S	0·149	0·210	0·192	0·190	0·163	0·192
Total	97·8	98·7	98·0	98·7	98·5	97·9
Cl (ppm)	800	840	650	710	390	820
H_2O (wt %)	0·94 (9)	0·60 (4)	0·78 (2)	0·52 (2)		0·66 (6)
H_2Omol (wt %)*	0·096 (14)	0·051 (8)	0·091 (14)	0·039 (6)		0·068 (10)
CO_2 (ppm)*	75 (16)	47 (15)	63 (4)	81 (6)		74 (10)
P_{equil}†	155	106	133	199		149
$(X_{CO_2})^v$†	0·32	0·68	0·53	0·88		0·72
Vesicles (vol. %)	28·3	4·3	5·6	2·0	4·1	5·1
Bulk CO_2 (ppm)‡	2964	529	682	612		931
Bulk H_2O (wt %)‡	1·19	0·61	0·81	0·52		0·67
Bulk vol. (wt %)‡	1·49	0·66	0·87	0·58		0·76

Table 2. Readers are referred to Garcia *et al.* (1993, 1995, 1998) for an overview of Loihi petrology. Here we focus on interpreting variations in volatile species. Data for Loihi glasses will be compared with data from Kilauea (Clague *et al.*, 1991, 1995; Dixon *et al.*, 1991), the North Arch volcanic field (Dixon *et al.*, 1997), and other submarine alkalic lavas erupted marginal to the Hawaiian plume (Clague *et al.*, in preparation).

Dissolved water and carbon dioxide in Loihi glasses
Concentrations

Dissolved water concentrations in Loihi glasses (0·38–1·01 wt %) correlate roughly linearly with K_2O (Fig. 3). Molecular water concentrations in most glasses lie along the predicted water speciation curve (Fig. 4). Several outliers lie slightly above (KK26-5 and KK29-12) or

Table 1: continued

Sample:	KK19I	KK20A	KK20-14	KK21A	KK21B	KK21C
Flow unit/type:	/AOB	/Trans.	E/Thol.	/AOB	/AOB	/Trans.
Depth (m):	1509 (144)	1517 (166)	1517 (166)	1092 (32)	1092 (32)	1092 (32)
SiO_2	47·5	48·3	49·3	49·5	48·6	48·5
Al_2O_3	13·3	13·9	12·9	13·6	14·8	14·1
FeO	11·4	11·7	11·5	12·9	12·6	11·8
MnO	0·16	0·19	0·18	0·21	0·21	0·17
MgO	6·11	6·49	7·12	4·39	4·59	6·76
CaO	11·3	11·4	12·1	8·9	9·4	11·6
Na_2O	3·12	2·87	2·47	3·36	3·48	2·58
K_2O	0·88	0·59	0·50	0·97	1·17	0·47
P_2O_5	0·42	0·30	0·24	0·48	0·48	0·27
TiO_2	3·26	2·85	2·44	3·76	3·82	2·67
S	0·183	0·167	0·158	0·104	0·132	0·149
Total	97·6	98·8	98·9	98·1	99·2	99·1
Cl (ppm)	1290	390	800	1160	2380	460
H_2O (wt %)			0·48 (5)			
H_2Omol (wt %)*						
CO_2 (ppm)*						
P_{equil}†						
$(X_{CO_2})^v$†						
Vesicles (vol. %)	5·5	4·4	5·2	32·1	14·5	1·8
Bulk CO_2 (ppm)‡						
Bulk H_2O (wt %)‡						
Bulk vol. (wt %)‡						

Sample:	KK22A	KK23-3	KK24-13	KK24-4	KK25A	KK26A
Flow unit/type:	/Thol.	B/Thol.	A/Trans.	B/AOB	/Trans.	/AOB
Depth (m):	1140 (21)	1093 (108)	1079 (26)	1079 (26)	2004 (90)	2458 (193)
SiO_2	48·6	49·5	48·1	48·5	48·1	47·1
Al_2O_3	13·9	13·5	13·6	13·6	14·0	14·3
FeO	11·8	11·8	11·8	12·7	12·2	12·4
MnO	0·18	0·18	0·18	0·19	0·19	0·19
MgO	6·73	7·24	7·12	5·18	6·00	5·85
CaO	11·5	11·1	11·9	9·9	11·0	11·7
Na_2O	2·55	2·42	2·66	3·26	2·95	3·21
K_2O	0·44	0·38	0·55	0·87	0·64	0·83
P_2O_5	0·26	0·26	0·26	0·45	0·31	0·40
TiO_2	2·69	2·54	2·50	3·67	2·96	3·32
S	0·154	0·137	0·173	0·085	0·181	0·215
Total	98·8	99·1	98·8	98·4	98·5	99·5
Cl (ppm)	460	410	355	1300	430	880
H_2O (wt %)		0·44 (4)	0·58 (3)	0·63 (6)		
H_2Omol (wt %)*		0·028 (4)				
CO_2 (ppm)*		32 (2)				
P_{equil}†		86				
$(X_{CO_2})v$†		0·81				
Vesicles (vol. %)	1·8	1·3	0·1	35·0	1·8	3·7
Bulk CO_2 (ppm)‡		168				
Bulk H_2O (wt %)‡		0·44				
Bulk vol. (wt %)‡		0·45				

below (KK15-5, KK17-17, KK27-14) the speciation curve, but the deviation from the predicted value is no more than 4% of the total water content; therefore the water contents of these glasses have not been significantly affected by post-eruptive, low-temperature processes. Dissolved CO_2 concentrations range from 29 to 111 ppm.

Degassing

The ubiquitous presence of vesicles in the Loihi glasses establishes that they were vapor saturated during eruption.

Calculated equilibration pressures (Dixon & Stolper, 1995; Dixon, 1997) are shown versus collection pressure in Fig. 5. Roughly half of the glasses are saturated for their depth of collection (within 25% of the 1:1 line) and half are undersaturated. We interpret the low equilibration pressures of the undersaturated glasses to be caused by downslope transport of these lavas after eruption.

Before we can estimate pre-eruptive magmatic volatile contents, we need to evaluate how the exsolution of gas has modified the dissolved concentrations of CO_2 and

Sample:	KK26-5	KK27-3	KK27-14	KK27-19	KK29-3	KK29-10
Flow unit/type:	B/Trans.	B/Thol.	E/AOB	G/Trans.	A/Trans.	B/Thol.
Depth (m):	2458 (193)	1847 (222)	1847 (222)	1847 (222)	1106 (71)	1106 (71)
SiO_2	48·8	49·7	46·1	48·7	48·1	49·9
Al_2O_3	13·5	13·6	13·6	14·0	13·7	13·5
FeO	11·0	11·6	11·7	11·8	11·6	11·0
MnO	0·17	0·19	0·18	0·18	0·18	0·16
MgO	7·04	7·23	8·25	6·95	7·28	8·03
CaO	12·1	11·1	12·6	11·9	12·2	11·1
Na_2O	2·69	2·43	2·65	2·62	2·55	2·21
K_2O	0·64	0·41	0·75	0·58	0·56	0·35
P_2O_5	0·29	0·20	0·27	0·27	0·23	0·22
TiO_2	2·52	2·28	2·62	2·64	2·34	2·41
S	0·152	0·181	0·134	0·215	0·177	0·125
Total	98·9	98·9	98·9	99·9	98·9	99·0
Cl (ppm)	870	940	690	1100	640	390
H_2O (wt %)	0·56 (2)	0·46 (1)	0·60 (0)	0·53 (3)	0·48 (7)	0·38 (2)
H_2Omol (wt %)*	0·071 (11)	0·033 (5)	0·026 (4)	0·035 (5)	0·034 (5)	0·019 (3)
CO_2 (ppm)*	111 (10)	61 (2)	108 (10)	60 (2)	44 (2)	44 (6)
P_{equil}†	248	150	139	140	89	108
$(X_{CO_2})^v$†	0·88	0·88	0·73	0·82	0·76	0·88
Vesicles (vol. %)	3·5	0·6	15·7	4·2	6·1	3·8
Bulk CO_2 (ppm)‡	1293	179	2918	804	699	603
Bulk H_2O (wt %)‡	0·56	0·46	0·64	0·54	0·49	0·38
Bulk vol. (wt %)‡	0·69	0·48	0·94	0·62	0·56	0·44

Sample:	KK29-12	KK29D	KK30A	KK30-9	KK31-12	KK31-15
Flow unit/type:	C/Thol.	/AOB	/AOB	E/AOB	A/AOB	B/AOB
Depth (m):	1106 (71)	1106 (71)	1217 (93)	1217 (93)	2186 (137)	2186 (137)
SiO_2	49·1	46·8	46·1	47·6	46·3	46·9
Al_2O_3	13·8	14·3	13·1	14·1	13·7	14·0
FeO	11·7	12·2	12·2	12·1	11·8	12·5
MnO	0·17	0·17	0·16	0·17	0·18	0·18
MgO	6·50	6·37	6·67	5·93	8·09	6·15
CaO	11·0	11·7	11·6	11·1	12·5	11·2
Na_2O	2·55	2·83	3·31	3·08	2·60	2·92
K_2O	0·53	0·77	0·95	0·78	0·67	0·70
P_2O_5	0·29	0·31	0·45	0·34	0·23	0·37
TiO_2	2·96	3·02	3·45	3·00	2·13	3·22
S	0·164	0·190	0·144	0·200	0·107	0·257
Total	98·8	98·7	98·1	98·4	98·3	98·4
Cl (ppm)	480	440	850	700	300	780
H_2O (wt %)	0·54 (2)			0·70 (5)	0·67 (4)	0·78 (4)
H_2Omol (wt %)*	0·063 (9)				0·065 (10)	0·086 (13)
CO_2 (ppm)*	32 (4)				92 (7)	62 (4)
P_{equil}†	96				136	131
$(X_{CO_2})^v$†	0·72				0·66	0·53
Vesicles (vol. %)	4·0	9·6	21·8	4·3	23·5	2·7
Bulk CO_2 (ppm)‡	462				4199	347
Bulk H_2O (wt %)‡	0·55				0·75	0·79
Bulk vol. (wt %)‡	0·59				1·17	0·82

Thol., tholeiite; Trans., transitional; AOB, alkali olivine basalt; Bas., basanite; P_{equil}, equilibration pressure. $(X_{CO_2})^v$ is mole percent CO_2 in the vapor. Values in parentheses are 1σ standard deviations in the last or last two decimal places.
*Background corrections for the molecular water and carbonate bands were performed on reference-subtracted spectra using interactive baseline and curve-fitting routines available in the OPUS software on the Brüker IFS-66 IR spectrometer. This technique makes use of fundamental peak shape information for the molecular water and carbonate bands based on well-defined standard bands with flat backgrounds. The carbonate bands are modeled as the sum of two gaussians of equal band height, 1515 and 1430 cm^{-1}, each with full-width at half height (FWHH) of $75 \pm 5 cm^{-1}$. The lowest point of the region of overlap between the 1515 and 1430 cm^{-1} bands is typically two-thirds of the maximum band height. The molecular water band at 1630 cm^{-1} is modeled as having a gaussian shape with an FWHH of $\sim 55 cm^{-1}$. Using this technique improves precision from $\sim 15\%$ to $\sim 7–10\%$.
†Equilibration pressure and vapor composition calculated according to Dixon (1997).
‡Bulk volatile contents (dissolved + vapor) provide minimum estimates of initial volatile contents and are calculated assuming (a) ideal gas behavior for the vesicle gases, (b) the calculated equilibration pressure, (c) a 'rigid temperature' of 1000°C (Moore et al., 1977), and (d) the calculated vapor composition.

Table 2: Trace element compositions of Loihi glasses

| Sample: | KK16-1 | KK17-2 | KK18-8 | KK20-14 | KK23-3 | KK24-13 |
	SIMS	INAA-XRF	SIMS	SIMS	SIMS	SIMS
Li	4·3		4·5	4·0	3·7	3·8
Be	0·5		0·8	0·7	0·7	0·8
Sc	31		34	32	31	30
Ti	12634		17031	15308	15213	15844
Cr	362		338	307	313	259
Rb	7·8	15·2	9·7	10·6	9·0	9·2
Sr	276	541	361	384	337	367
Y	20	21	21	21	22	24
Zr	125	182	157	143	154	163
Nb	11	26	17	16	15	16
Ba	67	218	124	136	96	120
La	8·3	22·1	13·9	12·7	11·6	13·1
Ce	21·1	49·9	33·1	30·1	28·1	31·5
Nd	14·8	27·3	20·5	19·2	18·7	20·4
Sm	4·12	6·81	4·93	4·90	5·00	5·13
Eu	1·47	2·37	1·67	1·86	1·74	1·84
Gd	4·82		5·50	5·55	5·57	5·75
Dy	4·35		4·45	4·71	4·73	4·66
Er	2·12		2·13	2·33	2·51	2·50
Yb	2·00	2·00	1·79	1·92	2·10	2·20
Hf	3·21	4·70	3·36	3·47	3·69	3·86
$(La/Sm)_n$	1·27	1·98	1·76	1·62	1·46	1·60
H_2O/Ce	237	170	181	159	155	183
$(H_2O/Ce)_{pmn}$	1·28	0·92	0·98	0·86	0·89	0·95
$^{87}Sr/^{86}Sr$	0·70353	0·70351	0·70368	0·70352	0·70354	0·70353
SD	0·00007	0·00005	0·00004	0·00002	0·00004	0·00002
$^{143}Nd/^{144}Nd$	0·512946	0·51305	0·512945	0·512954	0·512987	0·513053
SD	0·00002	0·00002	0·000015	0·000013	0·000018	0·000017
$^{206}Pb/^{204}Pb$	18·222	18·447	18·448	18·347	18·433	18·384
$^{207}Pb/^{204}Pb$	15·478	15·463	15·477	15·469	15·492	15·49
$^{208}Pb/^{204}Pb$	38·088	38·139	38·189	38·143	38·164	38·107
$^{3}He/^{4}He$ (1)	30·1	24·1	32·1	26·7	23·1	22·7
$^{3}He/^{4}He$ (2)		24·6		24·6		

H_2O. Because of the low solubility of CO_2 in basaltic liquids, initial (pre-eruptive) concentrations are notoriously difficult to obtain from the glassy rinds of submarine erupted basalts (Fine & Stolper, 1986; Stolper & Holloway, 1988; Dixon & Stolper, 1995). However, bulk CO_2 contents (exsolved vapor plus dissolved carbonate groups), can provide minimum estimates. Vapor compositions calculated to be in equilibrium with the measured dissolved H_2O and CO_2 concentrations (Dixon, 1997) range from 0 to 0·9 molar proportion CO_2. Vesicularity of the glasses analyzed for volatiles ranges from 0·1 to 35 vol. %, with most glasses having less than ∼7 vol. % vesicles. Estimated bulk CO_2 concentrations range from 0·017 to 0·630 wt %. The maximum estimated bulk CO_2 content (0·63 wt %) is virtually identical to the primary CO_2 content (0·65 wt %) estimated for Kilauea tholeiitic magma (Gerlach & Graeber, 1985). Estimated bulk CO_2/H_2O values (0·04–0·68) are significantly lower than the value of 2·5 ± 1·5 estimated for vesicular lavas from the North Arch (Dixon *et al.*, 1997). The relatively low vesicularity, low bulk CO_2 concentration, and low bulk CO_2/H_2O values could be the result of either low

Sample:	KK26-5 SIMS	KK27-3 SIMS	KK27-19 SIMS	KK29-3 SIMS	KK29-10 SIMS	KK31-12 SIMS
Li	4·8	3·9	4·0	4·2	3·3	4·3
Be	1·3	1·2	0·8	1·1	0·7	1·4
Sc	35	34	30	35	30	32
Ti	15786	13323	15660	13543	13763	13125
Cr	268	301	257	290	355	344
Rb	12·0	8·6	10·0	10·1	6·9	13·5
Sr	423	305	388	355	302	410
Y	22	20	21	19	20	21
Zr	159	134	137	133	132	143
Nb	18	13	18	15	13	17
Ba	176	83	140	142	77	214
La	15·1	10·4	15·0	12·8	14·1	15·1
Ce	34·6	25·0	34·6	29·7	24·3	34·1
Nd	20·8	16·5	20·4	18·0	16·1	20·3
Sm	5·17	4·20	4·80	4·33	4·07	4·92
Eu	1·93	1·57	1·63	1·50	1·42	1·99
Gd	5·97	4·89	5·09	4·89	4·36	5·52
Dy	4·72	4·14	4·40	3·94	4·12	4·62
Er	2·26	2·08	2·01	1·94	2·07	2·22
Yb	1·83	1·81	1·65	1·66	1·71	1·96
Hf	3·82	3·07	3·43	2·98	3·06	3·33
$(La/Sm)_n$	1·83	1·56	1·96	1·85	2·18	1·93
H_2O/Ce	161	183	153	161	157	196
$(H_2O/Ce)_{pmn}$	0·87	0·98	0·83	0·87	0·84	1·05
$^{87}Sr/^{86}Sr$					0·70358	0·70335
SD					0·00005	0·00003
$^{143}Nd/^{144}Nd$					0·512967	0·513052
SD					0·00002	0·000017
$^{206}Pb/^{204}Pb$					18·266	18·255
$^{207}Pb/^{204}Pb$					15·474	15·477
$^{208}Pb/^{204}Pb$					38·015	38·054
$^3He/^4He$ (1)					27·5	20·9
$^3He/^4He$ (2)	21·8					24·5

Trace element concentrations of glasses were measured using the Cameca IMS 6f ion microprobe at the Department of Terrestrial Magnetism following procedures of Shimizu & Hart (1982). INAA–XRF data are from Frey & Clague (1983). Sr, Nd, and Pb isotopic data are from Staudigel *et al.* (1984). He isotopic data are from (1) Kurz *et al.* (1983) and (2) Honda *et al.* (1993).

initial magmatic CO_2 contents or preferential loss of CO_2 through open-system degassing during storage of Loihi basalts at deep and/or shallow levels in the crust before eruption. Consistently high CO_2 concentrations in hydrothermal fluids from Loihi Seamount (Sedwick *et al.*, 1992, 1994; Loihi Science Team, 1997; Hilton *et al.*, 1998), provide evidence that significant quantities of CO_2 are being degassed from shallow magmatic intrusions. Therefore, we prefer the latter explanation for most samples.

Water is more soluble than CO_2 in basaltic melt and is thus less likely to degas from oceanic island basaltic magmas during submarine eruption and quenching (Moore, 1970; Dixon & Stolper, 1995; Dixon, 1997; Moore *et al.*, 1998). Exsolution of significant quantities of H_2O requires either high concentrations of H_2O (e.g. fractionated or strongly alkalic compositions) that are close to the solubility of H_2O at the pressure of eruption ($\sim$1·0 wt % at 10 MPa pressure; Dixon *et al.*, 1995) or
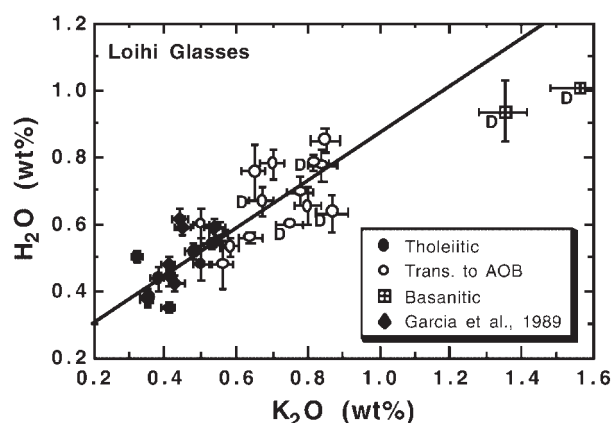
Fig. 3. Positive correlation between H_2O and K_2O in Loihi glasses. ●, tholeiites; ○, transitional to alkalic basalts; ⊞, basanites; ◆, from Garcia *et al.* (1989). Symbols marked with a 'D' have degassed water based on bulk water estimates (see text).
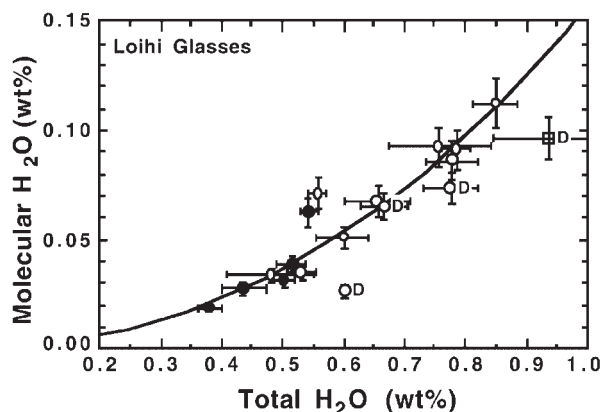

Fig. 4. Concentrations of molecular water ($1630\,cm^{-1}$ band, molar absorptivity = $20 \pm 3\,l/mol\,cm$) plotted against total water ($3550\,cm^{-1}$ band, molar absorptivity of $63\,l/mol\,cm$). Symbols as in Fig. 3. These data are consistent with the experimentally determined speciation model for water in tholeiitic glass (Dixon *et al.*, 1995). Depletion in molecular water may be related to rapid degassing of water before quenching.

Fig. 5. Equilibrium pressure calculated from dissolved CO_2 and H_2O concentrations (Dixon, 1997) plotted against collection pressure (10 m $H_2O = 0\cdot1\,MPa = 1$ bar pressure) for Loihi and marginal alkalic basalts (Dixon *et al.*, 1997; Clague *et al.*, in preparation). ●, Loihi (this study); ▲, Kilauea 41D; ◆, South Arch; ■, mean and 1σ standard deviation of all North Arch glasses; ⊞, Kauai–Oahu Channel. Error in calculated equilibration pressure is ~25%. Line is 1:1 line. Glasses are either saturated (within errors of line) or undersaturated (below line) with respect to CO_2–H_2O vapor. Undersaturated glasses were probably transported downslope during or after eruption.

closed-system degassing of a CO_2-rich system (e.g. highly vesicular glasses). We first consider a general model for degassing of Loihi magmas using the methods of Dixon (1997) and then examine evidence for water degassing for individual Loihi compositions.

To predict the effect of deep degassing on water concentrations, we model degassing as a three-stage process: stage 1—deep degassing at the crust–mantle boundary (~10 km depth, ~0·3 GPa); stage 2—shallow degassing within a crustal magma reservoir (~3 km depth, ~0·1 GPa); stage 3—during eruption at the summit of Loihi (1000 m water depth, 10 MPa). Evidence supporting ponding of magma near the crust–mantle

boundary (~10 km beneath Loihi) includes the fractionated character of Loihi lavas and the presence of only crustal cumulate and uppermost mantle lherzolite xenoliths in Loihi alkalic basalts (Clague, 1988). Garcia *et al.* (1998) also argued for fractionation of Loihi tholeiitic lavas in a deep storage zone located within the ocean crust (~8–9 km below the summit of Loihi). We have used conservative initial conditions designed to maximize possible water loss. Degassing is modeled as a closed system within each stage, but open between stages, as no detectable water loss could be produced if degassing were modeled as an open system throughout. An initial CO_2/H_2O ratio of three is assumed for all magmas based on results from the North Arch alkalic suite. Initial volatile contents for a magma having ~8 wt % MgO (more fractionated that the assumed primary magmas having ~16 wt % MgO; Clague *et al.*, 1991; Garcia *et al.*, 1995) are 0·4 wt % H_2O and 1·2 wt % CO_2 for tholeiite, 0·5 wt % H_2O and 1·5 wt % CO_2 for alkali olivine basalt, and 0·6 wt % H_2O and 1·8 wt % CO_2 for basanite.

Results of the degassing calculations are shown in Fig. 6. All compositions are vapor saturated by the time they reach the crust–mantle boundary. During deep degassing, all compositions have exsolved a CO_2-rich vapor resulting in loss of <1·3% of their initial water, but >80% of their initial CO_2. During shallow degassing, all compositions continue to lose a CO_2-rich vapor phase resulting in loss of <2% of their initial water, but >94% of their initial CO_2. During eruption at the summit, degassing is able to produce detectable losses of water (1·5% for tholeiite,
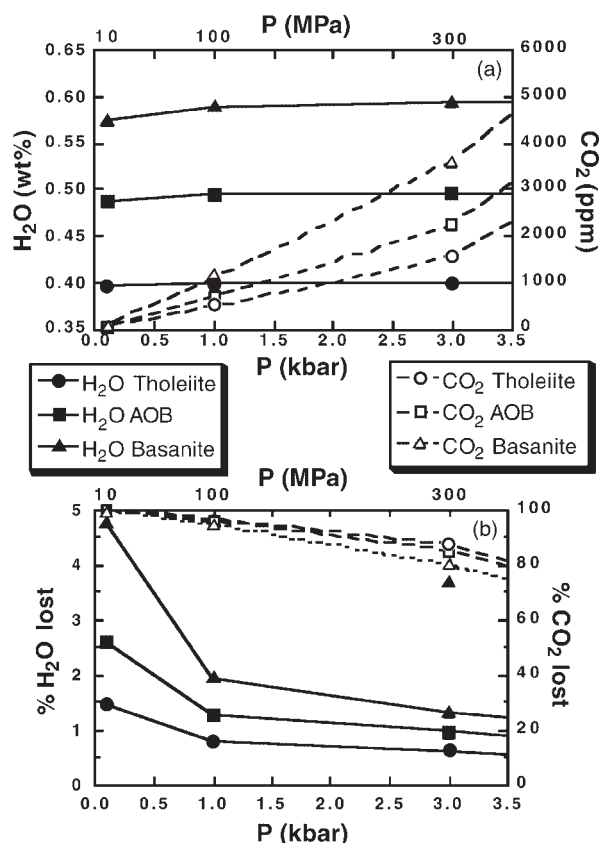
Fig. 6. Results of degassing calculations for Loihi magmas using the methods of Dixon (1997). Degassing is modeled as a three-stage process: stage 1—deep degassing at the crust–mantle boundary ($\sim$10 km depth, $\sim$0·3 GPa); stage 2—shallow degassing within a crustal magma reservoir ($\sim$3 km depth, $\sim$0·1 GPa); stage 3—during eruption at the summit of Loihi (1000 m water depth, 10 MPa). Degassing is modeled as a closed system within each stage, but open between stages with an initial CO_2/H_2O ratio of three. Initial water contents for magmas having $\sim$8 wt % MgO are 0·4 wt % H_2O and 1·2 wt % CO_2 for tholeiite, 0·5 wt % H_2O and 1·5 wt % CO_2 for alkali olivine basalt, and 0·6 wt % H_2O and 1·8 wt % CO_2 for basanite. (a) Concentrations of H_2O and CO_2 as a function of pressure and (b) % H_2O and % CO_2 lost as a function of pressure. Very little water is lost during deep and shallow degassing, therefore degassing cannot account for the water depletion observed in most Loihi basalts. In contrast, most CO_2, and presumably noble gases, is lost during degassing at the base of the crust.

2·6% for AOB, and 5% for the basanite) and has essentially stripped the magma of CO_2 (>99% CO_2 degassed). Predicted vesicularities for magmas erupted on the seafloor after degassing within the crust are 4–10%. If magmas erupt directly on the seafloor from the deep reservoir without residence at shallow levels, then vesicularities would be 13–33% for tholeiites to basanites, respectively. Observed vesicularities (up to 35 vol. %) within our sample suite are consistent with the values predicted by the degassing models.

There are two important results from the forward models. First, we were unable to produce significant water loss during stages 1 and 2, even though we used conservative initial conditions. In reality, evidence of noneruptive degassing of CO_2-rich vapor (Gerlach, 1986) suggests that degassing at crustal and subcrustal depths probably proceeds in a more open-system manner, thus decreasing the likelihood of water loss. Second, even though it is extremely difficult to modify water concentrations at pressures >0·1 GPa, at least 80% of the initial CO_2 has exsolved from the magma by a depth of 10 km. Because the solubility of He is similar to that of CO_2 (e.g. Carroll & Webster, 1994), this implies that most of the He would be degassed at the base of the crust as well. Deep degassing of CO_2 and He could explain the apparent 'paradox' (Anderson, 1998*a*, 1998*b*) that OIB magmas have higher $^3He/^4He$ ratios, but lower He concentrations, than MORB. Deep degassing also provides a source for the CO_2 fluid inclusions in cumulate and mantle xenoliths.

We can evaluate whether water has degassed during shallow storage and eruption from individual Loihi basalts, which may be more differentiated and have higher water concentrations than those used in the forward models, by comparing the measured dissolved H_2O with the estimated bulk H_2O concentrations (Table 1). Five glasses (KK15-4, KK15-5, KK17-17, KK27-14, and KK31-12) have dissolved H_2O concentrations significantly lower than their estimated bulk H_2O concentration and may have exsolved detectable amounts of H_2O. The proportion of initial H_2O lost correlates positively with the initial bulk volatile content (Fig. 7). Noise in the carbonate region of the IR spectrum prevented determination of the dissolved CO_2 content and calculation of bulk volatile content of glass 24-4, but it also appears to have degassed H_2O, as it falls below the general trends on plots of H_2O vs K_2O, P_2O_5 or MgO. These six glasses are alkalic, highly vesicular (16–35 vol. % vesicles), and all but samples KK27-14 and KK31-12 are highly fractionated (MgO <6·4 wt %). The relatively high MgO contents, vesicularity, and bulk CO_2/H_2O of several alkali olivine basalt samples (KK27-14 and KK31-12) are consistent with closed- or partially closed-system degassing during eruption (less time for escape of vapor and crystallization). We also note that all glasses having molecular water concentrations below the speciation curve have degassed water. We speculate that such depletion could result if diffusion of molecular water into vesicles and quenching of the glass occurred faster than equilibration of molecular water and hydroxyl groups. Samples that have degassed H_2O are marked with a 'D' in the figures. Degassing has not modified (<3% of the amount present) water concentrations of the other glasses.

A linear fit through the 'undegassed' samples in Fig. 3 intersects the H_2O axis at $\sim$0·17 wt %, therefore H_2O/K_2O is not constant and varies from $\sim$1·2 to 0·9 over a K_2O range of 0·35–0·85. The simplest explanation
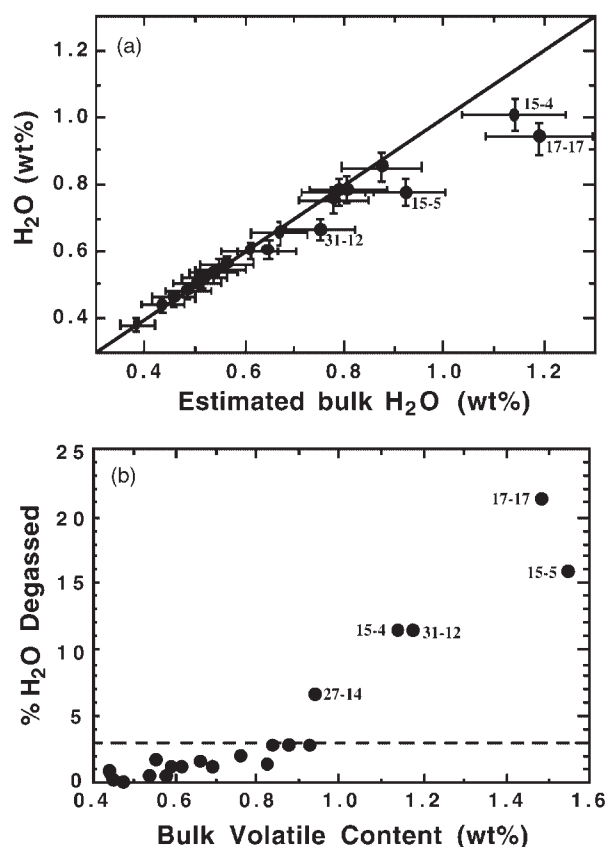
Fig. 7. (a) Dissolved H_2O plotted against estimated bulk H_2O. Bulk volatile calculations described in caption to Table 1. (b) Estimated percent water degassed plotted against bulk volatiles for Loihi lavas. Dashed line marks 3% water loss, roughly equal to the analytical precision. Water loss is greatest from samples with highest water concentrations.

is that K_2O is more incompatible than H_2O during melting and crystallization of gabbroic mineral assemblages, in contrast to the assumptions of Jambon & Zimmermann (1990) that water and potassium are equally incompatible.

Chlorine

Concentrations and assimilation of Cl-rich brines

Cl concentrations in Loihi glasses show a large range (240–2380 ppm) and do not correlate with proxies for melting or crystallization. Recent work on Loihi (Kent et al., 1999a, 1999b) and MORB (Michael & Schilling, 1989; Jambon et al., 1995; Michael & Cornell, 1998) has attributed excess Cl concentrations to assimilation of a Cl-rich brine derived from seawater unmixing at high temperature. We believe brine assimilation has affected the Cl concentrations in Loihi glasses, but several additional points are relevant to our ability to understand the origin of variations in magmatic volatiles.

First, not all Loihi magmas show anomalously high Cl concentrations. Chlorine is a highly incompatible element and its concentration should increase with increasing extents of crystallization and with decreasing extents of melting, as has been observed for alkalic lavas from the North Arch volcanic field (Dixon et al., 1997) and other Hawaiian and Reykjanes Ridge lavas (Unni, 1976). The behavior of Cl as a function of extent of melting is illustrated in Fig. 8a using SiO_2 as a proxy for extent of melting (e.g. Green & Ringwood, 1967; Frey et al., 1978; Hirose, 1997). Cl concentrations in the North Arch glasses increase linearly with decreasing SiO_2, consistent with generation by decreasing extents of melting of a homogeneous source region (Dixon et al., 1997). Cl concentrations in Loihi glasses at a given SiO_2 content overlap with the field of North Arch data. Furthermore, when Cl is plotted against a similarly incompatible element (Fig. 8b; we use La because of K_2O depletion in North Arch lavas), the lower one-quarter of the Cl concentrations in Loihi glasses at a given La content overlaps with the field of North Arch data. These data suggest that the baseline Cl contents of the two regions are controlled primarily by partial melting of source regions having similar Cl concentrations. Cl contents in the Puna Ridge glasses extend to lower values than those in Loihi and North Arch glasses because of higher average extents of melting and more complicated degassing history (Dixon et al., 1991). Thus it may be inappropriate to infer parental Cl contents for Loihi magmas based directly on Kilauea values.

Second, in contrast to most MORB results (Michael & Cornell, 1998), there is no correlation between amount of assimilation and extent of crystallization (MgO content) in the Loihi glasses. Evidence for assimilation is present for primitive and fractionated lavas, but the more differentiated compositions (MgO <7 wt %) have elevated Cl and La concentrations consistent with greater extents of crystal fractionation. A correlation between assimilation and crystallization makes sense in a steady-state magmatic system, such as moderately fast to fast spreading centers, because fractionated magmas reside longer in the crust, providing greater opportunities for assimilation. The absence of a correlation between Cl excesses and extent of crystal fractionation suggests that the magmatic system at Loihi has not yet reached a steady state. Each individual batch of magma breaks new ground and is affected by unique conditions within the crust through which it passes.

Third, in agreement with the results of Kent et al. (1999a), there is no correlation between water concentrations and the amount of excess Cl in Loihi glasses (Fig. 9). Glasses with moderate to high Cl concentrations are not anomalously enriched in H_2O. Although it is certainly possible for magmas to assimilate a more hydrous component (Kent et al., 1999b), it is remarkable how
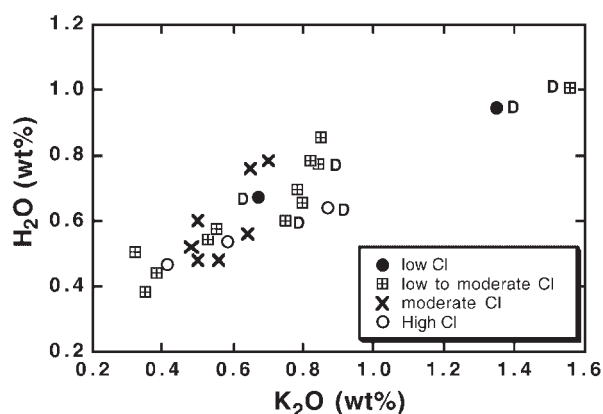
Fig. 9. H_2O plotted against K_2O for Loihi glasses. Symbols are grouped by amount of Cl in excess of North Arch trend ($63.5 + 844K_2O$). ● and ⊞, low to moderate Cl (<100 ppm excess Cl); ×, moderate Cl (100–00 ppm excess Cl); ○, high Cl (>400 ppm excess Cl). Samples that have degassed water are labelled with a 'D'. Absence of a correlation between water concentration and excess Cl suggests water is not affected by brine assimilation.

Fig. 8. (a) Cl concentration plotted against SiO_2 for Loihi [●, more primitive (MgO >7 wt %); ○, more differentiated (MgO <7 wt %); this study], Kilauea lavas and high MgO glass sands (KHMG) (▲; Clague *et al.*, 1991, in preparation; Dixon *et al.*, 1991), North Arch (■; Dixon *et al.*, 1997), South Arch (◆; Clague *et al.*, in preparation). Negative correlation between SiO_2 and Cl is caused by increase in incompatible element concentration with decrease in extent of melting. Large scatter in Loihi data is related to brine assimilation, but Loihi Cl concentrations bottom out on North Arch trend. (b) Cl concentrations plotted against La for Loihi, Kilauea (high MgO and 41D), North Arch, and South Arch (SA) glasses. Symbols are the same as in (a). Cl and La are roughly equally incompatible and concentrations of both increase with increasing extents of crystal fractionation and decreasing extents of partial melting. As in (a), larger scatter in Loihi data is related to brine assimilation, but lower Cl concentrations are consistent with North Arch trend. The highest La samples (NA23D and NA24D-a) have anomalously low Cl.

rarely it occurs. We wish to emphasize that assimilation of a Cl-rich component in most Loihi magmas does not appear to have modified their water concentrations.

Sulfur

Most Loihi glasses have S contents between 1200 and 2200 ppm similar to the North Arch basalts. The high S concentrations in Loihi and North Arch basalts compared with MORB with comparable total FeO contents are related to their higher oxygen fugacities (Dixon *et al.*, 1997). In general, S concentration correlates positively

with H_2O concentration. Loihi glasses that have degassed water (i.e. glasses KK15-4, KK15-5, KK17-17, KK24-4, KK27-14, and KK31-12) are offset to lower S concentrations, consistent with coupled H_2O and S degassing. The more differentiated compositions have more variable S concentrations (800–3000 ppm). Variations in S concentrations are a complex function of melt composition (primarily FeO content and Fe^{3+}/total iron), temperature, and degassing history (Wallace & Carmichael, 1992) and will not be discussed further in this paper.

The above results have established that degassing and assimilation have obscured information about primitive CO_2 and Cl concentrations in most Loihi glasses, but that useful information has been retained in many samples about primitive water and sulfur concentrations. Thus, it is valid to use these samples to investigate variations in primitive magmatic and mantle volatile concentrations.

DISCUSSION

The aim of this paper is to characterize the major volatile content of the mantle source regions for Hawaiian magmas. Hawaiian magmas are heterogeneous in major, trace, and volatile element concentrations, as well as their isotopic compositions. To explain this heterogeneity, petrologists have made use of the full spectrum of processes, including variations in degree and depth of fractional crystallization, mixing, degassing, assimilation, source region composition, and extent and style of partial melting. Each of these variables affects volatile element concentrations as well.

Although at first it may seem a daunting task to sort out the effects of these processes, it is useful to divide the

problem into shallow (magma chamber and eruption) and deep (thermal and geochemical plume structure) phenomena. For carefully selected samples, it is possible to accurately account for the shallow processes, allowing characterization of the deeper processes. First we will discuss the evolution of magmatic and degassing environments within Hawaiian volcanoes, and use this conceptual framework to select samples from a range of volcanic environments least affected by shallow-level effects. Next we discuss the volatile element variations within this 'least-affected' sample suite in the context of a thermal and geochemical model of plume structure.

Evolution of magmatic and degassing environments during growth of Hawaiian volcanoes

Hawaiian volcanoes grow in a series of well-documented stages (e.g. Stearns, 1940; Clague & Dalrymple, 1987): an alkalic preshield stage, a main tholeiitic shield stage, an alkalic post-shield stage, and a strongly alkalic rejuvenated stage. Lavas that are geochemically similar to rejuvenated stage, strongly alkalic lavas also erupt in front of (precursory, South Arch lavas, Lipman *et al.*, 1989; Clague *et al.*, in preparation) and to the sides of the island chain (peripheral, North Arch lavas, Clague *et al.*, 1990; Dixon *et al.*, 1997; Frey *et al.*, 2000). The shield stage can be further subdivided into submarine and subaerial phases, with the transition being marked by an explosive phase, which may produce thick hyaloclastite deposits. Clague & Dixon (2001) have presented a model of magma chamber evolution during growth of Hawaiian volcanoes. Below we describe five volcanic environments, which are critical to understanding volatile evolution.

(1) During precursory volcanism, as exemplified by alkalic series lavas from the South Arch volcanic field (Lipman *et al.*, 1989; Clague *et al.*, in preparation), small extents of melt of 'refertilized' lithospheric–asthenospheric mantle sources are erupted in advance of the plume center on the seafloor at depths of 4–5 km. Variation in the extent of melting is the dominant process controlling major and trace element concentrations. Because the flux of magma and heat is low, individual magma batches probably ascend directly to the seafloor without mixing. Because the extents of melting are low, the initial concentrations of volatiles are high relative to shield magmas and degassing of CO_2 and H_2O occurs as a single-stage, closed-system process during ascent. It is likely that exsolution of volatiles drives the rapid ascent of magmas. Primary volatile concentrations increase as extents of melting decrease, therefore water will more probably degas from nephelinitic than from alkali olivine basaltic compositions. Only rapidly quenched lavas close

to the eruptive vent will probably retain their full complement of mantle volatiles, including CO_2, in the form of dissolved and exsolved (bubbles) species. During flow on the seafloor, degassing proceeds as an open system, as bubbles are able to escape from the lava.

(2) During the submarine preshield to shield volcanism, as exemplified by Loihi, the volcano grows rapidly and the system is dominated by heterogeneity on all scales, including mantle source composition and extents of melting, crystallization, and assimilation. Magma compositions change from alkalic to tholeiitic as extents of melting increase. As the magmatic flux and temperature of the lithosphere and crust increase, magmas reside in one (or two) immature magma reservoirs at the base of the crust and/or at depths of $\sim$ 1–3 km below the summit. These chambers evolve from a region of intertwined intrusions and sills to a single, but probably zoned, reservoir. Cooling and prolonged crystallization in these magma reservoirs result in eruption of more differentiated compositions. During crustal residence of magmas in these submarine volcanoes, CO_2 is able to exsolve and escape, but hydrostatic pressure (>10 MPa) is sufficient to keep H_2O, S, and Cl dissolved in melts before and during eruption in all but the most differentiated or alkalic ones. Convection and mixing within the reservoir are minor, because dense, H_2O-poor melts do not form beneath the submarine summit, as they do in subaerial volcanoes (Dixon *et al.*, 1991). Without efficient mixing, erupted magmas tend to preserve a stronger signature of melting and source region heterogeneities. During its immature stage, the magma reservoir and feeder system have not yet dried out the surrounding crust (Connor *et al.*, 1997), and individual intrusions assimilate different amounts of a Cl-rich component as a function of their unique pathways through the volcanic pile. Except in isolated cases (Kent *et al.*, 1999*b*), assimilation does not affect the water contents of the melts. Therefore, water contents in most glasses may be used to infer their primary magmatic and mantle compositional variations.

(3) During the subaerial, shield-building volcanism, as exemplified by Kilauea, the summit of the volcano breaks through sea level. The melting region is squarely located over the center of the plume, resulting in generation of tholeiites by increased extents of melting. Higher extents of melting result in lower concentrations of dissolved volatile components. The significantly greater magmatic flux at this stage leads to the formation of a well-developed magma chamber in which different batches of magma may stratify or mix. As a long-lived heat source, the magma reservoir progressively dries out the surrounding crust (Connor *et al.*, 1997). As the volcano and magma chamber increase in elevation relative to sea level, the circulating fluid changes from seawater to fresh water. Thus, as the volcano grows, the likelihood of assimilation

of hydrous or Cl-rich components is diminished. Degassing from magma occurs in two stages (e.g. Gerlach, 1986; Dixon *et al.*, 1991). In the first stage, dominantly CO_2 exsolves and escapes from magmas within the summit reservoir. In the second stage, H_2O, S, Cl, and the remaining CO_2 exsolve and escape during eruption at the summit or along the rift. Subaerial degassing of magmas during sustained summit eruptions results in formation of H_2O-poor, dense, shallow lenses of melt that may be recycled deeper in magma reservoir (Dixon *et al.*, 1991; Clague *et al.*, 1995; Wallace & Anderson, 1998). Convection within the magma reservoir is a direct consequence of degassing through the subaerial summit. Variations in volatile components in submarine Kilauea basalts are dominated by mixing between subaerially degassed and relatively undegassed components within the magma reservoir and cannot be used to infer mantle volatile concentrations (Dixon *et al.*, 1991). Only those rare magmas that somehow manage to avoid the magma reservoir or pass through very quickly (i.e. high-MgO liquids) can reliably provide information about mantle volatile contents of mature, subaerial basaltic volcanoes.

(4) During subaerial or submarine rejuvenated volcanism, as exemplified by the Hana series on Haleakala, Maui (Chen *et al.*, 1991), the Honolulu series on Koolau, Oahu (Clague & Frey, 1982; Roden *et al.*, 1984), the Koloa series on Kauai (Clague & Dalrymple, 1988; Maaløe *et al.*, 1992; Reiners & Nelson, 1998), and submarine eruptions in the Kauai–Oahu Channel (Clague *et al.*, in preparation), melting extent is diminished, and melts generated from dominantly lithospheric–asthenospheric mantle sources erupt under conditions similar to precursory volcanics. Volatiles are generally lost from subaerially erupted lavas, but may be retained in glassy rinds on submarine lavas or in melt inclusions in phenocrysts.

(5) During peripheral volcanism, as exemplified by the North Arch volcanic field (Clague *et al.*, 1990; Dixon *et al.*, 1997) melting, eruption, and degassing conditions are essentially identical to (1) and (4).

The evolution of Hawaiian volcanoes described above can guide our selection of samples appropriate for use in separating shallow-level effects from heterogeneity in primary magma and mantle water concentrations. In sum, the following samples (Fig. 1) are most likely to have preserved their original (primary) H_2O concentrations:

(1) precursory—South Arch alkali olivine basalt 8D and basanite 9D (Clague *et al.*, in preparation);

(2) submarine preshield and shield—relatively primitive (MgO >7 wt %) magmas that have not had their initial water concentrations substantially increased by crystal fractionation or do not show evidence of closed-system degassing (Loihi glasses evaluated for H_2O degassing);

(3) subaerial shield—rapidly quenched magmas that did not reside in a magma reservoir (e.g. Iki-5 from the earliest stages of Kilauea Iki eruption; Wallace & Anderson, 1998; Kilauea high-MgO glass sands; Clague *et al.*, 1991; and alkali olivine basalt flow 41D collected in the moat at base of Puna Ridge; Clague *et al.*, in preparation);

(4) rejuvenated—Kauai–Oahu Channel 2D and 4D (Clague *et al.*, in preparation);

(5) peripheral—North Arch alkali olivine basalts 22D, 36D-b, and 17D-a (Dixon *et al.*, 1991). When we compare water concentrations in OIB and MORB, we assume most MORB erupted deeper than ∼1000 m has not degassed water (Moore & Schilling, 1973; Moore *et al.*, 1977; Jambon & Zimmermann, 1987; Dixon & Stolper, 1995).

Water concentrations in different mantle source regions for Hawaii and Pacific MORB

The use of element–element ratios of similarly incompatible elements is a useful way to normalize out the effects of fractional crystallization or partial melting (e.g. Langmuir *et al.*, 1977). Variability in water concentrations in tholeiitic basaltic melts is commonly investigated using variations in H_2O/K_2O or H_2O/P_2O_5 (Garcia *et al.*, 1989; Jambon & Zimmermann, 1990; Dixon *et al.*, 1991, 1997; Clague *et al.*, 1995; Wallace & Anderson, 1998). However, when we broaden our comparison base to include strongly alkalic compositions (North Arch) or significantly more incompatible-element-depleted source regions (MORB), variations in these ratios may also be affected by heterogeneity in K_2O and P_2O_5, as a result of differences in source region depletion or residual mantle mineralogy. To address this problem, we examine concentrations of water relative to other incompatible elements in the following section.

Primitive mantle normalized trace element diagrams

Trace element concentrations in Pacific MORB and Hawaiian glasses normalized to primitive mantle (Sun & McDonough, 1989) for elements Nb to Sm are shown in order of relative incompatibility in Fig. 10a–f. The figures are ordered roughly in order of eruptive stage, but will be discussed in reverse order.

To evaluate the relative enrichment or depletion of water with respect to other similarly incompatible elements, we have placed water on the spidergrams between La and Ce. We use a value of 330 ± 55 ppm for the primitive mantle water concentration. This value was selected to be consistent with available data, including similar bulk partition coefficients for H_2O and Ce during melting and crystallization (Dixon *et al.*, 1988; Michael,
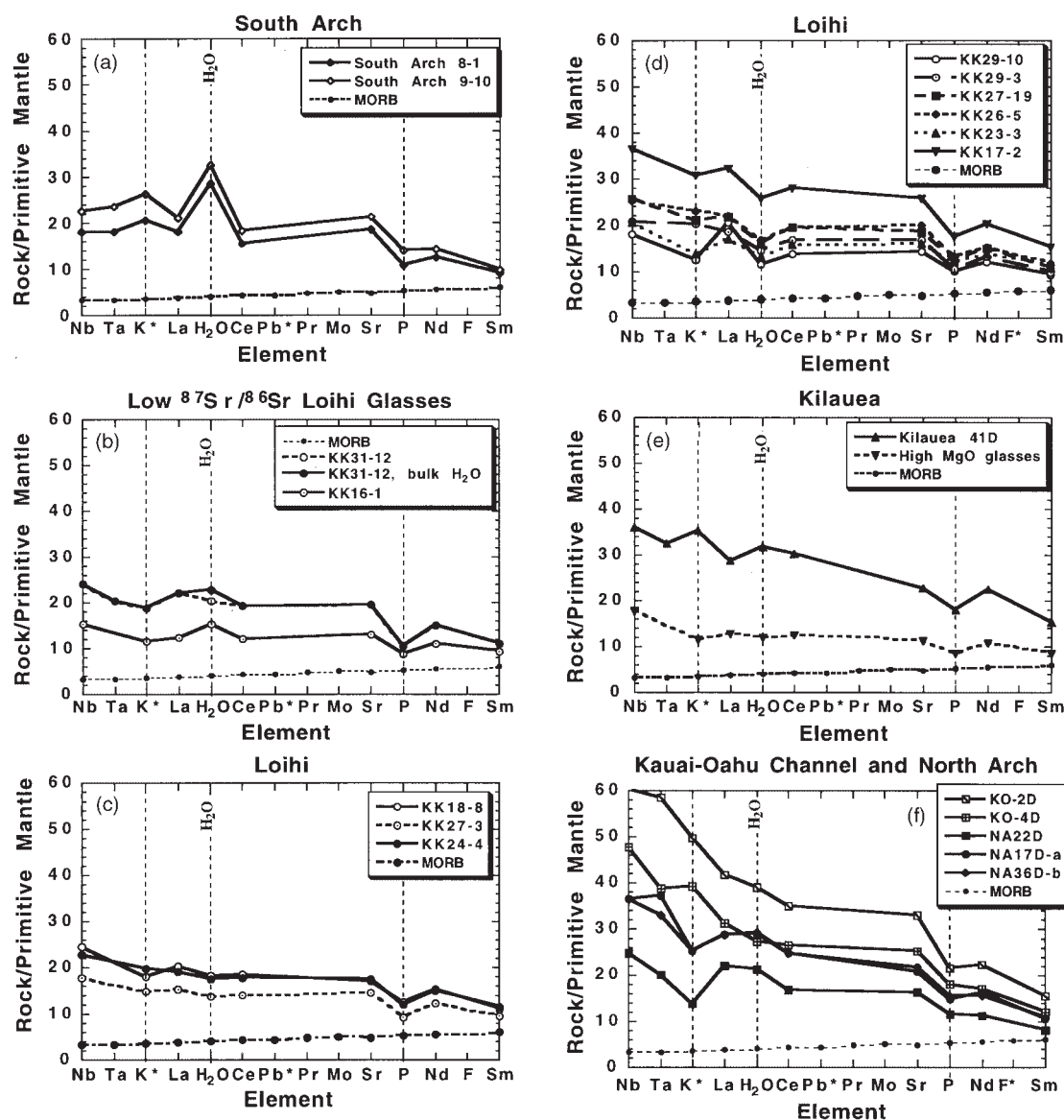
Fig. 10. Trace element concentrations normalized to primitive mantle for Hawaiian basalts between Nb and Sm. Elements are arranged in order of increasing compatibility. Each diagram shows average Pacific MORB as reference. (a) South Arch showing enrichment in H_2O relative to Ce. (b) Isotopically depleted Loihi glasses KK16-1 and KK31-12 (measured H_2O) and KK31-12* (calculated bulk H_2O) showing slight enrichment in H_2O relative to Ce. (c) Loihi KK18-8, KK27-3, and KK24-4 showing slight depletion in H_2O. (d) Loihi KK17-2, KK23-3, KK26-5, KK27-19, KK29-3, and KK29-10 showing strong depletions in H_2O. (e) Kilauea high-MgO primitive magma estimate and Kilauea alkalic basalt 41D showing no to slight enrichment in H_2O relative to Ce. It should be noted that the trace elements for the high-MgO glass (Wagner *et al.*, 1998) and volatiles (Clague *et al.*, 1991) were not measured on the same glass chips, therefore the spidergram shows trace element data for sample 57-13 having 14·8 wt % MgO (Wagner *et al.*, 1998) and a water concentration estimated from a linear correlation of H_2O with MgO (Clague *et al.*, 1991). (f) North Arch and Kauai–Oahu Channel showing no to slight enrichment in H_2O relative to Ce. Primitive mantle values used are 0·713 ppm Nb, 0·041 ppm Ta, 230 ppm K, 0·687 ppm La, 330 ppm H_2O, 1·775 ppm Ce, 0·071 ppm Pb, 0·276 ppm Pr, 0·063 ppm Mo, 21·1 ppm Sr, 95 ppm P, 1·354 ppm Nd, 26 ppm F, and 0·444 ppm Sm). Most primitive mantle values are from Sun & McDonough (1989), except H_2O and K_2O (we use 230 ppm instead of the 250 ppm listed as the preferred value to use in spidergrams). K, H_2O, and P are highlighted by vertical dashed lines.

1988, 1995; Danyushevsky *et al.*, 2000); a H_2O/Ce ratio of ∼180 ± 30 (2σ) for Pacific MORB (Michael, 1995); Ce concentrations of 1·78 ppm in the estimated primitive mantle and 7·5 in globally averaged primitive N-MORB (Sun & McDonough, 1989); and H_2O concentrations of ∼0·07–0·19 wt % in primitive N-MORB (Sobolev & Chaussidon, 1996). Adjustment of the primitive mantle water value will shift the normalized water concentrations

up or down together, but will not affect conclusions about relative water enrichment or depletion within the sample suite.

Our primitive mantle water estimate of 330 ppm, which results in a smooth depletion trend for highly incompatible elements in Pacific MORB, is lower than an estimate for bulk silicate Earth ($\sim$1000 ppm) based on addition of the exosphere (ocean, atmosphere, and crust) to the depleted mantle (O'Neill & Palme; 1998). As noted by Bell (1996), H_2O, like Pb, may be preferentially partitioned into the exosphere during subduction. If this were true, an isolated, relatively undepleted, lower-mantle component would have a higher H_2O/Ce than the upper mantle. Our estimate of primitive mantle water concentration is slightly higher than estimates of 245–290 ppm based on water concentrations in nominally anhydrous minerals in mantle xenoliths (Bell & Rossman, 1992) and identical to an estimate based on an H_2O/F ratio of 20 in oceanic basalts and a primitive mantle F content of 16·3 ppm (Dreibus *et al.*, 1997).

In general, the trace element patterns for these Hawaiian glasses are consistent with previously reported data (e.g. Frey & Clague, 1983; Garcia *et al.*, 1993, 1995; Frey *et al.*, 2000; Clague *et al.*, in preparation) and show light rare earth element (LREE) and highly incompatible element enriched patterns with absolute abundances increasing as extent of melting decreases. The heavy rare earth element (HREE) contents of all the Hawaiian glasses (higher Sm/Yb than MORB) indicate the presence of garnet in the residue (e.g. Leeman *et al.*, 1980; Hofmann *et al.*, 1984). Several differences between the Hawaiian and MORB patterns deserve mention. First, the North Arch glasses are depleted with respect to K and Rb (Frey *et al.*, 2000), and to a lesser extent P, relative to a smooth pattern (Fig. 10f). Loihi glasses do not have as large depletions in K and Rb, but instead have depletions in P (Fig. 10b–d) and relative enrichments in Ti and Zr (Frey *et al.*, 2000). It is beyond the scope of this paper to explain the underlying cause of these heterogeneities; however, the important point is that there are systematic differences in the K, Rb, and P contents of MORB and various Hawaiian basalts. Therefore, ratios of water to these elements (e.g. H_2O/K_2O and H_2O/P_2O_5) should be interpreted with caution and not simply attributed to water heterogeneity.

The elements La and Ce do not show such variability and have relative incompatibilities similar to H_2O (Dixon *et al.*, 1988; Michael, 1988, 1995; Danyushevsky *et al.*, 2000). Therefore, H_2O/Ce is a useful indicator of enrichment or depletion of H_2O relative to other incompatible trace elements. Melts with LREE-enriched patterns should have primitive-mantle-normalized water to Ce ratios [$(H_2O/Ce)_{pmn}$] slightly greater than unity, whereas MORB with LREE-depleted patterns should have ratios slightly less than unity. Also, H_2O/Ce should
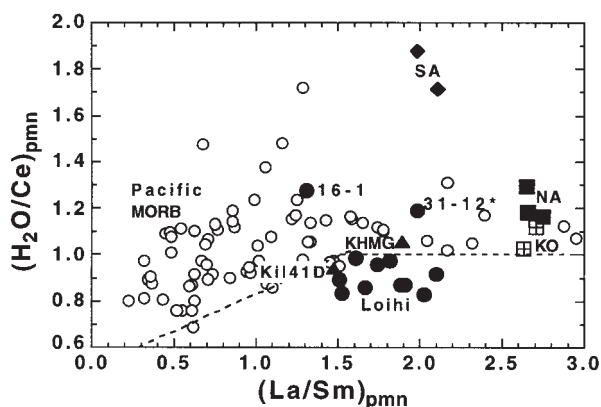
Fig. 11. $(H_2O/Ce)_{pmn}$ plotted against $(La/Sm)_{pmn}$. Primitive mantle values listed in caption to Fig. 10. Pacific MORB data (○) include East Pacific Rise and seamounts (Michael, 1995) and Easter Microplate and Easter–Salas y Gomez Seamount Chain (Simons, 2000). Other symbols as in Fig. 5. Dashed line drawn at lower limit of Pacific MORB data. Most Loihi glasses are below the dashed line. Kilauea glasses lie on the dashed line. Loihi KK16-1 and KK31-12, North Arch, and Kauai–Oahu Channel samples lie in the Pacific MORB field. South Arch samples lie above the Pacific MORB field. (Note La/Sm varies as a function of extent of melting and source region enrichment.)

increase slightly with indicators of trace element enrichment, such as La/Sm.

Trace element data for rejuvenated stage and peripheral alkalic (North Arch alkali olivine basalt 17D-a, 22D, 36D-b and Kauai-Oahu 2D and 4D) glasses are shown in Fig. 10f. Although these magmas are water rich (0·70–1·29 wt % H_2O), the amount of water is consistent with the concentrations of other incompatible elements (i.e. glasses enriched in LREE, but water is not enriched relative to La and Ce). The mean $(H_2O/Ce)_{pmn}$ is 1·19 $\pm$ 0·14 (H_2O/Ce = 214 $\pm$ 17), consistent with other LREE-enriched Pacific basalt values (Fig. 11; Michael, 1995; Simons, 2000).

Water concentrations in a high-MgO tholeiitic glass ($\sim$0·40 wt % H_2O at 14·8 wt % MgO) and alkalic basalt 41D (1·05 wt % H_2O at 7·16 wt % MgO) from Kilauea are very different, but each is consistent with the value expected based on their La and Ce concentrations (Fig. 10e). The $(H_2O/Ce)_{pmn}$ are 0·98 for the high-MgO glasses and 1·06 for 41D (H_2O/Ce of 182 and 196, respectively).

In contrast, concentrations of water relative to LREE in Loihi alkalic and tholeiitic glasses are heterogeneous, ranging from H_2O enriched to H_2O depleted. Loihi glasses from the summit region (10 out of 12 samples, excluding KK16-1 and KK31-12) are slightly to strongly depleted in H_2O relative to Ce (Fig. 10c and d). When $(H_2O/Ce)_{pmn}$ is plotted as a function of $(La/Sm)_{pmn}$, Loihi glasses form a cluster that is distinct from and lower than the field for other Pacific basalts (Fig. 11). Even though the trace element patterns are enriched in LREE, these Loihi glasses have a mean $(H_2O/Ce)_{pmn}$ of 0·90 $\pm$ 0·05

(H_2O/Ce = 166 ± 12). This represents an average depletion of ~14% relative to an expected $(H_2O/Ce)_{pmn}$ value of ~1·05 (e.g. Kilauea 41D). The sample most depleted in water (KK29-10) has a $(H_2O/Ce)_{pmn}$ of 0·84 (H_2O/Ce = 157), 20% lower than Kilauea 41D. The magnitude of the relative depletion in water does not correlate with degree of differentiation or silica saturation, therefore it is probably not due to a difference in the bulk distribution coefficient of water for crystallizing or melting mineral assemblages. In particular, the water depletion cannot be caused by residual garnet during melting, because all the Hawaiian lavas studied here have HREE contents indicative of residual garnet in the source region.

Only glasses KK16-1 and KK31-12* (undegassed value using bulk H_2O) have a $(H_2O/Ce)_{pmn}$ greater than unity (Fig. 10b) and plot within the field of North Arch and other Pacific basalts in Fig. 11. These two samples are distinct for several other reasons. First, both of these glasses have lower $^{206}Pb/^{204}Pb$ than the average Loihi value (see later discussion). Second, neither of these glasses is from the summit region and may be older eruptions. Sample KK31-12 is an alkalic basalt from a small hill on the flank of Loihi and KK16-1 is a tholeiitic basalt from the base of the northern rift zone, therefore their distinct $(H_2O/Ce)_{pmn}$ ratios are not a simple function of major element chemistry or extent of partial melting, and are more likely to be related to source region heterogeneity.

In stark contrast to all other Hawaiian and MORB glasses, the alkalic South Arch glasses are strongly enriched in water relative to their LREE element concentrations (Fig. 10a). The two glasses analyzed have $(H_2O/Ce)_{pmn}$ of 1·88 and 1·71 (H_2O/Ce of 349 and 318). These glasses are also enriched in Cl, although the spatial uniqueness of these samples upstream of the plume, lack of a hydrothermal system, and their probable rapid ascent, lead us to speculate that the water and Cl enrichments in these glasses are related to source region heterogeneity and not assimilation.

In summary, water concentrations relative to similarly incompatible elements in Hawaiian magmas are lower (Loihi), equivalent (Kilauea, North Arch, Kauai–Oahu), or higher (South Arch). These relative depletions and enrichments in water do not correlate with major element composition or extent of melting. We therefore explore possible correlations with radiogenic isotopic compositions of potential mantle endmembers.

Isotopic endmembers: mixing of mantle components and zoned plume models

Physical model of the Hawaiian plume

Numerous investigators have defined isotopically distinct mantle source regions involved in the generation of Hawaiian magmas (e.g. Chen & Frey, 1983, 1985; Clague et al., 1983; Hawkins & Melchior, 1983; Stille et al., 1983, 1986; Frey et al., 1984; Roden et al., 1984, 1994; Staudigel et al., 1984; Hofmann et al., 1987; Lanphere & Frey, 1987; Tatsumoto et al., 1987; West et al., 1987; Chen et al., 1991; Leeman et al., 1994; see review by Clague, 1987). Recent models (Maaløe et al., 1992; Frey & Rhodes, 1993; Yang et al., 1994, 1996; Kurz et al., 1995; DePaolo & Stolper, 1996; Hauri, 1996, Hauri et al., 1996; Lassiter et al., 1996; Lassiter & Hauri, 1998), arrange the various components in the form of a concentrically zoned plume whose core differs in composition and temperature from its margins. Extents of melting, depths of melt segregation, and mantle source compositions vary systematically with time and location relative to the hot core of the plume. We would place the center of the plume beneath Kilauea, on the basis of variations in magmatic flux rates. An example of such a model [modified from Hauri (1996)] is shown in Fig. 12. The main compositional zonations are as follows:

(1) the core of the zoned mantle plume (~45 km diameter) beneath Hawaii contains two components, consisting of the Koolau (KOO) and Kea (KEA) components. The KOO component may not be symmetrically distributed around the core, such that the Loa-trend volcanoes (Loihi) sample a higher proportion than the Kea-trend volcanoes (Kilauea).

(2) Surrounding the core is a thin zone of heated and entrained lower mantle with a composition similar to the hypothesized FOZO component.

(3) Surrounding (2) is a region of interaction between the upwelling plume and passively upwelling upper-mantle asthenosphere.

(4) The outermost zone is passively upwelling upper mantle (Hawaiian Asthenospheric component, HA).

Although several recent studies have suggested that much of the observed isotopic heterogeneity in oceanic island basalts is the result of interaction between melts and the oceanic crust or lithospheric mantle (e.g. Halliday et al., 1995; Eiler et al., 1996; Class & Goldstein, 1997), Lassiter & Hauri (1998) have presented strong arguments based on the covariation of Sr, Nd, Pb, O, and Os isotopes that both the KEA and KOO Hawaiian plume components result from subduction of the oceanic lithosphere, with the KOO component representing recycled upper crust + sediment and the KEA component representing recycled lower crust + lithospheric mantle. New Hf-isotopic data also provide evidence for pelagic sediments related to the KOO component in the source region of Hawaiian basalts (Blichert-Toft et al., 1999).

A vertical slice through the plume (Fig. 13) shows the compositional zonations. The main melt generation zonations are:

(1) within the hot plume core, alkalic to tholeiitic melts are produced by relatively moderate to high extents of
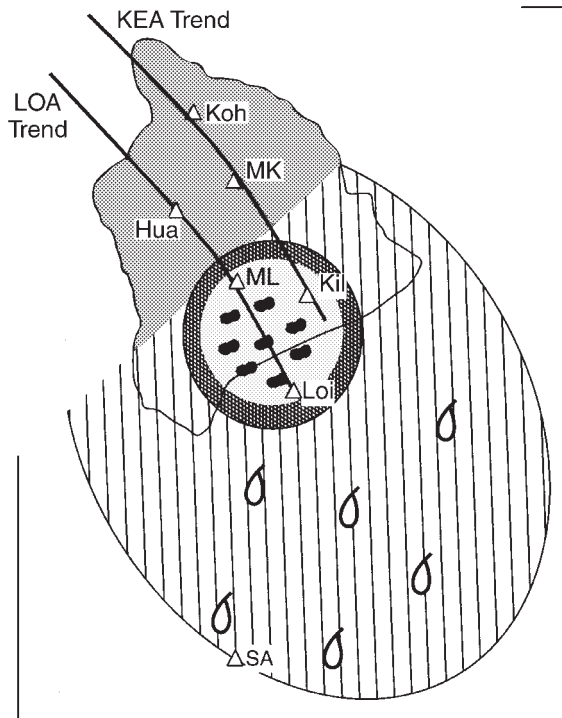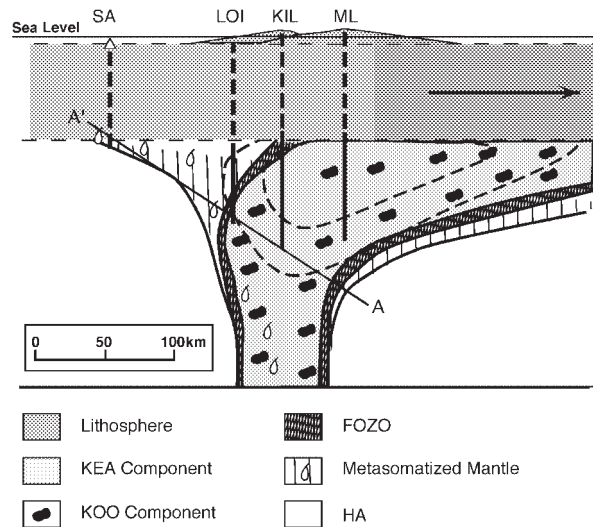
Fig. 12. Schematic model of a zoned plume under Hawaii [modified from Hauri (1996)]. The model is cut off at Mauna Loa because of uncertainty in the distribution of components in the plume as it is dragged over by Pacific plate motion. The core of the plume consists of recycled crust + sediment (relatively dry KOO component) and recycled lithosphere (KEA component). The distribution of the KOO component is not symmetric within the plume, such that the more southern LOA trend volcanoes sample a greater proportion of the KOO component than do the more northern KEA trend volcanoes (Hauri, 1996). Loihi lavas sample the heterogeneous margins of the plume that also includes entrained lower mantle (FOZO). In front of the plume is an area of hydrous metasomatism as sampled by the South Arch lavas. Downstream of the plume, North Arch and Kauai–Oahu Channel lavas (not shown in figure) are derived from metasomatized, but not anomalously wet, mantle (HA). Arrow shows Pacific plate motion. SA, South Arch; LOI, Loihi; KIL, Kilauea; ML, Mauna Loa; Hua, Hualalai; MK, Mauna Kea; Koh, Kohala.

Fig. 13. We have added the compositional zonations from Fig. 12 onto a schematic cross-section of the zoned plume [modified from Watson & McKenzie (1991) and Rhodes & Hart (1995); their model has an ~75 km diameter plume deflected by a 70 km thick lithosphere]. Bold vertical lines show melting initiating at a depth of ~130 km beneath Kilauea. The plume is tilted as a consequence of lithospheric drag in the direction of Pacific plate motion. [Note the plume core of recycled material is narrower (~60 km wide) and contained within a larger thermal plume.] We have added an outer zone of metasomatism to explain the isotopic characteristics of the South Arch lavas.

melting and shallow depths of melt segregation of the two plume components;

(2) marginal to the plume core, strongly alkalic melts are produced by lower extents of melting of asthenospheric and/or entrained lower-mantle components and at greater depths of segregation.

This model explains the observed change in mixing proportions of source components with age (e.g. Chen & Frey, 1983, 1985). As lava compositions change from tholeiitic to alkalic compositions (transition from shield to post-shield and rejuvenated stages), the more incompatible-element-depleted and low $^{87}Sr/^{86}Sr$ asthenospheric component becomes increasingly important. Because the extents of melting decrease as the volcano moves off the center of the plume, these more 'depleted'

isotopic compositions are commonly associated with relative enrichment in highly incompatible elements.

Radiogenic isotopic compositions of Hawaiian mantle endmembers

Table 3 lists the isotopic characteristics of the various mantle endmembers used in this study, as well as some values from previous studies. One modification of existing models is that we use the rejuvenated stage lavas and peripheral North Arch lavas as representative of the upper mantle surrounding the plume (Hawaiian Asthenosphere–Lithosphere or HA), instead of requiring a fully, depleted MORB source. Allowing the upper mantle and lithosphere near Hawaii to have been 'refertilized' by melts at some point in its 100 my history (Frey *et al.*, 2000) reduces the requirement for generation of alkalic melts by extremely low extents of melting (i.e. ≪1%; Sims *et al.*, 1995). Figure 14 plots $^{87}Sr/^{86}Sr$ vs $^{206}Pb/^{204}Pb$ for Hawaiian lavas, clearly showing the triangular array of Hawaiian isotopic data bounded by the KEA, KOO, and HA endmember compositions. In the subsequent discussion, we assume that Loihi lavas can be modeled as a mixture of KEA, KOO, and FOZO components (e.g. Bennett *et al.*, 1996; Lassiter & Hauri, 1998; Blichert-Toft *et al.*, 1999), although some other studies prefer to classify Loihi as yet another distinct component to explain

Table 3: Summary of isotopic characterization of mixing endmembers

Name	$^{87}Sr/^{86}Sr$	$^{143}Nd/^{144}Nd$	$^{206}Pb/^{204}Pb$	$^{207}Pb/^{204}Pb$	$^{208}Pb/^{204}Pb$	$^{3}He/^{4}He$
KEA	0·70352	0·51298	18·660	15·487	38·111	16·7
KOO	0·70440	0·51267	17·800	15·425	37·740	13·0
HA	0·70300	0·51310	18·100	15·438	37·700	8·0
FOZO	0·703–0·704	0·5128–0·5130	18·5–19·5	15·55–15·65	38·8–39·3	high
LOI	0·70365	0·51296	18·424	15·480	38·214	32·0

Endmember isotopic compositions are selected to lie just outside the range of Hawaiian isotopic data and to serve as visual aids in Fig. 14. KEA component is dominant in Kilauea and Mauna Kea lavas. KOO is Koolau. HA is Hawaiian asthenosphere–lithosphere and is assumed to be aged metasomatized Pacific upper mantle (Frey *et al.*, 2000). Entrained lower mantle is assumed to be FOZO (Hauri *et al.*, 1994), which is similar to 'C' as defined by Hanan & Graham (1996). We assume that the LOI component is composed of a mixture of KEA and KOO, and attribute the high $^{3}He/^{4}He$ values to complex entrainment and melting processes associated with the plume margin. Hawaiian data used for estimates are from Kurz *et al.* (1983), Staudigel *et al.* (1984), Stille *et al.* (1986), Honda *et al.* (1993), Garcia *et al.* (1995), Lassiter *et al.* (1996), Frey *et al.* (2000), and Clague *et al.* (in preparation).
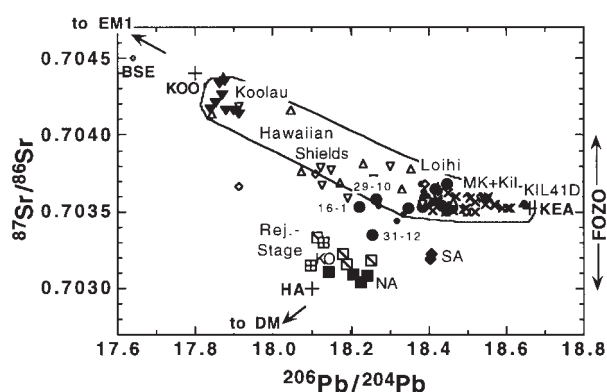
Fig. 14. $^{87}Sr/^{86}Sr$ vs $^{206}Pb/^{204}Pb$ for Hawaiian lavas. Radiogenic isotopes can be explained by mixing of three endmembers composed of two plume components (KOO and KEA) and a more depleted asthenospheric–lithospheric component (HA). Most Loihi lavas form a cluster to the left of the KEA component because of involvement of the KOO component. Loihi lava KK16-1, KK29-10, and KK31-12 have lower $^{206}Pb/^{204}Pb$ than the main Loihi group consistent with involvement of HA or KOO mantle during melting. Large ●, Loihi (Staudigel *et al.*, 1984); small ●, Loihi (Garcia *et al.*, 1995); ×, Mauna Kea (Lassiter *et al.*, 1996); △, ▽, other Hawaiian shield lavas including Kohala, Mauna Kea, Kilauea, Mauna Loa, West Molokai, East Molokai, West Maui, Haleakala, Koolau, and Kauai (△, Bennett *et al.*, 1996; ▽, Stille *et al.*, 1986); ◇, late-stage lavas including Hualalai, West Molokai, Honoloa series on West Maui, Kula series on Haleakala, and Waianae (Stille *et al.*, 1986); open squares with a slash, rejuvenated stage lavas including Lahaina series on West Maui, Hana series on Haleakala, Honolulu Series on Koolau, and the Koloa volcanics on Kauai (Stille *et al.*, 1986); open squares with a cross, the Kauai–Oahu Channel lavas (Clague *et al.*, in preparation); ■, North Arch lavas (Frey *et al.*, 2000).

the maximum in $^{3}He/^{4}He$ values (Kurz *et al.*, 1995; Hauri, 1996).

When the radiogenic isotopic data are considered with variations in H_2O/Ce, we can begin to characterize the variation in mantle water concentrations. The next two sections compare radiogenic isotopes and H_2O/Ce variations for Hawaiian lavas erupted outside (South Arch, North Arch, Kauai–Oahu) and inside (Loihi, Kilauea) the plume core.

Radiogenic isotopes and H_2O/Ce in lavas erupted outside the Hawaiian plume core

The peripheral North Arch and rejuvenated stage lavas form a cluster near the proposed HA component (Fig. 14) and have MORB-like $^{3}He/^{4}He$ ratios, reflecting melting of aged, possibly refertilized Pacific lithosphere–asthenosphere that is heated and possibly uplifted by the plume. These samples have H_2O/Ce ratios consistent with LREE-enriched Pacific MORB values (Fig. 11), therefore the 'refertilizing' melt was not anomalously wet.

In contrast, the precursory South Arch lavas have higher $^{206}Pb/^{204}Pb$ than the peripheral and rejuvenated stage lavas and have elevated $^{3}He/^{4}He$ ratios ($\sim 19\ R_a$, where R_a is the atmospheric ratio of $1·39 \times 10^{-6}$). In addition to these unique isotopic compositions, these and only these lavas have strong enrichments in water (Fig. 15). If the distinct isotopic and volatile character of the South Arch lavas were caused by preexisting heterogeneity within the Pacific asthenosphere–lithosphere, extent of melting, or depth of melt segregation, we would expect, but do not observe, equivalent enrichments in all the marginal alkalic lavas. The observation that lithophile ($^{206}Pb/^{204}Pb$) and volatile (H_2O/Ce, $^{3}He/^{4}He$) ratios are modified together implies that the mantle source composition was modified by addition of a melt, not a C–H–O fluid. We conclude that the distinct isotopic and volatile character of the South Arch lavas is caused by metasomatism by a hydrous melt derived from the Hawaiian plume of the mantle in advance of the plume. Small-scale hydrous regions within the plume will melt first
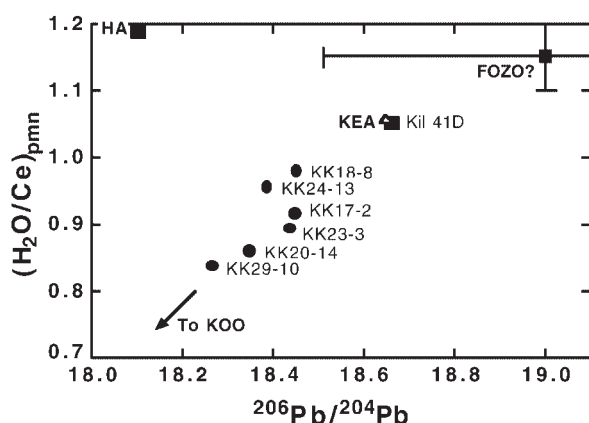
Fig. 15. Correlation between $^{206}Pb/^{204}Pb$ and H_2O/Ce for Loihi summit lavas. H_2O/Ce decreases as the proportion of the KOO component increases. Although there is no *a priori* reason to assume a linear correlation, a linear regression through the data yields an $(H_2O/Ce)_{pmn}$ of 0·6 at a $^{206}Pb/^{204}Pb$ of 17·8 for the KOO component.

during ascent of the plume material. These hydrous 'pods' must be volumetrically trivial, because the anomalous enrichment in water is not observed in later shield lavas produced by higher extents of melting or in peripheral and rejuvenated lavas erupted downdrift of the plume. In addition, the $^3He/^4He$ ratios of South Arch lavas are similar to those of Kilauea samples, suggesting that melting of the hydrous heterogeneities may involve at least the KEA mantle component (wet KEA?).

Radiogenic isotopes and H$_2$O/Ce within the Hawaiian plume core

Sample Kil41D is isotopically similar to the KEA end-member and has a normal H_2O/Ce ratio. Radiogenic isotopes have not been determined for the high-MgO glasses because of their small size (individual sand grains). Loihi lavas are isotopically heterogeneous. Most Loihi lavas form a cluster having $^{87}Sr/^{86}Sr$ of 0·70365 and $^{206}Pb/^{204}Pb$ of 18·424, shifted to lower $^{206}Pb/^{204}Pb$ (toward KOO) relative to Kilauea and Mauna Kea lavas (KEA). Three Loihi lavas (KK16-1, KK31-12, and KK29-10) are distinct from the main Loihi cluster and have lower $^{206}Pb/^{204}Pb$ ratios. These are the same three glasses that have the highest and lowest H_2O/Ce. Lava KK31-12 is shifted to lower $^{87}Sr/^{86}Sr$ (toward the rejuvenated stage lavas) indicating involvement of an asthenospheric–lithospheric component (HA) in melt generation. It has H_2O/Ce similar to other Pacific basalts, higher than samples in the main Loihi cluster. Lava KK29-10 is shifted toward the KOO component (lower $^{206}Pb/^{204}Pb$ and higher $^{87}Sr/^{86}Sr$) and has the lowest H_2O/Ce. Lava KK16-1 has radiogenic isotopic characteristics intermediate between KK31-12 and KK29-10, extremely high $^3He/^4He$ (30·1 R$_a$), and the highest H_2O/Ce of the Loihi lavas (237). This sample, collected at the base

of the northern rift zone, may be derived from the heterogeneous mixed region at the edge of the plume involving unknown proportions of HA, KOO, KEA, wet KEA, and FOZO endmembers.

The isotopically coherent Loihi glasses (KEA + KOO + FOZO) are enriched in incompatible elements (including water) relative to MORB, but the amount of water present is less than that predicted based on their REE concentrations. In other words, the mantle source for Loihi is depleted in water by $\sim 14\%$ relative to concentrations of similarly incompatible trace elements, resulting in H_2O/Ce significantly lower than the surrounding mantle.

We speculate that it is the KOO component that is strongly depleted in water, based on the following reasoning. The KOO component makes up <5% of the Loihi lavas, the remaining >95% representing KEA + FOZO components (e.g. Hauri, 1996). As there is no water-depletion signal in the Kilauea glasses (derived mainly from the KEA component), then the KEA component can be assumed to have normal water content. For the summit Loihi lavas, H_2O/Ce decreases as $^{206}Pb/^{204}Pb$ decreases (Fig. 15) in the direction toward KOO and away from KEA and FOZO. Thus, the water depletion signal observed in Loihi lavas must derive from the KOO component. As this component makes up only a small fraction of the Loihi lavas, it must be extremely dry. This conclusion is consistent with data from Hawaiian, silicic melt inclusions (Hauri *et al.*, 1999; Hauri, 2001). Hauri *et al.* (1999) found melt inclusions in phenocrysts from Koolau lavas with very low H_2O and Cl concentrations along with very low D/H ratios.

One possible source of this anomalously dry material is old oceanic lithosphere and sediments that have been 'recycled' through a subduction zone. If so, low H_2O/Ce ratios in the KOO component suggest that dehydration of oceanic crust and lithosphere during subduction that penetrates into the lower mantle must be efficient at extracting H_2O from the subducted slab and fractionating it into the overlying suprasubduction zone mantle wedge and eventually into the exosphere. The efficiency of this process varies with subduction rate and age of the subducting plate (e.g. Staudigel & King, 1992; Peacock, 1993). Therefore, other plumes with recycled oceanic crust and lithospheric components may have had different subduction histories and may have different relative enrichments or depletions in H_2O.

The mineralogy of the various mantle endmembers is an area of active speculation. For example, Hauri (1996) proposed that the Koolau component is dominantly quartz eclogite, whereas the KEA component is dominantly peridotite. The lower abundances of Sc, Y and Yb in Koolau lavas relative to shield lavas erupted at Kilauea and Mauna Loa are consistent with a more important role for residual garnet in the source region

of Koolau lavas (Jackson *et al.*, 1999). In contrast, Stracke *et al.* (1999) use Hf–Nd–Th isotopic data to argue against the existence of garnet pyroxenite or eclogite in the source of Hawaiian basalts. They concluded that both the KEA and KOO components are dominantly peridotitic. The relatively dry nature of the KOO component is consistent with the latter model, because water (OH) shows a strong preference for ortho- and clinopyroxenes over coexisting olivines (Bell & Rossman, 1992); therefore, pods of eclogite situated within peridotitic mantle might be expected to be local areas of comparatively high water concentration.

Estimates of mantle water concentrations

Although the H_2O/Ce ratios within the plume and surrounding upper mantle vary, the absolute water concentrations are similar. Mantle water concentration in the Loihi source region (KEA + KOO) is estimated to be ∼400 ppm based on H_2O/Ce from this study (167 ± 13) and 2·4 ppm Ce (four times chondrites) in the source region (Garcia *et al.*, 1995; this assumes primary Loihi tholeiites are generated by 10% non-modal, equilibrium partial melting of a garnet lherzolitic source). This mantle water estimate is greater than that for MORB mantle (∼100 ppm), but slightly lower than other estimates for Hawaiian source regions, including 525 ± 75 ppm for the source of the North Arch basalts (refertilized upper mantle; Dixon *et al.*, 1997) and 450 ± 190 ppm for the source of Kilauea basalts (Wallace, 1998). Although the differences in mantle water concentrations are small, our data are consistent with the 'wet-rim/dry-core' model of Sen *et al.* (1996) based on mineralogical variations in Hawaiian mantle xenoliths. Implications of this amount of water on enhancing partial melting and melt extraction within the upwelling plume compared with drier MORB mantle have been presented by Wallace (1998).

Summary of water in Hawaiian mantle source regions

We conclude that the concentration of water relative to that of similarly incompatible elements correlates with mantle source composition as identified by radiogenic isotopes. The most volatile-enriched lavas occur 'in front' or updrift of the plume, where small volumes of plume-derived hydrous melts have metasomatized the overlying asthenosphere–lithosphere. The core of the Hawaiian plume is wetter than the MORB source, but the amount of water present is equal to (not anomalously wet) or less than (relatively dry) that expected based on concentrations of other incompatible elements. The Hawaiian plume, therefore, does not represent primitive 'undegassed' lower mantle. The absence of major volatile-enriched components within the core of the Hawaiian plume has important implications for the origin of primitive noble gas signatures.

Noble gas isotopes

We argued above that the Loihi lavas are not enriched in water, suggesting that the plume is not derived from a primitive, undegassed lower-mantle source, yet the $^3He/^4He$ ratios at Loihi are some of the highest measured (Kurz *et al.*, 1982, 1983; Kaneoka *et al.*, 1983; Rison & Craig, 1983; Kurz & Kammer, 1991; Hiyagon *et al.*, 1992; Honda *et al.*, 1993; Kurz, 1993), suggesting involvement of a relatively undegassed source region. Even though Loihi is intermediate between the KEA and KOO endmembers in plots involving radiogenic isotopes or trace element ratios (e.g. Lassiter & Hauri, 1998), it erupts samples with the highest $^3He/^4He$ (Loihi). Previous workers have noted a lack of correlation between lithophile and noble gas isotopic ratios (e.g. Vance *et al.*, 1989; Poreda *et al.*, 1993; Valbracht *et al.*, 1996; Hilton *et al.*, 1997). Mechanisms proposed to explain this lack of correlation at Hawaii and at other hotspots include (1) 'plume degassing' (Valbracht *et al.*, 1996; Hilton *et al.*, 1997); (2) preferential extraction of helium during partial melting (e.g. Kurz & Geist, 1999); (3) kinetic decoupling of He and Ne from heavier elements over short length scales as a result of their greater diffusivities (e.g. Kaneoka, 1998); (4) incorporation of a unique mantle component (i.e. FOZO; Hauri, 1996).

In the plume degassing model, the volatile and lithophile systems are coupled in the deep mantle, but become decoupled when a gas-rich melt phase separates from the plume through the early separation of a CO_2-dominated melt phase, possibly when the plume begins to flex by the drag of the overriding plate (>100 km). Thus, the high $^3He/^4He$ Loihi basalts should also have elevated CO_2 contents compared with other Hawaiian basalts. Unfortunately, we cannot evaluate the differences in initial CO_2 contents in various Hawaiian magmas because of open-system CO_2 loss.

To support the plume degassing model, Valbrecht cited the ubiquitous presence of cogenetic CO_2 fluid inclusions, which record minimum trapping pressures of 1·3 GPa (43 km), in mantle xenoliths from various oceanic islands (Schiano *et al.*, 1992). Other work, however, indicates that primary fluid inclusions were trapped at lower pressures (∼0·22–0·47 GPa or ∼8–17 km depth; Roedder, 1983). The presence of CO_2 fluid inclusions can be accomplished simply by magma degassing, during storage and solidification within or at the base of the crust or in the upper lithospheric mantle, without requiring plume degassing. Dixon (1997) showed that a range of alkalic to tholeiitic basalt compositions will begin to exsolve a CO_2-rich fluid phase at 0·6–1·4 GPa (∼20–50 km).

Another study (Hilton *et al.*, 1997) supports the idea of plume degassing based on the low ^{3}He content of Kilauea's solfataras and steam fumaroles located within and around the central summit caldera of Kilauea volcano. We suggest that the low ^{3}He content measured by Hilton is the result of shallow (magma chamber degassing), not deep (plume degassing), processes. It should be noted that there is abundant geologic evidence for shallow-level, magmatic degassing; in contrast, there is no direct evidence for plume degassing.

In contrast to the plume degassing models, recent work (Kurz *et al.*, 1995, 1996; Lassiter *et al.*, 1996; Eiler *et al.*, 1998) on Mauna Loa and Mauna Kea has shown reasonably good covariation between helium and lead isotopic compositions, such that a three-component model of the sources of pre-shield and shield-building lavas can account simultaneously for their helium and lead isotope systematics. This is strong evidence that helium is not decoupled from the nonvolatile isotope systems in these mature shield and post-shield lavas, and it confirms previous inferences based upon correlations of helium and strontium isotope ratios among individual suites of Hawaiian lavas (Kurz *et al.*, 1987, 1996; Kurz & Kammer, 1991).

We propose that earlier models of volatile decoupling were misguided by the coincidence of the radiogenic isotopic composition of the KOO component with that of bulk silicate Earth (e.g. Roden *et al.*, 1994). When one assumes that the plume is representative of the bulk undegassed mantle, then the problem is how to remove ^{3}He from the core of the plume and concentrate it near the margin. If one instead assumes that the plume is composed of recycled oceanic crust and lithosphere (e.g. Lassiter & Hauri, 1998), then the problem becomes how to get ^{3}He into the plume.

When the spatial distributions of H_2O/Ce and ^{3}He/^{4}He ratios (Fig. 16) are compared, several important observations can be made. First, the location of maximum H_2O/Ce (South Arch) and ^{3}He/^{4}He (Loihi) do not coincide, thus the processes controlling water and helium are not coupled. We have proposed our own version of 'plume degassing', in which more hydrous regions within the plume melt early, segregate, and metasomatize the overlying asthenosphere and lithosphere in front of the plume, but this process cannot explain the helium isotopic variations. We therefore favor the unique mantle component to explain the high ^{3}He/^{4}He ratios at Loihi (e.g. Hauri, 1996). Thus, a thin, He-rich zone of entrained lower mantle (FOZO) adds He to the margin of the plume. Because the ^{3}He/^{4}He ratios of the South Arch lavas are similar to Kilauea, not Loihi, lavas, we conclude that the metasomatic melt component in front of the plume
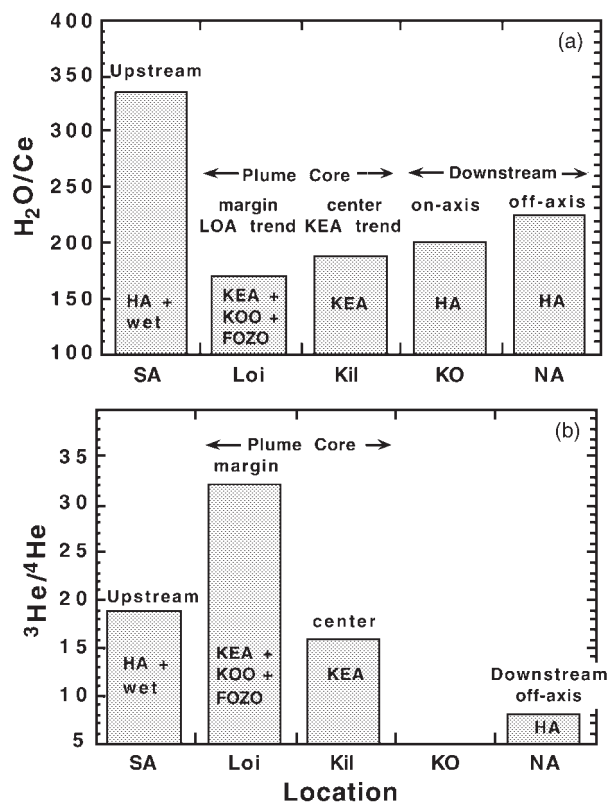

Fig. 16. Average H_2O/Ce and ^{3}He/^{4}He ratios for Hawaiian basalts as a function of location. The highest H_2O/Ce is seen in advance of, but not downstream of the plume. The maxima in H_2O/Ce and ^{3}He/^{4}He are offset, suggesting different mechanism are responsible for their behavior.

may be derived dominantly from the KEA component (wet KEA, rather than FOZO).

CONCLUSIONS

We present new volatile (H_2O, CO_2, Cl and S) concentration data for Loihi seamount southeast of the island of Hawaii, and discuss these data in the context of (1) degassing models that discriminate between shallow (degassing and assimilation) and deep processes, and (2) volatile concentrations in submarine Hawaiian basalts from a range of environments within and around the plume. Concentrations of CO_2 and Cl in Loihi glasses are dominated by shallow-level processes (CO_2 degassed, Cl assimilated). Bulk CO_2 concentrations in Loihi glasses are low because of degassing and loss of a CO_2-rich vapor phase from magmas stored at deep or shallow levels. Degassing of basalts stored at the base of the crust results in loss of 80–90% of the initial CO_2, and presumably He, explaining the characteristically low He concentrations in OIB. Cl concentrations are high and controlled by variable amounts of brine assimilation.

Water concentrations in most Loihi glasses (30 out of 36) are not affected by shallow degassing and assimilation, and can be used to estimate primary magmatic and mantle water concentrations. Most Loihi lavas have lower H_2O/Ce than other Hawaiian lavas.

We confirm that Hawaiian magmas have higher water concentrations than MORB, but our main goal was to answer the question: 'Are plumes anomalously wet relative to other trace elements?' The answer for Hawaii is no, except in advance of the plume. Variations in H_2O/Ce ratios in Hawaiian lavas do not correlate with major element composition, extents of melting, or depths of melting. Instead, these data are consistent with a zoned plume model, in which mantle components within the plume are drier than the exterior. Outside the plume core, strong enrichments in H_2O are observed only in advance of the plume (South Arch), suggesting that small-scale hydrous regions in the upwelling plume melt early, segregate, and metasomatize the overlying mantle. These hydrous regions must be volumetrically trivial because similar water enrichments are not observed in later shield (Kilauea), rejuvenated (Kauai–Oahu Channel) and peripheral (North Arch) lavas. Within the plume core, lavas have enrichments in water that are equivalent to (Kilauea) or less than (Loihi) those of similarly incompatible elements. The KOO mantle component, one of two components in the Hawaiian plume thought to derive from subducted oceanic lithosphere, and perhaps representing basaltic crust plus sedimentary cover, is strongly depleted in water, explaining the correlation between H_2O/Ce and $^{206}Pb/^{204}Pb$ in summit Loihi lavas. Lower H_2O/Ce in the KOO component may reflect efficient dehydration of the oceanic crust during subduction and recycling into the deep mantle. High $^3He/^4He$ ratios in Loihi glasses are not the result of plume degassing of a volatile-rich plume, but instead probably result from mixing with entrained lower mantle (FOZO) into the plume interior (KEA + KOO) along the outer rim of the plume.

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