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Compositional diversity of Mauna Kea shield lavas recovered by the Hawaii Scientific Drilling Project: Inferences on source lithology, magma supply, and the role of multiple volcanoes

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[1] The final Stage (Phase-2) of the Hawaii Scientific Drilling Project (HSDP) recovered 408 m of basaltic core (3098–3506 mbsl) attributed to Mauna Kea volcano. We determined the major and trace element composition of 40 samples from this core. Our results show that the incompatible element ratios, such as Zr/Nb, which are correlated with Pb isotopic ratios, are more variable in the lower 408 m of Mauna Kea shield lavas than in the overlying 2855 m (\sim 450 ka). We argue that this geochemical diversity was present in the mantle source of Mauna Kea shield lavas and does not require the inter-fingering of lavas from adjacent volcanoes. Because of uncertainties in Ni partitioning between olivine and melt and the wide range of Ni contents in peridotites, we show that all Mauna Kea lavas may have been derived from a peridotite source. We also obtained major and trace element compositions for 24 whole-rock clasts and hyaloclastites and 7 glasses from HSDP Phase-1 core between 1767 and 1808 mbs. These enigmatic lavas, previously recognized by the distinctive high CaO and K_2O contents of their glasses, are also relatively enriched in highly incompatible trace elements. We show that this group of lavas have affinities with post-shield lavas and argue that they are a consequence of lower degrees of melting (\sim a factor of two) than other Mauna Kea shield lavas, thereby providing evidence that magma supply varied significantly during the growth of the Mauna Kea shield.

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1. Introduction

- [2] A major impediment to understanding the magmatic history of Hawaiian volcanoes and the structure of the Hawaiian mantle plume is the lack of thick stratigraphic sections that sample most of the 800 to 1500 ka of volcano growth [e.g., Moore and Clague, 1992; Lipman, 1995; Garcia et al., 1995]. Subaerial sections of Hawaiian volcanoes reveal only a small fraction (5-10%) of this history and are biased toward the late stages of volcano growth. The Hawaii Scientific Drilling Project (HSDP) made a significant advance toward addressing this problem by drilling and coring a 1 km pilot hole, HSDP-1 [Stolper et al., 1996], followed by a 3.1 km hole (HSDP-2) [Garcia et al., 2007; Stolper et al., 2009], on the eastern flank of Mauna Kea volcano. This international, multidisciplinary study documented \sim 450 ka (\sim 209–647 ka) of Mauna Kea's magmatic history [Sharp and Renne, 2005], which began with a vigorous submarine shield-building stage, and ended with a marked decline in magma production as the volcano reached its post-shield stage [see Stolper et al., 2009, Figure 6].
- [3] Major results of the HSDP include information on the internal structure of a large oceanic volcano [Garcia et al., 2007], varying magma compositions erupted during the shield building stage [e.g., Huang and Frey, 2003; Rhodes and Vollinger, 2004; Stolper et al., 2004], and the isotopic diversity of the lavas [e.g., Blichert-Toft et al., 2003; Eisele et al., 2003; Kurz et al., 2004; Bryce and DePaolo, 2005; Blichert-Toft and Albarède, 2009]. The geochemical heterogeneity of the lavas requires either heterogeneity in their source, or perhaps the HSDP core contains lavas erupted from several volcanoes [e.g., Holcomb et al., 2000; Blichert-Toft and Albarède, 2009]. These HSDP results have significantly contributed to recent discussions of the nature and structure of mantle plumes [e.g., Abouchami et al., 2005; Bryce and DePaolo, 2005; Farnetani and Hofmann, 2009, 2010; Huang et al., 2011; Weis et al., 2011] and the relative roles of peridotite and pyroxenite as sources of plume-related magmas [e.g., Sobolev et al., 2005; Herzberg, 2006, 2011; Putirka et al., 2011].

- [4] Phase-1 of HSDP-2 (we use the terminology of Stolper et al. [2009, see Figure 3]) recovered 3100 m of core, documenting about 450 ka of Mauna Kea's eruptive history between 209 and 647 ka [Sharp and Renne, 2005; Stolper et al., 2009]. Here, we report on the composition and geochemical stratigraphy of an additional 408 m of core (3098-3506 mbsl) recovered during Phase-2 (2003–2007) of the HSDP-2 project [Stolper et al., 2009]. Assuming an eruption rate of 9 m/ka [see Stolper et al., 2009, Figure 6], this 408 m of core extends the eruptive history of Mauna Kea by an additional 48 ka from 647 to 695 ka. The forty analyzed Phase-2 samples are from 33 of the 45 identified flow and intrusive units and consist mostly of submarine pillow lavas, with lesser amounts of hyaloclastites, pillow breccias, and massive volcanic and intrusive units (Figure 1a).
- [5] We also sampled and determined whole-rock major and trace element abundances for 24 clasts and hyaloclastites from HSDP-2 Phase-1 flow units 248, 254, 255 and 256 higher in the core between 1767 and 1808 m (Figure 1b). These lavas, recognized previously by the distinctive major element compositions of glasses, were designated CaO-K2Orich glasses because of their high CaO and K2O content relative to other Mauna Kea glasses [Stolper et al., 2004]. Additionally, we determined trace element abundances in 7 of these high CaO-K₂O glasses previously analyzed for major elements by Stolper et al. [2004]. In a provocative paper, Herzberg [2006] suggested that these CaO-K₂O rich shield lavas may be the only Mauna Kea shield magmas derived from a peridotitic source and that all other shield lavas result from melting of pyroxenite sources.
- [6] In this paper we use published and newly obtained geochemical data to show that the compositional diversity of lavas from the deepest part of the core (3098–3506 mbsl) exceeds that of younger lavas at higher stratigraphic levels. We also assess: (1) the roles of peridotite and pyroxenite in the source of Mauna Kea magmas; (2) the possibility that the HSDP core includes Mauna Kea shield lavas intermingled with lavas derived from other shields;



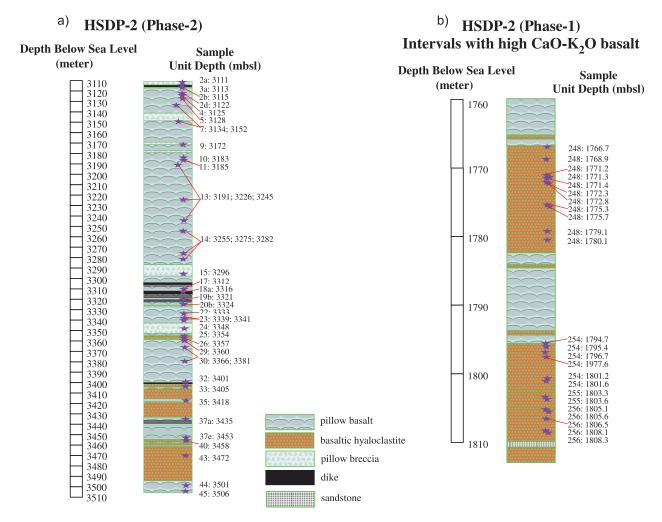


Figure 1. Simplified lithological sections of the Hawaii Scientific Drilling Project (HSDP) core, showing rock types, sample locations, flow unit numbers and depth in mbsl. (a) Core from Phase-2 of the project between 3098 and 3506 mbsl. (b) Core from Phase-1 of the project between 1767 and 1808 mbsl showing the location of High CaO-K₂O whole-rock samples.

and (3) the origin of the enigmatic CaO-K₂O-rich lavas erupted in the depth interval of 1767 to 1808 m.

2. Analytical Methods

2.1. X-Ray Fluorescence Analysis of Whole-Rocks

[7] Tables 1a and 1b report the whole-rock major and trace element compositions of 40 Phase-2 lavas. Twenty eight of these are pillow lavas, or pillow breccia, 10 are massive units, including both volcanic and intrusive, and 2 are hyaloclastites. The sampling density for the Phase-2 lavas is around 9 m/sample, roughly twice the 19 m/sample of Phase-1 lavas by *Rhodes and Vollinger* [2004], and three times (~26 m/sample) that of the Phase-1

reference samples distributed to different laboratories. Tables 2a and 2b contain whole-rock major and trace element compositions of 24 High CaO lavas from Phase-1 of the core, between 1767 and 1808 mbsl. The sampling density is about 1.7 m/sample. Nine of these samples are hyaloclastites and 15 are clasts from within this hyaloclastite sequence.

[8] The sample crushing and washing protocols were identical to those described by *Rhodes* [1996], and the X-ray fluorescence (XRF) analytical methods for major and trace elements are described by *Rhodes and Vollinger* [2004]. Estimates of the precision and accuracy of these data are given by *Rhodes* [1996] and *Rhodes and Vollinger* [2004]. In addition to the customary major and trace elements



Table 1a. XRF Major Element Analyses of Lavas Sampled by Phase-2 of the HSDP Core^a

	Geocl Geopl Geosy	hys ⁄ste	ics		G	<u> </u>]	RHO	DDE	ES I	ET .	AL.	: C	OM	POS	SITIO	ONA	AL I	DIV	ERS	SIT	Y C	F H	SDI	P LA	AVA	S		10	0.1	02	9/2	201	10	зС	003
Alkalic Index	-1.30	-0.19 -1.54	-1.43	-1.46	-1.32	-1.49	-1.44	-1.37	-1.53	-1.51	-1.55	-1.50	-1.40	/4·I-	1.42	1.57	-1.34 -1.34	-1.37	-1.47	-1.46	-1.83	-1.35	-1.79	-2.40	-1.83	-2.1 <i>/</i> -1 61	-1.68	-1.57	-0.94	-1.56	-1.41	-1.45	-1.13	-1.15	-1.69	77.77	0.55 0.56 -1.14
COI	0.75	5.05 0.91	0.72	98.0	-4.46	0.92	1.10	0.80	98.0	1.04	0.65	0.70	0.75	0.60	0.54	0.45	0.61	0.90	1.14	0.36	0.46	1.10	2.26	0.79	0.70	1.27	0.55	0.35	1.82	0.63	0.32	0.35	0.29	0.67	0.66	0.87	0.56
Mg#	0.58	0.00	0.58	0.58	0.58	0.58	0.59	0.58	0.58	0.58	0.59	0.58	0.58	95.0	0.00	0.20	0.59	0.58	0.55	69.0	0.55	0.73	0.75	0.55	0.55	0.03	0.63	0.62	0.67	0.74	0.78	0.79	0.81	0.82	0.64	0.64	
Total (%)	100.07	100.12	100.23	100.20	66.66	100.14	100.04	100.30	66.66	66.66	100.30	100.16	99.73	99.90	100.23	100 31	100.31	100.25	100.07	100.13	99.95	100.08	88.66	99.75	99.83	99.63	100.13	72.66	100.11	99.92	99.93	100.35	99.96	99.84	99.73	99.41	100.28
P_2O_5 (%)	0.25	0.20	0.25	0.25	0.25	0.25	0.24	0.25	0.25	0.25	0.24	0.23	0.24	0.23	0.70	0.23	0.23	0.24	0.24	0.20	0.25	0.16	0.18	0.25	0.24	0.23	0.22	0.22	0.21	0.18	0.17	0.15	0.13	0.12	0.26	0.77	0.26
K_2O	0.48	0.93	0.39	0.37	0.33	0.31	0.30	0.36	0.34	0.33	0.37	0.32	0.33	0.40	0.40	0.41	0.20	0.33	0.31	0.30	0.36	0.27	0.10	0.30	0.37	0.28	0.31	0.34	0.14	0.16	0.20	0.19	0.15	0.12	0.30	0.55	0.35
Na ₂ O (%)	2.39	1.91	2.37	2.35	2.49	2.35	2.40	2.46	2.27	2.28	2.28	2.35	2.35	87.7	2.4I	2.53	2.40	2.49	2.42	2.19	2.13	1.78	1.37	7. 4.	2.10	1.44	1.91	1.93	2.06	1.80	1.36	1.32	1.24	1.09	2.20	1.5/	2.54
CaO (%)	10.62	9.39 10.67	10.76	10.76	10.63	10.60	10.58	10.60	10.71	10.65	10.65	10.74	10.70	10.63	10.34	10.01	10.68	10.63	10.99	9.91	10.88	8.83	8.44	11.04	10.85	10.99	10.89	10.77	10.10	8.85	7.60	7.83	08.9	6.48	9.86	9.95	11.09
MgO (%)	7.75	7 96	7.71	7.72	7.77	8.01	8.16	8.03	7.86	7.91	8.14	8.00	7.97	8.IO	24.7 10.1	7.71 8 11	09.9	7.90	6.94	11.74	6.75	15.64	17.42	6.83	0.85	9.00	9.61	9.55	12.30	15.74	20.26	20.79	24.24	25.37	9.67	9.88	68.9
MnO (%)	0.17	0.17	0.18	0.18	0.17	0.17	0.18	0.18	0.18	0.17	0.18	0.17	0.17	0.16	0.18	0.10	0.10	0.18	0.17	0.17	0.18	0.19	0.18	0.19	0.18	0.19	0.19	0.19	0.19	0.18	0.18	0.18	0.18	0.19	0.19	0.19	0.19
Fe_2O_3* (%)	12.37	15.02	12.45	12.46	12.42	12.52	12.48	12.60	12.54	12.53	12.70	12.51	12.48	12.34	12.04	12.30	12.38	12.56	12.25	11.81	12.27	12.78	12.56	12.31	12.18	12.01	12.67	12.64	13.14	12.05	12.31	12.42	12.45	12.57	12.13	12.01	12.32 0.19 6.89 11.09 2.54 0.35 0.26 100.28
Al2O3 (%)	13.15	11.98	13.15	13.15	13.13	13.12	12.92	12.90	13.04	13.13	12.77	13.04	12.96	13.07	13.07	12.90	13.67	12.99	13.74	11.93	13.82	10.46	6.87	13.82	13.81	12.33	12.32	12.29	12.08	10.50	8.99	8.81	7.56	7.16	12.60	12.65	
TiO ₂ (%)	2.58	2.52	2.50	2.59	2.55	2.54	2.52	2.53	2.56	2.54	2.55	2.48	2.48	2.42	2.03	2.4.1 C.4.1	24.7 27.4 47.2	2.54	2.59	2.13	2.59	1.73	1.87	2.60	2.58	2.41	2.39	2.39	2.33	1.89	1.77	1.59	1.34	1.29	2.15	7.58	2.64
SiO ₂ (%)	50.31	47.31 5035	50.37	50.37	50.24	50.27	50.26	50.39	50.24	50.20	50.42	50.32	50.06	77.00	50.05	50.75	50.76	50.39	50.41	49.75	50.73	48.25	47.88	50.78	70.07	49.03 49.24	49.62	49.45	47.56	48.58	47.09	47.07	45.87	45.45	50.38	50.19	49.95
Rock Type	PI	MII PI	E I	PB	PI	PI	PI	PI	PB	PI	PI	PI	PI	MV	MV	MI V	Ы	ı W	PI	MI	PI	MV	MV	PB	Z À	Ы	Ы	PI	MI	ΡΙ	MV	Ы	Ξ ;	PI	HY	Z i	PI
Depth (mbsl)	3098	3102.4	3109.4	3111.5	3115.2	3122.5	3141.2	3160.8	3171.1	3173.4	3181.2	3215.5	3234.7	3244.8	9.5025	3285.8	3300.1	3305.9	3308.2	3313.5	3333.3	3339.5	3341.4	3348.3	3333.9	3359.8	3366.3	3381.3	3400.9	3405.3	3418.1	3435.2	3453.4	3458.4	3472.2	3500.9	3505.7
Unit	2a	ر بر	2d 2d	4	5	7	7	6	10	11	13				<u> </u>			65		9		23	23	24	57	20	30	30	32	33	35	37a	37e	940	2 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5	4 :	45
Run and Core Interval	R6-0.85-1.2	R8-2.13-3.0 R8-0 15-0 7	R10-4.35-5.7	R11-5.3-5.7	R13-0.1-0.5	R16-5.2-6.0	R30-4.25-5.2	R51-2.4-3.6	R56-1.0-1.5	R57-5.0-5.9	R60-7.6-8.4	R80-2.8-3.5	R93-1.4-2.0	K101-4.4-4.9	K108-0.0-0./	R112-7.1-7.7	R122-1.85-2.65	R125-4.9-5.3	R127-1.4-2.2	R129-5.8-6.5	R149-1.2-1.6	R154-2.1-2.95	R155-2.7-3.5	R158-1.75-2.10	K162-1.55-2.5	R165-0 75-1 45	R168-3.7-4.15	R176-5.93-6.5	R184-1.15-2.1	R187-0.9-2.5	R192-4.4-5.4	R198-0.5-1.9	R204-1.1-1.8	R205-7.5-8.15	R210-3.3-3.95	K219-5.5-7.7	R219-8.0-8.8 45 3505.7 PI 49.95 2.64 14.06



Table 1b. XRF Trace Element Analysis of Lavas Sampled by Phase-2 of the HSDP Core^a

					•											
Run and Core Interval	Unit	Depth (mbsl)	Rock Tvne	Nb (maa)	Zr (maa)	Y (maa)	Sr (man)	Rb (mm)	Pb (mom)	Ga (mm)	Zn (maa)	Ni (mad)	Cr (ppm)	V (maa)	Ce (mum)	Ba (nnm)
							616		,							
K6-0.85-1.2	7a	3097.7	Ы	14.9	166	8./7	313	4./	_	70	CII	134	313	761	30	123
R6-2.15-3.0	m	3098.2	M	11.6	117	20.8	212	21.0	_	17	107	437	534	214	24	103
R8-0.15-0.7	2b	3102.4	PI	14.2	159	27.1	311	5.8	-	21	113	162	359	262	31	127
R10-4.35-5.7	2d	3109.4	ΡΙ	15.1	167	28.2	310	6.2	_	20	117	139	356	267	32	103
R11-5.3-5.7	4	3111.5	PB	14.9	165	28.0	309	5.8	1	21	116	142	369	267	32	66
R13-0.1-0.5	5	3115.2	ΡΙ	14.7	164	27.8	311	5.9	7	20	113	149	361	265	56	86
R16-5.2-6.0	7	3122.5	PI	14.5	162	27.2	311	5.7	_	20	114	166	374	265	32	124
R30-4.25-5.2	7	3141.2	PI	14.4	160	27.1	308	5.8	1	20	114	168	364	259	30	120
R51-2.4-3.6	6	3160.8	PI	14.0	161	27.5	316	7.7	_	21	112	144	331	261	35	140
R56-1.0-1.5	10	3171.1	PB	14.7	163	27.7	308	5.7	_	21	118	155	381	265	27	103
R57-5.0-5.9	11	3173.4	PI	14.6	163	27.6	309	5.7	7	20	116	153	359	263	31	111
R60-7.6-8.4	13	3181.2	PI	13.8	159	27.5	314	4.8		21	113	146	328	259	33	156
R80-2.8-3.5	13	3215.5	PI	13.8	154	26.4	307	5.7	2	20	114	140	345	256	27	123
R93-1.4-2.0	13	3234.7	PI	13.9	154	56.6	305	5.9		20	116	144	366	255	27	123
R101-4.4-4.9	14	3244.8	MV	13.4	152	26.2	309	5.9		20	111	129	305	248	59	123
R108-0.0-0.7	14	3263.9	MV	15.0	170	28.7	322	7.1	-	22	116	120	287	265	32	144
R112-7.1-7.7	14	3277.0	MV	13.3	150	26.6	310	5.8		21	111	137	310	258	31	123
R116-6.25-7.2	15	3285.8	PI	13.2	149	26.2	311	5.7	_	21	111	139	343	255	27	119
R122-1.85-2.65	17	3300.1	PI	15.9	177	29.6	331	8.3	_	22	116	87	256	275	36	132
R125-4.9-5.3	18a	3305.9	MI	14.4	161	27.1	307	7.8	_	20	117	145	383	265	31	104
R127-1.4-2.2	19b	3308.2	PI	15.4	161	56.6	335	7.8	_	21	113	103	210	566	33	109
R129-5.8-6.5	20b	3313.5	MI	10.2	131	23.4	267	3.4		18	106	378	640	230	25	104
R149-1.2-1.6	22	3333.3	ΡΙ	15.0	163	26.0	335	6.4	_	21	112	92	199	252	30	102
R154-2.1-2.95	23	3339.5	MV	8.0	104	18.5	221	5.0		16	105	207	922	194	19	62
R155-2.7-3.5	23	3341.4	MV	9.3	117	20.0	241	2.7	7	16	105	869	948	198	22	06
R158-1.75-2.10	24	3348.3	PB	15.1	163	26.2	336	5.4	7	21	113	95	206	256	31	26
R162-1.55-2.3	25	3353.9	ΡΙ	15.0	163	25.7	329	6.3		21	114	66	203	255	32	100
R163-2.1-2.6	56	3357.0	HY	15.0	146	23.2	313	4.9	7	19	114	185	551	243	31	102
R165-0.75-1.45	59	3359.8	ΡΙ	14.3	144	22.8	312	4.3	7	18	113	196	593	241	50	87
R168-3.7-4.15	30	3366.3	ΡΙ	14.4	144	22.8	318	7.4	_	19	111	179	532	236	28	112
R176-5.93-6.5	30	3381.3	ΡΙ	14.3	146	23.3	322	5.2	2	20	110	173	519	238	28	126
R184-1.15-2.1	32	3400.9	MI	12.4	131	22.2	303	2.5	_	19	120	491	647	228	23	95
R187-0.9-2.5	33	3405.3	ΡΙ	0.6	117	20.1	234	3.0	1	16	105	715	833	194	22	69
R192-4.4-5.4	35	3418.1	MV	10.1	113	18.2	230	2.2	2	15	105	616	1091	178	24	83
R198-0.5-1.9	37a	3435.2	ΡΙ	8.7	95	16.0	204	3.3		13	103	935	1424	168	17	74
R204-1.1-1.8	37e	3453.4	ΡΙ	7.5	81	14.0	178	2.5	_	11	102	1179	1653	152	4	52
R205-7.5-8.15	40	3458.4	ΡΙ	7.1	78	13.4	165	1.9	0	11	103	1242	1612	147	16	65
R210-3.3-3.95	43	3472.2	НУ	10.1	153	26.3	264	4.8	7	19	110	277	548	234	27	99
R219-5.5-7.7	44	3500.9	ΡΙ	12.4	165	26.3	313	5.6	7	19	108	332	440	240	27	87
R219-8.0-8.8	45	3505.7	ΡΙ	15.1	160	25.4	382	3.8	7	22	107	86	193	273	37	125
1 48	11		20.4													

^aRock types: PI, pillows; HY, hyaloclastites; MI, massive intrusive units; MV, massive volcanic units.



Table 2a. XRF Major Element Analyses of Phase-1 High CaO Lavas^a

Run and Core Interval	Unit	Depth (mbsl)	Rock Type	SiO ₂ (%)	TiO ₂ (%)	Al ₂ O ₃ (%)	Fe ₂ O ₃ * (%)	MnO (%)	MgO (%)	CaO (%)	Na ₂ O (%)	K ₂ O (%)	P ₂ O ₅ (%)	Total (%)	Mg#	(%) TOI	Alkalic Index
R684-9.0-9.2	248	1766.7	HY	45.50	1.89	9.29	13.08	0.20	18.80	9.44	1.41	0.54	0.19	100.34	0.76	3.34	-0.43
R685-5.5-6.1	248	1768.9	CL	46.70	2.06	10.42	12.66	0.19	15.21	10.74	1.74	0.37	0.21	100.30	0.73	0.97	-0.71
R686-3.9-4.1	248	1771.2	HY	46.82	2.09	10.76	12.85	0.19	15.49	9.54	1.53	0.54	0.25	100.06	0.73	9.91	-0.80
R686-4.5-4.7	248	1771.3	CF	45.90	1.87	9.52	12.82	0.19	17.95	9.90	1.46	0.27	0.20	100.08	0.75	1.25	-0.80
R686-4.9-5.1	248	1771.4	CF	46.07	1.98	10.04	12.73	0.19	16.46	10.40	1.46	0.27	0.21	99.81	0.74	1.46	-0.86
R686-7.7-7.9	248	1772.3	CF	46.06	1.93	9.83	12.76	0.19	16.93	10.29	1.56	0.32	0.20	100.07	0.74	96.0	-0.70
R686-9.5-9.7	248	1772.8	CF	46.08	1.96	9.76	12.80	0.19	17.04	10.26	1.49	0.31	0.20	100.09	0.75	1.18	-0.79
R687-8.5-8.8	248	1775.3	CF	47.10	2.18	11.22	12.44	0.18	13.10	11.54	1.81	0.42	0.22	100.22	0.70	1.05	-0.74
R688-0.0-0.4	248	1775.7	CF	45.79	1.86	9.56	12.75	0.19	17.60	9.78	1.59	0.36	0.19	29.66	0.75	1.27	-0.53
R689-1.2-1.4	248	1779.1	CF	46.01	1.82	9.39	12.95	0.19	18.26	9.17	1.56	0.47	0.18	100.00	92.0	0.79	-0.54
R689-4.6-4.8	248	1780.1	CF	46.41	1.95	9.95	12.73	0.19	16.39	10.16	1.63	0.37	0.19	26.66	0.74	0.47	-0.71
R696-1.0-1.6	254	1794.7	HY	45.62	1.75	8.70	13.41	0.19	21.48	7.07	1.20	0.48	0.17	100.07	0.78	5.93	-0.74
R696-2.1-2.3	254	1795.4	CL	45.73	1.67	99.8	13.01	0.19	20.66	8.41	1.21	0.42	0.17	100.13	0.78	0.00	-0.83
R696-6.5-6.7	254	1796.7	HY	45.13	1.64	7.97	13.54	0.19	22.99	7.11	1.17	0.48	0.16	100.38	0.79	5.04	-0.59
R696-9.4-9.6	254	1797.6	CL	46.53	1.97	10.03	12.72	0.19	16.44	10.30	1.40	0.26	0.19	100.03	0.74	1.74	-1.10
R698-1.4-4.6	254	1801.2	CF	46.65	1.87	9.75	12.74	0.19	17.43	9.83	1.45	0.25	0.19	100.35	0.75	1.65	-1.10
R698-2.6-2.7	254	1801.6	CF	45.95	1.77	9.14	12.85	0.19	18.90	9.33	1.37	0.31	0.18	66.66	92.0	1.11	-0.86
R698-8.3-8.5	255	1803.3	HY	46.38	1.78	9.11	13.02	0.19	19.12	8.85	0.98	0.42	0.17	100.02	0.76	2.40	-1.30
R698-9.1-9.3	255	1803.6	HY	47.52	5.09	10.96	12.56	0.18	15.46	9.35	1.27	0.39	0.20	86.66	0.73	11.26	-1.47
R699-3.7-4.0	255	1805.1	CL	46.69	1.90	10.04	12.53	0.18	16.13	10.35	1.64	0.22	0.19	28.66	0.74	1.27	-0.96
R699-5.4-5.6	255	1805.6	HY	46.82	1.80	69.6	12.78	0.18	17.96	80.6	1.19	0.44	0.18	100.12	0.76	3.40	-1.24
R699-8.4-8.6	255	1806.5	HY	46.56	1.72	9.29	12.83	0.19	18.81	8.91	1.40	0.31	0.16	100.18	92.0	2.34	-1.06
R700-2.9-3.1	255	1808.1	CF	49.05	2.44	12.80	12.22	0.18	8.73	12.24	1.94	0.43	0.24	100.27	0.61	0.88	-1.33
R700-3.6-3.8	255	1808.3	HY	47.11	1.80	9.84	12.73	0.18	17.49	9.15	1.42	0.36	0.17	100.25	0.75	2.18	-1.19

^aMajor element analyses are based on ignited (1040°C), volatile-free, samples. Fe₂O₃* is total iron expressed as Fe₂O₃. Mg# is Mg/(Mg+Fe) after adjusting Fe³+/total Fe to 0.1. LOI is loss on ignition. Alkalic index = total alkali – (SiO₂ × 0.37 – 14.43). Rock types: PI, pillows; HY, hyaloclastites; MI, massive units; MV, massive volcanic units.



Table 2b. XRF Trace Element Analyses of Phase-1 High CaO Lavas^a

			•)											
Run and Core		Depth	Rock	N _P	Zr	Y	Sr	Rb	Pb	Ga	Zn	ïZ	Cr	Λ	Ce	Ba
Interval	Unit	(mbsl)	Type	(mdd)	(mdd)	(mdd)	(mdd)	(mdd)	(mdd)	(mdd)	(mdd)	(mdd)	(mdd)	(mdd)	(mdd)	(mdd)
R684-9.0-9.2	248	1766.7	HY	14.9	129	15.4	295	9.6	2	14	86	726	1470	279	31	186
R685-5.5-6.1	248	1768.9	CF	16.1	139	17.7	360	5.1	7	17	100	657	1407	284	33	147
R686-3.9-4.1	248	1771.2	HY	15.3	133	17.0	322	8.1	7	16	94	423	006	588	33	169
R686-4.5-4.7	248	1771.3	CL	14.7	127	16.4	332	1.7	2	15	104	833	1451	276	30	150
R686-4.9-5.1	248	1771.4	CF	15.6	135	17.6	355	2.5	В	16	101	402	1350	281	34	148
R686-7.7-7.9	248	1772.3	CL	15.4	131	16.9	340	4.6	2	16	101	748	1471	285	35	134
R686-9.5-9.7	248	1772.8	CF	15.1	132	16.6	338	3.6	_	14	101	167	1343	277	30	147
R687-8.5-8.8	248	1775.3	CF	16.9	146	18.6	375	5.9	2	16	66	551	1135	281	31	160
R688-0.0-0.4	248	1775.7	CF	14.3	125	16.0	329	4.7	2	15	100	816	1544	250	59	138
R689-1.2-1.4	248	1779.1	CF	14.7	125	16.1	325	7.3	2	14	101	785	1469	265	59	145
R689-4.6-4.8	248	1780.1	CF	15.5	132	17.0	340	4.5	-	15	100	715	1410	269	35	14 4
R696-1.0-1.6	254	1794.7	HY	13.2	115	15.1	240	7.9	2	14	107	792	1408	254	59	177
R696-2.1-2.3	254	1795.4	CL	13.5	115	14.7	286	6.7		13	100	965	1510	225	27	117
R696-6.5-6.7	254	1796.7	HY	11.9	104	13.2	256	6.7	5	12	94	790	1640	277	36	179
R696-9.4-9.6	254	1797.6	CL	15.2	132	17.3	340	2.9	2	15	102	889	1316	272	33	131
R698-1.4-4.6	254	1801.2	CF	14.2	125	16.7	320	2.5	2	15	102	262	1390	259	59	125
R698-2.6-2.7	254	1801.6	CF	13.7	119	15.4	310	3.9	2	14	101	864	1504	259	27	121
R698-8.3-8.5	255	1803.3	HY	13.5	120	16.3	296	6.5	2	14	100	714	1392	252	31	164
R698-9.1-9.3	255	1803.6	HY	14.5	129	17.4	569	5.3	2	16	26	370	833	284	31	187
R699-3.7-4.0	255	1805.1	CL	14.1	128	17.9	325	2.3	2	15	102	<i>L</i> 69	1279	259	59	114
R699-5.4-5.6	255	1805.6	HY	12.6	117	16.6	281	6.2	_	14	101	734	1286	261	28	174
R699-8.4-8.6	255	1806.5	HY	11.9	114	16.6	280	4.2	7	14	103	758	1327	251	25	130
R700-2.9-3.1	255	1808.1	CF	18.2	165	22.4	409	8.9	2	19	102	207	869	321	38	158
R700-3.6-3.8	255	1808.3	HY	12.3	116	17.0	279	5.2	2	14	104	738	1369	241	76	128

^aRock types: HY, hyaloclastites; CL, clasts in hyaloclastites.



Table 3 (Sample). ICP-MS Analyses of Lavas Sampled by Phase 2 of HSDP Core [The full Table [3] is available in the HTML version of this article]

Run and	TT '	Sc	Rb	Sr	Y	Zr	Nb	Ba	La	Ce	Pr	Nd	Sm	Eu
Core	Unit	(ppm)												
R6-0.85-1.2	2a	29	7.9	308	29.7	158	14.7	116	12.4	31.7	4.6	21.9	5.8	1.94
R6-2.15-3.0	3	27	20.1	201	22.4	115	11.5	84	9.1	23.2	3.4	16.2	4.3	1.46
R8-0.5-0.7	2b	30	6.3	305	28.8	154	14.0	117	11.7	29.8	4.4	20.8	5.6	1.87
R10-4.35-4.7	2d	33	6.9	313	30.6	164	14.9	101	12.3	31.2	4.6	21.5	5.8	1.94
R11-5.3-5.7	4	33	6.9	321	31.3	167	15.2	99	12.3	31.3	4.6	21.5	5.8	1.96
R13-0.1-0.5	5	31	6.5	310	30.2	160	14.6	107	12.1	30.5	4.5	21.3	5.6	1.92
R16-5.2-6.0	7	31	6.5	313	30.0	160	14.6	115	12.0	30.6	4.5	21.1	5.7	1.95
R30-4.25-5.2	7	32	6.5	307	29.6	158	14.3	107	11.9	29.9	4.4	20.9	5.6	1.92
R51-2.4-3.6	9	32	8.1	314	30.1	161	14.7	117	12.1	30.8	4.5	21.3	5.6	1.94
R56-1.0-1.5	10	32	6.3	307	29.5	158	14.4	96	11.8	30.0	4.4	21.0	5.6	1.90
R57-5-5.9	11	28	6.1	294	28.2	152	13.8	99	11.5	29.2	4.3	20.4	5.5	1.84
R60-7.6-8.4	13	28	5.2	299	28.1	151	13.7	133	11.8	29.6	4.4	20.8	5.6	1.88
R80-2.8-3.5	13	31	6.3	305	28.5	151	13.6	110	11.4	28.8	4.3	20.1	5.4	1.84
R93-1.4-2.0	13	31	6.4	303	28.6	151	13.7	122	11.3	28.7	4.3	20.1	5.4	1.83
R101-4.4-4.9	14	32	6.6	307	28.8	152	13.8	112	11.2	28.5	4.3	20.0	5.4	1.84
R108-0-0.7	14	33	8.1	321	31.4	169	15.3	125	12.4	31.6	4.7	22.1	5.8	1.97
R112-7.7-7.7	14	32	6.4	299	28.2	147	13.2	106	11.0	28.2	4.2	19.7	5.3	1.81
R116-6.25-7.2	15	33	6.5	312	28.9	151	13.6	102	11.2	28.4	4.2	19.7	5.4	1.83
R122-1.85-2.65	17	30	8.5	324	31.9	173	15.8	123	13.1	33.2	4.9	22.9	6.1	2.07
R125-4.9-5.3	18a	32	8.6	309	29.9	159	14.5	103	11.8	30.1	4.5	21.0	5.6	1.90
R127-1.4-2.2	19b	32	8.4	332	28.8	157	15.0	105	12.1	30.9	4.5	21.2	5.6	1.87
R129-5.8-6.5	20b	31	4.1	267	25.7	131	10.4	83	8.8	23.1	3.5	16.7	4.7	1.59
R149-1.2-1.6	22	33	7.3	336	29.7	160	15.6	108	12.6	31.4	4.6	21.4	5.8	1.94
R154-2.1-2.95	23	25	5.2	209	18.9	94	7.4	57	6.6	16.7	2.6	12.3	3.5	1.21
R155-2.7-3.5	23	26	3.2	236	22.3	112	9.6	73	7.8	20.6	3.1	14.7	4.1	1.41
R158-1.75-2.10	24	29	6.0	315	27.1	146	14.4	95	11.7	29.2	4.3	19.7	5.3	1.80
R162-1.55-2.3	25	32	7.1	325	28.6	154	15.2	106	12.1	30.3	4.4	20.7	5.5	1.89
R163-2.1-2.6	26	33	5.8	312	25.9	141	15.2	106	11.8	29.0	4.2	19.5	5.1	1.76
R165-0.75-1.45	29	33	5.3	321	26.1	142	14.7	94	11.6	29.1	4.2	19.6	5.1	1.71
R168-3.7-4.15	30	33	9.2	340	26.7	149	15.3	126	12.3	30.3	4.4	20.3	5.2	1.80
R176-5.93-6.5	30	34	6.2	330	26.7	148	15.3	128	12.0	29.7	4.3	19.9	5.3	1.77
R184-1.15-2.1	32	29	3.3	310	25.1	127	12.9	84	9.8	24.8	3.6	17.2	4.7	1.61
R187-0.9-2.5	33	27	3.6	232	22.1	111	9.1	69	7.5	19.8	3.0	14.4	4.0	1.40
R192-4.4-5.4	35	23	2.8	219	19.1	106	9.9	75	7.9	19.7	2.9	13.5	3.8	1.27
R198-0.5-1.9	37a	28	3.9	208	18.0	92	8.8	68	7.1	18.0	2.7	12.6	3.4	1.16
R204-1.1-1.8	37e	24	2.9	172	14.5	74	7.1	48	5.5	14.3	2.1	9.9	2.8	0.94
R205-7.5-8.15	40	24	2.2	173	15.1	79	7.6	68	5.8	14.7	2.2	10.3	2.8	0.97
R210-3.3-3.95	43	32	5.9	275	30.5	154	10.6	76	10.2	26.5	4.0	19.3	5.5	1.83
R219-5.5-7.7	44	30	6.4	307	29.5	154	12.2	90	11.3	28.5	4.3	20.2	5.5	1.85
R222-8.0-8.8	45	33	4.7	384	29.4	158	16.2	117	13.0	32.1	4.7	21.7	5.9	1.99
BHVO-2, $n = 9$		31	9.6	387	27.3	170	18.2	130	15.1	36.6	5.3	23.9	6.1	1.98
1 SD		2	0.3	9	0.8	4	0.4	3	0.4	1.0	0.2	0.5	0.2	0.07

determined by XRF, we also measured loss on ignition (LOI) on these samples [Rhodes and Vollinger, 2004] as an indicator of post-magmatic alteration. LOI is a loss in weight after ignition at 1040°C, reflecting a loss of volatiles which are mostly water and CO₂, but also S gases. However, LOI may also record a gain in weight. This is because FeO in minerals and glass are partially oxidized to ferric iron. Therefore with fresh basaltic lavas a LOI measurement can result in a weight gain (or negative LOI).

2.2. Solution ICP-MS Analyses of Whole-Rocks

[9] Trace element abundances of the 22 samples from Units 2 to 20 were analyzed using solution ICP-MS at MIT following the method described in the Appendix of *Huang and Frey* [2003], and the 18 samples from Units 22 to 45 were analyzed using solution ICP-MS at Harvard University using the following procedures (Table 3).

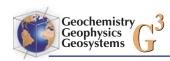


Table 4. LA-ICP-MS Analyses of High CaO Glasses Sampled by Phase-1 of HSDP Core^a

Core (Kb ; (ppm) (p	Sr Y (ppm) (ppm)	Y (mdc	Zr (ppm) (Np (bpm)	Ba (ppm)	La (ppm)	Ce (ppm)	Pr (ppm)	(mdd)	Sm (ppm)	Eu (ppm)	(bbm)	Tb (ppm)	Dy (ppm)	Ho (bbm)	Er (ppm)	Tm (ppm)	Yb (ppm)	Lu (ppm)	(mdd)	Ta (ppm)	Th (ppm)	(mdd)
R684-8.95	16.4 4		25.8	188	24.8	264	21.0	56.9	7.47	30.9	7.05	2.36	6.45	96.0	5.13	96.0	2.34	0.33	1.94	0.26	4.84	1.53	1.74	0.64
R686-5.10		541 2	23.7	167	22.4	235	18.4	49.8	6.51	27.0	6.22	2.12	5.74	98.0	4.68	0.87	2.16	0.30	1.77	0.24	4.27	1.36	1.60	0.59
R689-2.20		485	22.5	156	20.4	213	17.0	45.2	5.99	25.0	5.82	1.98	5.46	0.83	4.45	0.83	2.06	0.28	1.69	0.23	4.04	1.26	1.50	0.54
R697-8.10	11.1 4	481 2	23.2	158	19.2	192	16.1	39.7	5.52	23.8	5.66	1.87	5.47	0.82	4.50	0.84	2.09	0.29	1.70	0.23	4.04	1.23	1.48	0.46
R698-5.60			21.4	138	17.0	170	13.6	36.0	4.99	21.5	5.23	1.76	5.13	0.77	4.19	0.78	1.95	0.27	1.62	0.22	3.59	1.08	1.22	0.43
	13.8 4		24.3	165	22.4	225	17.4	48.0	6.29	26.2	6.13	2.13	5.75	98.0	4.69	0.87	2.18	0.30	1.82	0.24	4.12	1.33	1.51	0.58
R700-1.40		451 2	24.5	155	18.2	184	15.2	39.1	5.51	24.0	5.89	2.00	5.83	0.89	4.86	0.91	2.28	0.31	1.86	0.25	4.14	1.18	1.40	0.47
BCR-2g, $n = 5$		353 4	40.6	202	13.2	725	25.7	55.3	7.14	28.9	6.58	1.87	09.9	1.10	6.45	1.34	3.64	0.54	3.41	0.51	4.81	0.79	6.05	1.76
	0.7 6		1.0	5	0.2	14	0.5	8.0	0.10	0.3	80.0	0.03	0.18	0.03	0.17	0.02	0.10	0.01	0.07	0.01	0.09	0.02	0.12	0.04

'Major element contents of these glasses were reported by Stolper et al. [2004]

[10] About 0.05 g of rock powder was dissolved using 1:1 mixture of HF and HNO₃ acids. After complete dissolution, aliquots of solutions were diluted by a factor of 5000 with 1.5% HNO₃, and then analyzed for trace element abundances by traditional solution-ICP-MS technique using a GV Quadrupole ICP-MS at Harvard University. The monitored isotopes are in Table A1a of Huang and Frey [2003]. USGS standard samples, AGV-1, BCR-1 and BHVO-1, whose trace element abundances are in Table A2 of Huang and Frey [2003], were used to construct the standard calibration curve. Each analytical sequence contains three standard sample solutions (BHVO-1, BCR-1 and AGV-1), one procedure blank, four unknown sample solutions, and one BHVO-2 solution analyzed as an unknown sample. In order to monitor the sensitivity drift, beginning with the first solution in the analytical sequence, BHVO-1 solution was analyzed every fifth solution. Each analytical sequence takes about one hour. The sensitivity drifts for all analyzed isotopes are less than 20%, and most are less than 10%. Therefore, no internal drift monitor was used at Harvard. Analytical precision was estimated using multiple measurements (9) of BHVO-2 solution analyzed as an unknown sample during the analyses, and it is better than 5% for all measured trace elements.

2.3. LA-ICP-MS Analyses of Glasses

[11] Polished chips of HSDP High Ca-K glasses analyzed for major elements by Stolper et al. [2004], were analyzed for trace elements (Table 4) using LA-ICP-MS at Florida State University (FSU). The LA-ICP-MS analysis was conducted using a Finnigan® Element 1 ICP-MS coupled with a New Wave® UP 213 Nd-YAG 213 nm laser system at the National High Magnetic Field Laboratory, FSU. The laser ablation system was used in spot mode with a repetition rate of 10 Hz. The energy output of the laser during the course of analysis was \sim 1.1 mJ. Trace elements were determined at low resolution (R = 400) using a 100 micron spot size. Each spot was ablated for 75 s. Measured intensity ratios with respect to ⁴³Ca were converted to elemental ratios with respect to CaO using BHVO-2g glass standard for calibration. Trace element abundances of BHVO-2 analyzed using solution ICP-MS [Huang and Frey, 2003, Table A3] were used for BHVO-2g glass standard. Analytical uncertainty was estimated using multiple measurements (5) of BCR-2g analyzed as an unknown sample during the analyses, and it is better than 3% for all measured trace elements. The reported analytical uncertainties for



Mean 7

Mean]

MgO

Mean

 100.26 ± 0.30 100.42 ± 0.34 100.42 ± 0.17 100.69 ± 0.21 100.49 ± 0.21

 ± 0.0250

0.57 0.61

46.99

0.038 0.032

++

0.365

0.65 0.67

0.015 0.020 0.015

0.017 0.015 0.016

0.389

 $100.68 \pm 0.26 \\ 99.99 \pm 0.20$

0.19

 $\begin{array}{c} \pm \ 0.035 \\ \pm \ 0.021 \\ \pm \ 0.029 \\ \pm \ 0.035 \\ \pm \ 0.030 \end{array}$

0.375 0.368 0.387 0.396 0.361

46.99 46.92 46.76 47.31 46.38

0.013

 100.66 ± 0 100.68 ± 0 100.24 ± 0

Mean MnO 0.188 0.186 0.173 0.178 0.179 0.187 0.185 $\begin{array}{c} + 1.12 \\ + 1.12 \\ + 1.05 \\ + 1.07 \\ + 1.07 \\ + 1.05 \\ + 1.22 \\ + 1.05 \end{array}$ 13.30 13.30 12.60 12.70 12.90 13.00 13.03 13.03 $\begin{array}{c} + & + & + & + & 0.28 \\ 0.14 & + & + & + & + & 0.14 \\ 0.20 & + & + & + & + & 0.20 \\ 0.18 & + & 0.18 & + & 0.25 \\ 0.29 & + & 0.29 & + & 0.29 \end{array}$ Mean SiO₂ 40.26 40.17 40.12 40.37 0.6 0.9 1.1 1.0 1.0 0.9 0.8 86.3 H 1 86.4 H 1 86. 86.6 86.5 86.0 Range in Fo% 5 5 5 5 5 5 5 5 5 10 83.4 t 85.8 t \mathbf{z} Depth (mbsl) Unit

Summary of Olivine Composition in High CaO Lavas^a

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^aN is number of olivines analyzed. Oxide contents in wt% with 1 standard deviation

LA-ICP-MS measurements are slightly better than those for solution ICP-MS measurements reported in Section 2.2. The seven HSDP glass chips, as well as the BCR-2g, were analyzed in one LA-ICP-MS analytical session, and their estimated analytical uncertainty reflects the short-term reproducibility within an analytical session, typically less than 6 h. In contrast, the solution ICP-MS measurements for HSDP whole-rock samples include multiple analytical sessions conducted in several days, and the estimated analytical uncertainty for solution ICP-MS measurements reflects the long-term reproducibility.

2.4. Electron Microprobe Analyses of Olivine

[12] Major (Si, Mg, Fe) and minor (Mn, Ni) element abundances in olivine phenocrysts were measured simultaneously on the 5-channel Jeol 8200 microprobe at Massachusetts Institute of Technology (Table 5). Each olivine grain was analyzed near the geometric center using a 10 micron wide, 300 nA electron beam, 15 kV accelerating voltage, and 180 s counting time. All element abundances are reported relative to the San Carlos olivine standard using the values reported by Sobolev et al. [2007]; CITZAF corrections were applied after Armstrong [1995]. Major element abundances were reproducible to better than 0.05%, and minor elements to better than 3-5% (2 s.d.).

3. Results

3.1. Basalt Classification

[13] A significant result of the Phase-1 HSDP project was the recognition that magmas with distinctly different SiO₂ contents, described as "low" and "high" SiO2 were erupted throughout much of the shield-building stage of Mauna Kea volcano [Stolper et al., 2004; Rhodes and Vollinger, 2004]. This bimodality has not been observed at other Hawaiian volcanoes. The prevailing opinion has been that individual Hawaiian volcanoes erupt lavas with compositions characteristic of that volcano for a very large part of their eruptive history [e.g., Garcia et al., 1989; Frey and Rhodes, 1993]. At Mauna Kea the difference in SiO₂ content is most obvious in the glass data, which are clearly bi-modal [Stolper et al., 2004]. The whole-rock data are slightly more ambiguous because of the possible SiO₂ loss during alteration, and because of the added complexities of mixing and olivine

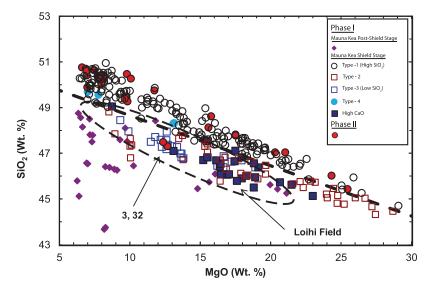


Figure 2. Variation of SiO_2 and MgO content in HSDP lavas. In Figures 2–14 the data of this study are compared with data for Phase-1 of HSDP [*Rhodes and Vollinger*, 2004; *Huang and Frey*, 2003]. The legend reconciles the classification of *Rhodes and Vollinger* [2004] with that of *Huang and Frey* [2003] (see Table 6). Except for the labeled Phase-2 dikes (units 3 and 32), Phase 2 lavas are high- SiO_2 . Phase-1 High CaO and post-shield lavas are low- SiO_2 . The heavy dashed line ($SiO_2 = 50.85 - 0.22 * MgO$) is a discriminant between high and low SiO_2 lavas. The dashed field for Loihi tholeiitic lavas is shown for comparison with the low SiO_2 Mauna Kea lavas.

accumulation. Nonetheless, as shown in Figure 2, there is a discriminant line between "high" and "low" SiO_2 lavas at a given MgO content. This point is emphasized further in a plot of SiO_2 normalized to 13% MgO versus depth (Figure 3a).

[14] Rhodes and Vollinger [2004] introduced a classificatory scheme for Phase-1 Mauna Kea shield-stage lavas based on normalized SiO₂ and Zr/Nb (Figure 4). The normalized SiO₂ content (to MgO = 13% and indicated by SiO_2 (13)) may reflect depth of melt segregation [Albarède, 1992; Lee et al., 2009]. In Hawaiian shield lavas Zr/Nb correlates with radiogenic isotopic ratios [e.g., Frey and Rhodes, 1993] and is inferred to reflect geochemical heterogeneity in the source of Mauna Kea shield lavas. Specifically, Type-1 lavas have high SiO₂ (13) and high Zr/Nb; Type-2 lavas have low SiO₂ (13) and high Zr/Nb; Type-3 lavas have low SiO₂ (13) and low Zr/Nb; and rare Type-4 lavas have high SiO₂ (13) and low Zr/Nb. This classification differs from that of Huang and Frey [2003], mainly with regard to the Type-2 lavas (see Table 6).

[15] With the exception of two intrusive units (3 and 32), all of the flow units from the Phase-2 core are high in SiO₂ at a given MgO (Figure 2), and are similar to all other Mauna Kea High SiO₂ lavas (Type-1 of *Rhodes and Vollinger* [2004]). Most are pillow lavas with minor hyaloclastites and

massive intrusive units (Figure 1a). The two Low SiO₂ samples (units 3 and 32) are similar to Low-SiO₂ pillow lavas (Type-3 of *Rhodes and Vollinger* [2004]) higher in the section between 2233 and 2481 mbsl. They are intrusive and most probably feeder dikes for the stratigraphically higher Low SiO₂ (Type-3) pillow lavas. In this respect, they correspond with other Low SiO₂ (Type-3) lavas between 2411 and 3098 mbsl sampled during Phase-1 of the project that are also intrusive [e.g., *Garcia et al.*, 2007].

[16] In an SiO₂(13) versus Zr/Nb plot (Figure 4), the two Low SiO₂ intrusives (units 3 and 32) have low Zr/Nb, overlapping with Low SiO₂ (Type-3) lavas higher in the section. In contrast, the Phase-2 lavas with high SiO₂ exhibit a wide range in Zr/Nb which correlates positively with normalized SiO₂. The range in Zr/Nb exceeds that for younger High SiO₂ lavas higher in the core. The sample from unit 43 has high Zr/Nb (>15) comparable to that of Mauna Loa lavas. The other Phase-2 samples range in Zr/Nb from 9.7–13, with the higher ratios overlapping with the overlying Type-1 (High SiO₂) and the lower ratios overlapping with Type-4 lavas (High SiO₂ and Zr/Nb < 10 in Figure 4).

[17] Another compositional type of Phase-1 lavas was recognized by $Stolper\ et\ al.$ [2004], who identified a group of glasses from 1767 to 1808 mbsl that are characterized by high CaO and K_2O

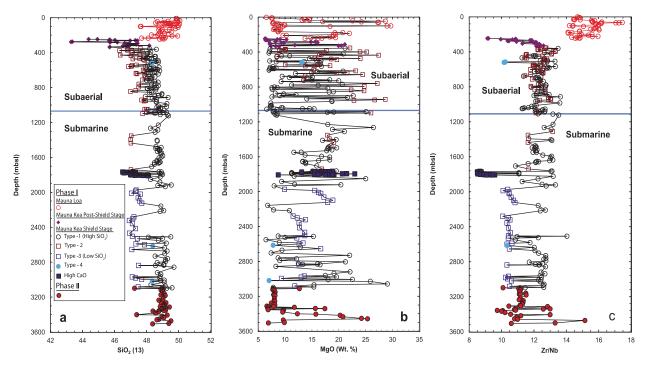


Figure 3. Variation with stratigraphic depth (mbsl) of (a) SiO₂ normalized to 13% MgO by addition or subtraction of olivine [after *Rhodes and Vollinger*, 2004], (b) MgO, and (c) Zr/Nb.

contents. In this depth interval the hyaloclastites consist of fresh, brown, basaltic glass fragments containing phenocrysts and fragments of olivine. The clast samples have a very fine-grained matrix containing clinopyroxene and plagioclase with phenocrysts of olivine. The olivine phenocrysts and fragments range from Fo₈₃ to Fo₈₉, but are predominantly Fo₈₆ (Table 5). However, no wholerock samples from this interval were included in the original Phase-1 reference suite samples. Our new

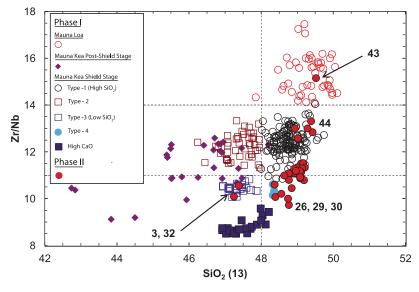


Figure 4. Classification of HSDP lavas based on variation of Zr/Nb with SiO₂ normalized to 13% MgO by addition or subtraction of olivine. With the exception of units 3 and 32, which correspond with low-SiO₂ (Type-3) lavas, the Phase-2 lavas are all high in SiO₂, and extend from Type-4 lavas to overlap with Mauna Loa lavas (unit 43). The Phase-1 High CaO lavas have low SiO₂ and Zr/Nb and are compositionally distinct. The thin dashed lines distinguish lava types 1, 2, 3 and 4 [*Rhodes and Vollinger*, 2004].



Table 6. Comparison of the Different Classifications used by *Rhodes and Vollinger* [2004] and *Huang and Frey* [2003]

Rhodes and Vollinger [2004]	Huang and Frey [2003]
Type-1	shield-stage: high SiO ₂
Type-3	shield-stage: low SiO ₂
Type-2	post-shield tholeiites (low SiO ₂ above 794 mbsl)
Type-4	not recognized

analyses of bulk rock samples of clasts and hyaloclastites from this interval have the distinctive high CaO and K₂O contents of glasses in this interval. At a given MgO content, these rocks have higher CaO content and CaO/Al₂O₃ than other Mauna Kea tholeiites (Figure 5) and are low in SiO₂ at a given MgO (Figure 2). They form a distinct compositional group of lavas with low, but variable, SiO₂ (13) and with Zr/Nb of 8.5 to 9.6. Low Zr/Nb values, such as these, are significantly lower than other Mauna Kea tholeiitic basalts, including postshield tholeiites (Figure 4), but are comparable with post-shield alkalic basalts and highly evolved tholeiites in the uppermost 56 m of the HSDP-1 core [e.g., Yang et al., 1996]. In addition to Zr/Nb, these samples, including glasses previously analyzed for major elements by Stolper et al. [2004] are high in incompatible elements such as La, K, Ba, Ce, and Sr. We classify them as a new "High CaO type."

3.2. MgO-FeO Relationships

[18] Picritic lavas (MgO > 12%) are common among Hawaiian submarine lavas [e.g., Garcia et al., 1989; Clague et al., 1995; Garcia et al., 1995; Norman and Garcia, 1999] and are exceedingly common in the HSDP lavas [Rhodes and Vollinger, 2004; Garcia et al., 2007]. Basaltic lavas with around 7–8% MgO, although common, along with picrites, in the subaerial section, are less common in the submarine section. The range in whole-rock MgO for Phase-2 lavas is 6-25%, comparable with the 6–27% found in overlying Phase-1 lavas (Figure 3b). In contrast glass compositions in these lavas range from 6% to 9% [Stolper et al., 2004]. The olivine phenocryst content of Phase-1 lavas varies from as little as 1% to up to 45% [Garcia et al., 2007]. There is a strong correlation of MgO with modal olivine phenocryst abundance [Garcia et al., 2007, Figure 17], a clear indication that the bulk composition of picritic whole-rock compositions are controlled mainly by olivine addition into magmas with lower MgO contents.

[19] However, between 3100 and 3350 mbsl there is a remarkable absence of picrites; in this interval most lavas have between 6–8% MgO (Figure 3b). They are also nearly homogeneous in isotopic ratios of Nd, Hf and Pb [see *Blichert-Toft and Albarède*, 2009, Figure 2]. We suggest that these geochemically similar lavas represent a 250 m interval formed at a relatively high eruption rate from a thoroughly mixed, steady state magma reservoir [e.g., *Rhodes*,

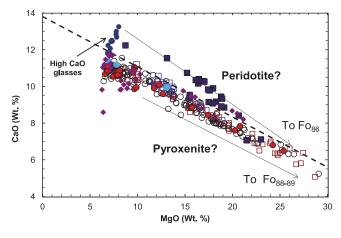


Figure 5. Variation of MgO and CaO content in HSDP lavas. The Phase-2 lavas overlap with younger Phase-1 shield tholeiites, but the Phase-1 High CaO lavas (this paper) and glasses [Stolper et al., 2004] are characteristically higher in CaO than other Mauna Kea lavas at a given MgO content. Symbols are as in Figure 4; in addition, High CaO glasses are shown as filled blue circles. The black dashed line is the boundary proposed by Herzberg [2006] to distinguish between partial melts of peridotite and pyroxenite. The arrow passing through most of the High CaO data shows the trend for accumulation of olivine Fo_{86} and the arrows parallel to the data for types 1, 2, 3 and 4 show the trend for accumulation of olivine Fo_{88-89} .

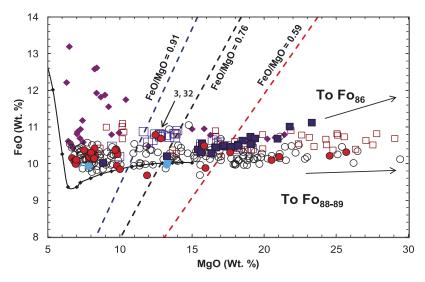


Figure 6. FeO versus MgO in HSDP lavas. FeO is calculated from total iron as Fe_2O_3 on the assumption that the oxygen fugacity of the lavas was close to magnetite-wüstite (MW) [*Rhodes and Vollinger*, 2005]. The Phase-2 lavas overlap with younger Phase-1 lavas along an almost horizontal trend due to the accumulation of olivine (Fo_{88-89}) in melts with lower MgO contents. Although the High CaO lavas also overlap with the Phase-1 lavas they define a steeper trend indicative of accumulation of olivine (Fo_{86}). The three oblique dashed lines represent the FeO/MgO of melts in equilibrium with $Fo_{90.5}$ (red), the maximum Fo content for olivine in these lavas [*Putirka et al.*, 2011]; with Fo_{89} (black), the typical Fo content for olivine in these lavas [*Putirka et al.*, 2011]; and with Fo_{86} (blue), the typical Fo content for olivine in the High CaO lavas (Table 5). The intersection of these lines with the whole-rock trend provides an estimate of the MgO content of parental and possibly primary magmas. Also shown (thin black line with diamonds) is a liquid line of descent for a hypothetical magma with 15% MgO [*Rhodes and Vollinger*, 2004].

1988]. Below 3350 mbsl the MgO variability resembles that in the rest of the core.

[20] Flow units from Phase-2 of HSDP have FeO abundances at a given MgO content comparable with younger Phase-1 lavas (Figure 6). Among the Phase-2 lavas, the two Low SiO₂ intrusives (units 3 and 32) have the highest FeO, a result consistent with the relatively high FeO of Low SiO₂ (Type-3) lavas higher in the section. The broad sub-horizontal trend in FeO versus MgO (Figure 6) in HSDP shield tholeiites is consistent with the crystallization and accumulation of olivine (Fo_{87–89}). Assuming a K_D(Fe-Mg) of 0.32 for partitioning between olivine and Mauna Kea melts, lavas crystallizing Fo₈₇₋₈₉ olivine will have FeO/MgO around 0.76 and contain about 13-15% MgO. Putirka et al. [2011] show that both High and Low SiO₂ Mauna Kea lavas contain olivine with a maximum forsterite content of Fo_{90.5}, indicating possible parental magmas with FeO/MgO around 0.59 containing about 17-18% MgO. Recently, Matzen et al. [2011] suggest that a K_D(Fe-Mg) of 0.34 for partitioning between olivine and melts is more appropriate for Mauna Kea lavas; in this case the inferred parental magmas will have higher MgO of 18–20%.

[21] The High CaO lavas differ from other compositional types of Mauna Kea lavas in that they define a slightly positive slope in FeO versus MgO (Figure 6). This slope is indicative of crystallization and accumulation of olivine (\sim Fo₈₆), the average olivine composition in these lavas (Table 5). This relatively low Fo olivine is unusual for shieldbuilding Mauna Kea tholeiites [Baker et al., 1996; Garcia, 1996; Putirka et al., 2011], requiring a more evolved magma with higher FeO/MgO of around 0.91 and MgO contents of about 11%. In this respect the olivines in the High CaO lavas are similar to olivines in the post-shield lavas with typical forsterite contents of around Fo₈₄₋₈₆ and maximum values of Fo₈₉ [Baker et al., 1996; *Garcia*, 1996; *Putirka et al.*, 2011].

3.3. MgO-Ni Relationships

[22] The Phase-2 lavas plot on positive trends of Ni versus MgO that overlap with data from lavas higher in the core (Figure 7). These trends are linear, not curved olivine fractionation trends, providing further evidence that the picritic whole-rock compositions are controlled mainly by olivine addition into magmas with lower MgO contents. The Ni

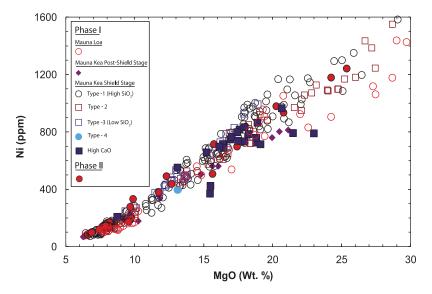


Figure 7. Variation in Ni and MgO content in HSDP lavas. The linear trend is indicative of olivine accumulation into melts with lower MgO content. Both Phase-2 lavas and High CaO lavas (with the exception of four hydrated High CaO lavas with >5% LOI; see Table 2a) overlap with Phase-1 lavas. Note that there is no discernable difference in Ni at a given MgO content for lavas with markedly different SiO₂ content, including lavas from Mauna Loa.

contents of the Low and High SiO₂ lavas are similar at a given MgO content. From this we infer similar Ni contents in olivines from both High and Low SiO₂ lavas, an inference that is consistent with the olivine data of Putirka et al. [2011]. Ni abundances in the High CaO lavas are also comparable to other shield lavas of similar MgO content, and the Ni content of their olivines (2400–3100 ppm; Table 5) is comparable to other Fo_{85–86} olivines in the core [Putirka et al., 2011]. Four (R686-3.9-4.1, R696-1.0-1.6, R696-6.5-6.7 and R698-9.1-9.3) of the 24 High CaO whole-rocks have lower Ni at a given MgO. Because they have unusually high LOI values $(\sim 5 \text{ to } 11\%; \text{ Table 2a})$, we suspect that their anomalously low Ni contents reflect alteration and/or dilution as a result of their high volatile contents.

[23] Putirka et al. [2011] propose that both High and Low SiO₂ Mauna Kea lavas with around 18% MgO are close to parental magma compositions. Melts with these whole-rock compositions would crystallize olivine corresponding to the most forsteritic olivines (Fo_{90.5}) found in these lavas [Putirka et al., 2011, Figure 2]. The Ni content of these proposed parental magmas is around 830 ppm. This estimate is significantly higher than the \sim 600 ppm Ni proposed by Sobolev et al. [2005] and Herzberg [2011] for partial melts from fertile peridotite with around 18% MgO.

3.4. MgO-CaO Relationships

[24] The CaO content and CaO/Al₂O₃ versus MgO content of the Phase-2 lavas are consistent with the

crystallization and accumulation of olivine (Fo_{88-89}) and are comparable with Phase-1 shield-stage Mauna Kea magmas (Figure 5). Consistent with their steeper FeO versus MgO trend (Figure 6), the whole-rock data for the High CaO samples plot on an olivine (Fo₈₆) accumulation trend emanating from the High CaO glass compositions (Figure 5). Like the high CaO - K2O glasses from flow units 248, 254 and 255 [Stolper et al. 2004], most of the clasts and hyaloclastites from these units have elevated CaO at a given MgO content (Figure 5) and higher CaO/Al₂O₃ (>0.9) than other Mauna Kea shield lavas. The High CaO lavas plot above the line proposed by Herzberg [2006] that discriminates magmas derived from peridotites from those produced by melting pyroxenite (Figure 5). According to Herzberg [2006, 2011], these rather unusual lavas are the only Mauna Kea shield lavas with a peridotite source; the rest were derived from pyroxenite.

3.5. Incompatible Trace Elements

[25] As expected of olivine fractionation and accumulation, abundances of incompatible trace elements are negatively correlated with MgO contents in HSDP lavas (Figures 8a–8c). At a given MgO content, Phase-1 Types 1, 2, 3 and 4 and Phase-2 samples have overlapping incompatible trace element abundances. Relative to other Mauna Kea shield lavas, all of the High CaO samples have higher abundances of incompatible elements (e.g., K₂O, Th and Nb), similar abundances of moderately incompatible elements (e.g., TiO₂, P₂O₅, Zr and Hf)

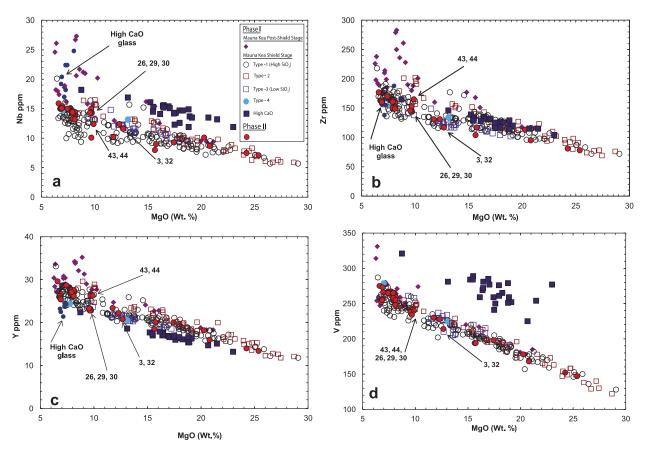


Figure 8. Variation of MgO and incompatible element contents in HSDP lavas (a) Nb, (b) Zr, (c) Y, and (d) V. Phase-2 lavas overlap with younger types 2, 2, 3 and 4 Phase-1 lavas; labeled samples are end-members (see Figure 13). In contrast, relative to other Phase-1 lavas the High CaO lavas and their glasses (shown as filled blue circles) are enriched in Nb and V (also K, Ba, Th, La, Ce and Sr) but not in moderately incompatible elements such as Zr and Y (also Ti and P). These results are consistent with a lower extent of melting for the High CaO lavas relative to other Mauna Kea shield tholeiites; see text for details.

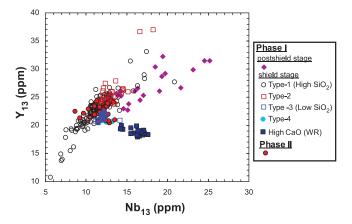


Figure 9. Y and Nb contents in HSDP lavas, normalized to MgO = 13%, using a simple MgO-trace element correlation, in order to reduce the effects of crystal fractionation and accumulation of olivine. The High CaO lavas are distinct from all other Phase-1 and -2 lavas in that they define a negative slope that may reflect lower extents of melting in the presence of garnet.

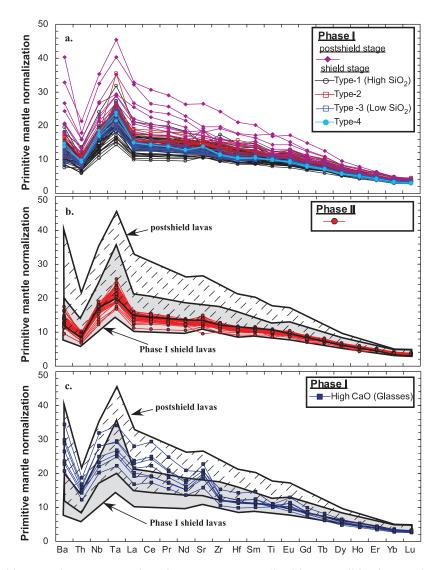


Figure 10. Primitive mantle [*McDonough and Sun*, 1995] normalized incompatible element data for HSDP lavas. The data have also been normalized to MgO = 13% to compensate for the effects of crystallization and accumulation of olivine. (a) Phase-1 lavas [*Huang and Frey*, 2003], (b) comparison of Phase-2 lavas (Table 3) with Phase-1 lavas indicated by shaded field, and (c) comparison of Phase-1 High CaO glasses (Table 4) with other Phase-1 lavas. Note the overlap with the diagonal hatched field defined by post-shield lavas.

and lower abundances of Y and HREE (Figures 8 and 10). Important features of the High-CaO lavas are their low Zr/Nb (Figure 4) and an inverse correlation between Nb and Y (Figure 9). They have ratios of Nb/Y, Zr/Y and La/Yb higher than other shield-stage lavas, and have similarities to post-shield lavas (Figure 10c). Their Zr/Nb extend to values lower than the most alkalic post-shield Mauna Kea lavas (Figure 4). The High CaO lavas, however, are not alkalic (alkalinity index ranges from -0.4 to -1.5; Table 1b).

[26] Stolper et al. [2004] noted that the High CaO glasses in the 1765–1810 mbsl interval also have high K₂O, compared to overlying and underlying

shield lavas, but this enrichment of potassium is not accompanied by elevated TiO_2 and P_2O_5 contents. Our whole-rock analyses of hyaloclastites from this interval are consistent with the glass analyses. Moreover, our results show that K_2O/P_2O_5 and K_2O/TiO_2 are elevated over a wide range in MgO content, \sim 7 to 23% (Figure 11). We infer that, in addition to high CaO content, the parental magmas of this group had high K_2O/P_2O_5 and K_2O/TiO_2 . In contrast to the hyaloclastites, the clasts from the 1782–1793 mbsl interval range from high K_2O/P_2O_5 and K_2O/TiO_2 to lower ratios that overlap with overlying and underlying shield lavas (Figure 11). The considerable scatter in the clasts, 0.11 to 0.26

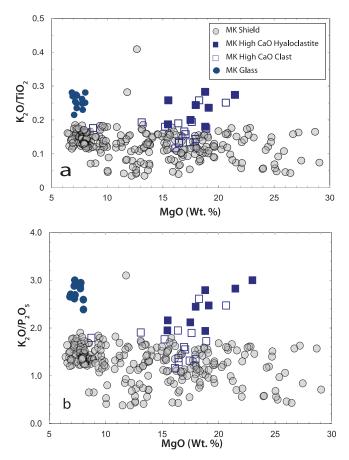


Figure 11. Comparison of K_2O/TiO_2 and K_2O/P_2O_5 in High CaO lavas and glasses (glass data from *Stolper et al.* [2004]) with other compositional types of Mauna Kea shield lavas (indicated by gray circles). The glasses and hyaloclastites have ratios that are higher than the shield lavas, whereas the High CaO clasts range from ratios that overlap with the hyaloclastites and glasses to lower values overlapping with the shield lavas. We interpret the scatter to lower ratios in the shield lavas and some clasts as a consequence of K_2O loss during post-eruption alteration.

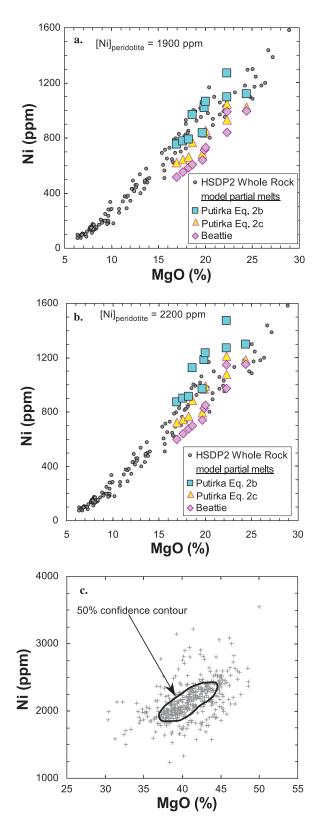
in K_2O/TiO_2 and 1.1 to 2.5 in K_2O/P_2O_5 is comparable with the scatter in other shield lavas and is attributed to post-magmatic alteration caused by interaction with fresh water [see *Huang and Frey*, 2003, Figure 4; *Rhodes and Vollinger*, 2004].

4. Discussion

4.1. Do Ni Contents in Mauna Kea Lavas Require a Pyroxenite Source?

[27] There was a broad consensus that basaltic magmas result from de-compression melting of a peridotite mantle [e.g., *Yoder and Tilley*, 1962; *Green and Ringwood*, 1967]. Recently, this consensus has been challenged and there is a vigorous debate on the relative roles of peridotite and eclogite/pyroxenite as mantle sources of Hawaiian magmas. For example, *Hauri* [1996] proposed that dacitic magmas, produced from melting lithologically

discrete domains of eclogite within the plume, mix with picritic melts of peridotite to produce the range in SiO₂ content and isotopic ratios of Hawaiian magmas. Others have adopted variants on this model [e.g., Takahashi and Nakajima, 2002; Huang and Frey, 2005], particularly in order to explain the high SiO₂ content of Makapuu-stage Koolau lavas. Sobolev and colleagues [Sobolev et al., 2005, 2007] have introduced a more complex model in which silicic melts from discrete eclogite domains react with surrounding peridotite to produce secondary pyroxenite. Subsequent melting of differing proportions of these peridotite - pyroxenite hybrids is thought to be responsible for differences in the compositions of Hawaiian magmas, and also for their correlated isotopic and compositional characteristics. Herzberg [2006] further argued that most Hawaiian magmas, with the exception of the High CaO Mauna Kea lavas and possibly some Loihi lavas, are derived solely through melting of pyroxenite.



[28] The driving force behind the secondary pyroxenite model is the observation that the Ni contents of olivines in Hawaiian magmas, and therefore their parental melts, are higher than would be expected from melting of peridotite. This discrepancy is most pronounced in lavas with a relatively high SiO₂ content. Our whole-rock data, showing similar Ni content at a given MgO in the Low and High SiO₂ lavas (Figure 7), are inconsistent with this model, which predicts higher Ni contents in the higher SiO₂ lavas (Type-1) relative to the Low SiO₂ lavas (Type-2). Similarly, *Putirka* et al. [2011] found comparable Ni contents in the olivines from both High and Low SiO₂ lavas. The Ni content of the High CaO lavas (with the exception of four altered samples) overlap the Ni content of other Mauna Kea lavas (Figure 7), as do the Ni content of their olivines (Table 5). If these lavas are derived from peridotite and all other Mauna Kea lavas from pyroxenite, as proposed by Herzberg [2006], then according to the Sobolev et al. [2005] model they should contain lower Ni at a given MgO. They do not. Additionally, the Ni content, at a given MgO, of Mauna Loa lavas is similar to those of Mauna Kea (Figure 7), despite the higher SiO₂ content of the Mauna Loa lavas (Figure 3a). Again this is inconsistent with the Sobolev et al. [2005] model.

4.1.1. Ni Partitioning Between Olivine and Melt

[29] Because the Ni content of peridotitic melts is dependent on the Ni content of the peridotite and the $D_{\rm Ni}^{\rm olivine/melt}$, we have re-visited the calculations of *Sobolev et al.* [2005], comparing the results obtained for different models for $D_{\rm Ni}^{\rm olivine/melt}$ and varying the peridotite Ni content (see section A in Text S1 in the auxiliary material and Figures 12a

Figure 12. Model calculations for Ni concentrations in partial melts of peridotite. The melting model is identical to that of Sobolev et al. [2005] and is based on the (3–5 GPa) melting experiments of Walter [1998]. (a) Comparison of Ni versus MgO in Mauna Kea shield-stage tholeiites with calculated partial melts of peridotite containing 1900 ppm Ni. The Ni kd's for olivine/melt are from Beattie et al. [1991] and Putirka et al. [2011]. (b) Same as in Figure 12a but the Ni content of the source peridotite has been increased to 2200 ppm. (c) Ni versus MgO in 413 peridotites taken from the GeoRoc website (georoc.mpch-mainz.gwdg.de/) and listed in Table S2. There is a wide range in Ni at a given MgO content. A 50% confidence contour shows that the Ni content in peridotites is highly variable and that the assumption of a 2200 ppm source is not unreasonable.



and 12b). Our calculations follow Sobolev et al. [2005, Table S1] and are based on the peridotite partial melting (3-5 GPa) experiments of Walter [1998]. We used the same $D_{Ni}^{mineral/melt}$ for garnet and pyroxenes as used by Sobolev et al. [2005], but for $\hat{D}_{N_i}^{\delta livine/melt}$ we used both the *Beattie et al.* [1991] equation, which was used by Sobolev et al. [2005], and also equations 2b and 2c from Putirka et al. [2011]. The model results are presented in Figure 12a. If the peridotite has 1900 ppm Ni, as proposed by Sobolev et al. [2005] and Herzberg [2011], then partial melts calculated using the Beattie et al. [1991] model should have significantly lower Ni content at a given MgO content than Mauna Kea whole-rocks. This is the original argument of Sobolev et al. [2005]. Partial melts calculated using equation 2b of *Putirka et al.* [2011] plot well within the Mauna Kea MgO-Ni whole- rock trend, and melts calculated using equation 2c of Putirka et al. [2011] plot slightly below the Mauna Kea whole-rock trend in Figure 12a. Therefore, if equation 2b of Putirka et al. [2011] describes the Ni partitioning between olivine and melt during mantle melting more satisfactorily than that of Beattie et al. [1991], then the original argument of Sobolev et al. [2005] does not hold.

4.1.2. Ni Content in Peridotite

[30] How constant are the Ni contents of mantle peridotites? Is the value of 1900 ppm Ni in fertile peridotite, used by both Sobolev et al. [2005] and Herzberg [2011], appropriate, or are other values plausible? These questions were addressed by Putirka et al. [2011, Appendix A3] and are evaluated in section A in Text S1. The data show a large range in Ni abundances in spinel and garnet peridotites. The mean is 2320 ppm, the median is 2198 ppm, and 50% of the samples are between 2029 and 2400 ppm. Figure 12c, taken from published data on mantle peridotites downloaded from the GeoRoc website (georoc.mpch-mainz.gwdg.de/), shows that at a given MgO content there is considerable Ni variation in peridotite. A 50% confidence contour shows that, in general, MgO and Ni contents are positively correlated, implying that the Ni content in peridotite is mainly controlled by the olivine abundance.

[31] The previous calculations (Figure 12a) followed *Sobolev et al.* [2005] and *Herzberg* [2011] in using "fertile" peridotite with 1900 ppm Ni.

However, there is considerable Ni variation at a given MgO content for peridotites (Figure 12c). If we use a Ni content of 2200 ppm for peridotite (which corresponds with the "depleted" peridotite of *Herzberg* [2011] but is well within the 50% confidence contour for peridotite compositions), partial melts calculated using the D_{Ni} model from *Beattie et al.* [1991] overlap with the Mauna Kea whole-rock trend in MgO-Ni (Figure 12b).

[32] Earlier, we showed that the Ni content of Mauna Kea lavas do not follow the predictions of the *Sobolev et al.* [2005] secondary pyroxenite model. There is no relationship between the Ni content of the lavas, or their olivines, and the SiO₂ content of HSDP lavas. We conclude, therefore, that because of the large range in the Ni content of possible source peridotites and the current uncertainties in estimating the partitioning of Ni between olivine and melt, there is no compelling reason to accept the model of *Sobolev et al.* [2005] and reject peridotite as the source of Mauna Kea magmas.

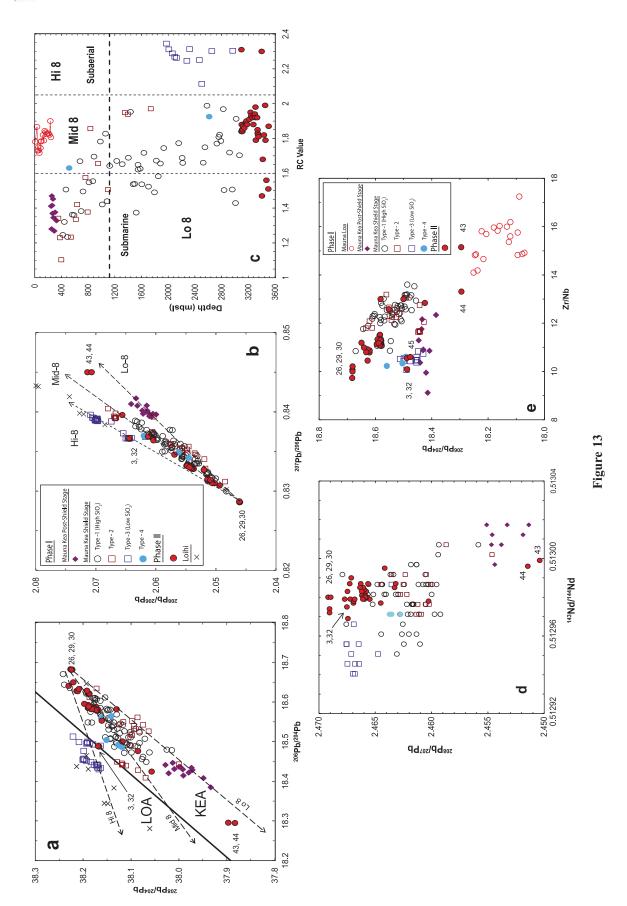
4.2. Zr/Nb and Pb Isotopic Ratios: Indicators of Geochemical Heterogeneity in the Source of Mauna Kea Shield Lavas

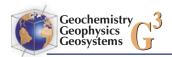
[33] Eisele et al. [2003] showed that in a 206 Pb/ 204 Pb versus 208 Pb/ 204 Pb plot, HSDP Mauna Kea Phase-1 lavas define three Pb-isotopic arrays that converge at a common, and relatively radiogenic end-point at $^{206}\text{Pb}/^{204}\text{Pb} \sim 18.7$ and $^{208}\text{Pb}/^{204}\text{Pb} \sim$ 38.25, the Kea end-member of *Tanaka et al.* [2008]. Eisele et al. [2003] designated these trends as Hi8, Mid8 and Lo8 to reflect the ²⁰⁸Pb/²⁰⁴Pb values at a given value of ²⁰⁶Pb/²⁰⁴Pb (Figure 13a). Subsequent studies have confirmed these trends in Phase-2 lavas [Nobre Silva et al., 2008; Blichert-Toft and Albarède, 2009]. The simplest explanation is that these trends represent mixing of a single radiogenic endmember with three end-members with relatively low ²⁰⁶Pb/²⁰⁴Pb, or, more plausibly, a continuum of depleted end-members. Alternatively, the three trends can be explained by a pseudobinary mixing process that involves three components with two components being mixed prior to the addition of the third [e.g., Bianco et al., 2011].

[34] The assignment of an individual sample to the Hi8, Mid8 or Lo8 trends is not always definitive in a $^{206}\text{Pb}/^{204}\text{Pb}$ versus $^{208}\text{Pb}/^{204}\text{Pb}$ plot (Figure 13a). Blichert-Toft and Albarède [2009] define a parameter R_C based on the slopes of these trends in plots of $^{208}\text{Pb}/^{206}\text{Pb}$ versus $^{207}\text{Pb}/^{206}\text{Pb}$, that provides better resolution of the three trends (Figures 13b and 13c). Hi8 lavas have $R_C > 2$, whereas an R_C

¹Auxiliary materials are available in the HTML. doi:10.1029/2011GC003812.







of \sim 1.6 separates Lo8 from Mid8 lavas. Lavas with $R_C > 2$ only occur below 1974 mbsl (Figure 13c), and they correspond to the Low-SiO₂ group of *Huang and Frey* [2003] and the Type-3 lavas of *Rhodes and Vollinger* [2004].

[35] Abouchami et al. [2005], developing an idea originated by *Tatsumoto* [1978], proposed a dividing line that separates lavas erupted at Loaand Kea-trend Hawaiian volcanoes, with Loa-trend lavas having higher ²⁰⁸Pb/²⁰⁴Pb at a given ²⁰⁶Pb/²⁰⁴Pb (Figure 13a). All Hi8 lavas plot on the Loa side of the dividing line, defining a mixing trend between the common high ²⁰⁶Pb/²⁰⁴Pb Kea end-member with a lower ²⁰⁶Pb/²⁰⁴Pb Loa endmember (Figure 13a). Consistent with a mixing interpretation, Huang and Frey [2003] found that the Hi8 lavas form a near horizontal Nb/Zr versus La/Yb trend that cannot be explained by partial melting of peridotite (Figure 14). Phase-2 units 3 and 32, the Low SiO₂ intrusives (Figures 1a and 2), are within the Hi8 trend at the least radiogenic end of this array (Figure 13a). This high ²⁰⁸Pb/²⁰⁴Pb Loa end-member has isotopic and geochemical similarities with Loihi lavas [e.g., Blichert-Toft et al., 2003; Huang and Frey, 2003; Kurz et al., 2004; Rhodes and Vollinger, 2004].

[36] The High SiO₂ lavas that occur throughout the shield-stage of the core belong to both the Mid8 and Lo8 arrays, although the distinction is somewhat arbitrary. The Low SiO₂ lavas erupted above 1974 mbsl (Type-2 lavas of *Rhodes and Vollinger* [2004]) also occur on both the Mid8 and Lo8 arrays (Figures 13a and 13b). Most of the Phase-2 lavas plot in the Mid8 field in a tight cluster toward the radiogenic end of the trend, which is defined by Phase-2 units 26, 29 and 30 (Figure 13a). In contrast, Phase-2 units 43 and 44 have the lowest ²⁰⁶Pb/²⁰⁴Pb and ²⁰⁸Pb/²⁰⁴Pb found in Mauna Kea lavas and plot on the Lo8 array (Figures 13a and 13b). Mauna Kea post-shield lavas fall exclusively on the Lo8 array, and like units 43 and 44 they

have relatively non-radiogenic Pb isotopic ratios (Figure 13a). *Frey et al.* [1991] and *Kennedy et al.* [1991] argued that the transition from shield stage volcanism to post-shield stage volcanism at Mauna Kea volcano is characterized by a decreasing degree of partial melting, and an increasing role for a depleted (i.e., high ¹⁴³Nd/¹⁴⁴Nd, low ⁸⁷Sr/⁸⁶Sr and low ²⁰⁶Pb/²⁰⁴Pb, ²⁰⁷Pb/²⁰⁴Pb and ²⁰⁸Pb/²⁰⁴Pb) source component.

[37] The similarity in Pb and Nd isotopic ratios of the relatively young post-shield Mauna Kea lavas and the relatively old units 43 and 44, deep in the shield-stage of the volcano (Figures 13a and 13d) show that the depleted source component sampled during the post-shield stage of volcanism was also sampled early during shield stage volcanism. This indicates that this depleted source component is long-lived and intrinsic to the Hawaiian plume. Similarly, the component with the most radiogenic Pb is present throughout the eruptive history of the volcano, that is, Phase-2 units 26, 29 and 30 and Phase-1 unit 305 (Figures 13a and 13b). It is also evident, from the plot of Rc versus depth (Figure 13c), that the Hi8 (Loihi-like) component with Rc > 2.0) that characterizes the Hi8 Low SiO₂ lavas also contributes to both younger high and low SiO_2 lavas with Rc = 1.8-2.

[38] Trace element ratios involving Nb, such as Zr/Nb, have long been established as a useful proxy for isotopic ratios in Hawaiian lavas [e.g., *Rhodes et al.*, 1989; *Frey and Rhodes*, 1993; *Frey et al.*, 1994], and in particular for Pb isotopes in Mauna Kea lavas [e.g., *Huang and Frey*, 2003; *Rhodes and Vollinger*, 2004]. There is an overall negative correlation between Zr/Nb and ²⁰⁶Pb/²⁰⁴Pb (Figure 13e); that is the depleted component with high Zr/Nb has relatively non-radiogenic Pb isotope ratios. Phase-2 lavas exhibit greater diversity in Pb isotopes [*Nobre Silva et al.*, 2008; *Blichert-Toft and Albarède*, 2009] and Zr/Nb than all of the younger shield-stage lavas recovered during

Figure 13. Pb isotopic and Zr/Nb ratios in HSDP lavas. The isotopic data are from *Eisele et al.* [2003], *Blichert-Toft et al.* [2003], *Abouchami et al.* [2005], and *Blichert-Toft and Albarède* [2009]. See legend in Figure 13b for an explanation of the symbols. Several Phase-2 lavas (labeled) have more extreme values than the more numerous Phase-1 lavas. (a) Plot of ²⁰⁸Pb/²⁰⁴Pb versus ²⁰⁶Pb/²⁰⁴Pb showing the Hi8, Mid8 and Lo8 trends of *Eisele et al.* [2003]. Phase-2 lavas fall on all three trends. Type-3 (low SiO₂) lavas define the Hi8 trend and are on the Loa side of the proposed line (shown as a heavy black line) that separates Loa and Kea trend volcanoes [*Abouchami et al.*, 2005]. Loihi data [*Abouchami et al.*, 2005], shown as black crosses, also plot along the Hi8 trend. (b) The same three trends in a plot of ²⁰⁸Pb/²⁰⁶Pb versus ²⁰⁷Pb/²⁰⁶Pb [*Blichert-Toft and Albarède*, 2009]. (c) Rc versus stratigraphic depth for HSDP lavas. Rc is defined by *Blichert-Toft and Albarède* [2009] and is a parameter based on the slopes of the Hi8, Mid8 and Lo8 trends in a plot of ²⁰⁸Pb/²⁰⁶Pb versus ²⁰⁷Pb/²⁰⁶Pb (see Figure 13b). Hi8 lavas have Rc > 2.0, Mid8 lavas 1.6 to 2.0, and Lo8 lavas <1.6. (d) Plot showing the inverse correlation of ²⁰⁸Pb/²⁰⁴Pb with Zr/Nb.

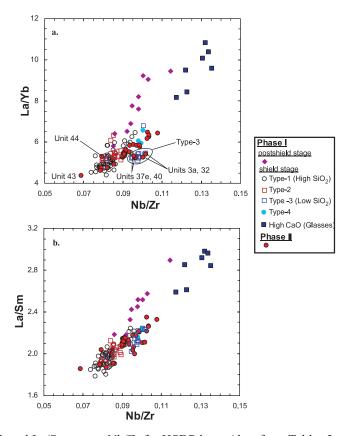


Figure 14. Plot of La/Yb and La/Sm versus Nb/Zr for HSDP lavas (data from Tables 3 and 4). The High CaO lavas have higher ratios than other Phase-1 and -2 lavas and are comparable with, and even higher than post-shield lavas. As inferred from Figure 8 their high abundances of highly incompatible elements indicate that the High CaO lavas formed by relatively low degrees of melting.

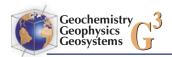
Phase-1 of HSDP. This is particularly pronounced at the very bottom of the core (>3357 m) where units 26, 29 and 30 have the lowest Zr/Nb (9.7 to 10.1) and the highest ²⁰⁶Pb/²⁰⁴Pb (>18.68) and units 43 and 44 have the highest Zr/Nb (13.3 to 15.1) and the lowest $^{206}\text{Pb}/^{204}\text{Pb}$ (~ 18.29) (Figure 13e). Units 43 and 44, near the bottom of the core, fall on the Lo8 trend and have the least radiogenic Pb isotopic ratios and highest Zr/Nb, supporting the conclusion that this depleted component was present throughout Mauna Kea's magmatic history, including the post-shield stage. In addition, there are members of all three Pb isotopic trends within the 3098–3506 mbsl part of the core (Figure 13c), thereby implying a wide range of endmember components at this stage in the magmatic history of the volcano.

4.3. The Origin of the High CaO Lavas

[39] The High CaO tholeitic shield basalts occur only over a very narrow stratigraphic range (1767 to 1808 mbsl) and have compositions unlike any other Hawaiian shield tholeites [Stolper et al.,

2004]. *Herzberg* [2006], in a provocative paper, suggested that these High CaO lavas are the only Mauna Kea shield lavas produced by melting of peridotite and that the other types of Mauna Kea shield lavas were derived from melting of pyroxenite.

[40] The High CaO lavas have many similarities to Mauna Kea post-shield lavas. For example, the dominant olivine composition in the High CaO shield lavas is Fo₈₅₋₈₆, similar to that of post-shield tholeiitic Mauna Kea lavas known as the Hamakua Volcanics (Table 5) [Baker et al., 1996; Garcia, 1996; Putirka et al., 2011]. Moreover, oxide versus MgO whole-rock trends for the High CaO shield lavas reflect the accumulation of Fo₈₅₋₈₆, rather than Fo_{88–89} as is common for other shield-building Mauna Kea tholeiites (e.g., Figures 5 and 6). There are phenocrysts of Fo₈₉ in the High CaO shield lavas (Table 5), but these are rare, as they are in post-shield tholeiites. Also, the overlying subaerial post-shield tholeiitic basalts [Frey et al., 1990, 1991] have similarly high CaO and K₂O contents [Stolper et al., 2004, Figure 18d].



- [41] In addition, the High CaO shield lavas are characterized by unusually high incompatible element abundances at a given MgO content (Figures 8 and 10) and relatively high ratios of Nb/Zr and La/Yb (Figure 14). These abundances and ratios overlap with those of Mauna Kea's post-shield lavas, and in some samples extend beyond the range of post-shield alkalic lavas (Figures 4 and 14). However, the post-shield lavas do not have the distinctive high K₂O/TiO₂ and K₂O/P₂O₅ of the High CaO group [Stolper et al., 2004, Figures 18a and 18b].
- [42] Currently, there are no isotopic data for the High CaO lavas, but their Zr/Nb, from 8.5 to 9.6, is lower than all other Mauna Kea tholeiites, including post-shield tholeiites. Therefore, based on the inverse trend of Zr/Nb versus ²⁰⁶Pb/²⁰⁴Pb (Figure 13e), we predict that their isotopic characteristics will extend the range of Mauna Kea magmas to more radiogenic Pb isotopic ratios, thereby shedding further light on the source characteristics of Mauna Kea lavas.
- [43] If we assume similar source compositions for all Mauna Kea shield lavas, several compositional features of the High CaO shield lavas are consistent with their formation by relatively low extents of melting (F), specifically: (1) their relative enrichment in highly incompatible elements, such as Th, K, Nb and La (Figures 8a, 10, 11, and 14); (2) the compatible behavior of Y and relatively low content of heavy rare earth elements in the High CaO lavas (Figures 9 and 10c) which are compatible in garnet and hence their low abundances of these elements suggest that the extent of melting was not sufficient to eliminate garnet from the residue; (3) their high K_2O/TiO_2 and K_2O/P_2O_5 (Figure 11) is also an expected consequence of low F, <5%, because at low F the low (<1) ratios of mineral/melt compound partition coefficients D_K/D_{Ti} and D_K/D_P for residual garnet and clinopyroxene will create melts with higher K₂O/TiO₂ and K₂O/P₂O₅ than the source ratios (section B in Text S1); (4) if D_{CaO} for cpx/ melt is <1, the CaO content of partial melts of garnet peridotite increase with decreasing F (see case 1 in Figure 6 of Huang et al. [2011]), and therefore relatively high CaO content may also reflect relatively low F.
- [44] Based on inverse correlations between Sr/Nb and 87 Sr/ 86 Sr with $\delta^{44/40}$ Ca, *Huang et al.* [2011] argued that the Hawaiian plume may contain up to 4% recycled ancient carbonate; the Makapuu-stage of Koolau shield lavas contain the largest amount of this carbonate component. Did the High CaO

- Mauna Kea lavas have such a carbonate component in their mantle source? We think not because they lack the geochemical characteristics of recycled ancient carbonate component, that is:
- [45] (1) The High CaO lavas do not have high Sr/Nb; their Sr/Nb ratios, 19–25, are similar to that of other Mauna Kea tholeites (16–33);
- [46] (2) Two High CaO lavas, R685–5.5–6.1 and R700–2.9–3.1 (labeled as SR685 and SR700 by *Huang et al.* [2011]), have $\delta^{44/40}$ Ca of 0.92 and 0.94. They define the high $\delta^{44/40}$ Ca_{SRM915a} end of the Ca isotopic spectrum of Hawaiian lavas, and are close to the upper mantle values (1.05) defined by measurements on peridotites [*Huang et al.*, 2010].
- [47] The high V abundances in High CaO lavas (Figure 8d) are also inconsistent with the source of High CaO lavas being Ca-rich. Huang et al. [2011] showed that the net effect of adding carbonate into a peridotite is to increase the clinopyroxene proportion at the expense of orthopyroxene [see Huang et al., 2011, section 5.2 and Table 4]. If the high CaO content in High CaO lavas reflects carbonate in their mantle source (e.g., Case I in Figure 6 and Table 4 of Huang et al. [2011]), then a clinopyroxene-rich source is inferred for High CaO lavas. Since V is compatible in clinopyroxene [e.g., Hart and Dunn, 1993], the High CaO lavas in equilibrium with abundant clinopyroxene should have relatively low V abundances, which is inconsistent with the higher V abundances in High CaO lavas (Figure 8d).
- [48] If the High CaO lavas were derived by lower degrees of melting than the other compositional types of Mauna Kea shield-building tholeiitic basalts, an important implication is that the magma supply to Mauna Kea diminished during the interval, 1765 to 1810 mbsl, of High CaO basalt production. Stolper et al. [2004] came to a similar conclusion regarding glasses sampled between 2233 and 2280 mbsl. Although these glasses do not have high CaO, they have relatively high K₂O and Na₂O contents: that is, they are transitional tholeiites formed by relatively low extents of melting. We agree with Stolper et al. [2004] that the magma supply to Mauna Kea waxed and waned during the shield-building stage. This is contrary to the common generalization for shield building, where magma supply is represented by a bell-shaped curve of initially increasing, and eventually decreasing magma supply as the volcano migrates toward and away from the plume center [e.g., Frey et al., 1990; Lipman, 1995; DePaolo and Stolper, 1996].



4.4. Does the HSDP-2 Core Include Lavas From Multiple Shields?

[49] The HSDP-2 core sampled an abrupt transition from shield-stage Mauna Loa lavas to older postshield Mauna Kea lavas at a depth of 245 mbsl [Rhodes and Vollinger, 2004]. Were there other inter-shield transitions recorded in the \sim 695 ka record of the core? Using Pb isotopic data Eisele et al. [2003], and more recently Blichert-Toft and Albarède [2009] show that there is a tendency for Lo8 lavas to occur high in the core, with Mid 8 lavas below, and inter-layered Hi8 and Mid8 lavas at greater depth (Figure 13c). Blichert-Toft and Albarède [2009] suggest that over ~366 ka, Mauna Kea has migrated over three volcanic centers, first Kilauea (Mid8), followed by Loihi-like (Hi8) and finally Mauna Kea (Lo8) as the Pacific Plate moved over the Hawaiian hot spot. This sequence is an oversimplification. Lo8 lavas also occur near the bottom of the core (3472–3501 mbsl) and Mid 8 lavas are found as high as 679 m (Figure 13c). Clearly, all of the geochemical components that contributed to Mauna Kea's magmas were available throughout much of the shieldbuilding history recorded in the core.

[50] The submarine pillows and hyaloclastites of the Hi8 group are Low SiO₂ lavas (Type-3), with major, trace and isotopic characteristics similar to those of Loihi magmas [Rhodes, 2000; Huang and Frey, 2003; Stolper et al., 2004, Rhodes and Vollinger, 2004]. They are inter-layered with "normal" High SiO2 (Type-1) Mauna Kea lavas at depths between 1974 and 2481 m. Their estimated ages, based on depth, are around 517-523 ka, a relatively short period of time. Stratigraphically below them, including units 3 and 32 from Phase-2 of HSDP, are intrusive units with similar compositions. They are probably feeders to the overlying extrusive units. These enigmatic lavas present a problem [Abouchami et al., 2005]. They either reflect the presence of relatively short-lived "Loa" source components on the "Kea" side of the plume, or they are lavas from an adjacent volcano with Loalike isotopic compositions. At that time (\sim 520 ka) it is unlikely that either Loihi or Kilauea were even in existence [Moore and Clague, 1992: DePaolo and Stolper, 1996; Lipman et al., 2002]. Early, Loihilike, stages of Mauna Loa or Hualalai are the most compelling candidates. Mauna Loa, however, can be ruled out. Recent Ar/Ar dating of submarine Mauna Loa lavas [Jicha et al., 2009] show that around 500-700 ka Mauna Loa was erupting High-SiO₂ lavas, similar to those of modern-day Mauna Loa. Hualalai would have been in a more advanced

stage of its evolution than Mauna Loa, making it an even more unlikely candidate.

[51] Holcomb et al. [2000] predicted that Kohala lavas would be sampled at depth by the HSDP core because, they argued, the southeast rift zone of Kohala (the Hilo Ridge) extends beneath Mauna Kea. Lipman and Calvert [2011] endorse this notion, based on an age of \sim 1140 ka for transitional tholeiitic lavas dredged from the toe of the Hilo ridge, which, because of their old age, they infer originates from Kohala volcano rather than Mauna Kea. Could these enigmatic Low SiO₂ lavas come from Kohala? At this time (\sim 520 ka) Kohala should have been in a vigorous stage of tholeiitic shield-growth [Moore and Clague, 1992; Lipman and Calvert, 2011] and Phase-2 drilling should have encountered more of these Low SiO₂ putative Kohala lavas as it penetrated further into the Kohala shield. It did not. The majority of the Phase-2 lavas are High SiO₂ lavas, similar to younger Mauna Kea units, and only two intrusive units (3, 32) are Low SiO₂ lavas. Finally, the presence of "Loa" type lavas at Kohala Volcano, which lies along the "Kea" trend, does not solve the problem: it merely shifts the presence of a Loa component to another "Kea" trend volcano.

[52] Recently, Blichert-Toft and Albarède [2009] suggested that these Low SiO₂ lavas come from a "lost" volcano with strong Loihi affinities. The problem with this alternative interpretation is that the low-SiO₂ lavas form a distinct trend (the Hi8 trend of *Eisele et al.* [2003]) in ²⁰⁶Pb/²⁰⁴Pb versus ²⁰⁸Pb/²⁰⁴Pb, converging at the same high radiogenic values of ²⁰⁶Pb/²⁰⁴Pb and ²⁰⁸Pb/²⁰⁴Pb as the Mid8 and Lo8 Mauna Kea lavas (Figures 13a and 13b). This is unlikely to be a coincidence. Therefore, we conclude that the Low-SiO₂ lavas were erupted from Mauna Kea, reflecting the presence of a relatively small-scale, and short-lived, "Loa" heterogeneity within the melting regime of Mauna Kea around 517 to 523 ka. This conclusion is not unprecedented. Ren et al. [2005] have shown that melt inclusions in olivine in submarine Haleakala and Koolau lavas have major and trace element characteristics of both "Kea" and "Loa" trend volcanoes. On a larger scale, Marske et al. [2007] show that for a brief period between 250-1400 AD the Pb, Sr and Nd isotopic ratios of both Kilauea and Mauna Loa volcanoes shifted from "typical" values, on either side of the Loa-Kea boundary (Figure 13a) toward ratios that were intermediate between the two volcanoes. Subsequently, lavas from both volcanoes returned to more "typical" values. They interpret this transient magmatic event as evidence



for the passage of a small-scale compositional heterogeneity through the melting regimes of both volcanoes. Finally, we predict that, given the distinctive compositional characteristics of the High CaO lavas, such as their low Zr/Nb (Figures 4 and 14), they are likely to have higher ²⁰⁶Pb/²⁰⁴Pb and ²⁰⁸Pb/²⁰⁴Pb than all the other Mauna Kea shield lavas (Figures 13a and 13d). Are we to infer from this that they too represent lavas from yet another unknown volcano? We think not, and conclude that these isotopic anomalies reflect small-scale source heterogeneities passing through the melting zone of Mauna Kea volcano. Supporting this conclusion we observe that, although Mauna Kea and adjacent Mauna Loa were both in their vigorous shield building stages for much of the last 600 ka [Jicha et al., 2009], there are no Mauna Loa lavas inter-layered with Mauna Kea lavas throughout the entire HSDP core.

5. Conclusions

[53] (1) SiO₂ and Ni abundance in Hawaiian shield lavas have been used to distinguish between pyroxenite and peridotite sources [e.g., Sobolev et al., 2005]. In the HSDP-2 core there are High and Low SiO₂ groups and they have similar Ni contents at a given MgO content. Hence, whole-rock Ni contents in Mauna Kea shield lavas do not reflect differences in source mineralogy for the High and Low SiO₂ groups. We conclude that, given the uncertainties in partitioning between olivine and melt, and in the Ni content of peridotites, it is premature to reject peridotite as the mantle source of these magmas.

[54] (2) There is more geochemical diversity, e.g., in Zr/Nb and Pb isotopic ratios, among Mauna Kea Shield lavas in the lower 408 m of the HSDP core than in the overlying 2745 m. of Mauna Kea shield lavas. Clearly, the range of mantle source components that formed the Mauna Kea shield was sampled early, and throughout the growth of the Mauna Kea shield. For example, a depleted component intrinsic to the plume contributed to basalt eruption early in the construction of the shield (units 43 and 44 in the Phase-2 core) and during post-shield volcanism.

[55] (3) A geochemically unique group of High CaO-K₂O lavas first identified by glass composition occur over a narrow depth interval, 1767 to 1808 mbsl in the HSDP core [*Stolper et al.*, 2004]. No whole-rocks from this group have been previously studied, therefore we sampled the core and

analyzed hyaloclastites and clasts associated with these compositionally distinct glasses. Relative to other Mauna Kea shield lavas these whole-rocks are also enriched in CaO, K₂O and highly incompatible elements at a given MgO. These shield-stage lavas have affinities with post-shield lavas, for example both groups formed by lower extents of melting than other compositional groups of Mauna Kea shield lavas. Contrary to a previous hypothesis [Herzberg, 2006], we find no evidence that these High CaO lavas were derived from a mantle source that was lithologically distinct, that is, peridotite rather than pyroxenite, from the source of other Mauna Kea lavas. The important implication is that melt production waxed and waned during shield growth and large, short-term fluctuations in extent of partial melting are superimposed on the longterm initial increase followed by eventual decrease in melt flux that characterizes growth of a Hawaiian shield as it passes over the Hawaiian plume.

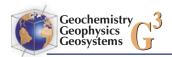
[56] (4) In order to explain the compositional diversity of lavas sampled by the HSDP, it has been suggested that the core contains basalts derived from several volcanoes [e.g., *Blichert-Toft and Albarède*, 2009]. We argue that this is unlikely and we infer that rather than geochemically distinct lavas from several volcanoes, a range of geochemically distinct mantle end-members contributed to basalts forming the Mauna Kea shield.

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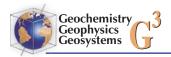
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