

# Cadmium, indium, tin, tellurium, and sulfur in oceanic basalts: Implications for chalcophile element fractionation in the Earth

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**Abstract.** Concentrations of S, Cd, In, Sn, and Te are reported for 80 samples of mid-ocean ridge basalt (MORB), submarine and subaerial ocean island basalt (OIB) and submarine arc lavas. Cadmium, In, and Sn are moderately incompatible, and Te is compatible during partial melting. Cadmium is particularly uniform, consistent with a homogeneous distribution in the mantle. Tellurium is more variable (1–6 ppb) and is notably higher in Loihi, ranging up to 29 ppb, the most likely explanation for which is accumulation of Cu-bearing sulfide. The average Cd/Dy ratio is the same (0.027) for OIB glasses, MORB glasses and the continental crust, yielding a primitive mantle Cd concentration of ~18 ppb. Indium, despite being more volatile, is less depleted than Cd and the other very volatile chalcophile elements Pb, Bi, Tl, and Hg. From the depletion of In we deduce that core formation depleted the silicate Earth in Cd, Pb, Bi, Tl, and Hg by between factors of 5 and 10. The In depletion yields concentrations of C, S, Se, and Te in the core of C ~ 1.2%, S > 2.4%, Se > 7.1 ppm, and Te > 0.89 ppm. The Moon appears to be enriched in Te relative to the silicate Earth. Either a significant fraction of the Moon was derived from a more Te-rich body or the silicate Earth's inventory of chalcophile and siderophile elements was depleted by further terrestrial core growth after formation of the Moon.

## 1. Introduction

The geochemistry of some volatile siderophile and chalcophile elements is only poorly understood because of the dearth of high-quality data. Accurate data could provide constraints on the role that sulfide plays in mantle melting and differentiation, the abundance of sulfur (S) in the mantle, and the processes of accretion and core formation. The Earth's core is estimated to contain roughly 11 wt % of light elements [Birch, 1952, 1961, 1964]. Most of the leading candidates for the light elements in the core (O, C, S, H) are also volatile and their abundances in the bulk Earth are very difficult to estimate because two separate processes, loss of volatile elements and core formation, will lead to nonchondritic relative proportions in the silicate Earth. Furthermore, the concentrations of highly volatile elements (such as H, C, S, and noble gases) in geological samples are often reduced by low-pressure degassing, making it a difficult challenge to estimate their abundances in the Earth's mantle. Ultramafic xenoliths are of questionable help in understanding such elements, since they have often experienced some degree of partial melting or perhaps alteration [Lorand, 1989]. For example, orogenic lherzolites have around

300 ppm S [Garuti *et al.*, 1984; Lorand, 1989], while spinel lherzolite xenoliths in continental alkali basalts are much more depleted, with between 0 and 150 ppm S [Mitchell and Keays, 1981; Harmon *et al.*, 1987]. Studies of trace siderophile and chalcophile elements in basalts have been used as proxies to partially circumvent the problems of estimating S budgets directly and, more importantly, to constrain models of accretion and core formation using independently determined metal-silicate and sulfide-silicate partition coefficients [Chou, 1978; Arculus and Delano, 1981; Newsom *et al.*, 1986; Jones and Drake, 1986]. However, making reliable estimates of primitive mantle abundances is not always straightforward, even for such proxy elements.

Key issues relevant to all trace chalcophile elements include the solubility of S in basaltic magmas, the partition coefficients between sulfide and silicate melts, and the dynamic P-T path of ascending magmas. Mathez [1976] and Wallace and Carmichael [1992] presented mechanisms by which physiochemical factors control the solubility of S in basaltic magmas. It is believed that increases in temperature, Fe<sup>2+</sup>, and  $f_{S_2}$  favor higher solubility of S. There is debate about whether S solubility is sensitive to pressure [Carroll and Webster, 1994]. The effect of  $f_{O_2}$  is also complicated. Sulfide will be the dominant S-bearing species at the oxygen fugacities ( $f_{O_2}$ ) thought to be characteristic of normal mid-ocean ridge basalts (MORB) and ocean island basalts (OIB). High  $f_{O_2}$  does not favor S<sup>-2</sup> solubility because the percentage of sulfate increases with increasing  $f_{O_2}$ , although this may increase the total amount of dissolved S.

Trace elements such as Se, Cd, In, Sn, and Te that may

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Paper number 2000JB900152.  
0148-0227/00/2000JB900152\$09.00

sometimes be siderophile or chalcophile may, like S, be volatile in igneous processes. Cadmium, In, Sn, and Te can be flushed out of magma systems by a degassing vapor phase [Symonds *et al.*, 1988; Greenland and Aruscavage, 1986]. So any study of these elements has to include data for submarine glasses as well as subaerial basalts. Studies of the relationships among these trace elements and S are scarce, partly because of analytical difficulties and the very low abundances, leading to a lack of reliable data. Laul *et al.* [1972] reported analyses of Cd and In in five MORB samples from the Atlantic Ocean. Hertogen *et al.* [1980] determined Cd and Te in several Atlantic MORB. Morgan [1986] reported Te concentrations in a suite of ultramafic xenoliths but offered no discussion of the data. All of these measurements were done by instrumental neutron activation analysis (INAA). Jochum *et al.* [1993] presented the first comprehensive data set on Sn using isotope dilution spark source mass spectrometry. Yi *et al.* [1995] provided the first high-precision concentrations of In and Sn for subaerial ocean island basalts (OIB) from the Atlantic Ocean determined using multiple collector inductively coupled plasma mass spectrometry (MC-ICPMS) [Halliday *et al.*, 1995b, 1998] and isotope dilution. In all of these studies, little evidence was found for chalcophile behavior for Cd, In, and Sn during mantle partial melting and magma differentiation. Cadmium, In, and Sn were considered to be lithophile. Indium has been thought to be roughly equivalent to a heavy rare earth or Y in incompatibility [Yi *et al.*, 1995]. Tin was shown to have a bulk distribution coefficient similar to Sm [Jochum *et al.*, 1993]. Cadmium was considered by Sun [1982] to be moderately incompatible, but the exact incompatibility was not clear. Tellurium was believed to be a compatible element [Sun, 1982] and highly enriched in sulfide because of its positive correlation with Se in some MORB [Hertogen *et al.*, 1980].

Here, we present the first high-precision isotope dilution analyses of Cd, In, Sn, and Te in a comprehensive suite of submarine glasses that include MORB, OIB, and submarine island arc and back arc trough basalts and andesites (referred to as IAB). These data are used to investigate the behavior of these elements in magmatic processes and to provide constraints on the early history of the Earth.

## 2. Sampling and Analytical Techniques

The sample set includes MORB glasses from the Mid-Atlantic Ridge (MAR), and various ridges in the Indian and Pacific Oceans. All MORB were dredged from the ocean floor or collected with submersibles at water depths greater than 1000 m. OIB include a suite of subaerial samples from the Atlantic Ocean islands [Halliday *et al.*, 1992, 1995a] and submarine lavas from Loihi seamount, just south of the island of Hawaii [Garcia *et al.*, 1993, 1995]. Analyzed samples from the arc environment are submarine glasses from the Mariana island arc and back arc trough [Alt *et al.*, 1993].

The major element compositions of all of the submarine samples are given in Table 1. All of the glasses are extremely fresh and most are basalts, with the exception of two of the submarine andesitic glasses from the Mariana arc. MgO contents in the MORB glasses (Table 1) are all lower than those in primary MORB (<9% versus 10–15% [Klein and Langmuir, 1987]). The Mid-Atlantic Ridge (MAR) glasses are from a transect around the Azores Islands [Langmuir, 1992] extending from the maximum influence of the Azores hot spot to south of the Hayes fracture zone, where the hot spot influence is no longer apparent. The MORB glasses have a wide range of rare

earth element (REE) patterns from light REE enriched to light REE depleted (Table 2). Glasses from Loihi include both alkali and tholeiitic basalts, with olivine being the major phenocryst phase (2–22%). All are light REE enriched. Pyroxene and plagioclase phenocrysts are rare or absent (<2% in lavas) and, if present, are often small in size (see Garcia *et al.* [1993, 1995] for detailed petrographic descriptions of these samples). Sulfide globules, although less common in OIB than in MORB glasses, are found both in glasses [Byers *et al.*, 1985] and in glass inclusions in olivine phenocrysts from Loihi. Two of the three Galapagos submarine glasses are of tholeiitic composition, and the third is an alkali basalt. They are strictly speaking ridge basalts but are geochemically more similar to OIB. The Mariana glasses were from two distinct tectonic settings. Two of three submarine glasses from Mariana island arc are slightly evolved with SiO<sub>2</sub> > 54% and Mg # of 22 and 44. (Mg # = molar 100 × (Mg/Mg + Fe) with total iron calculated as Fe<sup>2+</sup>.) The third one is tholeiitic in composition with a Mg # of 46. Two submarine glasses from the Mariana back arc trough are tholeiitic in composition. The arc basalts are highly vesiculated and experienced heavy degassing whereas the back arc trough experienced less degassing [Alt *et al.*, 1993]. The Mariana glasses contain rare sulfide globules up to ~20 μm in size [Alt *et al.*, 1993]. The subaerial OIBs consist of alkali olivine basalts, basanites, and nephelinites with the exceptions of tholeiitic lavas from Iceland [Halliday *et al.*, 1992, 1995a].

Each glass sample was gently crushed, ultrasonically cleaned in deionized H<sub>2</sub>O and then hand-picked under an optical microscope. No grains with visible sulfide globules were included in the aliquots. For the Loihi lavas the major elements (Table 1) were determined by electron microprobe [Garcia *et al.*, 1993, 1995]. The trace elements K, Co, Cr, Mn, Cu, Ni, Sc, Sr, V, Zn, and Zr (Tables 3 and 4) were determined by inductively coupled plasma emission spectrometry (ICP-ES) at the University of Washington using methods similar to those described by Xue *et al.* [1990]. The trace elements Rb, Cs, Ba, Th, Nb, Y, Hf, Ta, and U and the rare earth elements (REE) (Table 3) were determined by inductively coupled plasma mass spectrometry (ICP-MS) at Washington State University [Garcia *et al.*, 1993] for the numbered samples and by ICP-MS at Lamont-Doherty for the "D" samples. Major element concentrations for the MORB glasses from the Mid-Atlantic Ridge, East Pacific Rise, and Indian Ocean Ridge (Table 1) were determined by electron microprobe at Lamont-Doherty. Trace element concentrations (Tables 2 and 4) were determined by ICP-MS at the Lamont-Doherty Earth Observatory, Columbia University.

Some literature data were used in this study. Major and trace element data are from Puchelt and Emmerman [1983] for sample Sonne12-42a, from Garcia *et al.* [1993, 1995] for some of the Loihi samples, from a compilation by C. Sinton (personal communication, 1997) for samples from the Galapagos, and from Alt *et al.* [1993] for samples from Mariana arc and back arc trough and one MORB glass from the East Pacific Rise (MW8712-87-6). Relevant major and trace element and Sr, Nd, and Pb isotope compositions for the subaerial OIB lavas have been published by Halliday *et al.* [1992, 1995a].

The protocols for isotope dilution measurement of In and Sn by MC-ICPMS were described by Yi *et al.* [1995]. Details of the most recent chemical separation methods and isotope dilution techniques for Cd, In, and Te measurements were reported, along with data for standard rocks, by Yi *et al.* [1998]. In brief, the separation of Cd, In, Sn, and Te from the matrix involves a two-step anion/cation exchange resin separation. Spiked

**Table 1.** Major Element Concentrations of Submarine Basaltic Lavas

Sample	Lithology	Depth, m	SiO <sub>2</sub>	TiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	FeO*	MnO	MgO	CaO	Na <sub>2</sub> O	K <sub>2</sub> O	P <sub>2</sub> O <sub>5</sub>
<i>Mid-Atlantic Ridge</i>												
AII127 D1-5	tholeiite	2710	50.31	1.30	14.53	10.22	0.20	7.86	12.57	2.56	0.06	0.12
AII127 D5-5	tholeiite	3070	49.57	0.79	16.39	8.46	0.15	9.37	12.92	2.00	0.05	0.06
AII127 D8-2	tholeiite	2789	50.08	0.81	16.25	8.51	0.15	9.43	12.31	2.24	0.04	0.07
AII127 D11-1	tholeiite	3053	51.10	1.17	14.81	9.77	0.18	8.55	11.79	2.15	0.16	0.11
AII127 D17-3	tholeiite	1009	49.14	1.35	16.06	7.54	0.15	8.39	13.71	2.27	0.67	0.25
AII127 D21-3	tholeiite	2095	50.98	2.17	15.74	9.24	0.17	5.84	10.64	3.36	1.09	0.40
AII127 D22-5	tholeiite	1386	51.86	1.97	15.09	10.04	0.18	6.03	10.62	2.78	0.94	0.34
AII127 D26-5	tholeiite	2068	51.38	1.34	14.51	10.87	0.18	7.57	11.14	2.33	0.18	0.15
AII127 D27-5	tholeiite	2288	51.49	1.21	15.29	9.10	0.15	7.99	11.97	2.28	0.30	0.16
AII127 D15-1	tholeiite	1706	51.44	1.05	14.74	9.74	0.17	8.08	12.03	2.20	0.19	0.14
<i>Juan de Fuca</i>												
JDF D2-2	tholeiite		50.10	1.88	13.63	13.4	0.22	6.75	10.73	2.74	0.22	0.23
<i>East Pacific Rise</i>												
MW8712-87-6	tholeiite	2630	50.72	2.19	13.84	12.32	0.22	6.69	11.03	2.75	0.12	0.23
VNTR11-2	tholeiite		49.43	1.01	15.93	9.66	0.16	9.25	12.50	2.25	0.05	0.08
VNTR23-8	tholeiite		48.50	1.92	16.56	10.49	0.17	7.51	10.95	3.40	0.32	0.29
VNTR27-11	tholeiite		49.69	1.55	14.85	10.66	0.18	8.20	12.21	2.49	0.08	0.12
<i>Pacific-Cocos-Nazca Triple Junction</i>												
Sonne12 42 a	tholeiite		49.93	1.50	15.14	10.00	0.18	8.23	11.78	2.57	0.11	0.12
<i>Australian-Atlantic Discordance</i>												
VE33 D10-10	tholeiite		50.91	1.03	15.97	8.67	0.15	8.72	11.47	2.88	0.12	0.12
V33 D04-54	tholeiite		49.69	1.55	14.57	11.23	0.12	8.05	12.10	2.64	0.07	0.13
<i>Indian Ocean Ridge</i>												
KH93-3 D1-B2	tholeiite	4026	50.46	1.32	15.75	8.50	0.15	7.90	11.28	3.00	0.17	
KH93-3 D2-A3g	tholeiite	4184	50.67	1.53	15.05	9.61	0.20	7.89	10.98	2.83	0.12	
KH93-3 D3-B2	tholeiite	4093	50.48	1.30	15.21	8.72	0.27	7.87	11.47	2.73	0.08	
KH93-3 D6-A3	tholeiite	3672	50.21	1.28	15.63	8.77	0.16	7.82	11.37	2.99	0.10	
KH93-3 D6-B2	tholeiite	3672	50.66	1.02	15.83	7.85	0.16	8.35	11.79	2.66	0.08	
KH93-3 D9-F1g	tholeiite	4080	50.78	1.66	14.70	9.88	0.15	7.41	10.70	2.98	0.10	
KH93-3 D9-G2	tholeiite	4080	50.73	1.56	14.63	10.39	0.23	7.37	10.75	2.87	0.13	
ANTP 131-14	tholeiite		50.66	1.14	16.30	8.57	0.18	8.24	12.11	2.66	0.06	0.09
<i>Galapagos</i>												
PL02 24-32	tholeiite	2700	49.20	3.17	13.81	12.28	0.14	6.30	11.06	2.91	0.48	0.24
PL02 25-1	alkali basalt	2200	46.71	3.72	15.31	12.25	0.15	5.15	9.64	4.04	1.20	
PL02 30-1	tholeiite	2200	48.67	1.56	16.58	9.37	0.12	8.32	12.25	2.59	0.36	0.17
<i>Loihi Seamount</i>												
187-1	alkali basalt	2000	46.89	2.35	12.20	11.60	0.18	9.68	13.15	2.25	0.68	0.28
1802-4A	alkali basalt	1200	47.17	3.59	14.75	12.84	0.22	5.01	10.76	3.55	1.02	0.38
D2-11	alkali basalt	3050	47.40	3.75	14.34	12.99	0.24	4.97	9.90	3.20	0.80	0.47
D3-2	alkali basalt	4700	45.80	2.95	14.30	11.10	0.14	7.26	12.40	2.80	0.68	0.39
D4-6	alkali basalt	2500	46.80	3.24	15.80	11.06	0.17	6.00	10.60	3.00	0.56	0.38
D5-1	alkali basalt	3100	47.50	3.30	14.80	12.50	0.20	5.20	10.40	3.20	0.78	0.41
158-4	basanite	1925	45.40	3.38	16.10	12.05	0.18	4.59	10.76	4.25	1.75	0.68
187-8	tholeiite	1215	49.35	2.59	13.38	11.35	0.17	7.49	11.90	2.30	0.44	0.30
1801-22	tholeiite	1000	49.31	2.61	13.84	11.84	0.18	6.80	11.65	2.41	0.42	0.20
1804-1	tholeiite	1350	49.19	2.46	13.35	11.40	0.19	7.29	12.21	2.40	0.49	0.21
<i>Mariana Arc</i>												
1885-6	andesitic basalt	2865	54.60	0.79	16.32	7.23		5.80	10.25	2.49	0.98	0.20
77kk15161	andesitic basalt	1170	58.04	1.27	13.50	10.98		2.95	6.80	2.84	1.40	
1883-5	tholeiite	2760	52.26	0.77	16.42	7.21	0.13	5.46	10.46	2.27	1.61	0.29
ALV1846.9	tholeiite	3600	49.67	0.57	17.45	7.03	0.16	6.95	13.46	2.07	0.71	0.13
ALV1846.12	tholeiite	3600	50.75	1.11	17.30	7.56	0.15	7.00	11.39	2.75	0.40	0.18

Concentrations are in wt %. Data from *Langmuir* [1992] for Juan de Fuca sample, *Garcia et al.* [1993, 1995] for Loihi seamount, *Puchelt and Emmerman* [1983] for Sonne12-42a, C. Sinton (personal communication, 1997) for Galapagos seamount, *Alt et al.* [1993] for Mariana arc and back arc trough. Blank indicates data are unavailable.

sample solutions were first loaded on anion (AG1×8, 100–200 mesh) columns with a resin bed volume of 0.4 mL, pre-equilibrated with 6 M HCl. Indium is only weakly adsorbed by the anion resin and was collected with the matrix in 3 mL of 6 M HCl. After washing the columns with about 3 mL of 2.5 M HCl, Te, along with the remaining Fe, was collected with 3 mL of 0.5 M HCl. After this step, Cd and Sn were collected with 3 mL of

1 M HNO<sub>3</sub>. Tellurium and indium were further purified using the cation resin (AG50W×8, 100–200 mesh) columns with a resin bed volume of 0.2 mL, which were pre-equilibrated with 0.5 M HCl. After being loaded on the column in 0.5 mL of 0.5 M HCl, Te was collected in 2 mL of 0.5 M HCl. Indium was loaded on the column in a fashion similar to that of Te. However, an extra 0.5 mL of 2.5 M HCl was also used to collect In.

Table 2. Trace Element Concentrations of Mid-ocean Ridge Basalts

Sample	Rb	Sr	Y	Zr	Nb	Cs	Ba	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Yb	Lu	Hf	Ta	Pb	Th	U	
AH127 D1-5	0.39	98	31	78			3.9	1.83	6.26	1.26	7.09	2.69	1.02	3.97	0.75	4.95	1.08	3.1	3.09	0.48						
AH127 D5-5	0.67	83	17	37	1.3		8	1.24	3.76		3.7	1.5														
AH127 D8-2	0.68	87	20	43	1.5	0.01	6.2	1.86	5.18	0.89	4.72	1.69	0.69	2.47	0.48	3.14	0.7	1.97	1.97	0.33	1.18	0.1	0.14		0.04	
AH127 D11-1	3.02	90	23	59	8	0.05	42.5	4.74	10.9	1.57	7.46	2.29	0.82	3.07	0.59	3.79	0.84	2.35	2.34	0.39	1.67	0.5			0.03	
AH127 D17-3	18.8	295	19	85	28	0.24	244	16.7	32.6	3.96	16.2	3.55	1.19	4.12	0.64	3.79	0.76	2.04	1.94	0.31	2.31	1.48	0.84		0.59	
AH127 D21-3	23.3	405	29	194	36	0.25	258	23.7	47.6	6.17	25.2	5.49	1.81	5.94	0.92	5.16	1.13	2.68	2.49	0.4	4.31	2.08				
AH127 D22-5	20.5	282	27	148	32	0.22	235	20.4	40.0	5.09	20.7	4.49	1.51	5.06	0.83	4.64	1.12	2.54	2.43	0.39	3.43	1.81	1.19		0.6	
AH127 D26-5	3.98	94	31	81	7	0.04	47	4.96	11.7	1.85	9.11	2.92	1.01	4.03	0.78	4.97	1.23	3.08	3.1	0.51	2.12	0.43	0.49		0.14	
AH127 D27-5	7.53	134	25	84	12	0.08	82.6	7.69	17.2	2.3	10.4	2.85	1	3.64	0.68	4.12	1.14	2.51	2.44	0.41	2.06	0.69	0.92		0.22	
AH127 D15-1	4.64	104	24	56	8.7	0.05	60	5.24	11.4	1.64	7.74	2.34	0.86	3.01	0.59	3.86	0.87	2.44	2.46	0.41	1.7	0.51	0.41		0.16	
JDF D2-2		116	48	158			22		19.1		15.4	5.18	1.7	7.01		8.29			4.95							
VNTR11-2		83	26	58			4.2																			
VNTR23-8		219	37	185			37.7																			
VNTR27-11		111	31	91			6.9																			
Sonne 12 42 a		104	37	89				3.5	10.6		10	3.6	1.21	4.6	0.9		1	4	4	0.56	2.6	0.13				
VE33 D10-10		142	25	83			14.9	3.24	9.21		7.66	2.6	0.97	3.53		4.36		2.7	2.46							
V33D04-54		110	34	104			3.7	3	10.4		9.64	3.52	1.33	4.8		5.45		3.57	3.24							
KH93-3 D1-B2	1.5	153	31	103	3.4	0.02	17.4	4.03	11.5	1.89	10.1	3.24	1.18	4.49	0.76	5.08	1.08	3.11	2.98	0.44	2.44	0.21	0.67	0.23	0.07	
KH93-3 D2-A3g	0.84	114	38	112	1.9	0.01	10	3.62	11.6	2.02	11.6	3.78	1.39	5.44	0.94	6.26	1.37	3.93	3.72	0.56	2.9	0.13	0.73	0.14	0.04	
KH93-3 D3-B2	0.47	120	32	88	1.1	0.01	6.3	2.64	8.85	1.57	8.81	3.02	1.17	4.45	0.79	5.3	1.14	3.2	3.19	0.46	2.31	0.08	0.52	0.09	0.02	
KH93-3 D6-A3	0.91	131	31	89	1.7	0.01	11.9	2.77	8.96	1.61	8.72	3.01	1.15	4.32	0.75	4.96	1.07	3.1	2.92	0.44	2.21	0.12	0.54	0.13	0.04	
KH93-3 D6-B2	0.96	123	25	71	1.6	0.01	13.3	2.48	7.61	1.33	7.26	2.48	0.93	3.48	0.6	4.09	0.87	2.48	2.38	0.36	1.76	0.12	0.49	0.13	0.04	
KH93-3 D9-F1g	0.85	102	41	114	1.7	0.01	10.7	3.52	11.5	2.06	11.8	4.13	1.42	5.72	1.02	6.64	1.45	4.14	4.03	0.6	3.07	0.14	0.72	0.14	0.04	
KH93-3 D9-G2	0.82	102	41	113	1.7	0.01	10.1	3.49	11.5	2.04	11.5	4.01	1.49	5.6	1.01	6.65	1.45	4.1	3.87	0.6	2.99	0.13	0.72	0.14	0.04	
KH93 RCO2-sed-g	0.72	132	24	68	1.4	0.01	9.5	2.38	7.48	1.27	7.04	2.28	0.92	3.32	0.58	3.87	0.85	2.39	2.27	0.36	1.72	0.1	0.46	0.11	0.03	
KH93 RCO9-H	1.64	155	25	94	2.9	0.02	18.6	3.54	10.1	1.61	8.73	2.87	1.12	4.05	0.68	4.44	0.9	2.45	2.27	0.34	2.3	0.18	0.52	0.21	0.06	
ANTP 131-14*	0.44	109	26	74	1.4		7.11	2.56																		

Concentrations are in ppm. All glassy except as indicated otherwise. See Table 1 for data sources. Blank indicates data are not available.

\*Not glassy.



**Table 4.** Cd, In, Sn, Te, S, and Trace Transition Metal Concentrations in Submarine Lavas

Sample	V, ppm	Cr, ppm	Co, ppm	Ni, ppm	Cu, ppm	Zn, ppm	Cd, ppb	In, ppb	Sn, ppm	Te, ppb	S, ppm
<i>Mid-Atlantic Ridge</i>											
AII127 D1-5							123	63	1.01	2.33	880
AII127 D5-5							79	47	0.49	5.31	1050
AII127 D8-2							100	56	0.46	4.92	970
AII127 D11-1							113	60	0.71	4.9	1220
AII127 D17-3							102	50	0.83	0.83	460
AII127 D21-3							129	68	1.62	1.92	1000
AII127 D22-5							118	66	1.16	1.65	1220
AII127 D26-5							127	74	0.96	3.07	995
AII127 D27-5							109	60	0.78	3.15	800
AII127 D15-1							117	60	0.62	1.25	725
<i>Juan de Fuca</i>											
JDF D2-2	350	83		58	72		171	97	1.35	1.49	1690
<i>East Pacific Rise</i>											
MW8712-87-6							167	100	1.51	2.98	1570
R-82-1							108	52	0.58	6.2	1360
R-93-7							113	59	1.01	4.06	920
R-94-2							138	69	1.09	2.09	1010
VNTR11-2	251	379		138	77	70	86	56	0.58	4.91	950
VNTR23-8	280	226		92	70	79	134	74	1.52	3.27	
VNTR27-11	294	371		94	76	74	155	83	1.15	1.92	1150
<i>Pacific-Cocos-Nazca Triple Junction</i>											
Sonne12 42 a		277	43	109			120	68	0.83	3.99	950
<i>Australian-Antarctic Discordance</i>											
VE33 D10-10	219	375		119	63		118	51	0.72	3.11	920
V33D04-54	315	271		76	62	100	159	57	1.17	1.82	1410
<i>Indian Ocean</i>											
KH93-3 D1-B2	250	323	37	113	66	67	106	61	0.76	2.6	1070
KH93-3 D2-A3g	288	252	40	105	57	82	123	73	0.87	1.6	1240
KH93-3 D3-B2	248	366	39	121	61	71	110	61		2.2	1320
KH93-3 D6-A3	241	320	39	130	91	70	107	60	0.7	3.9	1250
KH93-3 D6-B2	215	381	40	146	76	63	95	52	0.55	4.1	1230
KH93-3 D9-F1g	296	218	39	91	54	88	132	78	0.9	1.2	1300
KH93-3 D9-G2	288	215	39	95	53	87	129	77	0.89	1.3	1330
KH93 RC02-sed-g	210	372	40	130	70	59	93	48	0.49	2.7	1090
KH93 RC09-H	183	319	40	136	83	78	104	62	0.78	2.4	840
ANTP 131-14	239	330	46	119	79	66	99	54	0.58	3.8	970
<i>Galapagos</i>											
PL02 24-32							123	84	1.39	4	1150
PL02 25-1							150	89	1.97	1.44	1160
PL02 30-1							111	60	0.9	7.45	1000
<i>Loihi</i>											
158-4							157	91	1.93	7.45	2320
187-1				1356	171		106	70	0.81	29.2	1640
187-8				265	109		124	91	1.31	12.0	1580
1801-22	371	397	50	122	128	112	126	83	1.21	8.05	1540
1802-4A	428	27	44	80	130	130	131	84	1.3	8.07	1600
1804-1	331	710	57	222	162	109	117	78	0.99	18.8	1820
D2-11							161	93	1.26	8.47	2400
D3-2							136	71	0.97	15.7	1880
D4-6							132	89		4.97	2140
D5-1							156	96	1.34	13.4	1300
<i>Mariana Arc</i>											
1883.5							114	44	0.68	3.6	120
1885.6							102	48	0.92	2.51	110
77kk15161							120	74	1.12	2.28	50
ALV1846.9							94	36	0.56	4.9	370
ALV1846.12							110	53	0.9	6.22	930

See Table 1 for additional data sources. Blank indicates data are not available.

chemistry literature [e.g., *Thirlwall*, 1997], and it is probably more practical to maintain the term standard deviation.

### 3. Results

#### 3.1. Concentrations of Cd, In, Sn, Te, and S in Basalt Glasses

The Cd concentrations for Atlantic, Pacific, and Indian MORB are nearly identical with means of  $112 \pm 15$  ppb,  $132 \pm 29$  ppb, and  $110 \pm 14$  ppb (Table 4). The Cd concentrations reported here are similar to the sparse literature data of *Laul et al.* [1972] and *Hertogen et al.* [1980]. Basaltic glasses from Loihi and Galapagos seamounts also have very similar Cd concentrations ( $133 \pm 18$  ppb) to MORB glasses ( $119 \pm 22$  ppb), as do submarine glasses from the Mariana arc ( $108 \pm 10$  ppb). These extremely small standard deviations are unmatched by those of any other incompatible elements except the heavy rare earths in OIB which also maintain very uniform concentrations through a range of samples, presumably because garnet maintains the bulk distribution coefficient close to unity [*Halliday et al.*, 1995a]. However, in the case of Cd, all basalts show the same effect despite a wide range of tectonic settings, magma types, and degrees of partial melting in the mantle. This immediately indicates that submicroscopic discrete sulfides, if they are present in our samples, have no effect on the Cd budgets. It also requires that the Earth's upper mantle is globally homogeneous in Cd concentration. Furthermore, either the degree of partial melting is approximately constant, which seems highly unlikely, or the bulk distribution coefficient for Cd must stay relatively close to unity (certainly  $> 0.01$ ) throughout the melting interval. The Cd concentration may be buffered by the presence of a minor phase such as a sulfide during melting. However, the arc environment does not appear to fractionate Cd significantly, which is surprising given the more strongly oxidizing conditions expected to be associated with magma generation. An alternative explanation is that all the silicates have generally similar mineral/melt distribution coefficients of  $>0.01$  for Cd.

Indium concentrations in MORB (Table 4) are similar (47–73 ppb) to the concentrations reported by *Laul et al.* [1972] (57–75 ppb) and by *Hertogen et al.* [1980] (44–99 ppb). The In concentrations in Loihi seamount (70–96 ppb) are similar to those in subaerial OIB reported by *Yi et al.* [1995]. Submarine lavas from Mariana arc and back arc trough also display similar In concentrations (Table 4). As with Cd, the overall variation of In concentrations is very limited. In our data set, In concentrations in Loihi submarine lavas ( $85 \pm 9$  ppb) are only slightly higher than those in MORB ( $61 \pm 7$  ppb). There seem to be no apparent differences between the In concentrations in the MORB from different oceans. As with Cd, the overall degree of variability in In in submarine basaltic glasses is small compared with most incompatible trace elements [*Halliday et al.*, 1995a], implicating a very uniform concentration in the mantle and bulk distribution coefficient close to unity. Again, this may be the result of being buffered by a minor phase such as sulfide present throughout the melting interval or indicate that all the phases that dominate the incompatible element budget (garnet and clinopyroxene) have similar mineral/melt distribution coefficients for In.

Tin concentrations (Table 4) in the submarine lavas measured in this study ( $1.00 \pm 0.37$  ppm) are similar to those reported by *Jochum et al.* [1993] and *Yi et al.* [1995]. There is no distinction between the range of Sn concentrations in the sub-

marine lavas from Loihi seamount and those of MORB. However, submarine lavas from Loihi seamount have, on average, higher Sn concentrations. Several evolved submarine basaltic and andesitic lavas from Mariana arc and back arc trough display Sn concentrations similar to submarine lavas from Loihi seamount. Tin is more variable than In or Cd and is more strongly fractionated by melting.

Tellurium concentrations are more variable than those of Cd, In, or Sn (Table 4). The range for East Pacific Rise (EPR), MAR, and Indian MORB glasses is similar ( $3 \pm 1$  ppb), but Te is much higher in submarine glasses from Loihi seamount ( $13 \pm 7$  ppb, ranging up to 29 ppb). One of the basaltic glasses from the Galapagos has Te concentrations similar to those of MORB glasses, but the other two are substantially enriched relative to MORB with the same MgO content, though not as enriched as the Loihi glasses. Submarine glasses from Mariana also have similar Te concentrations to those of MORB glasses ( $4 \pm 2$  ppb).

Like Te, the concentrations of S in submarine glasses are variable, ranging from 50 to 2400 ppm (Table 4). MORB glasses have S concentrations (range of 460–1690 ppm, mean of  $1096 \pm 256$  ppm,  $n = 30$ ), comparable to previously published data for other MORB glasses [*Wallace and Carmichael*, 1992]. The mean concentrations are broadly similar in each ocean basin as follows: Atlantic,  $932 \pm 230$  ppm,  $n = 10$ ; Pacific,  $1200 \pm 303$  ppm,  $n = 8$ ; Indian,  $1164 \pm 164$  ppm,  $n = 10$ . (These numbers exclude the Australian-Antarctic Discordance (AAD) data.) Glasses from Loihi seamount have higher S concentrations (range of 1300–2400 ppm, mean of  $1822 \pm 362$  ppm,  $n = 10$ ), whereas glasses from Galapagos seamount (range of 1000–1160 ppm, mean of  $1103 \pm 90$  ppm,  $n = 3$ ) have S concentrations comparable to the MORB glasses. Glasses from Mariana have the lowest S concentrations among the submarine glasses (range of 50–930 ppm).

#### 3.2. Comparisons Between Submarine and Subaerial Basalts and Evidence for Chalcophile Element Degassing

Overall, the Cd concentrations in subaerial basalts (Table 5) are more variable than in submarine basalts but with a similar mean ( $115 \pm 60$  ppb), possibly reflecting a more diverse range of magma types. However, this is a distorted picture. With the exception of a few enriched magmas (such as nephelinites) from the Cameroon line, Trinitade and Fernando de Noronho, the Cd concentrations in subaerial OIB are generally somewhat lower than in MORB and OIB glasses (Table 4). The In concentrations in Loihi seamount (70–96 ppb) are similar to those in subaerial OIB [*Yi et al.*, 1995], although the subaerial types are, in general, more enriched in incompatible elements [*Halliday et al.*, 1995]. Clearly, degassing does not affect In greatly but may cause some loss of Cd. Although Sn concentrations in subaerial basalts are very sensitive to alteration [*Jochum et al.*, 1993; *Yi et al.*, 1995], the data for subaerial lavas are comparable to those for submarine OIB glasses.

In contrast to Cd, In, and Sn it is well known that S is strongly degassed from subaerial OIB [*Wallace and Carmichael*, 1992], and so we have not analyzed these samples for S. A similar effect is found for Te. Tellurium concentrations in subaerial OIBs are mostly  $<1$  ppb (Table 5). This almost certainly reflects shallow degassing and the transport of Te into the walls of magma chambers. There is a tendency for Te to be higher in more enriched subaerial OIB. Some highly enriched Atlantic OIB (such as nephelinites) may have formed by small degrees of partial melting at high pressure and their generation

**Table 5.** Concentrations of Cd and Te in Subaerial OIB Lavas

Sample	Cd	Te
<i>Cameroon Line</i>		
AN7BM	115	0.43
C-25	107	0.55
FP-1	268	2.2
<i>Ascension</i>		
AS-1	139	0.24
<i>Azores-Pico</i>		
AZP-5	56	0.45
AZP-6	94	0.16
AZP-7	60	0.14
AZP-8	52	
<i>Iceland</i>		
CX-11 1	71	1.1
CX-19 2	103	0.76
<i>Easter Island</i>		
Easter 17678	90	0.22
Easter 17736	115	0.33
Easter 17736	113	0.24
<i>Fernando de Noronha</i>		
FDN-25	113	3.2
FDN-55	324	1.60
FDN-72	97	0.77
FDN-20	104	15
<i>Madeira</i>		
M-4	108	0.27
M-10	119	1.1
M-32	83	0.19
M-40	80	0.61
M-64	138	0.31
<i>Hawaii</i>		
Moiiliili flow	122	0.48
<i>Trinidad</i>		
TD-3	46	0.52
TD-4	235	2.6
<i>Tristan</i>		
Tristan 13	90	0.48
Tristan 167	96	0.65
Tristan 567	107	0.52

Concentrations are in ppb. See Halliday *et al.* [1995a] and Yi *et al.* [1995] for major and additional trace element data.

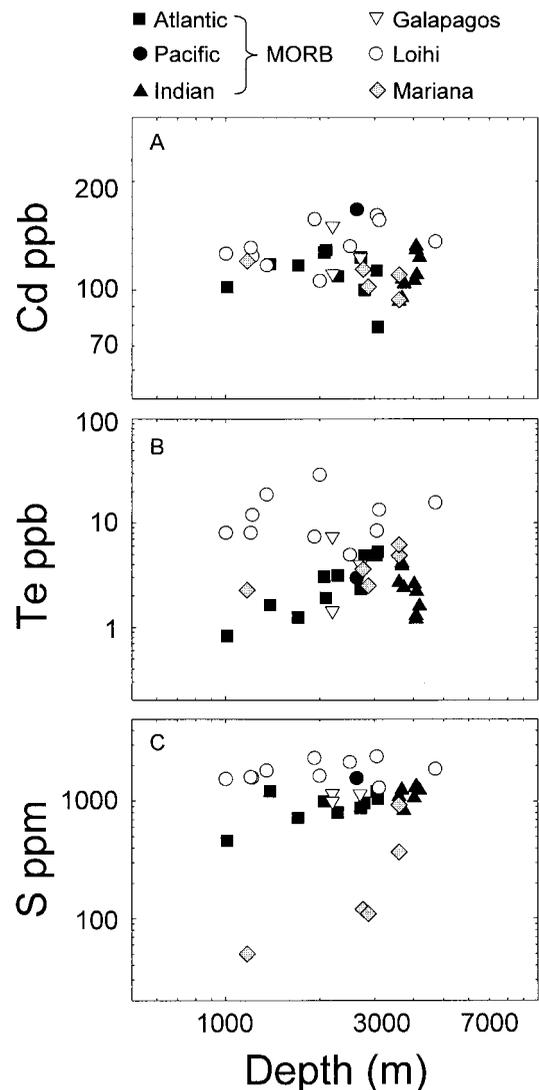
may have involved the formation of a free vapor phase into which Te might preferentially partition [Wyllie, 1988; Halliday *et al.*, 1992], but this is speculative.

The depth at which submarine degassing occurs varies greatly between different species. H<sub>2</sub>O, CO<sub>2</sub>, S, halogens, and other volatiles have long been recognized as being degassed from magmas at shallow levels, even in quenched submarine glasses [Moore and Fabbi, 1971; Moore and Schilling, 1973; Mathez, 1976; Garcia *et al.*, 1979], and this is generally believed to be controlled by ambient pressure. However, it is believed that S and H<sub>2</sub>O are not significantly degassed at water depths >1000 m at mid-ocean ridges, although CO<sub>2</sub> may be degassed at even greater depth [Moore and Fabbi, 1971; Moore and Schilling, 1973; Byers *et al.*, 1985; Dixon *et al.*, 1991]. Similarly, it has been shown that Cl and F are not significantly degassed from Icelandic MORB at water depths >500 m [Unni and Schilling, 1978; Rowe and Schilling, 1979].

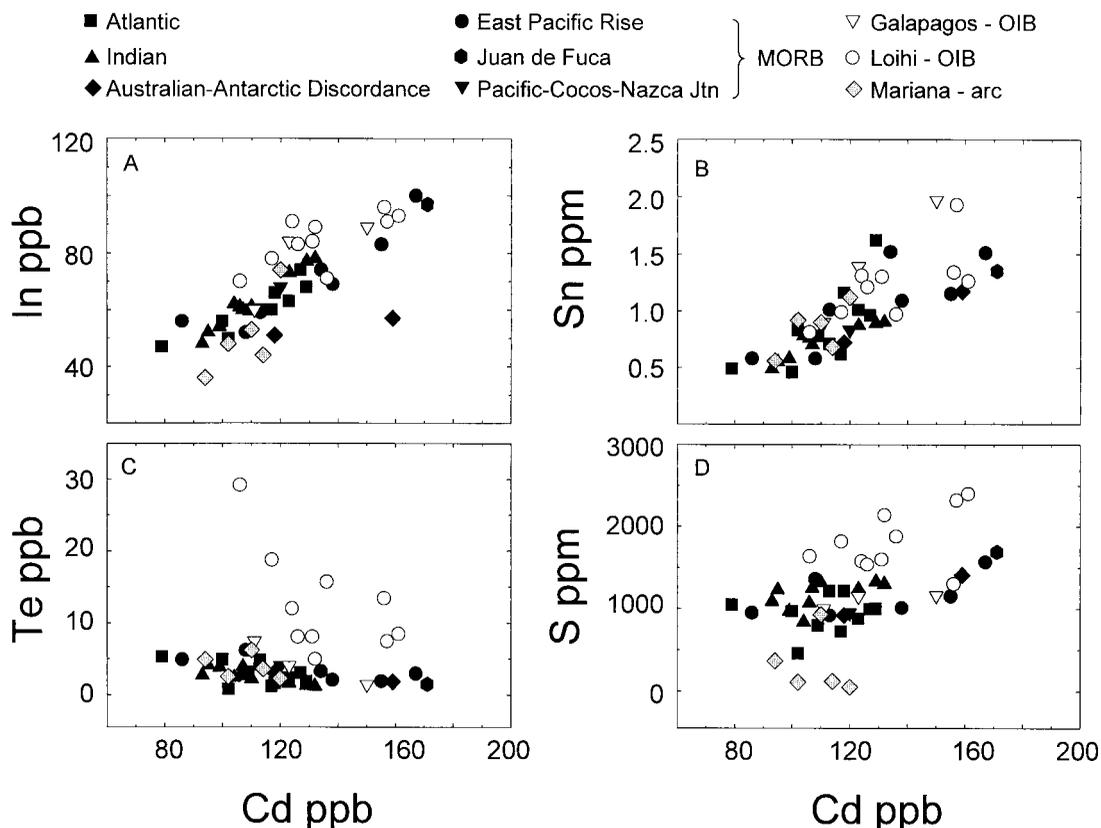
Although metals, including Cd, In, Sn, and Te, can be flushed out of magma systems by a degassing vapor phase

[Symonds *et al.*, 1988; Greenland and Aruscavage, 1986], it is unlikely that degassing has significantly affected the concentrations of these elements in most of the submarine basaltic glasses, as all the MORB investigated in this study were sampled at water depths >1000 m. In fact, Te displays an inverse correlation with depth in samples from the Indian Ocean, contrary to the effect that should be observed in a degassing situation (Figure 1). It is possible that some of the most volatile-rich glasses from the MAR have undergone some degassing. This may account for the very low Te contents in some enriched glasses from shallow depth (e.g., AII127-D17).

Byers *et al.* [1985] and Garcia *et al.* [1989] reported Cl and F data for submarine glasses recovered at water depths >1000 m from Loihi seamount. There is no simple correlation between Cl or F and depth. The glasses investigated in this study are either collected from same or greater depths than the glasses reported by Byers *et al.* [1985] and Garcia *et al.* [1989]. This, together with the evidence from Iceland [Unni and Schilling, 1978; Rowe and Schilling, 1979], lends confidence to the view that Loihi samples retain the original magmatic budgets of Te and S, as well as Cl and F.



**Figure 1.** (a) Cadmium, (b) Te, and (c) S plotted as a function of dredge depth for submarine basalts.



**Figure 2.** (a) Indium, (b) Sn, (c) Te, and (d) S plotted against Cd in submarine basalts.

Deeper glasses from Mariana tend to have much higher S contents, consistent with the conclusion that many Mariana arc glasses represent magmas that have experienced significant amounts of degassing [Alt *et al.*, 1993]. This is also supported by the observations that all the Mariana arc glasses are highly vesiculated and sulfide condensates are found on the walls of these vesicles [Alt *et al.*, 1993]. In contrast, submarine glasses from the Mariana back arc trough do not show such petrographic evidence of S degassing. There is no clear correlation between Te and S in these Mariana samples, and Te is not depleted in arc glasses relative to MORB glasses. This demonstrates that Te may not be affected by degassing to the extent of S.

### 3.3. Relationships Among Cd, In, Sn, Te, and S in Basalt Glasses

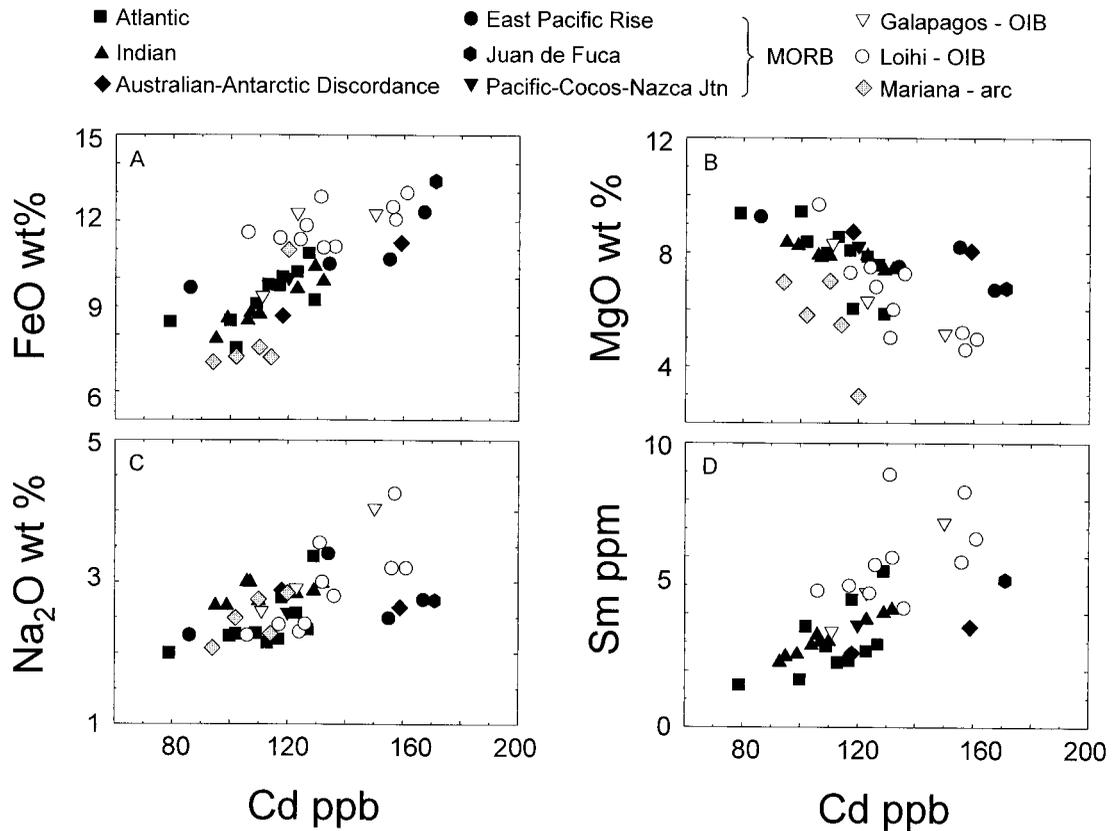
From the above it would appear that Cd and In concentrations in basalts vary only by a factor of  $\sim 2$ , Sn is somewhat more variable, Te can be highly enriched in submarine OIB, and S can be strongly depleted by degassing in IAB. These differences in behavior are paralleled by the degree of covariation among these elements. The concentrations of In and Sn are highly correlated with those of Cd, despite the limited range of concentrations (Figures 2a and 2b). Cadmium, In, and Sn concentrations increase with the concentrations of moderately incompatible elements such as Ti, Zr, and Sm (Figures 3d, 4a and 4b) but decrease with Mg (Figure 3b). MORB and OIB display highly variable (order of magnitude) enrichments and depletions in the highly incompatible elements Ba, U, K, La, and Ce (Tables 2 and 3), but no correlation is found

between these elements and the concentration of Cd, which varies by a factor of just 2 (Table 4).

There is a tendency for In/Cd to increase with In concentration, suggesting that In may be slightly more incompatible than Cd (Figure 5a). However, the only individual suite that displays such an effect is that from the Mariana arc. Samples with higher Sn and Cd have higher Sn/Cd ratios (Figure 5b), consistent with a lower bulk (mineral/melt) distribution coefficient for Sn than for Cd (or In). These results are consistent with previous interpretations of the relative degree of incompatibility of these elements [Sun, 1982; Jochum *et al.*, 1993; Yi *et al.*, 1995].

OIB and IAB are enriched and depleted, respectively, in Ti for a given Cd concentration, relative to MORB (Figure 4a). This is not surprising if OIB are the product of slab recycling [Chase, 1981; Hofmann and White, 1982; Ringwood, 1982]. In contrast, there is little distinction between the Cd, In, and Sn concentrations observed in different tectonic settings and therefore no sign that the processes of subduction and arc volcanism strongly fractionate these elements. Some arc basalts display a slightly lower In/Cd ratio (down to 0.4) than MORB for a given Cd concentration, but the effect is small (Figure 5a). Similarly, some OIB display a slightly higher In/Cd ratio (up to 0.8) than MORB for the same Cd concentration (Figure 5a). Tectonic setting appears to have no bearing on Sn-Cd relations (Figure 5b).

Among the major elements, Fe is positively correlated with Cd (Figure 3a). Sodium does not show such a clear trend (Figure 3c). In general terms, the concentration of Fe is ex-

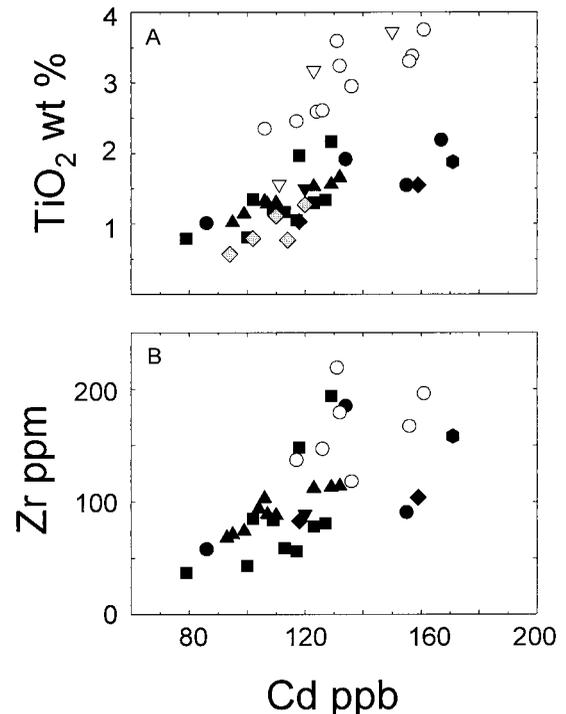


**Figure 3.** Cadmium plotted against (a) total Fe (calculated as FeO), (b) MgO, (c) Na<sub>2</sub>O, and (d) Sm. Cadmium displays a positive correlation with major elements FeO and Na<sub>2</sub>O and the moderately incompatible lithophile element Sm and an inverse correlation with MgO.

pected to be higher in basaltic liquids generated at greater depth [Klein and Langmuir, 1987]. A correlation between the S and Fe content of basalts was noted previously [Haughton *et al.*, 1974; Mathez, 1976; Wallace and Carmichael, 1992]. A similar effect is found here. There are overall correlations between the Cd, Fe, and S contents of basalts (Figures 2d, 3a, and 6b). However, in a given setting, certain of these relationships break down. For example, the Loihi, Galapagos, Mariana, and MORB data sets, on their own, display no correlation between Cd and S (Figure 2d). The same is true of the Fe-S relations (Figure 6b). Although Cd and Fe are correlated in MORB, there is no correlation for Loihi (Figure 3a). As with Ti, the Fe content of OIB is systematically high and the Fe content of IAB is systematically low relative to MORB (Figure 3a).

The uniformity of Cd and to a lesser extent In concentrations implies that these elements can only be moderately or slightly incompatible ( $D > 0.01$ ). Garnet and clinopyroxene control the abundances of most incompatible lithophile elements during mantle melting. The variable concentrations of heavy REEs is an indication of the relative importance of these two phases in MORB and OIB melting. The fact that there is at most a small distinction between the concentrations of Cd and In in OIB and MORB (in contrast to the heavy REEs) indicates that these two phases exert either a negligible or a very similar effect on Cd and In partitioning.

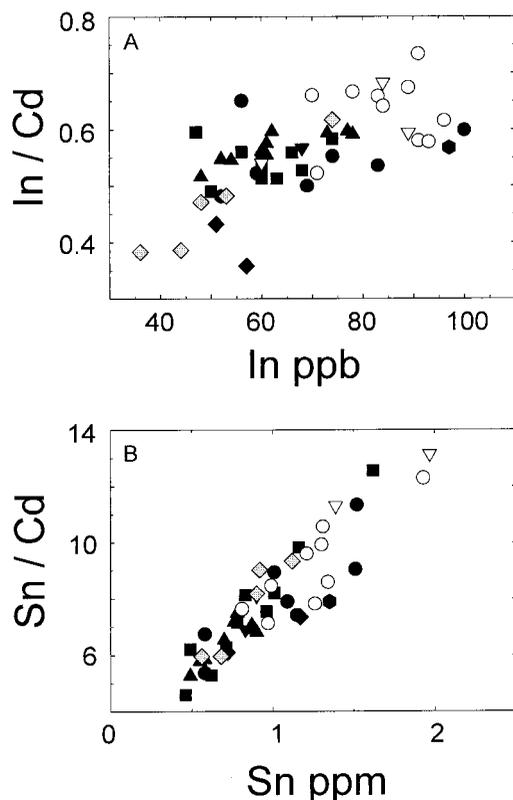
This is well illustrated by examining the ratios of Sn, In, or Cd to the middle and heavy REEs or Y. For example, the ratio of In/Y is independent of the small variation in In and was



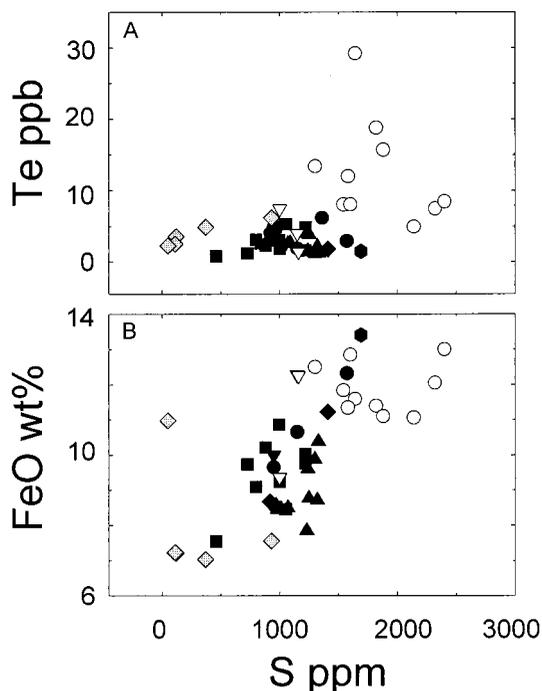
**Figure 4.** Cadmium displays positive correlations with the incompatible high field strength elements (a) TiO<sub>2</sub> and (b) Zr. Symbols are as in Figure 2.

therefore considered to provide evidence that In and Y are equally incompatible [Yi *et al.*, 1995]. However, the ratio of Y/In is positively correlated with the greater variability in Y resulting from garnet/clinopyroxene fractionation. Similarly, Sn/Sn shows a weak positive correlation with Sn even though the Sn/Sn ratio is independent of Sn [Jochum *et al.*, 1993; Yi *et al.*, 1995]. The same is found for Cd. The Dy/Cd ratio is positively correlated with Dy but displays no relationship with Cd (Figures 7a and 7b). This behavior of Cd relative to REEs is most extreme for Lu (Figures 7c and 7d). Lutetium is depleted in OIB relative to MORB, presumably because of greater garnet in the source of OIB magmas [Hofmann and Jochum, 1996]. So Lu/Cd correlates strongly with Lu but not with Cd (Figures 7c and 7d). These features can be explained if garnet and clinopyroxene have different partition coefficients for the middle and heavy REE but similar partition coefficients for Cd, In, and Sn.

However, there are clear complications that are well displayed by the relationships between In and Y (Figure 8). The Pacific and Indian MORB samples display a correlation between In and Y in which In varies a little less than Y. The same is true for Atlantic MORB but displaced to lower Y, possibly reflecting the garnet influence from the Azores hotspot. The Loihi lavas have the same range of Y as Atlantic MORB but are displaced to higher In. So most OIB have higher In/Y than MORB (Figure 8) but apparently not because of noticeable Y depletion. These relationships raise certain questions. Why



**Figure 5.** The relative incompatibilities of Cd, In, and Sn are illustrated in the standard plots of elemental concentration versus elemental ratio. There exist both positive correlations between In and In/Cd and between Sn and Sn/Cd, indicating that In and Sn are more incompatible than Cd. Symbols are as in Figure 2.

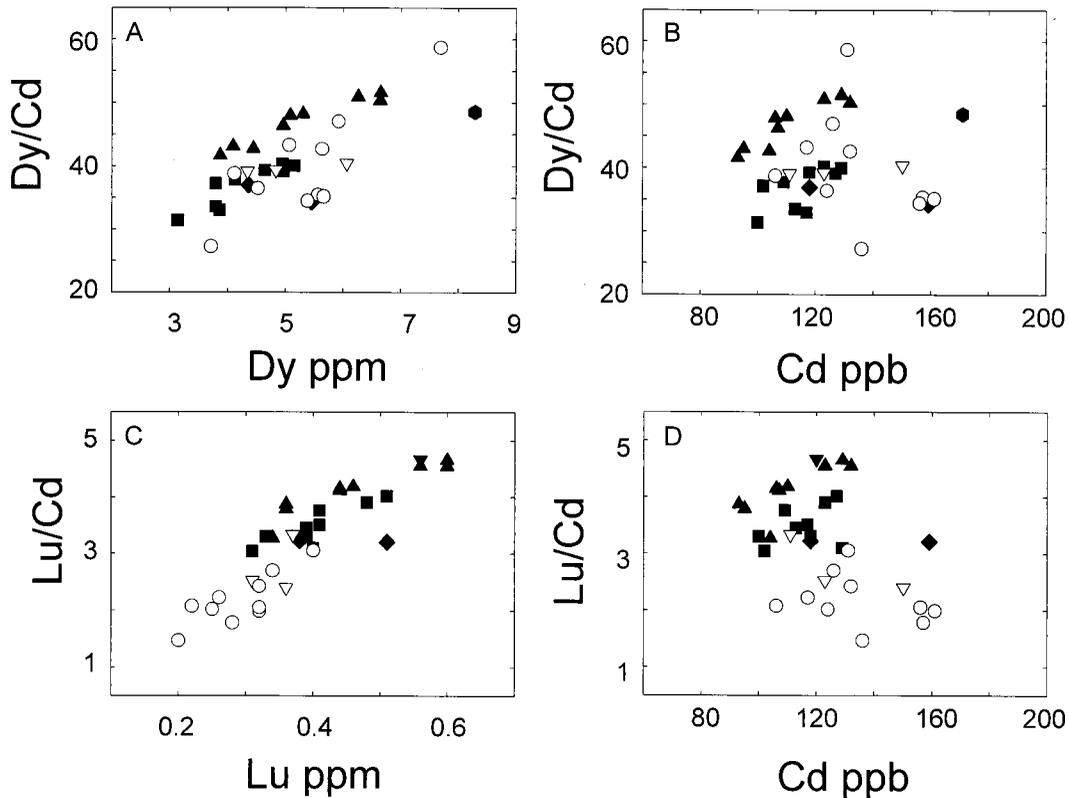


**Figure 6.** Sulfur versus (a) Te and (b) FeO\*. Overall, there is a positive correlation between S and Fe, but this breaks down at individual localities. There is no correlation between S and Te. Symbols are as in Figure 2.

does Y display a similar range in all of these magmatic suites if a garnet effect is important? Is this a result of combining a higher D for Y with a more enriched OIB source? Indium may, in fact, provide a better monitor of source enrichment because it is not sensitive to garnet versus clinopyroxene fractionation. However, the range for both elements is small. If the correlations between In and Y reflect partial melting and are displaced from each other by a garnet effect they should have distinct slopes but the data show no sign of this (Figure 8). An increased garnet effect should increase D and so reduce the degree of variability of Y relative to In. One explanation is that the trends between Cd and In on the one hand and the REEs and Y on the other reflect low-pressure differentiation and mixing rather than partial melting. The overall displacements between magma suites may indicate variable hot spot influence, together with the balancing effects of garnet partitioning versus source enrichment.

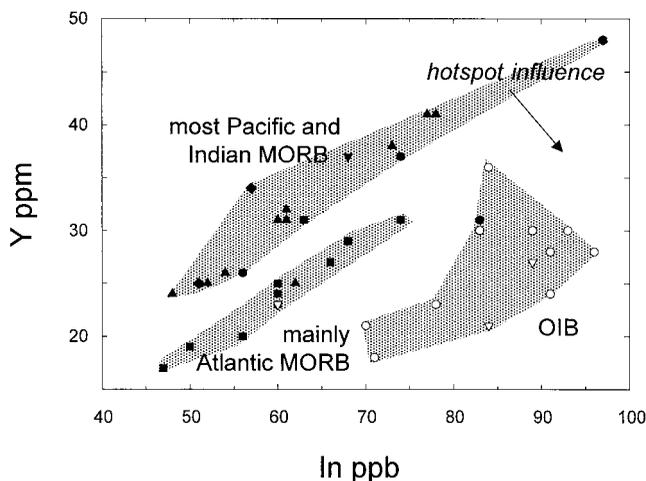
It is also possible that a minor phase attenuates and buffers the partitioning of the chalcophile elements Cd, In, and Sn. Despite poor correlations with S, the most likely candidate for this phase would be sulfide. Ubiquitous minor sulfide with a sulfide liquid/silicate liquid distribution coefficients for Cd and In slightly higher than unity might explain why Cd and In are so uniform in basalts. Sulfides are ubiquitous in basalts, indicating sulfide saturation. Sulfide is widespread in depleted peridotites, indicating that it is not entirely consumed in melting processes. Sulfide is likely to affect both Sn and Pb abundances as well and this has been invoked as an explanation for Pb depletions at small degrees of partial melting [Halliday *et al.*, 1995a].

Tellurium and S behave very differently from Cd, In and Sn (Figures 1b, 2c, and 6a). Tellurium is highly variable and en-



**Figure 7.** Dy/Cd versus (a) Dy and (b) Cd and Lu/Cd versus (c) Lu and (d) Cd. The ratio Dy/Cd does not correlate with Cd for submarine glasses but is positively correlated with Dy. This is also the case for Cd and Lu. For a given Cd concentration, Lu displays lower values (high Cd/Lu) in Loihi lavas, perhaps a result of garnet in the Loihi source region [see *Blundy et al.*, 1998]. Symbols are as in Figure 2.

riched in OIB. However, in MORB and arc basalts, Te decreases with increasing Cd concentrations (Figure 2c). This behavior is similar to that reported for Os [*Hauri and Hart*, 1993; *Roy-Barman and Allègre*, 1995; *Schiano et al.*, 1997]. Osmium is sulfide-controlled and behaves as a compatible element in MORB but is enriched in OIB relative to MORB. Sulfur is also enriched in OIB relative to MORB but less dramatically than Te. The correlations between S and Te are

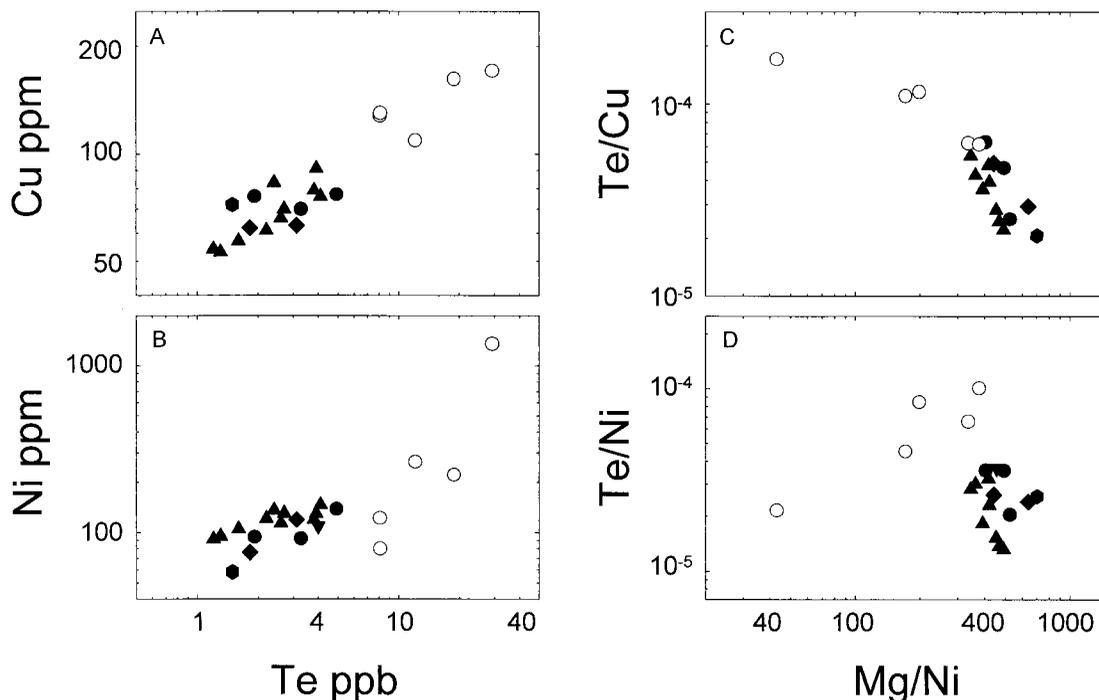


**Figure 8.** Indium versus Y showing the subparallel trends defined by separate MORB and OIB suites. Symbols are as in Figure 2.

not strong, even ignoring the data for arc basalts thought to be affected by degassing (Figure 6a). In contrast to Cd, Te shows no relationship, positive or negative, with Fe (Figure 6b), Mg, or Sn (not shown). Similarly, Te shows no relationship with the light and middle rare earth elements but is negatively correlated with the heavy rare earths. This is partly an artifact of plotting Te-rich, HREE-depleted OIB and MORB-like magmas. It is not clear that there is any functional relationship between Te and the rare earths. However, Te is strongly correlated with Cu and, to a lesser extent, with Ni (Figures 9a and 9b). This might seem surprising since Cu is considered to be incompatible during mantle melting, whereas Ni is thought to be highly compatible. However, Cu is known to be strongly partitioned by sulfide [*Czamanske and Moore*, 1977]. The Te/Cu ratio shows a very clear and systematic relationship with Mg/Ni (Figure 9c). Tellurium has been previously considered to be closely related to sulfide during the generation of basaltic magmas based on a positive correlation between Te and Se in MORB [*Hertogen et al.*, 1980]. Sulfide fractionation during the melting and crystallization of basaltic liquids appears to be dominating the budgets for Te, Se, and Cu, not by buffering the concentrations during melting, as may be happening with Cd and In, but by strongly controlling the concentrations during differentiation of the magmas.

#### 4. Cadmium, Indium, Tin, Tellurium, and Sulfide Fractionation

Sulfide globules are found in dredged basaltic glasses and in glass inclusions enclosed in olivine phenocrysts for a variety of



**Figure 9.** Tellurium versus (a) Cu and (b) Ni, (c) Te/Cu versus Mg/Ni, and (d) Te/Ni versus Mg/Ni. This group of diagrams illustrates the importance of concomitant segregation/assimilation of Cu-bearing sulfide and fractional crystallization/accumulation of olivine on the Te budgets of basaltic magmas.

oceanic basalts, indicating that sulfide liquids coexisted with silicate melts [Moore and Fabbi, 1971; Moore and Schilling, 1973; Mathez, 1976; Czamanske and Moore, 1977; Wallace and Carmichael, 1992]. Sulfide liquids are much denser than silicate melts so that if they are of sufficient size, sulfide globules are easily segregated. These sulfide liquids, even though not in large quantities (<0.01% by volume [Czamanske and Moore, 1977]), could have a profound effect on elements such as the platinum group elements [Garuti et al., 1984; Hamlyn et al., 1985; Stone et al., 1990; Peach et al., 1990; Rehkämper et al., 1999] and Te [Greenland and Aruscavage, 1986]. The formation of immiscible sulfide liquids is largely dictated by the solubility of sulfur in the silicate melts. It has been shown that S solubility is generally controlled by Fe concentration in basaltic magmas, although other factors like temperature and  $f_{O_2}$  are also important [Haughton et al., 1974; Mathez, 1976; Wallace and Carmichael, 1992]. This is confirmed in this study, as illustrated by the overall positive correlation between Fe and S (Figure 6b). Submarine lavas from Loihi seamount appear to deviate from the correlation to higher S. This may be the result of increased S solubility due to a higher temperature in the Hawaiian plume or selective incorporation of volatiles at Loihi [Garcia et al., 1989]. Because the majority of S is dissolved in basaltic magmas as sulfide [Carroll and Rutherford, 1988; Wallace and Carmichael, 1992] in all settings, it is unlikely that this enrichment reflects higher  $f_{O_2}$  in Loihi.

Copper is exclusively partitioned into sulfide [Czamanske and Moore, 1977] and the positive correlation between Te and Cu (Figure 9a) probably indicates Cu-bearing sulfides as the primary Te host phases. In contrast, Ni concentrations are primarily affected by fractional crystallization of olivine in a differentiating magma. Therefore the positive correlation between Te and Ni (Figure 9b) most likely reflects proportional

segregation of sulfide concomitant with fractional crystallization of olivine, rather than partitioning of Te and Ni into the same phase. The platinum group elements (PGEs) provide strong supporting evidence for this [Rehkämper et al., 1999]. Tellurium appears to be inversely correlated with Cd (also with In and Sn) for submarine lavas from specific localities (Figure 2c), consistent with the lower Te concentrations in MORB than ultramafic xenoliths [Morgan, 1986] and Te being compatible during mantle melting.

A spectrum of immiscible sulfide liquids exists in basalts, ranging from monosulfide (high in Ni, referred to as Ni-bearing sulfide thereafter) to intermediate solid solution sulfide (high in Cu, referred to as Cu-bearing sulfide thereafter) [Czamanske and Moore, 1977]. It has been shown that Ni/Cu in an immiscible sulfide varies with Ni content in the coexisting magma [Czamanske and Moore, 1977]. Early sulfide assemblages have higher Ni/Cu. If Te partitioning is the same between Ni and Cu sulfide, Te would have been largely depleted in the magma before Cu-bearing sulfide started being segregated in significant amounts and Te would be largely unrelated with Cu. Therefore Te must have higher partition coefficients in Cu-bearing sulfide than in Ni-bearing sulfide, consistent with the stronger correlation between Te and Cu.

The partition coefficient ( $D$ ) of Te between Cu sulfide and basaltic magmas can be estimated to be  $>10^4$  using the correlation between Te and Cu (Figure 9a). For this we have to assume that nearly all of the Cu and Te that were segregated from the magma was partitioned into sulfide and that segregated sulfide remained in equilibrium with magma. Therefore, from our MORB data, about 6 ng Te was partitioned into sulfide that had 60  $\mu\text{g}$  of Cu. Given 30% to be the average Cu content in Cu-bearing sulfide [Peach et al., 1990], a Te concentration of 30 ppm in the sulfide can be calculated. Using a value

of 1 ppb of Te concentration in residual magmas, a Nernst partition coefficient  $D$  ( $D$  is concentration ratio of Te between sulfide and silicate melt) [Peach *et al.*, 1990] of  $3 \times 10^4$  can be deduced. A  $D$  of  $6 \times 10^4$  can be calculated if the Loihi lavas are used. Tellurium is more strongly partitioned into sulfide over silicate melts than Cu ( $D = 200$ – $1300$  [Prendergast and Keays, 1989; Peach *et al.*, 1990]). These values are very uncertain but the  $D$  values for Te appear to be similar to those for PGEs between sulfide and basaltic melt [Hamlyn *et al.*, 1985; Peach *et al.*, 1990; Stone *et al.*, 1990; Fleet *et al.*, 1991; Bezmen *et al.*, 1994; Rehkämper *et al.*, 1999]. These  $D_{\text{sulf/melt}}$  values estimated for Te are really maximum values; much lower values would be obtained if you assumed fractional rather than batch equilibrium during sulfide segregation. In basaltic systems we probably have an incremental batch equilibrium between sulfides and melt [Rehkämper *et al.*, 1999].

Sulfide segregation occurs both at mid-ocean ridges and in plume settings and is an inevitable consequence of fractional crystallization [Rehkämper *et al.*, 1999]. Fractional crystallization of olivine, clinopyroxene and plagioclase is common in MORB [Batiza and Niu, 1992]. The proportions of the mineral assemblage of fractionated crystals for MORB has been estimated to be plagioclase 62%, clinopyroxene 22%, and olivine 16% [Batiza and Niu, 1992] which would generate Fe enrichment in the magmas. Using only olivine and plagioclase with a proportion of 3:10 as a fractionating assemblage, Mathez [1976] predicted that MORB would be enriched and kept saturated in S along the fractional crystallization path, assuming a constant temperature for the magmas. There appears to be an inverse correlation between FeO and MgO for the MORB in this study (not shown), consistent with enrichment of Fe in these samples as a result of fractional crystallization [Byers *et al.*, 1983].

The petrogenesis of Loihi magmas has been the subject of debate [Moore *et al.*, 1982; Frey and Clague, 1983; Garcia *et al.*, 1989, 1993, 1995; Hauri *et al.*, 1996; Hofmann and Jochum, 1996]. However, most agree that fractional crystallization and accumulation of olivine have played a vital role in the evolution of Loihi lavas [Marsh *et al.*, 1991]. The MgO concentrations of Loihi glasses range from 4 to 10% (Table 1). These are too low to be primary and must be the result of fractional crystallization of olivine [Garcia *et al.*, 1995]. As with MORB, there appears to be an inverse correlation between FeO and MgO for the submarine lavas from Loihi seamount (Table 1), also reflecting an enrichment of Fe in the Loihi lavas. With the increase in Fe contents, S solubility in both MORB and Loihi lavas would also increase (Figure 6). The degree of fractional crystallization of MORB can reach 50%, while FeO content changes by only 30% [Weaver and Langmuir, 1990; Batiza and Niu, 1992]. The total FeO concentrations for Loihi glasses are quite uniform (11–13%), and 40–70% of fractional crystallization is thought to have affected the lavas from Loihi seamount [Garcia *et al.*, 1993, 1995]. With these changes in FeO content and magma volume, the concentration of S in the magmas, in both MORB and Loihi lavas, probably exceeds the solubility, resulting in the formation of immiscible sulfide. So the concentration of S in the magmas would increase with differentiation, but sulfide formation and removal would fractionate and deplete strongly chalcophile elements such as Te. Given the high partition coefficient of Te ( $\sim 10^4$ ) in sulfide, segregation of small amounts of Cu-bearing sulfide would have a major impact on Cu and Te concentrations but only a small effect on S budgets. This would lead to the positive correlation between Cu and Te (Figure 9a) but no correlation between either Te

and S (Figure 6a) or Cu and S. For other chalcophile elements, such as Cd, In, and Sn, the partition coefficients are smaller, and the impact of sulfide segregation is much less dramatic.

## 5. High Tellurium in OIB Magmas

Whereas the variations in Cd among submarine lavas are small implying a broadly uniform distribution in the mantle, Te concentrations in Loihi are anomalously high and variable. Given that Te and Cu are both depleted by sulfide fractionation, it is unclear why Loihi OIB should display this enrichment. Here we discuss possible explanations of this feature.

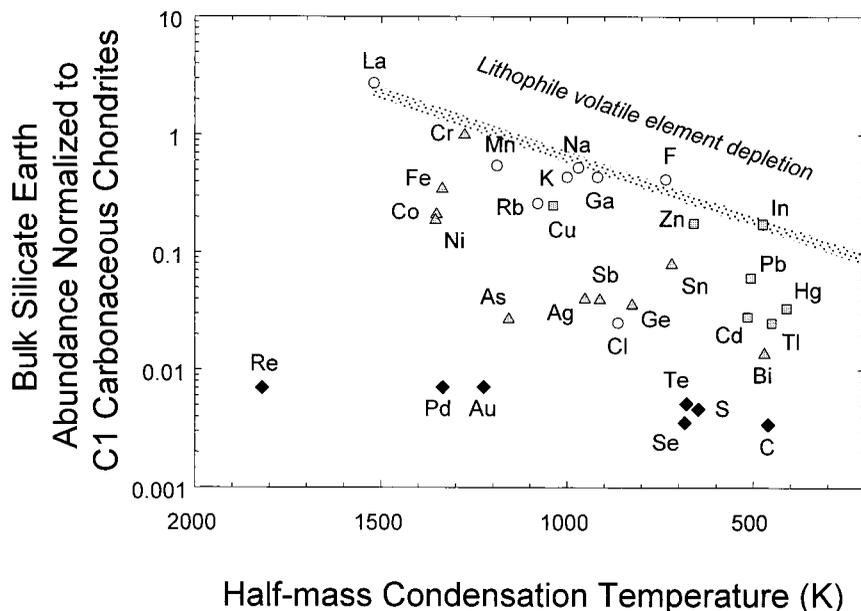
### 5.1. Differentiation of MORB

The abundances of highly chalcophile elements such as Te and PGEs in primary basaltic melts are largely dictated by the amounts of residual sulfide left in the source regions and by fractional crystallization and assimilation of sulfide-bearing cumulates. It is therefore conceivable that a greater percentage of sulfide was segregated from MORB (and other non-Loihi lavas) resulting in lower Te concentrations. PGE abundance data in MORB would be consistent with such segregation [Schiano *et al.*, 1997]. However, MORB is estimated to have experienced 30–50% of fractional crystallization [Weaver and Langmuir, 1990; Batiza and Niu, 1992], generally similar to that for Loihi lavas ( $>40\%$  [Garcia *et al.*, 1993, 1995]). Furthermore, the Cu concentrations cannot be reconciled with this model. It is estimated that about a third of the Cu in MORB has been lost by segregation of sulfide [Czamanske and Moore, 1977; Hamlyn *et al.*, 1985]. If this is true, no MORB in this study had an initial Cu content higher than 120 ppm, equivalent to an initial Te content  $<10$  ppb.

The relationships between the ratios of Mg/Ni and Te/Ni (Figure 9) can be used to calculate a more precise Te concentration of “primary MORB.” The ratios of Te/Ni for glasses from EPR are quite uniform ( $2$ – $3.5 \times 10^{-5}$ ), varying by a factor of  $<2$ , despite the 3.5-fold variation of Te (1.5–5 ppb). Given an average value of Te/Ni for EPR and AAD glasses of  $2.5 \times 10^{-5}$  and a concentration of 300 ppm Ni for primary MORB [Allègre and Minster, 1978; Tual *et al.*, 1985], a Te concentration of 7.5 ppb is calculated for primary MORB, consistent with the value  $<10$  ppb estimated from the correlation between Te and Cu. These values are comparable to the lower limit in Loihi glasses (8 ppb) (Table 4). Therefore the differences in Te between MORB and Loihi are not explicable by a greater degree of differentiation of MORB.

### 5.2. Higher Degrees of Melting in OIB or Less Residual Sulfide

MORB has been shown to be generated with a significant amount of residual sulfide such that the bulk of the PGE are left in the source regions [Helz, 1979; McGoldrick *et al.*, 1979; Mitchell and Keays, 1981; Roedder, 1981; Wendlandt, 1982]. Since Te has  $D$  values similar to those of PGEs, it is conceivable that MORB, and possibly arc lavas, are depleted in Te for the same reason. Moreover, the temperature of the Hawaiian plume is probably 100–200°C above the ambient values for the convecting upper mantle [Sleep, 1990; Eggins, 1992], resulting in increased S solubility and much higher MgO and Ni content in the primary melts of Loihi lavas (MgO, 15–16% [Eggins, 1992; Garcia, 1996; Garcia *et al.*, 1993, 1995; Rhodes, 1996], and Ni, 1000 ppm [Eggins, 1992]). The submarine lavas from Loihi have higher S ( $1822 \pm 362$  ppm) than not only MORB



**Figure 10.** Cl normalized [Anders and Grevesse, 1989] abundances of elements in the primitive mantle plotted against condensation temperature [Newsom, 1995]. Open circles, lithophile; shaded squares, chalcophile; shaded triangles, moderately siderophile; and solid diamonds, highly siderophile elements. Data are from this study, Yi *et al.* [1995], Newsom [1995], and McDonough and Sun [1995].

but also other Hawaiian volcanoes, interpreted as due to progressive melting and depletion of the source regions of the volcanoes at Hawaii [Garcia *et al.*, 1989]. If there is less residual sulfide left in the Loihi source region as a result of increased S solubility at higher temperatures, primary melts of Loihi lavas may have high initial Te concentration. If this is the case, an enrichment of PGEs in the Loihi lavas should also be observed, unless PGEs are depleted in the Loihi source.

Although scarce and limited to only Os, PGE concentrations for some Loihi lavas are indeed greater than those of MORB, indicating some degree of enrichment [Roy-Barman and Alègre, 1995; Hauri *et al.*, 1996; Schiano *et al.*, 1997]. However, the enrichment of PGEs in Loihi appears to be far less dramatic than is the enrichment of Te. So it is unlikely that this reflects partial melting. PGEs are quite uniform in all types of sulfide, being relatively enriched [Stone *et al.*, 1990; Bezmen *et al.*, 1994] or at least not depleted in Fe-Ni sulfide [Peach *et al.*, 1990] relatively to Cu-bearing sulfide. It could be argued therefore that the specific enrichment of Te in Cu sulfide is not paralleled by the behavior of the PGEs. So if Cu and Ni sulfides are segregated in different proportions, fractionation between Te and PGEs might occur. However, Cu-bearing sulfides are of relatively low abundance in fresh MORB glasses and in drilled gabbros from the oceanic crust [Peach *et al.*, 1990; Alt and Anderson, 1991]. Nickel-bearing sulfides are dominant at the early stage of magma differentiation and presumably during melting [Czamanske and Moore, 1977]. Therefore it is unlikely that Te was fractionated from the PGEs at the partial melting stage.

### 5.3. Core Entrainment

It is conceivable that some heterogeneity has been introduced via a plume into the upper mantle and is being tapped at Loihi. Several mechanisms are capable of generating such heterogeneity. Although recycled oceanic crust has been the

most widely cited as providing the sources for ocean island basalts [Chase, 1981; Hofmann and White, 1982; Ringwood, 1982], fresh and altered MORB and arc data [Yi, 1999, this study] provide no evidence that subducted slabs are enriched in Te.

Using Re-Os data, Walker *et al.* [1995] and Brandon *et al.* [1998] argue that core material has been brought to the surface by mantle plumes originating at the core-mantle boundary. If the Hawaiian plume-entrained core materials, it would result in various effects on siderophile element abundances. Using the degree of lithophile element depletion as a function of deduced volatility (Figure 10), the minimum Te concentration likely in the total Earth is  $\sim 600$  ppb. Assuming that effectively all of this Te was in the core, a concentration of  $\sim 900$  ppb is calculated for the total core. With this concentration a minimum of 1.2% of the source region of the Loihi magmas is required to be entrained core material in order to account for the excess Te in the Loihi source (with a minimum of 10 ppb higher than the upper mantle). This percentage is far too high. If bulk core material is added to the plume in such quantities, highly siderophile elements (e.g., platinum group elements) or S should be a more sensitive indicator. Our calculation shows that the Os concentrations in the Loihi source should be an order of magnitude higher than that found for the Hawaiian plume, even taking into consideration inner and outer core fractionation [Walker *et al.*, 1995].

However, Te could be added to the plume via a less dense sulfide liquid that was mixed into the silicate mantle in the  $D''$  layer at the core-mantle boundary. If such a sulfide had much higher Te concentration ( $>100$  ppm), a very small quantity (say, 50 ppm) would be needed to account for the Te concentration in the source region of Loihi magmas. This would also inject  $\sim 25$  ppm S into the Loihi source, contributing to, but not explaining, the higher S concentrations in Loihi glasses. Sulfide of this origin might have radiogenic Os isotopes but low PGE

abundances due to the relative partitioning between metal, liquid S-rich metal, and sulfide [Newsom, 1990]. So entrainment of material of this kind may have little effect on PGE abundances but significant impact on Os isotopic compositions in the entraining plume. So some form of outer core interchange with the lowermost mantle might be consistent with much of the data. However, the relationships between Te and other trace elements point to a more straightforward interpretation of the high Te in Loihi.

#### 5.4. Accumulation and Assimilation of Olivine and Sulfide

Garcia *et al.* [1989] presented progressive melting and depletion of the source region as an explanation for the relatively high volatile and K contents in Loihi lavas relative to lavas from other Hawaiian volcanoes. Another mechanism that might result in the enrichment of volatiles such as S, in Loihi lavas, is assimilation of sulfide in lithospheric mantle and oceanic crust. Lithospheric interaction has also been advanced to explain the Pb and O isotope data of Hawaiian magmas [Eiler *et al.*, 1996; Garcia *et al.*, 1998]. The REE patterns [Hofmann and Jochum, 1996] and Os isotope data [Hauri *et al.*, 1996] may also reflect the same, relatively shallow level assimilation, rather than the effects of long-term recycling, although this is a matter of some debate [Halliday, 1999]. It is clear that the process cannot be simple bulk assimilation [Lassiter and Hauri, 1998]. Fractionation between Te and PGEs could conceivably occur if magmas ascending through oceanic crust preferentially assimilate Cu-bearing sulfide, for which the melting temperature is significantly lower than that of Fe-Ni sulfide [Czamanske and Moore, 1977]. This process would also increase Cu and S contents in the Loihi lavas. Near normal PGE abundances in Loihi lavas would not be unexpected.

Interaction with oceanic crust is less of an issue for the majority of MORB. However, magmas from the Galapagos and Mariana back arc trough also migrated through older oceanic crust yet have Te concentrations similar to those of MORB. The 80–100 km thick oceanic lithosphere in Hawaii might be an explanation for this. Indeed, interaction with, or assimilation of, olivine-bearing cumulates is suggested by the data for Loihi. There is strong evidence that the highest concentrations of Te in Loihi are a reflection of such olivine and sulfide accumulation and/or assimilation. The Mg/Ni ratio of a basaltic magma is very sensitive to fractional crystallization and accumulation of olivines. Primary basaltic magmas have lower Mg/Ni than evolved ones. The inverse correlation between Mg/Ni and Te/Cu for the submarine lavas from Loihi seamount, Indian MORB and East Pacific Rise provides strong evidence for control by segregation/assimilation of sulfide associated with olivine (Figure 9c).

As discussed above, sulfide would be lost from the magmas concurrently with fractional crystallization of olivine [Rehkämper *et al.*, 1997]. However, this alone would not explain the anomalously high Te concentrations. Rather, the magmas have gained sulfide while accumulating olivine at some stage. Sulfide could easily be assimilated because of its low melting point. There is very strong evidence for this in certain samples. Sample 187-1 from Loihi seamount has a bulk MgO content of 23 wt % and an olivine phenocryst content of 22 vol %, far exceeding the MgO of 15–17 wt % postulated for primary Hawaiian magmas [Garcia, 1996; Garcia *et al.*, 1993, 1995; Rhodes, 1996]. Sample 187-1 also has the highest Te concentration (29 ppb) among all submarine glasses and bulk Ni and Cu concentrations of 1356 ppm and 171 ppm. It is likely that

sample 187-1 represents a magma that accumulated olivines and sulfide and thereby gained Ni, Cu, and Te. The olivines in this rock are euhedral and show no sign of being xenocrystic, whereas the sulfide could either be accumulated or assimilated. Assuming 30 ppm Te and 35% S in sulfide and a Te concentration of 2 ppb in the magma prior to sulfide assimilation, ~1000 ppm of sulfide would need to be assimilated, which would raise the S abundance of the magma by ~300–350 ppm. This is in good agreement with the high S abundance of the sample (~1650 ppm). However, this sample is extreme. The only other sample from Loihi with a significant amount of olivine phenocrysts is 187-8 (~3% olivine phenocrysts). This sample is also high in Te, Ni, and Cu relative to MORB but not exceptionally so relative to other Loihi samples. Indeed, with the exception of 187-1, all lavas have lower bulk MgO than Loihi primary melts. Note that S and Te are not well correlated, implying that the S concentration is mainly limited by the Fe concentration and hence S solubility of the magma.

In summary, accumulation of olivines accompanied by accumulation and/or assimilation of sulfide provides the most likely explanation for the highest Te concentrations in Loihi. The degree to which all the Loihi magmas have undergone equilibration with sulfide-bearing assemblages is unclear. Such processes could take place both during passage through the oceanic lithosphere and at the margins of magma chambers. The importance of this process for understanding melt compositions and Os isotope geochemistry needs to be evaluated carefully. While such processes could generate correlations between isotopic compositions of different elements, it is unlikely that such trends would extrapolate toward the bulk composition of any portion of the lithospheric mantle [Lassiter and Hauri, 1998].

## 6. Chalcophile Elements in the Primitive Mantle

The primitive mantle is generally considered to be chondritic in terms of the relative abundances of refractory lithophile elements [Ringwood, 1966; Chou, 1978; Jagoutz *et al.*, 1979; Sun, 1982; Wänke *et al.*, 1984; Palme and Nickel, 1985; Taylor and McLennan, 1985; Hart and Zindler, 1986; Newsom, 1990; Halliday *et al.*, 1996]. The standard method for estimating the abundance of volatile elements in the bulk Earth makes use of the volatile lithophile element depletion trend, defined by the primitive mantle abundances of the lithophile elements as a function of half-mass condensation temperature [Sun, 1982; Newsom, 1990; McDonough and Sun, 1995]. An alternative approach adopted by Allègre *et al.* [1995] is to use the trends defined by the ratios of volatile elements to refractory lithophile elements in chondrites to estimate abundances in the bulk Earth. This latter method circumvents the uncertainty over the exact volatility of the elements that accreted to form the Earth. However, it assumes that volatile element depletion processes recorded in carbonaceous chondrites, which probably come from the outer reaches of the asteroid belt, are analogous to those that affected the inner solar system. Both approaches assume that (1) volatile elements were lost before core formation, (2) condensation temperature is the only factor that affects the elemental abundances relative to chondrites, and (3) lithophile elements do not enter the Earth's core in significant amounts. Whichever approach is used, it is necessary to make a reasonable estimate of the primitive man-

the abundance of the element of interest in order to use the data to place constraints on models of core formation.

The relative degree of incompatibility during mantle melting can be used to estimate volatile/siderophile element abundances in the primitive mantle [Hofmann and White, 1983; Newsom *et al.*, 1986; Jochum *et al.*, 1993; Yi *et al.*, 1995]. The nearly constant ratio of Dy/Cd of submarine glasses from Loihi seamount and mid-ocean ridges (Figures 7a and 7b) appears to indicate that the bulk distribution coefficients for Cd and Dy are about the same during both melting and magma differentiation. Even though garnet affects the middle and heavy REEs, the primitive mantle abundance of Cd and In can be deduced. This is because the Cd/Dy and In/Y ratios are very uniform and about the same in MORB, OIB, IAB, and the continental crust [this study; Taylor and McLennan, 1985; McDonough and Sun, 1995; Yi *et al.*, 1995]. For both Cd and In, there is no indication that the continental crust has been selectively enriched over REEs by ocean floor hydrothermal or arc-related processes. This is somewhat surprising for Cd in particular because it is highly mobile in the alteration of the ocean floor [Yi, 1999]. However, it means that the primitive mantle abundances of these elements can be evaluated. It is difficult to conceive of circumstances whereby the Cd/Dy and In/Y ratios of the primitive mantle are any different from the consistent values found in all basalts and the continental crust. Yi *et al.* [1995] estimated the primitive mantle In/Y ratio to be 0.003 on this basis and deduced a primitive mantle In abundance of 14 ppb. In a similar manner we can conclude that the primitive mantle Cd/Dy is 0.027. Using a Dy abundance of 674 ppb [McDonough and Sun, 1995], an abundance of 18 ppb of Cd for the primitive mantle is obtained. This is at the low end of the range of existing estimates [see Newsom, 1995].

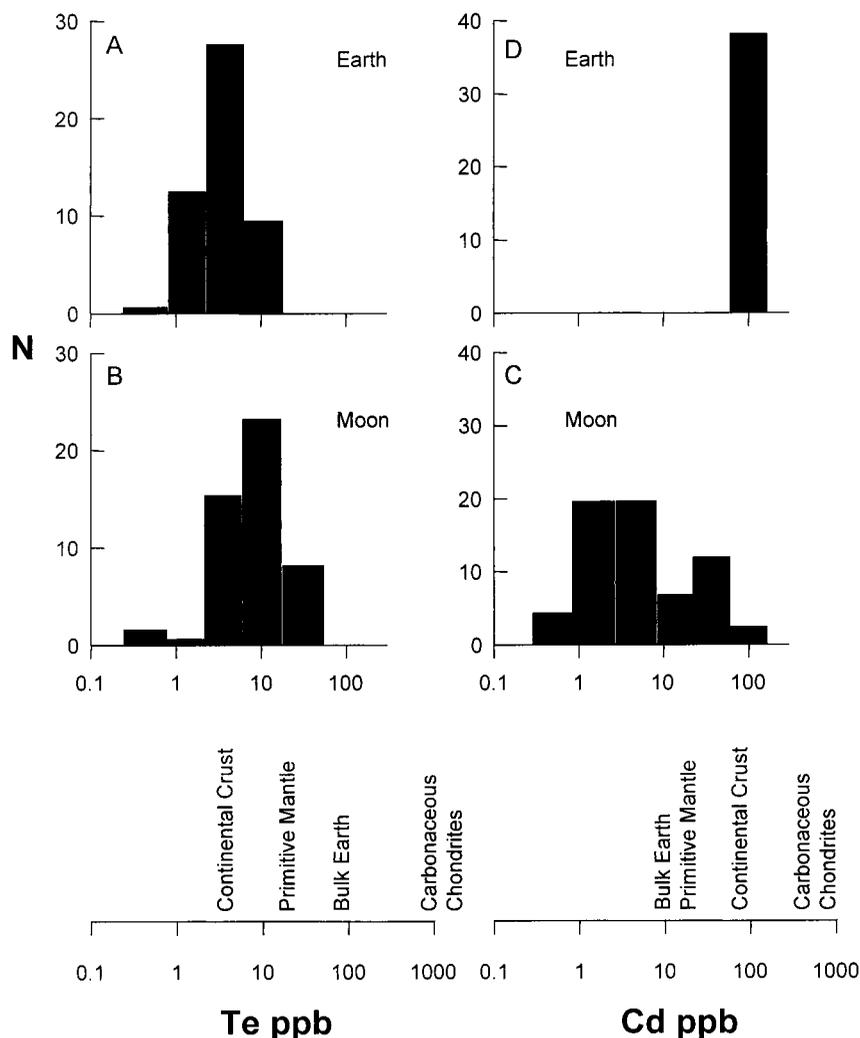
These primitive mantle abundances are plotted on Figure 10, from which it can be seen that there is a striking difference between the relative abundances of In and Cd. Despite being less volatile, Cd is far more depleted in the silicate Earth than is In. Other elements of similar volatility with very well defined primitive mantle abundances include Pb and Sn. All are less volatile than In, but more depleted. There are two likely explanations for this. The first is that In behaved as lithophile element whereas Cd, Sn, and Pb all behaved as siderophile and chalcophile elements during accretion of the Earth, such that Cd, Sn, and Pb were depleted by core formation. The second possibility is that In was not so volatile during the early development of the solar system. There are no unequivocally lithophile elements with the same volatility as In to allow a very clear estimate of how depleted Cd or In should be if they behaved in a purely lithophile manner. However, we prefer the former explanation because the abundance and volatility of In are consistent with the trend defined by data for other lithophile volatile elements such as F (Figure 10). If Cd and Pb have not been depleted by core formation, then both In and F are anomalously enriched for their volatility. There is no obvious explanation as to why both of these two very different elements should show this feature. A more likely explanation is that In was not segregated into the Earth's core and was lithophile, like F. This being the case, Pb has been depleted by at least a factor of 5 by core formation, (allowing for the increase in radiogenic Pb since then), somewhat less than the independent estimate deduced from the silicate Earth's K/U ratio [Allègre *et al.*, 1995]. The latter estimate is not dependent on assumptions regarding volatility. So one explanation for the difference is

that Pb was less volatile than considered theoretically and had a higher half-mass condensation temperature.

The concentration of Te in the primitive mantle has been estimated to be between 10 and 20 ppb [Taylor and McLennan, 1985; Morgan, 1986; McDonough and Sun, 1995], mostly based on data for fertile peridotites. Almost all the lavas studied here have experienced sulfide segregation and/or accumulation, making it difficult to deduce Te abundances for the primitive mantle directly. Given that Te is less compatible than Ni, the Te/Ni ratios of the glasses do provide an upper limit on the Te/Ni of the mantle sources and from this the primitive mantle should have <200 ppb Te. Given that Te is not very incompatible during melting and becomes compatible during magma differentiation, basalts and ultramafic xenoliths have comparable Te concentrations. Because both the continental crust and the oceanic crust represent insignificant fractions of the budget of the Earth, the values obtained from ultramafic xenoliths, should be, on average, similar to the primitive mantle concentration. Therefore the currently accepted values in the range  $15 \pm 5$  ppb are consistent with all the data.

## 7. Nature of the Late Veneer and the Composition of the Core

Highly siderophile elements, especially platinum group elements, have abundances in the mantle that are much higher than predicted based on low-pressure experiments of metal/silicate equilibrium [Chou, 1978; Jagoutz *et al.*, 1979; Morgan *et al.*, 1980; Jones and Drake, 1986; Newsom, 1990]. Although many models have been advanced to explain this, two are currently prevalent: the late chondritic veneer and high-temperature/high-pressure core-mantle equilibrium. The first model involves the late addition of a chondritic veneer into the Earth's mantle after core formation [Chou, 1978; Newsom, 1990; McDonough and Sun, 1995]. In the second model the excess siderophiles are the result of lower liquid metal/liquid silicate partition coefficients at pressures equivalent to that at the base of an ~700-km-deep magma ocean [Walker *et al.*, 1995; Hillgren *et al.*, 1994; Thibault and Walter, 1995; Li and Agee, 1996; Righter and Drake, 1996; Righter *et al.*, 1997]. The primitive mantle abundances of the highly volatile elements C, S, Se, and Te are strikingly similar to those of the refractory highly siderophile elements Pd (and other PGEs), Au, and Re (Figure 10). Note that this effect is so great that the validity of the observation is not greatly affected by the current uncertainties over the primitive mantle concentrations. These data provide compelling evidence that the highly siderophile and chalcophile elements were added to the Earth's mantle in relative proportions that were, on average, only somewhat volatile-depleted relative to carbonaceous chondrites in events postdating core formation [McDonough and Sun, 1995]. There is no reason why the relative abundances of C, S, Se, and Te should be so similar to those of the highly refractory siderophile elements unless they were established by the addition of such a component. If the effect of pressure is to render partition coefficients more uniform, it is a remarkable coincidence that the relative abundances of these elements with a huge range in volatility and chalcophile affinity would wind up being even closer to chondritic than is the Earth's relative abundances of lithophile elements! A corollary of this is that the entire budgets of C, S, Se, and Te in the silicate Earth were added by the late veneer. If instead some significant portion of the inventory in the silicate Earth represented the residue left



**Figure 11.** Histogram of Te and Cd concentrations for basalts from the Earth and Moon. Also shown are the abundances of these two elements in the continental crust, primitive mantle, bulk Earth, and carbonaceous chondrites. Data sources as for Figure 10 plus additional literature data [Anders *et al.*, 1971; Binz *et al.*, 1976; Brunfelt *et al.*, 1972; Compston *et al.*, 1971; Taylor and McLennan, 1985; Morrison *et al.*, 1970; Rose *et al.*, 1972; Taylor *et al.*, 1972; Wakita *et al.*, 1971; Wänke *et al.*, 1970, 1971].

behind from core formation, there should be less depletion in the less strongly siderophile elements. If this were the case it would imply that the PGEs are less siderophile than C, S, Se, and Te. That no major fractionation is found between all of these elements provides compelling support for the late veneer hypothesis. A further implication of this result is that C, S, Se, and Te must have been efficiently extracted by core formation prior to the addition of the late veneer. Therefore C and S must be significant light elements in the Earth's core. The budgets for these elements in the core can then be deduced from the volatile depletion trend for the lithophile elements. The primitive mantle values are irrelevant to this because they merely reflect the late veneer.

The well-defined degree of depletion of In in the Earth provides a monitor of the degree of volatile depletion in C that may have existed in the total Earth prior to addition of the veneer (Figure 10). This entire C was transferred to the core. Similarly, the degree of In depletion provides a maximum estimate for the volatile depletion of Te, Se, and S in the total Earth. On this basis we calculate the concentration of C, S, Se,

and Te in the core to be as follows: C ~ 1.2%, S > 2.4%, Se > 7.1 ppm, Te > 0.89 ppm. The S concentration is slightly higher than the limits provided by Dreibus and Palme [1996] based on Se/S and Zn, but it is similar to the value of 2.3% calculated by Allègre *et al.* [1995] based on the S/Ca and K/Ca ratios of carbonaceous chondrites. The C concentration is also somewhat lower than the estimates deployed by Wood [1993].

The fact that the primitive mantle abundances of the more volatile highly siderophile elements (C, S, Se, Te) are depleted relative to those of the more refractory highly siderophile elements (Re, Au, Pd) indicates that the material that was added to the Earth after core formation was, on average, somewhat volatile element depleted. This is scarcely surprising given that all average compositions of terrestrial planets and some asteroids are volatile element depleted. However, the composition is less volatile depleted than that indicated for the bulk Earth by the volatile depletion trend of the primitive mantle. The late veneer may have been added by a disproportionate amount of less volatile depleted material from a different "accretionary zone" of the solar system. Although the provenance of the

terrestrial planets is extremely broad [Wetherill, 1994], this effect is as expected if the early stages of terrestrial accretion attracted a disproportionate amount of material in the local vicinity that is the more volatile-depleted inner solar system. The later stages of accretion saw a relative increase in the proportion of material accreted from greater heliocentric distance such as the vicinity of the less volatile-depleted portions of the asteroid belt. It is also possible that the early Earth, prior to addition of the late veneer, lost a significant fraction of its volatile elements. The obvious event to cause such catastrophic loss of volatiles is a late giant impact such as is thought to have triggered the formation of the Moon [Cameron and Benz, 1991].

## 8. Origin of the Moon

There is a striking distinction in the abundance patterns of Cd and Te between the Moon and the Earth that may be fundamental to models for the formation of the Moon (Figure 11). For the Earth, Cd concentrations are relatively constant, and Te is highly variable but strongly depleted. The abundance patterns of Cd and Te on the Moon are reversed. Cadmium and In are highly depleted and strongly variable. Tellurium, in contrast, is less depleted than it is in terrestrial basalts and is less variable than Cd. There has been considerable debate concerning whether the materials which formed the Moon were derived from the silicate portion of the Earth [Wänke et al., 1983; Wänke and Dreibus, 1986; Ringwood, 1989, 1992] or the impactor [Jones and Drake, 1986; Newsom and Taylor, 1986; Cameron and Benz, 1991] with most dynamic simulations predicting that the material was derived from the impactor [Cameron and Benz, 1991; Cameron, 1997; Melosh and Sonett, 1986; Stevenson, 1987]. The similarity in the isotopic compositions of O [Clayton and Mayeda, 1975] and Cr [Lugmair et al., 1994] between the Earth and the Moon imply that if the material which formed the Moon were derived from the impactor, the impactor must have come from the same accretionary zone with a very similar early history of volatile depletion and siderophile element fractionation [Halliday et al., 1996]. The striking difference in Te is therefore of great interest. One explanation is that the impactor formed the Moon and that it was highly depleted in volatiles but was relatively enriched in chalcophile elements. SNC meteorites have similar levels of depletion in many volatile elements to that found in the Earth but are even more depleted in chalcophile elements relative to the Earth [Treiman et al., 1986]. Therefore the high Te on the Moon might indicate an origin for the impactor from closer in toward the Sun. Given that the late veneer was added from material that was less volatile element depleted than the average Earth, the provenance of the impactor and the late veneer would appear to be very different. Another explanation for the Te depletion in the silicate Earth relative to the Moon is that the core continued to grow and remove Te from the silicate Earth after the Moon had formed in the giant impact. There may also be pressure effects that complicate the partitioning of Te in different planetary bodies. Further work on the cosmochemistry of Cd, In, and Te must await the acquisition of isotope dilution data from these reservoirs.

**Acknowledgments.** We thank Bill White for providing some of the East Pacific Rise and Kane Fracture zone submarine glasses, Pete Baker for providing Tristan samples, and David Christie and the OSU core repository for providing the Galapagos submarine glasses. John

Blundy, Eric Essene, Al Hofmann, Henry Pollack, Bernie Wood, and Youxue Zhang are thanked for critical discussions. Comments from Matt Kohn, Bill Minarik, and Haibo Zou improved the manuscript. Marcus Johnson is thanked for general lab technical help. Donggao Zhao is thanked for helping with the electron microprobe analysis. This research was supported by DOE, NASA, and NSF.

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(Received December 30, 1998; revised March 8, 2000; accepted April 21, 2000.)