

## 7. DISTRIBUTION OF GOLD, PALLADIUM, PLATINUM, RHODIUM, RUTHENIUM, AND IRIDIUM IN LEG 115 HOTSPOT BASALTS: IMPLICATIONS FOR MAGMATIC PROCESSES<sup>1</sup>

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### ABSTRACT

A comparison of 50 basalts recovered at Sites 706, 707, 713, and 715 along the Réunion hotspot trace during Ocean Drilling Program Leg 115 in the Indian Ocean shows that seafloor alteration had little effect on noble metal concentrations (Au, Pd, Pt, Rh, Ru, and Ir), determined by inductively coupled plasma-mass spectrometry (ICP-MS), which generally tend to decrease with magma evolution. Their compatible-element behavior may be related to the precipitation of Ir-Os-based alloys, chromite, sulfides, and/or olivine and clinopyroxene in some combination. The simplest explanation indicates silicate control of concentrations during differentiation.

Basalts from the different sites show varying degrees of alkalinity. Noble metal abundances tend to increase with decreasing basalt alkalinity (i.e., with increasing percentages of mantle melting), indicating that the metals behave as compatible elements during mantle melting. The retention of low-melting-point Au, Pd, and Rh in mantle sulfides, which mostly dissolve before significant proportions of Ir-Os-based alloys melt, explains increasing Pd/Ir ratios with decreasing alkalinity (increasing melting percentages) in oceanic basalts. High noble metal concentrations in Indian Ocean basalts (weighted averages of Au, Pd, Rh, Pt, Ru, and Ir in Leg 115 basalts are 3.2, 8.1, 0.31, 7.3, 0.22, and 0.11 ppb, respectively), compared with basalts from some other ocean basins, may reflect fundamental primary variations in upper-mantle noble metal abundances.

### INTRODUCTION

In recent years a wide variety of processes have been proposed to account for the distribution and concentrations of the noble metals in mafic systems. Some of these include partial melting of the mantle (Campbell and Barnes, 1984; Brugmann et al., 1987); crystal fractionation of silicate phases (Crocket, 1981; Brugmann et al., 1987); oxide phases (Crocket and Chyi, 1972; Agiorgitis and Wolf, 1978); platinum-group-element-bearing (PGE-bearing) alloys (Bird and Basset, 1980; Keays, 1982); segregation of an immiscible sulfide liquid (Hertogen et al., 1980; Hamlyn et al., 1985); and processes related to the movement of volatiles at various stages in the evolutionary cooling history of a magma (Boudreau et al., 1986; Schiffries and Skinner, 1987; Wood, 1987).

The behavior of the noble metals during these processes is only poorly understood, but their net effect often results in element fractionation in order of descending melting point: Os, Ir, Ru, Rh, Pt, Pd, and Au (Barnes et al., 1985). The varied geochemical behavior of the noble metals indicates that they should provide new insights into mantle evolution, core-mantle differentiation, magma differentiation, and the formation of sulfide ore deposits that cannot easily be gleaned from the more commonly studied lithophile, siderophile, and chalcophile elements.

Investigations of oceanic-island basalts (OIB) have traditionally acted as cornerstones for understanding mantle evolution processes. Because they are present in ocean basins, the interpretation of OIB petrogenesis is simplified by the assumption that they have probably not assimilated continental crust. Oceanic-island magmas show compositional ranges that reflect various amounts of mantle-source enrichment in the large-ion litho-

phile elements (LILE; e.g., K and Rb) and high-field-strength elements (e.g., Zr and Nb; Sun and Hanson, 1975) relative to mid-ocean-ridge basalts (MORB), and various percentages of partial melting in their source regions (Gast, 1968). Magmas representing the cumulative effects of these and other mantle processes are variably alkaline and, as a result, follow assorted differentiation paths during evolution in lithospheric magma chambers. The OIB, therefore, are ideally suited to studies of noble metal behavior during mantle melting and differentiation processes. Curiously, no comprehensive studies of the noble metals in OIB have as yet been reported.

Basalts for this study were collected at four locations along the Réunion hotspot trace during Leg 115 (Fig. 1). Preliminary shipboard studies indicated that rocks from separate sites show different degrees of alkalinity and that basalts from any one site are variably evolved (Backman, Duncan, et al., 1988; Fisk et al., 1989). In this paper we document the concentrations of Au, Pd, Rh, Pt, Ru, and Ir in 49 Leg 115 basalts by means of ICP-MS methods of analysis developed at The Memorial University of Newfoundland, Canada. These data were used in conjunction with shipboard major and trace element data to place constraints on the behavior of noble metals during basalt petrogenesis. For thorough discussions of the geochemical and mineralogical attributes of Leg 115 basalts, the reader is referred to petrology studies elsewhere in this volume.

### DESCRIPTION OF SAMPLES

On the basis of petrographic descriptions as well as major and trace element analyses, samples were selected on board the *JOIDES Resolution* such that the maximum range of rock compositions from each site (706, 707, 713, and 715) were analyzed for their noble metal concentrations. Samples from each site can be placed into two groups according to their degree of evolution (based on Fe/Mg ratios). For each site, Group E basalts are always the most evolved and Group P the most primitive. Site 715 has two evolved groups (an upper, 715-UE, and a lower, 715-LE, on the basis of height in the hole) and two primitive groups (an upper and lower, symbolized as 715-UP and 715-LP, respectively). Samples lumped into one group could come from

<sup>1</sup> Duncan, R. A., Backman, J., Peterson, L. C., et al., 1990. *Proc. ODP, Sci. Results*, 115: College Station, TX (Ocean Drilling Program).

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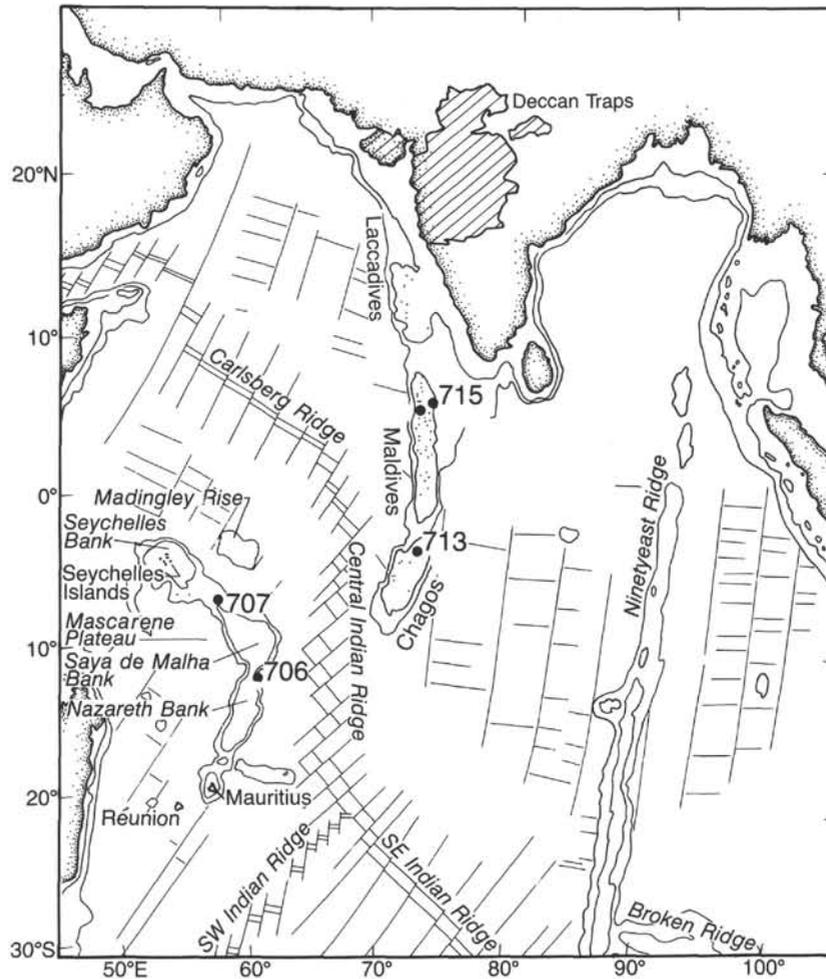


Figure 1. Map showing the location of Leg 115 hard-rock sites and the Réunion hotspot trace. Modified from Duncan et al., 1988.

several distinct lava flows or a single flow. The following background and petrographic information is derived from shipboard data (Backman, Duncan, et al., 1988; Duncan et al., 1989).

Basalts from Site 706 were dated paleontologically as early Oligocene (~35 Ma) and radiometrically at 33 Ma (Duncan and Hargraves, this volume). They erupted when the hotspot coincided with the Central Indian Ridge. Group 706-E samples come from Cores 115-706C-2R through -9R (17 samples analyzed for PGE; the sample locations appear as sample numbers in Table 1) and contain zoned plagioclase (~15%, 0.5 mm) and augite (~10%, 0.4 mm) microphenocrysts, the latter purplish in color (which indicates a high  $TiO_2$  content) and locally glomeroporphyritic. Olivine phenocrysts (1%–2%) are totally altered to clay minerals. The vesicular to highly vesicular (5%–20%) basalts have a fine-grained ( $\leq 0.1$  mm) to glassy (devitrified) matrix that often shows radiating crystals of clinopyroxene as well as Fe-Ti oxides that indicate quenching. Alteration phases (for the most part, celadonite) compose 10%–50% of each sample, replace glass and matrix minerals, and fill vesicles. Numerous glassy contacts, fine-grained textures, and high vesicularity indicate that these are pillow basalts erupted at fairly shallow water depths.

Group 706-P basalts (3 samples, bottom of Core 115-706C-9R) contain an abundance (15%) of large ( $\leq 7$  mm) equant plagioclase phenocrysts, but they tend to be poorer in augite phe-

nocrysts ( $\leq 10\%$ ,  $< 2$  mm) than Group 706-E basalts. They are medium to fine grained and less vesicular ( $\leq 10\%$ ) than the overlying basalts, but they do display similar alteration mineralogy.

The early Paleocene basalts (64 Ma, as per Duncan and Hargraves, this volume) from Site 707 (between the Mascarene Plateau and Seychelles Bank; see Fig. 1) can be linked in time and space with continental Deccan trap volcanic activity in western India, although it is now separated from the latter as a result of subsequent seafloor spreading. The basalts fall into two geochemical groups. Group 707-P samples (4 samples) contain augite and plagioclase microphenocrysts (5%–30% total) with augite dominant and locally glomeroporphyritic in samples from Core 115-707C-22R and plagioclase dominant in Core 115-707C-23R. Olivine phenocrysts (2%?) always appear altered to brown clay minerals. The lower basalts (Core 115-707C-23R) are medium to coarse grained, subophitic, and nonvesicular, whereas the upper ones are fine grained and often display intersertal and highly vesicular (10%–30%) textures. Alteration averages about 20% in the samples, with brown clay minerals and minor calcite replacing glass and matrix minerals as well as filling vesicles.

Group 707-E (3 samples) contains microphenocrysts of augite (7%,  $< 0.5$  mm), plagioclase (3%,  $< 2$  mm), and possibly olivine (1%, always altered). Vesicles ( $\leq 5\%$ ) are filled with calcite and brown clay minerals. Clay minerals also replace por-

Table 1. Noble metal abundances (ppb) in Leg 115 basalts.

Unit	Core, section, interval (cm)	Au	Pd	Rh	Pt	Ru	Ir
706-E	115-706A-6H-CC, 21-23	0.70	1.20	0.08	0.90	0.19	0.13
706-E	115-706C-2R-2, 74-77	0.55	0.99	0.08	1.30	0.08	0.12
706-E	115-706C-2R-2, 142-146	0.67	0.81	0.07	1.02	0.07	0.11
706-E	115-706C-3R-1, 83-85	0.58	1.01	0.05	0.94	0.05	0.07
706-E	115-706C-3R-2, 45-47	0.49	0.75	0.09	1.04	0.10	0.12
706-E	115-706C-4R-1, 78-80	0.61	1.14	0.07	1.83	0	0.12
706-E	115-706C-4R-2, 116-119	0.68	0.94	0.08	1.12	0	0.14
706-E	115-706C-5R-2, 52-56	0.70	0.71	0.04	0.59	0.06	0.09
706-E	115-706C-5R-2, 135-137	0.86	1.86	0.12	2.47	0	0.09
706-E	115-706C-5R-3, 59-62	0.47	1.03	0.11	1.09	0.06	0.12
706-E	115-706C-6R-1, 45-50	0.59	0.26	0.05	1.81	0.02	0.10
706-E	115-706C-6R-2, 17-19	0.49	1.20	0.09	1.16	0	0.08
706-E	115-706C-8R-1, 32-35	0.02	0.19	0.05	2.09	0.14	0.14
706-E	115-706C-8R-1, 67-77	0.26	0.08	0.02	0.34	0.16	0.07
706-E	115-706C-8R-2, 44-48	0.56	0.28	0	0.52	0.04	0.07
706-E	115-706C-8R-2, 125-128	0.36	0.19	0.05	0.21	0.40	0.14
706-E	115-706C-8R-3, 45-48	0.42	0.87	0.10	0.56	0.04	0.10
706-P	115-706C-9R-1, 13-16	2.93	3.18	0.12	2.41	1.17	0.26
706-P	115-706C-9R-1, 23-29	2.98	4.27	0.09	2.61	0	0.03
706-P	115-706C-9R-2, 36-39	1.48	0.93	0.05	0.84	0.10	0.04
707-P	115-707C-22R-1, 94-98	3.08	10.66	0.38	2.98	0.38	0.01
707-P	115-707C-22R-2, 40-42	3.88	16.89	0.51	3.22	0.41	0
707-P	115-707C-23R-1, 123-127	2.60	12.37	0.45	4.12	0.20	0.04
707-P	115-707C-23R-4, 32-34	4.55	17.18	0.48	4.48	0.39	0.03
707-E	115-707C-25R-1, 39-43	6.73	15.36	0.50	4.60	0.21	0.08
707-E	115-707C-26R-2, 126-128	4.81	22.54	0.62	4.64	0.25	0.11
707-E	115-707C-28R-4, 133-136	7.91	17.13	0.49	5.34	0.19	0.03
713-P	115-713A-13R-1, 63-69	5.50	13.55	0.51	9.31	0.20	0.23
713-P	115-713A-15R-4, 7-13	3.60	10.45	0.40	7.50	0.10	0.15
713-E	115-713A-15R-4, 143-146	2.33	2.67	0.28	4.31	0.08	0.14
713-E	115-713A-15R-5, 90-94	3.80	9.73	0.35	7.85	0.11	0.15
713-P	115-713C-19R-1, 27-29	3.80	13.08	0.50	9.21	0.12	0.21
713-P	115-713A-19R-3, 12-15	3.93	6.57	0.31	7.10	0.34	0.25
713-P	115-713A-20R-3, 51-54	3.76	12.31	0.58	9.76	0.06	0.24
713-P	115-713A-20R-3, 112-115	3.60	10.50	0.56	9.59	0.08	0.22
713-P	115-713A-20R-3, 137-139	3.57	17.97	0.46	21.55	0.10	0.21
713-P	115-713A-20R-5, 127-130	3.31	13.20	0.78	8.67	0.22	0.22
713-P	115-713A-21R-3, 55-59	4.74	13.17	0.58	13.02	0.22	0.28
715-UE	115-715A-23R-3, 91-95	0.40	2.20	0.04	8.31	0.09	0.03
715-UE	115-715A-24R-2, 30-38	0.20	2.66	0.02	12.17	0.02	0.02
715-UP	115-715A-25R-3, 25-34	6.06	8.82	0.36	28.55	0.43	0.41
715-UP	115-715A-25R-6, 38-47	14.08	13.17	0.39	32.06	0.45	0.26
715-UP	115-715A-29R-1, 33-38	0.60	8.43	0.33	20.41	0.38	0.15
715-LE	115-715A-29R-1, 113-119	3.74	7.01	0.28	2.54	0.14	0.02
715-LP	115-715A-29R-2, 42-48	1.78	16.53	0.70	7.79	0.22	0.20
715-LP	115-715A-30R-1, 52-61	1.34	3.67	0.31	5.26	0.20	0.12
715-LP	115-715A-30R-3, 41-51	0.89	2.82	0.36	3.21	0.25	0.13
715-LP	115-715A-30R-6, 0-9	1.78	4.77	0.28	4.95	0.28	0.15
715-LP	115-715A-31R-2, 89-94	0.54	5.39	0.24	4.30	0.25	0.12
Blank		0.70	0.61	0.04	0.26	0.03	0.01
DL		0.20	0.15	0.01	0.08	0.10	0.02

Note: DL = detection limit.

tions of the groundmass and compose  $\leq 25\%$  of each sample. The absence of pillows and the abundance of vesicles indicate subaerial or very shallow-water formation of Site 707 basalts.

Basalts from Site 713 are interbedded with chalks containing middle Eocene nannofossils and are dated radiometrically at 48 Ma (Duncan and Hargraves, this volume). Group 713-P samples come from Cores 115-713A-13R, -15R, and -19R through -21R (9 samples). They contain 5%–15% plagioclase ( $\leq 2$  mm) and 5%–10% augite ( $< 1$  mm) phenocrysts (locally glomerocrysts), and display medium- to fine-grained, subophitic, and, in some cases, intersertal textures. Vesicles are rare ( $< 2\%$ ) and filled with fibrous zeolites, gray clay minerals, and rarely calcite. Chlorite and clay minerals ( $\leq 40\%$ ) replace glass and matrix minerals in all samples.

Group 713-E samples (2 analyzed, Core 115-713A-15R) contain phenocrysts and locally glomerocrysts of augite (5%,  $< 0.8$  mm) and slightly aligned plagioclase (15%,  $< 1$  mm). In other respects, they resemble Group 713-P rocks. Intercalation of marine sediments with the vesicular basalts at Site 713 indicates extrusion at shallow-water depths.

Although four groups of early Paleogene (55–60 Ma) basalts (dated paleontologically from overlying reef limestones and radiometrically by Duncan and Hargraves, this volume) can be distinguished on the basis of Fe/Mg ratios and other chemical factors at Site 715, all basalts are petrographically similar. They are largely aphyric (augite and plagioclase phenocrysts  $< 3\%$ ), with olivine (usually altered) abundant in Group 715-UP basalts (up to 10%). Samples show subophitic and, near flow tops, vesicular (up to 50%) textures, with typically 20% of the rock consisting of pale green (celadonite?) to brown clay minerals and chlorite that replace matrix minerals and glass and, together with calcite, fill vesicles. Lateritic oxidation and weathering at the tops of flows indicates that the basalts are subaerial. One chemically analyzed sample (115-715A-23R-3, 91–95 cm) is lateritized.

## SAMPLE PREPARATION AND ANALYTICAL METHODS

The same powders used for major and trace element analyses on the *JOIDES Resolution* were used for noble metal analyses. Powders were prepared from vesicle-poor and fairly alteration-free portions of core. Cut surfaces were abraded on a diamond lap and ultrasonically cleaned with methanol and distilled water. After crushing in a hydraulic press, chips were powdered in a tungsten-carbide mill.

Noble metal analyses were determined by ICP-MS on 10% aqua regia solutions after NiS fire assay preconcentration of 10 g of rock powder. Reagent blanks are 0.70, 0.61, 0.04, 0.26, 0.03, and 0.01 ppb for Au, Pd, Rh, Pt, Ru, and Ir, respectively, and were subtracted from the concentrations reported. Average "detection limits" ( $3\sigma$ , above background) are equivalent to 0.20, 0.15, 0.01, 0.08, 0.10, and 0.02 ppb rock, respectively. Details of the procedure are being prepared for publication (S. Jackson, pers. comm., 1989). Replicate analyses of the standard SARM-7 have yielded values of 245, 1452, 227, 3923, 380, and 77 ppb for Au, Pd, Rh, Pt, Ru, and Ir, respectively, with relative standard deviations of 7% or better for all elements. All values are within 10% of the certified concentrations except for Au, which is 20% low.

## ANALYTICAL RESULTS

### Major and Trace Element Data

Major and trace element data appear in Figures 2 and 3 with average group compositions in Table 2. Site 715 basalts show the highest MgO contents and Site 706 basalts the lowest (Fig. 2). Aluminum concentrations tend to decrease or remain constant with decreasing MgO contents at all sites, whereas TiO<sub>2</sub> increases. Group 706-P basalts display the highest Al<sub>2</sub>O<sub>3</sub> concentrations, and Group 706-E, low Al<sub>2</sub>O<sub>3</sub> concentrations and very high TiO<sub>2</sub>. These characteristics indicate that plagioclase fractionation was important in magma evolution at all four sites and that TiO<sub>2</sub> behaved as an incompatible element.

Abundant plagioclase phenocrysts in basalts from all sites except Site 715 corroborate these suggestions and indicate a similarity to MORB. Indeed, these hypersthene normative (calculated assuming Fe<sup>3+</sup>/Fe<sup>2+</sup> = 0.15) tholeiites show more chemical similarities with MORB than with most OIB. Their K<sub>2</sub>O and TiO<sub>2</sub> contents are lower and Al<sub>2</sub>O<sub>3</sub> contents generally higher than in comparably evolved oceanic-island tholeiites such as in Hawaii (cf. Basaltic Volcanism Study Project [BVSP], 1981, pp. 161–192). Average major element compositions for Sites 707 and 713 show amazing similarities with average MORB compositions from Melson et al. (1976).

When plotted vs. the incompatible element Zr, both Ni and Cr display compatible behavior in Site 707 and 715 basalts and,

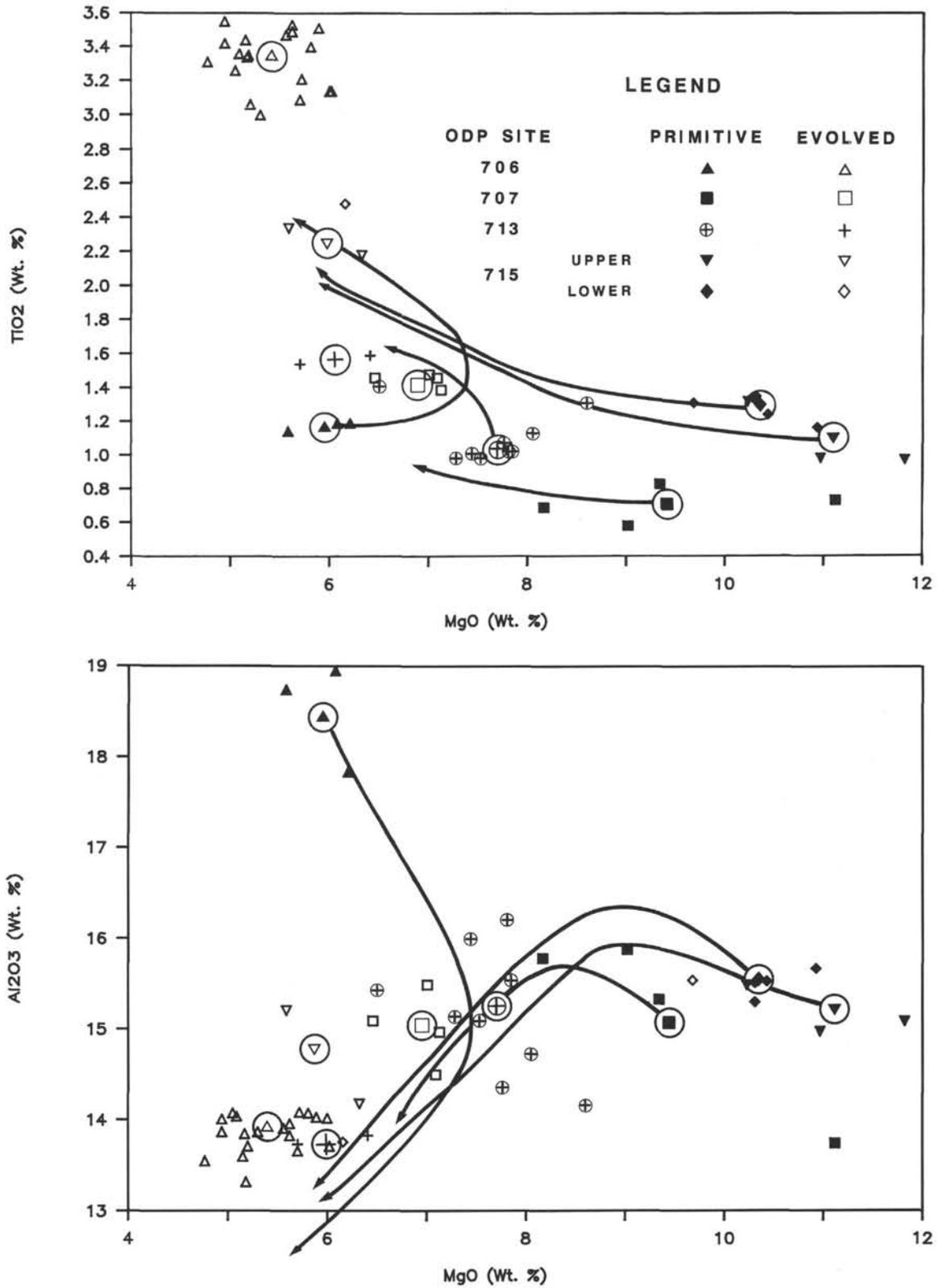


Figure 2. Al<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub> concentrations vs. MgO in Leg 115 basalts (all concentrations in wt% volatile free) from Sites 706, 707, 713, and 715. Average concentrations for each magma group are circled. Curves show the predicted fractional crystallization paths for each magma group from the Nathan and Van Kirk (1978) model. Data are from Backman, Duncan, et al. (1988).

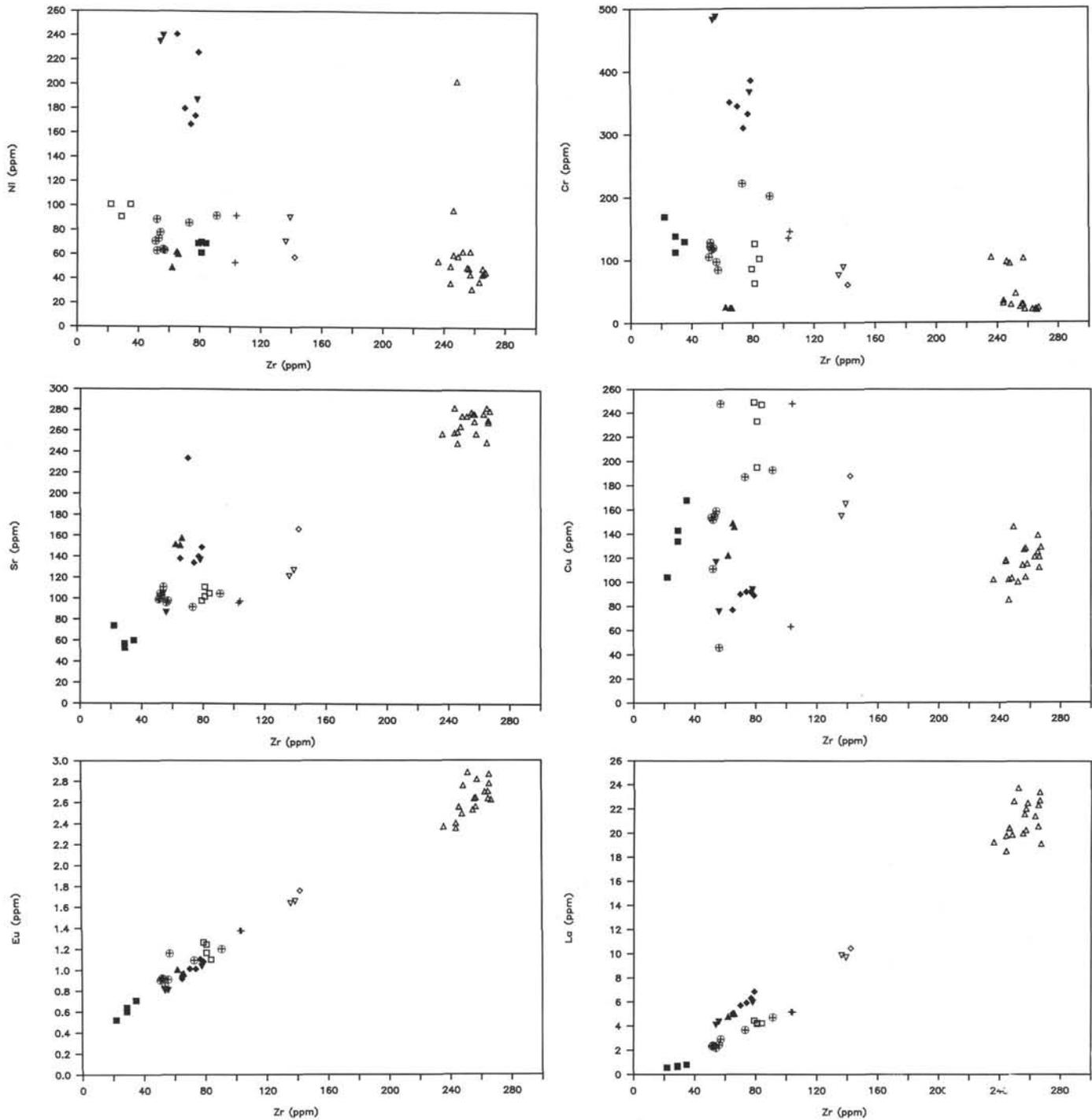


Figure 3. Selected trace elements (ppm) plotted vs. Zr (ppm) for Sites 706, 707, 713, and 715. Data are from Backman, Duncan, et al. (1988) and our unpublished data (La and Eu). Symbols are as in Figure 2.

to a lesser extent, in Site 706 basalts. Site 713 data, however, show no clear trends (Fig. 3). Concentrations of Cu, on the other hand, increase with Zr in Site 707 and 715 basalts, remain constant in Site 706 basalts, and display no coherent behavior in Site 713 basalts. Rubidium varies from 1 to 42 ppm in Group 706-E basalts but shows no correlation with other incompatible elements. Alkalinity indicators such as Nb/Y and La/Sm (Fig. 5) ratios indicate that all the rocks are tholeiitic (Pearce and Cann, 1973), with Site 713 and particularly Site 707 ratios very

similar to "normal" Type-1 MORB (Bryan et al., 1977; Langmuir et al., 1977). Sites 706 and 715 show ratios equivalent to "unenriched" tholeiitic basalts from oceanic-island volcanoes such as Mauna Loa in Hawaii (BVSP, 1981, p. 172). The ratios are only constant for Site 715 basalts, which demonstrates that basalts from the other sites cannot be comagmatic (or cannot be related by low-pressure fractionation processes) because no known low-pressure basaltic phenocryst phases can appreciably fractionate these elements (Schilling, 1971; Frey et al., 1974).

Table 2. Average group compositions of Leg 115 basalts and modeling results.

Group <i>N</i>	706-P 3	706-E 19(17)	Model 706-E	707-P 4	707-E 4(3)	Model 707-E	713-P 9	713-E 2	Model 713-E	715-UP 3	715-UE 2	Model 715-UE	715-LP 5	715-LE 1	Model 715-LE
<sup>a,c</sup> Major elements (wt%):															
SiO <sub>2</sub>	49.51	48.73	49.56	50.75	50.18	51.70	50.02	49.87	49.90	48.50	48.16	48.44	48.41	49.76	49.86
TiO <sub>2</sub>	1.18	3.35	2.23	0.70	1.45	0.84	1.11	1.57	1.49	1.10	2.29	2.01	1.28	2.50	2.07
Al <sub>2</sub> O <sub>3</sub>	18.54	13.95	14.24	15.09	15.07	15.06	15.25	13.82	13.88	15.31	14.90	15.09	15.61	13.86	13.91
FeO	8.91	14.10	14.67	11.00	12.34	12.00	10.55	13.25	13.34	10.75	14.99	15.21	10.93	12.79	12.88
MnO	0.14	0.20	0.23	0.11	0.17	0.10	0.19	0.24	0.22	0.18	0.20	0.23	0.18	0.21	0.21
MgO	5.97	5.45	5.44	9.34	6.95	6.96	7.68	6.07	6.11	11.09	6.04	6.08	10.40	6.20	6.19
CaO	13.20	10.35	10.67	10.74	11.42	10.84	12.81	12.20	12.34	11.07	10.18	10.36	10.46	11.47	11.53
Na <sub>2</sub> O	2.22	2.65	2.27	2.12	2.23	2.31	2.12	2.28	2.33	1.66	2.47	1.87	2.01	2.47	2.18
K <sub>2</sub> O	0.23	0.83	0.48	0.12	0.09	0.15	0.19	0.55	0.28	0.22	0.52	0.45	0.58	0.49	0.95
P <sub>2</sub> O <sub>5</sub>	0.10	0.39	0.22	0.03	0.11	0.04	0.07	0.14	0.10	0.12	0.24	0.26	0.13	0.25	0.22
Mg'	0.57	0.43		0.63	0.53		0.59	0.48		0.67	0.44		0.65	0.49	
<sup>b,c</sup> Trace elements (ppm):															
Cr	24.3	45.6	12	138	94	86	134	141	43	446	82	71	345	61	283
Ni	57.0	57.5	41	96	67	38	75	72	45	221	81	26	198	58	26
Cu	139	115	291	137	231	177	156	156	235	96	160	203	88	188	145
Sr	163	280	147	62	110	67	105	102	111	107	134	130	164	172	174
Y	20.7	42.9	43	17.5	29.5	29	23.9	35.0	36	19.3	38.5	41	21.8	38.0	36
Zr	64.0	255.	133	28.8	81.2	37	59.9	103.5	89	62.7	138.5	133	73.0	142	121
Nb	5.7	14.3	12	1.0	1.5	1.3	1.9	2.5	2.8	5.0	10.5	10.5	7.4	11	12
La	4.95	21.1	9.4	0.68	4.28	0.86	2.84	5.18	4.1	4.84	9.84	9.6	5.97	10.5	9.4
Sm	2.54	7.72	4.9	1.27	5.11	1.6	2.37	3.56	3.4	2.27	4.52	4.4	2.71	5.03	4.3
Eu	0.98	2.62	1.6	0.62	1.20	0.75	0.99	1.38	1.3	0.88	1.65	1.5	1.02	1.76	1.5
Noble metals (ppb):															
Au	2.46	0.55		3.53	6.48		3.98	3.06		6.91	0.30		1.27	3.74	
Pd	2.79	0.81		14.3	18.4		12.3	6.20		10.2	2.43		6.64	7.01	
Rh	0.09	0.07		0.46	0.54		0.52	0.32		0.36	0.03		0.38	0.28	
Pt	1.95	1.18		3.70	4.86		10.6	6.08		27.0	10.2		5.10	2.54	
Ru	0.42	0.09		0.35	0.22		0.16	0.09		0.42	0.05		0.24	0.14	
Ir	0.11	0.11		0.02	0.07		0.22	0.15		0.27	0.03		0.14	0.02	
Element ratios:															
Pd/Pt	1.43	0.69		3.86	3.79		1.16	1.02		0.38	0.24		1.30	2.76	
Pd/Ir	25.4	7.36		715	263		55.9	41.3		37.8	81.0		47.4	351	
Ru/Ir	3.82	0.82		17.5	3.14		0.73	0.6		1.56	1.7		1.71	7.0	
La/Sm	1.95	2.74		0.54	0.84		1.20	1.46		2.13	2.18		2.20	2.09	
Nb/Y	0.28	0.33		0.057	0.051		0.079	0.071		0.26	0.27		0.34	0.29	
<sup>a</sup> Modeling data:															
Olivine			0.072(1)			0.309(2)			0.096(1)			0.231(2)			0.379(1)
Augite			0.178(3)			0.223(4)			0.359(4)			0.298(4)			0.037(4)
Plagioclase			0.750(5)			0.468(6)			0.545(6)			0.471(6)			0.584(6)
% Crystallized			52			22			33			53			40
R <sup>2</sup>			2.775			3.144			0.116			0.656			0.500

Notes: Major element oxides are given in wt%, normalized to 100% volatile free. Total Fe as FeO. *N* = number of samples with number for PGE data in parentheses. Mg' = Mg/(Mg + 0.9 Fe) atomic.

<sup>a</sup> Major elements are modeled by means of mass balance calculations. Proportions of phases removed are shown under the modeling data, and the number in brackets corresponds to the mineral analysis used in the calculation, as follows: numbers 1, 2, and 3: analyses 22 and 13 and analysis 7 from BVSP, 1981, pp. 181 and 183, respectively; numbers 4 and 5: analyses 10 (augite) and 7 (plagioclase) from Frey et al., 1974; and number 6: analysis 4 (plagioclase) from Bryan et al., 1977.

<sup>b</sup> Trace elements are modeled by using phase proportions and % crystallization indicated from mass balance calculations. Partitioning coefficients are for Cr, Ni, Cu, Sr, Y, Zr, Nb, La, Sm, and Eu in olivine 2.0–2.7, 13, 0, 0.01, 0.01, 0.01, 0.01, 0.01, 0.01, 0.01, and 0.02; augite 10.0, 2.75, 0, 0.08, 0.01, 0.01, 0.01, 0.08, 0.30, and 0.35; and plagioclase 0.01, 0.04, 0, 1.5, 0.02, 0.02, 0.02, 0.15, 0.08, and 0.34. Partitioning coefficients compiled from Evans (1978), Frey et al. (1974), and Philpotts and Schnetzler (1970).

<sup>c</sup> Major elements and Cr, Ni, Cu, Sr, Zr, and Nb data for average of samples in Table 1 were compiled from Backman, Duncan, et al. (1988). La, Sm, and Eu = our unpublished data determined by ICP-MS at The Memorial University of Newfoundland, Canada.

### Noble Metal Concentrations

Noble metal abundances (Table 1; group averages, Table 2) are plotted in Figures 4 and 5 (there are three fewer samples—two from Site 706, one from 707—than in Fig. 3 as a result of analytical mishaps). Concentrations of Au and Pd (Table 2) are highest in Group 707-E (average = 6.5 and 18 ppb) and lowest in Groups 715-UE and 706-E basalts (0.3 and 0.8 ppb). One Group 715-UP sample shows anomalously high Au concentrations (Fig. 4). Gold and palladium concentrations resemble those reported for OIB (Table 3), but Group 707-E values are the highest yet noted in OIB and MORB. Most MORB Au and Pd values reported by Hertogen et al. (1980) are much lower ( $\sim 0.2$  and  $\leq 0.4$  ppb), but samples of these elements from Indian Ocean spreading centers display similar concentrations (3.5 and 5.7 ppb) to Leg 115 hotspot basalts.

Rhodium (Table 2) shows the highest concentrations in Group 707-E basalts (0.54 ppb) and the lowest concentrations in Group 715-UE lavas (0.03 ppb). Group 706-E basalts have the lowest Pt concentrations (1.2), and Group 715-UP by far the highest (27 ppb); the composite average for the basalts is 7.3 ppb. Comparison data for Rh and Pt in oceanic basalts are nonexistent.

Average Ru concentrations (Table 2) vary from  $\sim 0.42$  ppb (Group 715-UP) to 0.05 ppb (Group 715-UE). Group 715-UP basalts display the highest average (but concentrations are variable) Ir concentration (0.27 ppb), and Groups 707-P and 715-LE the lowest concentrations (0.02 ppb). Composite group averages for Ru and Ir are 0.22 and 0.11 ppb, respectively (Table 3). Indian MORBs show very similar Ir concentrations to average Leg 115 basalts, but most MORBs have much lower concentrations ( $\leq 0.035$  ppb), and other oceanic-island tholeiites slightly higher average values (0.25 ppb).

Plots of the noble metals vs. the differentiation index  $Mg'$  ( $Mg' = Mg/[Mg + (0.9 \times [Fe^{2+} + Fe^{3+}])]$  atomic) indicate their tendency toward compatible behavior because average concentrations at most sites either decrease with decreasing  $Mg'$  (i.e., they decrease with increasing differentiation) or they show little or no change (Fig. 4). Exceptions include Au and Pd in Site 707 basalts and the lower basalts at Site 715, as well as Rh and Ir in Site 707 basalts. Such PGE ratios as Pt/Pd, Pd/Ir, and Ru/Ir remain fairly constant in each magma group with changing  $Mg'$ . Palladium/iridium ratios are very high in Leg 115 basalts (particularly Site 707) compared with other oceanic-island tholeiitic magmas, but they appear similar to MORB (Table 3).

Indicators of alkalinity such as La/Sm (Fig. 5) imply that Au, Pd, Rh, and Ru abundances decrease with increasing alkalinity (i.e., increasing La/Sm ratios), although these trends do not take into account differentiation effects. Platinum and iridium show no clear dependency on La/Sm ratios, but Pt/Pd ratios tend to decrease, Pd/Ir ratios decrease, and Ru/Ir ratios remain constant with increasing alkalinity.

All of the noble metals can be mobile under certain types of metasomatic/hydrothermal conditions (e.g., Macdonald, 1987; Barnes et al., 1985), but there is little evidence for their mobility in our Leg 115 basalt samples. One of the Group 715-UP samples shows anomalous Au concentrations (Fig. 4). It also has slightly higher Rb (5 ppm) and Cu concentrations (120 ppm) compared with the other two Group 715-UP samples (2 and  $\sim 85$  ppm, respectively), so the possibility that Au was added to this sample cannot be eliminated. There is little or no relationship between noble metal concentrations at each site and various indicators of alteration such as LOI or alkali metal concentrations.

Samples selected for geochemical analysis from Site 706 show the greatest range of mineralogical and geochemical alteration effects, as detailed in Greenough et al. (this volume). Despite

this, when variations in the primary geochemistry of the rocks are taken into consideration, it is clear that much of the variation in noble metal concentrations and element ratios can be related to primary processes (and analytical uncertainty) as opposed to alteration processes. Low-grade alteration has a randomizing effect on element concentrations as rocks tend to be variably altered. Figures 4 and 5 show that, with but a few minor exceptions, the noble metals vary regularly with geochemical indicators of magma fractionation and alkalinity. Therefore, it is unlikely that alteration had any major effect on noble metal concentrations in most of the Leg 115 basalt samples used in this study.

### GENETIC RELATIONSHIPS BETWEEN MAGMAS

At most sites, variations in incompatible element ratios (e.g., Fig. 5) show that the basalts are not likely comagmatic, so it is necessary to obtain some appreciation for how closely they approach (or how much they depart from) a comagmatic ideal before interpreting the noble metal data. Mass balance calculations (Bryan et al., 1969) provide estimates of the mineral phases and proportions possibly removed during fractionation at each site. Only phenocryst phases observed in the basalts were used in the calculations. Analyses of phenocrysts in Leg 115 basalts were not available, so various analyses from MORB and OIB were used with analyses producing the best mix (lowest  $R^2$ ) reported in Table 2.

The  $R^2$  values (Table 2) indicate that evolved basalts can most easily be derived from primitive basalts at Sites 713 and 715 ( $R^2 < 1$ ). Basalts from Sites 706 and 707 depart farthest from the comagmatic ideal. Major elements that fit the mixing model the worst are those associated with magma alkalinity (e.g.,  $TiO_2$  and  $K_2O$ ; cf. Group 706-E with Model 706-E and Group 707-E with Model 707-E). Phase proportions and crystallization percentages (from mass balance) were used in trace element modeling (Table 2), assuming Rayleigh fractionation (Gast, 1968). In general, trace element modeling confirms the results of mass balance calculations (Table 2).

Curves in Figure 2 show the predicted behavior of selected major elements for each primitive magma group from the Nathan and Van Kirk (1978) magma crystallization model. The curves end (denoted by arrows) at the percentage of crystallization required (from mass balance) to produce evolved rocks from primitive rocks. Although information on fractionation lacks pressures (model applies to low pressure) and considering that crystallization always exceeds 20% (model loses accuracy beyond this percentage), it is amazing how closely the model predicts evolved compositions. Although magmas at each site may not be comagmatic, we think that these calculations demonstrate a close kinship. Considering the mass balance and trace element modeling results, primitive-to-evolved magma pairs can be subjectively ordered according to how closely they approach a comagmatic model, as follows: 715-UP  $\rightarrow$  715-UE (most closely); 715-LP  $\rightarrow$  715-LE; 713-P  $\rightarrow$  713-E; 706-P  $\rightarrow$  706-E; and 707-P  $\rightarrow$  707-E (greatest departure). In the following discussion, lavas at each site are considered comagmatic; however, the integrity of that assumption, and the conclusions derived from it, should be tempered according to the order of the magma pairs listed above.

### BEHAVIOR OF NOBLE METALS DURING MAGMA EVOLUTION

Noble metal abundances tend to decrease with increasing fractionation in many mafic magmas, but the process or processes responsible for these concentration decreases remain a subject of debate (e.g., Brugmann et al., 1987). In part, confusion over the merits of various processes probably stems from the fact that so many studies to date have concentrated on rocks associated with PGE ore deposits where exceptional conditions

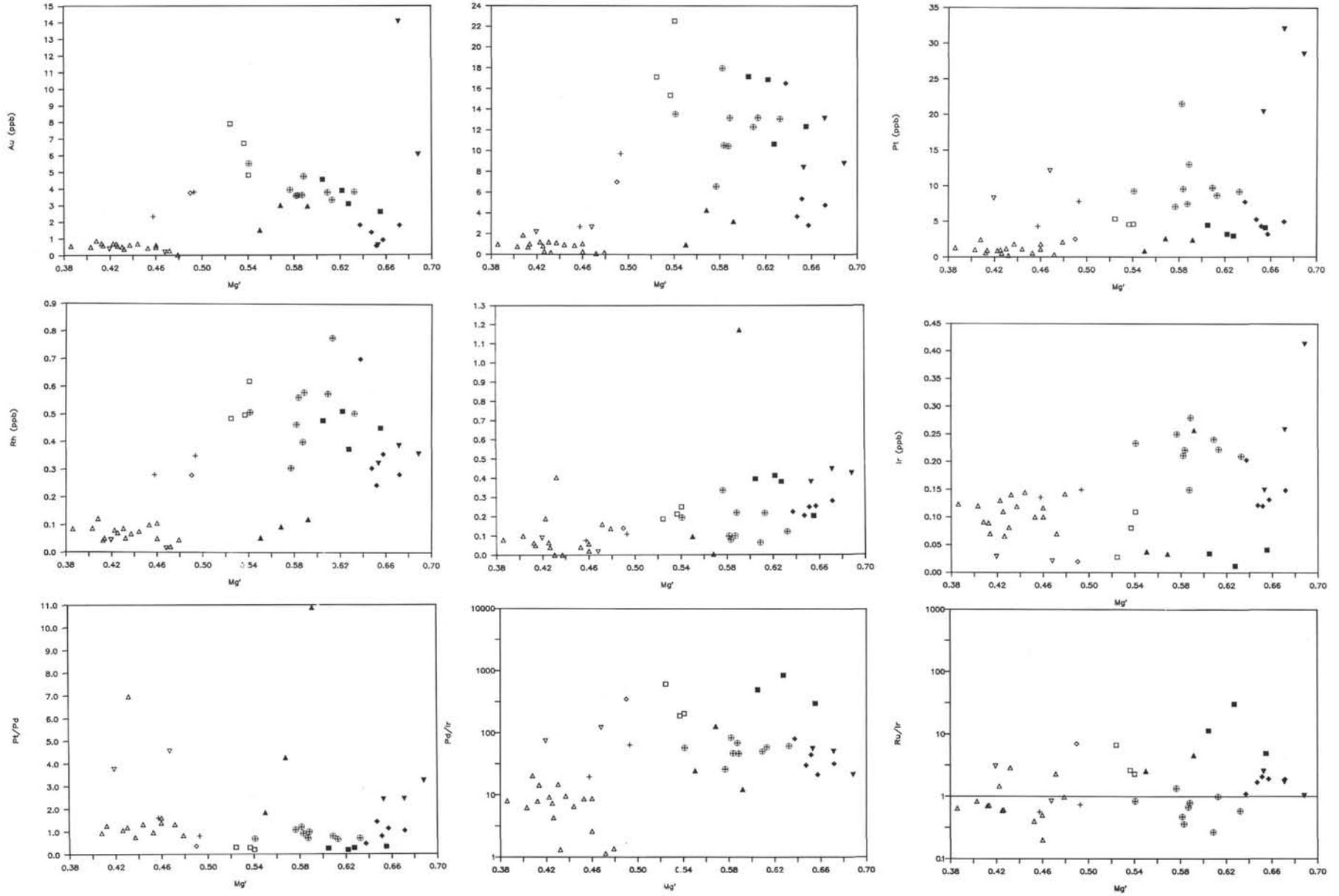


Figure 4. Noble metal abundances (ppb) and ratios in Leg 115 basalts plotted vs.  $Mg'$  ( $Mg' = Mg/[Mg + (0.9 \times \text{total Fe}) \text{ atomic}]$ ) for Sites 706, 707, 713, and 715. Symbols are as in Figure 2.

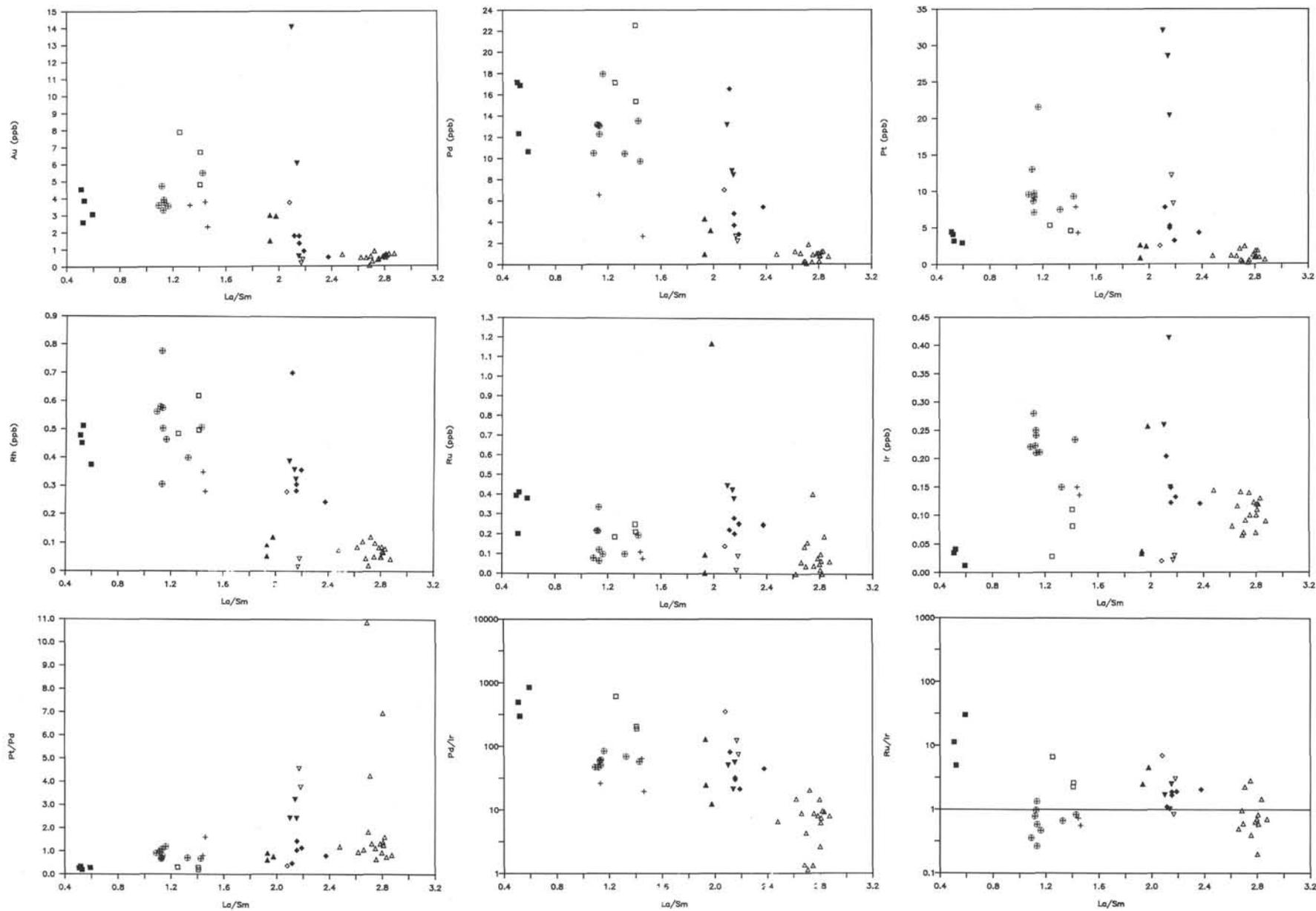


Figure 5. Noble metal abundances (ppb) and ratios in Leg 115 basalts plotted vs. La/Sm ratios (La/Sm from our unpubl. data) for Sites 706, 707, 713, and 715. Symbols are as in Figure 2.

**Table 3. Average noble metal abundances (ppb) in oceanic basalts.**

	Au	Pd	Rh	Pt	Ru	Os	Ir	Pd/Ir
<sup>a</sup> Average Leg 115	3.2	8.1	0.31	7.3	0.22	—	0.11	74.0
<sup>b</sup> Ocean-floor basalts	0.69	≤0.7	—	—	—	≤0.013	≤0.035	≥100
<sup>c</sup> Indian Ocean OFB	3.5	5.7	—	—	—	0.078	0.116	48.0
<sup>d</sup> Oceanic-island tholeiites	2.3	2.2	—	—	—	—	0.25	8.8
<sup>e</sup> Oceanic-island alkaline	0.50	1.5	—	—	—	—	0.30	4.5

<sup>a</sup> Composite average is made up of averages from Table 2, with each group given equal weight.

<sup>b</sup> Average of Leg 37, Hole 332B, Section 12 (13 samples); Southwest Triple Junction, Indian Ocean (1 sample); Mid-Atlantic Ridge, Vema Fracture Zone (1 sample), Mid-Atlantic Ridge 22°S (1 sample); Mid-Atlantic Ridge, FAMOUS area (1 sample); and South Atlantic, Bouvet Triple Junction (1 sample). Each sampling location is given equal weight. Sources: Leg 37 (Au, Pd, and Ir) from Crocket and Teruta (1977); all other data from Hertogen et al. (1980).

<sup>c</sup> Average of two Leg 24, Site 238 samples from Hertogen et al. (1980).

<sup>d</sup> Au = average of 26 Hawaiian basalts (Gottfried et al., 1972); Pd = average of 5 samples from Hawaii, Maui (Hawaii), James Island (Galapagos), Albemarle Island (Galapagos), and Réunion (Crocket and Skippen, 1966); Ir = average of 10 samples from Hawaii (Gottfried and Greenland, 1972).

<sup>e</sup> Au and Ir = average of 4 samples, Tahiti (Crocket et al., 1973); Pd = average of 4 samples from Tutuila (Samoa), Tahiti, St. Michael (Azores), and Ascension Island (Crocket and Skippen, 1966) plus average of 4 samples from Tahiti concentration (Crocket et al., 1973).

might have taken place. In this section, Leg 115 noble metal data were used to evaluate the effects of fractionating platinum group alloys, chromite, silicates, and an immiscible sulfide phase.

#### Fractionation of PGE Alloys

Keays (1982) argued that because Ir, Os, and Ru alloys represent residual mantle phases during mantle melting (Mitchell and Keays, 1981), partial melts should be saturated with Ir and would therefore precipitate an Ir-Os-Ru alloy early during magma evolution. If alloys do commonly form, their small size (e.g., in Bushveld rocks) requires that other minerals (e.g., chromite or olivine) remove them since they will not settle on their own (Hiemstra, 1979; Keays and Campbell, 1981; Talkington et al., 1983). Removal of alloys early in the process of magma evolution might explain the very high Pd/Ir of Leg 115 basalts. Brugmann et al. (1987) argued against alloy fractionation to explain the wide range (3 orders of magnitude) of Ir and Os concentrations in mafic and ultramafic rocks because a very special alloy composition would be required to maintain the chondritic Ir/Os ratios of these rocks.

Average Ru/Ir ratios (Table 2) remain fairly constant between primitive and evolved Indian Ocean rocks, in some cases rising slightly, in others decreasing slightly. Most are within a factor of 2 of chondritic ratios (1.53; Chou, 1978) except where near detection limits. Other ratios such as Pd/Pt also remain constant, whereas concentrations and Pd/Ir ratios tend to decrease between primitive and evolved rock types. Thus, alloy precipitation might explain decreases in Ir and Ru concentrations, but it cannot account for similar or larger decreases in Pd, Pt, and Rh. Finally, the early alloy precipitation may explain the high Pd/Ir ratios of Leg 115 basalts (all are somewhat evolved), but it would present difficulties in accounting for near-chondritic Ru/Ir ratios.

#### Fractionation of Chromite

Chrome-spinel contains appreciable concentrations of Ir, Os, and Ru (Agiorgitis and Wolf, 1978; Page and Talkington, 1984; Stockman and Hlava, 1984), and its early precipitation might account for the high Pd/Ir ratios of many basaltic rocks. Agiorgitis

and Wolf (1978) noted that Os, Ir, and Ru correlate with Cr in Greek chromites, implying that the metals substitute for Cr<sup>3+</sup>. Oshin and Crocket (1982) concluded that Ir alloys in some chromites formed through exsolution during cooling. Other workers (Prichard et al., 1981; Stockman and Hlava, 1984) found alloys and PGE-rich sulfides in ophiolitic chromites and hypothesized that both inclusions were engulfed during chromite growth. Agiorgitis and Wolf (1984) showed that chromite contains Os and Ir in near-chondritic proportions, indicating that its precipitation will not affect Ir/Os ratios.

Regardless of whether the PGE substitute for Cr in chromite or form inclusions, early chromite precipitation could account for the high Pd/Ir ratios of some basaltic rocks. Nevertheless, chromite precipitation was probably not an important process during the formation of evolved rocks from primitive Leg 115 rocks because clinopyroxene precipitation accounts for the total Cr depletion in all magma pairs except those from Site 715. In the latter case, bulk-rock similarities between primitive upper and lower lavas indicate a slight underestimation of the amount of clinopyroxene removed in modeling the lower lavas, a conclusion supported by the Nathan and Van Kirk (1978) modeling.

Removal of chromite might explain decreases in Ir and Ru concentrations, but it cannot account for similar or larger decreases in Pd, Pt, and Rh. It appears likely that early chromite precipitation (all Leg 115 basalts are evolved to some extent) had some effect on Pd/Ir ratios in the Leg 115 basalts, but it is questionable that this process can account for the important variations in average Pd/Ir ratios between different types of mafic magmas. Table 3 indicates that oceanic-island alkali basalts have lower Pd/Ir ratios than oceanic-island tholeiitic basalts, which are in turn lower than ocean-floor basalts and Leg 115 hotspot basalts (which have MORB affinities). If chromite precipitation controls Pd/Ir ratios, then chromite fractionation must be much more important in MORB than in alkaline OIB, a conclusion for which we know of no support.

#### Fractionation of Sulfides

The PGE have an affinity for, and associate with, sulfides in mafic rocks (Keays and Crocket, 1970; Naldrett et al., 1979;

Ross and Keays, 1979; Crocket, 1981; Naldrett, 1981; Barnes and Naldrett, 1985). Observations on glasses and the S content of mafic magmas (Moore and Schilling, 1973; Mathez, 1976; Czamanske and Moore, 1977) as well as high-temperature/pressure experiments (Haughton et al., 1974; Mysen and Popp, 1980; Wendlandt, 1982) show that many mafic magmas are saturated in sulfur and form immiscible sulfide globules. In some cases, the sulfides, which have great affinity for the PGE (measured sulfide/magma partitioning coefficients for Pd and Ir are  $2.3 \times 10^4$  and  $2.8 \times 10^4$ , respectively; C. Peach and E. Mathez, pers. comm., 1989) equilibrate with large volumes of magma and effectively scavenge it of PGE (Campbell and Barnes, 1984). Some magmatic PGE deposits have been attributed to concentration of the sulfides (Naldrett, 1981).

Trace element modeling calculations indicate that Cu behaved as an incompatible element in Site 715 magmas (Table 2), circumstantially implying that the PGE were not removed by sulfides. However, sulfide/magma partitioning coefficients for the PGE are much larger than the value for Cu (~250; Rajamani and Naldrett, 1978), such that minute amounts of sulfide removal (assuming equilibration with large amounts of magma) could drastically reduce PGE concentrations but have little effect on Cu concentrations (Campbell and Barnes, 1984). At the present time, it appears that the sulfide model cannot be quantitatively tested because the amount of sulfide removed (if any) cannot be ascertained. It remains to be demonstrated that tiny sulfide globules (like small alloy grains), despite their high density, would gravitationally settle from a magma. The similarity between Ir and Pd partitioning coefficients indicates that both metals should be equally removed by sulfide fractionation processes. Table 2 shows that, for the lower lavas at Site 715, Pd increases 6% whereas Ir shows an 86% decrease, thus arguing against sulfide removal as the only process controlling noble metal concentrations.

In trying to explain the low concentrations of PGE in many MORB, Brugmann et al. (1987) proposed sulfide removal as an answer. They explained the high Pd/Ir ratios of MORB basalts by concomitant removal of chromite or olivine. A combination of processes may be responsible for decreases in noble metal concentrations in Leg 115 basalts. The effects of silicate mineral removal are explored below.

#### Fractionation of Silicate Minerals

Commonly, silicate precipitation has been considered unimportant in controlling PGE concentrations in mafic magmas (Brugmann et al., 1987). However, various studies have shown that olivine-rich rocks contain high Ir values (Gijbels et al., 1976; Oshin and Crocket, 1982; Crocket and MacRae, 1986), and Ross and Keays (1979) reported high Ir contents (5.7 ppb) for cumulus olivine from an Australian komatiite flow. These data appear at odds with the low Ir contents of olivine from spinel and garnet lherzolites (0.07–0.5 ppb; Mitchell and Keays, 1981), but the lherzolite olivine probably equilibrated with sulfides that would scavenge most of the Ir (Brugmann et al., 1987). Ionic size and charge data (Shannon, 1976) indicate that Ir, Os, and Ru could substitute for  $Fe^{2+}$  and  $Mg^{2+}$  in olivine (Brugmann et al., 1987). Finally, Brugmann et al. (1987) rather convincingly show that Ir, Os, and Ru variations in two komatiite suites are probably related to olivine fractionation.

If silicate precipitation lowered noble metal abundances in Leg 115 basalts, then some mineral other than olivine removed Au, Pt, Pd, and Rh, or olivine-partitioning coefficients for these elements must be much higher in basaltic magmas than in komatiitic lavas. The PGE concentrations in lherzolite mineral separates (Mitchell and Keays, 1981) are interesting in this regard because noble metal abundances in clinopyroxene are con-

siderably greater (4–5 times for Pd) than in olivine. Lee and Tre-doux (1986) report that lower zone and lower critical zone pyroxenites from the eastern Bushveld complex contain more Ir than dunites, indicating that pyroxene might remove the PGE. Given the siderophile character of the noble metals, one might predict higher abundances in ferromagnesian minerals than in the feldspars. The silicate fractionation model is presently not testable because partitioning coefficient data are unavailable. Nevertheless, we think that olivine and pyroxene removal of the PGE is a possibility.

In summary, the most important argument against sulfide removal as the only process controlling the PGE in Leg 115 basalts is that Ir was preferentially removed relative to Pd in some Site 715 lavas. Control of PGE concentrations by chromite or PGE alloy removal is not supported by concentration decreases for all of the noble metals in most of the Leg 115 basalts (chromite and alloys mainly remove Ir, Os, and Ru). Trace element information does not support appreciable chromite removal. The available data do not unequivocally eliminate any of the above processes or the possibility that abundances were simply controlled by the precipitation of silicate phases.

#### MANTLE PROCESSES

Given that magma evolution unquestionably affects noble metal concentrations in magma series, it is necessary to determine whether major differences in average noble metal ratios (e.g., Pd/Ir) and concentrations between rock groups (Table 3) represent mantle processes or magma evolution processes or both. Hamlyn et al. (1985) and Brugmann et al. (1987) noted that MORB are depleted in Pd by a factor of 100 and Ir by 1000 compared with komatiites. They attributed the low concentrations to sulfide fractionation. However, when suites of rocks (showing a range of primitive to evolved rock types) from distinct localities were compared, major differences in PGE concentrations were apparent that could not easily be related to sulfide fractionation. Chou et al. (1983) showed that Pd decreases with fractionation from 2 to 0.1 ppb in Leg 37 basalts. In contrast, Site 707 basalts, which resemble MORB in many respects (e.g., La/Sm ratios), average 19 ppb in the most evolved rocks. Furthermore, Indian Ocean MORB samples reported by Hamlyn et al. (1985) average 5.7 ppb.

Average noble metal abundances decreased with evolution in all Leg 115 basalt suites (except noncomagmatic Site 707 rocks), but absolute abundances at any given degree of evolution (indicated by  $Mg'$  values) varied considerably between suites (Fig. 4). Our data also show that the more similar the basalts are to MORB, the higher the noble metal abundances are. In all probability, sulfide removal does in some cases decrease noble metal concentrations, but the major differences in abundances between variably alkaline rocks from similar localities (e.g., Indian Ocean) and between similar rocks from different localities (e.g., Indian vs. Atlantic ocean) more likely reflect source-region processes or variations in concentration.

The effects of magma evolution on Pd/Ir ratios have already been discussed. The high Pd/Ir ratios of MORB (~100) compared with the primitive komatiites (~4.5) have often been attributed to the removal of olivine, chromite (Hertogen et al., 1980; Crocket, 1981; Brugmann et al., 1987), or Ir-based alloys (Barnes et al., 1985) in the former. Our data show that Pd/Ir ratios are affected by magma evolution, but the data also indicate a greater tendency for the ratios to decrease with fractionation (cf. Pd/Ir in primitive vs. evolved rocks at Sites 706, 707, and 713, as shown in Table 2). Data for Leg 37 basalts (Atlantic Ocean) presented by Chou et al. (1983) showed that MORB evolution has little effect on Pd/Ir ratios. In summary, the above analysis implies that fractionation of MORB decreases, or has

little effect on, Pd/Ir ratios. For this reason, fractionation would only serve to decrease differences between the Pd/Ir ratios of MORB and primitive komatiites.

Following the above reasoning, one might conclude that the low Pd/Ir ratios of other types of basalts (e.g., oceanic-island alkali basalts; see Table 3) compared with MORB do not reflect magma evolution processes. A comparison of primitive groups of Leg 115 basalts (Table 2) shows that Pd/Ir ratios increase from 25 in Site 706 basalts (among the most alkaline of primitive Leg 115 basalts with La/Sm  $\sim$  2.0) to 707 in Site 715 basalts (the least alkaline, with La/Sm  $\sim$  0.54). This relationship between alkalinity and Pd/Ir ratios is mirrored in Table 3, with alkali basalts showing the lowest Pd/Ir ratios ( $\sim$  5) and MORB and Leg 115 data (keep in mind geochemical similarities between Leg 115 basalts and MORB) displaying the highest ratios ( $\sim$  100–74). It seems unlikely that the relationship between Pd/Ir ratios and alkalinity can easily be ascribed to magma evolution processes. It most likely reflects mantle processes.

### Mantle Processes and Magma Pd/Ir Ratios

Studies of purported upper-mantle materials provide an explanation for the wide variation in Pd/Ir ratios of mafic rocks. The chondrite-normalized PGE patterns of fairly undepleted spinel lherzolite xenoliths from alkaline rocks are flat, with the PGE predominantly held in intergranular sulfide phases apparently trapped during or after melting (Jagoutz et al., 1979; Morgan et al., 1981; Mitchell and Keays, 1981). Harzburgites and dunites representing post-melt extraction residues show normalized patterns enriched in Os, Ir, and Ru relative to Pt, Pd, and Rh with the PGE concentrated in alloy phases (Page and Talkington, 1984; Barnes et al., 1985; Rudashevskiy, 1987).

The details of PGE mineralogy are complicated (there are many minerals) in both the lherzolites and residue rocks; thus, the simple sulfide-alloy division of assemblages is only general. Bird and Bassett (1980) proposed that textural and compositional relationships of some Ir-Os alloys are consistent with high formation temperatures during accretion of the earth. However, the alloys apparently show increased abundances as the percentages of sulfide decrease (Rudashevskiy, 1987), which supports the hypothesis of F. A. Frey (1983, pers. comm. in Barnes et al., 1985) that they formed through incongruent melting of the sulfides.

The high Ir contents of komatiites compared with basalts (Table 3), and arguments that komatiites represent high percentage melts (BVSP, 1981, pp. 26–27), indicate that the low Pd/Ir ratios of komatiites (Brugmann et al., 1987) result from melting both alloys and sulfides (Barnes et al., 1985). Low Pd/Ir ratios in alkali basalts imply melting of a source with residual sulfides and alloys. Because sulfides are expected to dissolve before alloys, the high Pd/Ir ratios of basalts, which represent greater percentages of melting than alkali basalts, could be produced by fusion of the sulfides, with alloys remaining in the residue. The model implies that the increase in Pd/Ir ratios and Pd concentrations with decreasing alkalinity in Leg 115 basalts could reflect the highly compatible behavior of the noble metals during melting, with the progressive release of Pd from the sulfides with increased melting.

### Noble Metal Concentrations in the Mantle

The mantle may be extremely heterogeneous with regard to its noble metal content. Although there are few data for noble metal abundances in Atlantic OIB, LILE-enriched basalts from the FAMOUS area, like Atlantic MORB, show low noble metal abundances (Hertogen et al., 1980). Both tholeiitic basalts and LILE-enriched alkali basalts from the East Pacific Rise have low Ir concentrations (typically  $<0.05$  ppb) (Gottfried and Greenland, 1972). Relative to typical MORB, Leg 115 hotspot basalts with MORB affinities and Indian MORB display high noble

metal concentrations (Table 3). Crocket and Skippen (1966) found that Deccan flood basalts (northern end of Réunion hotspot trace) have higher Pd concentrations than flood basalts from the Parana Basin, Columbia-Snake River Plateau, or Karroo provinces. These observations suggest that mantle noble metal abundances vary dramatically from place to place. For example, mantle noble metal abundances for the Indian Ocean area may be anomalously high compared with the Atlantic Ocean area.

Gottfried and Greenland (1972) indicated that the apparently higher noble metal abundances of OIB compared with MORB reflect differences in source mineralogy, depth and degree of partial melting, and/or inherent variations in mantle concentrations. They also pointed out that noble metal concentrations appear to correlate with  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios in basalts and implied that the low Pd concentrations of MORB may be a result of previous melt extraction. We argued with our Leg 115 data that noble metal concentrations, particularly Au and Pd, rise as melting percentages increase because they are compatible in mantle minerals. The compatible melting behavior implies that concentrations in the residue will always be higher than in unmelted material and subsequent magmas generated from the same source will have higher concentrations than the initial magma. If so, the low Pd concentrations of many MORBs are difficult to explain by previous melt extraction because Pd should be enriched in subsequent magmas.

Some OIB contain too much Rb for their observed  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios, which implies that their sources were metasomatically enriched in LILE a short time prior to melt extraction (Sun and Hanson, 1975). Noble metal abundances decrease in Leg 115 basalts derived from sources most likely to show the effects of mantle metasomatism (i.e., those with the highest abundances of LILE). Similarly, Hamlyn et al. (1985) found no covariance between light rare-earth-element and PGE concentrations in low-titanium, magnesium-rich lavas from various localities. In their study of mantle xenoliths, Mitchell and Keays (1981) concluded that mantle metasomatism is probably not responsible for the intergranular sulfides that contain the bulk of the PGE because concentrations in the transporting fluids would have to be prohibitively high and the fluids would have to transport the metals in chondritic proportions. Jagoutz et al. (1979) reported that noble metal concentrations in mantle nodules show no relationship to elements commonly influenced by metasomatism. Apparently, processes other than previous melt extraction or mantle metasomatism are responsible for differences in noble metal concentrations in basalts from different areas.

### SUMMARY AND CONCLUSIONS

For any one site, evolved Leg 115 hotspot basalts generally show lower noble metal concentrations than more primitive basalts. The concentration decreases may be related to the removal of Ir-Os-based alloys, chromite, sulfides, or olivine and clinopyroxene in some combination. A lack of partitioning coefficients for the noble metals prevents the quantitative testing of the various possibilities, but the simplest explanation is that olivine and clinopyroxene fractionation is the major cause of removal of the noble metals.

The Pd/Ir ratios decrease with magma alkalinity in Leg 115 basalts and basalts worldwide. This observation is consistent with retention of the noble metals in mantle sulfide and Ir-Os-based alloy phases. Although the alloys retain high-melting-point metals up to high percentages of melting, the sulfides dissolve with increasing percentages of melting and thereby release the low-melting-point noble metals (e.g., Pd), which causes Pd/Ir ratios to increase.

Indian OIB and MORB are characterized by anomalously high noble metal concentrations, whereas Atlantic MORB and East Pacific Rise MORB show extremely low noble metal abun-

dances. These observations indicate a provinciality to noble metal abundances that cannot easily be related to percentages of melting or previous melt extraction. The concentration differences may reflect fundamental primary differences in mantle noble metal abundances related to core formation or cosmochemical processes.

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