

Contrasting behavior of noble-metal elements during magmatic differentiation in basalts from the Cook Islands, Polynesia

Yoshiyuki Tatsumi* Institute for Geothermal Sciences, Kyoto University, Beppu 874-0903, Japan, and
Ocean Research Institute, University of Tokyo, Tokyo 164-8639, Japan

Kiwamu Oguri School of Earth Sciences, Kyoto University, Kyoto 606-8501, Japan

Gen Shimoda Institute for Geothermal Sciences, Kyoto University, Beppu 874-0903, Japan

Tetsu Kogiso Department of Earth and Planetary Sciences, Tokyo Institute of Technology, Tokyo 152-8551, Japan

Hans G. Barszcz GBE-CNRS-ISTEEM, Université de Montpellier II Sciences et Techniques, 34095 Montpellier Cedex 5, France

ABSTRACT

Concentrations of noble metals (Ir, Ru, Rh, Pt, Pd, and Au) in ocean-island basalts from the Cook Islands, Polynesia, were determined by improved fire-assay and tellurium coprecipitation techniques with an inductively-coupled-plasma mass spectrometer. Isotope, major element, and trace element compositions of these basalts indicate that the present samples include distinctive HIMU (high μ = high $^{238}\text{U}/^{204}\text{Pb}$) and normal non-HIMU basalts. Examination based on Ni-Mg-Fe partitioning between olivine and liquid suggests an only minor effect of accumulation of phenocrysts in governing the compositional variations of the present samples. The fractionation trends obtained show monotonic decrease and increase in noble-metal elements with decreasing MgO content in HIMU and non-HIMU basalts, respectively. These characteristic trends indicate that HIMU magmas are differentiated by fractional crystallization and have higher sulfide/silicate ratios than non-HIMU basalts.

Keywords: noble-metal elements, magmatic fractionation, Pacific hotspots, HIMU basalts, sulfides.

INTRODUCTION

Noble metals are highly siderophilic and chalcophilic, and knowledge of their geochemical behavior in basaltic magmas is the key to understanding mantle processes such as partial melting and core-mantle interaction. It has been demonstrated that the mantle sources for some ocean-island basalts (OIBs) have elevated $^{187}\text{Os}/^{188}\text{Os}$ ratios compared with both chondrites and mid-oceanic ridge basalts (MORBs) (Martin, 1991; Hauri and Hart, 1993), which could be caused by addition of outer core materials with high Re/Os ratios to the base of the mantle (Walker et al., 1995). This is consistent with the idea that a possible location of the hot-spot source, from which a mantle plume rises to generate OIB magmas, is the D'' layer at the base of the mantle, where a relative reduction of seismic velocity takes place (e.g., Stacey and Loper, 1983). The following seismic observations further suggest that D'' may be the source for at least some mantle plumes: (1) the presence of an ultra low-velocity zone near the core-mantle boundary, which is consistent with partial melting in that region (Wen and Helmberger, 1998), and (2) the presence of a mantle-scale low-velocity anomaly beneath the South Pacific, probably related to upwelling of a large plume (Fukao, 1992).

Although the geochemistry of platinum-group elements (PGEs) in OIBs has the potential to provide key information on deep-mantle processes, few new data on PGE abundances in OIBs have appeared since the work of Crocket and Skippen (1966). The reason for this may be the difficulty in analyzing PGEs at such low concentration lev-

els in basalts. This paper presents the first complete data set of PGE and Au abundance in Polynesian OIBs and examines the behavior of these elements during magmatic differentiation.

GEOLOGIC SETTING AND SAMPLES

The Cook and Austral Islands form a 1500-km-long chain extending northwestward from MacDonal Seamount (Fig. 1). They are roughly parallel to other island chains of the South Pacific such as the Society and Tuamotu Islands. Radiometric dating of individual islands within the chain has demonstrated that there is not a simple correlation between the age and the distance of individual islands from a proposed Austral hot-

spot associated with an active volcano of the MacDonal Seamount (Duncan and McDougall, 1976; Turner and Jarrard, 1982; Diraison et al., 1991). Islands in the northern part of the island chain such as Rarotonga, Aitutaki, and Atiu, do not follow the age vs. distance relationship (Fig. 1).

Rarotonga Island in the Cook Islands is elliptical in shape, 11 km east to west and 8 km north to south, and represents the upper 650 m of a volcano, which rises 5000 m above the surrounding sea floor. The geology of Rarotonga (Thompson et al., 1998) together with radiometric dating (Dalrymple et al., 1975; Turner and Jarrard, 1982; Matsuda et al., 1984) indicate that two stages of volcanism took place on Rarotonga, an early phase of basaltic volcanism at 2.3–1.6 Ma and more evolved phonolitic volcanism at 1.4–1.1 Ma, although a simple model of the Austral plume suggests an age of ca. 20 Ma for Rarotonga volcanism. Samples used in this study were collected from the earlier basaltic group and include basalts and phenocryst-rich ankaramites.

Mangaia Island, also in the Cook Islands, has a diameter of ~7 km and a maximum height of 169 m. The island comprises a volcanic core of ankaramites and basalts and the surrounding Makatea limestone (Wood and Hay, 1970). The volcanism ca. 19.5 Ma (Diraison et al., 1991) also shows a greater geochronological affinity with the Austral plume (Fig. 1). The Mangaia volcanic

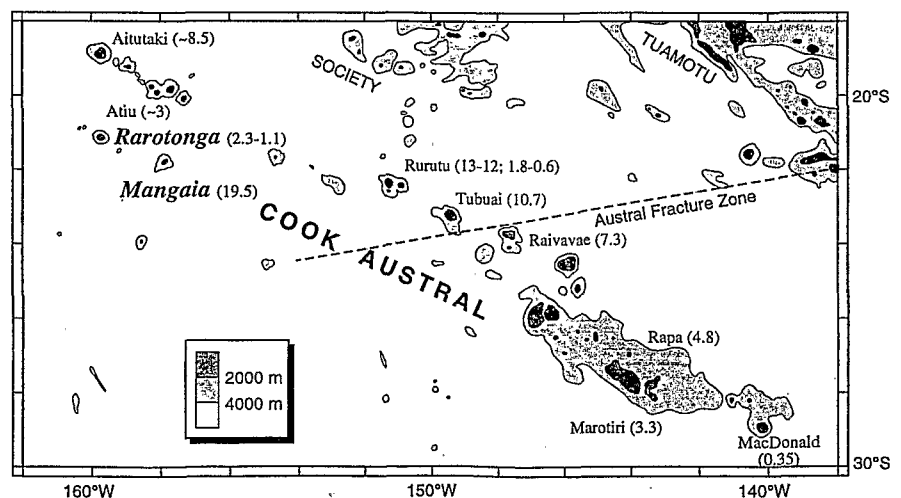


Figure 1. Cook-Austral archipelago, South Pacific. Bathymetry contour lines are shown at 2000 and 4000 m. Numbers in parentheses represent initiation of volcanism (Ma) at each edifice (Diraison et al., 1991). Samples were collected from Rarotonga and Mangaia Islands.

* E-mail: tatsumi@bep.vgs.kyoto-u.ac.jp.



rocks used in this study were collected from stream valleys near the central hills.

ANALYTICAL TECHNIQUES

Major and trace elements were analyzed with Rigaku 3550 and 3070 X-ray fluorescence spectrometers on fused glass beads and pressed powder pellets, respectively, following the methods of Goto and Tatsumi (1994, 1996).

The PGE and Au concentrations were determined by an inductively-coupled-plasma mass spectrometer (VG Plasma Quad 3) with improved techniques (described in Oguri et al., 1999). In these fire-assay and tellurium coprecipitation methods, fusion was repeated twice and was carried out under reduced conditions. Duplicate Te coprecipitation was also performed under suitable temperatures and durations. Total blanks were <42 pg/g sample except for Ru (220 pg) and Au (160 pg), and detection limits were 21, 3, 9, 2, 13, and 53 ppt for Ru, Rh, Pd, Ir, Pt, and Au, respectively. The values and 1 σ errors (all in ppb) obtained for UMT-1, a reference sample from the Canadian Centre for Mineral and Energy Technology, by duplicated analyses (n = 5) are Ru = 8.7 ± 0.7 (10.9 ± 1.5 in the reference sample), Rh = 8.8 ± 0.4 (9.5 ± 1.1), Pd = 95.6 ± 3.7 (106 ± 3), Ir = 10.0 ± 0.8 (8.8 ± 0.6), Pr = 132 ± 9 (129 ± 5), and Au = 50.5 ± 1.8 (48 ± 2).

Pb isotope compositions were measured with a Finnigan MAT 261 mass spectrometer with the analytical procedures given in Shimoda and Nohda (1995). The averages and standard deviations for NBS standard reference material (SRM) 981 Pb were $^{206}\text{Pb}/^{204}\text{Pb} = 16.900 \pm 0.005$, $^{207}\text{Pb}/^{204}\text{Pb} = 15.463 \pm 0.007$, and $^{208}\text{Pb}/^{204}\text{Pb} = 36.529 \pm 0.020$. The correction factors per amu for $^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$, and $^{208}\text{Pb}/^{204}\text{Pb}$ are 0.11%, 0.11%, and 0.13%, respectively. The values obtained from repeated analyses of the standard BCR-1 are $^{206}\text{Pb}/^{204}\text{Pb} = 18.813$ and 18.812 , $^{207}\text{Pb}/^{204}\text{Pb} = 15.626$ and 15.627 , and $^{208}\text{Pb}/^{204}\text{Pb} = 38.717$ and 38.727 . The total analytical blank of Pb is lower than 100 pg.

RESULTS AND DISCUSSION

Analytical results are presented in Table 1 with estimates of modal compositions of phenocryst phases. Element abundance data have been recalculated to 100% on a volatile-free basis for plotting in Figures 2 and 3.

Isotopes and Major and Trace Elements

Previous studies have shown that basalts from Mangaia are derived from an HIMU-type source (high $^{238}\text{U}/^{204}\text{Pb}$), whereas basalts from Rarotonga have been characterized as non-HIMU (Zindler and Hart, 1986; Hauri and Hart, 1993; Kogiso et al., 1997b). Isotopic data for three of the present samples are consistent with the previous categorizations (Fig. 2).

It has been documented that HIMU basalts are distinctive among OIBs in the relative enrichment of Nb to other incompatible elements (Weaver,

TABLE 1. COMPOSITIONS OF BASALTS IN MANGAIA AND RAROTONGA ISLANDS

	Mangaia					Rarotonga				
	M-C31	M-C32	M-304.3	M-307	M-306.1	R-304	R-305	R-301.1	R-302	R-C14
SiO ₂	42.75	43.28	43.59	43.98	44.54	43.13	44.04	44.23	44.28	45.06
TiO ₂	2.67	2.98	3.41	2.95	3.03	3.71	3.58	3.33	3.10	2.94
Al ₂ O ₃	10.82	11.69	14.75	11.57	13.13	11.80	14.31	12.54	11.58	11.32
Fe ₂ O ₃ *	13.16	13.42	14.06	13.44	13.48	13.68	12.86	12.83	13.08	12.50
MnO	0.17	0.18	0.19	0.17	0.18	0.17	0.17	0.17	0.17	0.16
MgO	13.57	9.91	5.65	10.34	9.00	9.82	7.41	9.76	11.55	12.37
CaO	12.16	13.33	12.18	13.81	12.47	11.66	10.90	11.56	11.23	9.97
Na ₂ O	2.18	2.60	3.79	2.25	2.45	2.53	2.90	2.22	2.19	2.49
K ₂ O	0.72	0.83	1.11	0.75	0.77	2.01	2.25	1.32	1.52	1.49
P ₂ O ₅	0.36	0.42	0.55	0.41	0.44	0.64	0.69	0.53	0.50	0.50
Total	98.56	98.64	99.30	99.68	99.49	99.14	99.11	98.49	99.20	98.80
Ba	181	224	246	206	206	574	692	490	399	362
Nb	32	43	54	40	42	55	63	45	43	34
Ni	295	151	42	151	101	141	94	149	186	294
Pb	1.2	1.8	2.0	2.7	2.1	5.2	6.3	4.2	3.0	2.4
Rb	13	16	24	16	18	39	49	40	31	27
Sr	409	471	610	466	511	840	1017	732	629	631
Th	-	3.3	5.4	4.1	4.5	6.1	7.9	5.1	4.7	-
Y	18	22	25	19	22	23	23	21	20	19
Zr	159	196	256	190	217	319	307	274	258	233
Ru	0.404	0.093	0.017	0.207	0.072	0.273	0.102	0.134	0.143	0.362
Rh	0.146	0.046	0.007	0.067	0.038	0.086	0.112	0.058	0.059	0.068
Pd	2.517	0.966	0.155	0.940	0.455	1.818	2.950	1.390	2.272	1.556
Ir	0.260	0.076	0.013	0.131	0.050	0.155	0.168	0.100	0.102	0.163
Pt	1.879	0.626	0.112	0.599	0.234	1.479	3.147	1.348	1.632	2.765
Au	1.838	0.772	0.312	0.671	0.539	1.809	1.910	1.471	1.696	1.218
²⁰⁶ Pb/ ²⁰⁴ Pb	21.151	21.465								18.342
²⁰⁷ Pb/ ²⁰⁴ Pb	15.752	15.810								15.534
²⁰⁸ Pb/ ²⁰⁴ Pb	40.252	40.484								38.648
olivine [†]	<5	-10	<5	<5	<5	<5	-10	-10	-10	<5
augite [†]	-10	-10	<5	<5	<5	-	-	-	-10	-

Note: Oxide contents in weight percent, trace elements in parts per millions, noble metals in parts per billion.
*Total iron as Fe₂O₃.
[†]Modal phenocryst percentages.

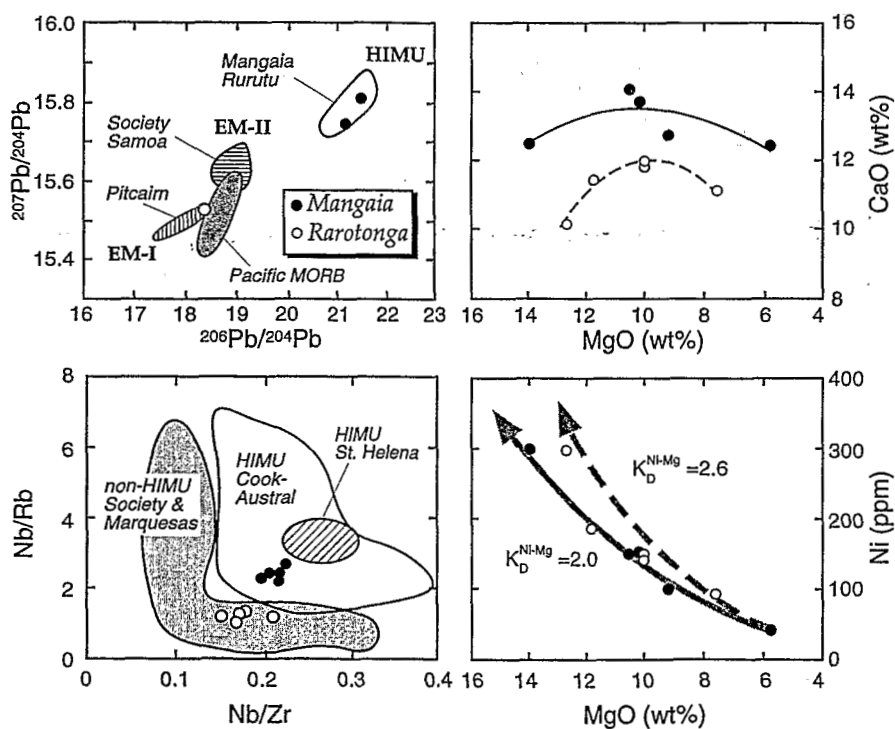


Figure 2. Isotopic and major and trace element characteristics of Mangaia and Rarotonga basalts. Pb isotope compositions of Pacific mid-ocean ridge basalt (MORB) and high $^{238}\text{U}/^{204}\text{Pb}$ (HIMU), EM-I, and EM-II ocean-island basalts (Wright and White, 1987; White et al., 1987; Chaffey et al., 1989; Devey et al., 1990; Hauri and Hart, 1993; Hémond et al., 1993) and Nb/Zr-Nb/Rb relationships for HIMU and non-HIMU basalts from Polynesia and St. Helena (Kogiso et al., 1997b) are also shown.

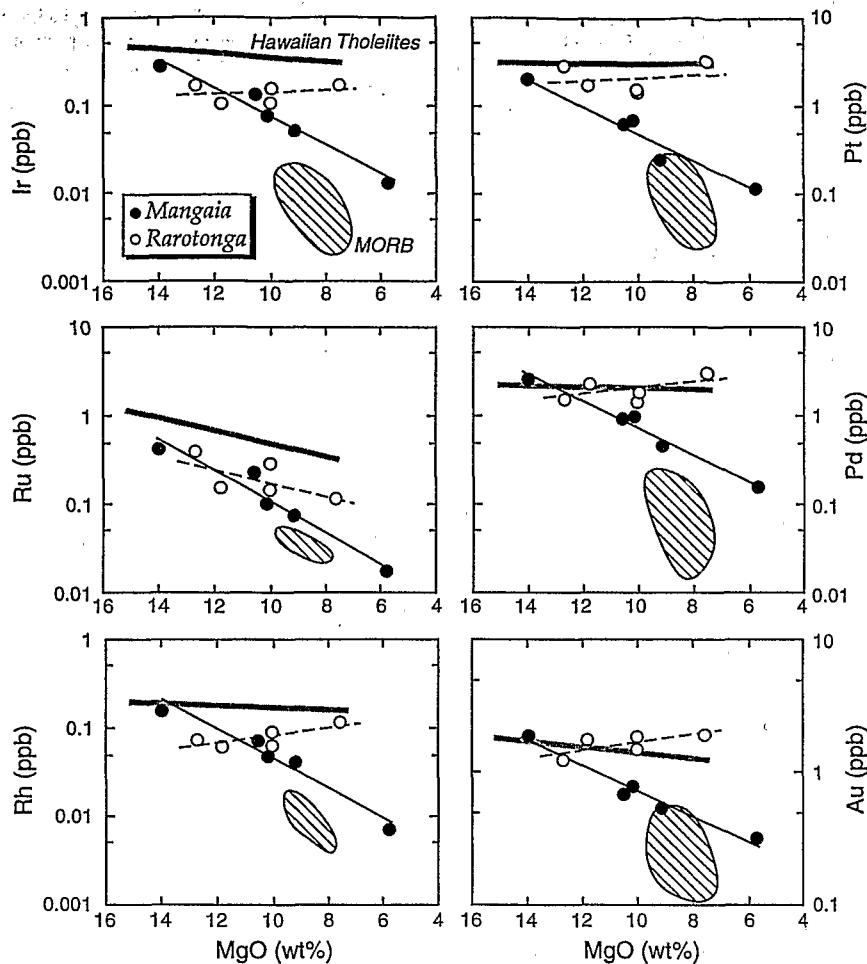


Figure 3. MgO-variation diagrams for platinum group elements (PGE) and Au in high $^{238}\text{U}/^{204}\text{Pb}$ (HIMU) and non-HIMU samples from Polynesia. Hawaiian trends are shown by thick gray lines. Concentrations of most PGEs and Au in non-HIMU basalts increase and those in HIMU samples decrease with decreasing MgO contents. MORB—mid-ocean ridge basalt.

1991). Kogiso et al. (1997b) attributed this both to higher degrees of partial melting of a more fertile source to produce HIMU magmas compared to other OIB magmas and to initial melting in the presence of silicate perovskites, i.e., under lower mantle conditions, to produce HIMU magmas. These geochemical features can be also used to discriminate HIMU from non-HIMU OIBs such as EM-I and EM-II basalts. Nb/Zr and Nb/Rb ratios in the present samples are shown in Figure 2 together with those of Polynesian and St. Helena basalts; the plot suggests that the samples from Mangaia and Rarotonga possess signatures characteristic of HIMU and non-HIMU basalts, respectively. We may thus regard samples from Mangaia and Rarotonga as HIMU and non-HIMU basalts, respectively, although isotope compositions have not been obtained for all samples.

Figure 2 indicates that HIMU basalts are more enriched in CaO than non-HIMU basalts, which can be explained by the involvement of subducted ancient MORB in forming the HIMU geochemical reservoir (Kogiso et al., 1997b). This process is consistent with high U/Pb ratios

in the HIMU source caused by selective extraction of Pb relative to U during dehydration processes in the sinking oceanic crust (Brenan et al., 1995; Kogiso et al., 1997a).

Most basalts in Mangaia and Rarotonga contain considerable amounts of mafic phenocrysts. Although phenocryst-poor samples were selected for the present analyses, we nevertheless examined the effect of crystal accumulation in bulk-rock compositions. In order to identify olivine and/or augite-cumulate rocks, the olivine fractionation trends for Ni and Mg were back-calculated on the basis of (1) the compositions of the olivine-bearing basalt containing the least MgO among the present samples, (2) Mg-Fe and Mg-Ni exchange partition coefficients of 0.3 and 2.0–2.6, respectively, between olivine and an equilibrium melt (Roeder and Emslie, 1970; Kinzler et al., 1990), and (3) $\text{Fe}^{2+}/(\text{Fe}^{2+} + \text{Fe}^{3+}) = 0.9$ in magmas. In this calculation, an iterative procedure was adopted by repeated addition of 0.5% of olivine, which is in equilibrium with the melt. The results shown in Figure 2 demonstrate that the compositional variation in the present samples

is largely explained by fractionation of olivine and not by an accumulation of phenocryst phases.

Noble-Metal Elements

In order to examine the behavior of noble metal concentrations in evolving magmas, the PGE and Au concentrations in HIMU and non-HIMU basalts were plotted against MgO in Figure 3. With the exception of Ru, which has large analytical errors, concentrations of PGEs and Au in non-HIMU basalts increase and those in HIMU samples decrease with decreasing MgO content.

The amount of phenocryst phases separated from the magma can be estimated based on mixing calculations for major elements and mineral compositions. Apparent bulk distribution coefficients of PGEs and Au, which were obtained from such estimates and a Rayleigh fractionation model, are >5 for HIMU basalts. Tatsumi et al. (1999) examined crystal-structure controls on the partitioning of noble-metal elements and considered chromite to be the only nonsulfide phase to crystallize in a basalt magma and fractionate most PGEs effectively. However, Pd and Au may behave as incompatible elements even for chromite (Tatsumi et al., 1999). It is thus suggested that the high bulk partition coefficients for all noble metals obtained for HIMU magmas cannot be explained solely by the separation of silicate and oxide phases from such magmas. Noble-metal elements are highly siderophilic and chalcophilic as indicated by extremely high sulfide/silicate distribution coefficients in the range of 10^3 – 10^5 (Peach et al., 1990, 1994; Fleet et al., 1991), and should be effectively fractionated from a magma that is precipitating sulfides. Therefore, the monotonic decrease in the concentrations of such elements during HIMU magma differentiation can be best explained by separation of sulfides as well as silicate and oxide phases.

In contrast, the differentiation trends of noble metals for non-HIMU magmas imply that effective sulfide separation may not take place in those magmas. Tatsumi et al. (1999) suggested that fractionation solely of silicate and oxide phases cannot account for differentiation trends in Hawaiian tholeiites (Fig. 3); small amounts of sulfides must play a role in the magmatic differentiation. Although the present trends for Rarotonga samples are almost identical to those of Hawaiian samples, it is difficult to define the sulfide saturation in Rarotonga magmas. Even if sulfides were separated from Rarotonga magmas, however, sulfide/silicate ratios in crystallizing phases should be much smaller in non-HIMU Rarotonga magmas than in HIMU Mangaia magmas.

What is the cause of different sulfide/silicate ratios in separating phases in HIMU and non-HIMU magmas? It has been repeatedly emphasized that oxygen fugacity in magmas is one key variable in the control of the PGE fractionation trend (e.g., Ballhaus, 1995). This finding is supported by the observation that the slopes of PGE and Au fractionation trends for MORBs (Peach

et al., 1990; Tatsumi et al., 1999) are much steeper than those for OIBs (Fig. 3), because (1) the S solubility in a silicate melt shows a minimum under the NNO (nickel-nickel oxide) buffer and increases with decreasing oxygen fugacity (Katsura and Nagashima, 1974) and (2) oxygen fugacity in MORB magma is one log unit lower than that in OIB magmas from around the FMQ (fayalite-magnetite-quartz) buffer (Ballhaus, 1993). If so, the fractionation trends of PGEs in the present samples may imply lower oxygen fugacity in HIMU than non-HIMU magmas.

The contrasting fractionation trends of most noble-metal elements for HIMU and non-HIMU basalts seem to cross each other at ~13 wt% MgO (Fig. 3). If values of 14–15 wt% are accepted as the MgO content in a primary Polynesian OIB magma (Kogiso et al., 1997b), then HIMU primary magmas could have higher concentrations of noble-metal elements than non-HIMU magmas. Examination of the behavior of such elements in OIB magmas could provide key constraints on the deep-mantle compositions and on the processes that govern the mantle composition, such as core-mantle interaction.

ACKNOWLEDGMENTS

We thank Richard Walker and Clive Neal for constructive comments on the manuscript, Susumu Nohda for isotope analyses, and Pochi-san for preparing the manuscript and figures. This work was sponsored by a Special Coordination Fund for Promoting Science and Technology (Superplume Project) from the Science and Technology Agency of Japan, a Grant-in-Aid (#08404029) from the Monbusho, and a Mitsubishi Foundation grant to Tatsumi.

REFERENCES CITED

Ballhaus, C., 1993, Redox states of lithospheric and asthenospheric upper mantle: *Contributions to Mineralogy and Petrology*, v. 114, p. 331–348.
 Ballhaus, C., 1995, Is the upper mantle metal-saturated?: *Earth and Planetary Science Letters*, v. 132, p. 75–86.
 Brennan, J. M., Shaw, H. F., and Ryerson, F. J., 1995, Experimental evidence for the origin of lead enrichment in convergent-margin magmas: *Nature*, v. 378, p. 54–56.
 Chaffey, D. J., Cliff, R. A., and Wilson, B. M., 1989, Characterization of the St. Helena magma source, in Saunders, A. D., and Norry, M. J., eds., *Magma-tism in the ocean basins*: Geological Society [London] Special Publication 42, p. 257–276.
 Crocket, J. H., and Skippen, G. B., 1966, Radioactivation determination of palladium in basaltic and ultrabasic rocks: *Geochimica et Cosmochimica Acta*, v. 30, p. 129–141.
 Dalrymple, G. B., Jarrard, R. D., and Clague, D. A., 1975, K-Ar ages of some volcanic rocks from the Cook and Austral Islands: *Geological Society of America Bulletin*, v. 86, p. 1463–1467.

Devey, C. W., Albarede, F., Chemin, J.-L., Michard, A., Muhe, R., and Stoffers, P., 1990, Active submarine volcanism on the Society hotspot swell (W. Pacific): A geochemical study: *Journal of Geophysical Research*, v. 95, p. 5049–5066.
 Diraison, C., Bellon, H., Lèotot, C., Brousse, R., and Barszcz, H. G., 1991, L'alignement de la Société (Polynésie française): volcanologie, géochronologie, proposition d'un modèle de point chaud: *Bulletin de la Société Géologique de France*, v. 162, p. 479–496.
 Duncan, R. A., and McDougall, I., 1976, Linear volcanism in French Polynesia: *Journal of Volcanology and Geothermal Research*, v. 1, p. 197–227.
 Fleet, M. E., Stone, W. E., and Crocket, J. H., 1991, Partitioning of palladium, iridium, and platinum between sulphide liquid and basalt melt: Effect of melt composition, concentration, and oxygen fugacity: *Geochimica et Cosmochimica Acta*, v. 55, p. 2545–2554.
 Fukao, Y., 1992, Seismic tomogram of the Earth's mantle: Geodynamic implications: *Science*, v. 258, p. 625–630.
 Goto, A., and Tatsumi, Y., 1994, Quantitative analysis of rock samples by an X-ray fluorescence spectrometer (I): *Rigaku Journal*, v. 11, p. 40–59.
 Goto, A., and Tatsumi, Y., 1996, Quantitative analysis of rock samples by an X-ray fluorescence spectrometer (II): *Rigaku Journal*, v. 13, p. 20–38.
 Hauri, E. H., and Hart, S. R., 1993, Re-Os isotope systematics of HIMU and EMII oceanic island basalts from the South Pacific Ocean: *Earth and Planetary Science Letters*, v. 114, p. 353–371.
 Hémond, C., Arndt, N. T., Lichtenstein, U., and Hofmann, A. W., 1993, The heterogeneous Iceland plume: Nd-Sr-O isotopes and trace element constraints: *Journal of Geophysical Research*, v. 98, p. 15,833–15,850.
 Katsura, T., and Nagashima, S., 1974, Solubility of sulfur in some magmas at 1 atmosphere: *Geochimica et Cosmochimica Acta*, v. 38, p. 517–531.
 Kinzler, B. J., Grove, T. L., and Recca, S. I., 1990, An experimental study on the effect of temperature and melt composition on the partitioning of nickel between olivine and silicate melt: *Geochimica et Cosmochimica Acta*, v. 54, p. 1255–1265.
 Kogiso, T., Tatsumi, Y., and Nakano, S., 1997a, Trace element transport during dehydration processes in the subducted oceanic crust: I. Experiments and implications for the origin of ocean island basalts: *Earth and Planetary Science Letters*, v. 148, p. 193–206.
 Kogiso, T., Tatsumi, Y., Shimoda, G., and Barszcz, H. G., 1997b, High- μ (HIMU) ocean island basalts in southern Polynesia: New evidence for whole-mantle scale recycling of subducted oceanic crust: *Journal of Geophysical Research*, v. 102, p. 8085–8103.
 Martin, C. E., 1991, Os isotopic characteristics of mantle derived rocks: *Geochimica et Cosmochimica Acta*, v. 55, p. 1421–1434.
 Matsuda, J., Notsu, K., Okano, J., Yaskawa, K., and Chungue, L., 1984, Geochemical implications from Sr isotopes and K-Ar age determinations for the Cook-Austral Islands chain: *Tectonophysics*, v. 104, p. 145–154.
 Oguri, K., Shimoda, G., and Tatsumi, Y., 1999, Quantitative determination of gold and the platinum-group elements in geological samples using improved NiS fire assay and tellurium coprecipitation with inductively coupled plasma-mass spectrometry (ICP-MS): *Chemical Geology*, v. 157, p. 189–197.
 Peach, C. L., Mathez, E. A., and Keays, R. R., 1990, Sulphide melt-silicate distribution coefficient for noble metals and other chalcophile elements as deduced from MORB: Implications for partial melting: *Geochimica et Cosmochimica Acta*, v. 54, p. 3379–3389.
 Peach, C. L., Mathez, E. A., Keays, R. R., and Reeves, S. J., 1994, Experimentally determined sulfide melt-silicate melt partition coefficients for iridium and palladium: *Chemical Geology*, v. 117, p. 361–377.
 Roeder, P. L., and Emslie, R. F., 1970, Olivine-liquid equilibrium: *Contributions to Mineralogy and Petrology*, v. 29, p. 275–289.
 Shimoda, H., and Nohda, S., 1995, Lead isotope analyses: An application to GSJ standard rock samples: *Kyoto University Bulletin of Human and Environmental Studies*, v. 4, p. 29–36.
 Stacey, F. D., and Loper, D. E., 1983, The thermal boundary-layer interpretation of D' and its role as a plume source: *Physics of Earth and Planetary Interiors*, v. 33, p. 45–55.
 Tatsumi, Y., Oguri, K., and Shimoda, G., 1999, The behaviour of platinum-group elements during magmatic differentiation in Hawaiian tholeiites: *Geochemical Journal*, v. 33, p. 237–247.
 Thompson, G. M., Malpas, J., and Smith, I. M., 1998, Volcanic geology of Rarotonga, southern Pacific Ocean: *New Zealand Journal of Geology and Geophysics*, v. 48, p. 95–104.
 Turner, D. L., and Jarrard, R. D., 1982, K-Ar dating of the Cook-Austral island chain: A test of the hotspot hypothesis: *Journal of Volcanology and Geothermal Research*, v. 12, p. 187–220.
 Walker, R. J., Morgan, J. W., and Horn, M. F., 1995, Osmium-187 enrichment in some plume: Evidence for core-mantle interaction?: *Science*, v. 269, p. 819–822.
 Weaver, B. L., 1991, The origin of ocean island basalt end-member compositions: Trace element and isotopic constraints: *Earth and Planetary Science Letters*, v. 104, p. 381–397.
 Wen, L., and Helmberger, D. V., 1998, Ultra-low velocity zone near the core-mantle boundary from broadband PKP precursors: *Science*, v. 279, p. 1701–1703.
 White, W. M., Hofmann, A. W., and Puchelt, H., 1987, Isotope geochemistry of Pacific mid-ocean ridge basalt: *Journal of Geophysical Research*, v. 92, p. 4881–4893.
 Wood, B. L., and Hay, R. F., 1970, Geology of the Cook Islands: *New Zealand Geological Survey Bulletin*, v. 82, 103 p.
 Wright, E., and White, W. M., 1987, The origin of Samoa: New evidence from Sr, Nd, and Pb isotopes: *Earth and Planetary Science Letters*, v. 81, p. 151–162.
 Zindler, A., and Hart, S., 1986, Chemical geodynamics: *Annual Review of Earth and Planetary Sciences*, v. 14, p. 493–571.

Manuscript received May 24, 1999
 Revised manuscript received September 24, 1999
 Manuscript accepted October 21, 1999