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Lead isotopic compositions in olivine-hosted melt inclusions from HIMU basalts and possible link to sulfide components

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Abstract

Pb isotopic compositions of melt inclusions in olivine phenocrysts of lava samples from Mangaia and Rarotonga, Cook-Austral islands, have been determined by secondary ion mass spectrometry. The Pb isotopic compositions of melt inclusions from Rarotonga are consistent with those of bulk rock. On the other hand, Pb isotopic compositions of sulfide-free melt inclusions from Mangaia Island are widely distributed along the join between HIMU (i.e. highly radiogenic Pb) and less radiogenic components. The variation is much wider than that in bulk-rock samples that are invariably end-member HIMU values. In contrast, Pb isotopic compositions of sulfide and carbonate inclusions are restricted to HIMU end-member values. The variations in Pb isotopic ratios can be explained by mixing between the HIMU component and another component with less radiogenic Pb, and suggests that the HIMU component is enriched in sulfide and carbonate phases as well as Pb compared with the less radiogenic component. It seems paradoxical that a sulfide-rich component is associated with highly radiogenic Pb, because sulfides generally have extremely low U/Pb and Th/Pb ratios, which result in quite unradiogenic Pb. Subducted oceanic crust is not a likely source for such a sulfide-rich component because sulfides in subducted crust may not survive dehydration processes in subduction zones, although it can produce highly radiogenic Pb. The association of highly radiogenic Pb and sulfides implies that sulfides and radiogenic Pb in the HIMU source originate from distinct reservoirs. A possible origin of the sulfides is the Earth's core, because the core is the largest sulfur budget in the Earth. The highly radiogenic Pb may originate from subducted oceanic crust which resides at the core-mantle boundary. Alternative source for radiogenic Pb is Ca-perovskite in the lower mantle, which is the main host of incompatible elements in the lower mantle and has high U/Pb and Th/Pb ratios. The core-derived sulfides would exchange Pb isotopes with subducted oceanic crust or Ca-perovskite during upwelling in the lower mantle, resulting in production of a sulfur-rich reservoir with highly radiogenic Pb. © 2004 Elsevier B.V. All rights reserved.

Keywords: Ocean island basalts; Mid ocean ridge basalt; HIMU lavas; Pb isotopes; Melt inclusion

1. Introduction

* Corresponding author. *E-mail address:* yuri@geo.titech.ac.jp (H. Yurimoto). There is significant isotopic diversity in mantlederived volcanic rocks, such as ocean island basalts

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(OIBs) and mid ocean ridge basalt (MORB) and it is believed to correspond to global chemical heterogeneity in the Earth's mantle (e.g., Gast et al., 1964; DePaolo and Wasserburg, 1976; White and Hofmann, 1982; Schilling et al., 1985). The isotopic variation in OIBs and MORB is expressed by four end-member components (Zindler and Hart, 1986): DMM (depleted MORB source mantle), EM1 (enriched mantle 1), EM2 (enriched mantle 2), and HIMU (high μ ; $\mu = ^{238} U/^{204}Pb$). Revealing the origin of these four components is essential in understanding physical and chemical evolution of the mantle.

There is a consensus that the DMM component represents the upper most mantle which has been depleted in incompatible elements by long-term extraction of crustal components, but there has been considerable debate on the origin of other isotopically extreme components, EM1, EM2, and HIMU (see review by Zindler and Hart, 1986). Nevertheless, the most widely appealing model is that all the three components are affected by recycling of subducted crustal materials including oceanic basaltic crust with or without continent-derived sediments (e.g., Chase, 1981; Hofmann and White, 1982; Zindler et al., 1982; Chauvel et al., 1992; Hauri and Hart, 1993). Many of the studies that proposed crustal recycling model suggested that HIMU originates solely from recycled basaltic crust but sources for EM1 and EM2 contain small amounts of sediments in addition to basaltic crust (Weaver, 1991; Chauvel et al., 1992; Hauri and Hart, 1993; Schiano, 2001). This implies that addition of sediment component to HIMU source can explain isotope signatures of EM1 and EM2. Thus, HIMU seems to play a key role in generating heterogeneity in the mantle.

HIMU is characterized by its extremely radiogenic Pb isotopes (typically 206 Pb/ 204 Pb > 20.5), which has been explained by entertainment of subducted oceanic crust enriched in U relative to Pb by subduction-related processes and/or hydrothermal activities at mid-ocean ridges (e.g., Weaver, 1991; Chauvel et al., 1992; Brenan et al., 1995; Kogiso et al., 1997a). Other mechanisms are also proposed for the origin of HIMU, such as metasomatism by CO₂- or H₂O-rich fluids (Hart et al., 1986; Halliday, 1990), extraction of Pb into the core (Vollmer, 1977; Vidal and Dosso, 1978), and U/Pb fractionation involving Ca-perovskite in the lower mantle (Taura et al., 2001).

A key point to reveal the origin of HIMU is to understand how HIMU lavas have obtained radiogenic Pb isotope characteristics in the mantle. Previous geochemical studies on HIMU lavas were restricted to isotope analyses of bulk rock samples, and have demonstrated that HIMU lavas have surprisingly homogeneous Pb isotopic ratios (see review by Stracke, 2003). This implies that the HIMU source have obtained homogeneous Pb isotope signatures prior to melting. However, Saal et al. (1998) reported Pb isotope analyses of melt inclusions in phenocrysts in HIMU and EM2 lavas from Polynesia, and demonstrated extensive variations of Pb isotopes within single rock specimens of HIMU, which extremely exceed those for whole-rock lavas. This observation strongly suggests that the homogeneous Pb isotope signature of erupted HIMU lavas was produced by processes related to volcanic plumbing system within the lithosphere (Saal et al., 1998). This further indicates that whole-rock composition of HIMU lavas represent mixing between a source with highly radiogenic Pb ("real" HIMU component) and another less radiogenic component.

Although the main scope of Saal et al. (1998) was argument for the origin of such small-scale heterogeneities in volcanic rocks, their data include another important inference: Pb isotopes of sulfideand carbonate-bearing melt inclusions are restricted to near HIMU end-member values while silicate-rich melt inclusions show a wide range of Pb isotopes (Fig. 3B of Saal et al., 1998). This implies some genetic linkage between carriers of HIMU-like Pb and sulfur- and carbon-bearing phases in the mantle, although this point has not been discussed deeply in Saal et al. (1998). Since Pb has a chalcophile character, sulfide phases can be principal hosts for Pb and therefore strongly influence the behavior of Pb during various differentiation processes in the mantle. In addition, as sulfur is one of the light elements potentially distributed in the Earth's core, the connection between sulfide phases and radiogenic Pb isotopes would be attributed to some processes in the core-mantle boundary region (e.g., Vollmer, 1977; Vidal and Dosso, 1978). For better understanding of the origin of HIMU, more data are needed to reveal how radiogenic Pb isotopes of HIMU are associated with sulfide phases.

Here we report new Pb isotope analyses of olivine-hosted melt inclusions of OIB lavas from Cook–Austral Islands using a secondary ion mass spectrometry (SIMS). The main scope of this paper is to compare Pb isotopic characteristics of inclusions between lavas of the most extreme HIMU (Mangaia) and those with isotope signatures furthest from HIMU in the same island chain (Rarotonga). We characterize Pb isotope features of individual phases in the melt inclusions from each island, and discuss possible scenarios for the origin of HIMU component.

2. Sample descriptions

We used lava samples from Mangaia and Rarotonga, Cook-Austral islands (Fig. 1). Detailed geological background of Mangaia and Rarotonga has been summarized in Kogiso et al. (1997b) and Tatsumi et al. (2000). The ages of volcanism are 19.5-17 Ma in Mangaia and 2.3-1.1 Ma in Rarotonga (Duncan and McDougall, 1976; Turner and Jarrard, 1982; Matsuda et al., 1984; Diraison et al., 1991). Isotopic compositions of Cook-Austral lavas form a linear array between HIMU and "bulk silicate Earth" (BSE: Zindler and Hart, 1986). Lavas from Mangaia have the most extreme HIMU signatures (i.e. the most radiogenic Pb isotopic composition) among worldwide OIB (Woodhead, 1996). Rarotonga lavas have isotope signatures furthest from HIMU among Cook-Austral lavas (i.e. closest to BSE), and their Pb isotopic ratios are plotted between EM1 and EM2 (Nakamura and Tatsumoto, 1988; Schiano, 2001).

We selected three samples (MGA-C8, MGA-C22, MGA-C23) from Mangaia and two samples (RTG-C8, RTG-C10) from Rarotonga for Pb isotope analyses of olivine-hosted inclusions. These samples are olivine-phyric alkali basalts and ankaramites containing abundant olivine, augite and plagioclase phenocrysts of mm–cm sizes. The groundmass mainly consists of augite, plagioclase, alkali feldspar, spinel, ilmenite and apatite. Sulfide phases are commonly observed in groundmass of the Mangaia samples but rare in the Rarotonga ones.

Shapes of olivine-hosted melt inclusions in this study are rounded in many cases, and the size is up to $150 \,\mu$ m. Melt inclusions from Rarotonga samples are smaller than those from Mangaia. We classified the melt inclusions into silicate-rich, sulfide-rich, and carbonate-rich melt-inclusions according to phase as-



Fig. 1. Location map showing hotspots in the Pacific Ocean (a) and the area of Cook–Austral Islands in the south Pacific (b). Stars in both panels indicate locations of hotspots (Duncan and Richards, 1991; Clouard and Bonneville, 2001). Names of hotspots are also shown in (b). The stippled area in (a) is the estimated location of "South Pacific Superplume" (Larson, 1991), beneath which there is a large seismic low-velocity anomaly region down to the core–mantle boundary (Zhao, 2001). Bathymetry contour lines are drawn in 1000 m interval, with thick lines at 3000 m depth. The seafloor bathymetry data are from Smith and Sandwell (1997).

semblage (Fig. 2). Samples from both Mangaia and Rarotonga contain all three types of melt inclusions.

Silicate-rich inclusions consist of glass, silicates (augite, apatite and hornblende), oxides (spinel and magnetite), and minor amounts of sulfides. Compositions of glasses are often evolved to phonolitic probably due to crystallization of the daughter minerals. Carbonate-rich inclusions contain predominantly carbonate minerals, often associated with sulfides and rarely silicate phases. Carbonate occurs as a globule and individual mineral phases cannot be recognized owing to very small size. Chemical compositions of Carbonates are dominant in calcite component with



Fig. 2. Back scattered electron images of olivine-hosted melt inclusions: (a) silicate-rich melt inclusion (MGA-c8-2); (b) sulfide-containing silicate-rich melt inclusion (MGA-c8-3); (c) sulfide-rich melt inclusion (MGA-c8-4s); (d) carbonate-rich melt inclusion (MGA-c8-4c); and (e) silicate-rich melt inclusion (RTG-c10-12). sp: Cr-spinel, mg: magnetite, ol: host olivine, cpx: augite, hbl: hornblende, po: pyrrhotite, pn: pentlandite, iss: intermediate solid solution-phase (Cu–Fe–S), car: carbonates, ap: apatite.

minor dolomite component. Many of sulfide-rich inclusions contain sulfides only, but some are accompanied with minor amounts of silicates. Sulfides consist of mixture of pyrrhotite, pentlandite and iss-phase (Fe–Cu–S), indicating that they crystallized from sulfide liquid of Cu–Fe–Ni–S system.

Silicate-rich melt inclusions in Rarotonga sample rarely contain sulfide and carbonate phases. Sulfide-rich or carbonate-rich melt-inclusions are also rare from Rarotonga samples.

3. Analytical procedures

Selected samples were roughly crushed in a stainless steel mill. Olivine crystals were picked up from these crushed samples by hand. The picked olivine crystals were observed with a binocular microscope to find melt inclusions. Inclusions connected with cracks or veins in host olivine crystal were excluded from analysis in order to eliminate any contaminations after olivine crystallization, such as late stage magma mixing in magma chambers and weathering after eruption.

Olivine crystals hosting melt inclusions were mounted in acrylic resin and ground until melt inclusions are exposed onto the olivine surface. The mounted olivine crystals were polished with $3 \mu m$ and $1 \mu m$ alumina film sheets. Before analysis by scanning electron microscopy, polished samples were coated with carbon of 20 nm thickness so as to eliminate electrostatic charge-up on the sample surface. For the same purpose, before analysis by secondary mass spectrometry, samples were coated with gold film of 40 nm in thickness after removing the carbon film.

Back-scattered electron images and quantitative X-ray analyses were collected using a JEOL JSM-5310LV scanning electron microscope equipped with an Oxford LINK-ISIS energy dispersive detector at Tokyo Institute of Technology (TiTech). In situ Pb isotope analyses were collected with the TiTech Cameca ims-1270 SIMS instrument. Primary ion beam of ${}^{16}O^{-}$ produced by duoplasmatron was used under 23 keV energy, 30-60 nA currents and $20-30 \,\mu\text{m}$ in diameter. Secondary ions were collected from the central area of $20 \,\mu\text{m}$ in square using a mechanical aperture. Mass resolution power was adjusted to about 4000 to exclude the molecular ion interferences.

Each analysis consisted of 50 cycles of sequential measurements of ²⁰⁴Pb, ²⁰⁶Pb, ²⁰⁷Pb, and ²⁰⁶Pb in peak jumping mode. Because counts of ²⁰⁴Pb from melt inclusions were close to or less than detection limit, we discussed ²⁰⁷Pb/²⁰⁶Pb and ²⁰⁸Pb/²⁰⁶Pb ratios in this study. Counting time was set to 10 s for ²⁰⁴Pb, ²⁰⁶Pb, ²⁰⁷Pb, ²⁰⁷Pb, and 5 s for ²⁰⁸Pb. Isotopic ratios of ²⁰⁷Pb/²⁰⁶Pb and ²⁰⁸Pb/²⁰⁶Pb were determined by the corresponding secondary ion ratios. Degrees of instrumental mass fractionation were expected to less than measurement uncertainties of repeated analyses (Fig. 3). Age corrections on Pb isotopic ratios were not applied because of relatively young ages of the samples (<20 Ma).

Lead concentrations were determined by 208 Pb/ 30 Si secondary ion ratios under the same analytical



Fig. 3. Repeated analyses of lead isotope ratios of a synthetic glass from JB-2 rock reference powder distributed by Geological Survey of Japan. A reference value of lead isotope ratios of JA-2 is plotted by a solid diamond (Koide and Nakamura, 1990). Error bars are estimated 2σ limits among the analyses. The mean value among analyses is plotted lower left of the reference value indicating ionization enhancement of secondary ions for lighter masses by primary beam sputtering. Note that the reference value is plotted within the range of 2σ confidence.

condition. A JA-2 glass, synthesized from wellcharacterized rock standard JA-2 distributed from Geological Survey of Japan, was used for determination of conversion factor from the secondary ion ratio to the concentration ratio. Si contents of the sputtered area by SIMS were determined by electron probe micro analysis before SIMS. Because glass pools in silicate-rich inclusions are smaller than the primary beam size, Pb concentrations and isotopic ratios for glasses are analyzed together with other crystal phases excluding sulfides. We mentioned these spots as "silicate" in Table 1. Also, the data for sulfide-rich inclusions are often affected by small amounts of silicates included there. In this case, we note it in Table 1.

4. Results

Lead isotopic compositions of olivine-hosted melt inclusions are listed in Table 1. Forsterite contents of host olivine crystals range from 0.78 to 0.84 (0.81 in average) and from 0.74 to 0.82 (0.79 in average) for Mangaia and Rarotonga samples, respectively. There is no detectible correlation between host olivine composition and Pb isotopic ratios of inclusions.

Pb concentrations of glasses in silicate-rich inclusions range from 1 to 10 ppm (Fig. 4). Some inclusions from Mangaia have much higher Pb concentrations up to several hundred ppm, which may be due to the presence of other phases within glass matrix.

Pb isotopic ratios in inclusions from Mangaia range from typical HIMU values $(^{207}\text{Pb}/^{206}\text{Pb} \sim 0.72$ and 208 Pb/ 206 Pb \sim 1.85) to less radiogenic (i.e. higher ²⁰⁷Pb/²⁰⁶Pb and ²⁰⁸Pb/²⁰⁶Pb) values, and the total ranges are much larger than those observed in Mangaia whole-rock lavas (Fig. 5). We measured Pb isotope ratios from different spots in an inclusion for several inclusions (Table 1). Degrees of beam overlap among different phases in an inclusion are different one another because of small daughter minerals in an inclusion. Note that Pb isotopic compositions among glasses and sulfides in a single inclusion show the same values within analytical uncertainties, indicating that isotopic equilibrium was achieved in single inclusion (Table 1). Less radiogenic Pb isotope values are observed only in silicate-rich inclusions, and all analyzed sulfides and carbonates have Pb isotopic ratios typical of end-member HIMU. These observations are

Rock no.	Olivine no.	Spot no.	Pb (ppm)	207 Pb/ 206 Pb ($2\sigma_{\rm m}$)	208 Pb/ 206 Pb ($2\sigma_{\rm m}$)	Phase
Mangaja					, , , , , , , , , , , , , , , , , , , ,	
MGA-c8	2	M8-02-3	na	0.730 ± 0.009	1.895 ± 0.017	Silicate
MGA-c8	2	M8-02a02	8.3	0.735 ± 0.009 0.735 ± 0.010	1.898 ± 0.028	Silicate
				0.732 ± 0.007	1.897 ± 0.005	Silicate
	2	M8 02-2		0.742 + 0.005	1 004 + 0.015	C16.1.0
MGA-c8	2	M8-02s2	n.a.	0.743 ± 0.005 0.723 \pm 0.005	1.884 ± 0.015 1.861 ± 0.014	Suinde ^a
MOA-CO	2	W18-0285	11.a.	0.735 ± 0.005	1.601 ± 0.014	Sunde
				0.738 ± 0.014	1.872 ± 0.033	Sulfide ^a
MGA-c8	3	M8-03a01	217	0.741 ± 0.003	1.889 ± 0.009	Silicate
MGA-c8	3	M8-03a03	54	0.738 ± 0.002	1.885 ± 0.008	Silicate
				0.740 ± 0.005	1.887 ± 0.006	Silicate
MGA-c8	3	M8-03a02s	n.a.	0.743 ± 0.003	1.906 ± 0.009	Sulfide ^a
MGA-c8	3	M8-03s	n.a.	0.726 ± 0.010	1.858 ± 0.036	Sulfide ^a
				0.734 ± 0.025	1.882 ± 0.068	Sulfide ^a
MGA-c8	40	M8-0s4c	na	0.728 ± 0.023	1.846 ± 0.059	Carbonate
MGA-c8	4s	M8-0s4s	n.a.	0.729 ± 0.007	1.846 ± 0.025	Sulfide
MGA-c8	5	M8-05s	n.a.	0.733 ± 0.002	1.874 ± 0.007	Sulfide
MGA-c8	7	M8-07-1	n.a.	0.772 ± 0.010	1.957 ± 0.025	Silicate
MGA-c8	7	M8-07-1-2	6.5	0.761 ± 0.006	1.920 ± 0.016	Silicate
MGA-c8	7	M8-07-2	n.a.	0.762 ± 0.011	1.935 ± 0.032	Silicate
MGA-c8	7	M8-07-2-2	4.5	0.754 ± 0.010	1.910 ± 0.025	Silicate
				0.762 ± 0.015	1.931 ± 0.041	Silicate
MGA-c8	9	M8-09-01	1.4	0.749 ± 0.018	1.912 ± 0.054	Silicate
MGA-c8	11	M8-11-1	n.a.	0.710 ± 0.013	1.878 ± 0.029	Silicate
MGA-c8	12	M8-12-2	n.a.	0.728 ± 0.010	1.856 ± 0.028	Silicate
MGA-c8	12	M8-12-4	n.a.	0.725 ± 0.024	1.884 ± 0.065	Silicate
				0.727 ± 0.004	1.870 ± 0.038	Silicate
MGA c8	21	M8 21 1	0.8	0.729 ± 0.009	1860 ± 0.017	Silicate
MGA-c8	21	M8-21-1 M8-21-2	5.0	0.729 ± 0.009 0.722 ± 0.005	1.809 ± 0.017 1.898 ± 0.017	Silicate
MGA-c8 MGA-c8	21	M8-21-3	11	0.724 ± 0.008	1.902 ± 0.019	Silicate
				0.725 ± 0.007	1.890 ± 0.037	Silicate
MGA-c8	21	M8-21-1s	na	0.739 ± 0.005	1.885 ± 0.018	Sulfidea
MGA-c8	21	M8-22-1	13	0.739 ± 0.009 0.720 ± 0.009	1.852 ± 0.030	Silicate
MGA-c8	23	M8-23-2	11	0.754 ± 0.010	1.919 ± 0.027	Silicate
MGA-c8	24	M8-24-1	n.a.	0.740 ± 0.009	1.887 ± 0.031	Silicate
MGA-c8	25	M8-25-01	3.4	0.756 ± 0.015	1.912 ± 0.038	Silicate
MGA-c22	20	M22-20-1	2.0	0.794 ± 0.016	1.967 ± 0.063	Silicate
MGA-c22	21	M22-21-1	1.4	0.750 ± 0.019	1.921 ± 0.045	Silicate
MGA-c22	24	M22-24-1	n.a.	0.728 ± 0.010	1.874 ± 0.035	Silicate
MGA-c23	1	M23-01-1	6.7	0.746 ± 0.008	1.907 ± 0.025	Silicate
MGA-c23	1	M23-01-2	10	0.741 ± 0.017	1.888 ± 0.067	Silicate
MGA-c23	1	M23-01-3	7.3	0.735 ± 0.014	1.848 ± 0.032	Silicate

Table 1 Pb isotopic compositions of olivine hosted melt inclusions

 $0.741 \pm 0.010 \qquad 1.881 \pm 0.060 \qquad \text{Silicate}$

Table 1 (Continued)

Rock no.	Olivine no.	Spot no.	Pb (ppm)	$^{207}{\rm Pb}/^{206}{\rm Pb}~(2\sigma_{\rm m})$	$^{208}{\rm Pb}/^{206}{\rm Pb}~(2\sigma_{\rm m})$	Phase
Rarotonga						
RTG-c8	1	R8-01-1	2.1	0.85 ± 0.016	2.146 ± 0.044	Silicate
RTG-c10	11	R10-11-1	n.a.	0.857 ± 0.011	2.115 ± 0.035	Silicate
RTG-c10	11	R10-11-2	5.4	0.839 ± 0.008	2.145 ± 0.056	Silicate
				0.848 ± 0.025	2.130 ± 0.043	Silicate
RTG-c10	12	R10-12-1	5.9	0.844 ± 0.015	2.095 ± 0.034	Silicate
RTG-c10	12	R10-12-2	1.3	0.835 ± 0.028	2.128 ± 0.056	Silicate
RTG-c10	12	R10-12a-2	2.7	0.838 ± 0.015	2.109 ± 0.041	Silicate
				0.839 ± 0.009	2.111 ± 0.033	Silicate
RTG-c10	13	R10-13-1s	n.a.	0.848 ± 0.015	2.048 ± 0.050	Sulfide
RTG-c10	14	R10-14-1	5.6	0.838 ± 0.010	2.106 ± 0.035	Silicate
RTG-c10	14	R10-14-2	3.6	0.838 ± 0.011	2.088 ± 0.033	Silicate
				0.838 ± 0.000	2.097 ± 0.025	Silicate
RTG-c10	15	R10-15-1	5.4	0.830 ± 0.010	2.102 ± 0.032	Silicate

n.a.: not analyzed.

^a Included silicate phases.



Fig. 4. Lead isotopic ratios against Pb concentrations of the analyzed point. Error bars for individual plot represent 2σ limits determined by statistics of secondary ion intensities.

consistent with the data by Saal et al. (1998), although the total range of Pb isotopic ratios in this study is about half of theirs. This may simply result from individual specificity of the samples. Pb isotopic ratios of inclusions from Rarotonga are plotted along the join between EM2 and EM1, which are similar to the range of whole-rock Pb isotopic compositions (Fig. 5).

5. Discussion

Large variations in Pb isotopic ratios of inclusions from Mangaia indicate that at least two geochemical components contributed to the genesis of Mangaia magmas. One component, which has highly radiogenic Pb, may be identical to the HIMU component observed in whole-rock lavas. The other component is characterized by less radiogenic Pb (hereafter called the less radiogenic component, as in Saal et al., 1998), and its signatures are not reflected in whole-rock Pb isotopes. Note again that Pb isotopic ratios of sulfide and carbonate inclusions are restricted to the HIMU end-member values (Fig. 5), as demonstrated by Saal et al. (1998). This implies that there may be some strong connection between sulfide- and carbonate-bearing agents and HIMU signature (i.e.



Fig. 5. Lead isotope compositions of olivine-hosted inclusions from Mangaia and Rarotonga. Isotopic mantle end-members of a depleted MORB source mantle (DMM), two enriched mantle components (EM1 and EM2) and a high μ component (HIMU) are also plotted. Error bars for individual plot represent 2σ limits determined by statistics of secondary ion intensities or by variations of independent measurements among different positions in a melt inclusion. The error bars tend to be larger than those of JA-2 glass in Fig. 3 mainly because of lower Pb concentrations of the melt inclusions. The Pb isotopic variations of melt inclusions from a hand specimen rock sample in Rarotonga is distributed over the range of whole rock Pb isotopic ratios (see Fig. 3 of Saal et al., 1998) reported previously. The Pb isotopic variations of silicate melt inclusions from Mangaia Island is widely distributed towards less radiogenic component whereas those of sulfide containing melt inclusions are concentrated in the whole rock Pb isotopic ratios that have HIMU characteristics.

highly radiogenic Pb) in the mantle. Saal et al. (1998) briefly mentioned the association of carbonates and sulfides with the HIMU signature, but they did not deeply discuss genetic relationship between them. Here we focus on the link between sulfides and radiogenic Pb, and discuss possible mechanisms for producing HIMU signature in the mantle with regard to the role of sulfides.

5.1. Characteristics of HIMU and less radiogenic components

In general, Pb abundances in sulfides are more than three orders of magnitude higher than those in silicates because of its chalcophile character, and therefore it is likely that Pb isotopic ratios of sulfide-bearing rocks are strongly controlled by sulfides. Typical secondary ion intensities of ²⁰⁸Pb from silicates and sulfides in this study were several tens counts per second (cps) and $\sim 10^4$ cps, respectively, supporting the general view. In Mangaia samples, sulfides are commonly present in groundmass and inclusions, and sulfides in inclusions have similar Pb isotopic ratios with whole-rock lavas (Fig. 5). In contrast, Rarotonga samples rarely contain sulfide minerals in groundmass and inclusions. Thus, sulfides occur in strong connection with highly radiogenic Pb signatures, suggesting that sulfides are chief host of radiogenic Pb that characterizes the HIMU signature of Mangaia lavas. On the other hand, large variations in Pb isotopes of glass inclusions and absence of sulfide inclusions with less radiogenic Pb indicate that the less radiogenic component is associated with silicate liquid. The absence of whole-rock lavas with less radiogenic Pb in Mangaia indicates that the source for the less radiogenic component is poor in Pb relative to the HIMU component. Thus, the Pb isotopic variations in inclusions can be explained by mixing between sulfide-rich liquid with HIMU signature and Pb-poor silicate liquid with less radiogenic Pb. This further indicates that the source for the HIMU component is more enriched in both sulfides and Pb than that for the less radiogenic component.

It is not clear whether the less radiogenic component of Mangaia has the same origin with the source for Rarotonga lavas. Although the Pb isotope trend of Mangaia inclusions extends toward the field of Rarotonga (Fig. 5), the Pb isotopic ratio of the unradiogenic end of the Mangaia trend is far from those of Rarotonga. Bulk Pb concentrations of Rarotonga lavas are higher than those of Mangaia lavas (Tatsumi et al., 2000), which does not seem to be consistent with expected low Pb concentrations of the less radiogenic component. However, contrasting fractionation trends of noble metal elements between Mangaia and Rarotonga lavas (Tatsumi et al., 2000) indicate higher sulfide/silicate ratios in Mangaia lavas relative to Rarotonga lavas, suggesting that larger amounts of Pb and sulfur were fractionated in Mangaia lavas than in Rarotonga lavas. This implies that the source of Rarotonga lavas could be depleted in Pb and sulfur and might have similar geochemical characteristics with the less radiogenic component in Mangaia. Further analytical data are required for better characterization of the less radiogenic component and its relevance to other OIB lavas.

A possible origin for the less radiogenic component is contaminations by oceanic lithosphere at shallow level. Addition of oceanic lithosphere material to HIMU magmas can produce the observed Pb isotopic trend of Mangaia (Fig. 5), because oceanic crust and lithosphere are expected to have MORB-like (i.e. DMM-like) Pb isotopic ratios (e.g., White, 1993). If the contamination occurs after sulfide phases were exsolved within HIMU magmas, the contaminant would alter significantly Pb isotopic ratios only of silicate phases but not of sulfides because of contrast in Pb concentration between silicates and sulfides. However, the effect of such "selective" contamination should appear in sulfide phases as well because sulfide fractionation occur continuously in HIMU magmas (Tatsumi et al., 2000). Also, sulfides contaminated by lithospheric material can be included in olivine crystals because sulfides fractionate simultaneously with olivine in Mangaia (Tatsumi et al., 2000). Thus, it is not likely that lithospheric contamination is the main cause of the variations in Pb isotopes that are observed only in silicate phases in inclusions, and it is plausible to consider that both the HIMU and less radiogenic components are inherited deep in Mangaia plume.

5.2. Origin of the HIMU component

Enrichment of sulfides and Pb in the HIMU source seems to be paradoxical. Because sulfide phases do not contain U and Th but favor Pb, sulfide itself has extremely low U/Pb and Th/Pb ratios, resulting in low Pb isotopic ratios even after long-term isotope evolution. This indicates that a reservoir enriched with sulfides tends to have unradiogenic Pb while it may have substantially high Pb concentration, unless radiogenic Pb is provided by other phases around sulfides. This dilemma can be solved if the sulfide-rich reservoir originally has highly radiogenic Pb. A candidate of such reservoir may be recycled oceanic crust. MORB has higher sulfur concentrations than peridotite (e.g., Bach et al., 1994; McDonough and Sun, 1995). Also, Pb isotopic ratios of subducted oceanic crust can evolve to highly radiogenic values because of relative enrichment of U relative to Pb during hydrothermal alteration at mid-oceanic ridges and/or during subduction, as suggested by many studies (e.g., Chase, 1981; Hauri and Hart, 1993; Brenan et al., 1995; Kogiso et al., 1997a). Thus, subducted oceanic crust could have higher sulfur and highly radiogenic Pb after long-term residence in the mantle. However, sulfur concentration in oceanic crust should be depleted as well as Pb by hydrothermal alteration (Brevart et al., 1981; Seccombe and Barnes, 1990; Alt, 1994) and probably by subduction-related dehydration processes. Therefore, it is not likely that subducted oceanic crust becomes a sulfur-rich reservoir in the mantle, although it is still a likely source for radiogenic Pb.

Alternative mechanism to produce sulfur-rich HIMU source is that sulfides and radiogenic Pb originate from distinct reservoirs (Fig. 6). If a sulfide-rich reservoir, which has unradiogenic Pb, passes through a reservoir of HIMU signature, the reservoir will equilibrate isotopically and chemically with the surrounding reservoir and finally have radiogenic Pb isotopes. A possible source for the sulfides is the core, because the core is expected to contain substantial amounts of light elements including sulfur. Considerable amounts of Pb are contained in sulfides from the core because of chalcophile character of Pb. In this



Fig. 6. Schematic diagram of HIMU forming processes. Sulfide-rich fluids are derived from the outer core possibly along with other light elements through cooling of the Earth. The sulfides exchange Pb isotopes with subducted oceanic crust at the core-mantle boundary (CMB) or Ca-perovskite during upwelling in the lower mantle, resulting in acquiring HIMU character. The HIMU-sulfides is mixed with silicate liquid with less radiogenic Pb beneath Mangaia volcano. The silicate liquid derives from the less radiogenic component, which might have similar geochemical characteristics with the source for Rarotonga lavas.

case, Pb isotopic composition of the sulfides from the core should be close to the value of iron meteorites (e.g., Tatsumoto et al., 1973). However, the initial Pb isotopic signature is easily disturbed by isotope exchange with other radiogenic-Pb reservoirs.

One of possible sources for radiogenic Pb is subducted oceanic crust, as mentioned above. Recent studies on whole-mantle seismic tomography (e.g., Gu et al., 2001) and high-pressure mineral physics (e.g., Ono et al., 2001) suggest that subducted oceanic crust sinks to the core-mantle boundary if it is cold enough. Subducted crust piled up at the core-mantle boundary can possess Pb isotopic ratios much higher than the HIMU end-member after a long residence (Brenan et al., 1995; Kogiso et al., 1997). When a sulfide-rich fluid derived from the core passes through the stacked subducted crust at the core-mantle boundary, it gains highly radiogenic Pb isotope signatures (Fig. 6).

Another potential source for radiogenic Pb is Ca-perovskite in the lower mantle. Ca-perovskite is one of the major mineral constituents in the lower mantle and is the only major budget for incompatible elements in the lower mantle (Taura et al., 2001), suggesting that Pb isotopic ratios in Ca-perovskite are expected to represent those of the bulk lower mantle. Since Ca-perovskite has high U and relatively low Pb concentrations, Pb isotopic ratios of Ca-perovskite increase to highly radiogenic values with time (Taura et al., 2001). If a sulfide-rich fluid ascends from the core-mantle boundary through the lower mantle, it gradually gets in equilibrium with surrounding mantle. Since Pb is concentrated in Ca-perovskite in the lower mantle, the sulfide-rich fluid exchanges Pb isotopes principally with Ca-perovskite and obtains HIMU characteristics (Fig. 6). The HIMU characteristics of the sulfides are preserved through upwelling in the upper mantle because Pb is highly depleted in the upper mantle (McDonough and Sun, 1995) and because the thickness of the upper mantle is about one fourth of that of the lower mantle. Such HIMU sulfides can be mixed with melts from the less radiogenic component at shallow level beneath Mangaia Island. One drawback for sulfide ascending process is that the sulfide fluid from the core may be much denser than silicate minerals in the lower mantle, preventing it from ascending up to shallower mantle. If sulfur is expelled from the core along with hydrogen (Okuchi, 1997) and/or other light elements, these core-derived elements could form a fluid lighter than the silicate mantle, although further experimental data are needed to constrain the composition and density of such a core-derived fluid.

Thus, the association between radiogenic Pb and sulfide-rich character in the HIMU component can be explained by a model in that sulfides and radiogenic Pb have distinct origins. Although this model is rather speculative and requires stronger constraints for detailed processes, a key point is that several geochemical features of a single geochemical component are not necessarily to be explained by processes in a single reservoir. Even if radiogenic Pb of the HIMU component originates from subducted oceanic crust at the core-mantle boundary, it does not mean that all of the geochemical signatures of subducted crust are reflected in geochemistry of erupted HIMU lavas. Indeed, contribution of subducted oceanic crust cannot explain the sulfide-rich signature of the HIMU component. Another significance of the model is that large-scale upwelling flow of solid mantle like a superplume is not essential for causing HIMU volcanism. Core-derived sulfide-rich fluids, if they exist and are sufficiently light, can bring geochemical features relevant to the core-mantle boundary processes to the surface, but they may not induce large upwelling flow in the solid mantle. This does not preclude the possible existence of a superplume in Polynesia region, but careful estimation of carriers of geochemical components in the mantle is important in considering geodynamical aspect of geochemistry of OIBs.

6. Concluding remarks

The Pb isotopic compositions of glass phases in olivine-hosted inclusions from Rarotonga Island are intermediate between EM1 and EM2. These Pb isotopic compositions of inclusions are consistent with those of bulk rock. On the other hand, Pb isotopic compositions of silicate phases in inclusions from Mangaia Island are distributed along the join between HIMU and a less radiogenic Pb component. The distribution is clearly wider than those of bulk rock. In contrast, Pb isotopic composition of sulfides and carbonates in Mangaia inclusions are invariably close to HIMU end-member values. This indicates that HIMU characteristics of Mangaia lavas are mainly controlled by Pb components of sulfides, suggesting that the HIMU source is enriched in sulfides compared with the less radiogenic component.

It seems paradoxical that the HIMU source is enriched in sulfides, because U abundance of sulfide is negligible but Pb concentrates into sulfides, which leads to quite unradiogenic Pb isotopes in sulfides. This dilemma can be solved if sulfides and radiogenic Pb in the HIMU source have different origins. Sulfides can be supplied from the core-mantle boundary, because the core is the largest budget for sulfur in the Earth. Radiogenic Pb which characterizes HIMU may originate from subducted oceanic crust or Ca-perovskite in the lower mantle.

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