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ENRICHMENT PROCESSES IN THE SUB-ARC MANTLE: A Sr–Nd–Pb ISOTOPIC AND *REE* STUDY OF PRIMITIVE ARC BASALTS FROM THE PHILIPPINES

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ABSTRACT

Within the Macolod Corridor, a SW–NE-trending extensional zone cross-cutting the Taiwan–Luzon arc in the Philippines, numerous centers of eruption have produced primitive to moderately evolved basalts. Those from the eastern part of the area (Macolod basalts) are characterized by increasing *LREE*/*HREE* with decreasing *HREE*. Whereas such a relationship might reflect variable degrees of melting of garnet peridotite, decreasing $^{143}Nd/^{144}Nd$ values with increasing *LREE*/*HREE* suggest that this feature is inherited from the source. Clear correlations exist among $^{143}Nd/^{144}Nd$, $^{87}Sr/^{86}Sr$, and *LREE*/*HREE* values, but there is no correlation between these data and Pb isotopic compositions. In addition, *LREE* enrichment is accompanied by *HFSE* enrichment. These relationships are interpreted to reflect infiltration of the source by melts (controlling the *REE* and *HFSE* geochemistry). Larger contributions from the slab, indicated by high *LREE*/*HREE* values and *HFSE* concentrations, are considered to result in higher degrees of partial melting and, hence, lower *HREE* concentrations.

Keywords: arc magmas, primitive basalts, isotopes, rare-earth elements, Philippines.

SOMMAIRE

Au sein du corridor de Macolod, zone en extension orientée SO–NE et recoupant l'arc de Taiwan–Luzon, dans les Philippines, de nombreux centres éruptifs ont produit des basaltes primitifs ou modérément évolués. Les centres situés dans le secteur est de la région (les basaltes de Macolod) montrent une augmentation dans le rapport des concentrations des terres rares légères à celles des terres rares lourdes à mesure que la concentration de ces dernières diminuent. Tandis qu'une telle augmentation du rapport pourrait résulter de taux variables de fusion d'une péridotite à grenat, une diminution parallèle des valeurs $^{143}Nd/^{144}Nd$ nous fait penser qu'il s'agit plutôt d'une caractéristique héritée de la source. Des corrélations nettes existent parmi $^{143}Nd/^{144}Nd$, $^{87}Sr/^{86}Sr$ et le rapport des terres rares légères à terres rares lourdes, mais aucune corrélation n'est évidente entre ces données et les rapports isotopiques du Pb. De plus, l'enrichissement en terres rares légères est accompagné d'un autre en éléments à potentiel ionique élevé. Ces relations résulteraient de l'infiltration de liquides silicatés à la source, ceux-ci exerçant un contrôle sur la répartition des terres rares et des éléments à potentiel ionique élevé. Une contribution accrue de liquides issus de la plaque, telle qu'indiquée par les teneurs dans ces éléments et le rapport impliquant les terres rares, donnerait des taux de fusion partielle plus élevés, et par conséquent des teneurs en terres rares légères plus faibles.

(Traduit par la Rédaction)

Mots-clés: magmas d'arc, basaltes primitifs, isotopes, terres rares, Philippines.

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INTRODUCTION

The compositional similarity of primitive magmas erupted in island arcs and along mid-ocean ridges (MORB), with regard to major element (Perfit *et al.* 1980), suggests that magmas in both settings are derived from mantle sources that are similar in terms of fertility. However, arc volcanic rocks are usually highly enriched in certain incompatible trace elements relative to MORB, in particular the large-ion lithophile elements (*LILE*), Th, U, and Pb, and, in many cases, the light rare-earth elements (*LREE*). In contrast, the incompatible high-field-strength elements (*HFSE*) in arc volcanic rocks are typically depleted relative to MORB. The enrichment in *LILE* and *LREE* is generally considered to reflect contributions from the subducted lithosphere and crust, but there is little agreement regarding the processes involved. In particular, it is not clear

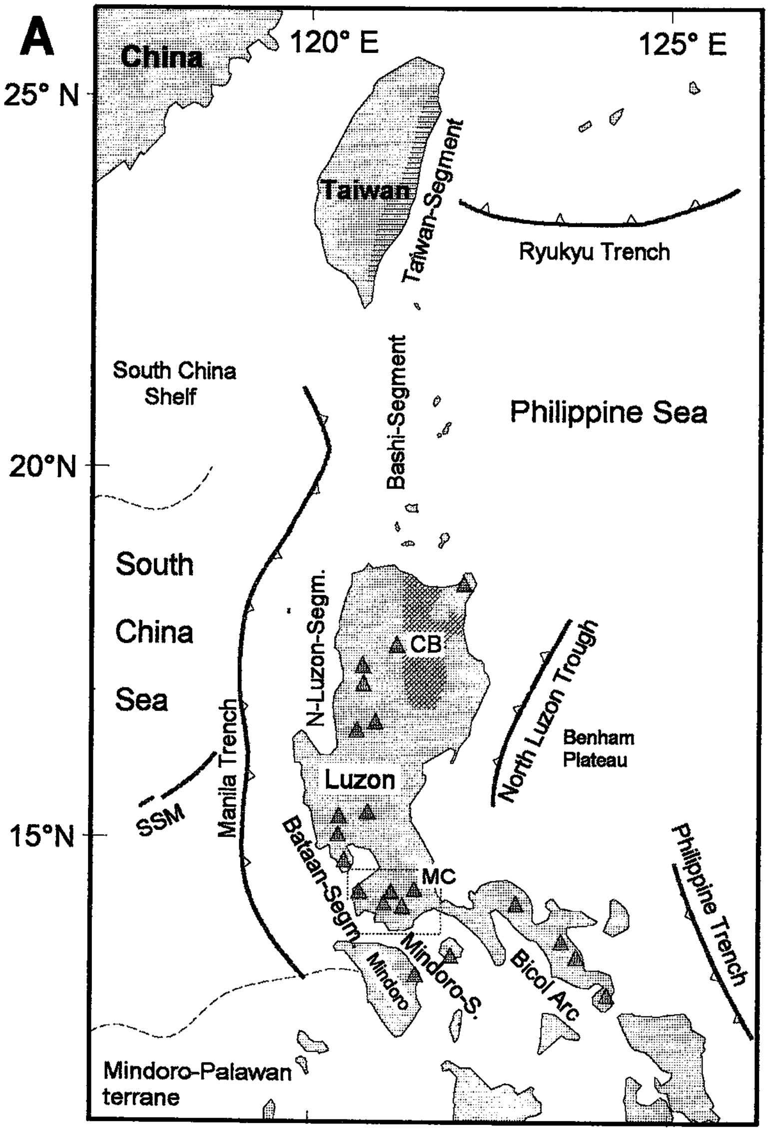

FIG. 1A. General tectonic setting of the Taiwan–Luzon arc system. CB: Cagayan Basin, MC: Macolod Corridor, SSM: Scarborough Seamount chain; triangles indicate major volcanoes (note that all islands of the Bashi Segment are the tips of volcanoes).

whether the geochemical signature of arc basalts represents largely the influence of the crustal input (*e.g.*, Plank & Langmuir 1993), equilibrium of fluids with mantle minerals (*e.g.*, Keppler 1996) or scavenging of elements from the mantle wedge (*e.g.*, Hawkesworth *et al.* 1991). Furthermore, the role of the transfer agents, melts or fluids or both, is currently not well constrained. The depletion in the *HFSE* may be explained by previous extraction of melt (*e.g.*, Woodhead *et al.* 1993, Knittel & Oles 1995), high degrees of partial melting, or accessory phases retaining these elements during the generation of arc magmas.

On the basis of isotopic compositions and *REE* fractionation, two groups of arc magmas may be recognized. In some arcs, the igneous rocks show little variation in isotopic composition, and the *LREE* are not significantly fractionated from the heavy rare-earth elements (*HREE*), whereas in other arcs, isotopic compositions are highly variable, and *LREE*/*HREE* fractionation is significant and variable (*e.g.*, White & Patchett 1984, Hawkesworth *et al.* 1991). The latter group offers the opportunity to obtain insights into the melting and mixing processes involved in the genesis of arc magmas, because the isotopic variations suggest the involvement of components with distinct geochemical signatures.

The volcanoes of the Taiwan–Luzon arc (Fig. 1), which formed in response to the subduction of the South China Sea lithosphere, are characterized by variable isotopic compositions (*e.g.*, Mukasa *et al.* 1987, Knittel *et al.* 1988). The isotopic diversity is most pronounced in post-Oligocene rocks, whereas pre-Miocene igneous rocks show little variation in Sr and Nd isotopic compositions and define shallow trends on Pb–Pb isotope diagrams (Mukasa *et al.* 1987, Knittel & Defant 1988, Knittel *et al.* 1988). Isotopic variability is greatest in the north (Taiwan) and south (Mindoro) (Knittel *et al.* 1988, Chen *et al.* 1990, McDermott *et al.* 1993), where the arc collided with continental Asia. This pattern suggests that the variability resulted from the introduction of "exotic" components into the magma sources during collision.

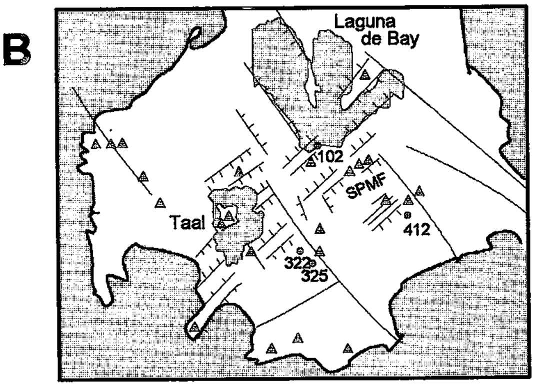

FIG. 1B. Simplified map of the Macolod Corridor, based on Oles (1988) and Förster *et al.* (1990), showing the location of major volcanoes (triangles) and of some maars (circles). The location of the younger SW–NE horst and graben system within the Macolod Corridor, which is superimposed on an older N–S system, is based on the map in Förster *et al.* (1990). Some sample localities are shown; for other sample localities, see Knittel & Oles (1995). SPMF: San Pablo maar field. The area shown is approximately 120 × 100 km.

Here, we report Sr, Nd, and Pb isotopic data and *REE* concentrations for primitive basalts from the Macolod Corridor, an area of intense volcanism cross-cutting the Taiwan–Luzon arc (Fig. 1). Though the primitive basalts should have suffered little contamination by crustal materials, we also analyzed an andesite and a dacite from Mt. Makiling, a stratovolcano located within the Macolod Corridor, to obtain information on the possible effects of crustal contamination. In addition, we report data for three older volcanic rocks from the Batangas Mountains (3–5 Ma), located to the south of the Macolod Corridor, in order to constrain the temporal evolution of the magma sources.

GEOLOGICAL SETTING

The Philippine archipelago, consisting of a collage of old arcs and exotic terranes (Karig 1983, McCabe *et al.* 1985), forms a wedge between the South China Sea and the Philippine Sea plate (Fig. 1). To the west, oceanic crust of the South China Sea is being subducted along the Manila Trench (Fig. 1). The onset of subduction along this trench system is not known, but is inferred to have occurred in the early Miocene, following a period of crustal extension. This extensional phase, which resulted in the subsidence of the Cagayan Graben and associated potassic alkaline volcanism from *ca.* 25–20 Ma (Knittel 1983), appears to have occurred during the reversal of the polarity of subduction, from westward along a trench system located east of the Philippine archipelago (Lewis & Hayes 1983), to eastward along the Manila Trench (Knittel 1983, 1986). Initially, the subduction system may have extended along the whole Philippine arc, but in the late Miocene, the northern and southern parts of the arc collided with the Asian continent in Taiwan and in the Mindoro–Palawan area (*e.g.*, McCabe *et al.* 1982, Ho 1986, Teng 1990). As a result, the pre-Miocene, westward-dipping subduction zone along the eastern margin of the northern Philippine archipelago is in the process of reactivation along the North Luzon Trough (Lewis & Hayes 1983). Along the southeastern margin of the Philippine archipelago, the Philippine Sea plate is being consumed along the Philippine Trench (Fig. 1).

Opposing polarities of the subduction in the northern and southern Philippines, respectively, cause the northern part of the archipelago to move westward owing to the consumption of the South China Sea along the

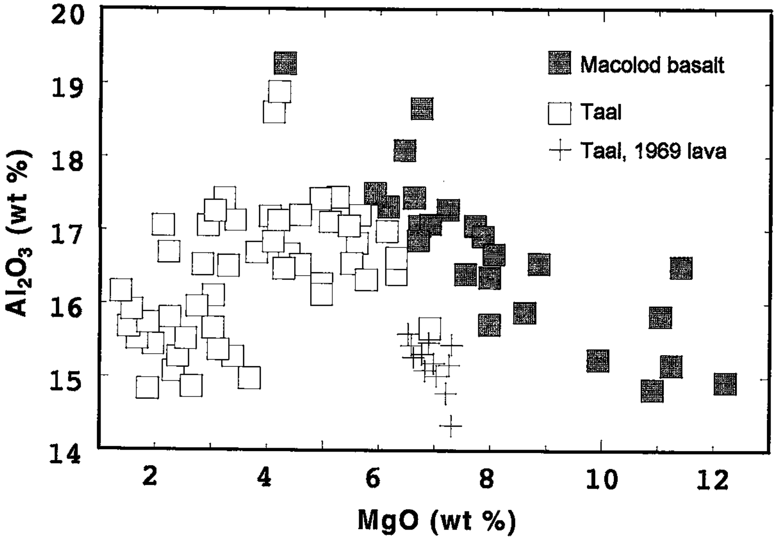

FIG. 2. Al_2O_3 *versus* MgO concentrations for volcanic rocks from the Macolod Corridor and the Taal system. The data are taken from Simon (1983), Oles (1988), Miklius *et al.* (1991), and Knittel & Oles (1995).

Manila Trench, whereas the southern parts move relatively eastward owing to subduction of the Philippine Sea plate along the Philippine Trench. The direction of movement is northwest for northern Luzon because it is coupled to the Philippine Sea plate. In contrast, south of the Mindoro collision zone, the southern parts of the archipelago may remain more or less stationary owing to coupling to the continental fragments of the Mindoro – North Palawan terrane.

These relative movements are accommodated in the Macolod Corridor, a horst-and-graben system 30 × 60 km wide (Knittel & Oles 1995), which is the site of intensive volcanism. This volcanism seems to be related to young horsts and grabens trending NE–SW (Fig. 1). This system is superimposed on an older, roughly N–S-trending system, with major centers of eruption located at the intersections of major faults (Oles 1988, Förster *et al.* 1990; Fig. 2). Several large and more than two hundred small centers of eruption (largely monogenetic scoria cones and maars) are scattered in the Macolod Corridor (Defant *et al.* 1988, Knittel & Oles 1995). This is in contrast to central Luzon and Mindoro, where the Taiwan–Luzon volcanic belt consists of a well-defined frontal arc with only a few volcanoes located behind the volcanic front.

The majority of the small centers of eruption in the Macolod Corridor are younger than 1 Ma (Oles 1988), whereas the major stratovolcanoes have a longer history (0.6–2.0 Ma; de Boer *et al.* 1980, Oles 1988). The small centers of eruption are concentrated within the Taal Caldera in the western part of the Macolod Corridor and the San Pablo Maar Field, a NE–SW-trending area east of Taal 4 × 18 km wide, where more than 200 ash and scoria cones and maars have been identified (Oles 1988). Historic activity is confined to Volcano Island, located in Taal Lake, and its immediate surroundings. More than 35 centers of eruption are located on this small (23 km^2) island.

PETROLOGY OF THE MACOLOD BASALTS

The monogenetic centers of eruption in the eastern part of the Macolod Corridor, which are predominantly located within the San Pablo Maar Field, have produced basalt ranging from near-primary compositions with 10–11% MgO to evolved high-Al basalts (<6% MgO, ~17.4% Al_2O_3: Table 1, Fig. 2). They are collectively referred to as Macolod basalts.

The most primitive basalts (>10% MgO, Mg# [= Mg/(Mg + Fe^{2+}] in the range 0.73–0.74) erupted from the Alligator Lake maar (samples SP102 and MC354) and the Mayabobo cone (sample MC412), and contain about 7% olivine and 7% clinopyroxene microphenocrysts (<1 mm), which are set in a matrix composed of plagioclase microlites and glass. The olivine crystals commonly contain numerous inclusions of chromite. The more evolved basalts contain less olivine than the near-primary lavas (largely free from chromite inclusions), whereas clinopyroxene and plagioclase phenocrysts are more prominent. The latter exhibit increasingly complex patterns of zoning. A glomeroporphyritic texture is common in evolved basalts.

TABLE 1. GEOCHEMICAL AND ISOTOPIC DATA FOR SELECTED SAMPLES OF THE MACOLOD BASALT

Sample	SP102	MC412	MC322	MC325	SP44	SP141	SP237	SP76
SiO_2 wt%	49.44	47.73	51.34	51.65	51.92	50.97	48.77	52.77
TiO_2	0.84	0.97	0.85	0.93	1.07	0.91	1.05	1.03
Al_2O_3	14.87	15.84	16.55	16.69	17.08	17.07	19.28	19.32
Fe_2O_3	8.89	9.49	8.45	9.14	9.44	9.58	10.96	9.49
MnO	0.16	0.17	0.15	0.16	0.16	0.17	0.20	0.16
MgO	10.88	11.00	8.79	8.07	6.68	7.70	4.29	4.27
CaO	10.17	8.91	9.30	8.98	10.31	10.41	10.19	9.33
Na_2O	2.58	2.27	3.02	3.07	3.23	2.35	2.35	3.52
K_2O	0.87	0.69	0.93	0.79	0.98	0.75	0.87	0.94
P_2O_5	0.22	0.29	0.23	0.19	0.23	0.11	0.16	0.30
LOI	0.17	1.90	0.17	0.29	0.04	0.23	0.39	0.24
Total	99.31	99.51	100.02	100.13	101.10	100.02	98.12	101,13
Mg#	0.74	0.73	0.71	0.67	0.62	0.65	0.48	0.51
Rb (XRF) ppm	14	5	17	14	18	15	16	19
Rb (ICP)	18.3	6.1	20.9	15.7	n.a.	15.0	15.6	19.8
Cs (ICP)	2.9	0.2	1.8	1.0	n.a.	1.5	0.3	1.4
Sr (XRF)	505	556	455	450	635	407	591	614
Sr (ICP)	494	609	499	470	n.a.	437	639	622
Ba (XRF)	277	542	209	225	330	206	297	298
Ba (ICP)	253	524	198	180	n.a.	177	259	372
Zr (XRF)	82-85	112-127	93-110	93-109	95	88	76	106
Zr (ICP)	86.4	117	97.8	94.1	n.a.	78.3	64.9	102
Nb (XRF)	6	9	6	4	6	5	4	6
Hf (ICP)	1.97	2.69	2.36	2.21	n.a.	1.93	1.72	2.37
Y (XRF)	13/19	20	16/18	22/23	22	21	19	24
Y (ICP)	15.3	20.6	19.1	22.4	n.a.	22.2	20.2	21.3
La	14.90	23.90	11.40	10.60	18.98	8.90	10.80	20.50
Ce	29.30	45.20	23.70	21.40	42.65	19.10	24.0	38.90
Pr	3.40	5.32	3.07	2.72	n.a.	2.44	3.22	4.47
Nd	13.70	21.10	13.10	12.70	16.81	10.80	14.7	18.10
Sm	3.23	4.51	3.27	3.14	4.15	2.87	3.75	4.07
Eu	1.16	1.59	1.19	1.13	1.29	1.17	1.41	1.43
Gd	3.51	4.49	3.76	3.85	3.73	3.62	4.10	4.50
Tb	0.56	0.72	0.61	0.61	n.a.	0.64	0.64	0.69
Dy	2.83	3.79	3.39	3.93	3.59	3.96	3.77	3.90
Ho	0.62	0.81	0.72	0.83	n.a.	0.83	0.74	0.79
Er	1.73	2.26	2.20	2.67	2.00	2.66	2.22	2.44
Tm	0.23	0.30	0.30	0.35	n.a.	0.34	0.32	0.30
Yb	1.63	1.88	2.20	2.45	1.86	2.51	2.03	2.19
Lu	0.27	0.36	0.33	0.40	0.37	0.39	0.34	0.31
Th	4.34	6.93	2.49	2.23	n.a.	2.23	2.06	5.29
U	1.13	1.33	0.88	0.53	n.a.	0.90	0.63	1.30
$^{87}Sr/^{86}Sr$	0.70457	0.70482	0.70446	0.70418	0.70471	0.70473	0.70448	0.70454
$^{143}Nd/^{144}Nd$	0.512851	0.512808	0.512898	0.512906	0.512812	0.512908	0.512865	0.512815
$^{206}Pb/^{204}Pb$	18.09	18.64	18.61	18.56	n.a.	18.64	n.a.	18.61
$^{207}Pb/^{204}Pb$	15.61	15.62	15.62	15.59	n.a.	15.61	n.a.	15.61
$^{208}Pb/^{204}Pb$	38.10	38.74	38.75	38.59	n.a.	38.68	n.a.	38.70

XRF data from Knittel & Oles (1995) [for samples SP102, MC412, MC322, and MC325, results of two XRF analyses from different laboratories are reported for Zr and Y]. Isotopic data for SP44 are taken from Knittel *et al.* (1988), and the REE data for SP44 are taken from Oles (1992). n.a.: not available.

The most primitive basalts are considered to have crystallized from near-primary magmas on the basis of the following observations. Olivine has a very small range of core (Fo_{90-87}) and rim (Fo_{87-84}) compositions (Fig. 3, Table 2). The core compositions are in equilibrium with the whole-rock Mg# values, 0.73–0.74, assuming $K_d(Fe/Mg)_{ol}/(Fe/Mg)_{liq} = 0.3 \pm 0.03$ (Roeder & Emslie 1970) and FeO to be in the range 0.80–0.90 FeO^{tot} (Nicholls & Whitford 1976). The small range of Fo contents and the equilibrium of core compositions and whole rocks suggest that significant accumulation of olivine did not occur (Knittel & Oles 1995, Fig. 3). Furthermore, the high Ni contents of the Fo-rich olivine cores (0.28–0.43% NiO: Table 2) suggest that they crystallized from melts that equilibrated with residual olivine in the mantle (Sato 1977).

Chromite inclusions in Fo-rich olivine ($Fo_{>85}$) typically have Cr/(Cr + Al) values in the range

TABLE 2. COMPOSITION OF THE MOST AND THE LEAST MAGNESIAN OLIVINE IN THE MOST PRIMITIVE BASALTS

Sample	MC412 (Mayabobo)				SP102 (Alligator maar)			
Analysis	04-25 ol8 core	04-26 ol8 rim	04-2 ol1 core	04-3 ol1 rim	04-34 ol1 core	04-35 ol1 rim	04-39 ol2 core	04-40 ol2 rim
SiO_2 wt%	40.44	39.57	39.78	38.99	39.72	39.16	39.73	39.67
MgO	49.40	46.44	47.38	44.31	48.19	45.32	47.18	46.90
FeO	9.33	12.73	11.80	15.06	10.57	12.64	11.81	12.93
MnO	0.15	0.22	0.23	0.30	0.18	0.24	0.21	0.21
NiO	0.43	0.14	0.19	0.08	0.28	0.15	0.20	0.14
CaO	0.15	0.20	0.20	0.24	0.19	0.25	0.22	0.26
Cr_2O_3	0.08	0.03	0.00	0.03	0.07	0.01	0.00	0.05
Total	99.97	99.33	99.58	99.01	99.20	97.77	99.34	100.16
Fo	90.4	86.6	87.7	84.0	89.1	86.5	87.7	86.6

Sample	MC322 (Anilao Hill)			MC325 (Rosario Hill)				MC141 (Candeleria)		
Analysis	A14 core	A16 rim	A17 core1)	A18 core	A20 rim	A21 core	A22 rim	18 core	19 rim	33 core1)
SiO_2 wt%	40.21	39.40	39.79	39.51	39.26	39.13	39.10	39.86	37.67	39.59
MgO	48.52	45.60	47.15	45.33	43.65	42.98	44.85	45.86	35.95	45.06
FeO	10.26	13.77	11.90	13.72	16.15	16.94	15.04	13.90	25.85	15.00
MnO	0.16	0.27	0.20	0.23	0.27	0.37	0.21	0.25	0.39	0.23
NiO	0.34	0.15	0.23	0.28	0.12	0.10	0.16	n.a.	n.a.	n.a.
CaO	0.13	0.16	0.19	0.18	0.20	0.19	0.16	0.19	0.23	0.16
Cr_2O_3	0.02	0.04	0.05	0.02	0.05	0.00	0.01	0.03	0.00	0.04
Total	99.64	99.39	99.51	99.27	99.70	99.71	99.53	100.09	100.09	100.07
Fo	89.4	85.4	87.6	85.5	82.8	81.8	84.2	85.5	71.2	84.2

[1] The composition of the rim is not available for this crystal.

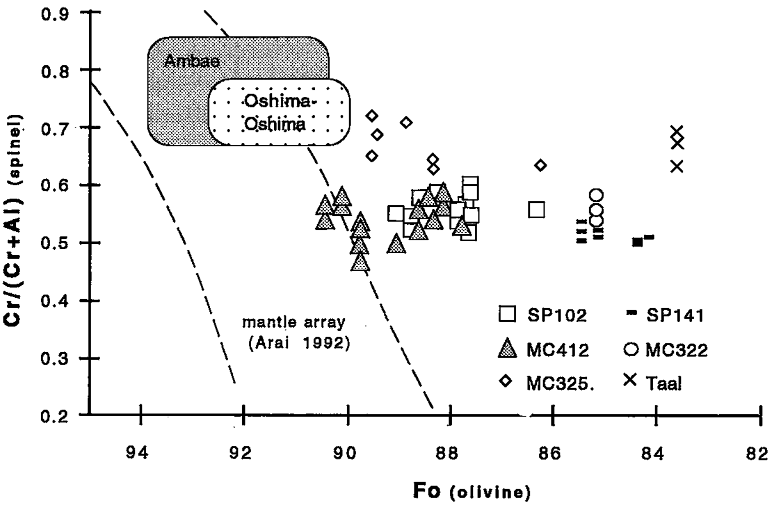

FIG. 3. Cr/(Cr + Al) values of chromite inclusions in olivine plotted *versus* Fo contents of host olivine. Mantle array based on Arai (1992). Generalized fields for arc picrites from Ambae and Oshima-Oshima are based on data in Eggins (1993) and Yamamoto (1983).

0.52–0.58 (Fig. 3, Table 3) and Mg/(Mg + Fe^{2+}) in the range 0.60–0.68, consistent with their coexistence with olivine Fo_{90} (Dick & Bullen 1984, Fig. 6a). Higher Cr/(Cr + Al) values (0.63–0.72) are observed for chromite from a single eruptive center (Anilao Hill, sample MC322; Table 3). Fe^{3+}/(Fe^{3+} + Cr + Al) values in the range 0.10–0.16 (here also sample MC322 is an exception) are slightly higher than the values observed

TABLE 3. SELECTED COMPOSITIONS OF CHROMITE IN THE MOST PRIMITIVE BASALTS

Sample	SP102 (Alligator maar)			MC 412 (Mayabobo)			MC322 (Anilao Hill)	
Analysis	04-41	04-38	04-44	04-31	04-8	04-19	P4	P3
comment	sp in ol2	sp in ol 1	sp in ol2	sp in ol9	sp in ol2	sp in ol 6	incl i ol	incl i ol
SiO_2 wt%	0.02	0.06	0.01	0.05	0.03	0.04	0.06	0.03
TiO_2	0.84	0.53	0.84	0.62	0.59	0.59	0.41	3.65
Fe_2O_3	12.65	9.06	12.49	8.77	9.62	10.01	7.15	19.53
Cr_2O_3	34.75	39.38	37.07	34.34	37.42	40.53	48.40	33.99
Al_2O_3	21.60	21.56	19.46	26.53	22.98	19.52	14.98	9.45
MgO	13.95	14.35	13.23	15.73	15.07	13.74	11.26	7.45
FeO	14.77	14.23	15.56	12.94	13.39	14.68	17.10	24.47
MnO	0.29	0.23	0.27	0.21	0.23	0.22	0.22	0.34
CaO	0.04	0.02	0.04	0.02	0.02	0.02	0.00	0.01
ZnO	0.06	0.04	0.09	0.08	0.11	0.05	0.17	0.11
NiO	0.13	0.15	0.12	0.23	0.19	0.14		
V_2O_5	0.15	0.14	0.16	0.10	0.14	0.09	0.11	0.36
Total	99.24	99.74	99.34	99.61	99.78	99.62	99.86	99.39
cations on the basis of 3 cations and 4 oxygens per formula unit								
Si	0.001	0.002	0.000	0.002	0.001	0.001	0.002	0.001
Ti	0.020	0.012	0.020	0.014	0.014	0.014	0.010	0.094
Fe^{3+}	0.295	0.210	0.295	0.198	0.221	0.235	0.175	0.510
Al	0.853	0.959	0.921	0.813	0.902	1.000	0.568	0.381
Cr	0.790	0.782	0.721	0.937	0.826	0.718	1.232	0.920
Mg	0.645	0.659	0.620	0.703	0.685	0.639	0.541	0.380
Fe^{2+}	0.383	0.366	0.409	0.324	0.341	0.383	0.460	0.699
Mn	0.008	0.006	0.007	0.005	0.006	0.006	0.006	0.010
Ca	0.001	0.001	0.001	0.001	0.000	0.001	0.000	0.000
Zn	0.001	0.001	0.002	0.002	0.003	0.001	0.004	0.003
Ni	0.003	0.004	0.003	0.005	0.005	0.004		
V	0.003	0.003	0.003	0.002	0.003	0.002	0.001	0.003
$Mg/Mg+Fe^{2+}$	0.63	0.64	0.60	0.68	0.67	0.63	0.54	0.35
Cr/Cr+Al	0.52	0.55	0.56	0.46	0.52	0.58	0.68	0.71
Fe^{3+}/R^{3+}	0.15	0.11	0.15	0.10	0.11	0.12	0.09	0.28
host ol[1)]	87.7	89.1	87.7	89.7	88.6	88.5	89.4	88.8

[1] Fo contents of the host olivine.

for chromite from MORB (Dick & Bullen 1984), and are typical for chromite from arc volcanic suites (*e.g.*, Arai 1992).

If the most primitive samples SP102 and MC412 are considered to be primary magmas, it may be possible to estimate the depth and temperature at which they were in equilibrium with the mantle. The significance of such estimates is uncertain, however, because recently MORB geochemistry has been interpreted to reflect mixing of incremental melts produced in the rising mantle over a range of depths (*e.g.*, Klein & Langmuir 1987). Similar processes may occur below arc volcanoes, since their source regions are frequently considered to be rising diapirs (*e.g.*, Marsh 1979, Sakuyama 1983, Plank & Langmuir 1988). In the present case, the mean equilibrium temperatures and pressure may be taken at face value, because it appears that the Macolod Corridor is not underlain by an active Benioff–Wadati zone (*e.g.*, Cardwell *et al.* 1980, Hamburger *et al.* 1983, Yang *et al.* 1996; Fig. 4); hence melting may not be related to decompression in a rising diapir, but to decompression caused by crustal extension, *i.e.*, unloading of the mantle, below the Macolod Corridor.

Using the formula given by Albarède (1992), mean temperatures of 1330° and 1343° ± 40°C are indicated for SP102 and MC412, respectively. Hirose & Kushiro (1993) also obtained melts with *ca.* 11% MgO from lherzolite at temperatures of 1300° – 1350°C. Equation (3) of Albarède (1992) allows us to estimate the mean equilibrium pressure to be 11.5 ± 2.7 kbar for SP102 and 14.6 ± 2.7 kbar for MC412. Based on SiO_2 contents alone, pressure estimates obtained from the melting experiments of Hirose & Kushiro (1993) are 10–15 kbar for SP102 and 15–20 kbar for MC412.

Lavas from the Taal volcanic system show a wide compositional variation, from moderately evolved basalts (7–8% MgO) to dacite (Fig. 2; Simon 1983, Miklius *et al.* 1991). The basalts differ from the Macolod basalts in their higher Ca contents and slightly lower Al contents (Fig. 2). A low Al content is in particular notable for the lava erupted in 1969 (Fig. 2).

The Fo contents in early crystallized, Ni-rich (NiO > 0.3%) olivine, and the Cr/(Cr + Al) values of chromite inclusions contained therein, are relatively low if compared to minerals crystallized from other examples of near-primary arc magma, as described in the literature

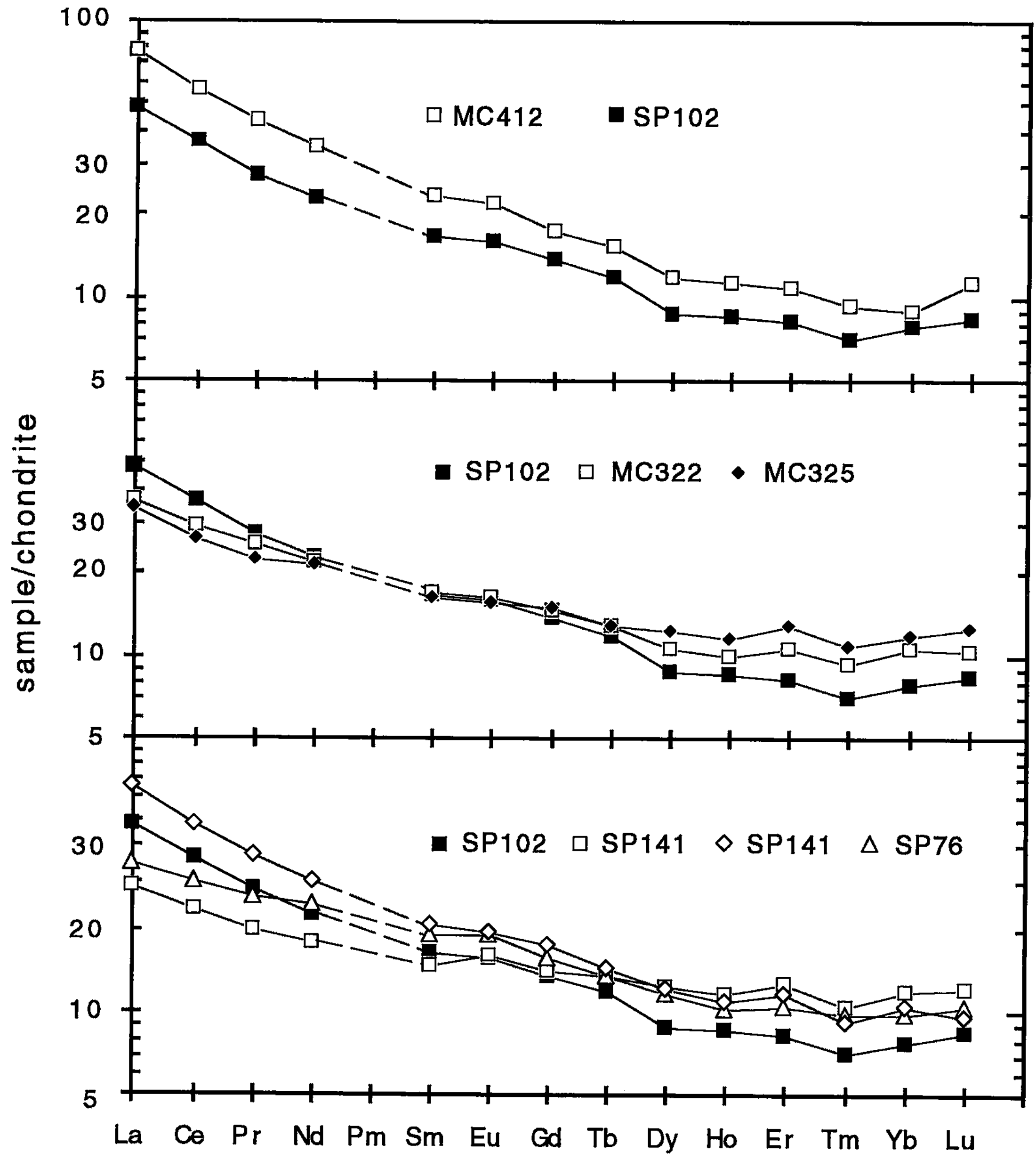

FIG. 4. *REE* patterns of Macolod basalts. The values used for normalization are from Boynton (1984).

(Fo_{90} *versus* Fo_{92-94} and Cr/(Cr + Al) < 0.6 *versus* 0.7–0.8; *e.g.*, Eggins 1993, Table 10). To Knittel & Oles (1995), these features suggest that the Macolod basalts are derived from relatively fertile sources. This conclusion is supported by comparatively high Zr, Y, and Nb contents and low Ti/Zr, which compare well with typical values for backarc basin basalts (Knittel & Oles 1995, Fig. 7; see Woodhead *et al.* 1993). In contrast, basalts from the Taal system may be derived from a more refractory source, as indicated by lower concentrations of Zr, Y, Ti, higher Ti/Zr, and higher Cr/(Cr + Al) in chromite (Fig. 3; Knittel & Oles 1995).

METHODS

Sr, Nd, and Pb isotopic ratios were determined at the University of Tübingen employing the methods described in Hegner *et al.* (1995). The measurements were performed on a Finnigan MAT 262 in static-collection mode. Proportions of Sr and Nd isotopes were measured on whole-rock powders and normalized to ^{86}Sr/^{88}Sr = 0.1194 and ^{146}Nd/^{144}Nd = 0.7219. Sr isotopic ratios are quoted relative to ^{87}Sr/^{86}Sr = 0.710265 for NBS 987, and Nd ratios, relative to ^{143}Nd/^{144}Nd = 0.511856 for the La Jolla Nd standard. Pb isotopic ratios were determined on rock chips and are corrected for thermal fractionation using 1.5‰ amu^{-1}. Procedure blanks were less than 100 pg.

Within-run precision (2σ mean) for ^{87}Sr/^{86}Sr is $\leq$0.0025%, for ^{143}Nd/^{144}Nd $\leq$0.0016%, and for Pb isotopic ratios, $\leq$0.005%. External precision (2σ) for ^{87}Sr/^{86}Sr is estimated to be ~0.0034%, for ^{143}Nd/^{144}Nd, ~0.003%, for ^{206}Pb/^{204}Pb ~0.08%, for ^{207}Pb/^{204}Pb ~0.11% and for ^{208}Pb/^{204}Pb ~0.13%.

Trace-element analyses have been carried out at the GeoForschungszentrum Potsdam using a Perkin Elmer/Sciex Elan inductively coupled plasma – mass-spectrometer (ICP–MS). Sample decomposition and analysis followed procedures described previously (Dulski 1994, Cotten *et al.* 1995). Sample powders were dissolved with HF and $HClO_4$ in a pressure vessel, and the solutions were evaporated to incipient dryness. The residues were redissolved with HCl in a pressure vessel, the resulting clear solutions evaporated again, and the residues taken up in HCl. Ru and Re were added as internal standards to allow correction for instrumental drift. Results were corrected for interference of analyte species on the basis of experimentally determined yields of M^+, MO^+, MOH^+, and MCl^+ (Dulski 1994).

Precision and accuracy of the ICP–MS results were frequently checked by analysis of international reference standards and by comparison of our data with results obtained in other laboratories employing different analytical techniques (*e.g.*, Dulski 1994, Cotten *et al.* 1995, Bau 1996). For reference standard W–2 (diabase), for example, precision (relative standard deviation 2σ) is as follows: rare-earth elements (*REE*) 1–10%, Y: 5%, Zr: 6%, Hf, 4%, Th 10%, U: 17%, Y/Ho: 12%, and Zr/Hf: 7%. The accuracy, with respect to the values of Govindaraju (1994), is: *REE* (except Pr, Nd, Er and Tm): 0–7%, Y: 5%, Zr: 12%, Hf: 2%, Th: 5%, U: 5%, Y/Ho: 6%, and Zr/Hf: 10%. The accuracy of data for Pr (49%), Nd (8%), Er (10%), and Tm (16%) is worse than for other *REE*, which partly results from the quality of the reference data [note that data for Nd, Er, and Tm are not given as "recommended", but as "proposed" values, and that Pr data are only suggested as "information values" by Govindaraju (1994)]. Thus, the accuracy of these data is assumed to be similar to that for other *REE*. Zr and Y concentrations previously determined at Aachen University and Melbourne University by XRF (Oles 1992, Knittel & Oles 1995) also are reported, because these data show systematic differences. The ICP data are mostly intermediate between the two XRF data sets.

RESULTS

The Macolod basalts are characterized by significant and variable enrichment in the light *REE* (*LREE*) [20–75 times chondritic abundances for La; chondritic values from Boynton (1984); Fig. 4]. The heavy *REE* (*HREE*) show only moderate enrichment (7–12 times chondritic abundances), as typically observed in subduction-related arc volcanic rocks (Gill 1981, White & Patchett 1984). The chondrite-normalized *REE* concentrations exhibit no Ce anomalies [Ce_N/Ce^* in the range 0.96–0.99; $Ce_N^* = (La_{N*}Pr_N)^{0.5}$] and, in some samples, small positive Eu anomalies [Eu_N/Eu_N^* in the range 1.00–1.11; $Eu_N^* = (Sm_N{*}Gd_N)^{0.5}$].

The most interesting feature of the *REE* patterns of the Macolod basalts is that they cut across each other, *i.e.*, high concentrations of the *LREE* are invariably associated with low concentrations of the *HREE* (Fig. 4), except for sample MC412. This is also illustrated in a plot of La/Yb *versus* Yb, where the Macolod basalts follow a trend of decreasing concentrations of *HREE* with increasing *LREE*/*HREE* (Fig. 5). These patterns are unusual, because fractional crystallization of the observed phenocrysts results in increasing *LREE*/*HREE and* increasing *HREE* (see arrow in Fig. 5). This is so because the *LREE* are less compatible in typical fractionating assemblages than the *HREE*, and because the bulk partition coefficients (K_d) for *all REE* are less than unity [see, for example, the compilation in Gill (1981)]. Fractionation of abundant amphibole could perhaps result in a bulk K_d greater than 1, but there is no evidence for the crystallization of this mineral in the basalts under consideration. The typical patterns resulting from fractionation are illustrated by samples from the Taal volcanic complex, which show increasing concentrations of Yb with increasing La/Yb (Fig. 5).

The isotopic data obtained for the Mg-rich basalts from the Macolod Corridor (Table 1) are likewise unexpected (Figs. 6, 7). Previously available data (Knittel *et al.* 1988, 1995, Defant *et al.* 1990, 1991) suggested a regular increase in ^{87}Sr/^{86}Sr with decreasing ^{143}Nd/^{144}Nd from the Baguio District in the North Luzon Segment, through the Bataan Segment and the Macolod Corridor, to the Mindoro Segment. The data obtained in our study show that: a) Nd isotopic compositions of the Macolod Basalts span virtually the same range as observed for the Bataan Segment, from Pinatubo (Bernard *et al.* 1997) to Mariveles [Knittel *et al.* (1988), and data from Table 4]. b) The data points for the Macolod basalt are clearly displaced toward higher ^{87}Sr/^{86}Sr for a given ^{143}Nd/^{144}Nd, relative to most

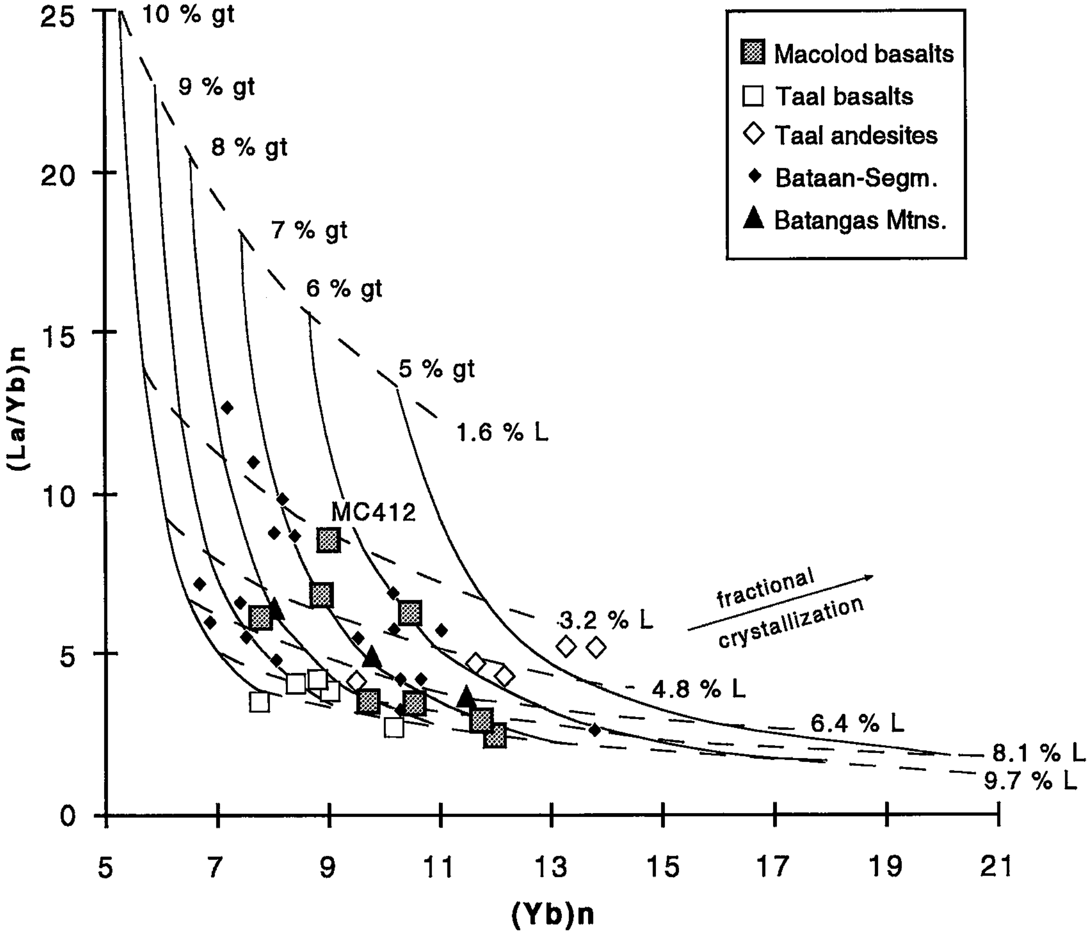

FIG. 5. Normalized La/Yb *versus* Yb correlation in Macolod and Taal basalts. The trend commonly produced by crystal fractionation is illustrated by basalts and andesites from the Taal system (Miklius *et al.* 1991). Data for the Bataan Segment (Bau & Knittel 1993; Table 4, this paper) and the 3- to 5-Ma-old volcanic rocks from southern Batangas are shown for comparison. Solid lines illustrate the composition of melts derived from garnet (gt) lherzolite with variable initial contents of garnet (percentages above the array). Degrees of partial melting (L) are shown at right side.

of the samples from the volcanic front in North Luzon and the Bataan and Mindoro segments (Fig. 6). In contrast, the data points for the andesite and dacite from Mt. Makiling (Table 4) plot within the field defined by volcanic suites of the Bataan Segment, which fall along a mixing array between depleted mantle and sediments from the South China Sea [Fig. 6; data from Chen *et al.* (1990) and McDermott *et al.* (1993)]. In addition, the isotopic shift is similar for near-primary and evolved basalts. Hence, contamination probably is not responsible for the radiogenic $^{87}Sr/^{86}Sr$ values. Compared to volcanic rocks from the South China Sea Basin and the Philippine Sea plate (Hickey-Vargas 1991, Tu *et al.* 1992), *all* arc volcanic rocks of the North Luzon, Bataan and Mindoro segments are displaced toward higher $^{87}Sr/^{86}Sr$ values for a given $^{143}Nd/^{144}Nd$. c) The 3- to 5-Ma-old volcanic rocks from the Batangas Mountains, located to the south of the Macolod Corridor, are characterized by $^{87}Sr/^{86}Sr$ values of less than 0.7040 (Table 4), similar to pre-Miocene igneous rocks and volcanic rocks from the North Luzon Segment (Knittel & Defant 1988, Defant *et al.* 1990, Knittel *et al.* 1995), but are slightly displaced toward lower $^{143}Nd/^{144}Nd$ values relative to the latter. This displacement is of much smaller magnitude than the shift toward low $^{143}Nd/^{144}Nd$ values observed for volcanic rocks erupted on several of the islands between Taiwan and Luzon (Fig. 6; Richard 1986, Defant *et al.* 1990, Chen *et al.* 1990, McDermott *et al.* 1993). d) Similar to igneous rocks from the South China Sea basin (Tu *et al.*

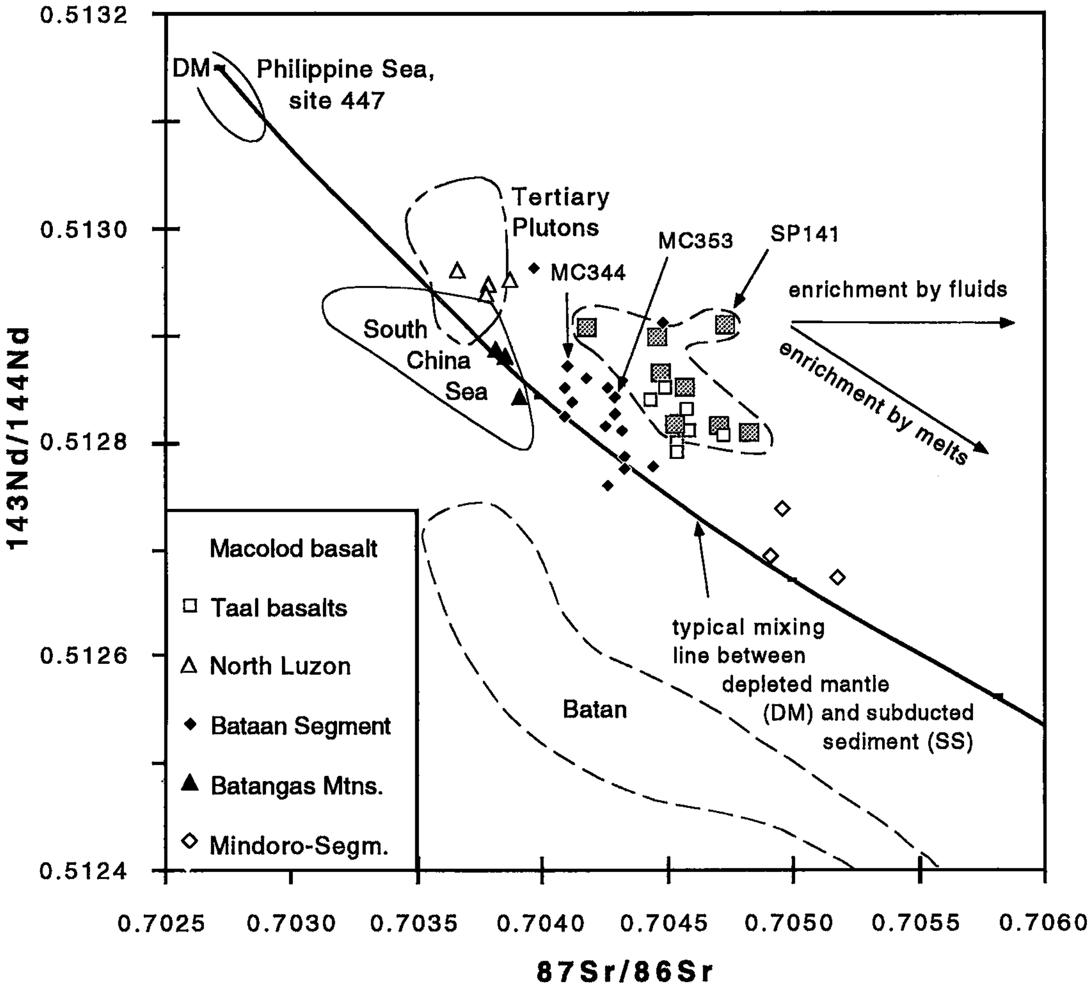

FIG. 6. $^{143}Nd/^{144}Nd$ *versus* $^{87}Sr/^{86}Sr$ plot showing significant displacement toward high $^{87}Sr/^{86}Sr$ values for Macolod basalts relative to volcanic rocks from the volcanic front of the Bataan Segment of the Taiwan–Luzon arc. All volcanic rocks of the Taiwan–Luzon arc are displaced toward high $^{87}Sr/^{86}Sr$ values relative to volcanic rocks from the South China Sea and the Philippine Sea, except those from Batan and some other islands of the Bashi Segment (Chen *et al.* 1990, McDermott *et al.* 1993). A typical mixing line between depleted mantle and sediment is shown for comparison. Sources of data: Taiwan–Luzon arc: Knittel *et al.* (1988); Defant *et al.* (1990, 1991), Mukasa *et al.* (1994), this paper; Philippine Sea basalts: Hickey-Vargas (1991); South China Sea basalts: Tu *et al.* (1992).

1992) and the Philippine Sea plate (Hickey-Vargas 1991), the arc volcanic rocks from the Taiwan Luzon arc plot above the northern hemisphere reference line (NHRL) of Hart (1984) (Fig. 7). Pb isotopic data for individual young volcanic complexes [Batan: Vidal *et al.* (1989), McDermott *et al.* (1993), Pinatubo: Bernard *et al.* (1997); Taal: Mukasa *et al.* (1994)] show steep trends in Pb isotope plots. Our data for the Mg-rich basalts follow the trend observed for the Taal system, though the spread is slightly smaller (Fig. 7). A possible explanation for the anomalous composition of sample SP102, which was checked by a replicate dissolution, is that it may be derived from a source containing old enriched mantle or lower continental crust. The evolved lavas of Mt. Mariveles, which plot within the Bataan Segment field in the Sr–Nd diagram, plot at the low $^{206}Pb/^{204}Pb$ end of the array. The data obtained for the 3- to 5-Ma-old samples from southern Batangas straddle the field defined by Batan samples, *i.e.*, are displaced toward lower $^{206}Pb/^{204}Pb$ values relative to data points for samples from the Bataan Segment and the Macolod Corridor.

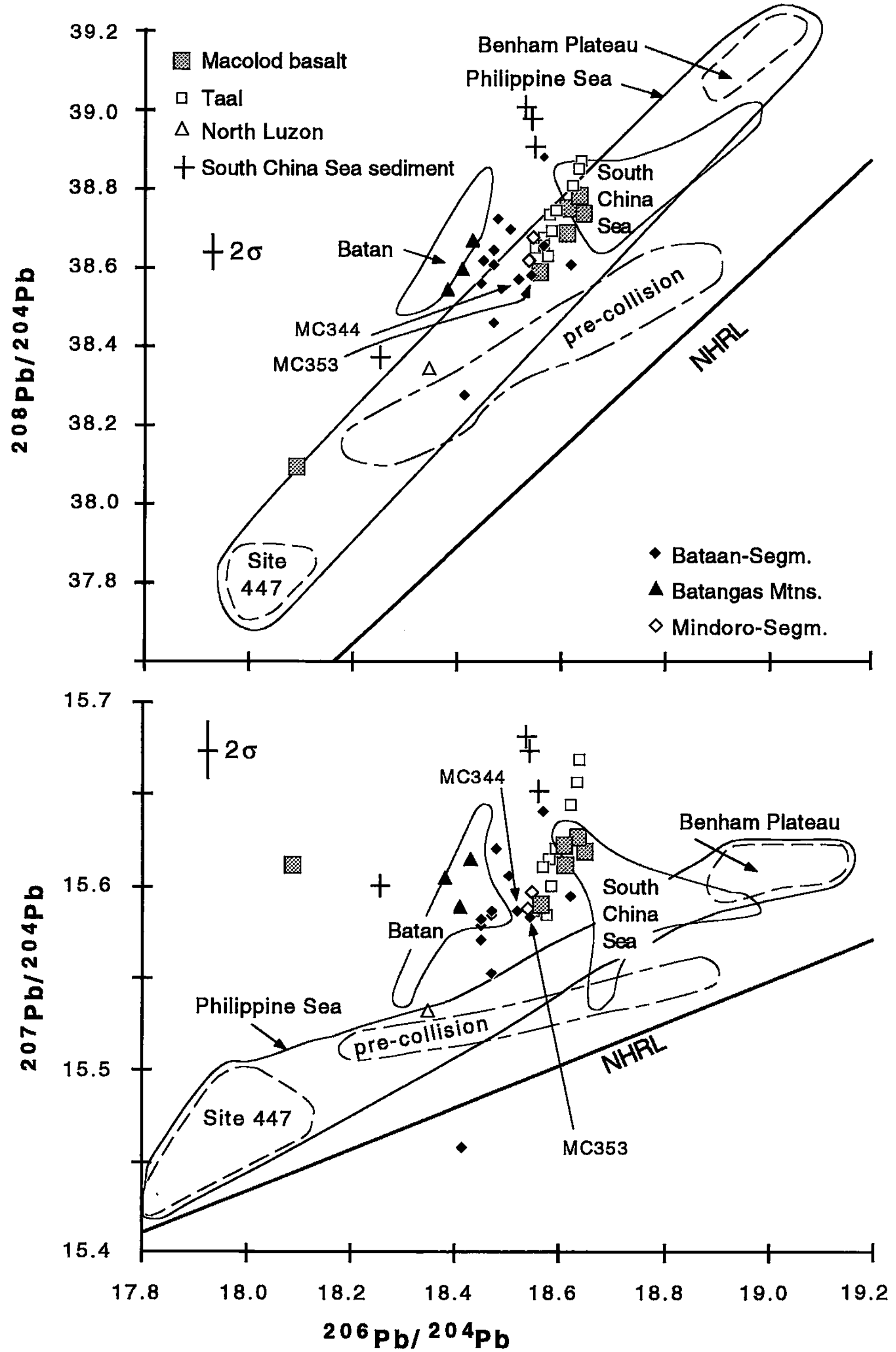

FIG. 7. Pb isotope plots for volcanic rocks from the Macolod Corridor, the Bataan Segment, and the 3- to 5-Ma-old volcanic suite from southern Batangas. The fields for pre-collision rocks from Panay (Mukasa *et al.* 1987) also are shown. Other sources of data are as given in the caption for Figure 6. The Northern Hemisphere reference line (NHRL) is from Hart (1984).

TABLE 4. GEOCHEMICAL AND ISOTOPIC DATA
FOR VOLCANIC ROCKS FROM MT. MAKILING
AND THE 3–5 Ma VOLCANIC SUITE
FROM THE SOUTHERN BATANGAS MOUNTAINS

Sample		MC344	MC353	MC382	MC418	MC421
SiO_2	wt%	64.65	69.45	58.36	64.67	58.95
TiO_2		0.62	0.37	0.64	0.49	0.62
Al_2O_3		16.07	15.02	16.60	16.75	16.94
Fe_2O_3		4.58	2.77	6.69	5.18	7.09
MnO		0.10	0.08	0.13	0.09	0.12
MgO		1.28	0.86	4.50	1.90	3.83
CaO		3.73	2.67	8.12	5.61	7.79
Na_2O		4.43	4.13	2.99	3.87	3.20
K_2O		2.97	3.42	1.60	1.74	0.96
P_2O_5		0.17	0.11	0.20	0.14	0.12
LOI		0.00	0.68	0.92	0.96	1.16
Total		98.61				
Rb (XRF)	ppm	75	87	40	39	15
Rb (ICP)		75.3	96.0	38.7	41.3	14.1
Cs (ICP)		2.1	5.4	2.3	1.0	0.7
Sr (XRF)		339	311	440	540	407
Sr (ICP)		352	322	484	636	460
Ba (XRF)		557	653	309	293	261
Ba (ICP)		569	686	304	298	260
Zr (XRF)		218	183	116	127	126
Zr (ICP)		195	158	105	102	111
Nb (XRF)		9	8	5	n.a.	n.a.
Hf (ICP)		4.72	3.68	2.80	2.83	3.12
Y (XRF)		25	14	15	20	21
Y (ICP)		24,3	13.2	15.2	19.7	21.0
La		23.90	22.10	15.90	15.10	13.30
Ce		46.40	43.92	32.90	25.30	27.50
Pr		5.47	4.05	4.05	3.88	3.90
Nd		20.80	13.70	16.20	16.60	16.70
Sm		4.33	2.52	3.52	3.61	3.89
Eu		1.15	0.80	0.99	1.03	1.03
Gd		4.06	2.22	3.25	3.68	3.77
Tb		0.69	0.36	0.51	0.59	0.62
Dy		4.32	2.04	2.87	3.25	3.98
Ho		0.88	0.44	0.56	0.76	0.80
Er		2.78	1.39	1.85	2.20	2.32
Tm		0.38	0.22	0.25	0.25	0.36
Yb		2.81	1.66	1.69	2.05	2.41
Lu		0.45	0.30	0.29	0.28	0.40
Th		9.23	12.13	4.89	3.58	3.66
U		2.45	3.30	1.13	1.01	0.82
$^{87}Sr/^{86}Sr$		0.70417	0.70429	0.70391	0.70382	0.70385
$^{143}Nd/^{144}Nd$		0.512859	0.512841	0.512842	0.512987	0.512880
$^{206}Pb/^{204}Pb$		18.52	18.55	18.41	18.38	18.43
$^{207}Pb/^{204}Pb$		15.59	15.58	15.59	15.60	15.61
$^{208}Pb/^{204}Pb$		38.57	38.58	38.59	38.54	38.66

Major element and XRF trace-element data from Oles (1992).

DISCUSSION

The basalts erupted from small centers in the eastern part of the Macolod Corridor show several features that set them apart from the volcanic rocks erupted along the volcanic front of the Taiwan–Luzon arc. Their *REE* patterns are unusual; they show increasing *LREE* enrichment with decreasing *HREE* abundances. In addition, they show relatively high $^{87}Sr/^{86}Sr$ values.

As pointed out above, the *REE* patterns are unlikely to result from processes of magmatic fractionation, because only fractionating assemblages containing large amounts of garnet would have a $K_{d(HREE)} > 1$ that is required to produce decreasing *HREE* abundances with increasing *LREE/HREE*. The consistency of the patterns from near-primary (SP102) to evolved basalts (SP237) suggests that assimilation of crustal rocks with high *LREE/HREE* and low levels of *HREE* likewise cannot account for the observed *REE* patterns. Significant crustal contamination also is considered unlikely on the basis of isotope systematics, as discussed above.

Garnet lherzolite, melted to variable degrees, may produce magmas with cross-cutting *REE* patterns if garnet preferentially enters the melt (non-modal melting), as demonstrated by Hanson (1989, his Fig. 8a). These calculations, in part repeated in Figures 5 and 8 using the K_d values of McKenzie & O'Nions (1991), show that with increasing degree of partial melting and diminishing amounts of residual garnet, *LREE* abundances will decrease, and *HREE* abundances will increase. For simple batch-melting models, the observed La/Yb fractionation could be explained by 3–10% partial melting of garnet lherzolite initially containing 6–9% garnet (Fig. 5).

Several observations, however, suggest that the observed *REE* patterns are not due to partial melting and assemblages of residual minerals. First, the calculated patterns involving residual garnet show a rather steep decrease of chondrite-normalized abundances from Ho to Lu, whereas the Macolod basalts show rather flat patterns for these elements. This is inconsistent with the presence of significant amounts of residual garnet, if known partition-coefficients are applicable. In addition, the primary melts probably were generated at pressures below the stability field of garnet lherzolite. Currently available experimental evidence regarding the transition from spinel to garnet lherzolite at temperatures close to the peridotite solidus indicate that this transition probably occurs at pressures in excess of 25 kbar (Hirschmann & Stolper 1996). As discussed in the section on the petrology of the Macolod basalts, the near-primary magmas equilibrated at about 10–15 kbar. Evidence for the presence of garnet in the sources of MORB (*e.g.*, Salters & Hart 1989), which are thought to be generated within the spinel lherzolite field of stability (*e.g.*, Albarède 1992), led Hirschmann & Stolper (1996) to suggest the presence of small amounts of garnet pyroxenite in the MORB sources.

The negative correlation between La/Yb and $^{143}Nd/^{144}Nd$ (Fig. 9) also is difficult to reconcile with non-modal melting of garnet peridotite. This correlation may reflect the evolution of a mantle with variable Sm/Nd or may be explained by mixing processes involving a component characterized by high *LREE/HREE* coupled with low *HREE* and low $^{143}Nd/^{144}Nd$.

If the Nd isotopic variations are considered to reflect variable Sm/Nd of a source that once had a common initial $^{143}Nd/^{144}Nd$, the source needs to have evolved as a closed system for about 600 Ma (assuming that Sm/Nd values in the basalts are lower than those in the source). We cannot exclude the possibility that old, enriched mantle invaded the wedge by asthenospheric flow. However, Knittel *et al.* (1988) have shown that magmas erupted in the Philippines prior to 20 Ma were derived from sources with overall uniform Sr and Nd

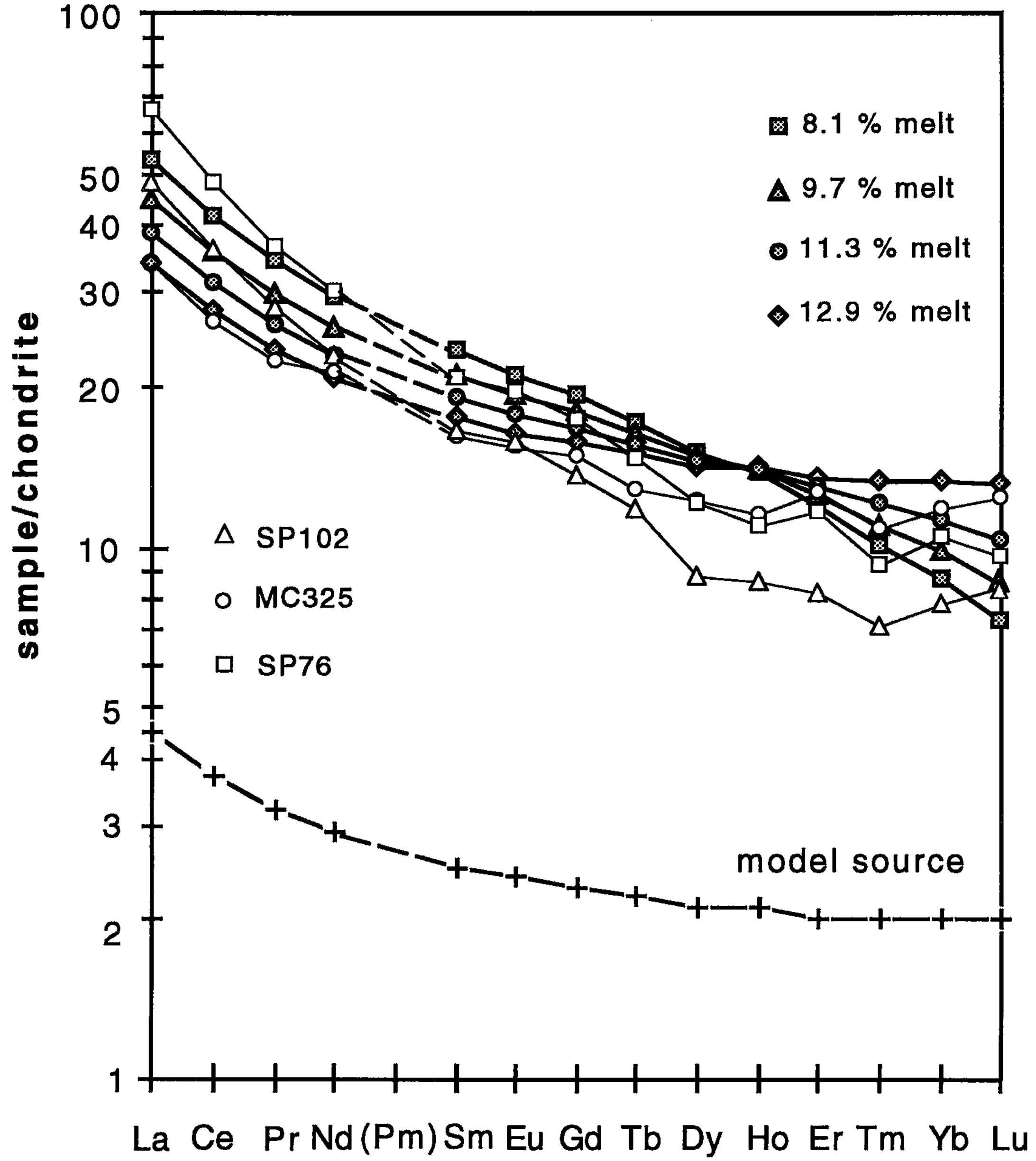

FIG. 8. Calculated *REE* patterns for melting of garnet lherzolite (solid symbols) compared to observed *REE* patterns for Macolod basalts (open symbols).

isotopic compositions. The data reported here for volcanic rocks from the Batangas Mountains show that even 3–5 Ma ago, the isotopic composition of the sources of arc magma had not changed significantly (Fig. 6). Hence, involvement of old enriched mantle is considered unlikely, in particular, since the collision of the Taiwan–Luzon arc with the continental Mindoro – North Palawan terrane has brought a source of old, enriched material, *i.e.*, material of the appropriate composition, into the geographic proximity of the area under consideration.

Mixing of the sources of the Macolod basalts with a component characterized by high La/Yb and $^{87}Sr/^{86}Sr$, and relatively low $^{143}Nd/^{144}Nd$, may explain the observed

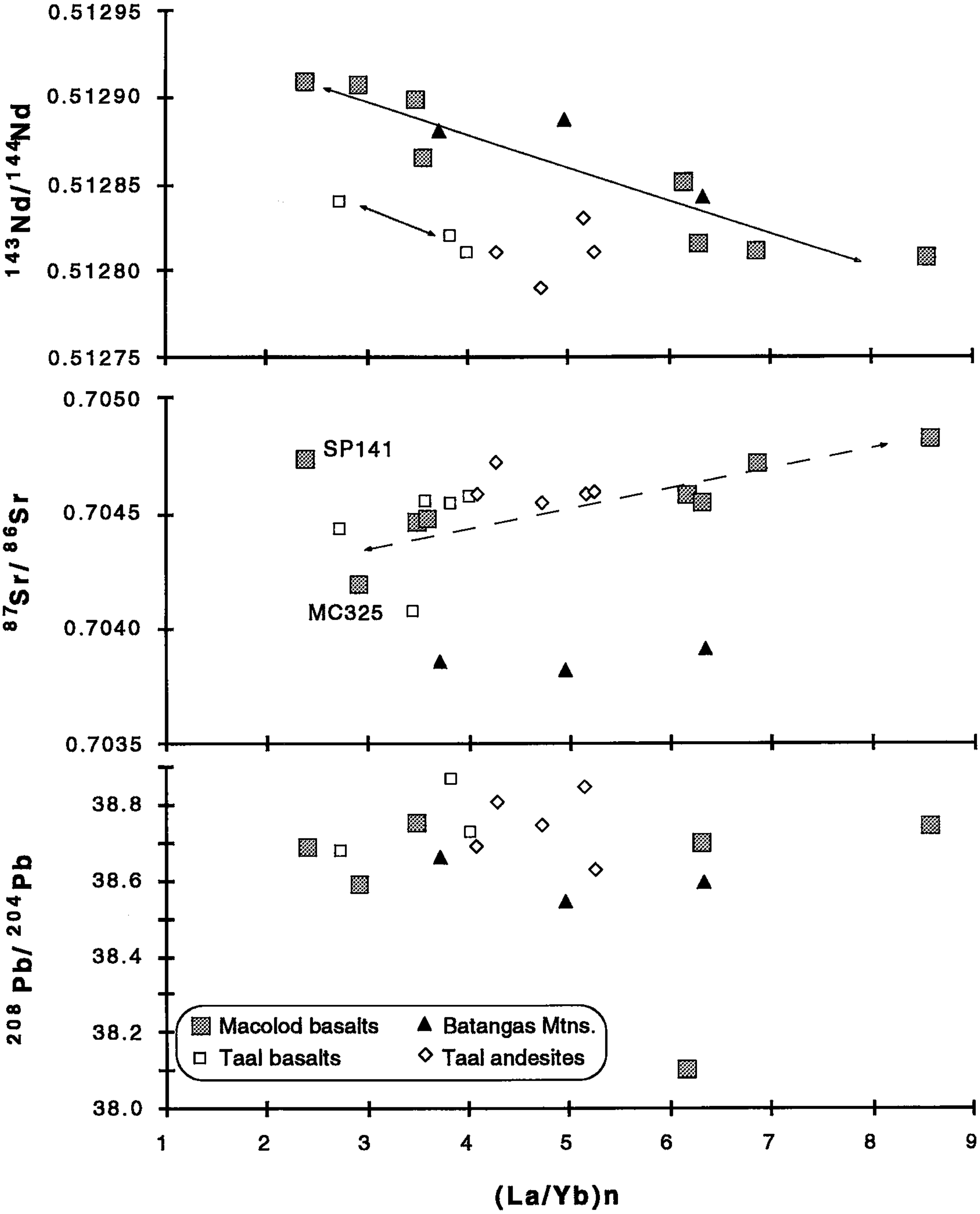

FIG. 9. ^{143}Nd/^{144}Nd, ^{87}Sr/^{86}Sr, and ^{208}Pb/^{204}Pb isotope ratios plotted as a function of $(La/Yb)_N$. Arrows illustrate the correlation between *LREE/HREE* and isotopic compositions of Nd and Sr.

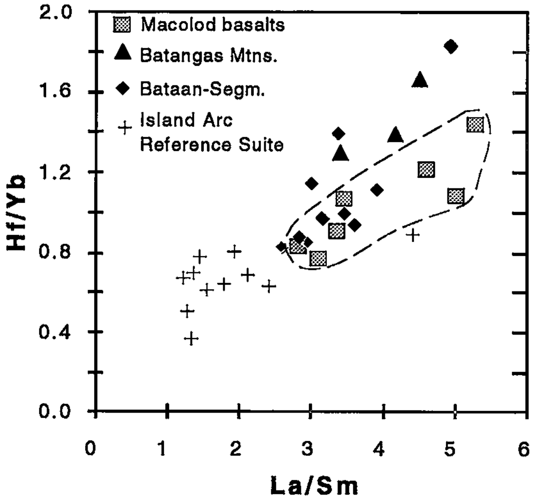

FIG. 10. Plot of Hf/Yb *versus* La/Sm values, illustrating a correlation of *LREE* and *HFSE* enrichment.

correlations between *REE* geochemistry and isotope systematics. We suggest that subduction of early Mesozoic granite and schist of the Mindoro – North Palawan continental terrane (Knittel & Daniels 1987, Faure *et al.* 1989), or subducted sediments derived therefrom, may explain the observed isotopic characteristics of the Macolod basalts.

In order to reduce the Yb concentration in the mixture of mantle and crustal material with increasing La/Yb relative to the abundance in the mantle prior to contamination, the contaminant needs to have a lower Yb content than the mantle (assuming similar degrees of partial melting). Estimates for the Yb_N concentration in the mantle are ~1.5. It is unlikely that any subducted material has such low *HREE* contents. Fluids appear to have have very low *HREE* contents (*e.g.*, Tatsumi *et al.* 1986, Keppler 1996), but it is unlikely that they are able to decrease the *HREE* concentration in the mixture significantly below 1.5 times chondritic values.

Melt derived from subducted crustal rocks that were transformed to eclogite may have the required low *HREE* contents provided that it equilibrates with a residue containing a high amount of garnet, and that the K_d for *HREE* between garnet and liquid is about 40, a value that has been observed for garnet in siliceous magma (*e.g.*, Irving & Frey 1978). Relics of hydrous, silica-rich melts, thought to be derived from the subducting slab, have been found by Schiano *et al.* (1995) in peridotite xenoliths erupted on Batan, an island of the Bashi Segment. These melts have Yb_N in the range 1.5 – 4.5; in other words, if they are typical of slab-derived melts, they are not capable of decreasing the Yb contents of the mixture peridotite + melt. Introduction of slab-derived melts into the mantle wedge would thus increase the *LREE*/*HREE* ratio of the mixture without changing its *HREE* contents. Further evidence for a melt-induced trace-element input from subducted continental crust or sediments into the sources of the Macolod basalts comes from the Y – *REE* – Zr – Hf systematics. The Macolod samples show a positive correlation between Hf/Yb and La/Sm (Fig. 10), suggesting that subduction-related *LREE*-enrichment is accompanied by enrichment of Hf (and other *HFSE*). In addition, the ratios Y/Ho and Zr/Hf, element pairs that are typically not fractionated by mantle melting, in Macolod basalts are close to the chondritic values ($25 < Y/Ho < 27$, and $38 < Zr/Hf < 44$) (Fig. 11). In contrast, Y/Ho and Zr/Hf are fractionated in aqueous fluids (Bau 1996).

The association of high *LREE*/*HREE*, indicating large slab-melt contributions to the source, and low *HREE*, may result from increasing degrees of partial melting of the mixtures with increasing slab-melt contributions. High degrees of partial melting result in low concentrations of the *HREE*, because the addition of slab-derived melt to the mantle does not change its *HREE* contents. Introduction of a fluid likewise may increase the degree of partial melting, but in this case, low-Yb melts should also have low abundances of those trace elements, which are considered to be immobile during element transfer by fluids. This is not observed. For example, the Zr contents increase slightly with decreasing Yb contents of the samples.

Hence we suggest that the *REE* geochemistry and Nd isotope compositions of the Macolod basalts are controlled by partial melts derived from subducted continental crust, or sediments derived therefrom. The Sr isotope ratio also is correlated with La/Yb if sample SP141, is considered to be an outlier (Fig. 9). The relation between $^{143}Nd/^{144}Nd$ and $^{87}Sr/^{86}Sr$ displayed in Figure 6 confirms this relationship.

In contrast to the $^{143}Nd/^{144}Nd$ values, Pb isotopes show no correlation with La/Yb (Fig. 9). The Pb isotope ratios of the samples form steep arrays relative to the NHRL, suggesting two-component mixing (except for sample SP102, which plots far away from the mixing array). A correlation of Pb isotope ratios with La/Yb values is not developed (Fig. 9), possibly because of the small overall variations of the Pb isotopic compositions of the lavas. The similar Pb isotopic compositions are possibly due to almost complete overprinting of mantle Pb by Pb from the slab-derived sediment.

The Pb isotope data reported by McDermott *et al.* (1993) for sediments from the South China Sea have only slightly higher $^{207}Pb/^{204}Pb$ and $^{208}Pb/^{204}Pb$ values than the volcanic rocks. Though we do not know whether the subducted sediments have similar Pb isotopic compositions, the available data do support the conclusion that the Pb of the lavas is nearly identical to the slab-derived Pb.

Commonly, mixing between depleted mantle peridotite and slab-derived Pb is envisioned to explain the steep array typically observed for subduction-related

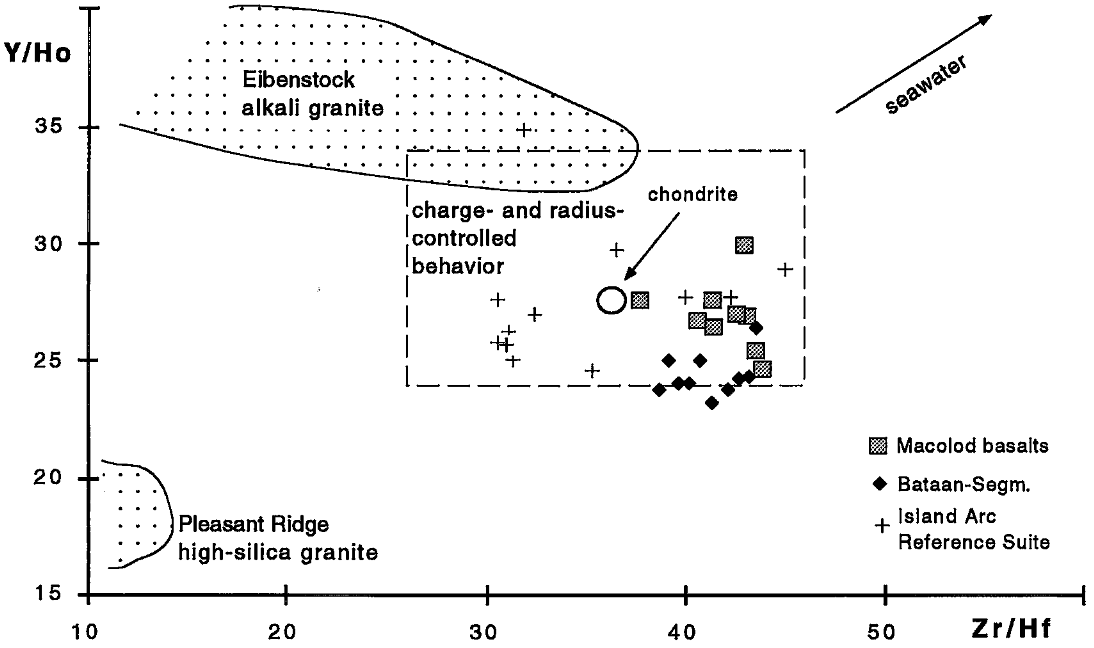

FIG. 11. Plot of Y/Ho *versus* Zr/Hf values, showing that Macolod and other arc basalts fall into a field considered to include magmas the Y/Ho and Zr/Hf values of which were only affected by partial melting processes, on the basis of data in Bau (1996).

igneous rocks. The lack of a correlation between La/Yb and Pb isotopic values suggests that the introduction of the slab-derived melt into the magma source discussed above is not the dominant mixing process for Pb. Rather, we suggest that Pb is preferentially transported by slab-derived fluid.

The shift toward high $^{87}Sr/^{86}Sr$ at a given $^{143}Nd/^{144}Nd$, generally seen in arc volcanic suites, commonly is considered to result from the involvement of a fluid phase with high Sr and low *REE* concentration (Tatsumi *et al.* 1986, Bau & Knittel 1993). The fluid transfer suggested for Pb may be responsible for the high $^{87}Sr/^{86}Sr$ at a given $^{143}Nd/^{144}Nd$ (Fig. 6). Two mixing processes of two end-members, *i.e.*, mixing of mantle peridotite and slab-derived fluids *and* melts, have previously been suggested by Ellam & Hawkesworth (1988) to explain some peculiarities of fractionation among the *LILE*.

CONCLUSIONS

The Nd isotope composition and *REE* and *HFSE* geochemistry, on one hand, and the Sr isotopic compositions, on the other, in primitive basalts from the Macolod Corridor appear to be controlled by different processes of mantle enrichment. Both processes are probably related to mixing of mantle peridotite, subducted sediments, and altered oceanic crust. The process that controls the *REE* chemistry may be considered to be melt infiltration, because *LREE* enrichment is coupled with *HFSE* enrichment. Decreasing *HREE* concentrations may result from increasing degrees of partial melting with increasing contributions of slab-derived melt, which are indicated by increasing *LREE/HREE* and *HFSE* concentrations. The other process may be the infiltration of slab-derived fluids, because isotopic shifts toward high $^{87}Sr/^{86}Sr$, as typically observed in ophiolitic rocks, are considered to be the result of seawater-induced alteration. Nd (and the *REE* in general) may be significantly less mobile in aqueous fluids (*e.g.*, Tatsumi *et al.* 1986), and hence contamination of the mantle by fluids may not affect its *REE* geochemistry significantly. Bau & Knittel (1993) likewise concluded that significant enrichment of the *REE* in the mantle wedge requires the involvement of partial melts derived from the subducted crust.

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