

## Research Article

# Insights into operation of the subduction factory from the oxygen isotopic values of the southern Izu–Bonin–Mariana Arc

EMI ITO,<sup>1,\*</sup> ROBERT J. STERN<sup>2</sup> AND CHUCK DOUTHITT<sup>3,†</sup>

<sup>1</sup>*Geology and Geophysics, University of Minnesota, 310 Pillsbury Drive SE, Minneapolis, MN 55455, USA (email: eito@umn.edu),* <sup>2</sup>*Department of Geosciences, University of Texas at Dallas, PO Box 830688, Richardson, TX 75083-0688, USA and* <sup>3</sup>*Division of Geological and Planetary Sciences, California Institute of Technology, Pasadena, CA 91125, USA*

**Abstract** Oxygen is the most abundant element in the earth, and isotopic analysis of this element in island arc lavas potentially provides sensitive constraints on the proportion of oxygen recycled from subducted material, relative to that extracted from the mantle. Here we report on 225 new oxygen isotopic analyses of whole-rock and glass samples, and clinopyroxene separates, from lavas collected from the southernmost 1500 km of the Izu–Bonin–Mariana (IBM) convergent margin. Whole-rock samples clustered around a mean of  $6.11 \pm 0.47\%$ , whereas Mariana Trough glasses and mafic melts, calculated to be in equilibrium with mafic phenocrysts, clustered narrowly around a mean of  $5.7\%$ . These data demonstrate that unequivocal identification of magmatic oxygen requires analysis of fresh glass or mafic minerals, and that the source of southern IBM Arc melts is entirely, or almost entirely, in equilibrium with normal mantle oxygen. If the elemental enrichments characteristic of the subduction component originate in subducted materials, these oxygen isotopic data are most consistent with the interaction of a small amount of sediment melt (<4%; mostly less than 1%) with mantle peridotite to yield the hybrid mantle that melts to form IBM Arc magmas.

**Key words:** clinopyroxene phenocryst, crustal recycling, island arc, magma, oxygen isotope, sediment, subduction.

## INTRODUCTION

Melts generated at convergent margins strongly manifest a “subduction component” in their composition, most simply defined as elevated concentrations of large ion lithophile elements (LILE) relative to high field strength elements (HFSE), and abundance of water up to 10-fold greater than that found in mid-ocean ridge basalt (MORB) or ocean-island basalt (OIB) (Pearce & Peate 1995). We still lack detailed understanding of how the subduction component forms, evolves, and is incorporated into the source of arc magmas. It can be

demonstrated that some constituents of arc lavas must have come from subducted sediments (e.g. cosmogenic <sup>10</sup>Be (Morris *et al.* 1990)), and nearly all of the water must ultimately come from the subducted lithosphere (Newman *et al.* 2000). Strong arguments have been made that the composition of subducted sediments controls the concentrations of LILE in arc lavas (Plank *et al.* 2002). Studies of western Pacific arc lavas have found correlation among  $\delta^{18}\text{O}$  and LILE concentrations and have concluded that the high values of both are associated with an increased extent of melting caused by the addition of slab-derived fluid (Macpherson & Matthey 1997; Macpherson *et al.* 1998; Eiler *et al.* 2000a). Nevertheless, constraining the proportions of elements other than water and <sup>10</sup>Be derived from the subducted slab or extracted from the mantle wedge remains depen-

\*Correspondence.

†Present address: 8848 South Raven Ridge, Safford, AZ 85546, USA.

Received 20 January 2003; accepted for publication 7 May 2003.

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dant on assumptions about the nature of the mantle source (e.g. normal (N)-MORB, enriched (E)-MORB or OIB) and what role, if any, is played by unusual residual minerals such as titanite.

Our objective in the present study was to contribute to our understanding of subduction components by using oxygen, the most common element in rocks, to constrain the relative contributions of mantle and subducted materials to arc melts. We achieve this aim by reporting new data on the oxygen isotopic composition of lavas and clinopyroxenes from the southern portion of the Izu–Bonin–Mariana (IBM) Arc system, an intraoceanic arc in the western Pacific where contamination of magmas by continental crust in the over-riding plate (having high  $\delta^{18}\text{O}$ ) is not a problem. This allows us to interpret the composition of unaltered samples as reflecting the composition of melts in equilibrium with their deeper sources, complicated only by relatively minor and predictable effects of fractionation. Subducted pelagic sediments have a very high  $\delta^{18}\text{O}$ , typically up to 30‰ (Anderson *et al.* 1976; Anderson & Lawrence 1976; Kolodny & Epstein 1976; Lawrence 1979; Ito & Stern 1986; O’Neil 1987). Locally derived volcanoclastic sediments contain  $\text{H}_2\text{O}$  of 6–11% (Plank & Langmuir 1998), which should have  $\delta^{18}\text{O}$  values between 18 and 28‰ (typically closer to 20‰) assuming all hydration reactions occurred at near-ambient seawater conditions (Muehlenbachs & Clayton 1972b). Together, the  $\delta^{18}\text{O}$  values of these sediments provide a potentially distinctive tracer; for example, lavas that inherit more than 1% of their oxygen from subducted sediments should be identifiable using modern analytical techniques. From our analysis, we show that many whole-rock samples have higher  $\delta^{18}\text{O}$  values than expected for MORB or OIB, whereas the melts calculated to be in equilibrium with clinopyroxene phenocrysts are isotopically very similar to mantle-derived MORB or OIB. We conclude that the disequilibrium between whole-rock and clinopyroxene oxygen isotopic compositions results from subtle alteration of whole-rock samples. We demonstrate that the oxygen isotopic composition of southern IBM Arc lavas mostly indicates a mantle origin. Our results are consistent with the conclusions reached by Eiler and others (e.g. Eiler *et al.* 2000a; Macpherson & Matthey 1997; and Macpherson *et al.* 1998).

This paper presents new  $\delta^{18}\text{O}$  data acquired from volcanic rocks and their pyroxene phenocrysts for the Mariana and Volcano Arcs and some Mariana Arc cross-chain seamounts. Our study demonstrates that (i) pyroxene phenocrysts retain

high-temperature  $\delta^{18}\text{O}$  values even when the matrix  $\delta^{18}\text{O}$  values are elevated due to subtle weathering; and (ii) the source of arc volcanics appears to receive little input of oxygen from subducted Pacific sediments in the Central Island Province, although samples from the Northern Seamount Province suggest that up to a few percent of the oxygen in these rocks may be ascribed to subducted sediments.

## GEOLOGICAL SETTING

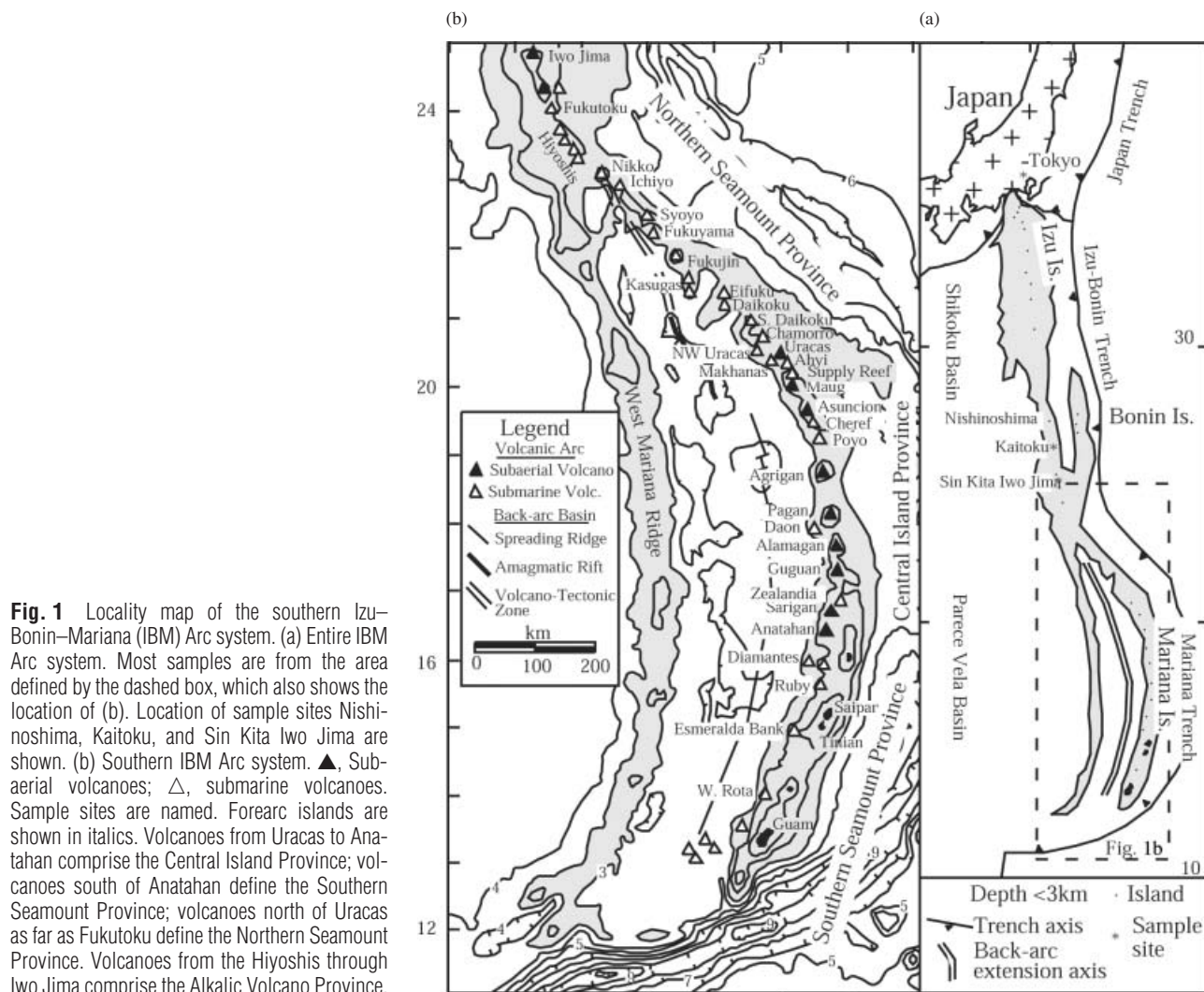
The IBM Arc system extends south from Japan along the eastern margin of the Philippine Sea plate. It formed approximately 45–50 Ma and has been subducting Pacific seafloor of Mesozoic age ever since. Jurassic seafloor is now being subducted, and this carries approximately 400 m of sediment (Plank & Langmuir 1998). Nearly everything on the Pacific plate that arrives at the IBM Trench is carried down into the subduction zone (Cloos & Shreve 1996); the IBM Arc has no accretionary prism. There is a well-developed volcanic chain that defines the active magmatic arc from the Izu Peninsula, Japan, to the south-east of Guam, spanning 23 degrees of latitude (approximately 2500 km; Fig. 1). For a more comprehensive overview of the IBM Arc system, see Stern *et al.* (2002). The samples examined in the present study encompass the southern two-thirds of the IBM Arc and include both volcanic islands and seamounts.

The southern IBM Arc has been subdivided into the Southern Seamount Subprovince (SSP; 14–16°N), the Central Island Subprovince (CIP; 16–21°N) and the Northern Seamount Subprovince (NSP; 21 to *ca* 24°N) (Bloomer *et al.* 1989b). The northern parts of the NSP, as far north as Iwo Jima, erupt shoshonitic lavas (Bloomer *et al.* 1989a). Volcanoes north of Iwo Jima (Sin Kita Iwo Jima, Kaitoku and Nishinoshima) erupt low-K arc tholeiites.

Some cross-chains extend from the magmatic arc rearwards; we examine rear-arc volcanoes of Daon and the Kasugas. An actively extending back-arc basin, the Mariana Trough, has been opening behind the Mariana Arc for the past few million years (Fig. 1).

## SAMPLES AND ANALYTICAL TECHNIQUES

Most of the submarine volcanic rock samples analyzed for this study were collected during the



**Fig. 1** Locality map of the southern Izu–Bonin–Mariana (IBM) Arc system. (a) Entire IBM Arc system. Most samples are from the area defined by the dashed box, which also shows the location of (b). Location of sample sites Nishinoshima, Kaitoku, and Sin Kita Iwo Jima are shown. (b) Southern IBM Arc system. ▲, Subaerial volcanoes; △, submarine volcanoes. Sample sites are named. Forearc islands are shown in italics. Volcanoes from Uracas to Anatahan comprise the Central Island Province; volcanoes south of Anatahan define the Southern Seamount Province; volcanoes north of Uracas as far as Fukutoku define the Northern Seamount Province. Volcanoes from the Hiyoshis through Iwo Jima comprise the Alkalic Volcano Province.

192nd cruise of the research vessel *R/V Thomas G. Thompson* (referred to as TT192 samples) of the University of Washington. Other samples were from subaerial (island) volcanic rocks collected by various researchers (A. Meijer, R. J. Stern, T. H. Dixon and I. Barnes), and submarine rocks collected by researchers from the University of Hawaii and from the Scripps Institution of Oceanography. Rocks included in this study were mostly basaltic to andesitic in composition, although some were dacitic. Some rocks were more alkalic, tending toward a trachytic composition.

The preparation of whole-rock powders from rocks recovered during the TT192 cruise has been described by Lin *et al.* (1990). All other whole-rock powders analyzed for  $\delta^{18}\text{O}$  at the University of Minnesota (UMN), or by the United States Geological Survey (USGS) (Barnes laboratory, Menlo Park, CA, USA), were prepared at UMN. The rocks were trimmed of all external surfaces, and

slabbed into 3–5-mm-thick slices. Each piece was visually inspected for saw marks (which were removed), and then split into domino-sized pieces of approximately  $1.5 \times 3$  cm. These were crushed to a small pea size and any weathered or altered matrix or olivine phenocrysts were removed. Clean pieces were ground with an alumina mortar and pestle to pass through a 0.180 mm sieve. Pyroxene phenocrysts were obtained from the same piece as that for whole-rock analysis. After the rock was crushed to pea size, a random aliquot was crushed using an iron mortar and pestle until phenocrysts largely separated from the matrix. Adhered fines were removed by repeated ultrasonic washing, and pyroxene phenocrysts were picked under binocular microscope. For several samples, a heavy liquid separation technique was used on 0.150 to 0.180 mm-sized grains.

Oxygen isotope analyses followed the  $\text{ClF}_3$  extraction technique (Borthwick & Harmon

1982), modified from the BrF<sub>5</sub> technique (Clayton & Mayeda 1963). The extracted CO<sub>2</sub> gas was analyzed using a Finnigan MAT delta E triple-collector isotope-ratio mass spectrometer (ThermoFinnigan, San Jose, CA, USA) at UMN, and using a Finnigan MAT 251 at both USGS laboratories (Barnes and O'Neil) in Menlo Park. A few (27) of the whole-rock samples from the SSP and CIP were analyzed in the USGS O'Neil laboratory in 1981 using a slightly different procedure (BrF<sub>5</sub>); these have been noted in Table 1. Forty-

seven analyses (including replicates) were performed at the USGS Barnes laboratory in 1989. The estimated overall error (1 SD) on USGS Barnes whole-rock analysis was  $\pm 0.3\%$ , based on more than 1000 replicate analyses of a granodiorite sample. More than 12 whole-rock samples were analyzed by both the USGS Barnes laboratory and the UMN laboratory. For each sample, the average  $\delta^{18}\text{O}$  value obtained at Barnes USGS and the average  $\delta^{18}\text{O}$  obtained at UMN agreed within  $0.1\%$ . All USGS analyses, regardless of extraction

**Table 1**  $\delta^{18}\text{O}$  values of southern Izu–Bonin–Mariana Arc, Cross Chain and Mariana Trough volcanic rocks

Sample ID	Lat.°N	SiO <sub>2</sub> <sup>†</sup>	K <sub>2</sub> O <sup>†</sup>	LOI <sup>‡</sup>	Rock <sup>§</sup>	Px <sup>§</sup>	Eq. mafic melt <sup>¶</sup>	Sample source <sup>††</sup>
<i>Mariana Arc</i>								
Southern Seamount Province								
Unnamed seamount	14.33							
MARA D47-A		55.9	1.25	ND	6.1*			D&S83
MARA D47-D1		65.0	1.80	ND	6.2*			D&S83
MARA D47-H		67.2	2.15	ND	6.7*			D&S83
Esmeralda Bank	15.00							
MARA D45-11		51.9	0.99	0.66	5.4*			D&S83
MARA D46-2		52.8	0.95	ND	5.8*			D&S83
MARA D46-3		52.9	0.91	ND	5.9*			Bibee
MARA D46-11		53.8	0.72	ND	6.2*			Bibee
MARA D46-12		52.8	0.89	0.85	5.6*			Bibee
Ruby, South	15.58							
D1-1		48.1	0.38	ND	5.9			S89
D1-16		50.6	0.46	ND	5.9			S89
D1-170		49.6	0.39	ND	6.3	5.67	6.1	S89
East Diamante	15.85							
MARA D59-A		53.5	1.18	1.22	5.8*			D&S83
MARA D59-C		51.9	0.73	0.84	5.9*			D&S83
West Diamante	16.02							
MARA D58-C		56.1	1.18	0.56	5.9*			D&S83
MARA D58-F		53.5	0.86	0.53	5.2*			D&S83
MARA D58-I		53.7	0.73	0.46	5.8*			D&S83
Central Island Province								
Anatahan								
	16.33							
ANT79.12		53.0	0.64	ND	6.2			Meijer
ANT79.36		ND	0.56	ND	6.0			Meijer
ANT79.17B		ND	ND	ND	6.2			Meijer
ANT79.4		59.8	0.82	ND	6.1			Meijer
ANT79.21		64.4	1.69	ND	6.2			Meijer
ANT79.28		52.8	0.53	ND	6.6			Meijer
Sarigan								
	16.70							
S-3		52.6	0.68	0.19	5.8*			D&B79
S-4		58.6	0.88	0.22	5.9*			D&B79
SA051		53.0	0.58	1.29	6.9	5.37	5.8	Meijer
SA053		57.1	0.89	0.91	6.4			Meijer
SA054		58.8	0.81	1.06	6.5			Meijer
SA057		65.9	ND	0.41	6.0			Meijer
SA61-1		52.7	0.53	2.13	8.7			Meijer
SA61-2		52.0	0.55	1.71	6.5	5.45	5.9	Meijer
SA065		55.1	0.90	1.10	6.7			Meijer
SA71B		50.9	0.70	1.05	6.4			Meijer
SA76B		59.9	1.05	0.95	6.4			Meijer
SA093		52.7	0.61	0.80	6.3	5.35	5.8	Meijer
SA096		52.8	0.76	0.67	6.0			Meijer
SA100		55.9	0.83	1.22	6.3			Meijer



Table 1 Continued

Sample ID	Lat. °N	SiO <sub>2</sub> <sup>†</sup>	K <sub>2</sub> O <sup>†</sup>	LOI <sup>‡</sup>	Rock <sup>§</sup>	Px <sup>§</sup>	Eq. mafic melt <sup>¶</sup>	Sample source <sup>††</sup>
SA120		55.3	0.91	0.65	6.3			Meijer
SA122		56.5	1.07	1.09	6.4			Meijer
SA123B		54.8	0.87	0.39	6.4			Meijer
SA130		53.4	0.61	0.82	6.1			Meijer
SA134		61.1	0.93	0.71	6.2			Meijer
SA134-2		ND	ND		6.3			Meijer
SA138		53.2	0.77	0.76	6.8	5.42	5.9	Meijer
1IB83		ND	ND		6.6			Barnes
Zealandia Bank	16.92							
MARA D57 A-1		48.6	0.64	1.44	6.2*			D&S83
MARA D57 A-2		48.7	0.61	1.40	5.6*			D&S83
MARA D57 C		49.0	0.58	1.30	6.0*			D&S83
Guguan	17.30							
GUG79.33 A		56.4	0.73	ND	6.2			Meijer
GUG79.31B		56.8	0.72	ND	6.4			Meijer
GUG1		51.9	ND	1.96	6.5			Meijer
GUG79.10		52.0	0.39	ND	6.9			Meijer
Gu-1		50.9	0.40	0.12	5.6*			D&B79
Gu-3		52.3	0.50	0.14	5.6*			D&B79
Alamagan	17.60							
AL30A		54.0	0.84	0.43	6.8			Meijer
AL69		ND	0.81	0.77	7.3			Meijer
AL53A		ND	ND	ND	6.7			Meijer
AL72		53.9	0.95	0.58	6.9			Meijer
AL27		52.8	1.05	0.50	6.6			Meijer
AL75		57.2	1.45	0.65	6.6			Meijer
AL71		65.5	0.90	0.52	6.5			Meijer
AL28		ND	ND	0.47	7.3			Meijer
AL65		51.4	0.77	0.34	6.5			Meijer
Pagan	18.12							
PA60C		51.3	0.67	1.33	6.8			Meijer
2IB83					6.1			Barnes
8IB83					6.1			Barnes
P-1		56.8	1.45	1.28	6.5*			D&B79
P-2		49.9	0.60	0.01	5.4*			D&B79
Agrigan	18.75							
Ag8-3B		52.6	0.76	ND	6.0			Stern
Ag8-3C		52.3	0.61	ND	5.7			Stern
Ag3-4		50.3	0.85	ND	5.7			Stern
Ag4-2		51.4	0.96	ND	5.8			Stern
Ag4-5		51.3	0.95	ND	5.6			Stern
Ag7-4		52.1	0.94	ND	6.0			Stern
Ag8-2B		53.7	1.11	ND	5.6			Stern
Ag1-6		53.4	1.45	ND	5.8			Stern
Ag4-9		53.4	1.16	ND	5.5			Stern
Ag7-2		56.1	1.57	ND	5.8			Stern
Ag-30		59.5	1.90	0.23	5.6*			D&B79
Ag-25		55.7	1.26	0.26	5.8*			D&B79
Ag-25a, chilled margin		55.7	1.26	0.26	5.6*			D&B79
Poyo	19.25							
D8-1		48.5	0.20	ND	6.6			B89, L89, L90
D8-3		48.2	0.22	ND	6.8			B89, L89, L90
Cheref	19.42							
D9-6		53.5	0.74	ND	5.7			B89, L89, L90
D9-7		55.4	0.59	ND	6.1			B89, L89, L90
D9-20		51.3	0.63	ND	5.9			B89, L89, L90
D10-1-2		64.0	1.22	ND	6.4			B89, L89, L90, P90
D10-2-6		56.3	0.65	ND	5.7			B89, L89, L90
D10-2-7		55.7	0.61	ND	6.2			B89, L89, L90
D10-2-11		49.5	0.55	ND	6.0			B89, L89, L90
D11-11		52.7	0.48	ND	6.3	5.09	5.5	B89, L89, L90

**Table 1** *Continued*

Sample ID	Lat.°N	SiO <sub>2</sub> <sup>†</sup>	K <sub>2</sub> O <sup>†</sup>	LOI <sup>‡</sup>	Rock <sup>§</sup>	Px <sup>§</sup>	Eq. mafic melt <sup>¶</sup>	Sample source <sup>††</sup>
Ascuncion	19.70							
A-3		54.9	0.60	ND	5.6			Stern
As-1		53.5	0.56	0.52	6.0*			D&B79
As-3		53.1	0.54	0.11	5.6*			D&B79
Maug	20.03							
MA1A		50.0	0.55	1.37	6.7			Meijer
MA3B		51.9	0.60	ND	6.2			Meijer
MA9		49.8	0.46	ND	6.8			Meijer
MA16		50.1	0.50	ND	6.0			Meijer
MA17		ND	ND	ND	6.5			Meijer
MA18		50.7	0.58	0.13	6.8			Meijer
MA20		49.3	0.43	ND	6.9			Meijer
MA26		51.7	0.46	ND	5.0			Meijer
MA29		59.7	0.86	ND	6.3			Meijer
MA30B		58.6	ND	ND	6.7			Meijer
MA30F		58.4	0.91	ND	6.2			Meijer
MA53		62.9	1.02	ND	6.2			Meijer
MA63		49.2	0.40	0.92	6.3			Meijer
MA-H9		54.8	0.71	ND	5.9			Hochstedter
MA-H12		52.5	0.59	ND	5.8			Hochstedter
Supply Reef	20.12							
D13-2		59.3	0.68	ND	6.2			L89, L90
D13-11		53.8	0.40	ND	5.3			B89, L89, L90
D14-1		56.0	0.45	ND	5.9			L89, L90
D14-15		52.8	0.48	ND	5.9			B89, L89, L90
Ahyi	20.40							
D15-3-2		52.8	0.70	ND	6.4	5.30	5.8	B89, L89, L90, P90
D15-3-3		53.0	0.57	ND		5.37	5.8	B89, L89, L90, P90
Makhahnas	20.53							
D18-9		56.3	1.12	ND	7.4	5.24	5.7	B89, L89, L90, P90
D18-11		57.7	1.31	ND	6.5	5.13	5.6	B89, L89, L90
North-west Uracas	20.58							
D19-3-5		52.1	0.39	ND	5.9			B89, L89, L90, P90
D19-3-10		52.1	0.39	ND	6.1			B89, L89, L90
Uracas	20.53							
UR23		53.8	0.71	ND	5.7			B89, L89, L90
UR31		53.8	0.65	0.58	6.3			Meijer
UR22		ND	0.61	0.31	6.6			Meijer
UR27		58.6	1.07	0.72	6.0			Meijer
UR1		54.0	0.67	0.52	6.0			Meijer
Northern Seamount Province								
Chamorro	20.75							
D23-3		65.8	1.32	ND	6.6			B89, L89, L90, P90
South Daikoku	21.05							
D26-3-1		61.8	0.92	ND	5.7			B89, L89
D26-4-5		60.0	0.94	ND	5.7			B89, L89
D26-4-6		59.0	0.99	ND	5.4			B89, L89
D25-1		58.2	1.50	ND	7.4			B89, L89, L90, P90
D25-8		54.3	0.70	ND	6.4			B89, L89, L90
D25-18		56.5	1.06	ND	5.8	5.38	5.8	B89, L89, L90, P90
Daikoku	21.33							
D29-1-1		59.1	1.83	ND	5.5			B89, L89
D29-1-2		59.9	1.74	ND	5.8			B89, L89, L90, P90
D29-2-2		63.3	2.06	ND	6.1			B89, L89, L90, P90
D29-2-3		62.5	2.04	ND	5.9			B89, L89
Eifuku	21.39							
D31-1-4		49.6	0.93	ND	5.5			B89, L89, L90, P90
D31-1-6		49.1	0.87	ND	5.5			B89, L89, L90, P90
D31-2-2		52.5	1.31	ND	6.4	5.11	5.6	B89, L89, L90, P90
D30-7		50.5	1.21	ND	5.4			B89, L89, L90, P90
D30-8		51.5	1.34	ND	5.7			B89, L89, L90, P90

Table 1 Continued

Sample ID	Lat. °N	SiO <sub>2</sub> <sup>†</sup>	K <sub>2</sub> O <sup>†</sup>	LOI <sup>‡</sup>	Rock <sup>§</sup>	Px <sup>§</sup>	Eq. mafic melt <sup>¶</sup>	Sample source <sup>**</sup>
Fukujuin	21.88							
D34-1-2		52.7	1.01	ND	5.9			B89, L89, L90
D34-2-2		53.1	1.19	ND	5.4			B89, L89, L90, P90
D35-1-2		55.4	1.27	ND	6.3	5.77	6.2	L89, L90
D35-2-1		56.4	1.39	ND	6.4			B89, L89, L90
Fukuyama	22.38							
D38-2		52.5	0.31	ND	4.2			B89, L89, L90, P90
Shoyo	22.50							
D41-52		ND	0.48	ND	6.1			L89, L90
Ichiyo	23.00							
D44-1-5		53.2	1.23	ND	6.5	5.84	6.3	B89, L89, L90, P90
Nikko	23.09							
D45-11		61.7	1.51	ND	5.9			B89, L89, L90
D46-1-1		45.9	0.34	ND	5.2			B89, L89, L90
84KK0402		ND	ND	ND	6.0			Fryer
Ko-hiyoshi	23.38							
D47-1-1		53.1	1.88	ND	7.8	5.43	5.9	B89, L89, L90, P90
South Hiyoshi	23.49							
D48-1-2		53.1	2.85	ND	6.3			B89, L89, L90, P90
D49-PB		50.1	1.97	ND	5.6			L89, L90
D49-1-2		50.2	2.00	ND	5.2	5.07	5.5	B89, L89, L90
D49-2-1		54.9	3.45	ND	6.5			B89, L89, L90
Central Hiyoshi	23.62							
D51-3		51.8	1.28	ND	5.9	5.20	5.7	B89, L89, L90, P90
D51-g-A		ND	3.85	ND	6.0			L89, L90
D51-g-B		ND	4.39	ND	5.9			L89, L90
D52-1-1		50.3	2.54	ND	5.9	5.34	5.8	B89, L89, L90, P90
D52-3-1		51.9	2.23	ND	6.2	5.63	6.1	B89, L89, L90, P90
North Hiyoshi	23.80							
D53-1-2		55.8	4.13	ND	6.0			B89, L89, L90
D53-1-3		55.4	4.19	ND	6.0	5.17	5.6	B89, L89, L90, P90
D54-1-1		46.2	1.38	ND	6.4			B89, L89, L90
Fukutoku	24.08							
D55-1-2		48.8	2.51	ND	6.4	5.67	6.1	B89, L89, L90, P90
D57-6		48.0	1.24	ND	6.0	5.86	6.3	B89, L89, L90, P90
<i>Volcano Arc</i>								
Sin Kita Iwo Jima	25.13							
D73-4-2		53.7	1.24	ND	6.4	5.33	5.8	B89, L89, L90, P90
D73-4-4		47.4	0.46	ND	6.2			B89, L89, L90, P90
Kaitoku	26.08							
D75-4		57.6	1.17	ND	6.5			B89, L89, L90, P90
D77-1		55.6	1.03	ND	7.0	5.40	5.9	B89, L89, L90
Nishi no shima	27.27							
D79-1		53.2	0.40	ND	ND	5.05	5.5	B89, L89, L90
D79-6		51.2	0.42	ND	5.4			B89, L89, L90, P90
D80-1		52.0	0.42	ND	5.7			B89, L89, L90, P90
73/74 flow		58.5	1.15	ND	6.1			L89, L90
<i>Central Cross Chain</i>								
Daon, cross chain	17.92							
D5-1		57.6	1.51	ND	6.4	5.05	5.5	TT192
D5-7		60.5	1.75	ND	6.3			TT192
D5-78		55.5	0.46	ND	6.4			TT192
Daon, summit	17.94							
D6-36		58.7	1.14	ND	6.8			TT192
D6-49		58.9	1.27	ND	6.2			TT192
D6-50		57.0	1.32	ND	6.1			TT192
<i>Northern Cross Chain</i>								
Kasuga 2	21.65							
83KK2406		50.2	ND	ND	5.5			Fryer
83KK2409		50.1	0.75	0.56	5.4			Fryer
83KK2501		48.0	2.14	0.18	5.7	5.53	6.0	F97
83KK2504		47.1	ND	ND	5.4	5.59	6.0	Fryer

Table 1 Continued

Sample ID	Lat. °N	SiO <sub>2</sub> <sup>†</sup>	K <sub>2</sub> O <sup>†</sup>	LOI <sup>‡</sup>	Rock <sup>§</sup>	Px <sup>§</sup>	Eq. mafic melt <sup>¶</sup>	Sample source <sup>††</sup>
83KK2508		51.5	1.27	0.43	5.5	5.65	6.1	Fryer
83KK2510		51.7	ND	ND	5.5	5.54	6.0	Fryer
<i>Mariana Trough</i>								
1838–1813	18.22	52.7	0.52	ND	6.0			V90
1841–1818	18.23	50.5	0.21	ND	5.8			H90
1839–1803	18.28	ND	ND	ND	5.8			V90
1846–1809	18.37	49.7	0.71	1.93	5.8			H90, V90, S94
1846–1812	18.37	50.8	0.40	1.58	5.8			H90, V90, S94
85KK0301	22.03	ND	ND	ND	5.3	5.48	5.9	Fryer
84KK0101	21.65	48.3	0.32	0.28	5.7			J89
84KK0102	21.65	48.2	0.37	0.59	5.6			J89
84KK0103	21.65	48.4	0.32	0.28	5.7			J89
84KK0205	22.80	52.2	1.04	0.98	6.0			J89

<sup>†</sup>SiO<sub>2</sub> and K<sub>2</sub>O reported in weight %. Chemistry data sources: Bloomer *et al.* (1989b); Bloomer (pers. comm.); Dixon and Batiza (1979); Dixon and Stern (1983); Hawkins and Melchior (1985); Hawkins *et al.* (1990); Ito and Stern (1986); Jackson (pers. comm.); Meijer and Reagan (1981); Meijer (pers. comm.); Stern and Bibee (1984), Stern (1979); Stern (1990); Stern *et al.* (1993); Stolper and Newman (1994); Volpe (1987); and Volpe (1990).

<sup>‡</sup>LOI, loss on ignition. Total H<sub>2</sub>O in weight %.

<sup>§</sup> $\delta^{18}\text{O}$  values in ‰ relative to VSMOW. Analyses marked \* by L. Adami, United States Geological Survey (USGS), Menlo Park (Geologic Division); all other analyses by I. S. Lee or J. Xia at the University of Minnesota, by C. Maley at USGS, Menlo Park (Water Resources Division), or by both institutions. All pyroxene analyses by J. Xia.

<sup>¶</sup>Eq. mafic melt, equilibrium mafic melt.  $\delta^{18}\text{O}$  for the melt of SiO<sub>2</sub> = 48% calculated from the  $\delta^{18}\text{O}$  (pyroxene) assuming that equilibrium isotope fractionation accompanies fractional crystallization (see Discussion).

<sup>††</sup>Samples that have previously reported data are so noted; samples with no previously published data are identified by the name of the donor. Many island samples (ANT, SA, GUG, AL, PA, MA and UR) were collected by Arend Meijer; other island samples were collected by Stern (1979) or Dixon and Batiza (1979) (D&B79), except those designated IB83 (collected by Ivan Barnes). D&S83 were collected by Dixon and Stern (1983). Submarine arc volcano samples were mostly collected during the *R/V Thomas G. Thompson* Cruise 192, with R. J. Stern and S. H. Bloomer as co-chief scientists; these samples have been studied by Bloomer *et al.* (1989a) (B89), Lin *et al.* (1989) (L89), Stern *et al.* (1989) (S89), Lin *et al.* (1990) (L90) and Peate and Pearce (1998) (P98). Samples labeled TT192 are unpublished results. Samples 1838, 1839, 1841 and 1846 were collected during *Alvin* dives and have been studied by Volpe (1990) (V90), Hawkins *et al.* (1990) (H90) and Stolper and Newman (1994) (S94). KK samples were collected during the *R/V Kana Keoki* cruises, and have been reported by Jackson (1989) (J89), Fryer *et al.* (1997) (F97), or are unpublished results from Fryer. Mariana Trough DS samples were studied for chemical compositions by Gribble *et al.* (1996) and for O isotopic compositions by Macpherson *et al.* (2000).

conditions or mass spectrometer performance, have been included because such information was not provided. All UMN analyses were performed between 1986 and 1992, with nearly half of the analyses performed in 1989. The error for UMN whole-rock analysis was  $\pm 0.2\%$ , based on 27 analyses of the sample D48-1-2. All pyroxene analyses reported here were performed at UMN and have been replicated at least once, and some as many as five times. For all pyroxene analyses, an error of 1 SD was  $\pm 0.1\%$  or better. Poor quality analyses from UMN were excluded (e.g. those resulting from (i) non-quantitative O<sub>2</sub> to CO<sub>2</sub> conversion identified by poor CO<sub>2</sub> yield; (ii) leaks in Ni bombs identified by the slow rate of O<sub>2</sub> to CO<sub>2</sub> conversion; and (iii) high residual non-condensibles). All results (mean value of replicate analyses) have been reported relative to VSMOW.

There is a serendipitous replication between our procedure and the laser-fluorination technique of Eiler *et al.* (2000a). Eiler *et al.* (2000a)

analyzed one olivine from Sarigan. Based on that analysis, accepting their preferred oxygen-isotope equilibrium fractionation factor ( $\Delta = 0.4$ ), a  $\delta^{18}\text{O}$  of 5.7 was calculated for the equilibrium melt. In the present paper, we report data for clinopyroxenes from four Sarigan lavas, which indicate that equilibrium mafic melts (see Discussion below for how this is calculated) had  $\delta^{18}\text{O}$  values of 5.7–5.8. Eiler *et al.* (2000a) also analyzed seven olivines from the North Hiyoshi Seamount, which indicated a very narrow range of  $\delta^{18}\text{O}$  for equilibrium melts (5.4–5.6‰). Our analysis of one clinopyroxene from North Hiyoshi also indicated equilibrium with a mafic melt with a  $\delta^{18}\text{O}$  value of 5.6‰. Two glasses from the Mariana Trough were also unknowingly replicated; Eiler *et al.* (2000a) report  $\delta^{18}\text{O}$  values for 1846–9 and 1846–1812 glasses of 5.55 and 5.61‰, respectively; our values for these samples are 5.8‰. In a previous study (Garcia *et al.* 1998), one Hawaiian glass sample was analyzed both at Wisconsin (Eiler)



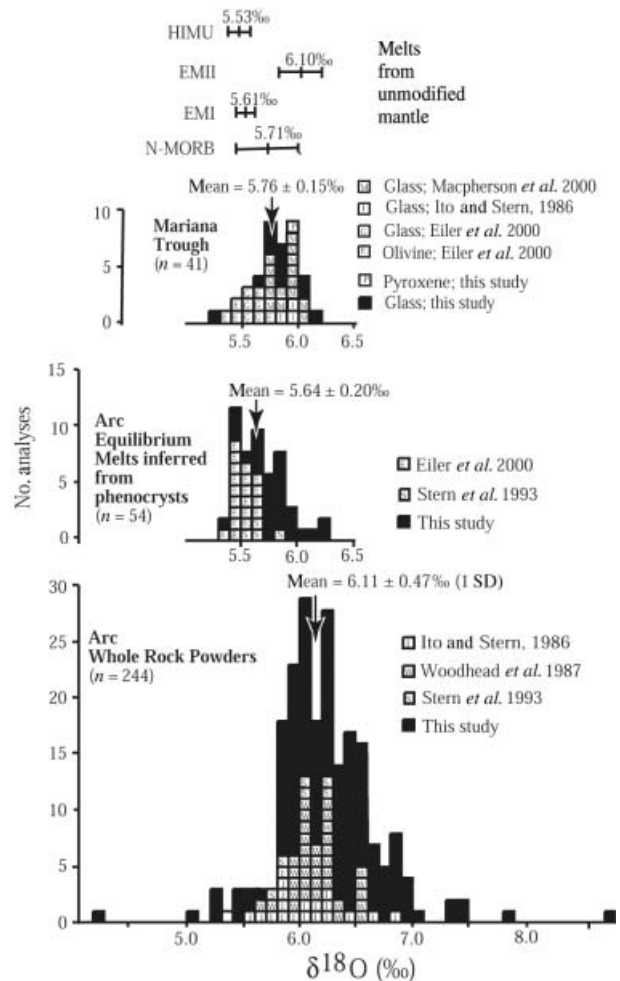
and at UMN (Ito) using the same techniques discussed here, with the former reporting  $4.91 \pm 0.08\text{‰}$  and the latter reporting  $4.76 \pm 0.05\text{‰}$ . Therefore, there seems to be no systematic difference in the analysis of glass samples between the two laboratories.

## RESULTS

The data set presented in Table 1 contains 225 analyses, including 184 whole rocks, 10 glasses and 31 clinopyroxenes. These results, together with previously published data (Ito & Stern 1986; Woodhead *et al.* 1987; Stern *et al.* 1993; Eiler *et al.* 2000a; Macpherson *et al.* 2000), are summarized in Figures 2 and 3. Whole-rock  $\delta^{18}\text{O}$  values of arc lavas ranged from 4.2 to 8.7‰, with a mean of  $6.11 \pm 0.46\text{‰}$  (1 SD). This is similar to the average oceanic arc basalt value of  $6.1 \pm 1.1\text{‰}$  reported by Harmon and Hoefs (1995). The pyroxene  $\delta^{18}\text{O}$  values spanned a lower and narrower range of 5.07–5.86‰. In the Discussion we explain how we inferred the oxygen isotopic composition of mafic melts in equilibrium with analyzed pyroxenes. The inferred equilibrium mafic melts have a mean  $\delta^{18}\text{O} = 5.72 \pm 0.22\text{‰}$ . Three elevated pyroxene  $\delta^{18}\text{O}$  values ( $>5.5\text{‰}$ ) were seen for samples collected from the NSP between  $21^{\circ}30'$  and  $24^{\circ}\text{N}$  (Fig. 3). A similar relationship was observed for pyroxenes in cross-chain volcanic rocks from Kasuga 2 and Daon, included in Figures 2 and 3 (includes three analyses for Kasuga 2 previously reported by Stern *et al.* (1993)). The whole-rock  $\delta^{18}\text{O}$  values of cross-chain volcanic rocks varied from 5.4 to 6.8‰ ( $n = 19$ ), with 10 samples below 6.0‰. Whole-rock  $\delta^{18}\text{O}$  values of back-arc basalt glasses ranged from 5.3 to 6.1‰ ( $n = 10$ ), which is similar to MORB (Ito *et al.* 1987), as originally suggested by Pineau *et al.* (1976): these values show no systematic north–south variation from  $16^{\circ}\text{N}$  to  $22^{\circ}\text{N}$ .

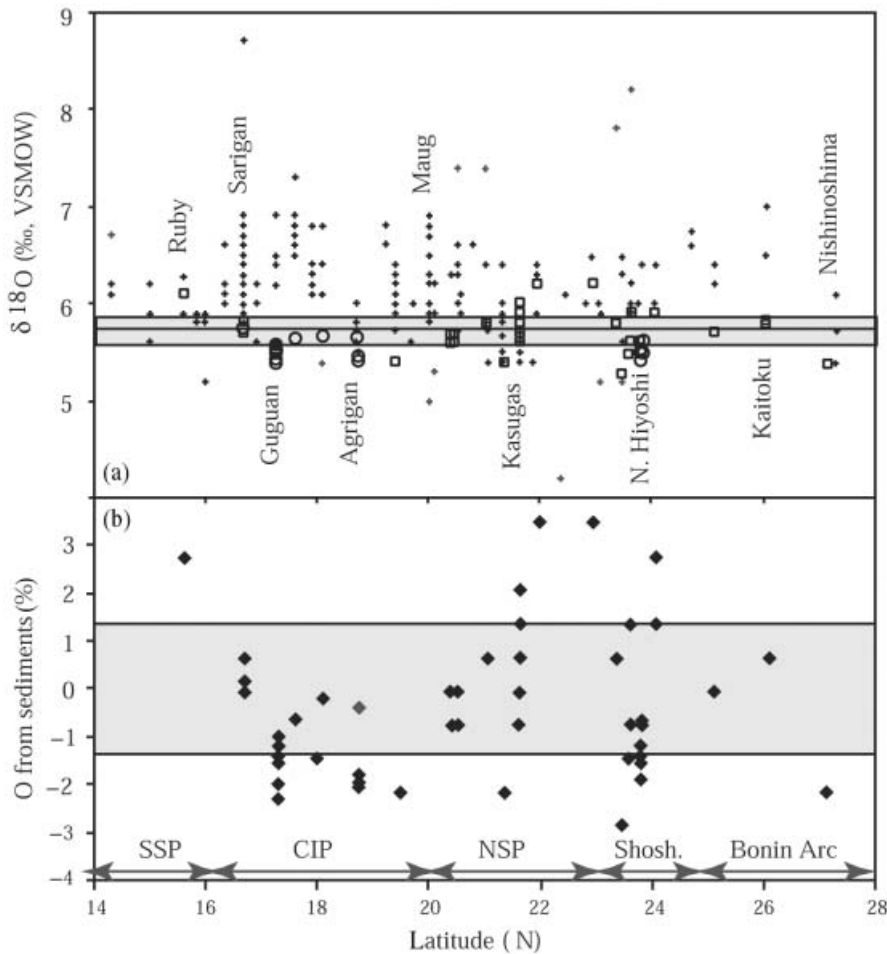
## DISCUSSION

Because oxygen is so common, its isotopic composition has long been recognized as important for understanding the relative contributions of the mantle wedge and subducted materials as sources for magmas generated at convergent plate margins. The IBM Arc has been the target of four efforts to understand the origin of these melts using oxygen isotopes, with similar results but conflicting interpretations. Matsuhisa (1979) analyzed whole rocks from Hachijo-jima and Oshima



**Fig. 2** Histograms of oxygen isotopic compositions of volcanic rocks and melts calculated to be in equilibrium with phenocrysts (olivine and clinopyroxene). The lower histogram plots data for whole-rock analyses for the southern Izu–Bonin–Mariana (IBM) Arc. The middle histogram plots compositions for equilibrium melts inferred from olivines analyzed using their preferred fractionation factor ( $\Delta = 0.4$ ) (Eiler *et al.* 2000a) and from mafic melts inferred from our clinopyroxene analyses. The top histogram plots the oxygen isotopic composition of back-arc basin basalt glasses and equilibrium melts inferred from phenocryst compositions. At the top of the diagram are the means  $\pm 1$  SD for mantle reservoirs, including two different means for N-mid-ocean ridge basalt (MORB) (Ito *et al.* 1987; Eiler *et al.* 2000b) and ocean-island basalt (OIB) EMI, EMII and HIMU (Eiler *et al.* 1997). Note that Mariana Arc whole-rock compositions are significantly heavier (on average by approximately 0.5‰) than the melts calculated to be in equilibrium with olivine and clinopyroxene phenocrysts. The oxygen isotopic composition of melts inferred to be in equilibrium with arc phenocrysts and Mariana Trough samples are largely indistinguishable from that of mantle-derived lavas such as N-MORB, EMI, EMII and HIMU.

in the northernmost part of the IBM Arc and found that mafic rocks were indistinguishable in terms of  $\delta^{18}\text{O}$  from mantle melts. He further documented that fractionation from 47%  $\text{SiO}_2$  basalt to 73%  $\text{SiO}_2$  dacite led to increases in  $\delta^{18}\text{O}$  of approximately 1‰. Ito and Stern (1986) studied



**Fig. 3** Latitudinal variation in oxygen isotopic composition of the southern Izu–Bonin–Mariana (IBM) Arc. Mariana Trough samples are excluded, but the cross-chain samples are included in the plot. (a) Plot of arc  $\delta^{18}\text{O}$  data for whole-rock samples (crosses), equilibrium mafic melts calculated from olivines (○) and equilibrium mafic melts calculated from clinopyroxenes (□). The horizontal line corresponds to the mean  $\delta^{18}\text{O}$  for N-mid-ocean ridge basalt (MORB) and the gray box corresponds to  $\pm 1$  SD (Ito *et al.* 1987). (b) Calculated amounts of subducted fluids involved in Mariana Arc melts (inferred from compositions of clinopyroxene and olivine). Fluid or melt derived from subducted sediments is inferred to have  $\delta^{18}\text{O} = 20\text{‰}$  (Eiler *et al.* 2000a) and mantle is assumed to have  $\delta^{18}\text{O} = 5.71\text{‰}$ . Grey box outlines amount of sediment-derived oxygen calculated from  $\pm 1$  SD in the  $\delta^{18}\text{O}$  of N-MORB. Location of arc segments is shown. CIP, Mariana Arc Central Island Province including the Central cross-chain (Daon); NSP, Mariana Arc Northern Seamount Province, including the Shoshonitic Province (Shosh) and Northern cross-chain (Kasuga); SSP, Mariana Arc Southern Seamount Province.

arc and back-arc basin lavas from southern IBM and concluded that there was insignificant (2%) involvement of sediment, in terms of oxygen and strontium, in the source of these melts. In contrast, Woodhead *et al.* (1987) concluded that oxygen derived from subducted sediment could be identified. They found a significant correlation between  $\text{SiO}_2$  concentration and  $\delta^{18}\text{O}$  of Mariana Arc lavas, and used that correlation to deduce that the  $\delta^{18}\text{O}$  of parental basalts ranged between 5.7 and 6.3‰. Because MORB oxygen clusters tightly around 5.5–5.7‰ (Fig. 2) (Ito *et al.* 1987), the  $\delta^{18}\text{O}$  range reported for Mariana parental magmas by these two studies permits identification of some sediment-derived oxygen, if the whole rocks preserve magmatic oxygen isotopic compositions. More recently, Eiler *et al.* (2000a) carried out laser-fluorination analyses of olivine and plagioclase phenocrysts from Mariana basalts and basaltic andesites, documenting  $\delta^{18}\text{O} = 4.98\text{--}5.33\text{‰}$  for 21 olivine and 5.66–5.96‰ for 11 plagioclase samples from seven Mariana Arc edifices. Applying their empirically determined oxygen-isotope frac-

tionation factor ( $\Delta = 0.4$ ) for olivine-melt equilibrium, magmatic  $\delta^{18}\text{O}$  for these basalts are calculated to be 5.5–5.7‰, significantly lower than the means reported from the studies of whole-rock samples.

It is well known that crystalline rocks and plagioclase minerals are easily altered by subtle sub-aerial and submarine weathering, which may not be petrographically detected (Muehlenbachs & Clayton 1972a; Ito & Clayton 1983). However, although plagioclase may exchange oxygen isotopes at an appreciable rate even at 100°C, experimental data suggest that other phenocryst phases such as olivine and pyroxene retain their high-temperature  $\delta^{18}\text{O}$  values as long as they are mineralogically unaltered (Cole & Ohmoto 1986; Gregory & Taylor 1986a, 1986b; Farver 1989). Empirical studies of hydrothermally altered oceanic crust corroborate this (Gregory & Taylor 1981; Ito & Clayton 1983; Gregory & Criss 1986). Hence, one way to get around the problems of detecting subtle alteration of volcanic rock samples and of deducing the  $\delta^{18}\text{O}$  of parental basaltic

magmas is to analyze phenocrysts that resist oxygen isotope exchange below magmatic temperatures. Recent studies by Thirlwall *et al.* (1996) for the Lesser Antilles, by Macpherson *et al.* (1998) for the Kermadec, by Eiler *et al.* (2000a) for the Vanuatu, Sandwich and Mariana, and by Vroon *et al.* (2001) for the Banda Arcs illustrate the use of analyzing these refractory phenocrysts. These workers carried out laser fluorination analyses of phenocrysts and obtained values that are as much as 2‰ lower than oxygen isotopic compositions reported for corresponding whole-rock samples thought to be fresh. They ascribed this difference to subtle, low-temperature alteration of the rock matrix. The results of Eiler *et al.* (2000a) also indicate that the studies of whole-rock samples (Ito & Stern 1986; Woodhead *et al.* 1987) give  $\delta^{18}\text{O}$  values for the Mariana Arc magmas that are as much as 0.5‰ too high.

Therefore, recognizing the problem of subtle alteration of fine-grained volcanic rocks, for the present study we focused our attention on clinopyroxene phenocrysts. We found that the difference in measured  $\delta^{18}\text{O}$  values between whole-rock and coexisting phenocryst pyroxene was too large to be the result of oxygen isotopic equilibration at a near-magmatic temperature (Anderson *et al.* 1971; Muehlenbachs & Byerly 1982; Sheppard & Harris 1985; Eiler *et al.* 2000b). Given that whole-rock matrix generally consists of much finer grained groundmass of plagioclase, pyroxene, olivine and oxide minerals, the original whole-rock  $\delta^{18}\text{O}$  values have probably been altered by weathering reactions. We agree that whole-rock  $\delta^{18}\text{O}$  values by themselves are suspect, without confirming analyses of refractory mafic phenocrysts (Eiler *et al.* 1995, 1996; Thirlwall *et al.* 1996; Garcia *et al.* 1998; Macpherson *et al.* 1998; Vroon *et al.* 2001).

Because whole-rock oxygen isotopic compositions of lavas are suspect, we used the more robust data from pyroxenes to infer the isotopic composition of oxygen in Mariana Arc mantle melts. Lavas hosting these pyroxenes are somewhat evolved, ranging from 47 to 58%  $\text{SiO}_2$  (mean = 52.6%). The formation of non-adakitic andesitic rocks in intra-oceanic rocks must result from magmatic processes in the crust, principally fractionation or mixing. Fractionation has been documented to be responsible for the formation of Mariana andesites (Stern 1979; Woodhead 1988; Sun & Stern 2001). Some andesites may also result from melting juvenile arc crust (Kawate & Arima 1998; Tatsumi 2000), but uncertainty about the isotopic composi-

tion of such crust, which is likely to consist of altered and metamorphosed igneous rocks, precludes modelling this possible mode of petrogenesis. If we assume that fractional crystallization is the cause of more silicic rocks, and assume that equilibrium oxygen isotope fractionation accompanies fractional crystallization (Matsuhisa & Kurasawa 1983; Ito & Stern 1986; Woodhead *et al.* 1987), then the  $\delta^{18}\text{O}$  of parental magma ( $\text{SiO}_2 = 48\%$ ) can be calculated for each sample that has undergone pyroxene analysis (column 10, Table 1, see footnote). The calculation assumes that (i)  $\delta^{18}\text{O}$  of melts changed at the same rate as rocks from Agrigan (Ito & Stern 1986); (ii) minerals that were involved in fractional crystallization can be approximated by normative minerals (Stern 1979); and (iii) the oxygen isotope fractionation between coexisting minerals occurred at 1200°C, following the temperature dependence determined by Chiba *et al.* (1989), with diopside approximating the behavior of augite pyroxene. The calculated  $\delta^{18}\text{O}$  values of mafic melts, based on either our clinopyroxene data or the olivine data of Eiler *et al.* (2000a), have a mean of  $5.64 \pm 0.20\%$  ( $n = 54$ ; Fig. 2), and range between 5.4 and 5.8‰ for rocks south of 21°30'N (with one exception from Ruby), and as high as 6.2‰ for rocks north of 21°30'N (Fig. 3). Not all calculated mafic-melt  $\delta^{18}\text{O}$  values for the northern NSP and Shoshonitic Province are high, which suggests that magma genesis is spatially heterogeneous. In the present study, the  $\delta^{18}\text{O}$  of equilibrium mafic melt calculated for some rocks was lower than that of the MORB source of Ito *et al.* (1987) ( $5.71 \pm 0.19\%$ , 1 SD), but was generally higher than data for 28 MORB glasses reported by Eiler *et al.* (2000b) ( $5.50 \pm 0.10\%$ , 1  $\sigma$ ). Eiler *et al.* (1997) have reported mean  $\delta^{18}\text{O}$  values for OIB that are slightly higher (EMII) or lower (HIMU; EMI) than the MORB mean (Fig. 2).

Mafic melts from many geological settings, including the lunar basalts, have  $\delta^{18}\text{O}$  values near 5.7‰ (Anderson *et al.* 1971; Clayton *et al.* 1971; Ito *et al.* 1987; Eiler *et al.* 1997; Garcia *et al.* 1998). This has been suggested as evidence that the earth's (upper) mantle is homogeneous with respect to oxygen isotopes. Consequently, the  $\delta^{18}\text{O}$  values of ca 5.5–5.9‰ are thought to be characteristic of mantle-derived partial melts. Based on this argument, most of the arc rocks south of 21°30'N, inferred from the oxygen isotopic composition of mafic phenocrysts, are indistinguishable from mantle-derived melts, whereas some rocks north of 21°30'N are distinct.



These results shed new light on the origin of the subduction component in IBM Arc lavas, as shown by elevated concentrations of K, Rb, Ba and other elements. Two principal sources in the subducted slab have been suggested as being responsible for these enrichments: hydrous fluids released principally from dehydration of oceanic crust (Woodhead *et al.* 1987; Ishikawa & Nakamura 1994; Elliott *et al.* 1997; Eiler *et al.* 2000a), and melts of subducted sediments (White & Patchett 1984; Lin 1992; Elliott *et al.* 1997). An origin as hydrous fluid released from dehydrating sediments is also plausible. Vroon *et al.* (2001) concluded that, for a given enrichment in incompatible elements delivered by the subduction component, oxygen isotopic compositions in the mantle source region (and in resultant melts) would be more strongly affected if the subduction component was delivered by a hydrous fluid than by a sediment melt, simply because the LILE:O ratio should be significantly higher in sediment melts compared to hydrous fluids. In fact, the origin of the subduction component is much more complex than this. In general, the limited range observed for IBM Arc  $\delta^{18}\text{O}$ , as inferred from mafic phenocrysts, makes it difficult to unequivocally identify any subducted component, particularly for the segment south of  $21^{\circ}30'\text{N}$ . The LILE-rich lavas of the Shoshonitic Province (*ca*  $22\text{--}25^{\circ}\text{N}$ ), which by some accounts reveal the largest proportion of subducted sediments in their source (Sun & Stern 2001), show some evidence (<4%) for oceanic sediments in their oxygen isotopic compositions (Fig. 3). Earlier studies (Stern *et al.* 1988; Bloomer *et al.* 1989a) identified distinct mantle source for the shoshonitic lavas and suggested that the generation of enriched magmas was related to the northward propagation of the Mariana Trough accompanied by the splitting of the arc (Stern *et al.* 1984). In general, though, if the subduction component does reflect contributions from the subducted slab, the oxygen isotopic compositions of IBM melts is qualitatively most consistent with a model of sediment melting.

## CONCLUSIONS

Analysis of mafic minerals contained in IBM Arc lavas indicates that whole-rock  $\delta^{18}\text{O}$  values higher than MORB or OIB  $\delta^{18}\text{O}$  values are mostly due to subtle alteration. In general, crystalline whole-rock oxygen-isotope values of arc rocks do not indicate magmatic compositions. The  $\delta^{18}\text{O}$  analysis of

refractory phenocryst minerals such as pyroxene or olivine is necessary before a sound interpretation of parental magmas and mantle sources is possible. Calculated equilibrium arc melts for the IBM Arc cannot be unequivocally distinguished from melts extracted from mantle sources that are not associated with a subduction zone, except for some of the melts for the NSP where up to 4% sediment component might be ascribed.

## ACKNOWLEDGEMENTS

We thank Cindy Maley, In-Sung Lee, Juanjuan Xia and Lanny Adami for oxygen isotope analysis, Juanjuan Xia for clinopyroxene phenocryst separation, and several undergraduate students at UMN, and P-N. Lin at the University of Texas (Dallas), for TT192 whole-rock powder sample preparation. E. Ito's participation on the *R/V Thomas G. Thompson* Cruise 192 and oxygen analytical work were supported by grants from the National Science Foundation (OCE-8515887) and the University of Minnesota. We benefited from the critical comments of Jim Gill and Terry Plank on an earlier version of this manuscript, and from thorough and constructive reviews by John Eiler and Yukihiro Matuhisa. This paper is dedicated to the memory of the late Ivan Barnes who was on the same cruise and became a dear friend to E. Ito despite his gruff and crusty demeanor.

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