

32. CHEMICAL AND SR-ISOTOPIC COMPOSITION OF IGNEOUS ROCKS FROM DEEP SEA DRILLING PROJECT LEGS 59 AND 60

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ABSTRACT

The igneous rocks of Holes 447A, 448, 448A, 458, and 459B are ocean-ridge type basalt, arc tholeiite, tholeiitic basalt, magnesian andesite (similar to boninite), and basaltic andesite (that is transitional between tholeiitic and calc-alkaline types), respectively. The magnesian andesites are notable for their low Na_2O (~1.7 wt. %) and TiO_2 (0.25 wt. %) and high $\text{Mg}/(\text{Mg} + \text{Fe}^{2+})$ (0.65 and 0.64) and for their degree of SiO_2 enrichment (51.11 and 56.00 wt. %).

Compared to ocean-ridge basalts, arc and remnant-arc volcanic rocks are markedly enriched in Rb, Sr, and Ba and depleted in Cr and Ni. V is variable—high in two remnant-arc (Site 448) samples (~400 ppm) and very low (~160 ppm) in the magnesian andesites. Zr shows only a slight decrease from ocean-ridge to arc rocks. The magnesian andesites are depleted in Sr, Zr, and Y and more enriched in Cr and Ni than other arc rocks. Highest K/Rb ratios (790) occur in Site 448 remnant-arc samples. For all sites the immobile elements Ti, Y, Zr, and Nb fall in the range characteristic of subalkaline basalts.

Initial $^{87}\text{Sr}/^{86}\text{Sr}$ isotopic ratios are low for the ridge-type basalts of Hole 447A (0.70261), just as these ratios are for other MORB. Mariana Arc samples (Holes 458 and 459B) average 0.70381 and 0.70364, distinctly more radiogenic than MORB, and thus are like other volcanic-arc samples from the circum-Pacific region. The remnant-arc samples (Holes 448 and 448A) are slightly less radiogenic (0.70356 and 0.70333) than MORB. The $^{87}\text{Sr}/^{86}\text{Sr}$ ratio for samples from Holes 448 and 448A appears to increase slightly as the rocks become younger and more differentiated.

INTRODUCTION

We were invited to participate in DSDP Legs 59 and 60 to provide precise Sr-isotopic data for igneous rocks of this transect across an active volcanic arc-marginal base region. The obvious long-term goal was to characterize completely suites of samples from each tectonic element of the transect as to petrography, major- and trace-element chemistry, and isotope composition (Sr, Pb, Nd, and O). This information would then be the foundation for speculations concerning the origin of the diverse types of igneous rocks and the geochemical evolution of the crust and mantle. In this chapter our contribution toward the long-term goal is largely descriptive—the chemistry and Sr-isotope composition of four suites of samples from the transect.

Our request to DSDP was for a limited number of the freshest rocks recovered on both Legs 59 and 60. We were provided with three samples from each of four sites. In many holes fresh basement was not encountered, and several of the samples we analyzed, although presumably the freshest available, are quite altered—with unknown additions from, losses to, or exchange with circulating pore fluids.

The relative topographic and longitudinal position of our sample suites is illustrated in Figure 1. The westernmost hole (447A) is located on the east side of the West Philippine Basin at a depth of 6022 meters. Holes 448 and 448A are on the west side of the Palau-Kyushu Ridge in a water depth of 3483 meters. Karig (1971; 1972; 1973) interprets this feature as a remnant arc.

We did not receive samples from the Parece Vela Basin, West Mariana Ridge, or Mariana Trough so that

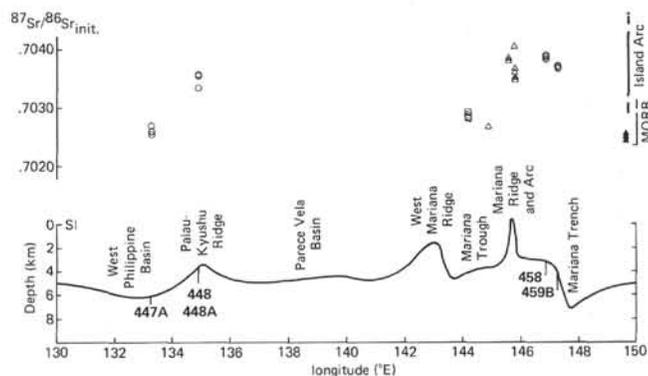


Figure 1. Sr-isotopic composition and topographic profile of Legs 59 and 60 transect across the Mariana Arc and West Philippine Basin. Open circles = our new data for Legs 59 and 60 samples; open squares = data from Hart et al. [1972]; open triangles = data from Meijer [1976]; closed triangles on the right-hand edge of the profile = our samples from the Juan de Fuca Ridge.)

our hopes of a complete isotopic profile across the arc-remnant arc system were not realized. Part of this gap is filled by published Sr-isotopic data for the Mariana Trough (Hart et al., 1972). Meijer (1976) reported isotopic data for islands in the Mariana Arc itself, and for one sample from the Mariana Trough. Stern (1979) presented four analyses for arc rocks about 2° north of the DSDP transect.

Our two easternmost holes (458 and 459B), in water depths of 3447 and 4121 meters, respectively, are in the Mariana Arc-Trench gap just west of the trench-slope break. The rocks at these two sites are subaqueously erupted arc volcanics, not accreted ocean floor (Meijer, 1978; Hussong, 1978).

SAMPLE DESCRIPTIONS

Leg 59

At Hole 447A, 113.5 meters of sediment and 183 meters of basalt flows were penetrated. The three samples supplied to us come from depths of 143.5, 170.1, and 191.5 meters below the seafloor and are assigned to Units 8a, 8c, and 10 in the Site 447 report, this volume. All three are relatively fresh.

Sample 447A-17-3, 49–53 and 58–61 cm is fresh basalt from pillow basalts with fresh glassy rims and phenocrysts of plagioclase, augite, and olivine. The two rock chips analyzed contain calcic andesine and clinopyroxene phenocrysts in a dark glassy groundmass partially altered to orange-brown clay and containing clay-filled vesicles.

Sample 447A-21-2, 114–119 cm is from the same lithologic unit as the previous sample. Phenocrysts and glomerocrysts of calcic andesine occur in a groundmass of plagioclase microlites, granular clinopyroxene, and <5% glass altered to orange-brown clay minerals.

Sample 447A-25-1, 49–54 cm is from the lower interior part of a thick flow with clinopyroxene and andesine to labradorite microphenocrysts in a medium-grained subophitic holocrystalline groundmass. It is quite fresh.

At Holes 448 and 448A, 337.5 meters of sediment and 576.5 meters of igneous and fragmental igneous rocks were penetrated. The three samples with which we were supplied come from depths of 549.3, 664, and 727 meters below the seafloor and represent Units 13, 20, and 26, respectively. All are moderately altered.

Sample 448-61-3, 26–32 cm is from a basalt flow near the bottom of Hole 448. Andesine and clinopyroxene phenocrysts occur in an intergranular groundmass composed of plagioclase, clinopyroxene, and ~10% to 15% dark orange-brown glass altered to clay.

Sample 448A-33-1, 100–108 cm is from altered aphyric basalt containing veins and granules of copper and green smectite (Site 448 report, this volume). Microphenocrysts of calcic andesine, clinopyroxene, and opaque oxide (titanomagnetite) occur in an intergranular, oxide-rich, altered glassy groundmass. Empty vesicles make up about 5% of the rock.

Sample 448A-41-1, 2–7 cm is from a dike or sill or steeply dipping flow of plagioclase-phyric basalt. Calcic-andesine phenocrysts and glomerocrysts occur in a hyalo-ophitic and vesicular groundmass with andesine laths, clinopyroxene, abundant opaque oxide, and glass altered to clay.

Leg 60

At Hole 458, 256.5 meters of sediment and 209 meters of igneous rock were penetrated. Two of our samples come from depths of 279 and 310 meters below the seafloor in the part of the section containing peculiar, glassy, two-pyroxene basaltic rocks called boninites in the initial descriptions (Units 1 and 2) (Saunders et al., 1978; Meijer, 1978). The third sample

comes from a depth of 438 meters in a section containing Unit 5 fractured basalts. The samples are moderately to highly altered.

Sample 458-30-2, 51–53 cm is from pillow basalts with irregular patches and streaks of small vesicles. Relict plagioclase and pyroxene occur in a cloudy, hydrated, and oxidized amygdaloidal groundmass.

Sample 458-33-2, 74–77 cm is from fractured and altered vesicular basalt. Andesine to labradorite, abundant augite, and opaque oxide occur in hyalo-ophitic texture in glass altered to dark brown clay. Vesicles contain green and brown clay minerals. Plagioclase is partially altered.

Sample 458-47-1, 131–134 cm is dark altered vesicular metabasalt from massive pillow lavas. Plagioclase and a few opaque oxide grains occur in an altered glassy groundmass—now yellowish brown clay. Brown clay minerals also fill vesicles.

At Hole 459B, 559 meters of sediment and 132.5 meters of basalt were penetrated. Our samples come from depths of 572, 617, and 644.5 meters below the seafloor and represent Units 1, 3, and 4, respectively. All three samples are moderately altered.

Sample 459B-61-2, 42–46 cm is from a thick flow or sill. Andesine to labradorite microlites and clinopyroxene grains occur in hyalo-ophitic texture in a dark brown glassy groundmass impregnated with opaque oxides. Vesicles are lined with green to yellow-brown clay. Scattered patches of calcite are present.

Sample 459B-66-1, 100–102 cm is from a coarse, vesicular, aphyric diabase sill. Partially altered calcic andesine, clinopyroxene, and magnetite occur in hyalo-ophitic texture in altered glass composed of clay and celadonite. Interstitial quartz and alkali feldspar are present.

Sample 459B-69-1, 47–50 cm is from vesicular pillow basalts. Plagioclase phenocrysts and laths and rare clinopyroxene grains occur in an altered fine-grained groundmass. Brown to green clay minerals line vesicles.

Comparison Suite

R. L. Chase (University of British Columbia) provided three dredge samples of basalt from the Juan de Fuca (JdF) Ridge, which represent fresh northwest Pacific ocean floor and are fairly typical of mid-ocean ridge basalt (MORB) in general.

JdF-P-269-6-4 (49°03'N, 130°54'W) is from the east flank of the Explorer Seamount at a depth of 1600 meters. The sample is spherulitic glass from the margin of a pillow with several per cent olivine phenocrysts.

JdF-70-025-2D-8 (50°53.7'N, 130°36.6'W) is from the northwest Dellwood Knoll at a depth of 1800 meters (Bertrand, 1972). The sample is composed of fragments of vesicular basalt with scattered olivine phenocrysts.

JdF-71-23-3 (48°31'N, 128°55'W) is from "West Ridge" at the north end of the Juan de Fuca Ridge at a depth of 2500 meters (Barr, 1972). The sample is a pillow fragment comprising glassy rim plus fine-grained interior, with about 10% olivine phenocrysts 0.5 to 2 mm across.

CHEMISTRY

Analyses and CIPW norms are presented in Table 1, arranged geographically from west to east and in order of increasing depth in each hole. Analytic techniques and precision are reported in the Appendix. Atomic $Mg/(Mg + Fe^{+2})$ values have been calculated after adjustment to a fixed oxidation state of iron such that $Fe_2O_3/(total\ iron\ as\ FeO) = 0.1$. The convention for oxidation in the CIPW norms was taken from the relationship $Fe_2O_3 = TiO_2 + 1.5$ (Irvine and Baragar, 1971).

Alteration

The effects of submarine weathering on ocean-floor basalts have been extensively documented (for example, Hart, 1969; 1971; Hart and Nalwalk, 1970; Hart et al., 1974) and various alteration parameters used to discriminate between fresh and altered oceanic basalts. Selected alteration parameters presented in Figure 2 show within- and between-site variation. On the basis of H_2O^+ contents (Hart and Nalwalk, 1970; Hart et al., 1974), the freshest samples are from the West Philippine Basin (Hole 447A) and Juan de Fuca Ridge. Arc and remnant-arc samples are moderately to extensively altered, with H_2O^+ in the range 0.55 to 1.38 wt.%. All samples except one from Hole 458 and one from Hole 459B have greater than 0.3 wt.% CO_2 , and oxidation ratios are generally high ($Fe^{+3}/[Fe^{+3} + Fe^{+2}] \geq 0.4$). Large amounts of absorbed water in samples from Hole 458 may have accompanied modification of other components. For example, 5.11 wt.% H_2O^- occurs in a magnesian andesite (Sample 458-30-2, 51–53 cm) whose chemistry suggests leaching of silica with possible addition of K_2O when compared to a petrographically identical sample (458-33-2, 74–77 cm). In general, however, no overall correlation exists between alteration parameters and the major oxides. Abundances and ratios of alkali elements, most likely to have been substantially changed by alteration processes, appear normal. $Mg/(Mg + Fe^{+2})$ values in samples from the Palau-Kyushu Ridge and Mariana fore-arc region exhibit a strong negative correlation with total iron as FeO and appear to be a reliable index of differentiation. Uniform $^{87}Sr/^{86}Sr$ within each site suggests that alteration has not greatly modified Sr-isotopic ratios or Sr concentrations. Trace elements generally considered "immobile," for example, Y, Zr, and Nb (Cann, 1970; Pearce and Cann, 1973), are probably also intact.

Major Elements

All samples studied are typical mid-ocean ridge basalts or island-arc tholeiites transitional to calc-alkaline compositions. Intra- and intersite variations of selected major-element oxides and average trends are shown in Figure 3. Arc and remnant-arc basalts and basaltic andesites are distinguished from ocean-floor tholeiites of the West Philippine Basin by higher overall SiO_2 and K_2O and lower CaO, TiO_2 and $Mg/(Mg + Fe^{+2})$. As a general guide to their chemical affinities, all island-arc rocks have been plotted in SiO_2 and FeO^1 ver-

sus FeO^1/MgO variation diagrams (Fig. 4, after Miyashiro, 1974; 1975).

Basalts of the Juan de Fuca comparison suite exhibit the general characteristics of MORB—low total alkalis, low K_2O and SiO_2 , and high CaO and MgO (Melson et al., 1976). The high alumina of JdF-70-025-2D-8 causes it to fall just within the field of calc-alkaline rocks on a cation normative-plagioclase versus Al_2O_3 diagram (Irvine and Baragar, 1971). All three basalts are relatively undifferentiated with respect to $Mg/(Mg + Fe^{+2})$ (0.68–0.75), the most primitive being JdF-71-23-3, which approaches a picritic composition with extremely low K_2O and high concentrations of compatible trace elements.

Ocean-floor basalts from Hole 447A in the West Philippine Basin are similar in composition to the Juan de Fuca suite and to MORB in general. Sample 447A-25-1, 49–54 cm, stratigraphically the lowest, is distinctly higher than the others in MgO and $Mg/(Mg + Fe^{+2})$ (0.72) and relatively depleted in K_2O (0.04 wt.%). The two samples higher in the section have greater abundances of K_2O (0.40–0.46 wt.%) and a greater degree of iron enrichment. Their $Mg/(Mg + Fe^{+2})$ values are too low for the lavas to be primary mantle-derived melts.

The arc rocks analyzed in this study are chemically diverse. Remnant-arc basalts at Holes 448 and 448A on the Palau-Kyushu Ridge show marked iron enrichment ($FeO^1 = 10.85$ – 12.72 wt.%), moderate CaO abundances (8.55–9.24 wt.%), and very low $Mg/(Mg + Fe^{+2})$ (0.41–0.47). In the classification scheme of Miyashiro (1974) these rocks fall well within the field of island-arc tholeiites (Figure 4). Relatively low Na_2O/K_2O and normal to very high K_2O concentrations (0.30–1.16 wt.%) distinguish these rocks from other arc tholeiites with similar silica contents (e.g., Jakeš and Gill, 1970). The high alumina of Samples 448-61-3, 26–32 cm and 448A-41-1, 2–7 cm may be partially a result of crystal accumulation in these plagioclase-phyric samples.

Samples from Hole 458 in the active arc-trench gap may be divided into two categories distinct in mineralogy and chemical composition: a tholeiitic metabasalt (Sample 458-47-1, 131–134 cm) with plagioclase and clinopyroxene phenocrysts at the base of the section; and magnesian andesites with affinity to boninite.

Sample 458-47-1, 131–134 cm, is a high-alumina basalt showing moderate iron enrichment ($Mg/[Mg + Fe^{+2}] = 0.46$) that falls well within the tholeiitic fields of Figure 4. Although this rock is obviously altered, with high volatile content and high $Fe^{+3}/(Fe^{+3} + Fe^{+2})$ value, the chemical differences between it and overlying magnesian andesites cannot be explained by alteration alone.

The upper stratigraphic units in this hole are characterized by low Na_2O (~1.7 wt.%), extremely low TiO_2 (~0.25 wt.%), and relatively high K_2O (0.78–1.16 wt.%). Both samples lie within the calc-alkaline fields in Miyashiro's diagrams (Fig. 4). The least altered sample is most extreme in having a high value for $Mg/(Mg + Fe^{+2})$ (0.64) relative to the degree of silica enrich-

Table 1. Volcanic rocks from DSDP Legs 59 and 60 and the Juan de Fuca Ridge: Chemical analyses, Sr-isotopic composition, and CIPW norms.

Sample (interval in cm)	447A-17-3, 49-53 and 58-61	447A-21-2, 114-119	447A-25-1, 49-54	448-61-3, 26-32	448A-33-1, 100-108	448A-41-1, 2-7	458-30-2, 51-53	458-33-2, 74-77	458-47-1, 131-134	459B-61-2, 42-46	459B-66-1, 100-102	459B-69-1, 47-50	JdF-70-025-2D-8	JdF-P-269-6-4	PdF-71-23-3
SiO ₂	50.62	49.93	48.56	50.14	52.50	50.03	51.11	56.00	51.85	52.39	57.16	56.97	47.87	47.00	49.20
TiO ₂	1.22	1.00	0.79	0.91	1.14	1.00	0.28	0.23	0.91	0.59	0.80	0.61	1.19	1.01	0.89
Al ₂ O ₃	15.17	15.66	16.68	17.15	14.75	16.80	14.93	14.48	16.92	15.09	14.90	16.42	17.38	16.00	15.44
Fe ₂ O ₃	4.06	4.68	2.15	5.45	5.89	6.62	5.84	3.26	6.99	3.82	6.32	3.72	4.17	1.84	0.93
FeO	5.94	5.21	5.86	5.52	7.03	4.48	2.14	4.09	3.20	5.26	3.25	3.46	4.53	8.56	7.22
MnO	0.17	0.16	0.14	0.14	0.18	0.16	0.09	0.11	0.09	0.14	0.12	0.09	0.16	0.18	0.15
MgO	6.94	6.74	10.12	3.97	4.33	4.61	6.98	6.25	4.04	6.08	3.34	3.23	8.76	12.42	11.99
CaO	11.33	12.22	11.56	9.24	8.62	8.55	8.54	10.83	6.65	11.29	7.30	8.65	11.89	10.64	11.23
Na ₂ O	2.21	1.98	2.21	2.15	1.89	1.60	1.72	1.69	2.10	2.34	2.80	2.65	2.39	2.11	1.96
K ₂ O	0.46	0.40	0.04	1.16	0.30	1.15	1.16	0.78	0.43	0.35	0.84	0.73	0.14	0.09	0.01
P ₂ O ₅	0.15	0.13	0.10	0.13	0.12	0.11	0.05	0.06	0.10	0.11	0.11	0.10	0.13	0.11	0.09
H ₂ O(+)	0.65	1.20	1.31	0.96	0.55	1.35	1.17	0.93	1.13	0.99	1.38	0.80	0.21	0.41	0.31
H ₂ O(-)	1.04	1.08	0.59	2.10	2.42	2.90	5.11	1.59	5.41	0.86	1.82	1.87	0.50	0.32	0.16
CO ₂	0.00	0.14	0.24	0.15	0.18	0.19	0.71	0.33	0.38	0.62	0.14	0.63	0.29	0.11	0.24
Total	99.96	100.53	100.35	99.17	99.60	99.55	99.83	100.73	100.20	99.93	100.28	99.93	99.61	100.80	100.32
FeO ^a	9.77	9.59	7.92	10.85	12.72	10.96	7.91	7.16	10.13	8.86	9.21	7.00	8.38	10.20	8.11
Mg/(Mg + Fe + 2 ^b)	0.59	0.59	0.72	0.43	0.41	0.47	0.65	0.64	0.46	0.58	0.43	0.48	0.68	0.71	0.75
Fe ³⁺ /(Fe ²⁺ + Fe ³⁺)	0.43	0.50	0.59	0.52	0.48	0.62	0.75	0.47	0.71	0.45	0.68	0.54	0.51	0.19	0.12
Cr	176	244	343	38	8	69	165	242	29	164	84	64	277	412	706
V	312	287	198	330	407	409	142	172	367	271	296	232	209	198	199
Ni	94	84	233	21	10	16	64	97	29	49	21	24	178	365	357
Rb	9	6	0.8	13	4	14	13	16	8	14	22	23	2	2.5	0.1
Sr	83	71	106	168	143	146	87	91	135	111	103	132	183	130	68
Ba	9	8	<8	71	44	45	23	34							
Zr	83	70	68	84	61	51	46	44	29	28	40	36	14	10	<8
Nb	<3	3	<3	<3	<3	3	<3	5	71	52	75	66	100	81	60
Y	32	27	21	26	24	19	4	8	3	5	4	<3	6	4	<3
Rb/Sr	0.108	0.085	0.008	0.077	0.025	0.096	0.149	0.176	0.059	0.126	0.214	0.174	0.011	0.019	0.0015
⁸⁷ Sr/ ⁸⁶ Sr obs.	0.70269	0.70270	0.70270	0.70367	0.70360	0.70345	0.70402	0.70404	0.70392	0.70390	0.70406	0.70392	0.70240	0.70250	0.70246
⁸⁷ Sr/ ⁸⁶ Sr init.	0.70254	0.70259	0.70269	0.70356	0.70356	0.70333	0.70381	0.70379	0.70384	0.70366	0.70367	0.70360	0.70240	0.70250	0.70246
CIPW Norms															
qz	3.10	2.60	0.00	5.30	12.19	8.23	8.20	12.74	15.34	6.43	15.77	16.59	0.00	0.00	0.00
or	2.74	2.40	0.21	7.15	1.86	7.15	7.37	4.73	2.76	2.14	5.15	4.42	0.85	0.54	0.07
ab	19.07	17.18	19.03	18.87	16.55	14.19	15.63	14.69	19.14	20.18	24.55	23.09	20.42	17.96	16.64
an	30.70	33.28	36.02	35.28	31.98	37.24	31.77	30.16	32.10	30.30	26.48	31.69	36.77	33.83	33.54
di	20.79	21.78	16.05	8.93	8.63	4.56	6.93	17.98	0.00	18.10	7.77	6.35	16.20	14.08	16.43
hy	16.90	16.54	16.15	18.44	21.96	22.20	25.05	15.82	21.87	16.94	14.75	11.85	11.50	6.51	19.13
ol	0.00	0.00	7.06	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	7.05	21.98	10.37
mt	3.98	3.65	3.16	3.55	3.88	3.70	2.61	2.52	3.58	3.05	3.37	3.09	3.92	2.66	1.35
il	2.37	1.93	1.52	1.81	2.24	2.01	0.58	0.46	1.85	1.15	1.58	1.20	2.29	1.92	1.71
ap	0.35	0.32	0.23	0.31	0.29	0.26	0.13	0.14	0.26	0.26	0.25	0.24	0.31	0.27	0.20
cc	0.00	0.33	0.56	0.36	0.43	0.46	1.74	0.77	0.93	1.45	0.33	1.48	0.67	0.25	0.55

^a FeO^t = total iron expressed as FeO.^b Mg/(Mg + Fe + 2) = atomic ratio with Fe + 2 standardized to Fe₂O₃/FeO^t = 0.1.

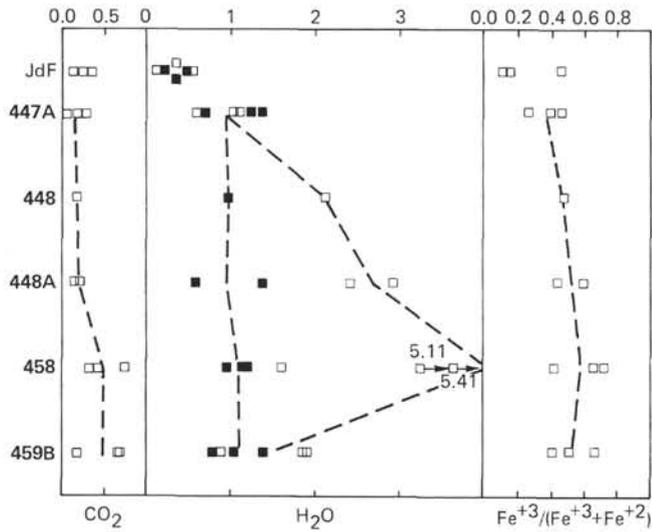


Figure 2. Variation of alteration parameters (wt. %) at each sample locality. (Dashed lines indicate average trends. H_2O^+ is shown as closed squares, H_2O^- as open squares.)

ment (56 wt.%; 12.74% normative quartz). It is interesting to note that rocks with similar characteristics but more extreme Al_2O_3 and CaO depletion and much higher MgO have been called boninites, and this term was used to describe some samples from Hole 458. In this paper we refer to Samples 458-30-2, 51-53 cm and 458-33-2, 74-77 cm as magnesian andesite (Kay, 1978). True boninites (Kikuchi, 1889) have been recognized in other fore-arc regions, notably in the inner wall of the Mariana Trench south of Guam (Hawkins et al., 1979), in the Bonin Islands (Kuroda et al., 1978), and in several ophiolite complexes (Cameron et al., 1979). Speculations by shipboard scientists concerning the origin of boninites (preliminary Site Report for DSDP Leg 60) involve partial melting of hydrous peridotite at fairly shallow mantle depths (<10 kb) at an early stage of island-arc development.

In contrast to the magnesian andesites of Hole 458, basaltic andesites at Hole 459B immediately to the east are some of the most evolved rocks in the suite. Samples 459B-66-1, 100-102 cm and 459B-69-1, 47-50 cm have SiO_2 contents of approximately 57 wt.%, moderate alumina (14.90 and 16.42 wt.%, respectively), and low

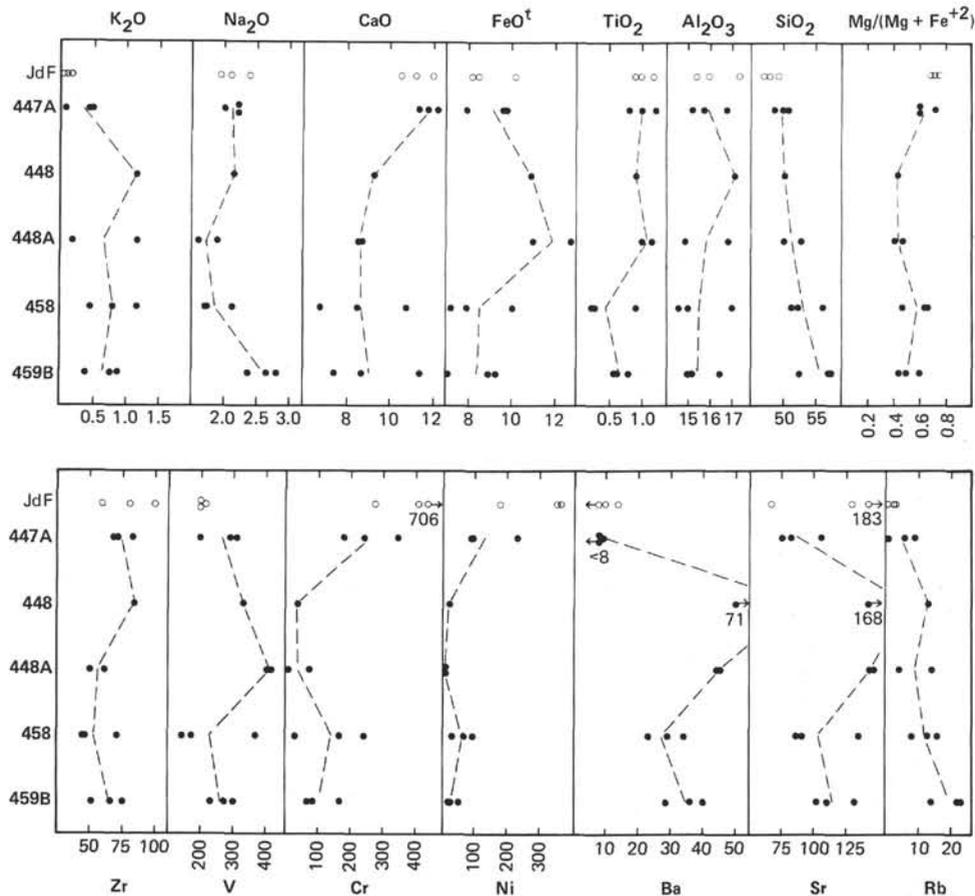


Figure 3. Selected major- and trace-element variations (wt. % and ppm, respectively) within and between sites sampled in this study. (Open circles represent Juan de Fuca basalts; dashed lines show average trends.)

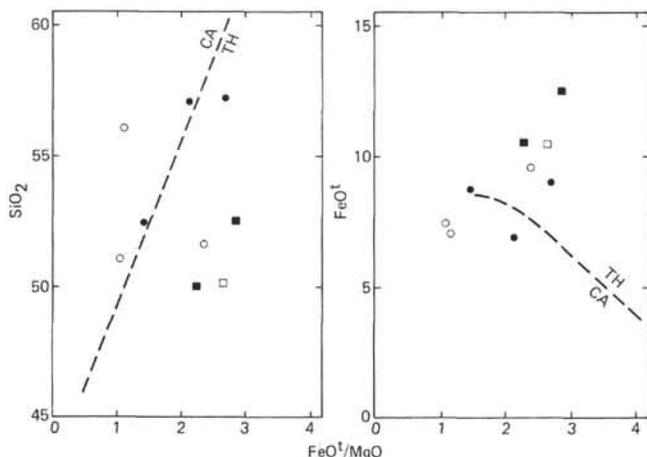


Figure 4. Silica and total iron as FeO^{\dagger} plotted as a function of the ratio $\text{FeO}^{\dagger}/\text{MgO}$ wt. % for arc and remnant-arc samples (after Miyashiro, 1974; 1975). (CA = calc-alkalic field; TH = tholeiitic field. Open square = Hole 448; filled squares = Hole 448A; open circles = Hole 458; filled circles = Hole 459B.)

$\text{Mg}/(\text{Mg} + \text{Fe}^{+2})$ (0.43 and 0.48). The youngest sample (459B-61-2, 42–46 cm) is a tholeiitic basalt with relatively low TiO_2 and K_2O and distinctly high CaO . In Figure 4 these rocks are transitional between typical tholeiite and calc-alkaline compositions. Higher Na_2O and $\text{Na}_2\text{O}/\text{CaO}$ distinguish all three samples from arc samples farther west.

Trace Elements

Variations of seven trace elements in our sample suite are shown in Figure 3. In general, Rb, Sr, and Ba are markedly enriched and Ni and Cr depleted in arc and remnant-arc samples relative to basalts from the West Philippine Basin and Juan de Fuca suite. In contrast, V behaves somewhat erratically. Perhaps most surprising is the depletion of Zr in arc rocks compared to ocean-floor basalts.

With respect to Ni, Cr, and V, basalts from the Juan de Fuca Ridge and West Philippine Basin fall in the normal range for MORB (Miyashiro and Shido, 1975). However, Cr abundances in JdF-P-269-6-4 and JdF-71-23-3 are rather high (412 ppm and 706 ppm respectively) and Ni concentrations unusually high (365 ppm and 357 ppm). Such Ni values are comparable to those calculated by Sato (1977; ~400 ppm) and Mysen (1978, ~300 ppm) for basaltic liquids in equilibrium with mantle peridotite, but they could also result in part from crystal accumulation in these olivine-phyric samples. The alkaline and alkaline-earth elements K, Rb, Sr, and Ba are generally low in basalts from the ocean floor, with typical values for "normal" ridge segments given as 732 ppm K, 0.75 ppm Rb, 92 ppm Sr, and 6 ppm Ba (White and Schilling, 1978). In comparison, basalts from the West Philippine Basin (Hole 447A) are normal to slightly low in Sr, have quite normal Ba abundances, but appear slightly enriched in Rb. Juan de Fuca basalts exhibit an anomalously large range of Sr (68–183 ppm) in spite of uniform $^{87}\text{Sr}/^{86}\text{Sr}$ ratios (~0.7025). Zr in

these samples varies from 60 ppm to 100 ppm, and V shows little variation from approximately 200 ppm.

Lavas from island arcs are typically more enriched in Rb, Sr, and Ba than are basalts from the ocean floor (Jakeš and White, 1972) and enable clear distinctions to be made between West Philippine Basin basalts and rocks of island-arc affinity farther east (Fig. 3). The relatively high Ba and Sr abundances in basalts of the Palau-Kyushu Ridge (Holes 448 and 448A) are particularly striking, whereas Ba and Sr in basalts and basaltic andesites (Holes 458 and 459B) in the active fore-arc region are enriched significantly over MORB but still somewhat low for typical arc tholeiites (Jakeš and Gill, 1970). At these sites, K and Rb are greater than typical MORB values by about an order of magnitude. The behavior of Cr, V, and Ni in calc-alkaline and tholeiite associations has been reviewed by Miyashiro and Shido (1975), who draw attention to the moderate increase of V in tholeiitic rocks with increasing differentiation, as opposed to its steady decline in the calc-alkalic series. Although the mean concentration of V in our arc samples is fairly typical, the high values (~408 ppm) found in low $\text{Mg}/(\text{Mg} + \text{Fe}^{+2})$ basalts at Hole 448A (Samples 448A-33-1, 100–108 cm and 448A-41-1, 2–7 cm) apparently reflect the presence of abundant titanomagnetite microphenocrysts. The lowest V abundances (142–172 ppm) are found in the magnesian andesites (Hole 458), which are also depleted in Sr, Zr, and Y but distinctly enriched in Cr (165–242 ppm) and Ni (64–97 ppm) compared to other arc samples. Y/Zr ratios are also notably low in the magnesian andesites.

K/Rb in our sample suites varies from 229 to 1384 for basalts from the Juan de Fuca Ridge, 415 to 553 for Philippine Basin basalts, 643–760 for the Palau-Kyushu samples, and 213 to 792 for active arc rocks. The higher values are found in the remnant arc (Holes 448 and 448A).

The relatively "immobile" elements Ti, Y, Zr, and Nb in volcanic rocks have been reviewed by Winchester and Floyd (1977). All the "immobile" trace-element data presented in Table 1 fall in the range of values that characterize subalkaline basalts. No further discriminations are evident.

SR-ISOTOPIC COMPOSITION

Observed Sr-isotopic compositions are reported in Table 1. The samples are old enough (ages were taken from the preliminary site reports) and sufficiently rich in Rb to require a small correction from observed to initial ratios, also given in Table 1. The isotopic pattern, shown graphically in Figure 1, is quite well defined and simple. At each site the initial ratios are remarkably uniform. Only at Holes 448 and 448A is there a suggestion of variability beyond analytic error, with the low value for the stratigraphically lowest sample being confirmed by triplicate analyses.

The variation of $^{87}\text{Sr}/^{86}\text{Sr}$ ratios with tectonic setting is as expected—ratios of basin rocks are low, similar to those of MORB, and arc ratios are distinctly higher. Our average for the Juan de Fuca basalts ($0.70246 \pm$

0.00005) is indistinguishable from the average value of 0.7026 ± 0.0002 reported for similar samples by Hedge and Peterman (1970) and comparable to the precise data of Hart (1971) for fast-spreading ridges of the Pacific Ocean (0.70238). The Sr-isotope composition of the three samples from the Philippine Basin (Hole 447A) is 0.70261 and falls in the range (0.7024–0.7031) expected for MORB (White and Bryan, 1977). Published data for the Mariana Trough (0.70263–0.70291 reported by Meijer, 1976, and Hart et al., 1972) are likewise in the normal range of MORB but slightly higher than Pacific Ridge or West Philippine Basin samples.

The most extensive isotopic and chemical work on rocks from the Mariana Arc is by Meijer (1976). His Sr-isotope ratios for frontal-arc and active volcanic-arc samples range from 0.70344 to 0.70400, with an average of approximately 0.7037. This is similar to western Pacific volcanic arcs in general (Gill and Compston, 1973). Stern (1979) reports somewhat lower values, 0.7032 to 0.7034, for basalt and andesite of the island Agrigan in the Mariana Arc north of our transect. These are more like our results for the remnant-arc samples discussed later.

Our new $^{87}\text{Sr}/^{86}\text{Sr}$ data for Holes 458 and 459B (for arc volcanics at the trench-slope break) average 0.70381 and 0.70364, respectively. They are identical to those of the arc rocks exposed above sea level and quite distinct from the ratios for deep basins or ocean floor.

Holes 448 and 448A on the Palau-Kyushu Ridge yield slightly less radiogenic Sr than the average Mariana Arc sample as well as a barely distinct down-hole difference in isotopic composition. All three samples are distinctly more radiogenic than is the ocean floor. The deepest basalt analyzed, giving an initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of 0.70333, is less radiogenic than the two overlying basalts (0.70356), suggesting an increase in isotopic ratio with time at the site. A similar increase in $^{87}\text{Sr}/^{86}\text{Sr}$ with time has been observed and discussed by Donnelly et al. (1971) for igneous rocks of the Caribbean Arc.

The Sr-isotope data are only part of the isotopic complexion of these rocks. They cannot be used alone to distinguish between crustal contamination, anomalous mantle source, subducted altered basalt, or subducted sediments as the cause of higher ratios in arc rocks than in ocean floor. Any lengthy speculations await a synthesis of data from many sources. We hope the new data presented in this chapter will influence such speculation.

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- trometer. Major elements were determined on fused glass discs prepared with a lanthanum-bearing lithium tetraborate fusion mixture (CHEMPLEX Grade III). According to the procedures described by Harvey et al. (1973), we constructed least-squares calibration lines for each oxide and used values for international standards recommended by Abbey (1977). In the data reduction we employed the matrix correction factors determined by Norrish and Hutton (1969).
- Na₂O was analyzed using a pressed powder pellet and not corrected for matrix effects. FeO was determined by titration with potassium dichromate using barium diphenylamine sulphate as indicator. Total H₂O and CO₂ were obtained gravimetrically by heating 1 g of sample in a furnace at approximately 1000°C under a constant flow of nitrogen. Magnesium perchlorate and Ascarite were used as chemical traps. H₂O⁻ was determined on a separate sample heated at 120°C for 8 h. H₂O⁺ was calculated by subtracting H₂O⁻ from total H₂O.
- During major-element oxide analysis, samples were excited using both Cr and W (Mn only) anodes operated at 50 kv and 40 ma. Coarse collimation (except in the case of Ca and Mn, where a fine collimator was used), flow-proportional counter, and TLAP and LiF (200) diffraction crystals were employed throughout. Backgrounds were measured for P, Mn, Na, and Mg.
- Trace-element analyses were performed on pressed powder briquettes and corrected for instrument drift, background, spectral interference, and matrix effects. Mass absorption coefficients were calculated from major-element data for Ba, Cr, and V but determined experimentally for the other elements using the Mo K_α Compton peak. We used LiF (200) crystal and evacuated x-ray path (<0.3 Torr) throughout trace analysis. Other operating conditions were as follows:
- Nb, Zr, Y: The W tube, operated at 50 kv and 40 ma, fine collimator and scintillation plus flow-proportional counters.
- Ba: The Cr tube, operated at 50 kv and 40 ma, flow-proportional counter, and a fine collimator.
- Ni, Cr, V: The Mo tube, operated at 60 kv and 40 ma, flow-proportional and scintillation counters, coarse collimator, and an Al filter (Cr and Ni K_α peaks only).
- Rb, Sr: The Mo tube, operated at 60 kb and 40 ma, scintillation counter, and fine collimator.
- Values of standards used in the calibrations were taken from Abbey (1977), except in the case of Ba, Rb, and Sr, where isotope dilution values were employed (de Laeter and Hosie, 1977; de Laeter and Rosman, 1977; Pankhurst and O'Nions, 1973).
- During the period of analysis, reference standards were used to estimate the precision and accuracy of the analytical techniques. The results are presented in Table 1. Replicate analysis for H₂O⁺, H₂O⁻, and CO₂ showed that precision is of the order of 5% to 10%; for FeO precision is approximately 2%.
- Sr-isotopic composition was measured on unspiked samples prepared using standard ion-exchange techniques. We washed all rock chips in warm 2.5N quartz-distilled HCl for 30 minutes prior to crushing. The mass spectrometer (60° sector, 30-cm radius, solid source) is of U.S. National Bureau of Standards design and modified by H. Faul. Data acquisition is digitized and automated using a NOVA computer. Experimental data have been normalized to a $^{86}\text{Sr}/^{88}\text{Sr}$ ratio of 0.1194 and adjusted so that the NBS standard SrCO₃ (SRM987) gives a $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of 0.71022 ± 2 and the Eimer and Amend Sr a ratio of 0.70800 ± 2 . The precision of a single $^{87}\text{Sr}/^{86}\text{Sr}$ ratio is 0.0001 (1σ).

APPENDIX

Analytical Procedures

Major- and trace-element analyses were obtained by X-ray fluorescence techniques (XRF) using a Phillips 1410 PW spec-

Table 1. Instrumental precision and accuracy of major- and trace-element data.

	BCR-1 (wt. %)		
	Analysis A ^a	Analysis B ^b	Precision (2 σ)
SiO ₂	54.71	54.66	0.42
TiO ₂	2.21	2.23	0.025
Al ₂ O ₃	13.65	13.78	0.25
Fe ₂ O ₃ ^t	13.51	13.54	0.24
MnO	0.19	0.19	0.005
MgO	3.48	3.48	0.13
CaO	6.96	7.15	0.10
Na ₂ O	3.26	3.28	0.06
K ₂ O	1.68	1.72	0.06
P ₂ O ₅	0.33	0.37	0.02
	W-1 (ppm)		
	Analysis A ^a	Analysis C ^c	Precision (2 σ)
Cr	120	110	11.3
V	240	248	2.7
Ni	78	79	2.7
Zr	105	107	2.7
Nb	9.5	9	2.0
Y	25	26	2.3
	GH (ppm)		
	Analysis D ^d	Analysis C ^c	Precision (2 σ)
Ba	17.2	15.8	8

Note: Rb/Sr ratios have a precision of 2% (or 0.003) (1 σ) and Rb and Sr concentrations a precision of 5% (or 0.3 ppm) (1 σ). Fe₂O₃^t = total iron expressed as Fe₂O₃.

^a Values recommended by Abbey (1977)—major-element oxides on a volatile-free basis.

^b Average of 12 determinations on a single fused disc.

^c Average of 10 determinations on pressed powder pellets.

^d Determined by isotope dilution (de Laeter and Hosie, 1977; de Laeter and Rosman, 1977).