

4. EFFECT OF ASSIMILATION OF ALTERED OCEANIC CRUST ON MAGMA CHEMISTRY: AN EXPERIMENTAL STUDY¹

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ABSTRACT

Altered basalt dikes from Hole 504B were partially melted at 1150°C and 1180°C to determine the composition of the first melts as oceanic Layer 2C is assimilated by a magma chamber. The partial melts are chemically similar to actinolite, the most abundant secondary mineral, but the melts are not simply melted actinolite. High TiO₂, P₂O₅, and K₂O abundances of the melts indicate that minor secondary minerals that are enriched in these elements also contribute to the melt. The incorporation of partial melts into a ridge-crest magma chamber may explain the local variability that is sometimes found in ocean ridge basalts that are not readily explained fractional crystallization or partial melting.

INTRODUCTION

Mid-ocean-ridge basalts (MORBs) have long been considered to be free of contamination by the oceanic crust because the tensional environment of ocean ridges creates an envelope of fresh basalt and mineral cumulates around the magma chamber. This envelope is difficult to assimilate because of its high melting temperature, but even if it is assimilated, it would produce little discernible effect on the chemistry of the erupted basalts. Recent studies (Michael and Schilling, 1989; Cornell et al., 1989), however, indicate that some oceanic basalts have chlorine and water abundances that result from the assimilation of a seawater-derived component in the oceanic crust. The abundance of Cl in fresh and altered MORBs is generally less than 0.10 wt% (Michael and Schilling, 1989), so either the selective assimilation of a Cl-rich component or other method of concentrating Cl is required to account for anomalously high Cl in basalts. Possible sources of Cl are hydrothermal brines in gabbros (Kelley and Delaney, 1987) or Cl-rich secondary minerals such as amphibole (Vanko, 1986).

If assimilation of secondary minerals is responsible for the high Cl of some evolved basalts, then this could be confirmed by other characteristic chemical signals of these minerals. The process of selective assimilation of the secondary minerals is likely to be complex. One means of determining what is assimilated is to partially melt altered oceanic crust, and the purpose of this study is to determine the composition of these partial melts. The dike rocks at Hole 504B are the best samples for this study because they are the only rocks where in-situ secondary mineralogy is preserved. In addition, they are representative of lower portions of the sheeted dike complex and are more likely to be assimilated than pillow basalts or upper levels of the crust.

SAMPLES

Samples from six lithologic units were selected for experimental study. Five of these units have similar primary mineralogy and are described as moderately phyrlic plagioclase-olivine basalts (Table 1). One sample is a highly phyrlic clinopyroxene-plagioclase-olivine basalt. These are typical dike rocks from Hole 504B in terms of mineralogy and grain size. The centimeter-depth intervals of the sample

numbers in the tables and figures differ slightly because the samples for different analyses (thin sections, bulk samples for chemical analysis, and samples for experiments) must be distributed along the core to prevent the core from being depleted.

The amount and type of secondary minerals of these samples are highly variable, and it was for this reason that they were chosen. Total alteration ranged from 18% to 100%, and in all but one sample this alteration is dominated by actinolite. The final sample has more clay than actinolite. Additional secondary minerals include clay, albite, titanite, epidote, anhydrite, and trace amounts of sulfides and secondary magnetite (Table 1). Detailed descriptions of the alteration of these samples are necessary to interpret the chemical composition of the partial melts.

Sample 140-504B-189R-2, 15–17 cm, is 80% to 90% altered. Clinopyroxene is extensively altered to amphibole and fine-grained magnetite. Plagioclase is altered to albite, orthoclase, and secondary anorthite. Olivine is completely altered to chlorite and actinolite, and titanomagnetite is recrystallized to titanite and minor ilmenite. One highly altered area in Sample 140-504B-189R-2, 15–17 cm, also contains epidote, laumontite, and prehnite.

Sample 140-504B-193R-1, 30–32 cm, also is extensively altered (ranging from 45% to 95%). The primary minerals, plagioclase, clinopyroxene, and olivine, are altered as in Sample 140-504B-189R-2, 15–17 cm. In addition, about 2% titanite is present as well as a trace of anhydrite and prehnite.

In Sample 140-504B-197R-1, 121–123 cm, olivine is completely altered to chlorite, minor talc, and magnetite. Clinopyroxene is slightly altered to actinolite and magnetite, and plagioclase is only slightly altered to chlorite along fractures. Titanomagnetite grains with ilmenite lamellae are partly altered to titanite.

Sample 140-504B-208R-1, 82–85 cm, has two regions with distinct alteration mineralogy: (1) a 2-mm-wide actinolite vein with a 1-cm-wide halo, and (2) the host rock (see photograph, fig. 46, p. 73, Dick, Erzinger, Stokking, et al., 1992). About 60% of the host rock has been altered in the halo. Clinopyroxene is partly replaced by amphibole and magnetite; plagioclase is slightly altered to albite-oligoclase; olivine is replaced by actinolitic amphibole and chlorite; and titanomagnetite that have ilmenite lamellae are extensively altered to titanite. In the host rock, which is only 15% altered, the alteration is the same as near the vein, except olivine is replaced by chlorite, mixed-layer chlorite-smectite, and quartz.

Sample 140-504B-214R-1, 71–72 cm, is extensively altered (about 90%) with clinopyroxene completely replaced by prismatic, pleochroic amphibole, and plagioclase extensively replaced by albite, anorthite, and a trace of epidote.

Sample 140-504B-227R-1, 65–67 cm, has a greenish patch that is filled with prismatic actinolitic amphibole. Clinopyroxene is com-

¹ Erzinger, J., Becker, K., Dick, H.J.B., and Stokking, L.B. (Eds.), 1995. *Proc. ODP, Sci. Results, 137/140*: College Station, TX (Ocean Drilling Program).

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Table 1. Samples selected for melting studies.

Core, section, interval (cm)	Unit	Name	Depth (mbsf)	Alteration (%)										
				Total	ac	ab	clay	ti	mt	qz	ep	anh	s	
140-504B-														
189R-2, 12-14	218	MPO	1653.5	86	57	22	6	1	tr			tr	tr	tr
193R-1, 30-32	220	MPO	1877.5	45	24	13	6	2	tr					tr
197R-1, 121-123	223	MPO	1709.5	18	9	1	8	tr	tr					
208R-1, 82-85	239	MPO	1780.7	62	48	5	9	tr	tr					tr
214R-1, 71-72	244	MPO	1819.8	100*	65	14		tr			1	3	4	
227R-1, 65-67	260	HCPO	1929.7	23	9	tr	13			tr	tr			tr

Notes: Sample numbers are those used in the experiments. Alteration mineralogy is for samples adjacent to the experimental samples. Rock names: MPO = moderately (2% to 10% phenocrysts) phryic plagioclase-olivine basalt; HCPO = highly (>10% phenocrysts) phryic clinopyroxene-plagioclase-olivine basalt. Alteration minerals: ac = actinolite; ab = albite; clay = chlorite + talc + smectite + mixed layer clays; ti = titanite; mt = magnetite; qz = quartz; ep = epidote; anh = anhydrite; and s = pyrite + chalcocopyrite + pyrrhotite. Tr = less than 0.5%. Chlorite is the dominant clay except in 197R-1, 122-123 cm, where chlorite is 2%, talc 4%, and smectite 2% of the rock. Talc also makes up 2% of 227R-1, 65-67 cm. Percentages are from Dick, Erzinger, Stokking, et al., 1992). *Sample 214R-1, 71-72 cm, also has 5% prehnite and 9% laumontite in amygdules.

pletely replaced by pleochroic, prismatic amphibole. Partial alteration of plagioclase to anorthite, minor albite-orthoclase, chlorite, and prehnite also has occurred. Olivine also is altered to chlorite and actinolite, and titanomagnetite to titanite.

The amphiboles are mainly calcic actinolitic hornblende but range to actinolite and magnesiohornblende with iron contents of 13 to 27 wt%. Na₂O abundances average less than 0.9 wt% and TiO₂ abundances are less than 0.6 wt%. Cl contents average less than 0.08 wt%.

In addition to the amphiboles mentioned above, Sample 140-504B-214R-1, 73-76 cm, contains edenite to edenitic hornblende. These are distinguished chemically by their low iron abundances (as low as 11 wt%), high Na₂O (1.5 wt%, average), high TiO₂ (up to 1.5 wt%), and by high Cl (0.2 wt% Cl, average of 10 analyses).

The chlorite and mixed-layer clays have between 15 and 25 wt% FeO and between 17 and 25 wt% MgO (Alt et al., this volume). TiO₂, Na₂O, and K₂O are all less than 0.1 wt%. Details of the compositions of the alteration minerals are reported elsewhere (Alt et al., this volume; Laverne et al., this volume).

The bulk-rock chemical compositions of these units were determined aboard ship by XRF (X-ray fluorescence) and CHNS (carbon-hydrogen-sulfur-nitrogen) analyzer (Table 2), and these are compared to the dikes from Hole 504B (Fig. 1) that were considered to be "less altered" (less than 1.5 wt% water; Sparks, pers. comm.). MgO abundance of the six samples ranges from 8.2 wt% to 9.7 wt%; the range for the all dikes is 7.6 wt% to 10 wt% (Fig. 1). Two dikes used for experiments (140-504B-193R-1, 30-32 cm, and 140-504B-214R-1, 71-72 cm) fall outside of the field range of "less altered" dikes, so the extreme alteration of these two samples appears to have affected their bulk chemistry. Except for these two samples, however, the alteration appears to have had little effect on most elements (Fig. 1); thus the alteration process appears to be nearly isochemical.

METHODS

Melting Procedure

The technique used here has been employed in previous studies (Fisk, 1989; Fisk and Nielsen, 1990). Pieces of each rock were cut into blocks that were about 10 mm by 10 mm by 5 mm. These blocks were polished and ultrasonically cleaned to remove any surface contamination. Individual blocks were held in the center of a one-atmosphere vertical quench furnace (Deltec design) that was set at the desired temperature. The time required for the sample to reach the furnace temperature was 20 to 30 min. The temperature was monitored with a thermocouple of pure platinum and platinum-rhodium alloy (Pt-Pt_{0.9}Rh_{0.1}) that was placed within a centimeter of the sample within the furnace. Oxygen content of the furnace atmosphere was maintained with a continuous flow of a mixture of CO₂ and H₂. After the sample reached the desired temperature, it was maintained there for 2 hr (except for Run 245, which lasted 2.5 hr) and then released and allowed to fall into distilled water. A polished thin section of the sample was

then made for petrographic observation and for analysis by electron microprobe and ion probe. All run conditions are reported in Table 3.

Microprobe Analyses

All analyses were done on a Cameca SX-50 four-spectrometer microprobe at Oregon State University Electron Microprobe Laboratory. Measured concentrations were corrected for atomic number, absorption, and fluorescence effects by software provided with the microprobe. Standards consisted of natural minerals and basalt glass from the Smithsonian reference collection (Jarosewich et al., 1980) and a commercially prepared standard block (Astimex Scientific LTD, 16 Edgewood Crescent, Toronto, Canada). Glasses were analyzed using the following standards: Kakanui anorthoclase for Na; Kakanui augite for Mg; Durango fluorapatite for P; Hohenfels sanidine for K; Makaopuhi basalt glass for Ca, Fe, Al, Ti, and Si; a pyroxmangite for Mn; and Tiebaghi chromite for Cr. Analytical conditions were 15-kV accelerating voltage, 50-nA beam current, defocused beam (approximately 30 μm), and 10-s counting times for all elements except Cr, which was counted for 20 s. Na was always analyzed first and showed no significant loss during analysis. Precision of this technique (based on multiple analyses of the Makaopuhi basalt glass) is reported elsewhere (Forsythe and Fisk, 1994). Glass in the experiments was analyzed seven to 12 times at several different locations within the sample. The averages of these analyses are given in Table 4, and all data are shown in Figure 1. Three experiments were not analyzed; two had areas of glass that were too small to analyze and one with 30% glass was redundant.

Ion Microprobe Analytical Technique

All ion probe analyses were done on the Cameca IMS 3-f located at Woods Hole Oceanographic Institution. For the elements ³⁰Si, ⁴⁷Ti, ⁵¹V, ⁵²Cr, ⁸⁸Sr, ⁸⁹Y, ⁹⁰Zr, and ⁹³Nb, a primary beam of negatively charged oxygen ions with a current of approximately 0.2 nA and a net energy of 12.55-12.65 keV was focused to a spot 5-10 μm in diameter. Positively charged secondary ions were mass analyzed by a double focusing mass spectrometer with a high energy offset of -90 eV and an energy bandpass of 110 eV for a net secondary accelerating voltage of 4400-4420 eV (a technique known as energy filtering was used to suppress molecular ion interferences; Shimizu et al. [1978]) and were detected and counted by a 17-stage Allen type electron multiplier in pulse counting mode. For rare-earth elements (REE) ¹³⁹La, ¹⁴⁰Ce, ¹⁴⁶Nd, ¹⁴⁷Sm, ¹⁵³Eu, ¹⁶³Dy, ¹⁶⁷Er, and ¹⁷⁴Yb, a primary beam current of 1-2 nA was focused to a 15-25 μm spot, and a high energy offset of -50 eV was used.

Individual points were analyzed by five cycles of measurements beginning with backgrounds and stepping progressively up mass to previously located peaks. Background and deadtime corrected secondary ion intensities were compared to either ¹⁶³Dy, for REE, or ³⁰Si for

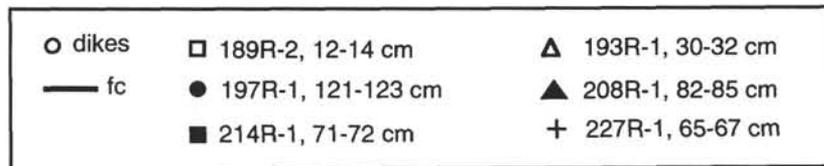
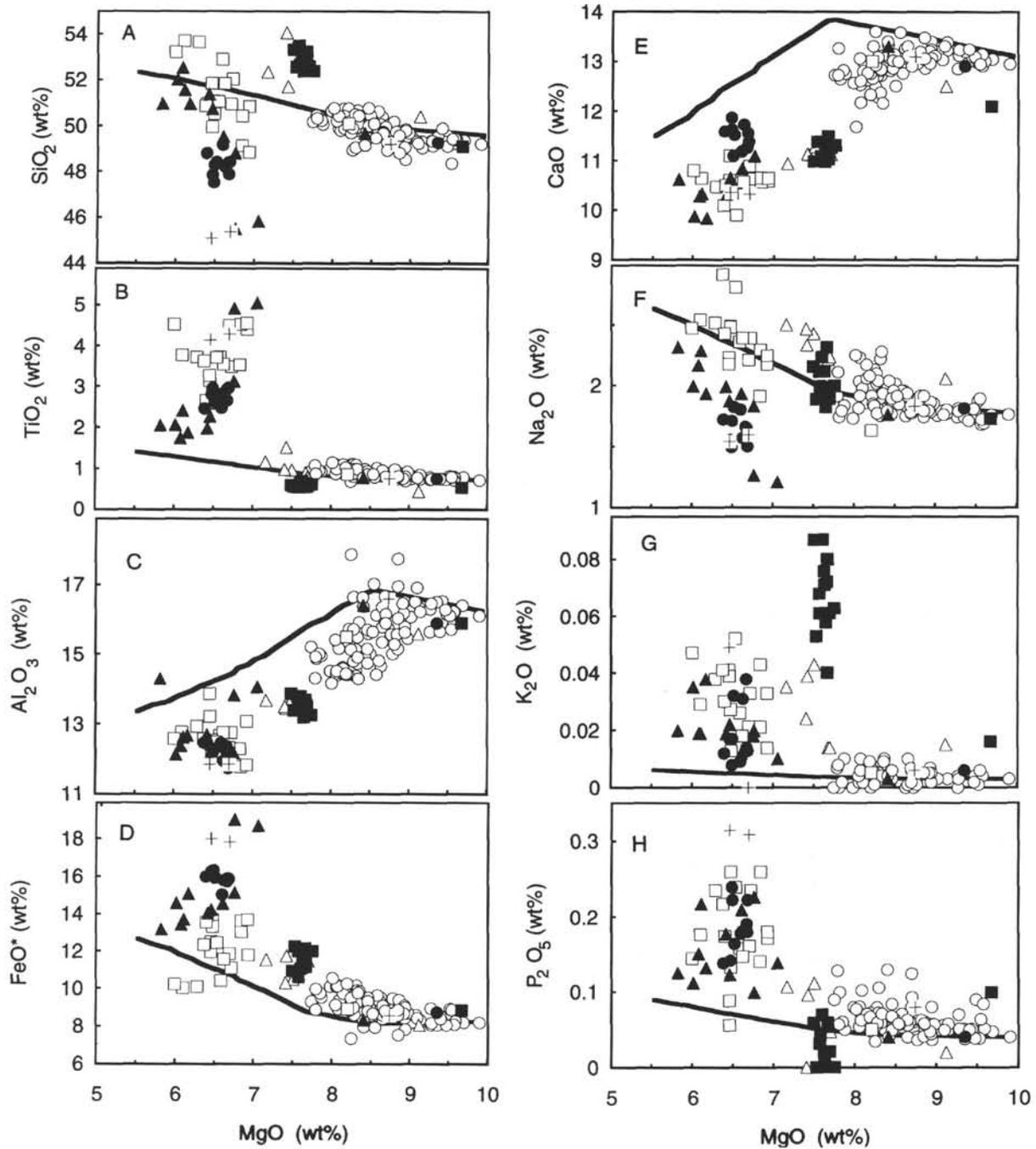


Figure 1. MgO-oxide variation diagrams showing the chemical composition of partial melts of dikes from Hole 504B. Symbols for starting materials and run products are indicated in the legend. Points are individual glass analyses. Starting materials have between 8 and 10 wt% MgO. Products of experiments at 1180°C have between 7 and 8 wt% MgO. Products of experiments at 1150°C have less than 7 wt% MgO. The solid line indicates the effect of fractional crystallization of a parent magma with 10 wt% MgO.

Table 2. Bulk rock chemical analyses of starting materials, Hole 504B.

Sample:	189R-2, 83–86 cm	193R-1, 28–31 cm	197R-2, 33–38 cm	208R-1, 50–53 cm	214R-1, 24–28 cm	227R-1, 90–94 cm
Unit:	218	220	223	239	244	260
SiO ₂	50.1	50.4	49.3	49.7	49.1	49.2
Al ₂ O ₃	15.5	15.6	15.9	16.4	15.9	16.6
TiO ₂	0.86	.43	0.75	0.77	0.53	0.76
Fe ₂ O ₃ *	9.91	8.95	9.72	9.22	9.86	9.51
MnO	0.17	0.15	0.16	0.17	0.13	0.16
MgO	8.20	9.12	9.35	8.41	9.67	8.74
CaO	13.0	12.5	12.9	13.3	12.1	13.1
Na ₂ O	1.63	2.06	1.81	1.76	1.73	1.83
K ₂ O	<0.005	0.015	0.006	0.003	0.016	0.006
P ₂ O ₅	0.05	0.02	0.04	0.04	0.10	0.08
H ₂ O ⁺	1.17	3.68	1.40	1.07	2.31	1.17
Cr	330	402	352	403	473	364
V	286	225	247	264	213	241
Nb	0.4	<0.3	0.5	0.4	<0.3	<0.3
Zr	42	18	36	39	26	38
Y	23	12	21	20	15	21
Sr	45	51	51	56	49	58

Notes: Shipboard XRF and water analyses (by CHNS) of bulk rocks within the same unit as the sample used for experiments. Oxides are in wt%. Cr, V, Nb, Zr, Y, and Sr are in ppm. Estimated errors are given in Dick, Erzinger, Stokking, et al. (1992).

the other trace elements. Doubly time-interpolated intensity ratios were converted to concentrations using empirically derived intensity-concentration correction factors (working curves) calculated from well-determined glass standards of similar Si composition. ¹⁵³Eu analyses are unreliable due to isobaric barium oxide and hydroxide molecular ion interferences (Johnson and Dick, 1992). Uncertainties in trace element measurements by ion microprobe are a function of uncertainty in slopes of working curves and from variations in counts in individual point analyses (counting statistics). Uncertainty in the working curve slope is itself a function of ion probe counting statistics and the quality of the standard (i.e., its homogeneity and the accuracy of its composition as determined by another analytical technique). Slope uncertainty influences the accuracy of the calculated unknown concentration and is minimized by using high quality standards, replicate measurements, and consistent operating conditions. Using standards with nearly the same major element concentrations as unknowns minimizes matrix effects. Slopes for each element were calculated based on normalized silica concentration in the standard to compensate for silicon-induced bias in the intensity ratios. Slopes and uncertainties calculated for this study are generally better than 1.5 relative percent, except for ¹⁵³Eu as noted above.

RESULTS

Heating the dike rocks to 1150°C or 1180°C melted some of the intergranular material and produced (after quenching) 1 to 30 modal percent of clear yellow to yellowish-brown interstitial glass (Table 3). The glass was often located in isolated patches, which made precise estimates of the amount of glass difficult. The glass often contained 1% to 2% of new crystals of pyroxene (1 to 10 μm). The residual crystals were primarily plagioclase, pyroxene, actinolite, and cryptocrystalline black patches. The cryptocrystalline areas often have a large number of voids that may have resulted from the collapse of vesicles produced by release of volatiles from the alteration minerals. In some cases new pyroxene crystallized around anhedral actinolite that appeared to be melting.

All major element compositions of the glass are shown in MgO-oxide variation diagrams in Figure 1. The compositions of dike rocks analyzed on Leg 140 are also shown, and the six starting compositions for the experiments fall within or near this field. The heavy lines indicate the expected evolution of the composition of the residual liquid during cooling of a dike (140-504B-200R-2, 26–31 cm) based on the fractional crystallization model of Nielsen (1990). This sample was chosen as the starting point of crystallization because of its high MgO abundance.

Table 3. Run conditions.

Core, section, interval (cm)	Unit	Depth (mbsf)	Run #	Conditions			
				Temperature (°C)	log fO ₂	Duration (hr)	Melt (%)
140-504B-							
189R-2, 12–14	218	1653.5	222	1150	-9.0	2.0	20
189R-2, 12–14	218	1653.5	244	1150	-9.1	2.0	5
193R-1, 30–32	220	1877.5	223	1150	-9.0	2.0	1
193R-1, 30–32	220	1877.5	242	1180	-8.8	2.0	10
197R-1, 121–123	223	1709.5	224	1150	-9.0	2.0	10
208R-1, 82–85	239	1780.7	225	1150	-9.0	2.0	10
214R-1, 71–72	244	1819.8	226	1150	-9.0	2.0	2
214R-1, 71–72	244	1819.8	243	1180	-8.8	2.0	30
227R-1, 65–67	260	1929.7	227	1150	-9.0	2.0	30
227R-1, 65–67	260	1929.7	245	1150	-9.1	2.5	20

The calculated path of chemical evolution passes through the fields of the compositions of the dikes (open circles in Fig. 1) for the oxides SiO₂, TiO₂, FeO, Na₂O, K₂O, and P₂O₅, but the path does not coincide with the Al₂O₃ and CaO of the dikes. The dike compositions are not strictly magmatic liquids because some of them contain phenocrysts, primarily plagioclase, so these dikes will have higher Al₂O₃ and CaO than the host liquids, and for this reason comparisons of dike chemistry with calculated liquids must be done with caution. It is the dikes with the lowest phenocryst abundance (and lowest Al₂O₃ and CaO) that resemble the magmatic liquids the closest. The difference between the Al₂O₃ and CaO of these nearly aphyric dikes and the calculated liquid line of descent is because the magmas crystallize at elevated pressures while the model is calibrated with one-atmosphere pressure experimental data (Nielsen, 1990). High-pressure crystallization will cause augite and plagioclase to crystallize at higher temperatures relative to olivine and thus make the Al₂O₃ and CaO liquid lines of descent coincide with the data.

The SiO₂ abundances in the partial melts range from 45 wt% to 54 wt% (Fig. 1A), and are inversely correlated with the abundance of iron. The MgO content ranges from 5.8 wt% to 7.0 wt% for the melts generated at 1150°C and from 7.0 wt% to 7.8 wt% for melts generated at 1180°C (Fig. 1). The MgO abundance in these partial melts is higher than the 1 to 4 wt% that would result from 5 to 30% equilibrium melting of the dikes. Thus the heating did not simply melt the last products of crystallization of the dikes but appears to have melted secondary minerals such as clay and actinolite with elevated MgO contents.

TiO₂ (Fig. 1B) is extremely variable, ranging from 1 to 5 wt% with the high-temperature experiments (1180°C) having lower TiO₂ than the low-temperature experiments. The partial melt of one high-temperature sample (140-504B-214R-1, 71–72 cm) has lower TiO₂ than most dike rocks, but it is marginally higher than the original bulk rock analysis for this sample of 0.53 wt%. The low-temperature experiments (1150°C) all have higher TiO₂ than the fractional crystallization line (Fig. 1B, solid line) that probably represents the groundmass of these slowly cooled dikes. The source of the TiO₂ in these glasses may be magnetite or titanite because the clays have less than 0.1 wt% TiO₂ and the actinolite generally has less than 0.5% TiO₂ (Ishizuka, 1989; Alt et al., this volume).

The Al₂O₃ abundances in the partial melts are all less than those observed in the bulk rocks (Fig. 1C), probably because plagioclase is a residual phase in the experiments. The primary contribution of Al₂O₃ to the melt is from actinolite that typically has less than 9 wt% Al₂O₃ (Ishizuka, 1989; Alt et al., this volume). The iron content of the partial melts varies from 10 to 19 wt% and the range may be a result of the type and extent of alteration within the samples. The samples that had the least alteration (140-504B-197R-1, 121–123 cm, and -227R-1, 65–67 cm) have the highest average iron content in their partial melts. Melting of the hornblende with 15 to 27 wt% FeO and less than 0.5 wt% TiO₂ would result in liquids with high iron contents but not necessarily high TiO₂. This would explain the iron and titanium abundances in some partial melts but not the high-Fe, high-Ti melt in 140-504B-227R-1, 65–67 cm, which probably results from the melting of the 5% primary iron-titanium oxides and their alteration products.

Table 4. Average major element abundance in wt% of partial melts.

Sample:	189R-2, 12–14 cm	189R-2, 12–14 cm	193R-1, 30–32 cm	197R-1, 121–123 cm	208R-1, 82–85 cm	214R-1, 71–72 cm	227R-1, 65–67 cm
Run:	222	244	242	224	225	243	245
SiO ₂	51.96	50.36	52.91	48.31	49.99	52.82	45.22
TiO ₂	3.78	3.47	1.05	2.76	2.75	0.59	4.22
Al ₂ O ₃	12.84	12.29	13.59	12.17	12.89	13.52	11.86
FeO	11.33	13.24	11.15	15.89	15.06	11.62	17.91
MnO	0.19	0.22	0.22	0.33	0.19	0.13	0.26
MgO	6.51	6.57	7.48	6.56	6.39	7.62	6.58
CaO	10.67	10.36	11.13	11.48	9.83	11.17	10.34
Na ₂ O	2.31	2.52	2.36	1.65	1.89	2.03	1.57
K ₂ O	0.03	0.03	0.03	0.02	0.02	0.07	0.02
P ₂ O ₅	0.16	0.21	0.06	0.19	0.16	0.03	0.31
Cr ₂ O ₃	0.01	0.02	0.01	0.01	0.01	0.03	0.00

Sodium abundance in the partial melts (Fig. 1F) is highly variable between samples and is not homogeneous within samples. Variation within samples is probably due to the localized alteration of plagioclase to albite and the formation of virtually sodium-free secondary minerals that contribute to the partial melt. Between-sample variation in Na₂O is probably due to the amount of secondary albite, which is lowest in Sample 140-504B-197R-1, 121–123 cm, and highest in 140-504B-189R-2, 12–14 cm (Table 1). Secondary albite abundance correlates to the relative abundance of Na₂O in the partial melts of these two samples but it does not correlate with the abundance of Na₂O in the starting compositions, as 140-504B-189R-2, 12–14 cm, has slightly lower Na₂O than 140-504B-197R-1, 121–123 cm. This suggests that it is the type of alteration that controls the composition of the partial melts and not the bulk composition of the rocks. In longer experiments where equilibrium is achieved between melts and residual crystals the melt compositions should be controlled by the bulk rock compositions for rocks with similar mineralogy.

Potassium in the dike rocks is extremely low (<0.02 wt% in all of the starting compositions; Table 2), and it is enriched relative to the dike rocks in all of the partial melts (Fig. 1G). In Sample 140-504B-214R-1, 71–72 cm, it is enriched by a factor of 5 over the K₂O content of the starting composition. The source of K₂O in these melts is not certain because amphibole, clays, and other secondary minerals (except for orthoclase) have little K₂O. The contribution of K₂O to the melt from orthoclase also does not appear to be significant because orthoclase is virtually absent from these samples. Edenitic hornblende with up to 0.1 wt% K₂O is present in Sample 140-504B-214R-1, 71–72 cm (Alt et al., this volume), which produced the highest K₂O melts, so edenite may be the source of the K₂O to the melt.

Phosphorus, like potassium, is highly variable within samples and for the 1150°C experiments seems to be enriched in the partial melts. The mineral that contributes P₂O₅ to the melt could be secondary apatite, which has been identified in some Leg 140 rocks (Laverne et al., this volume). The extremely low P₂O₅ of 140-504B-214R-1, 71–72 cm, suggests that phosphorus has been lost from this sample during alteration. Evidence of the mobility of phosphorus in Hole 504B has been observed (Zuleger et al., this volume).

Trace elements (by ion probe) were measured on the partial melts of three samples (Table 5). In two of the melts Zr and Y contents are enriched by a factor of about 2 over that present in the starting compositions, but a third sample (140-504B-208R-1, 82–85 cm) appears to have had no enrichment of Zr and Y relative to the starting composition (Fig. 2). The enrichment Zr and Y in two of the partial melts may have been due to the presence of primary iron-titanium oxides or secondary titanite for which these elements have an affinity.

Sr does not appear to be enriched in the partial melts and is even depleted in the melt of Sample 140-504B-208R-1, 82–85 cm (Fig. 2C), probably because calcic plagioclase is a residual mineral at 1150°C and Sr is retained there. (The choice of the initial composition for the model calculations is enriched in Sr relative to the starting compositions used in the experiments so the fractional crystallization line lies above most of the data). Vanadium is significantly enriched

relative to the starting compositions in only one sample (Fig. 2D), which may signify the importance of the contribution of iron-titanium oxides to this melt because of the preference of V for magnetite during crystallization (Ewart et al., 1973; Leeman et al., 1978). V also may be concentrated in amphibole (Luhr and Carmichael, 1980), so the melting of amphibole could contribute to the high V of this melt.

The heavy rare-earth elements in two of the three partial melts are extremely enriched relative to the basalts from Site 504 (Fig. 3) but the melt of the third sample is nearly identical to the depleted basalts. It is not clear why the REE abundances should be so different in these three samples that have similar alteration mineralogy and similar amounts of melting (Tables 1 and 3). The two heavy REE-enriched melts appear to have acquired their rare earth patterns from amphibole, which often has this shape. Even the sample without heavy REE enrichment may have been affected by amphibole because of its low Yb relative to Er, which is another characteristic of amphibole. One melt may also have a negative europium anomaly, but the source of this anomaly is not certain.

DISCUSSION

Assimilation of Partial Melts of Oceanic Layer 2C

In these experiments it appears that the chemistry of the partial melts of the oceanic Layer 2C is controlled by the composition of the secondary minerals and by the temperature of melting. Amphibole is the most abundant secondary mineral in the Hole 504B dike rocks, and it appears to be the major source of SiO₂, MgO, FeO, CaO, Na₂O, the REE, and possibly K₂O in the partial melts. Al₂O₃ appears to depend on the temperature of melting and is therefore probably controlled by the amount of feldspar that has melted. The low Sr in the melts probably results from the residual plagioclase in the experiments. The high abundance of TiO₂, Zr, Y, and V in some melts is probably the result of melting of primary and secondary iron-titanium oxides and secondary titanite. These oxides may also contribute to the high FeO in some of the partial melts. The source of P enrichment is not known, but it could be trace amounts of apatite.

These results show that partial melts of oceanic Layer 2C are chemically distinct from the bulk rocks from which they were derived. The questions remain: (1) Do these 1-atm-pressure experimental melts simulate the partial melting of oceanic Layer 2C when it is assimilated by a magma chamber? (2) Is it likely that oceanic Layer 2C is assimilated by ocean-ridge magma chambers? And (3) what are the magnitudes of the chemical signals that we should detect if assimilation does occur? We attempt to answer these questions in the following three sections.

Are the 1-atm Melts Relevant?

The one-atmosphere pressure and dry conditions of our experiments will cause the solidus temperatures, and the compositions of the experimental partial melts to be different from the partial melts of these same samples in-situ. Our starting compositions were collected from

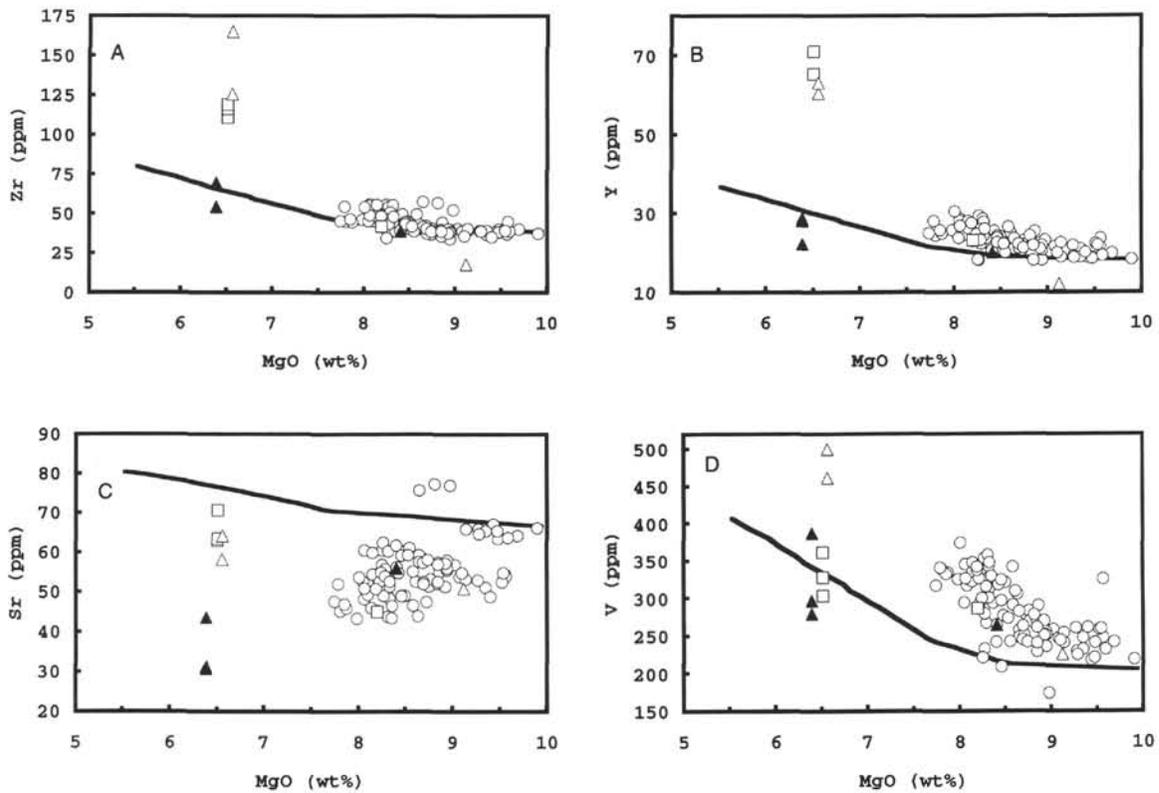


Figure 2. MgO-trace element variation diagrams. Symbols as in Figure 1.

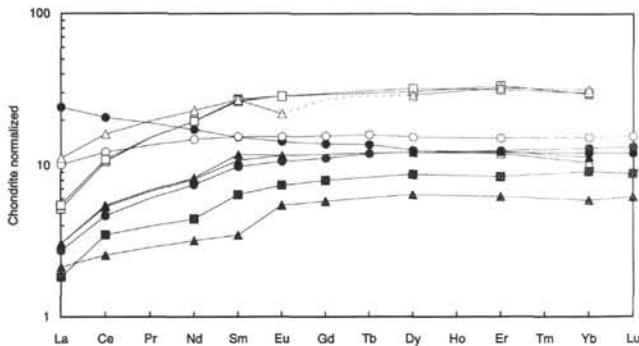


Figure 3. Rare earth-element diagram for five basalts and three partial melts analyzed by ion probe. Circles = three basalt types from the upper levels of Hole 504B (Tual et al., 1985). Shaded circle = depleted basalt (Type-D), Sample 83-504B-44R-1, 25–28 cm; open circle = MORB (M type), Sample 83-504B-56R-1, 139–148 cm; solid circle = enriched basalt, Sample 83-504B-19R-1, 73–74 cm. Open square and open and solid triangles are as in Figure 1. Shaded square = Sample 140-504B-189R-2, 15–17 cm; shaded triangle = Sample 140-504B-193R-1, 28–31 cm (Zuleger et al., this volume). These are the starting compositions for glasses indicated by the open squares and open triangles, respectively.

depths where the ambient pressure was about 100 MPa (1 kb), and because water lowers solidus temperatures, these compositions (with 1 wt% or more of H₂O, Table 2) would have a solidus of about 1000°C at about 100 MPa (Stern et al., 1975) rather than about 1150°, as observed in our experiments (Table 3). The melt chemistry may be affected by the presence of water because water increases the stability of amphibole and decreases the stability of feldspar (see for example Holloway and Burnham [1972] and Wyllie [1971]), and these minerals appear to be responsible for much of the unusual chemistry of the partial melts. The effects of wet melting compared to dry melting, however, will have little impact on this study, as discussed in the next paragraph.

Plagioclase is a residual mineral after amphibole melts at depths of less than 3 km (pressures less than 100 MPa) under water-saturated conditions (about 3 wt% H₂O at 100 MPa; Burnham [1979]). At lower water contents plagioclase will remain as a residual mineral to greater depths. The water contents of the Site 504 dike rocks are, on average, less than half of the saturation value (Dick, Erzinger, Stokking, et al., 1992), so plagioclase should be the residual mineral at all depths where mid-ocean ridges are likely to assimilate altered ocean crust. Thus, even though the solidus temperatures that we obtained in the experiments are higher than the in-situ solidus temperatures, our results are likely to be applicable to the ocean crust because amphibole is one of the first minerals to melt and plagioclase is a residual mineral in both situations. These two minerals appear to govern much of the melt chemistry so these experiments are probably relevant to melting of the ocean crust.

Melts extracted from blocks of diabase dike that have been partially digested within magma chambers appear to be responsible for the production of plagiogranites in Samail and Canyon Mountain ophiolites (Gregory and Taylor, 1981; Gerlach et al., 1981). In these cases the primary component of the melts is plagioclase and the residual is primarily amphibole. These observations are in contrast to our experiments and to the observations of the Skaergaard intrusion (next paragraph), and these differences may be due to the water content of the rocks and the pressure of melting. In tholeiites at 200 MPa with about 60 mole % water, amphibole starts to melt at 975°C and plagioclase starts to melt at 1025°C, but at 500 MPa plagioclase melts first at 925°C, followed by amphibole at 1025°C (Holloway and Burnham, 1972). Thus melting at lower pressure favors the stability of plagioclase, and it appears that amphibole should melt first at the pressures (100 MPa) where Layer 2C would be stopped into the magma chamber at ocean ridges.

Will Oceanic Layer 2C Be Assimilated?

One example of the type of assimilation that we think may occur at some locations on mid-ocean ridges has been documented in the

Skaergaard intrusion (Naslund, 1986). Blocks of anorthosite 100 m in diameter that are thought to be from the top of the intrusion are now near the floor of the intrusion. These blocks are rich in plagioclase relative to rocks still in place at the top of the intrusion, which suggests that mafic material was removed from the blocks and incorporated into the surrounding magma as the blocks sank (Naslund, 1986). This disequilibrium melting, leaving residual plagioclase, could also occur at mid-ocean ridges if blocks of Layer 2C fell into the magma chamber.

To partially melt oceanic Layer 2C it must be heated to at least 900°C if it is metamorphosed and hydrated. (We do not consider the assimilation of unaltered crust because of the high temperature, 1150°C, needed to melt it and because the melts are not likely to have much effect on the assimilating magma.) Greenschist metamorphism, similar to that seen at Hole 504B, appears to occur close to the rift axis (within tens of thousands of years of eruption; Alt et al., [1986]). This metamorphism results from the circulation of seawater near the rift axis. It is likely to be ubiquitous so that any near-axis or off-axis magma chamber could encounter Layer 2C that has been metamorphosed in a manner.

Thus at overlapping spreading centers, propagating rifts, off-axis volcanoes, and other areas where magma chambers expand into altered crust there is an opportunity for magma chambers to incorporate metamorphosed Layer 2C. As noted above, chlorine enrichment of some basalts from tips of propagating rifts may have occurred as a result of the assimilation of Cl-rich amphibole (Michael and Schilling, 1989; Cornell et al., 1989). Graham and Lupton (1992) have proposed that the low $^3\text{He}/^4\text{He}$ isotopic signatures of some basalts near ocean ridge offsets are due to the assimilation of altered wall rocks. Low helium isotopic ratios also have been interpreted as the result of assimilation of crust in Iceland (Condomines et al., 1983), and this data is supported by low oxygen isotopic ratios. Off-axis volcanoes may also assimilate altered crust, but presently there is little data to document this. Some basalts from the Cocos Seamounts near the East Pacific Rise, however, do have $^3\text{He}/^4\text{He}$ lower than the adjacent ridge axis, which may signify the incorporation of altered crust in some seamounts.

What Are the Chemical Signals of Assimilation of Layer 2C?

It is evident from the data presented here that there is a large variety in the compositions of partial melts of Layer 2C even from rocks with similar bulk chemistry. The range of partial melt compositions would probably be even larger than observed in these experiments if altered rocks were available from other ridge segments with different bulk chemistry. It appears, however, that much of the partial melt chemistry is due to the presence of amphibole and iron-titanium oxides that are likely to be ubiquitous in Layer 2C. In attempting to model the effects of assimilation of Layer 2C, we assume that a partial melt like that of 140-504B-189R-2, 12–14 cm (Tables 4 and 5), will be produced during melting of the crust.

In this partial melt the abundance of Ti, K, P, Zr, Y, and the heavy REEs are higher and abundance of Al, Ca, Cr, and Sr are lower than the parent rock. Ratios of elements that are often used to evaluate petrologic processes such as La/Sm, Zr/Y, K/Ti, and K/P will be lower in the partial melt than in the parent magma, and the Ti/Zr and Zr/Nb ratios will be higher. The effects of mixing of a depleted primitive magma with this partial melt are shown in Figures 4 and 5.

MORBs that evolve by fractional crystallization alone will have REE patterns that are nearly parallel to their parent because of the similarity of the bulk partition coefficients of the REE when olivine, plagioclase, and augite crystallize in eutectic proportions. The assimilation of a partial melt such as 140-504B-189R-2, 12–14 cm, by the same parent magma will result in a REE pattern that is rotated counterclockwise about La (Fig. 4). Thus the REE patterns generated by these two different processes will cross.

This is illustrated in Figure 4 where a Type-D parent is mixed with the partial melt of 140-504B-189R-2, 12–14. In the first example (Model 1, Fig. 4) 40% of the partial melt is added to the parent (140-

504B-200R-2, 53–57 cm; Zuleger et al., this volume) and the result is a rare earth pattern which crosses a Type-M basalt from the same hole (83-504B-56-1, 139–148 cm; Tual et al., 1985). In the Models 2 and 3, a steady state magma chamber (Nielsen, 1990) was allowed to assimilate either 2% or 4% of the partial melt (140-504B-189R-2, 12–14 cm; Tables 4 and 5) for each 10% of the magma that crystallized. The magma chamber was maintained at a constant size by balancing a recharge of 20% parent magma plus 2% or 4% partial melt with the eruption of 12% or 14% magma plus 10% crystallization. In these models rare earth patterns are generated that are similar to the pattern generated by the bulk assimilation of 40% of the partial melt. In all cases the rare earth pattern crosses that of the Type-M basalt.

Dynamic melting (Langmuir et al., 1977), melting of the garnet-bearing and garnet-free mantles, or variable degrees of melting and fractionation can also produce crossing rare earth patterns. Determining which process is responsible for the crossing rare earth patterns may only be decided if other evidence of assimilation is present, such as high Cl abundances or low $^3\text{He}/^4\text{He}$.

Another characteristic of the partial melts is the change from a pattern that has constant heavy rare earth enrichment relative to chondrites to a pattern that is curved downward with the maximum values near dysprosium or erbium (Figs. 3 and 4). This is a subtle effect but it is worth mentioning because it would result from the melting of amphibole, which has a greater affinity for the middle rare earths than for the light or heavy rare earths (Irving and Frey, 1984).

The effects of assimilation of 140-504B-189R-2, 12–14 cm, on La/Sm_(ef) and Ti/Zr are shown in Figure 5. La/Sm_(ef) decreases slightly and Yb increases as mixing proceeds (Fig. 5A). During fractional crystallization La/Sm_(ef) should increase slightly as Yb increases. The variation in the majority of the 504B rocks appears to be caused by fractional crystallization, although the rocks with the highest La/Sm_(ef) appear to have come from a different mantle source (Tual et al., 1985). Assimilation of melt 140-504B-189R-2, 12–14 cm (1150°C), results in an increase in the Ti/Zr of the derived magma, whereas fractional crystallization would decrease Ti/Zr (Fig. 5B). As expected, there is little evidence of significant assimilation of Layer 2C at Hole 504B.

The effect of assimilation of altered dikes on the Sr and Nd isotopic ratios of the host magma will probably be small because of the limited exchange of seawater Sr and Nd with the dikes (Friedrichsen, 1985; Kusakabe et al., 1989). Sr abundance in the partial melts is also low (Table 3), so the effects on the $^{87}\text{Sr}/^{86}\text{Sr}$ of the host magma would be less readily noticed than the effects on the $^{143}\text{Nd}/^{144}\text{Nd}$. The ratios $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{143}\text{Nd}/^{144}\text{Nd}$ in the dikes range from 0.70247 to 0.70283 and 0.513102 to 0.513212 and fall within the field for the East Pacific Rise (Kusakabe et al., 1989; Shimizu et al., 1989). These ratios appear to be little affected by alteration, and assimilation of this material would not be detected in the Sr or Nd isotopic ratios of the host magma.

Evidence of Assimilation of Layer 2C at Mid-ocean Ridges

On the East Pacific Rise closely associated basalts with crossing REE patterns occur at the 11°45'N overlapping spreading center (Thompson et al., 1989). In the Atlantic basalts, from Sites 332 and 335 (DSDP Leg 35) near the Mid-Atlantic Ridge near 37°N (Blanchard et al., 1976) also exhibit crossing rare-earth element patterns. Crossing rare-earth patterns do not necessarily indicate that assimilation has occurred, but other characteristics of the basalts may support assimilation. Some basalts from both arms of the overlapping spreading center at 11°45'N on the East Pacific Rise have high Zr/Nb and Ti/K and low Sr abundance (Thompson et al., 1989), which would be expected if magmas in this area assimilated a partial melt similar to 140-504B-189R-2, 12–14 cm (Tables 4 and 5). In addition, some basalts from this region have low He abundance and low $^3\text{He}/^4\text{He}$, which is another indication that material that equilibrated with seawater has been assimilated (Graham, pers. comm., 1993). A pair of basalts from 11°45'N are indicated in Figure 5, where they show variations in rare-earth ele-

Table 5. Trace element abundances of partial melts.

Sample:	189R-2, 12–14 cm	197R-1, 121–123 cm	208R-1, 82–85 cm
Run:	222	224	225
n	3	2	3
TiO ₂	3.30	2.70	3.34
V	330	481	321
Cr	29	61	348
Sr	66	61	35
Y	67	62	26
Zr	115	146	59
Nb	1.2	1.4	0.9
n	2	1	2
La	1.8	3.7	1.0
Ce	9.4	14.0	4.7
Nd	12.5	14.6	5.2
Sm	5.5	5.5	2.3
Eu	2.2	1.7	0.9
Dy	10.8	10.0	4.2
Er	7.3	7.3	2.8
Yb	6.6	6.9	2.4

Notes: TiO₂ in wt%; all others in ppm. Averages are given if the number of analyses (n) is greater than 1. TiO₂ through Nb were analyzed separately from the rare earths, so the number of analyses in the averages is different.

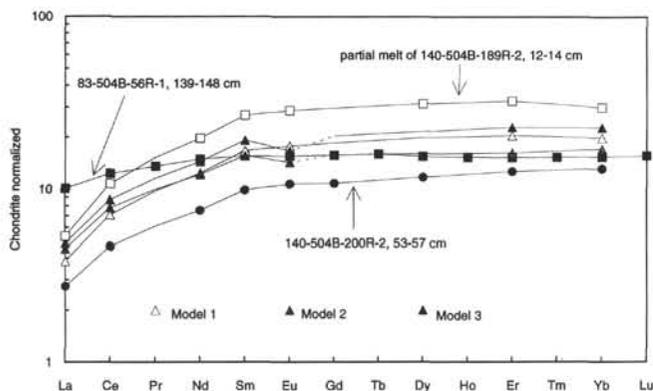


Figure 4. Rare-earth element patterns of two basalts from Hole 504B and three models for mixed partial melt and primitive dike 140-504B-189-2, 12–14 cm. Model 1 is a mix of 40% partial melt from 140-504B-189R-2, 12–14 cm, and -200R-2, 53–57 cm. Models 2 and 3 are for steady-state magma chambers in which assimilation of the partial melt is either 20% or 40%, respectively, of the amount crystallized. Details of the models are given in the text. Data for 140-504B-56R-1, 139–148 cm, from Tual et al. (1985) and for -200R-2, 53–57 cm, from Zuleger et al. (this volume).

ments and Ti and Zr which are consistent with assimilation of Layer 2C. This example is a strong indication that assimilation of altered oceanic crust can occur at overlapping spreading centers where magma chambers are established in older crust.

Subducted Oceanic Layer 2C

At low pressure, the melts of oceanic Layer 2C appear to have the chemistry of actinolitic hornblende plus other secondary minerals. At higher pressures, the melt will probably consist of melted feldspar and secondary minerals because, with water present, hornblende will be stable to depths of 100 km at 1000°C (Lambert and Wyllie, 1972). This implies that the melts produced in our experiments will be similar to the residual material if oceanic Layer 2C is melted after it subducts. This agrees with Woodhead et al. (1993), who indicate that the residual oceanic crust after extraction of arc melts would have a

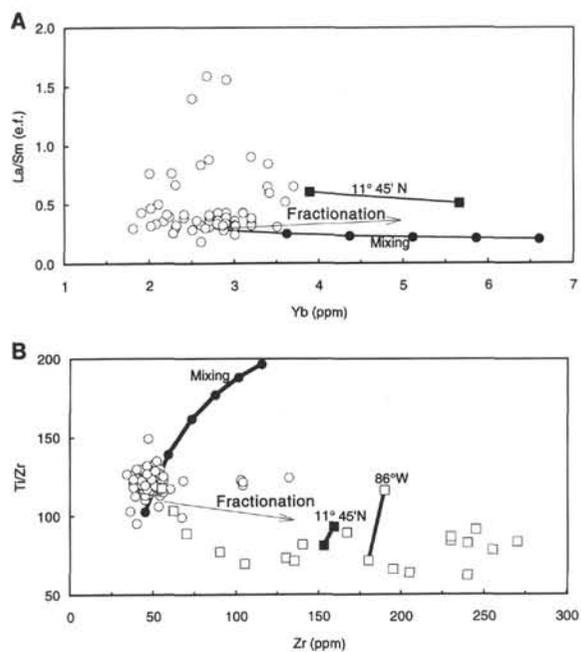


Figure 5. Mixing models for (A) La/Sm_(ef) vs. Yb and for (B) Ti/Zr vs. Zr. Open circles = basalts and dikes from Hole 504B. Solid circles = increments of 20% mixing of 140-504B-35R-1, 100 cm (Autio and Rhodes, 1983), with the partial melt of 140-504B-198R-2, 12–14 cm. Solid squares = rocks from 11°45'N on the East Pacific Rise (Thompson et al., 1989) that may be related by assimilation of altered crust. In (B), open squares = basalts from the Galapagos Spreading Center (Clague et al., 1981). Two rocks from 86°W are connected by a solid line. The rock with the higher Ti/Zr displays some of the characteristics of assimilation of altered crust. Arrows are 50% fractional crystallization in (A) and 80% fractional crystallization in (B).

Ti/Zr of 150 to 300 and a V/Ti of 0.01 to 0.05. The partial melts produced in our one-atmosphere experiments fall within these ranges.

McDonough (1991) suggests that a refractory eclogite reservoir exists in the mantle that is produced during the subduction of the oceanic lithosphere. This reservoir is enriched in Nb and Ti relative to MORB and has a Ti/Zr ratio greater than 115 (the ratio of chondrites). The reservoir is required to explain the lower-than-chondritic Ti/Zr ratio of the Earth's crust and the depleted abundances of Zr, Nb, and Ti in arc volcanics. The experimental melts produced in this study are chemically similar to the composition suggested by McDonough (1991) for the refractory eclogite. If this model is supported, then mineralogical changes associated with alteration of the ocean crust will have a significant impact on the evolution of the mantle.

CONCLUSIONS

Partial melts of oceanic Layer 2C from Site 504 have compositions that are distinct from the bulk compositions of the dike rocks from which they are derived. The major and trace element abundances in the partial melts result from the melting of secondary amphibole, although some element abundances appear to be controlled by the presence of iron-titanium oxides, titanite, and other minor secondary minerals. Some effects of assimilating this partial melt by a MORB magma would be lower La/Sm_(ef) and higher Ti, Y, Yb, and Zr in the mixture compared with basalts from the same area with similar MgO abundance. (This effect would produce a REE pattern in the contaminated basalt that crosses the REE pattern of an evolved, uncontaminated basalt.) These characteristics are observed in some MORBs from overlapping spreading centers and in propagating rifts. Additional evidence of this process can be found in the Cl and He abundance and He isotopic ratios of basalts from propagating

rifts. Assimilating partial melts should have little effect on the Sr and Nd isotopic ratios of the mixtures because the isotopic ratios of the dikes from Site 504 appear not to be modified by seawater alteration. The partial melts of the Hole 504B rocks have the chemical characteristics of the residual material that remains in subducted lithosphere (Woodhead et al., 1993; McDonough, 1991), and these melts may play an important part in the evolution of the mantle.

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*Abbreviations for names of organizations and publications in ODP reference lists follow the style given in *Chemical Abstracts Service Source Index* (published by American Chemical Society).

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