30. MAJOR- AND TRACE-ELEMENT SEAWATER ALTERATION PROFILES IN SERPENTINITE FORMED DURING THE DEVELOPMENT OF THE IBERIA MARGIN, SITE 897[1]

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ABSTRACT

Ocean Drilling Program Leg 149 Holes 897C and 897D penetrated 67 m and 143 m, respectively, into a buried serpentinite basement ridge. Approximately the upper half of each basement section is extensively oxidized and carbonatized. The alteration is much more intense than that observed at the top of the normal basaltic oceanic crust. The chemical changes during carbonatization involved primarily the addition of $CaCO_3$, and the oxidation of the existing iron in the rocks. Smaller quantities of K_2O, total iron, P_2O_5, V, Ba, Sr, and perhaps Zn were added to the serpentinite during carbonatization. The abundances of Al_2O_3, TiO_2, and Cr reflect the primary concentration of spinel in the rocks. This mineral is little changed by either serpentinization or the later calcitization. This results in lower abundances of these three constituents in the altered rocks as a result of dilution. Chlorine appears to have been added to the host ultramafic rocks during early serpentinization; however Cl concentrations are reduced in the upper calcitized zone. The origin of a local Cl-rich zone with up to 1.0% Cl, marked by the occurrence of iowaite, is uncertain but may result from alteration by chloride-rich brines circulating through fractures in the serpentinite. Textural evidence suggests that, although veining and fracture filling predominate, serpentine minerals are extensively replaced by $CaCO_3$. Large amounts of MgO and SiO_2 were probably removed during a protracted period of calcitization. These and the other changes associated with this process probably resulted from exposure to circulating cold seawater over an approximately 40 m.y. period following the cessation of tectonic activity at this site and prior to the burial of the rocks by the sediments of the Iberia Abyssal Plain.

INTRODUCTION

Leg 149 of the Ocean Drilling Program (ODP) was planned as an east-west transect of sites to examine the nature of the ocean/continent transition beneath the Iberia Abyssal Plain. Sites were designed to allow study of the different basement rocks within the area, and to identify the processes involved in continental fragmentation and the beginning of seafloor spreading. The *Initial Reports* volume (Sawyer, Whitmarsh, Klaus, et al., 1994) provides details of the shipboard observations made during Leg 149, and the present volume summarizes the postcruise results and conclusions drawn from the work.

The northwestern edge of the Galicia Bank is characterized by the presence of an elongate peridotite ridge intimately related to continental fragmentation and the development of the ocean/continent boundary (Boillot et al., 1980; Boillot et al., 1987; Boillot et al., 1988). Geophysical data suggested that this serpentinite ridge extends southward beneath the younger sediments of the Iberia Abyssal Plain (Whitmarsh et al., 1990; Beslier et al., 1993). Site 897 was positioned close to the summit of this southward-extending ridge at latitude 40°50.33'N, longitude 12°28.44'W, and the drilling was designed to determine the nature of the basement and its history and to test the geophysical predictions.

Holes 897C and 897D penetrated 67 m and 143 m, respectively, into basement. Core recovery exceeded 50% in both holes. The complete basement section consists of serpentinized peridotite. The rocks were originally relatively heterogeneous and included pyroxene-rich peridotites, plagioclase- and spinel-lherzolites, and harzburgites. Most of the primary mineralogy, except for spinel, has been destroyed by pervasive serpentinization, but the primary minerals are locally preserved.

In both holes, the upper part of the basement immediately underlying the lowest sediments is not only serpentinized but also pervasively calcitized, altered, and yellow to brown. In contrast, the lower parts of both serpentinite sections are pale green or dark greenish black. The spatial relationships of these two sections is shown in Figure 1. The degree of calcite veining and alteration is quite variable but the shipboard geochemical work, summarized here, indicates that the lower boundary of the alteration zone is quite sharp and can be drawn at about 675 m below seafloor (mbsf) in Hole 897C and at 760 mbsf in Hole 897D.

To better understand the nature of the alteration zone at the top of the serpentinite section, detailed sampling and major- and trace-element analytical work were undertaken during Leg 149. Some of these results are presented in the "Site 897" chapter of the *Initial Reports* volume (Shipboard Scientific Party, 1994). The remaining results are presented here, along with a discussion of the data and comparison with results from other Deep Sea Drilling Project (DSDP) and ODP sites.

METHODS AND ANALYTICAL RESULTS

Major element geochemical results for 15 serpentinite samples, determined by X-ray fluorescence (XRF) analysis, using the standard shipboard analytical techniques involving the preparation of lithium borate glass disks, are presented in the "Site 987" chapter (Shipboard Scientific Party, 1994, table 9). The results indicate that the variation

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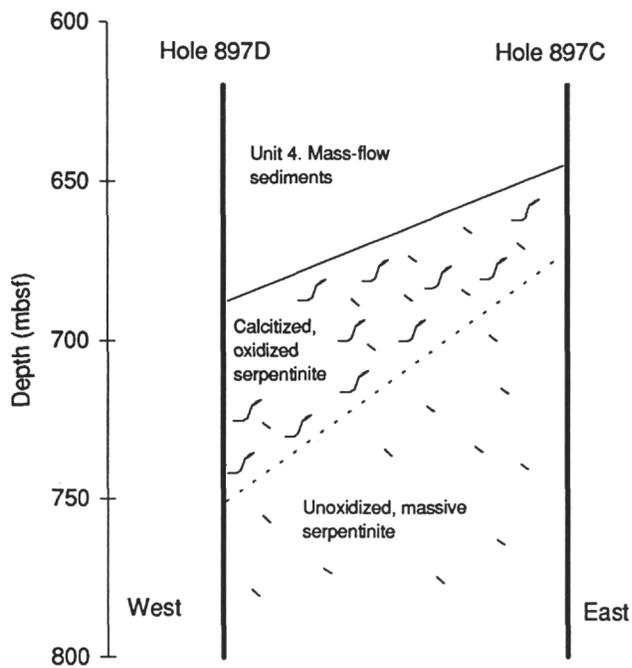
Figure 1. Diagram showing the relative positions and extent of the oxidized calcitized serpentinite horizons in Holes 897C and 897D. The two holes are approximately 105 m apart.

in the abundance of the oxides Al_2O_3, TiO_2, K_2O, and P_2O_5, is of the same order as the analytical error: the concentration of these oxides in the ultramafic rocks is very low. In addition, the shipboard identification of the mineral iowaite in serpentinite samples from both holes (see below) demonstrate that at least some of the rocks contain significant quantities of chlorine. We therefore instigated a shipboard analytical program involving the quantitative XRF analysis of Al_2O_3, CaO, K_2O, P_2O_5, TiO_2, and Cl on pressed powder pellets. The procedures followed were similar to those utilized on Leg 123 (Shipboard Scientific Party, 1990), except that ultramafic rocks were used to construct the calibrations. These results on 24 samples from Hole 897C (Table 1) and 39 samples from Hole 897D (Table 2) have higher precision (<10%) for elements at low concentrations relative to the analyses generated using the lithium borate glass disks. This allows the study of downhole variation in some of the major element components of the serpentinites.

XRF data for Nb, Zr, Y, Ba, Rb, Sr, Cu, Zn, Cr, and Ni for 66 samples from both holes are given in the "Site 987" chapter (Shipboard Scientific Party, 1994, tables 10, 11). Data for $CaCO_3$ and grain density (Hole 897D only) are also included. These trace-element data were discussed only very briefly in the "Site 987" chapter and a more comprehensive review of all the available analytical data in relation to the calcitized alteration zone is presented here

Vertical profiles showing the varying abundances of some of the major and trace elements are shown in Figures 2-5, 7, 9-11, 13-17 and included in the discussion along with other diagrams showing features of the geochemical data.

DISCUSSION

Primary Vertical Variations in the Bulk Composition of the Serpentinite

The core descriptions of the basement sections at Site 897 (Shipboard Scientific Party, 1994) show that the serpentinite is not uniform

Table 1. XRF analytical data for Al_2O_3, CaO, K_2O, P_2O_5, TiO_2, and Cl determined on pressed powder pellets of 24 samples from Hole 897C.

Core, section, interval (cm)	Depth (mbsf)	Al_2O_3 (ppm)	CaO (ppm)	Cl (ppm)	K_2O (ppm)	P_2O_5 (ppm)	TiO_2 (ppm)
149-897C-							
63R-2, 72–75	650.44	6,400	264,800	900	50	400	80
64R-3, 40–43	660.50	6,500	99,000	1,000	0	110	90
64R-3, 56–60	660.66	4,700	96,000	800	0	170	60
64R-4, 31–34	661.68	4,900	200,000	900	0	240	40
64R-5, 66–70	662.91	121,300	86,900	200	610	90	2130
65R-1, 38–41	668.38	38,000	161,900	2,200	20	300	940
65R-1, 53–56	668.53	20,000	195,100	1,600	60	310	570
65R-2, 48–51	669.94	6,500	56,400	1,200	0	120	110
65R-3, 41–43	671.24	9,000	366,200	1,400	250	750	150
66R-4, 8–12	680.81	30,000	1,000	1,700	0	80	1130
67R-2, 68–73	689.02	19,500	900	2,800	0	50	700
67R-3, 51–55	690.25	67,700	41,300	1,400	40	80	1520
69R-1, 41–43	706.61	5,500	1,200	8,600	0	70	220
69R-1, 92–95	707.12	4,200	900	7,000	0	80	180
70R-1, 62–64	710.82	7,800	800	8,900	0	70	600
70R-2, 19–22	711.81	1,900	800	8,200	0	20	130
70R-3, 57–60	713.24	1,600	700	7,500	0	70	100
71R-1, 58–61	716.48	3,800	600	7,800	0	110	50
71R-3, 57–59	719.47	4,300	700	11,100	0	50	90
71R-3, 115–118	720.05	4,700	700	5,600	0	10	130
72R-1, 55–58	726.15	4,500	400	4,600	0	0	90
72R-1, 64–66	726.24	4,500	600	5,600	0	30	100
73R-1, 50–52	735.80	5,100	700	4,500	0	50	70
73R-3, 50–52	737.58	5,000	600	4,600	0	80	50

Table 2. XRF analytical data for Al_2O_3, CaO, K_2O, P_2O_5, TiO_2, and Cl determined on pressed powder pellets of 39 samples from Hole 897D.

Core, section, interval (cm)	Depth (mbsf)	Al_2O_3 (ppm)	CaO (ppm)	Cl (ppm)	K_2O (ppm)	P_2O_5 (ppm)	TiO_2 (ppm)
149-897D-							
11R-3, 55–58	697.32	5,200	375,100	700	800	510	70
12R-1, 48–51	703.98	4,300	294,900	800	730	360	90
12R-3, 39–42	706.68	2,900	563,600	500	1860	1280	10
12R-5, 41–44	709.56	4,000	463,000	1100	640	800	20
13R-1, 38–41	713.38	5,200	201,700	900	620	210	50
13R-2, 14–18	714.64	4,600	479,900	300	650	940	20
13R-3, 40–43	715.82	5,000	220,500	600	210	200	50
13R-5, 39–42	718.46	3,400	346,400	800	650	410	20
14R-1, 39–42	723.09	4,200	473,800	1000	1030	650	60
14R-3, 38–41	725.92	3,900	570,000	1100	740	1080	90
15R-1, 38–41	732.68	5,100	525,400	2100	1120	1520	90
16R-1, 38–41	742.38	1,500	579,600	500	40	590	0
16R-2, 91–94	743.34	7,000	62,700	700	20	160	280
16R-3, 39–42	744.05	7,500	215,700	700	240	220	140
16R-5, 38–41	746.95	5,100	597,000	900	870	1710	60
16R-6, 116–119	749.23	5,500	546,000	200	1500	1330	50
17R-1, 26–32	751.86	3,800	458,600	2100	300	600	20
17R-1, 40–43	752.00	4,100	412,000	1400	710	590	20
17R-1, 73–78	752.33	1,400	630,900	700	240	1050	0
17R-3, 39–41	754.99	1,100	170,200	600	60	280	60
17R-5, 38–40	757.41	3,700	206,400	2900	0	140	20
18R-1, 39–41	761.59	8,900	86,700	4200	0	40	160
19R-1, 68–70	771.58	10,600	1,700	5400	0	130	360
19R-3, 42–44	773.72	31,800	2,100	4200	0	90	1000
19R-3, 57–63	773.87	37,500	9,600	2400	0	50	1100
19R-5, 41–43	776.26	59,300	6,100	3600	0	10	780
20R-1, 38–41	780.98	9,100	2,500	2700	0	100	460
20R-1, 84–87	781.44	8,100	1,700	1600	0	90	370
21R-1, 43–46	790.63	4,600	1,700	6900	0	70	110
21R-3, 38–41	792.46	4,700	1,700	6500	0	100	80
23R-1, 39–42	809.39	1,300	1,700	2500	0	60	70
23R-3, 44–47	812.16	3,100	2,200	3000	0	90	50
23R-5, 42–45	814.95	3,200	2,300	2800	0	50	90
24R-1, 38–41	818.98	15,000	2,100	3800	0	120	530
24R-3, 37–40	821.09	4,900	2,400	2900	0	30	110
25R-1, 38–40	828.58	6,100	2,300	3000	0	20	240
25R-3, 39–41	830.65	5,600	2,200	2200	0	50	270
25R-5, 58–62	833.68	4,900	2,700	2100	0	50	120
25R-5, 64–66	833.74	4,200	2,500	2300	0	40	100

in composition in that former dunitic, harzburgitic, and lherzolitic zones were all identified. Critical to the interpretation of the vertical geochemical profiles are variations in the primary abundances of spinel. This phase is of particular interest as it resists both serpentinization and the subsequent carbonatization. We therefore examined the vertical profiles for Al_2O_3 with particular care. These profiles

show five samples with anomalously high Al_2O_3 concentrations, two from Hole 897C (149-897C-64R-5, 66-70 cm; 149-897C-67R-3, 51-55 cm) and three from Hole 897D (149-897D-19R-3, 42-44 cm; 149-897D-19R-3, 57-63 cm; and 149-897D-19R-5, 41-43 cm). An examination of the profiles for TiO_2, Cr, and V shows that the concentrations of these three other elements are also anomalously high in the same five samples. Concentrations of Al_2O_3 and TiO_2 show a positive correlation. We interpret these results to indicate that these five samples, all from pyroxenitic or lherzolitic horizons, contain higher abundances of chrome-spinel, with some samples containing more that 10%—proportions compatible with those estimated petrographically.

Primary variations in the proportions of plagioclase, clinopyroxene, and orthopyroxene do occur. Examination of the elemental profiles suggest that these variations do not significantly affect the bulk composition of the serpentinite, perhaps because these minerals were mostly destroyed during serpentinization along with the olivine. As a result, with the exception of the variations induced by locally higher spinel abundances, the serpentinite can be considered to be a chemically uniform rock mass. This uniformity, and the low concentrations of many elements in the serpentinite, make the section particularly suitable for the study of elemental fluxes associated with the superimposed oxidation and carbonatization.

Impact of Large-scale Elemental Fluxes on Analytical Data for Altered Rocks

Data presented in the Site Report (Shipboard Scientific Party, 1994, table 9) show that the carbonatization of the serpentinite involved massive changes in the bulk composition of the rocks. Large amounts of $CaCO_3$ were added: the average $CaCO_3$ content of calcitized samples from Holes 897C and 897D (Shipboard Scientific Party, 1994, tables 10, 11) is 46%.

Morgan and Milliken (this volume) have shown that the calcitization process was complex and multistage. It involved both the addition of calcite in veins and fracture fillings and the large-scale replacement of the serpentine minerals by calcite. Although these two processes are intimately related, they are conveniently distinguished as the latter involves not only the addition of carbonate but the simultaneous removal of other components, principally MgO and SiO_2. In contrast, repeated fracturing and calcite veining of serpentinite, with no associated replacement, results in the dilution of the existing MgO and SiO_2 and only an apparent loss of these components. We show below that dilution effects appear to dominate in explaining the abundances of elements that have significantly lower concentrations in the calcitized zone relative to concentrations in the uncalcitized serpentinites. In some cases, we have examined the concentrations of a mobile element in relation to those of an element that was unaltered by oxidation and carbonatization. Al_2O_3 is commonly considered to be immobile and has frequently been used for this purpose. However, we have used Cr, as this element is present mainly in chromite, which is a mineral that clearly resisted both serpentinization and the subsequent carbonate alteration.

Calcium Carbonate Oxidizing Alteration on the Seafloor

It has been known for many years that an upper oxidized calcitized zone develops on the seafloor and that this results in the composition of the upper parts of the lava pile being extensively modified. The chemical effects, first summarized by Hart (1970) and by Scott and Hajash (1976), generally involve notable increases in H_2O, Fe_2O_3, K_2O, Rb, Cs, and U. Calcium carbonate alteration may also occur. The alteration has been shown to be the result of a low-temperature interaction between seawater and the rocks. The very similar nature of the alteration at Site 897 to the alteration zones modifying basaltic pillow piles on the seafloor suggests that the

Site 897 serpentinites were similarly modified by low-temperature circulating seawater, a conclusion supported by isotopic studies (Morgan and Milliken, this volume). In many of the depth plots (Figs. 2-5, 7, 9-11, 13-17), the base of this upper altered zone at Site 897 appears very sharp. This is an illusion. Although there is a well-defined front below which there is no carbonate alteration, within the altered zone the extent of carbonate alteration is very variable, and patches of greenish unaltered serpentinite are preserved. There is no evidence that the base of the altered zone is a structurally controlled stratigraphic break. However, there are a number of chemical features that are distinctive about the alteration at Site 897, and these are discussed below. In these discussions references are made to vertical profiles at three DSDP sites: Site 332 (Robinson et al., 1977), Site 417 (Donnelly et al., 1980), Site 504 (Alt et al., 1986) and to a study of the lava pile of the Troodos ophiolite (Gillis and Robinson, 1991).

Calcium Carbonate

Changes in the abundance of $CaCO_3$ dominate the alteration profile in the Site 897 serpentinites. Concentrations in the altered rocks average about 46%, but some samples contain more than 80% $CaCO_3$. The abundance profile indicates that the boundary of the calcitized zone is relatively sharp (Fig. 2). Qualitatively comparable calcitized horizons occur on the seafloor, and $CaCO_3$ concentrations are elevated in the upper parts of the basaltic section at Sites 332, 417, and 504. However the degree of calcite alteration is much less as $CaCO_3$ abundances only rarely exceed 10%. Concentrations in the upper parts of many ophiolitic basaltic sections are also elevated, but again the degree of alteration is much less and generally comparable to, or only slightly greater than, present-day seafloor sections (Bednarz et al., 1991) Some of the ophicalcite-breccia, gabbroic, and serpentinite sections exposed in the Apennines and Alps are very comparable to those drilled at Site 897. These are discussed below.

K_2O and Rb

Elevated levels of K_2O in rocks modified by seawater weathering are a feature predicted by experimental studies (e.g., Humphris and Thompson, 1978; Seyfried and Bischoff, 1979) and generally an obvious feature of seawater-altered basaltic rocks. For example, an approximately 300-m-thick zone of altered lavas from Hole 504B contains elevated concentrations of K_2O (0.16%), whereas fresh rocks from the deeper parts of the hole only contain on average 0.02% K_2O. The scale of the changes at Site 897 is similar, with K_2O concentrations in the altered rocks exceeding 0.1% (Fig. 3; Tables 1, 2). Where data are available, elevated levels of Rb have
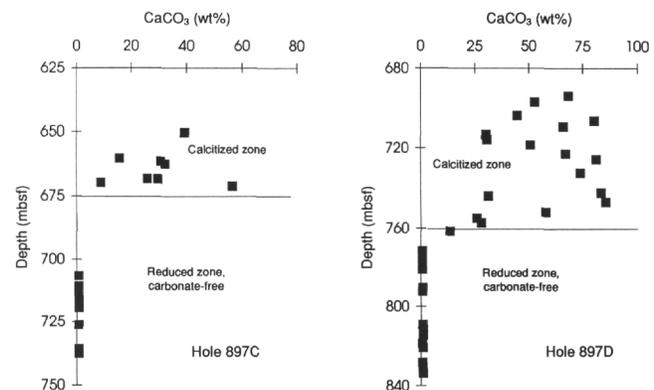

Figure 2. The concentration of $CaCO_3$ in serpentinites from Holes 897C and 897D plotted vs. depth. The approximate position of the lower boundary of the oxidized carbonated zone is shown in both cases.
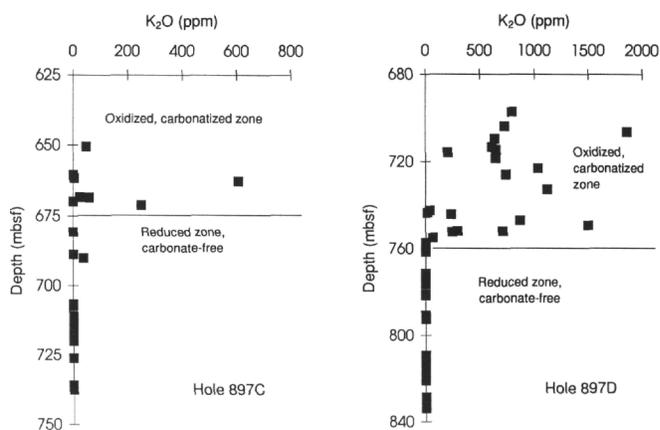
Figure 3. The concentration of K_2O in serpentinites from Holes 897C and 897D plotted vs. depth. The approximate position of the lower boundary of the oxidized carbonated zone is shown in both cases.

Figure 4. The concentration of Sr in serpentinites from Holes 897C and 897D plotted vs. depth. The approximate position of the lower boundary of the oxidized carbonated zone is shown in both cases.

Figure 5. The concentration of Ba in serpentinites from Holes 897C and 897D plotted vs. depth. The approximate position of the lower boundary of the oxidized carbonated zone is shown in both cases.

Figure 6. Graphs showing a positive correlation of Sr and Ba with $CaCO_3$ in serpentinites from Hole 897D.

also been reported. In contrast, at Site 897, levels of Rb in the altered and unaltered samples are similar (Shipboard Scientific Party, 1994, tables 10, 11). We find this surprising and there appears to be no obvious explanation. (We have not reanalyzed the shipboard samples for Rb during postcruise work). Generally Rb, Cs, and more particularly Tl are more sensitive to alteration that K (Hubberten et al., 1983).

Ba and Sr

Concentrations of these two elements are close to the detection limits in the carbonate-free serpentinites. Only one sample (149-897C-67R-3, 51-55 cm), a serpentinized plagioclase lherzolite in the carbonate-free zone, contains more than 10 ppm Sr. Changes in these two elements with alteration are very marked at Site 897 (Figs. 4, 5). Abundances correlate strongly with $CaCO_3$ concentrations (Fig. 6), and we assume that these two elements are present in the altered rocks as carbonates. Similar changes do not characterize the upper oxidized section of pillow basalts at Sites 332, 417, and 504. However, the top 300 m of the Troodos Ophiolite lava pile at Site CY1 has elevated Sr and Ba values (Gillis and Robinson, 1991) associated with calcium carbonate concentrations reaching 5%. Bednarz et al. (1991) note that the extent of the low-temperature seawater alteration at this ophiolite site is larger than in all the known sections through the present-day oceanic crust and speculate that this resulted from the section being located on a topographic high and being exposed to percolating seawater for a long time.

P_2O_5

Large changes in the concentration of P_2O_5 in seafloor rocks comparable to those seen at Site 897 (Fig. 7) have not been observed at Sites 332, 417, and 504. However, Miyashiro et al. (1969) showed that the yellow-brown oxidized rim of a basalt boulder from the seafloor was enriched in P_2O_5 relative to the unaltered dark core. Hart (1970) also suggested that small gains in P_2O_5 during the oxidative alteration of seafloor basalts were likely on the basis of analytical data for 112 deep ocean basalts collected at varying distances from ridge spreading centers.

Fe_2O_3 and MnO

No work was completed during Leg 149 on the oxidation state of the iron in the serpentinites. However, we assume that the very marked color change to a yellow-brow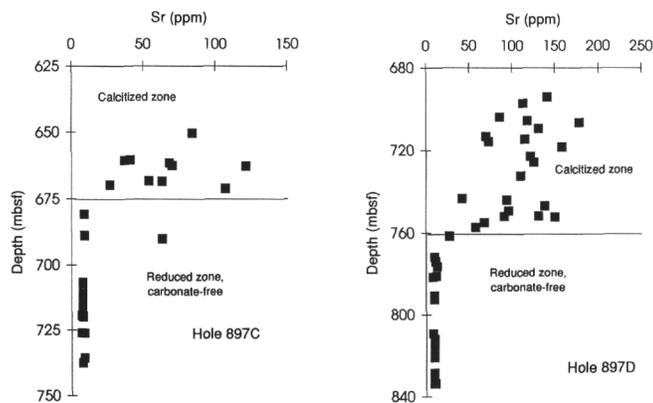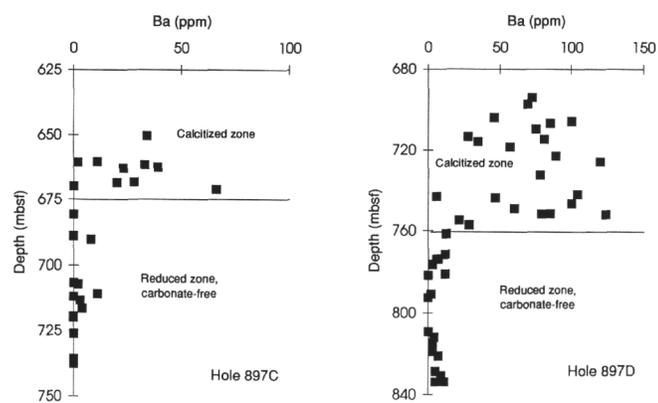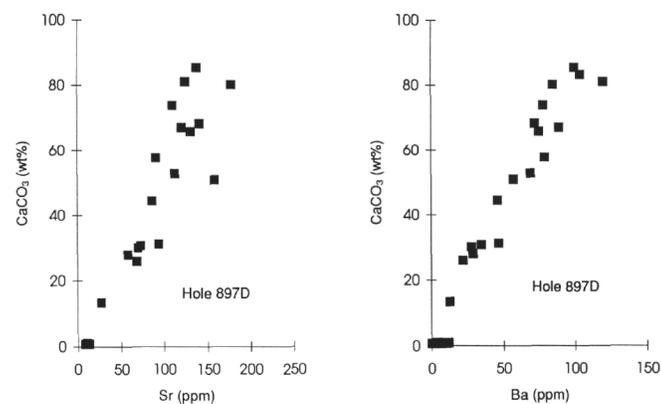n, carbonated serpentinite in the upper altered zone is associated with conversion of ferrous to ferric iron. Although the extent of oxidation seems particularly marked at Site 897, smaller changes have been described at Sites 504 in the Troodos lava pile, and in laboratory-based studies (e.g., Miyashiro et al., 1969). The previously published analytical data (Shipboard Scientific Party, 1994, table 9) shows that total iron (expressed as Fe_2O_3) correlates poorly but negatively with Cr and positively with $CaCO_3$. We tentatively interpret
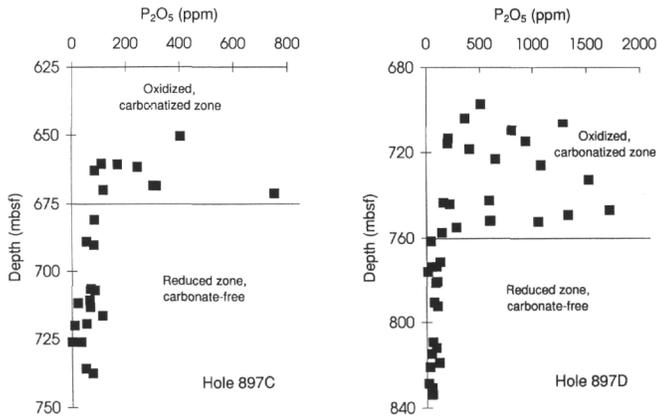
Figure 7. The concentration of P_2O_5 in serpentinites from Holes 897C and 897D plotted vs. depth. The approximate position of the lower boundary of the oxidized carbonated zone is shown in both cases.

this as indicating that iron was added during the carbonatization process. Hart (1970) demonstrated an enrichment in total iron and MnO in both small-scale and regional studies. The available bulk geochemical data for MnO are equivocal. However Morgan and Milliken (this volume) have shown that MnO was a very significant component and certainly added during the carbonatization process.

Al_2O_3, TiO_2, and Cr

As noted above, the abundances of these three constituents in vertical profiles through the serpentinite are influenced by variations in the primary modal concentrations of chrome-spinel in these rocks. As a result concentrations of these three constituents show a strong positive correlation (see for example Al_2O_3 vs. TiO_2, Fig. 8). However, if one ignores the perturbations produced by these spinel-rich rocks, the concentrations of TiO_2 are uniformly low (<1000 ppm). Cr concentrations are higher (averaging about 1600 ppm) and Al_2O_3 abundances average about 5000 ppm. In all cases, the abundances tend to be slightly lower in the carbonatized zone (Figs. 9-11), and in the case of Cr, there is a strong negative correlation of Cr with increasing $CaCO_3$ concentrations (Fig. 12). We interpret these results to indicate that these three components were not significantly mobilized during the oxidative alteration, almost certainly because of the stability of the host spinel. Concentrations were simply diluted by the addition of carbonate. Different relations have been observed during the alteration of pillow basalt sequences. Miyashiro et al. (1969) showed that an oxidized basalt rim was enriched in TiO_2 relative to the unaltered dark core. Hart (1970) also suggested that gains in TiO_2 during the oxidative alteration of seafloor basalts are likely. Results for Al_2O_3 and Cr are much more equivocal.

Vanadium

Although abundances of V are also influenced by variations in the chrome-spinel content of the host serpentinite, V concentrations in the rocks from Hole 897D are significantly higher in the calcitized zone (Fig. 13). Presumably small quantities of vanadium were precipitated from seawater as vanadates under the oxidizing conditions. The authors are unaware of comparable data for sections through the basaltic crust or for ophiolitic sections.

Nickel

The concentrations of nickel are lower in the upper calcitized zone (Fig. 14), but this appears to reflect the immobile nature of the element during seawater alteration, and its dilution by carbonate (Fig. 12). This stability may result from the formation of nickel silicates
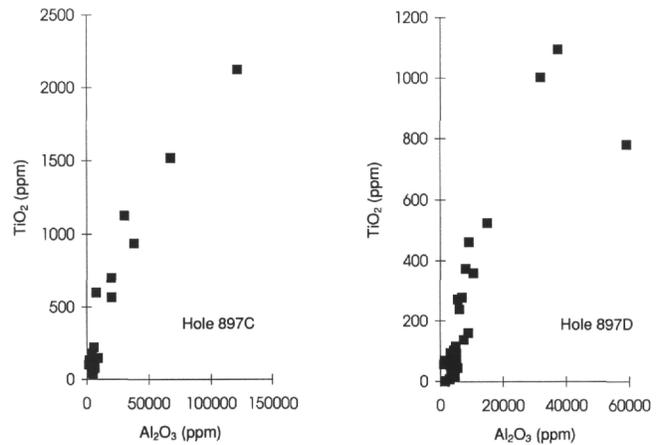

Figure 8. Graphs showing a positive correlation of Al_2O_3 and TiO_2 in serpentinites from Holes 897C and 897D. Samples that are relatively enriched in these two elements are interpreted to contain higher concentrations of spinel (for discussion, see text).
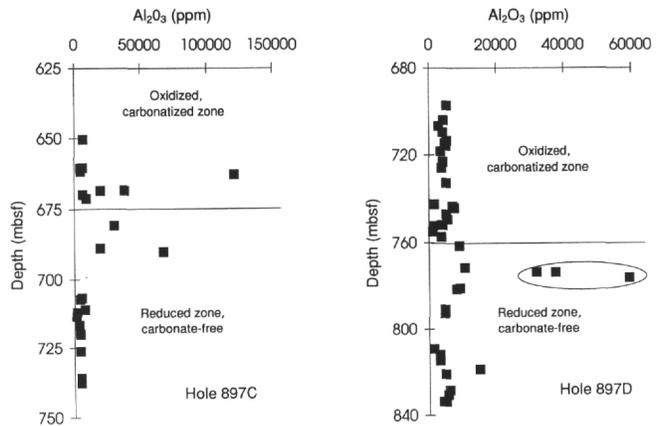

Figure 9. The concentration of Al_2O_3 in serpentinites from Holes 897C and 897D plotted vs. depth. The approximate position of the lower boundary of the oxidized carbonated zone is shown in both cases. The circled samples are assumed to have unusually high modal concentrations of spinel (for discussion, see text).
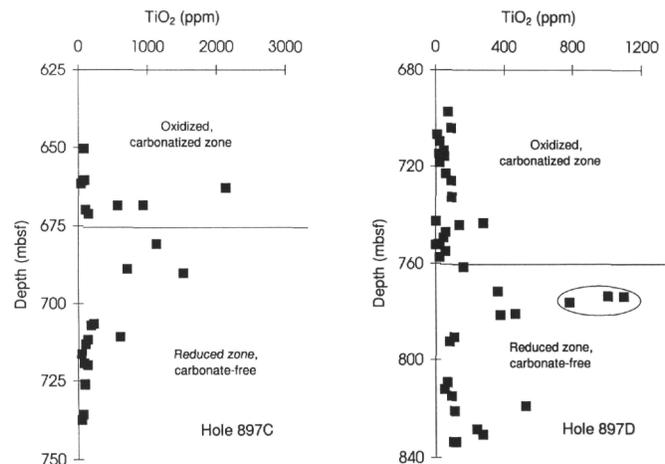

Figure 10. The concentration of TiO_2 in serpentinites from Holes 897C and 897D plotted vs. depth. The approximate position of the lower boundary of the oxidized carbonated zone is shown in both cases. The circled samples are assumed to have unusually high modal concentrations of spinel (for discussion, see text).
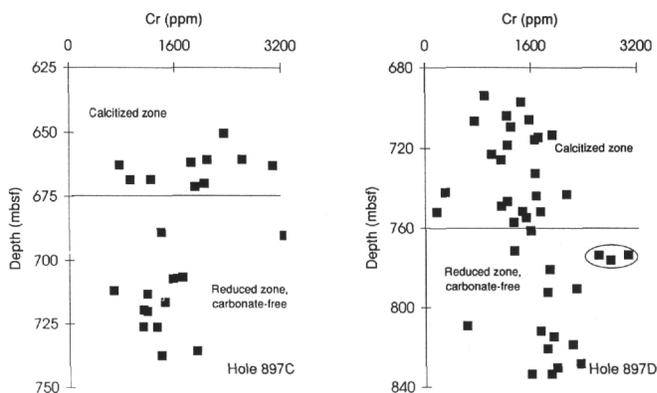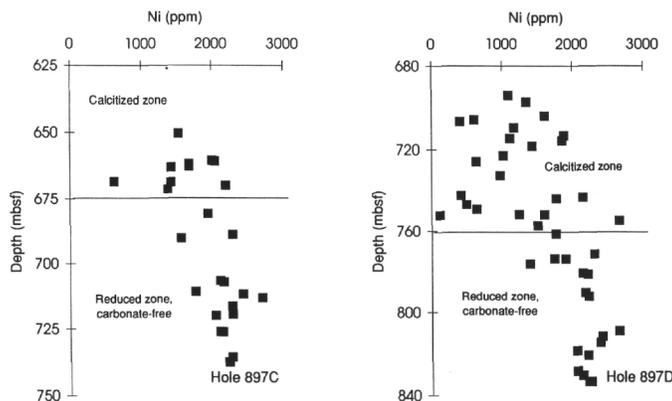
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Figure 11. The concentration of Cr in serpentinites from Holes 897C and 897D plotted vs. depth. The approximate position of the lower boundary of the oxidized carbonated zone is shown in both cases. The circled samples are assumed to have unusually high modal concentrations of spinel (for discussion, see text).

Figure 12. Graphs showing a negative correlation of Cr and Ni with CaCO$_3$ in serpentinites from Hole 897D. The scatter in both figures almost certainly reflects primary variations in the abundances of spinel (Cr) and olivine (Ni).

Figure 13. The concentration of V in serpentinites from Holes 897C and 897D plotted vs. depth. The approximate position of the lower boundary of the oxidized 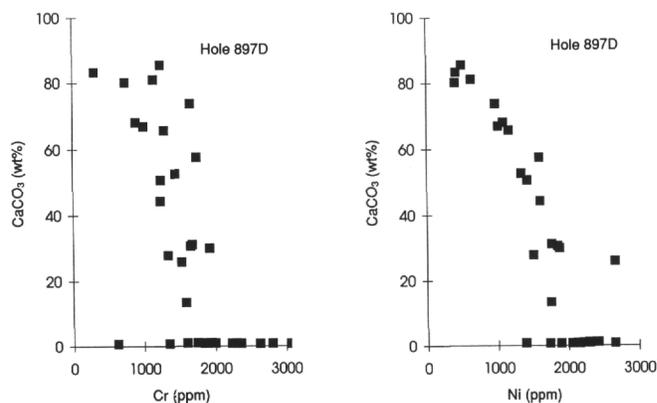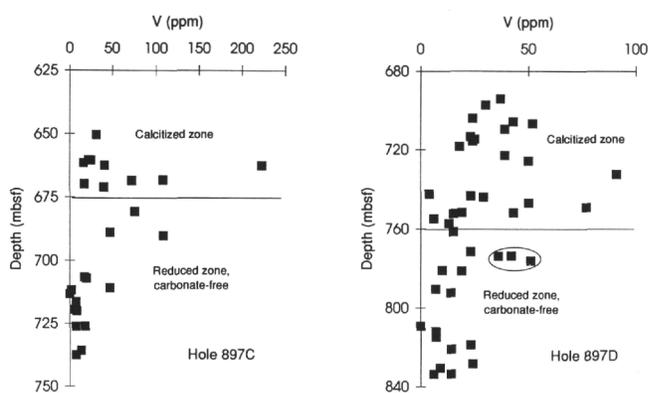carbonated zone is shown in both cases. The circled samples are assumed to have unusually high modal concentrations of spinel (for discussion, see text).

Figure 14. The concentration of Ni in serpentinites from Holes 897C and 897D plotted vs. depth. The approximate position of the lower boundary of the oxidized carbonated zone is shown in both cases.

following the destruction of Ni-bearing serpentine minerals and their replacement by carbonate.

Cu and Zn

The concentrations of Cu in the serpentinite are low, and the changes induced by the seawater oxidative alteration appear to be small (Figs. 15, 16). However, Zn, particularly in Hole 897D, appears to have been added during seawater alteration and was probably precipitated as zinc carbonate. No comparable changes in zinc concentrations in basaltic seafloor or ophiolitic sections are known to the authors.

Chlorine

The chlorine results (Fig. 17) are unique in the scientific literature at the present time in providing a picture of the downhole variation in the abundance of this element in a low-temperature seawater alteration profile through host serpentinites. The abundances are surprisingly high, exceeding 1% in sample 149-897C-71R-3, 57-59 cm, and reach a maximum in both holes in zones associated with the occurrence of the mineral iowaite, a rare secondary magnesium oxychloride. The abundance pattern is similar in both holes and distinct from that of any of the other elements studied here, and has the following features: (1) In the unoxidized serpentinites at the base of both holes, Cl abundances are moderate, ranging from about 2000 ppm to over 5000 ppm. (2) Above this is a zone up to 20 m thick in which iowaite occurs, either as a diffuse alteration product after serpentinite, or in narrow veins associated with brucite. Iowaite, a striking bluish mineral when fresh, is unstable in the laboratory and loses its color rapidly on exposure to air. We therefore confirmed the presence of this mineral by X-ray diffraction work. It occurs in eight closely spaced samples from Hole 897C and in three samples from Hole 897D. Iowaite was not found elsewhere in the core although more than 30 samples were examined. (3) Cl abundances above the iowaite zone are lower, and in general decline upward, reaching values of less than 1000 ppm in the oxidized carbonated rocks.

The relatively high abundance of Cl in the unoxidized serpentinites at the base of both holes is not unexpected. Earley (1958) reported between 0.1 wt% and 0.7 wt% Cl in samples of Archaean serpentinized dunite from Ontario. Steuber et al. (1968) showed that although unserpentinized ultramafic intrusions have a mean chlorine content of 88 ppm, similar rocks with more than 10% serpentine contain on average 300 ppm. Rucklidge (1972), in a microprobe study, then demonstrated that the Cl in similar ultramafic rocks is in fact in solid solution in the serpentine and restricted to serpentine veins in
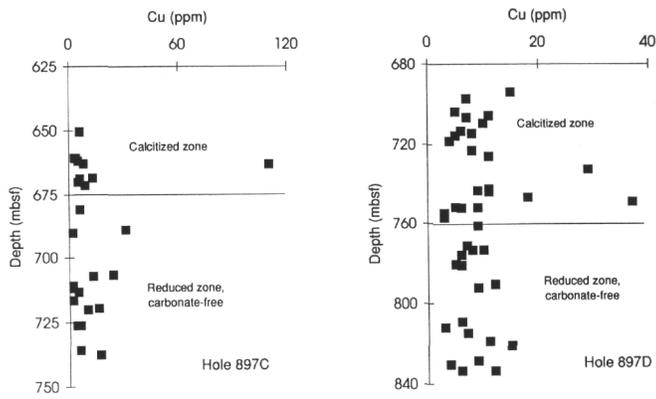
Figure 15. The concentration of Cu in serpentinites from Holes 897C and 897D plotted vs. depth. The approximate position of the lower boundary of the oxidized carbonated zone is shown in both cases.

Figure 16. The concentration of Zn in serpentinites from Holes 897C and 897D plotted vs. depth. The approximate position of the lower boundary of the oxidized carbonated zone is shown in both cases.

Figure 17. The concentration of Cl in serpentinites from Holes 897C and 897D plotted vs. depth. The approximate position of the lower boundary of the oxidized carbonated zone is shown in both cases. The open circles mark the occurrences of iowaite in the core.
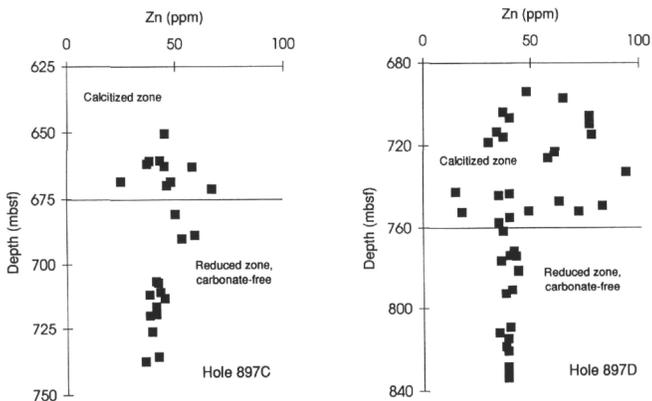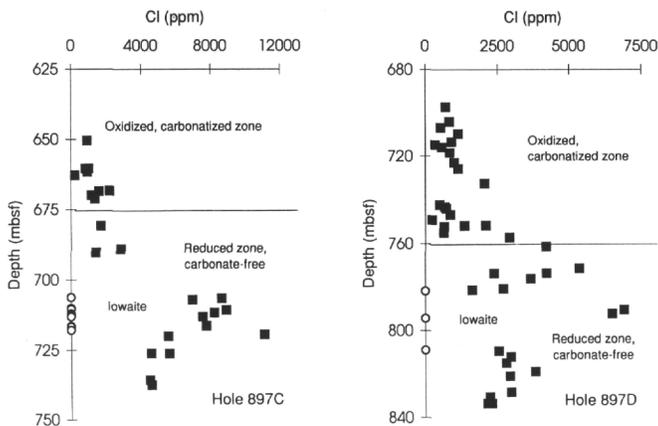
partially serpentinized samples. These studies indicate that the early serpentinization process at Site 897 involved not only the hydration of the primary silicates but probably the addition of chlorine.

The general destruction of the serpentine phases during the alteration that resulted in the oxidized zone must have released Cl into

these oxidizing fluids and the data suggest that this element on balance was removed during this process. Concentration in Hole 897D are mostly less than 1000 ppm in the oxidized rocks and about 2500 ppm in the reduced, carbonate-free rocks at the base of the hole.

Iowaite is a rare mineral, and was first described by Kohls and Rodda (1967) from a serpentinite mass in Precambrian rocks of Iowa. More recently it was described by Heling and Schwarz (1992) from serpentinite mud flows from two seamounts of the Mariana and Izu-Bonin forearcs. These authors considered that the iowaite was formed from preexisting brucite after the serpentinite muds had been extruded onto the seafloor. At Site 897, the relatively narrow iowaite zone in both holes is interpreted as a local zone of alteration associated with Cl-rich brines, probably independent of both the earlier sepentinization process and the later surficial oxidation. The association with brucite suggests that these Cl-rich brines are low temperature and clearly may be seawater derived. Local Cl-rich zones in metamorphosed oceanic plutonic rocks have been described previously. In a study of rocks from the Gorringe Bank, Mével (1988) noted that the Cl-rich amphiboles are present in highly recrystallized rocks with abundant hydrous minerals and textures suggesting that they formed late at temperatures below 700°C, perhaps from interaction with seawater. More recently, magnesiohornblende samples from the upper part of Hole 735B (Units I, II, and III) were shown to commonly contain up to 1.5 wt% Cl, with lower concentrations in Units IV, V, and VI. These results were interpreted by Vanko and Stakes (1991) as indicating seawater interaction. Similarly altered gabbroic rocks from the Mid-Cayman Rise contain some high-Cl amphiboles, which occur preferentially in the upper part of the gabbroic layer (Ito and Anderson, 1983, fig. 13). The authors interpreted the restricted nature of this zone as indicating "that either seawater-derived fluid was consumed by the formation of hydrous minerals or it underwent boiling and an enriched brine formed." Vanko (1986), considering the origin of Mathematician Ridge amphiboles, also noted that oxygen isotope data on the same samples clearly pointed to seawater as the agent of hydration and alteration.

Seafloor Alteration of In Situ Plutonic Mafic or Ultramafic Rocks

There are relatively few accounts of the in situ, low-temperature alteration of plutonic rocks on the seafloor, largely because of the very few long cores drilled through such rocks. The 500-m-thick section of gabbros drilled at Site 735 on the flank of the Southwest Indian Ridge provided the first opportunity to assess the nature and depth of metamorphism and alteration of rocks from oceanic layer 3. Robinson et al. (1991) identified five styles of alteration and metamorphism, the last of which involved an oxidative alteration and the development of ferric-oxides, carbonate, and clay minerals. They demonstrate that approximately the upper 100 m of the core shows concentrations of Fe_2O_3, H_2O, CO_2, and K_2O significantly above background values (Robinson et al., 1991, fig. 1), apparently resulting from oxygenated seawater reacting with olivine and orthopyroxene to form pseudomorphs of ferric oxides, clay minerals and carbonates. No related changes in the abundances of elements such as Ba and Sr were demonstrated, partly because of the relatively large primary variation in the composition of these elements, and also because the effect is small: the altered rocks at Site 735 all contain less than 0.5% CO_2, whereas some of the calcitized serpentinites from Site 897 contain over 50% CO_2.

We speculate that the relatively limited seawater alteration at Site 735 may be partly a result of the short duration (less than 9.5 m.y.) of seawater interaction at the site (Dick et al., 1991, fig. 35). In contrast, it is possible that the serpentinites at the top of the basement ridge at Site 897 were exposed to seawater alteration for as long as 40 m.y. before being buried by the sediments of the Iberia Abyssal Plain.

Bonatti et al. (1974) stressed the similarity of rocks described from the Romanche and Vema fracture zones to ultramafic breccias found in ophiolite occurrences in the Apennines and the South Pennine nappes of eastern Switzerland. The description by Bernoulli and Weissert (1985) of relations near Davos, Switzerland is very reminiscent of relations at Site 897 with sediments overlying brown, calcitized, brecciated serpentinites, which in turn overlay green massive serpentinites. The Davos breccias are described as polyphase in origin and forming in a transform zone. Barrett and Spooner (1977) described similar ophiolitic breccias from the East Ligurian Apennines and considered that most of the breccias represent talus accumulations at the base of major submarine fault scarps. In both of these areas, the ophiolites may indeed include landslide deposits, but in situ brecciation was probably important. The importance of the latter process was stressed by Folk and McBride (1976). In a particularly insightful article, these authors proposed that Ligurian ophicalcite complexes were formed in situ by prolonged calcite alteration on paleotopographic ridges. They observed caliche-like fabrics, favored a pedogenic origin for the carbonate, and suggested the rocks were subaerially exposed at times. Although we see no evidence for subaerial exposure, many other features at Site 897 are comparable to the Ligurian ophicalcite complexes. There is paleontologic and isotopic evidence that suggests that the serpentinite ridge at this site was subject to seawater alteration for up to 40 m.y., before it was buried by the sediments of the Iberia Abyssal Plain. This protracted period of exposure may account for the intensity of the alteration relative to other seafloor sites that are usually more rapidly buried by sediments.

CONCLUSIONS

The extensively oxidized and carbonatized zone forming the upper part of the serpentinized basement at Site 897 is interpreted as the result of protracted exposure to circulating cold seawater during an approximately 40 m.y. period following the cessation of tectonic activity at this site and prior to the burial of the rocks by the sediments of the Iberia Abyssal Plain. The alteration is much more intense than that observed at the top of normal basaltic oceanic crust. The chemical changes during carbonatization involved primarily the addition of $CaCO_3$, and the oxidation of the existing iron in the rocks. Smaller quantities of K_2O, total iron, P_2O_5, V, Ba, Sr, and perhaps Zn were also added to the serpentinite during carbonatization. The abundances of Al_2O_3, TiO_2, and Cr reflect the primary concentration of spinel in the rocks. This mineral is little changed by either serpentinization or the later pervasive calcite alteration. This results in lower abundances of these three constituents in the altered rocks as a result of dilution. Although we have not attempted to quantify losses from the serpentinite during calcitization, textural evidence suggests that serpentine minerals are extensively replaced by $CaCO_3$ and large amounts of MgO and SiO_2 must have been removed during this long period of alteration.

Chlorine appears to have been added to the host ultramafic rocks during early serpentinization. However, Cl concentrations are reduced in the upper calcitized zone. The origin of a local Cl-rich zone with up to 1.0% Cl and marked by the occurrence of iowaite is uncertain. The zone may result from alteration by chloride-rich brines circulating through fractures in the serpentinite.

Relations at Site 897 during the development of the Iberian continental margin were clearly unusual in that a zone of serpentinite was exposed on the seafloor for up to 40 m.y. However, such relationships are not unique in the geological record as indicated by the widespread occurrence of very similar calcitized rocks in the ophicalcite complexes of some Tethyan ophiolites.

REFERENCES

Alt, J.C., Honnorez, J., Laverne, C., and Emmermann, R., 1986. Hydrothermal alteration of a 1 km section through the upper oceanic crust, Deep Sea Drilling Project Hole 504B: mineralogy, chemistry, and evolution of seawater-basalt interactions. *J. Geophys. Res.,* 91:10309-10335.

Barrett, T.J., and Spooner, E.T.C., 1977. Ophiolite breccias associated with allochthonous oceanic crustal rocks in the East Ligurian Apennines, Italy—a comparison with observations from rifted ocean ridges. *Earth Planet. Sci. Lett.,* 35:79-91.

Bednarz, U., Gotte, P., and Schmincke, H.-U., 1991. The petrology of altered submarine lavas and major element mobility in Drillholes CY-1 and CY-1A, Cyprus. *In* Gibson, I.L., Malpas, J., Robinson, P.T., and Xenophontos, C. (Eds.), *Cyprus Crustal Study Project: Initial Report, Holes CY-1 and CY1A.* Pap.—Geol. Surv. Can., 90-20:95-116.

Bernoulli, D., and Weissert, H., 1985. Sedimentary fabrics in Alpine ophicalcites, South Pennine Arosa Zone, Switzerland. *Geology,* 13:755-758.

Beslier, M.-O., Ask, M., and Boillot, G., 1993. Ocean-continent boundary in the Iberia abyssal plain from multichannel seismic data. *Tectonophysics,* 218:383-393.

Boillot, G., Comas, M.C., Girardeau, J., Kornprobst, J., Loreau, J.-P., Malod, J., Mougenot, D., and Moullade, M., 1988. Preliminary results of the Galinaute cruise: dives of the submersible *Nautile* on the Western Galicia Margin, Spain. *In* Boillot, G., Winterer, E.L., et al., *Proc. ODP, Sci. Results,* 103: College Station, TX (Ocean Drilling Program), 37-51.

Boillot, G., Grimand, S., Mauffret, A., Mougenot, D., Kornprobst, J., Mergoil-Daniel, J., and Torrent, G., 1980. Ocean-continent boundary off the Iberian margin: a serpentinite diapir west of the Galicia Bank. *Earth Planet. Sci. Lett.,* 48:23-34.

Boillot, G., Recq, M., Winterer, E.L., Meyer, A.W., Applegate, J., Baltuck, M., Bergen, J.A., Comas, M.C., Davies, T.A., Dunham, K., Evans, C.A., Giradeau, J., Goldberg., D.G., Haggerty, J., Jansa, L.F., Johnson, J.A., Kasahara, J., Loreau J.-P., Luna-Sierra, E., Moullade, M., Ogg, J., Sarti, M., Thurow, J., and Willamson, M.A., 1987. Tectonic denudation of the upper mantle along passive margins: a model based on drilling results (ODP Leg 103, western Galicia margin, Spain). *Tectonophysics,* 132:335-342.

Bonatti, E., Emiliani, C., Ferrara, G., Honnorez, J., and Rydell, H., 1974. Ultramafic-carbonate breccias from the equatorial Mid Atlantic Ridge. *Mar. Geol.,* 16:83-102.

Dick, H.J.B., Meyer, P.S., Bloomer, S., Kirby, S., Stakes, D., and Mawer, C., 1991. Lithostratigraphic evolution of an in-situ section of oceanic Layer 3. *In* Von Herzen, R.P., Robinson, P.T., et al., *Proc. ODP, Sci. Results,* 118: College Station, TX (Ocean Drilling Program), 439-538.

Donnelly, T.W., Thompson, G., and Salisbury, M.H., 1980. The chemistry of altered basalts at Site 417, DSDP Leg 51. *In* Donnelly, T., Francheteau, J., Bryan, W., Robinson, P., Flower, M., Salisbury, M., et al., *Init. Repts. DSDP,* 51, 52, 53 (Pt. 2): Washington (U.S. Govt. Printing Office), 1319-1330.

Earley, J.W., 1958. On chlorine in serpentinized dunite. *Am. Mineral.* 43:148-155.

Folk, R.L., and McBride, E.F., 1976. Possible pedogenic origin of Ligurian ophicalcite: a Mesozoic calichified serpentinite. *Geology,* 4:327-332.

Gillis, K.M., and Robinson, P.T., 1991. Alteration of the ICRDG CY-1 and CY-1 A drill cores, Troodos Ophiolite: mineralogical and geochemical studies. *In* Gibson, I.L., Malpas, J., Robinson, P.T., and Xenophontos, C. (Eds.), *Cyprus Crustal Study Project: Initial Report, Holes CY-1 and CY1A.* Pap.—Geol. Surv. Can., 90-20:95-116.

Hart, R.A., 1970. Chemical exchange between seawater and deep ocean basalts. *Earth Planet. Sci. Lett.,* 9:269-279.

Heling, D., and Schwarz, A., 1992. Iowaite in serpentinite muds at Sites 778, 779, 780, and 784: a possible cause for the low chlorinity of pore waters. *In* Fryer, P., Pearce, J.A., Stokking, L.B., et al., *Proc. ODP, Sci. Results,* 125: College Station, TX (Ocean Drilling Program), 313-323.

Hubberten, H.-W., Emmermann, R., and Puchelt, H., 1983. Geochemistry of basalts from Costa Rica Rift Sites 504 and 505 (Deep Sea Drilling Project Legs 69 and 70). *In* Cann, J.R., Langseth, M.G., Honnorez, J., Von Herzen, R.P., White, S.M., et al., *Init. Repts. DSDP,* 69: Washington (U.S. Govt. Printing Office), 791-803.

Humphris, S.E., and Thompson, G., 1978. Hydrothermal alteration of oceanic basalts by seawater. *Geochim. Cosmochim. Acta,* 42:107-125.

Ito, E., and Anderson, A.T., Jr., 1983. Submarine metamorphism of gabbros from the Mid Cayman Rise: petrographic and mineralogic constraints on hydrothermal processes at slow-spreading ridges. *Contrib. Mineral. Petrol.,* 82:371-388.

Kohls, D.W., and Rodda, J.L., 1967. Iowaite, a new hydrous magnesium hydroxide-ferric oxychloride from the Precambrian of Iowa. *Am. Mineral.,* 52:1261-1271.

Mével, C., 1988. Metamorphism of oceanic layer 3, Gorringe Bank, eastern Atlantic. *Contrib. Mineral. Petrol.,* 100:496-509.

Miyashiro, A., Shido, F., and Ewing, M., 1969. Diversity and origin of abyssal tholeiite from the Mid-Atlantic ridge, 24° and 30°N latitude. *Contrib. Mineral. Petrol.,* 23:38-52.

Robinson, P.T., Dick, H.J.B., and Von Herzen, R.P., 1991. Metamorphism and alteration in oceanic layer 3: Hole 735B. *In* Von Herzen, R.P., Robinson, P.T., et al., *Proc. ODP, Sci. Results,* 118: College Station, TX (Ocean Drilling Program), 541-552.

Robinson, P.T., Flower, M.F.J., Schmincke, H.-U., and Ohnmacht, W., 1977. Low temperature alteration of oceanic basalts, DSDP Leg 37. *In* Aumento, F., Melson, W.G., et al., *Init. Repts. DSDP,* 37: Washington (U.S. Govt. Printing Office), 775-793.

Rucklidge, J.C., 1972. Chlorine in partially serpentinized dunite. *Econ. Geol.,* 67:38-40.

Sawyer, D.S., Whitmarsh, R.B., Klaus, A., et al., 1994. *Proc. ODP, Init. Repts.,* 149: College Station, TX (Ocean Drilling Program).

Scott, R.B., and Hajash, A., Jr., 1976. Initial submarine alteration of basaltic pillow lavas: a microprobe study. *Am. J. Sci.,* 276:480-501.

Seyfried, W.E., and Bischoff, J.L., 1979. Low temperature basalt alteration by seawater: an experimental study at 70°C and 150°C. *Geochim. Cosmochim. Acta.,* 43:1937-1947.

Shipboard Scientific Party, 1990. Explanatory notes. *In* Ludden, J.N., Gradstein, P.M., et al., *Proc. ODP, Init. Repts.,* 123: College Station, TX (Ocean Drilling Program), 27-59.

———, 1994. Site 897. *In* Sawyer, D.S., Whitmarsh, R.B., Klaus, A., et al., *Proc. ODP, Init. Repts.,* 149: College Station, TX (Ocean Drilling Program), 41-113.

Steuber, A.M., Huang, W.H., and Johns, W.D., 1968. Chlorine and fluorine abundances in ultramafic rocks. *Geochim. Cosmochim. Acta,* 32:353-358.

Vanko, D.A., 1986. High-chlorine amphiboles from oceanic rocks: product of highly saline hydrothermal fluids? *Am. Mineral.,* 71:51-59.

Vanko, D.A., and Stakes, D.S., 1991. Fluids in oceanic layer 3: evidence from veined rocks, Hole 735B, Southwest Indian Ridge. *In* Von Herzen, R.P., Robinson, P.T., et al., *Proc. ODP, Sci. Results,* 118: College Station, TX (Ocean Drilling Program), 181-215.

Whitmarsh, R.B., Miles, P.R., and Mauffret, A., 1990. The ocean-continent boundary off the western continental margin of Iberia, I. Crustal structure at 40°30'N. *Geophys. J. Int.,* 103:509-531.