17. ISOTOPIC CHARACTERIZATION OF SECONDARY CARBONATES FROM SULU AND CELEBES SEA BASALTS: CONTRASTING SCENARIOS OF BASALT-SEAWATER INTERACTION[1]

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ABSTRACT

Secondary carbonate minerals were recovered within the basalts at both ODP Sites 768 and 770 in the Sulu and Celebes seas. Petrographic and X-ray diffraction analyses indicate that the carbonates are calcites. Other alteration products recognized in the thin sections are smectites, iron oxides, and gypsum. The ^{13}C values of carbonates from both sites range from 1.6 ‰ to 2.3 ‰, which are indicative of inorganic carbonate formation with no contributions from ^{13}C-depleted sources such as oxidized organic carbon or methane. The oxygen isotopes at Site 770 range from 30.8‰ to 31.6‰, which indicates a pervasive circulation of cold seawater (9° to 12°C) during alteration of the Celebes Sea basalts. In contrast, carbonates associated with Site 768 basalts have less positive $\delta^{18}O$ values (21.0 ‰ to 27.3 ‰). A lighter ^{18}O isotopic signature indicates the formation of secondary calcite at either higher temperatures or in a system closed to seawater. The rapidly deposited pyroclastic flows at Site 768 would have limited water access to the crust very soon after its formation, which leads us to speculate that the carbonates in the Sulu Sea basalts were formed by isotopically modified fluids resulting from basalt alteration in a closed system.

INTRODUCTION

In the last decade, geochemical assessments of the heat loss from the oceanic crust has reinforced the view that large-scale mass transport through the crust is required to explain the large water/rock ratios inferred from chemical water-rock interactions (Sclater et al., 1976; Anderson and Hobart, 1976) The analysis of vein-filling material in drilled basalts have led to a good understanding of the basalt-seawater, post-deutiric alteration reactions. These studies have shown that such interactions have taken place to at least 500 m depth in the oceanic crust, and are at least in part controlled by the availability of fluid circulation through the crust. Such factors as the rate of sediment accumulation and the nature of the basalt (i.e., massive flow vs. pillow lavas), play a crucial role in controlling access of seawater to the oceanic crust. Effective water/rock ratio and extent of exchange between circulating seawater and young crust, influence the rate of heat loss and the chemical evolution of both fluid and rock (Staudigel and Hart, 1983).

The timing, duration, and chemical evolution of hydrothermal solutions have been fairly well established for oceanic crust generated at slow spreading ridges in the Atlantic. Based on the $^{87}Sr/^{86}Sr$ ratios in smectites, celadonites, analcites, and carbonates in the vein materials from drill holes ranging in age from 3.5 to 110 m.y. and the known variation of the $^{87}Sr/^{86}Sr$ with time, Hart and Staudigel (1978) and Richardson et al. (1980) have concluded that most reactions in the crust take place over a fairly short time. They have suggested four major low-temperature alteration stages that are thought to occur in characteristic temperature succession: Stage 1: formation of palagonites, Stage 2: formation of smectites, Stage 3: formation of carbonates, and Stage 4: compaction and dehydration of the crust.

Drilling and recovery of basaltic crust from both the Atlantic and Pacific oceans has provided new insights into the timing and duration of crustal alteration, and the chemical evolution of hydrothermal solutions. Two basic types have been described: seawater-dominated and rock-dominated systems. The abundance of massive flows and the thin sediment cover in fast-spreading centers are thought to result in high formation permeabilities and seawater-dominated hydrothermal solutions. Oxygen isotope data on the calcite veins at DSDP Site 597 in the Pacific Ocean reflect a low temperature of alteration, and the $^{87}Sr/^{86}Sr$ isotopic ratios and the Sr/Ca ratio of vein carbonates imply that the hydrothermal solutions at this site were not significantly altered from the interaction with the basalts (Staudigel et al., 1986).

On the other end of the spectrum, Hole 504B provides the first evidence that vein carbonates can in fact be deposited from solutions which are markedly different from ambient seawater. Based on Sr and $^{87}Sr/^{86}Sr$ data for carbonates from DSDP Hole 504B, Staudigel and Hart (1983) conclude that carbonate precipitattion occurred in a basalt-dominated, high-temperature system, where rapidly depositing sediments have sealed the crust form exchange with the overlying water column. Staudigel and Hart (1985) suggest that the calcium necessary for the precipitation of carbonates in DSDP Hole 504B must be derived from the alteration of basaltic glass and the breakdown of anorthic feldspar. Complex basalt alteration reactions and precipitation of secondary phases from fluids isolated from the overlying water column result in an hydrothermal solution that differ significantly from the composition of the original seawater.

To evaluate conditions of crustal alteration in two western Pacific basins, we have analyzed secondary vein carbonates of basalts from the Sulu and Celebes seas. Basement rocks from these two sites appear to have been formed in different tectonic settings and at different times. The Sulu Sea originated as a back-arc or intra-arc basin in the late early to early middle Miocene, the Celebes Sea originated in an open ocean setting in the middle Eocene (Rangin, Silver, von Breymann et al., 1990). Structural differences resulting from mechanisms of crust emplacement will have an effect on the amount of water flow. The
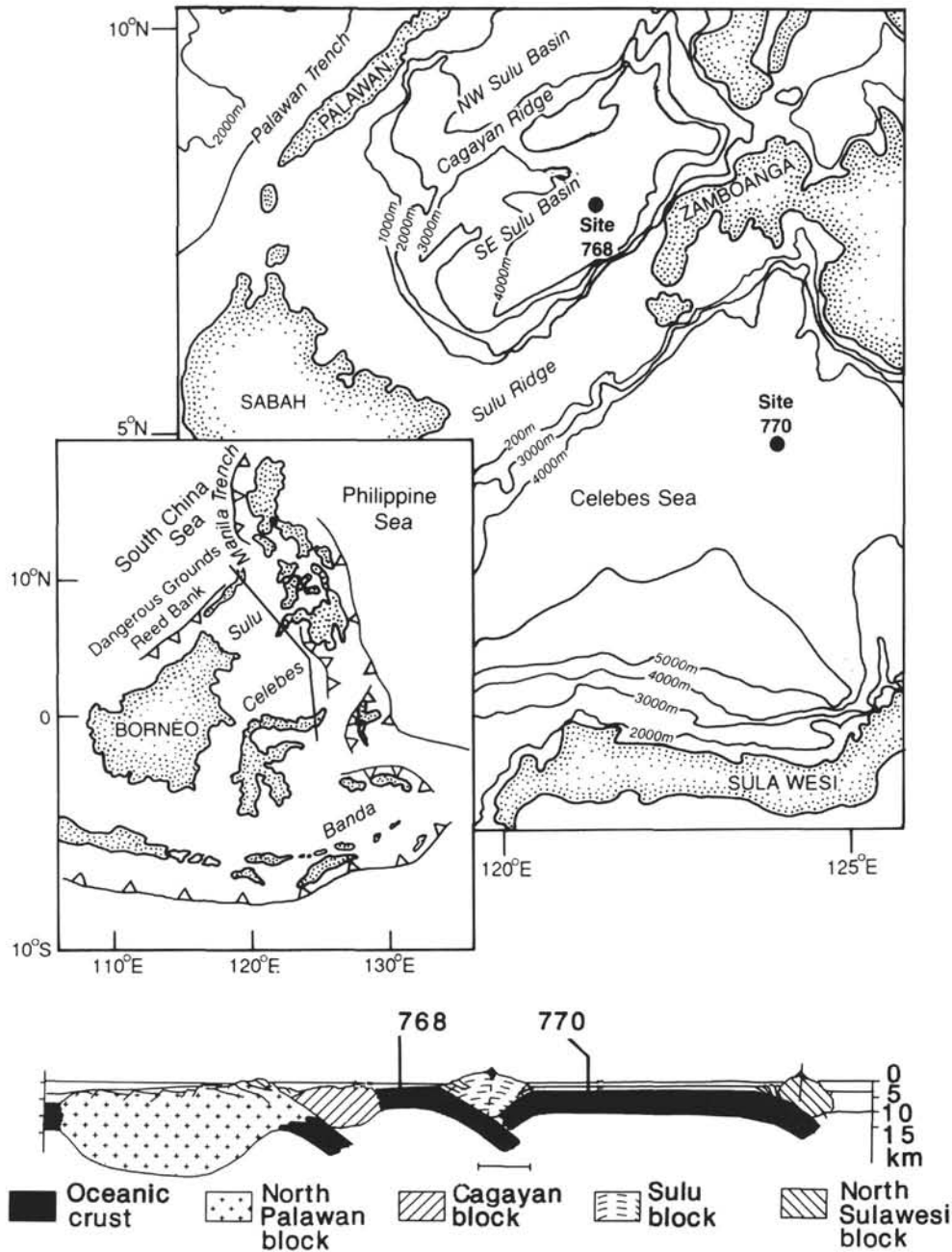
Figure 1. Location of the sites used in this study.

density of fault zones, general topography, sheet and massive flows vs. pillow-dominated environments might all contribute to the water circulation patterns. Massive flows are characterized by slower cooling rates than pillows, resulting in longer phases of deutiric alteration. Also very significant is the fact that the Sulu Sea site experienced rapid deposition of pyroclastics that sealed the crust soon after formation, while the Celebes Sea crust experienced very low sedimentation of red pelagic clays. The two different tectonic origins as well as the sedimentation patterns experienced by these basins soon after the formation of the crust would have played a mayor role in determining the mechanisms of seawater-basalt interaction.

GEOLOGICAL SETTINGS

Site 768 is located in the southeastern part of the Sulu Sea, in a water depth of 4386 m (Fig. 1). The Sulu Sea originated as a back-arc basin in the early part of the middle Miocene, nearly concurrent with the cessation of volcanism on the Cagayan Ridge. At this site, 221.8 m of basement was cored. The sequence has been divided into eight units, six of which occur as lavas, and two as olivine-dolerite sills (Fig. 2). The lavas are petrologically uniform and are composed of vesicular olivine-phyric basalts. Basement is overlain by 1047 m of sediments. Early outpourings of rhyolitic to dacidic flows are represented by a 250-m-thick sequence of pyroclastic deposits that probably accumulated during a short period of time after the oceanic crust of Site 768 was formed. Brown clay deposition continued above the tuffs for about 30 m, after which the dominant lithology was greenish claystone (Rangin, Silver, von Breymann et al., 1990).

Site 770 is located in the central Celebes Sea, in a water depth of 4505 m. The Celebes Sea originated in the middle
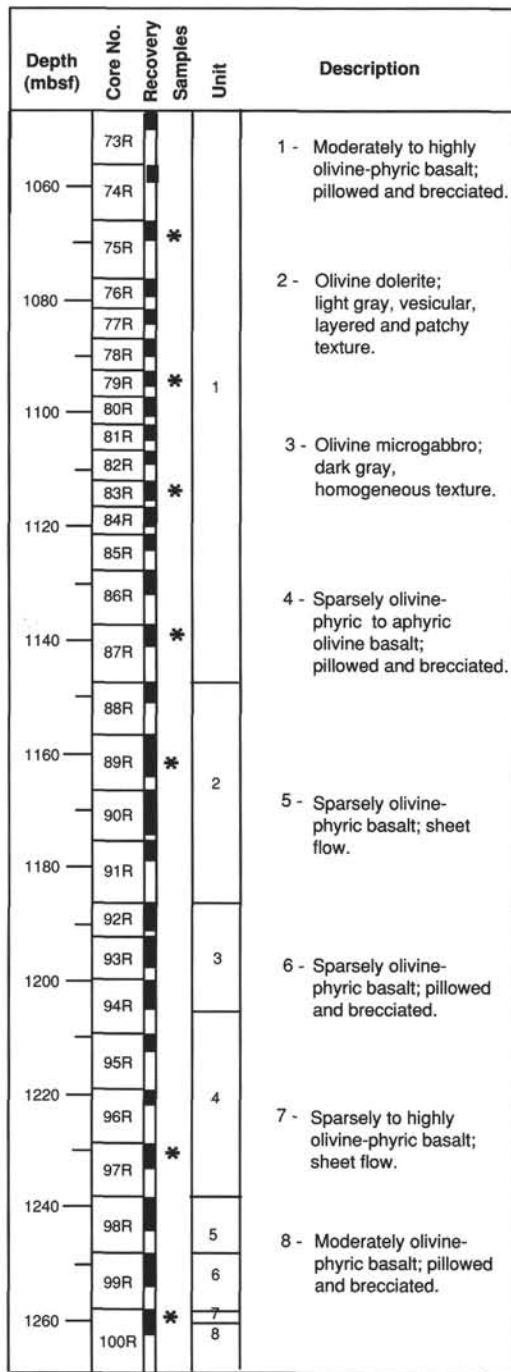
Hole 768C
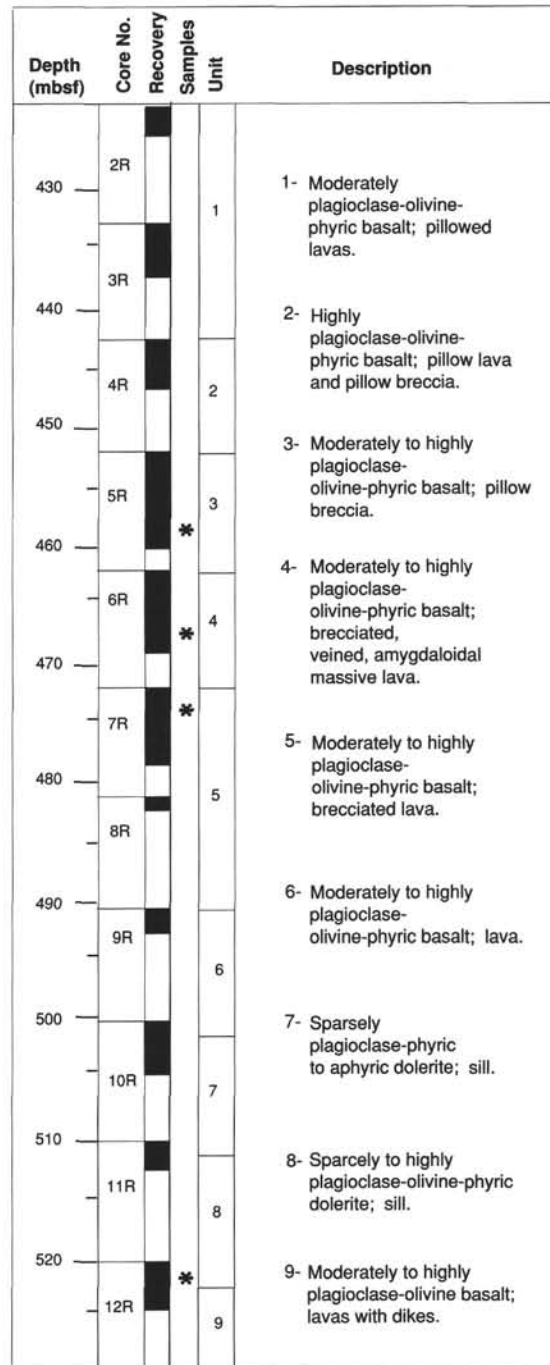
Hole 770C

Figure 2. Lithology of basement rocks from ODP Sites 768 and 770. Data are from Rangin, Silver, von Breymann, et al., 1990.

Eocene in an open ocean setting similar to that of the Philippine Sea. Basement was recovered from the interval 421 to 529 mbsf. Six lava units can be identified based on their mineralogy (Fig. 2); petrographical and geochemical studies show it to be a plagioclase-olivine phyric basalt with a normal mid-ocean ridge signature. Basement underlies 421 m of sediment, characterized by a middle Eocene to middle Miocene sequence of brown pelagic claystone overlain by 296 m of volcanogenic sitly clay. The basal red clays show low rates

of sedimentation, and the presence of manganese micronodules, fish teeth, and radiolarians is indicative of open ocean environments.

METHODS

Carbonate samples were selected from veins in basalts recovered from Holes 768C and 770C (Figs 2 and 3). The samples were analyzed for mineralogy by standard X-ray diffraction techniques at Texas A&M University. Carbonate
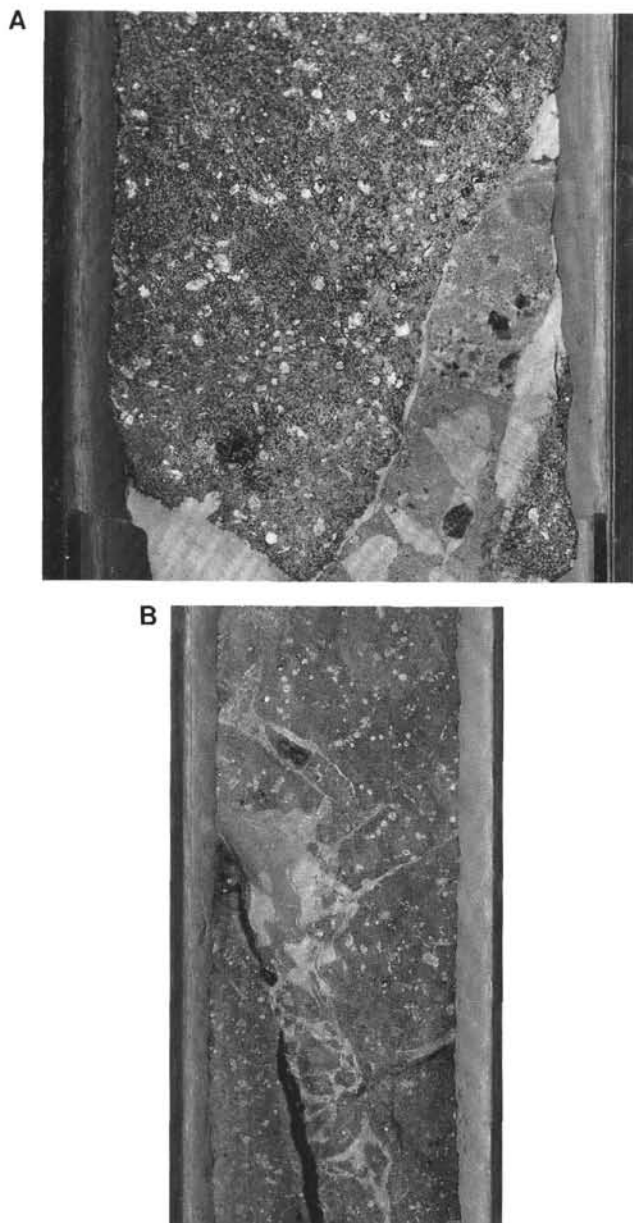
A

B

Figure 3. Core photographs with examples of secondary carbonates. **A.** Sample 124-770C-5R-5, 48–49 cm, and **B.** Sample 124-770C-6R-5, 63–65 cm.

$\delta^{18}O$ and $\delta^{13}C$ isotope values were determined according to the phosphoric acid method described by McCrea (1950). The stable isotope measurements on the CO_2 were carried out using a Finigan MAT 250 mass spectrometer at the BGR laboratories in Hannover.

RESULTS AND DISCUSSION

The petrographic and X-ray diffraction analysis indicates that the carbonates are mostly calcites. Other alteration products recognized in thin sections are smectites, gypsum, and iron oxides, in agreement with shipboard observations (Rangin, Silver, von Breymann et al., 1990).

The isotopic composition of the vein carbonates is given in Table 1 and plotted in Fig. 4. This figure also includes data from secondary carbonates recovered at other sites for comparison. The $\delta^{13}C$ values of both Sites 768 and 770 range from

1.6‰ to 2.3 ‰ relative to the PDB (Pee Dee Belemnite) standard, which are comparable with those found in most oceanic crusts (Muehlenbachs, 1979; Staudigel et al., 1986; Lawrence, 1979), and are fully compatible with inorganic carbonate formation in seawater. There is no indication of contributions from ^{13}C-depleted carbon reservoirs such as oxidized organic carbon or methane, which have been reported in carbonates from DSDP Legs 58 and 59 in the western Pacific (Anderson, 1980; Migdisov et al., 1981).

The oxygen isotopes at Site 770 range from 30.8‰ to 31.6‰ relative to SMOW. Site 768 carbonates have values ranging from 21.0 ‰ to 27.3 ‰, which constitute the lightest $\delta^{18}O$ values reported to date (Fig. 4). We have calculated the temperature of formation for these samples using the calcite-water temperature relationship of O'Neil et al. (1969), corrected for the CO_2-H_2O fractionation factor at 25°C of O'Neil et al. (1975) and assuming values for the $\delta^{18}O$ of seawater to be 0 ‰ and -1 ‰ (Table 1). In this temperature estimate we have also assumed that the fluid involved in the alteration is characteristic of carbonate deposited in equilibrium with seawater. Calcite precipitation temperatures for the Celebes Sea range from 9° to 12°C, and are in agreement with those reported for Atlantic and Pacific oceans. Temperatures estimated for the carbonates precipitated in the Sulu Sea (30° to 69°C) however, are higher than those reported previously.

The results indicate that either the carbonates in the Sulu Sea basalts precipitated at higher temperatures, or that they were formed in a system with restricted fluid circulation in which the oxygen isotope of the alteration fluid was lighter than that of seawater. Progressive alteration at small water/rock ratios results in a depletion of $\delta^{18}O$ of the water (Lawrence et al., 1979), and therefore secondary minerals formed in closed systems acquire progressively lighter δ18O. This "aging" effect was described by Anderson (1980) in relation to the light δ18O values of secondary carbonate veins from Hole 446A in the Daito Basin (DSDP Leg 58).

Water circulation through the crust is the main factor controlling deposition of secondary minerals. This has been inferred by comparison with mid-ocean ridge systems where the timing of secondary-mineral deposition closely follows the decay of the heat-flow anomaly (Sclater et al., 1976; Anderson and Hobart, 1976). The Celebes and Sulu basins experienced very different sedimentation patterns soon after emplacement, which would have influenced the water/rock ratio during alteration in these two basins. A thick sequence of pyroclastic flows accumulated over the newly formed Sulu Sea oceanic crust, sealing its communication with seawater. The Celebes Sea, on the other hand, experienced low rates of accumulation of red pelagic clays. The isotopic data on the secondary calcites indicate a pervasive circulation of cold seawater during alteration of the Celebes Sea basalts. With the available data it is not possible to unequivocally determine if the low $\delta^{18}O$ values in the Sulu Sea carbonates result from alteration at higher temperatures or in a closed system. However, the rapidly deposited pyroclastic flows at Site 768 would have limited access of water to the crust very soon after formation, a fact that can easily result in a low water rock ratio and depleted δ18O fluids during alteration of the basalts in the Sulu Sea.

ACKNOWLEDGMENTS

Table 1. Isotopic characterization and estimated temperature of formation of calcite veins, ODP Sites 768 and 770.

| Sample	Depth mbsf	Color	Mineralogy	$\delta^{13}C$ PDB	$\delta^{18}O$ PDB	$\delta^{18}O$ SMOW	Temp (0 ‰)	Temp (-1 ‰)
124-								
770C-5R-05, 48-49	458.7	light red	calcite	1.94	0.46	30.84	16	12
		dark red		1.64	0.77	31.16	15	11
770C-6R-5, 63-65	468.5	light red	calcite	1.97	0.77	31.16	15	11
		dark red		1.96	0.77	31.16	15	11
				1.70	0.47	30.85	16	12
				1.71	0.71	31.10	15	11
770C-7R-3, 93-95	475.4	white	calcite	1.94	0.65	31.04	15	11
770C-12R-3, 99-100	523.9	light brown	calcite	1.58	1.17	31.58	13	9
		light brown		1.61	1.16	31.57	13	9
768C-75R-1, 25-26	1066.2	gray	calcite	1.80	-6.22	23.96	50	45
768C-79R-2, 17-18	1092.2	gray		1.84	-8.19	21.93	63	57
		gray		1.86	-8.32	21.80	64	57
768C-83R-2, 17-18	1112.3	gray		1.89	-6.81	23.35	54	48
		gray		1.89	-6.75	23.42	54	48
768C-87R-1, 129-130	1137.6	gray	calcite	1.98	-9.08	21.01	70	63
		gray		1.95	-8.58	21.53	66	59
768C-89R-5, 59-60	1161.6	gray		2.11	-2.97	27.31	32	27
		gray		2.09	-3.01	27.27	32	27
768C-97R-1, 35-36	1230.1	gray	calcite	2.31	-4.78	25.44	42	37
		gray		2.31	-4.81	25.41	42	37
768C-100R-1, 97-99	1259.8	gray		2.30	-7.49	22.65	59	52
				2.28	-7.48	22.66	58	52
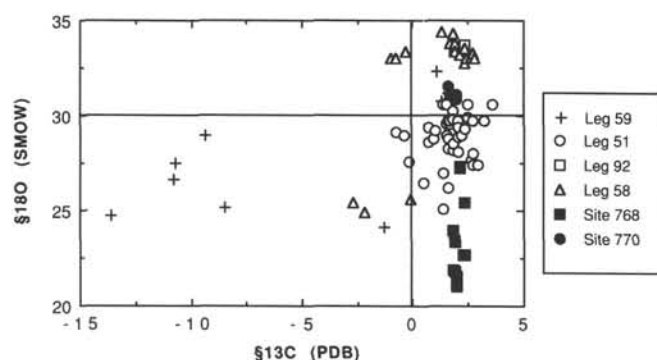
Figure 4. Plot of $\delta^{18}O$ vs. $\delta^{13}C$ for samples from ODP Sites 768 and 770. Isotopic composition of secondary carbonates from DSDP Legs 51 (Lawrence, 1979); 58 (Anderson, 1980); 59 (Migdisov et al., 1981); and 92 (Staudigel et al., 1986) is included for comparison. Note the low $\delta^{18}O$ values for Site 768 carbonates (closed squares).

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