

## 31. $\delta^{18}\text{O}$ AND $^{87}\text{Sr}/^{86}\text{Sr}$ OF CALCITES FROM THE BASALTIC BASEMENT OF DEEP SEA DRILLING PROJECT SITE 597: TIMING AND TEMPERATURE OF ALTERATION<sup>1</sup>

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### ABSTRACT

Calcites from the basaltic basement at Deep Sea Drilling Project Site 597, containing 3.4 to 4.4 mol%  $\text{MgCO}_3$ , were analyzed for  $\delta^{13}\text{C}$ ,  $\delta^{18}\text{O}$ ,  $^{87}\text{Sr}/^{86}\text{Sr}$ , K, Rb, and Sr concentrations. The  $\delta^{13}\text{C}$  values range from 1.9 to 2.4‰ (relative to PDB) and are typical for calcites from the extrusive layer of the oceanic crust. The  $\delta^{18}\text{O}$  values of calcites are very uniform and unusually high (2.33 to 2.77‰, PDB), which suggest temperatures of formation of 1.5 to 2.9°C and 0.03 to 1.7°C using the calibrations of O'Neil et al. (1969) and Epstein et al. (1953), respectively (after correction for  $\text{MgCO}_3$ ), and assuming -1‰ for the late Oligocene/early Miocene bottom water. Paleogene bottom waters are thought to have been warmer than those of present day, and hence the calibration of Epstein et al. (1953) yields more reasonable temperatures for late Oligocene/early Miocene bottom waters. K and Rb concentrations are very low, which is consistent with their incompatible character. Sr/Ca ratios of calcites from sub-basement depths less than 35 m are typical for calcites precipitated from pure seawater, whereas the lowermost sample, from a sub-basement depth of 78 m, appears to contain substantial amounts of basaltic Ca. The  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios of seawater calcites range from 0.708192 to 0.708349, suggesting that they precipitated from 20 to 28 Ma seawater, or within 8 m.y. after formation of the oceanic crust at Site 597. Our data for calcites from Site 597, drilled on fast-spreading oceanic crust, are similar to data for carbonates from slow-spreading crust, except that the high  $\delta^{18}\text{O}$  values of the former suggest low temperatures of formation. The low temperatures of calcite formation apparently indicate that the oceanic crust at Site 597 was unusually permeable, allowing rapid circulation of seawater.

### INTRODUCTION

Important advancements in our understanding of ocean-floor alteration were made on DSDP holes with high recovery rates, previously only drilled on oceanic crust generated at slow-spreading ridges in the Atlantic Ocean (e.g., Sites 332, 417/418, and 495) or at intermediate spreading ridges in the Pacific (Hole 504B). Cores drilled in fast-spreading crust typically lacked significant basement penetration and were plagued by poor recovery (e.g., those recovered during Legs 34 and 65). The DSDP sampling bias toward crust from slow-spreading ridges was ameliorated by drilling at Site 597, where 91 m of basalt were penetrated and recovery rates exceeded 50%. Site 597 is located in the Pacific Ocean at 18°48.38' S, and 129°46.23' W, on 28.6 Ma crust.

Site 597 may be typical of crust generated at fast-spreading ridges, having low sediment accumulation rates (1.25 mm/1000 yr.) and a predominance of massive flows (Site 597 chapter, this volume). Most fast-spreading ridges are characterized by slow sedimentation rates, because they are located far from major continental sources of detrital material. Massive flows have been linked to high mass eruption rates (Staudigel and Schmincke, 1984), which are particularly likely at mid-ocean ridges with high spreading rates.

Such factors as the abundance of massive flows and low sediment cover may affect the type and duration of

alteration. Slow sediment accumulation delays the sealing of the oceanic crust and may allow prolonged access to seawater. Massive flows are characterized by slower cooling rates than pillows and hyaloclastites, resulting in longer phases of deuteric alteration and low modal abundances of basaltic glass. Low modal abundance of basaltic glass may have two effects. First, glass alteration provides the major source of elements to form secondary phases in the upper oceanic crust, a source significantly more important than the ones resulting from the decay of olivine and plagioclase (Staudigel and Hart, 1983). For this reason, the chemical composition of hydrothermal solutions in crust generated at fast-spreading ridges may contain more seawater components and relatively larger amounts of components derived from olivine and plagioclase. A second effect of low modal glass abundance may be related to the swelling of glass upon hydration. Low glass abundance may thus provide an additional cause for relatively late sealing of oceanic crust from fast-spreading ridges. These considerations allow us to speculate that oceanic crust at Site 597 or at other fast-spreading ridge locations is characterized by more extensive deuteric alteration, high formation permeability, prolonged postdeuteric water-rock interaction, and more seawater-dominated hydrothermal solutions.

In oceanic crust, three major low-temperature secondary phases are thought to occur in a characteristic temporal succession: palagonite, smectites, and finally carbonates (see e.g., Bass, 1976; Andrews, 1977; Boehlke et al., 1980). This sequence of secondary mineral precipitation is evident in cross-cutting veins and sequential vein and vug fillings in oceanic crust of almost any origin and under a wide range of low-temperature conditions,

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although some hydrous layer silicates (e.g., celadonite) and zeolites may form after some early carbonates (Boehlke et al., 1980; Hay and Iijima, 1968). Carbonates, mostly formed late in the sequence of vein mineral deposition, assume a special role in ocean-floor alteration. Most vein calcites from the upper 500 m of oceanic crust having slow or intermediate sediment accumulation are thought to be formed from nearly pure seawater (Staudigel, Hart, et al., 1981; Staudigel, Muehlenbachs, et al., 1981; Staudigel and Hart, 1985). Thus, isotopic data from carbonates may provide constraints for the temperature ( $\delta^{18}\text{O}$ ) and age ( $^{87}\text{Sr}/^{86}\text{Sr}$ ) of alteration (Hart and Staudigel, 1978, 1982, 1983). In this initial report of our studies of vein mineral deposition at Site 597, we present  $\delta^{18}\text{O}$  and  $^{87}\text{Sr}/^{86}\text{Sr}$  isotope data of vein carbonates to evaluate the timing, temperature, and fluid composition during the late stages of alteration.

#### METHODS

Carbonate veins up to 2 mm thick were selected from representative portions of Holes 597A and 597C for isotopic analyses. Thin sections from these and other representative samples from Site 597 were prepared and petrographically analyzed. Carbonate veins were split open, the vein material broken off, and gently crushed and sieved. For hand picking, we selected the largest grain size yielding mostly monomineralic grains (generally an interval between 50 and 2000  $\mu\text{m}$ ). Carbonate separates were rapidly washed in distilled water under ultrasonic agitation, and then clean calcite grains were hand picked using a binocular microscope. Two different fractions were separated for  $\delta^{18}\text{O}$  and  $^{87}\text{Sr}/^{86}\text{Sr}$  isotopic analysis. Greatest care was used for separation of the Sr isotopic fraction by including only large, clear calcite grains that were free of inclusions, adhering basalt, and clay minerals. All fractions were analyzed by X-ray diffraction and binocular microscopy prior to isotopic analysis.  $\text{MgCO}_3$  contents of carbonates were determined by atomic absorption after selectively leaching the carbonate fractions from the fine-grained fractions of bulk vein material. Selective leaching included a step for removal of exchangeable ions by using  $\text{NH}_4\text{Cl}$ , followed by dissolution with acetic acid buffered at pH 4.8 with sodium acetate. We also analyzed the leachates for Si using the molybdate blue colorimetric technique of Mann and Gieskes (1975). We found the Si concentrations to be less than 30  $\mu\text{m}$  mol/l, suggesting that no silicates were dissolved during this selective leaching procedure. Mg concentration estimates by X-ray diffraction after Burton (1984) were approximately 30% higher than atomic absorption measurements. The error of atomic absorption is approximately 0.3 mol%  $\text{MgCO}_3$ . Calcite separates for Sr isotopic analyses generally were free of contaminants. The fraction for  $\delta^{18}\text{O}$  analyses contained minor amounts of plagioclase.

To establish an independent estimate of the temporal variation of  $^{87}\text{Sr}/^{86}\text{Sr}$  in seawater, we also analyzed some fish teeth from a variety of DSDP sites and from Scripps Institution of Oceanography piston cores. These separates were prepared by P. Doyle using  $\text{H}_2\text{O}_2$  digestion, heavy-liquid separation, and hand picking. Fish teeth were washed in alcohol and distilled water and were ion exchanged in ultrapure ammonium chloride prior to Sr isotopic analysis.

Carbonate  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  isotope values were determined according to the phosphoric acid method (McCrea, 1950). The isotopic analyses were carried out on a VG Micromass 602C mass spectrometer at Scripps and corrected according to Craig (1957); the results were reported as parts per mil (‰) relative to both PDB and SMOW standards. The standard deviation is  $\pm 0.10$  for  $\delta^{18}\text{O}$  and  $\pm 0.08$  for  $\delta^{13}\text{C}$  values.

Sr isotopic ratio measurements were carried out at the Lamont-Doherty Geological Observatory. K, Rb, and Sr were isolated with cation exchange techniques described by Hart and Brooks (1974). Isotopic dilution numbers are given to the last significant figure. The solid source mass spectrometric techniques are outlined by Zindler et al. (1984); isotopic ratios were normalized to  $^{87}\text{Sr}/^{86}\text{Sr} = 0.1194$ ; and the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio of the Eimer and Amend standard Sr carbonate was equal to 0.70800. Errors typically within  $2\sigma = \pm 0.000035$  are reported for the last significant figures (see Table 3).

## RESULTS

Thin-section observations and X-ray diffraction data largely confirm the data of the shipboard scientific party and Peterson et al. (this volume). Interstitial voids are filled with smectites and/or chlorite and Fe-oxides. According to Peterson et al., chlorite is particularly abundant in coarsely crystallized massive flows, replacing up to 60% of the interstitial groundmass. For example, Sample 597C-11-3, 82–88 cm, is a well-crystallized massive flow containing 3 to 5 mm average sized crystals which had 1 to 2 vol.% chlorite. Carbonate and celadonite veins, up to 2 mm thick, were formed late in the sequence of vein mineral deposition.

Table 1 summarizes the  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  values;  $\text{MgCO}_3$  contents and temperature estimates are shown in Table 2. The K, Rb, and Sr concentrations and  $^{87}\text{Sr}/^{86}\text{Sr}$  isotopic ratio are shown in Table 3. The  $\delta^{13}\text{C}$  values of Site 597 carbonates display a range of 1.9 to 2.4‰, which is typical for inorganically deposited carbonates in oceanic crust (e.g., Muehlenbachs, 1979). The carbonates from Site 597 display very uniform  $\delta^{18}\text{O}$  SMOW values ( $33.5 \pm 0.25$ ‰) independent of their position in the core. In Table 2, we summarize eight temperature estimates for every carbonate. We calculated the temperatures of formation for these samples based on the empirically and experimentally determined fractionation of  $^{18}\text{O}$  for calcite-water by Epstein et al. (1953) and O'Neil et al. (1969), respectively; the latter equation was corrected for the  $\text{CO}_2\text{-H}_2\text{O}$  fractionation factor at 25°C of O'Neil et al. (1975). For both curves, we calculated the temperatures for  $\delta^{18}\text{O}$  (seawater) as equal to 0‰ (SMOW) for present-day and late Oligocene/early Miocene bottom waters (Anderson and Arthur, 1983; Savin, 1977) and for pure calcite and calcite containing  $\text{MgCO}_3$  (Tarutani et al. 1969), which resulted in a total of eight temperature estimates for each sample giving a total temperature range of 7.2 to 0.03°C (Table 2).

The most significant discrepancies in calculated temperatures result from the different  $\delta^{18}\text{O}$  values of present-day and late Oligocene/early Miocene bottom waters (about 4°C) (Douglas and Savin, 1973, 1975). The  $\text{MgCO}_3$  correction is only 0.6 to 1.0°C for 3.4 to 4.4 mol %  $\text{MgCO}_3$ . Applying the Mg correction and the correction to the  $^{18}\text{O}$  depleted late Oligocene/early Miocene bottom waters gives two preferable temperature estimates. The fractionation expression of Epstein et al.

Table 1.  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  of secondary calcites from the basaltic basement of Holes 597A and 597C.

Sample (interval in cm)	Sub-basement depth (m)	$\delta^{13}\text{C}$ PDB (‰)	$\delta^{18}\text{O}$ SMOW (‰)	$\delta^{13}\text{C}$ (‰)
597A-7, CC	Top	2.33	33.26	2.25
		2.52	33.46	2.33
597C-3-1, 27-31, Piece 3	0.65	2.61	33.55	1.95
597C-6-5, 100-104, Piece 5d	34.87	2.77	33.72	2.37
597C-6-5, 139-143, Piece 9	35.31	2.52	33.46	2.17
		2.65	33.59	2.27
597C-11-3, 82-88, Piece 5f	78.25	2.52	33.46	1.92
		2.47	33.41	1.97

Table 2. Temperature estimates from the  $\delta^{18}\text{O}$  of Site 597 calcites.

Sample (interval in cm)	MgCO <sub>3</sub> (mol %)	Temperature (°C) after O'Neil et al. (1969) <sup>a</sup>				Temperature (°C) after Epstein et al. (1953) <sup>b</sup>			
		Pure calcite		Corrected for MgCO <sub>3</sub> <sup>c</sup>		Pure calcite		Corrected for MgCO <sub>3</sub> <sup>c</sup>	
		$\delta^{18}\text{O}_{\text{SW}} = 0\text{‰}$	$\delta^{18}\text{O}_{\text{SW}} = -1\text{‰}$	$\delta^{18}\text{O}_{\text{SW}} = 0\text{‰}$	$\delta^{18}\text{O}_{\text{SW}} = -1\text{‰}$	$\delta^{18}\text{O}_{\text{SW}} = 0\text{‰}$	$\delta^{18}\text{O}_{\text{SW}} = -1\text{‰}$	$\delta^{18}\text{O}_{\text{SW}} = 0\text{‰}$	$\delta^{18}\text{O}_{\text{SW}} = -1\text{‰}$
597A-7,CC	4.4	6.3	2.4	5.3	1.5	7.2	3.7	6.3	2.9
597C-3-1, 27-31, Piece 3	3.4	5.5	1.7	4.5	0.8	6.6	3.1	5.7	2.3
597C-6-5, 100-104, Piece 5d	3.4	5.2	1.4	4.4	0.7	6.2	2.8	5.6	2.2
597C-6-5, 100-104, Piece 5d	3.4	4.5	0.8	3.8	0.03	5.7	2.3	5.0	1.7
597C-6-5, 139-143, Piece 9	4.1	5.5	1.7	4.6	0.8	6.6	3.1	5.7	2.3
597C-6-5, 139-143, Piece 9	4.1	5.0	1.2	4.1	0.3	6.1	2.7	5.2	1.9
597C-11-3, 82-88, Piece 5d	4.3	5.5	1.7	4.5	0.8	6.6	3.1	5.7	2.3
597C-11-3, 82-88, Piece 5d	4.3	5.7	1.8	4.7	0.9	6.7	3.3	5.8	2.4

<sup>a</sup>  $10^3 \ln \alpha = 2.78(10^6 T^{-2}) - 2.89$ ; recalculated for CO<sub>2</sub>-H<sub>2</sub>O fractionation factor (25°C) = 1.0412 (O'Neil et al., 1975).

<sup>b</sup>  $t$  (°C) =  $16.5 - 4.3(\delta_c - \delta_w) + 0.14(\delta_c - \delta_w)^2$  (Epstein, 1953).

<sup>c</sup> After Tarutani et al. (1969).

Table 3. K, Rb, and Sr concentrations and  $^{87}\text{Sr}/^{86}\text{Sr}$  values of calcites from Site 597 and fish teeth from Sites 149, 502, and 576 and from Scripps Piston Cores Amph 116 and DODO 111.

Sample number (interval in cm)	Age (Ma) <sup>a</sup>	K (ppm)	Rb (ppm)	Sr (ppm)	$^{87}\text{Sr}/^{86}\text{Sr}$	$\sigma$
597A-7,CC	—	1780 ± 20	2.75	239.9	0.708227	35
597C-6-5, 139-143, Piece 9	—	21.22	nd	218	0.708300	49
597C-11-3, 82-88, Piece 5f	—	10.1	0.0310	27.1	0.708122	34
Amph 116P, 554-568	40.0-43.2	nd	nd	nd	0.707944	24
576-7-3, 69-75	52.0-57.6	nd	nd	nd	0.707743	36
DODO 111P, 125-140	21.5-26.0	nd	nd	nd	0.708504	33
502-15-1, 101-108	2.1-2.2	nd	nd	1933	0.708858	25
502-15-2, 100-107	2.1-2.2	106	7.65	1386	0.708785	35
149-11-6, 105-112	5.3-8.09	670	32.1	1016	0.708896	33
149-13-2, 68-75	8.1-8.4	nd	nd	1599	0.708823	34

Note: nd = no data.

<sup>a</sup> Numerical ages of fish teeth after Palmer, 1983; Berggren et al. (in press).

(1953) gives a total temperature range of 1.7 to 2.9°C for all samples analyzed, whereas the O'Neil et al. (1969) fractionation expression results in a range of 0.03 to 1.5°C. The latter temperature range appears to be unreasonably low for bottom waters and hydrothermal solutions within oceanic crust, particularly for the time between 20 and 30 Ma, when the ocean water temperatures were higher than today (see for review Anderson and Arthur, 1983). Giving preference to the equation of Epstein et al. (1953) is at odds with current convention, which uses O'Neil et al.'s equation for all igneous and metamorphic problems and Epstein et al.'s equation for biogenic sediments (e.g., Anderson and Arthur, 1983; Faure, 1977; Muehlenbachs, 1979; Lawrence, 1980). However, the temperature regime of calcite precipitation at Site 597 is much closer to diagenetic temperatures in sediments, and thus the Epstein et al. (1953) equation is better suited here. Calcite precipitation temperatures are substantially lower than the ones reported from other DSDP sites, such as Hole 418A, which had carbonate precipitation temperatures of 20 to 40°C (e.g., Muehlenbachs, 1979; Lawrence, 1980). They are similar, however, to pillow basalts dredged from the uppermost portion of the oceanic crust from the Mid-Atlantic Ridge at 45°N latitude (Muehlenbachs and Clayton, 1972).

Calcites show very low alkali concentrations, confirming the incompatibility of alkalis with the calcite structure. The K content of Sample 597A-7,CC is unusually high, whereas the two other samples contain as much K as most vein calcites (e.g., Staudigel, Hart, et al., 1981).

Sr concentrations from the upper two carbonate samples suggest that the carbonates may have precipitated close to equilibrium with seawater, assuming Sr/Ca partition coefficients of 0.055 to 0.058 (Katz et al., 1972; Baker et al., 1982). The low Sr/Ca ratio of the deepest calcite sample, in conjunction with its slightly lower  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio, suggests that this sample may have formed from solutions that had partially equilibrated with the basaltic host rock. For this reason, we have excluded the data from the lowermost Sample 597C-11-3, 82-88 cm, Piece 5f, from further analysis. Thus, the  $^{87}\text{Sr}/^{86}\text{Sr}$  of seawater-derived calcites of Site 597 range from 0.708192 to 0.708349 (Table 3).

To compare the range of  $^{87}\text{Sr}/^{86}\text{Sr}$  values for seawater-derived vein calcites to the variation in seawater Sr isotopic ratios through time, we also analyzed fish teeth of various ages. Such a test of the seawater variation, independent of previous determinations by Burke et al. (1982), was necessary, because Burke et al. (1982) did not provide data for the age control or possible diagenetic effects. Our seawater data, along with the data from Palmer and Elderfield (in press) (plotted in Fig. 1), support the findings of Burke et al. (1982).

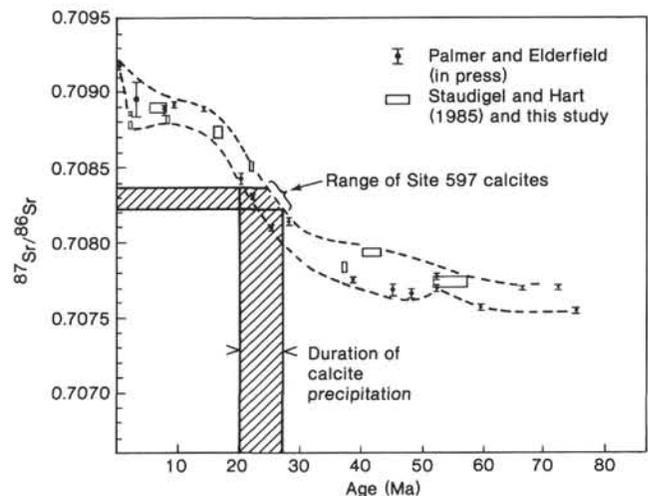


Figure 1.  $^{87}\text{Sr}/^{86}\text{Sr}$  of seawater versus age, after Palmer and Elderfield (in press) and Staudigel and Hart (1985) and this study. The shaded area illustrates the duration of calcite precipitation, inferred from the range of  $^{87}\text{Sr}/^{86}\text{Sr}$  in calcites.

## DISCUSSION

The abundance of chlorite as an interstitial phase, particularly in coarsely crystallized massive flows, supports the prediction of the high extent of deuteric alteration during the slow cooling of rapidly deposited massive flows. The petrographic evidence for the relatively late formation of carbonate and celadonite veins suggests that they may be used for determining the age of the latest phases of alteration. When comparing this age with the emplacement age of the crust, the duration of alteration can be inferred.

The age of calcite precipitation is approximately 20 to 28 Ma and is based on two calcites, one present at the basalt/sediment interface and one at 35.5 m sub-basement depth. Peterson et al. (this volume) determined K/Ar ages of celadonites from different portions of the Site 597 basement sections. These celadonites were formed at ages of 19.9, 19.3, and 13.1 Ma. Nannofossil evidence and magnetic lineations suggest that the crust at Site 597 was emplaced approximately 28.6 Ma (Rea, this volume). Thus, calcites and most celadonites formed as long as 8 m.y. after crustal formation, but one celadonite may have formed as late as 13 m.y. after crustal formation. These age estimates of ocean-floor alteration are also in agreement with data from Rb/Sr isochron dates on celadonites from slow-spreading ocean crust and from the Troodos ophiolite; this suggests that ocean-floor alteration probably lasts for about 13 m.y. and possibly as long as 20 m.y. (Staudigel et al., in press; Staudigel and Hart, 1985). Thus, there is currently no evidence for a difference in the duration of alteration in oceanic crust generated at different spreading rates.

The low oxygen isotopic temperatures of vein calcite formation at Site 597 indicate that the upper 100 m of oceanic crust at this site were practically at ambient bottom-water temperature during the time of calcite precipitation. We infer that seawater circulated freely in a very permeable environment, which was suggested from speculations based on the lithology at this site. The fairly constant  $^{87}\text{Sr}/^{86}\text{Sr}$  isotopic ratios, similar to 20 to 28 Ma seawater, as well as the high Sr/Ca ratios of vein carbonates, suggest that the two upper carbonates were probably derived from unaltered seawater. Thus, the hydrothermal solutions producing carbonates at this site in fast-spreading crust were not significantly altered from interaction with the basalts. The high Sr/Ca ratios also support the evidence of a highly permeable crust at Site 597 down to a sub-basement depth of 35 m. This site, however, is unique for its unusually low temperatures of alteration, because pure seawater-derived carbonates were also found at slow-spreading ocean crustal sections, such as at Sites 105, 417A, 418A, and 332B (e.g., Richardson et al., 1980).

These data suggest that alteration may not necessarily last longer in fast-spreading crust than in slow-spreading crust, but that the relatively low temperatures of calcite precipitation and the high modal abundance of chlorite in some massive flows may be unique for Site 597 and may be typical for crust from fast-spreading centers.

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