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Controls on temporal variability of the geochemistry of the deep Cariaco Basin

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Abstract

Studies of the Cariaco Basin on the continental shelf of Venezuela, as a part of the Carbon Retention In A Colored Ocean (CARIACO) program, have revealed that the chemistry of the deeper waters of the system is more variable than previously believed. Small oxygen maxima have been observed on a number of occasions at depths where oxygen was previously absent, suggesting the occurrence of intrusions of oxygenated water into the region of the oxic/anoxic interface (250–300 m). Apparently because of these events, the oxic/anoxic interface deepened by about 100 m during the period of our observations. We also observed a dramatic decrease in H_2S concentrations at all depths below the oxic/anoxic interface during this same period. Bottom waters, for example, had an H_2S concentration of about 75 μM in November 1995, but since November 1997, concentrations in bottom water have not exceeded 55 μM. Water of sufficient density to sink to the bottom of the Basin has been observed on one occasion at sill depth just north of the eastern sill. However, based on a simple box model, the decrease in deep-water sulfide does not appear to be due to intrusion of oxygenated water alone, as concentrations of other measured species, and of hydrographic parameters, have remained constant with time. Instead, we postulate that an earthquake that took place in July 1997 resulted in a turbidity current that transported large quantities of coastal sediment containing oxidized iron into the deep waters of the basin. If the final products of reaction were elemental sulfur and iron sulfide, the sediment associated with the oxidized iron would have produced a turbidite layer about 10 cm thick. Previous earthquakes have produced turbidites of similar thickness. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Anoxic basin; Oxic-anoxic interface; Temporal variability; Intrusion; Hydrogen sulfide Regional Index Terms: Caribbean Sea; Venezuela; Cariaco Basin

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1. Introduction

The Cariaco Basin is the largest, truly marine, anoxic basin on earth. It has been widely used as a laboratory for studying the biogeochemical processes that occur as carbon is degraded under oxic, sub-oxic, and anoxic conditions. The chemistry of the deep waters of the Basin has changed with time, resulting in monotonic increases in temperature, salinity, and concentrations of several nutrient species (Spencer and Brewer, 1972; Richards, 1975; Scranton, 1977, 1988; Scranton et al., 1987; Zhang and Millero, 1993). Shorter-term variability in the depth of the oxic/anoxic interface has also been noted (Richards, 1975; Herrera and Febres-Ortega, 1975). However, because of the relative infrequency of cruises, it has been difficult to determine the extent to which observed changes are affected by short-term phenomena (seasonal upwelling: Okuda et al., 1969; Herrera and Febres-Ortega, 1975), longer term climatic variations (El Niño), or episodic events (earthquakes: Zhang and Millero, 1993). Although Holmen and Rooth (1990) convincingly demonstrated from tritium data that relatively "young" water must reach the deep waters of the basin on a decadal time scale, previous studies have been unable to investigate processes of ventilation in any detail. In particular, there have been no data to permit assessment of the relative importance of intrusions of dense water over the sill as compared to entrainment of oxygenated water in turbidity currents induced by local earthquake activity.

In 1995, a time series of hydrographic and biogeochemical parameters was begun at a station located in the eastern Cariaco Basin as part of the CArbon Retention In A Colored Ocean (CARIACO) program. Monthly cruises have been carried out by the Estación de Investigaciones Marinas de Margarita (EDIMAR) of the Fundación La Salle de Ciencias Naturales on Isla Margarita, in collaboration with the Universidad de Oriente (Cumana), the University of South Florida (USF), the State University of New York (SUNY) at Stony Brook, and the University of South Carolina (USC). In addition, on three cruises a year, SUNY investigators provided detailed data on microbiological parameters. USC has maintained a sediment-trap time series at the site. After three years of monthly observations, it is clear that the system is neither the quiescent, steady-state environment, nor the gradually changing environment, envisioned by previous workers. In this paper, we examine the geochemical variations observed near the oxic/anoxic interface and in the deep water during our initial three-year period of observation.

2. Background

The Cariaco Basin is a deep, isolated depression on the continental margin of Venezuela located at about 10°30′N, 65°W. The Basin actually consists of two sub-basins about 1400 m deep separated by a saddle that extends to 900 m. Exchange of water with the open Caribbean is severely restricted by shallow sills. The two deepest connections are located, in the east, between Isla Margarita and Isla Tortuga, and, in the west, between Isla Tortuga and Cabo Codera. The eastern sill extends to 135 m (Febres-Ortega and Herrera, 1975) and the western sill to 146 m (Richards and Vaccaro, 1956) (Fig. 1).

The Cariaco Basin waters are stratified due to the temperature gradient rather than gradients in salinity as is the case in the Black Sea. The temperature contrast between waters at 150 m and the

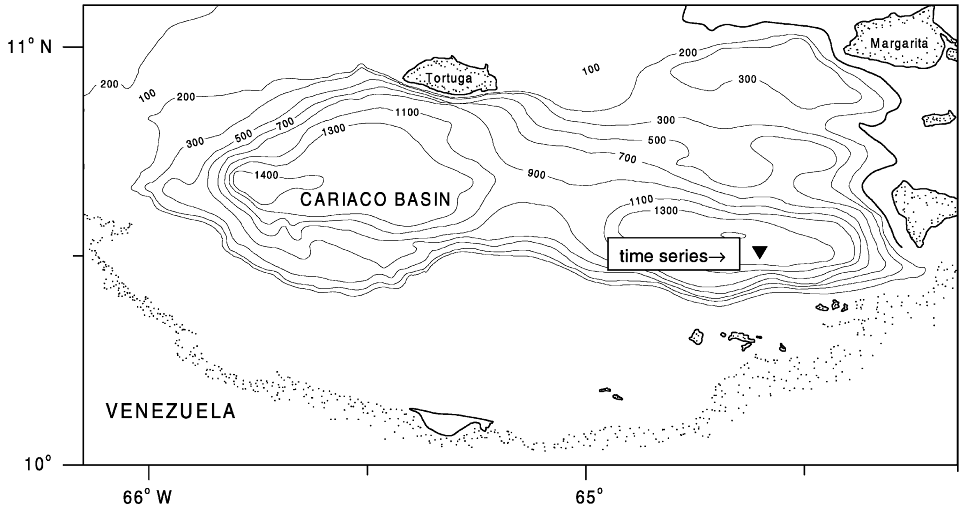

Fig. 1. Bathymetric map of the Cariaco Basin. The site of the CARIACO time series is indicated. Note the shallow sills surrounding the basin and the deeper channel to the North of the Cariaco station. Map from Thunell et al. (2000).

bottom (1400 m) is only 1.8°C, and the salinity contrast is only about 0.3. Potential temperatures at the bottom of the Basin are currently about 16.9°C, compared with about 4.4°C at comparable depths outside the basin (M. Bacon, personal communication), reflecting the shallow water source of deep basin waters. A strong pattern of seasonal upwelling is observed in waters shallower than 120 m, with maximum upwelling normally occurring between March and May (Herrera and Febres-Ortega, 1975; Muller-Karger and Aparicio, 1994). Primary production at the CARIACO station ranges from about 0.45 to 6.86 $\mathrm{g\,C\,m^{-2}\,d^{-1}}$ (Ramon Varela, EDIMAR, personal communication). The vertical flux of this carbon into the deep basin, combined with weak vertical mixing caused by a strong salinity maximum at about 100 m and the limitations in horizontal mixing that result from the shallow sills, results in a strong depletion of oxygen within the system below the top 100 m, and complete anoxia below about 250–350 m.

The Cariaco Basin has received considerable attention from chemical oceanographers over the years due to the relatively stable, permanently anoxic character of the system. These characteristics have allowed progressively more sophisticated studies of the processes controlling carbon cycling, and suboxic and anoxic diagenesis in the water column. Although modeling approaches are different, there is general consensus on the major factors of importance to the geochemistry of Cariaco Basin waters.

Scranton et al. (1987) and Scranton (1988) showed that temperature, salinity, and concentrations of silica, sulfide, and methane increased steadily with time between the middle 1950 s and the early 1980 s. Metabolism of organic matter is clearly a key process driving these changes. Scranton et al. (1987) and Scranton (1988) hypothesized that the major site of reaction was in sediments, although they suggested that mid-depth dissolution of silica and oxidation of methane near the oxic/anoxic interface were also important. Zhang and Millero (1993) found that increases in ΣCO_2, ammonium, phosphate, and hydrogen sulfide were consistent with the metabolic oxidation of organic matter during sulfate reduction as described by Richards (1975). Temperature and salinity increased as well, due to downward mixing of warm salty surface water, geothermal heating (in the case of temperature) (Scranton et al., 1987), and episodic deep intrusion events (Holmen and Rooth, 1990).

Holmen and Rooth (1990) proposed that injection of surface water into the deep portions of the Cariaco Basin occurs via two distinct mechanisms. They suggested that a high-salinity but low-volume source, originating along the Venezuelan coast, would be capable of sinking to the bottom. They also suggested that water injection at the sills represented a larger source providing water that sinks to mid-depths. Based on extrapolations of sulfide and ammonium trends, Zhang and Millero (1993) suggested that the entire basin had experienced overturn in about 1914–1916, and that, after overturn, both ammonium and sulfide concentrations of the deep water were close to zero, while the phosphate concentration was about 1 μM, and silicate 22 μM. They also noted that major earthquakes occurred in the area in 1900 and 1929. Since the early 1900 s, concentrations of hydrogen sulfide and the other nutrient elements have increased relatively linearly with time (Scranton et al., 1987). In this paper, we examine changes in oxygen and hydrogen sulfide over time at the CARIACO time-series site for the period November 1995–November 1998.

3. Methods

Water samples were collected with Teflon-lined 8 l Niskin bottles mounted on a Seabird Rosette system. Upon retrieval, and before being opened for sampling, Niskin bottles were fitted at the top with a source of pressured nitrogen gas to reduce oxygen contamination. Samples were drawn from one Niskin bottle at a time, to minimize the likelihood of oxygen diffusion into the sample.

Oxygen profiles were obtained using both Winkler titrations for discrete samples and a YSI oxygen probe mounted on a Seabird CTD system (SBE-19 and -25). The YSI oxygen probe tends to be affected negatively by contact with hydrogen sulfide, and must be replaced periodically. Therefore, we use the YSI data primarily to identify the presence of relative maxima in oxygen concentration, rather than for determination of absolute concentrations at low levels. The observed agreement between probe data and Winkler measurements suggests that this approach is appropriate. For the first two years (CAR1–CAR24: November 1995–October 1997), oxygen in discrete samples was measured using the standard Winkler technique described in Strickland and Parsons (1972). Precision for these samples was about ± 3 μM. After CAR24, the method used was a modified Winkler method similar to that described in the JGOFS manual and based on that of Strickland and Parsons (1972) as modified by Aminot (1983). Precision for the modified method was about 1.5 μM, especially at low values of oxygen such as are seen near the interface. The limit of detection of oxygen is estimated to be on the order of 5 μM. Winkler oxygen values below this level are questionable, due to possible artifacts associated with addition of reagents. Although the relative changes in oxygen concentration with depth seem the same between the two methods, the absolute concentrations measured are slightly offset (see below). Therefore, we have used the YSI-probe data only to identify the presence and the size of the maxima, as we are less confident about the absolute oxygen values provided by this system. For example, the YSI probe consistently reports deep-water oxygen values as 1–3 μM negative.

Sulfide concentrations were measured using a modification of the standard method of Cline (1969). Samples were taken with no bubbles using gas-tight syringes and were added to vials containing 0.5 ml of ZnAc (50 mM) or $ZnCl_2$ (5 mM) solution. ZnS_2 precipitates immediately, and samples can be stored for periods of several months refrigerated (Goldhaber, 1974; Robert Aller, personal communication). No difference was noted between samples fixed with the two reagents, or for samples stored for periods of a few days compared with periods of weeks. Standards were prepared from $NaS_2 \cdot 9H_2O$, and were diluted with N_2-purged surface seawater from the Cariaco Basin. Standard curves were run with each set of samples. For the later cruises, samples were taken in triplicate. Variation of molar absorptivity of the calibration curves obtained from six different cruises, including cruises before and after the sulfide decrease was noted, is about $\pm 10\%$. Precision of triplicate measurement was about $\pm 0.8\%$ for concentrations greater than 1 μM. Absolute accuracy is somewhat harder to estimate, but sample values more than one standard deviation above the value of the replicate error for the lowest samples (order of 1–2 μM) probably indicate the true presence of sulfide.

Methane samples were collected into 50 ml serum vials by overflowing several volumes and then sealing the vials with Teflon-coated septa and crimp seals. Samples were killed with 0.15 ml of 10 N KOH (which raises the pH to 12 or more) prior to capping. A headspace was produced in the vial in the laboratory using a double-ported needle to withdraw a small amount of water (3 ml) and replace it with "low-methane" air obtained from Scott-Marin, as described by Neill et al. (1997). Samples were equilibrated by shaking in a bath at a known temperature, and were analyzed in the laboratory on a Carle AGC 211 gas chromatograph using a Poropak R column. Data were quantified using commercially prepared methane gas mixtures. Because of trace amounts of methane in the air used to create the headspace, the detection limit for this method is about 10 nM. Precision is $\pm 3\%$.

Samples for phosphate and silicate were collected during the monthly CARIACO cruises in plastic bottles and were frozen until analysis at either UDO (Cumana) or USF. Standard techniques were used for both species (Strickland and Parsons, 1972). USF follows the recommendations of Gordon et al. (1993) for the WOCE WHP project for nutrient analysis.

4. Results

4.1. Hydrography

The overall hydrography of the Cariaco Basin as seen during CARIACO is very similar to that observed in previous studies. Surface temperature and salinity vary with upwelling strength. Subtropical Mode Water creates a salinity maximum at about 100 m. Data from CARIACO are plotted with data from a number of historical reports (listed in Table 1) in Fig. 2. All data were collected below 1200 m as in Scranton et al. (1987). There continues to be a trend toward increasing temperature and salinity as reported earlier. The potential temperature in the deep water is slightly higher after mid-1997 as compared with earlier cruises in the CARIACO series. However, the difference is less than the apparent cruise-to-cruise variability prior to CAR21 (July 1998) and within the 95% confidence limits of the long-term trend.

4.2. Oxygen

Oxygen concentrations decrease rapidly below the surface, and an oxic/anoxic interface is located below about 240 m (Figs. 2–4). During CAR1 (November 1995), the interface lay at 250 m,

Table 1
Sources of historical data

Cruise date	Years after Jan 1, 1954	Reference
Feb 1955	1.2	Richards and Vaccaro (1956)
Nov 1957	2.83	Richards and Benson (1961)
Nov 1965	11.8	Richards (1970)
Sep 1968	14.7	Fanning and Pilson (1972)
Jul 1971	17.6	Spencer and Brewer (1972)
Dec 1973	19.9	Bacon et al. (1980)
Feb 1974	20.2	Wiesenburg (1975) and Reeburgh (1976)
Feb 1975	21.3	Scranton (1977) and Scranton et al. (1987)
Nov 1982	28.9	Hastings and Emerson (1988), Scranton (1988) and Bacon (personal communication)
Mar 1986	32.2	Zafiriou (personal communication) and Scranton (1988)
Jun 1990	36.5	Zhang and Millero (1990)
Nov 1995–Nov 1998	41.8–44.8	CARIACO (this study)

while in contrast, during CAR36 (November 1998), oxygen levels did not reach zero until about 320 m. Between these dates, the interface depth has fluctuated, although generally between November 1995 and mid-1997, the oxic/anoxic interface appeared to lie at a depth of about 240–260 m based on the YSI-probe data, while after July 1997, the interface was typically below 300 m. This pattern has been confirmed with discrete samples. A comparison of discrete oxygen samples and the YSI-probe results is shown by the results in Fig. 3, where both discrete samples and probe data for CAR29 are plotted. The probe data for this date (March 1998) clearly show evidence for numerous small oxygen maxima at depths just above the oxic/anoxic interface.

The change in the depth of the interface seems to have been associated with lateral intrusion of oxygenated water, presumably from outside the sill, into the basin. The strongest evidence for such input is small oxygen maxima appearing below the depths at which oxygen concentrations first reach levels less than 20–30 μM (Figs. 3–5). We believe that these represent intrusions of oxygenated water, because on cruises to the same station in preceding months, oxygen concentrations at the depths of these maxima were either zero or much lower than that observed at the maximum. In addition, the maxima seem to disappear with time. Attempts to identify associated temperature or salinity anomalies have not been successful (Astor, unpublished data), probably due to the very small contrast between the temperature and salinity of intruding water and temperatures and salinities at the oxic/anoxic interface. Intrusion of water, more oxygenated than surrounding water, was first noted between 200–240 m in January 1997 (see Fig. 5). In January 1997, there was no evidence for intrusions in the discrete samples, but our sample at 200 m may have missed the feature. CTD data for August 1997, December 1997, and March 1998 also showed evidence of intrusions based on the presence of oxygen maxima near the oxic/anoxic interface. In addition, discrete samples indicated the presence of increases in oxygen to depths of 300 m in April and May 1996, and to 310 m in June 1997. Although no oxygen maxima were observed on these latter dates, oxygen concentrations above the interface were noticeably higher than in the preceding month.

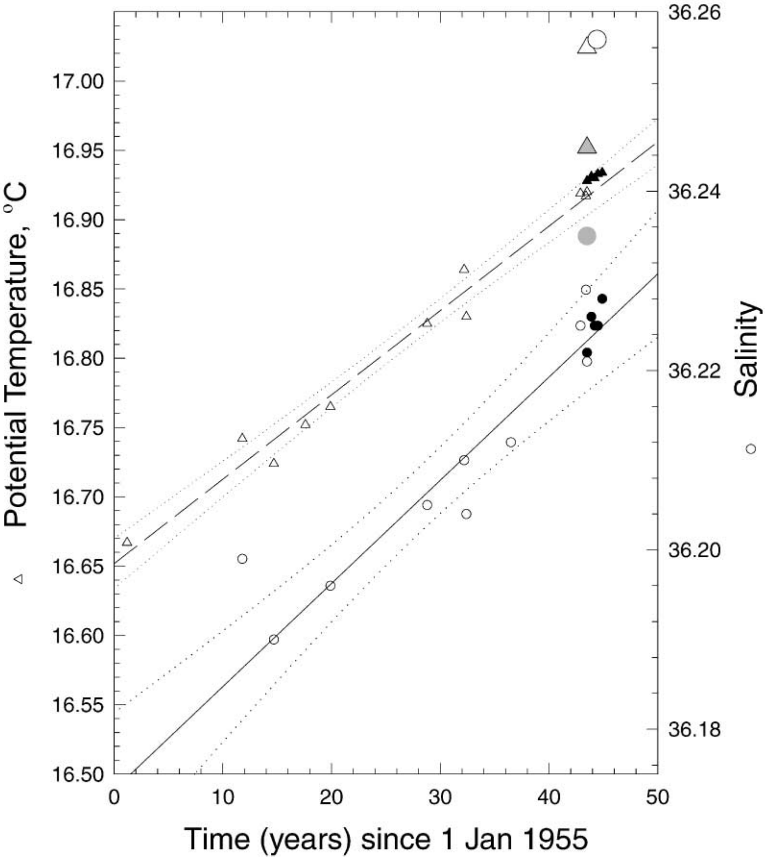

Fig. 2. Potential temperature and salinity trends with time for water below 1200 m. The open symbols are historical data, together with data taken on selected CARIACO cruises (those for which sulfide data are available) at depths greater than 1200 m prior to November 1997. Sources for historical data are listed in Table 1. Solid symbols represent data from cruises on or after November 1997. The larger symbols (salinity ○, ●; potential temperature △, ▲) are predictions from the models, with filled symbols indicating addition of 2.2×10^{14} l water and open symbols indicating an addition of 8.9×10^{14} l water.

When available, oxygen probe and discrete samples agreed well at depths above 270 and below 330 m (for example, Fig. 3). The discrepancies observed in the interface region (order of 2 μM) are probably partially due to lag in electrode response during down casts and possibly also due in part to trace amounts of oxygen that may be introduced into discrete samples during addition of the reagents. In addition, discrete samples are collected on up casts, but YSI-probe data are recorded on down casts, possibly resulting in mismatch due to ship's drift or the passage of internal waves between the up- and down-casts.

Table 2 provides a summary of the depths and thickness of the presumed intrusions. Maxima were seen at other times, at depths where maxima were seen on immediately previous cruises, and therefore may have been "relict" in some sense (Astor, personal communication). Because of our cruise schedule, we are unable to estimate whether the frequency of water injection at these depths

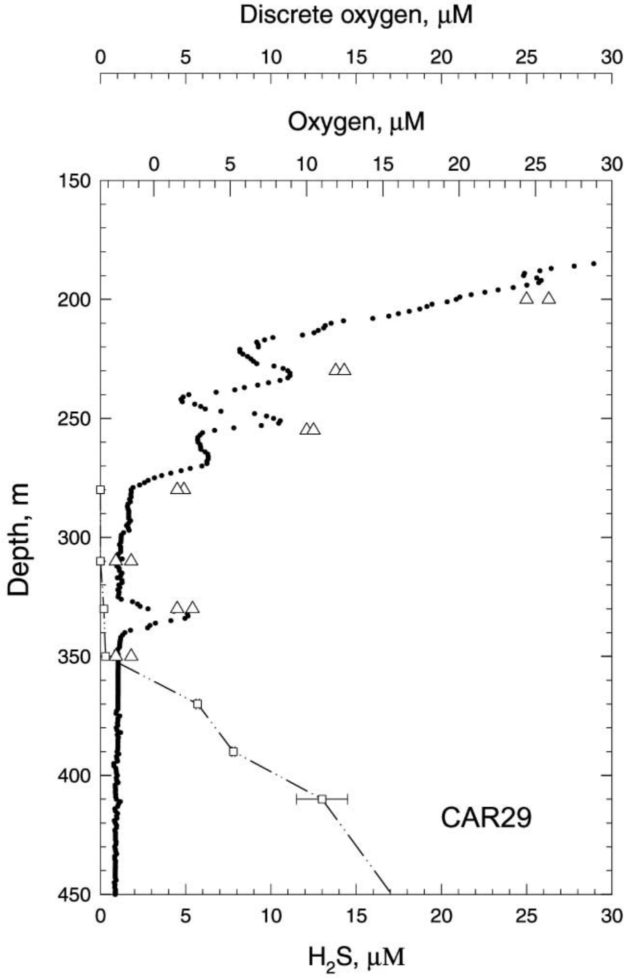

Fig. 3. YSI (●) and discrete (Winkler) data (△) for CAR29 (March 1998). The profile also includes data for H_2S (□).

is higher than at monthly scales. However, in mid-1997 the oxic–anoxic interface (the depth at which oxygen became undetectable and that at which sulfide was first measurable) shifted downward approximately 50–100 m.

4.3. Hydrogen sulfide

The hydrogen sulfide profiles measured during CARIACO are also shown in Fig. 4. Hydrogen sulfide was first measured (and detected by odor) at depths of 250 m during CAR1, but was not noted until below 310 m on CAR25, 350 m on CAR29, 330 m on CAR32, and 320 m on CAR36. Sulfide concentrations were consistently lower at all depths on and after November 1997 as compared to November 1995. Bottom-water sulfide concentrations for CAR25 and CAR29 were about 51 µM and for CAR32 and CAR36 were 40 and 46 µM respectively, compared to 76 µM for CAR1. Comparison of November 1995 data with data from Knorr 99, which were collected in 1982

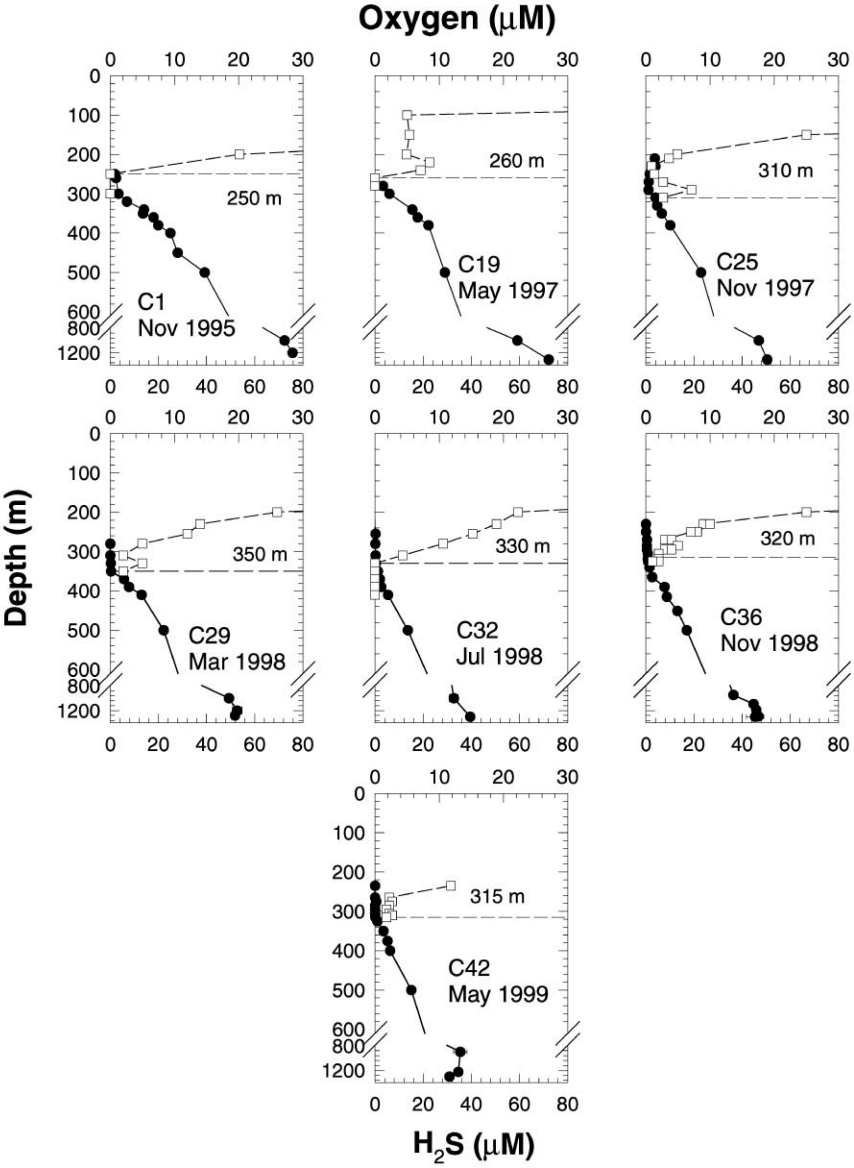

Fig. 4. Oxygen (□) and hydrogen sulfide (●) profiles for all CARIACO cruises for which there is hydrogen sulfide data and which were conducted between November 1995 and November 1998. The horizontal dashed line in each diagram represents our best estimate of the depth of the oxic/anoxic interface.

(Jacobs et al., 1987), indicates that oxygen concentrations were similar in 1982 and 1995, but sulfide concentrations had increased smoothly at all depths below the interface during this period. Knorr 99 data also show a zone less than 50 m thick where both oxygen and sulfide concentrations were less than 10 μM. During CAR1, this layer was about 100 m thick. In contrast, CARIACO cruises after May 1997 show broad regions of up to 200 m thick where both oxygen and sulfide values are below 10 μM (Fig. 4).

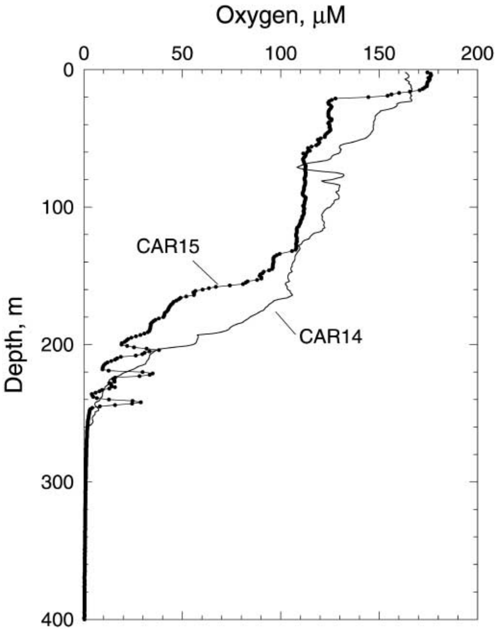

Fig. 5. Oxygen profile obtained by CTD on CAR15 (January 1997) showing evidence of mid-depth intrusion. Data from the previous cruise (CAR14 in December 1996) showed no sign of mid-depth maxima.

Table 2
Observations of intrusions into the Cariaco Basin

Date, intrusion first observed	Depth of deepest oxygen observed[a] (m)	Depth of secondary oxygen maximum[b] (m)	O_2 concentration at secondary oxygen maximum[b] (μM)	Thickness[c] (m)
Jan 1997	253	205	38	≈ 10
		222	35	≈ 15
		240	29	≈ 10
Jun 1997	310	None	—	–
Aug 1997	300	275	17	40
Dec 1997	300	230	45	≈ 10–20
Feb 1998	310	None	—	–
Mar 1998	300	277	20	27
Jun 1998	290	260	16	30

[a] Based on discrete oxygen samples.

[b] Based on data from the YSI oxygen probe on the CTD. The primary oxygen maximum was located at or near the sea surface. For dates where no maxima were observed, addition of oxygen was identified by increased oxygen penetration depths compared to the previous month, together with a broad increase in oxygen levels within the 50 m above the interface.

[c] Thickness of maximum determined from YSI-probe trace.

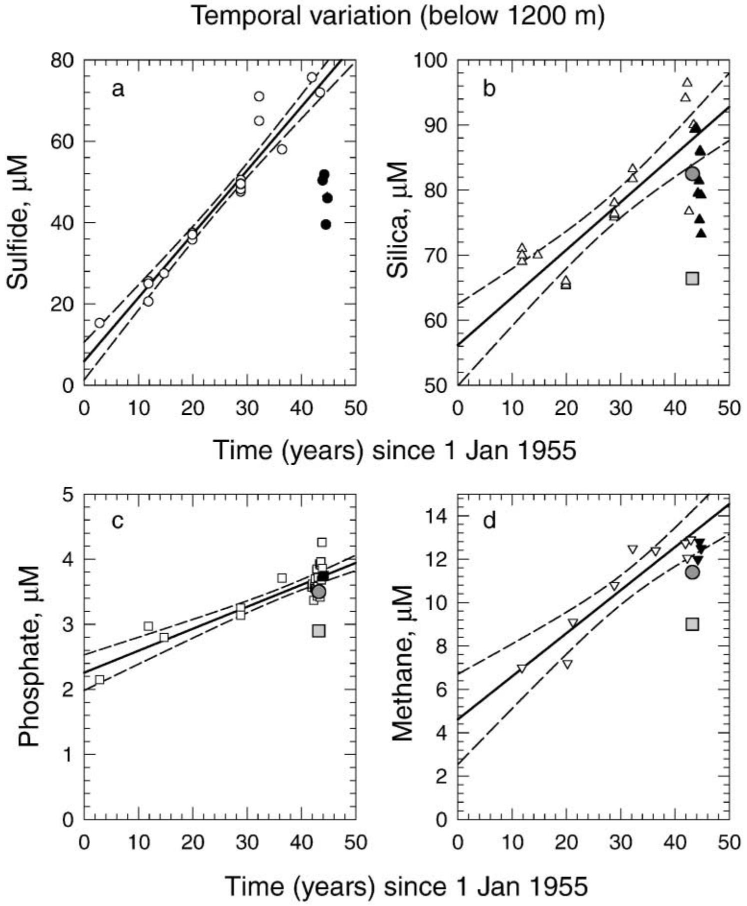

Fig. 6. Trends with time for (a) sulfide, (b) silica, (c) phosphate, and (d) methane in deep (> 1200 m) water of the Cariaco Basin. All data with which we are familiar are plotted. The lines represent best-fit linear regressions. Sources for data are listed in Table 1. On each panel, the small filled symbols represent data collected on or after November 1997. The larger symbols in b, c and d are predictions from the models, with the large filled circles indicating a sulfide oxidation product of elemental sulfur and the large filled squares indicating a sulfide oxidation product of sulfate.

Long-term rates of increase of hydrogen sulfide at the bottom of the Cariaco Basin (waters greater than 1200 m) estimated by Scranton et al. (1987) and by Zhang and Millero (1993) have been about 1.5 µM yr^{-1} since about 1954. The data from our November 1995 cruise are consistent with this long-term trend (Fig. 6a; open circles). However samples collected beginning in November 1997 (shown as solid circles) are considerably below the trend line.

4.4. Methane

Methane concentrations were measured on CAR1 (November 1995), CAR5 (May 1996), CAR13 (November 1996), CAR29 (March 1998), CAR32 (July 1998), and CAR36 (November 1998), and are shown in Fig. 7 with a detailed profile obtained on AII-86 in 1975 (Scranton, 1988). Methane

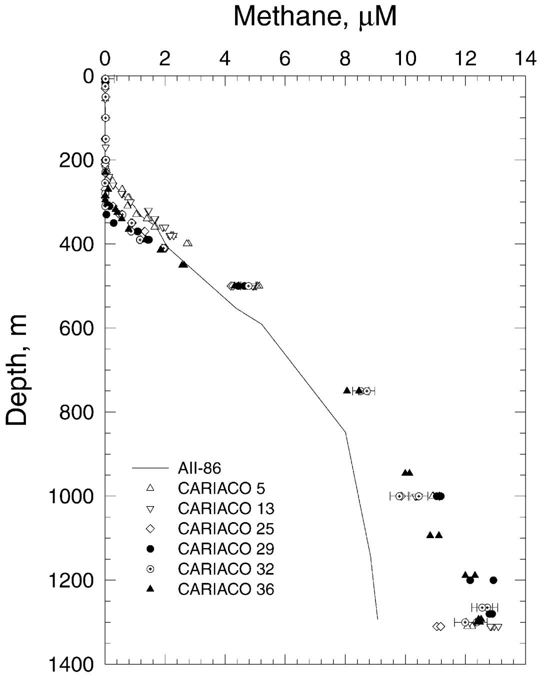

Fig. 7. Methane profiles from CARIACO cruises. The dotted line represents the profile from AII86 (station 2225) collected in the Eastern Basin of the Cariaco Basin in 1975 (Scranton, 1988). Error bars represent standard deviations calculated from triplicate analyses. There is no significant change in deep methane concentration over the period of the CARIACO program.

concentrations were very low in the upper portions of the water column (below our detection limit for the vial method) and increased sharply with depth at the O_2/H_2S interface. Compared with data from 1975, methane concentrations have increased at all depths below about 500 m, consistent with the predictions of Scranton (1988). Concentrations in deep water during the CARIACO program have consistently been about 12.5 ± 0.4 μM and agree with projections from previously reported long-term historical trends (Scranton, 1988; Fig. 6d). The deepest sample from CAR25 is slightly lower than those from other cruises, but we are not sure whether this value is real or not since it represents a single point. There is no indication of a decrease in concentrations, either in November 1997 or later.

4.5. Silica and phosphate

Nutrient data for CARIACO cruises before March 1998 were obtained from colleagues at UDO, Cumana. After that, measurements were conducted at USF. There are no systematic differences between the groups. Data from below 1200 m are consistent with previously reported values (Figs. 5b and c). USF silica concentrations for November 1997–November 1998 average 81.7 ± 5.3 μM (± 6.5%). Phosphate concentrations for the same period are 3.7 ± 0.04 (± 1.1%). We have no explanation for the variability seen in the silica data, although recent experiments (Kent Fanning, personal communication) suggest that frozen silicate standards of 80 μM are considerably more variable than expected. Although the reason for this variability has not yet been determined, it is possible that freezing may be responsible for the high cruise-to-cruise variability of measured deep silicate levels. Inspection of the data provides no reason to remove any particular observation. Results for CARIACO bottom-water data for both phosphate and silica are shown in Fig. 6b, together with the long-term trends. Phosphate concentrations in 1995–1998 lie on the long-term trend described by Zhang and Millero (1993), and there is no sign of a decrease following summer 1997. Silica concentrations are slightly lower after summer 1997, but given the scatter of the data, it is not possible to verify this trend.

5. Discussion

The CARIACO observations collected between 1995 and 1998 suggest that two processes have perturbed deep waters of the Cariaco Basin within this period. The first process involves an increase in the frequency of transport of oxygenated water below 200 m to depths as great as 350 m. The second process is related to the major earthquake that took place in July 1997.

5.1. *Mid-depth intrusions*

Variations in the depth at which oxygen disappears (the oxic–anoxic interface) have been reported in the past (Richards, 1975; Zhang and Millero, 1993), although temporal and depth resolution has been poor. Actual intrusion events, as evidenced by maxima in dissolved oxygen at mid-depth, have not been reported previously. Repeated observations of small increases in dissolved oxygen concentration within the oxic/anoxic transition region during the CARIACO program provide substantial evidence for mid-depth intrusions into the Cariaco Basin (Figs. 3 and 4). Unfortunately, we do not have adequate spatial coverage to track the oxygen maxima as they enter the Cariaco Basin and spread to the CARIACO site.

The effects of the intrusions on sulfide concentration are noticeable. Oxygen gradients are similar for 1995 (CAR1) and 1998 (CAR36) at depths above about 230 m (Fig. 4), but sulfide gradients are markedly less steep in 1998 than 1995. This implies that the vertical diffusive flux of oxygen to the interface remained roughly constant, but that the diffusive supply of sulfide decreased with time. This could affect chemoautotrophic activity of bacteria that mediate aerobic sulfide oxidation. In addition, accumulation of oxidation products such as particulate manganese and iron above the interface, resulting from oxygenated intrusions at depths which were previously anoxic, could provide an important oxidant pool to local bacterial populations (Taylor et al., 2001).

5.2. *Deep intrusions*

Temporal variation in deep-water concentration of selected chemical species is known to occur (Richards, 1975; Scranton et al., 1987; Zhang and Millero, 1993). These changes have seemed to be slow and predictable (Scranton et al., 1987) and have been typically represented by the long-term trends of θ (potential temperature), salinity, and several nutrient species as shown in Figs. 1 and 5.

The CARIACO time series has only been in operation for three years. Therefore, in the face of analytical and sampling variability, we have been unable to observe trends in deep-water hydrography and chemistry from our data alone. Relative to historical observations, potential temperature, salinity, phosphate, silica, and methane measurements from the CARIACO program generally lie on the linear trends predicted from previous studies (Scranton et al., 1987; Scranton, 1988; Zhang and Millero, 1993).

In contrast, sulfide concentrations show a major deviation from the long-term trend beginning in mid-1997. The abrupt shift in hydrogen sulfide concentrations occurred between May 1997 (CAR19) and November 1997 (CAR25). Indeed, hydrogen sulfide concentrations for CAR1 (November 1995) lie very close to the long-term line (Fig. 6). A few deep samples obtained from CAR19 (May 1997) also indicate deep-water values on the order of 75 μM. In contrast, sulfide values at all depths below the interface were significantly lower in November 1997 (CAR25), March 1998 (CAR29) July 1998 (CAR32), and November 1998 (CAR36) than was expected based on the CAR1 profile or on the long-term trend. Apparently, sulfide was removed from the water column in large quantities, without altering the concentrations of the other dissolved parameters measured.

One potential cause for decreased sulfide concentrations could be arrival of oxygenated water into the bottom of the Cariaco Basin. This mechanism would be comparable to the interface intrusions noted above. Table 3 shows the pre- and post-quake values of θ, S, and sulfide for waters below 1200 m at the CARIACO station. The volume of water below 550 m in the Cariaco Basin, excluding the western sub-basin below 900 m (the depth of the saddle separating the eastern and western basin), is 22.3×10^{14} l. We exclude the deep waters of the western sub-basin, as water intruding into the bottom of the eastern sub-basin would be prevented from reaching the western basin by the 900 m sill. Data for sill depth properties are taken from cruises at the NOR-A site (11°20′N 64°45′W; approximately 1000 m water depth). This station has been occupied approximately every 6–8 months as part of CARIACO in an effort to document the hydrography at the Tortuga sill. In February 1997, potential density at 130–160 m ($\sigma_\theta = 26.476$) at station NOR-A slightly exceeded the Cariaco Basin bottom-water density ($\sigma_\theta = 26.474$). Values of phosphate and

Table 3
Mass balance inputs and results

	Initial value in deep Cariaco Basin	Values outside sill at sill depth	Final observed value in deep Cariaco Basin	Predicted final value (product = S°)	Predicted final value (product = SO_4)
$V_{\text{below 550 m}}$	22.3×10^{14} l				
θ	16.919°C	17.286	16.932°C	16.952	17.024
S	36.225	36.340	36.226	36.235	36.258
H_2S	73 μM	0 μM	50 μM	Forced to balance[a]	Forced to balance[a]
O_2	0 μM	115 μM	0 μM	0 μM	0 μM
PO_4	3.8 μM	0.5–1 μM	3.7 μM	3.5 μM	2.9 μM
SiO_2	90 μM	7.5 μM	85 μM	82.5 μM	66.4 μM
CH_4	12.6 μM	≈ 0.1 μM	12.6 μM	11.4 μM	9.0 μM
$V_{\text{intrusion}}$				2.2×10^{14} l	8.9×10^{14} l

[a] Complete conversion of sulfide to either elemental sulfur or SO_4.

silica for this same station are listed, together with the temperature and salinity data, in Table 3. The nutrient data are estimated from a sample at 100 m (no samples were taken deeper on this date) since for other dates nutrient concentrations at 100 and 150 m were similar.

We will attempt to evaluate the effect of input of water of this type to deep basin chemistry as it is the only example of dense water outside the sill for which nutrient data are available. Denser water from outside the sill would be likely to have higher nutrient and lower oxygen concentrations than those we observed. Our approach uses a simple box model for a number of water column properties. We envision a bolus of water moving over the sill, entering the Cariaco basin, and sinking. This water would mix with waters within the basin as it reaches a stable depth. Oxygen in the intruding water and sulfide in Cariaco deeper waters could react to form either sulfate or elemental sulfur.

$$2O_2 + H_2S \rightarrow SO_4^{2-} + 2H^+,$$

$$O_2 + 2H_2S \rightarrow 2S_{solid} + 2H_2O.$$

In order to lower the hydrogen sulfide contained in 2.2×10^{15} l (volume of water below 550 m) by 23 μM (a total of 5×10^{10} mol of sulfide), between 2.5 and 10×10^{10} mol of O_2 must be supplied to the deep water. The lower number applies if the sulfide is converted to elemental sulfur and the higher number applies if the product of oxidation is sulfate. This represents between about 2×10^{14} and 9×10^{14} l of water with the sill depth composition noted in Table 3 (10–40 % of the water in the Cariaco Basin below 550 m).

Fig. 6 and Table 3 show that deep concentrations of phosphate, silica, and methane in late 1997 are consistent with intrusion of about 2×10^{14} l of water. However, the model calculations suggest that intrusions of 9×10^{14} l of water would produce much lower nutrient concentrations in deep water than the negligible changes observed. Temperature and salinity are more sensitive, and an intrusion of even 2×10^{14} l of water of properties such as those observed at NOR-A would have measurably altered deep-water properties outside of the observed range (Fig. 2). Potential temperature in late 1997 at 1200 m at CARIACO was 16.932, while the value predicted from intrusion of 2.2×10^{14} l of sill water would be 16.952. Similarly, the observed salinity was 36.226 while the predicted value is 36.235. Potential temperature and salinity shifts of the magnitude predicted from injection of sill depth water would have been easily detectable, but were not seen. These results suggest either that oxygenated sill depth water (at least of the properties observed) was not the cause of sulfide decrease, or that denser water (colder and less saline than observed) occurs occasionally at sill depth.

However, there is an alternative mechanism, which may have led to the observed decrease in sulfide. On 9 July 1997, a magnitude 6.8 earthquake struck the coast of Venezuela only 90 km from the CARIACO site. The monthly CARIACO cruise (CAR21) took place the day before the earthquake. Another cruise was conducted within a week of the earthquake to assess the effect of this event (Thunell et al., 1999), which included development of a large nepheloid layer in the bottom several hundred meters of the water column.

A connection between water chemistry and earthquakes has been suggested before. Zhang and Millero (1993) speculated that Cariaco Basin deep waters were oxic around 1915, and noted that this might have been related to earthquakes in 1900 and 1929. They based their argument, however, on extrapolations of data collected only between 1955 and 1969. Based on these early data, long-term linear trends of sulfide and ammonium concentrations with time reached zero concentration at about 1915. Our regression of silica versus time suggests that silica concentrations were near zero in 1913. However, if we use a more complete set of observations, providing a trend over a longer period of time, such as are presented in Fig. 6a, it appears that sulfide would have been zero in approximately 1953. Long-term trends of phosphate with time extrapolate to zero in about 1889, based on the regressions shown in Fig. 6c. Therefore, the arguments of Zhang and Millero that a major earthquake was somehow related to basin overturn or oxygenation near 1929 are somewhat in question, although intriguing.

Our results show that most parameter values (θ, S, PO_4, SiO_2) were unchanged following the earthquake. Therefore, there is no evidence for large-scale overturn of the basin in our data, although the magnitudes of the earthquakes of the early 1900s and the one in 1997 are similar. However, during the July 1997 earthquake, a large amount of sediment was transported into the middle of the basin, probably as a turbidity current (Thunell et al., 1999). This event was recorded both in a sediment trap located 200 m off the bottom and in a light scattering profile taken a few days after the earthquake. If this sediment originated above the oxic/anoxic interface, it might be expected to contain a significant amount of oxidized iron. Typical values for oxidized iron in marine sediment are 1% by weight. The iron oxides in the sediment must be reduced before they can be involved in FeS precipitation. Iron reduction could take place by several reactions. For example, if the S_{solid} is taken as S_8

$$Fe(OH)_3 + 2.5H^+ + 0.5HS^- \rightarrow Fe^{2+} + 0.0625S_{solid} + 3H_2O.$$

This reaction would result in release of soluble iron into the water column. Cariaco Basin waters historically contain about 0.5 μM dissolved iron (Jacobs et al., 1987), and recent analyses give similar, although slightly lower, results (Ho, unpublished data). In contrast, below 550 m, the sulfide decrease between CAR19 and CAR25 was about 24 μM. Therefore, we speculate that any Fe^{2+} released may have reacted with dissolved sulfide to give a form of FeS. Because the second dissociation coefficient for H_2S is not well known, most workers present the solubility of metal sulfides in terms of a reaction like

$$FeS(s) + H^+ = Fe^{2+} + HS^-$$

for which an equilibrium constant ($^*K_s$) can be assigned. Dyrrsen and Kremling (1990) give a value of $10^{-4.2}$ for $^*K_s$ for FeS based on data for the Baltic, and Davison (1991) gives a range of values from $10^{-2.95}$ to $10^{-5.2}$ for several different FeS minerals. By comparing the Ion Activity Product (IAP) for the above reaction to $^*K_s$, we can evaluate the extent to which the Cariaco Basin Deep Waters may be at or above saturation with FeS:

$$IAP = \frac{\gamma_{Fe}\,\gamma_{HS}[Fe^{2+}][HS^-]}{\gamma_H[H^+]}.$$

Hydrogen sulfide concentrations (almost exclusively HS^- at the pH of seawater) are between 0.5 and 50–70 μM. Fe^{2+} ranges from about 0.1 to 0.5 μM (Tung-Yuan Ho, unpublished data; Jacobs et al., 1987). pH values are about 7.6 (Bohrer, unpublished data). Activity coefficients for divalent and monovalent species in seawater, taken from Morel (1983), are $\gamma_{Fe} = 0.2$ and $\gamma_{HS} = \gamma_H = 0.7$. If we assume the activity of FeS = 1, then we obtain deep-water values of IAP of around $10^{-4.4}$ with a maximum value observed on CAR29 of $10^{-4.26}$ (Fig. 8). Values of IAP are very similar to the

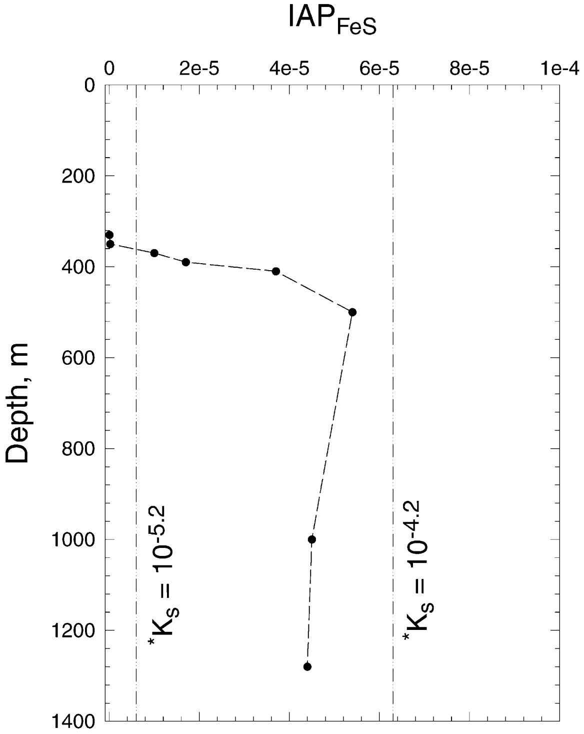

Fig. 8. Ion Activity Product (IAP) for FeS as a function of depth for May 1997 (CAR19). For comparison, two literature values of the solubility product of FeS are also plotted.

$^*K_s$ reported by Dyrrsen and Kremling (1990) for the Baltic, and to values of IAP for the Black Sea (estimated by us to be about $10^{-4.1}$ assuming deep-water pH is about 7.5). Therefore, it appears that waters of the deep Cariaco were close to saturation with iron sulfide about 8 months after the earthquake. Since iron concentrations probably were higher in and near the turbidite (as the 1% of oxidized iron dissolved), the waters would likely have been even more supersaturated with FeS shortly after the earthquake. Elevated turbidity was observed in the water for more than one month following the earthquake (Robert Thunell, personal communication).

The sum of the two reactions listed above is

$$\mathrm{Fe(OH)_3} + 1.5\mathrm{H}^+ + 1.5\mathrm{HS}^- \rightarrow 0.0625\mathrm{S}_{\mathrm{solid}} + 3\mathrm{H_2O} + \mathrm{FeS}.$$

This reaction should result in no net increase in alkalinity (defined as sum of weak bases, including OH^-, minus H^+), as one mole of H^+ is required for every mole of HS^- consumed. Measurements of alkalinity in the deep waters of the Cariaco are consistent with this result (Bohrer, unpublished data). We also would expect that this mechanism would yield enhanced concentrations of elemental sulfur in the deep waters of the basin. Unfortunately, elemental sulfur concentrations in the deep water are not known.

Reduced iron could also be produced by a reaction like

$$\mathrm{Fe(OH)_3} + \mathrm{HS}^- + 0.75\mathrm{H}^+ + 0.25\mathrm{CH_2O} = \mathrm{FeS} + 2.5\mathrm{H_2O} + 0.25\mathrm{HCO_3^-},$$

representing a coupling of organic matter reduction by iron-oxide-reducing bacteria with FeS precipitation. Iron-oxide-reducing bacteria are likely to be active in the Cariaco Basin. This equation would predict an increase in ΣCO_2 of about 0.25 times the decrease in sulfide (about 7 μM in this case). Results from Christopher Sabine and Richard Bohrer (unpublished observations) suggest that, while deep ΣCO_2 has been approximately constant, the data are sufficiently variable from cruise to cruise that an increase of 7 would be hard to distinguish from no change. However, it seems unlikely that this reaction would occur as rapidly as the simple inorganic reaction given above.

We can estimate the amount of sediment in the turbidite by considering the amount of iron required to scavenge the sulfide "missing" from the deep basin. The volume of the basin below 550 m is about 2.2×10^{15} l. If 5×10^{10} mol of sulfide were removed from the basin, and since we are considering an iron monosulfide precipitate, we would expect that 5×10^{10} mol or 2.8×10^{12} g iron is required. If the sediment were 1% iron, this would mean that 2.8×10^{14} g sediment has been transported to waters deeper than 550 m.

Thunell et al. (1999) estimated a flux of sediment of 1.45×10^{11} g into the deep basin following the earthquake, based on transmissometer and sediment trap measurements. However, their deepest trap was about 200 m above the bottom (and thus may have missed considerable sediment being transported near the bottom), and the transmissometer profile (which reached only to 1310 m although the bottom depth is 1380 m) was made a week after the earthquake (allowing some sediment to settle prior to our measurements).

The area of the basin between 550 and 900 m, and below 900 m in the eastern basin, is $2.6 \times 10^{10}\ \mathrm{m}^2$, so we estimate the flux of material to the bottom to be about $1.1 \times 10^4\ \mathrm{g\,m^{-2}}$ or $1.1\ \mathrm{g\,cm^{-2}}$. If the bulk wet density of the sediment were $1.13\ \mathrm{g\,cm^{-3}}$, this would imply a turbidite layer of 10 cm. Hughen et al. (1996a, b) have reported that the 1900 and 1927 earthquakes are associated with 3 and 7 cm thick turbidites, so our estimate of 10 cm is not unreasonable. If much oxygenated water were entrained with the turbidite sediments, or if there were more than 1% oxidized iron in the sediment, the amount of sediment would be proportionally decreased.

We only considered sulfide removal below 550 m. Fig. 4, however, shows that sulfide removal occurred at all depths below the interface, which deepened about 100 m during 1997. Therefore, the amount of mobilized iron-oxide-rich material may have been larger than has been calculated above. However, we feel it unlikely that the earthquake was the cause of the deepening interface. Intruding water parcels containing oxygen or other compounds (like nitrite/nitrate or iron or manganese oxides) were noted well before the earthquake, and it is most likely that these are the causes for the loss of sulfide at shallower depths.

Perhaps, the most troublesome part of this hypothesis is that it requires that sulfide be removed, more or less uniformly, from the waters of the entire Cariaco Basin over quite short periods (one or two months). Because of our lack of data at other stations, we do not, in fact, actually know whether sulfide concentrations in the entire basin changed simultaneously or whether they have remained laterally homogeneous as was the case in the past (Richards, 1975; Scranton et al., 1987). Until more complete studies of the Cariaco Basin examining the lateral variability of sulfide in the Cariaco Basin, the presence (or lack thereof) of a several cm thick turbidite deposited in 1997, or the identification of a slump scar of appropriate size, our suggestion of the role of earthquakes in removing sulfide from the Cariaco Basin will of necessity remain a hypothesis.

Conclusions

In conclusion, we have proposed two mechanisms for addition of oxidant to the Cariaco Basin (lateral intrusion of water near the interface and deep supply of sediment in the form of turbidites, together with some entrained surface water). These can be compared to the mechanisms for deep-water supply described by Holmen and Rooth (1990). They suggested, based on tritium data, that there are two sources of deep-water to the Cariaco Basin: a shallow intrusion of water with characteristics of water found near sill depth outside the basin at intermediate depths, together with much smaller amounts of high-salinity water from near shore that could be dense enough to reach the bottom. So far, a source of this coastal high-salinity water has not been identified (Paul Joyce, personal communication). In addition, our data do not show the sizeable changes in bottom-water potential temperature and salinity that would be required if water of properties seen outside the northeastern sill were to have been injected into the deep basin. Instead, it seems most likely that turbidites, which entrain surface water along with the sediment, may be the mechanism of transport of shallow water to the deep basin.

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