



High CO₂ content in hydrothermal vent water at the Snake Pit area, Mid-Atlantic Ridge

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Abstract: Carbon dioxide contents and partial pressures were measured during the MAR 93 cruise on several water samples collected from black smoker chimneys and around mussels and shrimps at the Snake Pit (MARK) vent field (Mid-Atlantic Ridge). High end-member values for total CO₂ (10.63 mmol l⁻¹) and CO₂ partial pressure (335 Torr directly measured at 33°C; 1 Torr = 0.133 kPa) were recorded for black smokers samples. Water sampled in close proximity of organisms was found moderately but significantly enriched in carbon dioxide.

Résumé : Concentration en CO₂ des fluides prélevés sur le site hydrothermal Snake Pit, Dorsale médio-atlantique.

Les concentrations et les pressions partielles de dioxyde de carbone ont été mesurées lors de la mission MAR 93 sur plusieurs échantillons d'eau collectés à la sortie de fumeurs noirs et au voisinage de populations de modioles et de crevettes sur le site hydrothermal Snake Pit (MARK) de la ride médio-atlantique. Les valeurs obtenues par extrapolation à concentration nulle de magnésium (représentatives de l'eau des événements hydrothermaux) sont élevées : 10.63 mmol l⁻¹ pour la concentration de dioxyde de carbone total et 335 Torr pour la pression partielle de dioxyde de carbone mesurée directement à 33 °C. L'eau prélevée au voisinage immédiat des organismes présente des valeurs beaucoup plus faibles mais reste néanmoins significativement, quoique modérément, enrichie en dioxyde de carbone par rapport à l'eau du fond.

Keywords : Carbon dioxide, hydrothermal vent water, Mid Atlantic Ridge.

Introduction

Water chemistry of hydrothermal fluid collected from several East Pacific Rise (EPR) and Mid-Atlantic Ridge (MAR) sites has received much attention with regard to major-element composition (Von Damm et al., 1985; Campbell et al., 1988a; 1988b). However, although it is well known that these waters have often very acid pH and low alkalinity values, their carbon dioxide content (ΣCO_2) and

especially partial pressure (P_{CO_2}) have remained only partially studied until recently. While very high ΣCO_2 values (up to 285 mmol kg⁻¹) have been reported from the Axial seamount of the Juan de Fuca Ridge (Butterfield et al., 1990; Von Damm, 1995), only modest enrichments (ΣCO_2 : 3 to 18 mmol kg⁻¹) were detected in the fluids from the EPR high temperature vent smokers (Von Damm, 1990, 1995). More recent, although limited, measurements have reported end-member ΣCO_2 values up to 40 mmol l⁻¹ corresponding to very high P_{CO_2} (34.5 kPa or 259 Torr measured at 10°C) in Pacific hydrothermal waters at the EPR Genesis vent site at 13° N (Childress et al., 1993). No published CO₂ values

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presently exist concerning vent fluids from the slowly spreading Mid Atlantic Ridge. But, as the pH values and major-element chemistry of these waters looks rather similar to those of fluids from the faster-spreading EPR (Campbell et al., 1988b), CO₂ enrichment, compared to bottom water, could also be expected.

A number of hydrothermal vent invertebrates harbor chemolithotrophic bacteria that are able to produce organic substances from inorganic carbon using energy derived from the oxidation of reduced sulphur compounds. It has been recently suggested that high ambient PCO₂ levels may facilitate CO₂ uptake by chemoautotrophic symbioses in the hydrothermal vent environment (Childress et al., 1993; Goffredi et al., 1997). As part of a shrimp physiology program during the MAR 93 cruise on the TAG and Snake Pit sites, we wanted to know which PCO₂ levels hydrothermal vent organisms could encounter in their specific environment. For this purpose, we had the opportunity to do some measurements on various water samples drawn from black smokers chimneys and other locations in this area by the submersible Alvin.

Material and Methods

The present account is based on seven water samples collected by titanium syringe samplers from both the Beehive and Moose vent fields in the Snake Pit area (23°22'N - 44°56'W, depth ca. 3500 m, also called MARK by Campbell et al., 1988b) during the MAR 93 cruise. The main characteristics of the collection sites are summarized in Table 1. Before sampling, the temperature was measured with Alvin probes and the sampling inlet was then positioned at approximately the same location. This positioning was rather imprecise and, due to the often steep temperature gradients in these areas, the measured temperature values can not be considered as very representative of the collected samples. On board, a 25-35 ml subsample was taken from the titanium bottle into a 50 ml glass syringe whose dead space had first been flushed with the sample fluid via a three-way tap, thus avoiding any contact with the atmosphere. Some gas-supersaturated samples progressively liberated a gas phase in the syringe (up to 10 ml gas for a 25-35 ml water sample), probably leading to an unknown loss of CO₂ from the water.

Measurements of carbon dioxide partial pressures and concentrations were begun immediately after recovery of the sample, using a Severinghaus-type (Severinghaus and Bradley, 1958) CO₂ electrode (Radiometer E5036/0) connected to the PCO₂ module of a blood gas Analyser (Radiometer PHA935/PHM72) and housed in a ca. 2 ml glass chamber thermostatted at 33°C (Cameron, 1971). For direct PCO₂ measurements, the chamber was flushed with

Table 1. Origin and characteristics of water samples obtained by titanium syringe samplers in the Snake Pit area during the MAR 93 cruise.

Tableau 1. Origine et caractéristiques des échantillons d'eau prélevés avec des seringues titane sur le site du Snake Pit pendant la mission MAR 93.

Sample n°	Alvin dive	Date	Location	Water temp. (°C)	Appearance
M8	2616	6/17/93	Beehive, black smoker	346-350	Black + gas and marked sulphide odour
M9	2617	6/18/93	Moose, shimmering water within mussels	20	Clear, without sulphide odour
M10	2618	6/19/93	Beehive, black smoker	349	Black + a few gas and marked sulphide odour
M11	2619	6/20/93	Beehive, black smoker	355	Black + a few gas and light sulphide odour
M12	2620	6/21/93	Beehive, black smoker	unknown	Black, without gas nor sulphide odour
M14(S+) 2622	2622	6/23/93	Beehive diffusor, among shrimps <i>Rimicaris</i>	30-35	Clear, without sulphide odour
M14(S-) 2622	2622	6/23/93	Beehive diffusor, area without shrimps <i>Rimicaris</i>	21	Clear, without sulphide odour

2-4 volumes of the temperature-equilibrated sample or standard before being closed with a glass bead. Readings were taken in arbitrary units at maximum gain after stabilization which took 1-2 min. For water samples that had liberated gas within the glass syringe, measurements were performed on both liquid and gas phases, leading to practically identical values. Calibration of the system was performed with physiological saline (10 g l⁻¹ NaCl) equilibrated at ambient temperature (26-28°C) with gas mixtures made up of ambient air and pure CO₂ (0.1 to 30 % by volume) using Wösthoff (Bochum, Germany) gas mixing pumps. Actual calibration values were re-calculated at 33°C using CO₂ solubility coefficients for a 10 PSU sea water (Skirrow, 1975). The relationship between the readings in arbitrary units and logPCO₂ was linear.

For measurements of total CO₂ concentration (ΣCO₂), the technique introduced by Cameron (1971) was used. The

glass chamber fitted with the P_{CO_2} electrode was first filled with a 0.01 N HCl solution pre-equilibrated at 33°C with 2 % CO_2 in air. After taking a first reading in arbitrary units at full gain, a known volume (30 or 50 μ l) of sample or standard was injected into the chamber and the resulting increase in P_{CO_2} was measured by taking a second reading. The system was calibrated with the same volume of standard solutions containing 5-15 mmol l^{-1} $NaHCO_3$. The relationship between ΣCO_2 in these standards and the difference between the two readings was not strictly linear. Thus, the sample values were estimated by interpolation between the two nearest standards.

Since we did not expect before the cruise to have access to water samples, we had no adequate equipment for water pH determination on board. Thus, although we were aware that such a procedure was largely open to criticism, the remaining water samples were kept preserved at -20°C for later pH measurements when back to the laboratory. In an attempt to limit the error on pH estimation, these samples were first equilibrated at 33°C against a gas mixture containing (air + CO_2) at a P_{CO_2} equal or very near to that of the original sample as measured on board. The pH was then measured electrometrically at 33°C with a Radiometer glass electrode GK 2401C connected to a pHM 84 pH/mV meter (Radiometer) and calibrated against NBS buffers. Bicarbonate concentration was calculated from measured

pH and P_{CO_2} using values for CO_2 solubility and pK'_1 of 0.0316 mmol l^{-1} Torr $^{-1}$ and 5.971, respectively, which are appropriate for a normal 35 PSU seawater at 33°C (Skirrow, 1975). Titratable alkalinity (TA) was determined with a Gran titration method using the same pH electrode as above. Chloride concentration was obtained by coulometric titration (CMT 10 Chloride Titrator, Radiometer) and the salinity S PSU was deduced from these measurements. Commercial kits were used for colorimetric determinations of calcium (Boehringer Mannheim MPR3 cat n° 1273574) and magnesium (Merck Merckotest cat n° 14102) concentrations. The precision obtained in these measurements was about 2 % for chloride and 4 % for calcium and magnesium.

Results and Discussion

To our knowledge, these are the first CO_2 measurements in water sampled at or near hydrothermal vents of the Mid-Atlantic Ridge. As shown in Table 1, the present set comprises samples obtained from black smokers as well as from sites around the most common animal species present in the Snake Pit area i.e. mussels of the genus *Bathymodiulus* and shrimps *Rimicaris exoculata*. The results of the various analyses are summarized in Table 2.

Table 2. Chemical characteristics of water samples obtained by titanium syringe samplers in the Snake Pit area during the MAR 93 cruise.

Tableau 2. Caractéristiques chimiques des échantillons d'eau prélevés avec des seringues titane sur le site du Snake Pit pendant la mission MAR 93.

Sample n°	P_{CO_2} at 33°C (Torr)	ΣCO_2 (mmol l^{-1})	pH at 33°C	TA ^a (meq l^{-1})	HCO_3^- calc ^b (mmol l^{-1})	Ca ²⁺ (mmol l^{-1})	Mg ²⁺ (mmol l^{-1})	Cl ⁻ (mmol l^{-1})	PSU
M8	278.0	8.71	3.36	- 0.440	0.021	9.9	3.9	581	36.4
M9	1.8	3.09	7.57	2.362	2.247	12.8	53.0	564	35.3
M10	302.1	10.61	3.45	- 0.366	0.029	10.9	11.4	575	36.0
M11	94.2	4.29	4.30	0.004	0.063	8.0	43.4	573	35.9
M12	74.6	4.10	4.37	- 0.001	0.059	7.7	47.5	553	34.6
M14(S+)	1.9	2.52	7.57	2.313	2.410	7.6	54.5	558	34.9
M14(S-)	8.7	2.81	6.89	2.150	2.271	7.6	55.2	563	35.3
Extrapolated end-member values									
	335.3	10.63	3.34	- 0.974			0 ^c	581	36.4

^a titratable alkalinity

^b calculated as $HCO_3^- = 10^{pH - pK'_1} \cdot \alpha_{CO_2} \cdot P_{CO_2}$,
with $\alpha_{CO_2} = 0.0316$ mmol l^{-1} Torr $^{-1}$ and $pK'_1 = 5.971$ (values for normal seawater at 33°C)

^c assumed

^a alcalinité de titration

^b calculé par $HCO_3^- = 10^{pH - pK'_1} \cdot \alpha_{CO_2} \cdot P_{CO_2}$,
avec $\alpha_{CO_2} = 0.0316$ mmol l^{-1} Torr $^{-1}$ et $pK'_1 = 5.971$ (valeurs pour l'eau de mer normale à 33°C)

^c admis

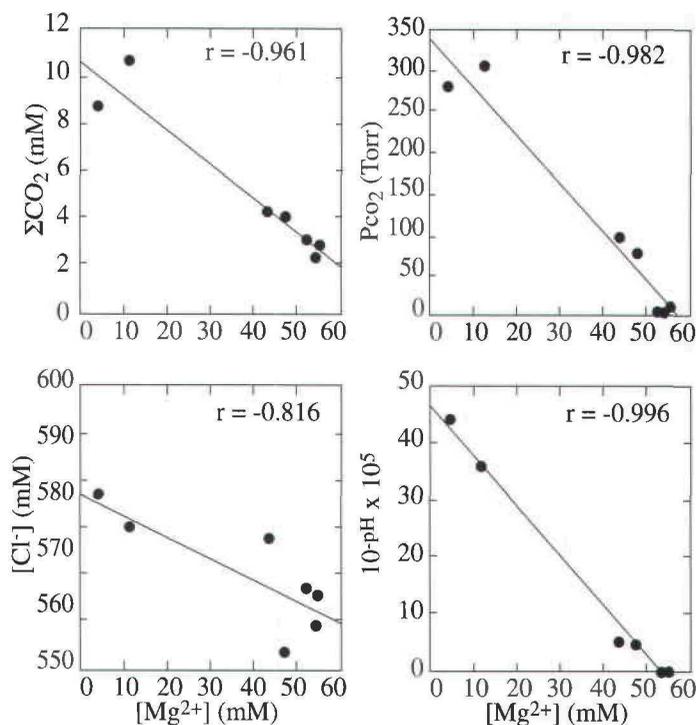


Figure 1. Plot of total concentration of carbon dioxide (ΣCO_2), carbon dioxide partial pressure (PCO_2), chloride concentration and 10-pH against magnesium concentration in water sampled in and around black smoker vents at the Snake Pit area of the Mid-Atlantic Ridge. CO_2 partial pressure was measured at 33°C . Extrapolation to zero magnesium concentration by linear regression gives an estimate of end-member values in undiluted hydrothermal fluid (values reported in Table 2). Correlation coefficients are given.

Figure 1. Concentration totale (ΣCO_2) et pression partielle (PCO_2) de dioxyde de carbone, concentration de chlorure et 10-pH , représentés en fonction de la concentration de magnésium mesurée dans l'eau collectée à l'intérieur et au voisinage des fumeurs noirs de l'aire hydrothermale du Snake Pit sur la rive médio-atlantique. L'extrapolation à une concentration nulle de magnésium par régression linéaire donne une estimation des valeurs dans le fluide hydrothermal non dilué (valeurs rapportées dans le Tableau 1). Les coefficients de corrélation sont indiqués.

As indicated by the recorded concentrations of magnesium, which is considered to have been practically removed from hot vent fluid (Von Damm, 1990, 1995), there are various degrees of mixing with bottom water in our samples. This allows to estimate end-member values in hydrothermal fluid by linear regression and extrapolation to zero magnesium concentration. These end-member extrapolated values are reported in Table 2 and illustrated in Fig. 1 for those parameters presenting the best correlations, i.e. PCO_2 , ΣCO_2 , Cl^- and pH. As a linear regression procedure is certainly not adequate to extrapolate end-member values for pH (Von Damm et al., 1985; Campbell et al., 1988a; Sarradin et al., 1998), a plot of 10-pH against Mg concentration was chosen as the best estimate. In agreement

with previous measurements at the same site (Campbell et al., 1988b; Edmond et al., 1995), the hydrothermal fluid from the Snake Pit has Cl^- contents and salinities which are very near those of a normal 35‰ S seawater, in contrast with the TAG site fluid which is markedly enriched in sodium chloride (Campbell et al., 1988b). The calcium concentrations are variable but much lower than in the TAG fluid ($7\text{-}13\text{ mmol l}^{-1}$ compared to 26 mmol l^{-1} , Campbell et al., 1988b). No significant correlation exist between calcium and magnesium concentrations, indicating that our calcium data can not be explained by mixing only. As is the case for almost all known hydrothermal fluids (Von Damm, 1995), our Snake Pit end-member values are strongly acid but with lower pH and titratable alkalinity values than previously reported (Campbell et al., 1988b; Edmond et al., 1995). However, for technical reasons explained above, these measurements have been performed on preserved samples several weeks after collection and they are probably not entirely reliable, especially because sulphide oxidation as well as precipitation of metal sulphides may acidify the sample (Sarradin et al., 1998).

In this work, both PCO_2 and ΣCO_2 were directly determined. We found very high PCO_2 in hot vent fluid leading to an end-member value of 335 Torr measured at 33°C , which is very similar to that extrapolated from the data of Childress et al. (1993) measured at 10°C for EPR hydrothermal fluid (337 Torr). The true PCO_2 values at in situ temperature of the hot fluid would obviously be much higher. Our derived end-member ΣCO_2 value was moderately high at 10.63 mmol l^{-1} , that is much lower than those ($26\text{-}31\text{ mmol l}^{-1}$) reported by Childress et al. (1993) for EPR fluids. However, as most of our black smoker samples had been outgassed, this value should probably be considered as an underestimate. Nevertheless, the internal consistency of our measurements is shown by the CO_2 solubility values calculated from experimentally determined PCO_2 and ΣCO_2 . For the most acid samples M8 and M10, in which carbon dioxide can be expected to be present almost only in dissolved form, these calculated values amount to 0.0313 and $0.0351\text{ mmol l}^{-1}\text{ Torr}^{-1}$, respectively, that is very near the value of $0.0316\text{ mmol l}^{-1}\text{ Torr}^{-1}$ for normal seawater at 33°C (Skirrow, 1975). Such was probably not the case for the data of Childress et al. (1993), since the solubility coefficient calculated from their values of ΣCO_2 and PCO_2 amounts to $0.119\text{ mmol l}^{-1}\text{ Torr}^{-1}$, that is much larger than the normal seawater CO_2 solubility of $0.059\text{ mmol l}^{-1}\text{ Torr}^{-1}$ at 10°C (Skirrow, 1975), indicating that their samples were probably less outgassed, or more supersaturated, at the time of ΣCO_2 compared to PCO_2 measurements.

These considerations highlight the difficulty in obtaining representative ΣCO_2 and PCO_2 data for vent water samples. As high CO_2 values were expected, handling of the samples on board was done with special care in order to prevent any loss of dissolved gas to the atmosphere. However, it is known that titanium syringe samplers are not perfectly gas tight, so that some of the CO_2 present in the richest black smoker samples may have been lost during ascent from the sea floor. In addition, outgassing took place on board during manipulation of some subsamples and this could also have occurred within titanium syringes, leading to substantial CO_2 depletion from the samples before analysis. All these problems have certainly caused underestimation to an unknown extent of the PCO_2 and ΣCO_2 values reported here for black smoker fluids. However, such an error may have been smaller or negligible for less CO_2 -rich samples.

Investigations of the chemistry of hydrothermal vent fluids have largely focused on black smokers emissions and very few measurements have been devoted to environmental chemistry of vent biota. In this work, PCO_2 values measured on water samples taken in the immediate proximity of vent organisms, e.g. mussels (sample M9) and shrimps (sample M14 S+) were elevated compared to those of bottom seawater, which is usually reported to correspond to atmosphere-equilibrated seawater (ca. 0.2-0.3 Torr, see for example Childress et al., 1993). Although lower than those prevailing among *Riftia* tubes on the EPR (ca 21.7 Torr measured at 10°C, Childress et al., 1993), they also indicate that such organisms might be naturally exposed to hypercapnic media. In addition, such media at the interface between fluid emission and bottom seawater could be expected to fluctuate greatly in PCO_2 , but much more measurements are required to evaluate the amplitude of these variations.

It has been regularly observed that shrimps *Rimicaris* crawling in dense swarms on bare sulfide deposits constituting porous structures, called diffusors, durably occupy well-defined locations but do not invade other ones (Segonzac, 1992; Segonzac et al., 1993). The purpose of samples M14 S+ and M14 S- was to compare water chemistry at both locations. Clearly, places not occupied by shrimps had higher PCO_2 and lower pH values than those where shrimps swam. This might suggest that these animals thrive only in locations of lower PCO_2 and higher pH values, but this clearly needs further observations to be confirmed.

In conclusion, present observations confirm a particular richness of hydrothermal fluids in dissolved carbon dioxide. Although certainly underestimated to an unknown extent, the values of PCO_2 and ΣCO_2 recorded on the MAR at the Snake Pit hydrothermal vent field are of the same order of magnitude as those reported for various sites of the EPR, but clearly lower than those measured in some fluids from the

Juan de Fuca Ridge (Von Damm, 1995). Mixing of these CO_2 -rich fluids with bottom waters can create a significantly hypercapnic environment for the organisms living in the immediate proximity of vent water emissions. This is probably beneficial in providing plenty of inorganic carbon to chemoautotrophic bacteria, either symbiotic (Childress et al., 1993; Goffredi et al., 1997) or not, but might also require specific adaptations for hydrothermal vent animals.

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