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A negligible contribution in terms of dissolved inorganic carbon from Haima cold seep in the South China Sea

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ABSTRACT

Cold seep can generate dissolved inorganic carbon (DIC) through various processes, such as anaerobic oxidation of methane. The DIC can be emitted into the sea surface via vertical movement of the water column. This part of DIC can bare the possibility of being released to the atmosphere through air-sea exchange. In this way, cold seep can be a carbon source. Yet the contribution in terms of DIC of cold seep has not been considered hitherto. The present study collected samples from four stations in the Haima cold seep from the South China Sea and measured the carbon content and isotope. The results show that cold seep is not a carbon source because of ocean fertilization by methane. Also, cold seep is not the only contribution of DIC. This part of the contribution demands more study to differentiate.

Keywords: Haima Cold Seep, Dissolved Inorganic Carbon, Carbon Isotope, Negligible Contribution

NONMENCLATURE

Abbreviations	
DIC	Dissolved inorganic carbon
SCS	South China Sea
AOM	Anaerobic oxidation of methane
OSR	Organoclastic sulfate reduction

1. INTRODUCTION

The increasing temperature trend has caused ocean warming, with the global ocean hitting a new record temperature of 21.1 ℃ in early April 2023, which is 0.1 ℃ higher than the last record in March 2016 [1]. The increasing trend has been accelerated since the last 100 years, with the global ocean area reaching the maximum yearly ocean heat content [2]. This has caused the slowdown of refreshment of Antarctic deep bottom water, which worsens the case by affecting the global heat content transferred by Antarctic deep bottom water, combined with a decline of dissolved oxygen level [3]. The warming trend has affected the whole ocean, including deep-sea areas. Ocean has been proven to be a carbon sink (-2.82 ± 0.85 Pg C yr^{-1} in global average) [4]. However, in the South China Sea (SCS), combined with the pCO2 measurements in this region, a net CO_2 flux rate of 0.54 ± 0.08 mol m^{-2} yr^{-1} was determined [5]. This indicates that the ocean has served as a carbon source in terms of dissolved inorganic carbon (DIC).

Cold seeps constitute seafloor ecosystems where methane-laden fluids migrate from beneath sedimentary layers to the seabed and ascend through the water column, potentially releasing methane into the atmosphere [6]. This makes it a well-focused topic, to evaluate if it can contribute to the global warming trend. The effect of methane is well studied, with a contemporary conclusion that its contribution to the greenhouse effect is negligible because the ancient-carbon methane with a highly damaging radiocarbon signature can barely reach the sea surface [7]. This is because the Anaerobic oxidation of methane (AOM) process is a major sink of the oceanic methane budget, consuming up to 300 Tg methane per year, equivalent to 88% of the methane released from subsurface reservoirs [8]. The previous research studied carbon sequestration by cold seep bivalves, whose shell comes from ambient DIC, while tissue comes from symbionts that feed on DIC and methane [9].

However, cold seeps can emit DIC, and this part of the contribution is yet unclear. Carbon dioxide from cold seeps can rise to the sea surface through upwelling processes, releasing aged carbon into the atmosphere above the

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South China Sea [10]. Through air-sea exchange, it can serve as a potential carbon source.

To our understanding, the previous study focuses on examining the dilution impact of methane emissions from cold seeps. Thus, it does not consider the dissolved inorganic effects caused by cold seeps. The DIC study about SCS concludes a net CO2 flux was emitted from the sea surface to the atmosphere while the sampling points were based on the general areas in SCS, with nearly none from cold seep position [5]. Furthermore, the carbon sequestration of deep sea remains unclear. The Global total carbon sequestration of the deep-sea ecosystem is 6.0 Tg·C·a-1, and comparatively, the coastal ecosystem is 237.6 Tg·C a-1. Yet, the contribution of the deep sea is not clear, and the estimation is based on a mathematical model and experimental parameters.

This study shed light on the potential DIC effect caused by cold seep from the South China Sea by measuring the DIC content as well as carbon isotope signature in seawater samples.

2. GEOLOGICAL SETTING

In this work, seawater samples were obtained from Haima cold seep. Haima site resides at an elevation of 1370-1390 meters within the southwestern sector of the Qiongdongnan Basin. Haima exhibits heightened activity as a cold seep, characterized by larger bubble diameters and accelerated release rates. (for Haima 6.17 mm and 22.6 bubbles s^{-1}) [11]. Thiotrophic species like tubeworms and bivalves *Archivesica marissinica*, indicating a higher concentration of sulfide, are found in Haima cold seep. More specifically, samples were collected from four stations in May 2022, including the middle cold seep development stage with strong methane seepage (ROV1), the middle cold seep development stage with weak methane seepage (ROV2), the early cold seep development stage (ROV3), and the non-seepage (ROV4) [12].

3. MATERIALS AND METHODS

As shown in Fig.1, the seawater samples were obtained in three locations and contained in empty brown bottles. The samples were delivered to Guangdong Ocean University for DIC content and carbon isotope determination. In short, 8 drops of anhydrous phosphoric acid were added to the 12 mL sample bottle (Labco). The bottle was then placed on the thermostatic sample plate in sequence. With the air-blowing needle fixed and the working procedure of the automatic sampler set, the sample bottle was emptied for up to 5 minutes to remove the influence of the air in the bottle on the determination of the sample C isotope ratio. 0.2 mL water was added to the sample bottle after emptying treatment. The 45° dry heater heated the bottle for 45 minutes and centrifuged. The samples were analyzed by GasBench Ⅱ-IRMS (Thermo Fisher Scientific, America). The carbon isotope is given in notation of $\delta^{13}C$(‰). The analytic precision is limited within 0.10 ‰.

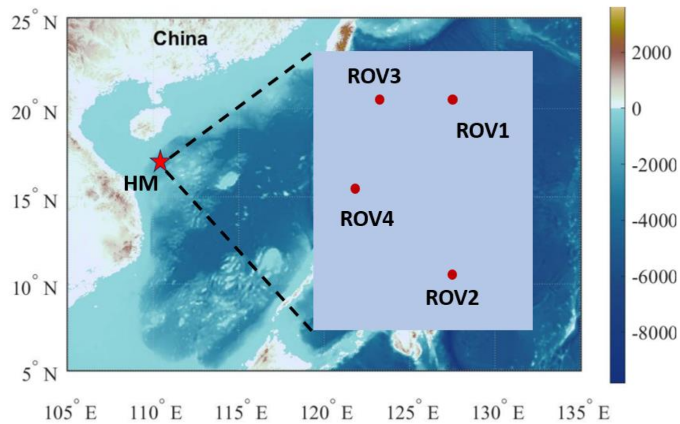

Figure.1 The sampling location (Red star or red points) of sampling locations of dissolved inorganic carbon. Water depth data is acquired from ETOPO 2 or 1-minute global bathymetry/topography from M_map.

4. RESULTS AND DISCUSSION

4.1 Different leakage intensity of cold seep DIC

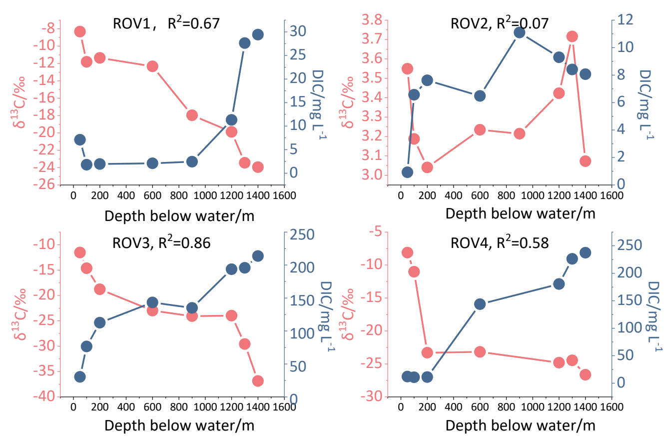

Figure 2. The DIC (blue color) and $\delta^{13}C$ (red color) versus depth profile of four stations. The relation coefficient between DIC and $\delta^{13}C$ is given.

As shown in Fig.2, the DIC varies from 1.8 mg/L to 29.4 mg/L for ROV1, from 0.9 mg/L to 11.1 mg/L for ROV2, from 30.4 mg/L to 213.7 mg/L for ROV3 and from 10.7 mg/L to 237.4 mg/L for ROV4. The station ROV2 seems to have the lowest DIC content, with a similar and slightly higher one of ROV1. DIC in ROV3 and ROV4 are the biggest ones similarly. This marks a possible transition that seepage does not increase but decreases the total DIC of the seawater in general, as is indicated in Fig.4. The methane-related bioreactions can generate DIC (alkalinity), including anaerobic oxidation of methane (AOM), organoclastic sulfate reduction (OSR) as well as thermogenic or biogenic methanogenesis. Therefore, the emergence of cold seep ecosystems should have improved the generation of DIC and the whole water depth profile as it is transferred from deeper to shallower in the water column. One possible mechanism is that the ocean fertilization by methane has improved the growth of phytoplankton, which in turn adsorbed more DIC for photosynthesis [13]. The same physical forces pushing the methane bubbles up also pump nutrient-rich cold waters from the sea bed to the surface, fertilizing phytoplankton blooms that soak up CO_2 (nearly 1900 times more CO2 is absorbed than methane emitted) [14]. Our results support the above study, which shows that cold seep does not contribute to the increasing temperature trend in terms of DIC. The R^2 of different stations between DIC and $\delta^{13}C$ shows a significant correlation, except ROV2. This indicates that the cold seep emits DIC with strong negative $\delta^{13}C$, which can be transferred to the upper sea surface through the water column. DIC generally decreased as the depth became shallower, also except ROV2. The decreasing trend of DIC and increasing trend of $\delta^{13}C$ indicate cold seep emits DIC as a source. The $\delta^{13}C$ of seawater DIC is reported to be a little negative near zero. More negative $\delta^{13}C$ is observed in all stations except ROV2; this indicates the whole water profile is affected by negative DIC emitted from the cold seep. ROV2, as the most extraordinary and distinct station, marks the stage of early transition when methane begins to emit. It is reported that the AOM process can generate DIC with extremely negative $\delta^{13}C$ while methanogenesis can generate that with positive $\delta^{13}C$ [15]. The middle cold seep development stage with weak methane seepage may have the characteristics of a stronger methane seepage and thus more positive DIC were mixed into the water column and overtake those from AOM. The previous study show the concentration of ROV2 is far bigger than that of ROV1 and ROV3, which is in support of this view [16]. However, the poor relationship between DIC and $\delta^{13}C$ shows the different source of DIC because if DIC emitted from AOM and methanogenesis integrated as one combined source, this should exhibits a good relationship anyway. $\delta^{13}C$ reaches a bottom and DIC reaches a peak at 200 m. However as the previous study shows the chlorophyll reach its maximum at around 100 m. This indicates that at 200 m there is a new $\delta^{13}C$ source but not cold seep and phytoplankton. This is most likely caused by terrestrial water input from human beings. The anthropogenic DIC, as one of the biogenic DICs, has lighter characteristics. This is compatible with the rise of DIC and decrease of $\delta^{13}C$. ROV2 station reveals the influences from anthropogenic DIC.

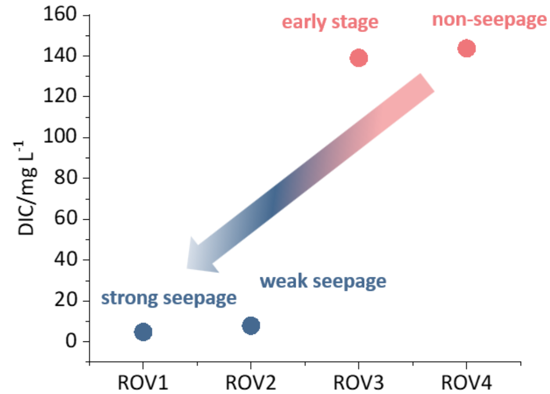

Figure.4 The DIC diminishing trend alongside with cold seep develops. The values were given above in the form of median values to represent the DIC leakage intensity in general.

4.2 Different DIC sources as well as diminishing trend as the cold seep develops

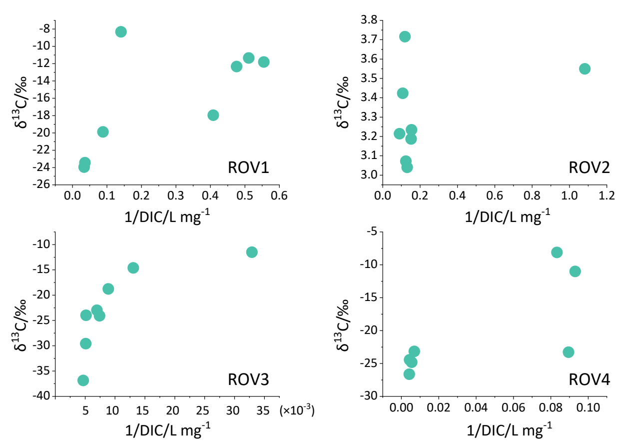

Figure.3 The carbon sequestration mechanism of shell and tissue of (a) Bathymodiolus platifrons (b) Gigantidas haimaensis and (c) Archivesica marissinica. (d) The methane-oxidation and sulfide-oxidation symbionts on the dissected gill filaments. (e) The carbon sequestration mechanism of shell. (modified from Ted A.M. et, 2008). Note that

The Keeling plot indicates the linear relationship between the isotope ratio and the reciprocal of the concentration, which indicates the diffusion process of one single source [17]. Otherwise, the non-linear trend indicates contributions from different sources.

As shown in Fig.3, the non-linear distributions of the keeling plot indicate that DIC affects the whole water profile from different sources for all stations. R^2 ranges from 0.42 to 0.57 for the entire water profile (except ROV2, with a low value of 0.16). This indicates the different sources, but mainly from cold seep environments. The poor R^2 of ROV2 indicates a strong effect from another source. After segregating the whole water profile into different sections, as shown in Table 1, the R2 becomes larger. It is obvious that different sources play a dominant role in different depths. This can be attributed to different water mass movements and mixing conditions. For instance, the different depth intervals show a stratification of three layers for ROV2 and ROV3, which is compatible with the water structure of SCS revealed by water mass isotopes [18].

All in all, cold seeps are not the mere contribution of DIC. Radiocarbon techniques can be applied to differentiate different sources in the future. But from this study, though DIC does be emitted from the seafloor to the sea surface, DIC diminishes in general with the development of the cold seep. Not to mention that these results do not tell the cold seep DIC from other origins.

Table. 1 The correlation coefficient of the Keeling plot (1/DIC-δ^{13}C). Different intervals indicate the data chosen according to different depth intervals; the non-mentioned ones do not show a good coefficient or show a too good result due to the small sample size. The poor relationship was highlighted in red color specifically.

Station	Depth intervals	R^2
ROV1	50-1400	0.42
	100-1400	0.90
ROV2	50-1400	0.16
	50-900	0.83
	1200-1400	0.12
ROV3	50-1400	0.55
	50-900	0.71
	1200-1400	0.87
ROV4	50-1400	0.57
	600-1400	0.66

5. CONCLUSION

This study tests the dissolved inorganic content and measures its isotope ratios from four stations of the Haima cold seep in the South China Sea. Based on these results, we evaluate the effect of DIC emitted from the Haima cold seep to see if it can contribute to greenhouse gases. The main conclusions can be drawn as follows:

(1) Cold seeps are the source of DIC, yet the development of the DIC content reveals a decreasing trend, possibly caused by methane fertilization resulting in the blossoming of phytoplankton. Cold seeps do not contribute to the greenhouse effect in terms of DIC.

(2) Cold seep is not the only contribution of DIC. Another identified source comes from freshwater input of anthropogenic DIC.

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DECLARATION OF INTEREST STATEMENT

We declare that we have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper. All authors read and approved the final manuscript.

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