

The Flux of Total Carbonate at the Southern East Pacific Rise

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Introduction

The study on the fate (behavior and diffusion) of carbon dioxide (CO_2) in the ocean is important in resolving the global climate issues, because the future CO_2 concentration in atmosphere can not be precisely predicted without full knowledge on the inventory of CO_2 in the ocean. Through deep-sea hydrothermal activities, a large amount of elements including carbon as a form of CO_2 are discharged to deep ocean. Deep-sea hydrothermal activities occur at the active lithosphere area, such as spreading ridges, back-arc basin and under-sea volcano. Hydrothermal fluids are highly enriched in CO_2 relative to seawater. The CO_2 in deep-sea hydrothermal vent fluids is mainly of magmatic origin. Seawater penetrates downward toward the magma chamber from the crack of oceanic crust, then rapid heating forces the buoyant hydrothermal fluid to the surface as a hydrothermal vent. This CO_2 is taken up from the basalt by the fluid during high temperature seawater-magma interaction. Furthermore at the back-arc basin, CO_2 is extracted from organic matter and calcium carbonate in the sediment over the subduction zone is added to the vent fluids. The vents of the natural CO_2 -rich fluid and hydrate formation were found in 1989 at the hydrothermal active area in the mid-Okinawa

Trough, back-arc basin (Sakai et al. 1990a). This fact suggest that CO_2 is discharged to deep ocean by hydrothermal activities at the seafloor where hydrothermal vents exist. The southern East Pacific Rise (S-EPR) is one of the super fast spreading ridge in the mid-ocean ridge, therefore it is expect that the hydrothermal flux is large at that area. Here, we focus on the observation of the flux of CO_2 from the hydrothermal systems to the ocean. This paper will report the observation results of the behavior of hydrothermal CO_2 in deep-sea at the S-EPR and consider that the influence of the input of hydrothermal CO_2 to carbon cycle in deep ocean.

Field observation of CO_2 discharge from Deep-Sea hydrothermal systems

Total carbonate (the sum of carbonic acid, bicarbonate ion and carbonate ion dissolved in seawater; total dissolved carbon dioxide) were determined in samples of the non-buoyant plume, the buoyant plume and the hydrothermal fluid collected at S-EPR by the R/V Melville (Nov.-Dec. 1993) and the DSRV SHINKAI 6500 (Sep.-Nov. 1994) under the RidgeFlux project (funded by Science & Technology Agency, Japan). The sampling location on S-EPR was shown in Figure 1. The total carbonate concentration in

seawater samples were determined by using the coulometric titration system (UIC Inc., Carbon Coulometer model 5011) explicated by Jhonson et al. (1985) with the modified CO₂ extraction system described by Shitashima et al. (1996). Samples for total carbonate analysis were drawn from the Niskin samplers and/or manifold-pump sampling system into a glass vial bottles and immediately poisoned with HgCl₂ in order to restrict biological alteration prior to sealing the bottles. All samples were stored in a refrigerator and analyzed on land. The total carbonate concentration in seawater was calculated using a calibration curve constructed by measuring six different concentrations of dissolved Na₂CO₃ (99.99% pure; Asahi Grass) used as a standard solutions (Dickson and Goyet, 1994). The standard deviation was $\pm 1.8 \mu\text{mol/kg}$ (n=19).

Analytical results of hydrothermal fluids sampled by the DSRV SHINKAI 6500 were defined the geochemical characteristics as follows (Ishibashi et al. 19965):

1. Hydrothermal fluids at the RM04, RM28 and RM29 sites were separated into gas phase and liquid phase under sea-floor.
2. Hydrothermal fluids collected from the RM23 and RM28 sites show remarkably high dissolved gas content, suggesting magmatic addition.

The concentration of total carbonate in the hydrothermal fluid samples from black smoker chimney ranged from 5 to 16 mM (2 to 8 times greater than ambient seawater). Total carbonate concentrations of the S-EPR vent fluids were relatively high in comparison to concentration reported for

other EPR hydrothermal vent fluids and 10^2 times lower than those of the vent fluid collected from hotspot volcano (Loihi Seamount: Sedwick et al., 1992) and back-arc basin (e.g. Okinawa Trough: Sakai et al., 1990b). Figure 2 shows Mg - total carbonate diagram in the hydrothermal fluid samples taken from hydrothermal active vents at the S-EPR. The diagram indicated three different lines at the each active sites. Hydrothermal fluids at RM28 site were highly enriched in total carbonate, are suggestive of contribution of gas component from magma body. The hydrothermal end-member fluids discharged from the vents are rapidly diluted between hydrothermal end-member fluid and ambient seawater by factors of $10^4 - 10^5$ (Lupton et al. 1985). Figure 3 indicates the distribution of total carbonate in the buoyant plume as a function of distance from hydrothermal active vents in the S-EPR. The buoyant plume samples were collected along with the trail of the buoyant plume by means of keeping the submersible buoyancy at natural and drifting with water current. Total carbonate concentration in the buoyant plume become close to that of ambient seawater within dozens meters from the vents due to drastic mixing and dilution of vent fluid with ambient seawater.

What happens to the hydrothermal CO₂ discharged by deep-sea hydrothermal systems in deep ocean? Along-axis transect of total carbonate anomaly in hydrothermal plumes over S-EPR axis is shown in Figure 4. The positive anomalies of total carbonate associated with hydrothermal plumes were observed on the seafloor along S-EPR axis. The highest concentration of total carbonate

anomaly detected near 16°S was 2.48 mM, but total carbonate concentration of ambient seawater in water column around S-EPR is about 2.36mM. Figure 5 represents the vertical profiles of total carbonate for a short east-west section along 15°S across the S-EPR axis. The total carbonate anomalies were observed in the bottom water over the slope of S-EPR axis, indicating the dispersion of a hydrothermal plumes at this depth. The total carbonate plumes spreaded out above the seafloor both westward and eastward along 15°S across the S-EPR. At the western stations, the concentrations of total carbonate were decreased due to mixing with the Pacific water with low total carbonate concentration. According to recent research for hydrothermal plumes, the carbon dioxide anomalies associated with hydrothermal plume have not been observed at various hydrothermal area. These results demonstrate that carbon dioxide is discharged through hydrothermal systems to the ocean in the same manner as ^3He , CH_4 and Mn. Schematic diagram of total carbonate plume for a short east-west section along 15°S across the S-EPR axis is presented in Figure 6. The distribution pattern of the total carbonate plumes were different from that of the ^3He plume reported by Lupton and Craig (1981). Low temperature diffuse discharge typically occurs in areas surrounding black smoker chimneys. This diffuse flow transports an order of magnitude more heat than the hydrothermal vent fluid from black smoker chimney (Schultz et al. 1992; Ginster et al. 1994). It is implied that the low temperature diffuse flow is significant source of heat and chemical, such as CO_2 , fluxes in

deep-sea hydrothermal systems. These observation results suggest the possibility of discharging of CO_2 through deep-sea hydrothermal systems to the ocean.

On the other hand, the other inputs of CO_2 into the deep-sea are the bacterial activity around hydrothermal vents, the oxidation of organic matter generated by hydrothermal bacteria, and the formation of calcium carbonate and CO_2 from calcium bicarbonate solution supplied by hydrothermal activity. However, these inputs in deep-sea are indirectly concerned with hydrothermal activity. In other word, CO_2 is supplied directly and indirectly from hydrothermal systems to deep ocean. Determination of carbon isotope ratio will be effective in order to distinguish the source of each carbon dioxide.

Flux of CO_2 to the ocean through mid ocean ridge

Recent estimate of CO_2 fluxes to the ocean through mid ocean ridge (MOR) from the $\text{CO}_2/^3\text{He}$ ratio of vent fluids and ^3He budget for the ocean were calculated at $0.7 \pm 0.25 \times 10^{12}$ mol C/year (Gerlach, 1989) and 15×10^{12} mol C/year (Javoy and Pineau, 1991). These results suggest that the input of CO_2 to the ocean from MOR is are 3-4 orders of magnitude smaller than the annual CO_2 fluxes through terrestrial and marine respiration, and an order of magnitude smaller than the flux of carbon to shelf and deep-sea sediments. The importance of CO_2 input from MOR on oceanic carbon cycle is thus minimal on shorter-term time scales (in several years order). However, the CO_2 input from MOR may be significant at longer time

scales ($10^6\sim10^7$ years), because ridge generation that cause the hydrothermal activity has been continuing from 100 million years ago, more active ridge generation might occur in the past or ridge generation rates might undergo rapid change. On a time scale of years, furthermore, the concentration of CO_2 in hydrothermal vent fluid at hotspot submarine volcano (*e.g.* Loihi Seamount) and back-arc basin (*e.g.* Okinawa Trough) is $10\sim10^2$ times higher than that of MOR, but the hydrothermal activities at back-arc basin and hotspot exist locally relative to MOR. The input of CO_2 from these hydrothermal systems to the ocean may be significant. The heat flux of the Megaplume, event plume of the episodic large-scale hydrothermal activity, is 1~3 orders larger than that of a normal plume (Baker et al., 1987), but the hydrothermal CO_2 flux from Megaplume is not made clear yet at present time.

From the facts presented above, it can be imagined that the flux of CO_2 from deep-sea hydrothermal systems to the deep ocean may be significant. It is necessary for the observation of CO_2 flux from the individual hydrothermal activity and the understanding of contribution or effect of the hydrothermal CO_2 flux to oceanic carbon cycle.

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Reference

- Baker, E.T., G.J. Massoth and R.A. Feely (1987): Cataclysmic hydrothermal venting on the Juan de Fuca Ridge. *Nature*, **329**, 149-151.
- Dickson, A. G. and C. Goyet. 1994. Handbook of methods for the analysis of the various parameters of the carbon dioxide system in sea water. Ver. 2 ORNL/CDIAC-74. A. G. Dickson and C. Goyet (eds.). Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory, Oak Ridge, Tenn.
- Gerlach, T.M. (1989): Degassing of carbon dioxide from basaltic magma at spreading centers: II. Mid-oceanic ridge basalts. *J. Volcanol. Geotherm. Res.*, **39**, 221-232.
- Ginster, U., M.J. Mottl and R.P. Von Herzen (1994): Heat flux from black smokers on the Endeavor and Cleft segments, Juan de Fuca Ridge. *J. Geophys. Res.*, **99**, 4937-4950.
- Ishibashi J., T. Oomori, A. Sonoda, J.E. Lupton, D.A. Butterfield, K. Shitashima, U. Tsumogai, K. Roe, G. Paradis, J. Gendron and G.J. Massoth (1995): Geochemical studies of hydrothermal activities along the S-EPR by "Shinkai 6500". *JAMSTEC Deep-Sea Res.*, **11**, 157-164. (in Japanese with English abstract).
- Javoy, M. and F. Pineau (1991): The volatile record of a "popping" rock from the Mid-Atlantic Ridge at 14°N : chemical and isotopic composition of gas trapped in the vesicles. *Earth Planet. Sci. Lett.*, **107**, 598-611.

- Jhonson, K. M., A. E. King, and J. M. Sieburth. 1985. Coulometric TCO_2 analysis for marine studies: An introduction. *Mar. Chem.* 16, 61-82.
- Lupton, J.E. and H. Graig (1981): A major helium-3 source at 15°S on the East Pacific Rise, *Science*, 214, 13-18.
- Lupton, J.E., J.R. Delaney, H.P. Johnson and M.K. Tivy (1985): Entertainement and vertical transport of deep-ocean water by buoyant hydrothermal plumes. *Nature*, 316, 621-623.
- Sakai, H., T. Gamo, E.-S. Kim, F. Yanagisawa, M. Tsutsumi, T. Tanaka, J. Ishibashi, H. Wakita, M. Yamano and T. Oomori (1990a): Venting of carbon dioxide-rich fluid and hydrate formation in mid-Okinawa Trough backarc basin. *Science*, 248, 1093-1096.
- Sakai, H., T. Gamo, E.-S. Kim, K. Shitashima, F. Yanagisawa, M. Tsutsumi, J. Ishibashi, Y. Sano, H. Wakita, T. Tanaka, T. Matsumoto, T. Naganuma and K. Mitsuzawa (1990b): Unique chemistry of the hydrothermal solution in the mid-Okinawa Trough backarc basin. *Geophys. Res. Lett.*, 17, 2133-2136.
- Sedwick, P.N., G.M. McMurtry and J.D. Macdougall (1992): Chemistry of hydrothermal solution from Pele's Vents, Loihi Seamount, Hawaii. *Geohim. Cosmochim. Acta*, 56, 3643-3667.
- Schultz, A., J.R. Delaney and R.E. McDuff (1992): On the partitioning of heat flux between diffuse and point source seafloor venting. *J. Geophys. Res.*, 97, 12229-12314.
- Shitashima, K., K. B. Steven, D. Tsumune, I. Asamuma, and T. Ono. 1996. The measurement of total carbonate in seawater.: In abstract of the 1996 spring meeting of the Oceanographic Society of Japan. 269pp (in Japanese)

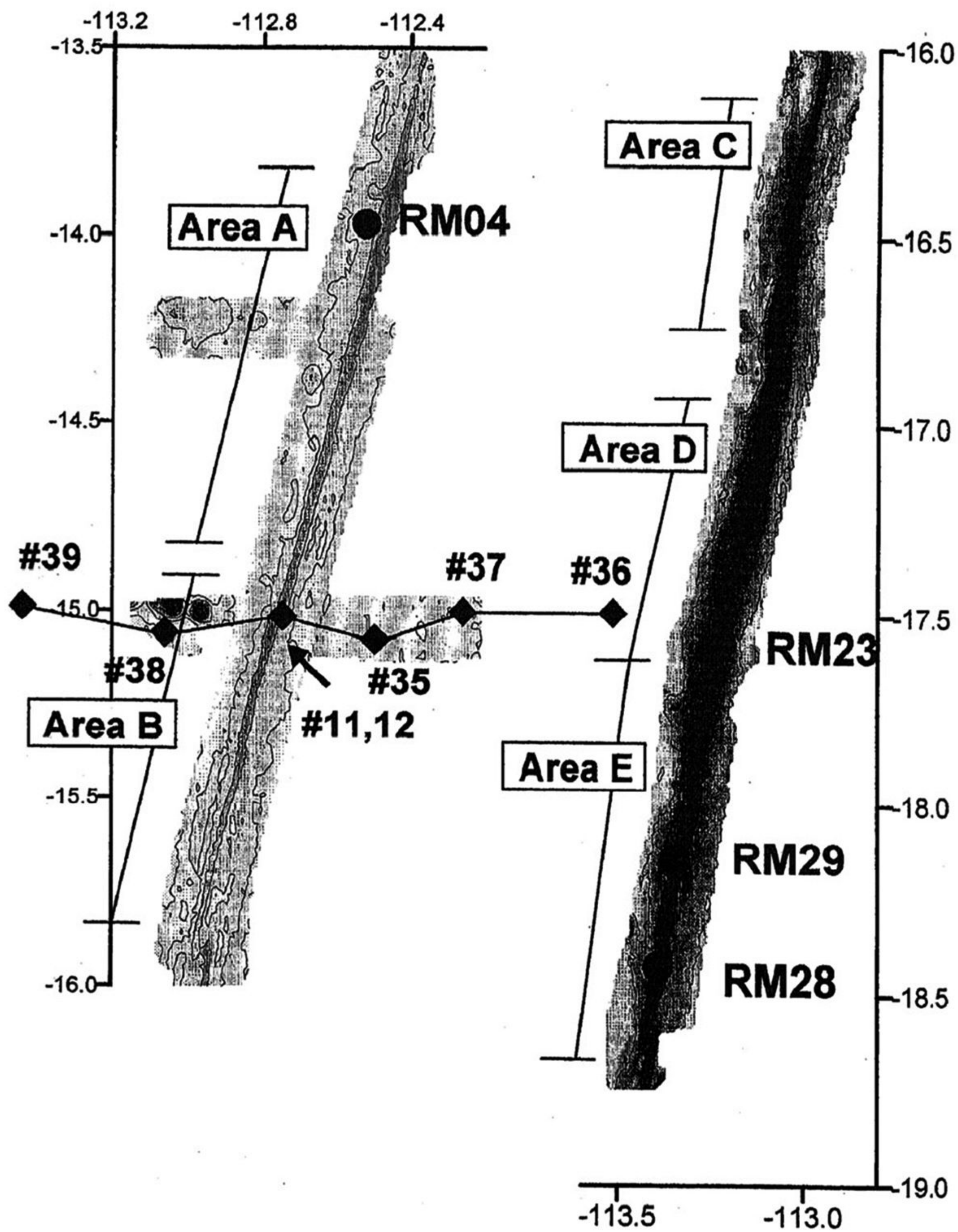


Figure-1: Sampling location on the S-EPR

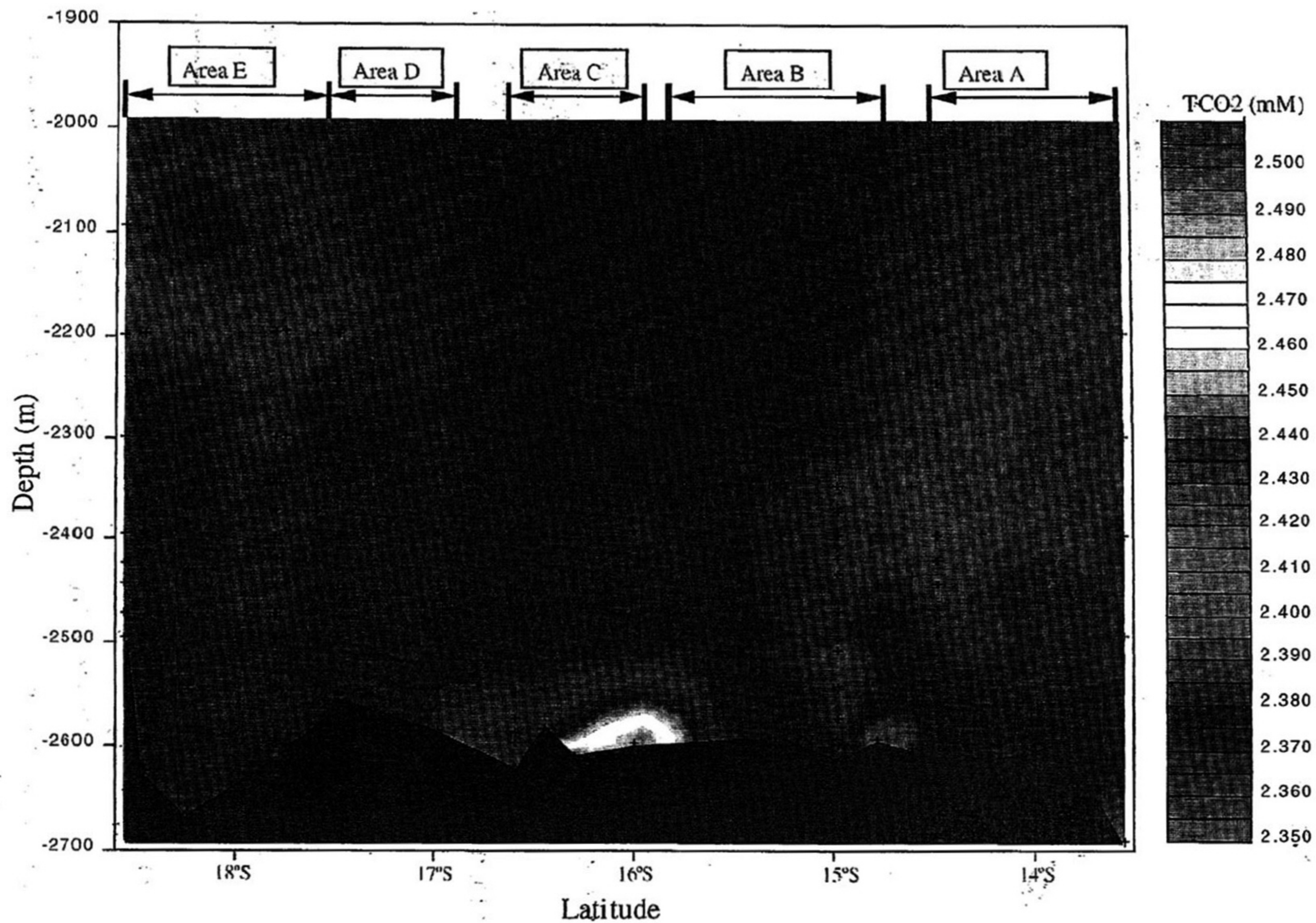


Figure-4: View of total carbonate in the water column over the S-EPR

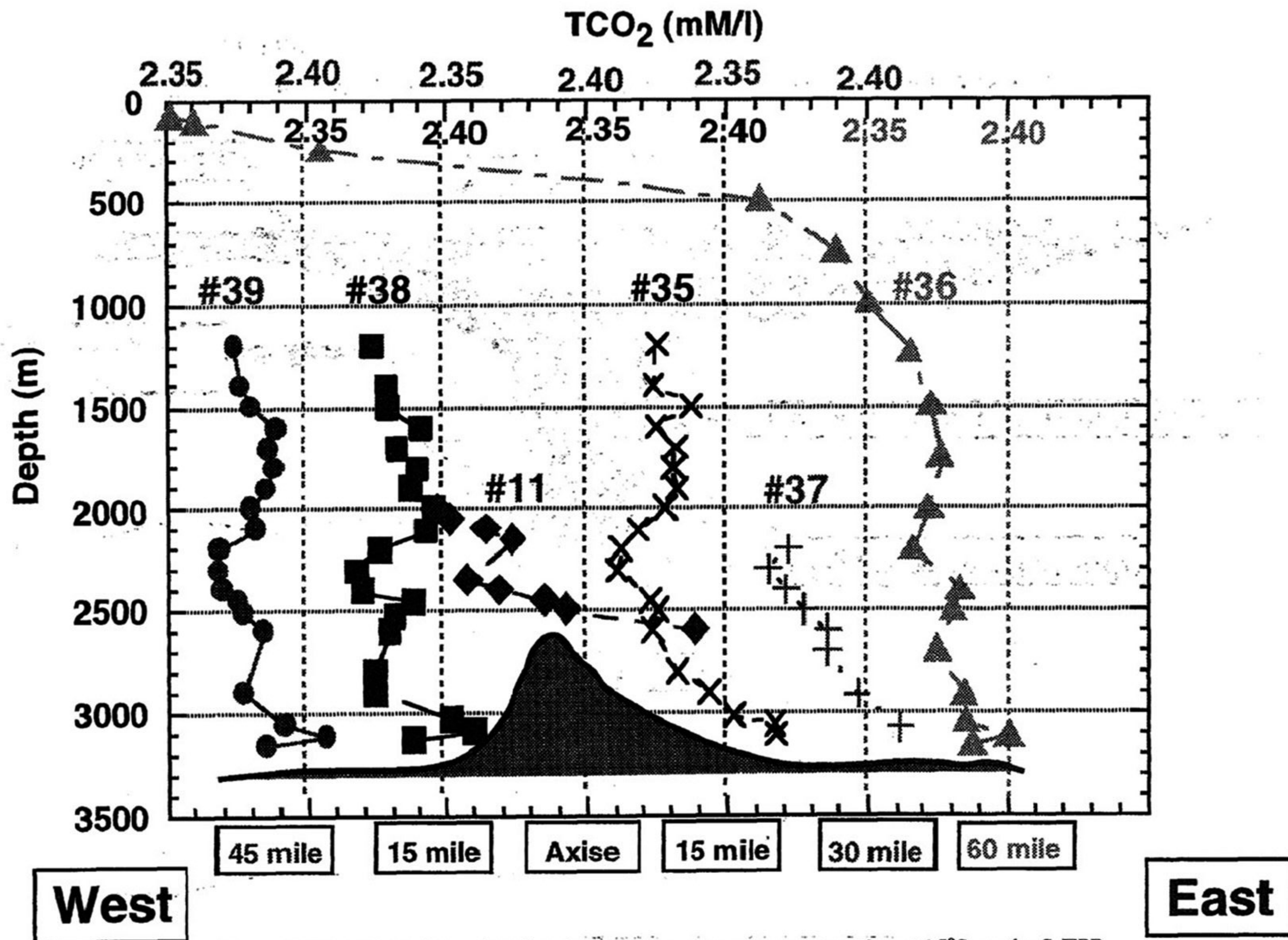


Figure-5: Vertical profiles of total carbonate for a short east-west section at 15°S on the S-EPR
 ("Axis" is the spreading center, each "mile" is distance from the spreading center)

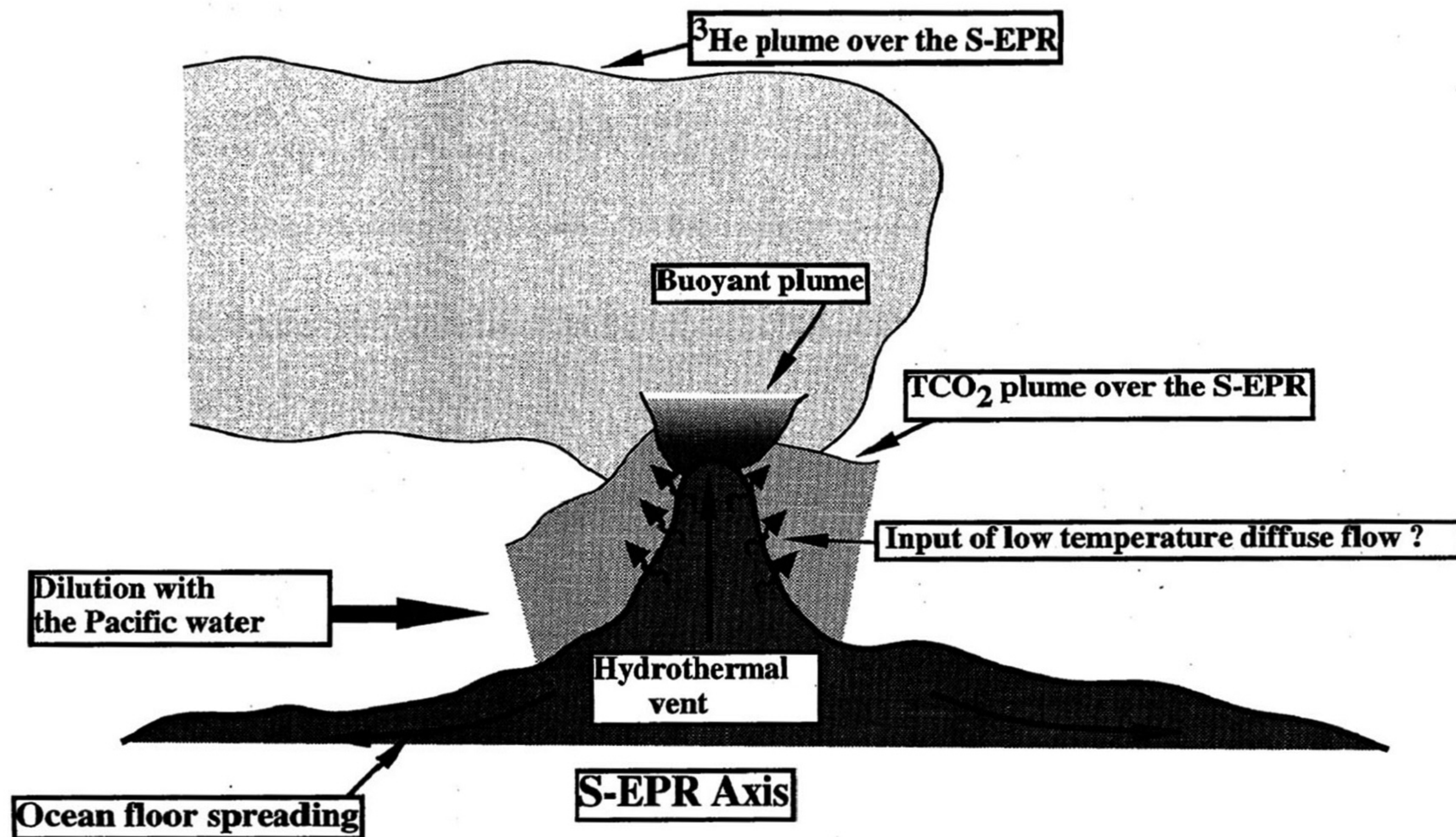


Figure-6: Schematic diagram of total carbonate plume for a short east-west section at 15°S on the S-EPR