

Stable carbon isotopes of DIC and dissolved methane concentrations on the western Iberian Margin

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Introduction

The $^{13}\text{C}/^{12}\text{C}$ ratio of total CO_2 ($\delta^{13}\text{C}$) and dissolved methane concentration are both tracers affected in some way by air-sea exchange, biogeochemical sources and sinks, and the ocean circulation and mixing. In deeper parts of the ocean, $\delta^{13}\text{C}$ is correlated with nutrient concentration, mainly due to biological cycling. In the upper ocean, additional effects come into play. These include sea-air fractionation from CO_2 gas exchange, fractionation by regional transfer of CO_2 through the atmosphere, and the penetration of isotopically light CO_2 produced in the atmosphere by fossil fuel burning [Keir *et al.*, 1998]. Because of these effects, the pattern of $\delta^{13}\text{C}$ versus dissolved phosphate in northeast Atlantic waters is not linear. The ocean plays an important role in sequestering a portion of the CO_2 that is being injected into the atmosphere by fossil fuel burning and deforestation. By measuring the contemporary $\delta^{13}\text{C}$ distribution and comparing this with proxies of the pre-industrial distribution, we are attempting to establish the pattern of the uptake of anthropogenic CO_2 in the OMEX II-II area. In the upper water column, the $\delta^{13}\text{C}$ measurements are being carried out on a seasonal basis in order to quantify the roles of biological production and air-sea exchange on the isotopic composition.

The principal control on the methane distribution in the northern Atlantic appears to be the “ventilation age” of the sub-surface waters formed over the last 100 years. This is seen from the close correlation of percent-saturation of CH_4 with that of chlorofluoromethane-11 throughout the Atlantic area between 50° and 60°N (Rehder *et al.*, 1999). This appears to be due to the atmospheric rise of methane on the one hand and the oxidation of methane on a 50-year time scale on the other. The methane distribution on the Iberian margin has not yet been investigated. Of special interest is the CH_4 content in the Mediterranean Outflow water (MOW), as the higher temperatures in these waters might favour higher microbial degradation rates.

Sampling

The objectives within Task II concerning the net flux of CO_2 across the air-sea interface have been further pursued. Water samples for carbon and oxygen isotopic analysis have been collected on two additional cruises, *Belgica BG9815* and *Meteor M43/2*. The analysis is being conducted in the Leibniz Laboratory of the University of Kiel. Acidification and extraction of the CO_2 for carbon isotopes is conducted on a multiple extraction manifold coupled to a Finnigan-MAT Delta E mass spectrometer. The analysis of $\delta^{13}\text{C}$ samples from *Belgica BG9714* and *Poseidon PS211* have been finished. Measurements of $\delta^{13}\text{C}$ samples of *Meteor M43/2* are almost accomplished, and data from *Belgica BG9815* will be analysed in the next few months. Since the Leibniz Laboratory is running the $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ in batch separately, the oxygen isotopes will be analysed in fall, 1999. Collection of radiocarbon samples took place on *Meteor M43/2*. In total, we will be able to provide a $\delta^{13}\text{C}$ data set from the OMEX II-II area from June 97, March 98, June 98 and January 99 (Figure 1).

Another area of attention in connection with the net flux of CO_2 between ocean and atmosphere is the measurement of the partial pressure of CO_2 in surface waters of the OMEX II-II area. Measurements are usually performed by ULg using IR spectroscopy. Intercalibration with the GEOMAR pCO_2 system based on gas chromatography was performed on *Meteor M43/2*, although the system had to be shut down on a part of the cruise to allow the measurement of CH_4 on discrete samples, as problems occurred with the gas chromatographic system usually used to run these samples. However, data

collection from both underway systems was long enough to allow intercalibration. Final data processing has not been finished yet.

Analysis of methane along OMEX Line S and some additional stations, tracing the Mediterranean outflow from near Cadiz to the OMEX working area, have been performed during *Meteor M43/2*. Methane was extracted by a vacuum degassing method and analysed for CH₄ by gas chromatography [Rehder *et al.*, 1999].

Results and Discussion.

The vertical pattern of $\delta^{13}\text{C}$ in the waters off Vigo are shown in Figure 2, based on data from June, 1997 (*Belgica BG9714*) and March, 1998 (*Poseidon PS211*). Below 200 m, the vertical distributions are quite similar. In summer '97, upwelling has brought light isotopic ratios closer to the surface, which is distinguishable in the upper 200 m of the profiles. The distribution of $\delta^{13}\text{C}$ in the upper 250 meters off of Vigo in summer '97 shows a sharp “frontal zone” in $\delta^{13}\text{C}$ at the edge of the shelf, presumably due to coastal upwelling (Figure 3).

Further to the north at the Goban Spur, phosphate concentrations of 0.5 mmol kg⁻¹ occur in the upper 300 m in winter (OMEX I). On the Galician margin, much lower concentrations (< 0.1 mmol kg⁻¹) are found in surface waters year-round, except close to the coast during summer upwelling. A plot of $\delta^{13}\text{C}$ versus phosphate from both regions shows an interesting comparison (Figure 4). Both patterns are similar and overlap. In the upper waters on the Galician margin, the slope of the linear segment is that expected from photosynthetic uptake of carbon and nutrients starting from a precursor with 1‰ $\delta^{13}\text{C}$ and 0.5 mmol kg⁻¹ phosphate - the composition of winter surface water at the Goban Spur. At $[\text{PO}_4] > 0.5$ mmol kg⁻¹, the patterns are not linear. It appears that $\delta^{13}\text{C}$ has been progressively shifted to lower values starting at $[\text{PO}_4] < 1.2$ mmol kg⁻¹, which may be due to penetration of isotopically light carbon into the upper 2000 m of the water column [Keir *et al.*, 1998].

The vertical distribution of CH₄ generally reflects the “ventilation age” of water masses in the region of the Iberian Peninsula. In the Gulf of Cadiz, the methane concentration in the core of Mediterranean Overflow Water is relatively high, and the concentration decreases “downstream” with the movement of this water mass in the direction of Cape Finisterre (Figure 5). The high concentrations in the core of MOW in the Gulf of Cadiz are higher than the expected equilibrium of this water mass with the atmosphere. Hence, it appears that the methane content of MOW during its formation is not completely controlled by the atmospheric CH₄ content. The fast decrease of CH₄ concentrations towards the north might be due to a combination of consumption and dilution of MOW with waters of lower methane concentration in the direction of flow. We suspect that the CH₄ consumption in the warm MOW is more rapid than in NADW [Rehder *et al.*, 1999]. Methane consumption rates are generally found to be highly dependent on temperature. The series of profiles normal to the Galician coast are generally similar (Figure 5). However, it can be seen that further off the coast, upper and lower MOW begin to be separated by an intrusion of lower-methane water at 900-m depth.

References

- Keir, R.S., G. Rehder, E. Suess, and H. Erlenkeuser, The $\delta^{13}\text{C}$ anomaly in the northeastern Atlantic, *Global Biogeochem. Cycl.*, 12, 467-477, 1998.
- Rehder, G., R.S. Keir, E. Suess, and M. Rhein, Methane in the northern Atlantic controlled by oxidation and atmospheric history, *Geophys. Res. Lett.*, 26, 587-590, 1999.

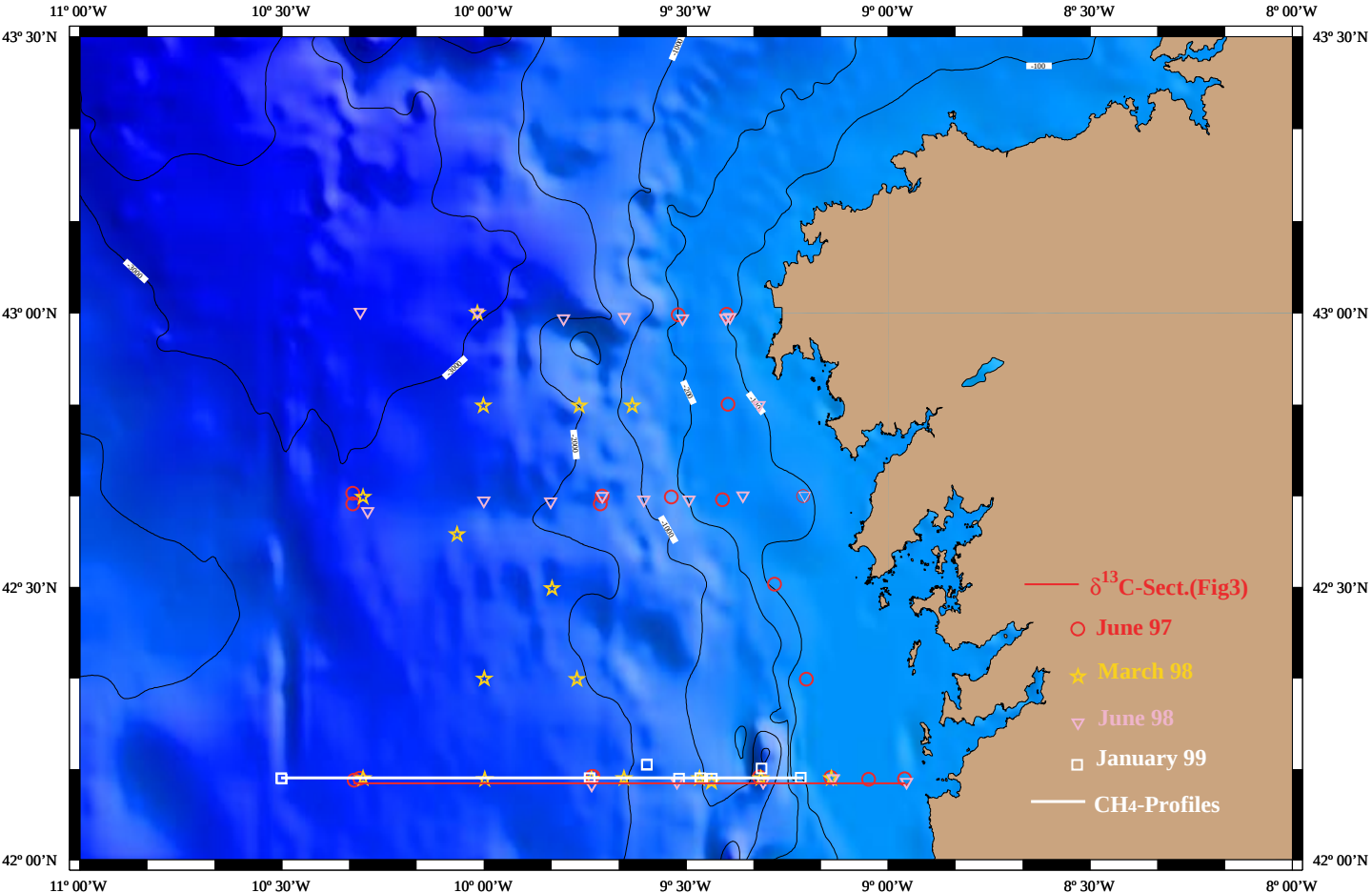


Fig. 1: Map showing all stations sampled for $\delta^{13}\text{C}_{\Sigma\text{CO}_2}$ during OMEX cruises Belgica 97/14 (June 97), Poseidon 237 (March 98), Belgica 98/15 (June 98), and Meteor 43/2 (January 99). Also shown are locations of the $\delta^{13}\text{C}$ section (Fig. 3).

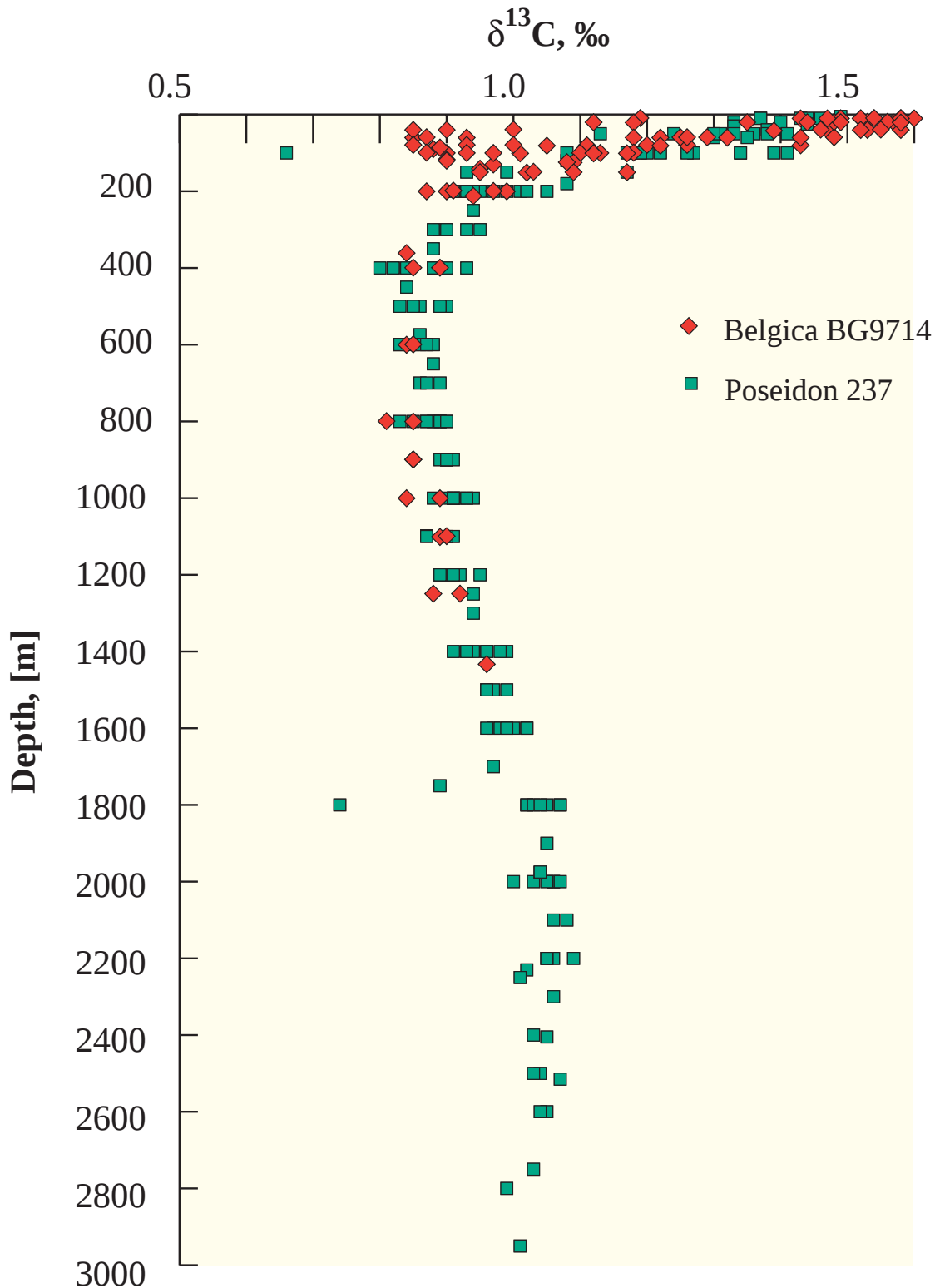


Fig. 2: $\delta^{13}\text{C}$ of total dissolved CO_2 versus depth. Red points show summer '97 (Belgica BG9714) data, green points show winter '98 (Poseidon P237) data.

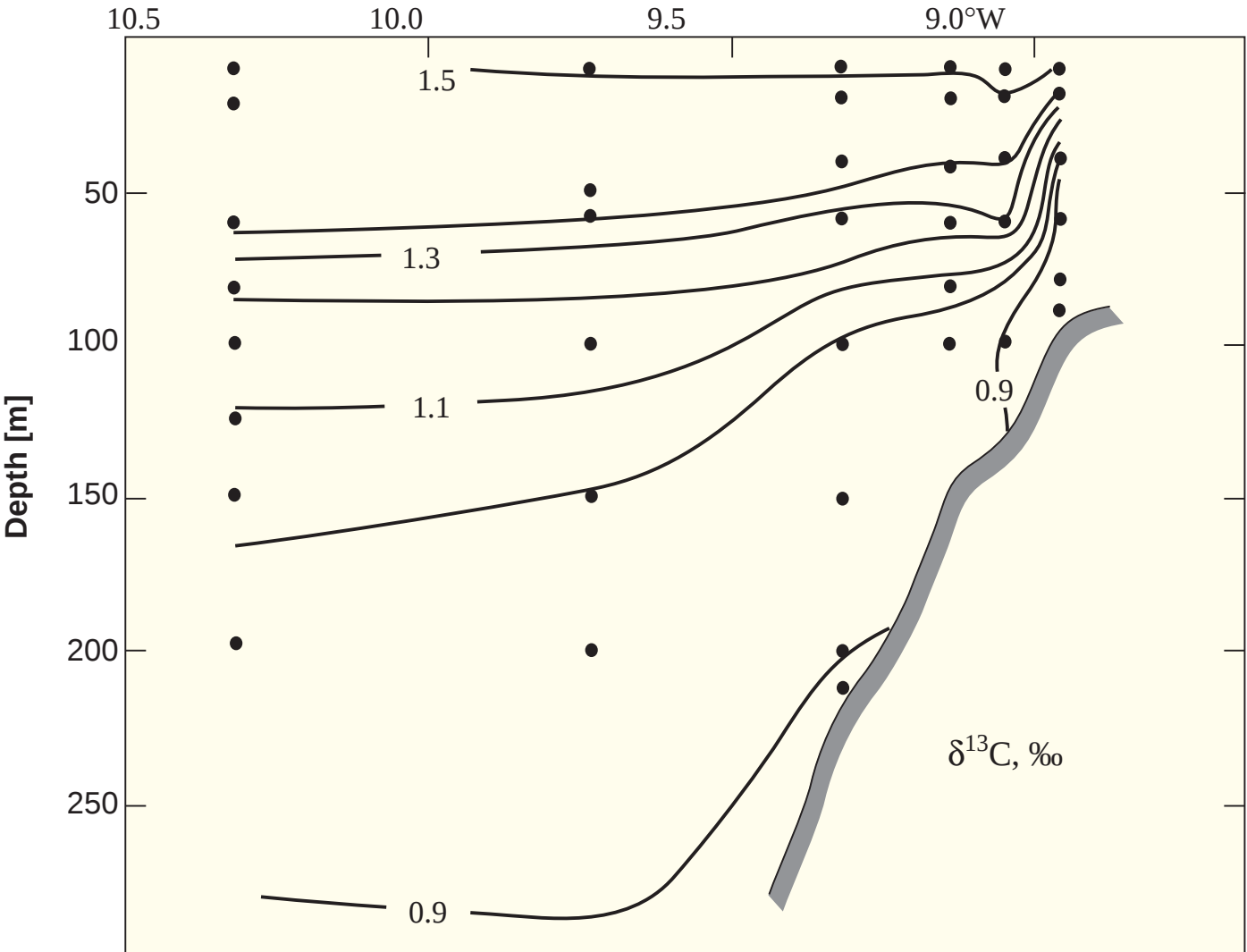


Fig. 3: Horizontal distribution of $\delta^{13}\text{C}$ in the upper 250m along $42^\circ 9' \text{ N}$ in summer '97. The frontal zone due to upwelling is clearly evident.

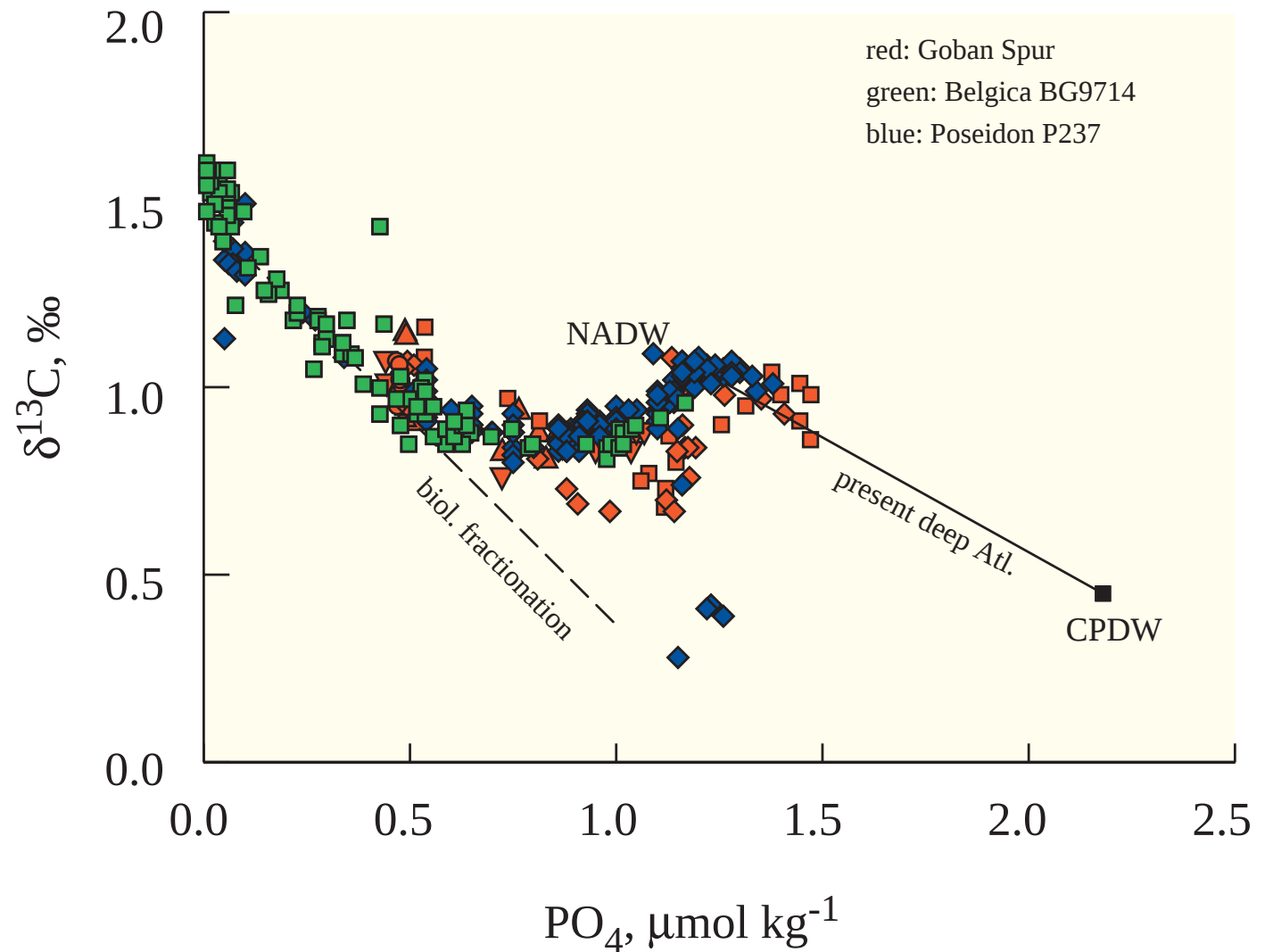


Fig. 4: $\delta^{13}\text{C}$ vs. phosphate. The data from OMEX II-II (Poseidon P237 and Belgica BG9714) are superimposed from earlier Goban Spur data (OMEX I). Lines show NADW-CPDW trend found in western Atlantic and slope expected from biological fractionation.

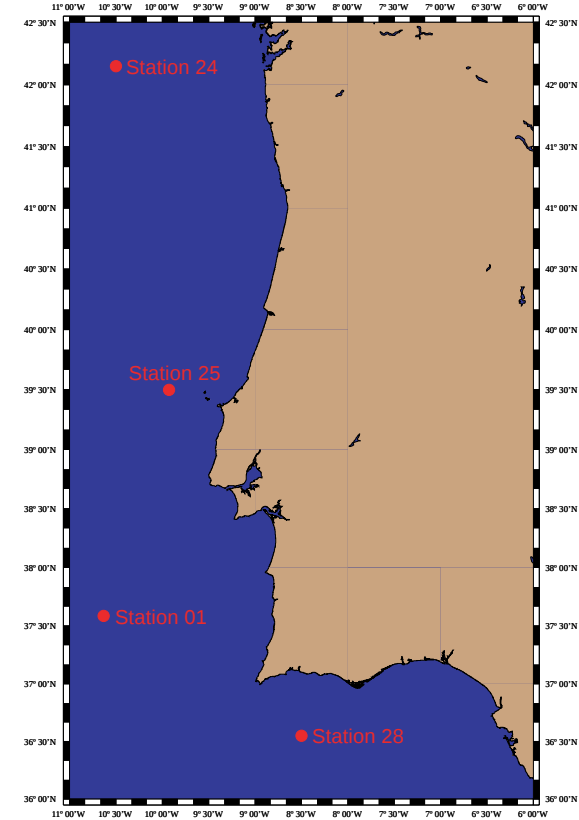
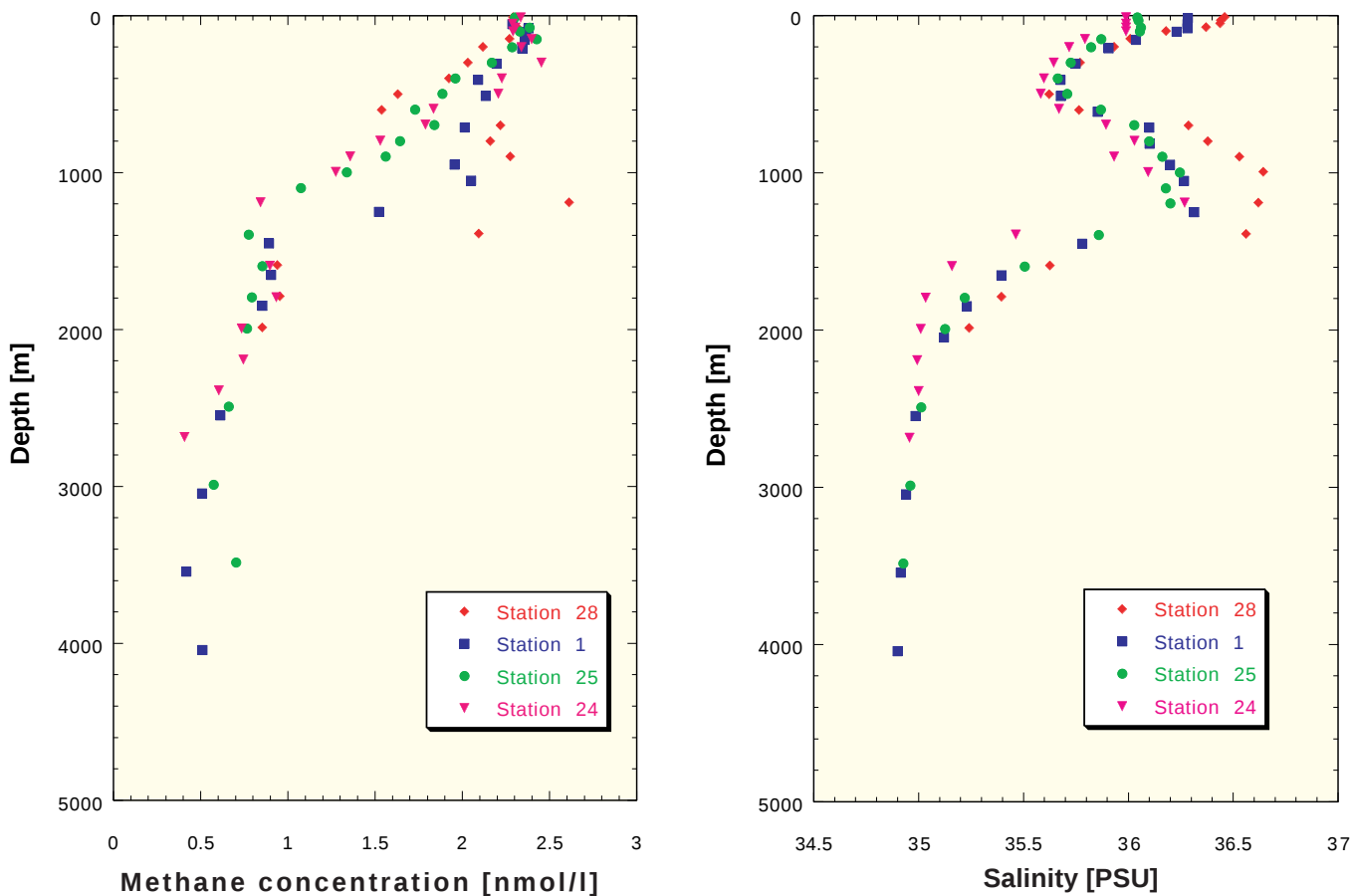


Fig. 5: CH_4 and Salinity distribution on 4 stations following the Mediterranean Outflow (MOW) along the Iberian Margin. The core of the MOW is characterized by high CH_4 concentrations near to its source. While salinity and potential

temperature (not shown) profiles indicate only small dilution of MOW between stations 01 and 24, the methane concentration shows considerable decrease.