European Science Foundation MedCLIVAR Exchange Grant 2362

Scientific Report

Purpose of the visit

The fellow has been awarded a European Science Foundation Exchange Grant (Mediterranean Climate Variability and Predictability – MedCLIVAR) to visit for a total of four weeks the Geochemistry Group at the Lamont-Doherty Earth Observatory (LDEO) of Columbia University (Palisades, New York, United States of America) and to work in close collaboration with Dr. Bärbel Hönisch.

The purpose of the visit was to perform species specific planktonic foraminiferal boron isotope ($\delta^{11}B$) measurements for paleo-pH reconstructions within the framework of the project entitled 'Biological calcification in the light of changing marine carbonate chemistry – a case study from sapropel 5 in the Mediterranean'.

Summary of the scientific rationale of the project

In the light of the pronounced impact of the ongoing atmospheric greenhouse gas rise on the chemistry of the world's ocean, dubbed ocean acidification, it is critical to advance our knowledge of the functioning of the marine carbonate system under 'natural', pre-anthropogenic conditions. Information concerning the present-day and past marine carbonate system in the Mediterranean Sea remains sparse and largely incomplete, thereby preventing a sound forecasting of the response(s) of the basin's seawater chemistry and calcifying biota to the continuing CO_2 forcing. The (few) available lines of evidence underscore the role of the efficient Mediterranean thermohaline circulation in promoting an active sink of CO_2 (Bethoux et al., 2005). Namely, carbon is taken up at the sea surface, exported first to the deep sea and eventually at depth to the North Atlantic by the dense water formation and by outflow of Mediterranean dense waters at Gibraltar, respectively (Bethoux et al., 2005).

Paleoceanographic evidence, however, demonstrates that nearly opposite oceanographic conditions prevailed during the insolation/monsoon maximum of the last interglacial period. During this interval, a positive shift in the eastern Mediterranean freshwater budget (Rohling et al., 2002) inhibited the process of dense water formation and dramatically weakened the basin's thermohaline circulation (Rohling et al., 2006; Marino et al., 2007). This, in turn, led to massive organic carbon burial (sapropel S5; C_{org} up to 14%) at the seafloor, accumulation of considerable amounts of respired CO_2 in the subsurface, and the development of a marked chemocline at ~300 m depth (Rohling et al., 2006; Marino et al., 2007).

Hence, the eastern Mediterranean sapropel S5 appears to markedly contrast the present-day conditions and, as such, represents an excellently suited target for us to elucidate the actual role played by the basin's thermohaline circulation on the marine carbonate system of the Mediterranean Sea.

Proposed methodological approach

We attempted the first reconstruction of the carbonate system changes and of the concomitant state of the marine calcifying biota during the period of sapropel S5 deposition. We focused on a high sedimentation rate marine archive, south-eastern Aegean core LC21 with evidence of well preserved carbonate fossils (Marino et al., 2007). A recently developed paleoceanographic proxy, namely the foraminiferal $\delta^{11}B$, permits to reconstruct pH changes in the past ocean surface and deep waters with relatively fine accuracy (e.g., Hönisch and Hemming, 2004, 2005; Hönisch et al., 2008, 2009). On the other hand, the response of the marine calcifiers – foraminifera and coccolithofores – to perturbations in the marine carbonate system is assessed

by performing foraminiferal and coccolith shell weight measurements (e.g., Young and Ziveri, 2000; Barker and Elderfield, 2002; Beaufort, 2005).

Description of the work carried out during the visit

Three planktonic foraminiferal species, namely *Orbulina universa*, *Globigerinoides ruber*, and *Neogloboquadrina pachyderma*, were hand picked by the fellow at his home institution. Fifty shells of *Orbulina universa*, which were picked within a very small size window (50 μm), were subsequently weighted to generate a size-normalized shell weight record across the studied interval.

At the host institution, the fellow progressed with the sample preparation for boron isotope analyses.

Foraminifera were gently crushed between clean glass plates to break open individual chambers. Subsequently, they were bleached with 4-6% sodium hypochlorite to remove organic matter. To allow the escape of evolving CO_2, vials were left open during the entire beaching process. After 24 hours in bleach, the samples were repeatedly rinsed with Milli-Q water, ultrasonicated, and centrifuged to remove soluble salt and any adsorbed boron.

Samples were dissolved in 2N quartz distilled HCl, and subsequently analyzed on a TRITON thermal ionization mass spectrometer. To help ionization, boron free seawater was added to both samples and boric acid standards. Each sample was analyzed al least eight times to eliminate analytical artifacts, e.g., an excessive fractionation and/or isobaric interferences on mass 42 with organic matter contamination ($^{12}C^{14}N^{16}O$ ions) on the reported data. Runs were considered acceptable when fractionation was estimated to be less than 1‰ (i.e., <0.004 in the absolute ratio) over a minimum acquisition time of 30 minutes.

A total of 12 samples were analyzed, although 3 of these samples were showing unexpectedly low isotopic values. Given that also boric acid standards were showing extremely low isotopic values, results from these analyses were discarded and they will be not considered for publication purposes. Following the analysis of these samples, the TRITON was baked out and only standards were run for a few days. For this reason and in order to complete the planned work, the appointment of the fellow as part-time post-doctoral research scientist at LDEO was extended by one week, that is, until September 1st 2009.

Notably, during his visit at LDEO the fellow participated in a 'boron isotope workshop', which was organized by Dr. Bärbel Hönisch at the host institution (August 17-18 2009) and was attended by several experts of the carbonate geochemistry research. During the workshop several different approaches to generate foraminiferal boron isotope/paleo-pH reconstructions were discussed in detail.

Description of the main results obtained

Variability of the *Orbulina universa* shell weights through the studied interval consists in rather small amplitude fluctuations, which are however not statistically significant. Concerning the $\delta^{11}B$ analyses, the most consistent picture derived from the measurements made on the summer mixed layer dweller *Globigerinoides ruber*. $\delta^{11}B$ values for this species range between 19.8 and 20.1‰ across the studied interval, with maximum values (high pH) that coincide with the interval of highest sea surface freshening and surface to intermediate water density stratification reported in previous studies (Rohling et al., 2006; Marino et al., 2007).

Future collaboration with host institution

The research visit carried out at the Geochemistry Group at the LDEO of Columbia University (Palisades, New York, United States of America) did undoubtedly foster the collaboration between the fellow, and the institution to which he is affiliated, and Dr. Bärbel Hönisch. Indeed, we are currently organizing another visit for the summer of 2010 in order to generate another foraminiferal $\delta^{11}B$ record from a core taken from the southern South Atlantic, offshore South Africa (Agulhas Bank). The scientific scope of the visit has been already set and we are in the process of exploring the funding opportunities to cover the travel expenses.

Projected publications/articles to result from the grant

The dataset generated during the visit of the fellow at the LDEO will be completed in the upcoming weeks/months. Namely, we are currently upgrading the software needed to generate the coccolith shell weight record. Publication will aim at a SCI-indexed Journal.

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