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FINAL REPORT

PALEOCEANOGRAPHIC CHANGES IN THE GULF OF CADIZ DURING THE LATE PLIOCENE

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1. Background and objectives

The Institute of Earth Sciences of the University of Graz (Austria) is involved in post-cruise research efforts of IODP Expedition 339 towards a better understanding of the environmental significance of Mediterranean Outflow Water (MOW) and its role in global climate (Stow et al., 2013). The research focus lies on the reconstruction of paleoceanographical changes in the NE Atlantic Ocean during the Pliocene caused by the onset of MOW after the opening of the Gibraltar Strait (~5.3 Ma).

Preliminary results from upper Pliocene sediments recovered at IODP Site U1389E (Figure 1) were ambiguous and difficult to interpret with respect to MOW. The methodology relied on micropaleontological and geochemical proxies as tracers of MOW: distinct benthic foraminiferal assemblages provide information on MOW intensity, velocity and bottom water ventilation, while the combination of $\delta^{18}\text{O}$ and Mg/Ca from benthic foraminifera indicates changes in the contribution of warm and highly saline MOW. The combination of these proxies is generally considered a reliable tool for MOW reconstruction (Rogerson et al., 2011). However, their application to the Pliocene sediments of IODP Site U1389E was complicated by Expedition 339 was complicated by preservation, the limited amount of suitable benthic foraminiferal shells, reworking and transport.

In addition, high-resolution records of total organic carbon (TOC), CaCO_3 and S contents were acquired from IODP Site U1389E to address changes in export productivity and bottom water ventilation. Preliminary results revealed distinct cyclic patterns in well recovered intervals potentially related to orbital forcing. However, the interpretation remained difficult as the source of CaCO_3 content of U1389E was not clear.

These difficulties resulted in the consideration of additional proxy records, which could provide reliable data in a time- and cost-efficient manner. Bahr et al. (2014) have recently introduced the Zr/Al ratio as a novel proxy for MOW reconstruction in upper Pleistocene sediments of IODP Sites U1387 and U1389. In their study, the authors demonstrate that the Zr/Al ratio follows occurrences of contourites, and therefore serves as a semi-quantitative indicator of bottom current strength (Bahr et al., 2014).

Furthermore, the origin of the carbonate in the sediment (biogenic vs detrital; continental runoff) is reflected in varying distributions of elements such as Sr, Ti and Fe (Hodell et al., 2008; Bahr et al., 2014). Input of biogenic organic matter is reflected in the Br content of the sediment, which in combination

with TOC and S records provides information about export productivity and bottom water oxygenation (Bahr et al., 2014).

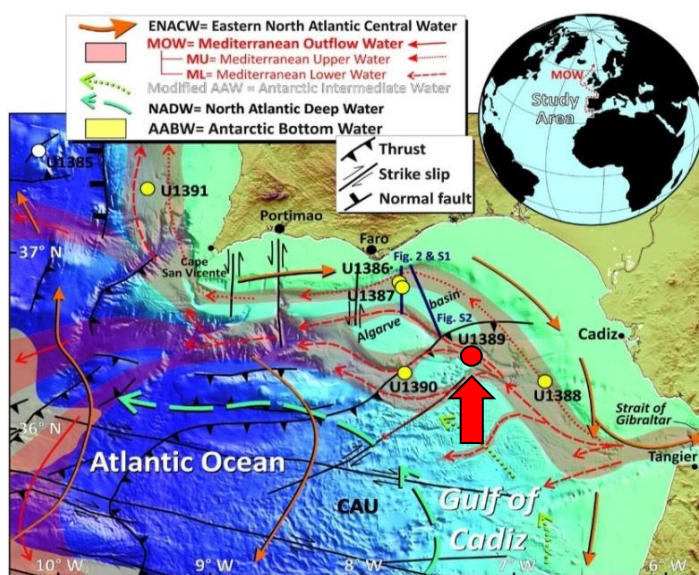


Figure 1. Hydrography of the Gulf of Cadiz and main flow paths of the Mediterranean Outflow Water (MOW). Location of IODP Site U1389 is indicated in red.

2. Material and methods

The studied sediments come from cores of IODP Site U1389E (Figure 1) collected during IODP Expedition 339 in the Gulf of Cádiz, and are stored at Bremen Core Repository at MARUM. The study focuses on the acquisition of an elemental record (in particular Zr, Al, Sr, Ca, Br, Ba, Fe, K and Ti) from upper Pliocene (~2.6-3.6 Ma) sediments of IODP Site U1389E on cores 41R through -70R (703.6-982.78 mbsf; total recovery: 127.8m) (Figure 1; Stow et al., 2013). XRF Core Scanner data were collected at MARUM, University of Bremen every 5 cm down-core over a 1.2 cm² area with down-core slit size of 12 mm using generator settings of 10, 30, and 50 kV, and currents of 0.2, 1.0, and 1.0 mA, respectively. A sampling time of 20 seconds directly at the split core surface of the archive half with an XRF Core Scanner II (AVAATECH Serial No. 2). The split core surface was covered with a 4 micron thin SPEXCerti Prep Ultralene1 foil to avoid contamination of the XRF measurement unit and desiccation of the sediment. The herein reported data have been acquired by a Canberra X-PIPS Silicon Drift Detector (SDD; Model SXD 15C-150-500) with 150eV X-ray resolution, the Canberra Digital Spectrum Analyzer DAS 1000, and an Oxford Instruments 50W XTF5011 X-Ray tube with rhodium (Rh) target material. Raw data spectra were processed by the analysis of X-ray spectra by Iterative Least square software (WIN AXIL) package from Canberra Eurisys.

3. Results and discussion

The results from XRF scanning on the sediment cores from IODP Site U1389E are consistent with the upper Pleistocene records for the same site in Bahr et al. (2014). Preliminary principal component analysis (PCA) reveals three principle components (PCs), together explaining 79% of the variance observed in the records (Figures 2, 3).

PC 1 (49% of variance) is characterized by positive loadings of Al, Si, Fe, Ti and negative loadings of Sr and Ca. This pattern is best explained by variations of detrital siliciclastic sediments (terrestrial input) and biogenic carbonate (productivity).

PC 2 (18% of variance) shows positive loadings for Zr and negative loadings of Al and Si. A comparison to occurrences of contourites observed in the sedimentary record strongly suggests a relation to bottom-current strength (Bahr et al., 2014). This allows to apply this new proxy for the first time to the Pliocene record of MOW.

Finally, PC 3 (12% of variance) shows strong positive loadings of Br and S, most likely reflecting export productivity and bottom water oxygenation.

In well recovered intervals, all three PCs show distinct cyclic patterns that vary in amplitude and frequency over the studied interval. A long-term increase in the amplitude of the cycles in PC 2 correlates with a general coarsening of the sediments, culminating in sections 41R-47R and indicating a significant strengthening of MOW < 2.7 Ma (Stow et al., 2013). The parallel increase in the length of the cycles in PC 1 and PC 2 supports preliminary results of the ongoing revision of the age model for the interval, which indicate a significant increase in sedimentation rates in sections 41R-47R. The completion of the revised age model in the near future will help to evaluate short-term fluctuations in the XRF records and their potential relation to orbital forcing.

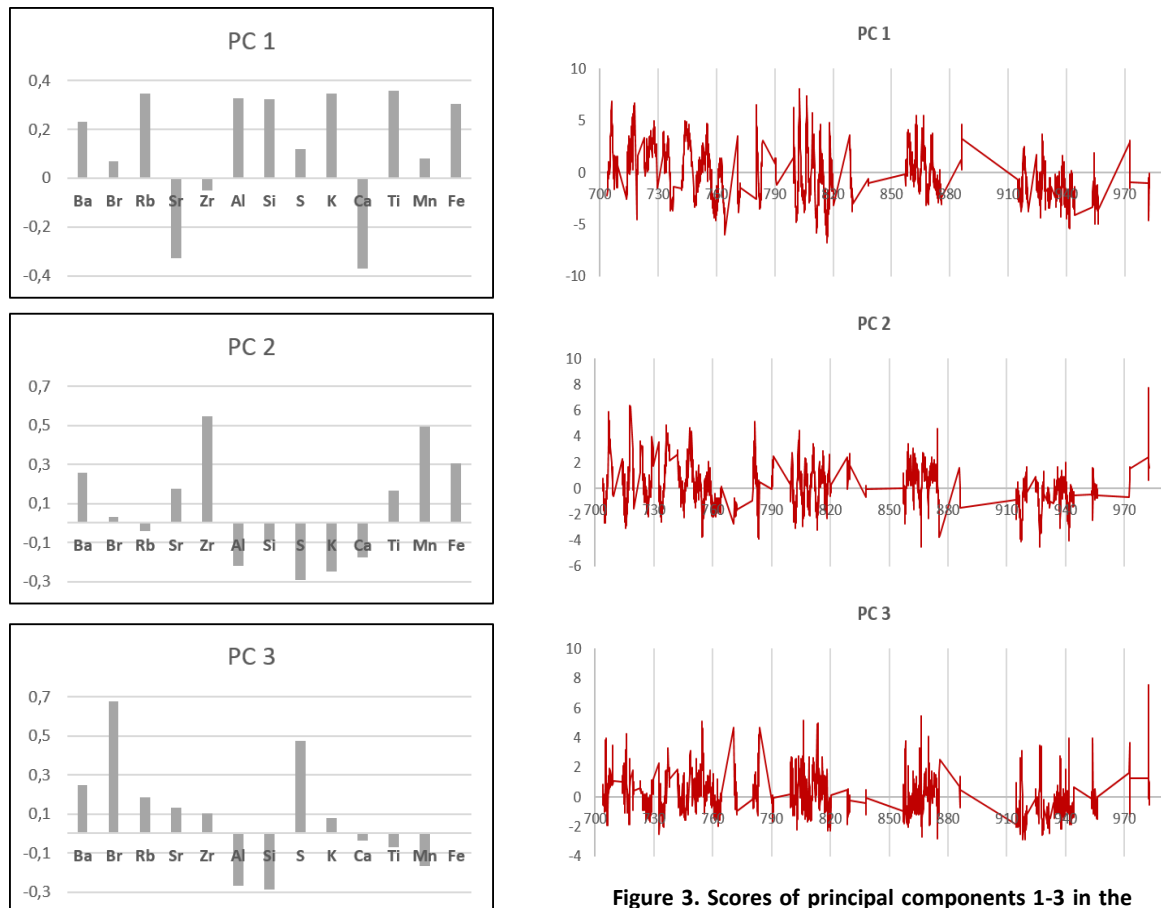


Figure 2. Principal components analysis for the XRF data of U1389E.

Figure 3. Scores of principal components 1-3 in the U1389E records. X-axis: depth in meters below seafloor.

The new Zr/Al proxy record for MOW will help to improve our understanding of benthic foraminifera as MOW proxies, specifically in comparison to early Pliocene records from U1387C (García-Gallardo, in prep). Schönfeld (2002a, 2002b) first described the elevated epifauna (benthic taxa inhabiting elevated substrates such as hard rocks, shells...) with greater settling heights above the

sediment surface under the influence of strong bottom currents in the Gulf of Cadiz. With this strategy, these foraminifera optimize food acquisition under strong bottom-currents, and the abundance of these epibenthic foraminifera is closely related to the ambient flow regime in the deep Gulf of Cadiz (Schönfeld, 2002 a,b). However, this potentially powerful proxy has been rarely applied to the sediment record (Schönfeld and Zahn, 2000). At U1389E, specifically *Planulina ariminensis* shows an exceptional correspondence in its abundance to the Zr/Al curve, and supports its reliability as MOW indicator at U1387C (García-Gallardo, in prep).

Preliminary results show that XRF-scanning provides multiple paleoceanographic proxy records that make an important contribution to the ongoing research at IODP Site U1389E and to the overall success of the research objectives of IODP Expedition 339.

4. Travel and lab expenses

XRF lab fee	656.10€
Flight Graz-Bremen-Graz	231.46€
Accommodation in Bremen	396.77€
Urban transport	24.40€
Total	1308.73€

5. Acknowledgements

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