SCAR Fellowship Report 2008/2009

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Institutions visited:

Leibniz-Institut für Meereswissenschaften, IFM-GEOMAR, Kiel, Germany - Host: Prof. Dirk Nürnberg

Institut de Ciència i Tecnologia Ambientals (ICTA), Universitat Autònoma de Barcelona (UAB), Bellaterra, Spain – Host: Prof. P. Graham Mortyn

Dates:

December 2008 – Kiel (Germany). Discussion on Mg/Ca data already acquired through LA-ICP MS (Laser Ablation – Inductively Coupled Plasma Mass Spectrometer) at Institute of Geosciences and Georesources (CNR of Pavia, Italy) on the planktonic foraminifer *Globigerina praebulloides* from ODP Site 747 (Kerguelen Plateau, Antarctica) with Prof. D. Nürnberg, and planning of Mg/Ca analysis to be carried out through ICP – OES (Inductively Coupled Plasma – Optical Emission Spectrophotometer) at Kiel.

June-August 2009 – Kiel (Germany). Laboratory work at GEOMAR Kiel: picking of *G. praebulloides* specimens for the analysis, cleaning procedure and analysis running (through ICP-OES). Interpretation of the results, discussion of the problems that arose.

November-December 2009 – Barcelona (Spain). Laboratory work at ICTA-UAB Barcelona: testing of four different cleaning procedures for Mg/Ca analysis (through ICP-MS). Interlaboratory comparison between the standard cleaning procedures applied at Kiel and Barcelona, and application of three other different cleaning procedures to a suite of samples from Site 747. Discussion of the results.

Work towards scientific objectives of the fellowship:

Middle Miocene Southern Ocean climatic and paleoceanographic evolution and Antarctic cryosphere expansion

Objectives:

The aim of this project was to study in detail the evolution and the growth phases and modality of the East Antarctic cryosphere from 14.8 to 11.9 Ma, during the Middle Miocene Climatic

Transition (MMCT), comparing quantitative data on planktonic foraminifers and stable isotope data (already acquired) with Mg/Ca data on the planktonic foraminifer *Globigerina praebulloides* (that were acquired during this project). This research included also a methodological study, consisting of Mg/Ca analysis on *Globigerina praebulloides* specimens treated with different cleaning procedures and analysed through different methodologies (*in situ* laser ablation and isotope dilution ICP OES and ICP MS) to test the robustness of Mg/Ca results, the validity and reproducibility of the methods and the best working conditions.

Comparison with a Mg/Ca record from the South Tasman Rise (ODP Site 1171, Shevenell et al., 2004) was carried out throughout each and every phase of the work and enabled us to highlight potential problems in SST estimation through Mg/Ca technique. Furthermore, the comparison of Site 747 (55°S) data with other from literature along a southward transect (Site 1171 at 50°S and Site 744 at 60°S) enabled us to elucidate the global meaning of the MMCT and the modality of development of this significant climatic phase in the Southern Ocean.

The key objectives addressed in this project are:

1) to evaluate the validity of the Mg/Ca method as a paleoclimatic tool, the reproducibility of data generated through different methods and on samples that underwent different cleaning procedures;

2) to reconstruct the Sea Surface Temperature (SST) changes that occurred in the Indian Ocean sector of the Southern Ocean (Kerguelen Plateau) during the MMCT, and its comparison with the oxygen and carbon isotope record from the same location;

3) to reconstruct the East Antarctic Ice Sheet (EAIS) development during the MMCT in correspondence to the isotopic event Mi3 (13.82 Ma according to Abels et al., 2005);

4) to reconstruct the Milankovitch cyclicity signal from trace metal, stable isotope and micropaleontological quantitative data to highlight the relation (if any) between insolation variations (particular combinations of the precession, eccentricity and obliquity cycles) and evolution of the EAIS;

5) to analyse the causes of the EAIS expansion: climatic change (temperature), carbon dioxide variation ($\delta^{13}C$ and nutrient/productivity proxies) and/or astronomical forcing?

Methods:

One of the most important application of Mg/Ca measurements on marine microfossils is the reconstruction of ocean paleotemperatures. Whereas the $\delta^{18}O$ measured on foraminiferal tests is a function of temperature, as well as ice volume and salinity signals, Mg/Ca on foraminiferal tests is an independent paleothermometer, since its variations are directly related to temperature changes

(Barker et al., 2005). Thus, its measurement may help in decoding the ice volume signal embedded in the $\delta^{18}O$. This is particularly important in evaluating the EAIS development and growth during key moments of the climatic evolution of the Earth, such as the MMCT.

To date, trace metal analyses have been performed mainly through isotope dilution and the employment of the ICP-MS (Inductively Coupled Plasma Mass Spectrometer). During this project we tested the validity of the laser ablation method (LA-ICP MS, Laser Ablation – Inductively Coupled Plasma Mass Spectrometer), which is based on *in situ* analysis, for the acquisition of Mg/Ca data on planktonic foraminifers. In fact, isotope dilution techniques require very long cleaning procedures (Barker et al., 2003) and do not allow *in situ* analyses of Mg, Sr and Ca. In the laser ablation technique, conversely, sample preparation is straightforward and contribution from anomalously coatings (whatever their origin) can be readily excluded from the analysis without invoking complex and time-consuming cleaning procedures. The high precision of the laser beam allows to sample through ablation a small portion of a single foraminiferal test instead of analysing twenty or more tests, like in the isotope dilution (Reichart et al., 2003; Eggins et al., 2003). The whole set of samples from the MMCT interval at ODP Site 747 was analysed for Mg/Ca by LA-ICP MS within the PNRA project "Climatic changes, paleoceanography of the Southern Ocean (Indian Ocean sector) and fluctuations of the EAIS in the middle Miocene, inferred from the analysis of the calcareous sediments of the Kerguelen Plateau, Antarctica". The SCAR fellowship gave me the opportunity to complete the methodological work on this topic, performing isotope dilution analysis on the same suite of samples.

Within the SCAR Fellowship program, we analysed 205 samples encompassing the MMCT from ODP Site 747 (at about 10.5 ka resolution). For each sample, about 30 specimens of the planktonic foraminifer *Globigerina praebulloides* were crashed between two glass plates, cleaned according to the standard cleaning protocol and analysed for the Mg/Ca content by ICP-OES (Inductively Coupled Plasma – Optical Emission Spectrophotometer) at IFM-GEOMAR of Kiel. The Mg/Ca data acquired *in situ* through laser ablation were compared with the data generated by ICP-OES on a solution. Since the results appeared to be rather different, we wondered if it was due to the analytical method or to the presence of contaminants on foraminiferal tests. Thus, further investigations were carried out to understand the causes of such results. At first we performed Field-Emission SEM (FESEM) analysis at the University of Granada (Spain) on selected samples (the ones that appeared to be the most contaminated on the basis of anomalous Mg/Ca values) to study the ultramicroscopic texture of the outer and inner part of the tests. The original texture of the test appeared to be partially modified by diagenesis. Subsequently, we tried to perform Mg/Ca analysis after applying three modified cleaning procedures in order to test the possibility to remove the

coating. Those analyses were performed through a third method (isotope dilution by ICP MS) on a suite of 13 samples at the Universitat Autònoma de Barcelona (Spain). These samples were splitted into four aliquots. One of them underwent the standard cleaning procedure (the same applied at Kiel), in order to test the interlaboratory reproducibility, while the other three were subjected to three different cleaning tests in the attempt to select the best method to eliminate the contamination.

At the same time, faunistic and stable isotope data were analysed by statistical methods and the spectral analysis was performed to highlight the astronomical forcing on middle Miocene climate.

Results:

Mg/Ca results

Comparison of the data showed that Mg/Ca results through LA-ICP MS differ from ICP-OES and ICP-MS results at ODP Site 747, while the latter two methodologies are fully comparable between each other. In particular, a close look revealed that the higher Mg/Ca values were usually associated to high Mn/Ca values. When processing the data obtained through LA-ICP MS, we can discard the head and the tail of the signal, which represent respectively the composition of the outermost and innermost part of the chamber wall. Those parts are the most contaminated by secondary minerals, which were deposited during diagenesis and do not represent a primary bio-mineralization. Investigation of the outer and inner surface of the tests through FESEM showed the presence of partial modifications of the original wall texture, probably caused by secondary processes ("frosty" tests according to Sexton et al., 2006). The four cleaning tests performed at the ICTA-UAB on a suite of 13 samples did not show significant differences in the Mg/Ca results, indicating that the contaminant coating was not (completely) eliminated. However, the perfect fit between foraminiferal abundance curve of cold and warm indices and the stable isotope data with the Mg/Ca data obtained at Kiel and Barcelona suggested that the overall Mg/Ca trend was real, even if the absolute SST values may have been overestimated a little. Consequently, we deduced that a careful cross-examination of many potential contaminants, such as Al, Mn, Fe, is necessary to choose properly the integration window of LA-ICP MS data in order to eliminate the bias introduced by diagenesis in the outermost and innermost part of the chamber wall and to make reliable the results of *in situ* analysis. Once a protocol on the procedure to eliminate contaminants will be released, this method may turn out to be the most powerful tool for paleoclimatic reconstructions, since it do not require long and time-consuming cleaning procedures and allows *in situ* determination of trace metals.

Statistical analysis and time series analysis

The quantitative faunal data and the stable isotope data that had been already acquired, were processed through statistical and time series analysis methods. Principal component analysis (PCA) and R-mode cluster analysis were carried out on quantitative faunal data, whereas Lomb spectral analysis and Foster wevelet analysis were performed on stable isotope records.

The PCA-1 discriminates between cold species living in polar areas or upwelling regions and warm or warm-temperate species. Therefore, we interpret PCA-1 as related to the sea surface temperature. From 14.8 to 13.8 Ma PCA-1 shows positive scores, thus indicating a relatively warm period. At 13.8 Ma PCA-1 scores decrease abruptly, becoming negative from that point onward. From 13.8 to 12.9 Ma, an interval of strongly negative scores identifies a cold regime. A third changes occurs at 12.9 Ma, when PCA-1 scores increase. It may represent a "cold-temperate" interval, marked by a slight climatic amelioration.

The PCA-2 discriminates between a group of species with positive loadings, consisting of both warm- and cold-water species, and a group with negative loadings, consisting of warm-water forms. This co-existence of warm and cold water taxa may point to an increased seasonality, whereas the group with negative loadings may indicate periods of reduced seasonality. At present, seasonality controls test flux patterns of planktonic foraminifers and influences assemblage diversity (Reynolds and Thunell, 1985; King and Howard, 2003). In the fossil record, stronger seasonality led to a greater planktonic foraminiferal diversity (Majewski, 2002). This is supported also by the variation of the Simpson index of species diversity calculated on Site 747 samples, which co-varies with the PCA-2.

The hierarchical cluster analysis highlights the presence of two main clusters, one composed of warm-temperate species and the other of cold species. The main change occurs at 13.8 Ma, when the warm forms are replaced by cold water taxa.

The spectral analysis reveals a strong response of the $\delta^{18}O$ record at obliquity and long-term eccentricity frequencies, and of the $\delta^{13}C$ signal to obliquity forcing with a dominant 1.2 Myr frequency.

Comparison of all the data

The most prominent faunal change took place at 13.8 Ma, when a fauna with warm-water affinity (marked by high abundance of *Globorotalia miozea* group and *Globoturborotalita woodi* plexus) was replaced by an oligotypic, opportunistic fauna with typical polar characters and dominated by neogloboquadrinids. This faunal change is interpreted as the result of foraminiferal migration from adjacent bioprovinces, caused by modifications in climate and hydrography. A positive 2.0‰ shift in $\delta^{18}O$ (interpreted as the Mi3 event) and a related positive 1.0‰ shift in $\delta^{13}C$ (corresponding to the CM6 event) accompanied this faunal turnover. These are interpreted to reflect

substantial reorganization of Southern Ocean waters, the northward migration of the Polar Front and a strong increase in primary productivity. The second faunal change took place at 12.9 Ma and was characterized by the gradual decrease in abundance of the neogloboquadrinids and the recovery of *Globorotalia praescitula/scitula* group and *Globigerinita glutinata*. A positive 1.5‰ shift in $\delta^{18}O$ (interpreted as the Mi4 event) and a concurrent gradual negative shift in $\delta^{13}C$ accompanied this faunal change, witnessing further modifications of the climate/ocean system. Variations in sea surface temperature, considered as the main factor causing changes of surface hydrography at the Kerguelen Plateau, seem to have been driven by obliquity and long-term eccentricity, thus suggesting a key role played by the astronomical forcing on the evolution of Southern Ocean dynamics during the middle Miocene. Also an evident 1.2 Myr modulation of the $\delta^{13}C$ record suggests a main control of the long-term obliquity cycles on the carbon cycle dynamics. Particularly, the Mi3/CM6 event exactly fits with a node of the 1.2 Myr modulation cycles. This confirms the key role played by orbital parameters on high-latitude temperatures and Antarctic ice volume, and indirectly on global carbon burial and/or surface sea water productivity.

Future work:

The laser ablation technique for Mg/Ca ratio measurements is a powerful tool for paleoclimatic and paleoceanographic reconstructions. It has many advantages over previously employed methods, e.g. the sample preparation is straightforward and contribution from anomalously coatings (whatever their origin) can be readily excluded from the analysis without invoking complex and time-consuming cleaning procedures; the accuracy of measurements is highly improved; the high precision of the laser beam allows to sample a small portion of a single foraminiferal test instead of analysing twenty or more tests, like in the isotope dilution by ICP-MS. Although the method is being increasingly employed in the analysis of recent or Holocenic sediments, its application on older sediments is still tentative. The major check on its application is represented by the necessity to eliminate coatings or contaminants coming from secondary processes, such as the diagenesis. Future work will be addressed to the solution of this problem and the standardization of this method.

Collaborations:

The work performed within the project funded by a SCAR Fellowship was carried out in collaboration with scientists from IFM-GEOMAR at Kiel and UAB at Barcelona. This led to the development of some international projects.

Milestones and deliverables:

The collaboration with Prof. Dirk Nürnberg (GEOMAR Kiel) has been very effective and allowed to fulfil the most important part of the work described in the proposal. Nevertheless, the interpretation of the Mg/Ca data collected at Kiel and their comparison with the laser ablation data already acquired highlighted strong differences between the two datasets. Those differences may be due to contaminants that were not properly eliminated during the cleaning procedures. Consequently, we decided to carry out further cleaning tests and contacted a group specialized in this type of testing, the GEPOC (Research group on oceanic and climatic processes) at ICTA-UAB (Barcelona). The collaboration with Prof. P. Graham Mortyn within this group allowed to reach the methodological objectives of the project and to understand the causes of the differences that were seen in the datasets.

Allocation and use of SCAR funds:

€ 5,217.50 = $ 8,000 were allocated for this project.

Funds has been spent mainly for covering accommodation and life expenses during a two and a half months stay in Germany, a one month stay in Spain and the round trip flights from/to Italy. Other minor expenses concerned some stationery and an external hard disk for data storage.

a) Air travel fares to/from Kiel (Germany) and to/from Barcelona (Spain): 956€

b) Transport tickets (bus, train, ferry, taxi): 581€

c) Accommodation and living costs 2375€

d) Some stationery and an external hard disk for data storage: 202€

e) Shipping of samples: 215€

f) Consumables for sample preparation: 600€

g) Travel to Pavia and accommodation to discuss comparison between LA-ICP MS data and ICP-OES and ICP-MS data: 278€

Total: 5207€

Talks and seminars:

24th September 2008: Invited lecturer on: 1- “Introduction to Foraminifera”; 2- “Foraminifera as paleoclimatic and paleoenvironmental proxies”; 3- “Foraminifera and trace metals: measurement techniques and data interpretation”. Institute of Marine Sciences (ISMAR) of the National Research Council (CNR), Venice, Italy.

5th February 2009: "Microfossils in the Southern Ocean: the Foraminifera". Seminar held to the students of the Doctoral School in Polar Sciences, University of Siena, Italy, on the theme: "Oceans and marine life in the Polar Regions", organised in occasion of the International Polar Year.

5th November 2010: Invited lecturer on "The history of climate and the evolution of the polar ice sheets: the archive of a shell", within the European Science Foundation public outreach initiative "Research Icebreaker Aurora Borealis in prospect: the technologic and scientific challenge of the future", Galata Science Museum, Genova, Italy.

Publications:

Verducci M., Foresi L.M., Scott G.H., Sprovieri M., Lirer F. and Pelosi N. (2009): The Middle Miocene climatic transition in the Southern Ocean: Evidence of paleoclimatic and hydrographic changes at Kerguelen Plateau from planktonic foraminifers and stable isotopes. *Palaeogeography, Palaeoclimatology, Palaeoecology*, 280: 371-386, doi:10.1016/j.palaeo.2009.06.024.

Two further manuscript on Mg/Ca data are in progress.

References:

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Shevenell, A.E., Kennett, J.P., Lea, D.W. 2004. Middle Miocene Southern Ocean cooling and Antarctic cryosphere expansion. Science 305, 1766-1770.