

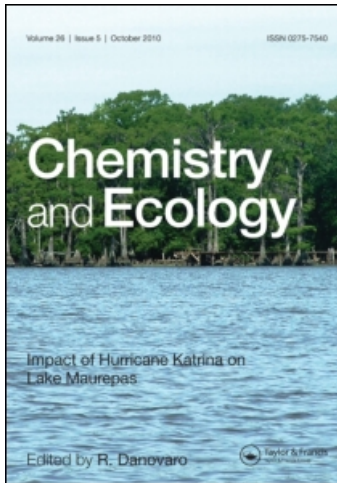
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Mg/Ca ratios in the planktonic foraminifer *Neogloboquadrina pachyderma* (sinistral) from plankton tows in the Ross Sea and the Pacific sector of the Southern Ocean (Antarctica): comparison of different methodological approaches

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Mg/Ca ratios in the planktonic foraminifer *Neogloboquadrina pachyderma* (sinistral) from plankton tows in the Ross Sea and the Pacific sector of the Southern Ocean (Antarctica): comparison of different methodological approaches

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Mg/Ca ratios in living specimens of the planktonic foraminifer *Neogloboquadrina pachyderma* (sin.) have been investigated using Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS) and ultracleaning procedures on 'bulk' foraminifera followed by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) and Inductively Coupled Plasma Atomic Emission Spectrophotometry (ICP-AES) analysis. Plankton tows were taken in the upper 250 m of the water column at different sites in the Ross Sea and at the Polar Front of the Pacific Ocean during 6 austral summers. We found high values of Mg/Ca ratios in *N. pachyderma* (s.) not previously reported in the literature. Our data suggest that at least two factors influence the results: (1) the presence of some protoplasm in the test of living specimens, which seems to control the actual Mg concentration and (2) the morphotype of the analysed specimens in term of test thickness.

Keywords: Mg/Ca ratios; *Neogloboquadrina pachyderma* (sin.); laser ablation ICP-MS; ICP-MS/ICP-AES; Antarctica

1. Introduction

Sea surface temperature (SST) is one of the most important parameters for palaeoclimate studies. The $\delta^{18}\text{O}$ ratios of planktonic foraminifera had long been used as a proxy for past SST (see overview in [1]). In particular, stable isotopes and metals concentration in tests of non-spinose planktonic foraminifera *Neogloboquadrina dutertrei* and *Neogloboquadrina pachyderma* are widely used to reconstruct past oceanic temperature in high latitude waters (e.g. [2]). $\delta^{18}\text{O}$ changes in planktonic foraminifera are controlled by SST, salinity and seawater $\delta^{18}\text{O}$ composition, and the latter is predominantly associated with changes of the global ice volume. Therefore,

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it is difficult to separate the signals of SST and ice volume change in the oxygen isotopic record without any other independent proxy.

Recent development in marine geochemistry indicates that the Mg/Ca ratio in planktonic foraminifera [3,4] is mainly controlled by SST [5–7]. The advantage of foraminiferal Mg/Ca thermometry over other marine paleotemperature proxy methods is that temperature estimates can be obtained from the same foraminiferal sample upon which data on oxygen isotopes are collected. The approach of measuring Mg/Ca and $\delta^{18}\text{O}$ in single species of foraminiferal calcite is potentially of great value in estimating both temperature and seawater $\delta^{18}\text{O}$ from the same sample.

Calibrations of Mg/Ca thermometry in planktonic foraminifera based on culture and core tops are invaluable but both have some problems. Culture calibrations have the great advantage that foraminifera calcify under prescribed and accurately measured temperatures but the disadvantage is that the ‘controlled’ environment may not fully reproduce natural growth conditions and that only a limited number of species can be studied. Core-top calibrations have the great advantage to directly handle the material that is buried to form the paleoceanographic record but it may be affected by secondary diagenetic effects, such as partial dissolution and overgrowth which, at times, render hard the establishment of a reliable link between Mg/Ca and SST. The third way to establish a calibration is through the analysis of living foraminifera collected from the water column, using both net and moored sediment traps [8].

Cleaning procedures are very important for obtaining Mg/Ca measurement in foraminifera because several mineral phases associated with the test, such as adhering clay minerals, organic materials, and Mn–Fe oxide coatings may engender Mg contamination of the foraminifera tests [9].

Moreover, elemental ratios measured in foraminiferal tests by different laboratories may differ for the following reasons: (1) offsets due to instrument calibration or incompatibility of the working standards; (2) offsets due to differences in methods applied by individual laboratories for cleaning foraminifera shells [8]; (3) differences due to natural variability in the sample assemblage [10].

We focus here on the analytical procedures for analysis of Mg/Ca in LA-ICP-MS and by application of ultracleaning procedures and consequent analysis of the bulk carbonate in ICP-MS and ICP-AES. Mg and Ca analyses were performed on tests of the planktonic foraminifer *Neogloboquadrina pachyderma* (sin.) from plankton tows collected in two sites located in the Ross Sea and at the Polar Front of the Pacific Ocean. The aim is to compare Mg/Ca ratios obtained from the two different cleaning and analytical procedures, applied on specimens of *N. pachyderma* (sin.) from the same sample.

2. Materials and methods

The plankton tows were conducted using a messenger-released net of 300 μm mesh size in the upper 250 m of the water column, divided into several depth intervals at one site in the Ross Sea (site B, 74° 00' S, 175° 00' E, water depth 600 m) and at the Polar Front of the Pacific Ocean (site O, 63° 00' S, 178° 00' E, water depth 4000 m) during austral summers of 1998 to 2003 (Figure 1). All samples were stored in 5% buffered formaldehyde seawater solution at 4°C to prevent dissolution.

The sampling was performed by subdividing the water column in discrete intervals on the base of the CTD information (Deep Chlorophyll Maximum, temperature, salinity, different water masses). For each sampling interval, mean temperature and mean salinity were calculated and for each site the DCM depth is indicated (Table 1).

The water column at site B is characterised by a marked and shallow stratification and a marked thermocline while at site O the mixed surface layer is deeper (60–70 m), the pycnocline and the thermocline less marked. *N. pachyderma* (sin.) seems to show abundance peaks at or just below the DCM.

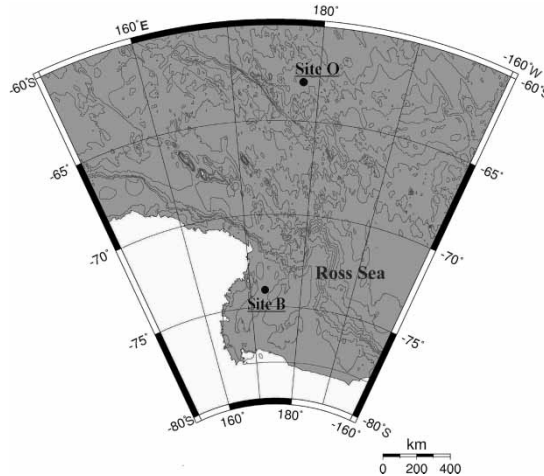


Figure 1. Location of site B and site O in the Ross Sea and in the Pacific sector of the Southern Ocean, respectively.

Table 1. Tow sampling depth, mean temperature, mean salinity and Deep Chlorophyll Maximum (DCM) depth at each site.

Year/Site	Sampling depth (m)	Mean temperature (°C)	Mean salinity (PSU)	DCM depth (m)
1999/B	200–260	−1.5	34.5	30
2000/O	60–150	1.0	34.2	50
2000/O	150–200	1.7	34.4	50
2001/O	90–150	0.1	34.0	60
2001/B	100–200	−1.6	34.6	50
2002/B	150–200	−1.7	34.6	30
2003/B	50–100	−1.6	34.4	30
2003/B	100–200	−1.7	34.6	30
2003/B	200–400	−1.9	34.7	30
2003/B2	0–50	−1.7	34.2	20
2003/B2	50–100	−1.7	34.5	20

2.1. LA-ICP-MS

Three specimens of *N. pachyderma* (sin.) were selected from each sample and ultrasonically cleaned twice with distilled water and twice with methanol to remove adhering detrital material, following the procedure described by Eggins et al. [11]. No treatment with H₂O₂ was applied to remove organic material from the tests in order to verify in which way the presence of protoplasm influences the Mg/Ca ratios. After cleaning, samples were thoroughly rinsed with water to ensure no reagent remained. For laser ablation analysis, dry foraminifera tests were secured on double-sided adhesive tape mounted on a glass microscope slides.

Laser Ablation (LA)-ICP-MS analyses were carried out at the CNR-IGG-U.O. of Pavia (Istituto di Geoscienze e Georisorse, Consiglio Nazionale delle Ricerche) using a sector field ICP-MS (Element-I from ThermoFinnigan) coupled to a 193 nm ArF excimer laser microprobe (GeoLas 200Q, MicroLas). The deep-ultraviolet-wavelength laser (193 nm) is essential for the reproducible ablation of the fragile tests, because carbonates do not absorb laser radiation well at higher wavelengths [12]. It should be noted also that poor absorption and catastrophic ablation of calcite may occur with use of significantly longer-wavelength laser light [11].

Since the variability of the results depends on the location of measurement sites in the primary calcite, the final chamber of the tests was selected for analysis. The laser was operated at a repetition rate of 5 Hz, with a fluence of 12 J/cm² and using a spot diameter of about 25 μm. The whole thickness of the chamber was ablated. Signals of masses ²⁴Mg, ²⁵Mg, ⁴³Ca and ⁴⁴Ca were acquired. Integration intervals for ablated signal and background were selected by inspecting the time resolved signals and using the GLITTER software [13]. The net signal for each mass was then normalised to the isotopic abundance and the raw Mg/Ca ratio was calculated as the ratio between the mean count rates from the two Mg (24 and 25) and Ca (43 and 44) isotopes. The raw Mg/Ca ratio was then corrected for fractionation effects adopting SRM-NIST610 reference glass as external standard. In order to reduce errors related to instrumental drifts the standard glass was measured every ten analysis.

2.2. ICP-MS/ICP-AES

For seven samples, specimens of *N. pachyderma* (sin.), corresponding to an average weight of about 0.6 mg, were picked and cleaned using a multistep trace metal protocol including reductive cleaning with buffered hydrazine [14]. Mg/Ca ratios were measured on a inductively coupled plasma mass spectrometer ICP-MS Varian and an inductively coupled plasma atomic emission spectrophotometer Varian MPX Vista at the Geochemistry Laboratory of the IAMC-CNR (Institute for Coastal Marine Environment) (Naples).

The tests were gently crushed and then cleaned following procedures modified from Lea and Boyle [15]. Briefly, samples were ultrasonically cleaned four times with ultrapure water (> 18 MΩ) and twice with methanol. Metal oxide coatings were reduced in a solution consisting of anhydrous-hydrazine, citric acid, and ammonium hydroxide and organic matter was oxidized in a solution of hydrogen-peroxide and sodium-hydroxide. All the water samples were treated under a laminar air flow clean bench to minimize contamination risks and the sampling materials were cleaned with high purity grade reagents. The remaining tests material was then dissolved in 0.1N nitric acid and simultaneously analysed for magnesium with the Varian ICP-MS inductively coupled plasma-mass spectrometer. A multi-element standard was prepared with ICP-MS grade High-Purity Standards. Based on repeated analyses of the standard and samples over several runs, on different days, the 2σ error in the ICP analyses is estimated at ±5%. Replicate analyses on five samples yielded an average external precision (1σ) of about 5%. Calcium was measured with a Varian Vista MPX inductively coupled plasma-optical emission spectrometer (ICP-OES). Metal to calcium ratios were determined from intensity ratios with an external matrix-matched standard using the method developed by Rosenthal et al. [16].

3. Results and discussion

Because *N. pachyderma* also adds a final, often thick, outer calcite crust (or ‘gametogenic crust’) in deeper colder water immediately prior to reproduction and ensuing death [17,18], there was a need to verify the influence of this crust on Mg/Ca ratios. For this reason, we analysed specimens of *N. pachyderma* (s.) from two different morphotypes present in this area: the first one (morph 1) is represented by specimens characterised by a subspheric and heavily encrusted test and lives in the outer continental shelf (site B), while the second one (morph 2) has a thin and lobate walled test and lives in the oceanic area (site O) (see [19] for details). The same two morphotypes were recognised by Asioli and Langone [20] in the Western Ross Sea in water sample from floating traps. In the literature [21,22], morph 2 is known to represent the early stage of the life cycle in the surface water and morph 1 is the terminal stage.

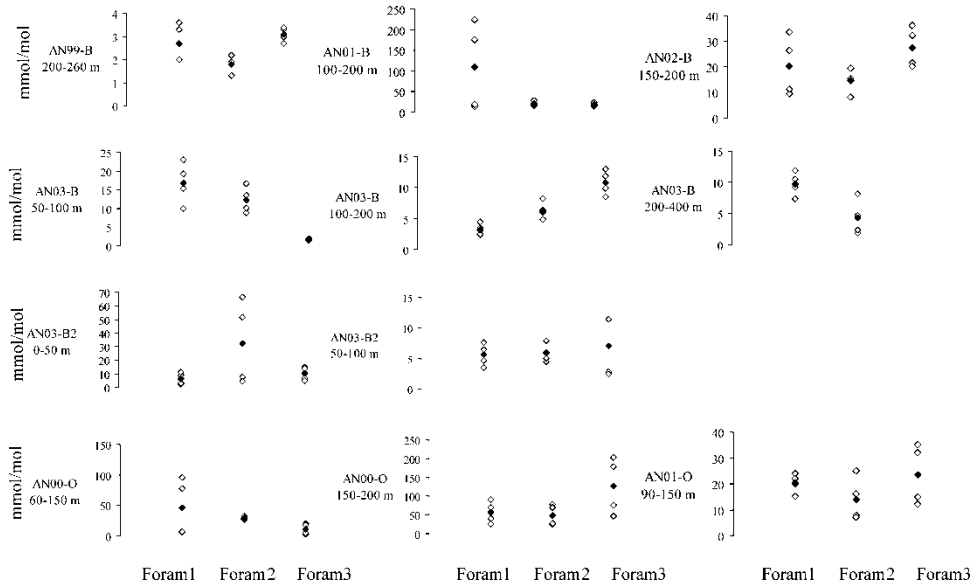


Figure 2. Mg/Ca values (mmol/mol) of the last chamber of three different specimens of *N. pachyderma* (s.) measured by LA-ICP-MS. We conducted two analyses on three different specimens (Foram1, Foram2, Foram3) for each sample. At the left of each graph are indicated the cruise name (AN), the year (99, 00, 01, 02, and 03), the site (B, B2, O) and the sampling depth in meters. Open symbols represent each of four replicates analyses; closed symbols represent the mean values.

Results obtained by LA-ICP-MS (Figure 2) showed values of Mg/Ca ratio ten or more times higher with respect to the ones present in the literature (between 0.5 and 2 mmol/mol) referred to the same species in Northern and Southern Atlantic Ocean [23]. In addition, we noted that Mg/Ca values for specimens of morph 2 typical of site O were even higher with respect to the values for morph 1 present in site B. The residual presence of some protoplasm in the tests of living specimens seems to influence the actual Mg concentration, yielding to higher Mg/Ca ratios in both sites. On the other hand, the different morphotypes collected in the two sites could produce different Mg/Ca ratios since the chemical composition of the shell and the different layers from which it is constituted vary according to the depth to which the specimens live. Furthermore, also the different oceanographic setting, in term of temperature and surface mixed layer depth, could impact the Mg incorporation into the calcitic tests. So far, we are unable to explain which factor affects more the Mg/Ca ratios in the tests.

However, samples characterised by higher averages of Mg/Ca ratios always show also very high standard deviation (Std) (Figure 3), which implies relevant compositional heterogeneity. Assuming that samples characterized by high Mg/Ca ratio and standard deviation are affected by effects of secondary contamination, they can be easily rejected. Samples with a coefficient of variation (this is the standard deviation divided by the mean and multiplied by 100) higher than 35% were removed and the mean Mg/Ca ratios for each sample re-calculated (Table 2).

The difference between the initial data and the averaged Mg/Ca after removal of the anomalous values was significant especially in terms of standard deviation. Of course, this operation is not possible using analytical procedures on 'bulk' foraminifera (ICP-MS/ICP-AES technique).

Mg/Ca ratios measured by both the two analytical procedures for the same samples are listed in Table 3. Again results from ICP-MS/ICP-AES technique show high values of Mg/Ca ratios in the tests when compared to those reported in the literature [23].

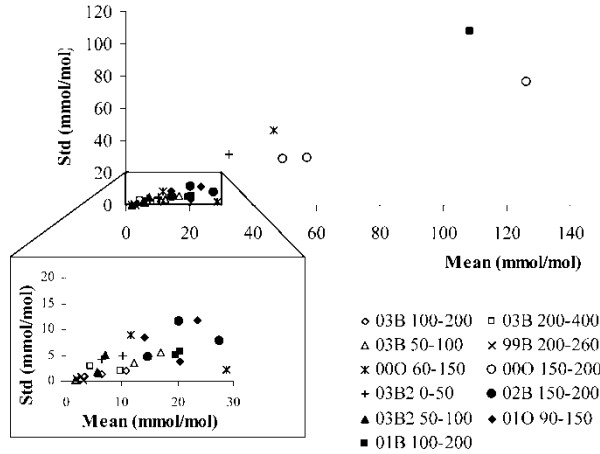


Figure 3. Mean Mg/Ca values (mmol/mol) versus standard deviation (Std, mmol/mol) for the three different specimens for each sample measured by LA-ICP-MS.

Table 2. Mean Mg/Ca value (averaged values between the three analysed specimens)(mmol/mol) and standard deviation for each sample analysed by LA-ICP-MS. In the fourth and fifth columns the corrected mean Mg/Ca and standard deviation are listed.

Sample ID	Mean Mg/Ca (mmol/mol)	Std (mmol/mol)	Corrected Mean Mg/Ca (mmol/mol)	Corrected Std (mmol/mol)
AN99 B 200-260	2.5	0.8		
AN00 O 60-150	29.0	29.0	28.7	2.2
AN00 O 150-200	77.6	57.8	Rejected	Rejected
AN01 O 90-150	19.4	8.8	20.4	3.7
AN01 B 100-200	49.5	71.2	20.1	5.0
AN02 B 150-200	20.8	9.5	21.1	8.1
AN03 B 50-100	10.3	7.5		
AN03 B 100-200	6.8	3.5		
AN03 B 200-400	7.0	3.9	9.7	1.9
AN03 B2 0-50	16.3	20.5	Rejected	Rejected
AN03 B2 50-100	6.2	3.0	5.7	1.6

Table 3. Mg/Ca ratios in the planktonic foraminifer *N. pachyderma* (s.) by ICP-MS/ICP-AES (second column) and by LA-ICP-MS (third column, corrected average values between the three analysed specimens) from the same samples.

Sample ID	Mg/Ca(mmol/mol) by ICP-MS/ICP-AES	Corrected Mg/Ca (mmol/mol) by LA-ICP-MS
AN99 B 200-260	13.1	2.5
AN01 O 90-100	6.1	20.4
AN03 B2 0-50	7.0	Rejected
AN03 B2 50-100	1.6	5.7
AN03 B 100-200	11.8	6.8
AN03 B 200-400	22.8	9.7

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Moreover, the results obtained by LA-ICP-MS analysis seem to be not comparable with the ones obtained by application of the ultracleaning protocol to the same samples. We tentatively attribute this fact to:

- (1) a relevant in-homogeneity of the investigated assemblages;
- (2) the fact that the final chambers of the organisms are contributing in different ways to the Mg and Ca contents of the specimens;
- (3) an adopted ultracleaning procedure that is not efficient and definitive.

In summary, our investigation documents that all the aspects above can contribute to a wrong evaluation of the Mg/Ca ratios and accordingly to an inaccurate estimate of Sea Surface Temperature. Such results should be held in consideration in paleoceanographic reconstructions.

Future work may involve the study of a box core collected in the same location to investigate the comparative effects of different cleaning procedures and the different results from the two different techniques in order to resolve discrepancies and conformities between methods.

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References

- [1] E.J. Rohling and S. Cooke, *Stable oxygen and carbon isotopes in foraminiferal carbonate shells*, in *Modern Foraminifera*, A. Sen Gupta, ed., Kluwer Academic Publishers, Dordrecht, The Netherlands, (1999), pp. 239–258.
- [2] D. Bauch, J. Carstens, and G. Wefer, *Oxygen isotope composition of living Neogloboquadrina pachyderma (sin.) in the Arctic Ocean*, *Earth Planet. Sci. Lett.* 146 (1997), p. 47.
- [3] D. Nürnberg, J. Bijma, and C. Hemleben, *Assessing the reliability of magnesium in foraminiferal calcite as a proxy for water mass temperatures*, *Geochim. Cosmochim. Acta* 60 (1996), p. 803.
- [4] D.W. Lea, T.A. Mashiotta, and H.J. Spero, *Controls on magnesium and strontium uptake in planktonic foraminifera determined by live culturing*, *Geochim. Cosmochim. Acta* 63 (1999), p. 2369.
- [5] T.A. Mashiotta, D.W. Lea, and H.J. Spero, *Glacial-interglacial changes in Subantarctic sea surface temperature and $\delta^{18}O$ water using foraminiferal Mg*, *Earth Planet. Sci. Lett.* 170 (1999), p. 417.
- [6] H. Elderfield and G. Gansenn, *Past temperature and $\delta^{18}O$ of surface ocean waters inferred from foraminiferal Mg/Ca ratios*, *Nature* 405 (2000), p. 442.
- [7] D.W. Lea, D.K. Pak, and H.J. Spero, *Climate impact of late quaternary equatorial Pacific sea surface temperature variations*, *Science* 289 (2000), p. 1719.
- [8] P. Anand, H. Elderfield, and M.H. Conte, *Calibration of Mg/Ca thermometry in planktonic foraminifera from a sediment trap time series*, *Paleoceanography* 18 (2003) p. 1050.
- [9] G. Wei, W. Deng, Y. Liu, and X. Li, *High-resolution sea surface temperature records derived from foraminiferal Mg/Ca ratios during the last 260 ka in the northern South China Sea*, *Palaeogeogr. Palaeoclimatol. Palaeoecol.* 250 (2007), p. 126.
- [10] Y. Rosenthal et al., *Laboratory inter-comparison study of Mg/Ca and Sr/Ca measurement in planktonic foraminifera for paleoceanographic research*, *Geochem. Geophys. Geosyst.* 5 (2004), Q04D09.
- [11] S. Eggins, P. De Deckker, and J. Marshall, *Mg/Ca variations in planktonic foraminifera tests: implications for reconstructing paleo-seawater temperature and habitat migration*, *Earth Planet. Sci. Lett.* 212 (2003), p. 291.
- [12] S.E. Jackson, H.P. Longrich, G.R. Dunning, and B.J. Fryer, *The application of laser-ablation microprobe-inductively-coupled-plasma-mass-spectrometry (LAM-ICP-MS) to in situ trace-element determinations in minerals*, *Can. Mineralogist* 30 (1992), p. 1049.
- [13] E. van Achtenbergh, C.G. Ryan, S.E. Jackson, and W. Griffin, *Data reduction software for LA-ICP-MS*, in *Laser Ablation-ICPMS in the Earth Science; principles and applications*, P. Sylvester, ed., Mineralogical Association of Canada Short Course 29 (2001), pp. 239–243.
- [14] E. A. Boyle and L. D. Keigwin, *Comparison of Atlantic and Pacific paleochemical records for the last 250,000 years: Changes in deep ocean circulation and chemical inventories*, *Earth Planet. Sci. Lett.* 76 (1985), p. 135.
- [15] D. W. Lea and E.A. Boyle, *Determination of carbonate-bound barium in corals and foraminifera by isotope dilution plasma mass spectrometry*, *Chem. Geol.* 103 (1993), p. 73.
- [16] Y. Rosenthal, M.P. Field, and R.M. Sherrell, *Precise determination of element-calcium ratios in calcareous samples using sector field inductively coupled plasma mass spectrometry*, *Anal. Chem.* 71 (1999), p. 3248.

- [17] C. Hemleben, *Modern Planktonic Foraminifera*, Springer, New York, 1989.
- [18] A.W.H. Bé, *Gametogenic calcification in a spinose planktonic foraminifer*, *Mar. Micropaleontol.* 5 (1980), p. 283.
- [19] C. Bergami, *Distribuzione attuale dei foraminiferi planctonici nell'Oceano meridionale (settoze pacifico)*. Degree thesis, University of Bologna, 2004.
- [20] A. Asioli and L. Langone, *Relationship between recent planktic foraminifera and water mass properties in the Western Ross Sea (Antarctica)*, *Geogr. Fis. Dinam. Quat.* 20 (1997), p. 193.
- [21] A.W.H. Bé, *Some observations on arctic planktonic Foraminifera*, *Contr. Cush. Found. Foram. Res.* 11 (1960), p. 64.
- [22] K.E. Kohfeld, R.G. Fairbanks, S.L. Smith, and I.D. Walsh, *Neogloboquadrina pachyderma (sinistral coiling) as paleoceanographic tracers in polar oceans: Evidence from Northeast Water Polynya plankton tow, sediment traps, and surface sediments*, *Paleoceanography* 11 (1996), p. 679.
- [23] D. Nürnberg, *Magnesium in tests of Neogloboquadrina pachyderma (sinistral) from high northern and southern latitude*, *J. Foraminifer. Res.* 25 (1995), p. 350.