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### **Research** paper

# Core-top calibration of $\delta^{18}$ O and $\delta^{13}$ C of *G. ruber (white)* and *U. mediterranea* along the southern Adriatic coast of Italy

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1. Introduction

ABSTRACT

We carried out an extensive survey of the oxygen and carbon isotope composition of the planktic species G. ruber (white) and of the benthic species U. mediterranea along the southern Italian coast of the Adriatic Sea and in the Gulf of Taranto. Comparison with seasonal satellite-based sea surface temperature maps and water column profiles as well as with several sets of water samples allows estimation of the effect of salinity and different nutrient supply on the  $\delta^{18}$ O and  $\delta^{13}$ C of foraminifera. The results indicate that *G. ruber (white)*, while being highly affected by different salinity and nutrient distributions related to circulation patterns of major water masses, dominantly record summer temperature conditions. U. mediterranea reflect the recent environmental conditions, such as nutrient supply and bottom water temperature characteristics, along the southern Italian coast and clearly show the transition from a near-coastal eutrophic system to an offshore oligotrophic system.

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The analysis of stable oxygen and carbon isotopes of foraminifera is an important tool for paleoceanography and paleoclimate reconstructions (Emiliani, 1955; Hemleben et al., 1989; Ravelo and Hillaire-Marcel, 2007; Shackleton, 1967). While in pelagic settings the factors controlling the geochemistry of foraminifera are relatively well understood, the application of this geochemical tool to near-coastal environments is more complex. Environmental parameters such as salinity, temperature and nutrient supply exhibit strong variability with distance to the coast (Martinez et al., 1998; Ding et al., 2006) and they have to be taken into consideration in the interpretations. Shallow-water near-coastal environments have generally higher sedimentation rates than pelagic environments and thus allow climate reconstructions of higher resolution. However, in near-coastal regions a wide range of factors may influence the stable isotopic composition of planktic and benthic foraminifera. Therefore, it is of paramount importance to carry out isotopic studies of recent samples to evaluate possible influences of sediment transport, water circulation patterns, temperature variability, seasonality and food availability (Schmiedl et al., 2000).

The objective of this study was to identify and isolate the main influences on the carbon and oxygen isotopic geochemistry of the species U. mediterranea and G. ruber (white) in a complex environment, the Gulf of Taranto, Italy. Sedimentation in the Gulf of Taranto is influenced by marine as well as terrestrial factors, and has a great potential for climate reconstruction at sub-decadal resolution (e.g. Versteegh et al., 2007). This calibration study was carried out on an extensive set of sediment surface samples taken during the POSEIDON cruise "CAPPUCCINO" in July 2006 (Zonneveld et al., 2008) and the PELAGIA cruise "DOPPIO" in October/November 2008 along the southern Italian coast. Due to input from the Po River and the complex hydrography of the Adriatic, it is very important to determine the different factors influencing geochemical signatures of benthic and planktic species under recent environmental conditions before applying them to paleoclimate reconstructions. In this study, we measured the oxygen isotope composition of the benthic and planktic foraminifera from the top 3 cm of multicores and compared them to seasonal satellite-based sea surface temperature maps and water column profiles, as well as to a set of water samples from the Gulf of Taranto in order to estimate the effect of salinity and nutrient supply on the  $\delta^{18}$ O and  $\delta^{13}$ C of foraminifera. With this calibration we are able to evaluate the robustness of reconstruction of past temperature and hydrographic conditions in the Gulf of Taranto from sediment cores in ongoing studies.

#### 1.1. Hydrography of the Adriatic Sea

The Adriatic Sea is an epicontinental basin with a low topographic gradient in the north and a deeper shelf further south (Turchetto et al., 2007; Artegiani et al., 1997a). It is located between the Italian Peninsula and the Balkans with the major axis in the northwestsoutheast direction. It can be divided into three sub-basins: the northern basin (~35 m depth) with shallow sea water mass

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characteristics, the middle Adriatic (~144 m depth), a transitions basin and the southern basin which is characterized by a wide depression-the southern Adriatic Pit (~1200 m depth)-and open sea water mass characteristics (Artegiani et al., 1997a). Due to these bathymetric features the circulation in the Adriatic Sea is mainly cyclonic (Sellschopp and Álvarez, 2003, Fig. 1). The water mass exchange with the Mediterranean Sea occurs through the Otranto channel where at the surface Ionian Surface Water (ISW) and the Levantine Intermediate Water (LIW) continuously enters the Adriatic. The ISW flows northward along the Croatian coast (Artegiani et al., 1997a; Turchetto et al., 2007; Grbec et al., 2007). Part of the entering water turns westward and recirculates towards the Italian coast. In addition, the discharge of the Po River has a significant influence on the circulation (Artegiani et al., 1997a; Turchetto et al., 2007) leading to the formation of the Western Adriatic Current (WAC) which is colder and less saline than the ISW and flows southward along the western Adriatic coast (Bignami et al., 2007). The Adriatic Sea behaves like a dilution basin in all seasons (Artegiani et al., 1997b). Besides the less saline water masses the river discharge brings large fluxes of nutrients into the basin (Marini et al., 2008).

The surface water undergoes a seasonal temperature cycle with maximal temperatures during summer and a maximum mixed layer depth during winter (Artegiani et al., 1997a). The salt balance of the surface layer is affected by freshwater river runoff in all three basins during spring and summer, and the fresh-coastal waters of the WAC are always separated and distinguishable from the open sea waters in all seasons (Artegiani et al., 1997a). During summer (July-August-September) the hydrographic conditions in the southern Adriatic are characterized by thermohaline stratification with low density and high temperatures in the surface layer (Turchetto et al., 2007). The lower salinity water coming from the north, however, is limited to a narrow belt near the Italian coast (Turchetto et al., 2007). According to Poulain (2001) the WAC has similar characteristics during fall, winter and summer but is characterized by a strongly reduced offshore transport during the warm season (April-September) (Bignami et al., 2007).



**Fig. 1.** Scheme of the circulation and major water masses pathways in the Adriatic Sea (ISW–Ionian Surface Water, LIW–Levantine Intermediate Water, WAC–Western Adriatic Current).

In the Gulf of Taranto we find complex water mass distributions (Sellschopp and Álvarez, 2003) because of the influence from the less saline water masses coming from the Adriatic Sea and flowing in a small band along the coast of the Gulf of Taranto, and the water masses coming from the Ionian Sea which have a higher temperature and salinity.

#### 2. Materials and methods

A number of multicores and water samples have been collected along the southern Adriatic coast, in the Strait of Otranto and in the Gulf of Taranto (Fig. 2) during the POSEIDON cruise "CAPPUCCINO" in June 2006 (Zonneveld et al., 2008), the PELAGIA cruise "DOPPIO" in October/November 2008 and the PELAGIA cruise "MACCHIATO" in November/December 2009. The multicores provided sediments with an undisturbed sediment–water interface (Zonneveld et al., 2008). For the sediment surface analysis we used the first 3 cm ( $3 \times 1$  cm slices) of 46 multicores (41 samples from the "CAPPUCCINO" cruise and 5 samples from the "DOPPIO" cruise) (Table 1). Information on the sedimentation rate based on <sup>210</sup>Pb dating is available for 15 of the study sites (Zonneveld et al., 2009) (Table 1).

#### 2.1. Isotope analysis of foraminifera

For the oxygen and carbon isotope analysis of planktic and benthic foraminifera approximately 10 g of wet sediment of the 0–1, 1–2 and 2–3 cm depth intervals were freeze–dried and then subsequently wet sieved into size fractions of >355  $\mu$ m, 355–250  $\mu$ m, 250–200  $\mu$ m and 200–125  $\mu$ m. At least 10 to 20 shells of *G. ruber (white)* and *U. mediterranea* were picked under the microscope from the fractions: >355  $\mu$ m, 355–250  $\mu$ m and 250–200  $\mu$ m. We did not separate different morphotypes of *G. ruber (white)* but the qualitatively most abundant



Fig. 2. Map of the sampling stations (circle: GeoB Stations CAPPUCCINO cruise (*sediment*), star: DP MC Stations DOPPIO cruise (*sediment/water*), rectangle: DP Stations DOPPIO cruise, MP Stations MACCHIATO cruise (*water*), triangle: VISCOMED2 Stations (*water*) Pierre (1999)).

#### Table 1

Geographic and bathymetric information of the 46 surface sediment samples and the 12 water samples.

ID	Cruise	Station	Number	Latitude	Longitude	Bottom depth [m]	Material	SR [cm/y]	Reference dating	
A. Trai	A. Transect Gargano peninsula									
1	CAPPUCCINO	GeoB 107 MUC	24	42°00 N	16°22 E	49	Sediment	0.46	Zonneveld et al. (2009)	
2	CAPPUCCINO	GeoB 107 MUC	32	41°50 N	16°41 E	51	Sediment	0.78	Zonneveld et al. (2009)	
3	CAPPUCCINO	GeoB 107 MUC	31	41°50 N	16°66 E	96	Sediment	0.32	Zonneveld et al. (2009)	
4	CAPPUCCINO	GeoB 107 MUC	25	42°00 N	16°37 E	98	Sediment	0.19	Zonneveld et al. (2009)	
5	CAPPUCCINO	GeoB 107 MUC	27	41°80 N	16°62 E	101	Sediment	0.19	Zonneveld et al. (2009)	
6	CAPPUCCINO	GeoB 107 MUC	23	42°17 N	16°00 E	114	Sediment	0.91	Zonneveld et al. (2009)	
7	CAPPUCCINO	GeoB 107 MUC	22	42°17 N	16°50 E	142	Sediment	0.19	Zonneveld et al. (2009)	
8	CAPPUCCINO	GeoB 107 MUC	26	42°00 N	16°72 E	183	Sediment			
9	CAPPUCCINO	GeoB 107 MUC	30	41°50 N	17°05 E	183	Sediment	0.19	Zonneveld et al. (2009)	
10	CAPPUCCINO	GeoB 107 MUC	28	41°78 N	16°86 E	194	Sediment			
11	CAPPUCCINO	GeoB 107 MUC	21	42°17 N	16°77 E	203	Sediment	0.06	Zonneveld et al. (2009)	
12	CAPPUCCINO	GeoB 107 MUC	29	41°65 N	17°19 E	712	Sediment	0.08	Zonneveld et al. (2009)	
13	CAPPUCCINO	GeoB 107 MUC	35	41°50 N	17°31 E	733	Sediment			
D Tran	agast Strait of Otrar									
D. 1101		CooP 107 MUC	26	40°76 N	10°10 E	100	Codimont	0.08	Zennoveld et al. (2000)	
14	CAPPUCCINO	Geob 107 MUC	27	40 70 N	10 19 E	125	Sediment	0.08	Zonnevelu et al. (2009)	
15	CAPPUCCINO	Geob 107 MUC	20	40 05 N	10 33 E 10º47 E	110	Sediment			
10	DODDIO	GEOD TOT MOC	20	40 55 N	10 47 E	11Z 527	Seulment Sedimont water			
1/	DUPPIU	DP MC	38	40 51 N	18 04 E	527	Seaiment, water			
18	CAPPUCCINO	Geob 107 MUC	39	40 50 N	18 64 E	565	Seaiment			
19	CAPPUCCINO	GeoB 107 MUC	40	40°39 N	18-58 E	128	Sediment			
20	CAPPUCCINO	GeoB 107 MUC	41	40°23 N	18°67 E	287	Sediment			
21	CAPPUCCINO	GeoB 107 MUC	44	39°85 N	18°60 E	117	Sediment			
22	CAPPUCCINO	GeoB 107 MUC	43	39°82 N	18°64 E	124	Sediment			
23	CAPPUCCINO	GeoB 107 MUC	42	39°72 N	18°78 E	599	Sediment			
C. Trai	C. Transect Gulf of Taranto (east)									
24	CAPPUCCINO	GeoB 107 MUC	4	40°00 N	17°83 E	219	Sediment	0.07	Zonneveld et al. (2009)	
25	CAPPUCCINO	GeoB 107 MUC	5	39°85 N	17°91 E	128	Sediment	0.07	Zonneveld et al. (2009)	
26	DOPPIO	DP MC	32	39°88 N	17°71 E	456	Sediment, water			
27	CAPPUCCINO	GeoB 107 MUC	6	39°83 N	17°83 E	218	Sediment	0.07	Zonneveld et al. (2009)	
28	DOPPIO	DP MC	29	39°83 N	17°80 E	270	Sediment, water			
29	CAPPUCCINO	GeoB 107 MUC	9	39°76 N	17°89 E	172	Sediment			
30	CAPPUCCINO	GeoB 107 MUC	18	39°69 N	18°06 E	220	Sediment			
31	CAPPUCCINO	GeoB 107 MUC	13	39°69 N	18°28 E	127	Sediment			
32	CAPPUCCINO	GeoB 107 MUC	12	39°73 N	17°86 E	618	Sediment			
33	CAPPUCCINO	GeoB 107 MUC	19	39°65 N	18°04 E	616	Sediment			
34	CAPPUCCINO	GeoB 107 MUC	14	39°64 N	18°28 E	207	Sediment			
35	CAPPUCCINO	GeoB 107 MUC	7	39°78 N	17°58 E	1598	Sediment			
36	CAPPUCCINO	GeoB 107 MUC	11	39°68 N	17°80 E	1049	Sediment			
37	CAPPUCCINO	GeoB 107 MUC	15	39°56 N	18°28 E	697	Sediment			
38	CAPPUCCINO	GeoB 107 MUC	10	39°59 N	17°68 E	2040	Sediment	0.07	Zonneveld et al. (2009)	
39	CAPPUCCINO	GeoB 107 MUC	20	39°51 N	17°98 E	1388	Sediment			
40	CAPPUCCINO	GeoB 107 MUC	16	39°34 N	18°28 E	1328	Sediment			
D Tra	nsect Gulf of Tarant	to (west)								
41	CAPPLICCINO	GeoB 107 MUC	46	39°91 N	16°76 F	157	Sediment			
12		DP MC	20	30°74 N	16°04 E	378	Sediment water			
12		CeoB 107 MUC	17	30°72 N	16°07 E	246	Sediment			
11	CAPPLICCINO	CooP 107 MUC	47	20°67 N	10 57 L 17°05 E	240	Sediment			
44	CAPPUCCINO	Geob 107 MUC	40	20°60 N	17 05 E	200	Sediment			
45	DOPPIO	DP MC	49 24	39°54 N	17 10 E 17°25 F	582	Sediment water			
40	DOITIO	DI MC	24	55 54 N	17 23 L	562	Seatment, water			
E. Wat	ter sampling station	IS DD CTD	20	20% (0.5)	10820 5	005	147-6			
4/	DOPPIO	DPCID	28	39°48 N	18-38 E	805	Water			
48	MACCHIATO	MP MC	30	38 53 N	19 18 E	1908	vvater			
49	MACCHIATO	MP MC	38	38-81 N	19-11 E	1359	water			
50	MACCHIATO	MP CTD	40	39°08 N	18°86 E	1057	Water			
51	MACCHIATO	MP CTD	42	39°29 N	18°31 E	789	Water			
52	MACCHIATO	MP BC	43	39°49 N	18°52 E	774	Water			
53	MACCHIATO	MP MC	45	40°22 N	17°37 E	475	Water			
54	MACCHIATO	MP MC	46	40°19 N	17°45 E	420	Water			
55	MACCHIATO	MP MC	47	40°11 N	17°58 E	407	Water			
56	MACCHIATO	MP PC	48	39°83 N	17°80 E	267	Water			

morphotype according to the nomenclature of Numberger et al. (2009) is type platys. The foraminifera shells were thoroughly cleaned to eliminate contaminations with a cleaning procedure modified after Barker et al. (2003) which includes (i) cracking of the chambers to remove internal filling (only for samples >20 specimen), (ii) cleaning twice with ultrapure water in an ultrasonic bath for 1 minute and (iii) cleaning twice with methanol in an ultrasonic bath for 30 seconds. Thereafter around 150 µg of the cleaned shells were weighed in the glass vials of a Thermo Fisher Scientific Kiel IV carbonate device for oxygen and carbon isotopic analyses. The Kiel V carbonate device was connected to a Thermo Fisher Scientific® Delta V Plus mass spectrometer and later to a Thermo Fisher Scientific® MAT 253 mass spectrometer. The carbonate was dissolved in vacuum with two drops of ~103% phosphoric acid at 70 °C, cleaned cryogenically and then transferred to the mass spectrometer. The mass spectrometers are calibrated with the international standards NBS 19 ( $\delta^{13}C_{VPDB} + 1.95\%$ ,  $\delta^{18}O_{VPDB} - 2.2\%$ , L-SVEC:  $\delta^{13}C - 46.6\%$ ,  $\delta^{18}O_{VPDB} - 26.41\%$ ). Reproducibility of the measurements based on repeated measurements of a *Carrara marble*–a laboratory standard–was better than 0.1‰ (1 $\sigma$ ). All results are reported in the conventional delta notation with respect to VPDB. All data were mapped with the Ocean Data View program of Schlitzer (2009).

#### 2.2. Water samples

The water samples were collected with a Rosette water sampling system equipped with 23 bottles and linked to a CTD guideline. The water sample set DP 28 taken during the DOPPIO cruise covers the depths from 5 m to 805 m. During the MACCHIATO cruise two further water sample sets were taken (MP 40 40 m to 1084 m and MP 42 29 m to 789 m). For  $\delta^{18}$ O analyses, the samples were poured into 20 ml Nalgene<sup>TM</sup> bottles and stored at 4 °C. Additionally, bottom water samples from ten multicores and one boxcore were taken during the DOPPIO cruise and the MACCHIATO cruise in the Gulf of Taranto, the southern Adriatic Sea and the western Ionian Sea (Table 1). Furthermore, two surface water samples covering the first 3 m of the water column were taken in the Gulf of Taranto during the MACCHIATO cruise. The oxygen isotope composition of the water samples was measured with the CO<sub>2</sub> equilibration method. Two hundred microliters of the sample was pipetted into glass and was flushed with a gas mixture of He and CO<sub>2</sub> (0.5% CO<sub>2</sub> in He). After an equilibration time of 18 hours at room temperature, the samples were measured with a Gas Bench device coupled to a Thermo Fisher Scientific® Delta V Plus mass spectrometer. The system was calibrated with the international reference waters SMOW, GISP and SLAP. All results are reported in the conventional delta notation with respect to VSMOW.

#### 3. Results

#### 3.1. Water isotopes

The  $\delta^{18}$ O values of the waters are plotted in Fig. 5 against depth. In the first 50 m the stations DP 28, MP 40 and MP 42 show mean values of ~ 1.47‰, ~ 1.33‰ and 1.41‰ respectively. The maximum values are found at 500 m depth (~ 1.59‰) at station DP 28 and at 800 m depth (~ 1.49‰) at station MP 40. Station MP 42 does not show a maximum in the intermediate layer probably because the weather conditions during the sampling were windy and with high waves. At greater depths the  $\delta^{18}$ O values decrease at stations DP 28 and MP 40 (~ 1.48‰ at depths of 700–800 m and 1.44‰ at 1084 m depth, respectively). At station MP 42 the mean value is ~ 1.48‰ at 800 m depth. The bottom water samples in the Gulf of Taranto show a similar pattern. The  $\delta^{18}$ O



**Fig. 3.** Spatial distribution of  $\delta^{18}$ O (a) and  $\delta^{13}$ C (b) of *G. ruber (white)*.

of the water at the stations in the western part of the Gulf of Taranto DP 22 and DP 24 is ~1.56‰. In the eastern part of the Gulf of Taranto the stations DP 29 and DP 32 show values of 1.43‰ and 1.53‰ respectively. The  $\delta^{18}$ O value of the surface water (first 3 m) at station DP 48 is ~1.31‰. Station MP 43 shows a  $\delta^{18}$ O value ~1.49‰ and Station DP 38 located in the Strait of Otranto shows a  $\delta^{18}$ O value of ~1.46‰ (Fig. 5). The two stations MP 36 and MP 38 located in the western Ionian Sea show a  $\delta^{18}$ O value of ~1.5‰ at 1908 m and 1359 m depth, respectively. These data are consistent with the data of Pierre (1999) from the VISCOMED2 cruise in February 1988 (Fig. 5).

#### 3.2. G. ruber (white)

Maps of the distribution of carbon and oxygen isotope compositions of *G. ruber (white)* in the top 3 cm of the sediment are presented in Fig. 3. Unfortunately due to varying amounts of material at different sample stations, it was not possible to carry out isotopic analyses for all sites (e.g. stations 36, 37, 38 and 47: no  $\delta^{18}$ O and  $\delta^{13}$ C value measurement at 0–1 cm and 2–3 cm). The  $\delta^{18}$ O of *G. ruber (white)* show similar patterns at all three depths although due to varying sedimentation rates at the different sites, the intervals may correspond to different sediment ages. Larger vertical changes in  $\delta^{18}$ O (~1‰) are observed only at the stations 22, 23, 24, and 25 along the Gargano Peninsula and at the stations 15, 16, DP29 and DP22 in the Gulf of Taranto (Fig. 3). In contrast, the spatial distribution of  $\delta^{18}$ O

values shows large changes in transects perpendicular to the coast along the depth gradient. The  $\delta^{18}$ O of the offshore station 16 has a mean value of around ~2‰ in comparison to the core closest to the coast DP 29 with a  $\delta^{18}$ O mean value of around ~0.06‰. The situation is quite similar around the Gargano Peninsula where the  $\delta^{18}$ O increases to ~0.16‰ close to the shore (station 24) to values of ~2‰ offshore (station 28).

The distribution maps of the carbon isotope compositions show relatively little change when comparing the first 3 cm (Fig. 3). In the Gulf of Taranto and around the Gargano Peninsula, the vertical changes of the  $\delta^{13}$ C values at stations 23 and 25 are approximately ~1‰, while at the stations 7, 28 and DP24 the values vary around 0.6–0.7‰. At the other stations the vertical changes of the  $\delta^{13}$ C values are <0.5‰. The largest change in  $\delta^{13}$ C, as for the oxygen isotopes, is observed in the gradient from the coastal to the offshore stations (coastal stations: 24 ~0.79‰, DP 29 ~0.59‰; offshore stations: 16 ~1.78‰, station 28 ~1.63‰).

#### 3.3. U. mediterranea

The  $\delta^{18}$ O of *U. mediterranea* in the first 3 cm is generally constant (Fig. 4). Only at the stations 31 ~0.55‰, 35 ~1‰, 39 ~0.7‰, and 42 ~0.5‰, a major  $\delta^{18}$ O gradient is observable in the first 3 cm. The spatial distribution of the  $\delta^{18}$ O, as for *G. ruber (white)*, shows significant gradients perpendicular to the coast. For example station



Fig. 4. Spatial distribution of  $\delta^{18}$ O (c) and  $\delta^{13}$ C (d) of U. mediterranea.

6 in the Gulf of Taranto has a mean value of ~2.17‰ and station 16 offshore a mean value of ~4.34‰. In the Gargano Peninsula coastal station 23 has a mean value of ~2.18‰ and the seaward station 29 a mean value of ~3.24‰.

The  $\delta^{13}$ C does not show significant vertical variations in the first 3 cm (Fig. 4). Merely the stations 23, 35 and 38 show larger changes of up to ~0.7–1‰. In comparison to the spatial distribution of the  $\delta^{18}$ O, the spatial distribution of the  $\delta^{13}$ C of *U. mediterranea* has a significant variation along the southern Adriatic whereby, the strongest gradient is again found perpendicular to the coast (coastal stations: 6 ~–0.63‰, 23 ~0.04‰; offshore stations: 16 ~1.72‰, 29 ~1.07).

#### 4. Discussion

#### 4.1. Isotopic composition of sea water

The  $\delta^{18}$ O of the samples from the upper 100 m of the water column of the DOPPIO. MACCHIATO and VISCOMED2 vary within a narrow range of  $1.4 \pm 0.1$ %. The  $\delta^{18}$ O of the waters also show only relatively small variations with depth (Fig. 5). The  $\delta^{18}$ O at station MP 40 shows a clear increase with depth, related to the presence of the LIW. At station DP 28 the  $\delta^{18}$ O value of the water is ~0.1‰ higher in the first 100 m compared to station MP 40. This is also the case at 500 m depth where we assume the presence of the LIW. The  $\delta^{18}$ O values of the bottom waters are in a narrow range of  $1.5 \pm 0.1$ %. The samples of Pierre (1999) were taken in the southern Adriatic Sea in February 1988. This suggests that the variability of the oxygen isotope composition of deep waters is very low in this region over the last 30 years. Site 12C and 12B' from Pierre (1999) show the same values as our sample sets DP 28, MP 40, and MP 42 and the bottom water samples (Fig. 5). Station 12C of Pierre (1999) shows the highest  $\delta^{18}$ O values of water, however because stations 12B and 12B' are similar to the ones taken during the DOPPIO and MACCHIATO this is probably not a seasonal signal.

#### 4.2. Isotope geochemistry of G. ruber (white)

The strong gradients in the oxygen isotope composition of G. ruber (white) show that the  $\delta^{18}$ O of this species is influenced by additional environmental parameters and does not simply reflect a temperature signal. The same is observed for the carbon isotope composition of this species, which also shows a heterogeneous distribution along the southern Adriatic coast. Although all cores show an undisturbed sediment-water interface, when interpreting the data two possible complicating factors have to be kept in mind: the cores do not all have the same sedimentation rate and, at some locations, the core-top may not represent modern sedimentation due to erosion/non sedimentation. We do not have data for all sites, but <sup>210</sup>Pb data from Zonneveld et al. (2009) summarized in Table 1 show that at all 15 stations for which data are available, the core-top is indeed modern. Along the Gargano peninsula sedimentation rates decrease offshore from 0.91 cm/y at station 23 to 0.06 cm/y at station 21. We assume that the same will be true in the Gulf of Taranto where the sedimentation rate is quite constant close to shore (stations 4, 5, 6, 10 show sedimentation rate of 0.07 cm/y) but likely decrease with distance from the shore (stations 15, 16 no <sup>210</sup>Pb data available). Nevertheless, the available <sup>210</sup>Pb data suggest a modern age between 3 years (coastal areas) to 50 years (offshore) for the top centimeter.

#### 4.2.1. Temperature and salinity

In general it is considered that *G. ruber (white)* inhabits the first 30 to 50 m of the water column and records a summer signal (Waelbroeck et al., 2005; Fraile et al., 2009). Using the  $\delta^{18}$ O of the foraminifera shells the calcification temperature can be calculated (Spero et al., 1997) if the  $\delta^{18}$ O of the ambient sea water is known. Here we compare the paleotemperature equations of Shackleton (1974)



Fig. 5.  $\delta^{18}$ O of the water samples versus water depth.

(1) and Mulitza et al. (2003) (2) for the reconstruction of the temperature and of the depth habitat of *G. ruber* (*white*):

$$T [^{\circ}C] = 16.9 - 4.38 \cdot \left(\delta^{18}O_{c} - \delta^{18}O_{w}\right) + 0.10 \cdot \left(\delta^{18}O_{c} - \delta^{18}O_{w}\right)^{2} \quad (1)$$

$$T [^{\circ}C] = 14.32 - 4.28 \cdot \left(\delta^{18}O_{c} - \delta^{18}O_{w}\right) + 0.07 \cdot \left(\delta^{18}O_{c} - \delta^{18}O_{w}\right)^{2}$$
(2)

where, *T* is the temperature in °C,  $\delta^{18}O_c$  is the  $\delta^{18}O$  of the carbonate of the shells and  $\delta^{18}O_w$  is the  $\delta^{18}O$  of ambient sea water. Based on our measurements and the data of Pierre (1999) we used an average value of 1.4‰ for  $\delta^{18}O_w$ . The equation of Mulitza et al. (2003) produces ~2.7 °C colder temperatures than the Shackleton (1974) equation. The comparison of the reconstructed temperatures by the Shackleton (1974) equation with CTD-temperature data of 2006 from the same sites would indicate that *C. ruber (white)* lives at depths of ~30 m in the coastal regions and ~30–50 m further offshore (Fig. 6). In contrast, the reconstructed temperatures using the Mulitza et al. (2003) equation



Fig. 6. Comparison of the temperature reconstructions of *G. ruber (white)* according to Shackleton (1974) (a) and Mulitza et al. (2003) (b) with the CTD-temperatures in July 2006 (Zonneveld et al. (2008)). The stations are arranged along the x-axes according to depth and distance from the coast. Details of the stations are described in Table 1. Right corner: map of transects A, B, C, and D.

for *G. ruber (white)* compared with the CTD-data would indicate a deeper habitat of ~30–50 m for the coastal areas. In the offshore regions, the calculated temperatures are below the measured bottom water temperature of  $13.7 \pm 0.5$  °C (Zonneveld et al., 2008) (Fig. 6) and thus unrealistically cold. By using the Shackleton (1974) equation the average habitat depth of *G. ruber (white)* agrees well with the other published estimates of 0–30 m and 30–50 m, respectively (Wang, 2000; Kuroyanagi et al., 2008; Numberger et al., 2009). Therefore, we use the Shackleton (1974) equation in the following discussion. The temperature reconstruction (Fig. 7) shows temperature gradients from 21 to 25 °C in the shelf area along the coast of the Gargano Peninsula and in the Gulf of Taranto decreasing seawards to ~15–16 °C and even down to 13 °C. This temperature gradient is significantly

higher than what could be explained with the variability in  $\delta^{18}O_w$  of  $\pm$ 0.1‰ observed in the surface water samples. Additional waters collected from several beaches in Apulia in October 2009 show similar average  $\delta^{18}O_w$  values closer to shore of  $1.2\text{--}1.3\pm0.1\%$ . Satellite-derived sea surface temperatures (SSTs) (Fig. 8 from Zonneveld et al., 2009) along the southern Italian coast do not show a strong temperature gradient towards the open sea, but rather show higher and more stable summer temperatures (June–August) of 25.15 $\pm$ 0.3 °C along the entire southern Italian coast (Zonneveld et al., 2009).

Measured  $\delta^{18}O_w$  and SST variations are not sufficient to explain the observed gradients in the foraminifera. There are different possibilities for the large range of temperatures reconstructed based on *G. ruber (white)*. One possible cause is the presence of at least three



Fig. 7. Spatial distribution of the temperature reconstructions according to Shackleton (1974) based on e) G. ruber (white) and f) U. mediterranea.

genetically distinct morphotypes within the white variety of G. ruber (Numberger et al., 2009). Kuroyanagi et al. (2008) found systematic morphological differences between two morphotypes which is consistent with the concept of Wang (2000). As defined in Numberger et al. (2009) G. ruber type normal, comparable to type sensu stricto (s.s.) according to the definition by Wang (2000), lives in the top 50 m of the water column during summer/early autumn and has a very constant depth habitat (Numberger et al., 2009). G. ruber type platys (Numberger et al., 2009) is comparable to the type sensu lato (s.l.) of Wang (2000) and lives in the upper 30 m of the water column during summer but according to Wang (2000) G. ruber s.l. appears to calcify in a deeper water layer then G. ruber s.s.. Numberger et al. (2009) defined a third type elongate of G. ruber which is comparable to the type G. ruber s.l. by Wang (2000). According to Numberger et al. (2009) type platys appears to share a similar habitat as type normal. For our analysis we mainly used the morphotype G. ruber type platys but we did not sort the species by their morphotypes. According to Kuroyanagi et al. (2008) the distribution of G. ruber s.l. is mostly dependent on the abundance of food and this morphotype is generally not found in the surface ocean in waters with low chlorophyll<sub>a</sub> content. The comparison of the reconstructed temperatures of G. ruber (white) with the CTD-temperature data of 2006 from the same site is consistent with the hypothesis that this species mainly inhabit the upper 30 m of the water column (Fig. 6). Around the Gargano Peninsula, a trend to deeper habitats correlates with the distance from the coast (Fig. 6, Transect A). One reason could be the heterogeneous bathymetry of the Adriatic Sea (Fig. 1). During summertime the circulation is mainly cyclonic in the southern Adriatic Sea (Artegiani et al., 1997b; Cushman-Roisin et al., 2001; Borzelli et al., 1999; Turchetto et al., 2007). From the eastern Mediterranean Sea warm, nutrient-poor ISW with high salinity enters the Adriatic Sea through the Strait of Otranto and flows northward along the Croatian coast (Borzelli et al., 1999). Part of the entering water masses turn westward in the southern Adriatic Sea and recirculate towards the Italian coast (Fig. 1) (Borzelli et al., 1999). From late spring to early fall the hydrographic conditions in the southern Adriatic are characterized by a thermohaline stratification due to surface warming and the gyres and coastal currents are prevailing (Turchetto et al., 2007; Bignami et al., 2007; Poulain, 2001). As a result, G. ruber (white) further away from the coast could be influenced by the nutrient-poor, more saline water masses from the eastern Mediterranean, Numberger et al. (2009) showed that along the African coast where the surface waters are oligotrophic during summer the species G. ruber type platys show a trend to deeper habitats (50 m). Along the southern Italian coast the nutrient content decreases offshore (Marini et al., 2008; Morović et al., 2006), which causes the species further away from the coast to live deeper in the water column. At stations 28 and 29 we already have a



Fig. 8. Satellite-derived SSTs and transect of salinity fluctuations in the Ionian Sea and the southern Adriatic Sea (Zonneveld et al. (2008), http://isramar.ocean.org.il).

relatively oligotrophic system (cf. 4.1.2), which possibly leads the foraminifera to live at depths of up to 50 m (Fig. 6). Thus, we propose that G. ruber (white) near the coast are influenced by the shallower and warmer coastal water and by the less saline WAC with a higher nutrient content coming from the North (Morović et al., 2006; Poulain, 2001; Vilibić and Orlić, 2002; Grbec et al., 2007). The nutrient content along the coast is higher in the surface waters (c.f. Section 4.1.2) which may allow the foraminifera to live in the upper 0–5 m of the water column which is also more influenced by the freshwater from the Po river, thus giving warmer temperature reconstructions. This model is consistent with lower  $\delta^{13}$ C values along the coast, which could also be related to freshwater influence. The salinity gradient away from the coast could also be an additional explanation for the gradient in  $\delta^{18}$ O. A map of the salinity distribution based on measurements of the cruises CAPPUCCINO (Zonneveld et al., 2008), PARO6RUS, PARO2RUS, GAK29RUS, GAK33RUS, GAK36RUS<sup>1</sup> along a transect from the central Ionian Sea to the southern Adriatic Sea shows an increase in salinity (Fig. 8) from 37.2 PSU (practical salinity units) along the southern Italian coast up to over 39.5 PSU in the central Ionian Sea (Fig. 8). Pierre (1999) determined the  $\delta^{18}$ O-salinity relationship for the Mediterranean to be 0.26%/PSU. Therefore, the observed salinity range of 2 PSU could explain up to 0.5% of the oxygen isotope range of *G. ruber* (*white*).

In the Gulf of Taranto the temperature reconstruction shows warmer temperatures (around 19.5-23.8 °C) in the shallower part decreasing towards the open sea to 13–17 °C (Fig. 6, Transect C). The situation is similar to the one along the Gargano Peninsula. The comparison of the reconstructed temperatures with the measured CTD-temperatures shows too, that the species mainly dwell in the upper 30 m of the water column with a trend to deeper habitats in the offshore regions with fewer nutrients. As the temperature reconstructions of the first 2 cm of stations 15 and 16 are very different from the other stations (Fig. 6), other factors must influence the  $\delta^{18}$ O of the species as well, for instance some intraspecific variability. According to Waelbroeck et al. (2005), the intraspecific variability could lead to a variance of up to 1.2–1.5‰ in  $\delta^{18}$ O values. To minimize this influence we measured only adult specimens in the sizes of 200-355 µm and used up to 20 individuals for one measurement. Another reason for the offset at station 15 and 16 could be that the species are reworked from sediments from the last glacial maximum.

So far we discussed changes in the isotopic composition of *G. ruber* (*white*) due to vertical distribution in the water column caused by

differences in food availability. The oxygen isotope gradient from the coast to the open sea, however, can also reflect seasonality. Far from the coast, nutrients are less abundant and may be consumed by early summer, thus reducing the abundance of foraminifera later in the season. In the shallow areas along the coast the higher nutrient supply may provide the foraminifera the possibility to live until late summer or early fall, thus recording higher temperatures. Satellite images (Marini et al., 2008; Morović et al., 2006) show a narrow band of nutrient-rich, freshwater during all seasons along the coast which corresponds to higher temperature and lower salinity conditions in the coastal regions during summer and early autumn (Marini et al., 2008) (c.f. 4.2.2).

The comparison of the satellite-derived SSTs (Fig. 8) with the measured CTD-data along the southern Italian coast (Zonneveld et al., 2008, 2009) shows several difficulties of using satellite-based SST measurements for a coastal environmental reconstruction. The satellite only measures the top of the surface ocean layer, the so called skin temperature (Barton, 2007; Reynolds et al., 2002) which does not represent the mean bulk temperature of the surface ocean layer (0-5 m). Other influencing factors which could cause a distorted temperature reflection of the surface ocean are for instance winds and high insolation which causes a daily skin temperature cycle but does only partially impact the bulk temperature beneath it (Reynolds et al., 2002). Another important factor is mentioned by Casey and Cornillon (1999) who pointed out that especially coastal regions tend to higher temperature variability. The CTD-data taken during the CAPPUCCINO cruise in July 2006 show a mean bulk temperature of ~23.7  $\pm$  2 °C for the first 5 m of the water column around the southern Italian coast. The temperature varies between 20 °C and 27 °C for the upper 5 m of the water column due to mixing and shows a large vertical temperature gradient of up to 10 °C (offshore stations) for the first 30 m of the water column (Turchetto et al., 2007).

In agreement with other core-top studies (e.g. Ding et al., 2006; Martinez et al., 1998; Mohtadi et al., 2007) we conclude that *G. ruber* (*white*) along the southern Italian coast is a warm and surfacedwelling species and records near surface temperatures (Wejnert et al., 2010). However, as Numberger et al. (2009) and Ding et al. (2006) already pointed out, the regional variability depending on the oceanographic setting and the influence of the environmental parameters (salinity, temperature and nutrients) play an important role. These factors have a large influence especially in near-coastal environments due to riverine influence and its variation along the coast.

<sup>&</sup>lt;sup>1</sup> Data source: http://isramar.ocean.org,il.

#### 4.2.2. $\delta^{13}C$ and nutrient supply

In contrast to the  $\delta^{18}$ O, the carbon isotope composition of *G*. ruber (white) shows somewhat larger vertical variations in the first 3 cm (Fig. 3). The  $\delta^{13}$ C is relatively constant (0.5–1‰) along the whole southern Italian coast but it increases to approximately ~2% towards the open sea along the Gargano Peninsula (station 28) as well as in the Gulf of Taranto (Fig. 2). In a pattern similar to that of  $\delta^{13}$ C of G. ruber (white) the chlorophyll<sub>a</sub> concentration during summer around the southern Italian coast (Zonneveld et al., 2008) shows a decrease towards the open sea. Satellite images (Marini et al., 2008) reveal that the nutrient supply is not constant in the area between the Gargano Peninsula and the Gulf of Taranto and show that chlorophyll<sub>a</sub> is mainly found in the plume of river-influenced WAC, thereby illustrating the separation of the nutrient-rich waters along the Italian coast from the more oligotrophic offshore regions in the central and southern Adriatic basins (Marini et al., 2008). The extended algal blooma documented by these satellite images also corresponds to higher temperature and lower salinity conditions in the coastal regions (Marini et al., 2008). The southward extension of the Po river plume within the WAC could allow G. ruber (white) to thrive in the upper 0–5 m of the water column in the coastal areas while the *G*. ruber (white) would have to dwell in the subsurface waters (0-30 m and up to 50 m) in the more oligotrophic offshore regions as well. This could explain the strong gradients expressed in the carbon isotopes of G. ruber (white).

Another influencing factor could be the decrease in  $\delta^{13}$ C of atmospheric CO<sub>2</sub> since the industrial revolution due to the burning of <sup>13</sup> C-depleted fossil fuels commonly referred to as the Suess effect (Beveridge and Shackleton, 1994; King and Howard, 2007). King and Howard (2007) have shown that foraminifera collected with sediment traps show a  $\delta^{13}$ C depletion of the surface waters by up to 0.65‰ in the Subantarctic Zone compared to core-tops of preindustrial age. The higher  $\delta^{13}$ C values at the offshore stations 28, 15 and 16 may correspond to an older sediment age thus the gradient from the offshore to the coastal stations could be also somewhat magnified by this effect.

# 4.2.3. Fluctuations $\delta^{13}C$ and $\delta^{18}O$ of *G*. ruber (white) in the Gulf of Taranto and their implications for paleoclimate reconstructions

The fluctuations of the  $\delta^{18}$ O and the  $\delta^{13}$ C of *G. ruber (white)* along the southern Italian coast are caused by the complex hydrography of the Adriatic Sea that influences nutrient supply and salinity. For paleoclimate reconstruction it is important to know that these fluctuations are caused by changes of the environmental conditions and are due to factors such as food availability that heavily influences the depths at which *G. ruber (white)* dominantly lives. Thus, we compare a transect of several sampling stations located on the shelf area in the eastern part of the Gulf of Taranto (4, 5, DP32, DP29, 9, 11, 12, 18, 19) with each other (Table 2): In the top centimeter the mean  $\delta^{18}$ O value is  $0.64 \pm 0.17\%$ , in the second the mean  $\delta^{18}$ O value is  $0.60 \pm$ 0.31% and in the third the mean  $\delta^{18}$ O value is  $0.50 \pm 0.55\%$ . The  $\delta^{13}$ C values are:  $0.63 \pm 0.25\%$  (0–1 cm),  $0.63 \pm 0.31\%$  (1–2 cm) and  $0.65 \pm$  0.36‰ (2–3 cm). If we compare the  $\delta^{18}$ O fluctuations to the temperature variability in the first 30 m of the water column (CTDtemperature data taken during the CAPPUCCINO cruise) we have also a mean temperature of  $20.4 \pm 2.1$  °C in this transect which corresponds well to the temperature calculated from the  $\delta^{18}$ O values of *G. ruber* (white) (0–1 cm 20.3  $^{\circ}C \pm 1.1 ^{\circ}C$ , 1–2 cm 20.5  $\pm 1.4 ^{\circ}C$  and 2–3 cm  $21.0 \pm 2.5$  °C). The measured CTD-temperature data is only a snapshot of a 1-day situation in the Gulf of Taranto and especially at the surface, the daily temperature fluctuations of  $\pm 1.6$  °C are relatively high. However, this comparison shows that the signal of *G. ruber (white)* in the Gulf of Taranto is stable and mainly reflects the summer temperature of the first 30 m of the water column. Nevertheless, we have to keep in mind that especially for a high-resolution reconstruction, a noise  $(\pm 2 \degree C)$  due to nutrient supply, temperature and salinity variability within the water column, may play an important role and has to be considered.

#### 4.3. U. mediterranea

#### 4.3.1. Temperature reconstructions

The oxygen isotope composition of U. mediterranea is relatively constant along the southern Italian coast and closely reflects the present temperature conditions. In addition, no clear trends are observed when comparing the first 3 cm at each location. We reconstruct the calcification temperature of *U. mediterranea* using the equation of Shackleton (1974) (Fig. 7) using a  $\delta^{18}$ O of sea water of 1.5% (Fig. 5). The reconstructed temperatures vary between 12 °C and 15 °C in the shallow stations and decrease down to 5 °C offshore (Fig. 7). There is only little variation of the reconstructed temperature at the shallow-water stations and they are consistent with the in situ bottom temperatures of  $13.7 \pm 0.5$  °C measured in 2006 (Zonneveld et al., 2008). However, the temperature reconstructed for the offshore stations, especially station 16 with ~5.3 °C and the stations 29 with ~9.6 °C and 15 with ~10.7 °C are well below the bottom water temperatures of  $13.7 \pm 0.5$  °C. Station 16 is an offshore station at 1328 m close to a slope. At the other two stations (10 and 20) below 1000 m depths U. mediterranea was absent. This suggests that this site is below the depth limit of *U. mediterranea* (De Rijk et al., 2000) and probably the analyzed tests, which were poorly preserved at this station, are possibly reworked from sediments from the last glacial maximum.

#### 4.3.2. $\delta^{13}C$ and nutrient supply

 $δ^{18}$ O and  $δ^{13}$ C values of *U. mediterranea* show only a weak correlation with each other. The  $δ^{13}$ C values of *U. mediterranea* exhibit no significant vertical variations in the first 3 cm, although the  $δ^{13}$ C varied slightly along the coast of Bari (0.1–0.4‰) (Fig. 4). Compared to the quite homogeneous spatial distribution of the  $δ^{18}$ O, the  $δ^{13}$ C values of *U. mediterranea* show a clear pattern with low values <0‰ in the coastal areas increasing to 1.5–2‰ offshore. The occurrence and  $δ^{13}$ C of *U. mediterranea*, a shallow infaunal species, are strongly controlled by the flux of organic carbon to the seafloor (Schmiedl

Table 2				
Fluctuations of the	recent conditions	in the	Gulf of	Taranto

Station	δ <sup>13</sup> C (0–1 cm)	δ <sup>18</sup> 0 (0–1 cm)	Temperature reconstruction	δ <sup>13</sup> C (1–2 cm)	δ <sup>18</sup> 0 (1–2 cm)	Temperature reconstruction	δ <sup>13</sup> C (2–3 cm)	δ <sup>18</sup> 0 (2-3 cm)	Temperature reconstruction	CTD-temperature first 5 m	CTD-temperature at 30 m depth
MUC 4				0.42	0.86	19.3	0.61	0.70	20.0	23.0	19.16
MUC 5	0.77	0.51	19.7	0.41	0.86	19.3				22.6	18.84
DP 32	0.29	0.29	21.9	0.50	0.55	20.7	0.26	-0.06	23.5		
DP 29	0.69	0.66	20.1	0.44	-0.06	23.5	0.64	-0.41	25.1		
MUC 9	0.64	0.69	20.3				0.80	0.38	21.5	20.2	18.78
MUC 18	0.46	0.83	21.1	0.93	0.61	20.4	0.67	0.98	18.7	21.0	18.57
MUC 12	0.67	0.64	20.2	0.46	0.85	19.3				20.2	18.52
MUC 19	0.42	0.72	21.3	0.61	0.41	21.3	0.25	0.95	18.9	24.3	18.45
MUC 11	1.09	0.79	18.3	1.26	0.72	19.9	1.32	0.92	19.0	23.4	18.43

et al., 2004; Jorissen et al., 1995). The gradient in  $\delta^{13}$ C can be related to the higher nutrient concentrations in the WAC (Jorissen et al., 1992) and the enhanced primary productivity which induces a higher organic carbon flux to the sediment and thus to a lowering of the  $\delta^{13}$ C of *U. mediterranea* along the coast. An influence of the Suess effect, as discussed above for *G. ruber (white)*, is also possible, although the magnitude of this signal would be much smaller than the observed gradient.

#### 5. Conclusions

The results of our study provide a detailed picture of the modern hydrological and environmental conditions along the southern Adriatic coast. Also they show the difficulties of using stable isotopes of foraminifera for temperature reconstruction in near-coastal environments. In this context, we were able to show that the oxygen and carbon isotope compositions of G. ruber (white) reflect the environmental conditions during summer, which are mainly influenced by the heterogeneous bathymetry of the southern Adriatic Sea causing the variations in nutrient supply and salinity. In the shallow near-coastal areas G. ruber (white) is influenced by shallow, warm water masses and by the less saline, nutrient-rich WAC. We explain the increase in  $\delta^{13}$ C and  $\delta^{18}$ O of G. ruber (white) with the distance from the coast as a combination of an increase in salinity and an expansion of the habitat towards deeper waters (30-50 m) as food availability decreases. The vertical  $\delta^{18}$ O fluctuations of G. ruber (white) at several stations in the Gulf of Taranto are very small in the first 3 cm of the cores (0–1 cm  $0.64 \pm 0.17\%$ , 1–2 cm  $0.60 \pm 0.31\%$ , 2–3 cm  $0.50 \pm 0.55\%$ ).

With regard to ongoing paleoclimate studies in this region, our study provides a snapshot of the recent conditions and how they are reflected in the isotopic composition of the species. Despite the difficulties introduced by the influence of the different environmental parameters, we conclude that the isotopic signal of *G. ruber (white)* is stable in the Gulf of Taranto and reflects summer conditions.

The  $\delta^{18}$ O of the benthic species *U. mediterranea* is stable and reproduces well the temperature conditions along the southern Italian coast. The  $\delta^{13}$ C on the other hand, shows larger variations mainly caused by changing nutrient supply. In the shallower areas, the sediment is enriched in organic carbon because of the high nutrient discharge of the Po River and their southward transport by the WAC. The carbon isotopes of *U. mediterranea* reflect this situation, with low  $\delta^{13}$ C along the coast increasing offshore. This highlights the transitions from the more eutrophic coastal system to the oligotrophic offshore system of the southern Adriatic Sea and the western Ionian Sea.

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#### Appendix A. Supplementary data

Supplementary data to this article can be found online at doi:10.1016/j.marmicro.2010.09.003.

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