Geochemical evidence for intermediate water circulation in the westernmost Mediterranean over the last 20 kyr BP and its impact on the Mediterranean outflow

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Abstract

The Mediterranean Outflow (MOW) is generated by deep and intermediate waters from different basins in the Mediterranean Sea.Despite the number of studies on Mediterranean water masses, little work hasbeen done onthe source and properties of intermediate waters in the westernmost Mediterranean Sea and their links with MOW. Here we examine three marine sediment records spanning the last 20 kyr, located at key depthsto trace intermediate waters along the Alboran Sea. We use a combination of redox-sensitive elements, which can serve as proxies to reconstruct variations in the water column oxygenationand the Nd isotopic composition of foraminiferalferromanganese coatings, in order to reconstruct water mass provenanceof Eastern/Western Mediterranean waters.

As measured,$\varepsilon_{Nd} < -9.2$ and a low U/Th ratioduring glacial periods can be attributed tothe presence of Western Mediterranean Deep Water (WMDW)at the study sites. During deglaciation, higher Nd isotopic compositions and U/Th ratios point to an enhanced contribution of themodifiedLevantine Intermediate Water (LIW). The comparison between our data and other LIW and MOW records suggeststhat i) the lower branchof MOW is linked to WMDW during the glacial period, ii)the middle MOW branch follows LIW activity during deglaciation, whileiii) the upper branch is more active during late Holocene,coinciding withLIW formation increase after sapropel deposits. This reconstruction has significant implications for anunderstanding of the MOW evolution.

1.Introduction

The Mediterranean Sea is connected with the northeastern Atlantic Ocean through the Strait of Gibraltar. The Mediterranean Outflow Water (MOW)has a strong impact on the composition of North Atlantic intermediate waters, henceplaying an important role in global thermohaline circulation (Johnson, 1997; Sierro et al., 2005; Rogerson et al., 2006; Hernandez-Molina et al., 2014; Ivanovic et al., 2014). A strong MOWinput has been associated,for example,with the recovery of the Atlantic thermohaline circulationafter the Last Glacial Maximum (e.g., Rogerson et al., 2006;Voelker et al., 2006). At present, the MOW is predominantly fedby intermediate and deep Mediterranean waters (Bryden and Stommel, 1984).

A key location for understanding MOW is the Alboran Sea,within the westernmost Mediterranean. Most previous studies involving the AlboranSea (e.g., Barcena et al., 2001; Cacho et al., 2001; Martrat et al., 2004;Moreno et al., 2005; Jimenez-Espejo et al., 2007; Rohling et al., 2015 and references therein) focus on reconstructing surface water and deep water conditions, while information about intermediate waters remains scarce. Yet compared to surface and deep water masses, intermediate waters displaydistinct hydrographic features (e.g. Font, 1987; Millot, 2009), and a very characteristic geochemical fingerprint(e.g. their Nd isotopic composition; Tachikawa et al., 2004).

A key open question is how to reconstruct the source and properties of Mediterranean intermediate waters and theirrelationship with the MOW. Instudying relativewater mass contributionsto the MOW during the last deglaciation and the Holocene, we deploy a range of geochemicalproxieson threesediment recordsrecovered in the Alboran Sea basin.The cores are located at depths between 1800 and 2400 mbsf,allowing for anintermediate/deep water mass reconstruction (De Lange et al., 2008, Tachikawa et al., 2015). The utilized proxies include the Nd isotopic composition of seawateras a quasi-conservative water massproxy, as well asredox sensitive trace elements to constrain the redox conditions in the water column.Our new data may provide novel insights into the evolution of Levantine Intermediate Water (LIW) and Mediterranean thermohaline circulation,leading to an improved understanding ofthe MOWover time.

Oceanographic setting

The general circulation in the Mediterranean is a result ofhigh evaporation rates and MOWactivity (Ovchinnikov et al., 1976; Millot et al., 2009; MerMex group, 2011). In the Western Mediterranean Sea (WMS),three main water massescan be distinguished: Modified Atlantic Water (MAW), Levantine Intermediate Water (LIW), and Western Mediterranean Deep Water (WMDW). The MAWforms as a resultof the comparatively fresh Atlantic water (S<36.5) entering the Mediterranean Sea via the strait of Gibraltar and mixing with the surface waters of the Alboran Sea. The MAW flows eastward as a 150-200 m thick surface layer.

On the other hand, the LIW originates in the Eastern Mediterranean Sea (EMS)through sinking during winter times (Cramp and O'Sullivan, 1999) and can be identified in the study area at depths between 200 and 600 m. Finally,WMDW is found below this water depth, being generated by surface cooling in the Gulf of Lion. Its main flow path isalong the Moroccan margin(Hernandez-Molina et al., 2002).

The MOW comprisesa mixture of these deep and intermediate water masses (Parrilla et al., 1986; Millot et al., 1999)(Figs. 1 and 2). Its formation has been relatedto the wind strength, predominant circulation patterns of source waters, freshwater input, temperatures andthe density of surface waters, among other factors (e.g., Rohling and Bryden, 1992; Bethoux et al., 1998; Cramp and O'Sullivan, 1999; Millot, 2009).

2. Materials and methods

2.1. Site description and age model

We obtained our data from Sites 300G, 302G and 304G, situated at different depths (1860m, 1989m, and 2382m, respectively; Table 1) along the west-east trending East Alboran basin slope; they are currently bathed in the WMDW(Figs. 1 and 2). The incoming MAW flow generates a quasi-permanent anticyclonic gyre in the western Alboran Sea and a transient gyre at the eastern part of the basin (Fig. 1). The hydrological front is characterized by a strong horizontal density gradient (>0.4 kg m^3) betweenMAW and the LIW (Tolosa et al., 2003).

Age models for the three siteshave been published previously(Jimenez-Espejo et al., 2008) and are based onmonospecific planktonic foraminifera ^{14}C-AMS dates (accelerator mass spectrometry), stable isotope stratigraphy, and the correlation of geochemical elemental ratio profiles among sites.The cores span the past 20 kyr BP (Table 1) and were collected during Training-Through-Research (TTR) Cruise 14 in order to track shifts in the water column structure. Recovered lithologies comprise homogenous greyish olive nannofossil clay and nannofossil-rich silty clay (Comas and Ivanov, 2006).The studied intervals and their detrital elemental composition show no indication of grain-sorting processes, indicative of strong bottom currents, or turbiditic sequences(Jimenez-Espejo et al., 2008). Sedimentation rates in the Alboran basins range from approximately 10 cm/ka during the late Holocene up to 20 cm/kyrduring some pre-Holocene periods. Sampling resolution was 3 cm atsite 300G and between 3 and 7 cmat sites 302 and 304,yielding atemporal resolutionof ~200 to ~500 yrs depending onsite and time interval.

2.2. Methods

Major element concentrations (Fig. 3)were obtained by atomic absorption spectrometry (AAS) (Perkin-Elmer 5100 spectrometer),with an analytical error of 2%, at the Instituto Andaluz de Ciencias de la Tierra (CSIC-UGR).Analysis of trace elements (U, Th and Ba) was performed using inductively coupled plasma-mass spectrometry (Perkin-Elmer Sciex Elan 5000 ICP-MS) following HNO_3 + HF digestion. Measurements were carried out as triplicates using Re and Rh as internal standards at the Centro de Instrumentación Científica (University of Granada). External reproducibility was determined by dissolving 10 replicates of powdered samples and results were in agreement within 3% for analyte concentrations of 50 ppm and within 8% for analyte concentrations of 5 ppm (Bea, 1996).From the suite of analyzed major and trace elements, U, Th and Ba (and corresponding normalized concentrations) were selected as proxies for water mass reconstructions.

Authigenic Nd isotopiccompositionsof bottom waterswere reconstructed based on the Fe-Mn oxide coatings around foraminifera tests in the MAGIC laboratories at Imperial College, London,following the pioneering work of Roberts et al. (2010) (Table 2). Briefly, ~80 mg of planktonic foraminifera were picked from the >125µm fraction of 11 sediment samples from two different coresites (304G and 302G)located in the western gyre of the Alboran Sea. Sampled tests were crushed between glass plates, ensuring that all chambers were opened. Thereafter, samples were ultrasonicated in glass beakers (with 5 ml de-ionized water) for ~1 minute before pipetting off the waste water. This step was repeated until the water was clear (i.e., no clay left). Thecleanliness of samples was checked under a microscope and visible pieces of pyrite and detrital particleswere removed. Digestion of foraminifera was achieved by addition of 1ml of 1M acetic acid.

Additionally, four samples from sites 302G and 304Gwere investigated for their detrital Nd isotopic composition following sequential extraction of authigenic carbonate and ferromanganese coatings as described previously (see Biscaye, 1965, and Rutberg et al., 2000) (Table 2). ~50mg of detrital material was digested on a hotplate using a mixture of 0.5ml 20M $HClO_4$, 1ml 15M HNO_3 and 3ml 27M HF. After conversion to nitrate form, Nd was separated from the sample matrix and other rare earth elements by means of two-step ion chromatography (TRU-spec and Ln-spec columns; modified after Pin and Zalduegui, 1997). Neodymium isotope measurements were carried out on a Nu Plasma-HR MC-ICPMS. Instrumental mass bias was corrected for using a $^{146}Nd/^{144}Nd$ ratio of 0.7219 and an exponential law. Samarium interferences were monitored and were significantly below the correctable level of 0.1% ^{144}Sm on ^{144}N in all samples. Repeated analyses of the JNdi-1 standard yielded values of 0.512107 ± 0.000014, 0.512133 ± 0.000015, 0.512121 ± 0.000014,and 0.512072 ± 0.000011 (2sd)over the course of the four days of sample analyses. All sample results are reported relative to a JNdi-1$^{143}Nd/^{144}Nd$ value of 0.512115 (Tanaka et al., 2000).

3. Paleoenviromentalproxies

3.1. Neodymium isotopes as water mass proxies

Neodymium isotope ratios in seawater are often used in paleoceanography as a quasi-conservative tracer of water masses (e.g., Frank et al., 2002; Goldstein and Hemming, 2003). Neodymium isotopes are expressed as ε_{Nd} and denote thedeviation of a measured $^{143}Nd/^{144}Nd$ ratio from the Chondritic Uniform Reservoir (CHUR) in parts per 10,000 (present day CHUR = 0.512638; Jacobsen and Wasserburg, 1980). Geological heterogeneity inthe continents and their subsequent erosion and delivery to the ocean, as well as exchange of seawater with the ocean margins, leave distinct Nd imprints on water masses, which can be traced spatially due to the short residence time of Nd in the seawater (~400 years; Tachikawa et al., 2003). Modern seawater Nd isotopic compositions range from values as low as $\varepsilon_{Nd}< -20$ in the Labrador Sea, which is surrounded by old continental crust, to values as high as $\varepsilon_{Nd} \sim 0$ in the North Pacific, close to young volcanic inputs (see Lacan et al.,2012, and Jeandel et al., 2007 for an overview). The origin and significance of ε_{Nd} in the Mediterranean Sea has been previously explored, indicating that LIW has an isotopic signature of $\varepsilon_{Nd} \sim -5$ in the EMS (Tachikawa et al., 2004; Vance et al., 2004). However, this value becomes less radiogenic in the WMS, where ε_{Nd}values of ~ -8.9 are observed at LIW depths (Henry et al., 1994; Tachikawa et al., 2004). LIW reaches these values after crossing the strait of Sicily. Hereafter we will refer to this signature at intermediate depths in the WMSasmodified LIW (mLIW). Less radiogenic values are characteristic of WMDW ($\varepsilon_{Nd} = -9.4$; Henry et al., 1994; Tachikawa et al., 2004), the least radiogenic values being recorded in MAW ($\varepsilon_{Nd} = \sim -10.4$; Spivack and Wasserburg, 1988; Tachikawa et al., 2004) (Fig. 3). When interpreting the Nd isotopic composition of seawater as derived from authigenic phases in sediments, it should be noted that intense sediment reworking and along-slope transport may alter the use of Nd isotopes as a water mass proxy (e.g., Gutjahr et al., 2008). The Gulf of Cadiz is one such area (Stumpf et al. 2010), though contourites are not described in the eastern Alboran region (Palomino et al., 2011); hencewe are confident that Nd isotopes can reliably trace water masses.

3.2. U aspaleoceanographic proxy

Uranium in sediments can be hosted in solid phases such as detrital lithogenic components (physically transported to and deposited at the site), in authigenic phases (associated with biogenic carbonate and organic biomass), or be derived from reductive authigenic pore-water precipitation (Andersen et al., 2014).

Because U concentrations in the sediment might be further biased by detrital input,the U/Th ratiois used. Normalization of trace element contents to an immobile element —usually Al or Th— is common in paleoceanographical studies, and a vast literature on geochemical proxies demonstrates the usefulness of this ratio (e.g., Van der Weijden, 2002; Calvert and Pedersen, 2007). In this sense, the U/Th ratio allows for correcting the dilution by sedimentary phases barren of a particular trace element. The U/Th ratio thus represents the excess of U with respect to Th (aluminosilicate fraction). The subtraction of the detrital influence on trace elements concentrations is an important issue discussed by different authors (e.g., Chase et al., 2001; Tribovillard et al., 2006; Andersen et al., 2014). Hence, it is important to distinguish whether uranium enrichment is linked to bottom water oxygenation and/or organic matter oxidation and consequent post-depositional sediment reduction forcing U deposition from pore waters (when pore-water nitrate vanishes in sediments beneath the redoxcline, U^{+6} is reduced to immobile U^{+4} and precipitates; Anderson, 1982; Barnes and Cochran, 1990; Mangini et al., 2001).Although thespecific behavior of U under oxic and suboxic conditions remains poorly understood,an increase in U deposition has been observed in suboxic basins with respect to oxidized conditions(Andersen et al., 2014).In the WMS,the last organic rich layer (ORL 1,between 14.5 and 8.2 ka) has been associated with the occurrence of sluggish bottom waters (Rogerson et al., 2006).U/Th enrichment is observed for sediments deposited during this ORL interval, and partially the GS-2a period, when Ba based proxies also support enhanced productivity (Fig. 3e). Consequently, the WMS U/Th ratio appears to be predominantly sensitive to suboxic conditionsat the sea floor,and furthermore correlates with organic matter deposition.

4. Results

Major element concentrations in 355 samples were obtained byAAS; 360 samples were analyzed using inductively coupled plasma-mass spectrometry. Nd isotopiccomposition was determined in 15 samples, 11 in the authigenic Fe-Mn oxide coatings around foraminifera tests and 4 in bulk samples (Table 2). All datasets are unpublished to date, except the Barium excess content during the 20 to 5 kyr interval, previously discussed in Jimenez-Espejo et al., 2008.

U content ranged between 1 and 5 ppm, showing the lowest values at site 304G during late Holocene. Higher values are associated to the deglaciation period (U > 3 ppm), whereas lower values can be found during the last Glacial maximum and after 8.0kyr. The content varies between 5 and 9 ppm, the highest values reached during late Holocene at site 302G.

The Ba content derived from marine barite (Baexcess)was obtained by subtracting the amount of terrigenous Ba from the total Ba content (Dymond et al., 1992; Eagle et al., 2003). The presence of marine barite was confirmed by Field Emission Scanning Electron Microscopy(FESEM).Barite crystals were found with sizes and morphologiescorresponding to typical marine barite(1-5 mm in size, with round and elliptical crystals). Ba excess is calculated as: Ba excess = (Ba-total) – Al $(Ba/Al)_c$, where Ba-total and Al are concentrations in ppm, and $(Ba/Al)_c$is the crustal ratio for these elements. In this study, we used the value $(Ba/Al)_c$= 0.033, as estimated by Sanchez-Vidal et al., 2005 in the Alboran basin. During the last 5 ka interval all studied sites show a nearly parallel and flat pattern, having Ba excess values around 250 ppm (Fig. 3e).

In turn, the ε_{Nd}values obtained for the authigenic fractionrange from ε_{Nd} -10.1 ± 0.3 for the deepest site (304G)during the last glacial period, to ε_{Nd} -9.09± 0.28 for the shallowest site (302G) during late Holocene. Measured ε_{Nd}values in bulk samples are clearly different from the authigenic ones, with ε_{Nd}values between -12.62± 0.28 and -12.82 ±0.28 (Table 2).

5. Discussion

5.1. Last Glacial Maximum and deglaciation

During the last glacial maximum,a low sea level combined with cold and arid conditions over the Gulf of Lion (Hayes et al., 2005)have been associated with intense deep water formation in the WMS (Rogerson et al., 2008). Around 19.8 ka cal BP we obtained aε_{Nd}value of -9.6 ± 0.29for site 302G and ε_{Nd} -10.1 ± 0.3for site 304G (Fig. 3b), values typically associated with modern water masses generated in the Gulf of Lion (Henry et al., 1994; Tachikawa et al., 2004) (Fig. 3b).At all our studied sites U/Th ratios show relatively lowvalues, between 0.25 and 0.4, suggestingwell ventilated water mass generated in the WMS. For the same time period, Toucanne et al. (2012) describedan intenseLIW flowat the Corsica Trough (MD01-2434; Fig.

3d). Furthermore, a dense MOW, flowing at deeper depths than today,has been reconstructed in the Gulf of Cadiz (Rogerson et al., 2005; Voelker et al., 2006; Llave et al., 2007), with low activity in the upper MOW branch (Bahr et al., 2014). We therefore conclude that WMDWpredominance in the Alboran basin is coincident with enhanced activity of the deeper MOW branch during the last glacial maximum. The probable causes of this relationship will be discussed in more detail below.

Environmental conditions in the Alboran Sea appear to change around 18 ka cal BP, contemporaneouswith progressive deglaciation affecting atmospheric CO_2 and methane contents (e.g., Marcott et al., 2014),as well as theAtlantic meridional circulation(McManus et al., 2004).OurNd records indicate a shift from values around -10.1± 0.3 during the glacial period, to less radiogenic ones reaching ε_{Nd} = -9.0 ± 0.3 at site 302G at 15.8 ka cal BP (Fig. 3b). Such higher values aretypically associated with water masses generated in the EMS (Henry et al., 1994; Tachikawa et al., 2004).Furthermore, from 17.5 ka cal BP onwardU/Th ratios increaseatall sites,with a subtle difference among them(Fig. 3 dashed line). At the shallower sites, 300G and 302G, oxygenation decreases before the same trend is observed at the deeper site 304G, pointing to a depth-dependent bottom and/or pore waters ventilation. Despite the dating uncertainties, similar depth-dependent ventilation variations have been invoked in the EMS basins related to sapropel S1 deposition (De Lange et al., 2008; Tachikawa et al., 2015). These changes can be explained byprogressivewater mass mixing or replacement of WMS-generated deep waters, and/or by deepening of EMS-generated intermediate waters (LIW) from 1,900 and 2,300 mbsf. It is noteworthythat we observe a peak in LIW intensity in the Corsica site (Toucanne et al., 2012: Fig. 3d) at the same time when themLIW influence appears to affect the shallowest sites in the Alboran Sea. This decrease in the WMDW contribution to the MOW should have increasedthe

MOW buoyancy and decreased the flux in the lower core of the MOW, as can be interpreted from the records in the Gulf of Cadiz (Voelker et al., 2006). Nevertheless, no changes are observed in the MOW upper branch (Fig. 3c) (Bahr et al., 2014). Hence,changes in water masses within the Alboran region can be tracked in the Gulf of Cadiz, in this case a mLIW intensification that is connected to a ceased MOW lower core.

The next change in environmental conditions that is recorded in the Alboran region took place during the GS-1 (Younger Dryas, YD) (Fig. 3).Ba/Al andU/Th ratiosshowan increaseduringthe YDat the deepest site (304G),pointing to lower oxygenation and higher productivity, whichcoincides with the maximum intensity ofLIW flow in the central Mediterranean Sea(Fig.3d) (Toucanne et al., 2012).This increase in marine productivity is also documented by the diatom recordfrom Alboran basin(Barcena et al., 2001). In the Gulf of Cadiz (Site U1387; Bahr et al., 2014), a concomitant reactivation of the upper branch of MOW,as reconstructed from Zr/Al ratios,indicateshigherMOW buoyancy during this period (Fig. 3c). A weak contribution of theWMDW to the MOW is fostered by the Nd data that point toa persistent influence of the LIW waters atsite 302G (Fig. 3b). Furthermore,the studiedproxies indicate that the cooling associated with the YD did not lead to a significant reactivation of WMDW formation. This observed low oxygenation in the WMS during the YD seems to contradict model results that predict high ventilation during this period (Rogerson et al., 2012a).Our data therefore reveal a marked difference betweenthe EMS, with intense thermohaline circulation,and the WMS, with sluggish circulation during the YD. It appearsthat theEastern Mediterranean Basin was more prone to alterations in the water mass structurethan the western basin(Sprovieri et al., 2002; Hayes et al., 2005; Hennekam et al., 2014).

5.2 Holocene and sapropel deposition

During the Holocene, the Eastern and Western Mediterranean Basins show distinctsignatures. In the Eastern basin, a characteristic feature was the deposition of the most recent sapropel(S1), an organic-rich black layer, depositedbetween 10.8± 0.4 and 6.1± 0.5 kacal BP(Ariztegui et al., 2000; De Lange et al., 2008). However, no such deposits can be found in the WMS, where the last ORL formed between 14.5 and 8.2 ka(Cacho et al., 2002; Rogerson et al., 2008; Rohling et al., 2015).

During the early/middle Holocene (until 8.2 ka BP), the studied records display high U/Th ratio values (around 0.6), indicating a relatively low oxygenation in agreement with the S1a deposition (Fig.3a).The Ndisotopic composition of seawater around 6.8ka cal BP at site 302G (ε_{Nd}-9.75± 0.27) shows values similar to those related with WMDW formation during the Last Glacial Maximum, pointing to a WMDW reactivation—or at least a LIW reduction—while sapropel S1 deposition was still active.Weak LIW formation has also been described in the EMS during sapropel deposition and has been linked with increase runoff and fluvial input from the Nile (Bosmans et al., 2015; Rohling et al., 2015).

During the late Holocene,more radiogenic Nd isotope valuesindicate a mLIW influence (Fig. 3b). This recovery of the EMS signal is coincident with a progressive increase in the MOW upper branch (Fig. 3c). Notably, the central Mediterranean LIW record (Fig. 3d) does not show any variationsassociated with the sapropel demise,nor does it reveal any significant changes throughout the entire Holocene. Previous work has described an antiphasedpatternbetween the EMS and the WMSin the late Holocene(Rimbu et al., 2004; Roberts et al., 2008; Felis and Rimbu, 2010;Martín-Puertas et al.,2010),with humid conditions in the WMS (Martín-Puertas et al., 2010) but dry conditions in the EMS (e.g., Nieto-Moreno et al., 2013). These differences between basins can berelated to the W-E gradients in salinityand temperature, different influences of riverine input, and diverging climate patterns especially during winter (e.g., Hayes et al., 2005).

Overall, observedvariations during the Holocene indicate a high sensitivity of the Mediterranean thermohaline circulation to fresh water input. In detail, model results indicate that as little as 5%-10% changes in the Mediterranean mean freshwater budgetmay have pronounced effects on the overturning circulation in the area (Skliris et al., 2007).

5.3. Origin and significance of simultaneous changes recorded between records from the Alboran Sea and MOW

Comparison between our records from the Alboran sites and previously published MOWrecords indicatesa complex regional picture. Despite the fact that the WMS thermohaline circulation is affected by a number of factors throughout time —such as interaction between sea-level rise, meltwater pulses, monsoon flooding, Gibraltar strait section and Alpine melt-water routing (e.g., Rohling et al., 2015)—our new data reveal some insightful patterns. In detail, our observationsindicate that (i) the MOW’s lower branch is linked to the WMDW evolution, (ii) its middle branch followsthe LIW activity,and (iii) itsupper branch is more active during times of minima inWMDW formation. This marked heterogeneity of the MOW is in agreement with present day oceanographic observations ofdifferent Mediterranean waters in the Gibraltar strait(Naranjo et al., 2012; Millot et al., 2014)and three distinct MOW branches (e.g., Ambar et al., 2002).

The described correlations between the two water masses can be causal or genetic. A causal relationwould have major consequences for understanding the MOW behavior, because the WMDW, formed in theGulf of Lion, is mainly driven by the North Atlantic climate realm (Cacho et al., 2002; Frigola et al., 2007). In contrast,the LIW is mainly affected by the Eastern Mediterranean realm and conditioned by variations in high and low latitude climates (e.g., Blanchet et al., 2013; Hennekan et al., 2014). If causal,the main mechanisms driving the MOW branch intensification could be fresheningof the Mediterranean Sea surface, thereby influencing bottom water formation (MerMex group, 2011). Enhanced fresh water input has been relatedto Nile run-off (Rossignol-Strick et al., 1982; Rohling, 1994; Rohling et al., 2015), meltwater fluxes (Ehrmann et al., 2007), and Black Sea influence (Grimm et al., 2015). Climate models indicate that precipitation patterns as well as runoff from the Nile aredriven by the strength of the North African monsoon, ultimately responding tonorthern hemisphere summer insolation(Bosmans et al., 2015). In such a scenario, water mass variations at the studied core sites can be interpreted to manifest the influence of surface processeson deep sea circulation in the Mediterranean.

Nonetheless, hydrodynamic models reject a causal link between downwelling in the Mediterranean and MOW evolution, and instead propose sea-levelvariability and water column density in the Eastern Atlantic as main driving factors for MOW deepening and branch activity (Rogerson et al., 2012a;b). In this case, the described correlation between both sides of the Gibraltar strait water masses could be linked genetically, through common climate and environmental variations. More specifically, the water column density gradient in the Gulf of Cadiz would have increasedduring deglaciation due to the production of meltwater from ice sheets and glaciers (Rogerson et al., 2012b). This gradient increase would in turn promote a

MOW shoaling due to the presence of dense Atlantic water masses at shallower depths and surface freshening in the Mediterranean, leading to reduced WMDW formationat the same time.This genetic link is,however,difficult to reconcile with observedchanges during the late Holocene, a period of almost stable sea level.

No matter which of the two mechanisms is preferred, our data certainly point to an intrinsic correlation between Mediterranean intermediate water masses and MOW branches. Deciphering this correlation in more detailcalls fora targeted study of geochemical proxies in all three MOW branches (lower, middle, and upper)to discernwhether they preserve an EMS or WMS climate realm signal. Based on the results presented here, we can speculate that the middle and upper branch were probably dominated by low latitude climate variations, whereas the lower branch would be more sensitive to a higher latitudinal signal.

6.Conclusions

Geochemical proxies provide evidence of significant paleoceanographic changes in the western Mediterranean during the last 20 ka BP. We observe a replacement (or reduced influence) of relatively cold and well oxygenated bottom waters generated in the WMS during GS-2a by less oxygenated intermediate water masses of Eastern Mediterranean provenance in key depth locations. The Eastern water mass appears to have influenced shallower water depths in the Alboran Sea during the entire deglaciation and until the early Holocene.

Comparison of the Alboran records with previously published records ofLIW intensity fromthe Central Mediterranean,as well asMOW intensity in the Gulf of Cadiz,suggestsa heterogeneous MOW linked to Mediterranean intermediate water variations. The lower branchseems to be mainly fed by the WMDW, while themiddle and upper branch would belinked to LIW activity. Nevertheless, we cannot determine whether the described relationshipsare causally or genetically based. Placing our results into the context of Northern Hemisphere climate variations,the lower branch of MOW is apparently dominated by high latitude climate variations, and the middle and upper branchesare insteadforced by low latitude evolution. More detailed studies are needed to fully resolve what drives changes in the different branches of MOW over time, and how they are associated with regional and global climate changes.

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Table and Figure captions

Figure 1. a) Map of the western Mediterranean Sea with setting of studied gravity cores 300G, 302G and 304G in the Alboran Sea. Also shown are sitesIODP-U1387 and MD01-2434 for comparison. Black and dashed gray lines represent the flow directions of major water masses, Western Mediterranean Deep Water (WMDW), Levantine Intermediate Water (LIW) and Modified Atlantic Water (MAW). b) Cross-section showing water mass stratification in the Mediterranean. Modified from Cramp and O'Sullivan (1999).

Figure 2. Gibraltar Strait and Alboran basin bathymetry and raised-relief maps with vertically exaggerated scale viewed from the East. Dashed lines represent the pathways of the main currents in the area (modified from Hernandez-Molina et al., 2002).Modified Atlantic Water (dark blue), Levantine Intermediate Water (green), and Western Mediterranean Deep Water (light blue). Red line represents the coast line.

Figure 3.Time series of geochemical proxies for studied sites TTR-300G, TTR-302G,and TTR-304G from the Alboran Sea (this study) in comparison to previously published records from the area. a) U/Th ratios for sites 300G (red), 302G (blue) and 304G (orange), used as a proxy for the degree of anoxia.b) Neodymium isotope composition ofplanktonic foraminifera ferromanganese coatings at sites 302G and 304G used as a water mass provenance indicator. Green and blue dark bands respectively display the main range of seawater Nd isotopic compositionsof modified Levantine Intermediate Water (mLIW) (εNd ~ - 8.9, Tachikawa et al., 2004) and the West Mediterranean Deep Water (WMDW) (εNd ~ - 9.4, Tachikawa et al., 2004). Extended light green and blue bands denote full values range.c) Ln Zr/Al ratio at site U1387

(Gulf of Cadiz), an upper MOW intensity proxy (Bahr et al., 2014). d) Sortable Silt content at site MD01-2434, an LIW intensity proxy (Toucanne et al., 2012). e)Barium excess (ppm) age plotted comparison among cores (Jimenez-Espejo et al., 2008).Light blue bars across the Figure indicate the African Humid Period and the last Organic Rich Layer (ORL) deposited in the Western Mediterranean. Light grey bars indicate Greenland Stadials 2a, Sapropel S1a and S1b (Ariztegui et al., 2000).

Table 1.Core data including location, water depth, studied interval and linear sedimentation rates.

Table 2. Nd isotopic compositions of foraminiferal coatings and bulk sediments from studied sites. (a) Measured Nd isotopic composition normalized to JNdi $^{143}Nd/^{144}Nd$ value of 0.512115 (Tanaka et al., 2000). JNdi results for the four measurement sessions are reported in the main text. (b) Internal 2σ standard error of the measurements. (c) ƐNd values are calculated relative to a CHUR value of 0.512638 (Jacobsen and Wasserburg, 1980). (d) External errors are the 2σ deviations derived from repeat analysis of the JNdi standard during the measurement sessions at similar concentrations to sample sizes (10-20 ng Nd). Uncertainties plotted in Figure 3 are internal 2σ standard errors.

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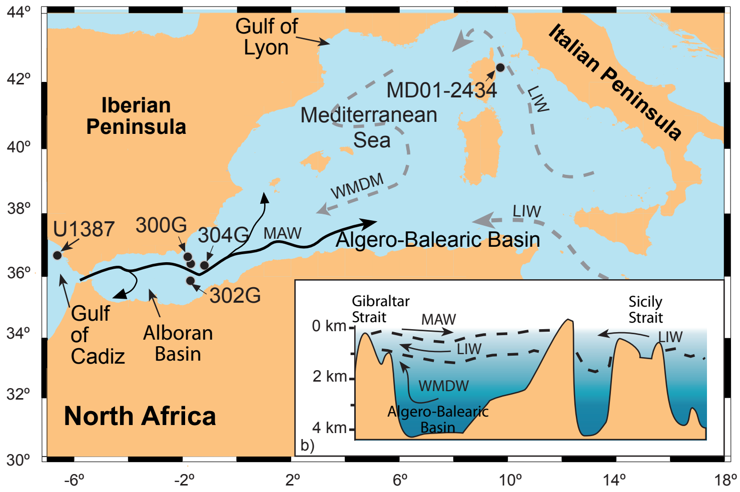
Figure 1



Gulf of Lyon
Italian Peninsula
Iberian Peninsula
MD01-2434
Mediterranean Sea
LIW
WMDM
LIW
U1387
300G
304G
MAW
Algero-Balearic Basin
302G
Gulf of Cadiz
Alboran Basin
North Africa
Gibraltar Strait
MAW
Sicily Strait
LIW
0 km
LIW
2 km
WMDW
Algero-Balearic Basin
4 km
b)
44º
42º
40º
38º
36º
34º
32º
30º
-6º
-2º
2º
6º
10º
14º
18º

Figure 2

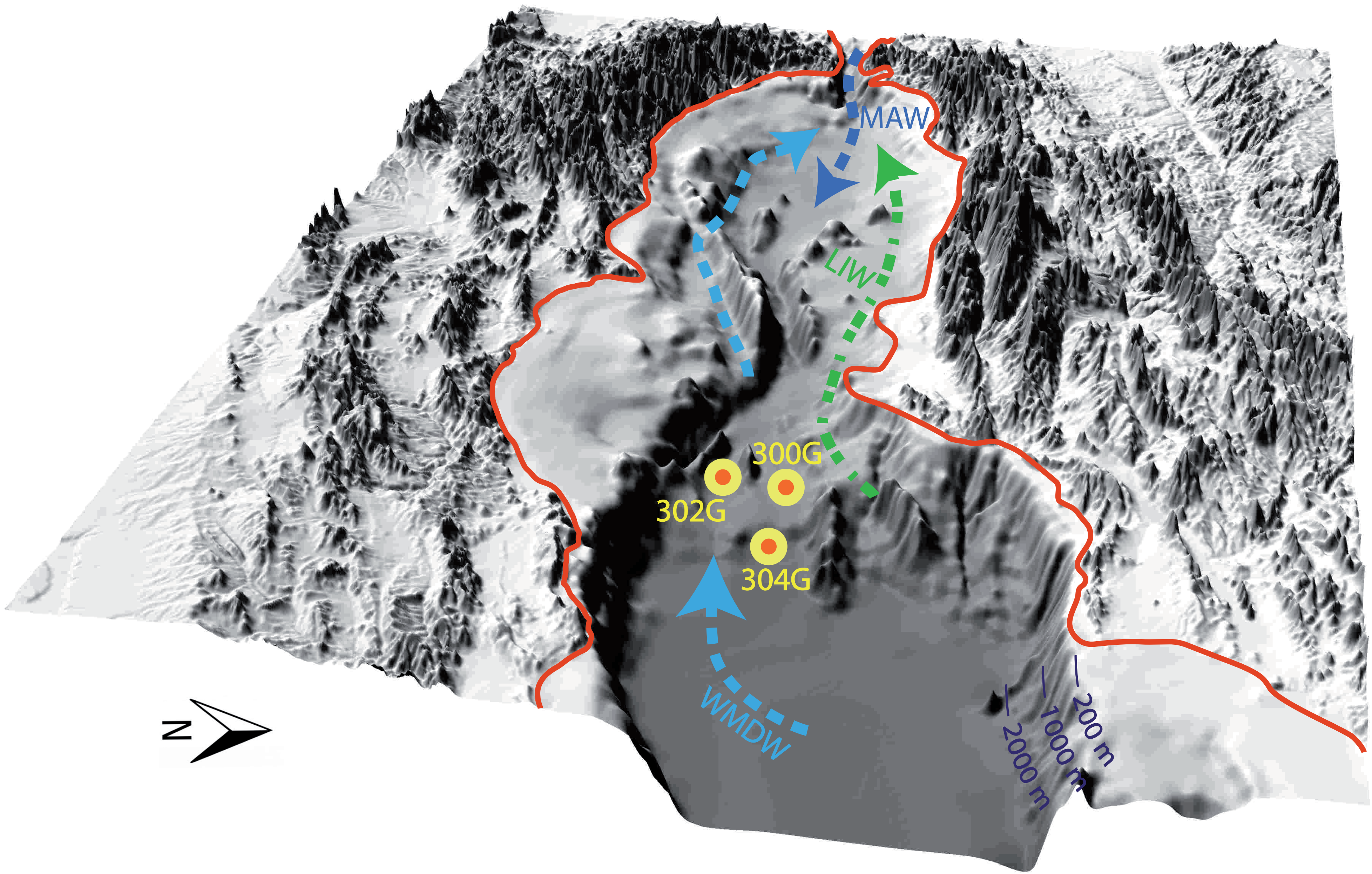


Figure 3
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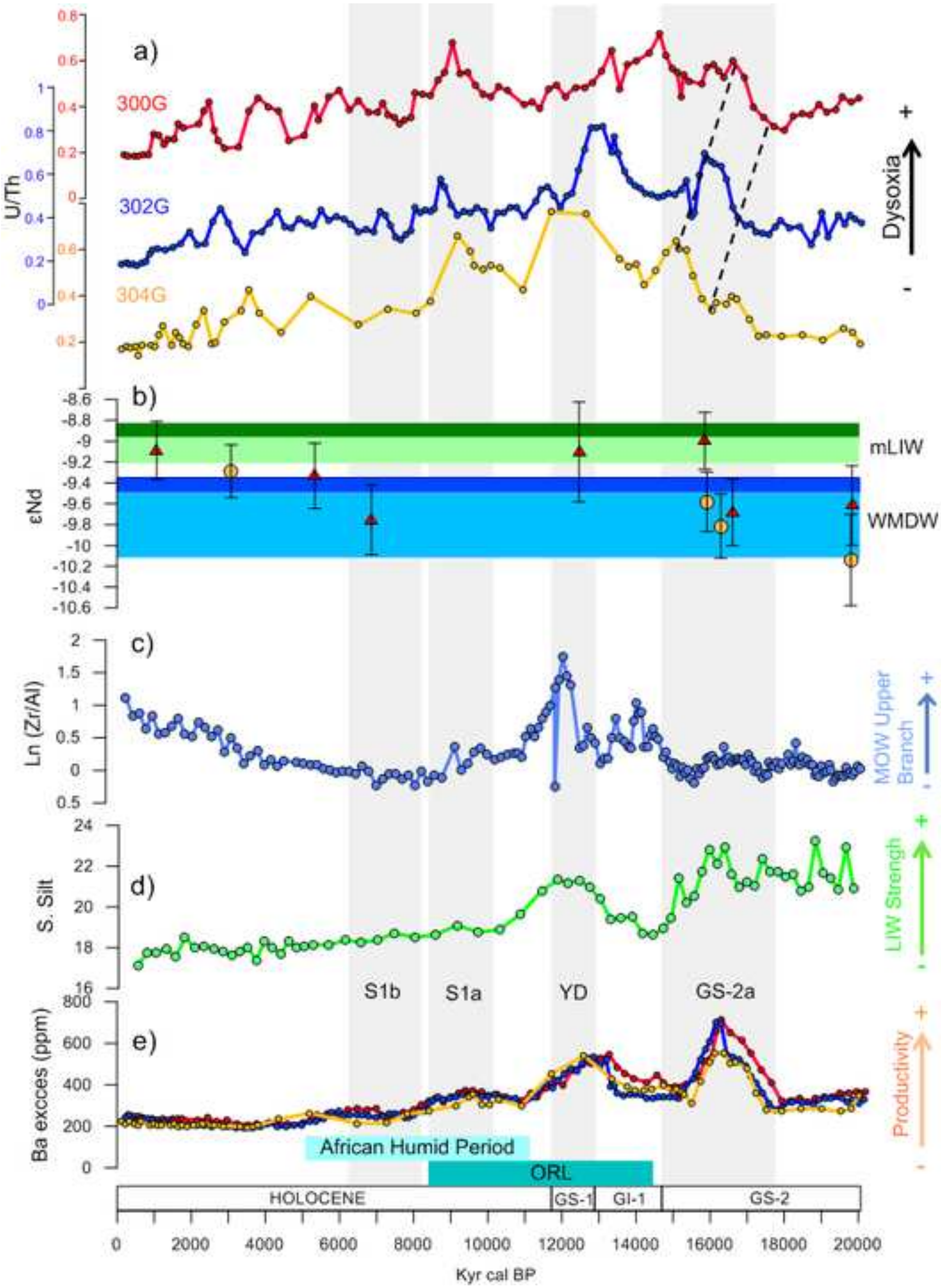

Data set Figure 3

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