Dissolved neodymium isotopes in the Mediterranean Sea

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Abstract

The neodymium isotopic composition (ε_{Nd}) of seawater is one of the most important geochemical tracers to investigate water mass provenance, which can also serve as a proxy to reconstruct past variations in ocean circulation. Nd isotopes have recently also been used to reconstruct past circulation changes in the Mediterranean Sea on different time scales. However, the modern seawater ε_{Nd} dataset for the Mediterranean Sea, which these reconstructions are based on, is limited and up to now only 160 isotopic measurements are available for the entire basin. The lack of present-day data also limits our understanding of the processes controlling the Nd cycle and Nd isotopic distribution in this semi-enclosed basin. Here we present new ε_{Nd} data from 24 depth profiles covering all Mediterranean sub-basins, which significantly increases the available dataset in the Mediterranean Sea. The main goal of our study is to better characterize the relationship between the dissolved Nd isotope distributions and major water masses in the Mediterranean Sea and to investigate the impact and relative importance of local non-conservative modifications, which include input of riverine particles and waters, aeolian-derived material and exchange with the sediments at continental margins. This comprehensive ε_{Nd} data set reveals a clear ε_{Nd} – salinity correlation and a zonal and depth gradient with ε_{Nd} systematically increasing from the western to the eastern Mediterranean basin (average ε_{Nd} = -8.8±0.8 and -6.7±1 for the entire water column, respectively), reflecting the large-scale basin circulation. We have evaluated the conservative ε_{Nd} behaviour in the Mediterranean Sea and quantified the non-conservative components of the ε_{Nd} signatures by applying an Optimum Multiparameter (OMP) analysis and results from the Parametric Optimum Multiparameter (POMP) analysis of Jullion et al. (2017). The results of the present study combined with previously published Nd isotope values indicate that dissolved ε_{Nd} behaves overall conservatively in the open Mediterranean Sea and show that its water masses are clearly distinguishable by their Nd isotope signature. However, misfits between measured and OMP- and POMP-derived ε_{Nd} values exist in almost all sub-basins, especially in the eastern Levantine Basin and Alboran Sea at intermediate-deep depths, which can be explained by the influence of detrital lithogenic ε_{Nd} signatures through interaction with highly radiogenic Nile sourced volcanic fractions and unradiogenic sediments, respectively.

The radiogenic signature acquired in the eastern Levantine Basin is carried by the Levantine Intermediate Water and transferred conservatively to the entire Mediterranean at intermediate depths. Our measured ε_{Nd} values and OMP- and POMP-derived results indicate that non-conservative contributions originating from sediment sources are then propagated by water mass circulation (with distinct preformed ε_{Nd}) along the Mediterranean Sea through advection and conservative mixing. Mediterranean ε_{Nd} effectively traces the mixing between the different water masses in this semi-enclosed basin and is a suitable water mass tracer.

Keywords: neodymium isotopes, seawater, Mediterranean Sea

1. Introduction

The Mediterranean Sea is a semi-enclosed and highly evaporative basin that is connected with the Atlantic Ocean through the Strait of Gibraltar (sill depth ~ 300 m) and with the Black Sea through the Strait of Dardanelles (sill depth ~100 m) and the Bosphorus Strait (sill depth ~65 m). The Atlantic water that enters the Mediterranean Sea spreads throughout the entire basin and participates in the formation of intermediate and deep waters that contribute to the Mediterranean thermohaline circulation (Millot and Taupier-Letage, 2005). This vigorous basin-wide overturning cell is characterized by a rapid mixing time of 75 to 150 years (Roether et al., 1996; Roether and Well, 2001) and is mainly driven by internal advection of salt and heat, freshwater exchange, deep convection and the external atmospheric forcing (Schroeder et al., 2012; Tanhua et al., 2013). The Mediterranean thermohaline circulation exhibits large seasonal and interannual variations and its variability in the past has been linked to major environmental changes that strongly modified the deep hydrology and heavily affected the marine ecosystems of the Mediterranean basin, which includes episodes of deep-sea oxygen starvation that led to the deposition of sapropels (Rohling et al., 2015). The reconstruction of past variations in ocean circulation requires fingerprinting the different water masses to track their origin and determine their relative exchange through time. One of the most useful tracers to investigate water mass provenance is the dissolved neodymium (Nd) isotopic composition of seawater (expressed as $\varepsilon_{Nd} = ([(^{143}Nd/^{144}Nd)_{sample}/(^{143}Nd/^{144}Nd)_{CHUR}]-1)*10^4$, where CHUR stands for Chondritic Uniform Reservoir, an estimate of the average value of the Earth), which is considered a direct water mass tracer as it "fingerprints" the different water masses as isotopically distinct entities and its changes in the open ocean are mainly attributed to water mass mixing (e.g. Piepgras et al., 1979; Albarede and Goldstein, 1992; Tachikawa et al., 2017).

The seawater ε_{Nd} signature is preserved in several natural archives, including Fe-Mn crusts (Frank et al., 2002), to (e.g. Rutberg et al., 2000), foraminifera (e.g. Klevenz et al., 2008; Vance and Burton, 1999), cold-water corals (Copard et al., 2010; van de Flierdt et al., 2010; Montagna and Taviani, 2019) and fish teeth (Martin and Haley, 2000) and it has been widely employed in paleoceanographic studies (Frank, 2002). This powerful tracer has also been used to reconstruct past circulation changes in the Mediterranean Sea on different time scales (Osborne et al., 2010; Jiménez-Espejo et al., 2015; Dubois-Dauphin et al., 2016, 2017a; Cornuault et al., 2018; Wu et al., 2019; Duhamel et al., 2020).

The seawater ε_{Nd} signature originates from the continental Nd supply through weathering of surrounding source rocks of different ages (Goldstein and Hemming, 2003) and mainly reflects lateral water mass advection and mixing. However, the use of ε_{Nd} as a water mass tracer is challenged by non-conservative modifications that can impact its "quasi-conservative" behaviour, which includes input of riverine particles and waters, aeolian-derived material, benthic fluxes of Nd, submarine groundwater discharge and exchange with the sediments at continental margins (e.g. Frank, 2002; Goldstein and Hemming, 2003; Lacan and Jeandel, 2005; Johannesson and Burdige, 2007; Abbott et al., 2015; Morrison et al., 2019). This has been observed in several regions of the global ocean, especially close to the continental margins, where seawater ε_{Nd} does not co-vary with other conservative hydrographic parameters, such as salinity and temperature (e.g. Grenier et al., 2013;

Stichel et al., 2015). The exchange between seawater and the sediments deposited on the continental margins has been termed “boundary exchange” (BE) and results in a modification of seawater ε_{Nd} without a net change in Nd concentration [Nd] (Lacan and Jeandel, 2005; Arsouze et al., 2007), although recent studies have shown that sediment-water interactions can affect [Nd] (Abbott, 2019). Local overprints from different Nd sources may strongly limit the use of ε_{Nd} as a conservative tracer for oceanographic and paleoceanographic studies but can also provide additional information on modern and past changes in ocean circulation. This can be especially the case in marginal and semi-enclosed basins, such as the Mediterranean Sea, where the local influence of different Nd sources may strongly modify the original ε_{Nd} signature of the water masses. Previous studies on the Nd budget of the Mediterranean Sea have documented higher Nd concentrations and more radiogenic ε_{Nd} values in most of the basin than in the surface Atlantic water entering through the Strait of Gibraltar, which reflects sources of radiogenic Nd within the basin (Spivack and Wasserburg, 1988; Henry et al., 1994; Tachikawa et al., 2004; Garcia-Solsona and Jeandel, 2020). In particular, the Atlantic Inflow shows [Nd] < 20 pmol/kg and ε_{Nd} < -10, whereas the Mediterranean seawater has [Nd] > 20 pmol/kg and ε_{Nd} values generally > -10.5, with the eastern basin showing a more radiogenic signature (i.e. higher ε_{Nd} values) compared to the western basin (~ -9 vs. -7) (Censi et al., 2004; Tachikawa et al., 2004; Garcia-Solsona and Jeandel, 2020). Results based on a high-resolution regional oceanic model also indicate a strong E-W ε_{Nd} gradient and the importance of the BE process in controlling the Nd cycle in the Mediterranean Sea (Ayache et al., 2016). However, our knowledge on the present-day seawater ε_{Nd} distribution in the Mediterranean Sea is still fragmentary with only about 160 ε_{Nd} measurements available for the entire basin. This strongly limits our understanding of the processes and sources that control seawater Nd cycling in the Mediterranean and restricts the interpretation of ε_{Nd}-based paleoceanographic reconstructions in this and other semi-enclosed basins.

Here we present dissolved ε_{Nd} compositions of 80 new seawater samples that were recovered at 24 stations covering different Mediterranean sub-basins, which significantly increases the available data set in the Mediterranean Sea. Combined with published ε_{Nd} values the data support that dissolved ε_{Nd} behaves overall conservatively in the open Mediterranean Sea and shows that most of the surface and sub-surface water masses can be depicted based on their Nd isotopic composition. A mixing analysis of the water masses has been performed to assess the degree of conservativeness of dissolved ε_{Nd} when used as a water mass tracer. This comprehensive ε_{Nd} database helps to identify the most relevant mechanisms and external sources driving the Nd isotopic composition of the different Mediterranean water masses including water mass mixing and advection, riverine fluxes, atmospheric deposition and water-sediment exchange along the continental margins in the different sub-basins.

2. General hydrography of the Mediterranean Sea

The Mediterranean Sea is characterized by two main basins, the western (WMED) and eastern (EMED) Mediterranean, which are separated by the Sicily Channel (sill depth ~500 m). Since evaporation exceeds precipitation and river runoff, the relatively fresh (salinity ~ 36.5) surface Atlantic Water (AW) entering the Mediterranean Sea across the Strait of Gibraltar at the surface becomes progressively saltier and denser during eastward advection, reaching values of 39.2 in the Cretan Sea (Velaoras et al., 2015). AW salinity also increases by mixing with the surrounding surface and underlying intermediate waters, leading to the gradual modification of this water mass, while it flows along the basin at 50-200 m water depth following a general cyclonic path including several eddies and meanders (Pinardi and Masetti, 2000). Evaporation and mixing together with intense cooling and strong wind-induced heat loss in specific areas in winter (Gulf of Lion, Adriatic Sea, Levantine and Aegean Seas) result in denser waters that sink via convection and form the intermediate and deep waters in the Mediterranean Sea (Pinardi and Masetti, 2000; Schroeder et al., 2012). In particular, the Levantine Intermediate Water (LIW) is formed by intermediate convection in the Cyprus-Rhodes area and it spreads in the EMED and WMED at intermediate depths (~ 200-600 m) (Fig. 1). LIW is the most abundant water mass in the Mediterranean Sea and is identifiable by its subsurface salinity maximum (Lascaratos et al., 1993). It flows westwards generally following a basin scale cyclonic circulation pattern and enters the Adriatic Sea through the Strait of Otranto and the WMED through the Sicily Channel at depths between 200 and 350 m (Ben Ismail et al., 2012). Based on transient tracer data and salinity anomalies, the transport time of LIW from the formation area to the Sicily Channel has been estimated to be between 8 and 13 years (Roether et al., 1998; Gačić et al., 2013). In the Adriatic Sea, LIW is involved in the formation of the Adriatic Deep Water (AdDW) that sinks to the deep EMED and together with the Aegean Deep Water (AeDW) contributes to the formation of the Eastern Mediterranean Deep Water (EMDW). After entering the WMED, the LIW, or the Eastern Intermediate Water as named by Millot (2013), breaks into current segments that flow across the Corsica Strait and the Algeria basin through the Sardinia Channel (Pinardi et al., 2015; Fig. 1). During advection in the WMED, LIW is gradually diluted with adjacent water masses thereby becoming less salty and colder (Schroeder et al., 2012). In the Tyrrhenian Sea, the depth of the core of LIW is observed between 350 and 550 m water depth (Wu and Haines, 1996) whereas in the

Sardinia Channel it is identified between 250 and 450 m depth (Gana et al., 2015). A fraction of the LIW then flows into the Ligurian Sea and the Provençal basin and its salt content contributes to the Western Mediterranean Deep Water (WMDW) formation in the Gulf of Lion during extreme meteorological conditions in winter (Millot and Taupier-Letage, 2005). Most of the LIW finally exits the Mediterranean through the Strait of Gibraltar as part of the Mediterranean Outflow Water (MOW). The WMDW spreads southward and westward into the Balearic basin and the Tyrrhenian Sea between ~ 2000 and 3000 m depth (Millot, 1999; Schroeder et al. 2012; Fig. 1) and also contributes to MOW (Bryden, 2009). The depth range between ~ 700 and 2000 m in the WMDW is filled by the Tyrrhenian Deep Water (TDW) (Millot et al., 2006), which results from the mixing between WMDW, LIW and the upper part of the EMDW (Sparnocchia et al., 1999). In the WMED, the depth layer between the AW and LIW (i.e. ~ 85-200 m) is occupied by the Winter Intermediate Water (WIW), which is formed by intense cooling and downward mixing of AW (Millot, 1999).

3. Materials and methods

3.1. Seawater sampling

Seawater samples were collected during the oceanographic cruises Medcor (December 2009), Arcadia (March-April 2010) and Record (November 2013) on the R/V *Urania*, Meteor 84/3 (April 2011) on the R/V *Meteor* and MedBlack GEOTRACES 64PE370 (May-June 2013) and 64PE374 (July-August 2013) on the R/V *Pelagia* (Fig. 1, Table 1). A total of 80 samples were recovered from 24 stations covering all Mediterranean sub-basins using either an ultraclean all-titanium frame CTD rosette system (cruises GEOTRACES 64PE370 and 64PE374; Rijkenberg et al., 2015) or a CTD rosette system equipped with 24 12L Niskin bottles. Four samples (Meteor 309-799m, 64PE374-17-25m, 64PE374-17-1500m and 64PE374-17-2824m) were collected in duplicate to check intra and inter-laboratory analytical reproducibility. At each station, continuous temperature and salinity were obtained from a CTD system SBE19 Sea-Bird Electronics (Table 1). Seawater samples were also collected for dissolved inorganic nutrient measurements. The analytical methods for nutrient determination and results for phosphate and nitrate concentration are reported in Tanhua et al. (2013b) and Tanhua (2013) for Meteor 84/3 cruise, Cruise reports 64PE370 (http://geotraces.imev-mer.fr/library-88/scientific-publications/cruise-reports/823-ga04) and 64PE374 (http://geotraces.imev-mer.fr/library-88/scientific-publications/cruise-reports/857-ga04-3) for MedBlack GEOTRACES cruise. The samples collected during the cruises Medcor, Arcadia and Record were syringe-filtered through Whatmann® GF/F and cellulose acetate Albet® filters (0.45 µm), and immediately frozen at -20°C. The concentrations of nitrite, nitrate and phosphate were determined by colorimetric methods using a Bran-Luebbe® autoanalyzer III at the Institute of Marine

Sciences (ICM-CSIC) in Barcelona. For the calibration, standards were run along with the samples after every set of 20 samples.

All seawater samples for Nd isotopes were filtered on board using AcroPak 500 (0.8–0.45μm) capsule filters connected to the spigot of the Niskin bottles through a Tygon tubing into acid-cleaned 5-liter and 20-liter LDPE-collapsible cubitainers. The filters had previously been cleaned with 1N ultra-clean HCl, rinsed with MilliQ water and flushed with seawater prior to sample collection. The same capsule filters were repeatedly used for similar depth ranges (i.e. surface, intermediate and deep). Upon recovery, all the samples from cruises Medcor, Arcadia, Record and Meteor 84/3 were immediately acidified to $pH \leq 2$ with ultra-clean HCl and mixed with ca. 20 mg of ultra-pure $FeCl_3$ solution for pre-concentration of REEs. After one day of equilibration the samples were treated with NH_4OH (Optima grade) to induce $Fe(OH)_3$ precipitation by adjusting the pH between 7.5 and 8.5. After precipitation of the Fe and the REEs, the supernatant was siphoned off and the cubitainers were sealed with Parafilm® and stored in double plastic bags for further processing in the home laboratories. Samples from cruise 64PE370 and 64PE374 were treated similarly but the entire procedure was conducted in the home laboratory. Seawater sampling followed established protocols for GEOTRACES cruises (Cutter et al., 2010).

3.2 Laboratory procedures

The cubitainers containing the Fe-REEs co-precipitated fraction were transferred to the Lamont-Doherty Earth Observatory (LDEO) of Columbia University (samples from cruises Medcor and Arcadia) and to the Laboratoire GEOsciences Paris-Sud (GEOPS), University of Paris-Saclay (samples from cruises Record and Meteor 84/3, and 17 samples from cruise 64PE374), whereas samples from cruise 64PE370 (and eleven samples from cruise 64PE374) were sent to GEOMAR Helmholtz Centre for Ocean Research in Kiel.

At LDEO, the samples were transferred to 250 mL acid-cleaned containers, centrifuged and dissolved in 3N HNO_3. The solutions were then transferred to Teflon beakers, dried down at ~ 120°C and re-dissolved in ultra-clean 1N HNO_3 before loading the samples into 100 μL columns containing Eichrom RE-resin to separate the rare earth elements (REEs) from the major and trace elements. Nd was subsequently isolated from the other REEs using 0.15M α-HIBA acid and a cation resin (Dowex AG50-X4, 100-200 mesh size). The Nd isotopes were analyzed as Nd-oxide on a VG Sector 54-30 thermal ionization mass spectrometer by dynamic multicollection in June 2010. The samples were analysed at $^{144}Nd^{16}O$ signal intensities between 160 and 360 mV for 250-300 ratios using 10^{11} ohm resistors on the amplifiers. The instrumental mass fractionation was corrected using a $^{146}Nd/^{144}Nd$ value of 0.7219. The external error, calculated as the standard deviation (2σ) of replicates of the international standard JNdi-1 performed during a 3-days analytical session, was ±0.000017 (average $^{143}Nd/^{144}Nd$ = 0.512076, n=9). The $^{143}Nd/^{144}Nd$ ratio for all the samples was corrected for instrumental bias to a JNdi-1 value of 0.512115 (Tanaka et al., 2000) and εNd was calculated using a $^{143}Nd/^{144}Nd$ CHUR value of 0.512638 (Jacobsen and Wasserburg, 1980). Three procedural blanks were analysed during the processing of the Medcor and Arcadia samples, with Nd concentration ranging between 40 and 70 pg, which represents <2 % of the typical concentration of the Mediterranean seawater samples (Tachikawa et al., 2004).

At GEOPS, the samples were transferred to 50 mL acid-cleaned Falcon tube, centrifuged, dissolved in 3N HNO_3 and transferred into Teflon beakers. After total evaporation, the samples were re-dissolved in 6N HCl and solutions were loaded onto anion exchange columns to remove Fe (AG1-X8 resin, 100-200 μm mesh-size resin). REEs were separated from the matrix using Eichrom TRU-spec resin (100-150 μm mesh-size) and finally Nd was purified using Eichrom Ln-spec resin (100-150 μm mesh-size), following the procedure reported in Copard et al. (2010). The Nd isotopes of the purified fractions were measured on a Thermo Scientific Neptune^{Plus} Multi-Collector Inductively Coupled Plasma Mass Spectrometer (MC-ICP-MS) at the Laboratoire des Sciences du Climat et de l'Environnement (LSCE) in Gif-sur-Yvette. For the Nd isotope analyses, sample and standard concentrations were matched at 5 ppb. The $^{143}Nd/^{144}Nd$ ratios were corrected for mass-dependent fractionation using a $^{146}Nd/^{144}Nd$ = 0.7219 (O'Nions et al., 1977) and an exponential law. The La Jolla standard was analysed after every two samples (sample-standard bracketing method). Multiple measurements of La Jolla standard during the analytical sessions yielded average $^{143}Nd/^{144}Nd$ values of 0.511844 ± 0.000025 (2σ, n = 14). The $^{143}Nd/^{144}Nd$ ratio of all the samples were normalized to the generally accepted La Jolla value of 0.511858 (Lugmair et al., 1983). The internal reproducibility ranged from 0.2 and 0.5 εNd units (2σ) and the external reproducibility was 0.5 εNd units (2σ). Procedural blanks corresponding to all analytical procedures after preconcentration of Nd from seawater matrix were < 25 pg, which represents < 1% of the typical concentration of the Mediterranean seawater samples (Tachikawa et al., 2004)

At GEOMAR, the Fe-REEs co-precipitated fraction were centrifuged, rinsed with MilliQ water and transferred into Teflon beakers. The samples were dissolved in 6N HCl and dried down at 80°C. Afterwards, the samples were treated with aqua regia to destroy organic components, evaporated to dryness and dissolved in 6N HCl. A back extraction method using a diethyl ether phase was applied (Stichel et al., 2012) to remove the large amounts of Fe while keeping Nd dissolved in the acid phase. Finally, the samples were evaporated again and dissolved in 1N HCl and 0.05N HF. Solutions were loaded onto cation exchange columns (AG50W-X8, 200-400 μm mesh-size resin) to separate Nd from the main matrix. Nd was finally separated from Sm and the other REEs using Eichrom Ln-spec resin (50-100 μm mesh-size), following a slightly modified procedure by Pin and Santos Zalduegui (1997). The Nd isotopes of the purified fractions were analyzed on a Thermo Scientific Neptune^{Plus} MC-ICP-MS matching concentrations of the analysed solutions and standards. The mass fractionation correction for the measured Nd isotopic compositions was carried out using a ^{146}Nd/^{144}Nd to 0.7219 (O'Nions et al., 1977) and applying an exponential fractionation law. The external reproducibility of ^{143}Nd/^{144}Nd measurements was estimated by repeated measurements of JNdi-1 standards (10, 20 and 40 ppb) over the course of a measuring session and varied between 0.18 and 0.83 ε_{Nd} (2σ). JNdi-1 solutions were measured at similar concentration and over a similar integration time as the samples. The ^{143}Nd/^{144}Nd ratios of the samples were normalized to the accepted JNdi-1 value of 0.512115 (Tanaka et al., 2000). Procedural blanks for Nd isotopes were less than 1% of the sample amounts and were considered negligible.

The three laboratories (LDEO, GEOPS and GEOMAR) participated in the international GEOTRACES intercalibration study for Nd isotopes and procedures followed the agreed protocols (van de Flierdt et al., 2012).

REE concentrations have been analysed only on a subset of the samples, since most of them had been entirely consumed for the ε_{Nd} analyses. In particular, aliquots of seawater samples were collected for REE analyses of 18 samples of the Record, Meteor 84/3 and GEOTRACES 64PE370 cruises (Table 1). The Record and Meteor 84/3 samples were processed at GEOPS following the method by Yu et al. (2017). Briefly, an ultra-pure $FeCl_3$ solution and a spike solution enriched in ^{141}Pr and ^{169}Tm were added to each sample (∼125 ml filtered seawater), with contents around 10-50 fold higher than REE concentration in the samples. After 48h of equilibration, the pH was adjusted to ~8 through the addition of ultraclean NH_4OH (Optima grade), leading to the formation of iron hydroxides, which in turn, efficiently scavenge REEs out of the seawater samples. The REE co-precipitated fractions were separated from the remaining solution through several centrifugations and MilliQ water rinsing, re-dissolved in ultra-clean 3N HNO_3 and evaporated to dryness. The dried samples were re-dissolved in 2 ml ultra-clean 8N HNO_3 and 50 μl HF to remove any possible hydrated silica residues precipitated during the Fe co-precipitation step. After drying, REEs were separated from the matrix through anion exchange columns (AG1-X8 resin, mesh 100-200). The solutions were analysed using a Thermo Scientific Element XR High-Resolution ICP-MS hosted at GEOPS. The added ^{141}Pr and ^{169}Tm spikes allowed the calculation of the REE extraction step recovery (~ 70-100%) and finally REE concentrations by taking into account the initial Pr and Tm content in the samples. Internal REE and seawater standards and BCR-1 standard solutions were analysed to monitor instrument drift.

The GEOTRACES 64PE370 samples were analysed at GEOMAR following Stichel et al. (2012), which is in accordance with accepted GEOTRACES protocols outlined in van de Flierdt et al. (2012).

3.3 Optimum Multiparameter Analysis

An Optimum Multiparameter (OMP) analysis (Tomczak and Large, 1989; Hainbucher et al., 2013) has been applied to a subsample of the dataset shown in Table S1, to estimate the water mass fractions in each water sample. In particular, we used the temperature and salinity values collected during cruises since 2009 (e.g. Medcor in 2009, Arcadia in 2010, Meteor 84/3 in 2011, Record in 2013, MedBlack GEOTRACES 64PE370 and 64PE374 in 2013, Dubois-Dauphin et al., 2017, Garcia-Solsona and Jeandel, 2020 and Garcia-Solsona et al., 2020) to avoid as much as possible the temporal differences in temperature and salinity related to the climate-induced warming and salinification of the Mediterranean Sea. This analysis is based on the assumption that mixing is a linear process that affects temperature and salinity (as well as other seawater properties) in the same way. The analysis allows to estimate the contributions of (m) water types (WTs) to each water sample, by solving a system of (m+1) linear mixing equations, with one equation for each seawater property and a mass conservation equation. The best mixing solution is found by minimizing the residuals for all parameters and in a non-negative least squares sense.

In the present study, the Mediterranean has been divided into 2 sub-basins, the Eastern Mediterranean and the Western Mediterranean Sea, to minimize the effect of the substantial differences in water masses properties between the two basins. In each sub-basin three WTs were defined by the average values of θ and S (Table S2) extracted from the decadal climatology (2006-2015) by Iona et al. (2018). This approach has been chosen, given that the OMP will be applied to data collected during different cruises and covering different years. For the WMED, the Atlantic Water (AW) WT was defined in the Gibraltar-Alboran region (where the “pure” AW inflows), the Intermediate Water (IW) WT was defined in the Sicily Channel (where the inflow of IW into the WMED occurs), while the Deep Water (DW) WT was defined offshore the Gulf of Lion region (where the DW of the WMED starts spreading through the basin, after it has been formed by open ocean convection and cascading of dense shelf waters). For the EMED, the AW-WT has been defined in the Sicily Channel (where the inflow of AW into the EMED occurs), the IW-WT has been defined in the Levantine sub-basin (where the IW starts spreading through the EMED, after it has been formed by open ocean convection), and the DW-WT has been defined at the exit of the Adriatic Sea (where the DW starts spreading through the EMED, after it has been formed by open ocean convection and cascading of dense shelf waters).

The set of mixing equations to solve is A × X = N, where A is the (3 × 3) matrix with the WT properties, X is the (3 × n) matrix with the WT fractions, N is the (3 × n) matrix with the measured θ and S properties, n being the number of samples. The linear equations are normalized and weighted. The normalization is done using the mean and standard deviation values for the three parameters in the WT matrix. Equations are weighted, considering the standard deviation of each parameter in the WT matrix and its uncertainty when estimating it. Weights of 10, 10 and 50 were assigned to θ, S and mass, respectively. All samples are thus considered as composed by these three WTs, with percentages that vary horizontally and vertically. The approach of using the basic OMP with θ and S only has certain limitations in complex basins as the Mediterranean Sea as a whole, with intense and regionally varying ocean-atmosphere interactions. The fact that the samples have been collected during different cruises and over a certain number of years (during which T and S are known to have changed, not because of different mixing fractions, but because of climate-induced warming and salinification of the Mediterranean water masses, e.g. Schroeder et al., 2017) place further limitations on the use of the OMP analysis. Indeed, the inclusion of additional source water types would be required to increase the degree of accuracy of mixing ratios. Beside samples in the surface mixed layer, where the conservativeness assumption does not hold, samples with slight departures of the total fraction percentage associated to tracers values beyond the selected end-members in the θ-S space (e.g., the Levantine Surface Waters and the Cretan Intermediate Waters in the Aegean/Cretan Seas) and samples with questionable mixing ratios by expert judgment due to unresolved physical processes, were intentionally excluded *a priori* from the subsequent analysis.

The mixing fractions obtained from the OMP analysis (Table S1; Figs. S1 and S2) have been used to reconstruct the conservative part of the seawater neodymium isotopic composition reflecting the large scale mass distribution in the Mediterranean Sea. The ε_{Nd} and [Nd] of the WTs (Supplementary Table S2) used to calculate the conservative mixing were defined by identifying the ε_{Nd} and [Nd] values corresponding to the salinity and potential temperature definitions of the WTs. The non-conservative component of ε_{Nd} was separated by removing the conservative component from the observations.

We also decided to estimate the non-conservative component of ε_{Nd} from the water mass fractions derived from the Parametric Optimum Multiparameter (POMP) analysis of Jullion et al. (2017) based on conservative (potential temperature and salinity) and quasi-conservative ($NO = 9NO_3 + O_2$ and $PO = 170PO_4 + O_2$) variables, acquired during the M84/3 cruise (Tahnua et al., 2013b). Jullion et al. (2017) defined 4 WTs (or source waters) for both WMED and EMED and their θ-S-PO-NO properties were used as input parameters for the POMP model (Table S3). Similarly to the OMP analysis performed in the present study, the conservative ε_{Nd} was calculated using the POMP-derived mixing fractions and the ε_{Nd} and [Nd] of the WTs (Table S3).

4. Results

4.1 Spatial distribution of measured ε_{Nd} values

Results of the dissolved Nd isotopic composition and [Nd] of the seawater samples analysed in the present study are reported in Table 1 and Figures 2, 3 and 4. Table 1 also shows the main physico-chemical parameters (potential temperature, salinity, potential density, phosphate and nitrate concentrations) at the sampling locations. The figures and Table S1 combine the ε_{Nd} values obtained in the present study and sourced from previous publications (Dubois-Dauphin et al., 2017b; Garcia-Solsona et al., 2020; Garcia-Solsona and Jeandel, 2020; Henry et al., 1994; Spivack and Wasserburg, 1988; Tachikawa et al., 2004; Vance et al., 2004). Note that samples from station C (1270 m), MST-1 (1500 m) and MNT-1 (120 m) from Tachikawa et al. (2004) have been excluded due to contamination by lithogenic material, as reported by the authors.

Two full replicates of sample Meteor 309, collected with two different Niskin bottles at 799 m water depth in the Ionian Sea and analysed at GEOPS, gave identical ε_{Nd} values (Table 1). Inter-laboratory reproducibility was tested on samples 64PE374-17 (25 m), 64PE374-17 (1500 m) and 64PE374-17 (2824 m), which were collected in duplicate in the Balearic Sea and analysed at GEOPS and GEOMAR. Samples 64PE374-17 (25 m) and 64PE374-17 (1500 m) gave consistent ε_{Nd} values within analytical uncertainty, whereas ε_{Nd} value for sample 64PE374-17 (2824 m) analysed at GEOMAR (-7.78) was slightly higher than that obtained at GEOPS (-8.73). However, the two values overlap when the external error (2σ SD) is considered.

On the θ-S-ε_{Nd} diagram in Figure 2 the end-member compositions of the five main water masses prevailing in the WMED and EMED and their Nd isotope composition are defined: the relatively fresh, warm and unradiogenic AW prevailing at the surface, and the more saline and more radiogenic WIW, WMDW, LIW, and EMDW.

The ε_{Nd} values obtained in the present study range from -9.75±0.33 at 60 m water depth in the Sicily Channel (Medcor 20) to -5.21±0.21 at 150 m water depth in the southern Aegean Sea (64PE370-28), with the most and least radiogenic values generally corresponding to high and low salinity water masses, respectively (Table 1). The ε_{Nd} – salinity relationship is even more evident when combining our results with previously published values (Figures 2 and 3). All samples (except MNT-1 in the northern Aegean Sea at 20 m water depth and 64PE370-10 in the Algerian basin at 25 m water depth), with ε_{Nd} values more radiogenic than -7, are characterized by salinities higher than 38.7 (Figures 2 and 3). The values outside the salinity – ε_{Nd} mixing envelopes (n = 31, which represents 13% of the total number; Figure 3) mostly correspond to samples collected at depths shallower than 150 m (68%), with 39% of these samples occurring in the uppermost 50 m of the water column and 32% in depths below 150 m.

Overall, the data display a clear ε_{Nd} – salinity correlation and a zonal gradient with ε_{Nd} systematically increasing from the western to the eastern Mediterranean basin (average ε_{Nd} = -8.81±0.79 and -6.65±1.02 for the entire water column, respectively) (Figures 3, 4 and 5). In particular, ε_{Nd} values higher than -7 are only found in the EMED (with the exception of station 64PE370-10 in the Algerian basin at 25 m) and values higher than -6 only occur in the Levantine basin east of 25°E and in the Aegean Sea (Figure 3). This zonal gradient is particularly evident in the surface layer where AW prevails. The surface waters in the western, central and part of the eastern Mediterranean are characterized by unradiogenic ε_{Nd} values (between -10.8 to -7.8), whereas in the eastern Levantine basin and the Aegean Sea the values are more radiogenic (between -7.3 to -4.2) (Figures 5 and 6).

The neodymium isotopic composition of the Mediterranean waters generally becomes more radiogenic with depth and shows the highest values for intermediate waters, notably in the eastern basin. The observed W-E and depth gradient reflects the general circulation pattern of the Mediterranean Sea, with the fresh (salinity < 36.5) and unradiogenic (ε_{Nd} -11.8; Spivack and Wasserburg, 1988) AW entering across the Strait of Gibraltar, mixing along the basin with more saline and radiogenic surrounding surface and underlying intermediate waters and flowing and meandering eastward at 50-200 m water depth as AW (Figure 6). The surface salinity increases from ~ 36.5 in the Alboran Sea to ~ 39 in the eastern Levantine basin (Figures 2, 3 and 5). In the Cyprus-Rhodes area the surface water sinks via intermediate convection and forms LIW that is characterized by a salinity of 39.19 and a potential temperature of 16.39°C, resulting in a density of 28.9 kg/m^3 and ε_{Nd} signature of -6.40±0.50 at 250 m water depth at station Meteor-294 (Table 1). LIW spreads throughout the Mediterranean Sea as an alongslope current circulating counterclockwise and it is involved in the formation of the Aegean Deep Water (AeDW), Adriatic Deep Water AdDW and Western Mediterranean Deep Water (WMDW) (Figures 1 and 6). LIW advection is very rapid and the transport time from the formation area to the Sicily Channel is on the order of 8-13 years (Gačić et al., 2013; Roether et al., 1998). The ε_{Nd} signature of LIW varies from -4.8±0.2 in the eastern Levantine basin at 227 m depth (station 74 from Tachikawa et al., 2004) to -8.94±0.26 in the western basin at 250 m water depth (station 20 from Garcia-Solsona and Jeandel, 2020). This shows that the tongue of radiogenic LIW is progressively diluted westwards but reaches the Alboran Sea and is part of the Mediterranean Outflow at the Strait of Gibraltar. The ε_{Nd} distribution along the W-E section matches very well the salinity pattern and closely follows the isohalines (Figure 5). However, in the eastern Levantine basin, the water masses generally display highly radiogenic values (> -6.5) that are associated with relatively low salinity (< 39) (Figures 3 and 5), hence not matching the isohalines in this region. Similarly, the highly unradiogenic values between 800 and 1000 m (< -8.9) in the Alboran Sea also do not follow the isohalines.

The W-E sections of potential temperature, salinity and ε_{Nd} (Figure 5) show the tongue of Adriatic Deep Water (AdDW) that is advected south in the deep Ionian Sea below ~ 2500 m water depth and becomes a major component of the EMDW (stations Meteor-306 and Meteor-307; stations 1 and 2 from Garcia-Solsona et al., 2020). These stations are located in the path of AdDW that brings colder, less salty, better ventilated, and less radiogenic water into the deep eastern Mediterranean Sea.

Overall, the ε_{Nd} values for the different Mediterranean sub-basins, except the Aegean Sea, gradually become more radiogenic from the surface to intermediate and deep waters (Figures 4, 5 and 6).

The mean ε_{Nd} values of the water masses flowing in the different Mediterranean sub-basins are reported in Table 2. The surface water masses prevailing in the Alboran Sea above 110 m water depth shows the least radiogenic values (-9.95±0.71), whereas the most radiogenic values are found in the surface (< 50 m) and intermediate (160-500 m) waters of the easternmost Levantine basin (-5.27±0.96 and -5.58±0.66, respectively). The largest depth gradient of more than 2 ε_{Nd} units difference between the surface water (60-75 m) and the intermediate (300-647 m) and deep (1020-1692 m) waters is observed in the Sicily Channel (stations Medcor 20 and 37; station 3 from Garcia-Solsona et al., 2020). The smallest depth gradient occurs in the southern Adriatic Sea where the difference between the ε_{Nd} values for the surface, intermediate and deep waters is within the analytical uncertainty (station Arcadia 50).

The property-property plots of ε_{Nd} vs. salinity, potential temperature and dissolved phosphate concentration at water depth above 200 m, between 200 and 500 m (LIW), between 500 and 2000 m and below 2000 m are shown in figure 7. The Nd isotope compositions of the water masses above

200 m show significant correlation only with salinity ($R^2 = 0.46$), whereas the ε_{Nd} values of the water masses below 200 m display highly significant linear correlations with salinity, potential temperature and dissolved phosphate concentration (Figure 7), which reflects mixing of water masses with distinct ε_{Nd} values. However, despite the high correlations, the deviations from conservative mixing are large, with values up to 2 ε_{Nd} units, which is consistent with previous studies (Lacan and Jeandel, 2005; Abbott et al., 2015; Du et al., 2016). The three oceanographic parameters show a continuous change along a W-E gradient, with the salinity and potential temperature increasing towards the eastern basin and phosphate concentration decreasing along the gradient. This is consistent with the presence of saltier, warmer and more oligotrophic waters in the EMED than in the WMED (Tanhua et al., 2013a) and their mixing.

One seawater sample was collected at 3552 m depth at station Meteor-301 in the deep hypersaline brine of the Urania basin (west of the Crete Island). This sample shows a less radiogenic Nd isotopic signature (ε_{Nd} = -8.40) than the other deep samples in the eastern basin (~ -7; Figure 6), likely reflecting the admixture of the brine that originates from the dissolution of Messinian evaporites (e.g. Cita, 2006).

The Nd concentrations of the seawater samples analysed in the present study range from 18.96 and 33.73 pmol/kg (Table 1 and S4), which are consistent with values reported in the literature for the Mediterranean Sea (Henry et al., 1994; Spivack and Wasserburg, 1998; Censi et al., 2004; Tachikawa et al., 2004; Vance et al., 2004; Garcia-Solana and Jeandel, 2020; Garcia-Solsona et al., 2020). In particular, the [Nd] values obtained from the station Record 10 in the Sicily Channel are very similar to those reported by Garcia-Solsona et al. (2020) for station 3, with a maximum difference of 1.5 pmol/kg at ~ 70 m water depth (Table S1). In addition, the relatively high [Nd] values obtained from sample Meteor-294 at 254 m in the Levantine basin (33.73 pmol/kg) and Meteor-288 at 27 m in the Aegean Sea (32.00 pmol/kg) are similar, within error, to those reported in Tachikawa et al. (2004) for the stations 74 at 202-252 m (33.6 pmol/kg) and MST-1 at 10 m (34.7 pmol/kg).

The shale (PAAS)-normalized REE patterns of all the samples are typical of seawater, showing a distinct negative Ce anomaly and an enrichment of heavy REE (HREE) over light REE (LREE) (Figure S3), which is indicative of preferential LREE scavenging by marine particles (e.g. Elderfield, 1988). All samples display a very similar pattern shape, however samples Meteor-288 (25 m) and Meteor-294 (254 m) have higher LREE and HREE concentrations, and Meteor-309 (5 m) and Record 28 (25 m) show higher LREE concentrations compared to the other samples. The four samples are also characterized by a less pronounced cerium anomaly, with values between 0.49 and 0.52, which is likely indicative of lithogenic input.

4.2 OMP- and POMP-derived ε_{Nd} values

Figures S1 and S2 show the overall results of the OMP analysis, with the vertical sections of the mixing fractions of the three WTs in each sub-region. The mixing analysis was characterized by small mass residuals (<3%) in the intermediate and deep layer. Fractions of AW as high as 60-70% were calculated for the western and eastern Mediterranean basins at shallower depths. The AW signal is progressively diluted going from the west to the east in both basins, in agreement with the eastward propagation of the Atlantic-sourced water mass from the Strait of Gibraltar to the Levantine basin. Intermediate water values up to 100% and 70-90% were calculated for depths of 254 m in the Levantine basin (Meteor-294) and 200-500 m in the Ionian Sea (Station 2 from Garcia-Solsona et al., 2020), respectively (Figure S2). In the WMED, IW values up to 90% were obtained at 200-700 m in the south and central Tyrrhenian Sea (stations 4, 5, 7, 8 and 9 from Garcia-Solsona et al., 2020; 64PE374-13). The DW fractions in the Balearic and Algerian basin below ca. 1000 m and in the Tyrrhenian Sea below ca. 2000 m are higher than 90%. DW values as high as 80% were calculated in the Gulf of Lion below 500 m (Station 20 from Garcia-Solsona and Jeandel, 2020), which is the site where the DW end-member has been defined for the WMED. Finally, DW fractions higher than 70% were calculated for the EMED at depths below 500-700 m and higher than 95% in the Ionian Sea at depths below 2500 m.

Overall, the OMP-derived fractions for AW, IW and DW correspond to the large-scale circulation pattern of the western and eastern Mediterranean Sea (Figure 1), although there are some inconsistencies, such as the high DW fraction values (> 50%) at relatively shallow depths (100-300 m), that are likely the result of the OMP limitations in complex basins such as the Mediterranean Sea and the fact that samples have been collected during different cruises and over a number of years. The inclusion of additional source water type end-members would likely increase the degree of accuracy of mixing ratios.

Figures 8 and 9 show the measured vs. OMP-derived (predicted) ε_{Nd} values for the WMED and EMED, respectively. The mean difference is very close to zero for both basins and residual values show a Gaussian type distribution, with the largest differences being 1.5-2 ε_{Nd} (inset in figures 8 and 9). About 75% and 55% of the OMP-derived ε_{Nd} values of the WMED and EMED fall inside the band formed by the 1:1 slope ± 0.5 epsilon units. The size of the band is based on the maximum 2σ external reproducibility of the $^{143}Nd/^{144}Nd$ measurements at GEOPS. However, if we consider the highest 2σ uncertainty from GEOMAR (i.e. 0.83 ε_{Nd}), the percentage of values increases to 88% and 77% for WMED and EMED, respectively. Both basins show positive and negative anomalies (Figures 8 and 9). In particular, 7 samples from the Balearic Sea (64PE374-17; Stations 20 and 22 from Garcia-Solsona and Jeandel, 2020), 1 from the Alboran Sea (Station BR-I from Dubois-Dauphin et al. 2017b), 4 from the Ionian Sea (Meteor-309) and the Aegean Sea (64PE370-28 and 64PE370-31) and 1 sample from the Levantine basin (Meteor-294) have a more radiogenic ε_{Nd} signature than expected from the OMP analysis. Conversely, 6 samples from the Tyrrhenian Sea (Stations 7 and 8 from Garcia-Solsona et al., 2020; 64PE374-13 and 64PE374-15), 2 from the Alboran Sea (Stations BR-I and OMS from Dubois-Dauphin et al. 2017b), 2 from the Balearic Sea (Station 22 from Garcia-Solsona and Jeandel, 2020; 64PE374-17), 2 from the Sicily Channel (Medcor 37), 5 from the Ionian Sea (Stations 1 and 2 from Garcia-Solsona et al., 2020) and 1 sample from the Adriatic Sea (64PE374-8) have lower ε_{Nd} values than predicted (Figures 8 and 9).

Figure 5 shows the comparison between the measured and the POMP-derived ε_{Nd} values along a W-E transect from the Strait of Gibraltar to the Levantine Basin. Overall, the two longitudinal sections show comparable values for the different sub-basins, which suggests a strong control of the water mass mixing over the large-scale Mediterranean seawater Nd isotopic composition. The differences between measured and calculated values are mostly within 1 ε_{Nd} unit, with the notable exception of the easternmost Levantine Basin and the Alboran Sea, where differences up to 2 units are observed, suggesting local and regional deviations from conservative behaviour. The radiogenic signature of the LIW flowing to the western Mediterranean is clearly visible also in the POMP-derived section, and it seems to propagate more westward in the Alboran Sea compared to the measured values.

5. Discussion

The present study reports a comprehensive compilation of the dissolved Nd isotopic composition of Mediterranean seawater, based on which a detailed assessment of the factors controlling its distribution is now possible for the entire Mediterranean basin.

The ε_{Nd} signature closely correlate with both conservative (i.e. salinity and potential temperature) and non-conservative (i.e. nutrients) tracers of water masses at depths > 200 m in the Mediterranean Sea, as already reported for other ocean basins (e.g. Goldstein and Hemming, 2003; Hu et al., 2016;

Piotrowski et al., 2008; Dubois-Dauphin et al., 2017b; Tachikawa et al., 2017). This is indicative of water mass mixing along a longitudinal gradient between saltier, warmer and oligotrophic intermediate-deep waters originating from the eastern basin with relatively colder, less saline and nutrient-rich intermediate-deep waters from the western basin, which are characterized by distinct ε_{Nd} values. The correlation between ε_{Nd} and the water mass properties is significantly weaker for seawater samples shallower than 200 m. In fact, 68% of the values outside the salinity-ε_{Nd} mixing lines (Figure 3) correspond to samples collected at depths shallower than 150 m suggesting that salinity in the surface waters of the Mediterranean Sea is not a conservative indicator of water masses, as previously observed by Tachikawa et al., (2004), due to the strong influence of evaporation processes on this oceanographic parameter.

Our results, combined with previously published ε_{Nd} values, show that the Mediterranean water masses are clearly distinguishable by their Nd isotope signatures.

5.1 Comparison between measured and OMP- and POMP-derived ε_{Nd} values

The comparison between measured and OMP and POMP-derived ε_{Nd} values allows evaluating to what extend the ε_{Nd} reflects conservative water mass mixing in the Mediterranean Sea and quantifying the variability related to non-conservative Nd addition locally and regionally. In general, the measured values are consistent with pure water mass mixing (Figures 5, 8 and 9), which indeed exerts the key control over the general Nd isotope composition in the Mediterranean basin, although deviations exist in almost all sub-basins. Considering also the water mass mixing envelopes in figure 3, the regions showing the largest deviations from conservative mixing are the Alboran Sea, the Tyrrhenian Sea, the Ionian Sea, the eastern Levantine Basin and the Aegean Sea. The 1-2 epsilon unit difference between predicted and measured values in the Tyrrhenian and Ionian Sea at shallow and bottom waters is consistent with results of the OMP analysis by Garcia-Solsona et al. (2020).

Intermediate and bottom waters in the Alboran Sea deviate from the conservative behaviour and are characterized by less radiogenic ε_{Nd} signature than expected from the OMP and POMP analysis (Figure 5 and 8). On the other hand, intermediate and deep water masses (shallower than 1500-2000 m) in the eastern Levantine Basin generally exhibit a radiogenic Nd isotope excess (i.e. negative difference between predicted and measured ε_{Nd}), which cannot be explained by physical seawater transport. Therefore, additional local and regional processes other than conservative water mass mixing are necessarily involved in modifying the ε_{Nd} signature of those water masses. These processes are discussed in chapters 5.3, 5.4 and 5.5.

5.2 Comparison between measured and modelled ε_{Nd} values

The new extended ε_{Nd} dataset obtained in this study was also compared to the modelled data obtained by Ayache et al. (2016) (Figures 10 and 11). These authors already carried out such comparison in their publication but the dataset of observed ε_{Nd} values was limited at that time. The Nd isotopic compositions of the different seawater masses in the Mediterranean Sea were simulated using the high-resolution (1/12°) regional oceanic model NEMO-MED12 and taking into account only the boundary exchange process as Nd source while excluding dust and river inputs. The boundary exchange was parameterized by a relaxing equation between the ocean and the continental margin, which considers the ε_{Nd} of the seawater and ε_{Nd} of the material deposited along the continental margin down to ~ 540 m. The Nd isotopic signature of the margins in the model corresponds to the ε_{Nd} values of the surface sediments collected on the shelf or the slope, or the erodible material deposited along the coasts (Supplementary material from Ayache et al., 2016).

The modelled ε_{Nd} distribution at 25 m water depth displays a clear W-E gradient, with values becoming more radiogenic from the western (~ -9) to the eastern (~ -5) Mediterranean basin, which is consistent with the overall gradient observed in the measured ε_{Nd} data (Figures 6 and 10). However, most of the measured values at shallow depths (< 62 m) are ~ 2-4 epsilon units less radiogenic than those obtained from the model simulation. The model-data difference for the surface waters is more pronounced in the eastern Mediterranean basin, in particular in the Ionian Sea, Aegean Sea and south of Crete, where modelled surface (25 m) ε_{Nd} values are up to 4.5 epsilon units more radiogenic than *in situ* measurements (Figure 10). Significant differences (up to 4.5 epsilon units) are also observed in the Sicily Channel at intermediate depth (Figure 11). Similarly, modelled ε_{Nd} values for the LIW are overestimated (i.e. too radiogenic) in the Alboran Sea by 4 epsilon units (Figure 11). The model-data misfit is also observed at deeper depths in the western Mediterranean basin, particularly in the Alboran Sea, Tyrrhenian Sea and Sicily Channel, corresponding to the WMDW, EMDW and TDW, whereas differences close to zero or slightly negative (i.e. measured data are more radiogenic than modelled values) are observed in the central part of the eastern basin at depths below ~ 1000 m and in the eastern Levantine basin along the entire water column (Figure 11).

Overall, this indicates that most of the ε_{Nd} signature simulated by the regional model of Ayache et al. (2016) at depths shallower than ~1000 m are too radiogenic compared to the observations, as also previously acknowledged by the same authors. Ayache et al. (2016) explained the model-data disagreement by the fact that their model only took into account the exchange between the continental margins and seawater as a Nd source, excluding the atmospheric dust and the dissolved river input. A similar mismatch between modelled and measured ε_{Nd} data was also observed by Vadsaria et al. (2019), which used a model configuration very similar to Ayache et al. (2016).

The large model-data difference in the Alboran Sea (Figure 11) was explained with a low simulated net water input from the Atlantic compared to the observed range, which reduces the advection of unradiogenic surface Atlantic waters (ε_{Nd} = -11.8; Spivack and Wasserburg, 1988) in the Mediterranean Sea (Ayache et al., 2016). Following this reasoning, it is possible that the effect of a reduced net water flux likely propagates to the other parts of the Mediterranean Sea and the modelled too radiogenic signature of the surface waters in the eastern basin is partially the result of the reduced advection of unradiogenic waters of Atlantic origin.

Ayache et al. (2016) and Vadsaria et al. (2019) noted that the seawater ε_{Nd} simulation slightly improved when also including the dust deposition and concluded that the highly radiogenic signatures simulated by the model might be corrected by taking into account all Nd sources and sinks. However, dust inputs only result in significant ε_{Nd} deviations in the surface layer of the water column (Tachikawa et al., 1999; Goldstein and Hemming, 2003; Sticher et al., 2015). Consequently the model-data differences for intermediate and deep waters in the Mediterranean Sea, especially in the western basin and in the Sicily Channel (Figure 11), are difficult to explain, even considering a dust contribution in the model. A working hypothesis is that these model-data misfits could be the result of a detrital lithogenic ε_{Nd} signature acquired through interaction with sediments at depth (e.g. > 540 m), which was not considered in the model by Ayache et al. (2016). The arbitrary choice of restricting BE to the margins shallower than ~ 540 m could in fact be a strong limitation of the model that should be fixed. Moreover, it is also known that the sedimentary ε_{Nd} flux is not necessarily equal to the sediment ε_{Nd}, as certain reactive sediment phases are likely more important contributors to sediment influence (Wilson et al., 2013; Abbott et al., 2016; Blaser et al., 2016; Du et al., 2016). The sediment flux ε_{Nd} map in the model may thus be wrong. Therefore, at present, it is difficult to say whether the model-data misfits are real or reflect inaccurate representation of boundary exchange in the model, which ultimately limits the interpretation of the observed discrepancies.

5.3 Evaluation of African dust input on dissolved ε_{Nd} in the eastern and western Mediterranean basins

The relative contribution of partial dissolution of Saharan dust to the Mediterranean Sea differs for the different sub-basins and depends on the ε_{Nd} composition of potential African source areas for dust production, as identified by Scheuvens et al. (2013). These authors compiled a large number of Nd and Sr isotope data from marine sediments, aerosols and soils from the Mediterranean Sea and from 6 major preferential source areas of dust generation (PSAs) in northern Africa. These areas represent the world's largest source of mineral dust, accounting for ~ 70% of the global dust budget (Laurent et al., 2008) and are the dominant sediment suppliers to the Mediterranean Sea (Weldeab et al., 2002). The geochemical data by Scheuvens et al. (2013) have been recently revised by Blanchet (2019) and made available at https://doi.org/10.5880/GFZ.4.3.2019.001. The ε_{Nd} values of the soil samples in the eastern part of northern Africa (Egypt) are relatively high (-10.5 to -3.9) and become less radiogenic in the central and western part of northern Africa (Libya: -15.3; Morocco: -13.6) (Figure 6; Scheuvens et al., 2013), reflecting the geology of the source rocks. This broad E-W geochemical trend has been also identified by Jewell et al. (2021) through the analysis of Sr and Nd isotopes of sediments from dried lakes and river beds in Chad, Morocco, Sudan and Mauritania (Figure 6). The ε_{Nd} values of the aerosol samples collected in the Mediterranean Sea vary from -12.1 to -8.2 in the Levantine basin (Frost et al., 1986) and from -14.6 to -10.9 in the Liguro-Balearic and Tyrrhenian basin (Colin, 1993; Grousset et al., 1988). This W-E isotopic gradient towards more radiogenic values in north-eastern Africa is consistent with the longitudinal gradient of the surface waters. Neodymium is released congruently from dust, which is reflected in surface ocean isotopic compositions being very close to those of the dust (Rickli et al., 2010). However, the quantitative contribution of the dust in the Mediterranean Nd cycle is not well constrained but it is generally considered not very significant also given its low fractional solubility and REE mobilization (Greaves et al., 1994; Tachikawa et al., 2004). Our new ε_{Nd} values for the surface waters in the WMED and EMED differ significantly from the unradiogenic isotope composition of Saharan dust, confirming the previous findings (Tachikawa et al., 2004). Moreover, the recent study by Garcia-Solsona et al. (2020) concluded that dust inputs cannot explain the negative correlation of light rare earth elements (LREE) concentrations with distance to the closest continental shelf for the Tyrrhenian surface samples, which is instead the result of dissolved LREE released from the continental margin sediments. Therefore, our new ε_{Nd} values, combined with previously published data, suggest that the relative importance of dust in modifying the ε_{Nd} signature of surface waters in the Mediterranean Sea is very minor.

5.4 ε_{Nd} of surface water masses

The distribution of the ε_{Nd} signatures in the surface layer follows the mean surface circulation patterns obtained from the reanalysis flow field (Figure 6; Pinardi et al., 2015). The Atlantic Water enters the Strait of Gibraltar with an isotopic signature of -11.8 (Spivack and Wasserburg, 1988) and circulates within the Mediterranean Sea meandering around small and large gyres and cyclonic and anticyclonic eddies. The AW propagates north-eastward and eastward along the Balearic Islands and the Sardinia Channel following the Western Mid-Mediterranean Current and the Southerly Sardinia Current (Pinardi et al., 2015). In the Sardinia Channel the AW splits into two branches, one flowing into the Tyrrhenian Sea and the other entering the Sicily Channel as the Algerian Current. The AW moves eastward along the Cretan passage via the Mid-Mediterranean jet and the Southern Levantine Current until if finally reaches the eastern Levantine basin (Pinardi et al., 2015). AW also enters the Aegean Sea between Crete and Rhodes via the Asia Minor Current and the Adriatic Sea across the Strait of Otranto. The pattern of surface ε_{Nd} values displayed in figure 6 closely follows the large-scale basin circulation. The Nd isotopic values become systematically more radiogenic along the W-E and S-N gradients, from the Alboran Sea (-9.95±0.71) to the Balearic and Tyrrhenian Sea (-9.22±0.17 and -9.07±0.45), Sicily Channel (-9.40±0.36), Adriatic Sea (-7.80) and the eastern Levantine basin (-5.27±0.96) (Table 2), consistent with the main surface currents and a general cyclonic flowpath with several eddies and meanders. According to our OMP analysis (Figure S2) and results from the multiparameter mixing model by Garcia-Solsona et al. (2020) that considers temperature, salinity and oxygen, the fraction of AW along the Sicily Channel is as high as 70-100% in the uppermost waters, which explains the highly unradiogenic values across the passage between WMED and EMED (e.g. -9.75±0.33 for Station Medcor 20 at 60 m depth and -9.52±0.25 for station 3 at 75 m from Garcia-Solsona et al., 2020). The ε_{Nd} difference between the surface water flowing through the Cretan passage (-9.30±0.20) and the eastern Levantine basin (-5.27±0.96) is very large (~ 4 epsilon units) and is the result of a sharp contrast between the unradiogenic AW and a highly radiogenic water mass. The most likely source of this radiogenic signature is the Nile river that supplies highly radiogenic dissolved and particulate Nd to the easternmost Levantine basin (~ -1.2 to -3.25; Goldstein et al., 1984; Tachikawa et al., 2004). Partially dissolved Nile river particles rather than river water likely contribute most of the radiogenic Nd to the eastern Mediterranean (Tachikawa et al., 2004). On the global scale, it has been calculated that the dissolution of less than 3% of the riverine particulate load in the water column can account for the “missing” Nd source in the ocean (Jeandel and Oelkers, 2015).

The north-eastward surface current in the eastern Levantine basin carries and distributes the Nile sediment load along the Egyptian-Israeli margin. Weldeab et al. (2002) analysed the lithogenic surface sediments of the eastern Mediterranean Sea and showed a pronounced E-W gradient in ε_{Nd}, with the easternmost sediment samples off the Israeli coast characterized by the highest values (~ -2.5). Weldeab et al. (2002) also observed a significant decrease in the Nile sediment contribution towards the west. Therefore, it is very likely that the most radiogenic surface seawater samples observed in the Mediterranean Sea north of Egypt acquired their signature from partial dissolution of Nile river particles. This also agrees with previous studies (Piepgras and Wasserburg, 1987; Jones et al., 2008; Siddall et al., 2008; Arsouze et al., 2009) that suggest that the surface water ε_{Nd} signature mainly reflects the river input and only to a minor extent atmospheric dust. Low-density hypopycnal plumes originating from the Nile mouth may have played a significant role in enhancing the dispersion of the Nile river particles in the surface layer and hence releasing Nd in the water column during flooding periods (Ducassou et al., 2008), especially prior the completion of the Aswan High Dam in 1964. Considering that the seawater samples in the easternmost Levantine basin were collected in the early 2000s and the residence time of seawater in the eastern Mediterranean Sea is on the order of 60 years, we consider that their Nd isotopic composition at least partly reflects pre-Aswan Dam conditions, when Nile discharge was extensive (~ 6 x 10^{10} m^3/yr; Béthoux and Gentili, 1996). A recent study has demonstrated the impact of riverine sediment discharge on the Nd isotopic composition of surface and intermediate waters in the Bay of Bengal, supporting a rapid exchange of Nd between riverine particles originating from hypopycnal plumes and seawater (Singh et al., 2012; Yu et al., 2017).

The observed surface ε_{Nd} values in the easternmost Levantine basin may also be the result of the exchange between the shelf sediments (ε_{Nd} up to +6 along the Israeli margin; Ayache et al., 2006) and seawater. In particular, post depositional Nd release driven by sediment diagenesis could play a key role in the Nd cycle (Abbott et al., 2016). However, the locally confined radiogenic values close to the Nile river delta supports the Nile particle load as the main Nd source for the surface waters. The mixing between AW flowing eastwards with local detrital signals from the Nile river particles at shallow depths ultimately results in an average ε_{Nd} signature of -5.27±0.96 in the surface waters of the eastern Levantine Basin.

5.5 ε_{Nd} of intermediate and deep water masses

The surface water of the Levantine basin contributes to the formation of the LIW in the Cyprus-Rhodes area and conveys its highly radiogenic signature derived from the Nile river and its suspend particles to the intermediate depths along the entire Mediterranean basin. The Nd isotopic signature of the LIW then becomes progressively less radiogenic along its westward flowpath (Fig. 6). The high Nd concentration (33.73 pmol/kg) and relatively high Ce/Ce* value (0.50) at station Meteor-294 (254 m) are comparable to the surface water samples and indicate an imprint of lithogenic supply (e.g. Solsona et al., 2020). This could be the result of partial dissolution of sinking particles or the advection of lithogenic supplies (BE) to the intermediate water depths south of Cyprus, or a combination of the two processes.

The comparison between measured and OMP- and POMP-derived ε_{Nd} values in the eastern Levantine Basin reveals a radiogenic Nd isotope excess, in particular for depths shallower than ~ 1500-2000 m (Figure 5, 6 and 9), with differences between predicted and measured ε_{Nd} values ranging from 0.6 to 1.4 epsilon units. The positive non-conservative ε_{Nd} signature at intermediate-deep depths most likely reflects the interaction with the reactive components of the Nile sourced detrital sediments, which contain highly radiogenic volcanic fractions (ε_{Nd} > -4; Padoan et al., 2011) derived from the weathering of Ethiopian Tertiary basaltic rocks. The eastern Levantine Basin thus offers a high ε_{Nd} sedimentary source that contributes (e.g. via benthic fluxes of pore water Nd; Abbott et al., 2016) to the non-conservative ε_{Nd} signature of the intermediate-deep waters (< ~ 1500-2000 m) in this region. This non-conservative radiogenic component is then advected laterally and vertically along the Mediterranean Sea, most likely through sinking particles. However, the measured values from bottom water samples for stations 74 at 2257 m (Tachikawa et al., 2004) and GeoB 7709-1 at 1080 m (Vance et al., 2004) in the easternmost Levantine basin, which represent the EMDW, have an isotopic composition that is up to 4 epsilon units lower than the lithogenic surface sediment below (Figure 12), as also observed by Tachikawa et al. (2004). This likely indicates that either the interaction with the sediment is not strong enough to substantially modify (overprint) the water ε_{Nd} signature in this region at deeper depths, or BE is still a significant process even in the deep eastern Mediterranean Sea but the residence time of the bottom waters in contact with the highly radiogenic sediments is short enough to prevent a full sediment-water isotopic equilibration (i.e. short benthic exposure time relative to circulation timescales).

The EMDW is formed primarily by the AdDW (ε_{Nd} ~ -7) and flows eastward (Figure 1) without changing its Nd isotopic composition significantly (Figure 6), even though it is in contact with highly radiogenic sediments in the easternmost Levantine basin that might modify its signature. The non-conservative component for waters deeper than ~ 1500-2000 m in this region is minor, with the difference between measured and POMP-derived ε_{Nd} values being lower than 0.5 epsilon units (Figure 5). Overall, this indicates that water mass mixing plays a major role in controlling the Nd isotopic composition of the bottom water in the Levantine basin (Figure 6), with minor sedimentary modification along the circulation pathway.

The strong negative non-conservative ε_{Nd} fraction in the Alboran Sea in intermediate and deep waters, with differences between predicted and measured ε_{Nd} values of up to 1.5-2 epsilon units (Figure 5 and 8), requires a sediment source with ε_{Nd} more negative than seawater ε_{Nd}. The isotopic signature of the marine surface sediments in the Alboran Sea is among the least radiogenic in the entire Mediterranean Sea (Blanchet, 2019), with ε_{Nd} values of ~ -11. This suggests that deviations of observed seawater ε_{Nd} from the conservative behaviour in this region might result from the interaction with a less radiogenic sediment source. This could also be the case for other specific sites in the Tyrrhenian Sea, showing negative non-conservative ε_{Nd} (Figure 8). The observed relationship between intermediate-deep water ε_{Nd} values and the detrital lithogenic signatures reflects the good correlation between non-conservative ε_{Nd} and coretop detrital sediment ε_{Nd} at global scale (Du et al., 2020), suggesting a major role of the sediment flux also in the Mediterranean Sea, especially in the eastern Levantine Basin and Alboran Sea.

However, most of the Mediterranean regions show less pronounced non-conservative behaviour (Figures 5, 8 and 9), which is consistent with rapid advection and mixing of eastern radiogenic and western unradiogenic water masses as the dominant processes controlling the Nd cycle and dissolved Nd isotope distribution in the present-day Mediterranean Sea, which is characterized by a highly efficient intermediate and deep-water ventilation.

6. Conclusions

This study presents the dissolved ε_{Nd} compositions of 80 new seawater samples that were recovered from 24 stations between 10 and 4087 m water depth covering the entire Mediterranean basin. The new dataset adds to the previous results and represents one third of the total number of samples (n = 240) obtained so far in the Mediterranean Sea for ε_{Nd}. Our new data support the strong W-E gradient, with the western basin mainly characterized by less radiogenic signature (< -7) and the eastern basin showing a highly radiogenic signature (> -7). In particular, values higher than -6 occur only in the Levantine basin east of 25°E and in the Aegean Sea. This longitudinal gradient is particularly evident in the surface layer that is dominated by AW. The radiogenic signature of the eastern basin is propagated westward at intermediate depth with Levantine Intermediate Water and is progressively diluted during advection from its source region in the eastern Levantine basin (-5.58±0.66) by the mixing with less radiogenic surface and bottom water along its flowpath towards the Alboran Sea (-9.33±0.69). Our data also show a highly significant ε_{Nd} – salinity correlation and a clear distinction between the different surface, intermediate and deep water masses of the Mediterranean Sea based on their ε_{Nd} signature. We used an Optimum Multiparameter (OMP) analysis and results from the Parametric Optimum Multiparameter (POMP) analysis of Jullion et al. (2017) to evaluate the conservative ε_{Nd} behaviour in the Mediterranean Sea and quantify the variability related to local and regional non-conservative Nd addition. Based on the comparison between observed and OMP- and POMP-derived ε_{Nd} values, we can conclude that most of the measured values are consistent with pure water mass mixing (Figures 5, 8 and 9), which indeed exerts a key overall control over the Nd isotope distribution in the Mediterranean basin. However, data-model ε_{Nd} misfits exist in almost all sub-basins, especially in the eastern Levantine Basin and Alboran Sea, which can be explained by the influence of highly radiogenic Nile sourced volcanic sediment fractions and unradiogenic detrital sediments, respectively. Therefore, we can conclude that partially dissolved Nile river particles and the sediment flux contributed by the boundary exchange process play a major role in specific regions of the Mediterranean Sea. The non-conservative contributions originating from sediment sources are then propagated by water mass circulation (with distinct preformed ε_{Nd}) along the Mediterranean Sea as conservative components. The results of the present study indicate that ε_{Nd} effectively traces the mixing between the different water masses in this semi-enclosed basin and is a suitable water mass tracer.

Measured ε_{Nd} values differ significantly (up to +4.8 epsilon units) from model outputs (Ayache et al., 2016), notably for surface waters in the eastern Mediterranean Sea and intermediate and deep waters in the western Mediterranean basin. The model-data disagreement is likely the result of a combination of different factors, such as low simulated net water input and advection from the Atlantic, the lacking inclusion of all external Nd inputs and sinks in the model simulation and the poor implementation of the BE term in the model. In particular, the model BE implementation does not seem to be able to capture boundary exchange or sediment influence in reality (Du et al. 2020). The use of a fully prognostic coupled dynamical/biogeochemical model with an explicit representation of all Nd sources and sinks, as suggested by Ayache et al. (2016), coupled with a better implementation of BE and comparison with this new extended ε_{Nd} dataset, could help improving model simulations and better quantifying the relative proportions of external Nd sources, which will allow us to improve our understanding of the relevant processes affecting the Nd cycle in the Mediterranean Sea.

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Figure captions

Fig. 1. Map of the Mediterranean Sea showing the locations of the new stations of this study (white dots) and those of previously published Nd isotope profiles (black dots), with geographic names reported in the main text. The schematic circulation pattern of the Levantine Intermediate Water (grey arrows) and deep water (dotted black arrows) is modified from Pinarti and Masetti (2000) and Schroeder et al. (2012).

Fig. 2. S-θ-ε_{Nd} plot for all stations discussed in the paper (coloured dots). Grey dots represent full T-S profiles for the Meteor 84/3 and MedBlack GEOTRACES 64PE370 and 64PE374 cruises. Stars correspond to the salinity and potential temperature values of the most important water masses in the Mediterranean Sea, based on water properties reported in Manca et al. (2004). AW = Atlantic Water; LIW = Levantine Intermediate Water; WIW = Winter Intermediate Water; EMDW = Eastern Mediterranean Deep Water; WMDW = Western Mediterranean Deep Water. The eNd signature for AW, LIW, WIW, EMDW and WMDW represent spatially averaged eNd values from the Gulf of Cadiz, Eastern Levantine Basin, Balearic Sea, Ionian Sea and Balearic Sea, respectively (Table 2).

Fig. 3. ε_{Nd}-S-longitude plot showing all the values available for the Mediterranean Sea (this study and previously published results) and calculated 2 end-member mixing lines. Mixing envelopes were calculated based on 1σ SD of the average ε_{Nd} signature for each end-member (Table 2). Grey stars represent surface, intermediate and deep water mass end-members (AW, LIW, EMDW, WMDW).

Fig. 4. ε_{Nd} depth profiles for the Aegean Sea, Adriatic Sea, Western and Eastern Mediterranean basins. Shaded areas indicate the depth range of the main water masses in the Mediterranean Sea (AW = Atlantic Water; LIW = Levantine Intermediate Water; WMDW = Western Mediterranean Deep Water; EMDW = Eastern Mediterranean Deep Water; AdDW = Adriatic Deep Water; MLD = Mixed Layer Depth; TMW = Transitional Mediterranean Water; CDW = Cretan Deep Water). MLD, TMW and CDW are observed in the South Aegean (Vervatis et al., 2011).

Fig. 5. Sections of potential temperature, salinity, measured and POMP-derived ε_{Nd} values along a longitudinal transect from the Strait of Gibraltar to the eastern Levantine Basin. The water mass

fractions used to calculate the POMP-derived ε_{Nd} values were obtained from the Parametric Optimum Multiparameter analysis of Jullion et al. (2017) based on conservative (potential temperature and salinity) and quasi-conservative ($NO = 9NO_3 + O_2$ and $PO = 170PO_4 + O_2$) variables, acquired during the M84/3 cruise (Tanhua et al., 2013b). The red and yellow lines in the map represent the W-E transects for the measured and calculated ε_{Nd} values, respectively. Sampled depths are indicated by grey and black dots. White lines superimposed on the ε_{Nd} values represent salinity contours.

Fig. 6. Maps of the ε_{Nd} signature for the Mediterranean Sea. A) Surface water (< 100 m); B) Intermediate water (200 – 500 m); C) Intermediate-deep waters (500 – 2000 m); D) Deep waters (> 2000 m). The schematic circulation pattern marked by grey arrows is modified by Pinardi and Masetti (2000), Pinardi et al. (2015) and Schroeder et al. (2012). The ε_{Nd} data for the rivers are from Goldstein et al. (1984), Frost et al. (1986), Henry et al. (1994) and Tachikawa et al. (2004). White dots represent average values for surface sediments from the eastern Levantine Basin (-2.5; Weldeab et al., 2002) and Nile River particles (-1.2; Tachikawa et al., 2004). The ε_{Nd} data of the soil samples in northern Africa are from Scheuvens et al. (2013) and Blanchet (2019). The ε_{Nd} composition of the three North African preferential dust source areas (Western, Central and Eastern PSA) is from Jewell et al. (2021). Coloured rectangles with ε_{Nd} values denote the isotopic composition of the aerosol samples analysed by Colin (1993), Frost et al. (1986) and Grousset et al. (1988). The dotted line off-shore the Nile mouth shows the potential extent of the hypopycnal plume from the Nile, based on Ducassou et al. (2008).

Fig. 7. Property-property plots (ε_{Nd} vs. salinity, potential temperature and phosphate) for data from water depths above 227 m (A, B and C), between 227 and 500 m (D, E and F), between 500 and 2000 m (G, H and I) and below 2000 m (J, K and L).

Fig. 8. Comparison between measured and OMP-derived ε_{Nd} values for the western Mediterranean Sea. Deviations from conservative mixing exceed ± 0.5 epsilon units (dotted lines) from the 1:1 line. Inset shows the histogram of the differences between OMP-derived and measured ε_{Nd} values.

Fig. 9. Comparison between measured and OMP-derived ε_{Nd} values for the eastern Mediterranean Sea. Deviations from conservative mixing exceed ± 0.5 epsilon units (dotted lines) from the 1:1 line. Inset shows the histogram of the differences between OMP-derived and measured ε_{Nd} values.

Fig. 10. Comparison between modelled and observed ε_{Nd} values. The colouring shows the modelled surface (25 m) ε_{Nd} distribution (from Ayache et al. 2016). Coloured dots represent measured ε_{Nd} values at shallow depths (< 62 m).

Fig. 11. E-W section of the modelled e_{Nd} distribution (from Ayache et al. 2016) (same track as in Fig. 5). Coloured dots in the upper panel represent measured ε_{Nd} values. Difference between modelled and measured values is displayed in the lower panel.

Fig. 12. Section of the ε_{Nd} distribution in the eastern Levantine basin. White numbers represent the Nd isotopic composition of lithogenic surface sediments from Weldeab et al. (2002). Inset shows the map of the eastern Levantine Basin with isolines of the Nd isotopic composition of lithogenic surface sediments (Weldeab et al., 2002).

Fig. S1. Sections showing the AW, IW and DW fractions for the western Mediterranean Sea, derived from the OMP analysis. Inset shows the transect from the Strait of Gibraltar to the Sicily Channel used to generate the seawater sections. Yellow stars represent the sites of the water type end-members for the OMP analysis. Potential temperature, salinity, ε_{Nd} and Nd concentration of the AW, IW and DW end-members used for the OMP analysis are different for the two basins (see section 3.3 and Table S2).

Fig. S2. Sections showing the AW, IW and DW fractions for the eastern Mediterranean Sea, derived from the OMP analysis. Inset shows the transect from the Sicily Channel to the Levantine Basin used to generate the seawater sections. Yellow stars represent the sites of the water type end-members for the OMP analysis. Potential temperature, salinity, ε_{Nd} and Nd concentration of the AW, IW and DW end-members used for the OMP analysis are different for the two basins (see section 3.3 and Table S2).

Fig. S3. REE patterns for the Mediterranean seawater samples analysed in this study. REE values are normalized to the Post Archean Australian Shale (PAAS, Taylor and MacLennan, 1985) and plotted on a log scale.

Cruise	Station	Lat [°N]	Long [°E]	Depth	θ	Salinity	σ_θ	Phosphate	Nitrate	^{143}Nd/^{144}Nd (bias corrected)	Internal error (2σ SE)	ε_{Nd}	External error (2σ SD)	Nd
				(m)	(°C)		(kg/m^3)	(μmol/kg)	(μmol/kg)					(pmol/kg)
Medcor	37	35.813	14.082	140	15.99	38.22	28.23	0.14	0.96	0.512154	0.000012	-9.44	0.33	
	37			300	14.17	38.79	29.08	0.09	3.31	0.512249	0.000012	-7.58	0.33	
	37			800	13.74	38.75	29.15	0.32	4.33	0.512291	0.000011	-6.78	0.33	
	37			1020	13.71	38.75	29.15	0.19	5.53	0.512278	0.000016	-7.02	0.33	
	20	35.504	14.078	60	17.97	37.87	27.48	0.10	0.11	0.512138	0.000011	-9.75	0.33	
	20			647	13.82	38.75	29.16	0.14	3.92	0.512252	0.000013	-7.54	0.33	
Arcadia	50	41.296	17.254	40	13.62	38.46	28.94	0.02	1.56	0.512238	0.000012	-7.80	0.33	
	50			170	13.38	38.58	29.09	0.04	2.55	0.512252	0.000011	-7.52	0.33	
	50			473	13.54	38.69	29.14	0.16	4.56	0.512263	0.000013	-7.31	0.33	
	50			718	13.44	38.70	29.17	0.13	4.43	0.512263	0.000012	-7.31	0.33	
Record	10	36.500	13.212	65	16.48	37.51	27.57	0.09	0.10					23.26
	10			200	14.67	38.83	29.00	0.13	1.73					23.79
	10			800	13.88	38.79	29.15	0.41	4.65					20.68
	10			1200	13.84	38.78	29.15	0.18	5.42					23.37
	10			1710	13.80	38.78	29.15	0.19	5.02					19.96
	28	38.702	8.912	25	19.04	38.06	27.35	0.01	0.16	0.512138	0.000022	-9.75	0.50	30.06
	28			451	13.80	38.68	29.08	0.34	6.5	0.512228	0.000023	-8.00	0.50	22.37
Meteor 84/3	287	37.667	25.600	25	16.42	39.21	28.89	0.01	0.13	0.512300	0.000013	-6.60	0.50	
	287			506	14.65	39.10	29.22	0.07	1.4	0.512320	0.000016	-6.20	0.50	
	287			807	14.39	39.09	29.27	0.06	1.09	0.512305	0.000014	-6.50	0.50	
	288	35.649	26.227	27	16.85	39.23	28.80	0.00	0.17	0.512320	0.000018	-6.20	0.50	32.00
	288			1015	14.31	39.02	29.23	0.12	3.52	0.512330	0.000018	-6.00	0.50	18.96
	294	33.700	31.002	26	18.11	39.03	28.34	0.01	0.07	0.512264	0.000015	-7.30	0.50	
	294			254	16.35	39.19	28.89	0.02	1.17	0.512310	0.000013	-6.40	0.50	33.73
	294			1776	13.62	38.78	29.19	0.21	4.9	0.512338	0.000016	-5.85	0.50	

	301	35.233	21.483	3552	15.36	152.00	119.80	1.29	0	0.512207	0.000014	-8.40	0.50	23.02
	305	35.600	17.240	4087	13.40	38.73	29.20	0.18	4.36	0.512269	0.000019	-7.20	0.50	22.05
	306	36.500	19.000	255	14.93	39.00	29.08	0.14	3.87	0.512284	0.000013	-6.90	0.50	
	306			3478	13.41	38.73	29.20	0.19	4.44	0.512259	0.000012	-7.40	0.50	
	307	38.000	19.300	3335	13.42	38.73	29.20	0.15	4.5	0.512284	0.000016	-6.90	0.50	
	309*	39.500	18.801	799	13.54	38.74	29.18	0.18	4.84	0.512317	0.000014	-6.26	0.50	22.88
	309*			799	13.54	38.74	29.18	0.18	4.84	0.512317	0.000011	-6.26	0.50	
	317	39.220	11.751	26	15.36	37.52	27.84	0.01	0.07	0.512141	0.000013	-9.70	0.50	
	317			811	13.64	38.67	29.11	0.31	6.56	0.512233	0.000015	-7.90	0.50	21.76
	317			3268	12.96	38.49	29.11	0.37	7.94	0.512192	0.000013	-8.70	0.50	
	338	35.951	-5.749	304	13.10	38.49	29.08	0.44	9.79	0.512177	0.000018	-9.00	0.50	
GEOTRACES-Med	*64PE370-10*	37.575	4.774	11	16.98	36.90	26.98	0.02	0.14	*0.512152*	*0.000005*	*-9.48*	*0.18*	24.61
	64PE370-10			25	16.81	36.91	27.03	0.10	2.47	*0.512346*	*0.000008*	*-5.70*	*0.21*	
	64PE370-10			40	15.99	37.00	27.30	0.17	4.04	*0.512211*	*0.000020*	*-8.34*	*0.46*	
	64PE370-10			80	14.37	37.69	28.19	0.16	4.17	*0.512164*	*0.000009*	*-9.25*	*0.34*	20.83
	64PE370-10			200	13.22	38.35	28.95	0.46	10.16	*0.512195*	*0.000021*	*-8.65*	*0.46*	
	64PE370-10			400	13.28	38.54	29.08	0.47	9.84	*0.512189*	*0.000019*	*-8.77*	*0.46*	
	64PE370-10			1000	12.95	38.48	29.11	0.43	9.02	*0.512180*	*0.000022*	*-8.93*	*0.46*	
	64PE370-10			1500	12.89	38.47	29.11	0.41	8.84	*0.512233*	*0.000022*	*-7.90*	*0.46*	
	64PE370-28	35.296	26.641	50	17.61	39.07	28.50	0.01	0.05	*0.512321*	*0.000025*	*-6.19*	*0.49*	
	64PE370-28			100	16.89	39.08	28.68	0.01	0.53	*0.512365*	*0.000022*	*-5.33*	*0.46*	
	64PE370-28			150	16.50	39.10	28.79	0.01	0.85	*0.512371*	*0.000005*	*-5.21*	*0.21*	
	64PE370-28			400	14.97	39.06	29.12	0.06	2.40	*0.512344*	*0.000006*	*-5.73*	*0.21*	
	64PE370-28			800	13.87	38.83	29.19	0.19	5.09	*0.512352*	*0.000005*	*-5.57*	*0.21*	
	64PE370-28			1000	14.00	38.88	29.20	0.17	4.69	*0.512366*	*0.000017*	*-5.30*	*0.46*	
	64PE370-28			1200	14.09	38.92	29.21	0.15	4.40	*0.512343*	*0.000021*	*-5.75*	*0.46*	
	64PE370-31	39.048	25.210	10	20.48	39.08	27.75	0.03	0.02	*0.512320*	*0.000005*	*-6.20*	*0.21*	
	64PE370-31			60	16.12	39.06	28.85	0.03	0.02	*0.512350*	*0.000007*	*-5.61*	*0.18*	24.81
	64PE370-31			120	15.43	39.00	28.97	0.03	0.93	*0.512355*	*0.000014*	*-5.52*	*0.46*	
	64PE370-31			200	15.07	38.99	29.04	0.04	1.25	*0.512340*	*0.000007*	*-5.82*	*0.18*	22.87
	64PE370-31			276	14.40	38.98	29.18	0.09	2.40	*0.512361*	*0.000017*	*-5.41*	*0.46*	
	64PE370-31			294	14.22	38.98	29.22	0.11	2.73	*0.512305*	*0.000019*	*-6.49*	*0.46*	
	64PE374-1	35.637	24.920	25	23.60	39.16	26.92	0.02	0.03	0.512280	0.000015	-6.99	0.50	
	64PE374-8	40.961	18.536	235	13.97	38.82	29.15	0.07	3.15	0.512239	0.000008	-7.78	0.50	
	64PE374-8			874	13.04	38.71	29.27	0.12	3.78	0.512263	0.000018	-7.31	0.50	
	64PE374-9	40.154	18.817	739	13.48	38.76	29.21	0.07	3.10	0.512250	0.000012	-7.57	0.50	
	64PE374-12	39.007	14.502	3464	13.00	38.50	29.11	0.37	8.25	0.512202	0.000009	-8.50	0.50	
	64PE374-13	39.878	13.010	20	21.13	37.90	26.67	0.02	0.02	0.512179	0.000019	-8.95	0.50	
	64PE374-13			400	14.12	38.76	29.07	0.24	6.01	0.512250	0.000014	-7.58	0.50	
	64PE374-13			499	14.03	38.76	29.09	0.26	6.22	0.512236	0.000011	-7.84	0.50	
	64PE374-13			1000	13.54	38.65	29.11	0.31	7.11	0.512260	0.000021	-7.38	0.50	
	64PE374-13			3576	12.98	38.50	29.11	0.39	8.36	0.512158	0.000015	-9.36	0.50	
	64PE374-15	42.051	10.568	25	17.87	38.11	27.70	0.03	0.01	0.512187	0.000011	-8.80	0.50	
	64PE374-15			299	13.98	38.67	29.04	0.27	6.26	0.512207	0.000017	-8.41	0.50	
	64PE374-15			1244	13.30	38.58	29.11	0.36	7.73	0.512210	0.000008	-8.35	0.50	
	64PE374-17**	40.070	5.947	25	20.44	37.11	26.26	0.02	0.01	0.512172	0.000011	-9.08	0.50	
	*64PE374-17***			25	20.44	37.11	26.26	0.02	0.01	*0.512153*	*0.000006*	*-9.46*	*0.21*	

	64PE374-17			55	15.74	37.22	27.52	0.03	0.02	*0.512170*	*0.000033*	*-9.13*	*0.66*	
	64PE374-17			85	14.59	38.13	28.48	0.03	0.02	*0.512167*	*0.000007*	*-9.19*	*0.21*	
	64PE374-17			175	13.28	38.34	28.93	0.27	6.94	*0.512209*	*0.000023*	*-8.38*	*0.46*	
	64PE374-17			199	13.34	38.41	28.97	0.31	7.58	0.512218	0.000016	-8.19	0.50	
	64PE374-17			500	13.27	38.56	29.10	0.41	8.93	*0.512218*	*0.000013*	*-8.19*	*0.46*	
	64PE374-17			1000	12.96	38.49	29.11	0.41	8.78	*0.512243*	*0.000020*	*-7.70*	*0.46*	
	64PE374-17**			1500	12.86	38.47	29.12	0.41	8.71	0.512198	0.000011	-8.58	0.50	
	*64PE374-17***			1500	12.86	38.47	29.12	0.41	8.71	*0.512209*	*0.000008*	*-8.37*	*0.21*	
	64PE374-17			2000	12.90	38.48	29.12	0.39	8.47	*0.512190*	*0.000006*	*-8.73*	*0.12*	
	64PE374-17			2500	12.90	38.49	29.12	0.39	8.46	*0.512245*	*0.000042*	*-7.67*	*0.83*	
	64PE374-17			2785	12.90	38.49	29.12	0.39	8.43	*0.512193*	*0.000020*	*-8.69*	*0.46*	
	64PE374-17**			2824	12.91	38.49	29.12	0.39	8.42	0.512190	0.000016	-8.73	0.50	
	*64PE374-17***			2824	12.91	38.49	29.12	0.39	8.42	*0.512239*	*0.000021*	*-7.78*	*0.46*	

Table 1. Hydrographic data, Nd isotopic composition, ε_{Nd} values and Nd concentration of the seawater samples analysed in the present study. The uncertainties are given at the two-sigma (2σ) level for the internal and external error. The external reproducibility of ^{143}Nd/^{144}Nd measurements was estimated by repeated measurements of the international standards JNdi-1 and La Jolla. * Intra-laboratory replicate samples (GEOPS); ** Inter-laboratory replicate samples (GEOPS and GEOMAR). Samples in italics were analysed at GEOMAR.

Basin	Sub-basin	Water mass	Depth (m)	ε_{Nd} ± 1SD		N. of samples	Reference
Western	Alboran Sea	AW	0-110	-9.95	±0.71	13	2, 3, 4
		LIW	200-400	-9.33	±0.69	8	3, 4
		WMDW	800-1270	-9.23	±0.25	4	3
	Balearic Sea	AW	25-85	-9.22	±0.17	4	1, 7
		WIW	100-250	-8.56	±0.44	6	1, 7
		LIW	250-501	-8.31	±0.52	6	1, 7
		WMDW	1000-2825	-8.61	±0.49	17	1, 7
	Tyrrhenian Sea	AW	20-140	-9.07	±0.45	15	1, 8
		LIW	240-580	-7.81	±0.35	13	1, 8
		TDW	811-1500	-8.26	±0.66	9	1, 8
		WMDW	2264-3576	-8.65	±0.34	7	1, 8
Eastern	Sicily Channel	AW	60-140	-9.40	±0.36	4	1, 8
		LIW	300-647	-7.46	±0.31	4	1, 5, 8
		EMDW	1020-1692	-7.03	±0.01	2	1, 8
	Ionian Sea	AW	25-130	-8.21	±0.58	4	8
		LIW	200-300	-6.88	±0.38	5	1, 8
		AdDW	799-874	-6.97	±0.48	4	1, 8
		EMDW	2718-4086	-6.87	±0.24	4	1, 8
	South Adriatic Sea	AW	40	-7.80		1	1

	LIW	235-473	-7.55	±0.33	2	1
	AdDW	718-874	-7.40	±0.15	3	1
South Crete	AW	11-62	-9.30	±0.00	2	3
	LIW	200-430	-7.43	±0.44	4	3
	EMDW	1313-2228	-7.34	±0.40	5	3
Eastern Levantine Basin	AW	1-50	-5.27	±0.96	7	6, 1
	LIW	160-500	-5.58	±0.66	6	1, 3, 6
	EMDW	800-2257	-6.39	±0.80	7	1, 3, 6
Aegean Sea	Surface water	10-75	-6.63	±0.74	10	1, 3
	Intermediate water	200-700	-5.89	±0.50	6	1, 3
	Deep water	1000-1500	-7.13	±2.61	6	1, 3

Table 2. Spatially averaged ε_{Nd} signature of the main water masses in the different Mediterranean sub-basins. Reference: 1 = this study; 2 = Spivack and Wasserburg (1988); 3 = Tachikawa et al. (2004); 4 = Dubois-Dauphin et al. (2017b); 5 = Henry et al. (1994); 6 = Vance et al. (2004); 7 = Garcia-Solsona and Jeandel (2020); 8 = Garcia-Solsona et al. (2020).

Table S1. Hydrographic data, Nd isotopic composition, ε_{Nd} values and Nd concentration of the seawater samples analysed in the present study and literature data. The uncertainties are given at the two-sigma (2σ) level for the internal and external error. The table reports also the water mass fractions calculated through the OMP analysis.

Table S2. Potential temperature, salinity, ε_{Nd} and Nd concentration of the source water type end-members used as input parameters for the OMP analysis in the WMED and EMED and the calculation of predicted ε_{Nd} values.

Table S3. Potential temperature, salinity, NO, PO, ε_{Nd} and Nd concentration of the source water type end-members used as input parameters for the POMP analysis in the WMED and EMED (Jullion et al., 2017) and to calculate the predicted ε_{Nd} values.

Table S4. Dissolved Rare Earth Elements concentrations (in pmol/kg of seawater) and Ce anomalies (Ce/Ce*) of the samples analysed in the present study.