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Paleoceanography and Paleoclimatology



RESEARCH ARTICLE

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Key Points:

- Precessional cyclicity is exhibited in records of seawater Pb isotopes from marginal Messinian Mediterranean marine sediments
- We hypothesize that dust from North Africa drives the observed cyclicity
- Seawater Pb isotopes in the Mediterranean potentially provide another tie point to anchor the insolation curve for orbital tuning

Supporting Information:

- Supporting Information S1
- Table S1

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Precessional Cyclicity of Seawater Pb Isotopes in the Late Miocene Mediterranean

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Abstract Astronomical tuning in the Mediterranean region is primarily based on organically-mediated proxies, such as cyclicity of organic rich layers or changes in foraminiferal assemblages. Both during and post deposition, organic proxies can be affected by complex processes not immediately related to the changes in precession (insolation) they are assumed to reflect. Here we present an isotopic proxy which exhibits precessional cyclicity yet is inorganic. Seawater lead (Pb) isotope records over four precessional cycles between 6.6 and 6.5 Ma, from bulk sediment leachates of three Messinian, circum-Mediterranean marginal locations, show variations consistent with precessional cyclicity. During insolation minima, the Pb isotope signatures from all three sites converge to similar values, suggesting a regional process is affecting all three locations at that time. Data from the marginal sites are compared with new data from ODP Site 978 and published data from a variety of geological archives from the Mediterranean region to determine the mechanism(s) causing the observed variability. While the comparisons are not fully conclusive, the timing of events suggest that increased dust production from North Africa during insolation minima is the most likely control. This hypothesis implies that authigenic marine Pb isotope records have the potential to provide a reliable inorganic tie point for Mediterranean cyclostratigraphy where sub-precessional resolution is required. An inorganic tie point could also provide the means to resolve long-standing problems in Mediterranean stratigraphy on precessional and sub-precessional timescales which have been obscured due to post-depositional changes (e.g., sapropel burn-down) or suboptimal ecological conditions (e.g., the Messinian Salinity Crisis).

Plain Language Summary Research into the geological and climate history of the Mediterranean region has been important globally, partly because the geologic timescale, back to about 23 million years ago, is pinned to the geological record of this region and partly because the water exiting the Mediterranean into the Atlantic is an important component of global ocean circulation. In this paper, we examine changes through time in the isotope ratios of the trace metal lead (Pb), which is present in tiny amounts even in unpolluted seawater. Our Pb isotope records, covering ~100 thousand years at about 6.5 million years ago, show distinctive regular cyclicity with time, with “peaks” at approximately 20 thousand year intervals. We hypothesize that wet-dry climate cycles in North Africa produced these peaks by supplying more dust to the Mediterranean during the driest part of the cycle, when Pb from dust would have more strongly influenced the seawater Pb isotope composition. This hypothesis is exciting because it suggests that seawater Pb isotopes have the potential to improve our understanding of the passage of time in the Mediterranean region, in particular at times and locations where existing techniques are inadequate.

1. Introduction

The near landlocked nature of the Mediterranean Sea reduces the buffering effect of the Atlantic, rendering this basin sensitive to regional climatic changes (Gladstone et al., 2007). Consequently, Mediterranean marine sediments reflect a dominantly precessional (approximately 20 ka) cyclicity. This has been documented for both marginal and open Mediterranean basin locations since at least 13.5 Ma, in terms of visible differences in sediment characteristics (Hüsing et al., 2009; Lourens et al., 1996; Murat, 1999), changes in faunal assemblages (Blanc-Valleron et al., 2002; Negri et al., 1999; Raffi et al., 2003; Sierro et al., 2003), and other geochemical signatures (see Rohling et al., 2015 for a review).

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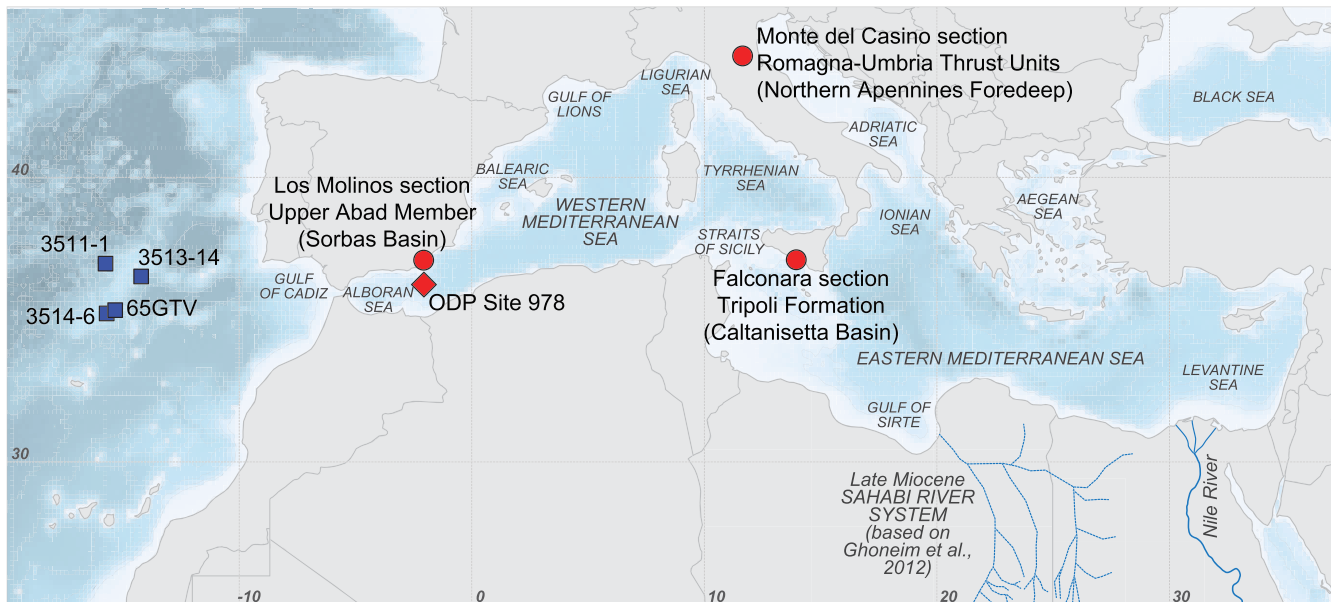


Figure 1. The Mediterranean region. Sample locations marked in red; published ferromanganese crust records referred to in the discussion marked in blue. Also indicated are the major rivers draining from North Africa to the Mediterranean, including the Nile and the now defunct Sahabi River system.

These cyclic marine sediments include sapropels, whose pattern over at least the last 7 Ma reproduces the strongly precession-modulated La04 solution for summer insolation at 65°N (Lourens et al., 1996) or the summer inter-tropical insolation gradient (SITIG) insolation curve (Bosmans et al., 2015; Reichert, 1997). Sapropels are finely laminated marine muds that typically contain a relatively high proportion of organic carbon ($\geq 2\%$; Kidd et al., 1978) and lack benthic fossils. Sapropel deposition is attributed to the disruption of deep water formation, leading to bottom water anoxia; this disruption is primarily ascribed to increased freshwater inputs during precession minima (Cramp & O'Sullivan, 1999; Emeis, Sakamoto, et al., 2000; Rohling, 1994; Rohling et al., 2015; Rohling & Hilgen, 1991; Rossignol-Strick, 1985; Schmiedl et al., 2010). Precessional oscillations in the latitude of the Intertropical Convergence Zone control the position of the African monsoon system (Marzocchi et al., 2015; Zhang et al., 2014). During precession minima (equivalent to insolation maxima), the African monsoon is situated further north, increasing the amount of rainfall over catchments which drain into the Mediterranean such as the Nile and the now defunct Sahabi river system (Figure 1; Griffin, 2011; Osborne et al., 2010). On a practical level, sapropels are visually distinctive and easy to identify, due to their dark color and laminations, making them an ideal sedimentary marker for building chronology. Sapropels, or more generally, the strong precessional cyclicity in Mediterranean sediments, have enabled high-resolution (precessional) astronomical tuning in the Mediterranean, vastly improving the precision of the Neogene to present geologic timescale and improving chronology even beyond the Neogene (Hilgen et al., 1995, 2012; Kuiper et al., 2008; Lourens et al., 2004).

Despite the revelations provided by astronomical tuning in the Mediterranean, important questions remain about the geological history of this region, including changes in the connection(s) to the Atlantic Ocean which may have had consequences for global thermohaline circulation (Flecker et al., 2015; Ivanovic, 2012). Answering these questions requires an improvement in the precision with which we can constrain time within the sedimentary expression of a precessional cycle; in other words, improving our ability to pinpoint the position where insolation maxima and minima occurred within a sedimentary sequence. Such sub-precessional resolution requires an understanding of the phasing between deposition of any given proxy and insolation. However, the proxies we currently rely on are affected by complex processes. One example is sapropel “burn-down” (top-down post-depositional oxidation of organic matter) which has been observed to remove up to half of the original layer (Thomson et al., 1999). Foraminiferal assemblages are another important proxy in this setting (e.g., Kouwenhoven et al., 1999; Pérez-Folgado et al., 2003; Sierro et al., 2003), but these have ecological interdependencies which in turn generate complications. Nutrient

concentrations, turbidity, ventilation, and temperature all affect faunal abundances and assemblages, but are also interdependent; for example, increased ventilation can lead to nutrient exhaustion due to biological activity (Filippelli et al., 2003). Moreover, there are significant differences in the temporal occurrence of several proxies between Mediterranean sub-basins; for example, sapropels in the Western Mediterranean are often less distinct, spatially less extensive, and sometimes missing entirely in the Plio-Pleistocene compared to the Eastern Mediterranean (Murat, 1999). The east-west spatial discrepancy is due to the fact that the intense increase in monsoon-driven runoff during insolation maxima is primarily channeled into the eastern basin (Marzocchi et al., 2019; Emeis, Struck, et al., 2000; Rossignol-Strick, 1985), suggesting different processes are responsible for sapropel development in the west (Emeis, Struck, et al., 2000; Murat, 1999). Finally, substantial changes in salinity occurred in the Mediterranean during the Messinian Salinity Crisis (MSC; 5.971–5.333 Ma; Krijgsman et al., 1999; Lourens et al., 1996; Manzi et al., 2013), which obscured normal marine sedimentation and the biological activity moderating organic proxies altogether.

To assess these issues, an independent, inorganic proxy is required. One candidate which has not been explored in the Mediterranean context is lead (Pb) isotopes. In seawater, Pb isotopes respond to changes in Earth's climate by recording shifts in weathering regimes. The best documented observations of this nature correspond to major periods of glaciation and glacial terminations, reflecting an increase in sediment and runoff release to the oceans during deglacial and early post-glacial intervals (Foster & Vance, 2006; Gutjahr et al., 2009; Kurzweil et al., 2010). Archives of seawater Pb isotopes preserve relatively short-term signals due to very high particle reactivity and a correspondingly low dissolved Pb concentration, reflected by the short (tens of years) marine residence time of Pb (Frank, 2002; Henderson & Maier-Reimer, 2002). These properties allow Pb isotope compositions to be very sensitive in marine environments, more so than other radiogenic isotope tracers such as neodymium (Nd; Abouchami & Goldstein, 1995). Paleo-seawater Pb isotopes can be extracted from the ferromanganese (FeMn) oxyhydroxides which precipitate directly out of the water column and pore waters onto or within other sediment particles. Extracting Pb from FeMn oxyhydroxides has proven robust and reliable for investigating past seawater Pb isotope compositions (Basak et al., 2011; Gutjahr et al., 2007).

For studies of the marginal Mediterranean sedimentary sequences which expose late Miocene deposits, paleo-seawater Pb isotopes provide several other advantages over Nd. The latter is difficult to interpret and often unreliable as a water mass tracer in the relatively shallow, near shore environments investigated here (Modestou, 2016) due to a strong influence of benthic flux and boundary exchange, processes which have the potential to disturb or completely replace seawater Nd signatures in the oxyhydroxide coating (Abbott et al., 2015; Lacan & Jeandel, 2005; Pearce et al., 2013; Rousseau et al., 2015; Wilson et al., 2013). By contrast, Pb has a high affinity to hydrous manganese oxide (Gadde & Laitinen, 1974) so that after complexation within FeMn oxyhydroxides Pb is unlikely to be remobilized, preserving the primary seawater signal. Besides the improved reliability, authigenic seawater Pb contained in FeMn oxyhydroxides is the result of inorganic complexation, indicating this isotope system is an ideal tool to avoid the ecological issues described above.

2. Materials and Methods

2.1. Geology and Sampling

The sediments investigated were recovered from three Messinian marine sedimentary sections exposed on the margins of the Western Mediterranean as well as Ocean Drilling Program (ODP) Leg 161 Site 978 (Figure 1). The sedimentary cyclicity at the three land-based sites has been demonstrated to follow precession; the chronostratigraphic tie points used in the astronomical tuning (including magneto- and bio-stratigraphic markers) rule out other options (Hilgen & Krijgsman, 1999; Hüsing et al., 2009; Krijgsman et al., 1997; Sierro et al., 1999). The stratigraphy at each site is based on similar principles used to astronomically tune the deep basin Plio-Pleistocene sections of the Mediterranean, assuming sapropelic layers coincide with precession minima (Lourens et al., 1996). The specific time interval and locations studied herein were selected because the requisite high-resolution stratigraphy and precessional nature of sedimentation had been previously determined (Hilgen & Krijgsman, 1999; Krijgsman et al., 1997, 1999; Negri et al., 1999; Pérez-Folgado et al., 2003). All samples were taken from the marine unit preceding evaporite deposition related to the MSC. Table 1 provides a comparison of various properties from each of the

Table 1
Details of Studied Sections

Basin	Sorbas	Caltanissetta	Apennine Foredeep
Section name	Los Molinos	Falconara	Monte del Casino
Location	Southern Spain 37°05'22"N 02°04'08"W	Sicily 37°06'11"N 13°57'07"E	Northern Italy 44°15'54"N 11°38'42"E
Unit exposed	Upper Abad member	Tripoli formation	Romagna-Umbria thrust units
Precessional sedimentary cyclicity?	Yes	Yes	Yes
Layers per cycle	4	3	2
	sapropelic, marl, diatomite, marl	sapropelic, diatomite, marl	sapropelic, marl
Maximum sapropelic layer TOC ^a (%)	1.8 ^b	0.15 ^c	N/A ^d
Sedimentation rate (cm/ka)	10–12	2–4	2–4
Time range included in this study (Ma)	6.61–6.55	6.61–6.53	6.62–6.53
Length of section (m)	7	2.5	3

^aTotal organic carbon. ^bVázquez et al., 2000. ^cBellanca et al., 2001. ^dNo data available.

marginal sequences. We use the term “sapropelic” rather than sapropel as these sequences tend to have lower and more variable total organic carbon than the classic definition.

2.1.1. The Sorbas Basin

Sediments from the Sorbas Basin were sampled from the Los Molinos section which exposes the Upper Abad marls (Southern Spain, Figure 1). These marls are characterized by repeating quadripartite cycles (Figure 2; Sierro et al., 2001, 2003), consisting of a brownish-grey sapropelic layer exhibiting laminations; a bioturbated, homogenous grey marl; diatomaceous marl (hereafter diatomite); and another grey homogenous marl. The sediments of the Sorbas Basin have been the focus of numerous sedimentological and paleoecological studies, and thus there is extensive information available; the evidence for climatic expression of precessional control on these sediment packages is summarized here. Fine laminations and the paucity of benthic foraminifera support the theory that bottom water anoxia caused sapropelic layer deposition in the Sorbas Basin, suggesting wetter conditions, lower surface salinity, and stratification prevailed (Pérez-Folgado et al., 2003; Sierro et al., 2003), mirroring the processes credited for sapropel development in the Eastern Mediterranean at insolation maxima. Linking the sapropelic layers in the Sorbas Basin to this part of an insolation cycle results in the diatomite layers being associated with insolation minima and drier conditions. Insolation minima are associated with higher surface water salinity and enhanced vertical mixing, promoting nutrient upwelling and phytoplankton production; evidence is available for these processes within the Sorbas Basin diatomites (Filippelli et al., 2003; Pérez-Folgado et al., 2003; Sierro et al., 1999, 2003; Vázquez et al., 2000). The interbedded marls contain benthic organisms and bioturbation, recording the transition between anoxic and well-ventilated bottom water conditions (Sierro et al., 2003). Based on benthic foraminiferal assemblages, the Sorbas Basin was approximately 150- to 250 m deep during the interval investigated in this study (Modestou et al., 2017). The cyclical changes in planktic foraminiferal assemblages, and the planktic assemblages themselves, are identical to the ~1,000 m deep sediments exposed at Gavdos, Crete in the Eastern Mediterranean (Kouwenhoven et al., 2003; Pérez-Folgado et al., 2003).

2.1.2. The Caltanissetta Basin

Sediments from the Caltanissetta Basin were sampled from the Falconara section (Sicily, Figure 1), one of many outcrops exposing the Tripoli Formation. This basin was the primary depozone of the Sicilian-Maghrebian foredeep (Jolivet et al., 2006 and references therein). Caltanissetta is significant because it is located beside the Strait of Sicily, which connects the Eastern and Western Mediterranean basins. The Tripoli sediments are characterized by tripartite cyclicity, each cycle comprised a sapropelic layer, a diatomite, and a homogeneous marl. As with the diatomites of the Sorbas Basin, the Tripoli diatomites are thought to coincide with insolation minima (Hilgen & Krijgsman, 1999). Unlike Sorbas, the diatomites of the Caltanissetta Basin are quite thick, dominating the sedimentary cyclicity. This may suggest that sedimentation rates increased during their deposition, although this cannot be verified since sub-precessional age constraints are currently unavailable.

2.1.3. The Apennine Foredeep

Sediments of the Apennine Foredeep were sampled at the Monte del Casino section, located about 10 km south of Imola (Bologna, Italy; Figure 1). Sediments exposed here comprise part of the Romagna-Umbria thrust units which overlie calcareous turbidites of the Marnoso-Arenacea Formation (Negri et al., 1999),

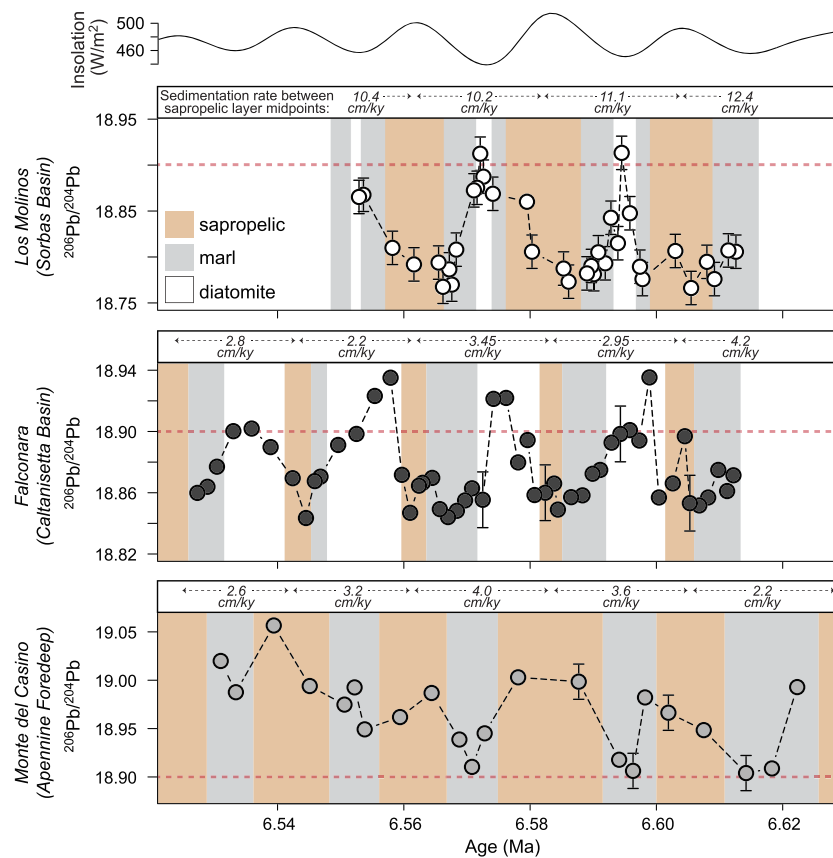


Figure 2. $^{206}\text{Pb}/^{204}\text{Pb}$ records from all three basins plotted against lithological variation and insolation. The sedimentation rate between sapropelic layer midpoints is indicated above each time series; note the difference between sites is an order of magnitude. Horizontal line at $^{206}\text{Pb}/^{204}\text{Pb} = 18.90$ emphasizes the approximate value where Pb isotope ratios converge at all three sites (see also Figure 3). Where multiple replicates of a sample have been measured, the average is plotted. Uncertainty is 2SD external analytical reproducibility; bars not visible where uncertainty is smaller than symbol size.

all of which were deposited in a marine basin created in the foredeep of the Northern Apennine mountains (Krijgsman et al., 1997). The sedimentary cyclicality here is bipartite (sapropelic layer—marl; Krijgsman et al., 1997), with the sapropelic and homogeneous marl layers roughly equal in thickness. The sapropelic layers here are also assumed to coincide with insolation maxima (Krijgsman et al., 1997) and the associated environmental conditions (Negri et al., 1999). Based on planktic/benthic foraminifera ratios and geochemical proxies, this basin experienced significant shallowing, with its paleodepth reduced from ~1,000 to 500 m in just a few hundred thousand years leading up to and including the time interval studied here (Kouwenhoven & van der Zwaan, 2006; Van Der Meulen et al., 1999).

For all sites, material was selected from curated sample sets. The Los Molinos samples, provided by Prof F. Sierro (University of Salamanca) span Upper Abad cycles 5 to 8 (~6.61 to 6.55 Ma; Sierro et al., 2001). For both the Falconara and Monte del Casino sections, samples were provided by Dr F. J. Hilgen (Utrecht University). The originally published age models for the Abad Formation (Krijgsman et al., 1999; Sierro et al., 2001) and Falconara (Hilgen & Krijgsman, 1999) were updated to the La04 solution (Laskar et al., 2004) for this work. The Monte del Casino age model was previously updated to La04 by Hüsing et al. (2009). Retuning was performed using the common assumption (e.g., Hilgen & Krijgsman, 1999) that sapropelic layer midpoints coincide with insolation maxima (precession minima).

2.1.4. ODP Site 978

ODP Leg 161 Site 978 was drilled in the Alborán Sea at 1,930 m water depth (36°13.867'N, 2°3.424'W; Figure 1). Its location would imply that it records the properties of Mediterranean water prior to its exit

into the Atlantic. The samples were collected from Hole 978A, cores 47 and 48, which contained dark greenish-grey to bluish-greenish-grey sediments, classified as siltstone to calcareous clayey siltstone throughout (Shipboard Scientific Party, 1996). This section of core does not show regular sedimentary alternations, and foraminifera are poorly preserved, precluding astronomical tuning based on color changes or stable isotopes. For this reason, the age model at this section is based solely on the nannofossil *Reticulofenestra rotaria* (Shipboard Scientific Party, 1996). However, several factors have called the age model into question. The Miocene sediments are capped by a hiatus, marked by a 10 to 25 m thick gravel bed that caused low core recovery. Subsequent to publication of the cruise reports, *R. rotaria* was excluded as a reliable biostratigraphic marker due to large spatial variability (Raffi et al., 2003). The lack of continuity between robust tie points and the inability to perform astronomical tuning by other means result in sample ages with very poor precision compared to the marginal successions. Consequently, only four Messinian samples were selected for analysis. We selected depths at or between *R. rotaria* events making the assumption that these events are sufficiently close to Messinian in age. Subsequently, we use these four samples simply to constrain the range of Messinian Pb isotope values for Alborán Sea water exiting the Mediterranean to the Atlantic, without attributing a precise age to these measurements.

2.2. Analytical Procedure

Pb isotope compositions were extracted from approximately 0.35 g of homogenized bulk sediment using acid-reductive leaching following Gutjahr et al. (2007) without prior decarbonation. All reagents used were either in-house distilled from analytical grade, or ultraclean quality, except MgCl_2 and ethanol (analytical grade). Deionized water was 18.2 M Ω . Disaggregated, unwashed sediment was agitated in 0.9 M MgCl_2 for 2 h to remove easily exchangeable ions via cation exchange (Tessier et al., 1979). After multiple rinses with deionized water and separation via centrifugation, 10 ml of the leaching solution (0.05 M hydroxylamine hydrochloride, 15% v/v acetic acid, 0.03 M ethylenediaminetetraacetic acid (EDTA), and 0.35 M NaOH) was agitated with samples for 2 h. Pb was separated using the column chromatography chemistry described by Lugmair and Galer (1992).

Strong leaching as well as total dissolution were performed on a subset of the Sorbas Basin samples in order to compare the signal of the detrital siliciclastic fraction. This subset spans all lithologies and the entire temporal range of the full Sorbas sample set. Strong leaching aims to extract metals from the more easily weathered siliciclastic sediment, while total dissolution provides the isotope composition of the complete detrital fraction. For the strong leachates, removal of the seawater signal was performed by repeated acid-reductive leaches with the same solution described in the previous paragraph, first for 2 h and then twice for 24 h, centrifuging and removing the supernatant after each leach. Samples were rinsed thrice with deionized water then agitated with 5 ml, 3 M HCl—3 M HNO_3 for 24 h.

The total dissolution procedure required several oxidation steps due to resistant organic matter. Initially, the seawater signal was removed by leaching first for 3 h and then 24 hr with centrifugation and removal of the leaching solution each time. Organic matter in the samples was oxidized by step-wise addition of a total of 2 ml, 30% H_2O_2 combined with ultrasonication and refluxing overnight at 100°C. After drying, aqua regia oxidation was performed, followed by dissolution in 5 ml, 14 M HNO_3 , 2 ml, 12 M HCl, and 3 mL, 29 M HF combined with microwave digestion. Both the strong leachates and totally dissolved samples were purified following the same column chemistry as the acid-reductive leachate. Further detail is included in the supporting information.

Pb isotope analysis was performed on either a Nu Plasma or Thermo Scientific Neptune Plus multi-collector inductively coupled plasma mass spectrometer (MC-ICP-MS; GEOMAR Helmholtz Centre for Ocean Research Kiel, Germany). Concentration-matched standard and sample Pb concentrations of 40 ppb (Nu Plasma) and 28 ppb (Neptune Plus) were prepared for analysis. Results from the Nu Plasma MC-ICP-MS were mass bias corrected using standard sample bracketing, correcting to the accepted value of primary standard NBS 981 (Baker et al., 2004). On the Neptune Plus MC-ICP-MS, mass bias correction was carried out using the thallium doping technique. NBS997 Tl standard was added aiming for a Pb/Tl \sim 4 (Belshaw et al., 1998). The most accurate $^{205}\text{Tl}/^{203}\text{Tl}$ ratio required for mass bias correction was determined on a session-by-session basis so that the sum of all offsets of all six Pb isotope pairs for NIST NBS 981 equaled 0 ppm compared with published compositions of Baker et al. (2004) (see Süfke et al., 2019). This always

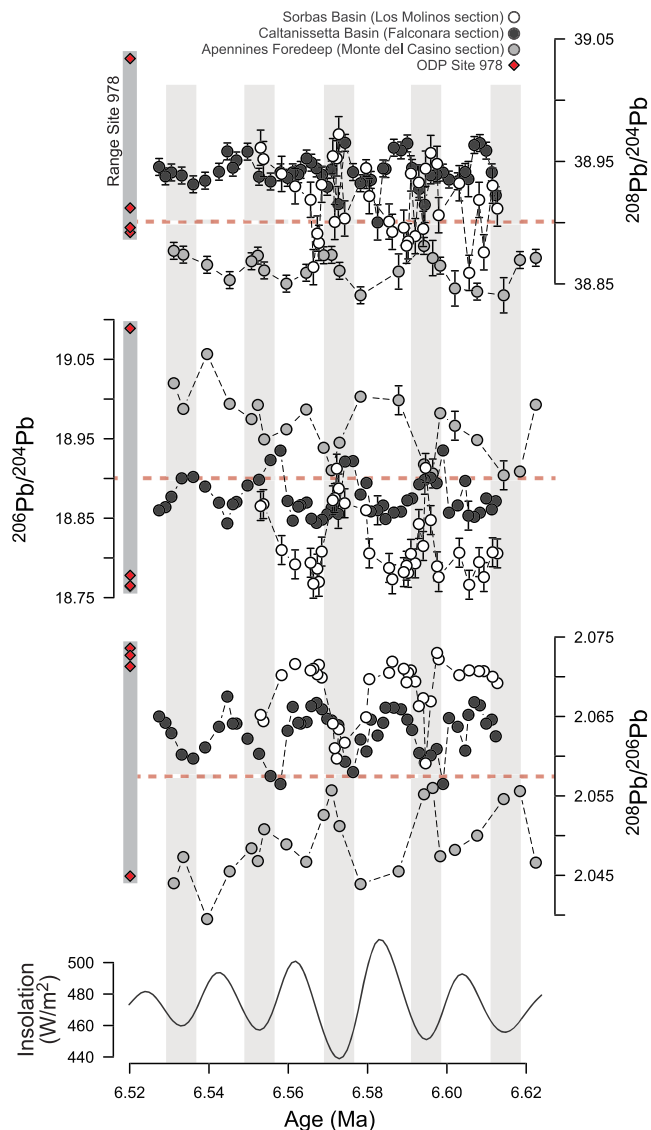


Figure 3. Changes in reconstructed basin water Pb isotope compositions compared to insolation. Data plotted with color corresponding to location. Vertical shaded bars highlight periods of insolation minima. Horizontal red dashed line corresponds to approximate Pb isotopic composition at times of convergence (see also Figure 2). See Figure 1 for locations. Where multiple replicates of a sample have been measured, the average is plotted. Uncertainty is 2SD external reproducibility unless internal was larger; where not visible, analytical uncertainty is smaller than symbol.

the values form a mirror image to those observed at the other locations. The Apennine Foredeep cycles also appear to be overprinted onto a long-term trend towards more radiogenic values. Despite the mirror-image behavior, the Pb isotope values for all ratios at all sites converge towards similar values at nearly the same time, near insolation minima (again, according to the tuning; Figures 2 and 3).

3.2. Preservation and Reliability of the Records

Gutjahr et al. (2007) previously raised concerns that anoxic conditions may result in remobilization of Pb. However, a recent study employing this leaching method on anoxic Holocene sediments in an Alpine lake extracted an unperturbed Pb isotope record (Süfke et al., 2019), suggesting that reliable authigenic Pb isotopic compositions can be extracted from anoxic sediments. Experiments with sediments from a temperate

led to slightly higher $^{205}\text{Tl}/^{203}\text{Tl}$ than certified for NIST NBS997 because of the slightly different ionization behavior of Tl compared with Pb (Thirlwall, 2002). NBS 982, USGS NOD-A1, and USGS NOD-P1 were used as secondary standards. Due to their similar matrix, the latter two standards were also used to monitor consistency of the methodological approach by processing them with the same purification treatment as the bulk sediments. External reproducibility for measurements with the Nu Plasma were $^{208}\text{Pb}/^{204}\text{Pb} = 0.014$, $^{207}\text{Pb}/^{204}\text{Pb} = 0.006$, $^{206}\text{Pb}/^{204}\text{Pb} = 0.018$, $^{208}\text{Pb}/^{206}\text{Pb} = 0.0004$, and $^{207}\text{Pb}/^{206}\text{Pb} = 0.00012$, based on secondary standard NBS 982 ($n = 65$). External reproducibility for measurements with the Neptune were $^{208}\text{Pb}/^{204}\text{Pb} = 0.007$, $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{206}\text{Pb}/^{204}\text{Pb} = 0.002$, $^{208}\text{Pb}/^{206}\text{Pb} = 0.0002$, and $^{207}\text{Pb}/^{206}\text{Pb} = 0.00004$, based on secondary standard USGS NOD-A-1 ($n = 32$). Procedural blanks, <0.7 ng for acid-reductive and strong leach samples, were less than 1% of the smallest sample mass and therefore negligible. The procedural blank for the total dissolution samples was 1.22 ng, between 0.8 and 3.4% of sample mass, necessitating blank correction (see supporting information).

3. Results

3.1. Marginal Basin Sediments

The Pb isotopic compositions of the acid-reductive bulk sediment leachates from all three sections show regular cyclicity, changing in phase with lithology (Figures 2 and 3; supporting information, Table S2, Figure S1). As the lithological cyclicity at all three sites is precessional (Hilgen & Krijgsman, 1999; Krijgsman et al., 1997; Negri et al., 1999; Sierro et al., 2001), the cyclicity of Pb isotope compositions is most likely related to precession. Acid-reductive leaching accesses the authigenic seawater signal stored within FeMn oxyhydroxides; therefore, the records indicate that seawater Pb isotope compositions at all three sites fluctuated with precession.

In the basins with diatomites (Sorbas and Caltanissetta), the Pb isotope compositions are similar in both the sapropelic and homogenous marls (Figure 2). In contrast, the values “peak” within the diatomites; this behavior is particularly clear in $^{206}\text{Pb}/^{204}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$. Caltanissetta Pb isotope compositions display a narrower range than those from Sorbas, although the two ranges overlap significantly. These two records behave comparably, with the change in Pb isotope values occurring somewhat similarly both temporally and in magnitude.

A mirror-image relationship is observed for the Apennine Foredeep. For sediments here, the time-equivalent layers to the diatomites of the other locations are the homogeneous marls, according to the tuning. While these marls do contain rhythmic changes in seawater Pb isotopes, the

acidic lake have similarly shown that post-depositional Pb mobility did not occur (Davis & Galloway, 1993). Another potential issue, particularly at Falconara, is that some sapropelic layers show signs of tectonic disturbance, another process which could alter Pb isotope signatures (if, e.g., tectonism or instability is associated with fluid movement). If anoxia or tectonic disturbance perturbed the preserved Pb isotope signatures post-deposition, this should be apparent as an identifiable change within the sapropelic layers compared to the others, in particular at Los Molinos and Falconara where more than two lithologies are present. Only Pb isotope values observed within the diatomites at these two sites show a significant difference (Figures 2 and 3), whereas the marls and sapropelic layers are very similar. We therefore conclude that no significant resetting has occurred and our Pb isotope records, derived by exploiting the FeMn oxyhydroxide particle coatings, preserves the original seawater Pb isotope compositions.

A further issue requiring consideration is our assumption that Pb isotope compositions archived in the FeMn oxyhydroxides reflect the compositions of seawater rather than porewater. Ideally, a study such as that performed by Du et al. (2016) for Nd isotopes would allow for the quantification of porewater control on the archived Pb signal. Unfortunately, core top sediments integrate over decades to centuries, while anthropogenic Pb inputs varied considerably over these time scales: increasing with the onset of industrial activity and the use of leaded gasoline and more recently decreasing with the implementation of environmental regulation and phasing out of leaded gasoline (Rusiecka et al., 2018). This is particularly true for the Mediterranean as it experiences a larger human impact by volume relative to the Atlantic or Pacific. The very short residence time of Pb in the troposphere (less than a week; Moore et al., 1973; Turekian et al., 1977) leads to a near-instantaneous change in Mediterranean Sea Pb (Nicolas et al., 1994). Consequently, core top sediment Pb isotope compositions are not necessarily expected to reflect the composition of modern seawater (e.g., Alleman et al., 2000; Huy et al., 2015; Kamenov et al., 2009), and correspondingly, there is a paucity of information in the literature dealing with Pb isotope compositions in marginal Mediterranean sediment porewaters. However, in addition to these studies which indicate that Pb mobility is low, a few have shown results consistent with our assumption of substantial seawater control. A recent study in Arctic waters found that Pb is largely in the colloidal phase (Marsay et al., 2018), implying at least a significant proportion of the Pb in oxyhydroxides is formed in the water column. The concentration of Pb in the oxyhydroxide fraction is generally much higher than in the detrital siliciclastic component (Gutjahr et al., 2007), implying that Pb released to pore waters from particles post-deposition would have the same composition as seawater at the time of deposition. Finally, the experiments performed by Davis and Galloway (1993) also showed that post-burial diffusion of Pb through the sediment profile does not occur, even with highly undersaturated porewaters at low pH. We therefore infer that changes in Pb isotope compositions of FeMn oxyhydroxides are primarily driven by changes in seawater and that these records are therefore likely to be reliable archives of primary seawater Pb isotope compositions.

The apparent stability of Pb in FeMn oxyhydroxides may be explained by the strong affinity between Pb and hydrous manganese oxides, in particular birnessite (δ -MnO₂; Gadde & Laitinen, 1974; Komárek et al., 2013; Slavek & Pickering, 1985). Mn-oxides including δ -MnO₂ exist in high concentrations in the authigenic FeMn oxyhydroxide fraction accessed by our leaching process. This affinity is so important that the use of manganese oxides is highly encouraged for remediation of Pb-contaminated soils and wastewater across a wide range of pH (Gasparatos, 2013; Islam et al., 2018; Komárek et al., 2013).

3.3. ODP Site 978

The results of acid-reductive leachates from ODP Site 978 are shown in Figure 3. The range of compositions generally encompasses those observed in the marginal basins, with the exception of some values observed from the Apennine Foredeep. Three of the four samples are very similar in composition, while one is quite high (radiogenic) in comparison (48R-1 W 13–15 cm). There is no obvious sedimentological reason for the difference. Analysis was repeated on a new portion of material and the radiogenic Pb isotopic composition was confirmed. These results are tabulated in the supporting information, Table S5. The samples from ODP Site 978 are all thought to be younger by ~250 to 300 ka than those of the marginal sites. Thus, while these results provide Pb isotope compositions for Alborán Sea water in the late Miocene, somewhat differing values from compositions observed in the marginal sites may be expected.

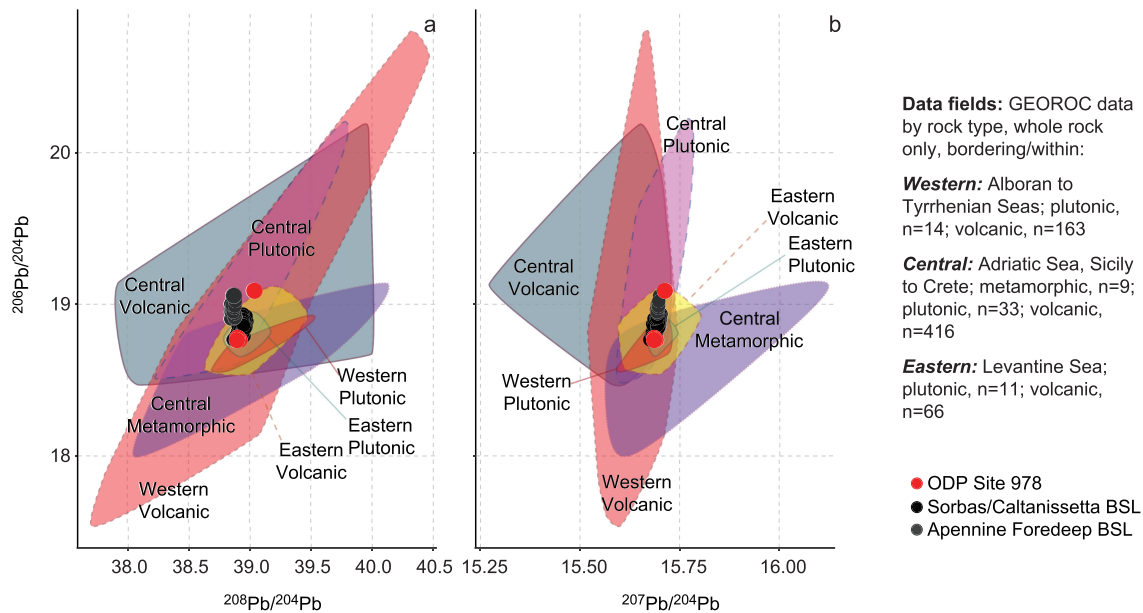


Figure 4. Seawater Pb isotope compositions compared to Miocene or older circum-Mediterranean whole rock data from the GEOROC database (see Figure 1 for sub-basins).

4. Discussion

In all three marginal basins, the Pb isotope signature changes with precession (Figure 2). The records presented here are, to the best of our knowledge, the first evidence that authigenic Pb isotope records preserve precessional cyclicity. Other locations, which might have been expected to show similar frequencies, have not (for example, the Indian Ocean; Wilson et al., 2015). This suggests the phenomenon may be restricted to the Mediterranean, though since Neogene stratigraphy is pinned exclusively to Mediterranean sediments, this result has global implications. Due to the short residence time and highly particle reactive nature of Pb in seawater, and the fact that post-depositional resetting is not observed, it is likely that these changes are climate-driven and reflect the strongly precessional cyclicity observed in other Mediterranean climate records. The challenge remaining is to identify the process(es) forcing Pb isotope changes across precessional cycles in the Mediterranean region. The following discussion presents the available data for the major Pb sources to the region, followed by an exploration of the most likely climatic drivers.

4.1. Regional Geology

Anthropogenic Pb has drastically altered natural Pb isotope signatures in Earth's atmosphere and surface waters (Bollhöfer & Rosman, 2001; Boyle et al., 1986; Chow & Patterson, 1962; Hamelin et al., 1997; Noble et al., 2015; Nriagu, 1979; Settle & Patterson, 1982). As a result, modern spatial patterns in seawater Pb isotope compositions cannot provide the necessary information to detect natural input sources, unlike other commonly employed water mass tracers such as Nd (e.g., Frank et al., 1999; Gutjahr et al., 2008; Jones et al., 2008). Fortunately, Pb isotope compositions from the surrounding geology fully account for the range of signatures recorded at the study sites during the late Miocene. Figure 4 compares the values observed at ODP Site 978 and the three marginal sites with all Neogene or older circum-Mediterranean whole rock data available from the GEOROC database (data set IDs listed in the supporting information). The seawater estimates from all four sites plot near the center of the whole rock data. This comparison implies, first, that the seawater Pb isotope compositions observed in our records reflect an average signal derived from circum-Mediterranean geology, and second, that processes such as incongruent weathering are not required to explain the observed seawater Pb isotope compositions. Furthermore, the relationship with the Site 978 data shows that all three marginal basin sediments are recording Pb isotope signatures similar to those expected for the main Mediterranean basin, at least periodically. The latter observation is important because access to marine sediments predating the MSC with precessional resolution age

control is limited to deposits from marginal, potentially restricted, basins like those investigated in this study, which are potentially not representative of the wider open Mediterranean. Finally, it is likely that this regional geological signal is transported fluvially towards the basins, which would help explain some of the variation between sites; particularly, the variation between sites observed from lithologies assumed to be deposited during wetter conditions (i.e., sapropelic layer and perhaps homogeneous marl deposition).

The record from the Apennine Foredeep is the only one which includes values outside the range observed at ODP Site 978 (Figure 3). It also has a pattern of Pb isotope cyclicity that mirrors that of the other two sections. The seawater values from the Apennine Foredeep are generally less radiogenic in $^{208}\text{Pb}/^{204}\text{Pb}$, more radiogenic in terms of $^{206}\text{Pb}/^{204}\text{Pb}$ (Figures 2, 3, and 4), and about the same in $^{207}\text{Pb}/^{204}\text{Pb}$ (Figures 4 and S1). $^{207}\text{Pb}/^{204}\text{Pb}$ is not expected to be diagnostic of environmental changes; there is restricted variability between sources for ^{207}Pb in the region, and thus, ^{207}Pb does not exhibit the range of ^{208}Pb or ^{206}Pb (Figure 4b; supporting information, Text S3). The most likely explanation for the observed differences is tectonic uplift causing local geology (and its Pb isotopic composition) to overwhelm regional signals via enhanced weathering and input. The observed trends are reflected in the whole rock data specific to the central and western Mediterranean (Figure 4). A large proportion of these data comes from the Italian Alps and Apennines, mountain ranges which bounded the Apennine Foredeep during the late Tortonian/early Messinian around the same time a marine connection spanning Northern Italy was closed (Jolivet et al., 2006). As uplift progressed, the foredeep narrowed to an east-west trending trough, with only a connection to the northern Adriatic Sea remaining at the time the sediments investigated here were deposited; in this setting, the local geology would be expected to play a much more important role in the Pb isotope composition of the sub-basin than signatures transported by currents from further afield. Compared to the other basins, it is possible that circulation of water originating from the open Mediterranean was more restricted, because the connection was only provided via the relatively long and shallow Adriatic. This interpretation is consistent with the long-term trend towards values increasingly different from the other two sub-basins as the Foredeep record gets younger (Figure 2). Furthermore, another source affecting all basins could be dust derived from North Africa (discussed further in section 4.4), while the Apennine Foredeep was situated northwards of the main Apennine range. In the modern environment, the mountain ranges bounding the Mediterranean to the north have been observed to block northwards transport of dust (Marinou et al., 2017), suggesting this potential source could have been diminished relative to the Sorbas and Caltanissetta Basins. Consequently, both restriction from the Mediterranean and ongoing uplift of local topography could explain why complete convergence does not occur during the youngest two precessional cycles in the Apennine Foredeep record.

4.2. Fluvial Transport

Fluvial input is an important mechanism for the transportation of Pb from the regional source rocks to a basin. Fluvial fluxes are also an important component of a basin's hydrologic budget, which could fluctuate with precession and impact the Pb budget. The behavior of other isotope systems, such as Sr or Nd, in the Mediterranean has been successfully modeled (e.g., Cornuault et al., 2018; Modestou et al., 2017; Tachikawa et al., 2004), providing much needed insight into the physical processes responsible for shifting isotope signatures, including changes in fluvial fluxes. However, in the case of Pb, so little is known about natural Pb riverine concentrations in the Mediterranean region that it is difficult to assess the validity of model results for isotopes of this element. For example, based on the short residence time of Pb in the oceans, it could be assumed that unaltered Pb concentrations in rivers may be similar to that of unpolluted seawater (<7 pg/L, Lee et al., 2015); therefore, a reasonable range of concentrations to test might range from 0.5 to 10 pg/L. Model results will be highly sensitive to concentration, yet this range spans two orders of magnitude. With available information, validation of the concentration parameter is essentially impossible; thus, it is difficult to know how informative modeling seawater Pb in this region might be.

For the reasons outlined above, we adopted a different approach, employing Sorbas Basin sediment Pb isotope compositions to test whether precessionally fluctuating fluvial discharge exerted control on the observed seawater Pb isotope compositions. The strong leach and total dissolution samples from Sorbas provide the signature of easily-weathered and refractory detrital siliciclastics, respectively, derived from local riverine transport. Considering the bulk leachate data, representing seawater values, from the Sorbas Basin in Pb-Pb space (Figure 5, all plots), the shift in Pb isotopic compositions from insolation maxima to minima occurs on a quasi-linear mixing line. While the compositions corresponding to insolation maxima

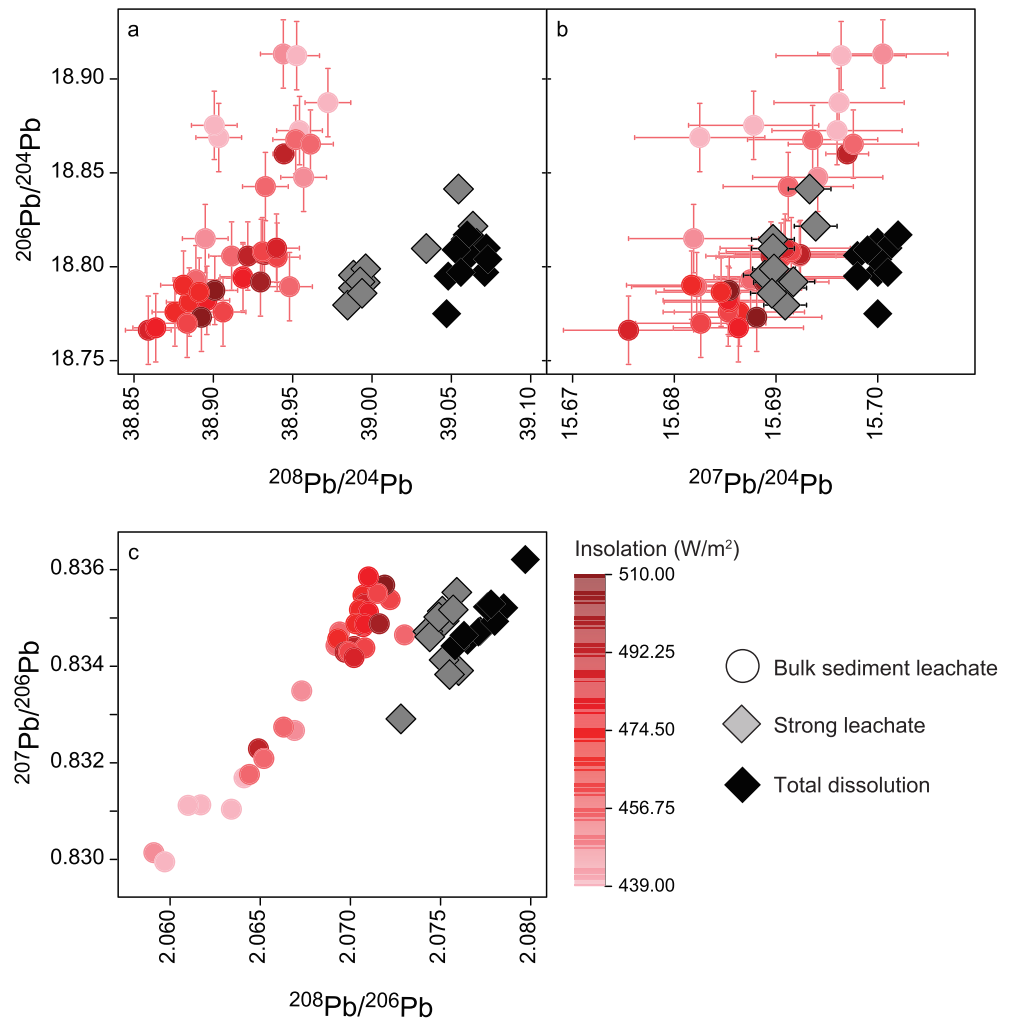


Figure 5. Pb/Pb crossplots of bulk sediment leachates, total dissolution, and strong leachates from the Sorbas Basin. Bulk sediment leachates are color-coded by insolation, with lighter colors indicating lower insolation. Any quasi-linear trend in the bulk sediment leachates (which provide the seawater value) between insolation maxima and minima does not encompass the local detrital siliciclastic signature (total dissolution and strong leach samples). Bars indicate 2SD external reproducibility; where not visible, uncertainty is smaller than the symbol.

are generally nearer the detrital signatures, the mixing line does not pass through the total dissolution compositions. The mixing line does pass through or at least move closer to the strong leachates; however, this does not occur near the more radiogenic endmember. These relationships suggest that while fluvial inputs may have influenced seawater Pb isotope compositions, they are not responsible for the more radiogenic compositions at insolation minima. This is consistent with the relatively small changes in the hydrologic budget across precessional cycles expected for the Western Mediterranean (Marzocchi et al., 2019; Modestou et al., 2017).

Additionally, increases in fluvial discharge are expected to occur concurrently with sapropelic layer deposition, but the sapropelic layers and homogeneous marls preserve essentially the same Pb isotope signatures at both Sorbas and Caltanissetta. Thus, the climate induced shifts in seawater Pb isotope signatures at insolation minima are not likely to be related to increased fluvial flux, since this is linked to sapropelic layer deposition.

4.3. Atlantic Inflow

In the modern configuration, there is significant exchange between the Northeastern Atlantic and the Mediterranean through the Gibraltar Strait (Atlantic inflow ~ 0.8 Sv, Mediterranean Outflow ~ 0.7 Sv,

Garcia-Lafuente et al., 2011; Tsimplis & Bryden, 2000; $1 \text{ Sv} = 10^6 \text{ m}^3/\text{s}$). Thus, water from the Atlantic is a significant source of dissolved Pb to the Mediterranean basin. While the connections between the Atlantic and Mediterranean were different in the late Miocene, exchange was not interrupted until at least onset of the MSC at 5.971 Ma (Flecker et al., 2015; Manzi et al., 2013). Long-term Pb isotope records from four hydrogenetic FeMn crusts from the Northeastern Atlantic (Figure 1) are available for comparison. These crusts (65GTV, Abouchami et al., 1999; 3514-6, 3511-1, and 3513-14, Muiños et al., 2008) were formed in a region strongly affected by the Mediterranean Outflow (MO) plume. Each crust precipitated at a different depth, recording different admixtures of local water masses, including the MO (3514-6, ~800 m; 65GTV, 1,500 m), Northeastern Atlantic Deep Water (3511-1, ~2,400 m), and Antarctic Intermediate Water (3513-14, ~4,600 m). The admixtures of Pb recorded in the crusts may be biased towards Mediterranean values, since other trace metal concentrations in MO are generally higher than in surrounding Atlantic waters (Duce et al., 1991; Maring & Duce, 1987). Only late Miocene crust Pb isotope compositions are compared to the compositions from ODP Site 978 and the marginal basin values in Figures 6a and 6b.

The Pb isotope compositions for the crusts is relatively close to the lowest ratios observed at the four Mediterranean sites, while the values fall along a sub-linear trend in Pb/Pb space similar to the trends observed in all sites except the Apennine Foredeep. This observation supports the influence of both the Atlantic and Mediterranean at the extra-Mediterranean locations of the crusts (Figures 6a and 6b). However, since the Pb isotope “peaks” in the Sorbas and Caltanissetta Basins trend towards higher values, it is unlikely that the precessional cyclicity observed is related to variation in Mediterranean-Atlantic exchange.

4.4. Dust

Dust has been hypothesized to provide 12% of oceanic Pb globally, while particulates with Pb-rich surface coatings are expected to contribute more Pb on a regional basis (Henderson & Maier-Reimer, 2002). Currently, the Sahara and Sahel regions of North Africa produce ~50% to 70% of global mineral dust, emitting 400 to 2,200 Tg/year (Ginoux et al., 2012; Huneus et al., 2011; Tanaka & Chiba, 2006). The Bodélé Depression in central Chad (Figure 7) is recognized as contributing more mineral dust to the global budget than any other single source in the world (Huneus et al., 2011; Tanaka & Chiba, 2006). While Saharan and other North African dust sources are known to contribute significant dust to the tropical Atlantic, and regions as far as the Caribbean and the Amazon, significant amounts of dust from these sources are also deposited over the Mediterranean region (Figure 7; Grousset & Biscaye, 2005; Prospero, 1996).

Drier conditions are linked to increased African dust production today (Prospero & Lamb, 2003). This relationship extends to the past, such that at times of decreased soil moisture and vegetation cover, a direct result of drier conditions, dust production, and subsequent transportation is expected to increase (Lunt & Valdes, 2002; Mahowald et al., 1999). Therefore, at insolation minima when hydrologic cycling over the Mediterranean and North Africa is predicted to decrease (Bosmans et al., 2014, 2015; Marzocchi et al., 2015; Zhang et al., 2014), dust input to the Mediterranean likely increased. Observational data supporting this argument extend well into the Pliocene. Over the past 240 ka, deep Atlantic dust fluxes off the West African margin increase in parallel with decreases in insolation (Skonieczny et al., 2019). The study by Skonieczny et al. (2019) confirmed that orbital forcing, at the frequency of precession, is the dominant control on the timing of North African dust production. Records from various locations in the Central and Eastern Mediterranean, spanning periods of the Plio-Pleistocene and Quaternary, show a distinct orbital precession control on dust deposition (Dinarès-Turell et al., 2003; Emeis, Sakamoto, et al., 2000; Foucault & Mélières, 2000; Wehausen & Brumsack, 2000). For the past 3 Ma, increased North African dust inputs to the Eastern Mediterranean during insolation minima are evidenced by increases in Ti/Al and hematite (Larrasoña et al., 2003).

The Sahara Desert is thought to have existed since at least the late Miocene (Schuster et al., 2006, 2009; Zhang et al., 2014). North African aridity likely first arose during the middle Miocene, after the connection between the proto-Mediterranean and the Indian Ocean was lost (Zhang et al., 2014). Evidence of Saharan dust as old as ~7.4 Ma is found north of the Eastern Mediterranean in present day Bulgaria (Böhme et al., 2018).

A compilation of available estimates for the Pb isotope composition of Saharan dust plots near the less radiogenic end of the marginal basin seawater values (red asterisk, Figures 6c and 6d; Abouchami & Zabel, 2003),

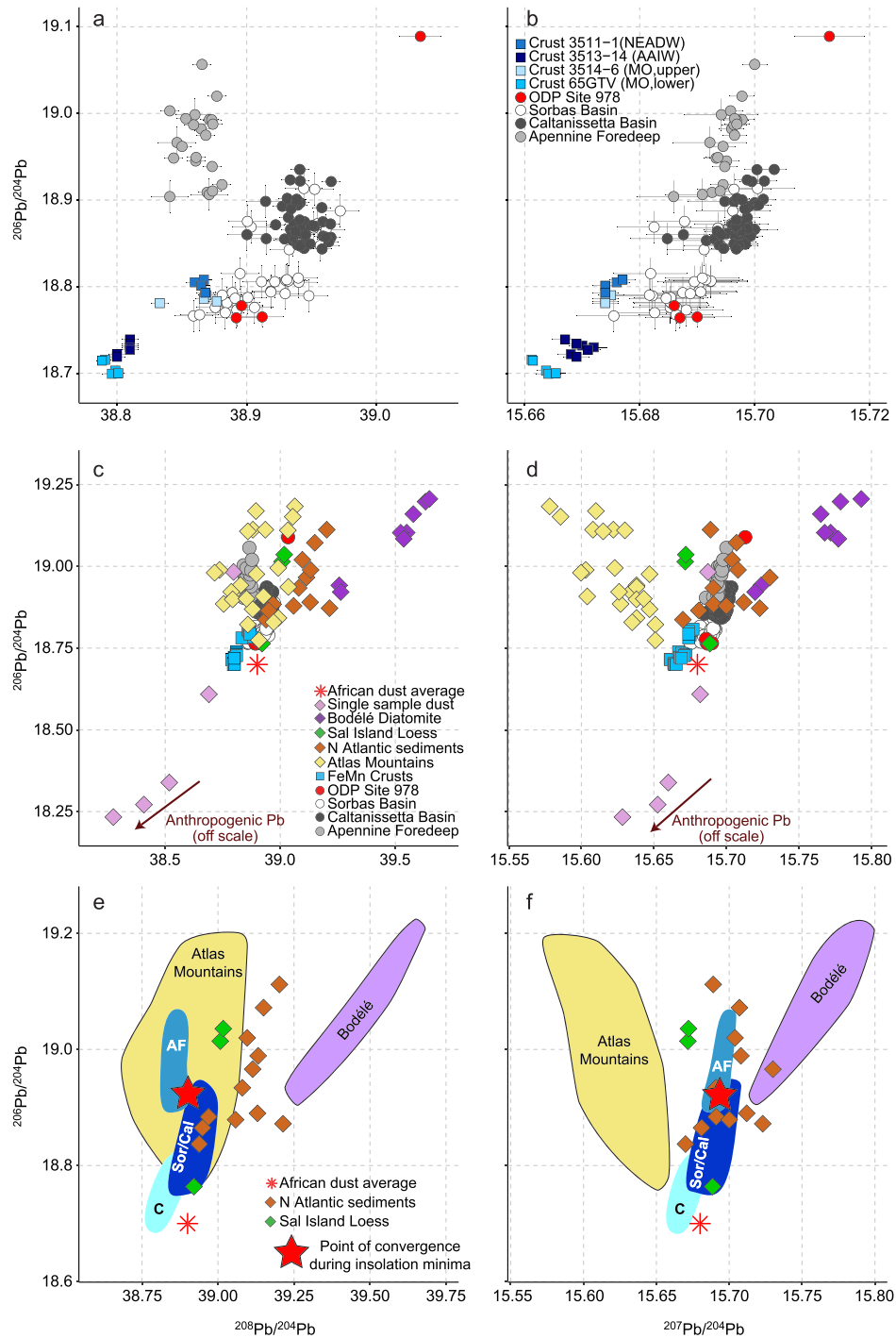


Figure 6. (a and b) Marginal basin Pb isotope compositions compared to open marine ODP Site 978 (this work) and crusts deposited on the Atlantic side of the Gibraltar gateway (Abouchami et al., 1999; Muñios et al., 2008). Abbreviations indicate water masses sampled by crusts: MO = Mediterranean Outflow (upper and lower indicate relative depths in plume), NEADW = North Eastern Atlantic Deep Water, AAIW = Antarctic Intermediate Water. (c and d) Seawater data compared to modern African dust measurements, modern dust sources, and deposits with significant dust content. Asterisk represents average computed by Abouchami and Zabel (2003); $^{208}\text{Pb}/^{204}\text{Pb} = 38.90$, $^{207}\text{Pb}/^{204}\text{Pb} = 15.68$, $^{206}\text{Pb}/^{204}\text{Pb} = 18.70$. Individual dust samples (pink diamonds), Sal Island loess (green diamonds), and Bodélé Depression diatomite (purple diamonds) from Abouchami et al. (2013), Northeastern Atlantic sediments from Sun (1980). Atlas Mountains (yellow diamonds) from GEOROC database (see supporting information). Anthropogenic Pb isotope values from Bollhöfer and Rosman (2001); $^{206}\text{Pb}/^{204}\text{Pb} = 17.02$ – 18.20 , $^{207}\text{Pb}/^{204}\text{Pb} = 15.43$ – 15.64 , $^{208}\text{Pb}/^{204}\text{Pb} = 36.66$ – 38.10 . (e and f) Simplified version of (c and d) with unreliable sources removed (discussion in text) and data groups reduced to fields for clarity. Fields and points with black outline indicate whole sample analyses, blue fields indicate seawater signatures derived from leachates (AF = Apennine Foredeep, Sor/Cal = Sorbas and Caltanissetta Basins) or crusts (C). Red star indicates point of convergence in Pb/Pb space between Apennine Foredeep, Sorbas, and Caltanissetta Basin values at insolation minima.

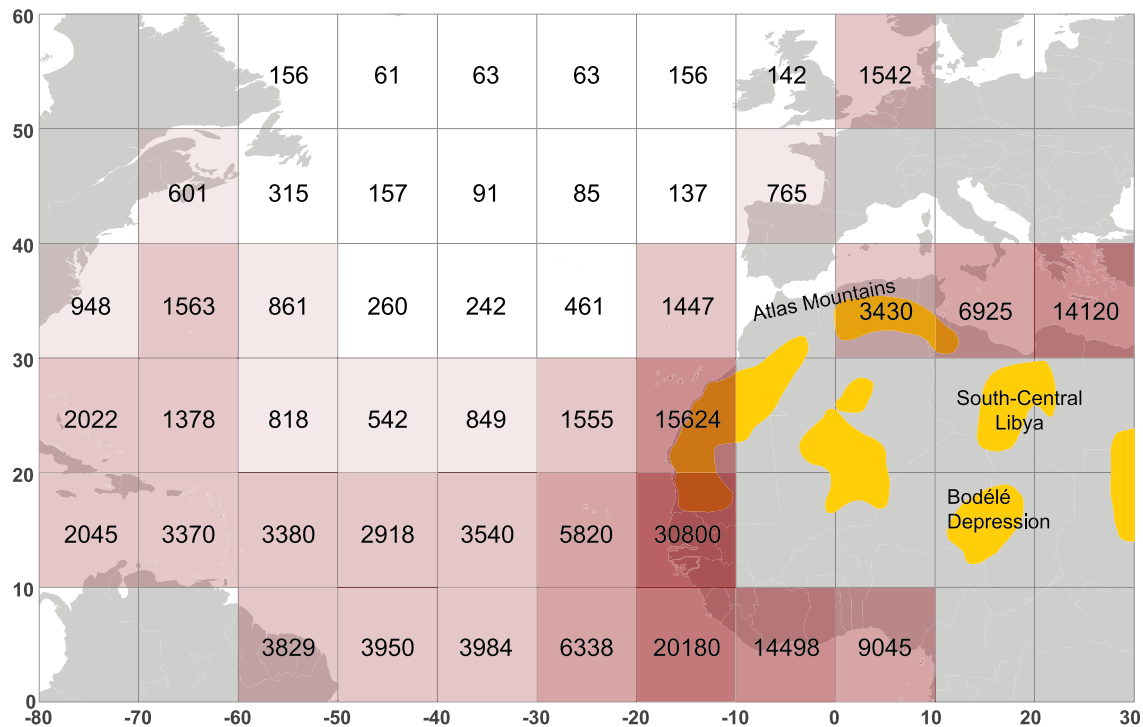


Figure 7. Estimated annual aerosol deposition rates (mg/m^2) for the North Atlantic and Mediterranean. Based on Goudie and Middleton (2001) and data from (Prospero, 1996). Important sources of African dust are highlighted, including the Principal Source Areas (yellow regions) proposed by Scheuven et al. (2013).

lower than the Pb ratios on which all three sections converge (red star, Figures 6e and 6f). At face value, this relationship suggests that African dust cannot account for the compositions observed during insolation minima. However, modern dust Pb isotope compositions are considered unreliable as indicators of natural sources because of anthropogenic contamination (Scheuven et al., 2013).

Data from the Bodélé Depression illustrate this point. Diatomite from this location, the primary sediment type transported as dust from the Bodélé Depression, has a relatively radiogenic Pb isotope signature compared to direct dust measurements. Both the African dust compilation value estimated by Abouchami and Zabel (2003) and modern-day individual dust samples from Niger and Chad (Abouchami et al., 2013) are unradiogenic in comparison (Figures 6c and 6d; compare African dust, pink diamonds, Bodélé Depression diatomite, purple diamonds, and marginal basin compositions, circles). Furthermore, individual dust sample Pb isotope compositions plot in a trend which deflects toward values observed for tetra-ethyl Pb additives in Europe, North Africa and the near East (arrows, Figures 6c and 6d; Bollhöfer & Rosman, 2001). Niger and Chad are the most proximal countries to the Bodélé Depression, confirming dust does not require long transport times in the atmosphere to acquire an anthropogenic signal. This validates the suspicion that approximations of natural Pb isotope signatures derived from modern dust do not represent natural Pb isotope compositions and therefore cannot be used to reconstruct past dust Pb isotope signatures (see supporting information for further discussion; Hamelin et al., 1989; MacLean et al., 2011).

Given that estimates of the natural Pb isotope compositions of North African dust are unreliable, the most appropriate sources available to represent natural North African dust Pb isotope signatures are the sources themselves or loess deposits near the region. In addition to diatomite from the Bodélé Depression, there are three other published data sets representing potential proxies for North African dust. Each of these data sets indicate North African dust includes more radiogenic Pb isotope compositions than the estimates of Abouchami and Zabel (2003) and the modern dust measurements of Abouchami et al. (2013) from the following deposits:

- Loess from Sal Island (Cape Verde, off NW Africa; Abouchami et al., 2013). Nd and Sr isotope provenance analysis indicates that 80 to 95% of Sal Island loess originates from the Sahara (Rognon et al., 1996), while

back trajectory analysis indicates that the dust deposited here is sourced from various locations across North Africa (Chiapello et al., 1997).

- Mid-Holocene pelagic Northeast Atlantic marine sediments (Sun, 1980). These are considered to contain a strong North African dust signal due to very low sedimentation rates.
- The Atlas Mountain range of Northern Morocco and Algeria (Figure 7; data from the GEOROC database) is another important source of dust (Prospero et al., 2002; Scheuven et al., 2013), including contributing to Sal Island loess (Chiapello et al., 1997).

A simplified comparison with the marginal basin seawater data, including only the more reliable African dust proxy values, is provided in Figure 6e and 6f. The two fields describing the most reliable source Pb isotope compositions (Atlas Mountains, Bodélé diatomite) fall on either side of the dust sinks (marginal basin seawater, Sal Island loess, and Northeastern Atlantic sediments). Note that while age control for the loess and North Atlantic sediment samples is relatively poor, no significant changes in the geology of North Africa are thought to have occurred between the late Miocene and deposition of Sal Island loess and North Atlantic sediments. Though a direct overlap of source and deposit does not exist, mixing between the Atlas Mountains and Bodélé sources could generate the values observed in the Sal Island loess and North Atlantic sediments. In $^{206}\text{Pb}/^{204}\text{Pb}$ versus $^{207}\text{Pb}/^{204}\text{Pb}$ space (Figure 6f), this observation holds for the authigenic Pb isotope compositions from the marginal basins. However, in $^{206}\text{Pb}/^{204}\text{Pb}$ versus $^{208}\text{Pb}/^{204}\text{Pb}$ space (Figure 6e), compositions from the Bodélé source are not required to explain the seawater compositions, suggesting that one or more sources are missing. Unfortunately, there is a paucity of relevant Pb isotope data available to assess the Pb isotope contribution of other known dust source regions (yellow areas, Figure 7), making full characterization of the total range of dust Pb isotope compositions currently impossible. Spatial and temporal inhomogeneity are also not likely to explain the discrepancy since in the modern environment, dust from across the entire span of North Africa is observed to be lofted and transported northwards towards and across the Mediterranean each year (Marinou et al., 2017). Marinou et al. (2017) demonstrated that some sources are more important than others during specific seasons. For example, the entire Sahara produces dust uniformly during spring, whereas the Western Sahara becomes more important in summer. However, seasonality should not be visible in our records since each individual sample represents approximately a century of deposition, while the residence time of Pb is on the order of decades, supporting mixing of seasonal signals in the water column. While the timing of the Pb isotope excursions in our records supports dust as the most likely explanation, more information is required to fully characterize this potential source.

4.5. Potential Role of Seawater Pb Isotopes in Mediterranean Astronomical Tuning

The development of precessional-scale astronomical tuning in the Mediterranean was revolutionary (e.g., Hilgen et al., 1995; Lourens et al., 1996) providing a high-resolution geological timescale for the entire Neogene (Hilgen et al., 2012; Lourens et al., 2004) and enabling a more accurate and precise understanding of the timing of specific events such as the Messinian Salinity Crisis (Krijgsman et al., 1999). At sub-precessional timescales, however, there are two issues which have hindered the ability to move beyond this resolution.

First, variability within a precessional cycle remains difficult to resolve. Lourens et al. (1996) observed a ~3-ky lag from precession minima to the midpoint of youngest Eastern Mediterranean sapropel S1 based on ^{14}C dating; similarly, Topper and Meijer (2015) found that responses in a “typical” marginal Mediterranean basin may lag precession minima by ~3 ka. However, Weber and Tuenter (2011) describe general circulation model results indicating there should be little to no time lag for precessional climate forcing at midlatitudes. The discrepancy here cannot be due to sapropel burn-down, which should cause the apparent mid-point of the remaining layer to be older rather than younger.

Second, marginal basins bordering the Mediterranean, from which almost all of our understanding of the events prior to and during the MSC are derived, are particularly prone to leads or lags compared to open-water conditions in the Mediterranean before and after the event. In the Sorbas Basin, Pérez-Folgado et al. (2003) determined from foraminiferal assemblages that sapropelic layers do not coincide with insolation maxima, but rather are triggered by the transition from insolation minima to insolation maxima, implying they lead insolation maxima. In contrast, Modestou et al. (2017) found that Sorbas Basin sediment layers

may lag open Mediterranean deposition by ~ 1 ka based on hydrological modeling of Sr isotopes preserved in foraminifera.

The leads and lags observed from data-based studies are partly due to the complex processes mediating sapropel deposition, the fact that these may not be identical in all parts of the Mediterranean region, and post-depositional changes. Another factor influencing these observations is the practice of tying sapropel midpoints to insolation maxima and then assuming constant sedimentation between tie points. Despite the findings of Weber and Tuenter (2011), it is still posited that mechanisms causing deposition of sapropelic layers may lag behind insolation, since the response to higher insolation (specifically, increased precipitation over North Africa) and the conditions appropriate for increased organic matter preservation in sediments may not be immediate (Rohling et al., 2015). Further complicating the issue, post-depositional processes such as sapropel burn-down mean that the true extent of sapropelic layers are not always preserved. This issue is only partly countered by considering Ba/Al, a proxy that is relatively resistant to degradation, or other proxies such as foraminiferal assemblages. Comparing data sets from different open Mediterranean sites for the same sapropels, Rohling et al. (2015) found that specific details in these proxies match only over short distances. One explanation may be that the complex ecological responses such as competition for nutrients and oxygen availability during periods of intense productivity are highly localized. Compounding the problem further, sapropels are not deposited equally throughout the entire Mediterranean; for example, the Western Mediterranean basin lacks several of the Plio-Pleistocene sapropels observed in the Eastern basin (Murat, 1999). These “missing” sapropels, added to the differences in lithology between different marginal sites as well as open Mediterranean ones, exacerbate the issue of assigning accurate tie points to individual cycles.

An important limitation on the precision of orbital tuning in the Mediterranean is, therefore, the incomplete understanding of the sub-precessional relationship between sedimentation, climate, and insolation. Assuming increased North African dust flux to Mediterranean sediments during insolation minima (Larrasoana et al., 2003; Skonieczny et al., 2019) extends back in time to at least the Tortonian (Rohling et al., 2015; Zhang et al., 2014) and that this process is the causal mechanism of the changes observed in our records as discussed in section 4.4, the use of seawater Pb isotopes has the potential to be particularly powerful. Based on modern observations (Marinou et al., 2017), dust is expected to have a widespread contribution across the entire Mediterranean region, affecting both the deeper, open Mediterranean, and the more restricted, marginal basins. Seawater Pb isotope records may also avoid the problems of the leads and lags associated to sapropels as mineral aerosol lifetime in the atmosphere is thought to be on the order of days (Huneus et al., 2011; Tanaka & Chiba, 2006). These two properties, a wide regional impact and near instantaneous response time, in combination with the short residence time of Pb in seawater, suggest that seawater Pb isotope records may provide the ability to link individual beds with greater accuracy at sub-precessional resolution across the entire Mediterranean region. If this is confirmed with further studies, added benefits include the fact that this proxy is independent from other proxies currently in use, and the fact that it could provide a second tie point per precessional cycle at the opposite phase in the insolation curve (insolation minima vs. insolation maxima). Furthermore, dust-driven Mediterranean seawater Pb isotope cyclicity would represent a means to tune stages where sub-optimal ecological conditions existed (e.g., the MSC) or where sapropels are missing (e.g., the Western Mediterranean). Further back in time, suitable Global Boundary Stratotype Section and Points for the bases of the Burdigalian and Langhian have not yet been ratified (Hilgen et al., 2012) because candidate sections are lacking in some component of stratigraphic control, for example having poor magneto- or bio-stratigraphy. If precessional Pb isotope cyclicity extends to these stages, it could provide a solution.

As shown by the records presented here (Figures 2 and 3), seawater Pb isotope records will not provide unique signatures for a given sapropel in all locations, nor can they provide numerical dates. Moreover, tuning insolation to sapropelic layers remains the easiest means to perform orbital tuning on long sequences in the Mediterranean, although the bulk sediment leaching technique is possibly less time-consuming than methods such as counting foraminifera. However, for problematic sections, to improve constraints on time or sedimentation rate over shorter intervals or to provide solutions to research questions for which sub-precessional temporal accuracy is a necessity, Pb isotopes hold substantial potential. To validate this hypothesis, similar studies need to be undertaken in a wide range of locations, settings, elevated sedimentation rates, and ages.

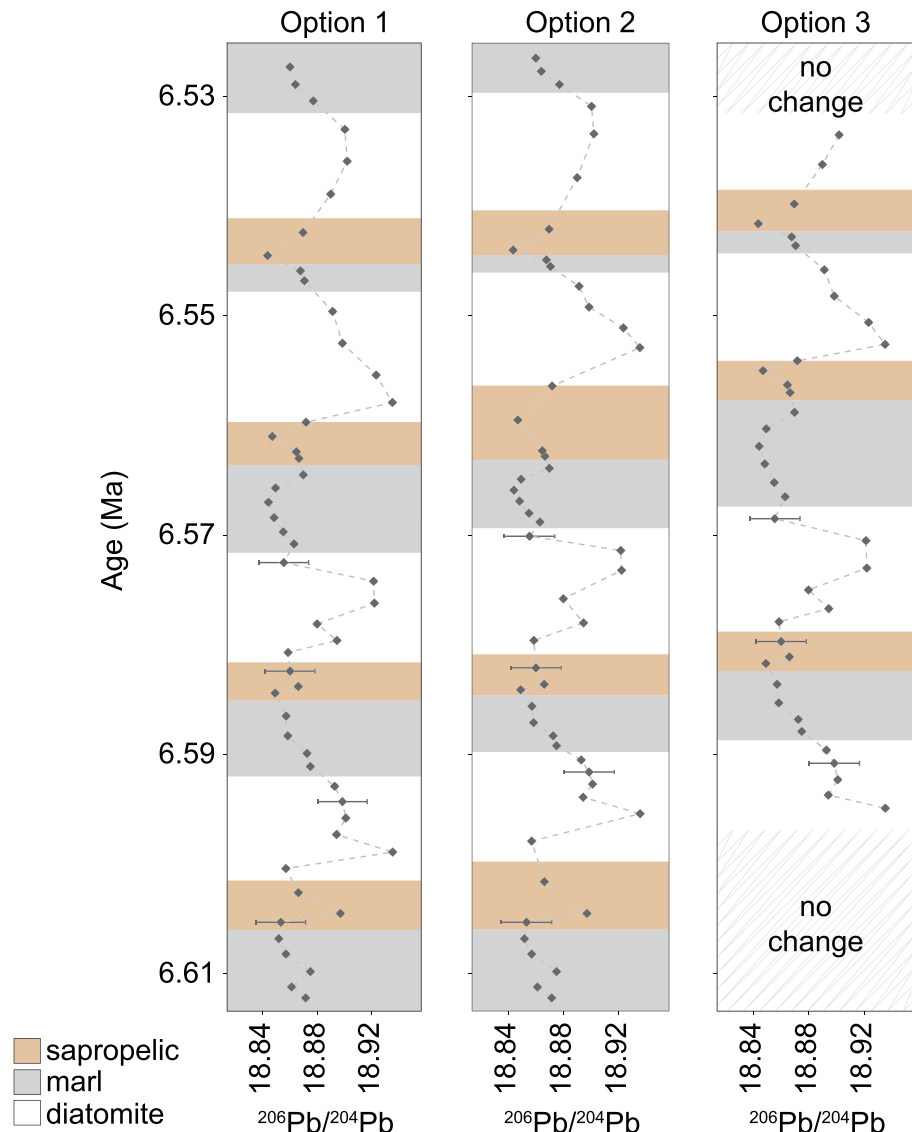


Figure 8. Comparison of alternative tuning options employing the tuning points provided by the peaks observed in the $^{206}\text{Pb}/^{204}\text{Pb}$ isotope record from the Caltanissetta Basin. “Option 1” indicates tuning of sapropelic layer midpoints to insolation maxima only. “Option 2” employs the $^{206}\text{Pb}/^{204}\text{Pb}$ peaks as second tie points tuned to insolation minima (in addition to the sapropelic layer midpoints); this leads to a maximum difference of 5 ka near insolation minima. “Option 3” solely employs the Pb isotope tie points and leads to a maximum difference of 6.2 ka. “No change” is indicated where the lack of an additional tie points does not permit retuning.

For the three sections investigated in this study, we tested the degree to which the tuning of the sections would change using the Pb isotope records (Figure 8). Three schemes were compared: the original tuning, using sapropelic layer midpoints as the sole tie point (option 1); applying a second tie point where peaks in the $^{206}\text{Pb}/^{204}\text{Pb}$ records were tied to insolation minima (option 2); and where the $^{206}\text{Pb}/^{204}\text{Pb}$ peaks are the sole tie point (option 3). For the Sorbas Basin, applying the different tuning regimes led to a maximum difference at any given point in the sequence of only ~1 ka, a small and rather negligible difference implying the original tuning of the Los Molinos section is very accurate. For the Apennines Foredeep, the lower temporal resolution of the data precludes this from being a useful exercise. However, for the Caltanissetta Basin, the maximum discrepancy was significant; 5.0 ka using option 2 and 6.2 ka using option 3 (Figure 8; see supporting information for tabulated age differences). The alternate tuning also affects the duration of each lithology; with option 2, the time span of the homogeneous marls is shortened, while that of the sapropelic layers is extended.

5. Conclusions

The three marginal basins investigated here in high resolution show clear precessional cyclicity in their seawater Pb isotope compositions. This indicates that Pb isotopes are a sensitive recorder of climate-driven shifts in inputs to the marginal Mediterranean marine system.

Determining the mechanism driving the cyclicity is more difficult, caused by the lack of reliable modern analogues. Comparing the different compositions observed between the sites, the Pb isotope ratios at all locations converge to similar values approximately at insolation minima. The most likely explanation for this is an increase in Mediterranean-wide dust deposition, transported from North Africa. Considering both the fact that the peaks in Pb isotope composition occur within the sedimentary layers associated with drier conditions, as well as the comparison with strong leachate and total dissolution data from the Sorbas Basin, it is unlikely that precessional changes in river runoff are responsible. More data on the Pb isotope composition of important dust source material and natural Pb concentration and isotope composition of rivers in the Mediterranean region are needed to test this hypothesis.

If Mediterranean seawater Pb isotopes are driven by dust patterns, this proxy may provide a crucial second tie point per astronomical cycle, one which may be more accurate considering the ambiguities related to tuning by sapropelic layer midpoint, and which does not require the presence of sapropels at all. Consequently, Pb isotope ratios may provide the means to correlate accurately between beds at widespread locations with varying depositional regimes. Testing different methods of tuning using the peaks in the $^{206}\text{Pb}/^{204}\text{Pb}$ records indicates little change in individual ages for the Sorbas Basin, but up to 6.2 ka change in Caltanissetta Basin sediments. Further research into spatiotemporal records of seawater Pb isotopes in the Mediterranean, for sediments deposited both in marginal and deep settings, and at various points in the Neogene, is warranted in order to test this proxy as a new tool for orbital tuning of Mediterranean stratigraphy.

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