



Invited review

Paleoclimate and paleoceanography over the past 20,000 yr in the Mediterranean Sea Basins as indicated by sediment elemental proxies



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ABSTRACT

Marine sediments record paleoenvironmental changes over time through variations in major and trace element concentrations. The main objective of this paper is to review such changes in the Mediterranean Sea basins over the last 20 ka, using the inorganic chemistry and mineralogy of marine sediment records. Elemental ratio proxies that are mostly used are discussed, and the uncertainties involved in using them for paleoclimate and paleoceanographic reconstructions are evaluated. The focus on the Mediterranean region is based on the sensitivity of this region to global climate changes due to its semi-enclosed nature. The elemental ratios that have been particularly useful for reconstructing terrigenous inputs into the Mediterranean have been Ti/Al and Zr/Al ratios as proxies for eolian dust input, and Mg/Al, K/Al and Rb/Al ratios as proxies for fluvial input. Redox sensitive elements (e.g., U, Mo, V, Co, Ni, Cr) have provided reliable reconstructions of oxygen conditions at the time of deposition. Some of these elements are also particularly susceptible to post-depositional remobilization and record diagenetic processes instead of the original environmental signatures. Regarding productivity fluctuations, most of the paleoproductivity reconstructions are based on the abundance of barite and Ba excess algorithms. The biogeochemistry of Ba is, however, not fully understood and mechanisms for barite precipitation in the water column are not yet known. Two case studies are presented: the eastern Mediterranean sapropel S1 (deposited between 10.8 and 6.1 cal ka BP) and the westernmost Mediterranean paleoclimate record over the last 20 ka.

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1. Introduction

The reconstruction of paleoclimate and paleoceanography relies on various established proxies for a spectrum of important physical, chemical, and biological environmental properties (e.g., Calvert and Pedersen, 2007). Globally, tree rings, pollen records, corals, speleothems, peat bogs, ice cores, and marine and lake sediments are the important paleo-archives used for paleoenvironmental studies. The resolution of these paleoenvironmental records depends on the quality of these natural archives.

This synthesis on the Mediterranean Sea Basins paleoenvironment in the past 20 ka is based on the extensive marine sediment

records available from this region. Marine sediments offer some unique aspects for paleoenvironmental studies because of the continuity of the records over the whole time span considered here. The resolutions provided are at the millennial to centennial time scale, or even decadal in certain regions of high-sedimentation rates. In order to unravel the highly diverse and interactive properties recorded in marine sediments, multiple geochemical methods have been used to develop proxies for paleoenvironmental studies, i.e., molecular biomarkers (e.g., Eglinton and Eglinton, 2008; Kim et al., 2010; Rampen et al., 2012, 2014; Rontani et al., 2013; Schouten et al., 2013; Weijers et al., 2014), stable isotopes (e.g., Pearson, 2012; Wit et al., 2013; Henkes et al., 2014; Levin et al., 2014) radiogenic isotopes (e.g., Frank, 2002; Bayon et al., 2009; Garçon et al., 2014), microfossil assemblages (e.g., Cléroux et al., 2013; Evans et al., 2013 and references therein), sediment grain size (e.g., McCave and Hall, 2006; Garzanti et al.,

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2009; deGelleke et al., 2013), and elemental ratios (e.g., Tribovillard et al., 2006; Calvert and Pedersen, 2007).

For the following properties, chemical composition and elemental ratios have turned out to become appropriate proxies: source of sediments, paleocirculation, paleoproductivity, depositional redox conditions, and diagenesis, as well as for reconstructing past climate variations and forcing mechanisms associated with climate variability at diverse scales. The use of these proxies has recently increased due to technical advances, such as X-ray Fluorescence (XRF) core scanners. Numerous paleoclimate studies have provided important information on regional and global scale patterns of climate variability in the Mediterranean region (e.g., Abrantes et al., 2012; Lionello, 2012; Malanotte-Rizzoli et al., 2014) (Fig. 1, Table Supplementary material). Its semi-enclosed nature and the relative short residence time of its water masses make it especially responsive to external forcing. In fact, it has been considered an exceptional natural laboratory for paleoenvironmental investigations (e.g., Krijgsman, 2002; Picotti et al., 2014) and it has also been identified as a “hotspot” for global change studies (Durrieu de Madron et al., 2011 and references therein). Furthermore, its latitudinal position where southern and northern climate regimes interact makes this region highly sensitive to climate changes (e.g., Lionello et al., 2006, Lionello, 2012). The excellent marine sediment paleoarchives provided a large database of sediment geochemistry in the Mediterranean basins.

High sedimentation rates in certain regions, such as the Alboran Sea or the Nile Delta have resulted in remarkably high-resolution records (Figs. 1 and 2). Special emphasis was placed on paleoclimate reconstruction over the last 20 ka. This time interval is of particular interest because of the significant climate and paleoceanographic restructuring that took place since the Last Glacial Maximum (LGM) (Table 1), of which the most important ones are the last Heinrich event (H1), the Bølling–Allerød (B–A) transition, the Younger Dryas (YD), and the Holocene climate oscillations, that have offered helpful insights on current climate variability (e.g., Schmittner et al., 2011).

Based on these considerations, in this paper a review and a synthesis of the diverse information acquired from the inorganic chemical composition and elemental ratios of marine sediments, in order to reconstruct the paleoclimate and paleoceanographic conditions in the Mediterranean basins over the past 20 ka, are the main focus. A brief summary of the use of chemical proxies for paleoenvironmental reconstruction in the Mediterranean is followed by a discussion of the sediment sources, depositional redox conditions, productivity fluctuations, and diagenesis. Case studies from the eastern and western Mediterranean basins are provided with an emphasis on the S1 sapropel record from the eastern Mediterranean basins, and on the Alboran Sea record. The main strengths and weaknesses of elemental proxies for paleoclimate and paleoceanographic reconstructions are as well discussed.

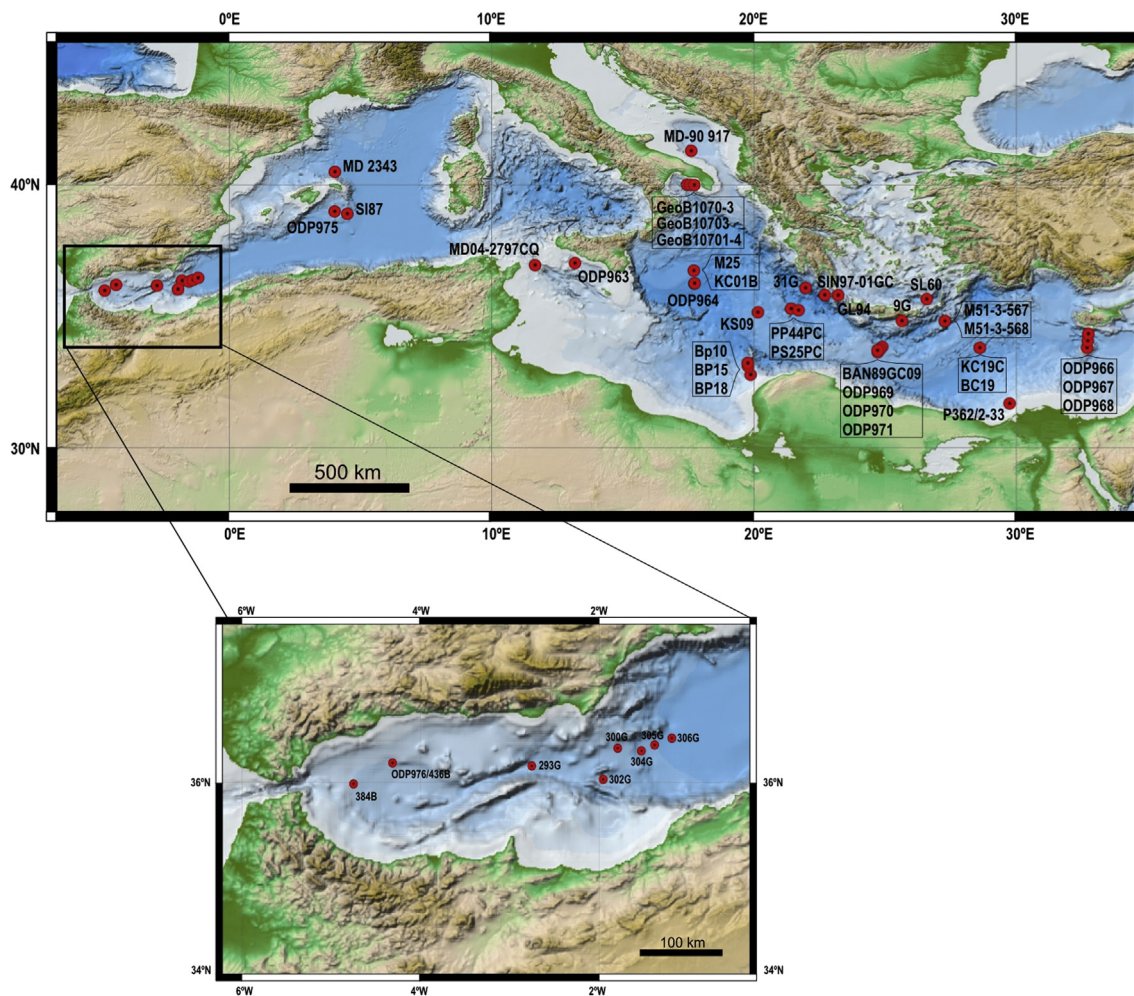


Fig. 1. Schematic map of the Mediterranean Sea showing the location of sites having records of elemental ratios for paleoenvironmental reconstruction over the last 20 ka (see Table as supplementary material for reference of proxies used at each site).



Fig. 2. Schematic map of the Mediterranean showing different basins and main rivers flowing to the Mediterranean. Sediment sources and major clay mineral inputs are indicated by theoretical arrows in green (riverine supply) and orange (aeolian input) (source data from Ehrmann et al., 2007; Bout-Roumzeilles et al., 2013).

2. Elemental ratios as paleoclimate and paleoceanographic proxies in the Mediterranean

The inorganic composition of marine sediments considered in this paper is to a large extent controlled by the sources (terrigenous, biogenic, and aeolian), sedimentation processes, and by post-depositional alteration. Sources, depositional and post-depositional processes are reconstructed by using suites of major and trace element proxies (e.g., Tribovillard et al., 2006; Calvert and Pedersen, 2007; Chang et al., 2014; Riedinger et al., 2014). In particular, paleoclimate and paleoceanographic reconstructions have been based on geochemical proxies, because climate changes often cause significant variations in the composition of marine sediments, influenced by terrigenous input, paleocirculation, and depositional redox conditions.

The chemical composition of the terrigenous fraction has been used to unravel the sources, provenance, and the fluctuations in the detrital input to the marine basins over time. Elemental ratios such as K/Al, Mg/Al and Rb/Al (Table 2), have usually been used to reconstruct the riverine supply of terrigenous material and Si/Al, Ti/Al and Zr/Al ratios to reconstruct the aeolian input (e.g., Calvert and Pedersen, 2007; Govin et al., 2012). Rare Earth Elements (REE) and their ratios have also provided relevant information on sources and detrital input variations (e.g., Révillon et al., 2011 and references therein), as REE patterns in sediments generally reflect the average REE pattern of the source rocks (e.g., McLennan, 1989, 2001; Condie, 1991; Taylor and McLennan, 1995). Regarding depositional conditions, redox sensitive elements concentrations (e.g., Mo, U, V, Ni, Ni, Mn) (Table 2) have offered essential information that characterize the redox conditions of deep-waters and of the sediments, as well as chemical and hydrographic properties of paleomarine systems (e.g., Algeo, 2004; Tribovillard et al., 2006; Algeo and Rowe, 2012; McKay and Pedersen, 2014). In addition, certain elements such as phosphorus, aluminum, and barium concentrations (Table 2) have helped to reconstruct marine paleo-productivity (e.g., Dymond et al., 1992; Paytan and Kastner, 1996; Schmidz et al., 1997; McManus et al., 1998; Paytan and Griffith, 2007). In general, all these geochemical proxies have become powerful tools in paleoceanographic studies (Tribovillard et al., 2006; Calvert and Pedersen, 2007).

As bulk elemental concentrations may be subjected to large fluctuations caused by variable proportions of biogenic versus detrital minerals, instead of using bulk major, minor, or trace element contents as paleoenvironmental proxies, normalized concentrations are being used. Although Al and Ti, which are the most refractory elements (Taylor and McLennan, 1985), have been regularly used for normalizations (Calvert and Pedersen, 1993; Morford and Emerson, 1999; Tribovillard et al., 2006), other refractory elements have also been considered for normalization, as Li (e.g., Loring, 1990; Loring and Rantala, 1992). Normalization, however, requires caution, in particular when the detrital fraction content is very low; the use of Al normalization is not appropriate in sediments with a detrital fraction lower than 3–5% or when there is a relative excess of Al (Kryc et al., 2003; Tribovillard et al., 2006). This is the case in the central Pacific, where the Al/Ti ratio is higher than the crustal ratio due to scavenging of oxy-hydroxides on biogenic particle surfaces (Murray and Leinen, 1993, 1996; Kryc et al., 2003). However, when the detrital contribution is high, as in the Mediterranean, Al could be considered as an indicator of the terrigenous aluminosilicate sediment fraction that generally behaves conservatively. Al-normalized concentrations have been therefore used in numerous sediment records to reconstruct paleoclimate and paleoceanographic changes in both the eastern and western Mediterranean basins (Fig. 2; Table supplementary material) (e.g., Wehausen and Brumsack, 1999, 2000; Calvert and Fontugne, 2001; Moreno et al., 2002, 2004; Jiménez-Espejo et al., 2007, 2008; Rodrigo-Gámiz et al., 2011; Nieto-Moreno et al., 2011, 2013a). In general, the Al-normalized ratios have offered important insights into past climate variations, providing a detailed reconstruction of paleoclimate fluctuations, climate cycles and forcing mechanisms associated at regional and global scales (for a detailed list of Mediterranean sites see Table in Supplementary material).

The eastern Mediterranean has been the subject of a larger amount of geochemical studies than the western Mediterranean, mainly focused on the origin of sapropels. They are organic-rich sediments with a total organic carbon content (TOC) > 2 wt% that were cyclically deposited by the combination of climatically induced increases in primary productivity and changes in bottom-water oxygenation (e.g., Calvert et al., 1992; Emeis et al., 2000a;

Table 1
Main climate intervals and events over the last 20 ka, time spanning for each event (ages expressed as calendar years before present, cal yr BP, where present is defined as 0 cal yr BP = 1950 yr AD), and paleoclimate conditions registered in southern Europe, the Mediterranean and northern Africa.

Climate intervals/Stratigraphic events	Calendar age (cal yr BP)	Cf. Reference (e.g.)	General paleoclimate conditions
2 nd half 20th century	Present day	Jansen et al., 2007	Dry
Industrial Period (IP)	150–0	Jansen et al., 2007	Humid
Little Ice Age (LIA)	650–150	Bradley and Jones, 1993	Humid
Medieval Climate Anomaly (MCA)	1150–650	Lamb, 1965; Hughes and Díaz et al., 1994;	Dry
Dark Ages (DA)	1600–1150	Berglund, 2003	Dry
Roman Humid Period (RHP)	2600–1600	Issar, 2003	Humid
Late Bronze Age–Iron Age (LBA-IA)	3600–2600	Van Geel et al., 1996	Dry
African Humid period (AHP)	14,800–5500 ^a	COHMAP Members, 1988; deMenocal et al., 2000; Gasse, 2000; Roberts, 1998	Humid
S1 Sapropel	10,800–6100	De Lange et al., 2008	Humid-warm
8.2 event	8200	Alley et al., 1997	Cold
Early-Middle Holocene	~11,500–5500	Siani et al., 2010	Dry-Humid
Organic Rich Layer 1 (ORL 1)	14,500–8900/8200 ^a	Cacho et al., 2002; Jiménez-Espejo et al., 2008; Rodrigo-Gámiz et al., 2011	Humid
Younger Dryas (YD)/GS1	12,890–11,650	Alley et al., 1993; Dansgaard et al., 1989	Cold, dry
Bölling–Alleröd/GI-1a-e	14,670–12,890	von Grafenstein et al., 1999	Humid-warm
Heinrich event 1 (H1)	16,500–15,700 ^a	Heinrich, 1988; Sierro et al., 2005	Cold, dry
Mystery Interval (MI)	17,500–14,500	Denton et al., 2006	Cold, dry
Oldest Dryas/GS-2a	18,000–14,670	Clement and Peterson, 2008	Cold
Last Glacial Maximum (LGM)/GS-2b	23,000–18,000	CLIMAP-Project-Members, 1976, 1981	Cold, dry

^a Differences in absolute date and time spanning depending on the paleorecord.

Meyers and Arnaboldi, 2005; Rohling et al., 2006). Although elemental ratios from western Mediterranean records have not been investigated as thoroughly as other paleoceanographic proxies, the available elemental ratios profiles (Table Supplementary material) have offered valuable information on climate fluctuations in this basin and their relationships to high latitude climates (e.g., Moreno et al., 2002, 2005; Jiménez-Espejo et al., 2007, 2008; Nieto-Moreno et al., 2011, 2013a, 2015; Rodrigo-Gámiz et al., 2011, 2014a).

With focus on the time window since the LGM, the evolution of the climate system leading to present day conditions has been punctuated by very significant climate events (Table 1). Some of these changes are still poorly understood, for example the Mystery Interval (MI) (17,500–14,500 cal yr BP), defined as the time period between the beginning of the H1 and the onset of the B–A transition. The frequency of these climate shifts is variable and many of the driving mechanism are as yet not fully constrained. However, the chemical composition of marine sediments has provided substantial insights on specific past climate variability, for instance on the dry and humid fluctuations during the H1, B–A, YD, the short-term late Holocene climate fluctuations (e.g., Nieto-Moreno et al., 2011, 2013a, b, 2015; Rodrigo-Gámiz et al., 2011; Moreno et al., 2012), and on paleoenvironmental changes leading to sapropel and other organic rich layer (ORL) depositions in the Mediterranean (e.g., Wehausen and Brumsack, 1999, 2000; Nijenhuis and de Lange, 2000; De Lange et al., 2008; Jiménez-Espejo et al., 2008; Rogerson et al., 2008; Gallego-Torres et al., 2010; Rodrigo-Gámiz et al., 2011; Hennekam et al., 2014; Konijnendijk et al., 2014).

Table 2
Main elements that have been normalized to Al and used as paleoenvironmental proxies in Mediterranean sediment paleorecords over the last 20 ka; common host mineral phases are also indicated. For references on the use of these proxies in particular records see Table in Supplementary material.

Elements	Proxy for	Host mineral
Zr, Si, Ti	Aeolian input	Zircon, quartz, rutile, sphene, and ilmenite
K, Mg, Rb	Fluvial input	Illite, chlorite, K-feldspars, fibrous clays, smectites, dolomite
Ba	Productivity	Authigenic barite
Oxidation state varies		
Mn, Fe, I, Cr, Mo, Re, U, V	Redox conditions/diagenesis	Oxides, oxi-hydroxides, sulfides
Oxidation state does not varies		
Cu, Ni and Zn	Redox conditions/diagenesis	Sulfides

3. Main sources of the elemental ratio proxies

3.1. Terrigenous sediment source proxies

The chemical composition of the sediment detrital fraction has been used to study Mediterranean paleorecords of terrigenous inputs and their sources. The most common element ratios that have been used as proxies for riverine terrigenous supplies are K/Al, Mg/Al and Rb/Al, and for aeolian inputs are Si/Al, Ti/Al, and Zr/Al (Table 2). REEs have also provided information on sediment sources and fluctuations in detrital input; in particular certain REE ratios such as the La/Lu ratio (e.g., Hamroush and Stanley, 1990), have been used to characterize fluctuations in the Nile input over time. In general, humid periods characterized by lower aeolian input, that for example led to sapropel deposition in the eastern Mediterranean, exhibit decreasing Si/Al, Ti/Al, Zr/Al ratios and enhanced K/Al, Mg/Al ratios (e.g., Wehausen and Brumsack, 1999, 2000; Warning and Brumsack, 2000; Nijenhuis et al., 2001). However, distinguishing between aeolian and fluvial sources of certain element ratios is challenging because both input sources may supply the same detrital minerals, thus have similar elemental ratios. Information on source rocks, transport processes, and mineral composition of the sediments is thus essential for precise interpretations of the sediment records. Grain size is as well a most important sediment property to be considered that could help to distinguish between fluvial and aeolian inputs and identify the presence of turbidites; the latter may significantly influence the mineralogy of the terrigenous sediment fraction, hence, the element ratios.

3.1.1. Riverine supply of terrigenous material

The composition of the sediments supplied by rivers to the Mediterranean basins is considerably variable. At present, the main supply to the eastern Mediterranean is derived from the Nile; southeastern European, and Turkish rivers also contribute to the eastern regions (Fig. 2). Other major sources are in central and western Mediterranean, the Po river, that is discharging into the Adriatic Sea, and the Rhône and the Ebro rivers that discharge into the western Mediterranean (see Bout-Roumzeilles et al., 2007, 2013 on sources and provenance) (Fig. 2). Detrital clays represent the major contribution from the rivers to deep basin areas, even though other minerals are also abundant, particularly in the coarse fractions. For instance, in the Rhône river calcite is the most abundant mineral in the coarse fraction of the suspended particulate material (up to 60% of non clay minerals), followed by quartz (up to 48%) and minor amounts of micas, feldspars, and dolomite (Ollivier et al., 2010). Relatively minor amounts of non-clay minerals are also transported by rivers offshore with the finer fractions.

Different source regions have different characteristic clay minerals that are transported by rivers to the Mediterranean basins (Fig. 2) (e.g., Ehrmann et al., 2007 and reference therein). In the eastern regions, such as the Levantine basin (Fig. 2) smectites are the dominant clay minerals delivered by rivers (e.g., Bout-Roumzeilles et al., 2007, 2013; Ehrmann et al., 2007; Hamann et al., 2009). The Nile-derived input, which is smectite-rich, has a strong influence in the eastern Mediterranean sediment composition. The Nile input is carried by the counter-clockwise surface water gyre that is transporting the sediments along the Israeli and Lebanese coasts and as far as the Mediterranean ridge (e.g., Stanley and Maldonado, 1981; Ehrmann et al., 2007). In the central Mediterranean, southern European rivers, for example the Po river that is flowing into the Adriatic Sea (Fig. 2), are transporting mostly illite and chlorite; the terrigenous material from the Alps is very rich in illite and also chlorite. In the western Mediterranean, where the Rhône is the most important source of sediments (Fig. 2), illite is the main clay mineral supplied by this river, though other minerals are also significant (e.g., Fanget et al., 2013); according to Ollivier et al. (2010) illite represents 38–84% of the clay mineral fraction, followed by smectite (3–43%), kaolinite (3–14%), chlorite (4–11%) and mixed illite/chlorite (0–9%). The Ebro river (Fig. 2) is as well rich in illite, although it also contributes some kaolinite and chlorite (Alonso and Maldonado, 1990). In the westernmost Mediterranean, in the Alboran Sea basin, the river contribution is from small drainage basins and is also very rich in illite (Fig. 2) (Martínez-Ruiz et al., 2003). In summary, the overall clay mineral assemblages in the central and western Mediterranean are dominated by illite with lesser proportions of smectite, chlorite, and kaolinite. A high input of illite in these regions derives from the rapid erosion of relative juvenile reliefs at the Alps and the Betic Cordillera.

Over time, changes in clay mineral assemblages reflect fluctuations in terrigenous provenance and transportation/distribution patterns that are influenced by climate conditions (e.g., Fagel, 2007). The substantial climate changes since the LGM (Table 1) have strongly affected the composition of the rivers sediment supply to the Mediterranean basins. In general, humid periods involving higher rainfall and freshwater runoff such as at the B–A transition or the S1 sapropel time interval resulted in increasing supply of fluvial detrital clays, which influence the major and trace element composition of the marine sediments. Indeed, Al normalized concentrations of terrigenous elements have served to characterize past climate fluctuations and river fluvial discharge (e.g., Blanchet et al., 2013). The relative supply of such elements mostly reflects the intensity of precipitation and erosional processes linked to climate conditions. As northern Mediterranean regions are a major source of illite, the increasing illite river supply

linked to humid intervals has led to increasing K/Al ratios in the sediments. In the eastern Mediterranean, for example in the Aegean and the Ionian seas (Fig. 1, ODP Sites 969 and 964), sapropel layers are characterized by higher K/Al ratios derived from increasing illite content (e.g., Wehausen and Brumsack, 2000). Likewise, this ratio has also been used in the study of paleorecords from the western Mediterranean to indicate humid periods (e.g., Jiménez-Espejo et al., 2007, 2008; Nieto-Moreno et al., 2011, 2013a; Rodrigo-Gámiz et al., 2011).

Because of substitution of Rb for K in some aluminosilicate minerals, the Rb/Al ratio has also served as a proxy for tracing fluvial inputs (e.g., Nieto-Moreno et al., 2011; Martín-Puertas et al., 2010; Rodrigo-Gámiz et al., 2011). However, it is important to note that in addition to illite the K/Al ratio is also influenced by the contribution of detrital K-feldspar that may be significant, particularly in the coarse fraction. The enrichment of Rb relative to K is greater in illite than in K feldspars. In fact Rb usually shows positive correlation with illite, and has been used as a grain-size proxy to indicate the amounts of fine-grained siliciclastic material in marine sediments (e.g., Dypvik and Harris, 2001). Therefore, thoughtful interpretations of the K/Al relative to Rb/Al ratios require careful mineralogical and grain size studies of the sediments analyzed.

Mg in the detrital fraction is associated with Mg-rich clays such as chlorite. In diverse eastern Mediterranean records, the profiles of Mg/Al parallel those of the K/Al ratios suggest a Mg input derived from northern European regions that are rich in illite and chlorite (e.g., Nijenhuis and de Lange, 2000; Wehausen and Brumsack, 2000). However, because chlorite abundance in the eastern Mediterranean Ridge region is sparse, it is rather difficult to explain the high Mg enrichments found in the sapropels from the Mediterranean Ridge area (Site 969) (Fig. 1), and another Mg-rich source is required. Wehausen and Brumsack (2000) suggested that during sapropel formation, the Greek rivers, draining catchment areas with ultramafic rocks and discharging into the northwestern Aegean Sea, supplied a greater volume of sediments particularly enriched in Mg due to its abundance in the source rocks. In the westernmost Mediterranean, diverse records have documented that Mg/Al and K/Al profiles are well correlated in certain intervals (Fig. 3) (e.g., Jiménez-Espejo et al., 2007, 2008; Rodrigo-Gámiz et al., 2011), suggesting that clays are the potential source for both K and Mg, which is consistent with illite and chlorite-rich source areas respectively. However, the link of Mg to chlorite is not always unique as other minerals such as dolomite, palygorskite (e.g., Sirocko et al., 2000) and to some extent Mg-rich smectites may also significantly contribute to the Mg input. As mentioned above, mineralogical analyses are also required for accurate interpretations of this elemental ratio.

The REE composition of marine sediments has also been used for terrigenous input reconstructions since it generally reflects the source rock REE patterns (e.g., McLennan, 1989; Condie, 1991). REEs are mostly hosted in clays and heavy minerals and they are mainly transported in detrital grains. Indeed Taylor and McLennan (1985) proposed that they are transferred almost in bulk from source to sediments. In the Mediterranean, REE composition has been used to reconstruct both fluvial and aeolian inputs (e.g., Censi et al., 2010). Regarding fluvial contribution it has been used as a tool for river sediment provenance (Révillon et al., 2011). As mentioned, certain REE ratios such as the La/Lu ratio, have as well served to document sediment sources and provenance in the eastern Mediterranean. This ratio offers a clear signature for the Nile riverine input. The North African regions exhibit lower La/Lu ratio than those from Central Africa, because of their different source rocks. Hence, as the North African region was particularly affected by the intensified monsoonal activity during insolation maxima, these areas were intensively eroded and provided a major source of

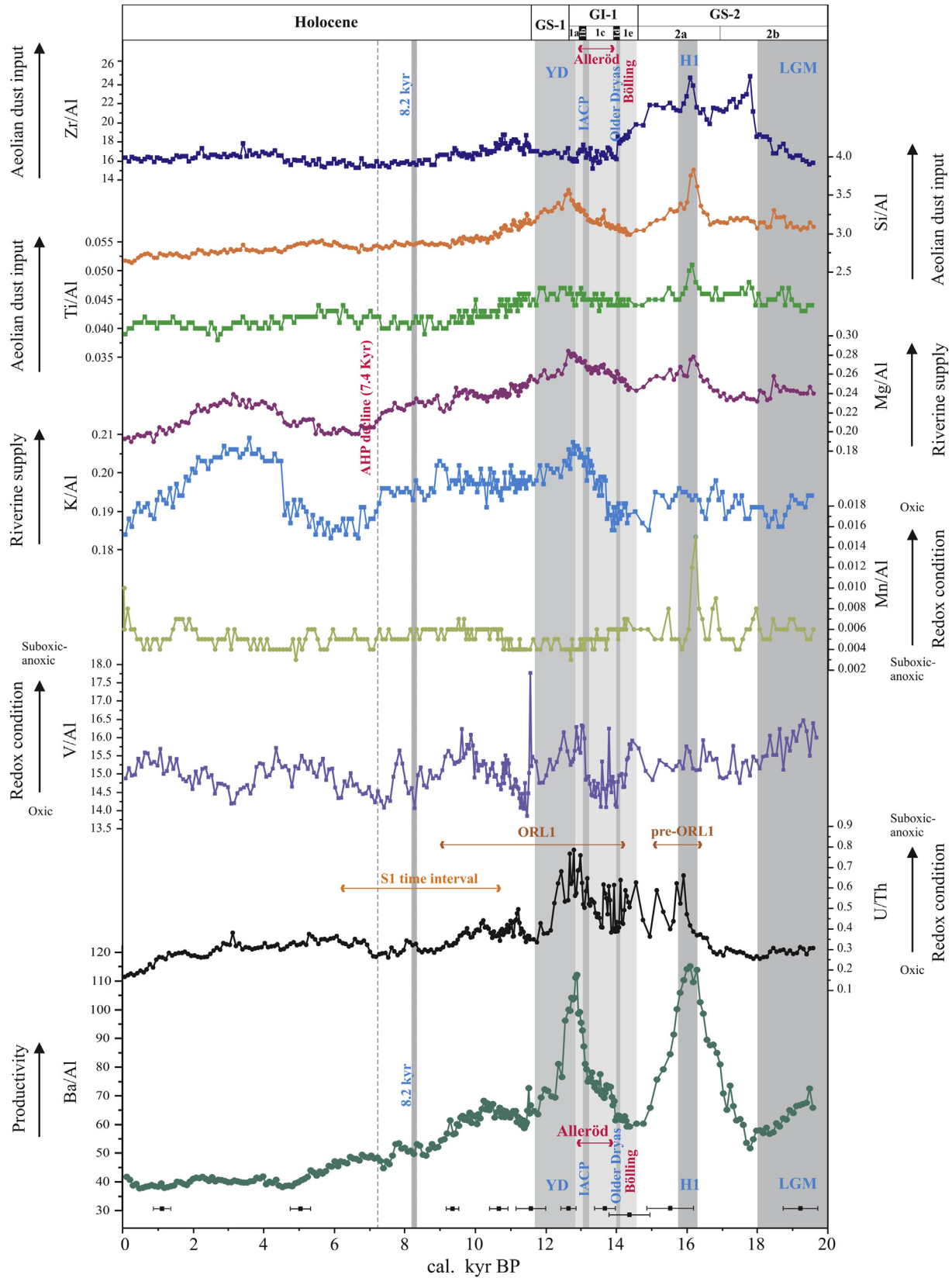


Fig. 3. Age profiles of the Al-normalized concentrations of elements used as detrital input proxies (K, Mg, Ti, Si, Zr), paleoredox proxies (U, V, Mn) and productivity proxies (Ba) in record 293 collected at the Alboran Sea basin (see Fig. 1 for location) (values correspond to Element/Al for major elements and Element/Al $\times 10^{-4}$ ppm for trace elements). Diverse climate-change periods specified in Table 1 are indicated. Warm periods such as Alleröd and Bölling time intervals are marked as well as cold intervals; gray-shaded vertical bars indicate, the 8,200 cold event, Younger Dryas (YD), Intra-Alleröd Cold Period (IACP), Older Dryas, the last Heinrich event (H1), and the Last Glacial Maximum (LGM). The Organic-Rich Layers (Pre-ORL1, ORL1) and S1 sapropel deposition time intervals are also indicated. Chronostratigraphic timing subdivisions are based on ^{14}C AMS dates and stable oxygen isotope stratigraphy from Greenland ice cores (source data and details on analytical methods provided in Rodrigo-Gámiz et al., 2011).

riverine detrital sediments that led to the lower La/Lu ratios in eastern Mediterranean sapropel layers (e.g., Hamroush and Stanley, 1990; Martínez-Ruiz et al., 2000; Gallego-Torres et al., 2007, 2010). However, other than mineral composition also grain size affects the REE contents of terrigenous sediments since heavy minerals represent a significant contribution of REE and other detrital elements to marine sediments (e.g., McLennan, 1989; Taylor and McLennan, 1995). In the particular case of REEs, their use as provenance proxies requires specific caution since different source regions may also have similar REE composition (e.g., Clift et al., 2008; Révillon et al., 2011).

3.1.2. Aeolian inputs

The aeolian input contribution to the Mediterranean sediments is extremely high in comparison with other regions as it is located next to the major dust source of the globe, which is the Sahara-Sahel region (e.g., Washington et al., 2009). Estimates of dust emission from the arid regions of North Africa are about 800 Tg yr^{-1} of soil material that accounts for 70% of the global total and it is six times higher than the next largest source, from Asia (e.g., Huneus et al., 2011; Prospero and Mayol-Bracero, 2013). The dust mobilized over Northern Africa is transported over the Mediterranean and southern Europe (e.g., Avila and Alarcón, 1999; Goudie and Middleton, 2001; Rodríguez et al., 2001; Escudero et al., 2005; Querol et al., 2009; Marconi et al., 2014), and also across the Atlantic (e.g., Prospero et al., 1995, 1999; Caquineau et al., 1998; Alastuey et al., 2005; Gangoiti et al., 2006; Moreno et al., 2006; Serra et al., 2014). In the Mediterranean regions, the amount of Sahara dust deposition varies depending on atmospheric trajectories and distance from the source. Indeed, there is a tendency for fluxes to be lowest at larger distances from the source. For instance, in Northeast Spain, a value of annual deposition of 5.1 g m^{-2} is recorded while 23.1 g m^{-2} are registered in Southeast Spain (Goudie and Middleton, 2001).

Saharan dust has been thoroughly studied, particularly the present day emissions because of its impact in the overall climate system (IPCC, 2007, 2013). It is mostly composed of silicates (clays, feldspars and quartz) with lesser amounts of carbonates, sulfates, oxides and hydroxides (e.g., Caquineau et al., 1998). The source areas of dust emission in North Africa are substantially variable, they are compositionally heterogeneous at regional scales and this heterogeneity has been used to distinguish source areas. Scheuven et al. (2013) have recently reviewed the composition of the northern African dust and its source sediments and have used the ratio $(\text{Ca} + \text{Mg})/\text{Fe}$, the carbonate content, palygorskite occurrence and abundance, illite/kaolinite ratio, $\epsilon_{\text{Nd}}(0)$ value, and the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio as the best tools to characterize active source regions in North Africa and dust input. Regarding the clay mineral composition, the North and East Sahara exhibit the highest illite/kaolinite proportion, the northwestern Sahara contributes more smectitic clays, whereas kaolinite is predominant in the Sahelian region as well as in the southern and central Sahara (e.g., Paquet et al., 1984; Avila et al., 1997, 1998; Caquineau et al., 1998; Prospero, 1999; Pey et al., 2009). In addition, there are more specific minerals that are also characteristic of particular regions, for instance palygorskite. Its formation is favored by evaporation and chemical precipitation in poorly drained areas, mainly derives from the northern and northwestern regions of North Africa (Morocco, Algeria, Tunisia) (Scheuven et al., 2013).

Dust input represents an important contribution to marine sediments. Both the amount supplied and its mineralogy are reflected in the composition of sediments. Because of the proximity to the source areas aeolian sediments deposited in the deep Mediterranean are usually coarser grained than the average hemipelagic sediments (e.g., Sirocko et al., 1991; Goudie and Middleton,

2001; Stuut et al., 2005, 2014; McGee et al., 2013). In fact, the aeolian sediment fraction has been generally recognized in deep-sea sediments by its coarser than clays grain size, which is one of the parameter used to identify aeolian input. The aeolian fraction has served to reconstruct paleoclimate changes, particularly humid and arid phase fluctuations that are reflected by corresponding increases or decreases in the concentration of dust derived elements (e.g., Cole et al., 2009) as well as the intensity of the transporting winds, since larger and denser particles require more energetic atmospheric circulation for transport (e.g., McGee et al., 2013; Stuut et al., 2014). Regarding paleoclimate reconstructions in the Mediterranean, the most useful proxies for past aeolian contribution have been the composition of clay mineral assemblages (e.g., Foucault and Mélières, 2000), and the element normalized to Al ratios. Geochemical proxies such as Si/Al, Zr/Al and Ti/Al ratios (e.g., Calvert and Pedersen, 2007) have been extensively used for reconstructing aeolian input variations to the Mediterranean basins over time. These ratios are proxies for sediment grain-size because they vary depending on the contribution of aeolian quartz and heavy minerals, respectively, to marine sediments. Both are extremely resistant to weathering and can survive multiple cycles of erosion and deposition. The interpretation of these ratios would require therefore of additional mineralogical, grain-size, and textural analyses.

In the Mediterranean, the Si from marine sediments is mostly derived from aluminosilicates and quartz. Because the biogenic Si contribution is in general very low (e.g., Masque et al., 2002), the Si/Al ratio is indicative of the relative proportion of quartz to aluminosilicates, and has been extensively used in the study of Mediterranean paleorecords. Because arid phases are characterized by increasing aeolian quartz input, this ratio has been used in the eastern basins to infer Saharan aeolian input during intervals of sapropel deposition (e.g., Wehausen and Brumsack, 1999, 2000; Calvert and Fontugne, 2001; Mercione et al., 2001), and in the western basins to reconstruct fluctuations in aridity (e.g., Moreno et al., 2002, 2004; Jiménez-Espejo et al., 2007, 2008; Rodrigo-Gámiz et al., 2011). For example, Moreno et al. (2002, 2005) have used the Si/Al ratio in combination with grain size measurements for reconstructing fluctuations of aeolian inputs in the Alboran Sea during the time window between 28 and 48 ka BP, and Rodrigo-Gámiz et al. (2011) have also shown an increase in the Si/Al ratio during the H1 cold event (Fig. 3), in agreement with other paleoclimate proxies, indicating aridity at that time. Increasing dust fluxes from North Africa during this cold interval are also well documented in records from the northwest African margin (McGee et al., 2013).

Regarding the Zr/Al and Ti/Al ratios, heavy minerals are the main carriers of Zr and Ti in aeolian dust (e.g., Sarnthein et al., 1982; Grousset et al., 1989). Zr occurs almost entirely in the mineral zircon. Due to its higher density it is usually transported with coarser quartz grains. Similarly, Ti resides in both aluminosilicates, substituting for some major elements, and as discrete Ti oxide and silicate mineral phases, mostly rutile, sphene and ilmenite. Because of their higher density they as well are transported with slightly coarser aeolian quartz grains. Ti/Al and Zr/Al ratios have thus been used to track changes in the supply of wind-blown dust because enhanced concentration of aeolian particles in marine sediments leads to elevated concentrations of these elements relative to the average hemipelagic sediments. In general, the supply of wind-blown dust appears to have increased under glacial conditions when the aridity and its areal extent in the Sahara increased significantly (e.g., Chylek et al., 2001; Harrison et al., 2001). In the eastern Mediterranean, the significant decrease in dust input from the African margin and the simultaneous increase of fluvial input from the northern margin during sapropel depositions are

recognized by lower Ti/Al and Zr/Al ratios (e.g., Wehausen and Brumsack, 1999, 2000; Calvert and Fontugne, 2001; Lourens et al., 2001; Ziegler et al., 2010). Similarly, in the western Mediterranean basins, the Ti/Al and Zr/Al ratios have indicated fluctuations in humidity linked to paleoclimate changes (e.g., Jiménez-Espejo et al., 2007, 2008; Rodrigo-Gámiz et al., 2011).

As discussed above, the Ti/Al and Zr/Al ratios have provided helpful insights for reconstructing aeolian input variability in the Mediterranean. However, they may be also affected by other factors that could complicate source interpretations. For example, the influence of ash layers, which are rich in Al, may result in decreasing concentrations of other elements and their ratios; ash layers can be significantly enriched in lanthanide REEs, and in Rb, Zr, Nb, Y and Th (e.g., Tamburrino et al., 2012). Turbidites characterized by grain size variations also affect the sediment chemical composition since coarser sediments may be relatively enriched in quartz and heavy minerals. For example, the sapropel S6 in the easternmost Mediterranean (Site 968, Fig. 1) that is characterized by its high TOC and Ba/Al ratios, does not show a decrease in the Ti/Al ratio. This sapropel has thin silty turbidite layers enriched in titanium minerals that are responsible for the observed relative higher Ti/Al ratio (Wehausen and Brumsack, 2000; Lourens et al., 2001; Ziegler et al., 2010). Fluvial contribution of Ti has been also demonstrated in sediments dominated by Nile inputs; it has been suggested that the Ti/Al record in the southeast Levantine Basin reflects variability in contribution of White Nile versus Blue Nile/Atbara sediments and weathering rates in the Ethiopian Highlands (Hennekam et al., 2014).

It is important to emphasize that distinguishing between fluvial and aeolian inputs across the Mediterranean basin based only on particular elements concentrated in marine sediments may be difficult because eventually the same terrigenous minerals may also be supplied by either rivers or dust. Indeed, the profiles of Si, Ti and Zr do not present always a good correspondence. For instance, the Alboran Sea record (core 293G) (Figs. 1 and 3) did show a good correlation between Si/Al, Zr/Al and Ti/Al ratios during the LGM and H1 cold events. In contrast, during the B–A transition and the YD the Si/Al ratio appears to be better correlated with the Mg/Al and K/Al ratios (Fig. 3), suggesting that likely Si was also supplied by increasing fluvial input during these times. Aeolian input to a particular region also depends on vegetation cover, wind direction, atmospheric configuration and transport efficiency; hence these factors also need to be considered for paleoclimate and source reconstructions. In the Alboran Sea for instance, atmospheric configuration and air mass trajectories have been reconstructed by combining mineralogical proxies and palynological assemblages, establishing the western Morocco as the major source of the clay mineral input during the North Atlantic cold events (Bout-Roumazeilles et al., 2007).

Therefore, it is important to realize that the characteristic element ratios that contribute information on variations in aeolian inputs over time, discussed above, may not be unique tracers for specific source regions, thus for the reconstructions of dust provenances. Relying on other proxies such as grain size and radiogenic isotopes (e.g., Scheuven et al., 2013) is often necessary to understand the paleoclimate conditions and history of aeolian deposition in the Mediterranean basins.

3.2. Redox conditions as proxies for depositional environments

Because deep-water oxygen conditions have played a key role in the deposition of the sapropel layers in the eastern Mediterranean Sea, particular attention was given to the distribution of redox sensitive elements; a vast literature exists concerning the reconstruction of redox conditions during deposition of sapropels (e.g., Thomson et al., 1995; van Santvoort et al., 1997; Passier et al.,

1999; Nijenhuis and de Lange, 2000; Warning and Brumsack, 2000; Gallego-Torres et al., 2010; Jilbert et al., 2010; Azrieli-Tal et al., 2014). Since the early ocean drilling expeditions in the seventies (DSDP Leg 13 and Leg 42) many hypotheses dealing with the origin of sapropels have been proposed, arguing both for increasing preservation of organic matter primarily deposited under anoxic conditions (e.g., Menzel et al., 2003), and for primary production in the surface waters leading to enhanced organic matter fluxes (e.g., Calvert et al., 1992). Even though the sapropel origin is still a matter of debate, a combination of the two origins that are not mutually exclusive (e.g., Rohling, 1994; Emeis et al., 2000a,b) is now broadly accepted (e.g., Incarbona et al., 2011; Azrieli-Tal et al., 2014; Taylforth et al., 2014). Other carbon-rich sediments, as black shales (e.g., Jenkyns, 2010) are similarly explained. The controls on preservation and diagenesis of organic matter in marine sediments are also the focus of ample interdisciplinary research (e.g., Zonneveld et al., 2010; Arndt et al., 2013). Although less thoroughly studied, other Mediterranean organic-rich sediment records, in particular those in the western Mediterranean named as organic rich layers (ORLs), have also been studied for their depositional and paleoredox histories (e.g., Zahn et al., 1999; Jiménez-Espejo et al., 2008; Rogerson et al., 2008; Rodrigo-Gámiz et al., 2011; Martrat et al., 2014).

An extensive suite of trace elements has been used in the study of Mediterranean paleorecords to infer bottom water oxygenation (Fig. 1, Table Supplementary material). The use of geochemical paleoredox proxies has been reviewed by Tribouillard et al. (2006), Calvert and Pedersen (2007), and Algeo and Rowe (2012). Some of this information is briefly summarized below with an emphasis on the use of these proxies in studies of Mediterranean sediments (Table Supplementary material). As discussed by Calvert and Pedersen (2007), redox-sensitive elements fall into two categories, (i) elements whose oxidation state can vary as a function of the prevailing redox potential: Mn, for example, forms highly insoluble oxo-hydroxides where oxic conditions prevail; I, as the iodate ion, has a strong adsorptive affinity for organic matter in the presence of oxygen; and Cr, Mo, Re, U and V, occur as highly soluble anionic species in oxic waters but are reduced to reactive or insoluble species under anoxic conditions; and (ii) elements whose oxidation state does not change, such as Ag, Cd, Cu, Ni and Zn, but which form highly insoluble sulfides and are usually removed from solution in the presence of H₂S. The use of elements, whose oxidation state can vary as a function of the redox potential, is based on their different oxidation states and the associated changes in solubility of the ionic species.

These redox-sensitive elements have been used as proxies for paleoredox conditions mainly in three different ways: (i) their concentration normalized to Al (e.g., Thomson et al., 1995, 1999; Van der Weijden, 2002), (ii) their enrichment Factor (EF) (e.g., Arthur and Sageman, 1994; Brumsack, 2006), and (iii) as trace metal ratios of two elements that show different redox behavior (e.g., Jones and Manning, 1994).

The justifications for using element/Al ratios have been already discussed above. This normalization has similarly been used in studies of redox sensitive-elements as paleoredox proxies (e.g., Werne et al., 2003; Lyons et al., 2003; Rimmer et al., 2004; Algeo, 2004; Algeo and Maynard, 2004; Tribouillard et al., 2004, 2005; Díaz-Ochoa et al., 2011 among others). In the Mediterranean, most of the studies of paleoredox conditions across sapropel intervals have been based on Al-normalized element concentrations. As shown by Thomson et al. (1995, 1999), the use of this normalization method in the S1 sapropel minimizes the effects of dilution by CaCO₃. With no diagenetic overprinting, increasing concentrations of trace metals, i.e. Mo, U, V, Cr, Co, Ni, Re, Cu and Zn, generally indicate deposition under reducing conditions.

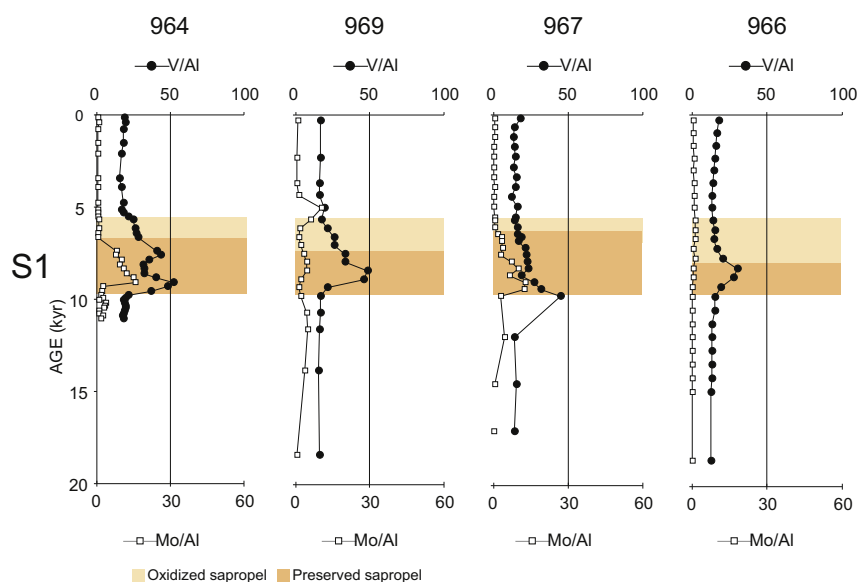


Fig. 4. Age profiles of redox sensitive elements normalized to Al (Mo/Al and V/Al ratios $\times 10^{-4}$ ppm) for the S1 sapropel layer at different ODP Sites (see Fig. 1 for location) (source data and details on analytical methods provided in Gallego-Torres et al., 2007, 2010). Dark orange shaded area corresponds to the visual sapropel enriched in TOC and light orange shaded area indicates the oxidized sapropel.

Since the end of the LGM (Table 1), the deposition of the S1 sapropel has been the most significant paleoenvironmental event in the eastern Mediterranean. In this sapropel, the Al-normalized trace metals profiles show increasing concentrations of redox sensitive trace metals (Fig. 4) that support decreasing bottom-water oxygenation during this time interval (e.g., Warning and Brumsack, 2000; De Lange et al., 2008; Jilbert et al., 2010; Hennekam et al., 2014). In the western Mediterranean, increasing element/Al ratios of redox-sensitive elements (Fig. 3) likewise indicate that the deposition of the last ORL involved important variations in bottom waters oxygenation (Jiménez-Espejo et al., 2008; Rogerson et al., 2008; Rodrigo-Gámiz et al., 2011). Similarly, during the late Holocene fluctuations in deep-water oxygenation derived from variations in paleo-current intensity are also indicated by trace metal contents (Nieto-Moreno et al., 2011, 2013a, 2015).

Al has also been used to calculate EF defined as: $EF = (\text{element}/Al)_{\text{sample}} / (\text{element}/Al)_{\text{shale}}$ (e.g., Brumsack, 2006). The EF indicates the element concentration enrichment relative to the corresponding concentration in average shale. Thus the deviation from average shale composition indicates either enrichment or depletion. The EF of Mo, U and V have been generally used as redox sensitive proxies, these elements change their speciation, thus their solubility under progressively decreasing redox conditions. V is particularly sensitive to minor changes in oxygen concentration, while more

oxidized forms of V ([IV] or [VI]) are soluble in oxic environments; V^{3+} is insoluble, and precipitates as oxy-hydroxides under dysoxic-suboxic conditions (Wanty and Goldhaber, 1992; Calvert and Pedersen, 1993). In reduced sediments under dysoxic to anoxic conditions, the soluble U^{6+} is reduced to relatively insoluble U^{4+} , thus precipitating (for a recent review see Andersen et al., 2014), whereas Mo precipitates only under anoxic to sulfidic conditions (Algeo and Tribovillard, 2009; Algeo and Rowe, 2012 and reference therein). In high-resolution studies it is thus possible to infer the timing of progressive oxygen depletion following the sequence of V, U, and Mo concentrations as showed by Azrieli-Tal et al. (2014) for the eastern Mediterranean sapropel S1 formation.

Recording the trace metal ratios of two elements that show different redox behavior is the third approach to studies of redox sensitive elements. While Al-normalized concentrations of redox sensitive elements provide information on relative enrichment or depletion, the ratios of these elements have helped to define “redox fields”, to distinguish between oxic, dysoxic (suboxic), anoxic, and sulfidic environments, since the diverse elements may precipitate under different redox potentials (e.g., Algeo and Jones and Manning, 1994; Powell et al., 2003; Tribovillard et al., 2006; Algeo and Rowe, 2012). These ratios indicate the different behavior of redox-sensitive elements under variable degrees of oxygen depletion. Nevertheless, the in-depth analysis of the

Table 3

Redox-sensitive element ratios used in marine sediments for paleoredox reconstructions. References in brackets correspond to Mediterranean sediment records.

Element ratio	Proxy for	References (e.g.)
Re/Mo	anoxic (ratio $< 9 \times 10^{-3}$)/suboxic environments (ratio $> 9 \times 10^{-3}$)	Crusius et al., 1996; (Scheiderich et al., 2010)
Authigenic U [$U_{\text{auth}} = U_{\text{total}} - (\text{Th}/3)$], U/Th	oxic, dysoxic, suboxic-anoxic environments	Jones and Manning, 1994; (Martinez-Ruiz et al., 2000; Gallego-Torres et al., 2007, 2010)
Mo–U co-variation	suboxic environments: U_{auth} exceeds Mo_{auth} ; oxic, dysoxic, suboxic-anoxic environments	Algeo and Tribovillard, 2009; (this paper)
V/Mo, V/Sc, V/CrV/(V + Ni)	oxic, dysoxic, suboxic-anoxic environments	Lewan, 1984; Jones and Manning, 1994; Kimura and Watanabe, 2001; Piper and Calvert, 2009; (Hatch and Leventhal, 1992; Gallego-Torres et al., 2007, 2010)
Ni/Co	oxic, dysoxic, suboxic-anoxic environments	Jones and Manning, 1994; (Martinez-Ruiz et al., 2000; Gallego-Torres et al., 2007)

*Values provided by Jones and Manning (1994) on some of the ratios for the three different redox fields that they distinguish are: oxic environments $U/Th < 0.75$, $U_{\text{auth}} < 5$, $V/Cr < 2$, $Ni/Co < 5$; dysoxic environments $U/Th 0.75-1.25$, $U_{\text{auth}} 5-12$, $V/Cr 2-4.25$, $Ni/Co 5-7$; suboxic-anoxic environments $U/Th > 1.25$, $U_{\text{auth}} > 12$, $V/Cr > 4.25$, $Ni/Co > 7$.

behavior of each of the elements used is out of the scope of this paper. Detailed discussions are provided in the aforementioned reviews as well as in more recent papers (Andersen et al., 2014; Azrieli-Tal et al., 2014; Chappaz et al., 2014; Large et al., 2014; Swanner et al., 2014 among others). The ratios that have been most commonly used in the study of Mediterranean paleorecords are presented in Table 3 and briefly discussed below.

In the Mediterranean, most of these ratios have been applied to investigate fluctuations in oxygen conditions at time of sapropel deposition in the eastern basins. The Re/Mo for instance (Table 3) has been used to support a sulfidic water column during the deposition of early Pleistocene sapropels in the Mediterranean Ridge area (Scheiderich et al., 2010). Authigenic U and the U/Th ratio have also provided important information on paleoredox conditions (Martinez-Ruiz et al., 2000; Gallego-Torres et al., 2007, 2010). The enrichment within sapropel layers indicates decreasing oxygen condition, though oxygen depletion varies at different Sites (Figs. 5 and 6). Regarding the Mo–U co-variation, Algeo and Tribovillard (2009) presented a comprehensive study on water column oxygenation in recent (eastern tropical Pacific, Cariaco and Orca Basins, and the Black Sea) and ancient environments (Late Pennsylvanian Midcontinent Sea and the Late Devonian Seaway of the North American craton). They have shown that in open-ocean systems with suboxic bottom waters the enrichment of U_{auth} tends to exceed that of Mo_{auth} . When the water column becomes increasingly reducing or even sulfidic, the rate of accumulation of

Mo_{auth} increases relative to that of U_{auth} . However, if long term stagnation prevails, dissolved Mo_{auth} fixation decelerates while U_{auth} continues to accumulate at a constant rate. Clear differences between sapropel events arise from this proxy, as shown in Fig. 7. There is a distinction between sapropels formed under depleted-oxygen conditions sustained by increased export productivity (S1 and S6) and those formed under anoxic conditions and likely partially stagnant waters, similar to the present day Black Sea (S5).

The ratios of V over other redox-sensitive elements (Table 3) have also been used as proxies for ancient redox conditions. The use of these ratios is based on the behavior of V versus the other elements at variable degrees of oxygen depletion (Emerson and Husted, 1991; Wanty and Goldhaber, 1992). For instance, Piper and Calvert (2009) studied the V/Mo ratio attempting to distinguish dysoxic from anoxic environments, as V precipitates under dysoxic conditions, whereas Mo requires an anoxic-sulfidic environment. The use of this ratio in the eastern Mediterranean sapropels has provided valuable information about different degrees of oxygen deficiencies during sapropel formation (Gallego-Torres et al., 2010). The overall decrease in V ratios within sapropel layers (Figs. 5 and 6) is supporting a major decrease in oxygen conditions during sapropel deposition.

Finally, the Ni/Co ratio also indicates paleoredox variations and delineates redox fields (Table 3) (e.g., Jones and Manning, 1994). Both elements form sulfide minerals and organometallic complexes and thus, their co-variation depends on sulfur and C_{org} contents

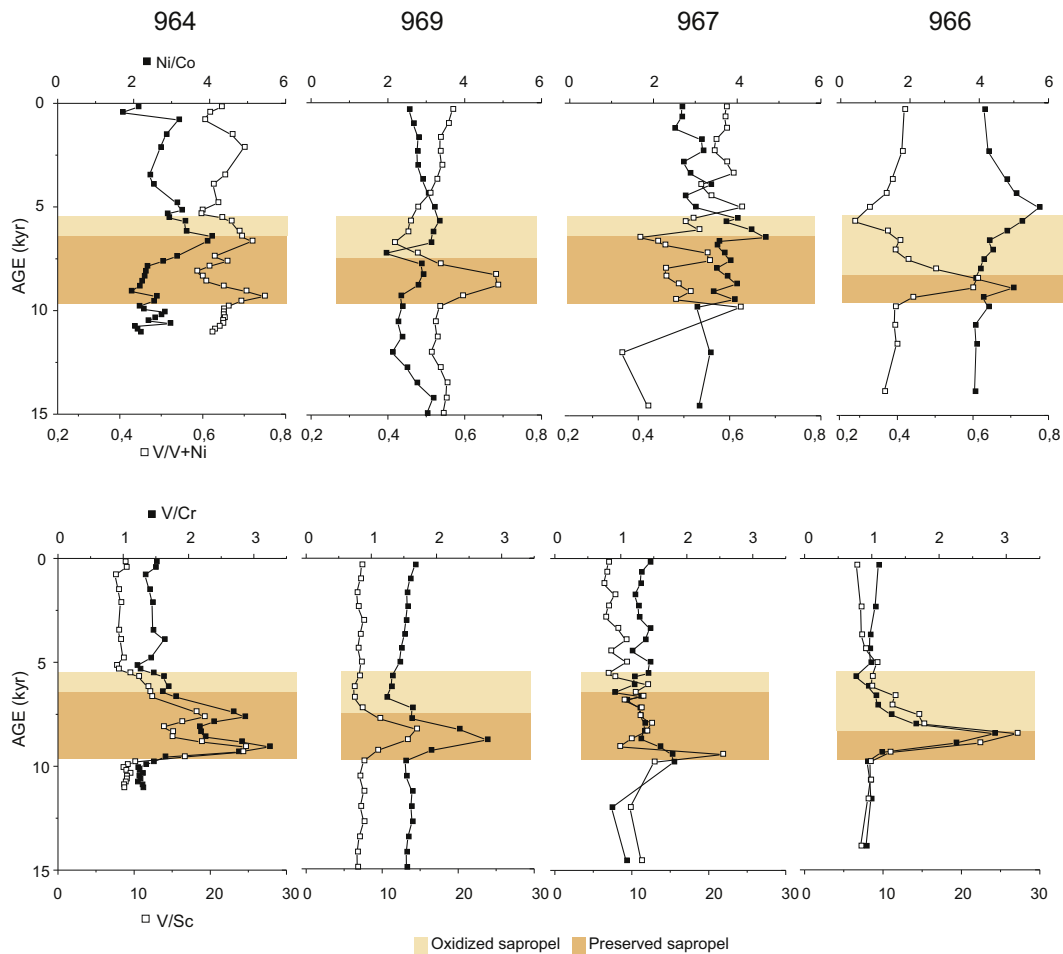


Fig. 5. Age profiles of redox-sensitive element ratios (Ni/Co, V/V + Ni, V/Cr and V/Sc) for S1 sapropel layer at different ODP Sites (see Fig. 1 for location) (source data and details on analytical methods provided in Gallego-Torres et al., 2007, 2010). Dark orange shaded area corresponds to the visual sapropel enriched in TOC and light orange shaded area indicates the oxidized sapropel.

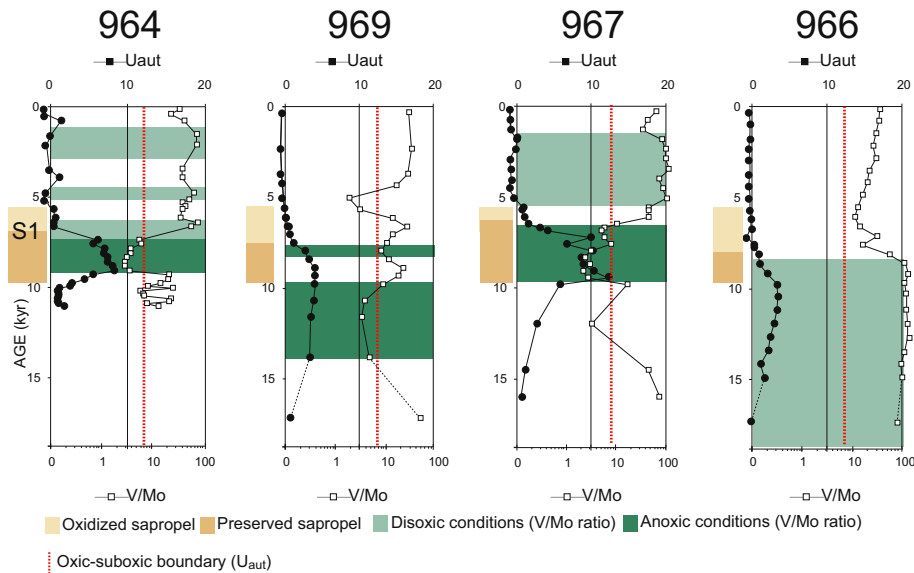


Fig. 6. Age profiles of redox conditions interpreted from U-authigenic and V/Mo ratio for S1 sapropel at the four studied sites (see Fig. 1 for site location). Light and dark green shading indicates disoxic and anoxic conditions, respectively, based on V/Mo. Note logarithmic scale for V/Mo. Red dash line marks the limit between oxic and low oxygen conditions based on U-authigenic. Orange shaded areas mark the visual and oxidized sapropel (source data and details on analytical methods provided in Gallego-Torres et al., 2007, 2010).

rather than on water column oxygen availability. Ni is usually associated with organic matter and is released its decay, that can be incorporated into pyrite under sulfate-reducing conditions. Similarly, Co in oxic environments is present as a dissolved cation, (Co^{2+}) or is complexed with humic/fulvic acids while in anoxic waters forms the insoluble sulfide (CoS), which is mostly in solid solution with Fe-sulfides (Tribovillard et al., 2006 and reference therein). However, Ni is easily oxidized and diffuses into seawater during post-depositional oxidation, which reduces its potential as a redox proxy. For example, the Ni/Co ratios in the S1 sapropel show random trends (Fig. 5) caused by the high TOC content in the sapropel and diagenetic remobilization of Ni. In contrast, in the western Mediterranean with lower C_{org} content, this ratio served more reliably to document redox variations associated to bottom water ventilation and deep current intensity during the late Holocene (Nieto-Moreno et al., 2013a, 2015).

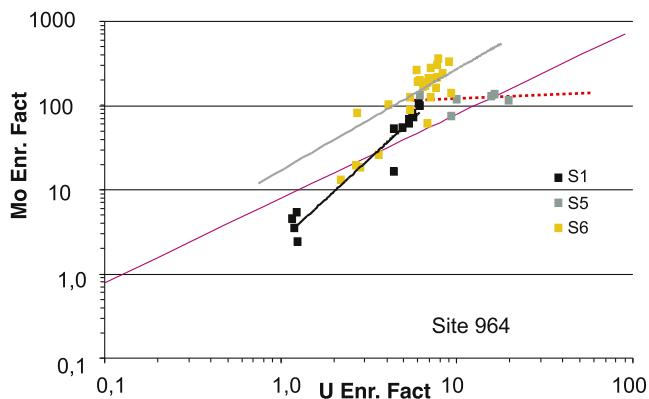


Fig. 7. Mo to U enrichment factors co-variation for sapropels S1, S5 and S6 on Site 964 (Ionian basin). Each sapropel present a different trend: S1 shows the same trend as the typical upwelling system (black line), S5 shows almost constant Mo E.F. (red dashed line) similar to a stagnant basin situation, and S6 draws the same pattern as in semi-stagnant basins (gray line) (see Algeo and Tribovillard, 2009 for details on the use of this proxy).

3.3. Productivity proxies and the barium records

Trace and major element concentrations as well as elemental ratios of marine sediments have also served to reconstruct marine paleoproductivity. The elements P, Al and Ba have been most widely used as productivity proxies (e.g., Murray and Leinen, 1993; Calvert and Pedersen, 2007). Br concentration profiles that generally mirror those of TOC were used to reflect well-preserved, non-oxidized TOC profiles (Ziegler et al., 2008; Lenggler et al., 2013). Since the early discoveries of Ba enrichment in marine sediments (e.g., Goldberg and Arrhenius, 1958; Chow and Goldberg, 1960), the extensive literature on Ba proxies that followed provided a large amount of data on export production in the past oceans. Paleoproductivity reconstructions were mostly based on Ba enrichment in pelagic sediments, using various Ba proxies, primarily Ba/Al ratios, Ba excess, and marine barite content (e.g., Paytan and Griffith, 2007 and references therein). Because Ba may be hosted in other mineral phases, calculations of Ba excess are based on normalization to terrigenous elements using Al or Ti, as discussed above. Most of the Ba enrichment in marine oxic sediments originates from the formation of the mineral barite (Table 2) in the water column. Marine barite occurs in distinct morphologies and sizes (Fig. 8), that differ from barites from other origins; it usually occurs as elliptical to spherical and euhedral particles $<5 \mu\text{m}$ in size (Dehairs et al., 1980; Bishop, 1988; Bertram and Cowen, 1997; Griffith and Paytan, 2012). Moored sediment traps have recorded the presence of marine barite in the water column and the correlation with organic carbon fluxes has been demonstrated (e.g., Jeandel et al., 2000; Stenberg et al., 2007; Dehairs et al., 2008).

In the Mediterranean, one of the most spectacular examples of productivity fluctuations recorded by Ba profiles is the sapropel paleoproductivity record. To date, a large dataset of paleoproductivity reconstructions based on Ba-excess exists (e.g., Thomson et al., 1995; van Santvoort et al., 1997; Wehausen and Brumsack, 1999; Emeis et al., 2000a,b; Mercone et al., 2000; Arnaboldi and Meyers, 2007; Jilbert et al., 2010; Hennekam et al., 2014). The enrichment of Ba by higher concentrations of authigenic marine barite (Fig. 8) within sapropel layers has also been

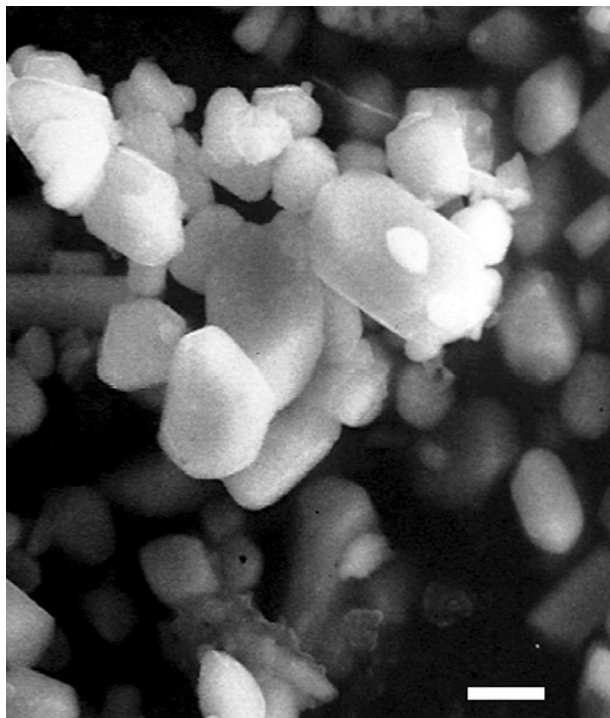


Fig. 8. Scanning Electron Microscopy photograph showing marine barite from sapropel layer S1 (core M25, [Martinez-Ruiz et al., 2000](#)). Scale bar 2 μm .

demonstrated (e.g., [Martinez-Ruiz et al., 2000](#); [Paytan et al., 2004](#)). Furthermore, the Ba/Al ratio has allowed delineating the original sapropel boundaries when C_{org} has been oxidized. Finally, the Ba/Al, rather than the C_{org} Mediterranean records, provided the astronomical tuning of productivity cycles (e.g., [Higgs et al., 1994](#); [van Santvoort et al., 1997](#)).

The eastern and western Mediterranean records have quite different Ba abundances (e.g., [Martinez-Ruiz et al., 2003](#)). Over time, during sapropel deposition events Ba accumulation rates have been considerably higher in the eastern basins than in the western Mediterranean, where sapropels were not deposited. The enhanced Nile and other North African rivers fluvial discharge was responsible for the considerably higher productivity in the eastern basin during sapropel formation. In the western records, Ba enrichments are recognized during the deposition of the ORL1, in particular during cold events as the H1 and the YD (Fig. 3) (e.g., [Jiménez-Espejo et al., 2008](#); [Rodrigo-Gámiz et al., 2011](#)). Even though a link to climate changes exists, productivity events recorded by Ba proxies are not correlated between eastern and western basins. This points to significant differences in nutrient supply and paleoceanographic conditions between both regions. In the modern Mediterranean some significant regional differences in productivity exist as well (e.g., [Turley et al., 2000](#); [Allen et al., 2002](#)).

Even though Ba proxies have been widely used in the Mediterranean and ocean basins in general, some unknowns still remain. The exact location of most barite formation in the ocean in high productivity regions is as yet unknown (e.g., [Dymond et al., 1992](#); [Francois et al., 1995](#); [Paytan et al., 1996](#); [Dehairs et al., 2000](#); [Eagle et al., 2003](#); [Sternberg et al., 2007](#)). Some of the barite formed may dissolve due to barite undersaturation in seawater ([Paytan and Kastner, 1996](#); [Monnin et al., 1999](#)), or in reducing settings, in the sulfate reduction zone barite dissolves (e.g., [Passier et al., 1999](#); [Henkel et al., 2012](#)). Only in oxic settings marine barite is a reliable proxy for paleoproductivity reconstruction. It is also important to note that the relationship between Ba-excess and

organic C fluxes show significant spatial variations ([Dymond et al., 1992](#); [Francois et al., 1995](#)), being different in margin and open-ocean sites ([Francois et al., 1995](#); [Sanchez-Vidal et al., 2005](#); [Sternberg et al., 2007](#)). Diverse processes have been considered to explain such differences; the most likely causes are sedimentation rates and water depth, thus the preferred oxidation of organic matter in open-ocean sites.

In addition to being a paleoproductivity proxy, marine barite, an authigenic marine mineral, reliably records the chemistry of seawater from which it precipitates. Thus, the chemical and isotopic compositions of marine barite also provide insights into seawater composition and therefore have been used to reconstruct ocean paleochemistry ([Paytan et al., 1993, 2002](#); [Griffith and Paytan, 2012](#)).

4. Diagenesis and proxy preservation

Late diagenesis is not discussed in this paper, as sediments deposited over the past 20 ka are unlikely to be affected by it (e.g., [Milliken, 2005](#)). The assessment of early diagenetic overprinting is crucial when using the chemical composition of marine sediments to reconstruct paleoenvironmental conditions. Understanding the factors that control the preservation of elements used as paleoenvironmental proxies discussed above is essential for reliable interpretations of sediment records. The most important physical and chemical processes that may alter or obliterate the original environmental records are bioturbation, winnowing, and redox reactions. After sedimentation, physical processes such as bioturbation may disturb the original record of major and trace element distributions, thus impacting the time resolution analyses in marine sediment cores; mineral winnowing or changes in the chemical environment, such as in the sediment redox condition, as well as may impact the original distribution of redox sensitive trace metals (e.g., [Pedersen et al., 1986](#); [Shaw et al., 1990](#)). The sediment redox condition could be impacted either by (i) the penetration of an oxic front that oxidizes the organic matter and modifies the distribution of key redox sensitive chemical proxies, e.g., Mn, Fe, U or Mo, or by (ii) the evolution of anoxic conditions in sediments with high TOC content. Certain trace metals will become soluble, e.g., Ni, Cu, Zn, increasing their concentration in the pore waters, causing their diffusion into more oxidized adjacent sediment horizons or into bottom water, where they will re-precipitate.

4.1. Trace metal remobilization

In the Mediterranean, post-depositional alteration has significantly modified original trace element distributions within sapropel layers (Fig. 9). Within the eastern Mediterranean, post-depositional oxidation of sapropel layers has been well documented (e.g., [Pruysers et al., 1993](#); [Higgs et al., 1994](#); [Thomson et al., 1995, 1997](#); [van Santvoort et al., 1996, 1997](#)). Likewise in the western Mediterranean, reventilation events have also led to active oxidation and reprecipitation of Mn (e.g., [Jiménez-Espejo et al., 2007](#)). In this paper, we are mostly focusing on the abundant elements Mn and Fe that are particularly sensitive to remobilization during early diagenetic processes. In marine sediments, particularly if they are organic rich, the oxidation of the organic matter leads to O_2 consumption. Under reducing condition, Mn, as well as other trace metals, are mobilized into the pore water, and will re-precipitate upon encountering oxic waters. Thus Mn and Fe (in that order) that precipitate in oxidation fronts are shifted within the sediment column (e.g., [Canfield et al., 1993](#); [März et al., 2011](#)). Mn and Fe oxides scavenge other trace metals such as Cu, Co, Mo and Ni that are as well mobilized by oxidation fronts (e.g., [Thomson et al., 1995, 1999](#)). The biogeochemistry of Mn has been thoroughly studied since it plays an important role in biogeochemical and diagenetic

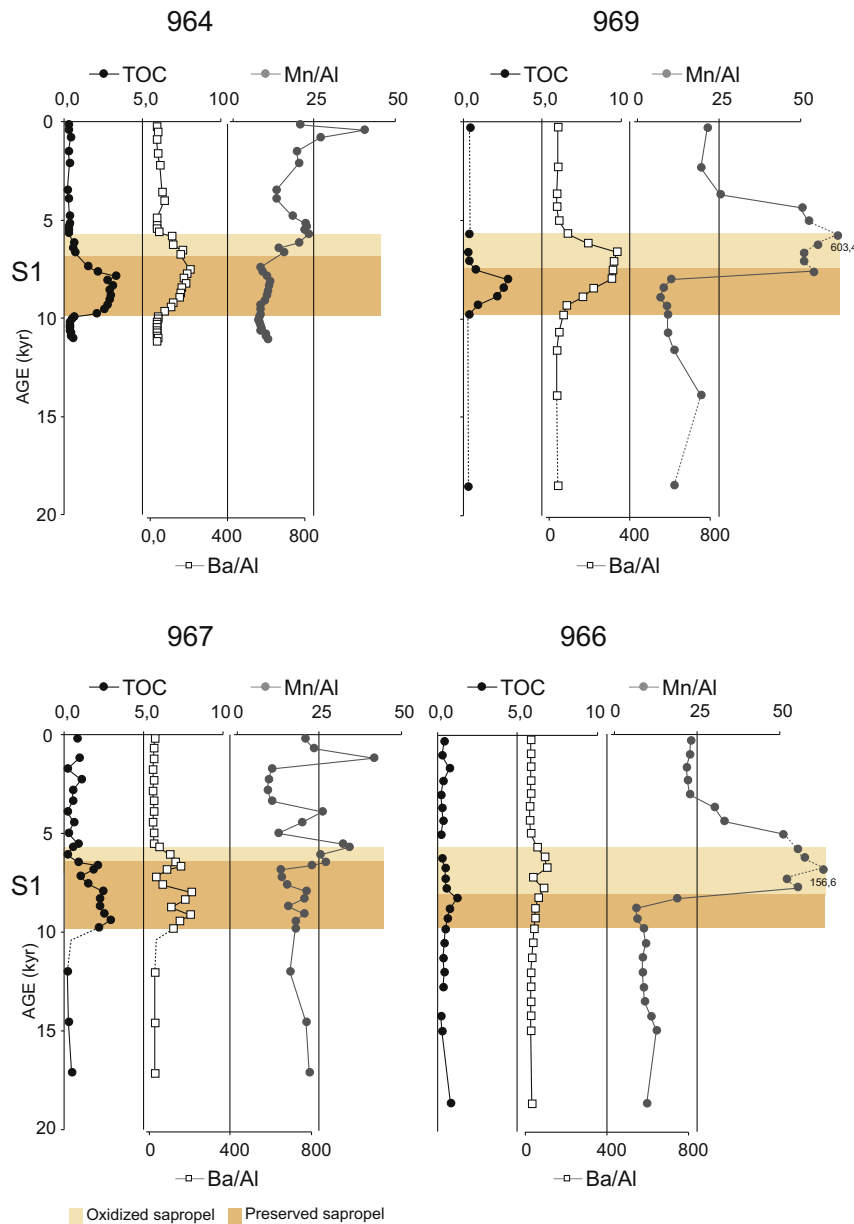


Fig. 9. Age profiles of TOC, Ba/Al and Mn/Al ratios ($\times 10^{-4}$ ppm) from the S1 sapropel interval at eastern Mediterranean ODP sites (see Fig. 1 for site location). The relationship between preserved or organic carbon (TOC), increased productivity signal (Ba/Al) and oxidation (Mn/Al) and the magnitude of the variations in the values of these ratios along the different sites are presented. Orange shaded areas mark the visual and the oxidized sapropel (source data and details on analytical methods provided in Gallego-Torres et al., 2007, 2010).

processes (e.g., McManus et al., 2012 and references therein). As its original distribution is rarely preserved, it rather indicates post-depositional conditions. The distribution of Mn in marine sediments, as in other environments, depends on its redox species; higher oxidation states (Mn^{3+} and Mn^{4+}) occur as insoluble oxihydroxides in oxygenated environments, and the lower oxidation state (Mn^{2+}) is soluble. In general, higher sediment and organic matter accumulation rates lead to oxygen consumption during burial of surface oxi-hydroxides that transport the oxidized Mn into the subsurface reducing environment; then dissolved Mn in the pore waters diffuses upwards to the oxic environment at or near bottom seawater. Where oxic and anoxic conditions are encountered within the sediments, Mn is recycled between the two environments; indeed diagenetic recycling is the main cause of Mn enrichment in sediments (e.g., Calvert and Pedersen, 1996, 2007; van Santvoort et al., 1996). In the Mediterranean, such fronts have been used to

identify events of deep-water renewal or invigoration of deep currents. In the particular case of the sapropel S1 the increases in the Mn/Al ratio define such an oxidation front (Fig. 9). In the western Mediterranean regions as well, Mn enrichments within the sediment records provide evidence for the progressive penetration of oxidation fronts linked to deep-water circulation and oxygenation (Jiménez-Espejo et al., 2007, 2008; Rogerson et al., 2008).

Regarding Fe, it is also subjected to post-depositional remobilization as dissolved Fe^{2+} . Fe and Mn are decoupled during diagenetic processes given that Mn reduction occurs prior to Fe reduction at a higher redox state. Because Fe oxidizes at a lower redox state than Mn, Fe typically precipitates below the Mn enrichment horizon (Passier and Dekkers, 2002; Rutten and Lange, 2002). The two adjacent enriched sediment layers, in oxidized Mn and Fe, define the progression of the oxidation front. Other trace elements are also subjected to active post-depositional

remobilization. Zn, Cu and Ni are preferentially trapped in the sediments via complexation as organo-metallic compounds. Thus, their concentrations are usually linked to organic matter accumulation. In sulfidic conditions, Zn, Cu and Ni precipitate in sulfide minerals (e.g., [Huerta-Diaz and Morse, 1992](#)). Even though these sulfide minerals are very stable and may persist even if later oxidation of organic matter occurs (e.g., [Tribovillard et al., 2006](#)), progressive oxidation may lead them to dissolve and subsequently they may re-precipitate in association with Mn–Fe oxides. U is particularly mobile, only suboxic conditions are required to redistribute this element, and thus to erase the original geochemical signal. This diagenetic U mobilization has been observed in recent sapropel layers, mainly affecting shallow water sites ([Fig. 5](#); [Gallego-Torres et al., 2010](#)), such as Site 966 (~900 m.b.s.l. [Fig. 1](#)). V and Mo are less prone to oxidation. In oxic conditions, Mo is diffused upwards, and it may become adsorbed onto Mn-oxides producing minor enrichments ([Fig. 4](#)). V is more stable and is not likely to be adsorbed onto Mn-oxides; indeed, no diagenetic enrichment in V has been observed in the Mediterranean region.

4.2. Preservation of the Ba record

The preservation of productivity proxies is discussed separately because Ba has been extensively used as a recorder of past productivity in all Mediterranean basins and deserves particular attention. Regardless of the poor understanding of the mechanisms of barite precipitation in the water column, barite has shown to be a useful proxy for reconstructing paleoproductivity responsible for sapropel deposition events in the eastern Mediterranean, and for other productivity fluctuations in the western regions as discussed above. Barite preservation in marine sediments has been discussed and investigated (e.g., [McManus et al., 1998](#); [Schenau et al., 2001](#); [Robin et al., 2003](#); [van Beek et al., 2003](#)) though uncertainties remain regarding the diverse parameters influencing such preservation ([Schenau et al., 2001](#); [Paytan and Griffith, 2007](#); [Griffith and Paytan, 2012](#)). Deep-water saturation state, sedimentation rates, and pore water chemistry are major controls on preservation. In high productivity regions and oxic pelagic settings, a substantial part of the marine barite that originated in the water column and/or sediment–water interface is preserved ([Paytan and Kastner, 1996](#)). Most of the known sapropel records show Ba profiles suggesting no diagenetic overprinting ([Fig. 9](#)). Especially the most recent sapropel, S1, shows a Ba profile that delineates the original sapropel layer, despite organic matter oxidation and Fe and Mn diagenetic remobilization; the Ba enrichment in S1 sapropel is associated with well-preserved marine barite ([Fig. 8](#)) ([Martínez-Ruiz et al., 2000](#)). Similarly, preserved marine barite has also been observed in western Mediterranean records of high productivity intervals ([Rodrigo-Gámiz et al., 2011](#)). Even though diagenetic remobilization of Ba has been observed in certain sapropel layers ([Van Os et al., 1994](#)), the overall Ba productivity record in the Mediterranean is well preserved. The marine origin of barite in the sapropels is supported by its size, habit and the contemporaneous seawater sulfate isotopic composition ([Paytan et al., 2004](#)). In the Black Sea for instance, there is an intense overprint of the Ba signal due to methanogenesis ([Henkel et al., 2012](#)). However, no correlation of Ba profiles with those of trace elements that have been mobilized has been observed in the Mediterranean.

5. Multi-proxy approaches and case studies

5.1. The Eastern Mediterranean S1 sapropel record

The most recent sapropel, S1, was deposited in the eastern Mediterranean Sea basins during the Holocene between 10.8 and

6.1 cal ka BP; [De Lange et al. \(2008\)](#) delimited the top and bottom of the Ba-enriched layer obtaining synchronous time limit basins-wide. This layer represents a sharp change in sedimentation, from organic carbon poor to organic rich sediments; the sapropel is characterized by enhanced TOC contents (~2%). As older sapropels, the S1 deposition also exhibits a significant enrichment in the Ba content ([Fig. 9](#)). However, the TOC and Ba profiles are not coincident in this sapropel, the Ba enrichment is extending several centimeters above the organic-rich layer ([Fig. 9](#)) due to an organic C oxidation of the upper sections of the sapropel, as mentioned above (e.g., [Higgs et al., 1994](#); [van Santvoort et al., 1996, 1997](#)). A peak in the Mn/Al ratio marks the boundary between the top of the TOC-rich sediment and the top of Ba-enriched layer (e.g., [Thomson et al., 1995, 1997](#)). The paleoenvironmental conditions during S1 deposition are indicated by the other proxy element ratios described above, as discussed below (e.g., [Sangiorgi et al., 2002](#); [Schmiedl et al., 2010](#); [Boere et al., 2011](#)). Decreasing values of Zr/Al, Si/Al and Ti/Al ratios indicate reduced aeolian input, while increasing K/Al and Mg/Al ratios provide evidence for increased fluvial-derived terrigenous material (e.g., [Wehausen and Brumsack, 1999](#)). The La/Lu ratio indicates a change in the source area of fluvial detrital sediment; in particular, a lower La/Lu ratio suggests an increase in fluvial derived sediment from the North African area during more intense precipitation (e.g., [Rossignol-Strick, 1985](#); [Hamroush and Stanley, 1990](#); [Martínez-Ruiz et al., 2000](#); [Gallego-Torres et al., 2007, 2010](#); [Liu et al., 2012](#)). These elemental ratios support a scenario in which a decrease in aeolian input and an enhanced supply of fluvial material occurred simultaneously. This has been traditionally interpreted by invoking a northward migration of the Inter-tropical Convergence Zone (ITCZ) and intensified monsoonal activity in northern Africa, associated with insolation maxima during astronomical precession minima (e.g., [Rohling et al., 2002](#); [Liu et al., 2012](#)). More intense rainfall induced lower sea surface salinity and higher nutrient input that also caused a change in the bacterial community, with the establishment of N-fixing bacteria (e.g., [Meyers and Arnaboldi, 2005](#); [Gallego-Torres et al., 2011](#)). The bacterial bloom of an N-fixing community would have also sustained high diatom productivity ([Kemp and Villareal, 2013](#)) and maintained a general high productivity level, which led to a high accumulation rate of organic matter in the sediment with an ultimately total oxygen consumption in deep waters (e.g., [Jilbert et al., 2010](#)). Bottom water circulation was also restricted due to lower surface salinity, which partially delayed the thermohaline circulation. These factors caused dysoxic to anoxic conditions in the deep basin as evidenced by the redox proxies ([Figs. 4–7](#)). Water column anoxia, however, did not reach shallower deposition sites (e.g., ODP Site 966, [Fig. 4](#)), where only V is enriched. The differences in oxygen conditions have also resulted in variations in preservation of the S1 layer depending on water depth ([De Lange et al., 2008](#)). In general, sulfidic conditions were not reached, since there is no evidence of sulfate reduction nor of Ba remobilization, as also discussed above. At the end of the high productivity event, there was a sharp return to pre-sapropel conditions, the deep waters were re-ventilated and the upper part of the organic-rich layer was oxidized ([Fig. 9](#)). This was probably caused by intense thermohaline circulation and a flush of cold deep water originated on the northern margins (e.g., [Gallego-Torres et al., 2010](#)).

High-resolution records of the S1 have also indicated a strong variability on multi-decadal to multi-centennial time scales in deep-water redox conditions throughout the S1 deposition time interval (e.g., [Jilbert et al., 2010](#)). Furthermore, in certain regions as the Adriatic or the Nile delta where high sedimentation rates provided high-resolution records, an interruption in the conditions leading to sapropel deposition has been recognized ([Rohling et al., 1997](#); [Aritztegui et al., 2000](#); [Hennekam et al., 2014](#)). Diverse

element ratios, i.e. Ti/Al, Ba/Al and V/Al, show an interruption around ~8.2–7.9 cal ka BP that splits the S1 into two parts “S1a” and “S1b”; within the interrupted sapropel, C_{org} and V/Al values are rather similar to non-sapropel values (Hennekam et al., 2014). The S1 represents therefore an excellent example where geochemical proxies, in particular element ratios, provide paleoclimate and paleoceanographic reconstructions, and also insights into global climate changes since the sapropel deposition records the various influences of the Indian, Asian and African monsoons, as well as of the Atlantic ocean climate variability.

5.2. The Westernmost Mediterranean paleoclimate record

In the westernmost Mediterranean because of less thorough paleoceanographic research using inorganic proxies than in the eastern Mediterranean, less geochemical records are available (see Table Supplementary material). However, the available proxy data that are based on elemental ratio proxies obtained from very high-resolution records have provided important information on past climate variations and oceanographic conditions. The exceptional high sedimentation rates in this region have helped to develop high-resolution records for paleoclimate reconstructions (e.g., Moreno et al., 2002, 2004, 2005, 2012; Martínez-Ruiz et al., 2003; Frigola et al., 2007, 2008; Jiménez-Espejo et al., 2007, 2008; Rogerson et al., 2008; Martín-Puertas et al., 2010; Nieto-Moreno et al., 2011, 2013a,b; Rodrigo-Gámiz et al., 2011, 2014a,b).

Over the last 20 ka the detrital input proxies have recorded major oscillations in sediment composition driven by climate changes. Since the LGM a major break in sediment composition occurred during the H1 cold interval (15,700–16,200 cal yr BP). At this time Zr/Al and Ti/Al ratios (Fig. 3) support a dusty period characterized by a major increase in aeolian input; this has also been documented in other paleorecords worldwide (e.g., Deplazes et al., 2014 and references therein). Dryness and arid conditions in the western Mediterranean and northern Africa at this time, suggest a northward migration of the ITCZ (Stager et al., 2011). The increased cyclonic activity and the stronger thermal gradient between high and low latitudes were similar to climate conditions during positive-mode phases of the North Atlantic Oscillation (Trouet et al., 2009; 2012).

During the entire Greenland Stadial-2a interval (Fig. 3) and particularly during the H1, redox proxies (Mn/Al, U/Th, V/Al) profiles also display significant oscillations (Fig. 3) and support reduced bottom water ventilation (Rodrigo-Gámiz et al., 2011). A collapse of the Western Mediterranean Deep Water (WMDW) formation and the injection of Atlantic water from iceberg melting have been proposed as an explanation for the reduced Mediterranean thermohaline circulation during this time interval (e.g., Sierro et al., 2005; Jiménez-Espejo et al., 2007, 2008; Rogerson et al., 2008). A marked peak in the Ba/Al ratio during the H1 supports enhanced marine productivity (Jiménez-Espejo et al., 2008; Rodrigo-Gámiz et al., 2011). Even though an influence of Ba-enriched melt-waters as proposed in the case of Atlantic records (Plewa et al., 2006) cannot be discarded, authigenic barite is relatively abundant within this sediment interval and support a Ba enrichment derived from marine barite, thus enhanced productivity (Rodrigo-Gámiz et al., 2011).

Significant changes in element ratios profiles are also observed during the B–A transition (12,890–14,670 cal yr BP), influenced, in particular, by a substantial increase in the values of fluvial input proxies (K/Al, Mg/Al ratios) (Fig. 3). Fluvial discharge would have mainly contributed clays from source regions, rich in illite and chlorite, leading to these increasing values. Over the B–A transition the Si/Al also increased suggesting that fluvial input and/or variations in circulation intensity may have led to greater Si content, in

fact quartz content clearly increases within this period (Rodrigo-Gámiz et al., 2011). Redox sensitive elements have also supported fluctuations in bottom water oxygen conditions during the B–A transition. The relative higher values of U/Th and V/Al ratios (Fig. 3) support reduced thermohaline circulation. In fact changes in thermohaline circulation are linked to the organic-rich sediment deposition in the Alboran Sea (ORL, from the H1 to around 8900 yr cal. BP; Rodrigo-Gámiz et al., 2011). The origin of this organic matter enrichment has been explained as a consequence of the strong reduction in surface Mediterranean water density and a shoaling of the interface between intermediate and deep waters (Rogerson et al., 2008). The subsequent bottom water re-oxygenation at 8.9 ka led to the termination of the ORL deposition. The increasing trend in the Ba/Al ratio during the B–A transition indicates enhanced productivity. A greater fluvial input may have contributed higher nutrient supply; in fact this increasing trend in the Ba/Al ratio culminates with a marked peak of this ratio by the end of the B–A transition and at the onset of the YD (Fig. 3). After this warm and humid transition, a decreasing trend in the values of fluvial input proxies characterizes the YD cold period as well as a decrease in the Ba/Al ratio that continued to decrease until the present day low productivity conditions. During the Holocene, even though the geochemical profiles suggest a more stable period (Fig. 3), fluvial proxies record significant changes in humidity caused by the decline of the African Humid Period (deMenocal et al., 2000).

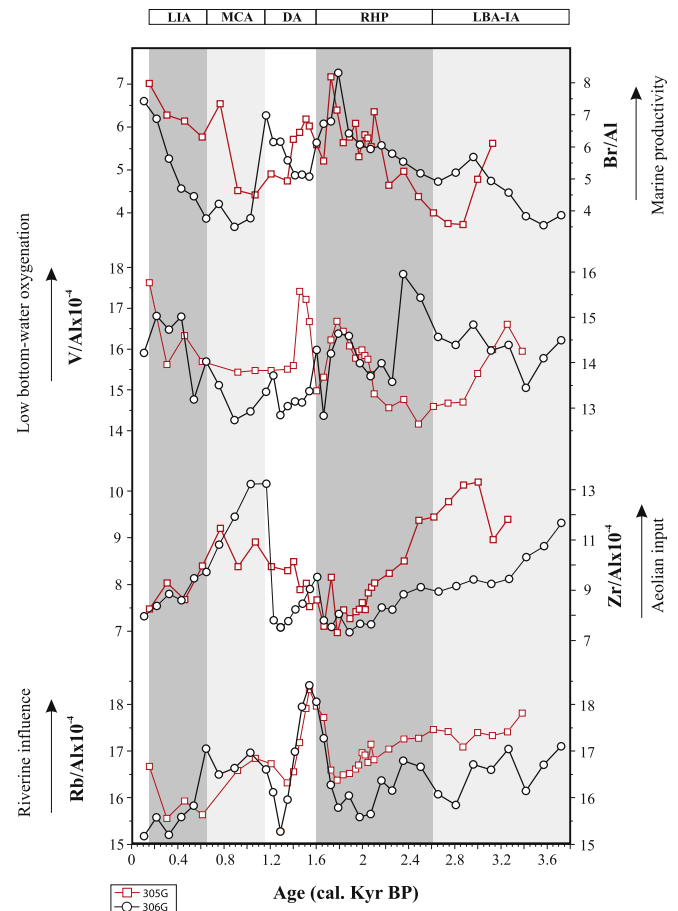


Fig. 10. Age profiles of elemental ratios (Rb/Al, Zr/Al, V/Al and Br/Al ratios) in cores from the westernmost Mediterranean, 305G (red squares) and 306G (black circles). Light gray shaded areas indicate humid periods (LIA: Little Ice Age, RHP: Roman Humid Period) and dry periods (MCA: Medieval Climate Anomaly, DA: Dark Ages, LBA-IA: Late Bronze Age-Iron Age) are also indicated in top bar (source data and details on analytical methods provided in Nieto-Moreno et al., 2011).

High-resolution studies over shorter time intervals have similarly provided detailed paleoclimate reconstructions based on element ratio proxies, as illustrated in Figs. 10 and 11. It has been shown that the late Holocene is punctuated by high frequency environmental changes. During the Roman Humid Period (RHP) and the Little Ice Age (LIA), fluctuations in the riverine input are indicated by detrital element ratios (e.g., Rb/Al, Si/Zr ratios), and aeolian input proxies (Zr/Al ratios, Figs. 10 and 11). For example, during the Late Bronze-Iron Age (LBA-IA) and the Medieval Climate Anomaly (MCA) drier conditions are supported by increasing Zr/Al ratios (Figs. 10 and 11). Even short and sharp dry/wet cycles during the LIA, that are coinciding with rainfall data and climate reconstructions for the last 0.5 ka in the South of the Iberian Peninsula, are indicated by these element ratios (Fig. 11) (Nieto-Moreno et al., 2013a, 2015). Reconstruction of climate variability at such a high resolution over the last millennia is of particular interest, it has a potential to be used as a “natural” analogue for the recent past in the 20th century greenhouse warming (Nieto-Moreno et al., 2013a, b; 2015).

Finally, in addition to documenting climate changes and climate responses, elemental ratio profiles have been shown to be a useful tool for cyclostratigraphic analysis. Marked periodicities in element ratios at 1300, 1515, 2000, and 5000 yr, sustained by spectral analysis data are recognized in the Alboran Sea record over the last 20 ka (Rodrigo-Gámiz et al., 2014a).

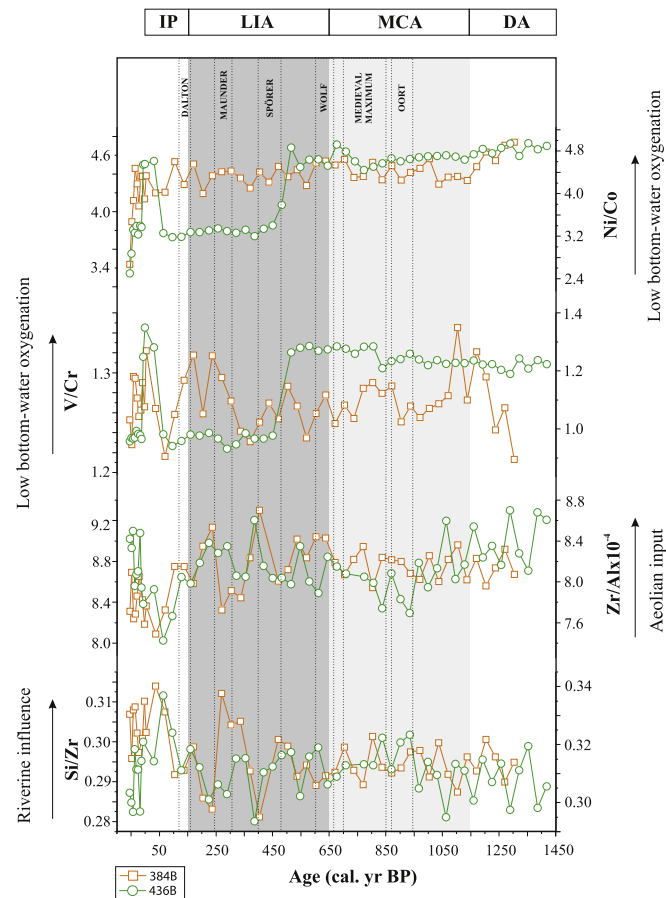


Fig. 11. Age profiles of detrital (Si/Zr and Zr/Al ratios) and redox proxies (V/Cr and Ni/Co ratios) from cores 384B (orange squares) and 436B (green circles), western Alboran basin. Time intervals corresponding to the IP: Industrial Period, LIA: Little Ice Age, MCA: Medieval Climate anomaly and DA: Dark Ages are indicated in top bar (source data and details on analytical methods provided in Nieto-Moreno et al., 2013a).

6. Concluding remarks

The reliability of geochemical proxy studies depends on the quality of the sediment records (e.g., McCave, 2007). A detailed chronology is as well essential for paleoenvironmental reconstructions. A well-known problem related to marine paleorecords is mixing, particularly by bioturbation. Depending on sedimentation rates and on the mixing depth, biomixing may mask or even erase original records on scales of years to thousands of years (e.g., Johannessen and Macdonald, 2012). Bioturbation plays an important role in remobilizing certain trace elements. For example, authigenic U is significantly remobilized in marine sediments by bioturbation (e.g., Zheng et al., 2002). Appropriate analytical procedures are also crucial for reliable paleoreconstructions based on elemental ratios. In particular, when sediment samples are digested, adequate procedures are essential to ensure dissolution of the heavy minerals that are important for the reliable interpretations of the detrital input proxies.

Technical advances have greatly contributed to the development of new geochemical proxies by improving detection limits, precision, accuracy, and calibration. With regard to marine sediments, during the last decade, the geochemical analyses of marine records have been deeply transformed by the development of the continuous nondestructive semiquantitative X-ray fluorescence (XRF) core scanner. However, XRF core scanning provides only qualitative to semi-quantitative data and relative element variations, affected by sediment water content, grain size, deviations from a flat split core surface, and by different penetration depths of the specific element X-rays (e.g., Hennekam and de Lange, 2012; Wilhelms-Dick et al., 2012).

In the particular case of the Mediterranean basins, major and trace element records have provided valuable archives for paleoenvironmental reconstructions. A large set of geochemical proxies has been obtained and elemental ratios have contributed crucial information on paleoclimate and paleoceanographic conditions. Suitable proxies used for aeolian input have been Zr/Al and Ti/Al ratios. Grain size distribution and composition of source rocks are important parameters to consider for reliable data interpretations since both elements are usually hosted in heavy minerals that could derive from either aeolian or fluvial transport, thus Ti may not be a suitable proxy for aeolian dust input in all regions (e.g., Govin et al., 2012). Furthermore, other than aridity in source regions, the distribution of aeolian dust depends on factors such as wind strength, wind direction, and provenance. Even though the Si/Al ratio has documented aeolian input fluctuations in some Mediterranean paleorecord, its interpretation is not always straightforward. Identification of the sources of Si may as well be problematic since both aeolian and fluvial inputs contain quartz and silicates. The same applies to Fe and it is also easily affected by diagenetic remobilization. K/Al, Mg/Al and Rb/Al have been used as fluvial input proxies, but for source identification knowledge of the mineral composition of the sediments is essential. Regarding paleoredox proxies, trace metals (such as Mn, Mo, Co, U, V, Cu, Ni and Zn) have been used for reconstructing oxygen conditions. They are useful proxies for original signatures when diagenetic remobilization is adequately constrained. The Ba proxies have been thoroughly documented in the Mediterranean. Ba enrichment is a reliable productivity proxy when derived from authigenic marine barite. The mechanism for barite precipitation in the ocean water column is, however, not known yet. The recently demonstrated capability of certain microbial groups to mediate barite precipitation (Gonzalez-Muñoz et al., 2012) suggests that microbial processes could have also played an important role in barite formation.

The proxies considered in this synthesis, although powerful, often may not provide unique information that could be used to

identify the sources or to characterize the various depositional environments. Additional proxies, not discussed here, exist, for example, radiogenic isotopes as proxies for detrital input and trace metal isotopes as proxies for redox conditions. Ultimately, it would be important to establish unique matrices of proxies for the various sources and depositional environments.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.quascirev.2014.09.018>.

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