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Precession driven changes in terrestrial organic matter input to the Eastern Mediterranean leading up to the Messinian Salinity Crisis

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ABSTRACT

Eastern Mediterranean sediments over the past 12 Myr commonly show strongly developed precessional cyclicity, thought to be a biogeochemical response to insolation-driven freshwater input from run-off. The Mediterranean's dominant freshwater source today and in the past, is the Nile, which is fed by North African monsoon rain; other, smaller, circum-Mediterranean rivers also contribute to Mediterranean hydrology. Crucially, run-off through all of these systems appears to vary with precession, but there is no direct evidence linking individual water sources to the biogeochemical response recorded in Mediterranean sediments. Consequently, it is not clear whether the North African monsoon is entirely responsible for the Mediterranean's sedimentary cyclicity, or whether other, precessional signals, such as Atlantic storm precipitation, drive it.

Organic matter in sediments derives from both marine and terrestrial sources and biomarker analysis can be used to discriminate between the two, thereby providing insight into sedimentary and ecological processes. We analysed a wide range of lipids from the Late Miocene (6.6–5.9 Ma) Pissouri section, southern Cyprus, and reconstructed the vegetation supplied to this region by measuring the carbon isotopes of the terrestrial component to identify its geographic source. BIT (Branched-Isoprenoidal-Tetraether) indices reflect changes in the relative abundance of marine vs terrestrial (soil) organic matter inputs, and with the exception of records from the last deglaciation, this work is the first application of the BIT approach to the reconstruction of orbital impacts on sedimentological processes. BIT indices show that the organic matter supplied to Cyprus changed over the course of each precession cycle and was dominantly terrestrial during insolation maxima when North African run-off was enhanced. The $\delta^{13}C$ values from these intervals are compatible with tropical North African vegetation. However, the $\delta^{13}C$ record indicates that during insolation minima, organic material supplied to southern Cyprus derives from a more arid source region. This is likely to have been aeolian-transported organic matter from the Anatolian Plateau demonstrating that even in Mediterranean sedimentary systems influenced by Nile run-off, there is more than one independent precessional organic matter contribution to the sedimentary cyclicity. Pissouri's organic geochemistry also illustrates a long-term trend towards more saline Mediterranean conditions during the 600 kyr leading up to the Messinian Salinity Crisis.

1. Introduction

Mediterranean sedimentary successions over the last 12 million years (Myr) are commonly dominated by strong cyclicity (Kidd et al., 1978; Rohling et al., 2015). These regular lithological alternations, comprising some combination of marls, limestones, diatomites and organic-rich sapropelic layers, are demonstrably precessional (Hilgen et al., 1997; Sierro et al., 2001) and are thought to be the Mediterranean's biogeochemical response to orbitally-driven variations in freshwater input (Rossignol-Strick, 1985). The largest source of this freshwater variation is derived from the North African monsoon (Rohling et al., 2015 and references therein). Precessional changes shift the position of the Intertropical Convergence Zone (ITCZ) northward during times of insolation maxima (July 65°N; Laskar et al., 2004) and increase the

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intensity of the monsoon in the catchment of northward draining rivers that flow into the Mediterranean (Marzocchi et al., 2015). These insolation-driven changes also affect the vegetation across North Africa (Larrasoaña et al., 2013), although model simulations fail to capture the full greening of the Sahara indicated by terrestrial data (Larrasoaña et al., 2013 and references therein). Precessional changes in the location and intensity of North Atlantic storm tracks also impact Mediterranean precipitation patterns, principally in the west and along the north Mediterranean margin (Kutzbach et al., 2014; Toucanne et al., 2015).

In the Late Miocene Mediterranean salinity rose significantly and thick, basin-wide evaporites were deposited during the Messinian Salinity Crisis (MSC, 5.97–5.33 Ma; Manzi et al., 2013 and references therein). While deep basinal evaporites have yet to be recovered, those preserved on the Mediterranean margins also show strong cyclicity which is thought to reflect an on-going precessional signal (Flecker et al., 2015), despite extreme environmental conditions. Although the transition to evaporite precipitation in the Mediterranean is synchronous and abrupt at 5.97 Ma (Manzi et al., 2013), geochemical evidence (Flecker et al., 2015 and references therein) as well as water column oxygenation and faunal data (Kouwenhoven et al., 2003; Sierro et al., 2001) indicate that the first environmental precursors of the MSC occurred several million years earlier.

The evidence of precessional-pacing of Mediterranean sedimentation is clear. However, the specific processes that generated the recorded biogeochemical response remain controversial. Debates over the role of freshwater driven productivity versus water column stratification in the generation of organic-rich sapropelic layers (Kidd et al., 1978) endure, while the question of whether deep-sea anoxia, promoted by enhanced export productivity, a freshwater cap, or a combination of both, can transfer the precessional run-off signal from the Eastern to Western Mediterranean Basins as advocated by Rohling et al. (2015), remains untested. One alternative possibility is that the North Atlantic storm-track generates the precessional biogeochemical response in the Western Mediterranean independent of, but in phase with precessional run-off to the Eastern Mediterranean (Toucanne et al., 2015). However, it is not clear whether the storm track precipitation is volumetrically sufficient to generate the biogeochemical response observed.

All of these controversies relate, in part, to the difficulty in identifying the fresh water sources responsible for driving the biogeochemical sedimentary product observed in the Mediterranean Basin. This study uses biomarkers preserved within the sedimentary record as tracers of the freshwater from which they were derived in order to explore and provide new insight into the underlying dynamics of the Mediterranean's sedimentary cyclicity.

Lipid biomarkers have been used to explore changes in the hydrological cycle in a variety of ways. Leaf wax δ^{13}C values differ between C_3- and C_4-plants where C_3-plants have lower δ^{13}C values than C_4-plants (O'Leary, 1981) as a result of their different morphology and carbon assimilation biochemistry (Edwards et al., 2010 and references therein). Because the distribution of C_3- and C_4-plants is governed by a combination of environmental factors, including temperature and aridity (Yang et al., 2014), leaf wax δ^{13}C values provide insight into both past vegetation and climatic conditions. Biomarkers can also provide insight into changes in marine versus terrestrial organic matter (OM) fluxes (Hopmans et al., 2004), from which changes in the OM source can be inferred. Other lipid biomarkers, including isoprenoidal and branched glycerol dialkyl glycerol tetraether (GDGT) lipids can be used to determine sea-surface temperatures (TEX_{86} [TetraEther indeX]; Schouten et al., 2013 and references therein) and land surface temperatures (MBT′ [Methylation of Branched Tetraether]/CBT [Cyclisation of Branched Tetraethers]; Weijers et al., 2007; Peterse et al., 2012), providing additional insights into environmental changes. This approach constrains the relative control of temperature versus aridity on C_3/C_4 plant abundances.

We have applied these approaches to the Late Miocene Pissouri section on Cyprus (5.98–6.51 Ma), which lies to the north of the Nile delta (Fig. 1). Today, the majority of the monsoon-derived North African run-off reaches the Mediterranean via the Nile which is its largest fluvial system. We extracted and characterised biomarkers from the strongly cyclic Pissouri succession and have used them to reconstruct the influence of Nile water and the precipitation in its catchment. In particular, we use the proportions branched-GDGTs (brGDGTs) to crenarchaeol (BIT index), distributions of *n*-alkyl lipids, and the δ^{13}C values of high molecular weight *n*-alkanes of terrestrial plant origin, to establish the nature of organic matter supplied to this central eastern Mediterranean region. The ~600 kyr interval preceding the MSC was targeted in order to evaluate the climatic changes that occur during the leading up to the MSC.

2. Methods

2.1. Site description and sampling strategy

The Pissouri basin on southern Cyprus (Fig. 1) is filled with Neogene sediments extending back to the Middle Miocene (Krijgsman et al., 2002). The Messinian succession of the basin comprises regular alternations of limestones and marls (Fig. 2; Krijgsman et al., 2002) where carbonate content (Krijgsman et al., 2002) has been used to distinguish them (e.g. limestone >75%; marl <75%; Sugden and McKerrow, 1962). The cyclicity of the succession has been used to astronomically tune the Pissouri section to orbital solutions (Laskar et al., 2004) using both bio- and magnetostratigraphic tie-points (Fig. 2; Krijgsman et al., 2002). At Pissouri, three biostratigraphic events occur in the 30 m of limestone–marl alternations that directly underlie the gypsum and are studied here (Fig. 2). These biostratigraphic tie points consistently link marl deposition to the area of the orbital curve that includes the insolation maxima (Fig. 2). In addition, three magnetostratigraphic boundaries also occur in this part of the section (Fig. 2) and these are consistent with the tuning based on biostratigraphic tie-points and confirm the lithological phase relationship with the orbital curve (Krijgsman et al., 2002). The marls have been correlated with sapropelic horizons (Krijgsman et al., 2002) that are observed in other Mediterranean successions (e.g. Sorbas; Sierro et al., 2001). In line with standard practice for astronomically tuned Mediterranean successions and consistent with the biostratigraphic and magnetostratigraphic tie points, the middle of each marl (or sapropel) layer is linked to the extremes of the 65°N summer insolation curve (Sierro et al., 2001; Fig. 2).

Forty-eight samples were collected in 1998 from the Pissouri section road cut (Kouwenhoven et al., 2006; Krijgsman et al., 2002) before it was sprayed with concrete. Where possible, one sample for every limestone and one for every marl was analysed throughout the section, starting at ~32 m below the gypsum and representing the 600 kyr preceding the MSC (6.52–5.98 Ma; Krijgsman et al., 2002). While this approach does not necessarily show the full range of values in relation to precession, it does allow us to compare data generated during two distinct phases of multiple orbital cycles. The slump layer (7–10 m, Fig. 2) towards the top of the section was not sampled because its age and orbital phasing is uncertain.

2.2. Extraction and separation

The sediments (~40 g) were homogenised and extracted via Soxhlet apparatus for 24 h using dichloromethane (DCM):

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