Earth and Planetary Science Letters 427 (2015) 226–235

Contents lists available at ScienceDirect

Earth and Planetary Science Letters

www.elsevier.com/locate/epsl

Evidence for deep-water deposition of abyssal Mediterranean evaporites during the Messinian salinity crisis

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ARTICLE INFO

Article history:
Received 24 March 2015
Received in revised form 28 June 2015
Accepted 29 June 2015
Available online 24 July 2015
Editor: D. Vance

Keywords:
Messinian salinity crisis
ACE index
TEX_{86}
Mediterranean sea
deep sea drilling project

ABSTRACT

Scientific drilling of the abyssal evaporites beneath the deepest parts of the Mediterranean basin gave rise to the idea that the Mediterranean sea completely evaporated at the end of the Messinian. Herein, we show, using new organic geochemical data, that those evaporites were deposited beneath a deep-water saline basin, not in a subaerial saltpan, as originally proposed. Abundant fossil organic lipids were extracted from evaporites in Mediterranean Deep Sea Drilling Project cores. The archaeal lipid distribution and new analyses, using the ACE salinity proxy and TEX_{86} temperature proxy, indicate that surface waters at the time of evaporite deposition had normal marine salinity, ranging from ∼26 to 34 practical salinity units, and temperatures of 25–28 °C. These conditions require a deep-water setting, with a mixed layer with normal marine salinity and an underlying brine layer at gypsum and halite saturation. After correction for isostatic rebound, our results indicate maximum drawdown of ∼2000 m and ∼2900 m relative to modern sea level in the western and eastern Mediterranean basins, respectively. Our results are consistent with previously proposed scenarios for sea level drawdown based on both subaerial and submarine incision and backfilling of the Rhone and Nile rivers, which require Messinian sea level drops of ∼1300 m and ∼200 m, respectively. This study provides new evidence for an old debate and also demonstrates the importance of further scientific drilling and sampling of deeper part of the abyssal Messinian units.

1. Introduction

Field studies dating back to the 1860s and renewed study in the 1950s of Late Miocene evaporites exposed around the margin of the Mediterranean provided the first evidence of widespread drawdown of the Mediterranean at about 6 Ma (Mottura, 1872; Ogniben, 1957). Seismic reflection profiling in the late 1960s revealed that the abyssal basins of the Mediterranean, such as the Sardino-Balearic basin in the western Mediterranean (∼2850 mbsl, meters below modern sea level), the Ionian basin in the central Mediterranean (∼4100 mbsl), and the Herodotus basin in the eastern Mediterranean (∼3000 mbsl), are also underlain by extensive Messinian-age evaporites, some 1 to 2 km thick (for details about this early history, see Ryan, 2009). These abyssal Messinian deposits were first sampled by deep-sea drilling in 1970 (Ryan et al., 1973a, 1973b; Hsü et al., 1978). That work gave rise to the surprising idea that the Mediterranean Sea may have fully evaporated during the Messinian salinity crisis, leaving behind a vast desert landscape ∼2 to 4 km below global sea level (Hsü, 1972; Hsü et al., 1973a, 1973b). This hypothesis, based partially on sedimentological features in the abyssal evaporites, has been hotly debated (e.g. Hardie and Lowenstein, 2004), but remains an enduring idea of the Messinian salinity crisis.

The Messinian salinity crisis is now precisely dated to 5.97 to 5.33 Ma (Krijgsman et al., 1999; Manzi et al., 2013). Drilling and seismic profiling have demonstrated deep incision and subsequent backfilling of the lower reaches of the Nile and Rhone rivers during the Messinian salinity crisis (Barber, 1981; Clauzon, 1982). Seismic profiling has also revealed an erosional unconformity around the higher parts of the Mediterranean, and reworking of evaporite detritus into the lower parts of the basin (e.g. Lofi et al., 2011). Hydrologic (Debenedetti, 1982; Blanc, 2006; Meijer and Krijgsman, 2005) and isostatic (Norman and Chase, 1986; Govers et al., 2009) modeling have helped clarify the response of the basin to changing climate, water supply, and sediment and water loads. These studies, and many others (see reviews by Ryan, 2009 and Roveri et al., 2014a), have aided our understanding of the Messinian salinity crisis. For example, in the original "shallow-water deep-basin" hypothesis, Hsü and colleagues (Hsü, 1972; Hsü et al., 1973a, 1973b) used the term "desiccated deep basin" to refer to a Mediterranean that was completely evaporated. Subsequent

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http://dx.doi.org/10.1016/j.epsl.2015.06.060

papers have refined this desiccation hypothesis and stretched the terminology to include various scenarios involving only partial evaporation of the Mediterranean (e.g. Meijer and Krijgsman, 2005; Ryan, 2009). There has also been much important work on the marginal Messinian, but those deposits formed in relative high positions within the basin and thus provide little direct evidence about the depositional setting of the deep Mediterranean basins. Apart from deep-sea cores, there is no direct evidence for the depositional environment of the abyssal Messinian evaporites.

Around the same time as the discovery of the Messinian salinity crisis, there was an active debate about the origin of "saline giants", which are massive evaporite deposits seen throughout the geologic record. It was well established that halite and gypsum could be deposited in deep-water silled basin, given the appropriate climatic constraints and basin geometry (e.g. Schmalz, 1969; Brongersma-Sanders, 1971). In this sense, "deep" refers to a water depth where storm waves cannot reach the bottom of the basin. For brine-filled basins, this transition occurs at about 50 m (Sonnenfeld, 1985). Several papers propose credible deep-water interpretations for the Messinian salinity crisis (Brongersma-Sanders, 1971; Debenedetti, 1982; Schmalz, 1991), but those ideas have been commonly discounted, mainly because there is no modern analogue for deep-water evaporite deposition (Hsü, 1972). It should be noted that there is also no modern analogue for a fully evaporated abyssal basin.

In the debate about the Messinian salinity crisis, what has been lacking is way to estimate the amount of evaporative drawdown of the deep Mediterranean basins during the deposition of the abyssal evaporites. This question cannot be addressed by studies of deposition and erosion in marginal settings. Instead, the key to this problem is determining the depositional environment of the abyssal evaporites. Our approach is to use organic geochemistry to estimate key paleoenvironmental indicators for the available core samples of abyssal evaporites. Relative abundances of fossil archaeal lipids are commonly used to determine the paleoenvironment of sediments, including temperature and salinity (Schouten et al., 2002; Turich and Freeman, 2011). Here we use this analysis to characterize the evaporite facies of the abyssal Mediterranean at the end of the Messinian, and provide an upper limit for the amount of sea level drawdown. We also integrate our new data with proposed scenarios for the Messinian salinity crisis by discussing other constraints on water depth.

2. Materials and methods

2.1. Sample locations

Samples of anhydrite, halite, and gypsum from three drill sites in the Sardino-Balearic and Ionian abyssal basins (Fig. 1) were obtained from the International Core Repository at the University of Bremen. The sites are in abyssal settings, 35–200 km from adjacent continental margins, located at modern water depths of 2.5–4 km.

The abyssal Messinian deposits are 1–2 km thick and are typically divided, on the basis of seismic reflection data, into the Lower Unit, middle Mobile Unit, and Upper Unit (Lofi et al., 2011; Roveri et al., 2014c). The Lower Unit is stratified, but the Mobile Unit shows extensive diapirism, which suggests it is dominated by halite. It is important to note that drilling has sampled no deeper than 160 m into the upper part of the abyssal Messinian evaporites, which amounts to only ∼10% of the section (Ryan et al., 1973a, 1973b; Hsü et al., 1978). Thus, our conclusions here are limited to the uppermost part of the abyssal Messinian evaporites. While there has been much speculation about deeper parts of the abyssal Messinian deposits, at present there are no samples from that part of the section.

Leg 42A Site 374 has a seafloor depth of 4088 m and is located in the eastern Mediterranean basin, 200 km east of the Malta Escarpment and 300 km from the European and African continents (Fig. 1). The evaporites are overlain by 373 m of Pleistocene and Pliocene nanofossil ooze, typical of an open-marine environment, with thin layers of siliciclastic silt, interpreted as distal turbidites (Hsü et al., 1978). The cored portion of the underlying Messinian contains alternating layers of dolomitic mudstone with gypsum crystals, and fine wavy laminae of gypsum and anhydrite (Figs. 2A and 2B).

Leg 13 Site 134 has a seafloor depth of 2864 m and is located at the base of the Sardinian continental slope (Fig. 1). The top 344 m of the drilled section consists of Quaternary and Pliocene nanofossil ooze, with minor pebbles and gravel of terrigenous material (Ryan et al., 1973b). The cored Messinian interval is composed mostly of halite with small anhydrite nodules (Fig. 2C) and thin silty layers with a minor component (<10%) of siliciclastic sediment, attributed to a windblown source (Hsü et al., 1973c).

Leg 13 Site 124 has a sea floor depth of 2726 m and is located in the western Sardino-Balearic abyssal plain, 300 km west of Sardinia and over 500 km from the Gulf of Lion, where the Rhone River empties into the Mediterranean (Fig. 1). The top 359 m of the drilled section consists of Quaternary and Pliocene nanofossil ooze, marls and sands (Ryan et al., 1973a). The cored Messinian interval contains abundant anhydrite nodules, up to 3 cm in diameter, with thin veins of carbonate and mud (Fig. 2D).

The evaporative textures in the cores deposits are not diagnostic of a particular depositional environment or water depth. For example, the shipboard scientists (Hsü et al., 1978) interpreted laminae in the dolomitic mudstone (site 374) as photic zone algal stromatolites, which would be diagnostic of a shallow-water setting. Hardie and Lowenstein (2004) note that wavy laminae are also formed in deep-water settings. The "hopper texture" of halite (site 134) was thought to be indicative of subaerial deposition (Hsü et al., 1973c). Hardie and Lowenstein (2004) and Roveri et al. (2014b) dispute this interpretation. Other early work argues that the similarity of anhydrite deposits (site 124) to "chicken-wire" anhydrite texture found in modern subaerial coastal salt flats (sabkhas) in the Persian Gulf is diagnostic of a subaerial setting (Hsü, 1972). Others suggest that nodular anhydrite is not diagnostic of subaerial deposition (Schreiber and El Tabakh, 2000; Hardie and Lowenstein, 2004).

2.2. Sample preparation and analysis

Organic compounds, including cell-membrane lipids of Archaea, were extracted and analyzed using standard procedures following Schouten et al. (2007). Samples were manually crushed, freeze dried for >48 h, and stored at −21 °C. Dry samples were then powdered and extracted using an accelerated solvent extractor (Dionex-ASE 300) with dichloromethane/methanol solution (2:1, by volume). Total lipid extracts were concentrated using a solvent evaporator (Zymark Turbovap II) and then dried under a stream of purified N_2. Silica-gel chromatography was then used to separate the lipid extract into compound-specific fractions. Ashed Pasteur pipettes loaded with approximately 0.5 g deactivated silica gel (70–230 mesh) were sequentially eluted with 4 ml hexane, 4 ml dichloromethane, and 4 ml of methanol to obtain aliphatic, aromatic, and polar fractions, respectively. The polar fraction, which contains diethers and tetraethers, was filtered through 0.7 μm glass microfiber filter, then dried under pure N_2 stream, and then loaded into a solution of hexane/isopropanol (99:1, by volume).

Extracted samples were analyzed on a high-performance liquid-chromatography atmospheric-pressure chemical-ionization mass spectrometer (Agilent 1200 Series HPLC-APCI-MS, equipped with automatic injector and HP Chemstation software). Liquid