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Impact of the Messinian Salinity Crisis on Black Sea hydrology—Insights from hydrogen isotopes analysis on biomarkers

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ABSTRACT

The Messinian Salinity Crisis (5.96–5.33 Ma ago) was a dramatic oceanographic event, when evaporites kilometers thick precipitated in a desiccating Mediterranean basin, trapping more than 5% of the world's oceanic salt. Hydrological changes in the adjacent Black Sea and water exchange with the Mediterranean region are crucial, but poorly understood factors, influencing Messinian evaporite formation. Here, we present compound specific hydrogen isotope (δD) data from Messinian Black Sea sedimentary rocks that show a rapid change to heavy waters at 5.8 Ma, when major glaciations occurred. At the same time, highly depleted δD values of long chain *n*-alkanes derived from plant waxes indicate that fresh, river transported water originated from colder northern latitudes. The δD values of alkenones, biosynthesized by haptophyte algae, show an unprecedented increase of 60‰ within $\sim$100 kyr. The corresponding rapid change to $+110$‰ for δD of the Black Sea waters seem unrealistic, being heavier than anywhere in the present day oceans. Regardless of the applied relation between the δD values of the alkenones and δD of the waters where they were produced, the 60‰ enrichment in the δD values of alkenones indicates strongly enhanced evaporitic conditions. Still, the relative distribution of the alkenones implies in-situ growth and reproduction of haptophyte algae, requiring sustained marine conditions in the Black Sea up to 5.6 Ma. This indicates that Mediterranean–Black Sea connectivity persisted during the first MSC phase when gypsum precipitated in the Mediterranean basin. When the Black Sea became isolated, at the peak of the MSC ($\sim$5.6 Ma), it had a strongly negative hydrological budget and rapidly desiccated due to excess evaporation.

1. Introduction

Intracontinental marine basins like the Mediterranean and Black Seas react rapidly to changing environments. Variations in rivers runoff, evaporation and precipitation are reflected quickly in seawater salinity and circulation patterns. For the Mediterranean, changes in the basin hydrology during the latest Miocene were dramatic. The region was affected by the so-called Messinian Salinity Crisis (MSC; 5.96–5.33 Ma), when evaporites kilometers thick accumulated in the desiccating Mediterranean basin (Hsü et al., 1973; Krijgsman et al., 1999). During the latest phase of the MSC, the Mediterranean basin seemed to have been affected by inflow of (fresh?) water from the Paratethys, area currently occupied by the circum Black and Caspian Seas regions (Cita et al., 1990, 1978). This resulted in a brackish to fresh water lake-sea (Lago Mare) system, extending over Mediterranean towards the northeast, in the regions of Black Sea, Caspian Sea and Aral Lake (Fig. 1). The MSC ended with Pliocene re-flooding when marine sedimentation resumed (Hsü et al., 1973).

An intermittent Black Sea–Mediterranean connection can be traced back during the late Miocene to early Pliocene ($\sim$11–3 Ma). During those times the Black Sea was the central part of the Eastern Paratethys (Fig. 1), an epicontinental sea whose connections to the open ocean became progressively restricted, resulting in the formation of several subbasins with environments marked by salinities varying from marine to brackish and fresh water conditions (e.g. Popov et al., 2006; Rögl, 1998). An impact of the Mediterranean's MSC on its neighboring Paratethyan sub-basins has been speculated, although the precise mechanism involved remains unknown (Hsü and Giovanoli, 1979). Frequent sea level changes in the Black Sea have been described from the Messinian (7.24–5.33 Ma) (Gillet et al., 2007), when the Black Sea area was still the central part of the eastern Paratethys (Fig. 1) (Rögl, 1996). Cores from the Deep Sea Drilling Project Leg 42 B revealed the presence of supratidal and intertidal Messinian deposits at more than 1700 m below current sea level (Hsü and Giovanoli, 1979). Also seismic data show deep

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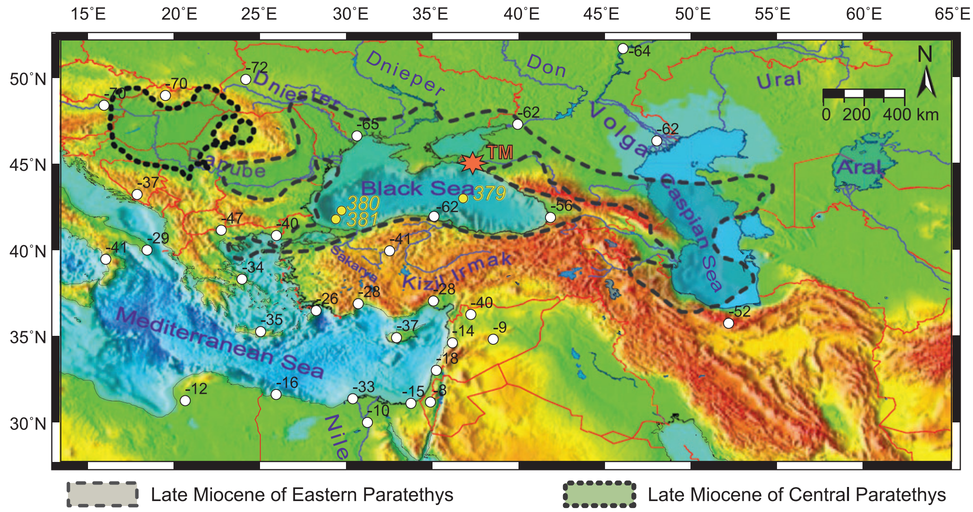

Fig. 1. Palaeogeographic map of the late Miocene, showing the Paratethys area on the presented day land configuration. Major rivers draining into the Paratethys are indicated. The values of the present day precipitation δD are reported according to IAEA (IAEA, 2001). Long-term means were calculated by selecting yearly means in which isotope content have been measured at least in 75% of the precipitation for that year and at least over eight months (IAEA, 2001). The star locates Taman peninsula (TM) with Zheleznyi Rog section. Deep sea drilling project 42B sites 379, 380 and 381 are located. Eastern and Western Paratethys (largely overlapping to the Pannonian basin) were subbasins exiting during Late Miocene.

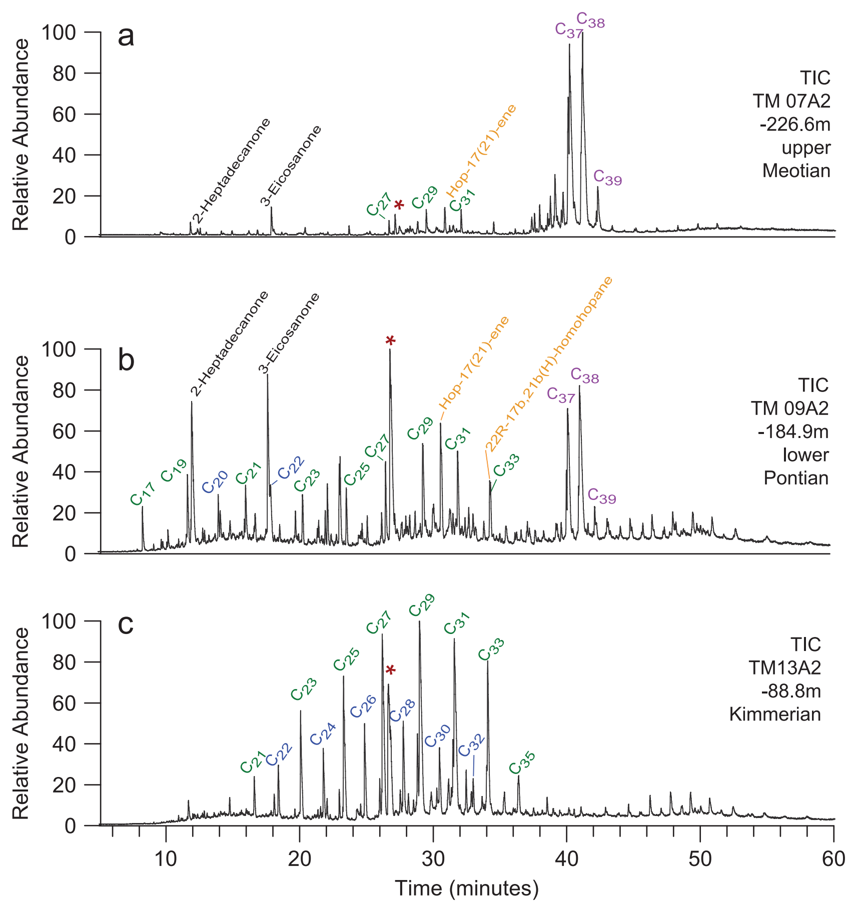

Fig. 2. Total-ion current chromatogram (TIC) of the apolar fraction with increasing predominance of the *n*-alkanes towards the younger sedimentary rocks. The examples are shown from old (a) to young (c), i.e. from upper Meotian to Kimmerian. Stratigraphic levels are in meters. C_{17}–C_{34} refers to *n*-alkanes with odd (green) over even (blue) predominance in chain length distribution; C_{37}–C_{39} (purple) are alkenones; other important compounds also indicated. The star represents co-injected standard. (a) TM 07 sample with the predominance of the alkenones; (b) TM 09 sample with comparable amplitudes of the *n*-alkanes and alkenones; (c) TM 13 sample where the *n*-alkanes are abundant in the a-polar fraction while the alkenones could not be detected. The stratigraphic level is indicated in all three panels. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Messinian erosional surfaces (Gillet et al., 2007), in agreement with a desiccating Black Sea as a consequence of a negative hydrological budget (Bartol and Govers, 2009). Still, evidence such as Late Miocene salt deposits are lacking from the Black Sea area. In contrast, overspilling of Black Sea water as a consequence of a positive rather than a negative hydrological budget has been suggested as well, since