

SEISMICALLY TRIGGERED ANOXIA AND BRINE SPILLOVER DURING THE CE 365 CRETE MEGA-EARTHQUAKE IN THE EASTERN MEDITERRANEAN SEA

SM1

EXTENDED MATERIALS AND METHODS

1 Geophysical data

Morphobathymetric maps were obtained using the GMT software package (Wessel et al., 2013), starting from multibeam swath bathymetry data collected onboard of the Italian CNR ship *Urania* in 2012 with a Kongsberg-Simrad EM-302 echosounder. Raw data were processed using CARIS, obtaining a 5 m resolution bathymetric grid. Bathymetric profiles were compiled using Global Mapper ver. 7.0.

Chirp data were collected using a 15 transducers Benthos Chirp III system. Processing and interpretation of the data, including seismic image compilation and reflector's analysis were carried out using the open-source software package SeisPrho (Gasperini and Stanghellini, 2009).

2 Sediment cores

The gravity core KR2_2 (298 cm long; 35° 04.0000' 22° 04.5500') was collected in the Hephaestus basin at 3398 m water depth during the SALINE cruise (21/10 – 03/11/2014) carried out on board of the R/V CNR-*Urania* in 2014. The core was cut in 1-m long sections that were scanned by a medical Core axial Tomography (CT) scan system, under *X-ray* energy of 120 kV and pitch of 0.3. The final CT scans have a voxel size of 0.5x0.5x1 mm³ with slice thickness of 1 mm. The intensity of the transmitted *X-ray* beams is expressed as *Hounsfield Unit* (HU), following the relation: $HU = (\mu_m - \mu_w) / (\mu_w) \times 1000$ where μ_w is the linear attenuation coefficient of the water. HU depends on properties of the material (m) of X-ray absorption. High-resolution magnetic susceptibility (MS) logs were acquired with a *Bartington*, model MS2, equipped with a 100 mm loop sensor at a sampling interval of 5 mm.

3 XRF core scanner

Geochemical data of core KR2_2 were collected by using an *Avaatech* XRF-CS at ISMAR CNR-Bologna, under 10 kV (10 s measuring time), 30 kV (20 s measuring time) and 50 kV (30 s measuring time) settings. Measurements were performed with a step size of 5 mm along the cores. We selected diagnostic elemental ratios which traditionally track detrital alumino-silicates, mainly the clay minerals (e.g., Al) and heavy

minerals (e.g., Zr, Fe, Ti), carbonates (e.g., mostly biogenic: Ca and Sr), diagenesis overprint (e.g. redox-sensitive elements: Fe, Mn, and S) and paleoproductivity (e.g. Ba, Br, Mo) as previously described in Polonia et al., 2021 [Fare clic o toccare qui per immettere il testo..](#)

4 Grain size

Grain-size analyses were performed on 80 samples with a varying sampling rate (1-6 cm) depending on visual characteristics. Sediment textures were analyzed using a coulter-counter laser MALVERN Mastersizer 2000 (Hydro 2000S), for size ranges between 0.02 and 2000 μm . Sediment samples were treated with 20 vol hydrogen peroxide solution for 48 hours. Results were classified according to Friedman and Sanders (1978) grain-size scale and are presented as % in sand, silt, clay and median particle size (Md) was expressed in μm .

5 Carbon and nitrogen analysis

Total nitrogen (TN), organic carbon (OC), inorganic carbon (IC) and stable carbon isotopes of OC ($\delta^{13}\text{C}$) were analysed in silver capsules using a Thermo Fischer Scientific DELTA Q mass spectrometer coupled with a Thermo Fisher Scientific FLASH 2000 Elemental Analyser via a ConFlo IV (EA-IRMS). Prior to elemental and $\delta^{13}\text{C}$ analyses, samples were acidified with HCl (1.5 N) to remove the inorganic carbon. TN, OC and IC contents are reported as weight % of the bulk sediment. Coefficient of variation for OC, IC and TN was lower than 4% based on replicates of in-house reference material (marine sediment). Reference gas $\delta^{13}\text{C}$ analyses was calibrated against the CH-7 reference NIST standard. Standard deviation for $\delta^{13}\text{C}$ values is better than 0.1‰. OC/TN ratio refers to the molar ratio.

6 Biomarkers

Microwave-assisted alkaline CuO oxidation was carried out following the method of Goñi & Montgomery (2000). Teflon extraction vessels were loaded with 2 – 4 mg OC, 500 mg CuO, 50 mg ferrous ammonium sulfate and 10 mL of degassed 2 N NaOH solution under oxygen-free conditions. The oxidation was performed using a MARS 6 microwave (CEM Cooperation) at 150 °C for 90 min. Extract was centrifuged, transferred to glass vials, and an internal recovery standard (Ethyl vanillin; Sigma-Aldrich) was added. Samples were acidified to pH 1 by adding concentrated HCl (37 %), and then extracted twice with ethyl acetate. The samples were dehydrated with anhydrous sodium sulfate, transferred to clean amber glass vials, and dried under N₂. Before analyses on an Agilent gas chromatograph-mass spectrometer (Agilent GC 7820 gas chromatograph coupled with a MSD EI 5977B mass spectrometer) samples were re-dissolved in pyridine and methylated with BSTFA. Quantification of individual lignin phenols, benzoic acids, was done by comparison with commercially available standards, and quantification of cutin-derived products was done using the response of trans-cinnamic acid and reported as weight % of the bulk sediment.

The lignin content, either normalized to OC (mg g⁻¹ OC), refers to the sum of vanillyl (V), syringyl (S) and cinnamyl (C) phenols, which is an indicator for the contribution of higher/vascular plant material to the total OM pool. These lignin-derived phenols have been extensively used to characterize and trace terrestrial

OC in different marine settings (Tesi et al., 2010a; Tommaso Tesi et al., 2007; T. Tesi et al., 2007). The ratios between these lignin phenol groups (S/V and C/V) can be used for tracing the various types of plants generating these phenols (Goñi and Hedges, 1992; Goñi and Montgomery, 2000; Hedges and Mann, 1979). Similarly, the cutin content refers to the sum of cutin-derived hydroxy fatty acids, which is a component of the leaves and needles of vascular plants used to trace the input of land-derived material (Tesi et al., 2010b).

To test the presence of salt-based brines rather than fluid escape rich in oil, we analysed the hydrocarbon fraction using the method presented in (Tesi et al., 2020). We targeted the upper core that exhibited an oily-like texture and that directly exchange with the brine-rich bottom waters. The hydrocarbon fraction was extracted from dried samples using a methanol/water/potassium hydroxide solution and subjected to alkaline hydrolysis by sonication. The neutral fraction was isolated through liquid-liquid extraction with hexane, followed by silica gel column chromatography to separate apolar and polar fractions. The apolar fraction was analyzed in GC-MS (Agilent 7820a-5977b) on an DB5-MS column (30 m × 250 µm × 0.25 µm) with a temperature program starting at 70 °C and reaching 320 °C. Mid- to long-chain n-alkanes (C22-C34) were identified by comparison to a n-alkane standard. To assess the degradation state and thermal maturity of the sedimentary organic matter, and to identify potential contamination from kerogene byproducts, the Carbon Preference Index (CPI) of n-alkanes (C25-C33) was calculated following the method of Marzi et al. (1993). CPI values of approximately 1 or lower suggest significant degradation or influence by oil and kerogene-derived products, while values exceeding 4 indicate a predominance of fresh terrestrial plant material (Collister et al., 1994). CPI₂₅₋₃₃ was calculated as follow: $(\sum_{\text{odd}} C_{25-31} + \sum_{\text{odd}} C_{27-33}) / 2 \times (\sum_{\text{even}} C_{26-32})$.

7 Foraminifera

7.1 Planktic foraminifera

Twenty-four sediment sub-samples 0.5-1 cm thick on average were taken from the uppermost and the lowermost part of the core KR02_2 for stratigraphic and paleoenvironmental purpose, according to lithological changes and sedimentary structures. The samples were dried at 50°C and washed through a 0.063mm mesh sieve. The fraction > 0.106 mm was counted for the planktic foraminifera content in fourteen samples in the lowermost part of the core. For the other samples a semiquantitative analysis was performed. For counting each subsample has been split into aliquots using a Jones-type microsplitter and for each sample enough aliquots were counted to reach 300-500 specimens. The results, expressed as percentages, are reported in Supplementary SM3. The taxonomy follows Schiebel and Hemleben (2017) and Morard et al. (2019), while the source of the ecological information is Pujol and Vergnaud-Grazzini (1995), Rigual-avnaimHernández et al. (2012), Hernández-Almeida et al. (2011), Mallo et al. (2017), Avnaim-Katav et al. (2020) and Schiebel and Hemleben (2017) for a review.

7.2 Benthic foraminifera

Benthic foraminifera analyses were carried out on a total of 54, 1cm thick, sub-samples from 28.5 cm to 296.5 cm along the core, according to lithological and sedimentary structures variations. The samples were

dried at 50°C and washed through a 0.063 mm mesh sieve. The fraction >0.063 mm has been counted for the benthic foraminifera content. Because the dried fraction contains insufficient microfauna, the samples were entirely studied and only for one sample (C2-II 27) at least 300 specimens of benthic taxa were picked, whereas eleven samples resulted barren. Foraminiferal benthic counts were performed considering only well-preserved specimens and data were reported as relative abundance (%) and as densities (FD = number of specimens/g of total sediment). Taxonomic identification was carried out following Loeblich and Tappan (1988, 1964) for genera, and Van Morkhoven et al. (1986), and Holbourn et al. (2013) for species. Some online databases, such as World Register of Marine Species – WoRMS (WoRMS Editorial Board, 2024. World Register of Marine Species. Available from <https://www.marinespecies.org> at VLIZ. Accessed 2024-11-15. doi:10.14284/170) were also examined.

Sixteen species present in more than two samples and/or with defined bathymetric distribution were grouped into 4 main groups (Supplementary SM4), following Berggren and Miller (1989) and Van Morkhoven et al. (1986), as follows: neritic taxa (0-200 m), upper-bathyal taxa (200-600 m), middle to lower bathyal taxa (600-2000 m), and abyssal taxa (>3000 m), the last only represented by *Articulina tubulosa*. Foraminiferal biodiversity was estimated using Shannon (H) diversity index.

8 Mineralogical analysis

Mineralogical analyses were carried out on 60 selected samples to define sediment composition and sources using Stereo Microscope (Zeiss STEMI, AXIO software), SEM with EDS attachment, XRD. Stereomicroscope allowed the identification of the main components (minerals and plant fragments), SEM/EDS and XRD were used to estimate proportions among components and identify minerals.

9 Radiometric dating

Accelerator mass spectrometry (AMS) radiocarbon dating of handpicked planktonic foraminifera with no evidence of carbonate overgrowth or pyritization was performed. We selected samples in the pelagic units within the slump deposit. About 5-6 mg of specimens (mixed or monospecific when possible) >125 µm in size from 1-cm thick samples were studied. The AMS analyses were performed at the Poznań Radiocarbon Laboratory - Foundation of the Adam Mickiewicz University (Poland). We also dated a black patch included in the basal part of a resedimented deposit and we obtained ages from bulk OC at the base of the anoxic sediment.

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