

ATTI DEI DIRETTORI DELLE SEZIONI DI RICERCA SCIENTIFICA O TECNOLOGICA, DELLE STRUTTURE TECNICHE DI SERVIZIO E DEI DIRIGENTI

Atto n. GEO 739 ADW del 03/12/2024

Oggetto: Servizio di pubblicazione dell'articolo scientifico, in open access, sulla rivista Nature Communications, dal titolo:" Chlorine isotopes constrain a major drawdown of the Mediterranean Sea during the Messinian Salinity Crisis". Importo complessivo € 1.896,00 IVA esclusa. Oneri di sicurezza interferenziale non soggetti a ribasso d'asta: € 0,00. Affidamento diretto, ai sensi dell'art. 50, comma 1, lettera b), del D.Lgs. n. 36/2023 e s.m.i., alla società Springer Nature Customer Service Center GmbH, di Heidelberg (Germania), VAT ID.DE209719094, CIG n. B47F556614.

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Richiamata la deliberazione del CdA n. 99 ADW adottata nella seduta del 30.10.2024 avente ad

Istituto nazionale di oceanografia e di geofisica sperimentale - OGS - Atto n. GEO 739 ADW del 03/12/2024

DETERMINA

Istituto nazionale di oceanografia e di geofisica sperimentale - OGS - Atto n. GEO 739 ADW del 03/12/2024 1. di procedere, per i motivi esposti in premessa, all'affidamento diretto alla società Springer Nature Customer Service Center GmbH, di Heidelberg (Germania), VAT ID.DE209719094, del servizio di pubblicazione dell'articolo scientifico, in open access, sulla rivista Nature Communications, dal titolo:" Chlorine isotopes constrain a major drawdown of the Mediterranean Sea during the Messinian Salinity Crisis", ai sensi dell'art. 50, comma 1, lettera b), del Codice, al prezzo complessivo di € 1.896,00 IVA esclusa;

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IL DIRETTORE Fausto Ferraccioli

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MODULO RICHIESTA FORNITURA IN ECONOMIA

LE RICHIESTE SARANNO NUMERATE A CURA DEL GRUPPO RICHIEDENTE

Chlorine isotopes constrain a major drawdown of the Mediterranean Sea during the Messinian Salinity Crisis

Received: 15 February 2024

Accepted: 17 October 2024

Published online: 18 November 2024

Check for updates

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Hydrological restriction from the Atlantic Ocean transformed the Mediterranean Sea into a giant saline basin during the Messinian Salinity Crisis (5.97– 5.33 million years ago). It is still unclear if the deposition of nearly one million km³ of evaporite salts during this event was triggered by a major (≥ 1 km) evaporative drawdown, or if it took place in a brine-filled Mediterranean connected to the Atlantic. Here we present evidence for a two-phase accumulation of the Mediterranean salt layer based on the chlorine stable isotope composition of halite. During the first phase, lasting approximately 35 kyr, halite deposition occurred only in the eastern Mediterranean, triggered by the restriction of Mediterranean outflow to the Atlantic, in an otherwise brinefilled Mediterranean basin. During the second phase, halite accumulation occurred across the entire Mediterranean, driven by a rapid (<10 kyr) evaporative drawdown event during which sea-level dropped 1.7–2.1 km and ~ 0.85 km in the eastern and western Mediterranean, respectively. During this extreme drawdown event, the eastern Mediterranean basin lost up to 83% of its water volume, and large parts of its margins were desiccated, while its deep Ionian and Herodotus sub-basins remained filled with >1 km-deep brine.

Today, more freshwater is extracted from the Mediterranean Sea by evaporation than is added by continental runoff¹. Blocking the net import of Atlantic Ocean waters through the Gibraltar sill would result in a Mediterranean sea level fall at a rate of about 0.5 m yr[−]¹ (ref. [2\)](#page-10-0). During the Messinian Salinity Crisis (MSC), the deposition of nearly one million km³ of evaporite salts^{3,4} (mainly gypsum, CaSO₄.2H₂O, and halite, NaCl) is a testimony of highly restricted hydrological exchange with the Atlantic Ocean. Whether or not evaporite deposition was accompanied by a major (≥1 km) sea level drawdown, however, is still debated. Estimates of the magnitude of the base-level fall during the MSC rely on geological indicators such as deeply incised canyons onland^{5-[9](#page-11-0)}, widespread erosional surfaces on the margins $10-13$ $10-13$ and in the basins $14-16$ $14-16$ $14-16$ and evaporite facies from drilled cores^{$17-20$ $17-20$}. However, these indicators are not interpreted unequivocally $21-24$ $21-24$ $21-24$ and drawdown estimates range from \sim 200 m to \sim 2 km^{[9](#page-11-0),[11,14,21,25](#page-11-0)-27}. Existing hydro-chemical models cannot solve the controversy because they show that the complete MSC halite body can be deposited in scenarios that include periods of Mediterranean isolation and sea level drawdown 28 , but also in scenarios involving exclusively a partially restricted, brine-filled Mediterranean^{9,10,[29](#page-11-0)}.

We use the chlorine stable isotope composition of halite to estimate the volumetric halite precipitation rate in the Mediterranean basins during the MSC. Compared to other geochemical tracers such as strontium isotopes $30,31$ $30,31$ $30,31$, chloride has the advantage of being a major constituent of halite and, for all practical purposes, is derived solely from inflowing seawater. Laboratory contamination issues are

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Fig. 1 | The Messinian Salt Giant of the Mediterranean sea. a Study area showing data and on-land and offshore Messinian evaporite thickness distribution⁴ over a Mediterranean Basin map (background relief and bathymetry maps taken from <https://www.geomapapp.org/>). Chloride isotope data included in this work comes from the hydrocarbon industry well Aphrodite (AP2) located in the Levantine basin (eastern Mediterranean) and from Deep Sea Drilling Project (DSDP) sites 134 (western Mediterranean), 374 (Ionian Basin, eastern Mediterranean) and 376 (Florence rise, eastern Mediterranean). b location of the seismic section (red dashed line) shown in **d**. c Petrophysics and associated lithologic log of the Aphrodite well. GR-Gamma Ray (graph ranges between 0 – left - and 100 API) and RES-

also minimal for this reason. At the basis of our approach is the Results and discussion Chloride isotope composition of halite CYB, Cyrenaica Basin; SB, Sirte Basin; IB Ionian Basin; TB, Tyrrhenian Basin; L-PB, Liguro-Provençal Basin; ALB, Algerian Basin; in the lithological log of c, orange layers represent clastic inclusions. Black horizon in seismic section of d is a highamplitude continuous reflection corresponding to a layer of clastics encased in halite; in d, vertical distance is in km below sea level.

chloride isotope reservoir effect which results from the preferential incorporation of the heavy isotope 37 Cl (as opposed to the lighter isotope 35 Cl) into precipitating halite³². The extent of the isotope reservoir effect depends on the balance between the rate of halite precipitation, which tends to decrease the ³⁷Cl/³⁵Cl ratio of dissolved chloride, and the rate of addition of dissolved chloride from the Atlantic Ocean, that tends to push Mediterranean 37 Cl $/35$ Cl towards heavier global ocean values. The faster the precipitation, the stronger the ³⁷Cl-depletion of the precipitating halite. Evaporative drawdown of a halite-saturated water column^{[33](#page-11-0)} results in very high rates of halite precipitation, and in the most extreme dissolved Cl, and thus halite, ³⁷Cl-depletion.

We analyzed 60 drill cuttings from the Aphrodite well (Levantine basin, eastern Mediterranean) starting from the onset of halite precipitation and spanning a thickness of 1393 m upcore (Fig. 1). All analytical results are presented in Supplementary Tables 1–3. In the Levantine basin, the Messinian evaporite package is divided into the following seven seismic subunits³⁴. Four transparent units are composed mainly of halite. Two intercalated, highly reflective units are composed of halite with a higher, albeit laterally variable, clay content. A seventh unit is composed of a mixture of anhydrite, clays and sands, separated from the underlying units by the Intra-Messinian Truncation Surface (IMTS, interpreted as a dissolution surface) 34 (Fig. 1d). Bulk XRD analyses of

d Composite seismic section (d-d') in the Levantine basin showing the Messinian evaporites composed of seven seismo-stratigraphic units³⁴. Notes: in a, symbols are as follows: RB, Rhodes Basin; FB, Finike Basin; AB, Antalya Basin; CB, Cilicia Basin; LRB, Larnaca Basin; LTB, Latakia Basin; LEB, Levant Basin; HB, Herodotus Basin;

Fig. 2 | Composite log and isotopic results. X-Ray Diffraction (XRD, colour legend as in Fig. [1c](#page-6-0)) (a), mineralogical $(c-f)$ and chloride isotopic (g) composition of cuttings from the Aphrodite 2 hydrocarbon exploration well from the deep Levant Basin, alongside a seismic line crossing the same well (b), and chloride isotopic composition (h) of halite samples from DSDP sites 134, 374 and 376. Notes: Quartz, $CaCO₃$ (calcite), $CaSO₄$ (anhydrite) and NaCl (halite) are in weight-% of dry sediment, discarding the presence of barite (BaSO₄) and sylvite (KCl) which were added to the drilling fluids. FBI stands for Foraminifer Barren Interval³⁶. The red dashed line in g and h represents the equilibrium chlorine stable isotope composition of

halite precipitating from seawater. In c–h, yellow layers (units 1, 2, 4 and 6) are nearly pure halite, gray layers (units 3 and 5) are halite mixed with terrigenous material. In g, the red circle and red star represent the $\delta^{37}Cl_{halite}$ data points used to fit the numerical model providing a range of drawdown estimates (Fig. [3\)](#page-8-0). The horizontal black line in b is the high-amplitude continuous seismic reflection corresponding to a layer of clastics encased in halite, also shown in Fig. [1d](#page-6-0); the dotted black line in c through g represents the vertical position of this reflector relative to the cuttings of core Aphrodite 2. Vertical distance is in meters below sea level. Source data are provided as a Source Data file.

the Aphrodite cuttings (Fig. 2) show that, within seismo-stratigraphic units 1 to 4 and the bottom 360 m of seismo-stratigraphic unit 5 (3943–2700 m depth interval), halite dominates the mineral assemblage (>80 wt-%), with minor ($<$ 20 wt-%) amounts of anhydrite (CaSO₄) and only trace amounts of $CaCO₃$ and quartz. In the topmost 140 m of seismo-stratigraphic unit 5, the abundance of halite decreases sharply, and that of all the other minerals increases. No samples are available from the well above 2550 m depth, hence no samples are available from unit 6. The drill cuttings also contain sylvite (KCl) and barite (BaSO₄) (Supplementary Fig. 1) which were artificially added to the drilling fluids to control their salinity and density, respectively.

Halite grains for Cl-isotope analyses were selected from the drill cuttings under a binocular microscope, excluding grains that contained evident signs of impurities. We cannot exclude, however, that minor amounts of Cl-bearing sylvite (KCl) contributed to the Clisotope signature we measured. Mass-balance calculations, however, suggest that the contribution is negligible (see supplementary materials). The δ^{37} Cl values at the base of the halite layer (0.4 % vs standard mean ocean chloride, hereafter SMOC) are in isotopic equilibrium with oceanic dissolved chloride (0 ‰ vs SMOC) (Fig. 2g). Subsequent halite, forming Levantine basin seismo-stratigraphic units 1 to 4 and the bottom 360 m of seismo-stratigraphic unit 5 (3943–2700 m depth interval), is slightly depleted in 37 Cl (average δ ³⁷Cl = 0.31 ‰ vs SMOC) compared to equilibrium with global ocean dissolved chloride. We interpret this as reflecting a modest isotope reservoir effect, in which the rate of dissolved chloride sequestration into halite becomes important relative to the influx of chloride from the Atlantic. In the topmost 140 m of seismo-stratigraphic unit 5, δ^{37} Cl values decrease abruptly, reaching a minimum of −0.30 ‰ vs SMOC at 2630 m depth (Fig. 2g). This is interpreted to reflect a sudden increase in the rate of halite precipitation relative to seawater chloride replenishment.

We also analyzed 9 halite samples from drill cores obtained by drilling the topmost few tens of meters of the deep-basin Mediterranean halite layer during Deep Sea Drilling Project (DSDP) Legs 13 and 42 A from the Florence Rise (Site 376, eastern Mediterranean), Ionian Abyssal Plain (Site 374, eastern Mediterranean) and west Sardinian margin (Site 134, western Mediterranean). A stratigraphic correlation between these sites and the Aphrodite section is not possible, although the position of the DSDP halite samples at the top of the halite body implies that they represent the final stages of the highsalinity evaporite phase of the MSC (Fig. 2). Halite from DSDP samples shows a range of 37Cl depletions from near-equilibrium with oceanic Cl at Site 376 (0.33 < δ^{37} Cl ‰ vs SMOC < 0.37), to a strong ³⁷Cl-depletion at Site 374 (−0.14 < δ³⁷Cl ‰ vs SMOC < 0.04). Halite from DSDP Site 134 has intermediate δ^{37} Cl (0.08 ‰ vs SMOC) (Fig. 2). The 37 Cl-depleted isotope signature of halite from DSDP sites cannot be influenced by the composition of drilling fluids, because the halite sub-samples were obtained by mechanically breaking solid halite layers in the DSDP cores, rather than extracted from an admixture of drill cuttings and drilling fluids like for the Aphrodite samples.

Two-phase deposition of the Mediterranean halite layer

We used a numerical model to quantify halite precipitation rates and the extent of sea-level drawdown during the MSC. The model is based on mass balances of water and dissolved ions $(^{35}Cl^-$, $(^{37}Cl^-$, Na⁺, Mg²⁺, SO_4^2 ⁻, Ca^{2+} , K⁺ and HCO₃⁻) in the western and eastern Mediterranean basins and is forced by the evaporative flux, continental runoff and hydrological restriction at the Gibraltar sill. Evaporation and continental runoff fluxes are based on the Miocene General Circulation Model results of Simon et al.³⁵. Starting from initial chemical and hydrologic conditions corresponding to the modern Mediterranean, the model is integrated forwards in time for 20 kyr, after which the hydrological connectivity at Gibraltar is impeded, salinity rises, and evaporitic minerals precipitate. With a salinity-corrected evaporation rate starting at the average value (1 m yr^{-1}) reported in Simon et al.³⁵ values of continental runoff and hydrological restriction at Gibraltar are found to obtain a good match between simulated and observed 4.25 halite volumes and halite δ^{37} Cl values. A full description of the numerical model, model forcing and model constraints is given in the supplementary material.

The best fit of the model to the volume and δ^{37} Cl values of halite (Fig. [3](#page-8-0)) is obtained if a two-phase hydrological restriction-isolation scenario at Gibraltar is considered. First, the deep-water outflow at Gibraltar is restricted but not blocked, leading to the precipitation of gypsum,

Fig. 3 | Results of the standard model run in the western (orange dashed line) and eastern (solid blue line) Mediterranean basins. a Salinity in g/kg; b water level in km; ${\bf c}$ volume (km 3) of precipitated calcite (CaCO₃); ${\bf d}$ volume (km 3) of precipitated gypsum ($CaSO_4.2H_2O$); e volume (km³) of precipitated halite (NaCl) and volume ($km³$) of total precipitated salts (faint black line); **f** volume ($km³$) of precipitated epsomite (MgSO₄.7H₂O); **g** volume (km³) of precipitated kainite (KClMgSO₄.3H₂O); **h** δ^{37} Cl of halite and kainite calculated by the model compared to the measured δ^{37} Cl values of halite form Units 1 to the bottom 2/3 of Unit 5 in the Aphrodite-2 core (AP-phase 1), halite from the top 1/3 of Unit 5 in the Aphrodite-2

core (AP-phase 2) and the halite samples at DSDP site 134 (west Sardinia margin). The blue shaded areas represent the ranges of water level (b), halite volume (e) and $\delta^{37}Cl_{halite}$ (h) in the eastern Mediterranean that result if the model is fitted to the lowest measured $\delta^{37}Cl_{halite}$ value (red circle in **h**) or the 2nd lowest $\delta^{37}Cl_{halite}$ value (red star in h), by increasing the freshwater continental input in the eastern basin during the drawdown phase (see text); these two $\delta^{37}Cl_{halite}$ data points are highlighted in Fig. [2;](#page-7-0) the green lines in b, e and h represent model results corresponding to this scenario of increased continental water input.

Fig. 4 | Modes of halite accumulation during the Messinian Salinity Crisis deduced from chlorine isotopes of halite and geochemical modeling presented in this work. a Two phases of halite accumulation. During phase 1, halite accumulates in a brine-filled Mediterranean basin that is connected to the Atlantic Ocean but has a hydrologically restricted outflow; during phase 2, the Mediterranean is fully isolated from the Atlantic Ocean and halite accumulates during a major evaporative drawdown event; **b** tentative comparison of the phases of halite accumulation (this work) with the Messinian Salinity Crisis (MSC) chrono-

stratigraphic stages after CIESM^{[38](#page-11-0)}, Roveri et al. (ref. [3](#page-10-0)) and Ryan³⁹. Notes: (i) while we can estimate the duration of the two phases of halite accumulation (a), we cannot date them. The tentative correlation with MSC chrono-stratigraphic stages (**b**) is based on the assumption that halite accumulation is restricted to phase 2 of the MSC[3,](#page-10-0)[38,39](#page-11-0); (ii) due to lateral erosion-transport processes, at the Aphrodite 2 site the relative thickness of halite layers is different from the halite volumetric ratios at the scale of the eastern Mediterranean basin.

followed by the precipitation of halite. This halite is characterized by a modest chloride isotope reservoir effect, and decreasing halite δ^{37} Cl from the value in equilibrium with oceanic dissolved chloride (0.4 ‰ vs SMOC) to the average value measured from seismo-stratigraphic unit 1 to the lower 360 m 360 m of unit 5 (0.31 % vs SMOC) (Fig. 3h). In this first phase, lasting about 35 kyr, halite precipitates exclusively in the brinefilled eastern Mediterranean; halite does not precipitate in the western Mediterranean (Fig. [3e](#page-8-0)) because the brine transferred from the eastern to the western Mediterranean basins across the Sicily sill is in thermodynamic equilibrium with halite, but not supersaturated.

After this first phase, the deep outflow at Gibraltar is blocked and the inflow of Atlantic water into the Mediterranean is stopped, leading to the complete isolation of the Mediterranean Sea from the Atlantic Ocean. As a result, the water level in the entire Mediterranean basin drops until the depth of the Sicily sill is reached, and then continues to fall independently in the western and eastern Mediterranean basins, forced by their respective freshwater budgets (Fig. [3](#page-8-0)b). The rate of water level fall is very rapid, with 50% of the total drawdown taking place in less than 3.5 kyr, 80% in less than 6 kyr, and the total drawdown attained in less than 10 kyr. Evaporative drawdown causes an abrupt increase in the rate of halite precipitation in the eastern Mediterranean, and to the initiation of halite precipitation in the western Mediterranean (Fig. [3e](#page-8-0)). The increased halite precipitation rate results in a strong Cl-isotope reservoir effect and an abrupt drop in the δ^{37} δ^{37} δ^{37} Cl of precipitating halite (Fig. 3h).

In the eastern Mediterranean basin, ~ 40% of the total halite volume formed in the standard model run accumulates in 35 kyr, while the total halite volume accumulates in ~ 50 kyr, in agreement with a "rapid^{36"} (~50–60 kyr), rather than a "slow^{37"} (~600 kyr), mode of halite accumulation. This time frame is consistent with the widely accepted stratigraphic position of the halite deposit being accumulated during phase 2 of the MSC across the Mediterranean basins $(5.60 - 5.55)$ Ma; e.g. CIESM³⁸; Roveri et al.³; Ryan et al.^{[39](#page-11-0)}) and, more specifically, in the Levant Basin (Manzi et al. 36).

After roughly 10 kyr from the beginning of the second phase, the calculated volume of halite in the western $(74,900 \text{ km}^3)$ and eastern $(492,300 \text{ km}^3)$ Mediterranean basins approaches the esti-mates of Heida et al.^{[25](#page-11-0)} (110,000-115,000 km³) and Haq et al.⁴ $(585,000-657,000 \text{ km}^3)$, respectively, while the δ^{37} Cl of halite in the eastern (−0.30 ‰ vs SMOC) and the western (0.08 ‰ vs SMOC) Mediterranean matches the minimum values measured from the upper 140 m of unit 5 in the Aphrodite well and the top of the salt layer at DSDP Site 374 (both in the eastern Mediterranean) and the value measured in the western Mediterranean at DSDP Site 134, respectively (Fig. [3h](#page-8-0)). Sensitivity tests (see supplementary material section) show that only a small range of continental runoff values and hydrological restriction at Gibraltar results in a good match of the model to the halite δ^{37} Cl data and halite volume estimates^{4,[25](#page-11-0)}, and that within this range, the calculated time to accumulate the halite body and the extent of the drawdown change little.

Our results solve a controversy regarding the mode of halite precipitation – deep basin, deep water⁴⁰ vs deep basin shallow water^{[17](#page-11-0)} that is outstanding since the discovery of the deep basin evaporites during DSDP Leg 13^{17} (Fig. 4). We show that in the eastern Mediterranean approximately 40% of the halite deposit was formed in a waterfilled Mediterranean basin, connected to the Atlantic Ocean by a twoway hydrological exchange, corresponding to the deep-basin, deepwater model⁴⁰. The remaining 60% of the eastern halite deposit was formed by evaporative drawdown of a halite-saturated water body, which is reminiscent of the deep-basin, shallow water model $\frac{17}{7}$ $\frac{17}{7}$ $\frac{17}{7}$, except that halite precipitation takes place during the drawdown, rather than in a deep, desiccated basin after the drawdown took place.

Drawdown of the Mediterranean sea

The water level drawdown we constrain is significant in the western Mediterranean (~850 m), and extreme in the eastern Mediterranean (~ 2100 m), implying that western and eastern sub-basins lost 43% and

83% of their water volume, respectively. In the eastern Mediterranean, large parts of the continental margins would have been completely desiccated, though the deep Ionian, Herodotus and Antalya basins were still covered by a > 1 km-thick brine layer. Our model also predicts that the drawdown in the eastern Mediterranean resulted in the precipitation of the Mg-K-salts epsomite (MgSO₄.7H₂O; 46,700 km³, Fig. $3f$ $3f$) and kainite (KMgClSO₄.3H₂O; 23,200 km³, Fig. 3g), although Mg-K salts were not detected by XRD in our samples, possibly due to a lateral heterogeneity of brine composition in the eastern Mediterranean, or their dissolution in the drilling fluids or during the washing of drill cuttings. The sequence of precipitation halite-epsomite-kainite is consistent with that observed in seawater evaporation experiments where the minerals are separated from the evaporating brine as they precipitated ("fractional precipitation) 41 .

In an attempt to obtain a more conservative estimate of the drawdown extent, we increased the continental freshwater input to the eastern Mediterranean basin in order for the model to reproduce the second-most negative halite δ^{37} Cl data point measured from cuttings of the Aphrodite well $(\delta^{37}Cl = -0.19$ ‰ vs SMOC; Fig. [2e](#page-7-0), star). In these conditions, a more limited drawdown of ~1700 m is calculated (Fig. [3b](#page-8-0), green line and star). Taken together these model runs imply that the eastern Mediterranean experienced a large-magnitude drawdown of 1.7–2.1 km during the MSC.

Independent evidence for the occurrence of a sea-level drop and for the subaerial exposure of the basin margins come from the decrease in halite concentration and the peak in Quartz abundance (up to 58 wt-%) in the top 140 m of Unit 5, suggesting significant terrigenous input into the basin during drawdown. The erosion that took place concomitant with the short-lived sea-level drawdown resulted in only a limited accumulation of halite during drawdown at the Aphrodite site (upper 1/3 of Unit 5 above the black horizon traced in the seismic line displayed in Fig. [1d](#page-6-0) and Fig. [2](#page-7-0)), compared to the underlying, thick halite layer deposited under a full Mediterranean water column (Units 1–4 and lower 2/3 of Unit 5), leading to a non-linear relation between thickness and volume.

The drawdown of 1.7–2.1 km estimated in this work contrasts with the smaller-magnitude (600 m) drawdown estimated from the restoration of the geomorphological base level of the buried Messinian Nile canyon⁹, although the canyon development cannot be precisely dated. If the two estimates refer to the same drawdown event, this implies that the large drawdown was too short-lived to be recorded in the Nile valley geomorphological profile. However, our work shows a complete disconnection of the eastern Mediterranean from the western Mediterranean, implying that, following the first, short-lived, large-scale drawdown, water levels in the eastern Mediterranean would have varied under the influence of an oscillating freshwater budget³⁵, and of the hydrological connection to the Paratethys drainage system 42 . This hydrological mode, which lasted until the reconnection with the Atlantic via the western Mediterranean, possibly as late as the Zanclean $(5.33 \text{ Ma})^{43,44}$, leaves ample time for intermediate water levels such as those deduced from the study of topographic profile of the Messinian Nile Canyon⁹ to develop.

Consequences of Mediterranean Sea drawdown

Our results have broader implications for the biological, geologic and climatic evolution of the Mediterranean realm, and beyond. In the western Mediterranean sub-basin, the 0.85 km sea-level drawdown we constrain would have resulted in the formation of a land-bridge connecting Africa and Europe through the Betic region and the Balearic Islands. This land bridge would have allowed continental-terrestrial vertebrate fauna to colonize the Balearic islands, a migration that is known to have taken place during the Messinian based on paleontological evidence⁴⁵. A drawdown of 1 km in the western and eastern Mediterranean may have resulted in enough lithospheric unloading to trigger a magmatic pulse in the form of volcanism and dykes in the pan-Mediterranean area at the end of the MSC^{46} . Our evidence for drawdowns of ~0.85 km and 1.7–2.1 km in the western and eastern Mediterranean, respectively, make this scenario even more likely. Alongside lithospheric unloading, the huge size of the Mediterranean depression created by MSC water level drawdown - corresponding to a volume loss of 69% of the Mediterranean water body - would have generated planetary-scale climate effects 47 , inducing changes in precipitation patterns, a scenario suggested by rainfall proxy data 47 .

Methods

X-Ray diffraction (XRD)

The XRD measurements were carried out on an Empyrean diffractometer (@Malvern-Panalytical), equipped with a copper tube and a PIXcel multi-channel detector. The configuration is Bragg-Brentano θ - θ and the sample holder is a spinner. The mineral phases are identified using Highscore plus (@Malvern-Panalytical) software and the ICSD-Panalytical database. Semi-quantitative evaluation of mineral abundances is obtained by scaling the intensities of the principal mineral diffraction peaks to those of reference materials applying reference intensity ratio (RIR) coefficients.

Cl-isotope measurements

We measured the chloride isotope composition of halite grains handpicked under a binocular microscope, which overwhelmingly reflects that of halite. First, the halite grains were dissolved in distilled water. Then, dissolved Cl ions were precipitated into AgCl and the AgCl converted into CH₃Cl^{48–[50](#page-12-0)}. The δ ³⁷Cl of CH₃Cl was measured with a Delta plus XP or Delta V ThermoFisher dual-inlet gas source mass spectrometer. The δ^{37} Cl compositions are reported in ‰ vs SMOC. The external reproducibility of the internal IPGP standard seawater dissolved chloride (Atlantique 2) was \pm 0.025 ‰ (1 σ , n = 48); note that this S.D. value is smaller than the size of the δ^{37} Cl symbols in Fig. [2g](#page-7-0).

Numerical model

A full description of the numerical model is provided in the supplementary material.

Data availability

All data generated or analyzed during this study are included in this published article (and its supplementary information). Source data are provided with this paper.

Code availability

The Mathematica code used to simulate the evolution of Mediterranean water mass chemistry and chloride isotope composition has been deposited in the Zenodo database [\(https://zenodo.org/records/](https://zenodo.org/records/13851502) [13851502](https://zenodo.org/records/13851502)) with <https://doi.org/10.5281/zenodo.13851502>.

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Acknowledgements

This study was supported by the European Union's Horizon 2020 research and innovation program under the Marie Skłodowska-Curie grant agreement number 765256 SALTGIANT and by the CNRS via IODP-France through a post-cruise grant. We acknowledge Modi'in Energy and Pelagic partnership for their permission to release data related to the well Aprodite-2. We thank HIS Markit for providing us the Kingdom academic licenses for seismic interpretation.

Author contributions

G.A. designed the study. G.A., L.G., G.B. and P.A. carried out the chloride isotope measurements of halite and interpreted the data. G.A. developed the numerical model and applied it to interpret the halite chloride isotope data with input from I.G., R.E. and J.M. G.A., J.M., L.G., A.C., I.G., G.B., P.A., R.E. and Z.G. contributed to the final manuscript preparation.

Competing interests

The authors declare no competing interests.

Additional information

Supplementary information The online version contains supplementary material available at <https://doi.org/10.1038/s41467-024-53781-6>.

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Peer review information Nature Communications thanks Jeremiah Bernau, Neil Mitchell and Mebrahtu Weldeghebriel for their contribution to the peer review of this work. A peer review file is available.

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