Causes and consequences of the Messinian salinity crisis

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Abstract

Salt giants are massive salt deposits (at least hundreds of m thick) that form during the evaporation of semi-enclosed seas. However, the drivers of salt giant formation and their feedbacks on global and regional environmental change remain debated. In this Review, we summarize the boundary conditions, causes and consequences of the Mediterranean Messinian salinity crisis (MSC; 5.97-5.33 Ma), and highlight the impacts of salt extraction and ion return on the Earth system. Salt giant formation is more complex than the simple evaporation of an enclosed sea. Instead, the tectonic setting of an evaporative basin largely determines the timing and mode of salt formation, with superimposed impacts of orbital-scale climate and sea-level fluctuations. These drivers triggered precipitation of carbonates, gypsum, halite, and even bittern salts in the Mediterranean, with well-defined orbital cyclicities in carbonate and gypsum phases. Removal of Ca^{2+} during salt deposition decouples the oceanic Ca^{2+} and HCO_3^- sinks, causing a $CaCO_3$ burial decrease and, consequently, increased ocean pH, lower atmospheric pCO_2, and global cooling. Salt giants, which reflect a ~7 to 10 % net evaporite-ion extraction from oceans that persists over million-year timescales, could therefore be an important climatic driver, but are currently not considered in long-term carbon cycle models. Future research should target more advanced hydrogeochemical models of water exchange with the open ocean to provide critical context for understanding interactions between salt giants and environmental change.

Website Summary:

Tectonic processes can lead to the formation of nearly enclosed seas and the deposition of extensive salt deposits. This Review explores the drivers and impacts of the Mediterranean Messinian salinity crisis, including previously under-considered impacts on the global carbon cycle.

Key points

1. Giant salt deposits (gypsum and halite) formed in the Mediterranean during the Messinian Salinity Crisis and their timing and mode depended on tectonic impacts on the evaporative basin.

2. Geodynamic and eustatic sea-level forcing are crucial for initiating and terminating salt giant formation with a subsidiary role for regional climate.

3. The main controls on evaporitic mineral precipitation are the freshwater deficit magnitude and the extent of water-exchange limitation between basin and ocean.

4. Evaluation of an updated sea-level record for the 6.4 to 5.0 Ma time interval demonstrates that sea level is a viable driver of the prominent MSC sedimentary cyclicity in addition to orbital freshwater budget variation.

5. The formation and dissolution of giant calcium sulphate (gypsum and anhydrite) deposits can have global consequences as an episodic driver of carbon cycle changes. Oceanic Ca^{2+} removal via $CaSO_4$ deposition decouples the oceanic Ca^{2+} and HCO_3^- sinks, causing a $CaCO_3$ burial decrease and, consequently, increased ocean pH, lower atmospheric pCO_2, and global cooling.

6. Most biogeochemical models assume that evaporite precipitation and weathering are balanced over timescales >100 kyr. However, salt giants can reflect a ~7 to 10 % net evaporite-ion extraction from ocean water that persist over million-year timescales, suggesting that current carbon cycle models could be missing an important long-term climatic driver.

[H1] Introduction

[Paragraph 1 – importance] The opening and closure of oceans and seas by plate tectonic processes is often marked by formation of marginal basins that have restricted water-exchange with the open ocean. Under negative hydrological budgets, where freshwater loss by evaporation exceeds the supply from rivers and rainfall, periods of limited exchange with the open ocean can lead to precipitation of enormous evaporite deposits in the incipient or dying basin, termed 'salt giants'. A small-scale modern example of an evaporative basin is the Dead Sea, a deep hypersaline lake that is entirely disconnected from the ocean. Salt giants have formed episodically through Earth's history, including the Palaeozoic (Australia, USA, Russia, NW Europe), Mesozoic (South Atlantic, Gulf of Mexico), and Cenozoic (Mediterranean, Red Sea, Central Europe) eras[1,2]. Halite (NaCl) and gypsum or anhydrite ($CaSO_4$) extraction from seawater during salt giant formation can represent >5% of the total ocean dissolved salt content[3,4], which disrupts local ecosystems in evaporitic seas and modifies global ocean chemistry[5].

[Paragraph 2 – MSC key features] The Mediterranean Messinian salinity crisis (MSC) is one of the youngest salt giants in Earth's history, having formed between 5.97 and 5.33 Ma when the Mediterranean became land-locked in the Late Miocene. During the MSC, more than one million cubic km of salt was extracted from the global ocean and precipitated as hundreds of m-thick gypsum deposits and km-thick halite units in the Mediterranean basins. The marine Atlantic connection progressively closed and Mediterranean water level has been interpreted to drop 800-2000 m[6–8]. During the final MSC stage, also known as "Lago Mare", the Mediterranean transformed into a megalake with highly fluctuating, hypersaline to brackish, conditions. The MSC was terminated by a massive flood from the Atlantic that reintroduced open marine conditions across the Miocene-Pliocene boundary in the Mediterranean[9–11].

[Paragraph 3 – motivation/recent developments] Seismic profiles across deep basinal sequences and outcrops along tectonically uplifted marginal basins provide a picture of the spatial distribution of Mediterranean evaporite units and their stratigraphy (Fig. 1)[12–16]. The Late Miocene land-locked Mediterranean configuration amplified its responses to regional and global climate fluctuations, and caused distinct cycles in pre- and post-MSC deposits, facilitating construction of a detailed chronostratigraphic framework, tuned with

precessional resolution (~20 kyr) to astronomical insolation curves[17–19]. This astrochronology has resulted in a stratigraphic consensus scenario for the Mediterranean salt giant[15] that provides a foundation for high-resolution geochemical evaporite fingerprinting[20,21] and for observational and modelling studies of the underlying forcing mechanisms[22,23]. These advances indicate that salt giants do not form in basins that simply isolate and desiccate; rather, complex sub-basin settings have a crucial role in determining the timing and mode of salt formation[24,25], with contributions from various forcing mechanisms such as tectonics, sea-level change, and hydrological connectivity with the ocean[26].

[Paragraph 4 – In this Review, we..] In this Review, we discuss the latest developments in MSC research, in terms of salt formation, hydrological conditions and drivers of basin desiccation. We build on previous detailed overviews of MSC stratigraphy[15,27], Mediterranean evaporite distribution patterns[4,16], and Atlantic-Mediterranean connectivity[26,28], and expand on the drivers and feedbacks of the MSC that are applicable to other salt giants more generally. In particular, we reflect on the regional and global environmental consequences of salt giant formation, rapid ion return during basin reconnection, and slow ion return during weathering over geological timescales, including impacts on the global carbon cycle.

[H1] The Mediterranean salt giant

Tectonic processes can lead to near-isolation of continental seas and deposition of extensive salt deposits. The onset of MSC evaporite deposition and establishment of earliest Pliocene marine conditions provide insights into both restriction and re-opening of such a marginal sea. The Mediterranean salt giant formed in a convergent plate tectonic setting with the African plate moving northward with respect to Europe and Iberia. This convergence is not complete, so it is possible that the Messinian evaporites will, in time, represent merely the initial phase of salt giant formation associated with ongoing Mediterranean basin closure.

[H2] Geological setting of the MSC

Salt giant formation requires the presence of a sill that restricts an evaporative basin from the open ocean. These sills generally form when continents collide or break apart by plate tectonic processes and provide the necessary raised lip across which exchange becomes restricted and allows development of water bodies with different

chemical and physical properties. The strait at Gibraltar that connects the Mediterranean with the Atlantic is presently 284 m deep at the Camarinal sill and 14.3 km wide at the Tarifa narrows[29]. Palaeogeographic reconstructions of the Gibraltar region indicate that the early Messinian Atlantic-Mediterranean connection was a foreland-basin system with multiple gateways through southern Iberia and northern Morocco[26,28]. These Betic and Rifian corridors, respectively, closed progressively in pre-MSC times, and marine connectivity evolved toward a single proto-Gibraltar strait gateway for the MSC[28,30]. Mediterranean-Atlantic connectivity could also have been partially controlled by an emergent volcanic chain on the eastern Alborán margin that formed a partial land-bridge between northern Morocco and southeastern Spain[31]. Water flux modelling indicates that exchange patterns with the Atlantic depended on relative sill depths[32]. Crucially, two-way flow exists in both corridors when the shallowest corridor is more than half as deep as the deepest corridor, whereas one-way flow exists in both corridors when the shallowest corridor is less than half as deep as the deepest corridor[32]. Uplift of the Rifian corridor at ~7 Ma[30] could, therefore, have altered exchange patterns in the Gibraltar strait from mainly Atlantic inflow to two-way flow, consistent with simultaneous Alborán Basin benthic faunal changes[33] and deep Mediterranean records in which the first signs of restricted conditions and increased water mass stratification occurred at ~7 Ma[34].

[H2] MSC stratigraphy

Mediterranean Messinian evaporites were first reported in 1867[35] and were later described by field geologists who documented ~100-m-thick gypsum units between marine sequences in several Italian basins[36,37]. In the 1970s, the widespread presence of evaporite units across the Mediterranean was confirmed by Deep Sea Drilling Project (DSDP) Leg 13[3,38,39], although coring only reached the uppermost MSC successions.

The depositional and stratigraphic architecture of Messinian evaporites varies across the Mediterranean, and depend mainly on tectonic settings and water depths. Four main settings are recognized (Fig. 2). First, marginal zones with mainly erosional features that have commonly been related to multiple drawdown events[6,16] in which subaqueous erosion by dense cascading waters might also have had a role[40]. Second, shallow, silled basins (Adriatic region, SE Spain basins) containing the most complete marine gypsum successions[41], overlain in places by erosional surfaces and/or younger lacustrine and continental deposits with intervals characterized by

brackish Lago Mare fauna[24,42–44]. Third, intermediate-depth basins (Sicily, Cyprus, Balearic Promontory), which can be complicated by substantial tectonic deformation during and since the MSC[45,46]. Basal MSC units in these intermediate settings comprise marine gypsum[47] or anoxic shales devoid of evaporites[48,49]. Where marine gypsum is observed, the evaporites might not be preserved *in situ* because they are commonly found as a range of reworked deposits from gypsarenites to gypsum olistostromes[15,50]. The final, fourth setting includes deep central basins that are found in the western (Liguro-Provençal, Algerian) and eastern (Ionian, Levant) Mediterranean, separated by the Strait of Sicily, which have strikingly different depositional architecture on seismic refection profiles[12,16].

Deep central western Mediterranean basins typically contain a seismic "trilogy" with a Lower Unit (mass-transport deposits), Mobile Unit (halite), and an Upper Unit (gypsum-clastic alternations)[12]. However, no direct lithological data are available for the deep central western salt giant where only the topmost MSC has been sampled, which generally contains gypsum with brackish water fauna[51]. The easternmost deep Mediterranean (Levant Basin) contains a >1-km-thick evaporitic succession with six seismic sub-units[52,53], four transparent units composed of halite and two units composed of claystones[54,55]. Cuttings from industrial drill holes suggest that evaporite deposition started with only a few metres of anhydrite[52,56], followed by the halite-dominated succession, which terminated after a truncation surface with a ~100 m thick "Unit 7" composed of shales, sands, and anhydrite[14]. This top unit of the MSC in the deep Levant Basin is interpreted as having been deposited above the Intra Messinian Truncation Surface (IMTS), a dissolution surface related to substantial dilution and stratification of the eastern Mediterranean water column[14].

Detailed stratigraphic studies from both onshore sequences and offshore seismic data indicate that the Mediterranean contains several different evaporite successions (Fig. 1, 2)[15]. There are at least four main evaporitic deposit types observed in MSC successions now exposed on land. Evaporitic carbonates known as the Calcare di Base (Sicily)[57,58] and the Terminal Carbonate Complex (SE Spain)[59,60] formed at the Messinian basin margins. Predominantly marine gypsum known as the Primary Lower Gypsum unit (PLG: Spain, Italy)[21,41] mainly precipitated in depocentres of shallow silled basins. Downslope reworking of PLG by tectonic activity and gravitational sliding is a common feature in intermediate-depth basins (Sicily, Balearic

Promontory, Cyprus)[46,61]. Thick gypsum-mudstone alternations and the absence of desiccation features indicate that Mediterranean-Atlantic connectivity persisted with two-way flow. Halite is only present in intermediate and deep central basins (Sicily, Liguro-Provençal, Levant)[62]. Marine inflow is still required to accommodate km-thick halite successions, but outflow was likely blocked. The youngest MSC evaporites are gypsum with continental geochemical signatures of the so-called Upper Gypsum unit (UG: Sicily, Cyprus)[24,63]. This gypsum unit requires additional fresh-water influx from the Paratethys and alternates with clastics that contain brackish Lago Mare fauna[24]. Also, volumetrically minor K-Mg-salts (bittern salts) are sometimes associated with halite. Except for the halite in the western Mediterranean, all of these evaporites are interbedded with detrital clastics and/or hemipelagic sediments. The transition from non-marine Messinian to deep marine Zanclean deposits marks the end of the MSC, and is often conformable without evidence of major erosion[10,64].

[H2] Astronomical cycles in Mediterranean evaporites

Miocene and Pliocene Mediterranean sedimentary successions are marked by precession-paced sapropel-marl cycles with characteristic patterns that can be correlated across the Mediterranean and to astronomical curves (Fig. 3)[17,18,65]. The sapropels record humid conditions at precession minima and insolation maxima and the marls reflect arid conditions at precession maxima and insolation minima. Cyclostratigraphic correlation and astronomical tuning of pre- and post-MSC sedimentary successions provide accurate ages for both the onset of PLG precipitation (5.97 Ma)[66], with evaporitic limestones in some intermediate and marginal basins forming slightly earlier (6.08-6.03 Ma)[13,67,68], and the marine sediments that immediately overlie the MSC successions throughout the Mediterranean (5.33 Ma)[69]. This astronomical tuning constrains the MSC duration to 640 kyr. Dating within the MSC interval itself is more uncertain because of a lack of high-resolution independent age control points; magnetostratigraphic constraints are lacking as the entire MSC occurred within a single reversed magnetic polarity subchron[18,70] (Fig. 3), biostratigraphic markers are absent because of the extreme environmental conditions, and datable volcanic ash layers are scarce[15,43].

During the PLG phase, marine carbonate-marl and gypsum-marl cycles accumulated subaqueously in both shallow and intermediate basins (Fig. 3)[41], which precludes a major Mediterranean sea-level fall at the onset of the MSC[71]. Moreover, marine strontium isotope data are broadly consistent with a high Mediterranean water

level that permitted restricted two-way Atlantic-Mediterranean exchange[21,72]. Assuming that cyclic gypsum-marl alternations followed the same regional precessional climate forcing as pre- and post-MSC Mediterranean sediments, correlation of 16-17 documented sedimentary cycles in the PLG to astronomical curves suggest that PLG deposition ended at <5.6 Ma (Fig. 3)[41,73]. However, numerical modelling of water and salt balances indicates that the gypsum-marl cycles could have resulted either from precession-driven ~20% hydrological budget changes and/or oscillating gateway restriction caused by sea-level fluctuations of ~10 m competing with tectonic uplift and marine gateway erosion[74,75].

Deep Mediterranean halite units lack absolute age control. In the western Mediterranean, halite is thought to have succeeded PLG deposition and is correlated tentatively with the TG12-14 glacial interval (5.59-5.55 Ma) in oxygen isotope ($\delta^{18}O$) records[27,76] (Figs. 3, 4). The timing of initial eastern Mediterranean halite deposition is contested, with suggested ages ranging from 5.97 Ma, equivalent to the PLG onset in marginal basins[77], to 5.59 Ma, at the end of the PLG[78]. There is a third possibility, that halite deposition partly coincided with the start of glacial stage TG22 at ~5.8 Ma, as demonstrated by comparing global sea level with MSC sill-depth scenarios (Fig. 4). Halite is thought to have been deposited when Atlantic-Mediterranean exchange was more restricted than during the PLG phase[79] (see also *Supplementary Note*). In geochemical models, a severely restricted scenario with no Mediterranean outflow (that is, with Mediterranean sea level close to, or below, sill depth) could support deposition within 80 kyr of the deep-basin halite body observed in seismic profiles[79]. In this scenario, evaporated freshwater is replaced continuously by Atlantic inflow, which generates the necessary ion fluxes for halite deposition. The evaporite mineral paragenesis resulting from this constant marine supply with no ion loss via Mediterranean outflow is distinctly different from that generated by evaporation of a fixed seawater volume. Instead of sequential evaporite phases precipitating as brine concentration increases, mineral precipitation fields overlap substantially, with carbonate, gypsum, and halite precipitation potentially coexisting up to bittern salt formation[80].

The final Mediterranean salt giant phase is the most enigmatic, with alternating UG beds and brackish Lago Mare deposits that contain biota of Paratethyan (former Black Sea-Caspian Sea system) affinity[43]. In intermediate basins (Sicily, Cyprus), 6-7 gypsum-brackish marl alternations are observed[27,81]. Strontium

isotope ratios from both gypsum crystals in the UG and ostracods from Lago Mare marl horizons suggest a dominantly freshwater system with only minor (~20%) Atlantic contribution[24,63]. Assuming that UG cycles were precession-driven, downward tuning from the lowermost Zanclean suggests that this final MSC phase started at 5.52 Ma[24]. In shallow silled basins, time-equivalent continental and lacustrine sediments contain influxes of high-diversity Paratethyan ostracods, but no gypsum [42,82].

[H1] Salt giant forcing mechanisms

Marine gateways have a critical role in the exchange of water, heat, salt, and nutrients between oceans and seas. During the MSC, water exchange with the open marine Atlantic Ocean and the brackish Paratethys Sea were influenced by a complex combination of geodynamic (tectonic movements in gateway regions), glacio-eustatic (global sea level fluctuations), and palaeoclimatic (hydrological budget changes) processes that all had a role in Messinian salt giant formation. Tectonic uplift and sea level lowering can have similar effects on water exchange through gateways and are difficult to unravel. Here, we present and evaluate current understanding of the geodynamic, ice-volume and sea-level forcings on the MSC and then revisit the role of superimposed regional palaeoclimatic forcing.

[H2] Geodynamic forcing

The main geodynamic processes in the Gibraltar orogenic system involve African-Iberian plate convergence[83], slab tearing under the eastern Betic Cordillera[84], and mantle resistance against Gibraltar slab drag[85]. Mantle tomography and other seismological investigations provide a clear present-day 3D image of Gibraltar slab geometry and lateral continuity with surface plates, and where it is detached and might have delaminated from continental lithospheric mantle (Fig. 5)[84,86]. Early to Late Miocene westward slab roll-back resulted in thrusting of the Alborán domain over the African and Iberian margins. Indentation of the Rif Mountains by slab dragging together with slab detachment beneath the Betic Cordillera (Fig. 5a, b) can explain gateway opening, closure, and re-opening[87]. During the late Tortonian (between 8 and 7 Ma), the Betic gateways were uplifted by isostatic rebound related to gradual slab tearing below Spain. Slab dragging initiated thick-skinned tectonics in Morocco that also closed the Rifian Corridor[88].

During the MSC, sills within the Mediterranean basin also had important roles. In shallow silled basins where PLG developed, geochemical evidence indicates that climate oscillations[89] modified conditions within the basins resulting in localised density contrasts across the sills, even before the MSC[90]. The Sicily sill, which separates the western and eastern Mediterranean basins, had a crucial role in water and salt transport across the Mediterranean before, during, and after the MSC[11,91,92], and likely generated the different MSC stratigraphies in the deep central basins. Other important sills were the tectonically active Gargano promontory (Italy)[93] and Cyclades region (Greece)[94] that separate, respectively, the Adriatic and North Aegean basins from the open eastern Mediterranean (Fig. 1). These restricted basins persisted as two evaporite-free largely isolated megalake systems during the halite and UG phases, probably influenced by extensive European river runoff (Fig. 1)[82,94].

In the eastern Mediterranean, the marine Neo-Tethys connection to the Indian Ocean had already closed in mid-Burdigalian times (~19-17 Ma), driven by Africa-Arabia-Eurasia collision[95,96], which created the first land bridge for mammal migration into and out of Africa. Consequently, this gateway probably played no role in Messinian salt giant evolution. Instead, the most important eastern connection during the MSC was with the Paratethys domain (Fig. 1). The present-day connection has sills 55 m deep and 1.2 km wide at the Dardanelles near Çanakkale, and 36 m deep and 698 m wide at the Bosporus near Istanbul[97] (Fig. 1a). Messinian palaeogeographic evolution of the Mediterranean-Paratethys gateway is poorly understood, but it affected hydrological, palaeoecological, and palaeoenvironmental conditions in both domains[94]. Palaeontological data indicative of marine faunal exchange[98,99] and strontium isotope data[23] suggest that Mediterranean-Paratethys connectivity was established at 6.1 Ma[100,101], before the onset of evaporite precipitation. Gateway geodynamics between the Mediterranean and Paratethys were then, as now, dominated by active westward growth and propagation of the North Anatolian Fault Zone, North Aegean extensional tectonics, and Cyclades domain uplift and exhumation[102]. These tectonic processes, combined with substantial lake-level fluctuations, resulted in episodic Mediterranean-Paratethys and Black Sea connection and disconnection ever since[103,104].

[H2] Glacio-eustatic forcing

To date, sea-level forcing of the MSC has been dismissed in most studies based on the assumption that its variations were obliquity controlled (~40 kyr); using this period for sedimentary cyclicity would result in an

MSC duration that is too long to match independent age constraints. However, an updated global $\delta^{18}O$ synthesis indicates that the periodicity of ice-volume and deep-sea temperature fluctuations across the Late Miocene was controlled by precession, similar to Mediterranean climate cycles (Fig. 4)[105]. To assess whether sea level was an important forcing mechanism for Mediterranean isolation from, and/or reconnection to, the Atlantic Ocean[106], we examine an updated sea-level record for the 6.4 to 5.0 Ma time interval relative to the present level (0 m; Fig. 4). By applying established box-model approaches to evaluate the evaporite implications of gateway restriction[74] (see *Supplementary Note*), this updated sea-level record indicates that sill depths >41 m favour basinal hemipelagic carbonate (marl) deposition. Evaporative carbonate deposition is favoured when the strait depth ranges between 22 and 41 m, gypsum deposition occurs between 13 and 22 m, and halite deposition occurs at depths <13 m. Friction would reduce exchange through the strait, so these threshold water depths are minimum estimates.

The updated high-resolution record of global mean sea-level variations[107] indicates that sea level alone cannot account for either the MSC onset, or rapid reestablishment of normal open marine conditions at the beginning of the Pliocene. Tectonic strait restriction is needed to trigger the transition from open marine hemipelagites to evaporative carbonates (6.08-6.03 Ma) followed by gypsum precipitation from 5.97 Ma (Fig. 4), while the MSC termination requires catastrophic, tectonic, strait opening to depths more than ~40 m below the lowest sea level of that time[9,11]. However, some stratigraphic features within the MSC are consistent with Late Miocene sea level fluctuations. For example, with a shallow Mediterranean-Atlantic sill depth of 13-22 m (with the uplifted sill ~18 m below present-day sea level), sea-level fluctuations could explain the 16 gypsum cycles (magenta arrows in Fig. 4b) deposited during the PLG phase. In this scenario, sea-level influence on the gypsum cycles could have been irregular, potentially accounting for at least some observed variability in their thickness and spacing. These lithological threshold depth calculations ignore Paratethys inputs and precession-scale Mediterranean hydrologic budget fluctuations, which are likely to have varied; threshold depths will be somewhat smaller under more humid conditions and somewhat greater under more arid conditions (see[72] for sensitivity analysis). Changes in Paratethys inputs and Mediterranean hydrology might explain the absence of halite between 5.8 and 5.7 Ma, when it should have been triggered by two marked sea-level falls (Fig. 4b). The

onset of well-documented halite precipitation (at ~5.6 Ma) requires further tectonic strait restriction (red shading in Fig. 4b). Maximum gateway restriction occurred at 5.55 Ma when global sea level was lowest, consistent with an episode of Mediterranean sea level fall. The end of halite deposition could have been terminated by the sea-level rise at ~5.53 Ma if the sill was below 6 m above present sea level.

For the UG phase (green shading in Fig. 4b), a (virtually) closed Atlantic connection with the basin in an essentially drawn-down state is required to obtain regional brackish to brine-water "lakes", non-marine evaporite deposition, and continental-dominated Sr-isotope ratios[11,24,25]. This high-resolution sea-level record is consistent with (potentially seven) partial reconnection events (green arrows in Fig. 4b) associated with minor Atlantic inflow that might correspond to the seven gypsum cycles observed in the UG[24,81].

[H2] Palaeoclimate forcing

Salt giant formation requires an excess of evaporation over precipitation and runoff into the basin. These factors are difficult to quantify from geological records and reconstructions. For example, palaeo-runoff requires robust knowledge of the palaeogeographic evolution of the complete catchment area of an evaporite basin, including its orography and palaeo-channels. However, global climate models can provide some constraints[65,108,109]. We here evaluate climatic variations over the Mediterranean basin and its catchment area, including the Paratethys and the north African monsoon region immediately before, during, and after the MSC.

Several records indicate that the Mediterranean salt giant formed during a period of global cooling between 7.2 and 5.5 Ma[110–112], which is likely to have been triggered by a global atmospheric pCO_2 decline to a minimum between 6.5 and 5.8 Ma[113]. The Late Miocene pCO_2 decrease has been linked to a ~1 ‰ global benthic foraminiferal $\delta^{13}C$ drop known as the Late Miocene Carbon Isotope Shift (LMCIS; Fig. 3) between 7.6 and 6.6 Ma[33,114]. This drop is amplified in the Mediterranean, probably because of progressive gateway restriction in the Gibraltar region since ~7.1 Ma[115]. The absence of a humidity decrease from the pre-evaporitic marls to the base of the PLG gypsum[116,117] implies that MSC salt giant formation was not likely triggered by Mediterranean climate change. As atmospheric pCO_2 began to rise after 5.5 Ma, warming occurred[113]. This warming trend started at the transition between isotope stages TG12 and TG11, coincident with the end of halite deposition

and the onset of Mediterranean UG formation (Figs. 3, 4). Ensuing long-term global warming was associated with long-term global sea level rise[106,107,118].

Lack of foraminifera hinders Mediterranean palaeoclimate reconstructions through the MSC, although Messinian palynological[119] and organic biomarker records[120–123] indicate that Mediterranean climate was warm and dry before, during, and after the MSC. Along the northern Mediterranean margin, climate was warm and humid, similar to present-day conditions, with important river runoff from the Alps (Rhone and Po)[124]. Lack of marked vegetation changes during the different evaporite phases suggests that Mediterranean climate did not force the MSC and that the MSC, in turn, did not have a substantial impact on Mediterranean climate[119].

The classic marl-sapropel alternations of pre-evaporitic MSC successions indicate conspicuous precession-paced climate oscillations (Fig. 3)[17,18,67], in which sapropels mark relatively wet conditions during precession minima (insolation maxima), when enhanced freshwater runoff increased Mediterranean water column stratification[125]. Whatever the role of eustatic sea-level variation, precessional forcing is assumed to have continued in the PLG deposits, with gypsum beds corresponding to relatively dry climates during precession maxima (insolation minima)[41,73]. Organic geochemical data from PLG cycles in northern Italy confirm this, revealing climatic oscillations[21] with gypsum deposition during relatively dry periods with reduced river runoff[116,117].

Most MSC scenarios envisage a maximum Mediterranean lowstand during or after halite deposition, with draw-down estimates of -600 to -2000 m[6–8], indicating a strong regional circum-Mediterranean negative hydrological balance. Mediterranean water level during the UG is still contested[43]. The presence of recurrent, high-diversity, shallow-water, brackish ostracod assemblages in most shallow, silled Mediterranean basins indicates considerable net freshwater influxes. Palaeoclimate models suggest that Mediterranean-wide Lago Mare conditions cannot be explained by Paratethys inflow alone, and that additional water sources are required[109,126]. Specifically, runoff from high-amplitude African monsoon maxima has been considered[127–130]. Alternatively, Atlantic input to the basin might have contributed during glacio-eustatic relative sea level highstands (Fig. 4), although fully marine conditions were not established until the Zanclean[69].

Given Mediterranean regional hydroclimate constancy through the MSC, periods of strong evaporative water-level drawdown must reflect low net precipitation over remote parts of the Mediterranean freshwater catchment (Paratethys and/or monsoonal Africa). Conversely, major freshwater influx periods must reflect high net precipitation over far reaches of its catchment. The Paratethys is a likely source of considerable Messinian freshwater variations because connection between the two basins[98,131] would have greatly extended the Mediterranean freshwater catchment area relative to today. Specifically, the Messinian Paratethys unified the Dacian, Black Sea, and Caspian Sea basins [100,131] , so that all major Eurasian rivers (Danube, Dnjepr, Don, Volga, Syr-Darya, Amu-Darya) drained into the Mediterranean[132]. In the Tortonian, hydrological variations associated with eccentricity-driven northward (southward) mid-latitude westerly displacement over the Paratethys could have already caused decreased (increased) Paratethys overspill and runoff into the Mediterranean[133]. Assuming that similar climate variability continued through the Messinian and that it also had a precession-timed component, the MSC net freshwater budget could have been affected substantially by Paratethys outflow[108,126].

African monsoon intensity tracked the northern summer insolation amplitude (hence the eccentricity-modulated amplitude of the precession cycle) throughout much of the Neogene[127,128], including the MSC[129,130]. During insolation maxima (precession minima), monsoon-driven humidity expanded over north Africa[127,128,134,135]. Large north African lakes, such as mega-lake Chad[108,109], might then have drained via the ancient Eosahabi river into the Mediterranean[136–138]. Although lake Chad lies well south of the modern central Saharan watershed, there is good evidence in younger geological periods of direct discharge via seasonal river floods and wadis[139,140]. The absence of high-amplitude insolation maxima between 5.73 and 5.53 Ma suggests an extended interval of relatively weak African monsoons, whereas several high-amplitude insolation maxima during the UG phase suggest potential high-amplitude African monsoon maxima, with enhanced monsoon runoff into the Mediterranean basin (Fig. 3).

Overall, it appears that the long-term evolution from pre-evaporitic marls to gypsum and salt deposition was not driven predominantly by Mediterranean climate change, and that relative sea level drops interacting with tectonic changes at gateways and their impact on ocean water exchange likely were the main mechanisms

leading to progressive salt concentration. This long-term trend was punctuated by both precession-based cycles in sea-level and Mediterranean (including Paratethys and African monsoon) hydrology. The influence of these astronomically driven variations was amplified progressively as Mediterranean restriction increased.

[H1] Global relevance of the MSC

The MSC provides an illustration that salt giant formation is much more complex than simply evaporating a sea water volume following its oceanic disconnection. The Messinian salt giant transitioned through three restriction phases from the open ocean (Fig. 1, 2). First, restricted two-way exchange with maintained sea-level connection between the Mediterranean and Atlantic resulted in gypsum precipitation with marine geochemical signatures (PLG phase). Second, severely restricted oceanic inflow, sufficient to maintain evaporite ion flux while Mediterranean sea-level fell, drove halite deposition. Third, extremely limited, intermittent oceanic inflow led to continental-dominated, non-marine evaporite deposition alternating with brackish water conditions (UG phase). The sequence was terminated by abrupt reconnection and progressive restoration of normal marine conditions throughout the basin, re-establishing two-way Mediterranean-Atlantic exchange in the early Pliocene[11,24]. Return flux of MSC residual brine ions into the open ocean occurred over ~30,000 years[11] (Fig. 6) and its impacts on open ocean circulation and climate have yet to be investigated.

Throughout all Mediterranean salt giant evaporitic phases, precession-timed runoff and/or global sea-level variations interacted to drive sedimentary environmental cyclicity due to greater or weaker freshwater admixtures and/or greater or weaker oceanic inflows to the basin, which overprinted marine connectivity changes due to tectonic gateway geometry changes. Model-based sensitivity tests indicate that even subtle freshwater budget and/or sea-level fluctuations would have sufficed to switch between gypsum and marl deposition[74]. Precession-timed arid-to-humid and precession-timed sea-level cycles both occurred at amplitudes relevant to the sedimentary regime, but the precise phase relationship between their impacts remains elusive; these processes could have partially amplified or cancelled each other. More advanced hydro-geochemical models that integrate both forcing mechanisms will be required to fully understand gypsum formation under restricted marine conditions. Hydro-geochemical modelling of salt giants can also provide

useful information about the link between seawater-exchange restriction at the gateway sill and salinity evolution of the evaporite basin[72,79,92]. These models track salinity as a single variable, or at most divide salinity into three contributions: gypsum (Ca and SO_4), halite (Na and Cl), and other salts (K, Mg, HCO_3^-). This simplification, which facilitates numerical model solution, comes at the expense of a more correct thermodynamic description of the brine and its evolution during salt giant formation.

The exact drawdown amount remains a key unknown regarding halite and non-marine gypsum precipitation, when the evaporite basin was semi-isolated from the ocean. Maximum lowstands based on seismic interpretations combined with numerical modelling differ between -600 and -2000 m, assuming that all observed Messinian erosional surfaces formed subaerially. At times of severely restricted or negligible Atlantic inflow, Mediterranean evaporites are expected to contain a mineralogical imprint of continental runoff. The low Ca^{2+}:Cl^- and SO_4^{2-}:Cl^- in continental runoff enables gypsum precipitation at much lower salinities than when forming from evaporating seawater[23,141]. Future hydro-geochemical models that integrate a sound thermodynamic description of high-salinity brines[80] will be able to test the hypothesis that increased relative importance of riverine inputs produces a substantial mineralogical assemblage change in a salt giant. Such models can also evaluate if a large (> 1.5 km) drawdown is required to attain brine saturation with respect to the highly soluble mineral bischofite, which is known to have precipitated during the MSC based on pore water geochemical tracers measured from the *Discovery*, *Hephaestus*, and *Kryos* deep-sea hypersaline brines on the Mediterranean Ridge[142–144].

Almost all salt giant-related research to date has focused on their nature and causes[15,145] with little consideration of their potential to drive wider environmental change[146,147], which is partly because of an assumption that impacts outside the salt basin will be synchronous with evaporite formation. Some MSC research has challenged that assumption [24,148] and in doing so, has initiated new research into the chemical and physical consequences of the MSC and salt giants more generally for regional and global climate.

While the impact of evaporite formation and subsequent weathering on ocean chemistry has been known for some time[147], their potential to drive rapid carbon cycle changes and associated climate change remains enigmatic[146]. Modelling of evaporite weathering and deposition suggests that despite the much larger halite

volume that is typically preserved in salt giants, it is the formation and dissolution of giant calcium sulphate (gypsum or anhydrite) deposits that can have global consequences as an episodic driver of carbon cycle changes[146]. These global consequences could occur because oceanic Ca^{2+} removal via $CaSO_4$ deposition decouples the oceanic Ca^{2+} and HCO_3^- sinks, causing a $CaCO_3$ burial decrease and, consequently, increased ocean pH, lower atmospheric pCO_2, and global cooling. Similarly, the return of Ca^{2+} ions to the ocean from weathered gypsum can drive warming[146].

Most biogeochemical models have ignored evaporite-driven perturbations to seawater chemistry[149,150], assuming that over timescales >100 kyr, evaporite precipitation and weathering are balanced. Formation of km-thick MSC evaporites, and their preservation over the subsequent ~5 million years of Earth history, reflects a ~7 to 10 % net evaporite-ion extraction from ocean water over this period[4,38]. Bearing in mind that the MSC is by no means the largest of the salt giants[147], this demonstrates that the evaporite precipitation-weathering balance assumption can only be true on multi-million year timescales at best, and suggests that current carbon cycle models could be missing an important intermediate timescale climatic driver[146].

Initial sensitivity experiments that explored the impact of gypsum precipitation and weathering on the carbon cycle recognised that precipitation and preservation of any gypsum represents a net reduction in oceanic $[Ca^{2+}]$ and expressed this as a constant Ca^{2+} forcing[146] for the duration of salt giant formation. However, in detail the Ca^{2+} ion flux associated with a salt giant is not constant, but far more complex, reflecting cyclic evaporite formation and the evolving connectivity history of the salt-bearing basin. For the MSC, this means that during the PLG, when gypsum-marl alternations formed under conditions of two-way Atlantic-Mediterranean exchange[26], Ca^{2+} ion loss from the global ocean occurred episodically, reflecting each precipitation event[24]. It is also likely that return flux to the global ocean occurred as the newly formed gypsum layers partially dissolved[24]. This return flux cannot have occurred during the later MSC stages, when there was no Mediterranean outflow[26]. Any ions liberated by exposure and weathering of evaporites during periods of lowered Mediterranean sea level would have remained trapped within the basin at least until early Pliocene reestablishment of two-way exchange and flushing of residual brines which took ~30,000 years (Fig. 6)[11]. New

model simulations that incorporate realistic Ca^{2+} ion flux records are, therefore, required to evaluate the magnitude of any evaporite-driven climate perturbation.

Reconstructing the magnitude and timing of evaporite ion fluxes is challenging. The salt volume preserved today is not a robust measure of the total evaporite ions extracted, but rather represents a minimum value for what was originally precipitated. Additional evaporites might have been precipitated and dissolved either before burial or during later exposure by orogenic processes[5]. Evaporite minerals also precipitate and dissolve three orders of magnitude more rapidly than other sediments[151]. Consequently, their impact on the carbon cycle can be an order of magnitude quicker than the carbonate-silicate weathering feedback[146]. Through burial, evaporites can also be stored in rock successions for long periods outside the ocean-climate system[28]. As a result, evaporite-mediated ion extraction from, and return to, the ocean can be both rapid (10^3-10^4 y), occurring during or shortly after salt giant formation, as is largely the case for the MSC, and/or gradual ($>>10^6$ y) where dissolution occurs post burial, as is occurring in Arctic Canada where a ~290-million-year-old gypsum salt giant is now emerging from beneath thawing and eroding permafrost[152].

Constraints on the evaporite-ion flux in addition to the salt giant succession itself are clearly required. One possibility is to use the seawater [Ca^{2+}] record[153]. To capture perturbations anticipated from salt giant formation, a high-resolution record is required. However, currently only a handful of [Ca^{2+}] measurements exist for the entire Cenozoic (ironically mainly from evaporite fluid inclusions[153]). These reveal a general decline over the past 100 million years[153], but are too few to detect a net $[Ca^{2+}]_{sw}$ reduction over the MSC duration, let alone the abrupt sub-precessional scale step-like structure that should be evident from evaporite ion extraction and return. By integrating Ca-evaporite formation and weathering processes, coupled carbon and calcium cycle models will provide more mechanistically sound explanations of the links between geological and geochemical cycles, and climate.

Physical processes associated with salt giant formation could also have a potential impact on global climate. Advection of dense, cold and/or salty overflow water from marginal basins strongly influences the oceanic distribution of heat and salt, exerting a powerful influence on thermohaline circulation and deep-water formation[154]. In the North Atlantic today, the densest of these overflows emanates from the Mediterranean

Sea[155] depositing a prominent overflow plume that contours around the Iberian margin[156]. Sensitivity experiments that exclude present-day Mediterranean-Atlantic exchange result in ~1° cooling over the North Atlantic, and a 0.7-2.3 Sv (1 Sv=10^6 m^3s^{-1}) reduction in the Atlantic Meridonal Overturning Circulation[154,157]. These results indicate that the negative Mediterranean hydrologic budget, combined with exchange through the Gibraltar Strait, is enough to generate a climatically important high-density water mass today. The outstanding question remains: what role did overflow have in driving Late Miocene climate?

[H1] Summary and future perspectives

In this Review we provide evidence that both geodynamic and eustatic sea-level forcing are crucial for initiating and terminating salt giant formation with a subsidiary role for regional climate. The formation and dissolution of giant calcium sulphate (gypsum and anhydrite) deposits can have global consequences as an episodic driver of carbon cycle changes. Mediterranean overflow was triggered by initial tectonic restriction of Mediterranean-Atlantic exchange as the two pre-Gibraltar marine gateways formed and closed, allowing a Mediterranean-Atlantic density contrast to develop[148]. This restriction process occurred at ~8 Ma[148] (Fig. 5), and pre-dated evaporite deposition by two million years and persisted after the MSC throughout the Pliocene and Pleistocene[156]. Similar dense overflows might be associated with every marginal basin in which a salt giant has formed and, like the MSC, their duration will not have been synchronous with salt giant formation. The impact of these overflows on thermohaline circulation should be a target for future research.

During salt giant formation, marginal basin water density will have been much higher, and evaporite-sediment alternations such as those of MSC successions, indicate fluctuating brine concentrations. However, only during two-way exchange episodes will this produce a high-density overflow plume that could impact thermohaline circulation. Modelling these extreme high-density overflows is challenging because the narrow, shallow marine gateways required for overflows to form are too small to be fully resolvable in current Earth System Models. Instead, numerical models use various parameterisations to mimic overflow mixing in model simulations[158,159]; none are currently compatible with densities that far exceed contemporary overflow observations[155]. Improved

model parameterisation of overflow mixing and development of proxies that allow overflow density reconstruction will be critical to addressing this challenge.

Finally, this Review provides context for the upcoming Land-2-Sea drilling project in 2024. IMMAGE (Investigating Miocene Mediterranean-Atlantic Gateway Exchange)[160] will recover 8- to 4-million-year-old sediments from both gateways and the Mediterranean outflow plume in the Atlantic before, during, and after the MSC. The project objective is to identify and quantify the impact of evolving Mediterranean-Atlantic exchange on regional and global environmental change and specifically its potential contribution to cooling during this period, which ultimately resulted in initiation of northern hemisphere glaciation[111]. This drilling project will combine offshore drilling with International Ocean Discovery Program Expedition 401 on either side of the Gibraltar Strait and onshore drilling with the International Continental Scientific Drilling Program in Morocco and Spain, targeting the two precursor Atlantic-Mediterranean marine connections that have been uplifted and preserved on land. IMMAGE, the first Land-2-Sea drilling project, offers great scope for addressing the many remaining unknowns outlined here.

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Supplementary Note

We constructed a sea-level record relative to the present level (0 m) for the 7.5 to 5.0 Ma time interval from the synthesis of Rohling et al.[107]. We include sea-level benchmarks from Mallorcan marine cave deposits and Patagonian coastal deposits, which have been corrected for tectonic changes, glacio-isostatic effects, and dynamic topography[161–163], and which corroborate the sea-level record from benthic $\delta^{18}O$ deconvolution before, and across, the Miocene-Pliocene boundary. Water exchange thresholds were calculated using the channel geometries of Krijgsman et al.[28], which we combine into an approximately triangular single width vs. depth profile (maximum width = 3.28 km; maximum depth = 136 m). Today, the Gibraltar Strait is 10.67 km wide at sea level with 136 m of water above the sill. Hence, the triangular cross-sectional area of the Messinian strait was 3.25 times more restricted than the modern triangular cross-sectional strait area for the same depth. We use this extra restriction in the Bryden and Kinder[164] model for water exchange through the strait, ignoring friction and assuming that excess evaporation (= evaporation − precipitation – runoff) over the basin was equal to that at present. We then calculate water depths in the Messinian strait required for key basin salinity thresholds of 350 (halite), 135 (gypsum), and ~75 ppt (evaporative carbonate); this yields depths of 13 m, 22 m, and 41 m, respectively.

Acknowledgements

This research was supported by the project SALTGIANT-Understanding the Mediterranean Salt Giant, funded by the European Union's Horizon 2020 program (Marie Skłodowska-Curie grant agreement No 765256). It also contributes to Australian Research Council projects FL120100050, DP2000101157 (E.J.R.), and DP190100874 (A.P.R.). D.V.P acknowledges project PNRR C9 - I8 "Multiproxy reconstruction of Eurasian Megalakes, connectivity and isolation patterns during Neogene-Quaternary times", code 97/15.11.2022, Contract No. 760115/23.05.2023 and the project "Impact of sea-level rise on anoxic basins: Paratethys vs. Black Sea" [grant Veni.212.136] of the research Talent programmed – Veni which is financed by the Dutch Research Council (NWO).

Competing interests

The authors declare no competing interests.

Author contributions

All authors contributed to the content, discussion, writing, and editing of the paper. DP, FR, VA, FS, EJR, and UA constructed the figures.

Peer review information

Nature Reviews Earth & Environment thanks [Referee#1 name], [Referee#2 name] and the other, anonymous, reviewer(s) for their contribution to the peer review of this work.

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Data availability

The data for figures X, Y, and Z are available …

Supplementary information

Supplementary information is available for this paper at https://doi.org/10.1038/s415XX-XXX-XXXX-X

Figures

Figure 1. ***Mediterranean MSC evaporite stages. a*** *| Map of the Mediterranean region with the most important seas, straits, and mountain ranges labelled.* ***b-d*** *| Schematic maps of the Mediterranean and Paratethys seas during three evaporite stages*[15] *with the main sites that crop out onshore.* ***b*** *| Non-marine upper gypsum (UG) stage with lacustrine deposits and Paratethyan fauna known as the "Lago Mare" in Mediterranean highstands and evaporites in lowstands;* ***c*** *| the desiccation stage during which halite was deposited; and* ***d*** *| water level during the marine primary lower gypsum (PLG) stage with Atlantic connectivity. For detailed distribution patterns from both offshore seismic and onshore field data, see refs.*[3,4,12–14,16,46,94,165]*. This series of maps illustrates the sequence of evaporite units that define the MSC during which the Mediterranean became restricted and isolated from the Atlantic .*

Figure 2. ***MSC stratigraphy in basinal settings. A*** *| Schematic Mediterranean map of Messinian marginal zones (MZ), shallow silled basins (SSB), intermediate basins (IB) and central deep basins (CDB).* ***B*** *| Schematic Mediterranean cross-section with MSC deposits in different basin settings. The numbers in the layers refer to: 1 - Primary Lower Gypsum (PLG) phase; 2 – Halite; 3 - Upper Gypsum (UG) phase.* ***C*** *| Age constraints and distribution of MSC deposits in different basin settings. The complexity of MSC stratigraphic records is illustrated based on depth and tectonic setting.*

Figure 3. ***Global benthic foraminiferal oxygen and carbon isotope records correlated to the main MSC phases. a*** *| Messinian magnetic polarity pattern.* ***b*** *| Messinian stratigraphic units. UG= Upper Gypsum, with 7 gypsum layers (white) interbedded with mudstones (grey)[24], PLG=Primary Lower Gypsum with 16 gypsum layers (white) interbedded with mudstones[15,27]. Precession-driven sedimentary cycles during the pre-evaporite stage: LA1 to LA21 and UA1 to UA34 indicate Lower and Upper Abad sedimentary cycles[19] (the thickness of each sedimentary cycle has been adjusted to its time span)[67]. Legend for the pre-evaporite cycles: pink, white, black and beige levels indicate indurated layers, homogeneous marls, sapropels and diatomaceous marls, respectively.* ***c*** *| Insolation at 65ºN for 21 June (black curve)[166].* ***d*** *| Changes in Earth´s orbital eccentricity (red curve)[166].* ***e*** *| Benthic foraminiferal $\delta^{18}O$ from ODP Site 982 (North Atlantic)[110].* ***f*** *| Changes in Earth´s tilt through the Messinian (red line)[166].* ***g*** *| Cenozoic benthic foraminiferal $\delta^{18}O$ reference record[105].* ***h*** *| Cenozoic benthic foraminiferal $\delta^{13}C$ reference record[105]. LMCIS: Late Miocene Carbon Isotope Shift.* ***i*** *| Northern Hemispheric sea surface temperature (SST, black line) stack and tropical sea surface temperature stack (yellow line)[111]. The scale reflects the difference in temperature from the present (note that the two SST scales are different).* ***j*** *| Messinian Geomagnetic Polarity Time Scale[105,110]. Vertical light-teal bands: main late Messinian global glacial isotope stages. Dashed vertical lines: main restriction steps for Atlantic-Mediterranean water exchange; the upper one results in the PLG onset. Red arrows indicate gypsum beds deposited during insolation minima. This figure is a summary of Mediterranean Messinian cyclostratigraphy that provides a detailed MSC chronology and a basis to correlate MSC events to global chronostratigraphic records.*

Figure 4. ***Sea-level reconstruction with MSC sill-depth scenarios****.* ***a*** *| Sea-level relative to present day over the last 10 Myr. The Plio-Pleistocene record (red) is based on benthic $\delta^{18}O$ deconvolution[107,118] using combined compilations from refs.[168] and [105]. For the Miocene (blue), we use the envelope between the main benthic $\delta^{18}O$ deconvolution and sensitivity scenario i of ref.[107] (see that study for rationale and details) based [105]on the benthic $\delta^{18}O$ compilation of ref.[105]. Sea-level benchmarks are also shown for Mallorcan marine cave deposits (black circles with error bars) and Patagonian coastal deposits (grey box), which have been corrected for tectonic changes, glacio-isostatic effects, and dynamic topography [161–163].* ***b*** *| Detail of the records from* ***a*** *between 5 and 6.4 Ma. We compare sea-level variations with the likely Atlantic-Mediterranean gateway geometry and calculate threshold values for water exchange through the strait that delimit precipitation of halite (H), gypsum (G), evaporative carbonate (EC), or hemipelagic marl deposition (M), as detailed in the Supplementary Note. The inferred MSC sill (grey shading) scenario assumes a disconnected (drawn down) condition during halite and UG deposition. MSC phases are coloured as in Figure 3. Purple up arrows indicate potential gypsum phases in the PLG, and green down arrows indicate ~7 potential (mostly continental) gypsum phases in the UG. From this sea level reconstruction it can be seen that eustatic sea level change was not a primary cause of the onset or end of the MSC, although seawater influxes over the sill during sea level highstands provided the water and ion resupply needed for ongoing evaporite formation.*

Figure 5. ***Geodynamic context of the MSC. a*** *| Schematic topography of the pre-MSC Gibraltar region with palaeogeographic projection of Mediterranean-Atlantic gateways. The labels illustrate the timing and mechanisms of vertical motion that restricted Atlantic-Mediterranean connectivity (~5.33–7 Ma).* ***b*** *| Cartoon of slab morphology below Gibraltar at ~8 Ma. Arrows illustrate absolute plate motions for Africa and Iberia with slower central-eastern Betic motion. Panel a adapted from ref.[87], CC BY 4.0. Panel b adapted from.[85], Springer Nature Limited. The Messinian landmass configuration required for Atlantic-Mediterranean connection or restriction was controlled by Africa-Iberia convergence and the illustrated geodynamics.*

Figure 6. ***Post-MSC removal of Messinian salts to the Atlantic, following an abrupt refilling event. a*** *| Sketch of the Mediterranean configuration immediately following abrupt basin refilling by Atlantic waters. The energetic Atlantic inflow transferred almost all western Mediterranean Messinian salt to the Eastern basin, which became stratified with salts to the Sicily sill level. Turbulent diffusion of salts from the lower dense layer (driven by energy input from winds and tides) slowly transferred Messinian salts back to the Atlantic across the Sicily and Camarinal sills, via the outflow.* ***b*** *| Timescale of complete salt removal (grey box: 10-40 kyr) for turbulent diffusivities of 1-5 $\times 10^{-5}$ m^2s^{-1}. The shaded area between the K_1 and K_5 curves represents all possible bottom water salinity reduction pathways. t_{k1}, t_{k5} = time taken to reach surface salinity values at K_1*

and K_5 turbulent diffusivities, respectively. S_{LIW} = Levantine intermediate water salinity. Panel b adapted from ref.[11], Springer Nature Limited. Illustration of how Atlantic inflow at Gibraltar at the MSC termination first filled the western basin then cascaded into the eastern basin at the Sicily sill to fill it with dense brines that required 26,000 years to flush back to the Atlantic[11]

Boxes

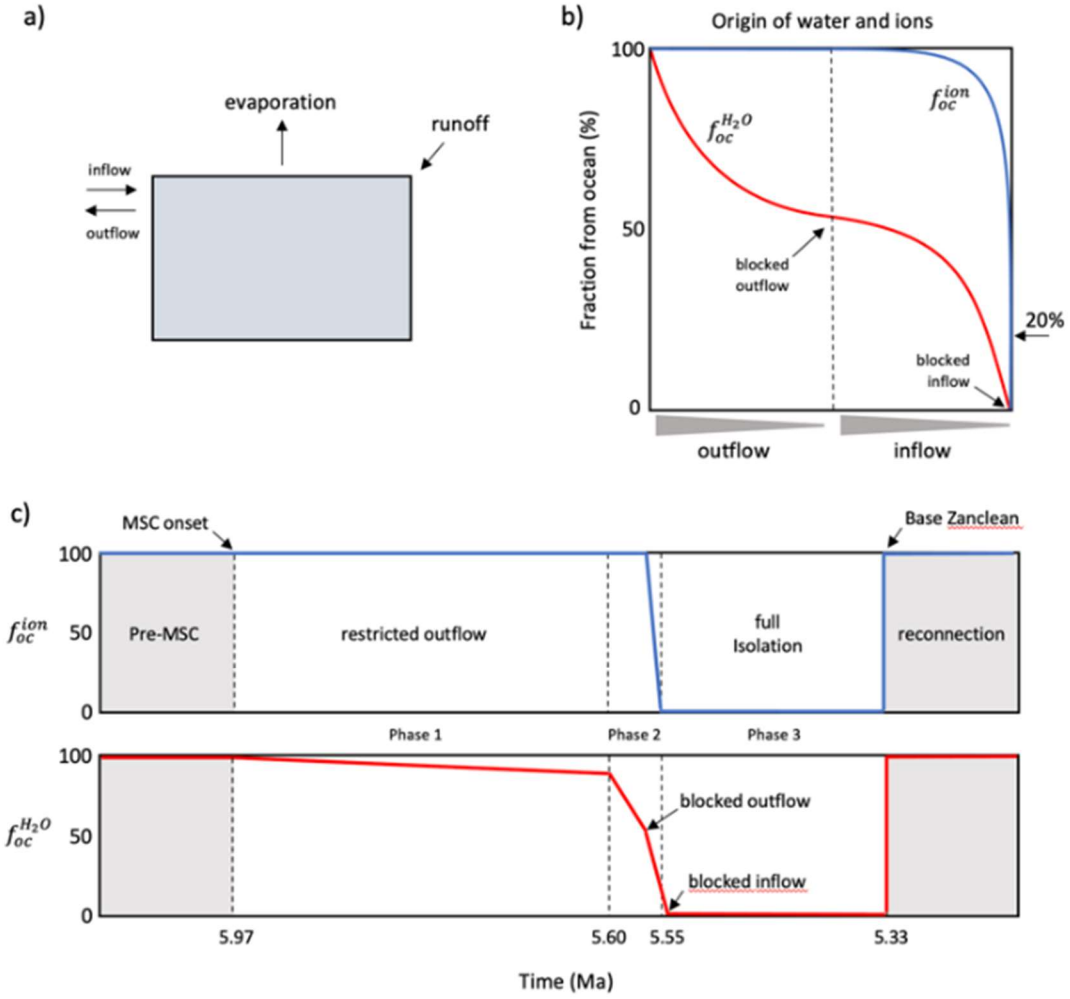
[B1] Evaporitic salt formation

Ocean chemistry has changed substantially over time[169]. One driver for this change is the precipitation and weathering of giant evaporite deposits. The most common marine evaporite minerals – carbonates, gypsum, anhydrite, halite, and the bittern salts (kainite, carnallite, bischofite) – precipitate from seawater when the concentration of their constituent ions (Na^+, Cl^-, Ca^{2+}, SO_4^{2-}, K^+, Mg^{2+}, HCO_3^-) exceeds a threshold known as the solubility product[170,171]. Ion concentration in evaporite basins depends both on water fluxes to, and the total water volume of, the marginal basin. Ions are added to these basins by water inflow from the ocean and rivers, and leave the basins only by outflow to the ocean or by mineral precipitation. The water volume in an evaporite basin is conserved if a sufficient oceanic connection exists, but it can decline through net evaporative draw-down if the connection becomes severely restricted or blocked; in both cases net evaporative freshwater removal raises the dissolved ion concentration in basin waters. The main controls on evaporitic mineral precipitation are, therefore, the magnitude of the freshwater deficit and the extent of water-exchange limitation between basin and ocean (see the figure, part a).

The simplest conceptual model for evaporitic salt formation considers a seawater volume disconnected from the ocean, subject to evaporative draw-down, while receiving no further ions from either seawater or river runoff. The Mediterranean salt giant, however, did not form under these conditions because complete evaporation of a 3,000 m-thick seawater column, with an average salinity of ~35 ‰, would leave behind only about 40 m of halite, a fraction of what is preserved in the deep central basins (~ 2.5 km of halite).

The evaporite-forming ion concentration in river water is, respectively, typically 1000 (Na^+, Cl^-), 100 (Mg^{2+}, SO_4^{2-}, K^+), and 10 (Ca^{2+}) times lower than in seawater[172,173]. Consequently, continental runoff influences marine evaporite mineral precipitation only if oceanic input is restricted severely or cut off entirely. A qualitative picture of the impact of ocean-continental water mixing on dissolved ions, as a function of seawater-exchange

restriction, is shown in the figure. Evaporites only evolve toward a "continental" mineralogical signature when the continental input dominates the oceanic source. This is the case for the Upper Gypsum succession on Sicily where non-oceanic Sr isotope data from both gypsum and ostracods suggest minimal Atlantic contribution[24]. The relative abundances of many other evaporite-forming ions are much higher in river water than in sea water (in brackets): Mg^{2+}:Cl^- = 0.7 (0.1), SO_4^{2-}:Cl^- = 0.6 (0.052), Ca^{2+}:Cl^- = 1.2 (0.019), K^+:Cl^- = 0.05 (0.018), and HCO_3^-:Cl^- = 2.5 (0.004). Thus, when oceanic connection is highly restricted or blocked, carbonate and gypsum precipitation dominate the typical halite-dominated marine association[141].



*In the figure, the controls on water and dissolved ion proportions from the ocean versus continental runoff during the MSC are shown in **part a**. Using a simplified water balance of an idealized marginal basin; **part b** is an illustration of how the fraction of water (red curve) and dissolved ions (blue curve) originating from the ocean change as a function of seawater-exchange flux, with the restriction at the sill separating the ocean from the marginal basin. In an idealized scheme for ocean water and ion fractions during the MSC (**part c**); note that continental runoff becomes a relevant ion source to the basin only when its marine connection is restricted severely, or cut off completely, from the ocean*[36].