

# Causes and consequences of the Messinian Salinity Crisis

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#### **Causes and consequences of the Messinian Salinity Crisis** 1 2 3 Wout Krijgsman<sup>1,†</sup>, Eelco J. Rohling<sup>2</sup>, Dan V. Palcu<sup>1</sup>, Fadl Raad<sup>3</sup>, Udara Amarathunga<sup>2</sup>, 4 5 Rachel Flecker<sup>4</sup>, Fabio Florindo<sup>5</sup>, Andrew P. Roberts<sup>2</sup>, Francisco J. Sierro<sup>6</sup>, and Giovanni Aloisi<sup>7</sup> 6 7 <sup>1</sup> Department of Earth Sciences, Utrecht University, Utrecht, The Netherlands. 8 9 <sup>2</sup> Research School of Earth Sciences, Australian National University, Canberra, Australia. 10 <sup>3</sup> Department of Hydrogeology, University of Corsica Pasquale Paoli, Corte, France. <sup>4</sup> BRIDGE, School of Geographical Sciences and Cabot Institute, University of Bristol, 11 Bristol, UK. 12 <sup>5</sup> Istituto Nazionale di Geofisica e Vulcanologia, Rome, Italy. 13 14 <sup>6</sup> Department of Geology, University of Salamanca, Salamanca, Spain. <sup>7</sup> Université Paris Cité, CNRS, Institut de Physique du Globe de Paris, Paris, France. 15

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- 17 Abstract
- 18

19 Salt giants are an intrinsic part of Earth's geological record and influence both regional and global climate and 20 environments. In this Review, we summarize the causes and consequences of the Mediterranean Messinian 21 salinity crisis (MSC; 5.97-5.33 million years ago), one of Earth's youngest and arguably best-studied salt giants. 22 We emphasize that salt giant formation is more complex than development of a palaeo-hydrological imbalance. 23 Instead, the tectonic setting of an evaporative basin largely determines the timing and mode of salt formation, 24 with superimposed impacts of orbital-scale climate and sea-level fluctuations. Combined, these drivers 25 triggered precipitation of carbonates, gypsum, halite, and even bittern salts in the Mediterranean, with well-26 defined orbital cyclicities in carbonate and gypsum phases. Salt extraction from the world ocean during 27 evaporite and residual brine formation, rapid ion return during basin reconnection, and slow ion return due to 28 evaporite weathering over geological timescales exert important feedbacks on global and regional 29 environmental change over millennial to million year timescales. Our compilation of MSC boundary conditions 30 highlights knowledge gaps for targeting future data collection campaigns and provides critical context to next-31 generation hydro-geochemical modelling of interactions between salt giants and environmental change. 32 33 34 35 36 37 38 Key points 39 1. Fifty years of Messinian salinity crisis research is summarized and general elements applicable to salt giant 40 formation are highlighted. 41 2. Geodynamic and eustatic sea-level forcing are crucial for initiating and terminating salt giant formation with

- 42 a subsidiary role for regional climate.
- 43 3. The main controls on evaporitic mineral precipitation are the freshwater deficit magnitude and the extent of 44 water-exchange limitation between basin and ocean.
- 45 4. Evaluation of a new sea-level record for the 6.4 to 5.0 Ma time interval demonstrates that sea level is a viable 46 driver of the prominent MSC sedimentary cyclicity in addition to orbital freshwater budget variation.
- 47 5. Formation and weathering of salt giants may be an important intermediate timescale carbon cycle driver.

#### 48 Introduction

49 The opening and closure of oceans and seas by plate tectonic processes is often marked by formation of 50 marginal basins that have restricted water-exchange with the open ocean. Under negative hydrological budgets, 51 where freshwater loss by evaporation exceeds the supply from rivers and rainfall, periods of limited exchange 52 with the open ocean can lead to precipitation of enormous evaporite deposits in the incipient or dving basin. 53 Such "salt giants" formed episodically through Earth's history, including the Palaeozoic (Australia, USA, 54 Russia, NW Europe), Mesozoic (South Atlantic, Gulf of Mexico), and Cenozoic (Mediterranean, Red Sea, 55 Central Europe) eras<sup>1,2</sup>. Halite (NaCl) and gypsum/anhydrite (CaSO<sub>4</sub>) extraction from seawater during salt giant 56 formation can represent >5% of the total ocean dissolved salt content<sup>3,4</sup>, which disrupts local ecosystems in 57 evaporitic seas and modifies global ocean chemistry<sup>5</sup>.

58 The Mediterranean Messinian salinity crisis (MSC) generated one of the youngest and arguably best-studied 59 salt giants in Earth's history, even though most MSC deposits are buried below the Mediterranean seafloor and 60 remain largely inaccessible to direct research<sup>6</sup>. Seismic profiles across deep basinal sequences and outcrops 61 along tectonically uplifted marginal basins provide a picture of the spatial distribution of evaporite units (Fig. 1)<sup>6-10</sup>. The Late Miocene land-locked Mediterranean configuration amplified its responses to regional and 62 63 global climate fluctuations, and caused distinct cycles in pre- and post-MSC deposits, facilitating construction 64 of a detailed chronostratigraphic framework, tuned with precessional resolution (~20 kyr) to astronomical 65 insolation curves<sup>11-13</sup>. This has resulted in a stratigraphic consensus scenario for the Mediterranean salt giant<sup>6</sup> 66 that provides a foundation for high-resolution geochemical evaporite fingerprinting<sup>14,15</sup> and for observational 67 and modelling studies of underlying forcing mechanisms<sup>16,17</sup>.

Fifty years of MSC research demonstrates that salt giants do not form in basins that simply isolate and desiccate;
rather, complex sub-basin settings play a crucial role in determining the timing and mode of salt formation<sup>18,19</sup>
with contributions from various forcing mechanisms such as tectonics, sea-level change, and hydrological
connectivity with the ocean<sup>20</sup>. In discussing the latest developments in MSC research here, we build from
previous detailed overviews of MSC stratigraphy<sup>6,21</sup>, Mediterranean evaporite distribution patterns<sup>4,10</sup>, and

- 73 Atlantic-Mediterranean connectivity<sup>20,22</sup>. We also consider which elements are applicable more generally to
- salt giants, and reflect on their consequences for regional and global environmental change.

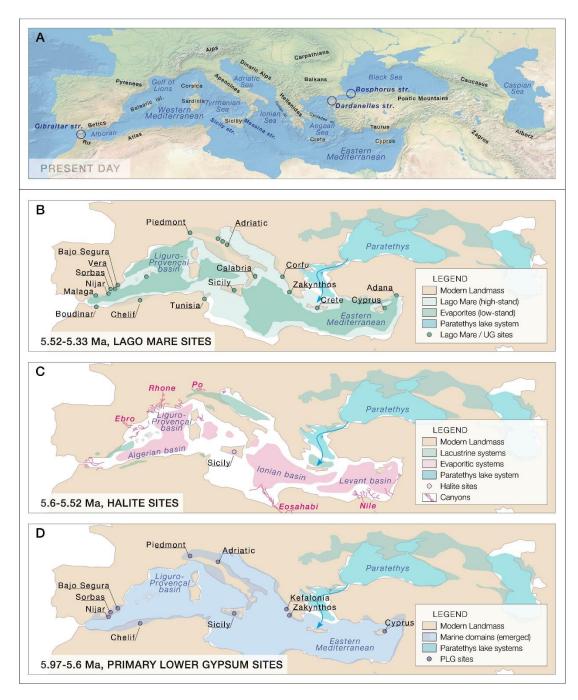


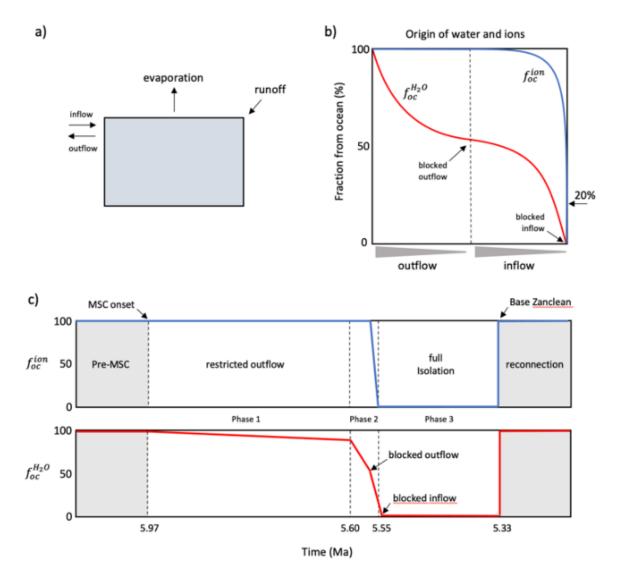
Figure 1. Mediterranean MSC evaporite stages. a | Map of the Mediterranean region with the most important
seas, straits, and mountain ranges labelled. b-d | Schematic maps of the Mediterranean and Paratethys seas
during three evaporite stages<sup>6</sup> showing the main sites that crop out onshore. 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 recent literature<sup>3,4,7-10,23-25</sup>.

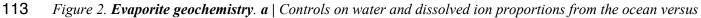
#### 83 Evaporitic salt formation

84 Ocean chemistry has changed substantially over time<sup>26</sup>. One driver for this change is the precipitation and 85 weathering of giant evaporite deposits. The most common marine evaporite minerals – carbonates, gypsum, 86 anhydrite, halite, and the bittern salts (kainite, carnallite, bischofite) - precipitate from seawater when the 87 concentration of their constituent ions (Na<sup>+</sup>, Cl<sup>-</sup>, Ca<sup>2+</sup>, SO<sub>4</sub><sup>2-</sup>, K<sup>+</sup>, Mg<sup>2+</sup>, HCO<sub>3</sub><sup>-</sup>) exceeds a threshold known as the solubility product<sup>27,28</sup>. Ion concentration in evaporite basins depends both on water fluxes to, and the total 88 89 water volume of, the marginal basin. Ions are added to these basins by water inflow from the ocean and rivers, 90 and leave the basins only by outflow to the ocean or by mineral precipitation. The water volume in an evaporite 91 basin is conserved if a sufficient oceanic connection exists, but it can decline through net evaporative draw-92 down if the connection becomes severely restricted or blocked; in both cases net evaporative freshwater 93 removal raises the dissolved ion concentration in basin waters. The main controls on evaporitic mineral 94 precipitation are, therefore, the magnitude of the freshwater deficit and the extent of water-exchange limitation 95 between basin and ocean (Fig. 2a).

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).

101 The evaporite-forming ion concentration in river water is, respectively, typically 1000 (Na<sup>+</sup>, Cl<sup>-</sup>), 100 (Mg<sup>2+</sup>,  $SO_4^{2-}$ , K<sup>+</sup>), and 10 (Ca<sup>2+</sup>) times lower than in seawater<sup>29,30</sup>. Consequently, continental runoff influences marine 102 103 evaporite mineral precipitation only if oceanic input is restricted severely or cut off entirely. A qualitative 104 picture of the impact of ocean-continental water mixing on dissolved ions, as a function of seawater-exchange 105 restriction, is shown in Fig. 2. Evaporites only evolve toward a "continental" mineralogical signature when the 106 continental input dominates the oceanic source. This is the case for the Upper Gypsum succession on Sicily 107 where non-oceanic Sr isotope data from both gypsum and ostracods suggests minimal Atlantic contribution<sup>18</sup>. 108 The relative abundances of many other evaporite-forming ions are much higher in river water than in sea water 109 (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 110  $HCO_3^{-}/Cl^{-} = 2.5$  (0.004). Thus, when oceanic connection is highly restricted or blocked, carbonate and gypsum 111 precipitation dominate the typical halite-dominated marine association<sup>31</sup>.





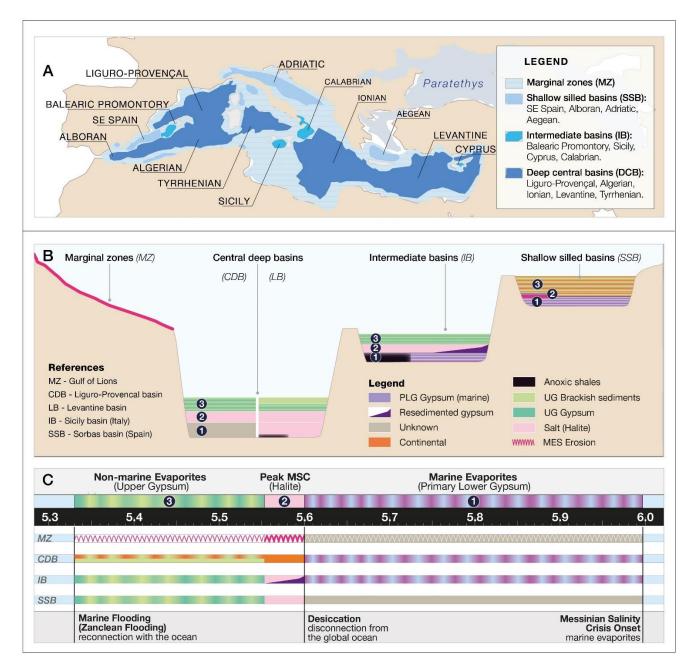
- 114 continental runoff during the MSC. Simplified water balance of an idealized marginal basin; **b** | fraction of
- 115 water (red curve) and dissolved ions (blue curve) originating from the ocean as a function of seawater-
- exchange flux restriction at the sill separating the ocean from the marginal basin;  $c \mid$  idealized scheme for ocean water and ion fractions during the MSC; note that continental runoff becomes a relevant ion source to
- 118 the basin only when its marine connection is restricted severely, or cut off completely, from the ocean<sup>36</sup>.

#### 119 The Mediterranean salt giant

120 The first scientific reports of Mediterranean Messinian evaporites were by field geologists who documented 121  $\sim 100$ -m-thick gypsum units between marine sequences in several Italian basins<sup>32,33</sup>. In the 1970s, Deep Sea 122 Drilling Project (DSDP) Leg 13 confirmed the widespread presence of evaporite units across the Mediterranean<sup>3,34</sup>, although coring only reached the uppermost MSC successions. The presence of these 123 124 evaporites led to the hypothesis that the Mediterranean became isolated from the Atlantic and desiccated almost 125 entirely during the terminal Miocene<sup>34,35</sup>. The Mediterranean salt giant extracted an estimated  $1.2 \pm 0.1$  km<sup>3</sup> ( $\sim$ 7 to 10 %) of salts from the global ocean<sup>4,34</sup>. Detailed stratigraphic studies from onshore sequences and 126 offshore seismic data indicate that the Mediterranean contains different evaporite successions (Fig. 1, 3)<sup>6</sup>. In 127 128 addition to volumetrically minor K-Mg-salts (bittern salts) associated with halite, there are at least four main 129 evaporitic deposit types observed in MSC successions now exposed on land: (1) evaporitic carbonates known as the Calcare di Base (Sicily)<sup>36,37</sup> and the Terminal Carbonate Complex (SE Spain)<sup>38,39</sup>; (2) predominantly 130 131 marine gypsum known as the Primary Lower Gypsum unit (PLG: Spain, Italy)<sup>15,40</sup>; (3) halite (Sicily, Liguro-132 Provencal, Levant)<sup>41</sup>; and (4) gypsum with continental geochemical signatures in the so-called Upper Gypsum unit (UG: Sicily, Cyprus)<sup>18,42</sup>. Except for the halite in the western Mediterranean, all of these evaporites are 133 134 interbedded with detrital clastics and/or hemipelagic sediments.

135 The depositional and stratigraphic architecture of Messinian evaporites varies across the Mediterranean 136 depending mainly on the tectonic setting and water depth. Four main settings are recognized. 1) Marginal zones with mainly erosional features (Fig. 3) that have commonly been related to multiple drawdown events<sup>10,43</sup> in 137 138 which subaqueous erosion by dense cascading waters might also have played a role<sup>44</sup>. 2) Shallow, silled basins 139 (Adriatic region, SE Spain basins) containing the most complete PLG successions<sup>38</sup>, overlain in places by 140 erosional surfaces and/or younger lacustrine and continental deposits with intervals characterized by brackish Lago Mare fauna<sup>18,45–47</sup>. 3) Intermediate-depth basins (Sicily, Cyprus, Balearic Promontory), which can be 141 142 complicated by substantial tectonism during and since the MSC<sup>23,48</sup>. Basal MSC units in these intermediate settings comprise PLG<sup>49</sup> or anoxic shales devoid of evaporites<sup>50,51</sup>. Where PLG is observed, the evaporites 143

- 144 might not be preserved *in situ* because they are commonly found as a range of reworked deposits from
- 145 gypsarenites to gypsum olistostromes, grouped into a Resedimented Lower Gypsum (RLG) unit<sup>6,52</sup>.



146

151 *basin settings*.

<sup>Figure 3. 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. 1 Primary Lower Gypsum (PLG)
phase, 2 Halite, 3 Upper Gypsum (UG) phase. C | Age constraints and distribution of MSC deposits in different</sup> 

153 Downslope reworking is considered time-equivalent with the halite observed in intermediate-depth basins 154 (Sicily, Balearic Promontory, Cyprus) $^{23,53}$ . The UG is commonly well developed, comprising gypsum 155 alternating with clastics that contain Lago Mare fauna<sup>18</sup>. The transition from non-marine Messinian to deep 156 marine Zanclean deposits is often conformable without evidence of major erosion<sup>54,55</sup>. 4) Deep central basins 157 are found in the western (Liguro-Provencal, Algerian) and eastern (Ionian, Levantine) Mediterranean, separated 158 by the Strait of Sicily, with strikingly different depositional architecture on seismic refection profiles<sup>7,10</sup>. Deep 159 central western Mediterranean basins typically contain a seismic "trilogy" with a Lower Unit (mass-transport 160 deposits), Mobile Unit (halite), and an Upper Unit (gypsum-clastic alternations)<sup>7</sup>. No direct lithological data 161 are available for the deep central western salt giant where only the topmost MSC has been sampled, which 162 generally contains UG with brackish water fauna<sup>56</sup>. The easternmost deep Mediterranean (Levantine Basin) 163 contains a >1-km thick evaporitic succession with six seismic sub-units<sup>57,58</sup>, four transparent units composed of halite and two units composed of claystones<sup>59,60</sup>. Cuttings from industrial drill holes suggest that evaporite 164 deposition started with only a few metres of anhydrite<sup>52,57</sup>, followed by the halite-dominated succession, which 165 166 terminated after a truncation surface with a ~100 m thick "Unit 7" composed of shales, sands, and anhydrite<sup>9</sup>. 167 This top unit of the MSC in the deep Levant Basin is interpreted as having been deposited above the Intra 168 Messinian Truncation Surface (IMTS), a dissolution surface related to significant dilution and stratification of 169 the eastern Mediterranean water column at the base of the UG-Lago Mare phase<sup>9</sup>.

170

#### 171 Age constraints and hydrological conditions for Mediterranean evaporites

172 Cyclostratigraphic correlation and astronomical tuning of pre- and post-MSC sedimentary successions provide 173 accurate ages for both the onset of PLG precipitation (5.97 Ma)<sup>61</sup>, with evaporitic limestones in some 174 intermediate and marginal basins forming slightly earlier (6.08-6.03 Ma)<sup>8,62,63</sup>, and the marine sediments that 175 immediately overlie the MSC successions throughout the Mediterranean (5.33 Ma)<sup>64</sup>. This constrains the MSC 176 duration to 640 kyr. Dating within the MSC interval itself is more uncertain because of a lack of high-resolution 177 independent age control points; the entire MSC occurred within a single reversed magnetic polarity subchron<sup>12,65</sup> (Fig. 4); biostratigraphic markers are absent because of the extreme environmental conditions,
and datable volcanic ash layers are scarce<sup>6,46</sup>.

180 During the PLG phase, marine carbonate-marl and gypsum-marl cycles accumulated subaqueously in both shallow and intermediate basins (Fig. 3)<sup>40</sup>, which precludes a major Mediterranean sea-level fall at the onset of 181 182 the MSC<sup>66</sup>. Moreover, marine strontium isotope data are broadly consistent with a high Mediterranean water 183 level that permitted restricted two-way Atlantic-Mediterranean exchange<sup>15,67</sup>. Assuming that cyclic gypsum-184 marl alternations followed the same regional precessional climate forcing as pre- and post-MSC Mediterranean 185 sediments, correlation of 16-17 documented sedimentary cycles in the PLG to astronomical curves suggest that PLG deposition ended at <5.6 Ma (Fig. 4)<sup>40,68</sup>. However, numerical modelling of water and salt balances 186 187 indicates

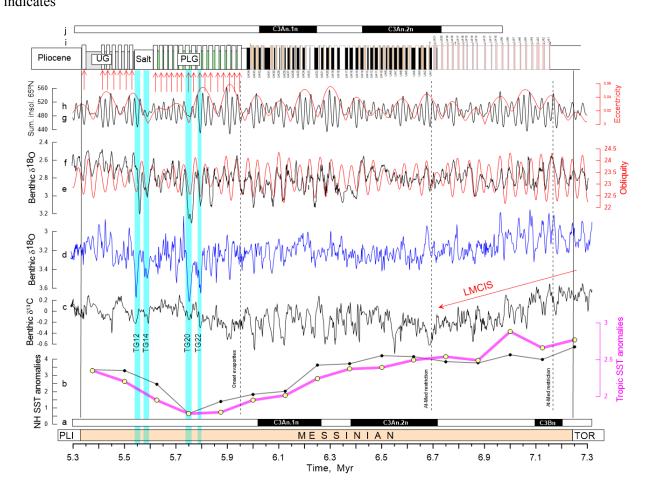


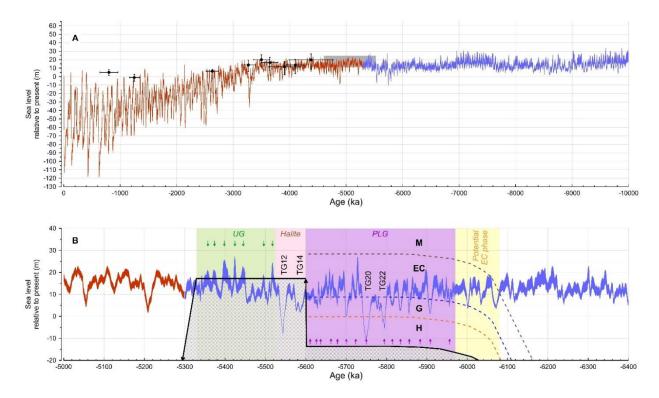
Figure 4. Global benthic foraminiferal oxygen and carbon isotope records correlated to the main MSC
 phases. a | Cenozoic Geomagnetic Polarity Time Scale<sup>69,70</sup>. b | Northern Hemispheric sea surface temperature
 (SST) stack in black and Tropical sea surface temperature stack in magenta<sup>71</sup>. The scale shows the difference
 in temperature from the present (note that the two SST scales are different). c | Cenozoic benthic foraminiferal

193  $\delta^{13}C$  reference record<sup>69</sup>. LMCIS: Late Miocene Carbon Isotope Shift. **d** | Cenozoic benthic foraminiferal  $\delta^{18}O$ reference record<sup>69</sup>.  $e \mid$  Changes in Earth's tilt through the Messinian<sup>72</sup>.  $f \mid$  Benthic foraminiferal  $\delta^{18}O$  from ODP 194 195 Site 982 (North Atlantic)<sup>70</sup>. g | Insolation at 65°N for 21 June<sup>72</sup>. h | Changes in the Earth's orbital eccentricity<sup>72</sup>. 196 i | Messinian stratigraphic units. UG= Upper Gypsum, with 7 gypsum layers (white) interbedded with 197 mudstones (grey)<sup>18</sup>, PLG=Primary Lower Gypsum with 16 gypsum layers (white) interbedded with 198 mudstones<sup>6,21</sup>. Precession-driven sedimentary cycles during the pre-evaporite stage. LA1 to LA21 and UA1 to UA34 indicate Lower and Upper Abad sedimentary cycles<sup>13</sup> (the thickness of each sedimentary cycle has been 199 200 adjusted to its time span)<sup>62</sup>. Legend for the pre-evaporite cycles: pink, white, black and beige levels indicate 201 indurated layers, homogeneous marls, sapropels and diatomaceous marls, respectively.  $\mathbf{i} \mid$  Geomagnetic 202 polarity time scale GPTS2012<sup>73</sup>. Blue bands: main global glacial isotope stages during the Late Messinian. 203 Dashed vertical lines: main restriction steps for Atlantic-Mediterranean water exchange; the upper one results 204 in the PLG onset. Red arrows indicate gypsum beds deposited during insolation minima. 205

- that the gypsum-marl cycles could have resulted either from precession-driven  $\sim 20\%$  hydrological budget changes and/or oscillating gateway restriction caused by sea-level fluctuations of  $\sim 10$  m competing with
- **208** tectonic uplift and marine gateway  $erosion^{74,75}$  (Fig. 5).

209 Deep Mediterranean halite units lack absolute age control. In the western Mediterranean, halite is thought to 210 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<sup>21,76</sup> (Figs. 4, 5). The timing of initial eastern Mediterranean halite deposition 211 212 is contested, with suggested ages ranging from 5.97 Ma, equivalent to the PLG onset in marginal basins<sup>77</sup>, to 213 5.59 Ma, at the end of the PLG<sup>78</sup>. Our sea-level analysis suggests a third possibility, namely ~5.8 Ma, which 214 coincided with the start of glacial stage TG22 (Fig. 5). Halite is thought to have been deposited when Atlantic-215 Mediterranean exchange was more restricted than during the PLG phase<sup>79</sup> (see also *Methods*). In geochemical 216 models, a severely restricted scenario with no Mediterranean outflow (that is, with Mediterranean sea level 217 close to, or below, sill depth) could support deposition within 80 kyr of the deep-basin halite body observed in seismic profiles<sup>79</sup>. In this scenario, evaporated freshwater is replaced continuously by Atlantic inflow, which 218 219 generates the necessary ion fluxes for halite deposition. The evaporite mineral paragenesis resulting from this 220 constant marine supply with no ion loss via Mediterranean outflow is distinctly different from that generated 221 by evaporation of a fixed seawater volume (Fig. 2). Instead of sequential evaporite phases precipitating as brine 222 concentration increases, mineral precipitation fields overlap substantially, with carbonate, gypsum, and halite 223 precipitation potentially coexisting up to bittern salt formation<sup>80</sup>.

224 The final Mediterranean salt giant phase is the most enigmatic, with alternating UG beds and brackish Lago 225 Mare deposits that contain biota of Paratethyan (former Black Sea-Caspian Sea system) affinity<sup>46</sup>. In 226 intermediate basins (Sicily, Cyprus), 6-7 gypsum-brackish marl alternations are observed<sup>21,81</sup>. Strontium 227 isotope ratios from both gypsum crystals in the UG and ostracods from Lago Mare marl horizons suggest a 228 dominantly freshwater system with only minor (~20%) Atlantic contribution<sup>18,42</sup>. Assuming that UG cycles 229 were precession-driven, downward tuning from the lowermost Zanclean suggests that this final MSC phase 230 started at 5.52 Ma<sup>18</sup>. In shallow silled basins, time-equivalent continental and lacustrine sediments contain 231 influxes of high-diversity Paratethyan ostracods, but no gypsum <sup>45,82</sup>.



232

233 Figure 5. Sea-level synthesis with MSC sill-depth scenarios. a | Last 10 Myr. The Plio-Pleistocene record 234 (red) is based on benthic  $\delta^{18}O$  deconvolution<sup>83,84</sup> using the combined compilations of Lisiecki and Raymo<sup>85</sup> and 235 Westerhold et al. <sup>69</sup>. For the Miocene (blue), we use the envelope between the main benthic  $\delta^{18}O$  deconvolution and the sensitivity scenario of Rohling et al.<sup>84</sup> (see that study for rationale and details) based on the Westerhold 236 237 et al.<sup>69</sup> benthic  $\delta^{18}O$  compilation. Sea-level benchmarks are also shown for Mallorcan marine cave deposits 238 (black circles with error bars) and Patagonian coastal deposits (grey box), which have been corrected for 239 tectonic changes, glacio-isostatic effects, and dynamic topography  $^{86-88}$ . **b** | Detail of the records from **a** between 240 5 and 6.4 Ma. We compare sea-level variations with the likely Atlantic-Mediterranean gateway geometry and 241 calculate threshold values for water exchange through the strait that delimit precipitation of halite (H), gypsum 242 (G), evaporative carbonate (EC), or hemipelagic marl deposition (M), as detailed in the Methods. The inferred 243 MSC sill (grey shading) scenario assumes a disconnected (drawn down) condition during halite and UG 244 deposition. MSC phases are coloured as in Figure 3. Purple arrows indicate potential gypsum phases in the 245 PLG, and green arrows indicate  $\sim$ 7 potential (mostly continental) gypsum phases in the UG.

#### 246 Salt giant forcing mechanisms: the roles of sills and straits

247 Marine gateways play a critical role in exchanging water, heat, salt, and nutrients between oceans and seas. 248 During the MSC, water exchange with the open marine Atlantic Ocean and the brackish Paratethys Sea were 249 influenced by a complex combination of geodynamic (tectonic movements in gateway regions), glacio-eustatic 250 (global sea level fluctuations), and palaeoclimatic (hydrological budget changes) processes that all played a 251 role in Messinian salt giant formation. Tectonic uplift and sea level lowering can have similar effects on water 252 exchange through gateways and are difficult to unravel. Here, we present and evaluate current understanding 253 of the geodynamic and ice-volume/sea-level forcings on the MSC and then revisit the role of superimposed 254 regional palaeoclimatic forcing.

255

#### 256 Geodynamic forcing

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<sup>89</sup>.

262 Palaeogeographic reconstructions of the Gibraltar region indicate that the early Messinian Atlantic-263 Mediterranean connection was a foreland-basin system with multiple gateways through southern Iberia and 264 northern Morocco (Fig. 6a). These Betic and Rifian corridors closed progressively in pre-MSC times, and marine connectivity evolved toward a single proto-Gibraltar strait gateway for the MSC<sup>22,90</sup>. Mediterranean-265 266 Atlantic connectivity may also have been partially controlled by an emergent volcanic chain on the eastern 267 Alborán margin that formed a partial land-bridge between northern Morocco and southeastern Spain (Fig. 6a)<sup>91</sup>. 268 Water flux modelling indicates that exchange patterns with the Atlantic depended on relative sill depths, with 269 two-way flow in two corridors when the shallow corridor was deeper than half the depth of the deep corridor, 270 and only one-way flow when the shallow corridor was shallower than this<sup>92</sup>. Uplift of the initially deep Rifian 271 corridor at  $\sim$ 7 Ma<sup>90</sup> could, therefore, have altered exchange patterns in the Gibraltar strait from mainly Atlantic 272 inflow to two-way flow, consistent with simultaneous Alborán Basin benthic faunal changes<sup>93</sup> and deep 273 Mediterranean records in which the first signs of restricted conditions and increased water mass stratification 274 occurred at  $\sim$ 7 Ma<sup>94</sup>.

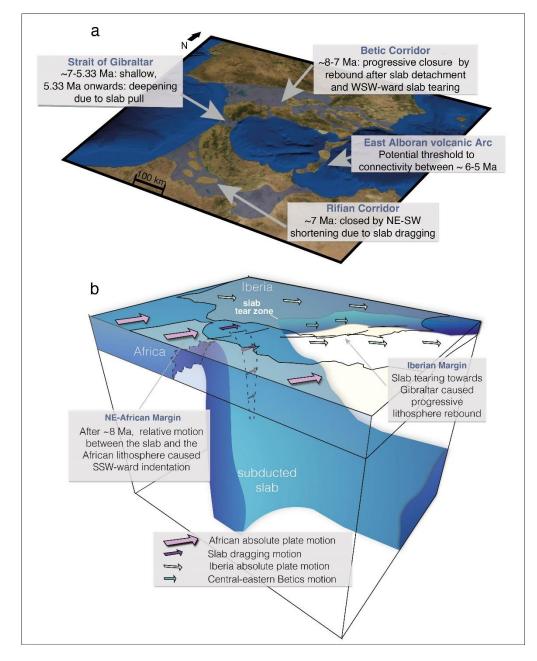


Figure 6. Geodynamic context of the MSC. a | Schematic topography of the pre-MSC Gibraltar region with
palaeogeographic projection of Mediterranean-Atlantic gateways. The labels illustrate the timing and
mechanisms of vertical motion that restricted Atlantic-Mediterranean connectivity (~5.33–7 Ma) (after Capella
et al.<sup>95</sup>). b | Cartoon of slab morphology below Gibraltar. Arrows illustrate absolute plate motions for Africa
and Iberia with slower central-eastern Betic motion (after Spakman et al.<sup>96</sup>).

The main geodynamic processes in the Gibraltar orogenic system involve African-Iberian plate convergence<sup>97</sup>. 281 282 slab tearing under the eastern Betic Cordillera<sup>98</sup>, and mantle resistance against Gibraltar slab drag<sup>96</sup>. Mantle 283 tomography and other seismological investigations provide a clear present-day 3D image of Gibraltar slab 284 geometry and lateral continuity with surface plates, and where it is detached and might have delaminated from 285 continental lithospheric mantle (Fig. 6b)<sup>98,99</sup>. Early to Late Miocene westward slab roll-back resulted in 286 thrusting of the Alborán domain over the African and Iberian margins. Indentation of the Rif Mountains by 287 slab dragging together with slab detachment beneath the Betic Cordillera (Fig. 6a, b) can explain gateway 288 opening, closure, and re-opening<sup>95</sup>. During the late Tortonian (between 8 and 7 Ma), the Betic gateways were 289 uplifted by isostatic rebound related to gradual slab tearing below Spain. Slab dragging initiated thick-skinned 290 tectonics in Morocco that also closed the Rifian Corridor<sup>100</sup>.

291 During the MSC, sills within the Mediterranean basin also played important roles. In shallow silled basins 292 where PLG developed, geochemical evidence indicates that climate oscillations<sup>101</sup> modified conditions within the basins resulting in localised density contrasts across the sills, even before the MSC<sup>102</sup>. The Sicily sill, which 293 294 separates the western and eastern Mediterranean basins, played a crucial role in water and salt transport across 295 the Mediterranean before, during, and after the MSC<sup>103-105</sup>, and likely generated the different MSC 296 stratigraphies in the deep central basins. Other important sills were the tectonically active Gargano promontory (Italy)<sup>106</sup> and Cyclades region (Greece)<sup>25</sup> that separate, respectively, the Adriatic and North Aegean basins from 297 298 the open eastern Mediterranean (Fig. 1). These restricted basins persisted as two evaporite-free largely isolated 299 megalake systems during the halite and UG phases, probably influenced by extensive European river runoff 300  $(Fig. 1)^{25,82}$ .

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<sup>107,108</sup>, 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<sup>109</sup> (Fig. 1a). Messinian 307 palaeogeographic evolution of the Mediterranean-Paratethys gateway is poorly understood, but it affected 308 hydrological, palaeoecological, and palaeoenvironmental conditions in both domains<sup>25</sup>. Palaeontological data 309 indicative of marine faunal exchange<sup>110,111</sup> and strontium isotope data<sup>17</sup> suggest that Mediterranean-Paratethys connectivity was established at 6.1 Ma<sup>112,113</sup>, before the onset of evaporite precipitation. Gateway geodynamics 310 311 between the Mediterranean and Paratethys were then, as now, dominated by active westward growth and 312 propagation of the North Anatolian Fault Zone, North Aegean extensional tectonics, and Cyclades domain 313 uplift/exhumation<sup>114</sup>. This, combined with substantial lake-level fluctuations, has resulted in episodic Mediterranean-Paratethys/Black Sea connection and disconnection ever since<sup>115,116</sup>. 314

315

#### 316 Glacio-eustatic forcing

317 To date, sea-level forcing of the MSC has been dismissed in most studies based on the assumption that its 318 variations were obliquity controlled (~40 kyr); using this period for sedimentary cyclicity would result in an 319 MSC duration that is too long to match independent age constraints. However, a recent global  $\delta^{18}$ O synthesis 320 indicates that the periodicity of ice-volume and deep-sea temperature fluctuations across the Late Miocene was 321 controlled by precession, similar to Mediterranean climate cycles (Fig. 5)<sup>69</sup>. To assess whether sea level was 322 an important forcing mechanism for Mediterranean isolation from, and/or reconnection to, the Atlantic 323 Ocean<sup>117</sup>, we examine a new sea-level record for the 6.4 to 5.0 Ma time interval relative to the present level (0 324 m; Fig. 5). By applying established box-model approaches to evaluate the evaporite implications of gateway restriction<sup>74</sup> (see *Methods*), this sea-level record indicates that sill depths >41 m favour basinal hemipelagic 325 326 carbonate (marl) deposition. Evaporative carbonate deposition is favoured when the strait depth ranges between 327 22 and 41 m, gypsum deposition occurs between 13 and 22 m, and halite deposition occurs at depths <13 m. 328 Friction would reduce exchange through the strait, so these threshold water depths are minimum estimates.

329 The new high-resolution record of global mean sea-level variations indicates that sea level alone cannot account

330 for either the MSC onset, or rapid reestablishment of normal open marine conditions at the beginning of the

331 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. 5), while the

333 MSC termination requires catastrophic, tectonic, strait opening to depths more than ~40 m below the lowest 334 sea level of that time<sup>104,118</sup>. However, some stratigraphic features within the MSC are consistent with Late 335 Miocene sea level fluctuations. For example, with a shallow Mediterranean-Atlantic sill depth of 13-22 m (with 336 the uplifted sill  $\sim 18$  m below present-day sea level), sea-level fluctuations could explain the 16 gypsum cycles 337 (magenta arrows in Fig. 5b) deposited during the PLG phase. In this scenario, sea-level influence on the gypsum 338 cycles may have been irregular, potentially accounting for at least some observed variability in their thickness 339 and spacing. These lithological threshold depth calculations ignore Paratethys inputs and precession-scale 340 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<sup>64</sup> for 341 342 sensitivity analysis). Changes in Paratethys inputs and Mediterranean hydrology might explain the absence of 343 halite between 5.8 and 5.7 Ma, when it should have been triggered by two marked sea-level falls (Fig. 5b). The 344 onset of well-documented halite precipitation (at ~5.6 Ma) requires further tectonic strait restriction (red 345 shading in Fig. 5b). Maximum gateway restriction occurred at 5.55 Ma when global sea level was lowest, 346 consistent with an episode of Mediterranean sea level fall. The end of halite deposition could have been 347 terminated by the sea-level rise at  $\sim$ 5.53 Ma if the sill was below 6 m above present sea level.

For the UG phase (green shading in Fig. 5b), 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<sup>18,19,104</sup>. This high-resolution sea-level record is consistent with (potentially seven) partial reconnection events (green arrows in Fig. 5b) associated with minor Atlantic inflow that might correspond to the seven gypsum cycles observed in the UG<sup>18,81</sup>.

353

#### 354 *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<sup>115–117</sup>. We

here evaluate climatic variations over the Mediterranean basin and its catchment area, including the Paratethysand the north African monsoon region immediately before, during, and after the MSC.

361 Several records indicate that the Mediterranean salt giant formed during a period of global cooling between 7.2 and 5.5 Ma<sup>70,71,119</sup>, which is likely to have been triggered by a global atmospheric  $pCO_2$  decline to a minimum 362 363 between 6.5 and 5.8 Ma<sup>120</sup>. The Late Miocene  $pCO_2$  decrease has been linked to a ~1 ‰ global benthic 364 for aminiferal  $\delta^{13}$ C drop known as the Late Miocene Carbon Isotope Shift (LMCIS; Fig. 4) between 7.6 and 6.6 365 Ma<sup>93,121</sup>. This drop is amplified in the Mediterranean, probably because of progressive gateway restriction in 366 the Gibraltar region since  $\sim 7.1$  Ma<sup>122</sup>. The absence of a humidity decrease from the pre-evaporitic marls to the 367 base of the PLG gypsum<sup>92,122</sup> implies that MSC salt giant formation was not likely triggered by Mediterranean 368 climate change. As atmospheric  $pCO_2$  began to rise after 5.5 Ma, warming occurred<sup>120</sup>. This warming trend 369 started at the transition between isotope stages TG12 and TG11, coincident with the end of halite deposition 370 and the onset of Mediterranean UG formation (Figs. 4, 5). Ensuing long-term global warming was associated with long-term global sea level rise (Figs. 4, 5) $^{83,84,117}$ . 371

372 Lack of foraminifera hinders Mediterranean palaeoclimate reconstructions through the MSC, although 373 Messinian palynological<sup>123</sup> and organic biomarker records<sup>124–127</sup> indicate that Mediterranean climate was warm 374 and dry before, during, and after the MSC. Along the northern Mediterranean margin, climate was warm and 375 humid, similar to present-day conditions, with important river runoff from the Alps (Rhone and Po)<sup>128</sup>. Lack of 376 marked vegetation changes during the different evaporite phases suggests that Mediterranean climate did not 377 force the MSC and that the MSC, in turn, did not have a substantial impact on Mediterranean climate<sup>123</sup>.

The classic marl-sapropel alternations of pre-evaporitic MSC successions indicate conspicuous precessionpaced climate oscillations (Fig. 4)<sup>11,12,62</sup>, in which sapropels mark relatively wet conditions during precession minima (insolation maxima), when enhanced freshwater runoff increased Mediterranean water column stratification<sup>129</sup>. 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)<sup>40,68</sup>. Organic geochemical data from PLG cycles in northern Italy confirm this, revealing climatic oscillations<sup>15</sup> with gypsum deposition during relatively dry periods with reduced river
 runoff<sup>130,131</sup>.

386 Most MSC scenarios envisage a maximum Mediterranean lowstand during or after halite deposition, with drawdown estimates of -600 to -2000 m<sup>43,132,133</sup>, indicating a strong regional circum-Mediterranean negative 387 388 hydrological balance. Mediterranean water level during the UG is still contested<sup>46</sup>. The presence of recurrent, 389 high-diversity, shallow-water, brackish ostracod assemblages in most shallow, silled Mediterranean basins 390 indicates considerable net freshwater influxes. Palaeoclimate models suggest that Mediterranean-wide Lago 391 Mare conditions cannot be explained by Paratethys inflow alone, and that additional water sources are required<sup>134,135</sup>. Specifically, runoff from high-amplitude African monsoon maxima has been considered<sup>136-140</sup>. 392 393 Alternatively, Atlantic input to the basin might have contributed during glacio-eustatic relative sea level 394 highstands (Fig. 5), although fully marine conditions were not established until the Zanclean<sup>95</sup>.

395 Given Mediterranean regional hydroclimate constancy through the MSC, periods of strong evaporative water-396 level drawdown must reflect low net precipitation over remote parts of the Mediterranean freshwater catchment 397 (Paratethys and/or monsoonal Africa). Conversely, major freshwater influx periods must reflect high net 398 precipitation over far reaches of its catchment. The Paratethys is a likely source of considerable Messinian freshwater variations because connection between the two basins<sup>110,136</sup> would have greatly extended the 399 400 Mediterranean freshwater catchment area relative to today<sup>19</sup>. Specifically, the Messinian Paratethys unified the 401 Dacian, Black Sea, and Caspian Sea basins<sup>105</sup>, so that all major Eurasian rivers (Danube, Dnjepr, Don, Volga, 402 Syr-Darya, Amu-Darya) drained into the Mediterranean<sup>137</sup>. In the Tortonian, hydrological variations associated 403 with eccentricity-driven northward (southward) mid-latitude westerly displacement over the Paratethys may 404 have already caused decreased (increased) Paratethys overspill/runoff into the Mediterranean<sup>138</sup>. Assuming that 405 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<sup>134,139</sup>. 406

407 African monsoon intensity tracked the northern summer insolation amplitude (hence the eccentricity 408 modulated amplitude of the precession cycle) throughout much of the Neogene<sup>140,141</sup>, including the MSC<sup>142,143</sup>.
 409 During insolation maxima (precession minima), monsoon-driven humidity expanded over north

410 Africa<sup>140,141,144,145</sup>. Large north African lakes, such as mega-lake Chad<sup>135,139</sup>, might then have drained via the 411 ancient Eosahabi river into the Mediterranean<sup>146–148</sup>. Although lake Chad lies well south of the modern central 412 Saharan watershed, there is good evidence in younger geological periods of direct discharge via seasonal river 413 floods and wadis<sup>149,150</sup>. The absence of high-amplitude insolation maxima between 5.73 and 5.53 Ma suggests 414 an extended interval of relatively weak African monsoons, whereas several high-amplitude insolation maxima 415 during the UG phase suggest potential high-amplitude African monsoon maxima, with enhanced monsoon 416 runoff into the Mediterranean basin (Fig. 4).

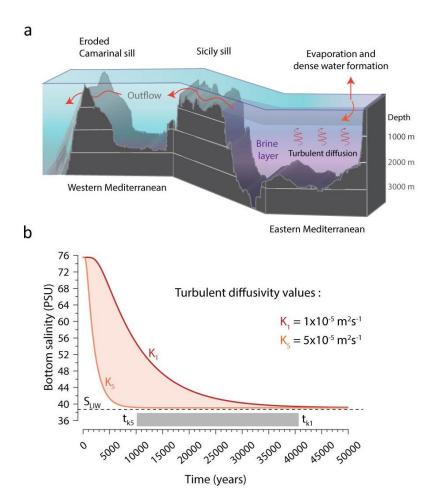
417 Overall, it appears that the long-term evolution from pre-evaporitic marls to gypsum and salt deposition was 418 not driven predominantly by Mediterranean climate change, and that relative sea level drops interacting with 419 tectonic changes at gateways and their impact on ocean water exchange likely were the main mechanisms 420 leading to progressive salt concentration. This long-term trend was punctuated by both precession-based cycles 421 in sea-level and Mediterranean (including Paratethys and African monsoon) hydrology. The influence of these 422 astronomically driven variations was amplified progressively as Mediterranean restriction increased.

423

#### 424 Global relevance and future perspectives

The Mediterranean MSC formed in a convergent tectonic setting. However, 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. The MSC sequence contains deposits that provide insights into both restriction and re-opening of a marginal sea (MSC onset and establishment of earliest Pliocene marine conditions).

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 pheses from the open ocean (Fig. 1,3). 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<sup>18,104</sup>. Return flux of MSC residual brine ions into the open ocean occurred over ~30,000
years<sup>104</sup> (Fig. 7) and its impacts on open ocean circulation and climate have yet to be investigated.



442 Figure 7. Post-MSC removal of Messinian salts to the Atlantic, following an abrupt refilling event. a | Sketch 443 of the Mediterranean configuration immediately following abrupt basin refilling by Atlantic waters. The 444 energetic Atlantic inflow transferred almost all western Mediterranean Messinian salt to the Eastern basin, 445 which became stratified with salts to the Sicily sill level. Turbulent diffusion of salts from the lower dense layer 446 (driven by energy input from winds and tides) slowly transferred Messinian salts back to the Atlantic across 447 the Sicily and Camarinal sills, via the outflow.  $\boldsymbol{b}$  | Diagram of complete salt removal time scale (grey box: 10-448 40 kyr) for turbulent diffusivities of  $1-5 \times 10^{-5} m^2 s^{-1}$ . The shaded area between the  $K_1$  and  $K_5$  curves represents 449 all possible bottom water salinity reduction pathways.  $t_{k1}$ ,  $t_{k5}$  = time taken to reach surface salinity values at 450  $K_1$  and  $K_5$  turbulent diffusivities.  $S_{LIW} =$  Levantine intermediate water salinity (after Amarathunga et al.<sup>104</sup>).

451 Throughout all Mediterranean salt giant evaporitic phases, precession-timed runoff and/or global sea-level 452 variations interacted to drive sedimentary environmental cyclicity due to greater/weaker freshwater admixtures 453 and/or greater/weaker oceanic inflows to the basin, which overprinted marine connectivity changes due to 454 tectonic gateway geometry changes. Model-based sensitivity tests indicate that even subtle freshwater budget 455 and/or sea-level fluctuations would have sufficed to switch between gypsum and marl deposition<sup>74</sup>. Precession-456 timed arid/humid and precession-timed sea-level cycles both occurred at amplitudes relevant to the sedimentary 457 regime, but the precise phase relationship between their impacts remains elusive; these processes could have 458 partially amplified or cancelled each other. More advanced hydro-geochemical models that integrate both 459 forcing mechanisms will be required to fully understand gypsum formation under restricted marine conditions. 460 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<sup>67,79,105</sup>. These 461 462 models track salinity as a single variable, or at most divide salinity into three contributions: gypsum (Ca and 463 SO<sub>4</sub>), halite (Na and Cl), and other salts (K, Mg, HCO<sub>3</sub><sup>-</sup>). This simplification, which facilitates numerical model 464 solution, comes at the expense of a more correct thermodynamic description of the brine and its evolution 465 during salt giant formation.

466 The exact drawdown amount remains a key unknown regarding halite and non-marine gypsum precipitation, 467 when the evaporite basin was semi-isolated from the ocean. Maximum lowstands based on seismic 468 interpretations combined with numerical modelling differ between -600 and -2000 m, assuming that all 469 observed Messinian erosional surfaces formed subaerially. At times of severely restricted or negligible Atlantic 470 inflow, Mediterranean evaporites are expected to contain a mineralogical imprint of continental runoff. The 471 low  $Ca^{2+}/Cl^{-}$  and  $SO_4^{2-}/Cl^{-}$  in continental runoff enables gypsum precipitation at much lower salinities than 472 when forming from evaporating seawater<sup>17,31</sup>. Future hydro-geochemical models that integrate a sound 473 thermodynamic description of high-salinity brines<sup>80</sup> will be able to test the hypothesis that increased relative 474 importance of riverine inputs produces a substantial mineralogical assemblage change in a salt giant. Such 475 models can also evaluate if a large (> 1.5 km) drawdown is required to attain brine saturation with respect to 476 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 lakes on the
Mediterranean Ridge<sup>151–153</sup>.

Almost all salt giant-related research to date has focused on their nature and causes<sup>6,154</sup> with little consideration
of their potential to drive wider environmental change<sup>18,155</sup>. This is partly because of an assumption that impacts
outside the salt basin will be synchronous with evaporite formation. Some recent MSC research has challenged
that assumption <sup>18,155</sup> 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.

484 While the impact of evaporite formation and subsequent weathering on ocean chemistry has been known for 485 some time<sup>162</sup>, their potential to drive rapid carbon cycle changes and associated climate change has only recently 486 been pointed out<sup>155</sup>. Modelling of evaporite weathering and deposition suggests that despite the much larger 487 halite volume that is typically preserved in salt giants, it is the formation and dissolution of giant calcium 488 sulphate (gypsum/anhydrite) deposits that can have global consequences as an episodic driver of carbon cycle changes<sup>155</sup>. This is because oceanic Ca<sup>2+</sup> removal via CaSO<sub>4</sub> deposition decouples the oceanic Ca<sup>2+</sup> and HCO<sub>3</sub><sup>-</sup> 489 490 sinks, causing a CaCO<sub>3</sub> burial decrease and, consequently, increased ocean pH, lower atmospheric pCO<sub>2</sub>, and 491 global cooling. Similarly, the return of  $Ca^{2+}$  ions to the ocean from weathered gypsum can drive warming<sup>155</sup>.

Most biogeochemical models have ignored evaporite-driven perturbations to seawater chemistry<sup>156,157</sup>, assuming that over timescales >100 kyr, evaporite precipitation and weathering are balanced. Formation of substantial 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<sup>4,39</sup>. Bearing in mind that the MSC is by no means the largest of the salt giants<sup>158</sup>, this demonstrates that the evaporite precipitationweathering balance assumption can only be true on multi-million year timescales at best, and suggests that current carbon cycle models may be missing an important intermediate timescale climatic driver<sup>155</sup>.

499 Initial sensitivity experiments that explored the impact of gypsum precipitation/weathering on the carbon cycle, 500 recognised that the precipitation and preservation of any gypsum represents a net reduction in oceanic  $[Ca^{2+}]$ 501 and expressed this as a constant  $Ca^{2+}$  forcing<sup>155</sup> for the duration of salt giant formation. However, in detail the

Ca<sup>2+</sup> ion flux associated with a salt giant is not constant, but far more complex, reflecting cyclic evaporite 502 503 formation and the evolving connectivity history of the salt-bearing basin. For the MSC, this means that during 504 the PLG, when gypsum-marl alternations formed under conditions of two-way Atlantic-Mediterranean exchange,  $Ca^{2+}$  ion loss from the global ocean occurred episodically, reflecting each precipitation event<sup>18</sup>. It is 505 506 also likely that return flux to the global ocean occurred as the newly formed gypsum layers partially dissolved<sup>18</sup>. 507 This return flux cannot have occurred during the later MSC stages, when there was no Mediterranean outflow. 508 Any ions liberated by exposure and weathering of evaporites during periods of lowered Mediterranean sea level 509 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<sup>104</sup>. New model simulations that incorporate realistic 510 511  $Ca^{2+}$  ion flux records are, therefore, required to evaluate the magnitude of any evaporite-driven climate 512 perturbation.

513 Reconstructing the magnitude and timing of evaporite ion fluxes, however, is challenging. The salt volume 514 preserved today is not a robust measure of the total evaporite ions extracted, but rather represents a minimum 515 value for what was originally precipitated. Additional evaporites may have been precipitated and dissolved 516 either before burial or during later exposure by orogenic processes<sup>5</sup>. Evaporite minerals also precipitate and 517 dissolve three orders of magnitude more rapidly than other sediments<sup>159</sup>. Consequently, their impact on the 518 carbon cycle can be an order of magnitude quicker than the carbonate-silicate weathering feedback<sup>155</sup>. Through 519 burial, evaporites can also be stored in rock successions for long periods outside the ocean-climate system<sup>25</sup>. As a result, evaporite-mediated ion extraction from, and return to, the ocean can be both rapid  $(10^3-10^4 \text{ y})$ , 520 521 occurring during or shortly after salt giant formation, as is largely the case for the MSC, and/or gradual (>>10<sup>6</sup> 522 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<sup>160</sup>. 523

524 Constraints on the evaporite-ion flux in addition to the salt giant succession itself are clearly required. One 525 possibility is to use the seawater  $[Ca^{2+}]$  record<sup>161</sup>. To capture perturbations anticipated from salt giant formation, 526 a high-resolution record is required. However, currently only a handful of  $[Ca^{2+}]$  measurements exist for the 527 entire Cenozoic (ironically mainly from evaporite fluid inclusions<sup>161</sup>). These reveal a general decline over the past 100 million years<sup>161</sup>, 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.

533 Physical processes associated with salt giant formation may also have a potential impact on global climate. 534 Advection of dense, cold/salty overflow water from marginal basins strongly influences the oceanic distribution 535 of heat and salt, exerting a powerful influence on thermohaline circulation and deep-water formation<sup>162</sup>. In the 536 North Atlantic today, the densest of these overflows emanates from the Mediterranean Sea<sup>163</sup> depositing a 537 prominent overflow plume that contours around the Iberian margin<sup>164</sup>. Sensitivity experiments that exclude 538 present-day Mediterranean-Atlantic exchange result in ~1° cooling over the North Atlantic, and a 0.7-2.3 Sv (1 Sv=10<sup>6</sup> m<sup>3</sup>/s) reduction in the Atlantic Meridonal Overturning Circulation<sup>162,165</sup>. These results indicate that 539 540 the negative Mediterranean hydrologic budget, combined with exchange through the Gibraltar Strait, is enough 541 to generate a climatically important high-density water mass today. The outstanding question is: what role did 542 this overflow play in driving Late Miocene climate?

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<sup>166</sup>. This restriction process occurred at ~8 Ma<sup>166</sup> (Fig. 6a), and pre-dated evaporite deposition by two million years and persisted after the MSC throughout the Pliocene and Pleistocene<sup>164</sup>. Similar dense overflows may 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 has yet to be explored.

550 During salt giant formation, marginal basin water density will have been much higher, and evaporite-sediment 551 alternations such as those of MSC successions, indicate fluctuating brine concentrations. However, only during 552 two-way exchange episodes will this produce a high-density overflow plume that could impact thermohaline 553 circulation. Modelling these extreme high-density overflows is challenging because the narrow, shallow marine 554 gateways required for overflows to form are too small to be fully resolvable in current Earth System Models.
555 Instead, models use various parameterisations to mimic overflow mixing in model simulations<sup>167,168</sup>; none are
556 currently compatible with densities that far exceed contemporary overflow observations<sup>163</sup>. Improved model
557 parameterisation of overflow mixing and development of proxies that allow overflow density reconstruction
558 will be critical to addressing this challenge.

559 Finally, this review provides context for the upcoming Land-2-Sea drilling project, IMMAGE (Investigating Miocene Mediterranean-Atlantic Gateway Exchange)<sup>169</sup>, which involves both offshore drilling with 560 561 International Ocean Discovery Program Expedition 401 on either side of the Gibraltar Strait and onshore 562 drilling with the International Continental Scientific Drilling Program in Morocco and Spain, targeting the two 563 precursor Atlantic-Mediterranean marine connections that have been uplifted and preserved on land. IMMAGE 564 will recover 8-4 million-year-old sediments from both gateways and the Mediterranean outflow plume in the 565 Atlantic before, during, and after the MSC. The objective is to identify and quantify the impact of evolving 566 Mediterranean-Atlantic exchange on regional and global environmental change and specifically its potential 567 contribution to cooling during this period, which ultimately resulted in initiation of northern hemisphere 568 glaciation<sup>71</sup>. IMMAGE, the first Land-2-Sea drilling project, offers great scope for addressing many remaining 569 unknowns outlined here.

570

#### 571 Methods

572 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.<sup>84</sup>. We include sea-level benchmarks from Mallorcan marine cave deposits and 573 574 Patagonian coastal deposits, which have been corrected for tectonic changes, glacio-isostatic effects, and 575 dynamic topography<sup>86–88</sup>, and which corroborate the sea-level record from benthic  $\delta^{18}$ O deconvolution before, 576 and across, the Miocene-Pliocene boundary. Water exchange thresholds were calculated using the channel 577 geometries of Krijgsman et al.<sup>22</sup>, which we combine into an approximately triangular single width vs. depth 578 profile (maximum width = 3.28 km; maximum depth = 136 m). Today, the Gibraltar Strait is 10.67 km wide at 579 sea level with 136 m of water above the sill. Hence, the triangular cross-sectional area of the Messinian strait 580 was 3.25 times more restricted than the modern triangular cross-sectional strait area for the same depth. We 581 use this extra restriction in the Bryden and Kinder<sup>170</sup> 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.

586

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592

#### 593 Competing interests

594 The authors declare that they have no known competing financial interests or personal relationships that could

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596

### 597 Author contributions

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

599 UA constructed the figures.

600

#### 601 References

- Camerlenghi, A. & Aloisi, V. Uncovering the Mediterranean salt giant (MEDSALT) scientific networking as incubator of cross-disciplinary research in Earth sciences. *Eur. Rev.* 28, 40–61 (2020).
- 604 2. Hübscher, C. et al. Global look at salt giants. Eos (Washington DC) 88, (2007).
- 3. Ryan, W. B. F. Decoding the Mediterranean salinity crisis. *Sedimentology* 56, 95–136 (2009).
- 4. Haq, B., Gorini, C., Baur, J., Moneron, J. & Rubino, J. Deep Mediterranean's Messinian evaporite giant: how much salt? *Glob. Planet. Change* 184, 103052 (2020).
- 6085.Wortmann, U. & Paytan, A. Rapid variability of seawater chemistry over the past 130 million years. Science609337, 334–336 (2012).
- 6. Roveri, M. *et al.* The Messinian Salinity Crisis: past and future of a great challenge for marine sciences. *Mar. Geol.* 352, 25–58 (2014).
- 612 7. Lofi, J. *et al.* Erosional processes and paleo-environmental changes in the Western Gulf of Lions (SW France) during the Messinian Salinity Crisis. *Mar. Geol.* 217, 1–30 (2005).
- 8. Rouchy, J. M. & Caruso, A. The Messinian salinity crisis in the Mediterranean basin: A reassessment of the data and an integrated scenario. *Sediment. Geol.* 188–189, 35–67 (2006).
- 616 9. Gvirtzman, Z. *et al.* Intra-Messinian truncation surface in the Levant Basin explained by subaqueous dissolution.
   617 *Geology* 45, 915–918 (2017).
- 618 10. Lofi, J. *et al.* Refining our knowledge of the Messinian salinity crisis records in the offshore domain through multi-site seismic analysis. *Bull Soc. Geol.France* 182, 163–180 (2011).
- Hilgen, F. J. *et al.* Extending the astronomical (polarity) time scale into the Miocene. *Earth Planet. Sci. Lett.*136, 495–510 (1995).
- Krijgsman, W., Hilgen, F. J., Raffi, I., Sierro, F. J. & Wilson, D. S. Chronology, causes and progression of the Messinian salinity crisis. *Nature* 400, 652–655 (1999).

- Sierro, F. J., Hilgen, F. J., Krijgsman, W. & Flores, J. A. The Abad composite (SE Spain): a Messinian reference section for the Mediterranean and the APTS. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* 168, 141–169 (2001).
- 14. Natalicchio, M. *et al.* Did late Miocene (Messinian) gypsum precipitate from evaporated marine brines? Insights from the Piedmont basin (Italy). *Geology* 42, 179–182 (2014).
- Reghizzi, M., Lugli, S., Manzi, V., Rossi, F. P. & Roveri, M. Orbitally forced hydrological balance during the Messinian Salinity Crisis: Insights from strontium isotopes (87Sr/86Sr) in the Vena del Gesso Basin (Northern Apennines, Italy). *Paleoceanogr. Paleoclimatol..*33, 716–731 (2018).
- 16. Topper, R. P. M. & Meijer, P. T. A modeling perspective on spatial and temporal variations in Messinian evaporite deposits. *Mar. Geol.* 336, 44–60 (2013).
- 633 17. Grothe, A. *et al.* Paratethys pacing of the Messinian Salinity Crisis : low salinity waters contributing to gypsum precipitation? *Earth Planet. Sci. Lett.* 532, 116029 (2020).
- Andreetto, F. *et al.* High-amplitude water-level fluctuations at the end of the Mediterranean Messinian Salinity Crisis: implications for gypsum formation, connectivity and global climate. *Earth Planet. Sci. Lett.* 595, 117767 (2022).
- Raad, F. *et al.* A song of volumes, surfaces and fluxes: the case study of the Central Mallorca Depression (Balearic Promontory) during the Messinian Salinity Crisis. *Basin Res.* 35, 1–27 (2023).
- 640 20. Flecker, R. *et al.* Evolution of the Late Miocene Mediterranean-Atlantic gateways and their impact on regional and global environmental change. *Earth Sci. Rev.* 150, 365–392 (2015).
- Hilgen, F., Kuiper, K., Krijgsman, W., Snel, E. & Van der Laan, E. Astronomical tuning as the basis for high resolution chronostratigraphy : the intricate history of the Messinian Salinity Crisis. *Stratigraphy* 4, 231–238 (2007).
- 645 22. Krijgsman, W. *et al.* The Gibraltar Corridor: Watergate of the Messinian Salinity Crisis. *Mar. Geol.* 403, 238–246 (2018).
- 847 83. Raad, F., Lofi, J., Maillard, A., Tzevahirtzian, A. & Caruso, A. The Messinian Salinity Crisis deposits in the Balearic Promontory: an undeformed analog of the MSC Sicilian basins?? *Mar. Pet. Geol.* 124, 104777 (2021).
- 649 24. Popov, S. V. *et al.* Late Miocene to Pliocene palaeogeography of the Paratethys and its relation to the Mediterranean. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* 238, 91–106 (2006).
- Krijgsman, W., Palcu, D. V., Andreetto, F., Stoica, M. & Mandic, O. Changing seas in the late Miocene
  Northern Aegean: a Paratethyan perspective to Mediterranean stratigraphy. *Earth Sci. Rev.* 210, 103386 (2020).
- 65326.Lowenstein, T. K., Timofeeff, M. N., Brennan, S. T., Hardie, L. A. & Demicco, R. V. Oscillations in654Phanerozoic seawater chemistry: evidence from fluid Inclusions. Science 294, 1086–1088 (2001).
- Babel, M. & Schreiber, B. C. *Geochemistry of Evaporites and Evolution of Seawater*. *Treatise on Geochemistry: Second Edition* vol. 9 (2014).
- Harvie, C. E. & Weare, J. H. The prediction of mineral solubilities in natural waters: the Na-K-Mg-Ca-Cl-S0<sub>4</sub>H<sub>2</sub>O system from zero to high concentration at 25°C. *Geochim Cosmochim Acta* 44, 723–751 (1980).
- 659 29. Gaillardet, J., Dupré, B., Louvat, P. & Allègre, C. J. Global silicate weathering and CO2 consumption rates deduced from the chemistry of large rivers. *Chem Geol* 159, 3–30 (1999).
- 30. Meybeck, M. Global analysis of river systems: from Earth system controls to Anthropocene syndromes. *Phil. Tran. R. Soc.Lond.* 358, 1935–1955 (2003).
- Aloisi, G. *et al.* The geochemical riddle of "low-salinity gypsum" deposits. *Geochim. Cosmochim. Acta* 327, 247–275 (2022).
- 665 32. Selli, R. Il Messiniano Mayer-Eymar 1867. Proposta di un neostratotipo. *Giornale di Geologia* 28, 1–33 (1960).
- 83. Ruggieri, G. The Miocene and later evolution of the Mediterranean Sea. Aspects of Tethyan Biogeography 283–290 (1967).
- 34. Hsü, K., Ryan, W. B. F. & Cita, M. Late Miocene desiccation of the Mediterranean. *Nature* 242, 240–244 (1973).
- 670 35. Ryan, W. B. F. 50th anniversary review of the Mediterranean desiccation hypothesis. *Rivista del Nuovo Cimento* 46 163 (2023).
- 672 36. Manzi, V., Lugli, S., Roveri, M., Schreiber, B. C. & Gennari, R. The Messinian 'Calcare di Base' (Sicily, Italy) revisited. *Bull. Geol. Soc. Am.* 123, 347–370 (2011).
- 674 37. Caruso, A., Pierre, C., Blanc-Valleron, M.-M. & Rouchy, J. M. Carbonate deposition and diagenesis in evaporitic environments: the evaporative and sulphur-bearing limestones during the settlement of the Messinian Salinity Crisis in Sicily and Calabria. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* 429, 136–162 (2015).
- 8. Bourillot, R. *et al.* Structure and evolution of a Messinian mixed carbonate-siliciclastic platform: the role of evaporites (Sorbas Basin, South-East Spain). *Sedimentology* 57, 477–512 (2010).

- 879 39. Roveri, M., Lugli, S., Manzi, V., Reghizzi, M. & Rossi, F. P. Stratigraphic relationships between shallow-water carbonates and primary gypsum: insights from the Messinian succession of the Sorbas Basin (Betic Cordillera, Southern Spain). *Sediment. Geol.* 404, 105678 (2020).
- 40. Lugli, S., Manzi, V., Roveri, M. & Schreiber, B. C. The Primary Lower Gypsum in the Mediterranean: a new facies interpretation for the first stage of the Messinian salinity crisis. *Palaeogeogr. Palaeoclimatol. Palaeoecol.*297, 83–99 (2010).
- 41. Manzi, V. *et al.* High-frequency cyclicity in the Mediterranean Messinian evaporites: evidence for solar-lunar climate forcing. *J. Sed. Res.* 82, 991–1005 (2012).
- 687 42. García-Veigas, J., Cendón, D. I., Gibert, L., Lowenstein, T. K. & Artiaga, D. Geochemical indicators in Western Mediterranean Messinian evaporites: Implications for the salinity crisis. *Mar. Geol.* 403, 197–214 (2018).
- 43. Heida, H. *et al.* Flexural-isostatic reconstruction of the Western Mediterranean during the Messinian Salinity Crisis: implications for water level and basin connectivity. *Basin Res.* 34, 50–80 (2022).
- 44. Roveri, M. *et al.* Dense shelf water cascading and Messinian Canyons: a new scenario for the Mediterranean salinity crisis. *Am. J. Sci.* 314, 751–784 (2014).
- 45. Stoica, M., Krijgsman, W., Fortuin, A. & Gliozzi, E. Paratethyan ostracods in the Spanish Lago-Mare: more evidence for interbasinal exchange at high Mediterranean sea level. *Palaeogeogr. Palaeoclimatol. Palaeoecol.*441, 854–870 (2016).
- 46. Andreetto, F. *et al.* Freshening of the Mediterranean Salt Giant: controversies and certainties around the terminal (Upper Gypsum and Lago-Mare) phases of the Messinian Salinity Crisis. *Earth Sci. Rev.* 216, 103577 (2021).
- 698 47. Gliozzi, E., Ceci, M. E., Grossi, F. & Ligios, S. Paratethyan ostracod immigrants in Italy during the Late Miocene. *Geobios* 40, 325–337 (2007).
- 48. Manzi, V., Lugli, S., Ricci Lucchi, F. & Roveri, M. Deep-water clastic evaporites deposition in the Messinian Adriatic foredeep (northern Apennines, Italy): did the Mediterranean ever dry out? *Sedimentology* 52, 875–902 (2005).
- 49. Ochoa, D. *et al.* Messinian Salinity Crisis deposits widespread over the Balearic Promontory : Insights from new high-resolution seismic data. Mar. Pet. Geol. 66 41–54 (2014)
- 70550.Manzi, V. et al. The deep-water counterpart of the Messinian Lower Evaporites in the Apennine foredeep: the<br/>Fanantello section (Northern Apennines, Italy). Palaeogeogr. Palaeoclimatol. Palaeoecol. 251, 470–499 (2007).
- 70751.de Lange, G. J. & Krijgsman, W. Messinian salinity crisis: a novel unifying shallow gypsum/deep dolomite<br/>formation mechanism. *Mar. Geol.* 275, 273–277 (2010).
- 52. Manzi, V., Roveri, M., Argnani, A., Cowan, D. & Lugli, S. Large-scale mass-transport deposits recording the collapse of an evaporitic platform during the Messinian salinity crisis (Caltanissetta basin, Sicily). *Sediment. Geol.* 424, 106003 (2021).
- 712 53. Roveri, M., Lugli, S., Manzi, V. & Schreiber, B. C. The Messinian Sicilian stratigraphy revisited: new insights for the Messinian salinity crisis. *Terra Nova* 20, 483–488 (2008).
- 54. Bulian, F., Kouwenhoven, T. J., Andersen, N., Krijgsman, W. & Sierro, F. J. Reflooding and repopulation of the Mediterranean Sea after the Messinian Salinity Crisis: benthic foraminifera assemblages and stable isotopes of Spanish basins. *Mar. Micropaleontol.* 176, 102160 (2022).
- 717 55. van Dijk, G. *et al.* A terminal Messinian flooding of the Mediterranean evidenced by contouritic deposits on Sicily. *Sedimentology* 70, 1195–1223 (2023).
- 56. Lugli, S., Manzi, V., Roveri, M. & Schreiber, B. C. The deep record of the Messinian salinity crisis: evidence of a non-desiccated Mediterranean Sea. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* 433, 201–218 (2015).
- 72157.Gvirtzman, Z., Reshef, M., Buch-Leviatan, O. & Ben-Avraham, Z. Intense salt deformation in the Levant Basin722in the middle of the Messinian Salinity Crisis. *Earth Planet. Sci. Lett.* **379**, 108–119 (2013).
- 58. Bertoni, C. & Cartwright, J. A. Controls on the basinwide architecture of late Miocene (Messinian) evaporites on the Levant margin (Eastern Mediterranean). *Sediment. Geol.* 188–189, 93–114 (2006).
- Feng, Y. E., Steinberg, J. & Reshef, M. Intra-salt deformation: implications for the evolution of the Messinian evaporites in the Levant Basin, eastern Mediterranean. *Mar. Pet. Geol.* 88, 251–267 (2017).
- 72760.Feng, Y. E., Yankelzon, A., Steinberg, J. & Reshef, M. Lithology and characteristics of the Messinian evaporite728sequence of the deep Levant Basin, Eastern Mediterranean. Mar. Geol. 376, 118–131 (2016).
- 72961.Manzi, V. et al. Age refinement of the Messinian salinity crisis onset in the Mediterranean. Terra Nova 25, 315–730322 (2013).
- 731 62. Zachariasse, W. J. & Lourens, L. J. The Messinian on Gavdos (Greece) and the status of currently used ages for the onset of the MSC and gypsum precipitation. *Newsl. Stratigr.* 55, 333–360 (2022).
- 733 63. Tzevahirtzian, A., Caruso, A., Andreetto, F., Bonomo, S. & Krijgsman, W. A bio-chronostratigraphic study of the upper Miocene from the northern Caltanissetta Basin, Sicily (core 3AGN2S04). implications for dating the Messinian Salinity Crisis onset. *Sediment. Geol.* 445, (2023).

- Van Couvering, J. A., Castradori, D., Cita, M. B., Hilgen, F. J. & Rio, D. The base of the Zanclean Stage and of the Pliocene Series. *Episodes* 23, 179–187 (2000).
- Clauzon, G., Suc, J.-P., Gautier, F., Berger, A. & Loutre, M.-F. Alternate interpretation of the Messinian salinity crisis: controversy resolved? *Geology* 24, 363–366 (1996).
- Krijgsman, W. *et al.* Revised astrochronology for the Ain el Beida section (Atlantic Morocco): No glacio-eustatic control for the onset of the Messinian Salinity Crisis. *Stratigraphy* 1, 87–101 (2004).
- 742 67. Topper, R. P. M., Flecker, R., Meijer, P. T. & Wortel, M. J. R. A box model of the Late Miocene Mediterranean Sea: Implications from combined <sup>87</sup>Sr/<sup>86</sup>Sr and salinity data. *Paleoceanography* 26, PA3223 (2011).
- Krijgsman, W., Fortuin, A. R., Hilgen, F. J. & Sierro, F. J. Astrochronology for the Messinian Sorbas basin (SE Spain) and orbital (precessional) forcing for evaporite cyclicity. *Sediment. Geol.* 140, 43–60 (2001).
- 74669.Westerhold, T. *et al.* An astronomically dated record of Earth's climate and its predictability over the last 66747million years. Science 369, 1383–1388 (2020).
- 748 70. Drury, A. J. *et al.* Late Miocene climate and time scale reconciliation: Accurate orbital calibration from a deep-sea perspective. *Earth Planet. Sci. Lett.* 475, 254–266 (2017).
- 750 71. Herbert, T. D. *et al.* Late Miocene global cooling and the rise of modern ecosystems. *Nat. Geosci.* 9, 843–847 (2016).
- 752 72. Laskar, J. *et al.* A long-term numerical solution for the insolation quantities of the Earth. *Astron. Astrophys.* 428, 261–285 (2004).
- 754 73. Hilgen, F. J., Lourens, L. J. & Van Dam, J. A. The Neogene Period. in *The Geological Time Scale 2012* (eds. Gradstein, F. M., Ogg, J. G., Schmitz, M. D. & Ogg, G. M.) 947–1002 (Elsevier B.V., 2012).
- 756 74. Rohling, E. J., Schiebel, R. & Siddall, M. Controls on Messinian Lower Evaporite cycles in the Mediterranean.
  757 *Earth Planet. Sci. Lett.* 275, 165–171 (2008).
- 758 75. Garcia-Castellanos, D. & Villaseñor, A. Messinian salinity crisis regulated by competing tectonics and erosion at the Gibraltar arc. *Nature* 480, 359–363 (2011).
- 760
  76. Krijgsman, W. & Meijer, P. T. Depositional environments of the Mediterranean "Lower Evaporites" of the Messinian salinity crisis: constraints from quantitative analyses. *Mar. Geol.* 253, 73–81 (2008).
- 762 77. Manzi, V. *et al.* The onset of the Messinian salinity crisis in the deep Eastern Mediterranean basin. *Terra Nova* 30, 189–198 (2018).
- 764 78. Meilijson, A. *et al.* Chronology with a pinch of salt: integrated stratigraphy of Messinian evaporites in the deep Eastern Mediterranean reveals long-lasting halite deposition during Atlantic connectivity. *Earth Sci. Rev.* 194, 374–398 (2019).
- 767 79. Meijer, P. Th. A box model of the blocked-outflow scenario for the Messinian Salinity Crisis. *Earth Planet. Sci. Lett.* 248, 486–494 (2006).
- 80. Sanford, W. E. & Wood, W. W. Brine evolution and mineral deposition in hydrologically open evaporite basins.
   770 Am. J. Sci. 291, 687–710 (1991).
- 81. Manzi, V., Lugli, S., Roveri, M. & Schreiber, B. C. A new facies model for the Upper Gypsum of Sicily (Italy):
  chronological and palaeoenvironmental constraints for the Messinian salinity crisis in the Mediterranean.
  Sedimentology 56, 1937–1960 (2009).
- Andreetto, F. *et al.* Multi-proxy investigation of the post-evaporitic succession of the Piedmont Basin (Pollenzo section, NW Italy): a new piece in the Stage 3 puzzle of the Messinian Salinity Crisis. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* 594, 110961 (2022).
- Rohling, E. J. *et al.* Sea level and deep-sea temperature reconstructions suggest quasi-stable states and critical transitions over the past 40 million years. *Sci. Adv.* 7, eabf5326 (2021).
- 77984.Rohling, E. J. *et al.* Comparison and synthesis of sea-level and deep-sea temperature variations over the past 40<br/>million years. *Rev. Geophys.* 60, e2002RG000775 (2022).
- 781 85. Lisiecki, L. E. & Raymo, M. E. A Pliocene-Pleistocene stack of 57 globally distributed benthic δ <sup>18</sup>O records.
   782 *Paleoceanography* 20, 1–17 (2005).
- 783 86. Dumitru, O. A. *et al.* Constraints on global mean sea level during Pliocene warmth. *Nature* 574, 233–236 (2019).
- 785 87. Dumitru, O. A. *et al.* Sea-level stands from the Western Mediterranean over the past 6.5 million years. *Sci. Rep.* 11, 261 (2021).
- 787 88. Hollyday, A. *et al.* A revised estimate of Early Pliocene global mean sea level using geodynamic models of the Patagonian slab window. *Geochem. Geophys. Geosyst.* 24, e2022GC010648 (2023).
- 89. Bryden, H. L., Candela, J. & Kinder, T. H. Exchange through the Strait of Gibraltar. *Prog. Oceanogr.* 33, 201–248 (1994).
- 791 90. Capella, W. *et al.* Palaeogeographic evolution of the late Miocene Rifian Corridor (Morocco): reconstructions from surface and subsurface data. *Earth Sci. Rev.* 180, 37–59 (2018).

- 91. Booth-Rea, G., Ranero, C. R. & Grevemeyer, I. The Alboran volcanic-arc modulated the Messinian faunal exchange and salinity crisis. *Sci. Rep.* 8, 13015 (2018).
- 795 92. De la Vara, A., Topper, R. P. M., Meijer, P. T. & Kouwenhoven, T. J. Water exchange through the Betic and Rifian corridors prior to the Messinian Salinity Crisis: a model study. *Paleoceanography* 30, 548–557 (2015).
- 797 93. Bulian, F. *et al.* Impact of the Mediterranean-Atlantic connectivity and the late Miocene carbon shift on deep-sea communities in the Western Alboran Basin. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* 589, 110841 (2022).
- 799 94. Kouwenhoven, T. J., Hilgen, F. J. & Van Der Zwaan, G. J. Late Tortonian-early Messinian stepwise disruption of the Mediterranean-Atlantic connections: constraints from benthic foraminiferal and geochemical data.
  801 Palaeogeogr. Palaeoclimatol. Palaeoecol. 198, 303–319 (2003).
- 802 95. Capella, W., Spakman, W., van Hinsbergen, D. J. J., Chertova, M. V. & Krijgsman, W. Mantle resistance
- against Gibraltar slab dragging as a key cause of the Messinian Salinity Crisis. *Terra Nova* **32**, 141–150 (2020).
- 804 96. Spakman, W., Chertova, M. V., Van Den Berg, A. & Van Hinsbergen, D. J. J. Puzzling features of western Mediterranean tectonics explained by slab dragging. *Nat. Geosci.* 11, 211–216 (2018).
- Jolivet, L., Augier, R., Robin, C., Suc, J.-P. & Rouchy, J. M. Lithospheric-scale geodynamic context of the Messinian salinity crisis. *Sediment. Geol.* 188–189, 9–33 (2006).
- 808 98. Mancilla, F. L. *et al.* Slab rupture and delamination under the Betics and Rif constrained from receiver functions. *Tectonophysics* 663, 225–237 (2015).
- 810 99. Wortel, M. J. R. & Spakman, W. Subduction and slab detachment in the Mediterranean-Carpathian region.
  811 Science 290, 1910–1917 (2000).
- 812 100. Capella, W. *et al.* Thick-skinned tectonics closing the Rifian Corridor. *Tectonophysics* 710–711, 249–265 (2017).
- 814 101. Sabino, M. *et al.* Climatic and hydrologic variability in the northern Mediterranean across the onset of the Messinian salinity crisis. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* 545, 109632 (2020).
- 816 102. Modestou, S. *et al.* Precessional variability of <sup>87</sup>Sr/<sup>86</sup>Sr in the late Miocene Sorbas Basin: an interdisciplinary study of drivers of interbasin exchange. *Paleoceanography* 32, 531–552 (2017).
- 818 103. Blanc, P.-L. Of sills and straits: a quantitative assessment of the Messinian Salinity Crisis. *Deep Sea Res. 1* 47, 1429–1460 (2000).
- 820 104. Amarathunga, U. *et al.* Sill-controlled salinity contrasts followed post-Messinian flooding of the Mediterranean.
   821 Nat. Geosci. 15, 720–725 (2022).
- 822 105. Meijer, P. & Krijgsman, W. A quantitative analysis of the desiccation and re-filling of the Mediterranean during the Messinian Salinity Crisis. *Earth Planet. Sci. Lett.* 240, 510–520 (2005).
- Pellen, R. *et al.* Structural and sedimentary origin of the Gargano-Pelagosa gateway and impact on sedimentary evolution during the Messinian Salinity Crisis. *Earth Sci. Rev.* 232, 104114 (2022).
- 826 107. Gülyüz, E., Durak, H., Özkaptan, M. & Krijgsman, W. Paleomagnetic constraints on the early Miocene closure of the southern Neo-Tethys (Van region; East Anatolia): inferences for the timing of Eurasia-Arabia collision. *Glob. Planet. Change* 185, 103089 (2020).
- 829 108. Harzhauser, M., Piller, W. E. & Steininger, F. F. Circum-Mediterranean Oligo–Miocene biogeographic evolution the gastropods' point of view. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* 183, 103–133 (2002).
- 831 109. Oguz, T., Özsoy, E., Latif, M. A., Sur, H. I. & Ünlüata, Ü. Modeling of hydraulically controlled exchange flow in the Bosphorus Strait. *J. Phys. Oceanogr.* 20, 945–965 (1990).
- Radionova, E. P. & Golovina, L. Upper Maeotian-Lower Pontian 'Transitional Strata' in the Taman Peninsula: stratigraphic position and paleogeographic interpretation. *Geol. Carpath.* 62, 77–90 (2011).
- 835
  111. Grothe, A., Sangiorgi, F., Brinkhuis, H., Stoica, M. & Krijgsman, W. Migration of the dinoflagellate *Galeacysta etrusca* and its implications for the Messinian Salinity Crisis. *Newsl. Stratigr.* 51, 73–91 (2018).
- 837 112. Van Baak, C. G. C., Stoica, M., Grothe, A., Aliyeva, E. & Krijgsman, W. Mediterranean-Paratethys connectivity during the Messinian salinity crisis: the Pontian of Azerbaijan. *Glob. Planet. Change* 141, 63–81 (2016).
- 839 113. Van Baak, C. G. C. *et al.* Paratethys response to the Messinian salinity crisis. *Earth Sci. Rev.* 172, 193–223 (2017).
- 841 114. Krijgsman, W. *et al.* Mediterranean-Black Sea gateway exchange: scientific drilling workshop on the BlackGate project. *Sci. Dril.* 31, 93–110 (2022).
- 843 115. Wegwerth, A. *et al.* Meltwater events and the Mediterranean reconnection at the Saalian–Eemian transition in the Black Sea. *Earth Planet. Sci. Lett.* 404, 124–135 (2014).
- 845
  846
  116. Bista, D. *et al.* Sr isotope-salinity modelling constraints on Quaternary Black Sea connectivity. *Quat. Sci. Rev.* 273, 107254 (2021).
- 847 117. Ohneiser, C. *et al.* Antarctic glacio-eustatic contributions to late Miocene Mediterranean desiccation and reflooding. *Nat. Commun.* 6, 8765 (2015).

- 849 118. Garcia-Castellanos, D. *et al.* Catastrophic flood of the Mediterranean after the Messinian salinity crisis. *Nature* 462, 778–781 (2009).
- 851 119. van der Laan, E. *et al.* Astronomical forcing of Northwest African climate and glacial history during the late
  852 Messinian (6.5-5.5Ma). *Palaeogeogr. Palaeoclimatol. Palaeoecol.* 313–314, 107–126 (2012).
- Holbourn, A. E. *et al.* Late Miocene climate cooling and intensification of southeast Asian winter monsoon. *Nat. Commun.* 9, (2018).
- Kontakiotis, G. *et al.* Decoding sea surface and paleoclimate conditions in the eastern Mediterranean over the Tortonian-Messinian Transition. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* 534, 109312 (2019).
- 857 122. Bulian, F., Sierro, F. J., Ledesma, S., Jiménez-Espejo, F. J. & Bassetti, M.-A. Messinian West Alboran Sea
  858 record in the proximity of Gibraltar: early signs of Atlantic-Mediterranean gateway restriction. *Mar. Geol.* 434, 106430 (2021).
- Fauquette, S. *et al.* How much did climate force the Messinian salinity crisis? quantified climatic conditions from pollen records in the Mediterranean region. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* 238, 281–301 (2006).
- 863 124. Vasiliev, I. *et al.* How dry was the Mediterranean during the Messinian salinity crisis? *Palaeogeogr. Palaeoclimatol. Palaeoecol.* 471, 120–133 (2017).
- Butiseacă, G. A. *et al.* Multiple crises preceded the Mediterranean Salinity Crisis: aridification and vegetation changes revealed by biomarkers and stable isotopes. *Glob. Planet. Change* 217, 103951 (2022).
- 867 126. Karakitsios, V. *et al.* Messinian salinity crisis record under strong freshwater input in marginal, intermediate, and deep environments: the case of the North Aegean. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* 485, 316–335 (2017).
- 870 127. Kontakiotis, G. *et al.* Hypersalinity accompanies tectonic restriction in the eastern Mediterranean prior to the Messinian Salinity Crisis. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* 592, (2022).
- 872 128. Bertini, A. The Northern Apennines palynological record as a contribute for the reconstruction of the Messinian palaeoenvironments. *Sediment. Geol.* 188–189, 235–258 (2006).
- Hilgen, F. J. Astronomical calibration of Gauss to Matuyama sapropels in the Mediterranean and implication for the Geomagnetic Polarity Time Scale. *Earth Planet. Sci. Lett.* 104, 226–244 (1991).
- 876
  130. Sabino, M. *et al.* Climatic and hydrologic variability in the northern Mediterranean across the onset of the Messinian salinity crisis. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* 545, 109632 (2020).
- 878 131. Natalicchio, M. *et al.* Paleoenvironmental change in a precession-paced succession across the onset of the Messinian salinity crisis: insight from element geochemistry and molecular fossils. *Palaeogeogr.*880 *Palaeoclimatol. Palaeoecol.* 518, 45–61 (2019).
- 132. Urgeles, R. *et al.* New constraints on the Messinian sealevel drawdown from 3D seismic data of the Ebro Margin, western Mediterranean. *Basin Res.* 23, 123–145 (2011).
- 133. Madof, A. S., Bertoni, C. & Lofi, J. Discovery of vast fluvial deposits provides evidence for drawdown during the late Miocene Messinian salinity crisis. *Geology* 47, 171–174 (2019).
- 885
  134. Marzocchi, A. *et al.* Orbital control on late Miocene climate and the North African monsoon: insight from an ensemble of sub-precessional simulations. *Clim. Past* 11, 1271–1295 (2015).
- 887
  135. Simon, D. *et al.* Quantifying the Mediterranean freshwater budget throughout the late Miocene: New implications for sapropel formation and the Messinian Salinity Crisis. *Earth Planet. Sci. Lett.* 472, 25–37 (2017).
- 890 136. Krijgsman, W., Stoica, M., Vasiliev, I. & Popov, V. V. Rise and fall of the Paratethys Sea during the Messinian Salinity Crisis. *Earth Planet. Sci. Lett.* 290, 183–191 (2010).
- 892 137. Palcu, D. V. et al. Late Miocene megalake regressions in Eurasia. Sci. Rep. 11, 1–12 (2021).
- 893
  138. Sprovieri, M., Sacchi, M. & Rohling, E. J. Climatically influenced interactions between the Mediterranean and the Paratethys during the Tortonian. *Paleoceanography* 18, 1034 (2003).
- 895 139. Gladstone, R., Flecker, R., Valdes, P., Lunt, D. & Markwick, P. The Mediterranean hydrologic budget from a Late Miocene global climate simulation. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* 251, 254–267 (2007).
- 140. Larrasoaña, J. C., Roberts, A. P. & Rohling, E. J. Dynamics of Green Sahara Periods and their role in hominin evolution. *PLoS One* 8, e76514 (2013).
- 899 141. Grant, K. M. *et al.* Organic carbon burial in Mediterranean sapropels intensified during Green Sahara Periods since 3.2 Myr ago. *Commun. Earth Environ.* 3, (2022).
- 901 142. Colin, C. *et al.* Reconstruction of Northern African monsoon between 6.2 and 4.9 Ma and possible relationships with Late Miocene events. *C. R. Geosci.* 340, 749–760 (2008).
- 903 143. Colin, C. *et al.* Late Miocene to early Pliocene climate variability off NW Africa (ODP Site 659). *Palaeogeogr.* 904 *Palaeoclimatol. Palaeoecol.* 401, 81–95 (2014).

- 44. Amies, J. D., Rohling, E. J., Grant, K. M., Rodríguez-Sanz, L. & Marino, G. Quantification of African monsoon runoff during last interglacial sapropel S5. *Paleoceanogr. Paleoclimatol.* 34, 1487–1516 (2019).
- 907 145. Bosmans, J. H. C. *et al.* Precession and obliquity forcing of the freshwater budget over the Mediterranean. *Quat. Sci. Rev.* 123, 16–30 (2015).
- 909 146. Griffin, D. L. The late Neogene Sahabi rivers of the Sahara and their climatic and environmental implications for the Chad Basin. J. Geol. Soc. Lond. 163, 905–921 (2006).
- 911 147. Griffin, D. L. Aridity and humidity: two aspects of the late Miocene climate of North Africa and the Mediterranean. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* 182, 65–91 (2002).
- 913148.Drake, N. A. *et al.* Reconstructing palaeoclimate and hydrological fluctuations in the Fezzan Basin (southern<br/>Libya) since 130 ka: a catchment-based approach. *Quat. Sci. Rev.* 200, 376–394 (2018).
- 915 149. Rohling, E. J. *et al.* African monsoon variability during the previous interglacial maximum. *Earth Planet. Sci. Lett.* 202, 61–75 (2002).
- 917 150. Coulthard, T. J., Ramirez, J. A., Barton, N., Rogerson, M. & Brücher, T. Were rivers flowing across the Sahara during the last interglacial? implications for human migration through Africa. *PLoS One* 8, e74834 (2013).
- 919 151. Wallmann, K. et al. Salty brines on the Mediterranean sea floor. Nature 387, 31–32 (1997).
- 152. La Cono, V. *et al.* The discovery of Lake Hephaestus, the youngest athalassohaline deep-sea formation on Earth. *Sci. Rep.* 9, 1679 (2019).
- 922 153. Yakimov, M. M. *et al.* Microbial community of the deep-sea brine Lake Kryos seawater-brine interface is active below the chaotropicity limit of life as revealed by recovery of mRNA. *Environ. Microbiol.* 17, 364–382 (2015).
- 924 154. Warren, J. K. Evaporites through time: tectonic, climatic and eustatic controls in marine and nonmarine deposits. *Earth Sci. Rev.* 98, 217–268 (2010).
- 926 155. Shields, G. A. & Mills, B. J. W. Evaporite weathering and deposition as a long-term climate forcing mechanism. *Geology* 49, 299–303 (2021).
- 928 156. Berner, R. A. A model for atmospheric CO<sub>2</sub> over Phanerozoic time. Am. J. Sci. 291, 339–376 (1991).
- 929 157. Lenton, T. M., Daines, S. J. & Mills, B. J. W. COPSE reloaded: an improved model of biogeochemical cycling over Phanerozoic time. *Earth Sci. Rev.* 178, 1–28 (2018).
- 931 158. Hay, W. W. *et al.* Evaporites and the salinity of the ocean during the Phanerozoic: implications for climate, ocean circulation and life. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* 240, 3–46 (2006).
- 933159.Nichols, G., Williams, E. & Paola, C. Sedimentary Processes, Environments and Basins. (Blackwell Publishing<br/>Ltd., 2007).
- 935
  936
  936
  937
  160. Hamilton, J. & Ford, D. Karst geomorphology and hydrogeology of the Bear Rock Formation a remarkable dolostone and gypsum megabreccia in the continuous permafrost zone of northwest territories, Canada. *Carbonates Evaporites* 17, 114–115 (2002).
- 938 161. Turchyn, A. V. & De Paolo, D. J. Seawater chemistry through Phanerozoic time. Ann. Rev. Earth Planet. Sci.
  939 47, 197-224 (2019).
- 940
  941
  942
  162. Ivanovic, R. F., Valdes, P. J., Gregoire, L., Flecker, R. & Gutjahr, M. Sensitivity of modern climate to the presence, strength and salinity of Mediterranean-Atlantic exchange in a global general circulation model. *Clim.*. *Dyn.* 42, 859–877 (2014).
- 943 163. Legg, S. *et al.* Improving oceanic overflow representation in climate models: the Gravity Current Entrainment Climate Process Team. *Bull. Am. Meteorol. Soc.* 90, 657–670 (2009).
- 945164.Hernández-Molina, F. J. et al. Onset of Mediterranean outflow into the North Atlantic. Science 344, 1244–1250<br/>(2014).
- 947 165. Bigg, G. R., Jickells, T. D., Liss, P. S. & Osborn, T. J. The role of the oceans in climate. *Int. J. Climatol.* 23, 1127–1159 (2003).
- 949 166. Capella, W. *et al.* Mediterranean isolation preconditioning the Earth System for late Miocene climate cooling. *Sci. Rep.* 9, 3795 (2019).
- 951 167. Adcroft, A. *et al.* The GFDL Global Ocean and Sea Ice Model OM4.0: model description and simulation features. *J. Adv. Model Earth Syst.* 11, 3167–3211 (2019).
- 953 168. Bruciaferri, D., Shapiro, G. I. & Wobus, F. A multi-envelope vertical coordinate system for numerical ocean modelling. *Ocean Dyn.* 68, 1239–1258 (2018).
- 955169.Flecker, R. et al. https://iodp.tamu.edu/scienceops/expeditions/mediterranean\_atlantic\_gateway\_exchange.html.956(2022).
- 957 170. Bryden, H. L. & Kinder, T. H. Steady two-layer exchange through the Strait of Gibraltar. *Deep-Sea Res.* 38 (Suppl. 1), S445–S463 (1991).