

Pleistocene water intrusions from the Mediterranean and Caspian seas into the Black Sea

S. Badertscher^{1,2*}, D. Fleitmann^{1,2*}, H. Cheng^{3,4}, R. L. Edwards⁴, O. M. Göktürk^{1,2}, A. Zumbühl², M. Leuenberger^{2,5} and O. Tüysüz⁶

The hydrological balance of the Black Sea is governed by riverine input and by the exchange with the Mediterranean Sea through the shallow Bosphorus Strait. These sources have distinctly different oxygen isotope ($\delta^{18}\text{O}$) signatures. Therefore, the $\delta^{18}\text{O}$ of Black Sea water directly reflects the presence or absence of a connection with the Mediterranean Sea, as well as hydrological changes in the vast watersheds of the Black and Caspian seas^{1–3}. However, the timing of late to middle Pleistocene water intrusions to the Black Sea is poorly constrained in sedimentary sequences^{4,5}. Here we present a stacked speleothem $\delta^{18}\text{O}$ record from Sofular Cave in northern Turkey that tracks the isotopic signature of Black Sea surface water, and thus allows a reconstruction of the precise timing of hydrological shifts of the Black Sea. Our record, which extends discontinuously over the last 670,000 years, suggests that the connection between the Black Sea and Mediterranean Sea has been open for a significant period at least twelve times since 670,000 yr ago, more often than previously suggested^{4,5}. Distinct minima in the Sofular $\delta^{18}\text{O}$ record indicate at least seven intervals when isotopically depleted freshwater from the Caspian Sea entered the Black Sea. Our data provide precisely dated evidence for a highly dynamic hydrological history of the Black Sea.

The modern hydrology of the Black Sea (BS) is strongly governed by the discharge of major Eurasian rivers (for example, the Danube, Dniester and Dnieper) and water exchange with the Mediterranean Sea (MS) through the shallow Bosphorus Strait (~35 mbsl) (Supplementary Fig. S1). The connection with the MS has been interrupted repeatedly over the last ~3 Myr, causing the BS to oscillate between lacustrine and marine conditions¹. However, only the last incursion, at ~9.4 kyr BP, has been studied in detail^{2,3,6}. The precise timing and nature of earlier shifts between a fresh to brackish BS are not known because BS sediment sequences older than 50 kyr cannot be dated accurately^{1,4,5}. Thus, it remains elusive whether earlier intrusions of MS water resulted from global sea level oscillations or changes in the Bosphorus sill depth due to erosion, sedimentation or local tectonics⁷. Furthermore, there have been episodic intrusions of water from the Caspian Sea (CS) through the Manych–Kerch spillway into the BS, the last one occurring between ~16.5 and ~14.5 kyr BP (refs 2–4,8). However, the precise timing

and nature of earlier intrusions is, like their Mediterranean counterparts, unknown.

To provide more precise dates for major hydrological shifts of the BS, we present an absolutely dated speleothem $\delta^{18}\text{O}$ record, extending back to 670 kyr BP, from six stalagmites (So-1, 2, 4, 6, 14B, 17A) collected from Sofular Cave. The cave is located 10 km from the southern BS coast in Turkey (Fig. 1; Supplementary Fig. S1), and the $\delta^{18}\text{O}$ of its speleothems is an excellent recorder of fluctuations in the $\delta^{18}\text{O}$ of BS surface water due to transitions between lacustrine and marine phases, and to intrusions of CS water⁹. The cave's climate is characterized by high relative humidity (>90%) and constant temperatures ($11.8 \pm 0.2^\circ\text{C}$). Local precipitation averages $1,200 \text{ mm yr}^{-1}$. The prevalence of northerly and north-westerly winds throughout the year⁹ (Supplementary Figs S2–S4) results in the BS being an important source of moisture (see Supplementary Information). A total of 224 ²³⁰Th-ages reveal that the stalagmites are up to ~670 kyr old. However, the stacked Sofular record is not continuous, with gaps that span the intervals ~21.6–24.1, 81.8–86.3, 122.9–127.7, 133.2–159.6, 235.8–284.9, 307.0–476.0 and 516.0–563.0 kyr BP (Supplementary Fig. S5, Tables S1 and S2). The Sofular $\delta^{18}\text{O}$ record consists of 9,300 stable isotope measurements, with values ranging between -7.5 and -17.5‰ (VPDB; Figs 2, 3; Supplementary Table S3).

Given the excellent reproducibility of the Sofular $\delta^{18}\text{O}$ profiles (Fig. 2c), we conclude that calcite $\delta^{18}\text{O}$ values are not compromised by kinetic effects, and thus constitute a reliable proxy for the $\delta^{18}\text{O}$ of meteoric precipitation. Today, the $\delta^{18}\text{O}$ of precipitation in Turkey is influenced by air temperature ('temperature effect'; ref. 10). At our cave site this effect is in the order of $+0.26\text{‰ }^\circ\text{C}^{-1}$ (Supplementary Fig. S6). When this temperature effect is added to the temperature effect associated with calcite precipitation from water ($-0.24\text{‰ }^\circ\text{C}^{-1}$; ref. 11), the net effect between air temperature and stalagmite $\delta^{18}\text{O}$ is almost zero, indicating that the 10‰ range in $\delta^{18}\text{O}$ is not directly related to temperature (Fig. 3). Furthermore, the long-term trend in the Sofular $\delta^{18}\text{O}$ profile is markedly different from that seen in the Lake Ammersee record¹² (located in the drainage basin of the BS), which reflects temperature-driven changes in the $\delta^{18}\text{O}$ of precipitation in central Europe (Fig. 2a). In contrast to Ammersee, the Sofular $\delta^{18}\text{O}$ profile (Fig. 2c) shows no clear Bølling–Allerød (BA) and Younger Dryas (YD), and a smooth linear increase into the Holocene. Between

¹Institute of Geological Sciences, University of Bern, Baltzerstr. 1 + 3, 3012 Bern, Switzerland, ²Oeschger Centre for Climate Change Research, University of Bern, Zähringerstr. 25, 3012 Bern, Switzerland, ³Institute of Global Environmental Change, Xi'an Jiaotong University, 710049 Xi'an, Shaanxi, China,

⁴Department of Geology and Geophysics, University of Minnesota, 310 Pillsbury Drive SE, Minneapolis, Minnesota 55455-0231, USA, ⁵Climate and Environmental Physics, University of Bern, Siedlerstr. 5, 3012 Bern, Switzerland, ⁶Eurasia Institute of Earth Sciences, Istanbul Technical University, Maslak 34469, Istanbul, Turkey. *e-mail: badertscher@geo.unibe.ch; fleitmann@geo.unibe.ch.

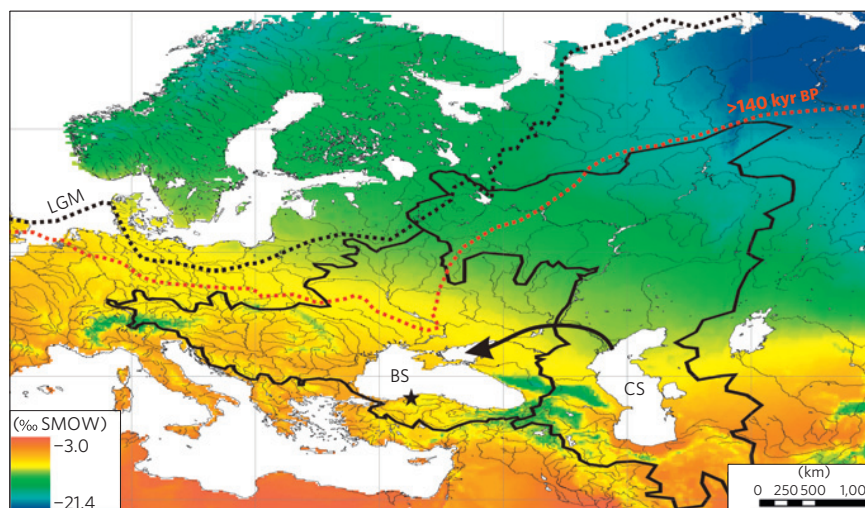


Figure 1 | Map of Black Sea (BS) and Caspian Sea (CS) drainage basins (black lines). Colours denote the interpolated mean annual oxygen isotope composition of precipitation (after www.waterisotopes.org). The black star marks Sofular Cave. The arrow denotes the Manych-Kerch spillway, which connects the CS with the BS. The maximum ice sheet extent during the last glacial maximum (LGM) and the Saalian (140–180 kyr BP) (redrawn after ref. 25) are also shown.

10.5 and 7 kyr BP, the Sofular $\delta^{18}\text{O}$ values increase by $\sim 2.5\text{‰}$ whereas Ammersee increases by only $\sim 0.4\text{‰}$. These disparities reveal that long-term changes in the Sofular $\delta^{18}\text{O}$ record are strongly influenced by other factors.

A major change in the source of moisture, for example from a BS to a MS water vapour source, is also unlikely. The deglacial trend in the Sofular $\delta^{18}\text{O}$ record is opposite to that in the Soreq Cave (Fig. 2b) and Mediterranean lake records, which are closely related to the $\delta^{18}\text{O}$ of MS surface water^{13,14}. Rather, we suggest that the mean $\delta^{18}\text{O}$ of precipitation reaching Sofular exhibits a greater dependence on the $\delta^{18}\text{O}$ of the BS surface water ('water vapour source effect'; ref. 11). This sea-land oxygen isotopic coupling is substantiated by the close correspondence between the Sofular and the BS ostracod $\delta^{18}\text{O}$ records (Fig. 2d). The decrease in $\delta^{18}\text{O}$ between ~ 16.5 and 14.8 kyr BP (related to the inflow of isotopically depleted water from the CS; refs 2–5), the subdued nature of the BA and YD, and the near-monotonic increase of $\sim 6\text{‰}$ in $\delta^{18}\text{O}$ between ~ 15 and 9 kyr BP are visible in both the terrestrial and the marine isotopic records (Fig. 2c,d). This long-term increase in $\delta^{18}\text{O}$ across the last deglaciation reflects the slow adjustment of the large water body of the BS ($517,000 \text{ km}^3$) to the relatively small volume of riverine input (presently at $\sim 350 \text{ km}^3 \text{ yr}^{-1}$; -6 to -10‰ VSMOW), and precipitation (presently at $\sim 230 \text{ km}^3 \text{ yr}^{-1}$; $\sim -10\text{‰}$ VSMOW; refs 15–17). In addition, the inflow of isotopically enriched Mediterranean water (presently at $\sim 300 \text{ km}^3 \text{ yr}^{-1}$; 1.8‰ VSMOW, ref. 15) since 9.4 ± 0.5 kyr BP has further increased the $\delta^{18}\text{O}$ of BS deep water (presently at -1.7‰ VSMOW), resulting in a slow equilibration (within $\sim 1,000$ – $2,000$ yr) of the BS surface water (presently at $\sim -2.4\text{‰}$ VSMOW) with deep water^{2,3,15–17}. The inflow of more enriched MS water has been estimated to account for a change of $\sim 2\text{‰}$ of BS water^{3,15}, which is in good agreement with the observed slow increase of 1.7‰ in the Sofular $\delta^{18}\text{O}$ record since ~ 9.5 kyr BP. Overall, there is strong evidence for a close coupling between changes in the $\delta^{18}\text{O}$ of BS water and stalagmite calcite. This sea-land relationship allows us to use our precisely dated stalagmites to reconstruct hydrological oscillations of the BS in detail.

On the basis of the clear visual correlation between the documented isotopic evolution during the last deglaciation and early Holocene (Fig. 2), we suggest that stalagmite $\delta^{18}\text{O}$ values of around $-8.5 \pm 1\text{‰}$ (error accounts for possible second order effects of evaporation, temperature and isotopic composition of precipitation) are characteristic of time intervals when a connection

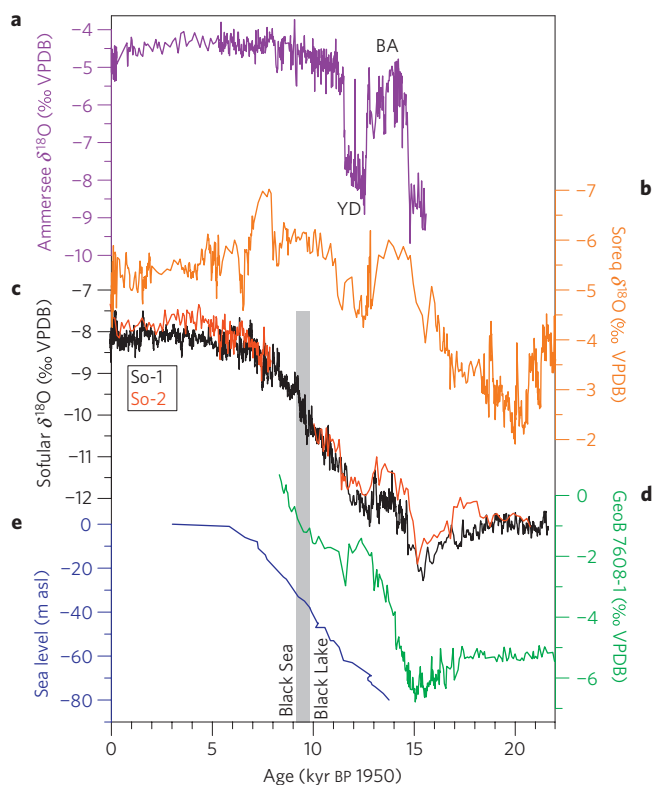


Figure 2 | Last deglacial and Holocene $\delta^{18}\text{O}$ variations and global sea level. Grey vertical bar indicates the timing of the connection between the Black Sea and Mediterranean Sea. **a**, Ammersee $\delta^{18}\text{O}$ record¹². **b**, Soreq Cave $\delta^{18}\text{O}$ record¹³. **c**, $\delta^{18}\text{O}$ profiles of stalagmites So-1 and So-2 from Sofular Cave. **d**, $\delta^{18}\text{O}$ record of Black Sea core GeoB 7608-1 (ref. 2). **e**, Sea-level record from Tahitian corals²⁹.

between the BS and MS was established. Thus, the Sofular $\delta^{18}\text{O}$ profile provides evidence for at least twelve time intervals (Fig. 3; Supplementary Table S4) within the last 670 kyr when water exchange between the BS and MS was established. These intervals coincide (within age uncertainties) with sea levels^{18,19} higher than the current Bosphorus sill depth of ~ 35 mbsl for at least the period spanning currently available sea-level reconstructions (that is, the

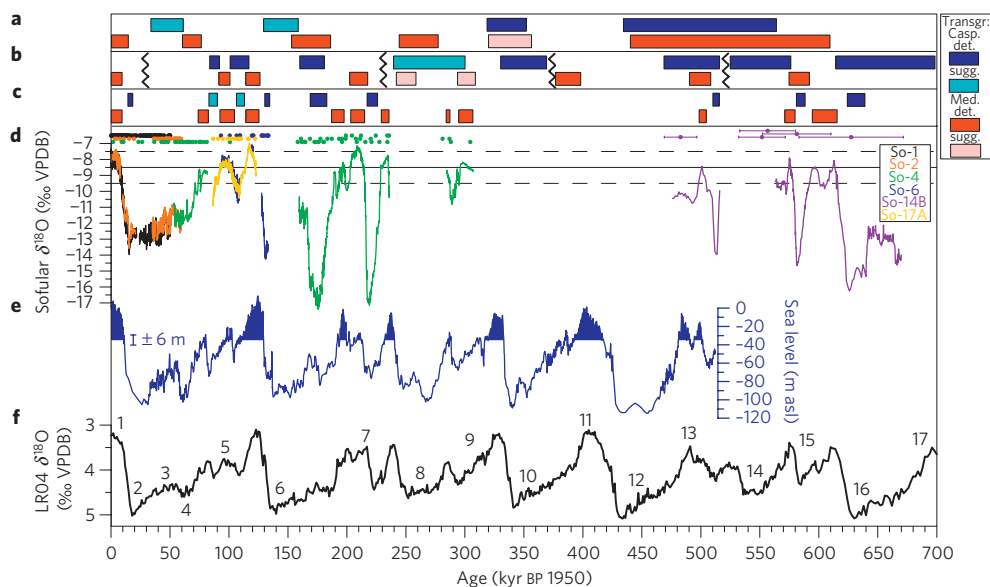


Figure 3 | Stacked Sofular $\delta^{18}\text{O}$ record in comparison with sedimentary records from the Black Sea and global sea level. a, Faunal evidence for water intrusions from the MS (red) and CS (blue) into the BS (ref. 5). **b**, Faunal evidence for water intrusions from the MS (red) and CS (blue) into the BS (ref. 4). Black lines denote discontinuities in the sedimentary sequence. **c**, Sofular stalagmite evidence for water intrusions from the MS (red) and CS (blue) into the BS. **d**, Sofular $\delta^{18}\text{O}$ record, with the colours and colour-coded dots with error bars denoting different stalagmites and ^{230}Th -ages respectively. Solid horizontal line (black) indicates the threshold value of $-8.5 \pm 1\%$ VPDB. **e**, Global sea-level curve^{18,19} (the error is ± 6 m). Blue shaded area marks periods when global sea level was above the Bosphorus sill depth of ~ -35 mbsl. **f**, LR04 stacked isotope record³⁰. Numbers denote marine isotope stages (MIS).

last 520 kyr BP; refs 18,19). For the last 240 kyr BP, the number of intrusions of Mediterranean water in the Sofular record is broadly consistent with those identified in poorly dated sediment sequences from the BS (refs 4,5). The close association between sea level and intrusion of MS water suggests that the Bosphorus sill depth only fluctuated slightly around its present depth of ~ 35 mbsl from at least marine isotope stage (MIS) 15 (~ 520 kyr BP; Fig. 3). Although this is surprising, considering local tectonic uplift (North Anatolian fault) and isostatic response²⁰, it is plausible that these processes, combined with sedimentation and stream downcutting, have resulted in the sill depth remaining fairly constant. As intrusions of Mediterranean water were apparently intimately linked to global sea level, there were most likely more intrusions during MIS 9, 11 and 13, when sea levels were also above ~ 35 mbsl. Unfortunately, MIS 9, 11 and 13 have yet to be recovered from Sofular Cave speleothems.

The Sofular time series shows distinct negative isotope excursions with $\delta^{18}\text{O}$ values as low as -17.5% at around 175, 220, 515, 580 and 630 kyr BP, and before Terminations I and II (Fig. 3; Supplementary Fig. S7). Such negative Sofular $\delta^{18}\text{O}$ values have been interpreted as reflecting the inflow of isotopically depleted water from the CS via the shallow Manych–Kerch (currently at 26 masl) spillway into the BS (refs 2,3,8). Although the modern $\delta^{18}\text{O}$ of CS water (-2.7 to -1.7% VSMOW) is almost identical to that of BS water (-2.4 to -1.7% VSMOW) (ref. 21), the $\delta^{18}\text{O}$ of CS water was significantly lower at times of increased freshwater discharge because of the inflow of melt water from the Eurasian ice sheets, diversion of rivers, and higher runoff coefficients and reduced evaporation under colder climatic conditions^{22–25}. This is also because of the generally more negative $\delta^{18}\text{O}$ values of precipitation in the drainage area of the CS compared with the BS (Fig. 1), as is evident, for instance, from the difference of $\sim 3\%$ in $\delta^{18}\text{O}$ between runoff from the Volga ($\sim -12.5\%$ VSMOW; $\sim 80\%$ of total water inflow into the CS) and Danube Rivers ($\sim -10\%$ VSMOW; $\sim 60\%$ of total water inflow into the BS; ref. 26). Estimates for maximum total annual runoff of CS water into the BS during Termination I range from 1,000 to 1,500 $\text{km}^3 \text{yr}^{-1}$, which is up to five times higher than current total river discharge into the BS (ref. 8). Clearly, such a high

discharge of isotopically depleted water would lead to more negative $\delta^{18}\text{O}$ values of BS water, and, thus, of precipitation at Sofular (Fig. 3). Furthermore, the marked negative shifts in the Sofular $\delta^{18}\text{O}$ profile are broadly consistent with faunal evidence for intrusions of CS water identified in sediment sequences from the BS (Fig. 3). In addition to CS water, a larger volume of isotopically depleted riverine water (melt water) could also have been delivered from the northern BS drainage area (for example, via the Dniestr and Dniepr) where the $\delta^{18}\text{O}$ of precipitation is more depleted (Fig. 1).

It is striking that the negative excursions in the Sofular $\delta^{18}\text{O}$ profile are $\sim 3\%$ lower before ~ 160 kyr BP than during the well-documented enhanced input of CS water between 16.5 and 14.5 kyr BP (Fig. 2; ref. 2). This suggests that the discharge of isotopically depleted water into the BS was considerably higher before ~ 160 kyr BP owing to a greater extent of ice sheets in the northern drainage basin of the BS and CS during the middle Pleistocene^{24,25,27} (Fig. 1). Our hypothesis is supported by the reconstruction of ice-sheet extent in Eurasia for different glacial periods. Compared with the last glacial maximum, the Late Saalian (180–140 kyr BP) ice sheet was $\sim 56\%$ larger and extended further east and southeast over Eurasia²⁸. Furthermore, there is clear evidence that ice sheets in Eurasia were much larger during the middle than during the late Pleistocene²⁷. This implies that runoff of isotopically depleted water into the BS and CS was considerably higher than during the late Pleistocene, as indicated by very low Sofular $\delta^{18}\text{O}$ values at around 175, 220, 515, 580 and 630 kyr BP.

Overall, the Sofular record shows strong evidence for a highly dynamic hydrological history of the BS, with more inundations of water from the Mediterranean and Caspian seas than previously thought. Precisely dated records such as ours are crucial for providing more accurate chronologies for ice sheet dynamics in Eurasia and for long sediment sequences from the BS, which in turn can be used to reconstruct the paleoclimate in this poorly explored region⁹.

Methods

Stable isotope measurements were performed on a Finnigan Delta V Advantage mass spectrometer equipped with an automated carbonate preparation system

(Gas-Bench-II) at the Institute of Geological Sciences, University of Bern. The precision of the $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ measurements is 0.06‰ and 0.07‰ (1σ -error), respectively.

^{230}Th dating was conducted using a multicollector inductively coupled mass spectrometer (MC-ICP-MS, Nu Instruments) at the Institute of Geological Sciences, University of Bern (Supplementary Table S1) and a MC-ICP-MS (Thermo-Finnigan Neptune) at the Department of Geology and Geophysics, University of Minnesota (Supplementary Table S2). Detailed information on analytical procedures is provided in the Supplementary Information accompanying this article.

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Author contributions

D.F. and O.T. initiated the project. S.B., A.Z., O.M.G. and D.F. performed the stable isotope analysis. H.C., S.B. and R.L.E. conducted the uranium-series analysis. S.B. and D.F. wrote the paper.

Additional information

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