Cryptotephra in the Lateglacial ICDP Dead Sea sediment record and their implications for chronology

INA NEUGEBAUER, DANIELA MÜLLER, MARKUS J. SCHWAB, SIMON BLOCKLEY, CHRISTINE S. LANE, SABINE WULF, OONA APPELT AND ACHIM BRAUER

Due to a lack of visible tephras in the Dead Sea record, this unique palaeoenvironmental archive is largely unconnected to the well-established Mediterranean tephr stratigraphy. Here we present first results of the ongoing search for cryptotephra in the International Continental Drilling Program (ICDP) sediment core from the deep Dead Sea basin. This study focuses on the Lateglacial (~15–11.4 cal. ka BP), when Lake Lisan – the precursor of the Dead Sea – shrank from its glacial highstand to the Holocene low levels. We developed a glass shard separation protocol and counting procedure that is adapted to the extreme salinity and sediment recycling of the Dead Sea. Cryptotephras are abundant in the Dead Sea record (up to ~100 shards cm~3), but often glasses are physically and/or chemically altered. Six glass samples from five tephra horizons reveal a heterogeneous geochemical composition, with mainly rhyolitic and some trachytic glasses potentially sourced from Italian, Aegean and Anatolian volcanoes. Most shards likely originate from the eastern Anatolian volcanic provinces and can be correlated using major element analyses with tephra deposits from swarm eruptions of the Süphan Volcano (~13 ka BP) and with ashes from Nemrut Volcano, presumably the Lake Van V-16 volcanic layer at ~13.8 ka BP. In addition to glasses that match the TM-10-1 from Lago Grande di Monticchio (19.82±1.790 cal. a BP) tentatively correlated with the St. Angelo Tuff of Ischia, we further identified a cryptotephras with glass analyses which are chemically identical with those of the P&T1 tephra in the Philippion peat record (13.9–10.5 ka BP), and also a compositional match for the glass analyses of the Santorini Cape Riva Tephra (Y-2 marine tephra, 22.024±642 cal. a BP). These first results demonstrate the great potential of cryptotephrachronology in the Dead Sea record for improving its chronology and connecting the Levantine region to the Mediterranean tephra framework.

In the drought-affected eastern Mediterranean region, a better understanding of the past hydroclimate variability is a prerequisite to improving our capability for estimating future changes of the water balance. In this respect, palaeoclimatic records from marine or lake sediments provide invaluable information about natural hydroclimatic changes. The hypersaline Dead Sea is a key palaeoclimatic archive in the southeastern Mediterranean region, situated at a critical position between more humid Mediterranean climate and the hyper-arid Saharo-Arabian desert belt (e.g. Enzel et al. 2003; Migowski et al. 2006; Stein et al. 2011; Torfstein & Enzel 2017). As such, the Dead Sea is particularly sensitive for recording even small changes in the atmospheric circulation and precipitation by varying lake levels and sedimentary facies (e.g. Stein 2001). The ~450-m-long International Continental Drilling Program (ICDP) drill-core 5017-1, recovered from the deepest part of the Dead Sea, spans the last ~220 000 years (Stein et al. 2011; Neugebauer et al. 2014; Torfstein et al. 2015). Despite the recent refinement of the age model of the ICDP Dead Sea core (Goldstein et al. 2020), it still mainly relies on wiggle matching of δ18O data and U–Th ages with comparably large dating uncertainties, hence, hampering the identification of lead- and lag-phase relationships of changing hydroclimate in comparison to other palaeoclimatic records.

The timing and hydroclimatic response to abrupt climate change can only be unequivocally synchronized and compared between different climate records if each of their chronologies are precise and robust. In this respect, tephrachronology, i.e. identifying volcanic ash (tephra) of past volcanic eruptions in lacustrine and marine sediment records and using them as time-parallel markers, is the ideal method to achieve unambiguous synchronisation (Lowe 2011; Davies et al. 2012; Lane et al. 2017). In recent years, methodological advances have enabled the identification of macroscopically invisible traces of volcanic ash – so-called cryptotephra – in sedimentary climate records, which have multiplied the
number of identified tephras, in regions that can be several thousand kilometres away from the volcanic source (Lane et al. 2014; Davies 2015).

For the central and eastern Mediterranean region (Fig. 1A), comprehensive tephrostratigraphical efforts have led to a good understanding of the chemical compositions and spatial distribution of late Quaternary tephras deposited in marine and terrestrial sediment records (e.g. Keller et al. 1978; Narcisi & Vezzoli 1999; Bourne et al. 2010; Wulf et al. 2012; Matthews et al. 2015). The main volcanic source regions for late Quaternary tephra dispersals in the eastern Mediterranean region are the Italian volcanic provinces, the Hellenic Arc including Santorini, central Anatolia and eastern Anatolia (Fig. 1A). So far, there is no evidence for regionally significant volcanic eruptions and tephra dispersal from the Arabian volcanic province including the Harrat Ash Shaam field (Fig. 1A) of the southern Levant and northern Arabia in the late Quaternary (Hamann et al. 2010; Zanchetta et al. 2011). Therefore, the tephrostratigraphical work accomplished in recent decades is mainly based on the study of visible tephra layers identified in marine and lacustrine sediment records located in relative proximity to the highly active Italian and Aegean provinces (e.g. Keller et al. 1978; Federman & Carey 1980; Narcisi & Vezzoli 1999; Wulf et al. 2004, 2008, 2012, 2020; Bourne et al. 2010, 2015; Çağatay et al. 2015; Matthews et al. 2015; Tomlinson et al. 2015).

Despite being located in a favourable wind direction for receiving tephra from the central and eastern Mediterranean volcanoes via the westerlies, there are so far no tephra layers reported in palaeoclimate records from the southeastern Levantine region. The only exception is the Early Holocene (~9000 cal. a BP) Dikkartin eruption of the Erciyes Dagi in central Anatolia that was identified as a distal tephra layer in the Yammounach palaeolake record in Lebanon, and in a marine sediment core from the SE Levantine Sea (Develle et al. 2009; Hamann et al. 2010). Recently, the first finding of this so-called ‘S1’ tephra as a cryptotephrad in the Dead Sea and in the Tayma palaeolake record from NW Arabia allowed precise synchronization of these records and a discussion of lead- and lag-phase relationships of precipitation patterns in the Levantine-Arabian region during the Early Holocene humid period (Neugebauer et al. 2017). Moreover, this discovery encouraged a systematic search for tephra time-markers in the ICDP deep-basin core 5017-1 (Fig. 1B, C), with the aim of improving the chronology of the deep record and providing a tool for precise regional synchronization of proxy records.

The present study focusses on the last glacial–interglacial transition in the ICDP Dead Sea sediment core. Strong lake level fluctuations occurred at the last glacial precursor of the Dead Sea (Lake Lisan) during the Lateglacial; however, the hydroclimatic conditions in the central Levantine region in particular during Greenland Stadial 1 are uncertain (Stein et al. 2010). An improved chronology of the Dead Sea sediment record is a prerequisite for a precise synchronization with other palaeoclimate records, particularly in the eastern Mediterranean, in order to prove or disprove apparent large regional hydroclimatic differences like, for example a wet Younger Dryas in the Levant (Stein et al. 2010) and an arid Younger Dryas in Anatolia (e.g. Wick et al. 2003). This study aims at deciphering the Lateglacial hydroclimatic conditions in the Levantine region through the identification of cryptotephras in the Dead Sea sediment record and the improvement of its Lateglacial chronology. Such advanced insights into past regional climatic responses to global change are crucial to better anticipate possible future developments.

The ICDP Dead Sea record

Previous studies of the Dead Sea sediments were mainly restricted to sediment formations that are exposed at the margins of the lake (e.g. Bartov et al. 2002; Bookman (Ken-Tor) et al. 2004; Torfstein et al. 2009; Waldmann et al. 2009), or that were drilled along the western shoreline (Migowski et al. 2006). These outcrops and shallow cores, however, lack information especially about drier periods and low lake stands. Earlier attempts to drill in the deep basin were hampered by thick salt sequences that could not be penetrated (Heim et al. 1997). Therefore, a promising way to gain a continuous, long sediment record from the deep Dead Sea basin was through an ICDP drilling. From the ICDP Dead Sea Deep Drilling Project (DSDDP; ‘The Dead Sea as a Global Paleoenviromental, Tectonic, and Seismological Archive’), a ~450-m-long sediment record was recovered from the deepest part of the Dead Sea basin in 2010/11, comprising a continuous record of the last ~220 000 years of climate history in the southern Levantine region (Stein et al. 2011; Neugebauer et al. 2014).

The efforts to establish a robust chronology for the exposed sequences of the Dead Sea lacustrine formations have continued for more than two decades, applying radiocarbon, U–Th dating and floating δ18O stratigraphy methods (see Stein & Goldstein 2006 for an overview; Torfstein et al. 2009, 2013a). Accordingly, this approach has also been applied to constrain the chronology of the ICDP deep core 5017-1. For the upper ~150 m of the core, the age-depth model is based on 38 14C dates of terrestrial plant remains that provide a relatively solid chronology for the last ~50 ka, i.e. back to the limit of the radiocarbon dating method (Neugebauer et al. 2014, 2015; Kitagawa et al. 2017). Unfortunately, this chronology includes unknown uncertainties because all dated plant remains could only be extracted from the base of turbidites so that reworking and resulting age/depth reversals cannot be excluded. Slumping of sediments and erosion by mass-transport deposits are very
Fig. 1. A. Distribution map of central and eastern Mediterranean volcanic provinces and selected palaeoenvironmental sediment records with established late Quaternary tephrochronologies; the Dead Sea is highlighted (yellow star). B. Dead Sea map with drilling locations of the ICDP 5017 expedition (diamonds; core 5017-1 is analysed in this study) and selected onshore sites studied earlier (circles). C. Core 5017-1 lithostratigraphy (Neugebauer et al. 2014) and selected $^{14}C$ (Kitagawa et al. 2017) and U–Th ages (Torfstein et al. 2015); corresponding marine isotope stages (MIS) and Dead Sea sediment formations (Fm.) are also marked. [Colour figure can be viewed at www.boreas.dk]
common features in the core (Neugebauer et al. 2014; Kagan et al. 2018) and further add to the uncertainty of the chronology, but this can hardly be quantified. The age model of the older part of the core, reaching to ~220 000 years, was constructed by U–Th dating on primary aragonite that was combined with wiggle matching of stable oxygen isotope signals from aragonite layers and lithological changes that have been tied to exposed sediment formations, and to stable oxygen isotope data from the Soreq Cave speleothem and the LR04 global marine stack (Torfstein et al. 2015; Goldstein et al. 2020). Also, this approach is problematic, since (i) U–Th dating of authigenic carbonate requires a comprehensive correction procedure to account for the presence of detrital U and Th, and hydrogenic Th in Dead Sea sediments (Stein & Goldstein 2006 and references therein), which results in large age uncertainties of U–Th ages of up to several thousand years (Torfstein et al. 2013a); and because (ii) wiggle matching of oxygen isotope and lithological data to very different types of records is not independent.

Sediments of the ~450-m-long 5017-1 core, retrieved from a water depth of ~300 m (in 2010), mainly consist of alternating aragonite-detritus laminae, massive gypsum deposits, laminated marl, and halite sequences that are characteristic for the Amora (MIS 7-6), Samra (MIS 5), Lisan (MIS 4-2) and Zeelim (Holocene) sediment formations deposited in the Dead Sea basin (Fig. 1C; Neugebauer et al. 2014). One of the best-studied sections of the Dead Sea sediment formations is the Upper Lisan Formation, deposited in the Dead Sea basin during MIS 2 and building iconic sediment exposures in Masada (M1 outcrop) and the Perazim Valley (PZ1 outcrop) (e.g. Begin et al. 1980; Machlus et al. 2000; Bartov et al. 2002; Prasad et al. 2004, 2009; Torfstein et al. 2013b). The so-called ‘White Cliff’, finely laminated white aragonite and detritus sediments, formed during the Last Glacial Maximum when Lake Lisan was at its maximum highstand of ~160 m below sea level (b.s.l.; Torfstein et al. 2013b). The White Cliff is topped by the ‘Upper and Additional Gypsum Units’, which announce the Lake Lisan level retreat at the end of the last glacial at ~17.1–15.5±0.5 and at ~14.5±0.5 ka (Torfstein et al. 2013a) down to Holocene levels of ~400±30 m b.s.l. (Migowski et al. 2006). Due to this lake level decline, Lateglacial sediments and the transition to the Holocene between ~13 and 11 cal. ka BP are not exposed in the onshore deposits, but these can now be studied in the ICDP deep-basin core.

Material and methods

Sampling and glass shard extraction

Sediment cores of ICDP expedition 5017 are stored at the Marum Core Repository in Bremen, Germany. Sampling for glass shard analyses of cryptotephras of core 5017-1 is principally done in contiguous 5-cm steps with sample volumes of 5 cm$^3$, excluding mass-transported deposits (turbidites and slumps) thicker than 5 cm. Rock salts and other consolidated sediment sections that are too hard for sampling with a spatula were cut using a band saw at GFZ Potsdam, Germany.

The cryptotephra glass extraction protocol followed established physical and chemical separation procedures (Blockley et al. 2005), and has been further developed to account for the specific conditions of Dead Sea sediments. First, samples were repeatedly rinsed with deionized water in a shaking bath to dissolve salts and remove highly saline pore waters. Second, 10% HCl and 15% H$_2$O$_2$ solutions were added to remove carbonates and organic matter. This step was followed by wet-sieving into a 20–100 µm grain-size fraction, and sodium polytungstate (SPT) liquid density mineral separation, with volcanic glass shards being concentrated in the 2–2.55 g cm$^{-3}$ fraction. Residual clays that disaggregated during this process were then removed by a second sieving through a 20-µm mesh.

The remaining sediment material still contains high concentrations of mineral grains (Fig. 2), which would prevent time-efficient glass shard counting of these samples. Therefore, Lycopodium spores (Fig. 2) with a defined number of spores per tablet (10 679±426 spores per tablet, batch no. 938934, Laboratory of Quaternary Geology University Lund, Sweden; Stockmarr 1971) were added to the samples. About 10% (at least 5%) of the total residue was mounted on glass slides for glass shard counting under a transmitted light polarization microscope. Along with counting Lycopodium spores in this subsample, the glass shard concentration per cubic centimetre of sediment or per gram dry weight can be estimated based on the given total number of spores (one tablet) in the total sample residue.

Geochemical characterization of tephra-derived glass

Glass shards of identified tephra horizons were picked under the microscope from the remaining ~90% of suspended sample material using a 100-µm-diameter gas-chromatography syringe attached to a micromanipulator (see Lane et al. 2014). Shards were transferred into single-hole-stubs, embedded in Araldite 2014 epoxy resin, ground and polished for electron probe microanalyses (EPMA). The major element composition of individual glass shards was measured using a JEOL JXA-8230 electron microprobe at GFZ Potsdam, Germany, with operating conditions of 15 kV voltage, 5 nA beam current, and a beam size of 5–10 µm depending on glass shard size. Exposure times were for each analysis 20 s for the elements Fe, Cl, Mn, Ti, Mg and P, and 10 s for Si, Al, K, Ca and Na. Instrumental calibration used natural mineral standards, and the glass standards Lipari obsidian (Hunt & Hill 1996; Kuehn et al. 2011) and MPI-Ding glasses ATHO-G, StHs-6-80-G and...
GOR-132-G (Jochum et al. 2006) were used during analytical runs to monitor the precision and accuracy of measurements (Table S1).

Lateglacial Dead Sea samples

For the present study, 56 samples between 89.30 and 94.09 m sediment depth below lake floor (m b.l.f.) from cores 5017-1-A-43 and 5017-1-A-44 were analysed for crypto-terphrostratigraphy, following the procedure illustrated above. These samples cover the top-most ~5 m of the Upper Lisan Formation in the ICDP core (Figs 1C, 3), i.e. immediately underlying the Early Holocene salt section (~73–89 m b.l.f. in 5017-1; Fig. 1C). From six of these samples, at least 10 glass shards per sample were measured by EPMA. Replicate measurements on a different set of glass shards from the sample were performed initially using 10 nA and later 5 nA beam currents for three samples, resulting in a total of 107 glass geochemical measurements (Table S1). Five values with raw totals of <90% were excluded from further evaluation.

Results

Glass shard counting

Of the 56 samples inspected here, 45 contain volcanic glass shards with concentrations of 4 to 107 shards cm$^{-3}$ wet sediment (Fig. 3). Shards are concentrated in several 10–20 cm thick tephra horizons (TH) within finely laminated $a a d$ (alternating aragonite and detritus) sediments around 89.80, 90.05, 90.75, 92.00, 92.55, 93.30 and 93.95 m b.l.f. (Fig. 3). Even though turbidites thicker than 5 cm were excluded from cryptotephra sampling, evidence of smaller reworking events is still common and included in the samples. This reworking likely explains the physical alteration (rounding) of glass shards of at least 17 samples. In addition, particularly vesicular shards are often chemically altered at their surface and rims (Fig. 4), potentially as a result of the alkaline composition of the Dead Sea brine. The frequent occurrence of ‘volcaniform’ phytoliths, which have similar optical properties to these altered volcanic glasses, further complicates glass and hence tephra identification under the microscope. The maximum estimate of the shard concentration in Fig. 3 considers such ambiguous cases.

Glass shard morphologies

Glass shards are typically clear, devoid of microlites or other inclusions, and range in size mostly between 30 and 80 µm (Fig. 4). Some glass morphologies are preferentially found within specific TH. In the upper tephra horizons TH(89.80; 90.05; 90.75), glasses are mostly cuspatte/butterfly-shaped or contain elongated vesicles (Fig. 4), and some are fluted. Tiny platy shards almost exclusively occur in TH(89.80). Glasses in TH(92.00) have cuspatte or fluted shapes. In TH(92.55), glasses with elongated vesicles are noticeably thin. Vesicular and highly vesicular bubble-wall shards are characteristic in TH(93.30). Very thin butterfly shards occur in the lowermost tephra horizon TH(93.95).

Glass geochemical compositions

Major element EPMA data ($n = 102$; Table S1) of glass from the six samples analysed here show mostly rhyolitic and some trachytic glass compositions (Fig. 5). Seven
tephra populations can be distinguished that are mostly spread over several samples, i.e. they occur in several tephra horizons. These tephra populations (POP) are described in the following; their major element glass chemistry is shown in Figs 5 and 6 and summarized in Table 1. The analyses reported in the following text are on a normalized (volatile-free) basis (Table 1).

**POP1 (trachytic).** – Seven shards are trachytic in composition (five in sample 5017-C2-45, two in sample 5017-C2-25), close to the phonolite boundary, with 61.7–64.3 wt% SiO₂ and on average 6.5 wt% Na₂O and 6.5 wt% K₂O. These glasses are further characterized by ~18.7 wt% Al₂O₃, 0.5 wt% TiO₂ and 2.6 wt% FeO (total iron sum reported as FeO). CaO values in glass differ between the two samples, with ~1.1 wt% in sample 5017-C2-45 and ~1.8 wt% in sample 5017-C2-25 (Fig. 5).

**POP2 (rhyolitic).** – The composition of glass in population POP2 (n = 13) is characterized by a rhyolitic, close to dacitic, narrow cluster of 71.5–72.4 wt% SiO₂ and total alkalis of 6.6–8 wt%, whereas K₂O values are constant and low (~2.9 wt%). One glass shard with
lower SiO₂ (70 wt%), but high Na₂O (6.5 wt%) was assigned to this cluster as well (Fig. 6), as all other major elements occur in similar concentrations, e.g. ~14.7 wt% Al₂O₃, 3.1 wt% FeO, 0.5 wt% MgO and 1.7 wt% CaO (Table 1). Single glass shards of this population occur in nearly all analysed samples, except for sample 5017-C2-33, but most of them are located in sample 5017-C2-27 of TH(92.00) (Fig. 5).

**POP3–POP7 (rhyolitic).** The majority of the glass shards analysed have rhyolitic compositions with 74–79 wt% SiO₂ and 6–9.5 wt% total alkalis (Fig. 5). Based on small differences in Ti, Al, Fe and Ca oxide contents and alkali ratios, five different tephra populations (POP3 to POP7) can be differentiated that describe n = 66 of all analysed shards (Fig. 6).

POP3 (n = 23) is characterized by particularly low TiO₂ (~0.05 wt%) and FeO (0.7 wt%), CaO is ~0.6 wt% and Na₂O is <4 wt%, and most glasses of this population were analysed in sample 5017-C2-33. Of the 14 analysed shards from this sample, 11 shards have compositions that fall into POP3 (Table S1).

POP4 (n = 16) shows very depleted CaO values (0.1–0.2 wt%), lower Al₂O₃ (~11.7 wt%) compared to POP3 (~12.9 wt%), higher FeO values (~2.6 wt%), and Na₂O >4 wt%. Glasses of POP4 occurred in all analysed samples; most in both the lowermost and uppermost samples 5017-C2-45 and 5017-C2-11, respectively.

The composition of POP5 (n = 13) is overall very similar to that of POP3 and POP4, with slightly higher TiO₂ (0.3 wt%) and Al₂O₃ (12.1 wt%), but similar FeO (2.4 wt%) compared to that of POP4, whereas CaO values of ~0.6 wt% compare with those of glass of POP3. However, the very low alkali-sum (~7 wt%) and higher K₂O/Na₂O (~1.6) ratio clearly distinguish POP5 from POP3 and POP4. Shards of this population occur in all analysed samples, except for sample 5017-C2-33.

POP6 (n = 8) shows the largest similarity with POP3; only SiO₂ is slightly lower (~75.6 wt%), and Al₂O₃ (13.4 wt%) and FeO (1.7 wt%) are somewhat higher. This population (POP6) mostly occurs in sample 5017-C2-27 of TH(92.00) and only occasionally in the overlying tephra horizons.

POP7 (n = 6) differs from POP3 to POP6 by having lower SiO₂ (72.7–76.8 wt%) and Al₂O₃ (8.2–11.7 wt%) concentrations, but much enhanced FeO values (4.6–5.9 wt%) (Fig. 6). Like POP6, most shards of this population were analysed in sample 5017-C2-27, while analyses of only single shards occur above.

**Undefined glasses.** Sixteen glass compositions, eight of which were from sample 5017-C2-11, could not be assigned to any of the tephra populations defined above, and do not build a separate cluster (Figs 5, 6). Some of these glasses show apparent similarities with POP3, 4, 5 and 6, and others plot in between trachytic and rhyolitic compositions. One single glass shard is of trachydacitic composition.

**Discussion**

**Lateglacial tephra record ~15–11 cal. ka BP in the Dead Sea**

Considering that the Dead Sea in the southern Levantine region is largely influenced by westerly winds from the Mediterranean Sea, we would expect the majority of cryptotephrae detected in the Dead Sea record to originate from Italian and Aegean volcanic centres. As the only visible tephra layer in the Levant – the Early Holocene S1’ tephra from Erciyes volcano (Develle et al. 2009; Hamann et al. 2010), detected as a cryptotephra in the Dead Sea record (Neugebauer et al. 2017) – originates from central Anatolia, we also include the western, central and eastern Anatolian volcanic provinces as potential tephra sources.
Fig. 5. Total alkali-silica diagram and bivariate elemental plots of EPMA normalized glass data from Lateglacial Dead Sea sediments (~15–11 cal. ka BP). Note that analytical errors are smaller than the symbol size. [Colour figure can be viewed at www.boreas.dk]
Fig. 6. Total alkali-silica diagram and bivariate elemental plots of EPMA normalized glass data of tephra populations identified in Lateglacial Dead Sea sediments (~15–11 cal. ka BP). Tephra populations were defined visually and by sorting the EPMA data table. Note that analytical errors are smaller than the symbol size. [Colour figure can be viewed at www.boreas.dk]
Due to the large number and frequent activity of highly explosive volcanoes in the central and eastern Mediterranean during the Lateglacial and beyond, and because successive eruptions from the same source often have very similar glass compositions (e.g. Tomlinson et al. 2012a, 2015), assigning a particular volcanic eruption to a tephra population defined in our data is difficult. Also, a very distal cryptotephra record with low shard concentrations, as is the case for our record, may not represent the full compositional range of an eruption (Tomlinson et al. 2015), which might lead to false correlation, if the full geochemical range of a proximal deposit is also unknown. A further complication is the strong reworking of sediments in the Deep Sea basin, which requires extending the search for tephra correlatives beyond the Lateglacial period analysed here to consider those from older eruptions.

We first followed the attempt by Tomlinson et al. (2015) to discriminate the Mediterranean volcanic centres captured in our data, based on major element glass variations that are typical for different tectonic settings and volcanic provinces, before discussing the correlation of tephra populations with particular eruptives. In addition, we consulted the RESET Database (https://c14.arch.ox.ac.uk/resetdb/db.php; Bronk Ramsey et al. 2015b; Lowe et al. 2015) for available tephra data also from Anatolian provinces. Accordingly, we can distinguish at least three different sources – (i) the Neapolitan volcanic centre and probably western Anatolia, (ii) Santorini, and (iii) eastern Anatolia and probably central Anatolia (Fig. 7).

**POP1 (Campanian and potentially western Anatolian volcanic provinces).** – The trachytic composition of POP1 is similar to products of the Neapolitan volcanic district (Campi Flegrei, Ischia and Somma Vesuvius) that formed in a post-subduction setting (Tomlinson et al. 2015). Chemical biplots of Ca-Si, Na/K-Ca and Ca-Mg oxides, which are useful to discriminate Neapolitan volcanic products, place the five glass shards of POP1 from sample 5017-C2-45 that have low CaO (~1.1 wt%) in the field of the Ischia Island (Tomlinson et al. 2015). We found a good correlation of four glasses of this low-Ca subgroup of POP1 (Fig. 8) with the glass analyses of Ischia tephra layer TM-10-1 (15820±790 cal. a BP) in the Lago Grande di Monticchio (LGdM) record (Wulf et al. 2008), which was suggested to relate to the St. Angelo Tuff from the Campotese volcano of Ischia (17800±3200 K/Ar a; Poli et al. 1987). Glass of the marine C-3 tephra in deep-sea cores in the Tyrrhenian Sea has similar age and trachytic composition (Paterne et al. 1988), and was considered to represent the same explosive event (Wulf et al. 2008). Finding the product of a sub-Plinian eruption in the Dead Sea record, more than 2000 km away from the source, is noteworthy. In addition, the cryptotephra age of ~14.5 cal. ka BP in the Deep Sea core (sample 5017-1-C2-45, TH(93.30)) would be younger than TM-10-1 by at least ~500 years. Therefore, a correlation of the low-CaO glasses of POP1 with those of the TM-10-1 tephra from Ischia must be considered with caution.

Two POP1 glasses in sample 5017-C2-25 (~1.8 wt% CaO) overlap with Campi Flegrei Campanian Ignimbrite (CI)/pre-CI products in Tomlinson et al. (2015), and are similar to the glass composition of the Campanian Ignimbrite super-eruption (~39 ka, marine Y-5 tephra) itself (e.g. Tomlinson et al. 2012a; Giaccio et al. 2017) (TM-18 in LGdM, Fig. 8; Wulf et al. 2004). However, CI glasses in this stratigraphical position in the Dead Sea record are unlikely, and Tomlinson et al. (2012a) reported that Post-CI/Pre-NYT (Neapolitan Yellow Tuff) tephras can hardly be discriminated based on major element compositions alone (see TM tephra layers of LGdM originating from the Phlegrean fields in Fig. 8; Wulf et al. 2004, 2008). Therefore, we do not consider the CI as a likely source of the two high-CaO

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**Table 1.** Mean glass geochemical data in wt% (normalized, volatile-free) of the identified tephra populations (POP). Std = standard deviation; * = total iron is reported as FeO.

| Tephra population | Total | SiO₂ | TiO₂ | Al₂O₃ | FeO* | MnO | MgO | CaO | Na₂O | K₂O | P₂O₅ | Na₂O+K₂O | K₂O/Na₂O |
|-------------------|-------|------|------|-------|------|-----|-----|-----|------|-----|------|---------|----------|
| POP1 (n = 7)      | 93.76 | 63.04 | 0.51 | 18.74 | 2.64 | 0.23 | 0.35 | 1.30 | 6.55 | 6.58 | 0.05 | 13.13   | 1.02     |
| std               | 1.11  | 0.71  | 0.09 | 0.21  | 0.19 | 0.02 | 0.04 | 0.32 | 0.55 | 0.32 | 0.02 | 0.36    | 0.13     |
| POP2 (n = 13)     | 95.14 | 71.90 | 0.48 | 14.72 | 3.08 | 0.12 | 0.49 | 1.69 | 4.56 | 2.89 | 0.08 | 7.45    | 0.65     |
| std               | 1.31  | 0.61  | 0.08 | 0.15  | 0.20 | 0.04 | 0.07 | 0.10 | 0.70 | 0.11 | 0.02 | 0.68    | 0.10     |
| POP3 (n = 23)     | 95.75 | 77.39 | 0.05 | 12.93 | 0.68 | 0.04 | 0.05 | 0.64 | 3.43 | 4.77 | 0.02 | 8.20    | 1.43     |
| std               | 1.6   | 0.26  | 0.03 | 0.20  | 0.10 | 0.03 | 0.02 | 0.07 | 0.38 | 0.46 | 0.02 | 0.30    | 0.37     |
| POP4 (n = 16)     | 95.93 | 76.43 | 0.19 | 11.69 | 2.62 | 0.11 | 0.03 | 0.16 | 4.15 | 4.62 | 0.01 | 8.77    | 1.14     |
| std               | 1.45  | 0.79  | 0.09 | 0.39  | 0.40 | 0.03 | 0.04 | 0.05 | 0.53 | 0.38 | 0.01 | 0.61    | 0.21     |
| POP5 (n = 13)     | 92.96 | 77.59 | 0.26 | 12.08 | 2.41 | 0.10 | 0.02 | 0.55 | 2.77 | 4.21 | 0.01 | 6.97    | 1.60     |
| std               | 1.54  | 1.01  | 0.06 | 0.26  | 0.32 | 0.03 | 0.04 | 0.12 | 0.64 | 0.21 | 0.01 | 0.74    | 0.39     |
| POP6 (n = 8)      | 94.90 | 75.61 | 0.10 | 13.35 | 1.65 | 0.06 | 0.02 | 0.59 | 3.75 | 4.85 | 0.02 | 8.61    | 1.34     |
| std               | 1.12  | 1.05  | 0.04 | 0.14  | 0.48 | 0.03 | 0.01 | 0.10 | 0.67 | 0.39 | 0.02 | 0.54    | 0.28     |
| POP7 (n = 6)      | 93.92 | 75.08 | 0.33 | 9.85  | 3.87 | 0.24 | 0.04 | 0.29 | 3.96 | 4.32 | 0.01 | 8.28    | 1.15     |
| std               | 2.26  | 1.25  | 0.05 | 1.00  | 1.40 | 0.04 | 0.03 | 0.08 | 0.88 | 0.29 | 0.02 | 0.88    | 0.28     |
glasses of POP1, even though reworking of older CI glasses cannot be entirely excluded.

A widely dispersed trachytic phreato-plinian deposit is the Neapolitan Yellow Tuff (NYT; marine C-2 tephra) that is the product of a high-magnitude, caldera-forming eruption of Campi Flegrei (Deino et al. 2004; Siani et al. 2004). Its $^{40}$Ar/$^{39}$Ar isochron age of 14.9±0.4 ka (2σ) (Deino et al. 2004) and revised age of 14 194±172 cal. a BP (Bronk Ramsey et al. 2015a), considering $^{14}$C dating and varve counting in Lago Grande di Monticchio (Wulf et al. 2004, 2008), would make the NYT a likely candidate for correlation with POP1. However, the NYT was rather dispersed to the north and has never been reported from eastern Mediterranean archives (Bronk Ramsey et al. 2015a). The slight mismatch of the major element compositions of the NYT (TM-8 in LGdM, Fig. 8; Wulf et al. 2004) and POP1 leave us to reject the NYT as a tephra correlative.

Trachytic tephra of the western Anatolian Gölçük volcano (Isparta, SW Turkey; Platevoet et al. 2008; Coban et al. 2019), located much closer to the Dead Sea than the Campanian province and with most recent activity during the Late-glacial ((U–Th)/He zircon eruption ages 14.1±0.5 and 12.9±0.4 ka, 1σ; Schmitt et al. 2018), would make the NYT a likely candidate for correlation with POP1. However, the NYT was rather dispersed to the north and has never been reported from eastern Mediterranean archives (Bronk Ramsey et al. 2015a). The slight mismatch of the major element compositions of the NYT (TM-8 in LGdM, Fig. 8; Wulf et al. 2004) and POP1 leave us to reject the NYT as a tephra correlative.

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Fig. 7. Discrimination of Mediterranean volcanic centres captured in tephra data of Late-glacial Dead Sea sediments (~15–11 cal. ka BP). Note that the highlighted fields do not represent the full range of geochemical glass compositions of tephras from Neapolitan, Santorini and western, central and eastern Anatolian volcanic centres, and that available proximal tephra data from central and eastern Anatolia largely overlap. Only glasses from Nemrut volcano (eastern Anatolia) can be discriminated due to characteristically low CaO. [Colour figure can be viewed at www.boreas.dk]

Fig. 8. Elemental biplots (normalized to 100%, volatile-free) of Dead Sea POP1 EPMA glass data (green triangles) compared with data of Ischia/Campanian eruptives, as recorded in the Lago Grande di Monticchio record (TM tephra layers; Wulf et al. 2004, 2008). Tephras related to the Phlegrean fields (grey shades): TM-7b = Pomici Principali; TM-8 = Neapolitan Yellow Tuff; TM-9 = Tufi Biancastri; TM-10a = Lagno Amendolare; TM-15 = marine Y-3 tephra; TM-18 = Campanian Ignimbrite (CI)/marine Y-5 tephra. Tephras related to Ischia (yellow shades): TM-10-1 = tentative correlation to St. Angelo Tuff/marine C-3 tephra (Wulf et al. 2008, and S. Wulf, unpublished data); FPI = Faro di Punta Imperatore in marine core PRAD 1-2, central Adriatic Sea (Bourne et al. 2010). Also shown are pumice data of Gölçük cycle III (orange field) from western Anatolia (Tomlinson et al. 2015). [Colour figure can be viewed at www.boreas.dk]
is considered as a more likely candidate for correlation with ‘high-CaO’ glasses of POP1. Indeed, geochemical data of glass from the most recent eruption sequence Gölçük cycle III (Tomlinson et al. 2015) plot very close to our data, of which one glass lies directly within this field (Fig. 8).

**POP2 (Santorini).** – The major element composition of glass of the rhyolitic POP2 can be correlated with the active subduction setting of the Aegean volcanic province (Tomlinson et al. 2015), and more specifically with glass of the rhyodacitic Cape Riva Ash of Santorini (marine Y-2 tephra) (Federman & Carey 1980; Drütt et al. 1999; Fabbro et al. 2013; Wulf et al. 2020; Fig. 9). The Cape Riva eruption, radiocarbon-dated at 22 024±642 (2σ) cal. a BP (Bronk Ramsey et al. 2015a), formed prominent proximal pyroclastic fall deposits and far-spread distal tephra layers in the eastern Mediterranean region (e.g. St. Seymour et al. 2004; Satow et al. 2015; Wulf et al. 2020). Still, the appearance of the ~22 ka Cape Riva Ash in Lateglacial sediments of the Dead Sea is considered unlikely due to the large age difference that would imply considerable reworking of sediments.

However, there is distal evidence from the Tenaghi Philippon peat basin of northern Greece for deposition of a Lateglacial Santorini eruption that has glass chemically identical to that of Cape Riva tephra (St. Seymour et al. 2004; Wulf et al. 2018), but this has not yet been proven in the proximal or marine distal database (Drütt et al. 1999; Wulf et al. 2020). St. Seymour et al. (2004) described a visible tephra layer (PhT1) in the Philippi peat basin, radiocarbon-dated to 11 818±139 cal. a BP (IntCal13) but with conflicting estimates from ~13.9 to 10.5 cal. ka BP, which has glass with a chemical affinity to Y-2 and which was recognized some decimetres above the primary, several-centimetre-thick Y-2 (PhT2) tephra. Similarly, Wulf et al. (2018) identified two cryptotephra layers (that have comparably high shard concentrations >10 000 shards g⁻¹ dwt; TP-05-7.07 and TP-05-7.26 in Fig. 9) that are chemically identical to those of the Cape Riva/Y-2 tephra in the Tenaghi Philippon TP-2005 core ~40–60 cm overlying the Y-2 tephra. Due to the lack of field and geochronological evidence for a Lateglacial eruption of Thera (Santorini) volcano, and because of the identical trace element composition of glass with that of the Y-2 tephra, the PhT1 tephra has been interpreted as a result of postdepositional recycling of Y-2 material (Wulf et al. 2018). Although we cannot exclude reworking in the Dead Sea sediments either, the occurrence of a cryptotephra with Cape Riva glass chemical affinity also in the Lateglacial sediments of the Dead Sea (sample 5017-C2-27 of TH(92.00); previously dated to ~14 cal. ka BP, see discussion below) might be another hint for a yet unknown Inter-Plinian eruption of the Santorini volcano during this period that so far has not yet been found in proximal sites.

**POP3–POP6 (central/eastern Anatolia).** – Glasses of the highly evolved, silicic tephra populations POP3 to POP6 overlap in their chemical composition with those of the products of several active subduction volcanic centres in the eastern Mediterranean; these are the
Hellenic Arc islands Nisyros, Kos and Yali (without Santorini) and central Anatolia (Kuzucuoglu et al. 1998; Tomlinson et al. 2015), as well as eastern Anatolia (Sumita & Schmincke 2013b; Schmincke & Sumita 2014). Only for four major eruptives from Hellenic Arc volcanoes, geochemical glass data are available: the Yali-2 tephra, dated to ~95 ka BP based on orbitally tuned marine core KB28 (Vinci 1985), shows a similar glass chemical composition as that of the Cape Riva Ash (Tomlinson et al. 2015) and may be considered for potential correlation with POP2 (Fig. 9). The Nisyros Upper and Lower Pumices (~47 and 52 ka BP, respectively; Limburg & Varekamp 1991; Tomlinson et al. 2012b), and the Kos Plateau Tuff (KPT, marine W-3 tephra, ~166 ka BP; Bachmann et al. 2010) overlap in their glass shard compositions with POP3 to POP6. Even though we cannot entirely exclude these tephras as potential correlatives to our data, we also do not consider these as very likely due to their much older eruption ages.

The tephrostratigraphical framework for central and eastern Anatolian volcanic provinces is sparse in comparison to that of the comprehensive Italian and Aegean databases. While the Early Holocene Dikkartin, Perikartın and Karagüllü eruptives of Erciyes Dagi in central Anatolia (Hamann et al. 2010) do not match with POP3 to POP6 data (Fig. 10), eruptives of the central Anatolian Acigöl volcano at ~25–20 ka BP or younger, the so-called western Acigöl rhyolites, might fit in composition with our data (Schmitt et al. 2011; Siebel et al. 2011). However, only mean chemical analysis data of six rock samples are available for comparison (Fig. 10), restricting a proper interpretation of these data in comparison to our glass-based cryptotephra record. Kuzucuoglu et al. (1998) reported three rhyolitic tephras of Lateglacial age (GÖLT1, GÖLT5 and GÖLT11) from the Eski Acigöl lacustrine sequence and one (GOCU 1 potentially correlating with the Korudagi Tuff of Acigöl) from the Gocü beach deposit sequence in the Konya Plain. The major element glass compositions, given only as mean values for these tephras (Kuzucuoglu et al. 1998), do not agree well with Dead Sea POPs when several elements are considered (Fig. 10).

Our POP3 to POP6 major element glass data show the best correlation with eastern Anatolian Süphan swarm eruptives around 13 cal. ka BP and with glass analyses of Nemrut Dagi ashes, as reported from tephra layers in the ICDP Lake Van sediment core (Schmincke & Sumita 2014). The Lateglacial Süphan tephra swarm occurred during a short time interval of ~338 years between ~13 078 and 12 740 varve years BP, labelled as V-8 to V-15 volcanic layers in Lake Van varved (annually laminated) sediments (Schmincke & Sumita 2014). POP3 and likely POP5 correlate with these chemically very similar Süphan eruptives around 13 cal. ka BP, and POP6 might correlate with V-13 that has glass with a somewhat higher FeO than other Süphan eruptives of this swarm (Fig. 10; Schmincke & Sumita 2014). POP4 most likely represents the V-16 layer of a Nemrut eruption ~13.8 cal. ka BP, as can be seen in the characteristically low CaO values (~0.2–0.3 wt% of glass of the rhyolitic Nemrut tephras. However, higher FeO in glass of POP4 could also suggest a correlation to Nemrut V-17 that is dated to >30 ka BP in the Lake Van core. Schmincke & Sumita (2014) postulate a tephra gap between 30 ka BP (V-17) and ~14 ka BP (V-16); hence, a match with V-17 in our data would imply reworking of tephra over more than 15 000 years in the Dead Sea record, which we consider as highly unlikely. It should also be noted that only single representative values of glass compositions for Lake Van tephra layers are reported, which cannot illustrate the whole range of glass compositions of these tephras.

**POP7 and ‘not defined’ glasses (not identified).** – The tephra population POP7 and glasses that could not be defined here potentially originate from eruptives of central and eastern Anatolian volcanic centres as well (Fig. 10). Unfortunately, the current, very limited proximal glass chemical database does not allow any conclusive correlation with our cryptotephra-derived glass data set.

**Implications for the Lateglacial chronology of the Dead Sea record**

The Lateglacial is of particular interest for palaeoclimate research at the Dead Sea because several strong lake level drops occurred between the Last Glacial Maximum highstand of Lake Lisan and the Holocene low-level of the Dead Sea. However, the last glacial–interglacial transition (LGIT) could not be studied for its entire duration before the ICDP deep drilling because of the lack of exposed sediments dating to this time. This gap particularly concerns the sedimentological and hydro-climatic signature of the Greenland Stadial 1 (GS-1) in the Levantine region, which is under debate (Stein et al. 2010).

The oldest Holocene Dead Sea sediments comprise the ‘Early Holocene salt section’ that has been radiocarbon-dated in marginal shallow cores to between 10 and 11 cal. ka BP (Stein et al. 2010). In the ICDP core, this Early Holocene salt is evident at ~71 to 88.5 m sediment depth (Figs 1C, 11). No radiocarbon or U–Th ages exist from this section of the core, but a ~75-cm-thick turbidite directly below is radiocarbon-dated at its base at 89.25 m b.l.f. to 11 440 ± 119 cal. a BP (Neugebauer et al. 2014; Kitagawa et al. 2017), supporting an age for the start of the salt sequence of ~11 cal. ka BP in the marginal cores (Stein et al. 2010) if significant reworking of the dated sample is excluded. So far, the only available age estimates for the LGIT in the ICDP core are from below a massive gypsum deposit at ~91–92 m b.l.f. (Fig. 11); a 14C age of 14 144 ± 110 cal. a BP retrieved from the base of a ~15-cm-thick turbidite at 92.06 m b.l.f. (Neugebauer
et al. 2014; Kitagawa et al. 2017) and an U–Th isochron age of 14 067±1140 a BP measured on aragonite at 92.20 m b.l.f. (Torfstein et al. 2015). These ages suggest deposition of this gypsum unit, labelled as ‘Additional Gypsum Unit’ (AGU) in the Masada section by Torfstein et al. (2013a), during Greenland Interstadial 1a-c. In contrast, our tephrochronological correlation provides evidence for a ~1000-years younger bottom-age of the gypsum deposit. Volcanic glass shards directly below the gypsum deposit (tephra horizons TH(92.00) and TH(92.55)) correlate with products of the Süphan swarm eruptions, which have been varve-dated at between 12 740 and 13 078 varve years BP in the Lake Van core (V8–V15 tephra layers) (Schmincke & Sumita 2014). Furthermore, we are confident that glass shards found at ~93 m b.l.f. in the ICDP core (TH(93.30))
correlate with those of the V-16 tephra layer in Lake Van, originating from an eruption of Nemrut Volcano at \( \sim 13.8 \) cal. ka BP (Schmincke & Sumita 2014). Our revised age for the gypsum deposit in the core further agrees within dating uncertainties with U–Th ages of \( \sim 13\)–14.5 ka BP for the corresponding onshore ‘Additional Gypsum Unit’ that has been dated at the M1 section in Masada and the PZ1 section in Perazim Valley (Figs 1B, 11; Torfstein et al. 2013a) and Perazim Valley (PZ1 section; Haase-Schramm et al. 2004). va = varve years. [Colour figure can be viewed at www.boreas.dk]

Further implies that the major lake level decline did not occur at the onset of the Lateglacial interstadial as previously assumed (Torfstein et al. 2013a) but only at around the transition to the Younger Dryas. Consequently, also previous interpretation of the Younger Dryas as a wet period in the Levant (Stein et al. 2010) must be questioned. An arid Younger Dryas as indicated by gypsum deposition is in accord with the observed coupling between millennial-scale lake level declines of the Dead Sea and cold Heinrich events in the North Atlantic (Torfstein et al. 2013b). This would reconcile the apparent contradiction of the Younger Dryas as the only cold period in the North Atlantic causing lake level rise (Stein et al. 2010) rather than decline of the Dead Sea. Furthermore, an arid Younger Dryas in the Levant is congruent with a dry eastern Mediterranean (Rossignol-Strick 1995) and major lake level lowering in Lake Van (Landmann et al. 1996; Wick et al. 2003) during that time.
Conclusions

In the Lateglacial (~11–15 cal. ka BP) time interval of the ICDP Dead Sea core, we have identified numerous cryptotephra horizons, from at least three different sources of Italian, Aegean and Anatolian volcanic centres. First glass geochemical data suggest that the majority of volcanic ash in the Dead Sea sediments originates from eruptions of the Anatolian volcanic provinces. Even though proximal Anatolian tephra data (glass shard analyses) for comparison are still limited, the identification of cryptotephra in the long Dead Sea record provides novel opportunities to advance the tephrostratigraphical framework in this region, e.g. not only through synchronizing the Dead Sea and Lake Van (eastern Anatolia) sediment records, but also with archaeological and palaeoenvironmental sites that are currently investigated in the Levant and in Arabia. Furthermore, the glass composition-based correlation of tephra populations in the Dead Sea with well-dated Lateglacial tephras of the Suphan and Nemrut volcanoes at Lake Van enabled us to improve the chronology of the Dead Sea record significantly, in a critical time-window for better understanding the hydroclimatic conditions in the region during abrupt climate changes at the end of the last glacial. The results of this study pave the way for extending the tephra work at the Dead Sea, and for synchronization with other important palaeoclimate records in the Mediterranean region, like Lago Grande di Monticchio, Italy, Lake Ohrid, Albania/Macedonia, Tenaghi Philippion, Greece, and Lake Van, Turkey.

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Author contributions. – IN, DM and MJS developed the project idea, and performed the sampling and sample preparation. IN and OA analysed glass shards using EPMA. Data evaluation was done by IN, DM, SB, CSL and SW. IN and AB wrote the manuscript with contributions from all co-authors.

Data availability statement. – Data of this article will be publicly available on PANGAEA.

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