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Journal of Ecology and Natural Resources

ISSN: 2578-4994

Calcareous Tufa Deposition in Connection with Late Pleistocene Abrupt Warming Events

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Short Communication

Volume 5 Issue 2

Received Date: March 30, 2021

Published Date: April 27, 2021

DOI: 10.23880/jenr-16000236

Abstract

Based on the comparison between the U/Th dates of samples obtained by different authors and the trend of the 180/160 ratios in the MIS 4-3-2 interval, this short note investigates the relationships between the deposition of calcareous tufa and surface temperature changes. The data analysis indicates that the deposition is decidedly favoured with rising temperatures, as happened repeatedly during the abrupt thermal rises of the Dansgaard-Oeschger events. The above observations confirm the role of climate-induced anomalies of surface/ground thermal gradients in controlling calcareous tufa deposition rates.

Keywords: Calcareous Tufa; Climate Change; Thermal Gradient

Introduction

Calcareous tufa or freshwater travertine is commonly deposited by spring water fed by limestone aquifers, in swamps and lakes, or at stream knickpoints and waterfalls where it builds dams up to several tens of meters high. These features, whose remains are widespread in limestone areas [1], consist of massive bodies of phytothermal travertine [2], encrusted over remnants of mosses and algae which contribute through respiration and photosynthesis to water spraying degassing of CO₂ and CaCO₃ precipitation [3]. Behind tufa dams, swampy-lacustrine clayey deposits with peaty levels and alternations of phytoclastic travertine layers and buried soils are locally present [4]. The growth of tufa dams occurs where the deposition rate of calcium carbonate from water is high enough to balance the streamflow erosion [5].

There is general agreement in referring to climate controls the deposition of calcareous tufa, particularly the

aggradation/erosion of tufa dams during geological times. Warm/wet climates are believed to favor tufa aggradation because of higher levels of biogenic CO₂ in soil layers, resulting in higher rates of limestone dissolution [6], higher air temperature at the springs favoring water outgassing [7], and absorption of CO₂ by aquatic plants [2]. Conversely, cold/dry climates are considered to be less favorable for CaCO₃ deposition due to: (1) reduction of biological activity in soils; (2) lower air temperatures at the springs; and (3) lesser development of aquatic plants [8,4].

A further model to explain the increase/decrease of tufa deposition rates refers to anomalies of thermal gradients between the ground surface and the limestone aquifer induced by climate changes [9]. Because of the low thermal conductivity of the rocks Vasseur, et al. [10] and the related slow ground penetration of thermal changes, reversed thermal gradients with differences of temperature up to several degrees may be produced between the ground surface and the underlying bedrock over timescales ranging

from years to thousands of years in relation to thermal change magnitude and the aquifer thickness [11]. With climatic changes to warmer conditions, such as that which occurred at the Pleistocene-Holocene transition, water percolating through progressively colder layers in the vadose belt and the phreatic zone undergoes a progressive enrichment in dissolved CaCO_3 [12,5]. At the emergence, because of higher surface temperatures, the spring water becomes over-saturated with CaCO_3 inducing deposition of tufa at waterfalls, knick-points, or on the river bed itself. Tufa aggradation may continue for a long time, even if with progressively lower deposition rates, till the thermal disturbance's exhaustion in the ground. Opposite effects, such as deposition of dissolved carbonate in the upper bedrock fractures and emergence of "aggressive" spring waters, under-saturated with CaCO_3 , should be expected with climate shifting to cold conditions.

The rapid growth of tufa dams observed in both East Africa and Europe during the Holocene with changes from cold to warm temperatures and the fall of tufa deposition rates at warm to cold transition [13-15] provide some support to the above model.

Investigations carried out in different parts of the world indicates that deposition of calcareous tufa also occurred in earlier Quaternary times, especially during the Interglacials, typically characterized by warm temperatures [16-19,8]. However, a more limited deposition of calcareous tufa was also recognized during the last glacial period by different authors (see Table 1).

This short note aims to investigate in detail the relationships between climatic changes and tufa deposition during the Late Pleistocene (MIS 4-3-2), a time interval characterized by the occurrence of several very cold periods known as Heinrich (H) events [20,21] and much warmer periods named Dansgaard-Oeschger (D-O) events [22,23] inducing abrupt increases of surface temperature up to 15°C [24-26] and related advances of arboreal vegetation cover [27].

Climate Changes during the MIS 4-3-2

The so-called "marine isotope stages" (MIS) are periods of Earth evolution showing a specific trend of the $^{18}\text{O}/^{16}\text{O}$ ratio ($\delta^{18}\text{O}$) in atmospheric and marine water, continental ice, and organic carbonates, indicating moments with different global temperatures and climates. MIS 4, 3, and 2 are interposed between MIS 5, the last interglacial period, and MIS 1, the

present interglacial, the Holocene in the geological scale. MIS 3 is a relatively warmer interval lasting approximately 30 ka, between ca. 59.5 and 29.5 ka BP; MIS 4 (ca. 71 - 57 ka BP), and MIS 2 (ca. 29.5 - 14 ka BP) correspond to cold stadial events, the latter including the Last Glacial Maximum (LGM), ca. 24 ka BP [28,24,29,25].

In the MIS 4-3-2 interval, six major Heinrich (H) events have been recognized, ending at about 16.8 (H1), 24 (H2), 31 (H3), 39.5 (H4), 48.5 (H5), and 59.9 (H6) ka BP, and at least 17 Dansgaard-Oeschger (D-O) events at about 14 (D-O 1), 22.8 (D-O 2), 27.5 (D-O 3), 28.6 (D-O 4), 32 (D-O 5), 33.8 (D-O 6), 35 (D-O 7), 38.8 (D-O 8), 39.4 (D-O 9), 41.5 (D-O 10), 43.4 (D-O 11), 46.8 (D-O 12), 48.8 (D-O 13), 54.5 (D-O 14), 56.8 (D-O 15), 59.5 (D-O 16), 59.9 (D-O 17), and 64.5 ka BP [30,31]. The "Younger Dryas" cold event (12.8 - 11.5 ka BP) could be considered as the last Heinrich event [32]. Not all of these events were of identical magnitude and total duration that was, for each whole cycle, probably around 1–2 kyr long on average [32]. During the D-O events, the sea-surface temperatures increased by ca. 4–6°C, resulting in a reinforcement of the thermohaline circulation and the Gulf Stream; the surface temperatures in the northern Atlantic Ocean were perhaps slightly colder than the present ones but much warmer than during the full glacial conditions [33,32].

Research Methods

In this research, we compare a large number of U/Th dates of calcareous tufa (excluding those related to thermal waters) obtained by different authors in the Mediterranean region over the 71 - 14 ka BP interval (MIS 4-3-2) with the $\delta^{18}\text{O}$ and related surface temperatures record provided by the Greenland ice-sheet coring [31] and the abundance of foraminifera (*Globigerina Bulloides* and *Neogloboquadrina Pachyderma*) in cores drilled from the bottom of the Atlantic Ocean [34].

More specifically, we have examined all the U/Th tufa dates available in scientific publications regarding nine countries from the northern hemisphere (Ethiopia, Egypt, Hungary, Israel, Italy, Morocco, Spain, Sweden, and the United States of America), omitting those with uncertainty intervals greater than one-fifth of the central value. Thus, we have obtained a list of 102 dates to which we have added two other unpublished dates from Central Italy, provided by the Environmental and Isotope Geochemistry Laboratory of Roma Tre University. The relative information (sampling countries and bibliographic references) is shown in Table 1.

Ethiopia	Moeyersons, et al. [35]
Egypt	Crombie [36] and Smith [37]
Hungary	Sierralta, et al. [38]
Israel	Schwarcz [39] and Kronfeld [40]
Italy	Carrara [41], Carrara [42]; Soligo, et al. [43]; Carrara, et al. [44]; Dramis [45]; Fubelli [4]; Environmental and Isotope Geochemistry Laboratory of Roma Tre University (13)
Morocco	Boudad [46]; Weisrock [47]
Spain	Peña [48]; Martín-Algarra, et al. [49]; Díaz-Hernández and Juliá [50]; Valero-Garcés, et al. [51]; Pérez-Peña, et al. [52]; González-Pellejero, et al. [53]; Peña, et al. [54]; Scotti, et al. [55]
Sweden	Gustavsson and Hogberg [56]
U.S.A.	Lao and Benson [57]; Szabo, et al. [58]

Table 1: Consulted publications and related investigation countries.

Results

By comparing the dates with the distribution of the relevant warm/cold temperatures peaks in the MIS 2-3-4 chronological interval (Table 2), we can observe that

most of tufa deposition (87 out of 104 dates) has occurred during periods of rising temperatures to relatively warm peaks (mostly corresponding with D-O events), after colder intervals, marked in six cases by the occurrence of H events (Figure 1).

Warm Peak 14 ka BP- DO-1	Cold Peak 24.4 ka BP - H2	Cold Peak 38.5 ka BP	50.2 ± 3.7 ka BP (21)
14.0 ± 3.0 ka BP (25) *	25.0 ± 1.8 ka BP (5)	Warm Peak 38.8 BP	Cold Peak 5*-0.2 ka BP
14.1 ± 0.5 ka BP (1)	26.2 ± 1.3 ka BP (21)	38.9 ± 2.1 ka BP (6)	Warm Peak 50.5 ka BP
14.2 ± 2.7 ka BP (7)	Warm Peak 27.5 ka BP- DO-3	Cold Peak 39.2 ka BP – H4	50.7 ± 2.5 ka BP (5)
15.4 ± 0.3 ka BP (15)	27.7 ± 4.9 ka BP (15)	Warm Peak 39.4 ka BP– DO-9	Cold Peak 51.4 ka BP
15.7 ± 1.3 ka BP (10)	Cold Peak 28 ka BP	40.5 ± 2.1 ka BP (6)	53.0 ± 2.0 ka BP (22)
15.8 ± 1.1 ka BP (1)	Warm Peak 28.6 ka BP- DO-4	Cold Peak 40.5 ka BP	Warm Peak 54.5 ka BP- DO-14
16.0 ± 0.7 ka BP (17)	28.7 ± 1.4 ka BP (1)	Warm Peak 40.8 ka BP	55.0 ± 6.0 ka BP (13)
16.1 ± 0.1 ka BP (26)	29.4 ± 1.6 ka BP (6)	41.0 ± 2.0 ka BP (23)	55.0 ± 9.0 ka BP (20)
16.3 ± 1.7 ka BP (26)	Cold Peak 29.5 ka BP	41.8 ± 3.1 ka BP (5)	55.9 ± 9.1 ka BP (15)
16.5 ± 1.5 ka BP (7)	29.9 ± ka BP (14)	42.0 ± 5.5 ka BP (7)	Cold Peak 56 ka BP
16.6 ± 0.7 ka BP (26)	Warm Peak 30 ka BP	42.5 ± 6.0 ka BP (15)	Warm Peak 56.8 ka BP- DO-15
16.8 ± 0.5 ka BP (14)	30.2 ± 5.5 ka BP (15)	Cold Peak 42.5 ka BP	57.0 ± 5.5 ka BP (7)
Cold Peak 16.8 ka BP – H1	30.9 ± 0.5 ka BP (26)	Warm Peak 43.4 ka BP- DO-11	57.3 ± 3.0 ka BP (26)
16.9 ± 1.2 ka BP (26)	Cold Peak 31 ka BP – H3	43.9 ± 1.5 ka BP (19)	57.4 ± 5.5 ka BP (8)
Warm Peak 17.5 ka BP	31.8 ± 1.1 ka BP (1)	44.0 ± 1.0 ka BP (22)	57.5 ± 5.3 ka BP (9)
17.8 ± 0.1 ka BP (26)	Warm Peak 32 ka BP- DO-5	Cold Peak 44.2 ka BP	Cold Peak 57.5 ka BP
17.8 ± 0.5 ka BP (22)	32.1 ± 1.3 ka BP (15)	44.4 ± 1.0 ka BP (1)	Warm Peak 58 ka BP
17.9 ± 1.0 ka BP (10)	Cold Peak 32.2 ka BP	45.0 ± 2.0 ka BP (26)	58.5 ± 4.0 ka BP (8)
18.1 ± 0.1 ka BP (26)	32.4 ± 0.6 ka BP (26)	Warm Peak 45.5 ka BP	Cold Peak 59 ka BP
18.1 ± 0.2 ka BP (26)	33.0 ± 5.0 ka BP (26)	45.7 ± 1.6 ka BP (18)	Warm Peak 59.5 ka BP- DO-16
18.1 ± 0.2 ka BP (26)	Warm Peak 33.8 ka BP	46.3 ± 3.0 ka BP (26)	Cold Peak 60 ka BP – H6
18.4 ± 0.6 ka BP (26)	33.9 ± 1.9 ka BP (15)	46.0 ± 4.2 ka BP (5)	Warm Peak 59.9 ka BP- DO-17

19.0 ± 3.0 ka BP (7)	34.0 ± 3 ka BP (8)	46.0 ± 5.0 ka BP (12)	Cold Peak 60 ka BP
19.0 ± 2.0 ka BP (25)	34.3 ± 1.3 ka BP (15)	46.0 ± 6.0 ka BP (11)	61.0 ± 1.3 ka BP (16)
19.3 ± 1.0 ka BP (10)	34.3 ± 2.2 ka BP (10)	Cold Peak 45.8 ka BP	Cold Peak 61.2 ka BP
19.5 ± 1.0 ka BP (26)	34.4 ± 1.3 ka BP (26)	46.5 ± 2.9 ka BP (5)	Warm Peak 62.8 ka BP
20.2 ± 0.1 ka BP (26)	Cold Peak 34.4 ka BP	Warm Peak 46.8 ka BP- DO-12	Cold Peak 63.5 ka BP
20.3 ± 1.4 ka BP (14)	Warm Peak 35 ka BP- DO-7	47.3 ± 3.6 ka BP (5)	Warm Peak 64.5 ka BP- DO-18
20.4 ± 0.1 ka BP (26)	35.0 ± 3.0 ka BP (26)	48.0 ± 3.0 ka BP (26)	62.3 ± 3.0 ka BP 26)
21.2 ± 1.7 ka BP (21)	35.0 ± 3.2 ka BP (15)	48.0 ± 6.5 ka BP (7)	64.8 ± 4.5 ka BP (11)
Cold Peak 21.2 ka BP	35.2 ± 1.2 ka BP (10)	48.4 ± 0.7 ka BP (15)	67.0 ± 5.6 ka BP (13)
21.6 ± 4.3 ka BP (15)	35.5 ± 0.4 ka BP (24)	Cold Peak 48.5 ka BP - H5	68.0 ± 1.0 ka BP (25)
21.9 ± 0.3 ka BP (26)	36.2 ± 1.0 ka BP (15)	Warm Peak 48.8 ka BP- DO-13	68.0 ± 2.0 ka BP (2)
22.5 ± 0.4 ka BP (1)	Cold Peak 37 ka BP	49.0 ± 2.0 ka BP (5)	68.0 ± 6.0 ka BP (20)
22.6 ± 1.3 ka BP (6)	37.4 ± 2.0 ka BP (15)	49.0 ± 2.0 ka BP (25)	69.2 ± 4.3 ka BP (15)
Warm Peak 22.8 ka BP- DO-2	Warm Peak 38 ka BP- DO-8	49.5 ± 5.0 ka BP (25)	69.3 ± 2.2 ka BP (15)
23.2 ± 1.3 ka BP (10)	38.2 ± 2.7 ka BP (15)	49.8 ± 0.1 ka BP (3)	
24.4 ± 1.6 ka BP (10)	38.4 ± 1.6 ka BP (15)	50.0 ± 2.0 ka BP (26)	

Table 2: Tufa dates and surface temperature cold/warm peaks in the MIS 2-3-4 chronological interval. All dates have been reset to one decimal place. *The numbers in brackets refer the consulted publications in Table 1.

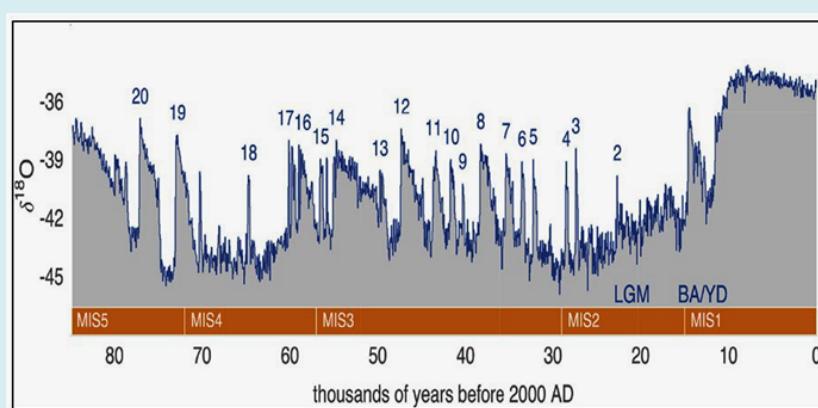


Figure 1: Variation of $\delta^{18}\text{O}$ during the MIS 1 to MIS 5 intervals from the Greenland ice-sheet coring. The top numbers mark the Dansgaard-Oeschger (D-O) events; LGM and BA/YD indicate the Last Glacial Maximum and the Bølling-Allerød/Younger-Dryas transition, respectively. after Li and Benson 2019.

Concluding Remarks

Despite the intrinsic approximation of the cold/warm peak ages and the uncertainty ranges of the tufa dates, sometimes too high in relation with the considered cold-warm intervals, the distribution of their central (most probable) values indicates how the deposition of calcareous tufa has occurred, above all, during the transition intervals from the cold peaks to the warm ones, even in the case of significantly low surface temperatures, commonly considered not favorable to the deposition of calcareous tufa.

Many dates are located just after the thermal minima in the rising temperature trends.

On the contrary, definitely less frequent are tufa deposition dates in the same ranges of surface temperatures but with a cooling climate trend. It is interesting that the number of tufa dates is quite high even in MIS 2, in decidedly colder climatic conditions. Without questioning the general control of temperature and aridity on the deposition of calcareous tufa [59,8,14], the comparison between the tufa dates and the $^{18}\text{O}/^{16}\text{O}$ ratios trend in the MIS 4-3-2 interval

indicates that the deposition of calcareous tufa is more active with rising surface temperatures [60]. The above observations seem to confirm further the role of climate-induced anomalies of surface/ground thermal gradients in controlling the rates of calcareous tufa deposition [61,62].

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