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Cuprins

STUDII // MATERIALE // NOTE

RECENZII // PREZENTĂRI DE CARTE

The transition from the Mediaeval Warming Period to the Little Ice Age in northeastern Romania (Târgu Neamț, *La Damian* Site)

Geanina A. Butiseacă[1,2*], Vasile Diaconu[3],
Maria Ilie[4], Iuliana Vasiliev[2]

Abstract. The European mediaeval climate was marked by important continental-scale changes in temperature and moisture availability, with a direct impact on human communities. The drastic changes in climate conditions during the Mediaeval Climatic Optimum to the Little Ice Age and the associated transition between the two have been extensively investigated in western Europe and depicted in historical records through literature or art; however, little information is available for Eastern Europe. The present study focuses on a Mediaeval archaeological site in NE Romania (Târgu Neamț – *La Damian*) from the XIVth century to assess the changes associated with the transition between the two major events. We analysed biomarkers from the sedimentary record coupled with previously published charcoal and archaeobotanical remains. Our data indicate a fluctuating temperature with a regional pattern for this time interval, marked by two slightly colder episodes (as low as 7 °C) and two important warmings (up to ~11.3 °C), three degrees more than the present-day average of 8.2 °C. The warming episodes were associated with changes in moisture and vegetation, with the greatest impact on cultivated plants (i.e. cereals and beans), indicating that climatic conditions impacted the community and food availability in the region.

Keywords*:* biomarkers, temperatures, vegetation, Middle Ages, Eastern Carpathians, Romania.

Tranziția de la perioada medievală de încălzire la Mica Eră Glaciară în nord-estul României (Târgu Neamț, situl *La Damian*). Climatul european medieval a fost marcat de importante schimbări de temperatură și umiditate la scară continentală, cu impact direct asupra

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comunităților umane. Schimbările climatice drastice care au avut loc în Optimul Climatic Medieval și Mica Eră Glaciară, precum și în perioada de tranziție asociată, au fost cercetate exhaustiv in Europa vestică și ilustrate în sursele istorice prin artă sau literatură, însă pentru Europa estică nu există multe informații privitoare la acestea. Studiul de față se focusează pe un sit arheologic medieval din nord-estul României (Târgu Neamț-*La Damian*), din secolul al XIV-lea, pentru a analiza schimbările asociate cu tranziția dintre cele două evenimente majore. Astfel, am analizat biomarkeri extrași din arhiva sedimentară, la care am adăugat datele rezultate din analiza cărbunilor si arheobotanică analizate anterior. Rezultatele obținute indică o temperatură variabilă și cu un pronunțat caracter regional pentru acest interval temporar, cu două episoade mai reci (până la 7°C) și două episoade calde (până la 11,3°C), cu trei grade peste media de 8,2°C din prezent. Episoadele cu temperaturi mai ridicate sunt asociate cu schimbări importante în umiditate si vegetație, cel mai mare impact fiind înregistrat asupra plantelor cultivate (cereale și boboase), ceea ce indică un impact climatic major asupra producției de hrană și a comunităților din zonă.

Cuvinte cheie: biomarkeri, temperaturi, vegetație, Evul Mediu, Carpații Orientali, România.

……………………

1. Introduction

The last millennium is one of the most dynamic periods in recent human history, with important changes in all aspects of society, but also in terms of climate. This period is marked by two major climate anomalies: the Mediaeval Warming Period (MWP) and the Little Ice Age (LIA), which mainly affected the northern hemisphere. The first represents a preindustrial natural phase of pronounced warming between ~900-1300 AD, with an estimated increase in global temperatures of ~1°C (Luterbacher *et alii* 2016). MWP is followed by intense cooling (~1400-1800 AD) by up to 1.4°C, although the detailed temperature evolution differs among the various continent-wide or hemispheric reconstructions (Lüning *et alii* 2019). Here we build upon the available charcoal and archaeobotanical record (Butiseacă, Diaconu 2021) and provide further organic geochemistry data (i.e., mean annual air temperature, pH, BIT index, vegetation composition and distribution) to constrain the short scale climate evolution in NE Romania (Eastern Europe) during the MWP – LIA transition.

2. Material and Methods

2.1. Stratigraphy and age

La Damian site (47°12’30.76” N; 26°21’9.25” E) is located in the western side of Târgu Neamț city in NE Romania and it was part of the city mediaeval urban center (**Fig. 1A**). Its position is between Neamț river plain (possibly flooded in the past) and Pleșu Hill (**Fig. 2B**), both acting as source areas for sediments. In this study, we are focusing on the remains of a dwelling that was excavated in 2021. The entire excavated sedimentary succession is ~ 75 cm thick, with the best preservation on the northern side. It consists of a mix of detrital elements (in the upper half) and multiple levels of building fillings with organic remains and mudbrick fragments (in the lower part). The filling contains several layers of burned organic matter (Butiseacă, Diaconu 2021) covered by alluvial sediments and modern debris. The sampling was focused on the archaeological horizon; therefore, the upper part of the profile was not analysed.

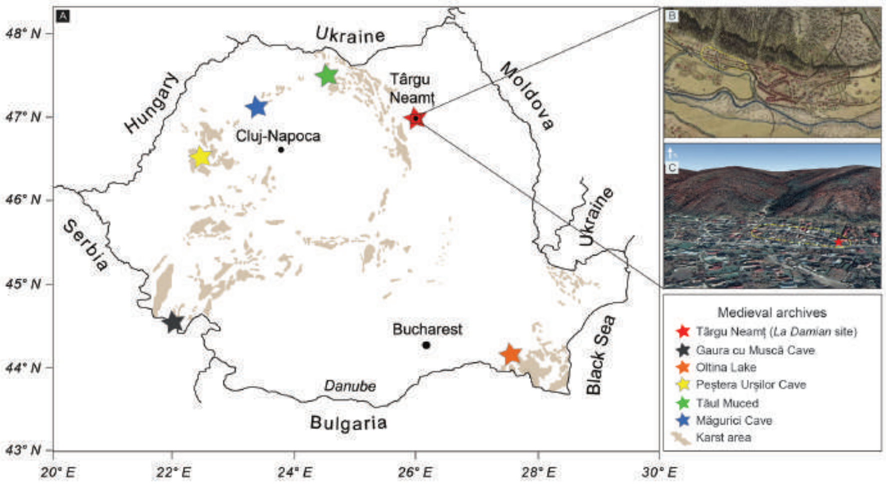

Fig. 1. Map showing the location of Târgu Neamț *La Damian* site and other mediaeval archives (panel A). Base map modified after Onac *et alii* (2015). In the right site of the figure is depicted the exact location of the site on a mediaeval map (B; *maps.arcanum.com*) and today (C). With coloured stars are marked the location of other available records.

Fig. 1. Hartă care arată localizarea sitului *La Damian* Târgu Neamț și altor arhive medievale (panoul A). Harta este modificată după Onac *et alii* (2015). În partea dreaptă a figurii este marcat locul exact al sitului pe harta medievală (B; *maps.arcanum.com*) și în prezent (C). Cu simboluri colorate sunt marcate locurile celorlalte înregistrări.

The present organic material mainly consists of cereals and wood fragments (Butiseacă, Diaconu 2021). Several *Vicia faba* beans, which are dominant in the upper part of the filling, were dated from sample P2_N at the Horia Hulubei National Institute for Physics and Nuclear Engineering Research (RoAMS Laboratory) in Romania in 2022.

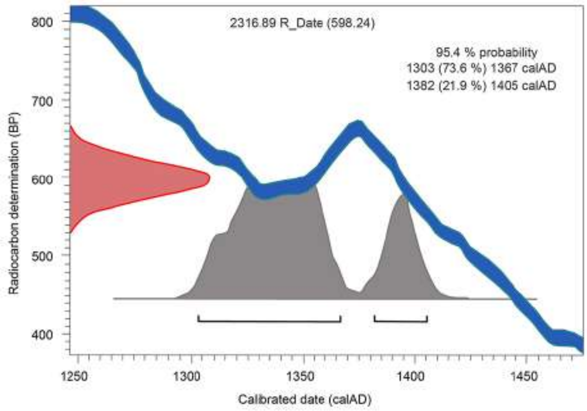

Fig. 2. Radiocarbon dating report ($\delta^{14}C$) based on *Vicia faba* seeds.
Fig. 2. Raportul de datare cu radiocarbon ($\delta^{14}C$) bazat pe semințe de *Vicia faba*.

2.2. Organic geochemistry

2.2.1. Lipids extraction and measurements

Five sediment samples were collected from the stratigraphic succession of an inhabited area from *La Damian* site (Târgu Neamț, Romania): four from the northern wall (P1_N, P2_N, P5_N and P3_N samples) and one from the eastern wall (P4_E). The samples were further dried, weighed, and manually ground. Lipids were extracted using a Soxhlet apparatus with a mixture of dichloromethane and methanol 7.5:1 (*v:v*) and pre-extracted cellulose thimbles. The extracts were evaporated to near dryness under continuous N_2 flow using a TurboVap LV. Subsequently, elemental sulphur was removed from the total lipid extracts (TLE) using Cu shreds activated with 10% HCl. The vials containing TLE, activated Cu, and magnetic rods were placed on a rotary table for ~20 hours. Subsequently, the TLEs were filtered over a Na_2SO_4 column. The remaining solvents were evaporated using N_2. The desulphurization step was repeated until no reaction with the Cu was observed. Up to 50% of the TLE was archived while the rest was further separated into fractions containing different lipids using Al_2O_3 column chromatography.

The polar fraction containing glycerol dialkyl glycerol tetraether lipids (GDGTs) was dissolved in a 1 ml mixture of *n*-hexane (*n*-hex)/isopropanol (IPA)-(99:1, *v:v*) and slightly dispersed using an ultrasonic bath (~ 10s/sample), then filtered over a 0.45 mm PTFE filter using a 1 ml syringe. Polars were measured using an HPLC Shimadzu, UFLC performance, double column; eluents *n*-hex (A) and IPA (B) coupled with an ABSciex 3200 QTrap chemical ionization mass spectrometer (HPLC/APCIeMS) at the Senckenberg Biodiversity and Climate Research Centre (SBiK-F) in Frankfurt am Main, Germany. For each sample, a 5 ml injection volume was used, and GDGTs detection was achieved through single ion monitoring. Branched GDGTs quantification was performed using the Analyst software, and the peaks were integrated manually for each sample multiple times. The average value was calculated for the samples with multiple integrations.

The apolar fraction containing *n*-alkanes was measured using Gas Chromatography-Mass Spectrometry (GC-MS) at the Senckenberg Biodiversity and Climate Research Centre (SBiK-F) in Frankfurt using a ThermoScientific Trace GC Ultra - DSQII equipped with a HP-5MS column (30 m × 0.25 nm × 0.25 μm). The GC oven was held at 70°C for 1 min, ramped at 10°C/min to 180°C (5 min. hold), ramped at 3°C/min to 320°C (15 min. hold). *N*-alkanes were identified by comparing their retention time and mass spectrum to an external standard (n-C_7 to n-C_{40}; Supelco) and quantified using peak areas calibrated against the corresponding standard peak. Peak assessment and quantification were performed using the Thermo Xcalibur 2.2 SP1.48 software.

2.2.2. Mean annual air temperature calculation and soil pH

Mean air annual temperature (MAAT) estimations are based on the relative distribution of brGDGT membrane lipids originating in the soil and catchment area. For MAAT and soil pH calculation, we used the calibration of de Jonge *et alii* (2014) where:

MAAT’ = 7.17 + (17.8 × GDGT Ia) + (25.9 × GDHT Ib) + (34.4 × GDGT Ic) – (28.6 × GDGT IIa)

pH = 7.15 + 1.59 × CBT’

CBT’ is expressed as:

CBT= log10 ((GDGT Ic + GDGT IIa’ + GDGT IIb’ + GDGT IIc’ + GDGT IIIa’ + GDGT IIIb’ + GDGT IIIc’) / (GDGT Ia + GDGT IIa + GDGT IIIa))

where GDGT I - GDGT III are branched GDGTs.

Root Mean Square Error (RMSE) of biomarker-based MAAT is ~4.6 °C.

2.2.3. BIT Index

The BIT (Branched and Isoprenoid Tetraethers) index defines the terrigenous versus aquatic components of organic input. The BIT index is the ratio of the three major brGDGTs (mostly terrigenous) to isoGDGT crenarchaeol (aquatic) (Hopmans *et alii* 2004):

BIT= [(GDGT-I) + (GDGT-II) + (GDGT-III)] /
[(crenarchaeol) + (GDGT-I) + (GDGT-II) + (GDGT-III)]

Crenarchaeol is a compound derived from Thaumarchaeota (Sinninghe Damsté *et alii* 2002) and is abundant mostly in the water column, although in small percentages it can also occur in soils (Weijers *et alii* 2007). BrGDGTs are highly abundant in terrestrial settings, including soils and peats (Hopmans *et alii* 2004; Peterse *et alii* 2012). BIT values close to 1 indicate a predominantly terrigenous source, whereas low values (close to 0) indicate a strong aquatic source of organic matter (Schouten *et alii* 2013).

2.2.4. N-alkanes ratios

N-alkanes were identified and quantified using a known external standard mixture (Alk C_7 – C_{40} – Supelco 49452-U, 1000 ng/µl) using the Xcalibur software. In order to identify *n*-alkanes sources and distribution we have calculated two ratios: average chain length (ACL; Gagosian, Peltzer 1986) and carbon preference index (CPI; Marzi *et alii* 1993), respectively.

$ACL = ((C_{21} \times 21) + (C_{23} \times 23) + (C_{25} \times 25) + (C_{27} \times 27) + (C_{29} \times 29) + (C_{31} \times 31) + (C_{33} \times 33)) / (C_{21} + C_{23} + C_{25} + C_{27} + C_{29} + C_{31} + C_{33})$;

$CPI = ((C_{23} + C_{25} + C_{27} + C_{29} + C_{31}) + (C_{25} + C_{27} + C_{29} + C_{31} + C_{33})) / (2 \times (C_{24} + C_{26} + C_{28} + C_{30} + C_{32}))$

3. Results

3.1. ^{14}C dating

The estimated calibrated ages (**Fig. 2**; 2σ 95.5% probability) indicate a match of 73.6% for the age of 1303-1367 AD and a match of 21.9% for the age of 1382-1405 AD, placing the analysed samples in the 14th century. Automatically, the samples below the dated interval are slightly older, whereas the samples above are slightly younger. Additionally, the ceramic fragments found at the site are specific to the second half of the 14th century, while coins from the other two excavated dwellings were placed in the same period (Bătrîna, Sion 2006) based on the depiction of Petru the Ist ruler (1375-1391 BC). Overall, the site covers most of the 14th century and the beginning of the 15th, a time frame known as the transition from the Mediaeval Warming Period to the Little Ice Age, both with global consequences.

3.2. Mean annual air temperature

In the northern profile, MAAT values vary between 7.14°C and 11.27°C, with an average value of 9.09°C (**Fig. 3**; **Table 1**). The lowest value is registered at the base of the profile (– 0.7 cm; P1_N sample), followed by a warming of 4.2°C, reaching the maximum registered in the section (– 0.7 cm; sample P2_N). The temperature drops again after this sample to 8.01°C (– 0.55 cm, P5_N sample), then increase once more to 11.01°C at the top of the profile (– 0.50 cm, P3_N sample). Overall, MAAT follows a warming trend from the base towards the top. Sample P4_E from the eastern profile (– 0.7 cm stratigraphically) has a value of 8.05°C.

3.3. Soil pH estimates

pH values correspond to slightly alkaline soils with values between 7.20 and 7.46 and an average value of 7.36 (**Fig. 3**; **Table 1**). The pH is following the same trend as the temperature (MAAT), with lower values when colder and higher values when warmer.

3.4. BIT index

BIT values range from 0.43 (sample P5_N) to 0.73 (sample P4_E) (**Fig. 3**; **Table 1**). BIT values correlate positively with MAAT and pH curves and follow a general decreasing trend towards the top.

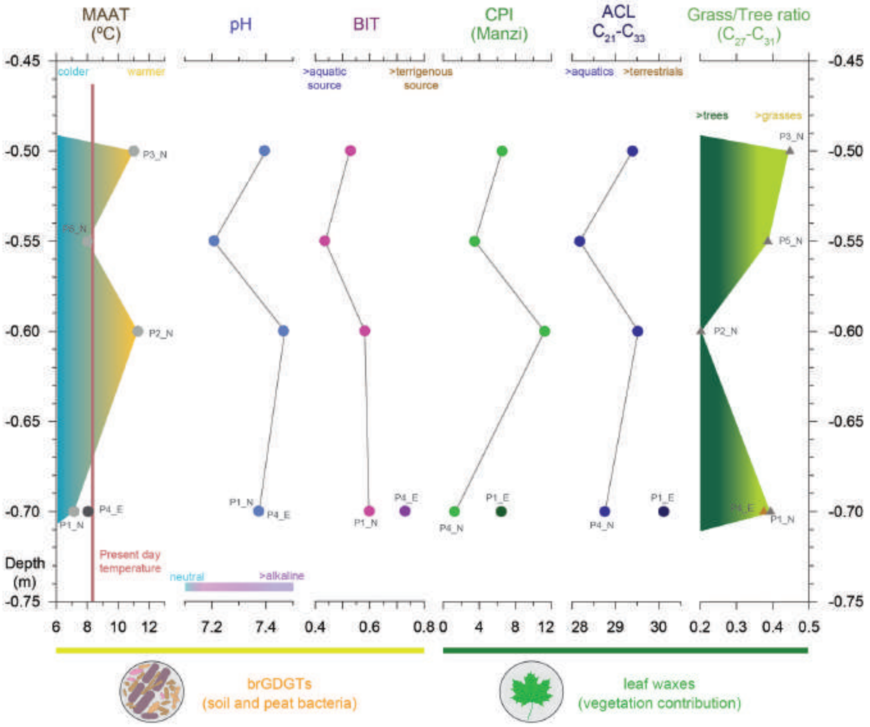

Fig. 3. Biomarker results from *La Damian* site: MAAT = mean annual air temperature; pH = acidity or alkalinity; BIT index = Branched and isoprenoid tetraether index; CPI = carbon preference index; ACL = average chain length. Below the graphs is marked the provenance of biomarkers: with yellow of branched GDGTs (brGDGTs) and with green the leaf wax.
Fig. 3. Rezultatele biomarkerilor de pe situl *La Damian*: TMA = temperatura medie anuală; pH = aciditate sau alcalinitate; BIT index = indexul tetraetherilor ramificați și izoprenoizi; CPI = indicele de preferință pentru carbon; ACL = lungimea medie a lanțurilor de *n*-alkani. La baza graficelor este marcată proveniența biomarkerilor: cu galben – brGDGT, iar cu verde – ceruri din frunze.

Sample name	Str. level (m)	MAAT	pH	BIT	CPI	ACL (C_{21}-C_{33})	Grass/Tree ratio C_{27}/C_{31}
P3_N	-0.50	11.01	7.77	0.53	6.54	29.39	0.45
P5_N	-0.55	8.01	7.34	0.43	3.48	28.17	0.39
P2_N	-0.60	11.27	7.75	0.58	11.26	29.52	0.20
P1_N	-0.70	7.14	7.54	0.60	6.44	30.12	0.39
P4_E	-0.70	8.06	7.50	0.73	1.26	28.75	0.38

Table 1. GDGTs and leaf wax derived proxies for *La Damian* site (Târgu Neamț).
Tab. 1. Date derivate din GDGT și ceruri de pe frunze pentru situl *La Damian* (Târgu Neamț).

3.5. *N*-alkanes indices

The *n*-alkanes chain lengths of the analysed samples from *La Damian* site range between C_{19} – C_{35}, with dominant C_{25} – C_{35} chains (**Fig. 4**, **Table 2**). Shorter (< C_{19}) or longer (>C_{36}) chain lengths were below the detection limit (**Fig. 4**). CPI varies between 1.25 and 11.26, with an average value of 5.97. The values show high variability, especially towards the base of the profile. ACL fluctuates between 20.17 and 30.11, with a mean value of 29.19 (**Fig. 4**; **Table 2**). The general trend indicates an increase in terrigenous components towards the top, except for sample P5_N (the minimum value), which has an increased aquatic component source of organic matter. The grass vs. tree ratio (grass/tree ratio; C_{27} – C_{31}) shows a dominance of open land vegetation (shrubs and grasses) around the site. Only one sample indicates the dominance of trees in the catchment area (P2_N) (**Fig. 4**; **Table 2**).

N-alk number	P3_N sample	P5_N sample	P2_N sample	P1_N sample	P4_E sample
C_{19}		4E+07			
C_{20}		9E+07	4E+07		6E+07
C_{21}		2E+08	9E+07		1E+08
C_{22}		1E+08	5E+07		9E+07
C_{23}		1E+08	6E+07		8E+07
C_{24}		1E+08	5E+07	1E+07	8E+07
C_{25}	2.7E+08	1E+08	1E+08	2E+07	6E+07
C_{26}	1.2E+08	8E+07	5E+07	7E+06	3E+07
C_{27}	5.6E+08	2E+08	4E+08	3E+07	1E+08
C_{28}	1.5E+08	8E+07	1E+08	1E+07	4E+07
C_{29}	1.3E+09	6E+08	2E+09	9E+07	2E+08
C_{30}	1.8E+08	1E+08	1E+08	6E+06	5E+08
C_{31}	1.3E+09	6E+08	2E+09	7E+07	3E+08
C_{32}	9E+07	5E+07	6E+07	4E+06	3E+07
C_{33}	2.9E+08	1E+08	2E+08	8E+07	2E+08
C_{34}	4.8E+07	2E+07	5E+07	4E+06	3E+07
C_{35}	6.6E+07	3E+07	5E+07	7E+06	4E+07

Table 2. Distribution of *n*-alkanes for each sample.
Tab. 2. Distribuția *n*-alkanilor pentru fiecare probă.

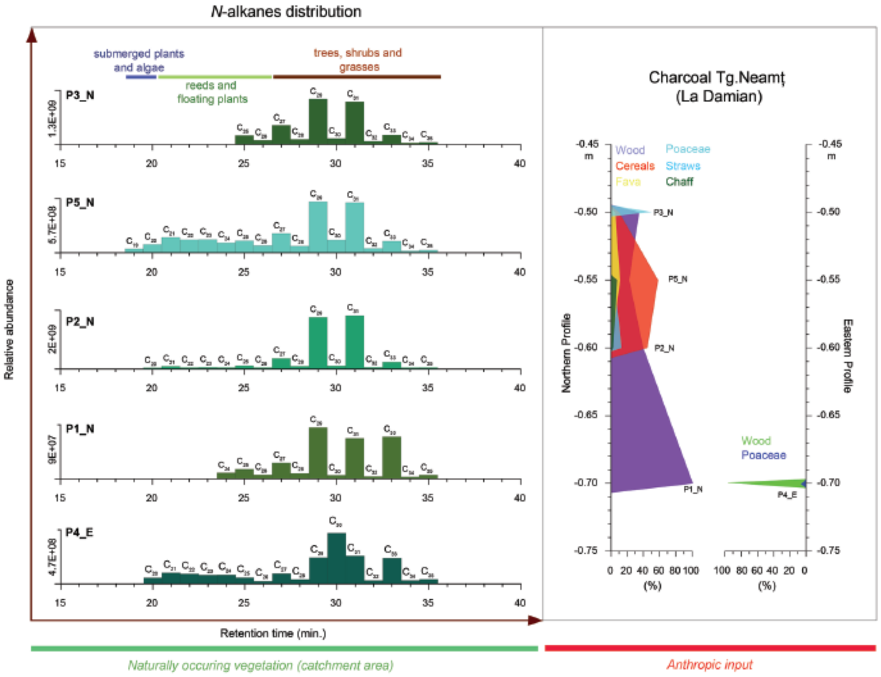

Fig. 4. *N*-alkanes most probable sources and distribution for *La Damian* site (left panel) and charred material (right panel) previously described in Butiseacă, Diaconu (2021). The two panels show the natural vegetation vs. the anthropic input of vegetation on the archaeological site.

Fig. 4. Sursele probabile și distribuția de *n*-alkanilor pentru situl *La Damian* (panoul stâng) și materialul ars (panoul din dreapta) descris anterior de Butiseacă, Diaconu (2021). Cele două panouri arată distribuția vegetației naturale *versus* antropice de pe sit.

4. Discussion

4.1. Temperature variability and consequences over food availability

According to the National Meteorology Administration[5], present day mean annual air temperature in Târgu Neamț area is 8.2°C, with cold winters rich in solid precipitations and mild to hot summers, specific to the moderate temperate-continental climate in the region. The values obtained for the *La Damian* site are either lower or higher than present-day values (**Fig. 4**), indicating a highly fluctuating climate during the MWP – LIA transition, with an amplitude of ~4.3°C.

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[5] www.meteoromania.ro

Our data reveal two cooling peaks (P1_N and P5_N), as well as two important warmings (samples P2_N and P3_N). The sedimentary succession starts with MAATs as low as 7°C (first cooling peak, sample P1_N; – 0.7 m). This interval corresponds approximately to the mid-14th century, which in the northern hemisphere correlates with the end of a temperature drop induced by a decrease in solar activity (i.e., the end of the Wolf minimum solar excursion; **Fig. 5**).

The record continues with a warming, reaching the maximum in the section of ~11.3°C (first warming event, sample P2_N; – 0.6 m), three degrees warmer than the present day temperature (**Fig. 4, 5**). The previously analysed charcoal and archaeobotanical material (Butiseacă, Diaconu 2021) shows that cereals found in this particular layer are poorly developed and show numerous traces of insect activity, indicating that the crops were affected by an intense drought. Poor crops would have had a major impact on the local population, most likely causing famine.

Further up in the record (sample P5_N), the temperature drops again up to ~8°C (second cooling event). The pH and BIT values are also decreasing implying an increase in humidity/precipitations, as well as a dominant aquatic source of organic matter. The charred material described by Butiseacă, Diaconu (2021) shows an increase in cereal production for this time interval, as well as a better seed quality. The last sample in the profile shows a second increase in temperature (~11°C) correlated yet again with a decrease in cereal/food quality, but less than the previous one.

Famine is a common theme for 14th century Europe, with couple of episodes between 1315-1390 AD of different extent and consequences, overlapped by bubonic plague (Ruiz 1996). Bad weather and failed crops are recorded mainly in northern and western Europe (William 1996), but the *La Damian* site suggests this was a recurrence in the NE Romania as well. Positive temperature fluctuations in a short time have affected the capacity of crops for development (i.e. cereals and beans), leading to local food shortages. A food crisis could have potentially caused conflictual situations. Successive fire episodes (at least four) over the analysed dwelling remains (Butiseacă, Diaconu 2021) might suggest an intentional cause. Records of famine in the Romanian and Balkan space for this time period are usually mentioned as being associated with war (Tofan 2003); for example, ottoman invasion of the Balkan Peninsula in 1371 (Bănescu 1946) or the Mongol invasion and expansion in Europe (13th-14th centuries; Ducas 1956), which in turn were the consequence of the prolonged warming during the MWP and the droughts it provoked in Eurasia. The life expectancy in Romanian territories between the 14th-16th centuries was between 23-28 years (Cernovodeanu 1993).

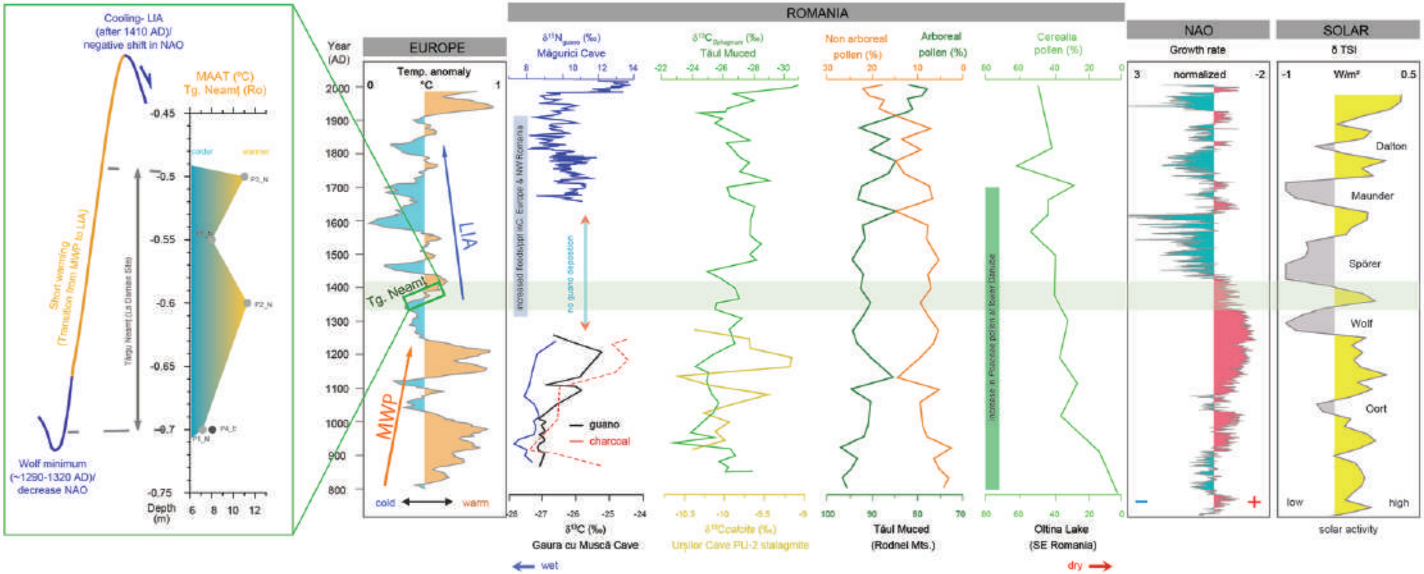

Fig. 5. MAAT data from *La Damian* site and summarised mediaeval records from literature.

From left to right: European summer land temperature curve (Luterbacher *et alii* 2016); δ^{14}C$_{guano}$ in Măgurici Cave (western Carpahians, Romania; Cleary *et alii* 2017); δ^{13}C$_{guano\ and\ charcoal}$ Gaura cu Muscă Cave (southern Carpahians, Romania; Onac *et alii* 2015); δ^{13}C$_{Sphagnum}$ Tăul Muced bog (northern Carpahians, Romania; Feurdean *et alii* 2015); δ^{13}C$_{calcite}$ Urșilor Cave (western Carpahians, Romania; Onac *et alii* 2014); Arboreal and non-arboreal pollen percentages (Tăul Muced bog (northern Carpahians, Romania; Feurdean *et alii* 2015); Cereals pollen from Oltina Lake (southern Romania; Feurdean *et alii* 2021); NAO (Baker *et alii* 2015), and solar activity changes with named minima (Steinhilber *et alii* 2012). European summer land temperature, NAO and solar activity plots are modified after Lüning *et alii* (2019). On the figure is marked with a blue band the increase in precipitations based on Starkel *et alii* 2002 and Chiriloaiei *et alii* 2012, while with green band is marked the increase in Poaceae pollen in south Romania (Feurdean *et alii* 2021).

Fig. 5. TMA pentru situl *La Damian* și arhive medievale sumarizate din literatură.

De la stânga spre dreapta: temperatura europeană în timpul verii (Luterbacher *et alii* 2016) ; δ^{14}C$_{guano}$ în Peștera Măgurici (Carpații vestici România; Cleary *et alii* 2017); δ^{13}C$_{guano\ and\ charcoal}$ în Peștera Gaura cu Muscă (Carpații sudici; România); δ^{13}C$_{Sphagnum}$ în mlaștina Tăul Muced (Carpații de nord România; Feurdean *et alii* 2015); δ^{13}C$_{calcite}$ Peștera Urșilor (Carpații vestici România; Onac *et alii* 2014); procentajele de polen arboricol și non-arboricol (mlaștina Tăul Muced, Carpații de nord România; Feurdean *et alii* 2015); Polen de cereale din Lacul Oltina (sudul României; Feurdean *et alii* 2021); NAO (Baker *et alii* 2015) și activitatea solară (Steinhilber *et alii* 2012). Temperatura europeană în timpul verii și activitatea solară sunt modificate după Lüning *et alii* (2019). Cu bandă albastră sunt marcate precipitațiile după Starkel *et alii* 2002 și Chiriloaiei *et alii* 2012, în timp ce cu bandă verde este marcată creșterea de polen de Poacee în sudul României (Feurdean *et alii* 2021).

4.2. Vegetation composition and sources

Chain length distribution in a sample is expressed through average chain length (ACL; Gagosian, Peltzer 1986) and carbon preference index (CPI; the ratio of odd-over-even *n*-chain lengths; Marzi *et alii* 1993). Homologues with chain lengths shorter than *n*-C_{21} are produced by aquatic elements such as algae and submerged plants, whereas higher homologues (*e.g.*, *n*-C_{21} to *n*-C_{25}) are produced by macrophytes, reeds, and mosses. Chain lengths above *n*-C_{27} have as source herbaceous plants and trees (Ficken *et alii* 2000). The abundance of C_{27} – C_{35} chain lengths indicates that the main sources of *n*-alkanes in the *La Damian* record are terrestrial plants, subsequently semi-aquatic plants, and rare submerged ones (**Fig. 3, 4**). The grass/tree ratio (C_{27} – C_{31}) indicate a dominance of grasses in the catchment for most of the record (**Fig. 3**), except for sample P2_N, where woody elements (i.e., trees) are dominant. If we look at the *n*-alkanes distributions (**Fig. 4**) we can see differences. At the base of the profile, sample P4_E (– 0.7 m) *n*-alkanes contribution suggest the presence of both aquatic and terrestrial flora. Sample P1_N (also – 0.7 m, but ~2 m distance; northern wall of the dwelling/main profile) still preserves some aquatic signal, but significant are terrestrial elements (most abundant C_{29}, C_{31} and C_{29} – wood). Samples P2_N (– 0.6 m) and P5_N (– 0.55 m) show again the presence of both aquatic and terrestrial elements, while the last sample (P3_N; – 0.45 m) shows a clear abundance of terrestrial elements.

Remarkably, the *n*-alkane composition is strictly matching the temperature fluctuations only at the upper part of the profile (P3_N; **Fig. 4**). In the rest of the record, the vegetation lags the changes in temperature and humidity, indicating fast changes in the environment, possibly seasonal or annual, between samples. In the case of the last sample, the climatic conditions seem to be more stable, possibly over a longer time period (*i.e.*, decadal scale). Sediments from this layer show a higher thickness as well. Additionally, the site location close to the riverbed makes it prone to flooding. In this case, the river course could change rapidly and advance towards the site (resulting in increased humidity), or the water could stagnate for longer periods of time, resulting in the development of local small ponds or marshy areas, hence the aquatic signal. The *n*-alkanes specific to woody elements and other grasses could have as origins the higher elevations areas around the site as Neamț river is draining all the hilly area north and west of the site. Overall, the *n*-alkanes composition at the site location shows a local source indicated by the dominance of aquatic and semi-aquatic taxa (specific to the river plain) and a more regional one, indicated by the higher chain lengths (trees and shrubs).

Combusted material found on the site (Butiseacă, Diaconu 2021) shows also a strong anthropogenic input of vegetation, mainly through cereals (*e.g.*, *Triticum aestivum, Hordeum vulgare, Avena sativa*), beans (*i.e.*, *Vicia faba*) and fragments of various woody elements (conifers and deciduous). While the cereals and beans were cultivated in-situ (or close by), the wood provenance is probably the forest in the hilly area north of the city (*i.e.*, Pleșu Hill) indicating a similar forest composition with the present day.

4.3. MWP – LIA Transition in Romania vs. Europe

La Damian record is the first in literature able to quantify directly climatic events from the second half of 14th century Romania in an archeological record, identifying two warming peaks (P3_N and P2_N; 3 °C more than present day MAAT) associated with the transition from MWP to LIA, suggesting milder climatic conditions at the site location.

Mediaeval climatic records are scarce in Romania (*e.g.*, Cleary *et alii* 2017; 2018; Onac *et alii* 2014; 2015), continuous ones even scarcer (*e.g.*, Feurdean *et alii* 2015; 2021) (**Fig. 5**). The carbon isotopic composition of calcite ($\delta^{13}C_{calcite}$) in cave formations in Urșilor Cave (PO-2 stalagmite; Onac *et alii* 2014) and nitrogen and carbon isotopic compositions of bat guano ($\delta^{15}N_{guano}$; $\delta^{13}C_{guano}$) in Măgurici and Gaura cu Muscă caves from the western and southern Carpathians (**Fig. 5**) show a gap in the sediment records from ~1300 AD to ~1650 AD (Onac *et alii* 2014: 2015; Cleary *et alii* 2017) in the caves. The multiproxy analysis of the ombrothrofic bog Tăul Muced from the Rodnei Mountains (north Romania; Feurdean *et alii* 2015) also shows a dried mire surface between 1300-1450 AD, suggesting dry conditions in the Carpathian Mountains at high altitudes. Additionally, a decrease in arboreal pollen is registered in the Rodnei Mountains for the same interval, and an increase in non-arboreal taxa (**Fig. 5**; Feurdean *et alii* 2015).

Geomorphological, sedimentological and tree fossils analyses of Moldova river plain (the next big river north of Neamț; Chiriloaei *et alii* 2012) show an intensification of floods after ~1300 AD, which infers a significant increase in precipitations in the Eastern Carpathians. Temperature reconstructions on tree rings in the Călimani Mountains (west of Târgu Neamț; Popa, Kern 2009) show that major cooling in the area took place after 1370 AD (1370-1630 AD). Our data from the *La Damian* site also indicate a lag in cooling on the eastern periphery of the Carpathians, suggesting decoupling of the Eastern Carpathians from other mountainous regions (*e.g.,* Alps; Popa, Kern 2009) caused by variations in large-scale atmosphere circulation patterns (Feurdean *et alii* 2015; Cleary *et alii* 2017), both latitudinal and elevation induced (Hurell, Loon 1997).

The main driver of the long-term European climate is the North Atlantic Oscillation (NAO, Baker *et alii* 2015; Lüning *et alii* 2019), which is modulating the North Atlantic storm track, thus controlling the changes in temperature and precipitations over the continent. The positive phase of NAO (NAO+) induces dry winters over southern and Eastern Europe, whereas the negative phase (NAO–) wet winters. Europe was under prolonged NAO+ between ~900-1400 AD (Baker *et alii* 2015), resulting in dry and warm conditions (**Fig. 5**). The end of this period is overlapping with the development of the *La Damian* archaeological site. Its position in Eastern Europe and on the margin of the Carpathian orogeny induced a strong regional pattern over the temperature record, explaining the +3°C (relative to present day) temperature anomaly at the site location for the second half of the 14th century.

Overall, the analysed data from Romanian archives slightly differ with the periodicity of the hydro-climatic records in the rest of Europe due to regional climatic differences (Feurdean *et alii* 2015), suggesting a diachronic transition from MWP to LIA in eastern Europe.

5. Conclusions

Our biomarker record from the *La Damian* site (Târgu Neamț, NE Romania) is the first palaeoclimatic reconstruction from an archaeological site in Romania and covers most of the 14th century, which represents the transition from MWP to LIA in Eastern Europe. The transitional phase at the site location is not uniform but registers two slightly colder peaks (MAAT as low as 7 °C) and two warming ones (MAAT up to 11.3°C), indicating an overall 3°C warmer climate than the present day 8.2°C, under a positive NAO influence. The warming phases are associated with poor quality crops, showing a direct correlation between high temperatures and drought effects on food availability in the region. The *n*-alkanes distribution and ratios register a local signal dominated by herbaceous and swamp vegetation, overlapped by a more regional/higher altitude signal dominated by forest.

Collectively, the *La Damian* site supports the climatic decoupling of the Carpathian area from the rest of Europe during the MWP – LIA transition, process that occurs diachronically at continental scale due to regional differences in atmospheric circulation patterns and topography.

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