The ‘Roxolany Tephra’ (Ukraine) – new evidence for an origin from Ciomadul volcano, East Carpathians

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Abstract

We present major element glass data and correlations of the ‘Roxolany Tephra’ – a so far geochemically unconstrained volcanic ash layer previously described in last glacial (MIS2) loess deposits of the Roxolany loess-palaeosol complex in the SW Ukraine. This exceptionally well preserved, 2-3 cm thick tephra layer is characterised by a rhyolitic glass composition that is comparable to that of proximal tephra units from Ciomadul volcano in the East Carpathians, central Romania. The chemistry particularly matches that of the final LSPA pyroclastic fall unit of St. Ana crater that is radiocarbon dated in the proximal Mohoș coring site (MOH-2) at 29.6±0.62 cal ka BP. The age of the tephra correlative is in agreement with the newest radiocarbon and IR-OSL age constraints from overlying palaeosols and tephra-embedding loess of the Roxolany sequence, respectively, which place the tephra between ca. 33 and 24 cal ka BP, and thus confirm the long-debated chronostratigraphy of this important
environmental archive. The occurrence of a distal Ciomadul tephra ca. 350 km east of its source indicates a great potential of further tephra and cryptotephra findings from this volcanic complex in the south-eastern Mediterranean and Black Sea region.

1. Introduction

The loess-palaeosol complex near the village of Roxolany in the SW Ukraine (Fig. 1) provides an almost complete Pleistocene terrestrial sedimentary record and is therefore the most representative sequence for the reconstruction of long-term palaeoclimatic and environmental changes in the Northern Black Sea region. The ca. 48 m thick Roxolany loess-palaeosol sequence was first studied by P. Gozhik with his research team (Putievoditel, 1976; Gozhik et al., 1995), demonstrating its potential for palaeoenvironmental reconstruction on the basis of granulometric, mineralogical, palaeomagnetic, palaeontological (molluscs, mammal fauna) analyses as well as radiocarbon and Thermoluminescence (TL) dating. Within these first studies, the authors suggested that the Brunhes/Matuyama magnetic reversal (ca. 780 ka) is in the lower part of the profile. Later, Tsatskin et al. (1998) provided a detailed description, proposing a revised stratigraphic interpretation of the loess-palaeosol horizons and palaeomagnetic data, and their correlation with the marine oxygen isotope stages (MIS). The authors re-identified the Brunhes/Matuyama boundary in the middle part of the section in loess unit L6 at ca. 35 m depth of the Roxolany loess-palaeosol complex, which now enabled a solid correlation with other loess profiles in Europe and China (e.g. Tsatskin et al., 2001; Dodonov et al., 2006; Gendler et al., 2006; Faustov et al., 2009).

Tsatskin et al. (1998) were the first to describe a macroscopic visible tephra (volcanic ash fall) layer, the so-called ‘Roxolany Tephra’, within the initially proposed L3 loess unit (corresponding to MIS 12, i.e. the period from 450 to 400 ka; Sartori, 2000). Tephra, in general, are useful chronological and/or synchronisation markers in terrestrial and marine palaeoenvironmental archives, if correlated via glass geochemical fingerprinting with known and dated volcanic events (e.g. Lowe, 2011). Loess-palaeosol complexes in the Middle and Lower Danube Basin have proven the preservation of tephra in different stratigraphic positions, although their chemical compositions, and thus their precise ages, were often poorly constrained due to the strong alteration of volcanic glass shards under the prevailing humid to semi-humid temperate climate (e.g. Horváth, 2001; Panaiotu et al., 2001; Fitzsimmons et al., 2013; Veres et al., 2013; Marković et al., 2015). Fedorowicz et al. (2012) provided a first detailed description of the mineralogical components of the Roxolany Tephra and suggested a
possible genetic link with Carpathian volcanic activity. However, this assumption still lacked the geochemical and chronological evidence from proximal and other distal tephra deposits. Many years of comprehensive research focusing on Roxolany have brought up a number of new, partially contradictory data in the chronostratigraphic diagnosis of the upper three loess units (Fig. 2), and, implicitly, the timing of tephra deposition varied depending on such interpretations (Putivnyk, 2000; Gozhik et al., 2007; Boguckyi et al. [eds], 2013; Gozhik, 2013). According to the latest data, the ‘Roxolany Tephra’ is embedded within the Bug loess (bg) from the upper Pleniglacial of the Weichselian glaciation (MIS 2) (Gozhik et al., 2007) (Fig. 2). It is overlain by two palaeosol layers of an interphase or interstadial rank, the Prychornomorsk (pc) and the Dofinivka (df) units, that have recently been radiocarbon dated at ca. 23.0 cal ka BP and 34.0 cal ka BP, respectively (Fedorowicz et al., 2012; Łanczont et al., 2015; this study Fig. 2, Table 1). The palaeosol underlying the tephra-bearing bg loess, the Vytachiv (vt) unit, has been attributed to the middle Pleniglacial (MIS 3) and is AMS radiocarbon dated between ca. 21.3 and 25.6 cal ka BP (Fedorowicz et al., 2012; Łanczont et al., 2015; this study Fig. 2, Table 1). The vt unit developed on the Uday (ud) loess, which is correlated with MIS 4 (Fig. 2). Infrared optically-stimulated luminescence (IR-OSL) dates of loess samples from ca. 9 m below the tephra revealed an age of 33.1±2.6 ka (Fedorowicz et al., 2012; this study Table 3), supporting both the radiocarbon-based chronology and the stratigraphic scheme developed by Gozhik et al. (1995; 2007). Further attempts to directly date phenocrysts of the Roxolany Tephra, however, led to unrealistically old ages of 50±3 Ma (40Ar/39Ar; Tsatskin et al., 1998; Sartori, 2000) and 11.83-14.54 Ma (K/Ar on amphibole and biotite; Fedorowicz et al., 2012).

In this study, we provide the first geochemical glass data of the ‘Roxolany Tephra’ and a solid correlation scheme with its dated volcanic source in order to (1) clarify the younger chronostratigraphy of the Roxolany loess-palaeosol complex, and (2) extend the tephrostratigraphic framework in south-eastern Europe with the principal aim of providing means for comparing various records on a wider scale.

2. Samples and methods

2.1 Roxolany sampling site

The Roxolany outcrop is situated on the eastern bank of the Dniester estuary, about 40 km southwest of Odessa and ca. 1.5 km northwest of the village of Roxolany (Ukrainian: Roksolany), SW Ukraine (46°10'N, 30°27'E) (Fig. 1). The ca. 48 m thick loess-palaeosol complex crops out along the ‘Zayach’ya Balka’ gully, which is deeply incised into the
sedimentary mantle of the VII Dniester terrace containing the late Tamanian mammal complex (Chepalyga, 1967; Putivnyk, 2000; Gozhik et al., 2007; Gozhik, 2013). A sample was taken from the 2-3 cm thick, white-greyish tephra layer that occurs in the third upper loess unit at ca. 9.5 m depth (Fig. 2).

2.2 Ciomadul proximal samples

Potential sources for the Roxolany Tephra encompass nearby Eastern Mediterranean volcanoes, e.g. the Aegean Arc (ca. 1100 km to the SSW), southern Italian volcanic provinces (ca. 1500 km to the SW), Anatolian volcanoes (ca. 900-1300 km to the SSE and SE), and the East Carpathians volcanic complexes (i.e. Ciomadul, ca. 350 km to the W) (Fig. 1). Late Quaternary tephrostratigraphies of Eastern Mediterranean volcanoes have been well constrained during the past decades (e.g. Keller et al., 1978; Federman and Carey, 1980; Deniel et al., 1998; Kuzucuoglu et al., 1998; Druitt et al., 1999; Narcisi and Vezzoli, 1999), while a detailed tephrostratigraphic framework of the East Carpathians is still in its infancy. Here, the Ciomadul volcanic massif in Romania, which is among the few candidates with Quaternary eruptions, is proposed to be the site of the youngest activity in the Carpatho-Pannonian Region. The timing of its activity is confined either to the past 1 Ma (Szakács et al., 2015) or only to the past 250-200 ka (Karátson et al., 2013; Harangi et al., 2015) and requires further studies. The Ciomadul volcanic massif is located in the South Harghita Mountains at the southernmost tip of the 140 km-long Călimani-Gurghiu-Harghita (CGH) volcanic range, representing the south-eastern part of the Miocene to Pleistocene volcanic range of the East Carpathians (e.g. Seghedi et al., 2004, Pécskay et al., 2006). Compared to other parts of the calc-alkaline Neogene Carpathian volcanic region, complex, subduction-related, post-collisional volcanism occurred along the CGH (Mason et al., 1998; Chalot-Prat and Gîrbacea, 2000; Seghedi et al., 2004), which is characterised by an obvious along-arc migration from the northwest to the southeast since ca. 10 Ma (Pécskay et al., 1995, 2006). The Ciomadul volcanic massif is a dome complex built on top of folded and thrustsed Cretaceous flysch sediments. Its central edifice (Ciomadul Mare, 1301 m a.s.l.) is truncated by two explosion craters: the older Mohoş crater peat bog in the east and the younger St. Ana crater lake in the west (Fig. 1). The latest volcanism at the Ciomadul/South Harghita volcanic complex produced pyroclastic deposits and lavas of fairly homogeneous high-K dacitic bulk-rock composition with a typical enrichment in incompatible trace elements (e.g. Szakács and Seghedi 1986; Szakács et al., 1993; Mason et al., 1998), and a main mineral assemblage of plagioclase, amphibole, biotite, occasional clinopyroxene, quartz, K-feldspar, orthopyroxene
and olivine (e.g. Szakács and Seghedi, 1986; Mason et al., 1998; Kiss et al., 2014). However, in contrast to the bulk rock composition, the first volcanic glass chemical data obtained by Vinkler et al. (2007) on a pumiceous pyroclastic sequence near Bâile Tușnad indicate a more evolved (rhyolitic) composition of juvenile clasts.

A new and comprehensive tephrostratigraphic study has now been undertaken to characterize the glass compositions of numerous (>100) pyroclastic fall deposits from Ciomadul’s latest activity in proximal and medial-distal settings around the volcanic complex and to provide solid chronostratigraphical constraints. The first results have revealed at least three eruptive stages from, probably, the Mohoș and St. Ana craters producing tephra of distinct rhyolitic glass compositions (Karátson et al., 2016): The Early Phreatomagmatic and Plinian Activity (EPPA) at ≥51 ka - 43 cal ka BP, the Middle Plinian Activity (MPA) at ca. 31.5 cal ka BP and the Latest St. Ana Phreatomagmatic Activity (LSPA) at ca. 29.6 cal ka BP. Representative tephras from each eruptive stage have been chosen for this study to undertake a detailed geochemical comparison with the Roxolany Tephra (Fig. 5). Single-grain glass chemical data of these selected samples are published in Karátson et al. (2016) and are, additionally, presented here in the Supplementary Information. Representative samples include two pyroclastic fall units from an outcrop along community road no. 113, ca. 0.5 km W of Turia village and 11 km ESE of Lake St. Ana (hereafter referred to as “TUR-2” locality). This exposure at an abandoned gas pipeline reveals a basal, >1.5-m-thick stratified tuff and tuffaceous sand sequence (unit TUR-2.1) overlain by loess and loessy sands that are intercalated by a ca. 10-cm-thin pumiceous lapillistone bed (unit TUR-2.2) (Karátson et al., 2016). On the basis of major element glass chemical data of pumices from both pyroclastic units it was possible to assign unit TUR-2.1 to the early phase of the EPPA stage (≥51 ka) and unit TUR-2.2 to the ‘TGS’ pumice fall eruption of the MPA stage at ca. 31.5 cal ka BP (Karátson et al., 2016). Two further tephra layers were sampled from a lacustrine sediment sequence from the central part of the Mohoș crater (Fig 1). Core MOH-2 was retrieved by a UWITECH piston corer in 2014 and encompasses a ca. 30m-long sequence of Holocene peat (ca. 10 m) and last glacial lacustrine deposits that are intercalated with several dm-thick, coarse primary and reworked tephra layers. The two uppermost tephra layers at 1521.5-1544 cm and 1552-1564 cm depth, namely samples RO-1/2/3 and RO-4/5, are interpreted as primary fall layers that correspond to the LSPA (ca. 29.6 cal ka BP) and MPA eruptive stages (ca. 31.5 cal ka BP), respectively (Karátson et al., 2016). Last but not least, we obtained geochemical glass data of coarse pumice fragments from the basal part of the St. Ana lake
core SZA-2013 from 1605-1612 cm depth. The SZA-2013 core retrieval also used a UWITECH piston corer and encompasses a total of 1700 cm of lacustrine sediments (Magyari et al., 2014; Karátson et al., 2016). The coarse pumice layers in the lowermost part of the sequence are interpreted as re-deposited pyroclastic material from the final (LSPA) eruption that formed the recent St. Ana crater, indicating that core SZA-2013 likely reached the bottom of the lacustrine deposits (Magyari et al., 2014).

2.3 Radiocarbon dating

Radiocarbon (AMS) dating of the Roxolany Tephra’s over- and underlying palaeosols of interphase or interstadial rank included ten organic soil samples, and was performed at the Poznan Radiocarbon Laboratory, Poland. All palaeosols represent dry steppe soils with A-Bk profiles and are affected by pedogenetic processes (i.e. rubification) of different degrees. Two samples were taken from the humus horizon of the palaeosol within the pc loess unit at 4.05 m (sample Roksolany 1) and 4.25 m depth (Roksolany 2). Three samples were collected from the underlying humus horizon of the upper df1 palaeosol at 6.75 m (Roksolany 3) and 6.85 m depth (Roksolany 4, 4a), and two samples from the lower df2 palaeosol at 7.05 m depth (Roksolany 5, 5a) (Table 1, Fig. 2). The humus horizon of the vt palaeosol (underlying the Roxolany Tephra) was sampled for radiocarbon dating at 20.2 m (Roksolany 6), 20.4 m (Roksolany 7) and 20.7 m depth (Roksolany 8). Radiocarbon dating results are published in Łanczont et al. (2015), but have been re-calibrated and presented as 2σ ranges in Table 1.

AMS-14C dating of the MOH-2 core (Mohoş crater, Ciomadul) was carried out at the University of Cologne (CologneAMS), Germany, and encompassed three measurements on charcoal and bulk sediments above tephra RO-1/2/3 (two samples at 1369-1371 cm and 1519-1521.5 cm depth) and below tephra RO-4/5 (one sample at 1591-1593 cm depth), respectively (Table 2). All samples were pre-treated according to Rethemeyer et al. (2013), with the graphite targets measured by the accelerator mass spectrometry (AMS) at the University of Cologne.

Radiocarbon ages of the Roxolany and MOH-2 sequences were converted into calendar ages using the OxCal programme v4.2.2 (Bronk Ramsey 2008, 2009; Bronk Ramsey et al., 2013) and the INTCAL13 calibration curve after Reimer et al. (2013), and are presented as calibrated age ranges with a confidence level of 95.4% in calendar years before present (cal yr BP).
2.4 IR-OSL dating

Dating of the Roxolany loess was performed by infrared optically stimulated luminescence (IR-OSL) dating at the Tallinn University of Technology, Estonia (Research Laboratory for Quaternary Geochronology). The luminescence dating method used potassium feldspar grains of the grain size range 100–150 µm. Palaeodose ‘P’ (or equivalent dose ‘D_e’) determinations were made by extrapolating the dose-response curves to zero IR-OSL intensities using the multiple-aliquot additive-dose protocol. Additive-dose growth curves were constructed using natural and ten-laboratory dose points each consisting of measurements of six separate aliquots. Aliquots of each sample were gamma-irradiated using a 60Co source to a maximum dose of 1000 Gy. Preheating of the K-feldspar samples before the measurements was not applied. Instead, we stored samples for about 1 month at room temperature to allow the decay of post-irradiation phosphorescence (for details see Molodkov and Bitinas, 2006). Sediment matrix dose rates for the samples were calculated from the data of laboratory gamma-ray spectrometric analysis. Results of IR-OSL dating are displayed in Table 3.

2.5 Tephrochronological methods

Pumice samples from Ciomadul proximal sites were cleaned in deionized water, dried and crushed with a hammer into smaller grain sizes. The Roxolany Tephra was subsequently treated with a 15% hydrogen peroxide (H_2O_2) and a 10% hydrochloric acid (HCl) solution to remove organic remains and carbonates, respectively. Both Ciomadul and Roxolany tephras were wet-sieved into a 32-125 µm grain size fraction. Dried tephra components were embedded on a slide with Araldit©2020 resin, sectioned by hand on silicon paper, polished and finally carbon coated for electron probe microanalyses (EPMA). The major element compositions of single glass shards were determined using a JEOL-JXA8230 instrument at the GFZ Potsdam using a 15 kV voltage, 10 nA beam current and beam sizes of 5-10 µm, respectively. Exposure times were 20 seconds for the elements Fe, Cl, Mn, Ti, Mg and P, as well as 10 seconds for Si, Al, K, Ca and Na. Instrumental calibration used natural minerals and the rhyolitic Lipari obsidian glass standard (Hunt and Hill, 1996; Kuehn et al., 2011). Glass data are reported in Table 4 (Roxolany Tephra) and in the Supplementary Information (Ciomadul tephras) and are compared in bivariate plots with published EPMA glass data of potential Eastern Mediterranean tephra correlatives (Figs. 4, 5). Back-scattered electron (BSE) images of volcanic glass shards from different grain size fractions (32-63 µm, 63-125 µm and >125 µm) of the Roxolany Tephra were acquired with a
Hitachi TM3000 Tabletop Scanning Electron Microscope (SEM) at Keele University, U.K., using an accelerating voltage of 15 kV.

3. Results

3.1 Composition of the Roxolany tephra

The Roxolany Tephra is a fine-grained ($d_{\text{max}} = 200 \mu\text{m}$) volcanic ash that is dominated by lithic clasts (dacitic rock fragments, clumped particles), phenocrysts (plagioclase, green pyroxene and biotite) and minor amounts of juvenile clasts (Figs. 3A-D). The latter consist of highly vesicular, microlite-rich (feldspars, pyroxenes) pumices (Fig. 3B) and blocky, low-vesicular glass shards (Figs. 3C, 3D), indicative of an origin from a phreatomagmatic eruption. Due to the mean low analytical totals of ca. 94-95 wt%, volcanic glasses are interpreted to be only slightly altered (Table 1). The major element glass composition is calc-alkaline rhyolitic with $\text{SiO}_2$ and $\text{Al}_2\text{O}_3$ concentrations of 75.6-77.6 wt% and 12.9-14.0 wt% (normalized, volatile-free data), respectively. Concentrations of $\text{FeO}$ (0.5-0.9 wt%) and $\text{CaO}$ (0.8-1.1 wt%) are low, and alkali ratios ($\text{K}_2\text{O}/\text{Na}_2\text{O}$) vary between 1.1 and 1.5 (Table 4, Figs. 4, 5).

3.2 Composition of Ciomadul proximal tephras

The representative samples from Ciomadul’s late stage activity reveal three distinct, partly overlapping major element glass compositions that indicate a clear compositional trend of matrix glass from highly evolved phreatomagmatic products (EPPA tephra) followed by the less evolved MPA/TGS pyroclastic units, and, finally, the slightly more evolved LSPA tephras, the latter forming a group that falls compositionally in between the older eruption products (Karátson et al., 2016) (Supplementary Information, Fig. 5). Pumice clasts of all three types are characterized by either a highly vesicular groundmass (MPA/TGS stage) and/or a larger number of microlite inclusions of feldspars, clinopyroxenes, amphiboles and Fe-Ti oxides (EPPA and LSPA stages). Therefore, a thorough evaluation of the major element glass data was required to avoid misinterpretations based on crystal contamination effects on groundmass glass composition. For this reason, beam sizes of EPMA were restricted to relatively small sizes that may have resulted in sodium migration during measurements (slightly higher $\text{SiO}_2$ and lower $\text{Al}_2\text{O}_3$ and $\text{Na}_2\text{O}$ concentrations). However, the instrumental setup, including the beam sizes for EPMA of the Roxolany Tephra and potential Ciomadul correlatives were similar, and thus a reliable comparison of chemical glass data was achieved. In turn, attempts to obtain trace element glass data of both the Roxolany and Ciomadul
proximal tephras by larger-beam (>10 µm) Laser Ablation (LA)-ICP-MS failed so far due to the high vesicularity and/or microlite content of juvenile clasts.

3.2.1 Sample TUR-2.1 (Early phreatomagmatic eruptions of EPPA stage, ≥51 ka)
Unit TUR-2.1 consists of low to medium vesicular pumice fragments that are characterised by a large amount of feldspar and Fe-oxide microlite inclusions. Matrix glass shows a heterogeneous, highly evolved rhyolitic composition, with ranges in concentrations (normalized volatile-free data) in SiO₂ of 76.4-79.7 wt%, Al₂O₃ of 11.5-13.4 wt%, FeO of 0.5-0.8 wt%, CaO of 0.6-1.1 wt% and K₂O/Na₂O of 1.1-1.7 (Fig. 5).

3.2.2 Samples TUR-2.2 and RO-4/5 (Plinian eruption of MPA stage, ca. 31.5 cal ka BP)
Sample TUR-2.2 and tephra layer RO-4/5 in Mohoş core MOH-2, 15.52-15.64 m depth, comprise highly vesicular pumice fragments with a minor microlite assemblage. Volcanic glass of both samples revealed a similar rhyolitic composition that is less evolved than that of the older EPPA sample TUR-2.1. Major element concentrations show ranges in SiO₂ of 70.3-73.9 wt%, Al₂O₃ of 14.7-16.8 wt%, FeO of 0.9-1.6 wt%, CaO of 1.0-2.0 wt% and K₂O/Na₂O of 0.7-1.2 (Fig. 5).

3.2.3 Samples RO-1/2/3 and SZA-2013, 1605-1612 cm (LSPA phreatomagmatic eruption, ca. 29.6 cal ka BP)
The uppermost tephra RO-1/2/3 at 1521.5-1544 cm depth in Mohoş core MOH-2 is a coarse, reversely graded pumice fallout that was deposited in a lacustrine environment. Pumices are slightly blocky-angular, low to medium vesicular and rich in feldspar microlites. The major element glass composition shows a heterogeneous, intermediate rhyolitic composition that is slightly less evolved than that of EPPA-type tephra units with SiO₂ concentrations of 74.7-78.0 wt%, slightly higher Al₂O₃ (12.3-14.0 wt%), FeO (0.3-1.0 wt%) and CaO (0.6-1.1 wt%) values, as well as alkali ratios K₂O/Na₂O of 1.1-1.6. This LSPA-type glass composition is comparable with that of the re-deposited pyroclastic layers from the basal part of the Lake St. Ana sediment core (sample SZA-2013 from 1605 to 1612 cm depth; Fig. 5).

4. Source and associated age of the Roxolany Tephra
The glass composition of the Roxolany Tephra was compared with EPMA glass data of other Late Pleistocene tephras occurring in the Eastern Mediterranean. Calc-alkaline rhyolitic
Tephra were produced from several volcanic centres of the Aeolian (Italy) and Aegean Arcs (Greece), Anatolia (Turkey) and the East Carpathians (Romania) during the considered time span between ca. 50 and 20 ka (Fig. 1). Lipari Island in southern Italy (ca. 1530 km SW of Roxolany), for example, erupted the Monte Guardia rhyolites between 27 and 24 cal ka BP (e.g. Forni et al., 2013). However, this sub-plinian eruption had only limited regional tephra dispersal (e.g. Crisci et al., 1991; Lucchi et al., 2008; Forni et al., 2013), and the respective juvenile pyroclasts show a distinct major-element composition with lower concentrations in SiO₂ and higher FeO concentrations compared to the Roxolany Tephra (Fig. 4). The Lower and Upper Pumices from Nisyros (Aegean Arc, ca. 1100 km SSW of Roxolany) are dated at >50 ka (Margari et al., 2007; Tomlinson et al., 2012; Karkanas et al., 2015) and show a similar glass composition to the Roxolany Tephra except for higher FeO and slightly lower Al₂O₃ values. Both Nisyros tephras have been found as discrete layers in marine sites south of the vent (Keller et al., 1978), but were not identified in northern locations so far except for the Upper Pumice that was recently reported as a cryptotephra within the Theopetra cave where it is stratigraphically overlain by the Pantellerian Y6/Green Tuff, dated at 45.7 ka (Karkanas et al., 2015). In the more proximal marine stratigraphy, the Upper Nisyros Pumice is overlain by the ca. 31 ka Yali-C (Yali-2) tephra (Federman and Carey, 1980), which in turn has a limited regional dispersal and a distinct rhyolitic composition compared to the Roxolany tephra (Fig. 4). The Y-2/Cape Riva tephra (22 cal ka BP) from Thera volcano (Santorini, Aegean Arc, ca. 1150 SSW of Roxolany) has been widely distributed towards the north (>500 km) and the northeast (>700 km) (e.g. Wulf et al., 2002; Kwiecien et al., 2008; Müller et al., 2011). However, the glass chemical composition of the Y-2 tephra is less silicic rhyolitic (Fig. 4), and thus this tephra can be excluded as a potential correlative of the Roxolany Tephra. Anatolian stratovolcanoes and caldera complexes, i.e. Acigöl and Erciyes Dağı (Central Anatolian Volcanic Province (CAVP), ca. 900-950 km SSE of Roxolany), and Süphan and Nemrut Dağı (East Anatolian Volcanic Province (EAVP), ca. 1280 km SE of Roxolany), produced numerous pyroclastic fallout deposits of highly silicic rhyolitic glass compositions during the considered time frame (e.g. Druitt et al., 1995; Deniel et al., 1998; Kuzucuoglu et al., 1998; Sumita and Schmincke, 2013b) (Fig. 4). Especially the MIS2 tephras from Acigöl and Süphan Dağı come close to the major element composition of the Roxolany Tephra (Fig. 4). Those tephras, however, have so far only been recognized close to their volcanic centres (e.g. visible tephra layers from Süphan Dağı in Lake Van sediments; Sumita and Schmincke, 2013a; Schmincke et al., 2014) and potentially as cryptotephra layers (macroscopic non-
visible tephra layers) in south-eastern Black Sea sediments (Cullen et al., 2014) (Figs. 1 and 5). Other CAVP tephras that show compositions comparable to the Roxolany Tephra, e.g. early Holocene deposits from Erciyes Dağı, are dispersed towards the south (Develle et al., 2009; Hamann et al., 2010) and too young to be considered as correlatives.

The large thickness and maximum grain sizes of the Roxolany tephra, however, suggest a rather nearby source, e.g. the Ciomadul volcano in the southern East Carpathians located ca. 350 km W of the Roxolany site. Ciomadul’s latest tephras are dispersed towards the N (e.g. EPPA-stage tephras), the S/SE (both EPPA- and MPA/TGS-stage tephras), and likely towards the E (LSPA-stage tephra) (Karátson et al., 2016). Representative rhyolitic glass compositions of the older EPPA (≥51 ka) and MPA/TGS tephras (ca. 31.5 cal ka BP) are distinct from that of the Roxolany Tephra, with the oldest EPPA tephra (e.g. sample TUR-2.1) being the more evolved (mean high SiO₂ values of ca. 78 wt%) and the MPA/TGS tephra (e.g. samples TUR-2.2 and RO-4/5) the less silicic products (mean SiO₂ concentration of ca. 73 wt%) (Fig. 5). Major-element glass data of the youngest, chemically intermediate LSPA tephra (mean SiO₂ values of 76.5 wt%), e.g. samples RO-1/2/3 and SZA-2013, 1605-1612 cm, in turn, match the glass data composition of the Roxolany Tephra and are here proposed as the correlative pyroclastic deposit (Fig. 5). The phreatomagmatic character, as inferred from low vesicularity pumice fragments, furthermore supports the geochemical evidence, as well as the large thickness and maximum grain sizes of the Roxolany Tephra, which imply a relatively short transport from the St. Ana crater by prevailing westerly winds. The LSPA tephra is dated at 29.6±0.62 cal yr BP by radiocarbon age interpolation of tephra sample RO-1/2/3 in the MOH-2 core (Fig. 6A, Table 2). A second age approximation is given at >27.18±0.46 cal yr BP from 14C dates on pollen concentrates from the lowermost part of the St. Ana SZA-2013 sediment sequence, which can be considered as a minimum age of the onset of lake sedimentation after the final, crater-forming eruption (Karátson et al., 2016).

5. Roxolany chronostratigraphy

The correlation of the Roxolany Tephra with the final eruptive products of Ciomadul volcano confirms the proposed time constraints of tephra-embedding sediments at Roxolany during the Last Glacial Maximum (Figs. 2, 6B). Therefore, the chronostratigraphy of the uppermost part of the Roxolany loess-palaeosol sequence is constrained by three different dating methods encompassing radiocarbon dating of palaeosols, IR-OSL loess dating and tephrochronology.
Radiocarbon dating of palaeosols in loess deposits is generally problematic, as the soil system remains open for a relatively long period (Orlova and Panychev, 1993). Thus, AMS-\(^{14}\)C dating of the organic soil samples at Roxolany gave partly mixed ages, i.e. in the upper two palaeosols of interphase rank between ca. 23,000 and 34,000 cal yr BP, and partly reversed ages, i.e. in the lower \(vt\) pedocomplex between 21,350 and 25,600 cal yr BP (Łanczont et al., 2015) (Table 1, Fig. 2). Mixed ages of the studied palaeosols can have a complex origin. They likely resulted from the low humus content of 0.13 to 0.18wt% (Łanczont et al., 2015) but also from the specific features of loess, which was the parent material of these soils. Silt alluvia with a high admixture of organic matter were very likely the source material for loess. They were deposited by the Dniester River in the shelf area, which was widely exposed as a result of the Late Pleistocene sea regression, and consequently very intensively blown during the formation of \(ud\) and \(bg\) loess deposits (Gozhik, 2013). Reversed ages in the lower \(vt\) pedocomplex are also difficult to explain. Those samples were obtained from the bottom part of a wall at a deep ravine, which is strongly overgrown by shrubs, i.e. in the zone of penetration of roots and concentrated flow of rainwater. Thus, we cannot exclude contamination of the samples by modern organic material, which in turn resulted in younger radiocarbon dates. In order to construct a consistent deposition (age-depth) model using Bayesian statistics we only selected radiocarbon dates that were most likely not influenced by older carbon, i.e. samples Roksolany 1, 2, combined 4/4a and 5/5a from the two upper palaeosols (Table 1, Fig. 6B). Radiocarbon dates of the lower \(vt\) pedocomplex are interpreted as too young based on the IR-OSL date of the overlying \(bg\) loess of 33.1±2.6 ka (Table 3) and thus have been rejected.

The imported Roxolany Tephra age of 29,589±620 cal yr BP derives from linear interpolation of two Bayesian modelled AMS-\(^{14}\)C dates at 27,832±652 and ca. 29,575±618 cal yr BP, ca. 151.5 cm and 1.25 cm (mean depths) above the RO-1/2/3 tephra, respectively, in the proximal MOH-2 core (Fig. 6A). It is chronostratigraphically in agreement with the age of the underlying MPA/TGS tephra (sample RO-4/5) at ca. 31,450±260 cal yr BP (Harangi et al., 2010; Karátson et al., 2016) and a radiocarbon age of bulk sediments at 31,749±894 cal yr BP ca. 27 cm below the RO-4/5 tephra. The Roxolany Tephra age at ca. 29.6 cal ka BP obtained at Ciomadul volcano is consistent within the radiocarbon and IR-OSL age based age-depth model of the upper Roxolany sequence and thus can be integrated into the Bayesian age model (Fig. 6B). Accordingly, we can estimate a mean sedimentation rate of the Bug loess unit of ca. 2-3 mm/yr, pointing to
very high accumulation rates during the last glacial period that also favoured the preservation of tephra within the loess sequence.

6. Implication for the distal tephostratigraphy of Ciomadul volcano

The identification of the LSPA tephra from Ciomadul volcano at the distal site of Roxolany has further implications on the tephostratigraphic framework of the Eastern Mediterranean – Black Sea region, particularly for linking the widespread loess records, the detailed correlation which is still hampered by limited chronological control (Veres et al., 2013; Markovic et al., 2015). The finding of a 2-3 cm thick tephra layer indicates on the one hand an exceptional preservation in loess sediments, probably due to high sedimentation rates and related rapid covering of the tephra by wind-blown sediments (Chlebowski et al., 2003; Boguckyi et al. [eds], 2013). This minimum thickness in combination with the relatively large grain size of tephra components at ca. 350 km distance suggests an origin from a violent, possibly even phreatoplinian eruption and widespread dispersal of the LSPA tephra by strong westerly winds. We thus expect further LSPA tephra and cryptotephra findings beyond the Roxolany site (e.g. in Eastern Romania, Ukraine and southern Russia) in the near future. Similarly, a wider dispersal of the older EPPA and MPA/TGS tephras from Ciomadul in a southerly/south-easterly direction, i.e. at sites in southern Romania, the Balkans, Black Sea and beyond, can be anticipated. Sediment core M72/5-25-GC1 from the south-eastern Black Sea (Fig.1), located ca. 1050 km ESE of Ciomadul, has already been proposed as such a potential site of Ciomadul cryptotephra preservation, but no solid tephra correlation was possible so far (Cullen et al., 2014). The comparison of new major-element glass chemical and chronostratigraphic data from Ciomadul’s latest explosive activity with 48.3-25 ka cryptotephra data of the Black Sea core (BSC) allows as well only tentative correlations (Fig. 4). For instance, the less evolved glass population of cryptotephra BSC_651, dated between 25 ka and 34.4 ka (Nowaczyk et al., 2012; Cullen et al., 2014), has a strong affinity to the 31.5 ka MPA/TGS tephra except for the lower CaO concentrations (Fig. 4). Older cryptotephras from the Black Sea core dated between 34.4 ka and 48.3 ka are geochemically indistinctive from each other and may correlate either with the older EPPA tephras from Ciomadul or the EAPV (Süphan) tephras (Figs. 3,4). In these cases, trace element and isotopic data sets of glass shards from all – proximal and distal – archives will be required for further detangling.

6. Summary and Conclusions
The tephrochronological study of the Roxolany loess site in combination with new geochemical and chronostratigraphic tephra constraints from the latest explosive activity of Ciomadul volcano (East Carpathians) allows a robust correlation of the long-discussed Roxolany Tephra with the final LSPA eruption of Ciomadul. The age of the LSPA tephra is constrained at the source volcano at ca. 29.6 cal ka BP and is in good agreement with the recently obtained dates for the Roxolany Tephra embedding sediments. Therefore, we propose that the Roxolany Tephra was deposited during the onset of the Last Glacial Maximum of the Weichselian phase, a period of intense aeolian activity. The occurrence of a visible Ciomadul tephra layer ca. 350 km east of its vent has important implications for future (crypto) tephra findings in the south-eastern Mediterranean and Black Sea region that would integrate Carpathian volcanism into establishing a regional tephra framework that focuses on linking terrestrial (loess and alluvial) and marine records.

Acknowledgements

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References


**Figure captions**

**Figure 1**: (A) Landsat image (Google Earth 2015) of the central and eastern Mediterranean showing the location of main silicic volcanic centres and sites mentioned in the text. (B) Landsat image of the Ciomadul volcanic complex with St. Ana and Mohoș crater drilling sites and TUR-2 sampling location. (C) Schematic map of the Roxolany sampling site (red arrow).

**Figure 2**: Stratigraphy, lithology and dating results for the upper loess section at Roxolany. (A) General overview of the top loess-soil section with position of the volcanic ash layer. Radiocarbon age ranges of palaeosols include a 2σ error and used the OxCal program v4.2.4
after Bronk Ramsey (2008, 2009) and Bronk Ramsey et al. (2013) in combination with the INTCAL13 calibration curve (Reimer et al., 2013). Original radiocarbon data from Łanczont et al. (2015). (B) MIS2 sediments at the Roxolany site, showing the Dofinivka soils (red-brownish top layer) and upper section of the Bug loess unit that contains the 2-3 cm thick white-greyish Roxolany tephra.

**Figure 3**: Backscattered electron (BSE) images of Roxolany Tephra components. (A) Overview of the 63-125 μm grain size fraction, (B) highly vesicular, microlite-rich pumiceous ash of the >125 μm fraction, (C) low-vesicular, microlite-rich glass shards with (D) attached feldspar micro-phenocryst of the 63-125 μm fraction. gl = volcanic glass; fs = feldspar; lt = lithic clast (clumped particles).

**Figure 4**: Geochemical bivariate plots of glass data of the Roxolany tephra in comparison with published data of potential eastern Mediterranean tephra sources. EPMA data are obtained from: Roxolany tephra (red stars): this study; Lipari: Crisci et al. (1991); Cape Riva/Y-2, Santorini: Çağatay et al. (2015), Tomlinson et al. (2015), Wulf et al. (2002); Yali-C: Federman and Carey (1980), Vinci (1985); Nisyros Lower and Upper Pumices: Tomlinson et al. (2012); Erciyes Dag and Acigöl: Tomlinson et al. (2015); Süphan Dagi and Nemrut Dagi: Schmincke et al. (2014).

**Figure 5**: Geochemical bivariate plots of glass data for discriminating between the Roxolany tephra (red stars, this study), proximal tephra deposits from the latest activity of Ciomadul volcano (black envelope = EPPA stage, orange envelope = MPA stage including TGS eruption, blue envelope = LSPA stage; after Karátson et al., 2016), representative Ciomadul pumice samples (black, orange and blue symbols; this study and Karátson et al., 2016) and cryptotephras of the last glacial period from Black Sea Core (BSC) M72/5-25-GC1 (grey fields; data from Cullen et al., 2014).

**Figure 6**: Deposition models of (A) Mohoş MOH-2 core (1350-1600 cm depth, with core photographs) and (B) the upper Roxolany sequence (4-21m, with schematic lithological profile, for legend see Fig. 2) using the OxCal program v4.2.4 after Bronk Ramsey (2008, 2009) and Bronk Ramsey et al. (2013) in combination with the INTCAL13 calibration curve (Reimer et al., 2013).
Table captions

Table 1: Results of radiocarbon AMS dating of palaeosols (bulk sediment) of the Roxolany site after Łanczont et al. (2015). Calibration used the OxCal software v4.2.4 (Bronk Ramsey 2008, 2009; Bronk Ramsey et al., 2013) with the INTCAL13 calibration curve of Reimer et al. (2013). # Radiometric date not used for the Bayesian deposition model (see Fig. 6B).

Table 2: Results of radiocarbon AMS dating of sediments of the MOH-2 core from the Mohoş crater, Ciomadul, partly modified from Karátson et al. (2016). Calibration used the OxCal software v4.2.4 (Bronk Ramsey 2008, 2009; Bronk Ramsey et al., 2013) with the INTCAL13 calibration curve of Reimer et al. (2013). *Mean radiocarbon age obtained from two charcoal samples from the Bixad outcrop south of Lake St. Ana, Ciomadul volcano (Harangi et al., 2010; Vinkler et al., 2007).

Table 3: IR-OSL results and radioactivity data of the loess sample from 18.7 m depth (Bug loess) of the Roxolany sequence.

Table 4: EPMA raw data of single point glass analyses of the Roxolany tephra and results of the rhyolitic Lipari Obsidian glass standard.
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Hunt and Hill (1996) provide data for Lipari Obsidian.
Figure 3
Figure 4

Al_{2}O_{3} (wt%) vs. SiO_{2} (wt%)

FeO (wt%) vs. SiO_{2} (wt%)

CaO (wt%) vs. SiO_{2} (wt%)

K_{2}O/Na_{2}O vs. SiO_{2} (wt%)