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

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Keywords: Tephra; Roxolany loess; Ukraine; Ciomadul; Lake St. Ana.

Abstract

We present major element glass data and correlations of the so-called 'Roxolany Tephra' – a so far geochemically unconstrained volcanic ash layer previously described in last glacial (MIS2) loess deposits in SW Ukraine. This exceptional well preserved, 2-3 cm thick tephra shows a rhyolitic glass composition that is comparable with that of proximal tephra units from the Ciomadul volcano in the East Carpathians, central Romania. The chemistry particularly matches that of the final pyroclastic fall unit of Sf. Ana crater that is radiocarbon dated at ca. 29.6 cal ka BP. The age of the tephra correlative is in agreement with the newest radiocarbon and OSL age constraints that place it between ca. 33 and 24 cal ka BP within the Roxolany loess sequence and thus confirms the long-debated chronostratigraphic position of the tephra in 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-paleosoil complex near the village of Roxolany in the SW Ukraine (Fig. 1) provides an almost complete Pleistocene terrestrial sedimentary record and is thus 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 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 TL dating. Within these first studies, the authors suggested the Brunhes/Matuyama magnetic reversal (ca. 780 ka) in the lower part of the profile. Later, Tsatskin *et al*. (1998) provided a more detailed description, proposing a revised stratigraphic interpretation of the loess-paleosoil 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 profile in loess unit L_6 at ca. 35 m depth of the Roxolany loess-palaeosoil complex, which now enabled a solid correlation with other loess profiles in Europe and China (e.g. Dodonov *et al*., 2006; Faustov *et al*., 2009; Gendler *et al*., 2006; Tsatskin *et al*., 2001).

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 L_3 loess unit (corresponding to MIS 12, i.e. the period from 450 to 400 ka; Sartori, 2000). Tephras, 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). Remarkably, Loess-Paleosoil complexes in the Middle and Lower Danube Basin revealed evidence for stratigraphic consistent tephras of diverse stratigraphic position, their precise geochemistry and age, however, is often poorly constraint (e.g. Fitzsimmons *et al*., 2013; Horváth, 2001; Marković *et al*., 2015; Panaiotu *et al*., 2001; Veres *et al*., 2013). 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 contradicting 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 (Boguckyi *et al*. (eds), 2013; Gozhik *et al*., 2007; Putivnyk, 2000). According to the newest 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 paleosol layers of an interphase rank, the *Prychornomorsk* (pc) and the *Dofinivka* (df) units, that have recently been radiocarbon dated at ca. 23.5 cal ka BP and 34.7 cal ka BP, respectively (Boguckyi *et al*. (eds), 2013; Fedorowicz *et al*., 2012) (Fig. 2). The paleosol 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 21 and 25.5 cal ka BP (Boguckyi *et al*. (eds), 2013; Fedorowicz *et al*., 2012) (Fig. 2). Optically-stimulated luminescence (OSL) dates of loess samples from ca. 9 m below the tephra revealed an age of 33.1±2.6 ka (Boguckyi *et al*. (eds), 2013; Fedorowicz *et al*., 2012), confirming both the radiocarbon-based chronology and the stratigraphic scheme developed by Gozhik *et al*. (1995; 2007) pointing to very high accumulation rates, that also favoured tephra preservation within loess. Further attempts to directly date phenocrysts of the Roxolany Tephra, however, led to unrealistic old ages of 50±3 Ma ($^{40}Ar/^{39}Ar$; Sartori, 2000; Tsatskin *et al*., 1998) 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 as a contribution to (1) the clarification of the chronostratigraphy of the Roxolany loess-paleosoil complex, and (2) the extension of the tephrostratigraphical framework in south-eastern Europe with the principal aim at 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, SW Ukraine (46°10'N, 30°27'E) (Fig. 1). The ca. 48 m thick Loess-Paleosol 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). 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 Tephrochronological methods

The tephra sample from the Roxolany loess sequence was treated with a 15% hydrogen peroxide (H_2O_2) solution to remove organic remains and subsequently 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 composition of single glass shards was determined at a CAMECA SX-100 and a JEOL-JXA8230 instrument at the GFZ Potsdam using a 15 kV voltage, a 20 nA and 10 nA beam current and a beam size of 15 µm and 8 µm, respectively. Exposure times were 20 seconds for the elements Fe, Cl, Mn, Ti, Mg and P, as well as 10 seconds for F, 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 1 and compared in bivariate plots with published EPMA glass data of potential tephra correlatives (Figs. 3, 4).

Back-scattered electron (BSE) images of volcanic glass shards from different grain size fractions (32-63 µm, 63-125 µm and >125 µm) were acquired with a 15 kV accelerating voltage with a Hitachi TM3000 Tabletop Scanning Electron Microscope (SEM) at Keele University.

3. Composition of the Roxolany tephra

The Roxolany Tephra is a fine-grained (d_{max} = 200 µm) volcanic ash that is dominated by lithics, plagioclase, green pyroxene and biotite crystals (Fig. 3A). It also consists of highly vesicular, microcryst-rich (feldspars, pyroxenes) pumices (Fig. 3B) and blocky, low-vesicular glass shards (Figs. 3C, 3D) that indicate an phreatomagmatic origin. Due to the mean low analytical totals of ca. 94-95 wt%, volcanic glasses are interpreted to be slightly altered (Table 1). Analytical data from both EPMA instruments using different setups are comparable with each other except for slightly higher SiO_2 and lower Al_2O_3 values for the JEOL probe data that used a smaller beam size (Table 1). Accordingly, the major element glass composition is calc-alkaline rhyolitic with SiO_2 and Al_2O_3 concentrations of 75.6-77.6 wt% and 12.9-14.0 wt% (normalized, volatile-free data), respectively. Concentrations in FeO (0.5-0.9 wt%) and CaO (0.8-1.1 wt%) are low, and alkali ratios (K_2O/Na_2O) vary between 1.1 and 1.5 (Figs. 4 and 5).

4. Source and associated age of the Roxolany Tephra

The glass composition of the Roxolany Tephra was compared to EPMA glass data of other Late Pleistocene tephras occurring in the Eastern Mediterranean. Calc-alkaline rhyolitic tephras 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; Forni *et al*., 2013; Lucchi *et al*., 2008), and the respective juvenile pyroclasts show a distinct major-element composition with lower concentrations in SiO_2 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 Al_2O_3 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 recently reported as a cryptotephra within the Theopetra cave, stratigraphically overlain by the Pantellerian Y6/Green Tuff, dated to 45.7 ka (Karkanas *et al*., 2015). In the more proximal marine stratigraphy, the Upper Nisyros Pumices are 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. Kwiecien *et al*., 2008; Müller *et al*., 2011; Wulf *et al*., 2002). 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 Dağ (Central Anatolian Volcanic Province CAVP, ca. 900-950 km SSE of Roxolany), and Süphan and Nemrut Dagi (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. Deniel *et al*., 1998; Druitt *et al*., 1995; Kuzucuoglu *et al*., 1998; Sumita and Schmincke, 2013b) (Fig. 4). Especially the MIS2 tephras from Acigöl and Süphan Dagi 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 in Lake Van sediments; Schmincke *et al*., 2014; Sumita and Schmincke, 2013a) 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 Dağ, 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 southern East Carpathians. New chronostratigraphic data of the latest pyroclastic deposits of the Ciomadul andesitic-dacitic lava dome complex in the East Carpathians (Romania, ca. 350 km W of Roxolany; Fig. 1) indicate that this site was indeed explosively active (e.g. Harangi *et al*., 2015; Karátson *et al*., 2013; Szakács and Seghedi, 1990, 1995), especially during its final eruptive stage at 52-29 ka BP (Karátson *et al*., submitted). The last eruptions of Ciomadul were characterized by successive crater formations (e.g. Mohoş, St. Ana) and by widespread dispersal of at least three tephra units (Karátson *et al*., submitted). The phreatomagmatic 'Turia' (ca. 52 ka) and plinian 'TGS' deposits (ca. 31.5 ka), for example, are widely dispersed towards the southeast (Karátson *et al*., submitted). The final phreatomagmatic LSA eruption likely originated from the St. Ana crater and is radiocarbon dated on the basis of lacustrine deposits of the Mohoş and St. Ana craters at ≥29.6 ± 0.6 cal ka BP and >27 cal ka BP, respectively (Karátson *et al*., submitted). The dispersal direction of the LSA tephra has been tentatively proposed towards the east (Karátson *et al*., submitted; Veres *et al*., in prep.). Glass chemical data show a distinct and relatively heterogeneous rhyolitic composition for all three Ciomadul tephras, with the oldest Turia tephra being the most evolved (mean high SiO_2 values of ca. 78 wt%) and the TGS tephra the least silicic products (mean SiO_2 concentration of ca. 73 wt%) (Fig. 5). Major-element glass data of the chemically intermediate LSA tephra (mean SiO_2 values of 76.5 wt%), especially those of the uppermost dated tephra layer RO-1/2/3 in the Mohoş core (Karátson *et al*., submitted), show the best agreement with the glass data of the Roxolany Tephra (Fig. 5). The chemical correlation with the LSA tephra is furthermore supported by the thickness and maximum grain sizes of the Roxolany Tephra, which imply a transport from the St. Ana crater over a relatively short distance (>350 km) and by favourable westerly winds, the prevailing atmospheric circulation in the region. The correlation of the Roxolany Tephra with the final eruptive products of Ciomadul volcano, in turn, confirms the proposed time constraints (33-24 cal ka BP) of tephra embedding loess deposits at Roxolany during the last Glacial Maximum (Fig. 2).

5. Implication for the distal tephrostratigraphy of Ciomadul volcano

The identification of the LSA tephra from Ciomadul volcano at the distal site of Roxolany has further implications on the tephrostratigraphic framework of the Eastern Mediterranean – Black Sea region, particularly for the linking of the widespread loess records, whose detailed correlation 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 sizes of tephra components at ca. 350 km distance suggests an origin from a violent, even phreatoplinian eruption and a widespread dispersal of the LSA tephra by strong westerly winds. We thus expect further LSA 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 Turia and TGS tephras from Ciomadul in a southerly/south-easterly direction, i.e. at sites in southern Romania, the Balkans, the 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 stage activity with 48.3-25 ka cryptotephra data of the Black Sea core (BSC) also only allows tentative correlations (Fig. 4). For instance, the less evolved glass population of cryptotephra BSC_651, dated between 25 ka and 34.4±0.65 ka (Cullen *et al*., 2014; Nowaczyk *et al*., 2012), has a strong affinity to the 31.5 ka 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, the Turia tephras from Ciomadul and 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 stage activity of Ciomadul volcano (East Carpathians) allow a robust correlation of the long-discussed Roxolany Tephra with the final LSA eruption of Ciomadul. The age of the LSA tephra is constrained at the source volcano at ca. 29.6 cal ka BP and is in good agreement with the latest dates obtained for the Roxolany Tephra embedding sediments. Therefore, the Roxolany Tephra was deposited during the onset of the 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 the Carpathian volcanism into the building of a regional tephra framework focusing on linking terrestrial (loess and alluvial) and marine records.

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Figure captions

Figure 1. 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. Left inlet map: Landset image of the Ciomadul volcanic complex with St. Ana and Mohoş craters. Right inlet map: location 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. (**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: Backscatter electron (BSE) images of Roxolany Tephra components. Overview of the 63-125 µm grain size fraction (A); highly vesicular, microcryst-rich pumice of the >125 µm fraction (B); low-vesicular, microcryst-rich glass shards (C) with attached feldspar phenocrystal (D) of the 63-125 µm fraction. gl = volcanic glass; fs = feldspar; lt = lithic.

Figure 4: Geochemical bivariate plots of glass data of the Roxolany tephra in comparison to published data of potential central and 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 (Turia, TGS, LSA including sample RO-1/2/3) from the latest activity of Ciomadul volcano (Karátson *et al*., submitted) and Black Sea Core (BSC) cryptotephras of the last Glacial (Cullen *et al*., 2014).

Table captions

Table 1: EPMA raw data of single point glass analyses, mean values and 2σ standard deviation (*sd*) of the Roxolany tephra, and results of the rhyolitic Lipari Obsidian glass standard.

Table 1:

CAMECA SX-100 (23/07/2004)

Sample	SiO_2	TiO_2	Al_2O_3	FeO_t	MnO	MgO	CaO	Na_2O	K_2O	P_2O_5	Total	-Cl-
Roxolany #A1	71.25	0.05	12.87	0.65	0.04	0.05	0.95	3.36	4.36	0.04	93.62	0.21
#A2	71.45	0.10	13.19	0.68	0.05	0.07	1.04	3.40	4.23	0.05	94.26	0.19
#A3	72.05	0.07	13.23	0.72	0.02	0.10	1.08	3.83	4.25	0.01	95.36	0.16
#A4	71.09	0.09	13.01	0.62	0.08	0.05	0.86	3.79	4.82	0.02	94.43	0.20
#A5	73.34	0.10	13.08	0.64	0.00	0.06	0.98	3.80	4.38	0.06	96.44	0.17
#A6	73.53	0.06	12.99	0.51	0.00	0.02	0.87	3.76	4.78	0.02	96.54	0.17
#A7	71.01	0.06	12.86	0.58	0.05	0.04	0.98	3.75	4.16	0.04	93.53	0.17
#A8	72.37	0.09	12.96	0.66	0.03	0.04	0.94	3.28	4.42	0.03	94.82	0.19
#A9	73.40	0.07	12.72	0.61	0.02	0.05	0.90	3.28	4.62	0.00	95.67	0.21
#A10	74.02	0.08	13.07	0.56	0.01	0.01	0.87	3.99	4.32	0.00	96.93	0.16
#A11	72.50	0.09	12.92	0.69	0.03	0.05	1.03	3.45	4.50	0.08	95.34	0.17
#A12	73.39	0.06	12.04	0.61	0.03	0.06	0.87	2.96	4.53	0.00	94.55	0.13
#A13	72.60	0.09	12.90	0.54	0.05	0.04	0.92	3.47	4.39	0.00	95.00	0.22
#A14	72.22	0.06	12.83	0.50	0.03	0.04	0.92	3.34	4.26	0.00	94.20	0.15
#A15	72.92	0.10	12.81	0.74	0.05	0.06	0.93	3.44	4.49	0.04	95.58	0.20
Mean	**72.48**	**0.08**	**12.90**	**0.62**	**0.03**	**0.05**	**0.94**	**3.53**	**4.43**	**0.03**	**95.05**	**0.18**
SD	*0.93*	*0.02*	*0.27*	*0.07*	*0.02*	*0.02*	*0.07*	*0.27*	*0.19*	*0.02*	*1.87*	*0.02*
Lipari Obsidian												
15 µm-beam	74.07	0.08	13.18	1.67	0.05	0.05	0.72	4.09	5.15	0.00	98.96	0.31

JEOL JXA-8230 (23/10/2014)

Sample	SiO_2	TiO_2	Al_2O_3	FeO_t	MnO	MgO	CaO	Na_2O	K_2O	P_2O_5	Total	-Cl-
Roxolany #B1	73.35	0.06	12.33	0.54	0.05	0.03	0.89	3.17	4.41	0.03	94.86	0.14
#B2	72.44	0.09	12.49	0.58	0.06	0.03	0.71	3.33	4.85	0.00	94.58	0.17
#B3	71.94	0.09	12.54	0.74	0.03	0.06	0.92	3.54	4.52	0.03	94.41	0.18
#B4	71.97	0.05	12.03	0.67	0.06	0.05	0.89	3.26	4.13	0.00	93.11	0.17
#B5	72.97	0.07	12.25	0.59	0.02	0.04	0.86	3.34	4.44	0.02	94.60	0.21
#B6	71.78	0.07	12.22	0.45	0.06	0.01	0.97	3.49	3.78	0.03	92.86	0.16
#B7	73.62	0.10	12.21	0.60	0.01	0.03	0.77	3.76	3.82	0.00	94.92	0.18
#B8	72.46	0.10	12.80	0.83	0.02	0.01	0.86	3.75	4.62	0.00	95.45	0.26
#B9	72.33	0.04	12.12	0.49	0.05	0.01	0.92	2.99	4.51	0.07	93.53	0.17
#B10	72.58	0.10	12.43	0.68	0.08	0.04	0.88	3.40	4.44	0.00	94.63	0.21
#B11	73.10	0.07	12.30	0.50	0.04	0.02	0.93	3.34	4.41	0.00	94.71	0.17
#B12	72.81	0.06	12.32	0.54	0.02	0.02	0.93	3.37	4.14	0.00	94.21	0.19
#B13	72.83	0.05	12.35	0.54	0.07	0.05	0.86	3.02	4.63	0.00	94.40	0.17
#B14	71.07	0.08	12.28	0.63	0.05	0.05	0.89	3.30	4.19	0.01	92.55	0.19
#B15	71.77	0.12	12.57	0.64	0.01	0.05	0.89	3.59	4.58	0.04	94.26	0.17
#B16	71.25	0.09	12.62	0.72	0.05	0.04	0.91	3.53	4.51	0.00	93.72	0.19
Mean	**72.39**	**0.08**	**12.37**	**0.61**	**0.04**	**0.03**	**0.88**	**3.39**	**4.37**	**0.01**	**94.18**	**0.18**
SD	*0.70*	*0.02*	*0.19*	*0.10*	*0.02*	*0.02*	*0.06*	*0.21*	*0.28*	*0.02*	*0.77*	*0.03*
Lipari Obsidian												
10 µm-beam	73.61	0.09	12.87	1.55	0.06	0.03	0.71	4.02	5.22	0.02	98.18	0.37
15 µm-beam	73.53	0.10	12.85	1.61	0.11	0.02	0.72	4.06	5.30	0.00	98.30	0.37
20 µm-beam	73.56	0.05	12.78	1.49	0.11	0.05	0.72	4.01	5.26	0.00	98.03	0.34


Mohoş
Ciomadul
St. Ana
1 km
UKRAINE
Ciomadul
Roxolany
ROMANIA
MOLDOVA
Odessa
Dniester
UKRAINE
Roxolany
Black Sea
20 km
ITALY
BALKAN
Black Sea
M72/5-25-GC1
Lipari
TURKEY
Acigöl
Erciyes Dagi
Süphan Dagi
Nemrut Dagi
Yali
Thera/Santorini
Nisyros
N
500 km
Levantine Sea

Figure 1

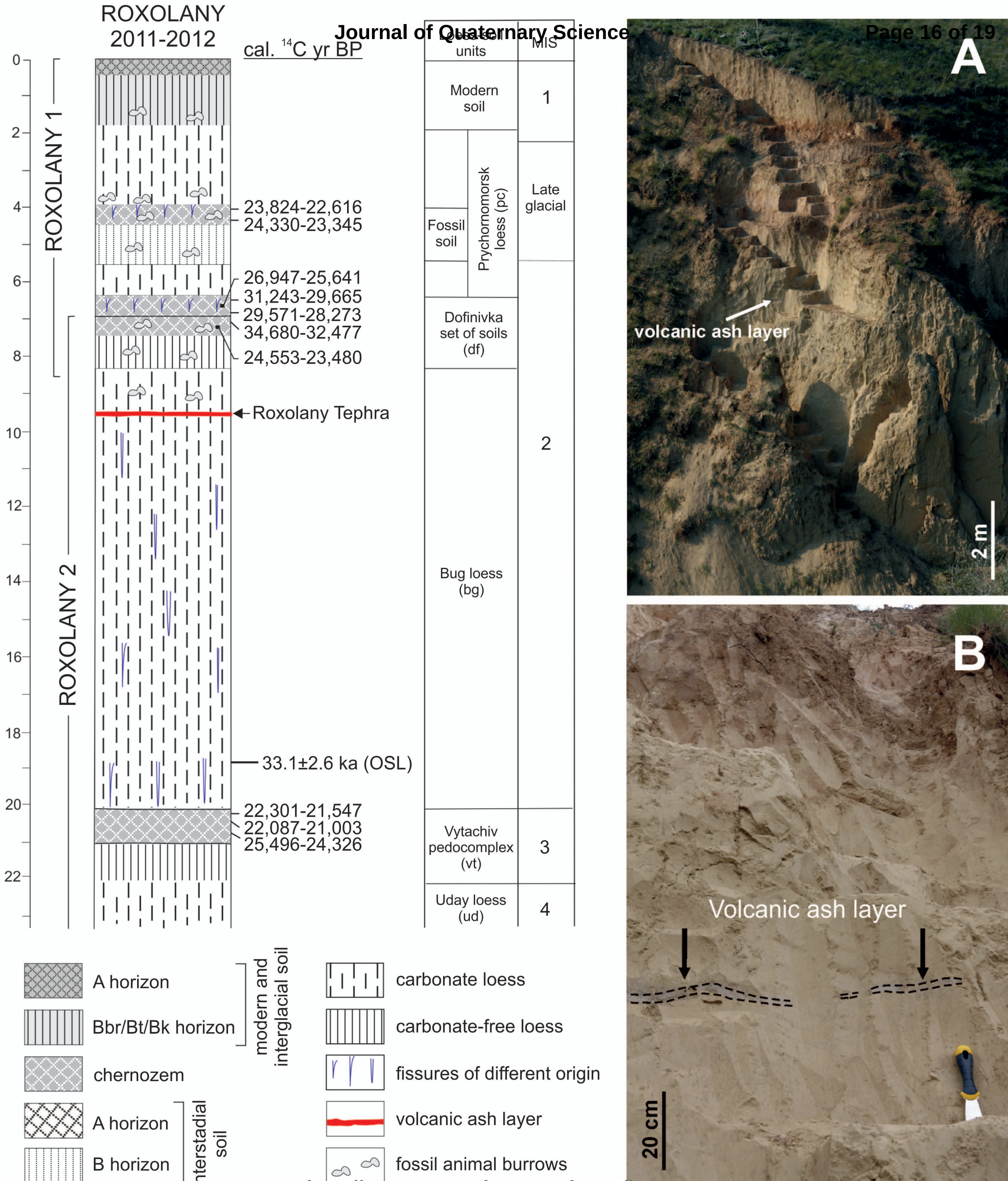

ROXOLANY
2011-2012
cal. 14C yr BP
Depth (m)
0
2
4
6
8
10
12
14
16
18
20
22
ROXOLANY 1
ROXOLANY 2
23,824-22,616
24,330-23,345
26,947-25,641
31,243-29,665
29,571-28,273
34,680-32,477
24,553-23,480
Roxolany Tephra
33.1±2.6 ka (OSL)
22,301-21,547
22,087-21,003
25,496-24,326
Loess-soil units
MIS
Modern soil
1
Fossil soil
Prychornomorsk loess (pc)
Late glacial
Dofinivka set of soils (df)
Bug loess (bg)
2
Vytachiv pedocomplex (vt)
3
Uday loess (ud)
4
A horizon
Bbr/Bt/Bk horizon
chernozem
modern and interglacial soil
A horizon
B horizon
interstadial soil
carbonate loess
carbonate-free loess
fissures of different origin
volcanic ash layer
fossil animal burrows
A
volcanic ash layer
2 m
B
Volcanic ash layer
20 cm

Figure 2

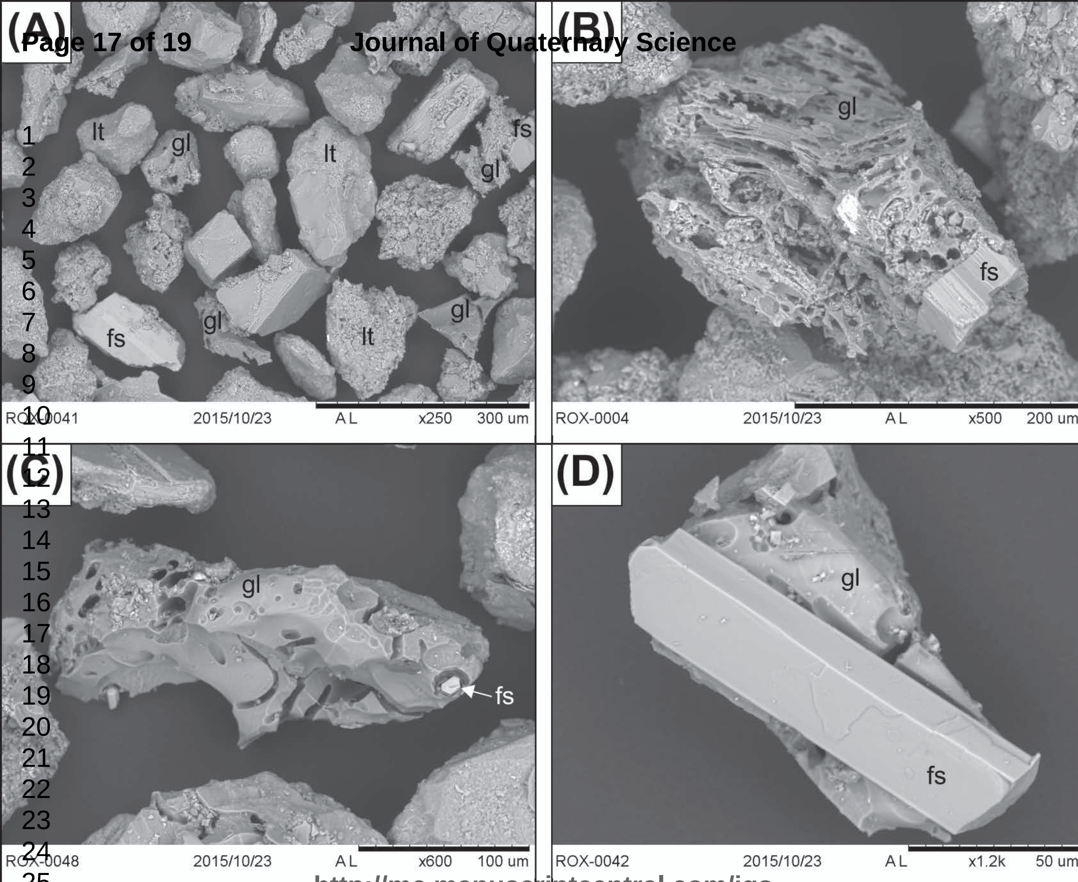
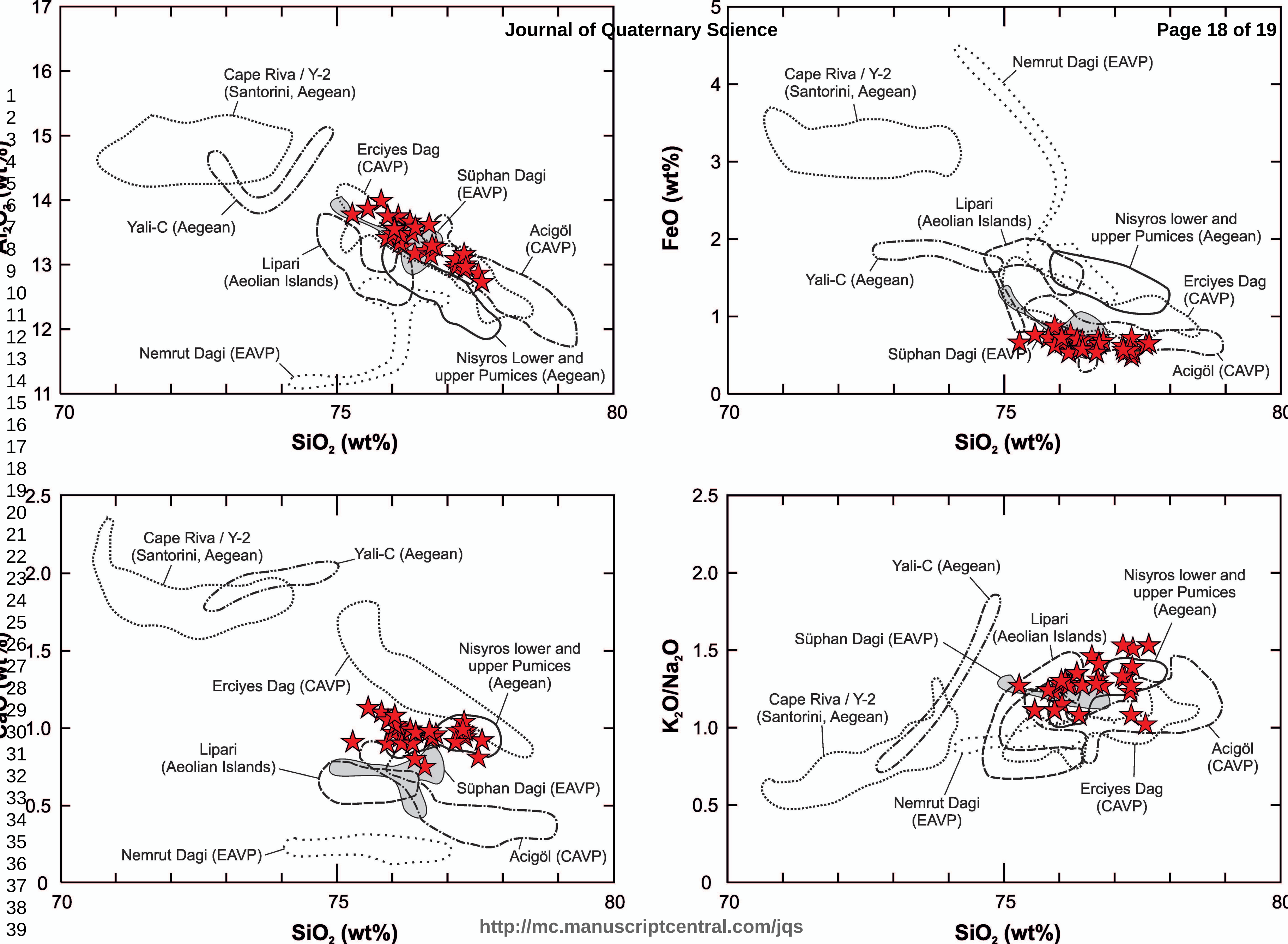

(A)
lt
gl
lt
fs
gl
fs
gl
gl
lt
gl
ROX-0041
2015/10/23
A L
x250
300 um
(B)
gl
fs
ROX-0004
2015/10/23
A L
x500
200 um
(C)
gl
fs
ROX-0048
2015/10/23
A L
x600
100 um
(D)
gl
fs
ROX-0042
2015/10/23
A L
x1.2k
50 um

Figure 3



Al2O3 (wt%)
SiO2 (wt%)
Cape Riva / Y-2 (Santorini, Aegean)
Yali-C (Aegean)
Erciyes Dag (CAVP)
Süphan Dagi (EAVP)
Acigöl (CAVP)
Lipari (Aeolian Islands)
Nemrut Dagi (EAVP)
Nisyros Lower and upper Pumices (Aegean)
FeO (wt%)
Nisyros lower and upper Pumices (Aegean)
CaO (wt%)
K2O/Na2O

Figure 4

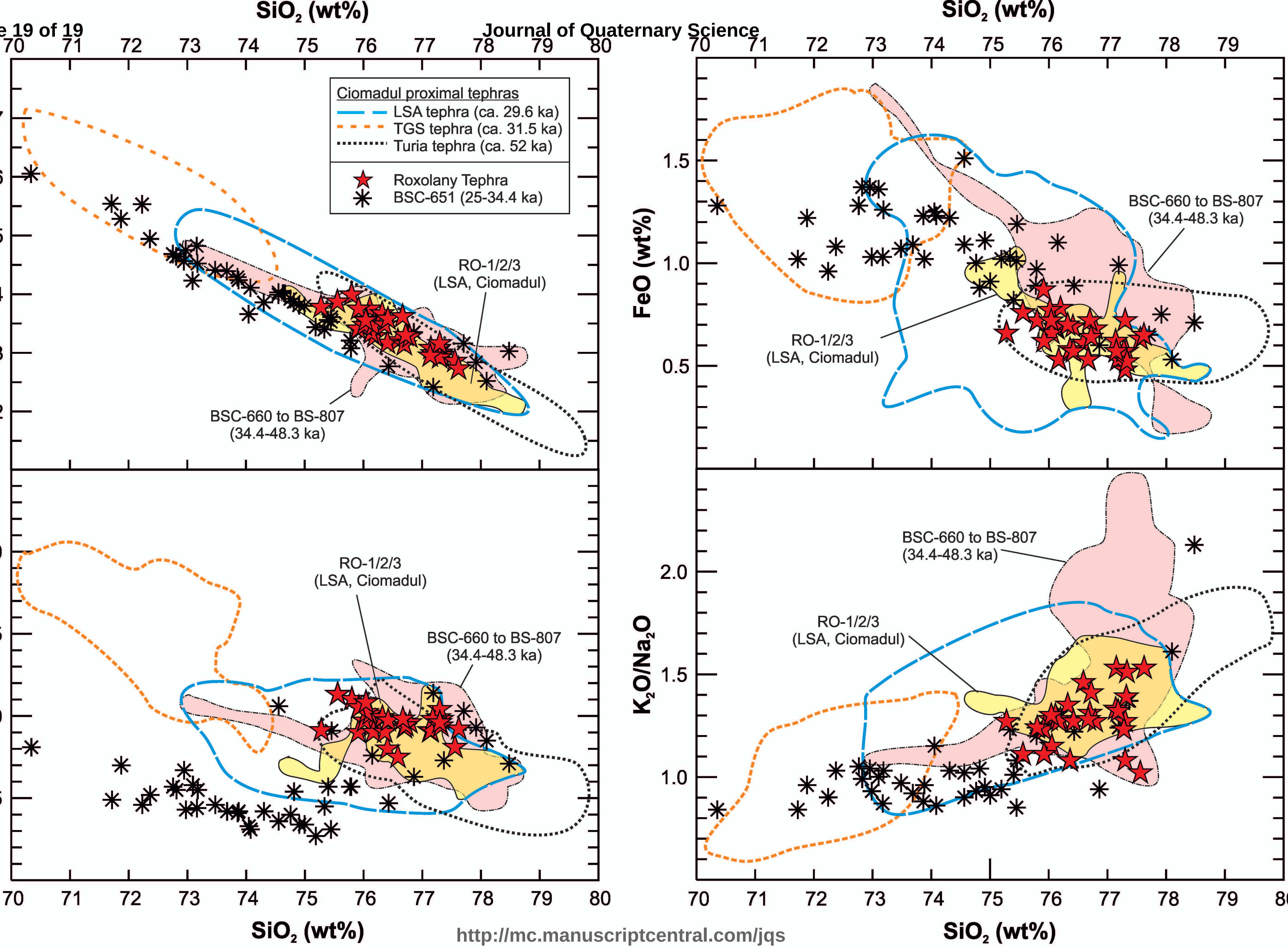

SiO2 (wt%)
Al2O3 (wt%)
Ciomadul proximal tephras
LSA tephra (ca. 29.6 ka)
TGS tephra (ca. 31.5 ka)
Turia tephra (ca. 52 ka)
Roxolany Tephra
BSC-651 (25-34.4 ka)
RO-1/2/3
(LSA, Ciomadul)
BSC-660 to BS-807
(34.4-48.3 ka)
FeO (wt%)
CaO (wt%)
K2O/Na2O

Figure 5