ORIGINAL PAPER



# Evidence of open-air late prehistoric occupation in the Trieste area (north-eastern Italy): dating, 3D clay plaster characterization and obsidian provenancing

F. Bernardini<sup>1,2</sup> · E. Sibilia<sup>3</sup> · Zs. Kasztovszky<sup>4</sup> · F. Boscutti<sup>5</sup> · A. De Min<sup>6</sup> · D. Lenaz<sup>6</sup> · G. Turco<sup>7</sup> · R. Micheli<sup>8</sup> · C. Tuniz<sup>2,1,9</sup> · M. Montagnari Kokelj<sup>10</sup>

Received: 29 November 2016 / Accepted: 3 May 2017 / Published online: 3 June 2017 © Springer-Verlag Berlin Heidelberg 2017

Abstract Abundant clay burnt plaster remains and a few flaked tools, including an obsidian artefact, found on the ground surface not far from Trieste (north-eastern Italy) provide rare evidence of a possible prehistoric open-air occupation in the area. To confirm and detail their ancient origin, a plaster sample has been dated between 4000 and 2000 B.C. via thermoluminescence. Outer and inner structure of selected plaster samples has been characterized using several techniques, i.e. X-ray diffraction, scanning electron microscopy and X-ray computed micro-tomography, obtaining information about their production technology. The last technique has allowed to image and virtually extract vegetal remains and imprints. Their 3D morphological study has contributed to collect information about the ancient environment and has provided clues to define the plaster production season. The provenance of the obsidian artefact from Lipari Island, revealed by prompt gamma activation analysis, suggests that the finding site was part of long-distance connection systems and probably worked as intermediate point between the northeastern Adriatic coastal areas and the inner Karst plateau.

Keywords Late Neolithic-Copper Age · North-eastern Italy · Clay plaster · Thermoluminescence dating · X-ray diffraction · Scanning electron microscopy · X-ray computed micro-tomography · Obsidian provenance · Prompt gamma activation analysis

#### Introduction

In the Trieste area (north-eastern Italy), almost all the known Neolithic and Copper Age sites identified so far are caves and rock shelters of the Karst plateau (Boschian and Montagnari Kokelj 2000, Montagnari Kokelj et al. 2013). Only a few findings are reported from the coastal hilly belt formed by relatively fertile Eocene turbiditic rocks (Flysch of Trieste) and alluvial deposits (Montagnari Kokelj 1997; Bernardini and Betic 2008; Fig. 1). The discovery of three flaked artefacts and abundant burnt clay plaster remains on the ground surface, along the southern slope of a marly-arenaceous hill (San Rocco), is therefore interesting. These findings could help to

F. Bernardini fbernard@ictp.it

- <sup>1</sup> Centro Fermi, Museo Storico della Fisica e Centro di Studi e Ricerche "Enrico Fermi", Piazza del Viminale 1, 00184 Rome, Italy
- <sup>2</sup> Multidisciplinary Laboratory, The "Abdus Salam" International Centre for Theoretical Physics, Strada Costiera 11, 34151 Trieste, Italy
- <sup>3</sup> INFN and Department of Materials Science, University of Milano-Bicocca, Via R. Cozzi 53, 20125 Milan, Italy
- <sup>4</sup> Nuclear Analysis and Radiography Department, MTA Centre for Energy Research, Konkoly Thege 29-33, Budapest H-1121, Hungary

- <sup>5</sup> Department of Agricultural, Food, Environmental and Animal Sciences, University of Udine, via delle Scienze 91, 33100 Udine, Italy
- <sup>6</sup> Department of Mathematics and Geosciences, University of Trieste, Via Weiss 8, 34127 Trieste, Italy
- <sup>7</sup> Department of Medical Sciences, University of Trieste, Piazza dell'Ospitale 1, 34125 Trieste, Italy
- <sup>8</sup> Soprintendenza Archeologia, Belle Arti e Paesaggio del Friuli Venezia Giulia, Piazza della Libertà 7, 34135 Trieste, Italy
- <sup>9</sup> Centre for Archaeological Science, University of Wollongong, Northfields Ave, Wollongong, NSW 2522, Australia
- <sup>10</sup> Department of Humanities, University of Trieste, Via Lazzaretto Vecchio 6, 34123 Trieste, Italy

Fig. 1 a Location of the studied area. b Elevation model of the north-eastern Adriatic regions with the position of the San Rocco hill. c LiDAR-derived hillshade of San Rocco hill with contour lines at 5 m showing the position of the archaeological findings. Big and small white circles 1-4: large distribution area and isolated findings of plaster remains; black, grey and white diamonds: obsidian flake, truncated flint bladelet and flint pebble with retouches, respectively; the red area corresponds to the fields without vegetation where the archaeological survey was more accurate



understand the settlement strategies adopted in the late prehistoric period by groups moving between the relatively fertile coast and the inner karstic areas. Their possible chronological and cultural association is however dubious. There are, in fact, two basic elements to consider. First, while the production of flaked tools ended before Roman times, the wall clay plaster remains are relatively common in prehistoric settlements (e.g. Anderson et al. 2014), but they are also reported from Roman (e.g. Morgan 1992) and later archaeological contexts (e.g. Staffa 1993). In Friuli Venezia Giulia, clay plaster remains were discovered in both prehistoric/protohistoric (e.g. Fabbri et al. 2007) and Roman sites (e.g. Prenc 2012). Secondly, the San Rocco hill—a strategic elevation that stands in the low Rosandra valley in front of the Muggia bay (Fig. 1)—was later occupied by a large Roman camp, probably built in the first half of the second century B.C. (Bernardini et al. 2015b).

To try solving the problem, several analyses were applied to the artefacts. A plaster sample from San Rocco was dated by thermoluminescence (TL) in order to ascertain its ancient origin. Although this dating technique is not one of the most accurate, it was the only available method to obtain at least a broad chronological attribution since well-preserved organic materials were not identified inside the plaster fragments. Several analytical techniques were then applied to selected plaster samples in order to study their mineralogical composition (X-ray diffraction—XRD) and image their outer and inner morphology (scanning electron microscope—SEM and X-ray computed micro-tomography—microCT), including vegetal imprints and remains. The microCT analysis was performed to obtain non-destructive 3D structural information, which cannot be achieved by other traditional techniques. The collected data have partially revealed the plaster production technology and have given some information about the natural past environment surrounding the site. As far as the flaked artefacts are concerned, a provenance study of an obsidian tool, found close to the plaster remains, has been carried out by non-destructive prompt gamma activation analysis (PGAA).

# Location and findings

The San Rocco hill is located in a strategic position, 2 km away from the innermost present-day shore of the Muggia bay, and its south-eastern slope is surrounded by the Rosandra River. The hill, formed by Eocene turbiditic rocks (mainly sandstones and marls), is part of a fertile semicircular area delimited to the north and east by the steep slope karstic plateau and to the south, towards the Istrian peninsula, by the Montedoro ridge. Its northern part was destroyed by construction excavations, while a large sector of the hill top was covered by a landfill. However, the north-eastern and southern sides of the hill have survived and the remains of a large republican Roman military camp have been identified (Bernardini et al. 2015b). Most of the area is covered by bushes and grasslands with the exception of modern paths and two small fields (Fig. 1c), where accurate archaeological surveys were carried out and repeated several times, especially after heavy rains and ploughings. In addition to secure republican Roman findings (see Bernardini et al. 2015b), several tens of fragments of burnt black-reddish plaster remains (Figs. 1c and 2a) were found together with an obsidian flake without retouch (Figs. 1c and 2b, 1), a truncated flint bladelet (Figs. 1c and 2b, 2) and a small grey flint pebble with few, weathered retouches (Figs. 1c and 2b, 3). The obsidian artefact shows the typical black partially translucent colour, while the flint bladelet found nearby shows a pinkish colour and a calcareous cortex.

About 30 fragments of burnt plaster remains with variable sizes (from a few cm up to about 10 cm large samples) were collected on the south-western slope of the San Rocco hill, especially in correspondence of point 3 of Fig. 1c. They partially derive from the soil excavated during the twentieth century to create two military posts still visible in the area. The plaster fragments, showing a reddish external colour with black areas (probably produced by fire), are characterised by a coarse texture with imprints of branches (Fig. 2a), small twigs and plants of variable dimension.

Among the collected samples, four plaster fragments (P1– P4) with particularly evident traces of vegetal imprints have been selected for the XRD, SEM and microCT analyses. Sample P1, found still partially buried in the soil, has been selected for TL dating.

# **Analytical methods**

#### **Burnt plaster remains**

#### X-ray diffraction

X-ray diffraction patterns of four samples (P1–P4) were obtained on powdered samples spread out on aluminium plates using a STOE D 500 X-ray diffractometer at room temperature at the Department of Mathematics and Geosciences of the Trieste University. CuK $\alpha$  radiation was used through a flat graphite crystal monochromator. The current used was 20 mA and the voltage was set at 40 kV. The scanning angle ranged from 2 to 40° of 2 $\theta$ , steps were of 0.01° of 2 $\theta$  and the counting time was of 2 s/step.

#### Thermoluminescence dating

Thermoluminescence dating (Aitken 1985) provides the time elapsed since the last high temperature heating experienced by a clay artefact (that, in the case of pottery samples, usually coincides with its firing in kiln).

One burnt plaster fragment (sample P1) was analysed according to the fine-grain technique (Zimmermann 1971) which uses the polymineral fraction of the material with size between 1 and 8 µm. The TL measurements of the sample were carried out at the Department of Materials Science of Milano-Bicocca University using a home-made system consisting of an oven for controlled heating in ultra pure nitrogen atmosphere (heating rate 15 °C/s) using a photon counting technique with a bialkali EMI 9635QB photomultiplier coupled to Corning BG12 blue filters. Laboratory irradiations were made with a 1400 MBq <sup>90</sup>Sr-<sup>90</sup>Y beta source and a 37 MBq <sup>241</sup>Am alpha source delivering, respectively,  $1.48 \pm 0.01$  and  $14.80 \pm 0.1$  Gy/min to the sample position. To evaluate the palaeodose (the numerator of the above mentioned age equation), the Multiple Aliquot Additive Dose protocol was applied (Zimmermann 1971). To evaluate the annual dose-rate, the concentrations of the natural radioelements of both sample and burial soil were measured.

For the internal contribution of the annual dose-rate, <sup>238</sup>U and <sup>232</sup>Th concentrations of the plaster were derived from total alpha counting using ZnS (Ag) scintillator discs and assuming a Th/U concentration ratio equal to 3.16. The contribution due to <sup>40</sup>K content was obtained from the total concentration of K measured by flame photometry (Aitken, 1985). The gamma external contribution mainly derives from the radioactivity of a 30 cm diameter sphere centred at the sampling point (Aitken,

Fig. 2 a One of the plaster fragments from San Rocco hill (P3) with a vertical imprint of a branch visible in the right part. **b** The chipped stone artefacts from San Rocco hill (drawings by A. Fragiacomo). *Scale bars*: 1 cm



1985). Such contribution was evaluated from the radioactivity concentrations of the plaster itself and of the surrounding burial soil, allowing 0,15 mGy/year due to the cosmic rays (Prescott and Hutton, 1994). Appropriate correction factors for the effects of humidity on the absorption of the radiation were applied (Aitken 1985) and the possible dating results corresponding to low and high humidity conditions during burial were evaluated.

#### Scanning electron microscope

The surfaces of the two plaster samples (P1–P2) were observed by means of a Quanta250 Scanning Electron Microscope (FEI, Oregon, USA), operating in secondary electron detection mode at the Department of Medical Sciences of the University of Trieste, in order to image plant remains and imprints.

#### X-ray computed micro-tomography

Three plaster samples (P1-P3) were analysed by X-ray computed micro-tomography to detail their inner structure and extract possible 3D virtual casts or partially preserved remains of plants. The analyses were carried out at the Multidisciplinary Laboratory of the "Abdus Salam" International Centre of Theoretical Physics (hereafter ICTP; Tuniz et al. 2013). The ICTP system, successfully used to study several types of archaeological materials (e.g. Bernardini et al. 2015a, 2016), is based on a microfocus Xray source (minimum focal spot size 5 mm, voltage up to 150 kV) and a large area flat panel sensor. The microCT scans were carried out with a source voltage of 110 kV, a current of 90 µA and recording 2400 projections of the sample over 360°. The final volume renderings were reconstructed using DigiXCT in 32-bit format, at an isotropic voxel size of 20.6 µm (samples P1-P2) and 36.93 µm (sample P3). Ring artefacts correction was applied in order to improve the image

quality. The segmentation of the samples was obtained using Amira 5.3.

A vegetal remain, identified in sample P1 thanks to microCT and SEM, was later re-analysed by microCT (voltage: 60 kV; current: 140  $\mu$ A; 1440 projections) in the same laboratory with a higher spatial resolution (voxel size: 7  $\mu$ m) in order to image possibly preserved inner structure of the plant.

# **Obsidian artefact**

#### Prompt gamma activation analysis

Major and few trace elements analysis of the obsidian artefact was carried out at the prompt gamma activation analysis (PGAA) facility of the Budapest Neutron Centre, operating at the  $10^8 \text{ cm}^{-2} \text{ s}^{-1}$  intensity horizontal cold neutron beam (for the recent developments of the Budapest PGAA system, see Szentmiklósi et al. 2010). This technique is a nondestructive method for quantitative determination of all major and some trace elements. Since neutrons can penetrate deep into the sample material, the method provides an average bulk composition for the irradiated volume of a few cubic centimetres. It is known from neutron radiography of rocks that a typical silicate rock of a few centimetres width decreases the neutron beam intensity by 10% relative to the value at the entrance, and the neutrons can pass along the whole width of the sample (Belgya et al. 2008). PGAA is based on the detection of characteristic gamma photons, emitted in  $(n, \gamma)$  reactions (Révay and Belgya 2004). The prompt gamma spectra were collected by a Compton-suppressed HPGe detector, which has been accurately calibrated. The gamma-ray spectra were evaluated using the Hypermet-PC program (Révay et al. 2005). The quantitative analysis is based on the  $k_0$  principle (for a detailed description see Révay 2009 and Kasztovszky et al. 2008), using the spectroscopic data libraries developed at the Budapest laboratory (Choi et al. 2007). The composition was determined using the methods described by Révay (2009). The accuracy of the results is about 3 and 10% for major and trace elements, respectively (Révay 2009).

PGAA has been successfully applied in the characterisation of various archaeological stone objects (Kasztovszky et al. 2008; Szakmány et al. 2011; Bernardini et al. 2014a, 2014b), including obsidian artefacts and geological samples (Kasztovszky and Biró 2004, 2006; Kasztovszky et al. 2014).

# Results

## Burnt plaster remains

#### X-ray diffraction

X-ray diffraction patterns of the artefacts indicate that the main mineral phases present in the samples are quartz (more than 95%) and very little feldspar (Fig. 3). The absence of clear peaks related to clay minerals can be probably due to their vitrification during a heating event, most likely a fire. This happens when the firing temperature rises over about 400 °C (Thorez 1976). In P2 and perhaps P3 samples, this

vitrification process was probably not complete because a small peak at  $20^{\circ} 2\theta$  can be attributed to clay minerals.

#### Thermoluminescence dating

The TL dating results are shown in (Table 1). Taking into account the overall experimental errors (Aitken 1985) and the possible values of water content, the last firing of the sample probably took place sometime between 4000 and 2000 B.C., confirming the ancient age of the plaster.

# Scanning Electron Microscope and X-ray computed micro-tomography analysis of plaster remains

SEM analysis have allowed to image superficial plant remains and imprints in samples P1–P2. In particular, a leaf imprint has been clearly recognized in the sample P1. It is about 3-mm wide and presents a linear shape with parallel venation (Fig. 4a; Fig. 5, sample P1, 1a). On the other hand, in sample P2, part of a plant stem with a polygonal cross-section, about 150-mm long and 2-mm wide, has been identified (Fig. 4b; Fig. 5, sample P2, 1b).



Fig. 3 X-ray diffractograms of samples P1-P4; 2 theta: 2 theta angle; Feld feldspar, Qtz quartz, CM clay minerals

Table 1 Experimental thermoluminescence dating results											
		High humidity conditions				Low humidity conditions					
Palaeodose (Gy)	238 U ppm	232Th ppm	K <sub>2</sub> O (%)	Dose rate (mGy/a)	Years BP	Date B.C.	Dose rate (mGy/a)	Years BP	Date B.C.		
$19.9 \pm 1.4$	2.9–3.1	9.3–9.9	1.6–1.7	$3.61 \pm 0.18$	$5500\pm500$	$3500\pm500$	$4.2\pm0.18$	$4700\pm450$	$2700\pm450$		

MicroCT analysis has shown that all the samples have a similar paste characterized by a prevalent relatively low-dense and fine-grained material, rare small lithic fragments with variable density and numerous elongated empty areas with subcircular sections, corresponding to the spaces that were originally occupied by vegetal materials (Fig. 5). The segmentation of the empty areas and the virtual extraction of their cast have allowed us to identify the shape and orientation of the plants that were mixed to the clay and other materials to produce the plaster. The plants do not show a preferential orientation in any of the analysed samples (Fig. 5). Moreover, the segmentation process has shown the presence of small seeds (from 0.5 to about 1 mm wide) of circular or flat-circular shape (Fig. 5).

In addition, rare plants are preserved as 3D remains showing a relatively high density (Fig. 5, sample P2, 1b, sections 1– 2). The plant stem, re-analysed with a higher resolution, has revealed details of its inner structure. In particular, microCTderived cross-sections of the stem have shown several voids evenly distributed especially in its external part (Fig. 6). The microCT-based renderings have allowed to depict the interruption of most of the voids towards the probable apex of the stem (i.e. from S1 to S3 of Fig. 6). It has also been possible to recognise a lateral outgrowth concurrent with one of the main voids (Fig. 6).

# **Obsidian** artefact

#### Prompt gamma activation analysis

Major and some trace element concentrations (in weight %) of the obsidian artefact from San Rocco are reported in (Table 2). The Cl/SiO<sub>2</sub> versus B/SiO<sub>2</sub> diagram allows the discrimination among different obsidian sources (Kasztovszky and Biró 2004, 2006; Kasztovszky et al. 2014). For the graphic reasons, the mass ratios are multiplied by 10,000. The San Rocco sample falls in the field of the Lipari Island, well separated from all the other sources (Fig. 7).

# **Discussion and conclusions**

The application of various analytical methods to burnt clay plaster remains and few flaked tools discovered on the San Rocco hill (Trieste) has helped understanding how and when this part of the Trieste territory was used during recent prehistory.

From a methodological point of view, the application of X-ray microCT to the study of plaster remains has given encouraging results, allowing to image and virtually extract vegetal remains and imprints. Their non destructive 3D morphological study can

**Fig. 4** SEM images of plant remains in sample P1 (**a**) and P2 (**b**)



**Fig. 5** MicroCT-based virtual renderings showing the plaster fragments P1-P3 *in yellow* (1), the plants remains (*in green*) inside the plaster in transparency (2), the extracted plants remains (*in green*) (3). *a* leaf imprint in P1 (see SEM images of Fig. 4a); *b* plant stem in P2 (see SEM images of Fig. 4b); *c*–*e* seeds extracted from P1; f: seed extracted from P2; S1 and S2 are virtual sections of P2 fragment; in the *white boxes* the polygonal cross-sections of

plant stem b are visible. Where not specified *scale bars*: 1 cm



contribute to collect information about plaster production season and past environments, although the nature of vegetal material remains inside the plaster is clearly influenced by human selection and related technological needs.

More specifically, the investigated clay plaster samples show similar pastes produced mixing together clay, rare small lithic fragments and abundant plants, which do not show any preferential orientation. Thanks to SEM and microCT analysis, information about external and internal morphology of some vegetal remains has been obtained.

In detail, the leaf imprint in sample P1 (Fig. 4a) is consistent with an apical portion of a monocot grass leaf (*Magnoliidae*, *Lilianae*, *Poales*; Angiosperm Phylogeny Group 2009). It shows a characteristic linear shape, with parallel margin, approximately 3-mm wide, convergent toward the apex. The presence of remarkable parallel venation and narrow width of the leaf suggests a putative attribution to *Poaeceae* family; nonetheless, these features are shared with species of other monocot families (e.g. *Cyperaceae*).

The shape of the stem section in sample P2 (Figs. 4, 5, and 6) is consistent with typical cross-sections of apical twigs of a

particular taxonomical group of the tribe *Genisteae* (family *Fabaceae*; Polhill 1976; Angiosperm Phylogeny Group 2009). In particular, the five-angled section matches with some species of *Cystisus* genus (e.g. *Cystisus scoparius*). In *Genisteae*, the cross-section of the stem is of taxonomical value because of the correspondence with anatomical presence and distribution of ribs (Metcalfe and Chalk 1950; Norverto et al. 1994, Schweingruber et al. 2006). More specifically, *Cytisus* usually present ribs (from 5 to 8) made of fibres and chollenchyma (Norverto et al. 1994).

The gaps within the stem, circularly arranged along the central pith (Fig. 6, sections 1–3), are consistent with the distribution of vascular bundles in the primary structure of dicots stems (i.e. eustele). In brooms, vascular bundles can be either embedded or in between the ribs (Norverto et al. 1994). The 3D distribution pattern of these bundles (ending toward the probable apex of the stem, as occurs in all the meristematic tips) corresponds well to an apical structure of a twig (Fig. 6b–c). Additionally, the presence of a vascular bundle in the lateral outgrowth of the stem matches with a typical scheme of stem branching (Fig. 6). Moreover, other small gaps, detectable as voids and mainly as

Fig. 6 MicroCT-based renderings showing the plant stem in P2 with the position of virtual sections S.1-S.3 displayed on the right (a), the voids inside the stem in transparency probably corresponding to former vascular bundles (b) and the extracted voids (c). Scale bars: 1 mm



low dense spots, are scattered in the central part of the stem probably representing breaks in the pith tissue (Fig. 6, sections 1-3). It was also possible to recognize a globose-ovoid remain compatible with the size and shape of the seeds of some Cytisus (Fig. 5, seed f).

Brooms belonging to Cytisus genus are circum-Mediterranean species, which underwent a high differentiation in the Balkan region during Miocene (Cristofolini 1997). They thrive in heaths, open woods and abandoned pastures on different substrates in both Mediterranean and European regions. On the other hand, grasses are a cosmopolitan taxon widespread in all terrestrial ecosystems. In temperate zone, they occur mainly in grassland, marshes and open woods.

The presence of seeds, probably incorporated within the paste together with their seedcase, suggests that the plaster was probably produced during the late summer season. In fact, most of the brooms show a late spring flowering producing mature seeds some months later.

From a strictly archaeological point of view, one basic result has been the assessment of the ancient age of the burnt plaster remains: moreover, the indication given by the TL dating-i.e. 4000 B.C. as terminus post quem for the last firing of these remains-would not exclude a possible contemporaneity (lato sensu) with the few flaked stone artefacts. However, further studies are necessary to confirm the dating of the plaster.

Obsidian artefacts are rather rare in the Trieste Karst and all of them were found in caves or rock-shelters (Williams Thorpe et al. 1979). Fourteen artefacts are reported from seven sites (three from Grotta della Tartaruga, four from Vlaška Jama, three from Riparo di Monrupino and one in each of the following caves: Orso di Gabrovizza, Lonza, Zingari and Ansa), plus an unspecified number of artefacts from Grotta Moser/Jama na Dolech. Among them, ten were provenanced (Williams Thorpe et al. 1979) revealing a prevalence of Liparian obsidians (eight artefacts: one from Tartaruga, Lonza, Zingari and Ansa caves each, two from Vlaška Jama and two from Riparo di Monrupino) and a sporadic presence of Carpathian (one from Grotta della Tartaruga) and Pontine Islands (one from Vlaška Jama) obsidians. The cultural attribution of many findings is uncertain but most of them are correlated with the Vlaška Group (Williams Thorpe et al. 1979) or Cultura dei vasi a coppa (Barfield 1972; Bagolini and Biagi 1983), approximately dated to the second half of the sixth and the first half of the fifth millennium B.C. Instead, the Liparian obsidian from Grotta dell'Ansa is attributed to Copper Age (Williams Thorpe et al. 1979).

Close to the Karst plateau, other obsidian artefacts, mainly discovered on surface and therefore without a reliable

Table 2 Major and   some trace elements of	SiO <sub>2</sub>	(wt%)	73.90		
the obsidian artefact	TiO <sub>2</sub>		0.08		
from San Rocco analysed by PGAA, in wt%. Fe <sub>2</sub> O <sub>3</sub> : total Fe content	Al <sub>2</sub> O <sub>3</sub> Fe <sub>2</sub> O <sub>3</sub>		13.10		
			1.60		
	MnO		0.07		
	CaO Na <sub>2</sub> O		0.77		
			4.41		
	K <sub>2</sub> O		5.31		
	$H_2O$		0.29		
	Sum		99.53		
	Cl	(wt%)	0.32		
	В		0.0205		
	Sm		0.000580		
	Gd		0.000670		



Fig. 7 Cl/SiO<sub>2</sub> vs. B/SiO<sub>2</sub> diagram based on PGAA results of the main Mediterranean and central European obsidian sources. On the axes, the mass ratios\*10,000 values are displayed. The San Rocco sample (*blue cross*) falls within the Lipari field, well separated from the other types

chronological framework, are reported from open-air sites mainly concentrated in the eastern part of Friuli Venezia Giulia, northwest of the Trieste Karst (Pessina and Radi 2006; Maddaleni et al. 2014). The site with the highest number of obsidian artefacts (11) is Sammardenchia in the Friuli plain (Pessina and Radi 2006), dated between 5500 and 4800 (Improta and Pessina 1998) or 4500 B.C. (Ferrari and Pessina 2014). Similarly to the Trieste area, most of the analysed specimens originate from Lipari, while a single artefact has a probable Carpathian origin (Pessina 1999).

In the Croatian part of the Istrian peninsula, the available data are comparable in terms of provenance and number of obsidian artefacts: 30 Liparian and just 2 Carpathian obsidians are reported form Kargadur and other Istrian sites (Tykot 2014).

The small flint pebble could come from the upper course of Reka river or an area located between Sežana and Divača (south-western Slovenia) where deposits containing small flint pebbles are reported (Turk 2004). The raw material of the truncated bladelet is different from the primary flint deposits outcropping in the northern part of Karst plateau, which show a dark grey to black colour and a low quality (Boschian 2005). Its calcareous cortex, texture and colour are compatible with the so-called Alpine or Lessini flint originating from the Jurassic-Cretaceous formations of the southern Alps (Ferrari and Mazzieri 1998; Barfield 2000).

The numerous clay plaster fragments discovered on the slope of San Rocco are probably an indirect evidence of open-air occupation of the hill. Unfortunately, they cannot be correlated to any archaeological structure but the imprints of branches detected in the large samples suggest they could be interpreted as remains of wall plaster belonging to huts or other structures. However, the absence of prehistoric pottery fragments and the scarcity of chipped stone industry are difficult to explain. If the thermoluminescence dating is correct, the occupation of the hill should anyway be referred to a late prehistoric phase between late Neolithic and Copper age, excluding a Roman or later attribution. It is worth mentioning that at Zaule, less than 1 km west of San Rocco hill, a small group of archaeological materials, including a few fragments of pottery vessels, a single-flaked tool and a putative plaster fragment, has been approximately attributed to the same period (Bernardini and Betic 2008). Moreover, a very small polished stone axe blade and a flaked tool were discovered not far from San Rocco, at Stramare (Montagnari Kokelj 1997; Betic et al. 2008). These findings are among the few rare open-air Neolithic-Copper Age evidence in the Trieste area, suggesting that the low Rosandra valley probably acted as midway point between the north-eastern Adriatic coastal areas (and related connection systems) and the inner Karst plateau, as perhaps indicated also by the Liparian obsidians found both at San Rocco and in some caves around Trieste. Moreover, the geomorphological differences between the Karst, used for millennia by shepherds to graze their sheeps and goats (Boschian and Montagnari Kokelj 2000; Montagnari Kokelj et al. 2012), and the relatively fertile and

water-rich coastal belt, where sea salt was available (Montagnari Kokelj et al. 2012), could have induced a diversified seasonal use of the territory by the same groups. Unfortunately, the available archaeological data are too scarce to test this hypothesis.

The position of San Rocco, a hill partially surrounded by a river at the centre of the coast of the Muggia bay, and its long archaeological occupation, spanning from prehistory to Roman time (Bernardini et al. 2015b), find a significant analogy with Sermin in the close bay of Koper (Slovenia; Horvat 1997). The prosperity and long-life continuity of these sites along the coast of northern Istria are probably related to their strategic position with respect to "commercial" routes and to the exploitation of salt, with "industrial" installations from Roman times to the nineteenth, or even twentieth centuries A.D.

Acknowledgements The authors are grateful to M. Di Giovannantonio for the review of the draft and A. Fragiacomo for the drawings of the chipped stone artefacts. This research was supported by the University of Trieste (Finanziamento per la Ricerca di Ateneo-FRA project 2014, coordinated by A. Favretto) and is part of the ICTP, Università di Trieste, Soprintendenza Archeologia FVG agreement "Accordo di collaborazione per lo sviluppo di tecnologie scientifiche avanzate per la conoscenza, la tutela e la valorizzazione delle evidenze archeologiche e del paesaggio antico della regione Friuli Venezia Giulia". The PGAA measurements of the obsidian samples were performed with the support of K100385 Nr. project of the National Research, Development and Innovation Office (NKFIH). The study was conceived and designed by FBe; FBe carried out archaeological surveys; ES performed TL dating and wrote the related chapter; DL and ADM performed XRD analyses; GT performed SEM analyses; FBe and CT performed microCT analyses; ZK performed PGAA analyses; RM performed research; FBo wrote the paleobothanical parts; FBe and MMK wrote the paper.

# References

Aitken MJ (1985) Thermoluminescence dating. Academic Press, Oxford

- Anderson E, Almond MJ, Matthews W (2014) Analysis of wall plasters and natural sediments from the Neolithic town of Çatalhöyük (Turkey) by a range of analytical techniques. Spectrochim Acta A 133:326–334
- Angiosperm Phylogeny Group (2009) An update of the Angiosperm Phylogeny Group classification for the orders and families of flowering plants: APG III (2009). Bot J Linn Soc 161(2):105–121
- Bagolini B, Biagi P (1983) Il Carso ed il Friuli nell'ambito del neolitico dell'Italia settentrionale e dell'area balcanico-adriatica. Atti della Società per la Preistoria e Protostoria della Regione Friuli-Venezia Giulia 4:187–206
- Barfield LH (1972) The first Neolithic cultures of north-eastern Italy. Fundamenta A/3 VII: 182-216.
- Barfield LH (2000) Commercio e scambio nel Neolitico dell'Italia settentrionale. In: Pessina A, Muscio G (eds) La neolitizzazione tra oriente e occidente. Museo Friulano di Storia Naturale, Udine, pp 55–66
- Belgya T, Kis Z, Szentmiklósi L, Zs K, Kudejova P, Schulze R, Materna T, Festa G, Caroppi PA (2008) The ancient charm collaboration, first elemental imaging experiments on a combined PGAI and NT setup at the Budapest Research Reactor. J Radioanal Nucl Chem 278(3): 751–754

- Bernardini F, Betic A (2008) Il sito di Zaule presso Trieste (Italia nordorientale). In: Auriemma R, Karinja S (eds) Terre di mare. L'archeologia dei paesaggi costieri e le variazioni climatiche. Stampa Luglio Fotocomposizioni, Trieste, pp 38–43
- Bernardini F, De Min A, Lenaz D, Kasztovszky Z, Turk P, Velušček A, Szilágyi V, Tuniz C, Montagnari Kokelj E (2014a) Mineralogical and chemical constraints about the provenance of Copper Age polished stone axes of "Ljubljana type" from Caput Adriae. Archaeometry 56(2):175–202
- Bernardini F, De Min A, Lenaz D, Kasztovszky Z, Turk P, Velušček A, Tuniz C, Montagnari Kokelj E (2014b) Petrographic and geochemical comparison between the Copper Age "Ljubljana type" axes and similar lithotypes from Eisenkappler Diabaszug complex (southern Austria). J Archaeol Sci 41:511–522
- Bernardini F, De Min A, Lenaz D, Mendoza Cuevas A, Nuviadenu CK, Tuniz C, Montagnari Kokelj E (2015a) Whetstones from Bronze Age hill forts of north-eastern Italy. Archaeometry 57(S1):36–53
- Bernardini F, Vecchiet A, De Min A, Lenaz D, Mendoza Cuevas A, Gianoncelli A, Dreossi D, Tuniz C, Montagnari Kokelj M (2016) Neolithic pottery from the Trieste Karst (northeastern Italy): a multianalytical study. Microchem J 124:600–607
- Bernardini F, Vinci G, Horvat J, De Min A, Forte E, Furlani S, Lenaz D, Pipan M, Zhao W, Sgambati A, Potleca M, Micheli R, Fragiacomo A, Tuniz C (2015b) Early Roman military fortifications and the origin of Trieste (Italy). PNAS 112(13):1520–1529
- Betic A, Bernardini F, Montagnari Kokelj M (2008) I castellieri di Trieste tra Carso e mare. In: Auriemma R, Karinja S (eds) Terre di mare. L'archeologia dei paesaggi costieri e le variazioni climatiche. Stampa Luglio Fotocomposizioni, Trieste, pp 25–37
- Boschian G (2005) Environment and hunters-gatherers mobility in the northern Adriatic Region. Preistoria Alpina 39:91–102
- Boschian G, Montagnari Kokelj E (2000) Prehistoric shepherds and caves in the Trieste Karst (Northeastern Italy). Geoarchaeology 15(4): 331–371
- Choi HD, Firestone RB, Lindstrom RM, Molnár GL, Mughabghab SF, Paviotti-Corcuera R, Révay ZS, Trkov A, Zerkin V, Chunmei Z (2007) Database of prompt gamma rays from slow neutron capture for elemental analysis. International Atomic Energy Agency, Vienna
- Cristofolini G (1997) The biodiversity of Leguminosae *Genisteae* and its genesis. Lagascalia 19(1–2):121–128
- Fabbri B, Gualtieri S, Rottoli M, Tasca G, Vitri S, Visentini P (2007) Materiali concotti dell'abitato tardoneolitico di Palù di Livenza (PN). In: Fabbri B, Gualtieri S, Rigoni AN (eds) Materiali argillosi non vascolari: un'occasione in più per l'archeologia, Atti dell 9° Giornata di Archeometria della Ceramica (Pordenone, 18–19 aprile 2005). Lithostampa, Pasian di Prato (UD), pp 66–80
- Ferrari A, Mazzieri P (1998) Fonti e processi di scambio di rocce silicee scheggiabili. In: Pessina A, Muscio G (eds) Settemila anni fa il primo pane: ambienti e culture delle società neolitiche. Museo Friulano di Storia Naturale, Udine, pp 165–170
- Ferrari A, Pessina A (2014) Sammardenchia. In: Visentini P, Podrug E (eds) Adriatico senza confini. Via di comunicazione e crocevia di popoli nel 6000 a. C.. Civici Musei di Udine, Museo Friulano di Storia Naturale, Udine, pp 124–127
- Horvat J (1997) Sermin: A Prehistoric and Early Roman Settlement in Northwestern Istria, Opera Instituti Archaeologici Sloveniae 3. Institut za Arheologijo ZRC SAZU, Založba ZRC, Ljubljana.
- Improta S, Pessina A (1998) La neolitizzazione dell'Italia settentrionale, il nuovo quadro cronologico. In: Pessina A, Muscio G (eds) Settemila anni fa il primo pane: ambienti e culture delle società neolitiche. Museo Friulano di Storia Naturale, Udine, pp 107–115
- Kasztovszky Z, Biró KT (2004) A kárpáti obszidiánok osztályozása prompt gamma aktivációs analízis segítségével: geológiai és régészeti mintákra vonatkozó első eredmények ("Fingerprinting Carpathian Obsidians by PGAA: First results on geological and archaeological specimens"). Archeometriai Műhely 1(1):9–15

- Kasztovszky Z, Biró KT (2006) Fingerprinting Carpathian obsidians by PGAA: first results on geological and archaeological specimens. In: Proceedings of the 34th International Symposium on Archaeometry. Institución «Fernando el Católico», Zaragoza, pp 301–308
- Kasztovszky Z, Biró KT, Kis Z (2014) Prompt Gamma Activation Analysis of the Nyírlugos obsidian core depot find. Journal of Lithic Studies 1(1):151–163
- Kasztovszky Z, Biró KT, Markó A, Dobosi V (2008) Cold neutron prompt gamma activation analysis - a non-destructive method for characterisation of high silica content chipped stone tools and raw materials. Archaeometry 50(1):12–29
- Maddaleni P, Micheli R, Monai GS, Pagano F (2014) Nuovi dati dal territorio di Cividale del Friuli (UD): l'insediamento preistorico tra il fiume Natisone e il torrente Lesa in località Madriolo. In: Riassunti Comunicazioni e Poster, XLIX Riunione Scientifica dell'Istituto Italiano di Preistoria e Protostoria Preistoria e Protostoria del Caput Adriae (Udine, 8–12 ottobre 2014), p 44
- Metcalfe CR, Chalk L (1950) Anatomy of the Dicotyledons. University Press, Oxford
- Montagnari Kokelj E (1997) Il territorio di Muggia prima della costruzione dei castellieri. In Maselli Scotti F (ed) Il Civico Museo Archeologico di Muggia. Trieste, pp 35–37
- Montagnari Kokelj M, Bernardini F, Boscarol C, Velušček A (2013) Le Karst et les Alpes d'Italie nord-orientale: éléments pour une reconstruction de l'évolution culturelle au cours de la préhistoire récente. In: Borello MA (ed) Les hommes et les Alpes. Chasseurs, agricultures et premiers metallurgists, BAR International Series 2476. Archaeopress, Oxford, pp 147–161
- Montagnari Kokelj E, Boscarol C, Peretti G (2012) Sulle tracce dei pastori-allevatori pre-protostorici nel Carso (e altrove): esempi di uso integrato di indicatori diversi. In: Busana MS, Basso P (eds) La lana nella Cisalpina Romana. Economia e società. Studi in onore di Stefania Pesavento Mattioli, Antenor Quaderni 27. Padova University Press, Padova, pp 29–42
- Morgan GC (1992) Romano-British mortars and plasters. PhD thesis, University of Leicester
- Norverto CA, González-Andrés F, Ortiz JM (1994) Leaf and stem anatomy of species of Cytisophyllum, Cytisus, Chamaecytisus, Genista, and Genista sect. Teline (fabaceae: Genisteae) as an aid for taxonomy. Israel Journal of Plant Sciences 42(3):213–225
- Pessina A (1999) Manufatti in ossidiana dal sito di Sammardenchia-Cûeis. In: Ferrari A, Pessina A (eds) Sammardenchia-Cûeis. Contributi per la conoscenza di una comunità del primo neolitico. Museo Friulano di Storia Naturale, Tavagnacco (UD), pp 287–290
- Pessina A, Radi G (2006) La diffusione dell'ossidiana nell'Italia centrosettentrionale. In: Materie prime e scambi nella preistoria italiana nel cinquantenario della fondazione dell'Istituto Italiano di Preistoria e Protostoria, Atti della XXXIX Riunione Scientifica (Firenze, 25–27 novembre 2004). Istituto Italiano di Preistoria e Protostoria, Firenze, pp 435–460
- Polhill RM (1976) Genisteae (Adans.) Benth. and related tribes (Leguminosae). Academic Press.

- Prenc F (2012) Dinamiche insediative e tipologie edilizie nella Bassa Friulana. In: Bonetto J, Salvadori M (eds) L'architettura privata ad Aquileia in età romana. Atti del convegno di studio (Padova, 21–22 febbraio 2011). Padova University Press, Padova, pp 475–486
- Prescott JR, Hutton JT (1994) Cosmic ray contributions to dose-rates for luminescence and ESR dating: large depths and long-term time variations. Radiat Meas 23(2/3):497–500
- Révay ZS (2009) Determining elemental composition using prompt gamma activation analysis. Anal Chem 81(16):6851–6859
- Révay ZS, Belgya T (2004) Principles of PGAA method. In: Molnár GL (ed) Handbook of prompt gamma activation analysis with neutron beams. Kluwer Academic Publishers, Dordrecht/Boston/New York, pp 1–30
- Révay ZS, Belgya T, Molnár GL (2005) Application of Hypermet-PC in PGAA. J Radioanal Nucl Chem 265(2):261–265
- Schweingruber FH, Börner A, Schulze ED (2006) Atlas of woody plant stems: evolution, structure, and environmental modifications. Springer, New York
- Staffa AR (1993) Forme di abitato altomedievale in Abruzzo: un approccio etnoarcheologico. In Brogiolo GP (ed) L'edilizia residenziale tra V e VIII secolo, Atti del IV Seminario sul tardo antico e l'alto medioevo in Italia Centrosettentrionale (Monte Barro, settembre 1993). Mantova, pp 67–88
- Szakmány G, Kasztovszky Z, Szilágyi V, Starnini E, Friedel O, Biró KT (2011) Discrimination of prehistoric polished stone tools from Hungary with non-destructive chemical Prompt Gamma Activation Analyses (PGAA). Eur J Mineral 23(6):883–893
- Szentmiklósi L, Belgya T, Révay ZS, Kis Z (2010) Upgrade of the prompt gamma activation analysis and the neutron-induced prompt gamma spectroscopy facilities at the Budapest research reactor. J Radioanal Nucl Chem 286(2):501–505
- Thorez J (1976) Practical identification of clay minerals. Editions Lelotte, Dison, Belgium
- Tuniz C, Bernardini F, Cicuttin A, Crespo ML, Dreossi D, Gianoncelli A, Mancini L, Mendoza Cuevas A, Sodini N, Tromba G, Zanini F, Zanolli C (2013) The ICTP-Elettra X-ray laboratory for cultural heritage and archaeology. Nucl Instr Meth A 711:106–110
- Turk P (2004) Viktorjev Spodmol and Mala Triglavca, Contributions to understanding the Mesolithic period in Slovenia, Opera Instituti Archaeologici Sloveniae 9. Institut za Arheologijo ZRC SAZU, Založba ZRC, Ljubljana.
- Tykot RH (2014) Utilizzo e commercio dell'ossidiana in adriatico. In: Visentini P, Podrug E (eds) Adriatico senza confini. Via di comunicazione e crocevia di popoli nel 6000 a.C.. Civici Musei di Udine, Museo Friulano di Storia Naturale, Udine, pp 171–181
- Williams Thorpe O, Warren SE, Barfield LH (1979) The sources and distribution of archaeological obsidian in Northern Italy. Preistoria Alpina 15:73–92
- Zimmermann DW (1971) Thermoluminescence dating using fine grains from pottery. Archaeometry 13(1):29–52