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Archaeological ash deposits and soils formed on ash in the south of the East European Plain

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ABSTRACT

Ash as an anthropogenic substrate is widely found at archaeological sites in the south of the East European Plain. Investigations of archaeological ashes, the results of which are presented here, have been conducted in three regions that differ in climate and extent of forest cover (from 29 to 1.5%): 1) typical forest–steppe; 2) piedmont forest-steppe with islands of groves; 3) steppe, almost woodless landscapes. Using spectrometry and X-ray analysis, the present study investigates the chemical composition of ancient ash and ash experimentally produced from different sorts of fuel, as well as the geochemistry of soils developed on ash deposits. For ashing, 25 samples of plants that potentially might have been used as fuel were selected, as well as dung from cattle and horses. Using the geometric mean values of concentrations of diagnostic elements, a formula was proposed for evaluating the pedogenetic transformation of ash, which is based on the ratio of accumulation elements (Cu, As, SiO_2, Al_2O_3 and Pb) and dispersion elements (Sr, Ca, Co, Mg and Na_2O). The procedure makes it possible to date the pedogenetically transformed ash through the stable associations of chemical elements diagnostic of the geochemical accumulation and dispersion in the soils formed on ash. Geochemical criteria were established for identifying ash that results from the combustion of dung, wood or a combination of different fuels. This study opens prospects for further research into archaeological ash deposits in varying cultural, temporal and environmental conditions.

1. Introduction

The pyrogenic processes and related combustion products have had considerable influence on the micromorphology and mineral composition of archaeological deposits (Courty et al., 1989; Canti, 2003). Ash as a common component of archaeological deposits, along with different methods of identification of its sources, is considered in a number of studies (Braadbaart et al., 2012, 2017; Powell et al., 2012; Shahack-Gross and Ayalon 2013; Mentzer, 2014; Kovács et al., 2017). As various plant taxa and other fuels differ in their elemental composition, chemical analysis of ash, along with other methods, is an important tool for identifying different types of fuel (Hillis, 1987; Etiégni and Campbell, 1991; Steenari et al., 1999; Canti, 2003; Liodakis et al., 2005; Miller and Miller, 2007; Ntinou and Tsartsidou, 2017). In the northern Black Sea region, the chemical composition of "ashy" deposits has only been studied in Moldova, in connection with archaeological sites of the Noua-Sabatinovka cultural complex (Daszkiewicz and Schneider, 2011; Demkin, 2011; Facklam, 2011) and some sites in Crimea (Lisetskii and Ergina, 2010; Lisetskii et al., 2016). Identification of various fuels contributes to a better understanding of the palaeoecological conditions and economic activities of ancient societies. Assessing the pedogenic transformation of ashy deposits makes it possible to establish their age and the age of related cultural strata, which is particularly valuable when other datable archaeological material is absent.

As a common attribute of human habitations, special ash deposits, the so-called "zol'niki" or ashy mounds, are known in the vast territory from the Southern Ural through the Danube Region, ranging in date from the Bronze Age to the late medieval and sub-modern periods (Kruglikova, 1975; Rusanova, 1998; Sava, 2005a; Rusjaeva, 2006; Nosova, 2008; Stolba and Andresen, 2015; Kovalčuk, 2015). In the north-western and northern Black Sea regions, such ashy deposits are particularly characteristic of the Noua and Sabatinovka cultures, as well as the subsequent cultures of the late Bronze Age and early Iron Age (Belogrudovka, Belozerka and Chernoles cultures). In the Greek settlements of the Black Sea coast and in the Scythian settlements of the forest-steppe zone, they also constituted a notable feature of their

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cultural landscape. In the ancient city of Olbia, ash has been used in the layered foundations of its buildings, while in the city's rural territory it served as fertilizer (Lisetskii and Rodionova, 2015). In Crimea, the soils rich in ash and ashy deposits occupy an area of 14,200 ha, including 2100 ha of ploughed land (Kogel', 1969). The height of ashy mounds varies from 0.5 to 2 to 10–13 m (Kruglikova, 1975; Dirin, 1896, 120; Stolba and Andresen, 2015). Their number varies too, amounting at the Bronze Age sites and the Scythian settlements of the forest-steppe zone to 10–25 and occasionally over 50 (Petrenko, 1989; Sava, 2005a; Sava and Kaiser, 2011). The youngest ashy deposits are recorded at the abandoned, mainly Tatar and Russian, rural settlements of the 18th through the first half of the 20th century.

While the nature of the Bronze Age and Early Iron Age ashy mounds in the northern Black Sea region remains a matter of debate, the three principal hypotheses explain them as: 1) household waste, 2) places of cult and ritual activities or 3) the ruins of dwellings covered with ashy remains (Rusanova, 1998; Belozor, 2012; Gerškovič, 1999, 2004). With regard to the "zol'niki" of the Noua and Sabatinovka cultures, it has been argued that they contain no proper ash, as no visual traces of burning could be discerned and the content of C_{org} (2.1–2.3%) is relatively high (Daszkiewicz and Schneider, 2011; Demkin, 2011). According to this hypothesis, each "ashy mound" conceals the remains of an estate, and the deposits of the characteristic light-grey "ashy" colour are the naturally decayed organic remains of plant or animal origin (straw, grass, etc.) accumulated in households by the time they were abandoned (Gerškovič, 2004; Sava and Kaiser, 2011). The economic structure of these societies, which practiced transhumance, periodically changing settlement places, is thought to account for the large number of sites with "zol'niki" in this region (Gershkovich, 2003).

Traditional sources of fuel in forestlands are wood and peat. In the steppe regions, where resources of firewood are limited, the need for fuel was compensated by alternative sources. According to Herodotus, animal bones were one of the alternative sources of fuel among the nomads of the northern Black Sea region (Hdt. 4.61; Godley, 1920). Of special importance was, traditionally, also the dung of herbivore animals, the use of which as fuel is recorded in different parts of the globe from the Neolithic to modern day (Miller, 1984; Brink, 2008; Mlekuž, 2009; Shahack-Gross, 2011; Portillo et al., 2017). Also in Crimea, this practice is well-documented (Çelebi, 2008; Stolba and Andresen, 2015). According to the mid–19th century ethnographic descriptions, manuring was alien to the agricultural practices of the Crimean Tatars, all the dung being used as fuel (Radde, 1856). Ash was not used as a fertilizer either, being brought by the villagers to the common ash mounds. These ash mounds, which reached 2 m and more in height, constituted an important feature of the natural and cultural landscape of the Tatar villages.

The ready fuel (Russ. *kizyak*, Turk. *tezek*) was a mixture of dung and straw. After drying, the stores of *kizyak* were kept in the homestead courtyards, forming long, oval, up to 2 m-high heaps that were daubed with fresh excrements as protection against moisture (Radde, 1856). According to Radde, the quality of the sheep dung *kizyak* is higher than that of cattle dung, and its heat emission is higher than that of the European beech (*Fagus silvatica*). As demonstrated experimentally, even though cow dung can produce a higher temperature than the sheep dung (up to 630°C and 570°C correspondingly), the latter burns longer (Shahack-Gross et al., 2005; Shahack-Gross, 2008).

An important advantage of this fuel for nomadic and agricultural communities is its wide availability. According to the archaeozoological evidence from the south of the East European Plain, cattle clearly dominated in the Bronze Age herds, making in some places up to 44% of the total (Bibikova, 1970; Kolotuchin, 1996, 2003; Gershkovich, 2003; Sava, 2005b; Sava and Kaiser, 2011; Lisetskii et al., 2017). Calculations suggest that one cow is able to produce about 10,000 kg of dung annually, while one sheep yields over 500 kg per year or about 1.5 kg per day (Slicher van Bath, 1963; Mlekuž, 2009).

In this work, we aim to experimentally investigate the chemical composition of the potential ancient fuels and identify the differences in types of ash and the soils formed on ashy strata in various regions of the East European Plain that differ in vegetation cover. Attempts have also been made to work out criteria for identifying ash and its genetic types, as well as to develop a method for dating ashy deposits.

2. Research area

Investigations of ash from the cultural strata of archaeological sites were conducted in three regions that differ significantly in climate and vegetation cover: 1) typical forest-steppe with hill groves on the right bank of the Vorskla River (50°37′15.5″N, 36°0′13.4″E; average annual temperature 6.1°C, annual precipitation 574 mm); 2) forest-steppe of piedmont Crimea with islands of groves (an area with coordinates from 45°7′2.0″N, 34°38′5.8″E to 45°8′28.5″N, 34°39′52.5″E) with an average annual temperature of 10.3 °C and an annual precipitation of 450 mm; 3) steppe landscapes of north-western Crimea (45°29′21.3″N, 32°43′17.9″E) with an average annual temperature of 9.8–10.2 °C and an annual precipitation of 340 mm.

Palaeopedological and palaeobotanical data from the forest-steppe of the Central Russian Upland suggests that the landscapes with deciduous forest on watersheds began to develop as early as the late Sub-Boreal (3500–2800 BP) (Čendev et al., 2014). Prior to the economic development of the Vorskla River region in the first half of the 17th century, woodlands amounted to 40% of the total area (Matveev et al., 2017), in contrast to only 29% at present. In Crimea, woodland makes up only 11.5% of the total area, the majority of which (66.5%) is represented by oak forests. For the area of Pantikapaion in eastern Crimea, Theophrastus, the 4th-century BC author of *Historia Plantarum* (HP 4.5.3; Hort, 1916), attests a number of deciduous species, including oak, elm, ash and others, but no pines or firs. For other parts of Crimea, no such literary evidence is available. In north-western Crimea, at present, no oak or pine grows in natural conditions, arboreal and shrub vegetation being found only at the bottoms of larger ravines (1.5% of the total area). However, the finds of charred wood, along with pollen and the archaeozoological data from archaeological sites, testify to the presence of oak, maple, elm, hazel, hornbeam, juniper, alder, poplar and other deciduous trees in the 4th–1st centuries BC, as well as to the presence of forest-steppe fauna (Levkovskaja, 1970; Maslov and Filin, 1976; Ščeglov, 1978; Podgorodeckij, 1979; Hannestad, 2007; Stolba, 2014. For the finds of the phytoliths of coniferous trees at the classical and Bronze-Age sites in the area, see Lisetskii et al., 2020). Geoarcheological and palinological studies in the area of ancient Chersonesos also suggest that in the period of the Greek colonisation, the territory of south-western Crimea must have been considerably more wooded than now (Cordova and Lehman, 2003). In the central part of Crimean piedmonts (Belogorsk District), woodland makes up 29.4% of the total area, of which only 12 small oak grove plots are protected (Garkusha and Bagrova, 2012). Buried forest soils discovered under the 4th century BC Scythian barrows suggest that these are the remnants of ancient forestland deforested by humans.

3. Data and methods

3.1. Archaeological sites with ash deposits

Sampling ash deposits (A) and soils formed on ash (S) in the south of the East European Plain (Fig. 1) was carried out in each of the soil-stratigraphic sections at archaeological sites of different ages. Most indicative stratigraphic columns with ash deposits and soils formed on them are presented in supplementary materials (Figs. S2–S4).

In Region 1, our investigations were focused on the fortified settlement of Borisovka situated in the forest-steppe zone, in the basin of the Vorskla River (Belgorod Oblast). The Scythian settlements of this region fall into two chronological groups: the early group (7th–5th century BC) and the late group (5th–3rd century BC) (Moruženko, 1985). In a soil

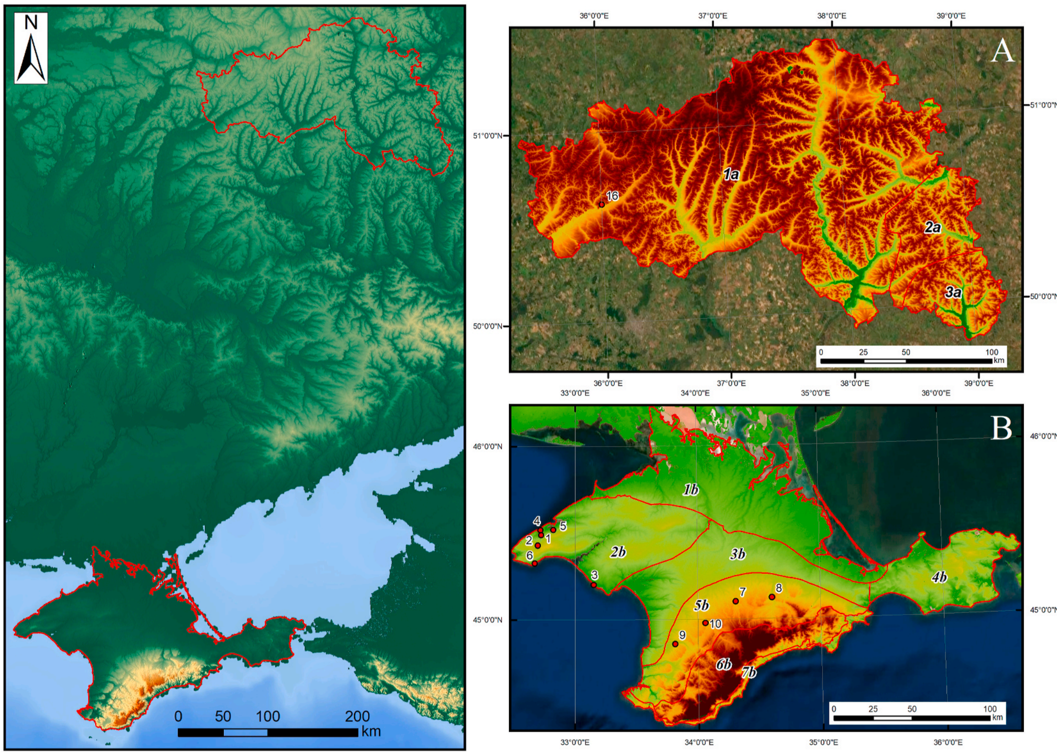

Fig. 1. Location of research objects (ashy soils and ash deposits) in the continental forest-steppe, Belgorod Oblast (A) and in the Plain (steppe) and Piedmont (forest-steppe) Crimea (B). Archaeological sites: Borisovka, mid-5th c. BC (16); Multiperiod settlement S11-022 (1); Kunan, 2nd c. BC (2); Airchi, 2nd c. BC – 1st c. AD (3); Kalos Limen, 4th c. BC – 2nd c. AD (4); former village of Saya, before 1944 (5); former village of Oirat, before 1944 (6); Borut-Khane, 1st c. BC – 1st c. AD (7); Ak-Kaya, c. 225–250 AD (8); Zayachye, 2nd – 3rd c. AD (9); Kermen-Kyr, 2nd – 3rd c. AD (10). Natural areas: 1a – Typical forest-steppe; 2a – Southern forest-steppe; 3a – Steppe; 1b – North Crimean lowland steppe; 2b – Tarkhankut elevated plain; 3b – Central Crimean plain steppe; 4b – Kerch hilly-ridged steppe; 5b – Foothill forest-steppe; 6b – Main ridge, mountainous meadows and forests; 7b – Southern Coast.

section made at the periphery of the Borisovka settlement (A16), an ashy layer dating to the mid-5th century BC was excavated to a depth of 1.0 m.

In Region 2 (Piedmont Crimea), the late Scythian fortified settlements of Borut-Khane, Ak-Kaya (Fig. 2) and Kermen-Kyr, as well as the unfortified settlement of Zayachye, were investigated (Fig. 1, nos. 7–10). At Borut-Khane, which dates to the period from the 3rd–2nd century BC to the 1st century AD (Smekalova et al., 2017), several ash mounds measuring from 0.5 to 2.0 m in height were identified. At this site, near the rampart, at the depth of 46–98 cm, a layer of pure ash was also discovered. A sample of ash for chemical analysis was taken from the depth of 63–73 cm (A167). The modern forest tracts, closest to the settlement, are situated at a distance of 4.3 km. For the regional reconstruction of the palaeogeographic conditions, we also used the data on the buried soils and wood remains uncovered under the tumuli, in particular under the burial mound of Ak-Kaya IX. The main burial of the kurgan, dating to 350–325 BC, was covered with oak logs. A sample of ancient wood for experimental ashing was taken from a log of 42–47 cm in circumference (P22).

Object numbers (ash [A], soils formed on ash [S]) are consistent with Table 1.

In Region 3 (north-western Crimea), archaeological sites sampled for ash (Fig. 1, nos. 1–6). included a multi-period, Bronze Age and Early Iron Age settlement S11–022, the Hellenistic and Roman period sites of Kunan, Airchi and Kalos Limen, and the abandoned sub-modern Tatar villages of Saya (45°31′7.9″N, 32°49′14.5″E; Table 1, no. S5) and Ojrat

Fig. 2. Ancient settlement of Ak-Kaya (Piedmont Crimea; excavations by Yu.P. Zaitsev). The soils formed after the demise of the settlement (c. 225–250 AD); the thickness of horizon A: 0–23 cm, of horizon AB: 23–34 cm. The depth of the ash deposit: 34–80 cm below the modern top-surface.

Table 1
Objects of study at archaeological sites of three investigated regions (soils formed on ash [S] and ash from cultural strata [A]).

No.	Object	Place of sampling	Horizon, depth (cm)	Soil colour, Munsell (dry)
S1/1	Settl. S11-022, area of Chernomorskoe	Soil on ash; archaeological horizon of the 10th c. BC	Hor. A, 0–18 Hor. AB, 18–50 Ash, >50	10 YR 5/2 10 YR 6/2 10 YR 7/2
S1/2	Settl. S11–022	Soil on ash	Hor. A, 5–26 Hor. AB, 26–55.5 Hor. B1, 47–55.5 Ash, 55.5–60.5	10 YR 5/3 10 YR 5/2 10 YR 5/2.5 10 YR 6/2.5
A1/3	Settl. S11–022	Cultural layer containing ash (section, 2 m W of stone structure)	Hor. C. Top section of the layer (60–70 cm) Hor. C. Lower section of the layer (80–90 cm)	10 YR 6/2 10 YR 6/2
A2/1	Kunan, 2nd c. BC	Ash intercalation with traces of fire	39–41	10 YR 5/1.5
A2/2	Kunan, 2nd c. BC	Cultural layer with ash	>41	10 YR 5/3
A3/1	Airchi, 2nd c. BC – 1st c. AD	Defensive ditch	235	10 YR 7/1
A3/2	Airchi, 2nd c. BC – 1st c. AD	A 3.5–3.8 m wide and 1.2 m deep pit with a 33 cm thick layer of ash	200	10 YR 6/2
A3/3	Airchi, 2nd c. BC – 1st c. AD	Hearth (93 × 41 cm); ash on the hearthstone	152	10 YR 6/4
A4/1	Kalos Limen, 1st c. BC – 1st c. AD	Top of ashy layer	Hor. A, 0–22	10 YR 6/2
A4/2	Kalos Limen, 4th c. BC – 2nd c. AD	Citadel (late 3rd–2nd c. BC), cultural stratum	>20	10 YR 7/2
S5	Former village of Saya, before 1944	Top of ashy layer	20 50	10 YR 5/2.5 10 YR 5/3
S6	Former village of Oirat, before 1944	Top of ashy layer	Hor. A, 0–16 Hor. AB 16–28	10 YR 6/2 10 YR 6/2
A7	Borut-Khane, 1st c. BC – 1st c. AD	Ash deposit ("zol'nik")	Hor. B1, >37	10 YR 6/2
A167	Borut-Khane, 1st c. BC – 1st c. AD	Rampart	Ash, 63–73	10 YR 7/1
A8	Ak-Kaya, 225–250 AD	Settlement	Hor. B1, >33.5	10 YR 6/2
A9	Zayachye, 2nd – 3rd c. AD	Village	Hor. B1, >32	10 YR 6/1
A10	Kermen-Kyr, 2nd – 3rd c. AD	Settlement	Hor. B1, 30–35	10 YR 6/1
A16	Borisovka, mid-5th c. BC	Settlement	Ash, 62–72	10 YR 6/2

(45°19′37.0″N, 32°40′14.3″E; Table 1, no. S6). Unlike the short-lived fortified Greek farmhouse of Kunan, where only two habitation phases were distinguished, i.e. of the second half of the 4th through the early 3rd century BC and of the last third of the 3rd through the mid-2nd century BC (Smekalova and Stolba, 2009), the chronology of Kalos Limen and Airchi is considerably broader, including also the Roman period. At Kunan, the upper ashy horizon bears witness of a fire that destroyed the farmhouse in the mid-2nd century BC (Smekalova and Kutajsov, 2017). The objects sampled at the fortified coastal settlement of Airchi, situated 9 km west of Yevpatoriya, included an ashy fill of a household pit and a well-preserved late-Scythian furnace, which was discovered at a depth of 1.5 m (Fig. 3) and penetrated the cultural layer of the Hellenistic period. Ash sample A3/3 has been taken at the bottom of this furnace.

3.2. Plant and dung samples

In 2016, 25 samples of arboreal and grass plants (P no.) that potentially could have served as fuel were taken for experimental ashing (Table 2). These were collected in the ravines of the Tarkhankut Peninsula (P1–9), in the Vorontsov Park of the township of Chernomorskoe (P10–13) and in the Belogorsk District of Crimea (P25, P22). Further, cattle and horse dung has been collected on pastures in the Chernomorskoe district of Crimea (Region 3). Moreover, in the typical forest-steppe of the Belgorod region, five types of arboreal species that no longer grow in the natural conditions of the Tarkhankut Peninsula were collected. The collection of plants selected for experimental ashing and chemical analysis was supplemented by a typical ash sample (A167) that comes from the foothill forest-steppe, where both wood and manure could be used as fuel.

3.3. Geochemical methods for the study of soils and ash

The chemical composition of ash prepared from plant samples was investigated using a variety of techniques, including emission spectrometry (Zn, Cu, Mn and Co; spectrometer ICPE–9000 with induction-bound plasma), atomic absorption spectroscopy (Pb and Cd: spectrometer Quant–2AT; Hg: spectrometer Quant–Z) and photocolorimetry (As; photocolorimeter KFK–3–01). Ashing of samples was carried out in a muffle furnace at 450 °C. To facilitate accurate comparison of the results, the same methods were used to analyse sample A167 that derives from an archaeological site. Colours of ash and soil (dry and moist) were recorded using the Munsell system.

Chemical analyses of soils included the following standard procedures (Arinushkina, 1970): the C_{org} content by Tyurin's method (by oxidation with a solution of potassium dichromate in sulphuric acid); CO_2 in carbonates by acidometry; pH (H_2O) by potentiometric method; the available P_2O_5 (mg· kg^{-1}) by Machigin's method (spectrophotometer UNICO–1200), and K_2O on a fiery photometer. The determination of cation exchange capacity (CEC) in calcareous soils was performed using EDTA–Na_2.

Concentrations of 22 chemical elements in ash and soils were determined by measuring the fractions of metal mass and oxides in powdered samples using XRF by a spectrometer Spectroscan Max–GV. Chemical elements analysed included ten macroelements (Ca, Si, Al, Fe, Ti, Mn, Mg, P, K, Na) and twelve trace elements (V, Cr, Ni, Co, Cu, Zn, As, Sr, Pb, Ba, Zr, Rb).

Using these data, the value of $SiO_2/(RO + R_2O)$, which characterizes the degree of the eluviation, was calculated by the formula:

Fig. 3. Ash sampling spot in the 2nd cent. BC–1st cent. AD furnace at the Airchi settlement.

Table 2
Plant (P1–18, P21–26 and P28) and dung (P19 and P20) samples used for ashing.

No.	Plants/dung types	Plant parts	Munsell; dry
P1	*Crataegus taurica* Pojark.	wood	10 YR 6/1
P2	*Salsola australis* R. Br	stalks	10 YR 5/1
P3	*Ligustrum vulgare* L.	wood	10 YR 5/1
P4	*Juniperus foetidissima* Willd.	wood	10 YR 5/1
P5	*Malus praecox* (Pall.) Borkh.	wood	10 YR 5/1
P6	*Pyrus pyraster* Burgsd.	wood	10 YR 5/1
P7	*Prunus spinosa* L.	wood	10 YR 5/1
P8	*Artemisia taurica* Willd.	stalks	10 YR 5/1
P9	*Padellus mahaleb* (L.) Vass.	wood	10 YR 5/1
P10	*Quercus pubescens* Willd.	wood	10 YR 5/1
P11	*Carpinus betulus* L.	wood	10 YR 6/1
P12	*Ulmus minor* Mill.	wood	7.5 YR 3/0
P13	*Fraxinus pennsylvanica* Marsh.	wood	10 YR 6/1
P14	*Acer campestre* L.	wood	10 YR 6/1
P15	*Sorbus aucuparia* L.	wood	2.5 YR 3/0
P16	*Populus nígra* L.	wood	10 YR 5/1
P17	*Salix fragilis* L.	wood	2.5 YR 2.5/0
P18	*Tilia cordata* Mill.	wood	10 YR 4/1
P22	*Quercus pubescens* Willd.	wood	10 YR 8/1
P25	*Pinus pallasiana* D. Don	wood	10 YR 4/1
P21	*Vitis*	base of the trunk and vine	10 YR 5/1
P23	*Phragmites australis* (Cav.) Trin. ex Steud.	stalks	7.5 YR 2/0
P24	Herbs; *Stipa capillata* L.	grass	2.5 YR 3/0
P26	*Hordeum vulgare* L.	straw	2.5 YR 3/0
P28	Grasses; *Setaria glauca* (L.) P. Beauv., *Festuca pratensis* Huds.	decayed grass	2.5 YR 3/0
P19	Cattle dung on pastures	*kizyak*	10 YR 5/1
P20	Horse dung on pastures	*kizyak*	10 YR 5/1
A167	Ash layer, Borut-Khane settl.	ash from the depth of 63–73 cm	10 YR 7/1

$$SiO_2/(RO+R_2O) = SiO_2/[(CaO+MgO)+(K_2O+Na_2O)] \tag{1}$$

Using the method of a geometric mean calculation, the duration of the pedogenetic transformation of ash (T, years) can be determined by the following expression:

$$T = \frac{\left(P_1^n EL_i\right)^{1/n}}{\left(P_1^n EA_i\right)^{1/n}}, \tag{2}$$

where P is product, EL_i is dispersed elements in the ash soil, and EA_i is accumulated elements in the ash soil.

The dating of soils was carried out using the method of pedogenetic chronology that is based on the regional chronofunction of the humus horizon formation of the soil (Lisetskii et al., 2016). Grouping of the objects (samples of the plant and dung ash, ash soils) is based on the most informative chemical elements, using cluster analysis (unification by Ward's method, on the criterion of squared Euclidean distance) normalized by mean-square deviation.

4. Results and discussion

4.1. Comparison of chemical properties of ash and soils formed on ash

The studied soils have different zero-moment of pedogenesis, which makes it difficult to classify them generally. However, the principles used for the classification of volcanic ash soils according to the World Reference Base for Soil Resources (WRB) Classification (FAO, 1998; Takahashi and Shoji, 2002) permit to term the different-age soils of our study Calcic Chernozems formed on ashy deposits.

The analysis of ash from a deposit at the former village of Ojrat (S6) gives an idea about its granulometric composition. The soils formed on ash contain 70–71% of particles with a size of >0.05 mm (sand) and 2–8% of particles measuring <0.002 mm (clay), which makes it possible to classify them as loam.

Ash of archaeological sites (Table 3) is characterized by its grey, light grey and light brownish grey colour. Due to both leaching and fixation in the mineral part of soil formation products, the soils formed on ashy substrates become more brownish: from light brownish grey (10 YR 6/2) to greyish brown (10 YR 5/2). The ash from a fireplace of the Late Scythian period (A3/3) differs from all other samples by its light yellowish brown colour (10 YR 6/4) and, as will be shown below, by its chemical composition.

Compared to ash deposited at a greater depth, soils formed on ash are richer in organic carbon, labile phosphorus and potassium, and if the initial reaction of the solutions was weakly alkaline, it becomes strongly alkaline over time. This shows a significant transformation of ash in the process of pedogenesis.

Comparing the chemical properties of ashy soils and ash with those of the background arable Chernozem (0–20 cm) (Table 3) confirms the well-known opinion about the ash fertilization effect on soils. Ashy soils of different age are on average 85 times richer in labile phosphorus, 31 times in exchangeable potassium, and 1.7 times in organic carbon, as compared to the arable horizon of loamy Chernozems.

4.2. Colour and chemical characteristics of ash from the sites of different age

The colour of ash from sampled archaeological sites varies from grey to light grey or light brownish grey. The diagnostic hue of the ash – grey, greyish brown or, more frequently, light brownish grey (10 YR 6/2) – appears after drying due to an increase in intensity (value) and a decrease in hue (chroma) (on average, two and one units on the Munsell scale respectively). One of its main physical properties is its low density, which, even after having been buried for a long time, remains lower than that of the soils. According to our observations, the density of ash in the subsoil strata of the Crimean ash deposits varies from 0.68 to 0.92 g cm^{-3}.

At a multi-period settlement S11-022 where soil sections S1/1, S1/2 and A1/3 (see Table 1) had been made, ash samples from different depths were compared.

In section S1/1, horizon A (0–18 cm), the soil colour varied from dark greyish brown (moist) to greyish brown (dry). The reaction of the soil solution throughout the entire profile was medium alkaline. Horizon BC was an unstructured, powder-like ashy stratum coloured from yellowish brown (moist) to light grey (dry), which also had the highest content of carbonates.

The stratigraphy of S1/2 and other Bronze Age sites in this region demonstrates that the strata of light brown ash (10 YR 6/2) are always overlaid by the strata of light grey ash (10 YR 7/2; dry), thus suggesting their relative chronology. The difference in colour also seems to suggest different geneses of these ashy horizons. The geochemical analysis (by 22 chemical elements) of the light grey ash from section S1/1 and light brown ash from A1/3, and an integral evaluation of their relative differences, demonstrate how they differ, first of all in a higher (>60%) content of Pb, Sr, Co, Na and Zn in the light grey ash. However, in explaining these differences, one cannot rule out the effect of the post-depositional chemical processes and their different duration (Pierce et al., 1998).

The thickness of the humus horizon (A+AB) of the newly formed soil was defined using the data from two sections: the average values in sections A1/3 and S1/1 amounted to 467 and 468 mm correspondingly. The soil age established using the method of pedogenetic chronology (Lisetskii et al., 2016) appeared to be c. 2.9 ka. Hence its formation must have started in the second half of the 10th century BC, what in the northern Black Sea area corresponds to the Belozerka stage of the late Bronze Age.

The chemical composition of parent materials of the Crimean soils was investigated in Lisetskii and Ergina (2010). In parts of the region where ashy deposits cover larger areas, they can also be considered a soil

Table 3
Chemical properties of soils formed on ash (S) and ash (A) from the cultural layers of archaeological sites of North-West Crimea.

Sample No.[a]	Depth, cm	Munsell colour		pH (H_2O)	Corg, %	$CaCO_3$, %	P_2O_5, mg·kg^{-1}	K_2O, mg·kg^{-1}	CEC, cmol$^+$·kg^{-1}		
		Dry	Moist						Ca^{2+}	Mg^{2+}	Na^+
S1/1	0–18	10 YR 5/2	10 YR 3/3	8.2	4.86	9.1	10.4	45.5	24.4	2.5	0.5
	18–50	10 YR 6/2	10 YR 3/2	8.2	3.76	12.8	13.9	61.0	21.6	1.7	0.7
	>50	10 YR 7/2	10 YR 5/4	8.0	2.55	25.7	8.2	951.7	22.2	5.2	0.1
A2/1	0–19	10 YR 5/2	10 YR 2/2	7.9	5.27	34.7	22.6	21.1	23.3	6.0	0.5
	19–38	10 YR 5/1	10 YR 3/2	8.1	4.11	18.9	27.8	154.7	21.4	5.4	0.6
S4/1	0–22	10 YR 6/2	10 YR 3/3	8.9	2.83	37.5	16.7	101.5	9.6	3.0	1.30
S6	0–16	10 YR 6/1.5	10 YR 3/2	9.1	3.29	44.0	1.5	36.7	16.2	8.9	0.5
	16–28	10 YR 6/2	10 YR 4/3	9.5	2.59	54.0	1.2	42.7	19.8	4.4	1.6
A3/1	235	10 YR 7/1	10 YR 5/2	7.4	0.84	17.0	0.8	5.1	–	–	–
A3/2	200	10 YR 6/2	10 YR 5/3	7.3	0.70	16.2	1.1	9.6	–	–	–
Mean (S)	–	–	–	8.5	3.70	29.6	12.8	93.5	19.8	4.6	0.7
Mean (A)	–	–	–	7.3	0.77	16.6	1.0	7.3	–	–	–
Chernozem[b]				6.8-7.4	1.5-2.1	17–28	0.15	2–4	23.4–37.2	2.2–7.6	0.3-1.6

Note.
[a] Sample numbers correspond to those in Table 1.
[b] The analytical data for the background Chernozems (0–20 cm) in the study area are after Kogel', 1969.

parent material. The comparison of the composition of the two predominant types of parent material, the carbonate loams and limestone eluvium, with that of the ash of archaeological sites and of the soils formed on ash showed significant differences. The ash proved to have a higher (by more than 30%) content of P, Ca and Sr (as compared to loams), and of P, Co, Sr, Zn, Pb and Cu (as compared to eluvium). Moreover, ash contains a smaller proportion of Cu, Pb, Fe and Ni (as compared to loams), and of Ca (as compared to eluvium). For the soils formed on ash, regardless of the time of leaching, a decrease (as compared to ash) in the concentrations of Ca > Sr > Mg > P was observed.

Along with the combustion temperature and the post-depositional processes, the chemical composition of ash may be influenced by some inclusions such as, for example, limestone and especially bones. The ash of the late Scythian hearth (A3/3) differed from all other samples (Table 1), not only in colour (10 YR 6/4) but also, as will be shown below, in chemical composition. As heating and cooking activities usually result in complete consumption of fuel, it should not be surprising that all examined ash samples proved to contain no trace of charcoal.

A cluster analysis by the 12 most diagnostic chemical elements has demonstrated typological differences between ash and the soils formed on it. Comparing the chemistry of the soils and ash of archaeological sites of north-western and piedmont Crimea shows certain regional differences in how the elemental composition of ash is transformed by pedogenesis. At the same time, despite the considerable differences in precipitation, the loss of sesquioxides in the soils of these regions (as compared to ash) is identical, amounting to c. 140%.

The comparison of ash from two forest regions (Crimean piedmonts and the continental forest-steppe) by 22 chemical elements (Table 4) has demonstrated that only two of these elements had a comparable concentration with the difference not exceeding 10 percent. This suggests that the ancient population of these regions must have been using completely different types of fuel. Ash with a high concentration of animal bones, as it was at the Scythian settlement of Borisovka, is distinguished, among other things, by a high phosphorus content. While Horizon A (0–25 cm) of this region's background soils contains 0.21–0.35% of total phosphorus and has an average degree of supply of mobile phosphates (P_2O_5 is 1.7 mg kg^{-1}) (Lukin et al., 2000), the ash from the depth of 62–72 cm contained 0.95% of total phosphorus. As compared to the Crimean ash, the fossil ash of the continental forest-steppe shows lower content of K, As, Al, Cu, Ca, V and Si, while the concentration of the 13 other elements is higher.

Fourteen samples of fossil ash from all three investigated regions were subjected to the cluster analysis by 18 chemical elements (Fig. 4); the insignificantly variable elements with the variation coefficient of ≤14% (Ti, Fe, Mg and Rb) were excluded from calculations. Judging by the threshold distance (D), two close objects, A1 and A2, and two other groups of ash that differ significantly in their chemical composition could be identified.

Table 4
Chemical composition of ash from cultural strata of the Scythian settlements: A167 – Borut-Khane, Piedmont Crimea; A16 – Borisovka, forest-steppe zone.

Chemical elements	A167	A16	Percentage of differences:
	63–73 cm	62–72 cm	100*[(A167/A16) – 1]
Accumulated elements in the ash of the Crimean piedmonts as compared to the ash of the continental forest-steppe			
K	1.62	0.91	+78.0
As	4.66	2.78	+67.6
Al	4.00	2.39	+67.4
Cu	19.22	12.70	+51.3
Ca	12.66	8.39	+50.9
V	63.80	48.52	+31.5
Si	16.75	14.97	+11.9
Dispersed elements in the ash of the Crimean piedmonts as compared to the ash of the continental forest-steppe			
Zr	161.99	444.15	−63.5
Sr	304.39	783.79	−61.2
Mn	0.07	0.16	−56.3
Zn	133.22	272.84	−51.2
Pb	16.07	27.37	−41.3
P_2O_5	0.61	0.95	−35.8
Co	10.42	15.76	−33.9
Na	2.03	2.81	−27.8
Ba	505.56	692.97	−27.0
Ti	0.27	0.36	−25.0
Ni	36.65	44.98	−18.5
Cr	73.04	88.94	−17.9
Fe	2.18	2.51	−13.1
Concentrations with a difference of no more than 10%			
Rb	62.21	68.32	−8.9
Mg	1.37	1.37	0.0

The comparison of the average chemical element content in the objects and groups (Table 5) has shown that, judging by the quantity of extremes (maxima and minima), sample A1 (ash from the forest-steppe settlement of Borisovka) is the most distinct.

4.3. Geochemical transformation of ash by pedogenesis and the dating of ash deposits

Combustion of plant-based fuels produces calcite, potash and other carbonates (Aleksandrovskii, 2007). The study of the chemical

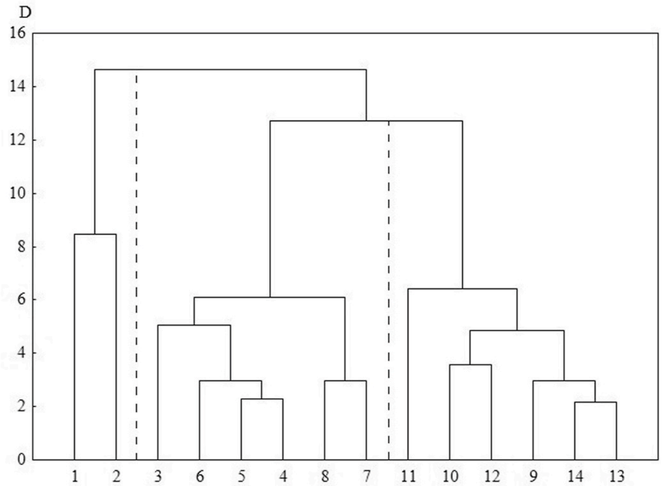

Fig. 4. Dendrogram of the ash sample distribution (A) according to 18 chemical elements (macroelements (Ca, Si, Al, Mn, P, K, Na) and trace elements (V, Cr, Ni, Co, Cu, Zn, As, Sr, Pb, Ba, Zr)). Key to the figure: 1 – A16; 2 – S1/1 (>50 cm); 3 – A2/2; 4 – A1/3 (60–70 cm); 5 – A1/3 (80–90 cm); 6 – S1/2 (56–61 cm); 7 – A3/1; 8 – A3/3; 9 – A7 (>37 cm); 10 – A8 (>33.5 cm); 11 – A9 (>32 cm); 12 – A2/1 (39–41 cm); 13 – A167 (63–73 cm); 14 – A10 (>30 cm).

Table 5
Colour and chemical composition of ash in the groups identified by the cluster analysis.

Indicator	Units	A1	A2	Group 1	Group 2
Colour (Munsell; dry)	–	10 YR 6/2	10 YR 7/2	10 YR 7/1 to 10 YR 6/2	10 YR 7/1 to 10 YR 5/1.5
CaO	%	11.7	13.7	12.5	17.9
MnO	%	0.2	0.1	0.1	0.1
SiO_2	%	32.1	33.9	50.5	35.0
P_2O_5	%	2.2	0.7	0.6	1.2
K_2O	%	1.1	1.5	1.9	1.8
Na_2O	%	2.8	2.9	1.6	2.2
Al_2O_3	%	4.5	6.1	9.5	7.2
Sr	mg kg^{-1}	783.8	431.6	329.2	349.4
Zn	mg kg^{-1}	272.8	157.7	89.8	132.3
Co	mg kg^{-1}	15.8	34.2	16.8	16.1
Pb	mg kg^{-1}	27.4	35.0	13.3	19.3
Zr	mg kg^{-1}	444.2	281.7	239.5	169.3
Cu	mg kg^{-1}	12.7	23.9	38.3	20.3
As	mg kg^{-1}	2.8	5.3	5.7	5.2
V	mg kg^{-1}	48.5	86.7	64.5	66.2
Ba	mg kg^{-1}	693.0	611.7	482.0	455.5
Ni	mg kg^{-1}	45.0	53.9	46.2	38.7
Cr	mg kg^{-1}	88.9	108.3	80.5	84.7

composition of the soils and ash at four archaeological sites in our study region 2 (Piedmont Crimea) has demonstrated that in the course of pedogenesis, the soils (as compared to ash) accumulate Cu, As, Pb and SiO_2, while losing Sr, Ca, Mg, P_2O_5 and K_2O. As shown in Lisetskii et al., 2016), in the conditions of regional pedogenesis, Cu and Pb, which are actively accumulated by plants, accumulate in the soil in higher concentrations than in parental rocks (loams and limestone eluvium).

As compared to the buried ash, the soils formed on ash have a higher content of organic carbon, labile phosphorus and potassium, with the solution reaction changing from alkalescent to strongly alkaline. This demonstrates a considerable transformation of ash in the process of pedogenesis.

A method for calculating the soil formation rate was proposed in Alexander (1986) and is based on the ratio of the concentration of elements in the soil and in the weathered rock, respectively. After 17–19 centuries of pedogenesis, the soils of the piedmont Crimea become, on average (judging by the value of $SiO_2/(RO + R_2O)$), 36% less alkaline as compared to the initial state of the ash of which they were formed. In contrast to the underlying ashy stratum, which is insignificantly affected by the pedogenesis, the overlying 35–37 cm thick layer of soil shows higher concentration of Cu > As > SiO_2>Al_2O_3>Pb (in the ranged sequence), whereas the concentration of Sr, Ca, Co, Mg and Na_2O decreases. Based on these elements, and using the formula (2), we rated the duration of the pedogenetic transformation of the ash (T, years). For the sites of Ak-Kaya, Kermen-Kyr and Zayachye Vostochnoye, which are of similar age, Formula (2) gives close values of T (1.73–1.84), whereas for the ash of Borut-Khane (sample from the depth of 63–73 cm) T equals 2.23. The close T values for the newly formed soils at these three sites indicate a practically synchronous beginning of the pedogenetic transformation of their ashy deposits. The fact that life at these settlements stopped simultaneously in the 3rd century AD is also confirmed archaeologically. At the same time, the soils of the Borut-Khane settlement which, judging by the pottery from the ashy mound, has a narrower chronology (1st century BC – 1st century AD), prove to be more leached, which implies a longer period of pedogenesis. Calculations of differences on the basis of the T values suggest that the formation of the new soil on the ashy deposits of Borut-Khane began in the early 1st century AD.

Hence, stable associations of chemical elements, indicating the processes of accumulation and leaching in the soils formed on ashy deposits of archaeological sites, make it possible to date the end of occupation at these sites.

4.4. *Properties of ash of different geneses*

Out of the 28 ash samples produced from different sorts of potential fuel, 18 (64%) were close in colour to the ash of archaeological sites where light grey (10 YR 7/1 and 7/2) and light brownish grey (10 YR 6/2) hues predominate (Table 1). Less often, the experimental ash shows dark grey and very dark grey colour (10 YR 4/1 and 3/1), and only rarely (willow and reed) is it black (7.5 YR 2/0, 2.5 YR 2.5/0).

Out of the examined fuel types, the most distinctive prove to be the Crimean wormwood (by Cu, Mn, As and Co), horse dung (by Pb, As, Co and Mn) and cow dung (by Mo and Mn). As can be seen in Fig. 5, in terms of their chemical composition, the ash of Borut-Khane (A167) and the experimental ash of dung and plant-based fuels that constitute Group 2, as well as samples from Group 1 (wood of small-leaved species such as willow and poplar), which have similar properties, form a separate cluster with high values of the threshold distance (D).

The other groups, which include ashes of both arboreal and gramineous plants (Groups 3–7 in Fig. 5) differ markedly in their chemical composition from both the dung ash (P19, P20) and the ash of Borut-Khane (A167).

An integral evaluation of the properties of the plants and other organic substances using the PP indicator (plant properties) shows (Table 6) that samples of Group 2 (horse and cattle dung, pine, wormwood and southern saltwort (P2)) demonstrate the closest similarity with the ash of Borut-Khane (A167).

In agreement with other works (Etiégni and Campbell, 1991; Aleksandrovskii, 2007), the comparative analysis of ash from different sources has shown that different kinds of wood, as well as gramineous plants and straw differ significantly in their chemical composition from the dung ash. This makes it possible to use the concentrations of Zn, Cu,

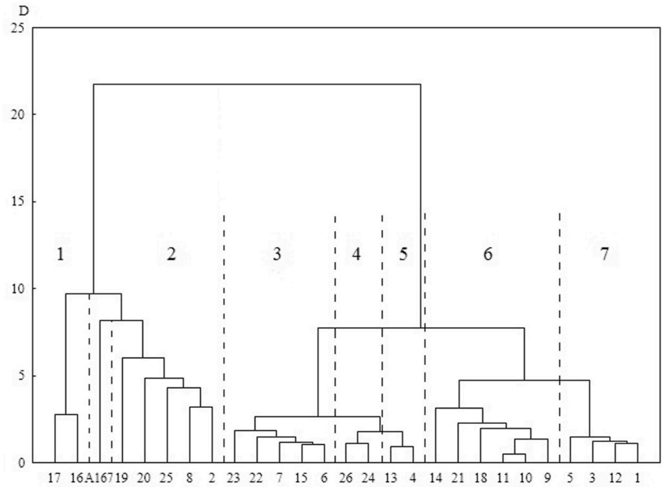

Fig. 5. Cluster analysis of samples of the plant and dung ash (numbers correspond to those in Table 2).

Mn, Cd, Pb, As, Hg, Mo and Co, along with other techniques, such as the study of phytoliths and dung spherulites, to identify ash of different geneses in archaeological contexts.

4.5. Different types of fuel and their indications in the composition of ash

The elemental composition of the ash produced from grasses that largely determine the composition of dung on pastures was compared with that of the ash produced from the fossil oak wood of the mid-4th century BC (Table 2, sample P22). This comparison showed significant differences between oak wood and steppe hay in chemical elements and oxides. Only in the amount of Cr and Ti, the values obtained were close. By contrast, the concentrations of As and Ca for wood, and, predictably, of silicon dioxide (SiO_2) for grasses appear as indicators of the differences.

Taking into account those 13 elements whose content in the ash from the Borisovka settlement was higher than in the ash of Borut-Khane (Table 1), the oak ash (P22) demonstrated a higher concentration of Sr, Na, Zr, Fe and Ba, as compared to that of grasses (P28). Possibly, this can be explained by the fact that other species of tree beside oak were used for fuel by the dwellers of Borisovka.

Having evaluated the relative differences between the objects, using the formula 100·[(X/У)-1], the data in Table 6 makes it possible to arrive at the following conclusions: 1) the wood ash and the dung ash have the maximum differences; 2) the elemental composition of the oak ash and the ash of the Borut-Khane settlement differ fundamentally; in the wood ash, the concentration of eight elements is lower, showing similar values only for Cd; 3) despite certain differences, the ash from Borut-Khane is close to the horse and cow dung, being a bit closer to the former.

Table 6
Chemical composition of the plant and dung ash in samples (P, mg kg^{-1}) and their quality (PP).

Group[a]	PNo	Zn	Cu	Mn	Cd	Pb	As	Hg (n·1000)	Mo	Co	PP[b]
2	19	162.7	41.5	544.7	0.7	12.6	2.93	2.3	5.8	3.3	5.47
	20	155.3	30.3	935.5	1.5	20.9	2.91	2.2	3.9	3.6	
	25	200.9	20.0	423.4	0.6	6.5	1.86	< LOD	1.7	4.2	
	8	144.5	76.2	480.0	0.6	10.9	4.68	3.8	2.8	4.4	
	2	164.4	46.1	218.1	0.4	12.4	3.79	4.0	5.4	2.1	
	$\bar{X}$	165.6	42.8	520.3	0.8	12.7	3.20	2.5	3.9	3.5	
6	14	65.8	24.1	147.2	0.7	10.2	0.94	3.4	1.6	1.0	2.72
	21	45.5	39.7	252.2	0.8	5.9	1.13	3.7	1.6	1.4	
	18	69.4	22.2	45.2	0.5	13.7	0.32	1.9	3.3	0.5	
	11	67.6	22.5	113.0	0.3	10.2	1.42	3.6	1.8	1.1	
	10	64.3	22.9	94.2	0.3	8.4	1.22	2.1	1.5	1.1	
	9	102.7	25.7	117.4	0.7	7.6	0.90	5.6	0.8	1.4	
	$\bar{X}$	69.2	26.2	128.2	0.5	9.3	1.00	3.4	1.7	1.1	
1	16	210.2	30.1	74.9	2.4	14.8	0.49	1.4	0.7	0.9	2.69
	17	204.0	46.6	87.9	1.9	14.3	0.50	1.8	0.7	1.1	
	$\bar{X}$	207.1	38.3	81.4	2.1	14.6	0.50	1.6	0.7	1.0	
7	5	143.0	33.5	114.0	0.2	5.9	0.93	2.6	1.7	1.2	2.40
	3	164.6	36.9	126.5	0.1	4.4	1.23	< LOD	2.6	1.0	
	12	121.3	29.9	150.0	0.2	3.0	1.01	2.7	1.3	1.4	
	1	115.2	34.3	59.9	0.2	7.0	0.88	4.2	1.4	0.8	
	$\bar{X}$	136.0	33.7	112.6	0.2	5.0	1.00	2.4	1.7	1.1	
4	26	35.6	9.8	204.8	0.2	1.0	0.97	4.7	2.2	1.1	1.70
	24	44.9	11.9	279.4	0.2	1.1	1.37	4.0	2.7	1.2	
	$\bar{X}$	40.3	10.8	242.1	0.2	1.0	1.20	4.3	2.5	1.1	
3	23	60.0	14.4	104.0	0.4	4.8	0.24	2.6	0.9	0.6	1.58
	22	22.6	22.3	106.5	0.3	4.3	0.14	2.8	1.2	1.2	
	7	100.4	20.5	57.1	0.3	2.7	0.32	2.1	0.9	0.4	
	15	64.3	13.3	30.4	0.8	4.8	0.27	1.9	0.9	0.3	
	6	54.4	9.8	47.6	0.1	4.7	0.29	2.2	0.7	0.5	
	$\bar{X}$	60.4	16.1	69.1	0.4	4.3	0.30	2.3	0.9	0.6	
5	13	23.7	10.8	38.0	0.2	3.4	0.95	7.3	0.7	0.5	1.36
	4	33.7	11.9	56.5	0.2	4.9	1.01	8.9	0.8	0.6	
	$\bar{X}$	28.7	11.4	47.2	0.2	4.2	1.00	8.1	0.7	0.5	
Ash deposit	A167	59.3	27.0	428.8	0.3	9.3	5.20	38.7	1.5	4.5	5.18

Note.
[a] The sequence of groups in the table follows the PP indicator.
[b] Calculation of the PP indicator has been made according to the formula of geometric mean: PP = $(x_1 \cdot x_2 \cdot \ldots \cdot x_9)^{1/9}$, where x_1, x_2 … x_9 is the content of chemical elements; LOD – limit of detection.

Given the chemical composition of the ash from the late Scythian settlements of piedmont Crimea, the 25 wood and plant species studied by us (Table 2) are very unlikely to have been used there as the main fuel. The closest relationship to the Borut-Khane ash is demonstrated by Group 2 in Table 6 (horse and cow dung, Crimean pine, Crimean wormwood and southern saltwort). For the ignition of dung, the easily available stalks of wormwood and saltwort, as well as pine twigs, could have been used too. Unlike the other six clusters (Fig. 5), Group 2 features higher concentrations of Mn, Cu, As, Mo and Co. The closeness relation (r) between ash A167 and the average content of the nine chemical elements is 0.987, which means that the contribution of this group to the ash deposits of Borut-Khane has amounted to 97%.

In its chemical composition, the ash from the Scythian settlement of Borut-Khane is closest to the horse dung, essential differences emerging only in the quantity of Mo. Certain similarities can also be observed with the pine ash, except for Zn and As. At the same time, it differs significantly, in five elements out of nine, from cow dung.

4.6. *Geochemical indicators of ash of different geneses*

The analysis of relative differences was conducted using the ensemble of chemical elements (P, K, Mn, Zn, Co, Pb, Sr and Zr) that best characterise the differences between the wood ash and dung ash. Using the formula 100*[(A/B(C))-1], where A, B and C are samples S1/2, A16 and A167 respectively, the following summary estimate of differences was obtained: A and B: -52, A and C: +443. Hence, it can be assumed that the ash of colour 10 YR 7/2 is primarily a product of wood combustion (Type 1). Employing the same formula 100*[(A/B(C))-1], where A, B and C are samples A1/3, A16 and A167 respectively, a similar calculation was made to estimate the differences between the light brownish grey ash (A1/2) and the ash deriving from wood and dung. In this case, the summary estimate of differences was as follows: A and B: -301, A and C: 45. This suggests that this variety of ash (central cluster [from A3 to A7] in Fig. 4) is likely to result from the combustion of *kizyak* with a significant addition of wood, i.e. what may be called a mixed type of ash (Type 2). Despite certain differences in the chemical composition, the ash of all late Scythian settlements and the ash of the Greek farmhouse of Kunan (burnt roof of felt and straw) can be ascribed to Type 3, with the animal components prevailing over the plant-based (Group 2 in Table 5). This type can be interpreted as dung (*kizyak*).

Comparison of objects A1 (A16) (pale brown ash) and A2 (S1/1) (light grey ash) in terms of relative (%) differences in the content of 22 chemical elements, using the criterion of differences $> \pm 50\%$, has demonstrated that A1 has a twice as high content of bulk phosphorus and higher concentrations in the group Sr > Zn > Mn > Zr, while the amount of cobalt is lower. With regard to the remaining 16 elements, the differences were small. This fact suggests that at multiperiod settlement S11-022 (S1/2), along with wood (perhaps not only oak), other fuels were also used. However, when A1 is compared to the ash from piedmont Crimea (A13 = A167, Borut-Khane), relative differences of >50% occur on the basis of a completely different (except Sr) ensemble of elements: Sr > Co > Ca > Pb > Na. Thus, the chemical signature of wood ash and of that of mixed fuels differs significantly from the ash resulting from the combustion of dung.

The distribution of geochemical properties in objects of Group 1 (Table 5) suggests ash of mixed origin, by contrast to Group 2, which primarily characterizes dung ash. Taking object A1 and Group 2 (A13) as typical examples of wood and dung ash respectively, and considering their relative (%) differences in the content of 22 chemical elements, a set of elements diagnostic of these two kinds of fuel was identified. In a ranged sequence, these elements appear as follows: Zr > Mn > Sr > Zn > P_2O_5>Pb. A higher concentration of these six elements, and in this order, distinguishes wood ash from the ash deriving from dung.

5. Conclusion

In the south of the East European Plain, where the cold period amounts from 34% to 50% of a calendar year, there was a constant need of fuel for both cooking and heating. This explains the wide distribution of ashy soils and massive ashy deposits in this region of long and intensive human activities. On the arable lands of Plain Crimea alone, they cover an area of 14,200 ha. From the Bronze Age to the sub-modern period, in the steppes of the northern Black Sea region, *kizyak*, a mixture of dung and straw, was the main fuel. In the conditions of the East European Plain, the assemblage of chemical elements Zr, Mn, Sr, Zn, P_2O_5 and Pb proved to be diagnostic of ash of different geneses. Their diagnostic effectiveness has to be tested also in other regions of the world. The prevalence of dung fuel among the Scythian and Tatar population of the Crimean piedmonts in the 3rd century BC through the 19th century AD was an effect of not only the unavailability of firewood but also of the traditional mode of life with the changing, but ever-important, role of livestock breeding. Based on the ratio of the stable associations of chemical elements indicating the processes of accumulation (Cu, As, Si, Al and Pb) and leaching (Sr, Ca, Co, Mg and Na) in the soils of different age formed on ash, it is possible to establish the age of ashy deposits by determining the time at which they stopped to form.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix. ASupplementary data

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