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Anthropic dark soils horizons in western Siberian taiga: origin, soil chemistry and sustainability of organic matter

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ABSTRACT

The impact of human activity on soil carbon stock and soil fertility is at the forefront of scientific research. In the past, human practices improved soil fertility and increased carbon storage over long periods of time. Studying the resulting anthrosols provides access to their evolution over time scales that are unavailable otherwise. These archeological Anthrosols have been extensively investigated in Amazonia and Europe, but are virtually unknown in Siberia. Here we examined four soil profiles from two archeological sites in western Siberia, along with two corresponding control profiles. The first site, Ketskii Ostrog, is an ancient 18th century fortress occupied by an agricultural population. The second site, Shaitan III, is a historical settlement of metallurgists and horse-breeders active from the 10th through the 17th century. We aimed to understand whether human activity at these two sites modified soil carbon and chemical fertility, and to compare these soils with other studied global anthrosols. We revealed a contrasting impact of human activity for these two sites. At Ketskii Ostrog, ancient agricultural practices improved soil chemical fertility, with the effects persisting until present day. Human activities exhibited a beneficial influence on deep horizons through improvements in their cation exchange capacity, pH and nutrient (P and Ca) concentrations. The Ketskii Ostrog soils were similar to plaggic soils documented in Northern Europe, which are characterized by the addition of fresh organic matter (OM) in the form of manure which was purposefully added to improve soil fertility. At Shaitan III, chemical fertility has also been improved, but to a lesser extent. In contrast to Ketskii Ostrog, Shaitan III soils are rich in charred organic matter and strongly resemble Amazonian Dark Earths with their physico-chemical properties. The Shaitan III soils also have a different origin, as the result of unintentional human impact. Anthropisation has increased carbon stocks in the soil at both sites; however, Shaitan III soils prove to be a more effective carbon sink than at Ketskii Ostrog. This two-fold dichotomy (intentional/unintentional vs. fresh OM/charred OM) is not limited by geographical borders (Amazonia, Europe, or Siberia) and soil typology as currently proposed in the WRB. This highlights the need for concerted studies on anthropised archaeological soils in regard to their importance for both soil fertility and carbon storage.

1. Introduction

To mitigate the effects of climate change, global public policies are considering strategies to not only limit greenhouse gases emissions but remove carbon from the atmosphere. In this context, soil organic (C_{org}) and inorganic (C_{inorg}) carbon storage has become an important focus (Lal et al., 2007; Paustian et al., 2016; Amelung et al., 2020) as soils have been greatly depleted in carbon particularly since the start of the

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agricultural revolution (Lal, 2004; Sanderman et al., 2017; Raza et al., 2020) in large part due to soil organic matter (SOM) mineralization, loss of inorganic carbon by nitrogen-induced soil acidification and soil erosion and carbon leaching. To remedy this, several measures have been implemented to increase soil carbon sequestration and storage. These are achieved via changing agricultural practices (Lal, 2007; DeJong et al., 2010; Jorat et al., 2015; Lal, 2020; Rumpel et al. 2020). However, the implementation of enhanced C storage in soils takes several years or decades, which is insufficient to assess their long-term carbon cycle impact. To assess optimal agricultural practices and maximize carbon sequestration, it's important to study archaeological soils and ancient farm sites where stable carbon compound rich soils were developed (Kern et al., 2019).

Unlike current human impacts that deplete soil carbon, past anthropic practices alternatively enriched soils in C and this enrichment has persisted over long periods of time lasting up to several millennia. Such soils are termed Anthropogenic Dark Earths and the most emblematic examples, the Amazonian Dark Earth (ADE), locally called *Terra Pretas de Indio*, are found in the Amazon from Pre-Columbian era (Smith, 1980; Lehmann et al., 2004; Woods et al., 2008; Alho et al., 2019). Other examples are known in Europe, and referred to as European Dark Earths (EDE) (Courty et al. 1989; Macphail et al., 2003; Nicosia et al., 2017; Howard, 2017). Dark soils are also found in temperate zones at locations with historical charcoal production (Schneider et al., 2022; Hardy et al., 2017).

In addition to Dark Earths, formed mainly by sedentarisation amid human settlements, in Europe some regions utilized plaggenic agriculture which modified soil nutrient status forming carbon enriched soils that are termed Plaggen soils or Plaggic Anthrosols by WRB (IUSS Working Group WRB, 2022). In the strict definition of plaggic agriculture, pieces of heather or grass, including roots and humus, are cut and used as litter for cattle during the winter. The resulting product is then mixed with domestic organic waste and spread over fields in spring (Giani et al., 2014; Urbanski et al., 2022; Vasilchenko & Vasilchenko, 2024). In recent years, these soils have been recognized as valuable resources to be protected, as highlighted in the FAO's 2022 report, which details their diversity and global distribution. All these soils are often characterized by a dark color and higher levels of SOM compared to control sites. These soils may also contain anthropic artifacts such as pottery, charcoal and bones. Addition of such materials often impact the main physico-chemical parameters of soils by increasing Corg stocks, pH and the cation exchange capacity (CEC) (Smith, 1980; Kämpf et al., 2004; Solomon et al., 2016; Asare et al., 2021). Both ADEs and Plaggic Anthrosol sites exhibit higher levels of macro and micronutrients (K, P, Ca, Mg, Zn, Mn and Cu) (Entwistle et al., 2000; Kern et al., 2019; Bintliff and Degryse, 2022; Asare, 2022; Urbanski et al., 2022; Raghothama, 2005; Gransee and Führs, 2013; Malhotra et al., 2018; Johnson et al., 2022; Nizamutdinov et al., 2023). Presence of micronutrients is necessary and beneficial for the plant functioning (Raghothama, 2005; Gransee and Führs, 2013; Malhotra et al., 2018; Johnson et al., 2022) but can be harmful in excessive quantities and may cause oxidative stress, especially when accompanied by an accumulation of toxicants such as Pb or Cd (Skórka et al., 2023; Stanton et al., 2022). Other elements can serve as markers of anthropisation such as Sr, which is often associated with bone-rich kitchen wastes, or Sn, which is linked to bronze metallurgy (Entwistle et al., 2000; Bintliff and Degryse, 2022; Asare, 2022). The study by Sátiro et al. 2021 noted that the quantity of the extractable elements - and therefore available to plants - in ADEs can decrease or increase depending on the element considered and the type of land use. In addition, mineral phases distinct from the local mineralogical background may be created by human activities such as metallurgy, pottery or pigment creation, or transported in by human populations (Mangueira et al., 2011; Portillo et al., 2018).

Across the boreal region of northen Eurasia, the documented number of anthropic soil horizons findings decreases, progressing from west to east. While dozens of studies have been covered this issue in western and central Europe (Courty et al., 1989; Macphail et al., 2003; Nicosia et al., 2017; Asare, 2022; Urbanski et al., 2022; Schneider et al., 2022; Hardy et al., 2017), only a limited number of works cover the subject in eastern Europe (Trofimov et al., 2004; Zazovskaya, 2013; Bobrovsky et al., 2022; Smirnov et al., 2023). Furthermore, for locations such as Western Siberia, no anthropic soil horizons have been described at all. It remains unknown whether this is due to a lack of environmental conditions capable of forming anthropic soil horizons or simply insufficient study of these territories.

In Western Siberia, human settlements date back to the end of the Neolithic period (Kosarev, 1984). However, there are no available studies on the historical impact of human activity on soils. Recent research has shown a relationship between the occurrence of forest fires and past cultures (Loiko et al., 2022), which is associated with the high density of archaeological sites along major rivers (Zolnikov et al., 2020). Therefore, past human presence likely influenced soil pedogenesis. Here we test this hypothesis via presenting an archaeological and pedological study based on two recently discovered archaeological sites in Western Siberia. These sites are very different in terms of their history, settlement practices and time of settlement; however, the sites have similar pedoclimatic conditions. The first site, Ketskii Ostrog, was a fortress that housed Russian populations during the 18th and 19th centuries. The second site, Shaitan III, served as a settlement for a population of Turkic speaking horse breeders and metallurgists from the 10th through the 17th century. Both sites are located on terraces of the Ob River that are comprised of layered sandy-loam rocks which are exposed to continental climate conditions and long-season (six to seven months a year) soil freezing (Dukarev and Pologova, 2002).

Our investigation aims to understand how has human activity served as a pedogenic process leading to the formation of dark earths at two sites in Western Siberia by addressing three main questions: 1) How has anthropisation changed soil physico-chemical parameters, nutritional status, SOM dynamics and C storage? 2) Do these changes differ between the two sites, and 3) Are these changes consistent with those observed in other global Anthrosols (specifically ADEs or Plaggic Anthrosols)?

To address these key questions, analytical approaches including field soil description and physico-chemical characterization (pH, exchangeable cations, major and trace elements concentrations, texture and density parameters) were used. Soil mineralogy was assessed by X-ray diffractometry (XRD), with special focus on minerals controlling SOM stabilization (i.e., phyllosilicates, carbonates (Barré et al., 2014). Rock-Eval® thermal analysis was employed to analyze the SOM, offering quantitative data on both C_{inorg} and C_{org} content. Additionally, this method provides insight into the SOM composition by assessing the levels of C-H and C-O bonds (Disnar et al., 2003; Albrecht et al., 2015; Sebag et al., 2016; Malou et al., 2023).

2. Study site, materials and methods

2.1. Environmental context

The two study sites are located in the Tomsk region of Western Siberia (Russia); they reside within a boreal taiga abundant with wetlands (Fig. 1). The mean annual air temperature (MAAT) for Shaitan III (southern site) is $1.2 \degree$ C and Ketskii Ostrog (northern site) is $-0.2 \degree$ C. However, temperatures can drop as low as -18 and $-20.6 \degree$ C, respectively, in January (climatebase.ru). The climate is continental and cold, without a dry season and a temperate summer (Kottek et al., 2006). Major soil types in the region consist of Fluvisols, Arenosols, Podzols, Histosols, Phaeozem and Retisols (Stolbovoi, 2000).

2.2. Historical context

Archaeologists actively began studying the region during the second half of the 19th century. The majority of the archaeological monuments are located in the valley of the Ob and its first-order tributaries. The Ket



Fig. 1. Site locations. Circles: anthropic profiles (Ket: Ket_DE1; Ket_DE2 Shaitan III: Shai_DE1; Shai_DE2), Triangles: control profiles (Ket: Ket_C1, Shaitan III: Shai_C1).

River is the second major right tributary of the Ob River (Lim et al., 2022). The archaeological contexts are very diverse and date from the Upper Paleolithic to the modern ethnographic period (Zolnikov et al., 2020).

2.2.1. Ketskii Ostrog

Ketskii Ostrog (often referred to as the fortress of Ket) is an archaeological site in a meadow along the Ket River that is surrounded by taiga. The site occupies a portion of a 10-meter-high bedrock terrace, extending as a promontory to the river bed. Initially, the area was occupied by hunter-gatherer populations (Vajda, 2009), but toward the end of the 16th century impact on the soil became significant with the arrival of Russian populations and the development of infrastructure. This transition was accompanied by significant agricultural development and Ketskii Ostrog is a good illustration of this dynamic in the region (Dolgikh, 1960). In the 17th and 18th centuries, Ketskii Ostrog became the main waterway for Russians travelling from western to eastern Siberia because of its connection with the Ob and Yenisey River basins. While fortress location has changed throughout history (Rezun and Vasilevski, 1989; Dolgikh, 1960) here, the last known location of the Ketskii Ostrog will be studied where activity is documented to have occurred during the 18th and late 19th centuries (Spafariev and Arseniev, 1882; Miller, 1996). Initially, a major problem for fortress functionality was access to food. Despite unfavorable geo-climatic conditions, adoption of suitable farming techniques allowed for development of localized agriculture in the region. However, by the end of the 19th century, food production tendencies shifted toward (more lucrative) fishing, hunting and nut harvesting. For this reason, agriculturally suitable lands tended to become overgrown with trees in summer and at best used as cattle pastures (Plotnikov, 1901). As human pressure further decreased, ecological succession took its course allowing for recolonization of more forested environments.

2.2.2. Shaitan III

Shaitan III is located in southern Tomsk, on the right bank of the Ob River, situated within a taiga biome (Barsukov, 2013; Barsukov, 2016). Shaitan III occupies the upper part of a slope extending from the Ob floodplain to the uplands. Site relief has been considerably transformed by medieval human impact (Zaitceva et al., 2010). The remains of buildings, refuse pits and a metallurgical installation were excavated in 2007. The site possesses a rather thick anthropic layer (up to 1.5 m) and a high density of archaeological finds (over 100 objects per m²). Archaeological research has made it possible to date the site as between the 10th and 17th centuries and also identifies the presence of two chronologically distinct ceramic groups (Zaitceva et al., 2010). The first group is analogous to materials found in monuments from the developed Middle Ages (10th-14th centuries AD) and is known as the Basanda culture (Pletneeva, 1990). During Basanda times horse breeding was of particular importance to this microdistrict population. The second group of pottery dates back to the late Middle Ages (15th-17th centuries AD) and is most likely linked to local Turkic speaking populations (Pletneeva, 1990). The economy during this period became more complex, while hunting and fishing increased the herding of livestock and small horned animals also played an important role (Pletneeva, 1990). Further, materials from Shaitan III indicate there was a high level of iron production (Vodyasov, 2018; Konovalenko et al., 2010) which must have resulted in the accumulation of ashes, embers and slags. This lengthy period of functionality for this site partly explains the thickness of the anthropic layer and the high density of archaeological finds.

2.3. Profile description and sampling

The area covered by the Ketskii ostrog site was estimated at ~ 54 180 m² and that of the Shaitan III site ~ 2900 m². In order to carry out pedological investigations, the representative zones to be studied were first determined by archaeological work. Thus, in 2020, two soil profiles were opened on the Ketskii Ostrog site, the first Ket_DE1 located closest

Location of sampled profiles. Mean annual air temperature (MAAT). Mean annual precipitation (MAP).

| Site | MAAT (C°) | MAP (mm) | Profile | Category | Latitude | Longitude |
|-------------|----------------------|----------|-------------------------------|-----------------------------------|---|--|
| Ket | −0.7 °C | 515.9 | Ket_C1 Ket_DE1 Ket_DE2 | Control Anthropic Anthropic | 58°26′12,41′' 58°25′56,85′' 58°25′55,99′' | 83° 37′24,37′' 83° 39′01,71′' 83° 39′01,96′' |
| Shaitan III | 0.6 °C | 556.0 | Shai_C1 Ket_DE1 Ket_DE2 | Control Anthropic Anthropic | 56°18′26,70′' 56°18′26,25′' 56°18′25,38′' | 84°06′36,93'' 84°06′32,51'' 84°06′30,74'' |

to the ancient remains of houses and the second Ket_DE2 the furthest away. In addition, a Ket_C1 control profile was taken 1.5 km to the west of the site, where the impact of human activity would be low or absent. This profile will serve as a reference for the regional natural pedogenesis. For the Shaitan III site, in 2021 two profiles Shai_DE1 and Shai_DE2 were opened directly on the site as well as a control profile Shai_C1 located 150 m northeast of the site (Fig. 1; Table 1).

First, these different profiles were described in situ, making it possible to determine the thickness of the different horizons, and more particularly the anthropic horizons. Subsequently, in order to be able to classify the soil profiles according to WRB criteria (IUSS Working Group WRB, 2022), all the soil profiles were sampled according to the visible horizons with a step size varying from five to ten cm for analyses such as color, texture, pH, CEC, exchangeable cations, elemental composition more particularly P content, which is essential for classifying Anthrosols (Kabala et al., 2018), and C_{org} content, the methodologies of which are described below. Also, samples were taken from visible horizons for bulk density calculation using a cylinder with a volume of 200 cm³. Taken samples were first dried in an oven at 40 °C before measuring their final weight. Since the samples did not contain coarse elements, the bulk density was calculated by dividing the obtained weight by the volume. This measurement subsequently enabled carbon stock calculations to be carried out.

2.4. Radiocarbon dating

Four radiocarbon dates on charcoal were performed on Shaitan_DE1 at the Poznan radiocarbon laboratory in Poland. On Ket, dating could not be carried out due to a lack of sampleable charcoal in the profiles. Calibration was based on the Northern Hemisphere radiocarbon age calibration curve published in Reimer et al., 2020.

2.5. Soil characterization and elemental composition

The texture of studied soils and underlaying sediments was determined using an LS 13 320 Beckman Coulter (Beckman Coulter, Indianapolis, USA) analyzer with the preliminary dispersion of samples in the sodium pyrophosphate followed by sonication. The analysis first produced eight granulometric categories ($<1 \,\mu$ m, $<2 \,\mu$ m, $1-5 \,\mu$ m, $5-10 \,\mu$ m, $10-50 \,\mu$ m, $50-250 \,\mu$ m, $250-500 \,\mu$ m, $500-2000 \,\mu$ m) and then these categories were grouped into three fractions: Sands ($50-250 \,\mu$ m, $250-500 \,\mu$ m, $500-2000 \,\mu$ m), Silt ($1-5 \,\mu$ m, $5-10 \,\mu$ m, $10-50 \,\mu$ m) and Clay ($<1 \,\mu$ m, $<2 \,\mu$ m). Based on the percentages obtained for each fraction, the soil texture classes could be estimated using the soil texture triangle with major textural classes defined by USDA.

After drying, sample color was determined in the Munsell system using 450 X-Rite spectrophotometer (Michigan, USA). Soil pH was measured following the procedures described in Burt, 2004: one volume of soil was placed in contact with five volumes of distilled water for two hours. The pH was then measured using a Sartorius Professional Meter PP-15. CEC was measured using the modified cobaltihexamine method, which uses absorbances at 380 and 475 nm to subtract the proportion of organic matter (Ciesielski et al., 1997). The exchangeable soil cations Ca^{2+} , Mg^{2+} , K^+ and Na^+ were quantified from the cobaltihexamine exchange solutions by ICP-OES. Base saturation rate was calculated by dividing the sum of exchangeable cations by the CEC.

For analysis of major and trace elements, soils were acid digested in a clean room in the GET Laboratory following the procedures described in details elsewhere (Stepanova et al., 2015; Vasyukova et al., 2019). The analysis was performed with the iCAP TQ ICP-MS Thermo ScientificTM analyzer. Internal calibration of the instrument was performed with indium/rhenium, with certified material used for analysis LKSD-3. The elemental concentrations in soil samples were determined after total acid digestion of ~ 100 mg of dried soil in a class A 10 000 clean room. For the majority of elements, measurement error was estimated to be < 10 %. Elemental concentrations in samples were normalized relative to upper continental crust (U.C.; Taylor and McLennan, 1995), following standard practices (Delplace et al., 2022; Stepanova et al., 2015). The C_{tot} and N_{tot} concentration in soil samples was measured using catalytic combustion with CuO at 900 °C, with an uncertainty of < 0.5 % using a Thermo Flash 2000 CN Analyzer.

2.6. X-ray diffractometry

The mineralogical composition of total soil fraction was assessed in all horizons using X-ray diffraction (XRD). XRD measurements for random powder analysis were performed on D8 Advance diffractometers (Cu-K α radiation, Brag Brentano theta/theta setup, 2-30°). Diffraction patterns were interpreted using ICDD and COD databases using EVA software (Bruker).

2.7. Rock-Eval® thermal analysis

Finely ground and dried samples (approximately 65 mg) were analyzed using a Rock-Eval® 6 instrument, following the procedure described in Behar et al. (2001) (Fig. S1; Fig. S2). Five thermograms were obtained for each sample, showing the evolution of compound release during progressive pyrolytic and oxidative heating. Using these thermograms, thermolabile (TOC) and thermoresistant (MINC) carbon contents could be calculated (Lafargue et al., 1998; Behar et al., 2001). In addition, thermograms obtained from the oxidation step can be used to determine the presence or absence of carbonates (peaking after 650 °C for the CO₂ oxidative thermogram). In the absence of carbonates, C_{org} is calculated by summing the TOC and MINC parameters. After pyrolysis, parameters S2 (mg HC g^{-1} Soil) and S3 (mg CO₂ g^{-1} Soil) were calculated to provide insights into the composition of the OM. S2 represents the quantity of H-C bonds, while S3 corresponds to the quantity of C-O bonds (Behar et al., 2001). The index R, between 0 and 1, quantifies the part of the S2 thermogram integrated after 400 °C and measures the contribution of the most thermally stable SOM, which corresponds to the most persistent SOM fraction (Sebag et al., 2016). For these parameters, the analytical error was below 10 %.

2.8. Carbon stock calculation

The C_{org} obtained from the Rock-Eval analysis were associated with different soil horizons in order to calculate organic carbon stocks for each horizon. The absence of rock fragments in the soil allowed calculating the stocks following (Tadiello et al., 2022; De Feudis et al., 2022):

 C_{org} stock = $C_{org} \times$ Horizon Thickness \times Bulk Density.

The obtained stocks of each horizon were summarized down to 30 cm and 100 cm respectively, for consistency with conventional C stock evaluation. This estimation is particularly useful for comparing anthropic soils featured in this study with other global soils (Glaser et al., 2001; Alho et al., 2019; Urbanski et al., 2022).

2.9. Statistical analysis

To compare the results between the control and anthropized profiles the Kruskal-Wallis non-parametric test was used with the Wilcoxon-Mann-Whitney as a post-hoc test. To measure the linear correlation between the two parameters, the Pearson coefficient was calculated. All statistical analyses were performed with Rstudio (v. 4.2.1).

3. Results

3.1. Soil profile descriptions

3.1.1. Ketskii Ostrog

Ket C1 was observed until a depth of 100 cm but was only sampled to a depth of 80 cm. Indeed, the deepest part of the soil profile appears to

be the result of complex processes suggesting either burial of horizons in the past due to mineral matter inputs (e.g., sediment or colluvium inputs) or ancient deep cryoturbated horizons. The topsoil corresponds to organo-mineral horizons (i.e., Apg and EAg) until a depth of 20 cm; however, mineral horizons from the subsoil (i.e., Bg, Bt) demonstrated a gradient of evolution texture, evolving from sandy to more clayey as depth progressed (i.e., argic horizon). Despite the fact that soil profile Ket C1 serves as an experimental control, the 5-20 cm deep horizons showed very clear demarcation with the deeper horizons (20-50 cm), thereby indicating anthropic impact on the surface. This soil was classified as a Protoargic Folic Arenosol (Ochric, Katostagnic) due to its surface-depth textural gradient, carbon content ≥ 0.2 % and the presence of orange spots (0.5-1 cm size) throughout the entire soil profile, which is characteristic of Fe oxy(hydr)oxide precipitation due to temporary soil waterlogging.

Ket DE1 was located closest to the former habitations and was sampled to a depth of 97 cm even though it has been observed up to 135 cm. Plow marks ranged from 3 to 38 cm deep, and defined the topsoil (i. e., organo-mineral horizons Apu1 and Apu2) and the subsoil with horizons Bh, Bhg, Bg and Cg. This soil was classified as a Pretic Plaggic Anthrosol (Arenic, Stagnic, Eutric), due to its predominantly sandy

140/150. 150 -

С



Fig. 2. Profiles descriptions.

150

160

180

3pyr

4C/pyr

| Information on Ket samples: | the depth at w | hich the sample wa | as collected, the | e colour according | to the Munsell system | , and the texture |
|-----------------------------|----------------|--------------------|-------------------|--------------------|-----------------------|-------------------|
|-----------------------------|----------------|--------------------|-------------------|--------------------|-----------------------|-------------------|

| Sample information | | | | Munsell color system | | | Texture | | |
|--------------------|--------------|-----------|------------|----------------------|-------|--------|----------|----------|----------|
| Profile | Horizon type | Sample | Depth (cm) | Hue | Value | Chroma | Sand (%) | Silt (%) | Clay (%) |
| Ket_C1 | topsoil | K_C1_9 | 6_9 | 0,137Y | 5,514 | 2,09 | 34,10 | 55,08 | 10,81 |
| | | K_C1_16 | 10_16 | 0,526Y | 5,34 | 2,087 | 68,01 | 26,44 | 5,55 |
| | subsoil | K_C1_27 | 17_27 | 0,798Y | 5,928 | 2,592 | 61,77 | 30,55 | 7,68 |
| | | K_C1_35 | 30_35 | 0,761Y | 5,942 | 2,703 | 68,30 | 25,31 | 6,39 |
| | | K_C1_45 | 40_45 | 0,871Y | 5,922 | 2,642 | 70,90 | 23,30 | 5,80 |
| | | K_C1_60 | 55_60 | 0,854Y | 5,677 | 2,495 | 71,31 | 23,23 | 5,46 |
| | | K_C1_80 | 75_80 | 1,132Y | 6,111 | 2,599 | 12,30 | 69,61 | 18,09 |
| Ket_DE1 | topsoil | K_DE1_10 | 4_10 | 0,358Y | 3,958 | 1,582 | 69,11 | 24,42 | 6,48 |
| | | K_DE1_17 | 12_17 | 0,423Y | 4,028 | 1,543 | 83,08 | 12,94 | 3,98 |
| | | K_DE1_27 | 20_27 | 0,328Y | 4,143 | 1,588 | 71,79 | 23,13 | 5,07 |
| | | K_DE1_37 | 31_37 | 0,365Y | 4,236 | 1,616 | 56,04 | 36,60 | 7,36 |
| | subsoil | K_DE1_44 | 39_44 | 0,849Y | 4,945 | 1,861 | 42,51 | 46,22 | 11,27 |
| | | K_DE1_60 | 50_60 | 0,954Y | 5,124 | 1,896 | 62,20 | 30,03 | 7,78 |
| | | K_DE1_80 | 70_80 | 1,009Y | 5,548 | 2,002 | 68,46 | 25,18 | 6,36 |
| | | K_DE1_97 | 90_97 | 1,209Y | 5,84 | 2,046 | 68,22 | 25,82 | 5,96 |
| Ket_DE2 | topsoil | K_DE2_7 | 2_7 | 0,227Y | 4,094 | 1,726 | 68,22 | 25,82 | 5,96 |
| | | K_DE2_12 | 7_12 | 10,008YR | 4,497 | 1,859 | 39,60 | 51,27 | 9,12 |
| | | K_DE2_20 | 12_20 | 10,079YR | 4,394 | 1,822 | 58,84 | 34,99 | 6,17 |
| | | K_DE2_26 | 20_26 | 10,065YR | 4,428 | 1,815 | 56,03 | 36,82 | 7,16 |
| | | K_DE2_35 | 28_35 | 0,113Y | 4,443 | 1,824 | 56,29 | 37,07 | 6,64 |
| | subsoil | K_DE2_43 | 37_43 | 10,086YR | 5,185 | 2,401 | 43,21 | 48,32 | 8,47 |
| | | K_DE2_55 | 45_55 | 2,695Y | 6,693 | 2,473 | 70,11 | 23,70 | 6,19 |
| | | K_DE2_72 | 67_72 | 0,318Y | 5,576 | 2,447 | 68,46 | 24,77 | 6,78 |
| | | K_DE2_85 | 80_85 | 0,383Y | 5,745 | 2,575 | 68,24 | 24,98 | 6,78 |
| | | K_DE2_105 | 95_105 | 0,459Y | 5,843 | 2,663 | 42,31 | 47,36 | 10,33 |
| | | K_DE2_145 | 135_145 | 0,927Y | 6,208 | 2,472 | 72,06 | 22,19 | 5,75 |

texture, C content > 0.6 % in the topsoil (ranging from 0.91 to 2.10 %), P content > 0.3 mg g⁻¹ in the topsoil (ranging from 1.3 to 1.5 mg g⁻¹), presence of anthropic artifacts such as bricks and charcoal to a depth of 56 cm, and the dark colour of the ploughed horizon (topsoil) followed by the presence of orange spots in the subsoil due to temporary waterlogging at depth.

Ket_DE2 was sampled to a depth of 145 cm. Visible plough marks ranged from 3 to 35 cm in depth and defined the topsoil (i.e., organomineral horizon Ap) from underlying subsoil (i.e., mineral horizons: Bh, B, Bg). This soil was classified as a *Brunic Arenosol (Humic)* because of its predominantly sandy texture, C content > 0.6 % in the topsoil (ranging from 1.7 to 2.4 %), P content > 0.03 % in the topsoil (0.08 to 0.09 %), and the dark colour of the ploughed horizon (topsoil). The ploughed topsoil is not thick enough to classify this soil as Anthrosol (<50 cm) according to WRB criteria (Fig. 2; Table 2; Table S1; Table S2).

3.1.2. Shaitan III

Shai_C1 included an organo-mineral layer which extended from 2 to 24/29 cm dividing the topsoil (i.e., organo-mineral horizons A1 and A2) from the subsoil (B, Cg, 2Cg, 3Cg). To a depth of 56 cm, this soil was made up of a homogeneous material, after which it showed structural and textural irregularities likely resulting from geological heterogeneity of its parent material. This soil profile also exhibited orange patches due to soil hydromorphy. This soil was classified as a *Stagnic Cambisol (Ochric)*.

Shai_DE1 was opened up to a depth of 190 cm. Anthropic impact was visible to a depth of 180 cm through the very dark coloration and of large quantities of charcoal and pottery debris. The organo-mineral section extended from 0-160 cm and formed topsoil organo-mineral horizons: Au1, Au2, Au3, 2Au, 3Au/pyr and 3pyr (pyr is a pyrogenic horizon composed exclusively of charcoal). Obviously, the 3pyr horizon constituted the upper part of the profile in the past and has been buried since, justifying its position as a topsoil. The subsoil was represented by horizons 4C /pyr and C. The texture was predominantly loam silt. This soil has been classified as a *Pretic Anthrosol (Siltic, Eutric)*, due to C content > 0.6 % in the topsoil (ranging from 3.53 to 8.80 %), P content > 0.03 % in the topsoil (0.57 to 1.13 %), exchangeable Ca plus Mg ≥ 1

cmolc kg-1 in topsoil (ranging from 19.71 to 4.67 cmol kg⁻¹), presence of anthropic artifacts (to a depth of 160 cm) and the dark color. Charcoal radiocarbon dates obtained from this profile confirmed that the formation of the Anthrosol was contemporaneous with the establishment of the archaeological site: at 60 cm depth 870 BP, at 125 cm depth 1020 BP, at 143 cm depth 940 BP and finally at 170 cm depth 1160 BP (Fig. S3).

Shai_DE2 was opened up to a depth of 150 cm. Visible anthropisation markings extended down to between 100 and 118 cm. These anthropic horizons formed the topsoil (i.e., organo-mineral horizons Au1, Au2, 2Au/B/pyr) and whereas deeper horizons represented the subsoil (i.e., mineral horizons B and C). The soil was also classified as a *Pretic Anthrosol (Siltic,Eutric)* using the same justification as soil profile Shai_DE1: C content > 0.6 % in the topsoil (ranging from 0.17 to 7.23 %), high P content > 0.03 % in the topsoil (0.20 to 0.72 %), exchangeable Ca plus Mg \geq 1 cmol kg⁻¹ in topsoil (ranging from 19.10 to 2.65 cmol kg⁻¹), presence of anthropic artifacts (to a depth of 160 cm) and the dark colour (Fig. 2; Table 3; Table S1; Table S2).

3.2. X-ray diffractometry

3.2.1. Ketskii Ostrog

Four samples from the control profile (Ket_C1) and three samples from the anthropic profile (Ket_DE1) of the Ketskii Ostrog that were analyzed by XRD showed similar mineral compositions. The mineralogical nature of the soil is predominantly quartzitic, which corresponds well with the predominantly sandy texture. Plagioclase and feldspar are also found in varying proportions. Clays were found to a minor extent, being represented by chlorite, illite and/or micas. Additionally, amphiboles were also detected in association with other major phases (Fig. 3). Two soil horizons could be distinguished following the occurrence of particular mineral phases: 1) from the control soil profile, sample K_C1_80 demonstrated ilmenite, an iron/titanium oxide, known to accumulate in certain levels during fluvial sedimentary deposition and 2) from anthropic soil profile Ket_DE1, sample K_DE1_80 marked by the presence of apatite, a calcium phosphate.

| Information on Shaitan III samples: the depth at which the sample was collected, the colour according to the Munsell syste | n, and the texture |
|--|--------------------|
|--|--------------------|

| Sample information | | | | Munsell color system | | | Texture | | |
|--------------------|--------------|-----------|------------|----------------------|-------|--------|----------|----------|----------|
| Profile | Horizon type | Sample | Depth (cm) | Hue | Value | Chroma | Sand (%) | Silt (%) | Clay (%) |
| Shai_C1 | topsoil | S_C1_5 | 0_5 | 9,725YR | 4,118 | 1,637 | 21,80 | 69,02 | 9,18 |
| | | S_C1_10 | 5_10 | 10,034YR | 4,615 | 1,864 | 31,82 | 61,75 | 6,43 |
| | | S_C1_15 | 10_15 | 0,279Y | 5,311 | 2,252 | 23,05 | 63,82 | 13,12 |
| | | S_C1_20 | 15_20 | 0,459Y | 5,619 | 2,379 | 20,28 | 65,42 | 14,30 |
| | subsoil | S_C1_30 | 20_30 | 0,497Y | 6,079 | 2,41 | 17,72 | 64,72 | 17,56 |
| | | S_C1_40 | 30_40 | 0,854Y | 6,491 | 2,621 | 18,12 | 65,11 | 16,76 |
| | | S_C1_50 | 40_50 | 0,916Y | 6,452 | 2,607 | 29,25 | 57,44 | 13,30 |
| | | S_C1_67 | 57_67 | 0,482Y | 5,689 | 2,976 | 33,25 | 50,37 | 16,38 |
| | | S_C1_85 | 75_85 | 1,144Y | 6,222 | 2,709 | 70,60 | 22,53 | 6,87 |
| | | S_C1_100 | 90_100 | 0,286Y | 5,488 | 3,083 | 36,33 | 48,39 | 15,28 |
| | | S_C1_110 | 100_110 | 0,194Y | 5,071 | 2,877 | 76,79 | 16,08 | 7,13 |
| | | S_C1_130 | 120_130 | 0,777Y | 5,942 | 3,176 | 4,52 | 69,35 | 26,13 |
| Shai_DE1 | topsoil | S_DE1_10 | 0_10 | 0,686Y | 2,752 | 1,084 | 20,14 | 71,86 | 8,00 |
| | | S_DE1_20 | 10_20 | 0,732Y | 3,003 | 1,103 | 16,50 | 74,18 | 9,32 |
| | | S_DE1_30 | 20_30 | 1,048Y | 3,063 | 1,162 | 26,33 | 63,92 | 9,75 |
| | | S_DE1_40 | 30_40 | 1,076Y | 3,378 | 1,291 | 14,48 | 72,69 | 12,83 |
| | | S_DE1_60 | 50_60 | 1,222Y | 3,362 | 1,32 | 28,39 | 61,26 | 10,36 |
| | | S_DE1_70 | 60_70 | 1,027Y | 3,379 | 1,331 | 29,62 | 58,04 | 12,33 |
| | | S_DE1_80 | 70_80 | 0,799Y | 3,571 | 1,375 | 23,37 | 62,71 | 13,92 |
| | | S_DE1_100 | 90_100 | 0,678Y | 3,774 | 1,465 | 15,90 | 69,80 | 14,29 |
| | | S_DE1_110 | 100_110 | 9,962YR | 3,347 | 1,499 | 17,81 | 65,44 | 16,75 |
| | | S_DE1_120 | 110_120 | 0,506Y | 3,836 | 1,517 | 36,69 | 53,21 | 10,10 |
| | | S_DE1_130 | 120_130 | 0,849Y | 3,992 | 1,545 | 18,98 | 66,21 | 14,81 |
| | | S_DE1_140 | 130_140 | 0,945Y | 3,982 | 1,52 | 26,39 | 60,46 | 13,16 |
| | | S_DE1_160 | 150_160 | 0,161Y | 2,954 | 1,345 | 16,25 | 68,17 | 15,59 |
| | subsoil | S_DE1_175 | 165_175 | 0,757Y | 5,041 | 1,859 | 33,05 | 54,16 | 12,79 |
| | | S_DE1_190 | 180_190 | 9,953YR | 5,571 | 3,906 | 52,02 | 37,77 | 10,20 |
| Shai_DE2 | topsoil | S_DE2_5 | 0_5 | 0,634Y | 3,002 | 1,312 | 27,23 | 64,91 | 7,87 |
| | | S_DE2_10 | 5_10 | 0,753Y | 3,025 | 1,221 | 27,07 | 64,31 | 8,63 |
| | | S_DE2_15 | 10_15 | 0,812Y | 3,008 | 1,208 | 20,11 | 69,70 | 10,19 |
| | | S_DE2_20 | 15_20 | 1,109Y | 2,983 | 1,218 | 24,11 | 67,69 | 8,20 |
| | | S_DE2_30 | 20_30 | 0,921Y | 3,313 | 1,388 | 32,30 | 57,04 | 10,66 |
| | | S_DE2_40 | 30_40 | 0,985Y | 3,381 | 1,41 | 52,57 | 38,79 | 8,63 |
| | | S_DE2_50 | 40_50 | 1,067Y | 3,53 | 1,41 | 52,37 | 40,25 | 7,38 |
| | | S_DE2_60 | 50_60 | 1,481Y | 3,753 | 1,331 | 50,51 | 39,06 | 10,43 |
| | | S_DE2_70 | 60_70 | 1,468Y | 3,75 | 1,321 | 52,95 | 37,73 | 9,31 |
| | | S_DE2_80 | 70_80 | 1,507Y | 3,665 | 1,21 | 43,64 | 45,17 | 11,19 |
| | | S_DE2_90 | 80_90 | 1,638Y | 3,755 | 1,266 | 41,70 | 47,15 | 11,15 |
| | | S_DE2_100 | 90_100 | 1,638Y | 3,755 | 1,266 | 52,14 | 38,97 | 8,89 |
| | | S_DE2_110 | 100_110 | 1,322Y | 3,789 | 1,409 | 27,14 | 60,98 | 11,88 |
| | | S_DE2_125 | 115_125 | 10,012YR | 5,118 | 3,404 | 48,96 | 39,76 | 11,29 |
| | subsoil | S_DE2_140 | 130_140 | 9,742YR | 5,007 | 3,735 | 58,58 | 32,04 | 9,38 |
| | | S_DE2_170 | 160_170 | 1,181Y | 5,566 | 3,343 | 67,46 | 25,78 | 6,76 |

3.2.2. Shaitan III

There were mineralogical differences between the Shaitan III anthropic (Shai_DE1) and control soil (Shai_C1) profiles. For the control profile, mineralogy was very similar to the Ketskii Ostrog samples with a dominant assemblage of quartz, feldspar, chlorite and amphibole. This mineralogical assemblage was found in the S_DE1_160 and S_DE1_190 samples for the anthropic soil profile. For samples taken above 150 cm depth, a quartz, feldspar and illite assemblage was dominant with much less marked or even complete absence of chlorite (Fig. 4). In contrast, the anthropic soil profile included mineral phases such as celsian (a Ba enriched feldspar), monazite, epidote, vernadite, and pyrolusite or metallic iron occurred; these phases occurred non-systematically from one horizon to another over the entire profile.

3.3. pH H₂O/ CEC/C_{tot}/N_{tot}

3.3.1. Ketskii Ostrog

For the Ketskii ostrog site, all the profiles (control and anthropic) show a bimodal distribution in the values of CEC, C_{tot} and N_{tot} : the topsoil has higher values than the subsoil. So, in order to make better comparisons for these parameters, control topsoil samples were compared with anthropic topsoil samples and the same for the subsoil's samples. For pH and base saturation, the bimodal distribution is absent, and the values for these parameters vary slightly with depth, so the

profiles as a whole could be compared.

The pH values for the site suggest that the soils are acidic to slightly acidic and comparable to other regional values (Dukarev and Pologova, 2011). The control profile has significantly lower pH and base saturation values compared with the anthropic profiles. With regard to CEC, the values of both topsoils and control subsoils are significantly lower than those of anthropic topsoils and subsoils; the highest CEC values were observed for the Ket_DE1 located closest to the old dwellings. The main exchangeable cation in these soils is Ca²⁺. Finally, C_{tot} and N_{tot} values were significantly lower for the control topsoils than for the anthropic topsoils, but no significant difference was observed for these parameters in the subsoils (Fig. 5; Table 4; Table S1).

3.3.2. Shaitan III

For the Shaitan III site, the variations over depth in pH and CEC are marked, with an overall trend that seems to be that of a gradual decrease in values with depth for the topsoil samples followed by a gradual increase for the subsoil samples. For base saturation, with the exception of two samples from the Shai_DE profile (S_DE2_10; S_DE2_140) which show a lower base saturation, the values do not seem to vary much with depth for the three studied profiles. The main exchangeable cation in these soils is Ca²⁺. Finally, C_{tot} and N_{tot} show very similar patterns, with a gradual decrease with depth in the topsoil samples and a stabilisation of values in the subsoil samples for both the control and anthropic



Fig. 3. XRD spectrogram for Ket samples.



Fig. 4. XRD spectrogram for Shaitan III samples.

profiles.

Finally, for pH, C_{tot} and N_{tot} significant differences were observed between the anthropic and control profiles, with the highest pH values observed for the Shai_DE2 profile and for C_{tot} and N_{tot} for the Shai_DE1 profile (Fig. 5; Table 4; Table S1).

3.4. Elemental composition

3.4.1. Ketskii Ostrog

All studied profiles exhibited a depleted upper-crust-normalised pattern (Sample/Upper Crust < 1). Exceptions to this observation were P and Cd for certain samples from anthropics profiles. In addition, for all profiles there were two types of patterns which corresponded to



Fig. 5. pH H₂O, CEC, Base saturation and C_{tot} as a function of depth. Control (orange) and anthropic profiles (green). Filled dots: topsoil samples, empty dots: subsoil samples.

topsoil/subsoil distinction. When comparing topsoils, the overall trend consisted of elemental enrichment in the anthropic soil profiles relative to the upper crust. One group of elements stood out, with marked topsoil enrichment: P, Ca, Mn, Cu, Zn, Cd, Sn and Pb. For the subsoil, P enrichment was quite systematic (Fig. S4).

The evolution of elements along the soil profiles demonstrated a clear difference between the topsoils of the three studied soil profiles: profile Ket_DE1 had higher values than profile Ket_DE2 and control profile Ket_C1. The exception was Pb, for which there seems to be no difference between topsoils. At the subsoil level, all soil profiles converged towards the same values except for P: Ket_DE1 displayed higher values than Ket_DE2 and Ket_C1 (Fig. 4; Table S2).

3.4.2. Shaitan III

For most of the elements measured, the control profile Shai_C1 had the highest enrichment factor with anthropic profile Shai_DE1 as the most depleted relative to Earth's crust. However, this trend was not observed for Na, P, Ca, Mn, Fe, Co, Ni, Cu, Zn, Sr, Cd and Sn. More specifically, for P, Ca, Cu, Zn, Sr and Cd, the anthropic profiles showed greater enrichment factors than the control soil profile (Fig. S5).

By observing an enrichment factor along the profiles, it appears that Ca, P and Cd in the anthropic soil profile Shai_DE1 possessed much higher values compared to anthropic profile Shai_DE2. For Cu, Sr and Zn, the difference between the two anthropic profiles was smaller, although still significant. Finally, sample S_DE1_160 from the pyrogenic horizon of soil profile Shai_DE1 exhibited particularly high enrichment factors for Ca, P, Cu, Zn and Cd (Fig. 4; Table S2).

3.5. Rock-Eval analysis

3.5.1. Ketskii Ostrog

Examination of the thermograms confirms the absence of carbonates, with no oxidation signal after 650 °C. The Corg was calculated by summing the values of the TOC and the MinC parameters. Along the two profiles Ket_C1 and Ket_DE1, the topsoils show higher Corg values compared with the subsoils. Corg values in Ket_C1 topsoil are lower than in Ket_DE1 topsoil, while the subsoils have comparable values. As Corg decreases, the S2 and S3 parameters also decrease. Also, for both soil profiles, the proportion of S3 was greater than of S2. Thus, compounds with C-O bonds are dominant in the SOM composition. However, the S2/S3 ratio seems lower for Ket_DE1, although sample size was too small to confirm the significance of this finding. There was no difference in the R-index between Ket_DE1 and Ket_C1 profiles; however, Ket_C1 did show greater variability for this parameter (Fig. 7; Table S3).

3.5.2. Shaitan III

Examination of the thermograms showed that for some samples from Shai_DE1, there was a weak presence of carbonates. In these cases, necessary corrections were made to calculate C_{org} . Shai_C1 contained less C_{org} than the Shai_DE1, and this difference was particularly marked in the topsoil. Beyond the quantitative differences, there were also differences in spatial patterns. In Shai_C1, there was a drastic drop in C_{org} content in the topsoil, with further stabilisation in the subsoil. For Shai_DE1, the first 30 cm horizon was similar to that of Shai_C1, it showed a drastic drop in C_{org} contents from at a depth of 5 cm to 25 cm



Fig. 6. Elemental enrichment as a function of depth for different elements. Control (orange) and anthropic profiles (green).

(layer A) followed by stabilisation of C_{org} values between 35 and 135 cm depth (layer B). A slight increase at the 155 cm depth was observed for the sample exhibiting the pyrogenic horizon (3pyr). Finally, the subsoil exhibited C_{org} values similar to those in Shai_C1, however, the sample size was not sufficient to assess the significance level. Similar to Ketskii Ostrog, as Corg decreases, the S2 and S3 parameters also decrease. Thus, the presence of layer A and layer B is also reflected in the S2 vs S3 diagram. For both profiles, the proportion of S3 was greater than that of S2. Thus, compounds with C-O bonds are dominant in the SOM composition. However, the S2/S3 ratio seems lower for Shai_DE1 topsoil samples. The R-index of Shai_DE1 was greater than that of the Shai_C1, suggesting a greater proportion of thermostable organic matter (Fig. 7; Table S3).

4. Discussion

When placing the results of this study within a regional context, there are almost 1400 known archaeological sites from different periods with varying past uses in the Tomsk region (Zolnikov et al., 2020). A new perspective on these numerous archaeological sites is that, in addition to representing a cultural diversity already studied by archeologists, these sites can provide various ecosystem services such as carbon storage and/ or soil fertility locales in boreal zones. In our study, we only studied two archaeological sites where soil pedogenesis was strongly impacted by human activity, although in very different ways. The Ketskii ostrog site is an ancient agricultural site that was active for almost two centuries. The human activities at the site created some of the richest soils in the

Statistical comparison of physico-chemical results: The p-value indicates the results of comparison: highly significant: 0 '***' significant: 0.001 '**' weakly significant: 0.01 '*' no significant 0.1 '-'.

| Site | Profile | pH H ₂ O | CEC (cmol/kg) | Base saturation (%) | Ctot (%) | Ntot (%) |
|------|----------------|------------------------|------------------|------------------------|-------------|-------------|
| Ket | All profils | *** | *** | *** | _ | - |
| | topsoils | * | * | * | * | * |
| | subsoils | ** | ** | ** | _ | - |
| Shai | All | *** | _ | - | ** | ** |
| | profils | | | | | |
| | topsoils | * | _ | _ | - | - |
| | subsoils | * | - | - | - | - |

region, as it was recognized more than a century ago (Plotnikov, 1901). Historical sources report that in the late 19th century, 400 to 500 carts of manure were used to fertilize the land every two years (Plotnikov, 1901). Indeed, for villages in Western Siberia, the number of livestock per inhabitant was much higher than in Europe which posed the problem of manure disposal; to resolve this manure disposal issue much of it was spread across the soil of vegetable gardens (Turov, 1997). At the Shaitan III site, the prolonged sedentarisation of the metallurgist and horse-breeding populations had the effect of enriching the soil with manure, pottery and, above all, charcoal, which was observed in large quantities in the soil.

In fact, anthropisation is already considered by some researchers to be the sixth factor in soil formation (Effland and Pouyat 1997; Dudal, 2005; Howard, 2017). However, the classification of anthropic soils remains unsatisfactory (Hartman et al., 2004; Capra et al., 2015; Howard, 2017; Kuzyakov and Zamanian, 2019). Mckey (2021) highlighted by two main types of organic matter management with the aim of improving soil fertility. The first involves fire, which plays a main role in mineralisation of nutrients, exemplified by paring and burning or slash-and-burn agriculture (Portères, 1972; Pülschln and Koch, 1990; Olarieta et al., 2011). The second involves decomposition of fresh organic matter, with a typical example being plaggen soils (Urbanski et al., 2022; Vasilchenko and Vasilchenko, 2024). The present study demonstrates that, in addition to the dichotomy between adding



Fig. 7. Rock-Eval results: C_{org} as a function of depth, S2 (mg/g) as a function of S3 (mg/g), and R-index comparison. Orange: samples from the control profiles (Ket_C1 and Shai_C1), green: samples from the anthropic profiles (Ket_DE1 and Shai_DE1). Filled dots: topsoil samples, empty dots: subsoil samples. Orange area: area of topsoil control samples, green area: area of anthropics topsoil samples (layer A for Shaitan III), grey area: area of subsoil samples, area circled in black: samples from layer B that are specific to Shai_DE1.



Fig. 8. Conceptual framework for studies on the SOM of anthropic carbon rich soils.

pyrogenic or fresh SOM decomposition, there is a second dichotomy between an intentional impact aimed at improving soil fertility (Ketskii Ostrog) and an unintentional impact when the transformation of the soil merely results from prolonged sedentarisation (Shaitan III). This brings us back to the problems of ADE, where the question of intentionality is still being debated (Steiner et al., 2009; Glaser and Birk, 2012; Kern et al., 2017). Perhaps, in order to better consider the fertility of archaeological anthroposols, one has to integrate the presence or absence of intention behind their creation. Fig. 8 proposes a sketch of this conceptual framework, integrating the different soils featured in this article and the type of organic matter added and/or transformed in particular through fire activities. We suggest that anthropic archaeological soils should be considered as a continuum of this double dichotomy (intentional/unintentional vs. fresh OM/charred OM), not limited either by geographical borders (Amazonia, Europe, Siberia, etc.) or by typology as currently proposed in the WRB.

In the following, it will be discussed how pedogenesis has been transformed by human activities through the key parameters studied in the article, such as the quantity and quality of organic matter, soil physico-chemistry and elemental composition. It will also be shown that the soils of Ketskii Ostrog are very similar to the Plaggic Anthrosols of Northern Europe and that the soils of Shaitan III are similar to the Prettic Anthrosols, *Terra Pretas de Indio*, of Amazonia, despite the very different biogeoclimatic conditions between these biomes. Following these findings, it would be appropriate to discuss the convergence of archaeo-anthropic soil formation.

4.1. Impact of anthropisation on Corg quantity, SOM composition and dynamics

At both sites, the anthropic topsoils have been enriched in C_{org} compared with control soils, reflecting the addition of organic matter (Fig. 7). At Shaitan III, C_{org} enrichment in anthropic profiles compared to the control profile (40 and 12 g C kg⁻¹, respectively) can partially

explain the depletion of other elements that are not constituents of organic matter and are unrelated to anthropic activities. In terms of C storage at both sites, anthropic profiles had higher C stocks than the control profiles. The difference obtained for the Shaitan III between anthropic and control soils (270 and 57 t C ha⁻¹ respectively for the 0-100 cm depth) is comparable to that reported for the most emblematic anthropic soils such as Terra Pretas de Indio or Plaggic Anthrosols at the Markhausen site (Germany) (Fig. 9) (Glaser et al., 2001; Alho et al., 2019; Urbanski et al., 2022). For Ketskii Ostrog, farming practices have not increased carbon stocks as much (95 and 64 t C ha^{-1} for the first 100 cm depth of the anthropic and control profile, respectively). Furthermore, the stocks at Ketskii Ostrog are close to values obtained for plaggen Anthrosols at the Druffel site in Germany (Urbanski et al., 2022; Fig. 9). However, it should be noted that human activity at Shaitan III lasted almost 700 years whereas at Ketskii Ostrog human activity only lasted 200-300 years. This can partially explain the difference in the degree of C enrichment between the two sites.

Also, spatial SOM dynamics have been differentially impacted at both sites. A natural trend consisted of gradual loss of C_{org} in the first few centimeters of soil followed by its stabilization at depth. For Ketskii Ostrog, this natural dynamic has not yet been restored. In fact, the formerly ploughed topsoil exhibited high and homogeneous C_{org} values followed by a sudden decrease in the subsoil. For Shaitan III, the dynamics of organic matter degradation along the profile were clearly visible. Anthropics horizons can be divided into two categories: 1) a topsoil layer which behaved in the same way as the control topsoil, subject to a loss of C_{org} over depth (layer A) demonstrated recent dynamics of organic matter degradation, and 2) an underlaying homogeneous layer which can be considered as anthropic subsoil, which has been enriched with carbon in the past (layer B) (Fig. 7).

Various mechanisms, such as a) chemical recalcitrance of SOM compounds (Sebag et al., 2016), b) occlusion of SOM in aggregates, c) microbial activity and d) associations with minerals are known to control the persistence of SOM in soils (Derrien et al., 2023). In the case of



Fig. 9. Comparison of the carbon stocks in the soils from this study compared with plaggic and prettic soils from the literature (Glaser et al., 2002; Urbanski et al., 2022) In orange: control profiles, in green:anthropic profiles.

Shaitan III, organic matter was significantly more thermoresistant compared to the control soil profile. XRD analysis did not show any differences in clay content and mineralogy between the control and anthropic soil profiles. Therefore, thermoresistance appears to be inherent in the nature of SOM at Shaitan III. For Ketskii Ostrog, there does not appear to be any difference in SOM thermoresistance between anthropic and control soil profiles (Fig. 7). Analysis of SOM composition at both sites demonstrated that anthropics horizons are more oxygenated than non-anthropic horizons. The oxygenation degree of organic matter can be linked to the initial composition of the litter, ageing of organic matter leading to oxygenation of plant biopolymers (Kleber, 2010) or ageing of biochar leading to oxygenation of its surface (Wang et al, 2020; Fan et al., 2018). Finally, Anthropic Ketskii Ostrog soil profiles had a lower C/N ratio than the control soil profile, indicating that SOM degraded more efficiently in anthropic soils; this remains consistent with other studies of Plaggic Anthrosols such as those for Oldenburg in northwestern Germany or Chitaevo located in the Komi Republic of Russia (Dymov et al., 2018; Kern et al., 2019). In fact, the original soils were nitrogen poor (Vasilchenko and Vasilchenko, 2024) and, if the additions consisted solely of manure or vegetable waste, the nitrogen content would have also increased. In the case of Shaitan III, the oxygenated and heat-resistant nature of SOM with higher C/N values compared to control soils confirms that the characteristics of OM are strongly influenced by the addition of charcoal (Fig. 10).

Moreover, although Ketskii ostrog these soils have been carbon enriched compared to control soils, this carbon was also vulnerable to degradation. In contrast, Shaitan III's anthropic soils have been greatly enriched in carbon by addition of SOM in the form of charcoal, manure and domestic waste similar to *Terras Pretas de Indio*. As a result, added soil carbon was more resistant to degradation. This similarity makes Shaitan III a more sustainable carbon storage system. Until now, charcoal was not considered in soil classification, although it has been evidenced as a major component for the Pretic horizons from Anthrosols as also proposed in Fig. 8. However, charcoal quantification still remains challenging. A recent study from Aubertin et al. (2024) seems to open up new and promising prospects via the use of the Rock-Eval® method.

4.2. Impact on soil chemical fertility

The results on pH, CEC, macro- and micronutrient and toxic metal content in the studied soils are helpful for assessing chemical fertility of Western Siberian soils. At Ketskii Ostrog, where soil transformation was intentional to assist in developing agricultural fertility (Fig. 8), anthropic activity had a positive impact on pH and CEC and enriched soil in certain macro- and micronutrients compared to control soil. Although anthropic activity was mainly concentrated within the topsoil, pH, CEC and P increased downward through the soil profiles, likely due to enhanced vertical migration in the humid climate (Fig. 5; Fig. 6). This profound impact of human activity on soil chemistry raises questions about the current WRB classification for these anthropics soils. According to WRB classification, to classify a soil as an Anthrosol the thickness of the anthropic horizon must be > 50 cm (IUSS Working



Fig. 10. C/N as a function of depth. In orange: control profiles (Ket_C1 and Shai_C1), in green: anthropic profiles (Ket_DE1 and Shai_DE1). Filled dots: topsoil samples, empty dots: subsoil samples.

Group WRB, 2022). Thus, depending on the limitations set on the basis of depth, Ket_DE2 may not truly be considered Plaggic Anthrosols, despite the fact anthropic impact was observed beyond the plaggic horizon. Thus, a new perspective for classification would require integration of anthropic impact propagation over the entire soil profile, notably in those regions with excessive precipitation occurring over evapotranspiration.

Anthropization at Shaitan III was not intended to improve the soil for agriculture (Fig. 8), but did have a positive impact on chemical fertility. For this site, soil acidity decreased, whereas the concentration of nutrients (P, Ca, N, Zn, Cu and Mn) and some toxicants (Cd) increased (Fig. 6). However, it is not yet possible to characterize the bioavailability of these nutrients and toxic elements for plants. Performing selective extractions on these soils could give a better idea of the role these elements play in soil chemical fertility (Chojnacka et al., 2005; Adamo et al., 2014; Kumpiene et al., 2017). Furthermore, while the presence of biochar is known to reduce bioavailability of toxicants, especially Cd (Park et al., 2011; Ni et al., 2020; Liu and Chen 2022), certain studies suggest it has an indirect positive effect on nutrient bioavailability (Xu et al., 2013; Zheng et al., 2013).

4.3. Impact of anthropisation on elemental composition

For both sites, we observed a sizable enrichment in macro- and micronutrients such as P, Ca, Cu, Zn, Mn and other elements which serve as markers of anthropisation (i.e. Cd, Pb, Sn and Sr) in the anthropics horizons of the soil profiles (Entwistle et al., 2000; Asare and Afriyie, 2021; Bintliff and Degryse, 2022). Normalization of element concentration to that of the Upper Crust showed variability detected cannot be explained by different fluvial or erosional inputs within the soil profiles at each site (Fig. S4; Fig. S5). The most drastic difference between control and anthropic soil profiles was evident in measured P and Ca concentrations (Fig. 6). These elements are known to be good markers of



Fig. 11. C_{tot} as a function of Ca^{2+} . Circles: Ketskii Ostrog, triangles:Shaitan III. In orange: Control profile, in green: anthropic profile samples.

anthropisation, as documented for ADE (Alho et al., 2019). For the Ketskii Ostrog, enrichment in P can be explained by the presence of apatite, a calcium phosphate originating from bones. It is also known that adding manure to the soil has the effect of enriching the soil in C, P, Ca, Zn, Cu and Mn (Wong et al., 1999; Ogiyama et al., 2005; Acksel

et al., 2019).

In the case of Shaitan III, the products derived from domestic waste could have enriched soil nutrients like C, P, Ca, Mn, Cu, Zn or other elements like Sr, as is the case with other Dark Earths around the world (Robellato et al., 2009; Solomon et al., 2016; Asare, 2022). Secondly, breeding of horses and cattle can be an important source of manure that can enrich soil in C, P, Ca, Zn, Cu, Zn and Mn (Wong et al., 1999; Ogiyama et al., 2005; Acksel et al., 2019). Finally, combustion of wood, which was necessary for domestic (cooking, home heating, making pottery) and metallurgical needs, produced a large quantity of charcoal and ash, thereby providing large amounts of C and nutrients (P, Ca, Zn, Cu and Mn) and heavy metals (Cd or Pb) to the soil (Demeyer et al., 2001; Rumpf et al., 2001). Presence of minerals such as pyrolusite or iron metal within the anthropic soil profiles are known to be indicative of these metallurgical practices (Georgakopoulou and Rehren, 2013; Amicone et al., 2020).

It has long been shown that adsorption mechanisms on minerals such as Al, Fe and Mn oxides can participate in SOM stabilisation (Torn et al., 1997; Grand and Lavkulich, 2011). The link with other elements in the stabilisation of SOM remains less studied, but recent studies show that organo-cationic interactions can participate in the stabilisation of SOM through sorption mechanisms (Rowley et al., 2018; Wan et al., 2021; Rowley et al., 2023). Our results also show that there is a significant correlation between C_{tot} and Ca^{2+} , the major cation in the studied soils (Fig. 11). Thus, anthropic Ca enrichment in soils could also partially explain the long-term stability of SOM in these Anthrosols.

It has been shown that, at the Ketskii Ostrog site, the human-induced transformation of soil for the purpose of agriculture led to a radical improvement in the chemical fertility of the soil. Moreover, this transformation was not restricted to the layer directly impacted by the addition of manure and ploughing, but the subsoil was also impacted by subsequent pedogenetic processes. The soils of Ketskii ostrog are quite similar to the Plaggic soils of northern Europe in terms of the quantity and quality of organic matter and soil physico-chemical parameters. However, because of their low carbon stability, these vulnerable soils (e. g., Giani et al, 2014) could become potential sources of carbon as a result of climate warming. In contrast, at the Shaitan III site, transformation of the soil was not intentional, but resulted from prolonged sedentarisation of the population. Chemical fertility has also improved, but less than at the Ketskii Ostrog. The greatest impact of anthropisation was on carbon stock, which increased by a factor of three. Because of SOM's great stability, this soil remains a carbon sink, comparable to the documented Terra Pretas de Indio. Thus, there is a need for further studies of anthropic soils in this vast region, with the aim of establishing management practices for these environments.

5. Conclusion

This study shows that anthropisation is not only the sixth factor in the formation of anthropic soils, but also the main agent. Using only two examples of anthropic soils from Western Siberia, we have shown that there are soils that are very similar to those found in very distant biomes, like Northern Europe or Amazonia. The present study highlights the need to reconsider the anthropogenic classification of archaeological soils according to the WRB, via accounting for both the initial intention of human population to modify the fertility of anthropogenic soils and the stability of the produced SOM. For this, several aspects of the classification should be addressed. Firstly, regarding soil fertility, beyond the chemical characteristics of horizons impacted by human activity, we recommend examining how anthropogenic effects propagate through the soil profile via pedogenesis. For instance, phosphorus has been identified as a marker of anthropisation (Alho et al., 2019), and its migration beyond anthropogenic horizons could be considered in future soil classifications. Secondly, concerning soil organic matter (SOM) stability, charcoal appears to play a crucial role, particularly in archaeological soils. We propose that this parameter be assessed

quantitatively rather than solely qualitatively, aligning with the perspective of Mastrolonardo and Certini (2020). New studies aimed at quantifying charcoal via thermal analysis are underway (Aubertin et al., 2024), offering promising advancements in analytical methodologies. Finally, a more precise definition of archaeological contexts would provide essential insights for developing a more accurate classification of archaeological Anthrosols.

CRediT authorship contribution statement

Daria S. Derbilova: Writing – review & editing, Writing – original draft, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. Priscia Oliva: Writing – review & editing, Validation, Supervision, Resources, Methodology, Investigation, Formal analysis, Conceptualization. David Sebag: Writing – review & editing, Validation, Resources, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. Sergei Loiko: Writing – review & editing, Validation, Resources, Methodology, Investigation, Conceptualization. Sergei Loiko: Writing – review & editing, Validation, Resources, Methodology, Investigation, Conceptualization. Asap Idimeshev: Writing – review & editing, Validation, Investigation. Liudmila S. Shirokova: Writing – review & editing, Validation, Resources, Methodology, Conceptualization. Jean-Jacques Braun: Resources, Project administration, Funding acquisition. Oleg S. Pokrovsky: Writing – review & editing, Validation, Resources, Project administration, Supervision, Resources, Project administration, Methodology, Conceptualization.

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 A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.geoderma.2024.117101.

Data availability

Much of the data is available in Supplementary matérials. More exaustive data will be published on PANGEA in open access after publication of the manuscript. Otherwise, please contact the authors.

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