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Dorota Riegert[1], Katarzyna Konopka[1], Urszula Kobylińska[2]

[1] Politechnika Warszawska, Wydział Inżynierii Materiałowej, ul. Wołoska 141, 02-507 Warszawa, Poland
[2] Polska Akademia Nauk, Instytut Archeologii i Etnologii, al. Solidarności 105, 00-140 Warszawa, Poland
** Corresponding author. E-mail: dorota.riegert@inmat.pw.edu.pl*

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USING SCANNING ELECTRON MICROSCOPY FOR IDENTIFICATION OF ADMIXTURES IN ARCHAEOLOGICAL POTTERY

The work presented in this article describes the use of scanning electron microscopy (SEM) with an EDS attachment in studying Early Medieval ceramic vessels from archaeological sites. These studies have allowed us to observe the shape and size of temper particles as well as analyze the chemical composition of mineral admixtures. The analyzed material consisted of fragments of Menkendorf-Szczecin type clay vessels from Polish and German archaeological sites of the 9th-11th centuries. Studies using scanning electron microscopy at various magnifications allow for the observation of mineral admixtures of different fractions, large temper particles which were added intentionally, as well as small particles which are a normal fraction of natural clay. Scanning electron microscopy studies also made it possible to classify minerals on the basis of their shapes. A group of admixtures of spherical shape and a group of polygons were identified. Point analysis of their chemical composition (SEM-EDS) allowed us to separate the minerals into groups containing quartz and those made up of other minerals containing titanium or barium in their chemical composition.

Keywords: **archaeological pottery, scanning electron microscopy, SEM-EDS**

WYKORZYSTANIE MIKROSKOPII SKANINGOWEJ DO IDENTYFIKACJI DOMIESZEK W CERAMICE ARCHEOLOGICZNEJ

Głównym celem prac przedstawionych w artykule było wykorzystanie skaningowej mikroskopii elektronowej (SEM) z przystawką EDS do badania wczesnośredniowiecznych ceramicznych naczyń pochodzących z wykopalisk archeologicznych. Badania te pozwoliły na obserwację kształtu i rozmiaru domieszek, a także analizę składu chemicznego mineralnych domieszek. Materiał do badań stanowiły fragmenty glinianych naczyń typu Menkendorf-Szczecin pochodzących z terenów Polski i Niemiec z IX-XI wieku. Badania z użyciem skaningowej mikroskopii elektronowej pozwalają przy różnych powiększeniach na obserwację domieszek pochodzenia mineralnego o różnej frakcji, grubej - która była dodawana celowo, a także frakcji drobnej, która mogła stanowić naturalny składnik gliny. Badania SEM pozwoliły także na sklasyfikowanie minerałów na podstawie kryterium ich kształtów. Wyróżniono grupę ziaren domieszki o kształcie kulistym oraz grupę o kształcie wieloboków. Badania punktowej analizy składu chemicznego (SEM-EDS) pozwoliły na podział grup minerałów na kwarce oraz minerały zawierające w swoim składzie chemicznym tytan lub bar.

Słowa kluczowe: **ceramika archeologiczna, skaningowa mikroskopia elektronowa, SEM-EDS**

INTRODUCTION

Clay ceramic vessels have been known to man for over 8000 years [1]. Their continuing popularity is due to the abundance of clay raw materials needed for their manufacture on the one hand, and to the relatively simple technology required to manufacture ordinary vessel forms on the other. Clay as a raw material contains mineral particles which are diverse in their chemical composition, size and shape. In addition, a variety of materials was intentionally added to potter's clay, including mineral particles, called temper or admixture by potters, which were intended to improve the quality of the final product. Sand grains, crushed stone, marl, or broken and fragmented pieces of other vessels were mainly used as mineral temper. Admixtures were added to the clay at the preparation stage of the ceramic paste. The addition of mineral filler increases the mechanical strength of the clay during drying and firing, and reduces susceptibility to thermal shock to which the products are exposed when they are fired and later used in household activities [2].

Although ceramics - along with stone, bronze and glass - is one of the historic materials which is most resistant to degradation [3], and fragments of pottery are found abundantly on archaeological sites from the Neolithic epoch onwards, the complex determinants of the manufacturing process involved in its production are still not fully understood by archaeologists. Precise knowledge of the structure and properties of ceramics from archaeological sites is therefore an important objective. A vital facet of this process is reconstructing ancient pottery recipes, which - as we know from ethnographic parallels - were not only composed for technological and environmental reasons but also reflect social and cultural factors [4].

The archeometry of pottery in Poland, despite its long history [5], is still in the phase of searching for and optimizing methods and tools of cognition. The study of archaeological finds, including pottery, is also a useful research area for materials science with its research techniques [6]. Analytic tools for studying ceramics from archaeological sites can include - among others - optical microscopy, scanning electron microscopy [7], scanning electron microscopy with an EDS attachment [8], and X-ray diffraction XRD [9].

STUDY MATERIAL AND RESEARCH METHODOLOGY

The material used in this study consisted of selected fragments of pottery of the Early Medieval Menkendorf-Szczecin type [10] dated from the late 9th to early 11th century AD, found during archaeological excavations conducted both in the territory of Poland and Germany (Fig. 1).

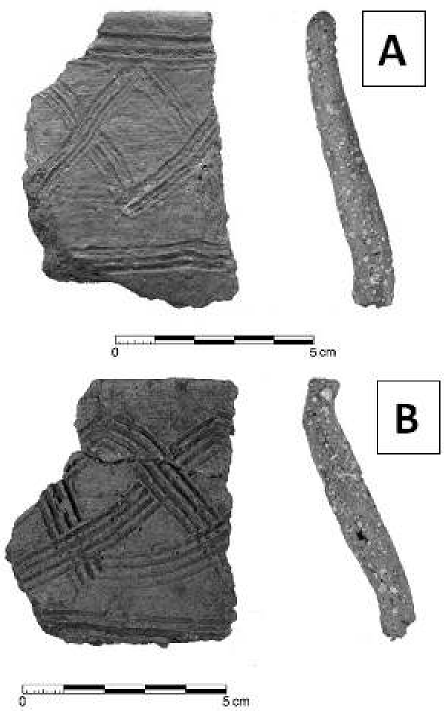

Fig. 1. Examples of fragments of vessels of Menkendorf-Szczecin type (photo: M. Osiadacz from Institute of Archaeology and Ethnology of Polish Academy of Sciences in Warsaw): A. Ottersburg, Saxony-Anhalt, Lkr. Stendal B. Kołuda Wielka, Kujawsko-Pomorskie Province

Rys. 1. Przykłady fragmentów naczyń typu Menkendorf-Szczecin (fot. M. Osiadacz z Instytutu Archeologii i Etnologii Polskiej Akademii Nauk w Warszawie): A. Ottersburg, Saksonia-Anhalt, Lkr. Stendal; B. Kołuda Wielka, woj. kujawsko-pomorskie

The results presented here are the effects of collaboration between the Department of Materials Science and Engineering of the Warsaw University of Technology and the Institute of Archaeology and Ethnology of the Polish Academy of Sciences in Warsaw.

This study was performed using scanning electron microscopes HITACHI 2600N and TM 1000 in order to observe the microstructure and morphology of grains of mineral temper and their relationship to each other. The observations described below were carried out on a cut surface created during the preparation of samples for testing. These studies allowed us to observe admixtures of different sizes and shapes.

These microscopic observations were enhanced by the point analysis of the chemical composition (SEM - EDS) of mineral admixtures and temper using a Hitachi 3500 microscope.

RESULTS AND DISCUSSION

An important element of the structure of ceramic vessels are the mineral admixtures which are intentionally added to the clay matrix or are a natural ingredient of the raw material. Observations using scanning electron microscopy allowed us to observe the shape and morphology of the added particles, i.e. temper. The selection of SEM images show the admixtures in the investigated fragments of the vessels (Fig. 2).

Observations using scanning electron microscopy showed the variety of shapes, sizes and morphology of the admixtures. The shapes of the particles include spherical forms (Fig. 2A, 2I), polygons (Fig. 2D, 2E) and irregular forms (Fig. 2G, 2H). Similarly, there are agglomerates of small particles (Fig. 2F) and clusters of a few admixtures (Fig. 2B). Some show a lamellar structure (Fig. 2C, Fig. 2J). The size of particular admixtures varied in size from 0.5 μm (Fig. 2J) to 1 mm (Fig. 2F).

The observed particles also have different chemical composition, as evidenced by differences in the contrast. This is confirmed further by the test point analysis of the chemical composition using scanning electron microscopy with an EDS attachment. These tests make it possible to identify these elements, which are likely to form particles of the mineral class.

In the analyzed microarea shown in Figure 3A for instance, a spherical grain of temper with a diameter of about 700 μm is visible. The chemical composition of this admixture showed a high content of silicon and oxygen and trace amounts of iron and aluminum. The intensity of the spectral lines of Si indicates that this temper particle is a mineral admixture from the group of silicates [11].

In the analyzed microarea shown in Figure 4A, an irregularly shaped temper grain is visible, the size of which is ca 30 by 50 μm. The chemical composition of this admixture showed a high content of titanium, iron, silicon and oxygen, as well as smaller amounts of aluminum, potassium and manganese. The high intensity of the spectral lines of titanium, iron, silicon and oxygen indicates that this is a titanium mineral - it may be, for example ilmenite [11].

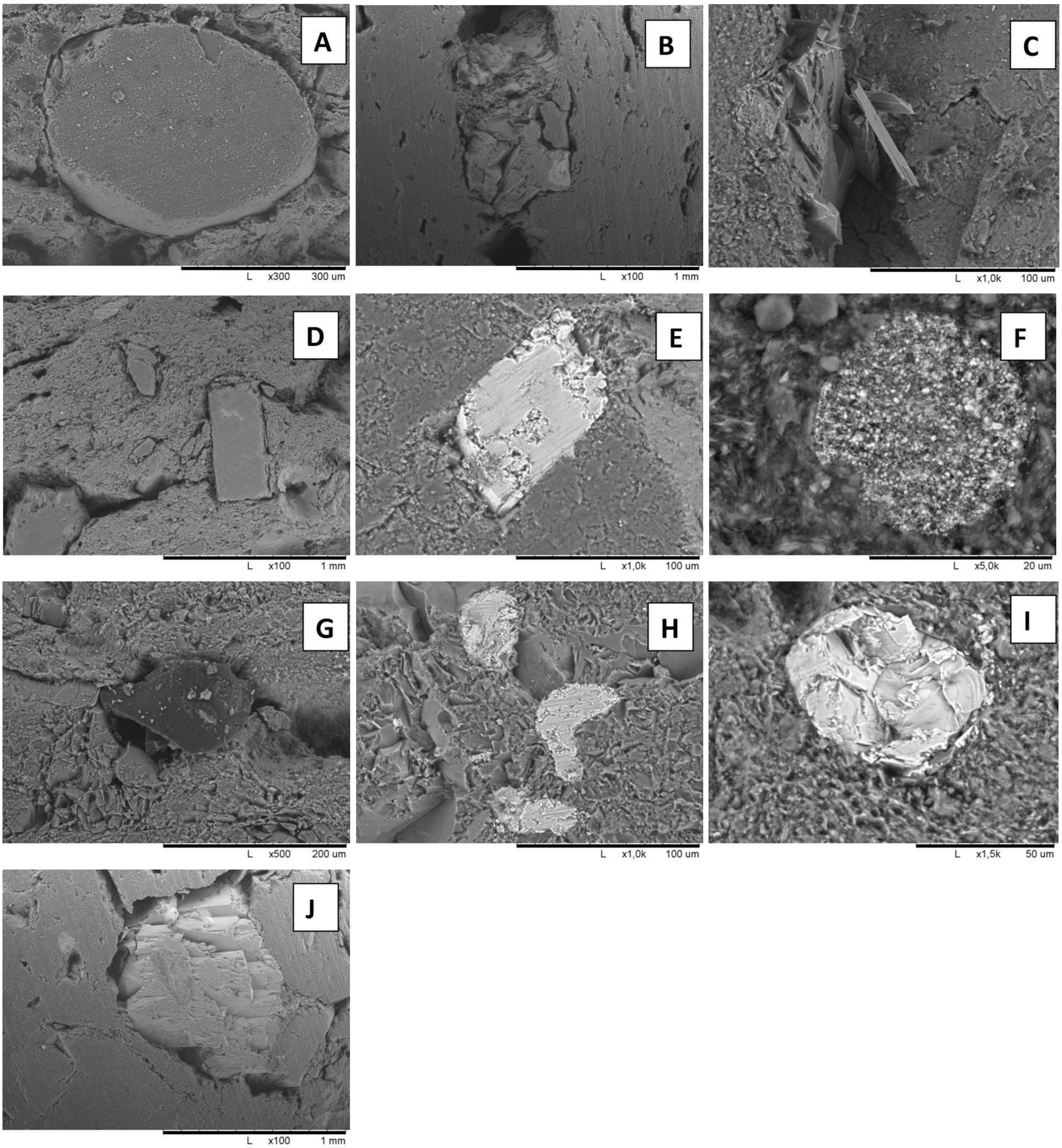

Fig. 2. SEM images of mineral admixtures in investigated pottery fragments: A. Święck-Strumiany, Podlaskie Province: large admixture of spherical shapes; B. Lubicz, Kujawsko-Pomorskie Province: agglomerate of of small particles; C. Lubicz, Kujawsko-Pomorskie Province: admixture of lamellar structure; D. Kołuda Wielka, Kujawsko-Pomorskie Province: large admixture of angular shapes; E. Kołuda Wielka, Kujawsko-Pomorskie Province: large admixture of angular shapes and bright contrast; F. Kołuda Wielka, Kujawsko-Pomorskie Province: agglomerate of small particles; G. Ottersburg, Saxony-Anhalt, Lkr. Stendal: admixture of irregular shape; H. Ottersburg, Saxony-Anhalt, Lkr. Stendal: admixture of irregular, rounded shapes; I. Objezierze, Wielkopolskie Province: admixture of spherical shapes; J. Lubicz, Kujawsko-Pomorskie Province: admixture of lamellar structure

Rys. 2. Zdjęcia SEM domieszek mineralnych w badanych fragmentach naczyń: A. Święck-Strumiany, woj. podlaskie: duża domieszka o kulistych kształtach; B. Lubicz, woj. kujawsko-pomorskie: aglomerat drobnych cząstek; C. Lubicz, woj. kujawsko-pomorskie: domieszka o budowie płytkowej; D. Kołuda Wielka, woj. kujawsko-pomorskie: duża domieszka o kanciastych kształtach; E. Kołuda Wielka, woj. kujawsko-pomorskie: duża domieszka o kanciastych kształtach i jasnym kontraście; F. Kołuda Wielka, woj. kujawsko-pomorskie: aglomerat drobnych cząstek; G. Ottersburg, Saksonia-Anhalt, Lkr. Stendal: domieszka o nieregularnych kształtach; H. Ottersburg, Saksonia-Anhalt, Lkr. Stendal: domieszki o nieregularnych, obłych kształtach; I. Objezierze, woj. wielkopolskie: domieszka kulistych kształtów; J. Lubicz, woj. kujawsko-pomorskie: domieszka o budowie płytkowej

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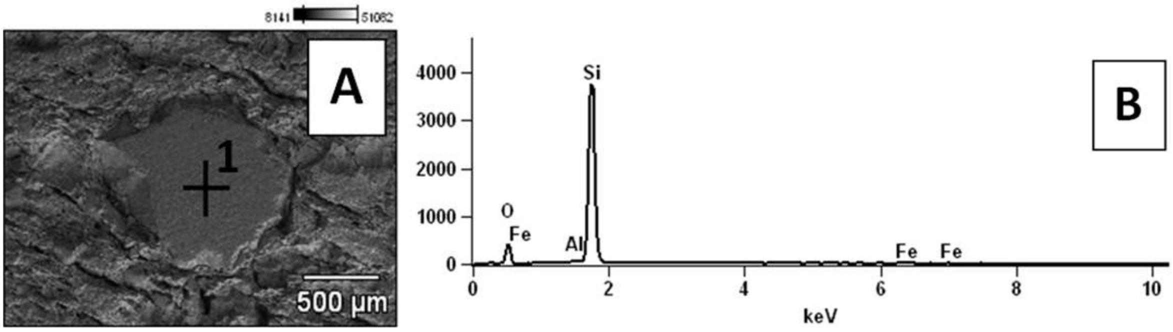

Fig. 3. Analyzed area on surface of pottery sample from Święck, Podlaskie Province: A. place of analysis in section 1; B. spectrum of elemental composition of test area (point 1 in Figure A)

Rys. 3. Analizowany obszar na powierzchni próbki ceramiki ze Święcka, woj. podlaskie: A. miejsce analizy w punkcie 1; B. spektrum składu pierwiastkowego badanego mikroobszaru (punkt 1 na rysunku A)

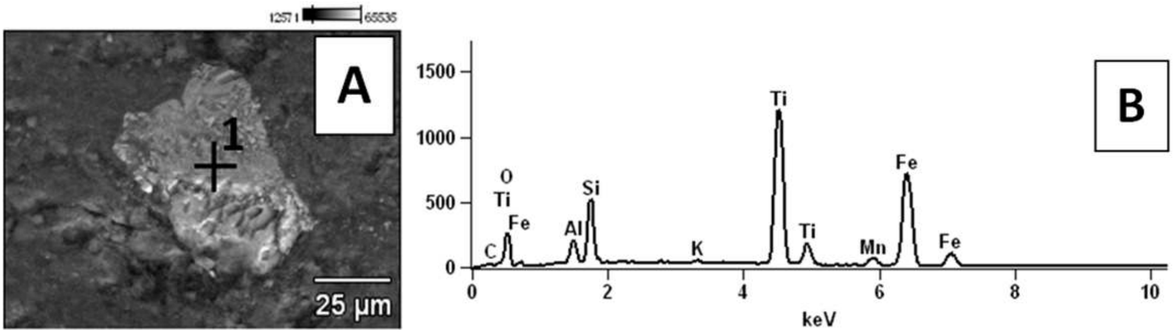

Fig. 4. Analyzed area on sample surface from Kołuda Wielka, Kujawsko-Pomorskie Province: A. place of analysis in section 1; B. spectrum of elemental composition of test area (point 1 in Figure A)

Rys. 4. Analizowany obszar na powierzchni próbki z Kołudy Wielkiej, woj. kujawsko-pomorskie: A. miejsce analizy w punkcie 1; B. spektrum składu pierwiastkowego badanego mikroobszaru (punkt 1 na rysunku A)

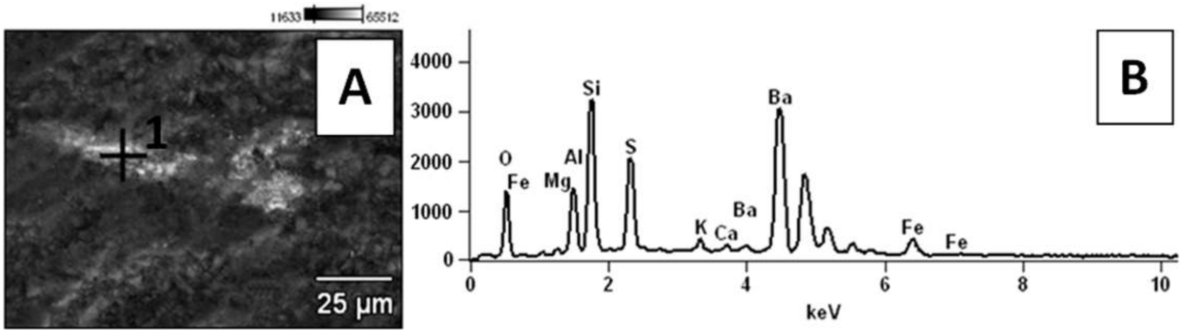

Fig. 5. Analyzed area on sample surface from Ottersburg, Saxony-Anhalt: A: place of analysis in section 1; B. spectrum of elemental composition of test area (point 1 in Figure A)

Rys. 5. Analizowany obszar na powierzchni próbki z Ottersburga, Saksonia-Anhalt: A. miejsce analizy w punkcie 1; B. spektrum składu pierwiastkowego badanego mikroobszaru (punkt 1 na rysunku A)

In other investigated pottery sherds, e.g. these presented in Figure 5, a cluster of small mineral particles can be seen. The study of its chemical composition showed a high content of barium, silicon, aluminum, sulfur and oxygen and traces of magnesium, potassium, calcium and iron. The high intensity of spectral lines of barium, sulfur and silicon shows that this may be a barium mineral called barite [11].

CONCLUSION

Studies using scanning electron microscopy allow for the observation of mineral admixtures or temper added intentionally during the manufacture of clay pots as well as of small particles that are a natural component of raw clay. The observations showed a variety of shapes of temper grains: spherical, angular and irregularly shaped. These observations showed differences in the contrast of admixtures, which supplies us with evidence of the variation of their chemical compositions.

The analysis of the chemical composition of these particles using an EDS analyzer allows for the identification of elements contained in the temper. However, this analysis only gives us general information about the elemental composition of mineral particles and does not allow for clear identification of the mineral. On the other hand, EDS analysis allows one to specify the groups of minerals, from which the admixture may come.

The differentiation of grain size and mineralogy of the admixtures found during the research presented above shows clearly that despite their chronological and typological homogeneity, the vessels of the Menkendorf-Szczecin type, which we examined, were manufactured using different sources of raw clay. This is a result which we expected, if we take into account the geographical distance between the archaeological sites from which the analysed pottery samples were obtained, as well as the different environmental conditions of the locations of these sites and the different clay deposits available in their vicinity. What is much more important from the point of view of both the history of technology and research on the social and cultural relationship between human groups in the past is ,however, the conclusion that the analysed vessels were manufactured using different recipes for preparing ceramic paste. Various amounts of tempering admixture, as well as different granulation and chemical composition of the temper which was deliberately added to the raw material (clay matrix) by potters in different places means that the cultural transfer of stylistic characteristics within the north-western Slavic settlement region, which lead to the adoption of common forms of pots and their ornaments, did not necessarily go hand in hand with a simultaneous transfer of technology. This implies that despite the intensive contacts between various human groups, the recipes for the preparation of ceramic paste remained a feature specifically local and culturally determined.

Acknowledgements

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