SEM-EDS AS INVESTIGATION TOOL FOR ARCHAEOLOGICAL ARTIFACTS – THE CASE OF NEPHRITE ADORNMENTS

P. MEREUTA[1], B. CONSTANTINESCU[1], D. CRISTEA-STAN[1], D. SERBANESCU[2]

[1] "Horia Hulubei" National Institute for Physics and Nuclear Engineering,
P.O. Box MG-6, Magurele, Romania
E-mail: *paul.mereuta@nipne.ro*, *daniela@nipne.ro*
[2] Museum of Gumelnitza Civilization, Oltenita, Romania
E-mail: *enod2009@gmail.com*

Abstract. Scanning Electron Microscope (SEM) coupled with Energy Dispersive X-Ray Spectroscopy (EDS) proved to be an efficient tool for analyzing archaeological samples. We illustrate with some Neolithic adornments – pendants, presumed nephrite and jadeite items, to verify if geologists' visual examination is confirmed by EDS elemental composition. SEM-EDS must be complementary to X-Ray Fluorescence (XRF), Proton Induced X-ray Emission (PIXE) or Inductively Coupled Plasma – Mass Spectrometry (ICP-MS) methods.

Key words: scanning electron microscope, energy dispersive X-ray spectroscopy, prehistory, Gumelnitza culture, nephrite adornments.

1. INTRODUCTION

The application of scanning electron microscopy and microanalysis (SEM-EDS) to the study of materials, manufacturing methods and deterioration processes of objects from ancient through to contemporary cultures, often used in conjunction with other microscopic and analytical instrumentation, has a huge influence in the last years on the understanding of material technologies that produced such objects and on the conservation and preservation of these items for the long-term benefit of world cultural heritage [1]. Some examples of SEM-EDS studies on ancient artifacts:
- Solder characterization on ancient gold artifacts with an electron microprobe [2]
- Electron microprobe analysis of ancient ceramics: a case study from Romania [3]
- Metallurgical and chemical characterization of Roman Imperial and Venetian silver denarii dating to the late twelfth century [4]
- Scanning electron microscopy of wood replaced by iron corrosion products [5].

Usually SEM analyses are complementary to other methods like micro-Proton Induced X-ray Emission (micro-PIXE), X-ray Fluorescence (XRF), Induced

Coupled Plasma-Mass Spectroscopy (ICP-MS), X-ray Diffraction (XRD), Fourier-Transform Infrared Spectroscopy (FTIR) – [6, 7, 8, 9]. Our group used SEM-EDS together with XRF and micro-PIXE to study the silver-copper-lead in-homogeneities in some ancient silver artifacts – a Dacian bracelet fragment and some Roman coins [10].

In the present work we applied SEM-EDS method to some Neolithic adornments suspected by geologists after visual examination to be nephrite and jadeite to confirm this suspicion by determination of their chemical composition.

2. METHOD

Scanning Electron Microscope (SEM) uses an electron beam in order to obtain surface images of different samples [11]. The beam scans point by point a predefined area, the point where the electron beam hits being correlated with the signal in the electron detectors and then the image reconstructed. A special type of analysis coupled with SEM is Energy Dispersive X-ray Spectroscopy (EDS) providing elemental analysis from Carbon to Uranium. The EDS system detects the characteristic X-rays due to excitation by the electron beam of atoms from the sample [11, 12, 13].

The SEM-EDS in our department is produced by Zeiss, model EVO MA15 coupled with an EDS system provided by Thermo Scientific. Technical characteristics of SEM: an acceleration voltage from 1 to 30 kV and a current that can go up to 400 mA. We have the possibility to analyze up to 9 samples at once using different sample holders. Our SEM has three detectors: one for BSE (Back-Scattered Electrons) and two for SE (Secondary Electrons) – one for high vacuum (HV) and one for variable pressure (VP) in the microscope. The EDS detector is a Silicon Drift Detector (SDD), with 129 eV (Mn) energy resolution, used to obtain X-ray spectra for a certain area, for a point in the case of point analysis and elemental maps.

Other important characteristics of our SEM-EDS system are the resolution: 3 nm at 30 kV – HV and 3.4 nm at 30 kV – VP. At lower accelerating voltages we have 20 nm at 1 kV and 3 nm at 3 kV, both in the case of high vacuum. We can obtain images with EDS having a maximum frame of 1024 × 768 pixels, with the field of view at a maximum value of 6 mm in diameter at an analytical working distance of 8.5 mm. The magnification range for our SEM is between 5x and 1000000x but the values depend a lot on the sample type, the working distance, the used accelerating voltage and the current values. For the VP mode the pressure range is 10–400 Pa, the gas being nitrogen and this mode is important when making X-ray analysis on non-conducting samples as is prevents surface charging that can give false signal to the EDS detector. For the current studies we used exclusively the EDS detector as nephrite is homogeneous.

Small archaeological artifacts like earrings, beads, pendants can fit in the SEM sample holder and can be analyzed as they are, without being necessary to cut them in smaller pieces. This is very important because in many cases invasive procedures on the artifacts are prohibited and also some cleaning methods and/or sample preparations are not suitable for such precious samples, because cleaning/preparing can affect their integrity and aspect.

3. SAMPLES

The sample to be analyzed must fit the dimensions required by the holders and must have a clean surface because SEM-EDS analysis cover only 1–4 microns in depth, depending of the sample chemical composition. We have two types of holders: a carousel that can hold up to 9 samples with the diameter of 20 mm and a vise that can hold bigger samples (50 mm × 50 mm). Many archaeological artifacts are adornments and they must not be modified in any way as they are important historical pieces, part of museum collections that can be put up on display. That is why their surface needs to be gently cleaned (*e.g.* with a cotton tissue and alcohol) to ensure that handling contaminants like C, Na, Cl are not present on the sample. However, even after cleaning a carbon component is present due to the oil vacuum pumps and must be evaluated using a carbon free material.

The samples we analyzed were Neolithic adornments suspected to be nephrite: two earrings (Fig. 1). The goal was to confirm the samples artifacts are indeed made from nephrite, as suspected from visual inspection by geologists, using SEM-EDS to determine their chemical (elemental) composition and at the same time to test our device capabilities in minerals studies.

Nephrite is a mineral part of the jade species, the other type of jade being jadeite. The difference between them is made by their elemental main constituents: for jadeite chemical formula is $NaAlSi_2O_6$ and for nephrite $Ca_2(Mg, Fe)_5Si_8O_{22}(OH)_2$ [13]. So, to identify the nephrite we focused on the main constituents Ca, Mg, Fe, Si and O, also verifying if their weight concentrations values are as close as possible to the theoretical values reflected in their ratios (*e.g.* Ca/Mg, Mg/Si). To verify the correctitude of our analysis a modern pendant confirmed as nephrite by geologists was also measured under the same conditions (similar parameters used for SEM-EDS analysis).

The artifacts were found in two settlements of Boian and Gumelniţa cultures (Cascioarele, Sultana [15]). The Balkans area holds numerous settlements dating to the Neolithic time where jade – nephrite and jadeite – artifacts were discovered (Bulgaria [16], Serbia [17]). The problem is if jade mineral was brought in the Balkan area from known European geological deposits (and if so from where – *e.g.* Southern Poland) or there was a jade deposit in the Balkans now exhausted. Until now this problem is not solved [18].

Fig. 1 – The two earrings with inventory numbers 12019 (top)
and 12020 (bottom).

Fig. 2 – Modern nephrite pendant (left) and Neolithic jadeite pendants,
inventory numbers 8750 and 3055.

Each object was analyzed in several points (at least three) across its surface in order to verify its homogeneity – see Fig. 3 (elemental maps for O, Mg, Si, Ca, Fe); for good statistics each spectrum had over 1000000 counts. The parameters used for the analyses were: accelerating voltage (EHT) – 20 kV with a current of approximately 690 pA, working distance (WD) – 10.5 mm and a magnification of 3000× for the spectra, resulting a $80 \times 80 \ \mu m^2$ scanned surface. Electron penetration depth is approximately 4 μm for these experimental conditions (EHT = 20 kV).
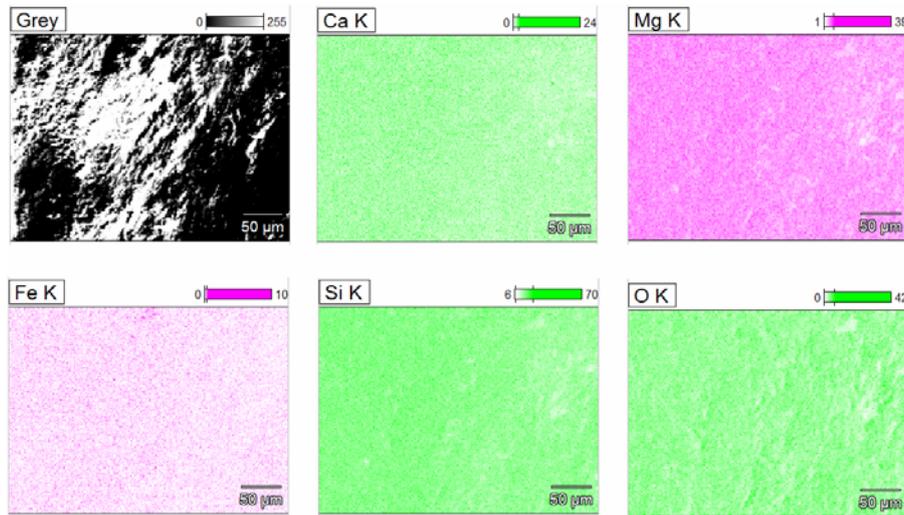
Fig. 3 – Elemental maps for earring with inventory number 12020.

4. RESULTS AND DISCUSSIONS

In Figs. 4 and 5 the spectra for the two earrings (12019 and 12020) are represented, indicating Mg, Si, Ca and Fe as main components. Also the compositional values (Tables 1 and 2) are close to the theoretical values for nephrite. So, with a high degree of certainty we can confirm that the earrings are indeed nephrite.
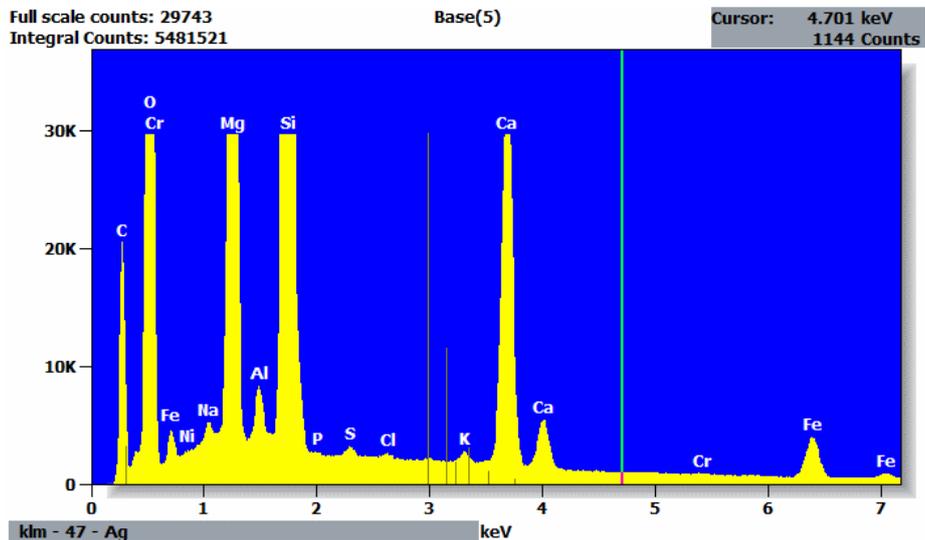

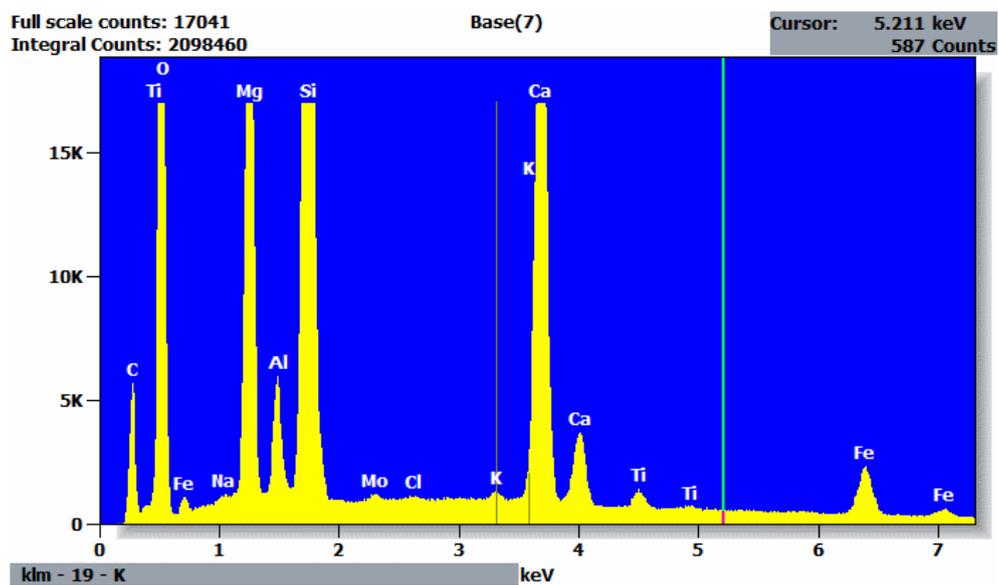Fig. 4 – X-ray spectrum of earring with inventory number 12019.

Fig. 5 – X-ray spectrum of earring with inventory number 12020.

Table 1

Composition of earring with inventory number 12019

Element	Net Counts	Weight (%)	Atom (%)
O	847922	48.04	62.8
Na	22311	0.6	0.54
Mg	795596	12.16	10.46
Al	47568	0.79	0.61
Si	1746567	26.15	19.47
P	6000	0.18	0.12
S	11298	0.24	0.16
Cl	7159	0.16	0.1
K	13556	0.26	0.14
Ca	434459	8.97	4.68
Cr	1341	0.04	0.02
Fe	52747	2.33	0.87
Ni	988	0.05	0.02

Table 2

Composition of earring with inventory number 12020 (Na, K, Mo – under detection limits)

Element	Net Counts	Weight (%)	Atom (%)
O	204836	44.26	46.48
Mg	179861	8.6	7.8
Al	16136	0.81	0.66
Si	557471	24.31	19.09
Ca	292874	17.58	9.67
Ti	6324	0.57	0.26
Fe	29641	3.88	1.53

As concerning the beads we found that only some of them are nephrite, while the rest are malachite ($Cu_2CO_3(OH)_2$). In the nephrite beads we found significant contributions from Ca, Mg, Fe, Si but also other elements from possible surface contamination – *e.g.* Cu.

To verify the capabilities of our SEM-EDS analysis we also investigated a modern nephrite pendant (previously identified by geologists) and two Neolithic jadeite pendants from Cascioarele previously analyzed by spectro-radiometry by Pierre Petrequin [19]. For the modern nephrite pendant (Fig. 6, Table 3) the main components have weight concentrations close to the theoretical ones. For the jadeite pendants (Fig. 7, Table 4 – only pendant with inventory number 8750 is represented) we observed that the values for Mg (0.66%, respectively 1.28%) and Ca (3.67%, respectively 1.21%) decrease considerably while the values for Na (5.54%, respectively 9.43%) and Al (7.37%, respectively 8.30%) increase in order to make them significant, confirming the jadeite. We made these analyses in order to establish a comparison database between previously confirmed nephrite and jadeite items and our SEM-EDS measurements.

The results we have obtained confirmed the initial supposition from visual inspection by geologists that the earrings are nephrite items, the data showing that the chemical elements of nephrite are the dominant ones; even though some other elements are present, their contribution is minor. The other elements are either characteristic to the soil (an area fingerprint) or due to handling contamination.
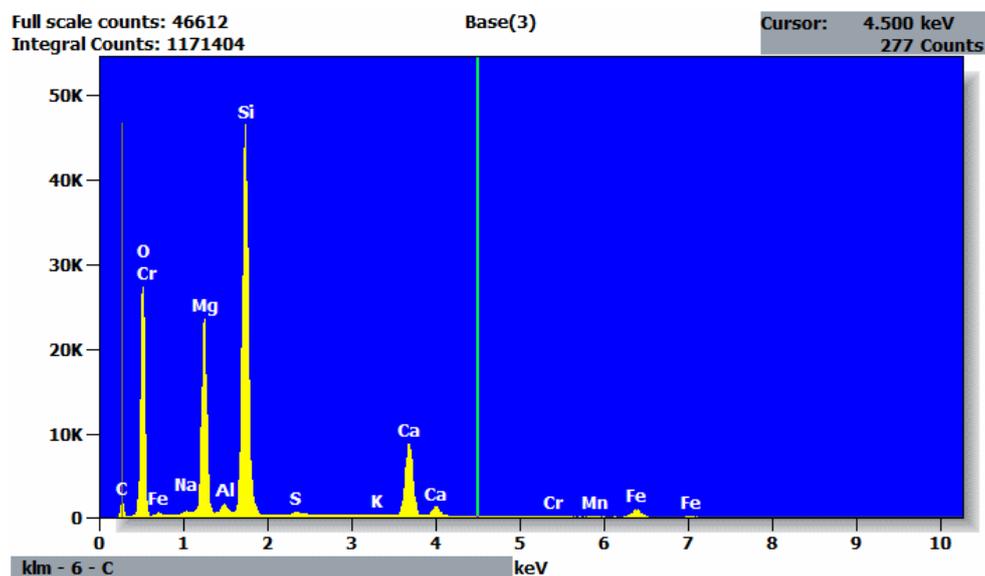
Fig. 6 – X-ray spectrum of modern nephrite pendant.

Table 3

Composition of modern nephrite pendant

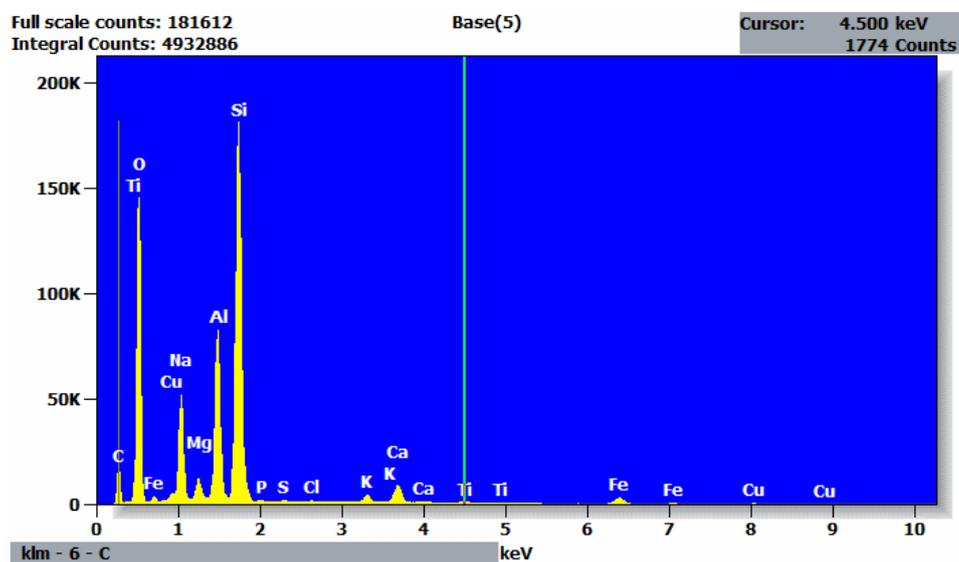| Element	Net Counts	Weight %	Atom %
O	158632	44.66	59.97
Na	1626	0.23	0.22
Mg	169627	12.18	10.76
Al	10582	0.83	0.66
Si	386318	27.43	20.98
S	4026	0.35	0.23
K	1934	0.17	0.1
Ca	107151	10.72	5.75
Cr	1378	0.23	0.09
Mn	641	0.13	0.05
Fe	14271	3.08	1.18

Fig. 7 – X-ray spectrum of Neolithic jadeite pendant inventory number 8750.

Table 4

Composition of Neolithic jadeite pendant 8750

Element	Net Counts	Weight %	Atom %
O	835263	44.32	58.14
Na	334335	10.33	9.43
Mg	79334	1.48	1.28
Al	631158	10.67	8.3
Si	1501015	26.19	19.57
P	12693	0.29	0.2
S	10605	0.21	0.14
Cl	10595	0.22	0.13
K	40126	0.83	0.45
Ca	101159	2.3	1.21
Ti	9153	0.29	0.13
Fe	47723	2.28	0.86
Cu	7507	0.58	0.19

5. CONCLUSION

The goal of our paper was to demonstrate how our SEM-EDS device can be successfully used to characterize gemstones-based archaeological samples, nephrite and jadeite in our case. The main result was the confirmation after SEM-EDS analysis of initial suspicion formulated after visual inspection by geologists that the analyzed adornments are nephrite or jadeite items. However for a complete characterization of archaeological artifacts besides SEM-EDS examination other analytical methods must be added: XRF, (micro) PIXE, ICPMS, depending on the nature of material – metals, glass, ceramics, pigments of paintings.

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