SEM-EDS AS INVESTIGATION TOOL FOR ARCHAEOLOGICAL ARTIFACTS

Paul MEREUTA[1], Bogdan CONSTANTINESCU[1], Daniela STAN[1], Done SERBANESCU[2]

[1] Horia Hulubei National Institute for Physics and Nuclear Engineering, P.O. Box MG-6, Magurele, Romania
[2] Museum of Gumelnitza Civilization, Oltenita, Romania

Introduction

The Scanning Electron Microscope (SEM) uses an electron beam in order to obtain surface images of different samples [1]. The beam is used to scan point by point a predefined area and the point where the electron beam hits is correlated with the signal in the electron detectors and the image is then reconstructed. Another type of analysis used with the SEM is the Energy Dispersive X-ray Spectroscopy (EDS) and this allows us to make studies when elemental analysis is necessary. The EDS system detects the characteristic X-rays due to the electron beam excitation of the atoms that can be found in the sample [1], [4]. In image 1 we have a sketch of a SEM system (left side) with the filament from which electrons are generated and the principle of SEM with the production of backscattered electrons (BSE), secondary electrons (SE) and X-rays.

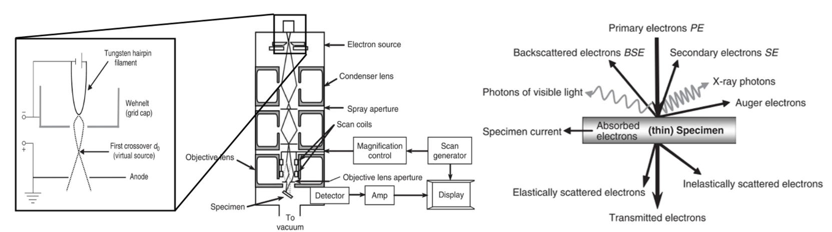


Figure 1. SEM system sketch (left) and SEM principle [1]

The SEM-EDS in our department is produced by Zeiss, the model EVO MA15 coupled with a EDS system provided by Thermo Scientific. Technical characteristics of SEM: an acceleration voltage that can be from 1 to 30 kV having different sample holders that allows us to analyze up to 9 samples at once. The SEM has three detectors : a BSE detector and two SE detectors – one for high vacuum (HV) and one for variable pressure (VP). The EDS detector is a SDD with 129 eV (Mn) resolution used to perform X-ray spectrum of a certain area, a point by point analysis and an elemental maps.

Figure 2. SEM-EDS Zeiss EVO MA15

Methods and Samples

We have analyzed some Neolithic adornments (two earings, three pendants and some beads), the goal being to determine their elemental composition to identify the minerals used by Neolithic people . The artifacts are found in settlements of Boian and Gumelnița cultures (Cascioarele, Sultana - see figure 3) supposed to be from nephrite.

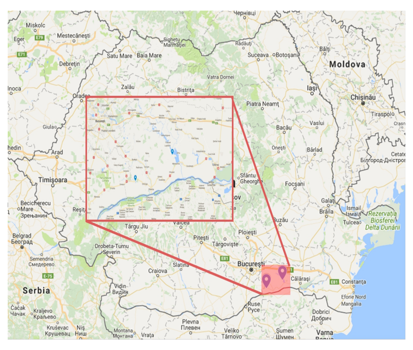


Figure 3. Map of artifacts

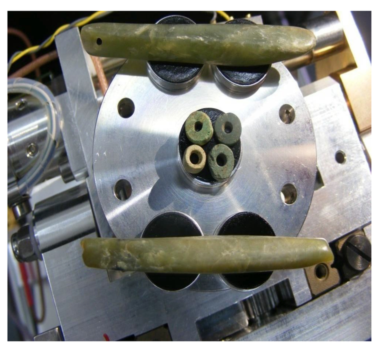


Figure 4. Nephrite artifacts

Another goal was to demonstrate that SEM-EDS can be successfully used used in archaeometrical studies. The SEM-EDS system is very versatile and can give us the necessary information in order to reach conclusions for the archaeological domain, even if sometimes the results must be completed by other methods (XRF, PIXE). The VP method was highly used due to the nature of the samples (non-conducting).

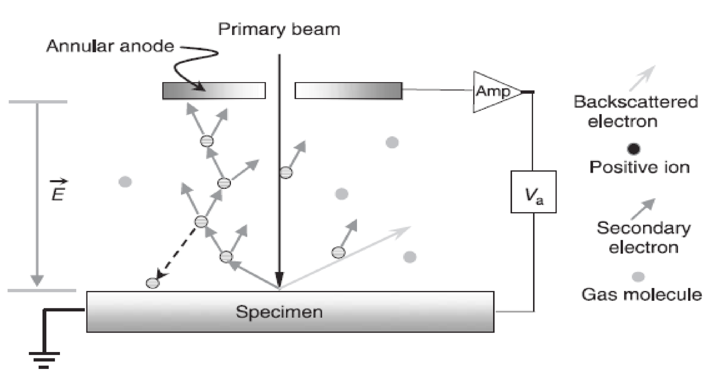
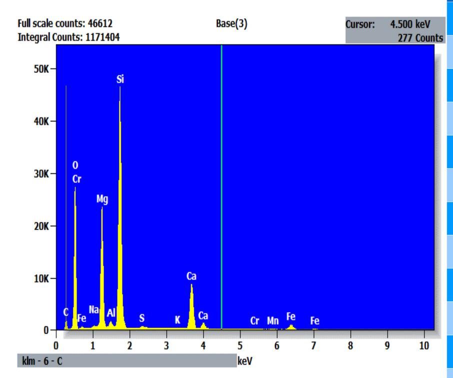


Figure 5. VP method for SEM [1]

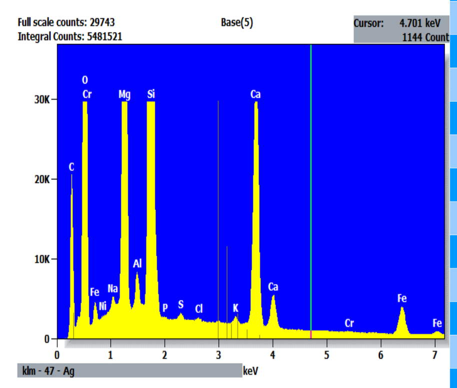
Results

The results obtained using SEM-EDS has offered us the information necessary to conclude that indeed the samples are made out of nephrite (see figure 6, 7, 8), because the elemental composition has shown the main components of nephrite Ca, Mg, Fe, Si and O are dominant in the samples and their weight values are very close to the theoretical values obtained from the formula $Ca_2(Mg,Fe)_5Si_8O_{22}(OH)_2$. We have also compared our spectra and the weight values to those from modern pendants geologically confirmed to be made out of nephrite and jadeite .



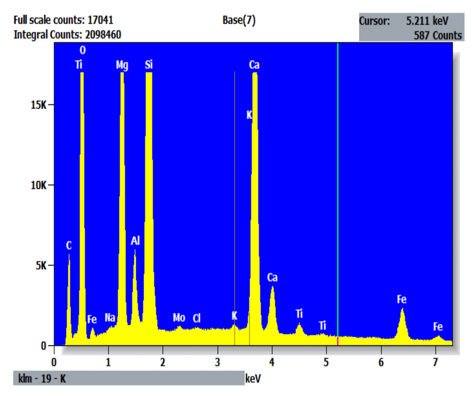
Element	Net Counts	Weight %	Atom %
C	10847	11.05	17.91
O	161012	42.45	51.62
Na	2989	0.36	0.3
Mg	168949	10.3	8.25
Al	10018	0.65	0.47
Si	385518	22.83	15.82
S	3571	0.25	0.15
K	1787	0.13	0.07
Ca	106991	9.03	4.38
Cr	1384	0.19	0.07
Mn	658	0.11	0.04
Fe	14302	2.63	0.92

Figure 6. Spectrum and elemental composition table for nephrite pendant



Element	Net Counts	Weight (%)	Atom (%)
C	127969	20.65	30.43
O	847922	42.94	47.5
Na	22311	0.49	0.37
Mg	795596	8.72	6.35
Al	47568	0.55	0.36
Si	1746567	18.07	11.39
P	6000	0.08	0.05
S	11298	0.13	0.07
Cl	7159	0.09	0.04
K	13556	0.18	0.08
Ca	434459	6.35	2.8
Cr	1341	0.03	0.01
Fe	52747	1.68	0.53
Ni	988	0.04	0.01

Figure 7. Spectrum and elemental composition table for nephrite earing, inventory number 12019



Element	Net Counts	Weight (%)	Atom (%)
C	36670	18.14	28.37
O	204836	39.58	46.48
Mg	179861	6.53	5.05
Al	16136	0.58	0.41
Si	557471	18.23	12.19
Ca	292874	13.49	6.32
Ti	6324	0.43	0.17
Fe	29641	3.02	1.02

Figure 8. Spectrum and elemental composition table for nephrite earing, inventory number 12020

Similarities can very well be observed between the pendant spetrum (figure 6) and the earings spectra (figures 7 and 8).

Element	Net Counts	Weight %	Atom %
C	8736	7.58	12.41
O	262543	48.16	59.24
Na	4034	0.4	0.35
Mg	13541	0.68	0.55
Al	139021	6.43	4.69
Si	566941	26.31	18.44
P	1407	0.09	0.06
S	4788	0.27	0.17
K	14840	0.89	0.45
Ca	78161	5.22	2.56
Fe	12883	1.85	0.65
Cu	3265	0.76	0.24
Ba	9663	1.37	0.2

Element	Net Counts	Weight %	Atom %
C	48453	12.28%	19.26
O	838048	42.73	50.31
Na	337337	8.7	7.13
Mg	80102	1.21	0.94
Al	631673	8.67	6.05
Si	1499267	20.85	13.98
P	9961	0.18	0.11
S	8286	0.13	0.08
Cl	8751	0.14	0.08
K	39063	0.65	0.31
Ca	100138	1.85	0.87
Ti	8879	0.23	0.09
Fe	47610	1.88	0.63
Cu	7525	0.48	0.14

Figure 9. Elemental composition tables for nephrite beads (left) and jadeite pendants (right)

Figure 10. Jadeite pendants samples

Conclusions

For the earrings the data shows that the 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 handling contamination. For the earings comparison with the nephrite pendants shows similar spectra and similar values thus confirming the hypothesis that they are made out of nephrite.

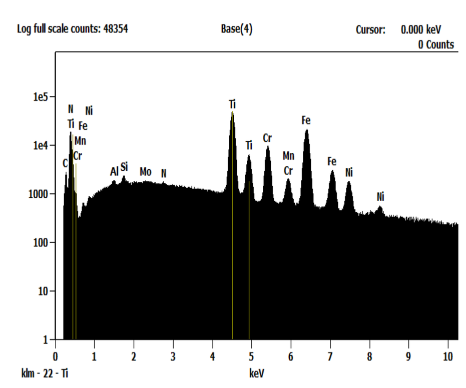
Although the beads have some elements from the other type of jade (jadeite) they are missing an important element: Na. In the comparison with the jadeite pendants (figure 9 right) we can see a significant contribution from Na, that is characteristic for jadeite. But in the beads Na is insignificant (less than 0.5 %) even though other jadeite elements are found (like Al – see figure 9 left). But the elements that are constituents of nephrite are all found with significant values. So the SEM-EDS spectra have shown that even though the beads could have been mistaken as jadeite they are in fact nephrite.

The penetration depth of the electron beam is around 4 μm for jade samples; jade is a homogeneous mineral. These discoveries made using SEM-EDS give rise to questions regarding the nephrite's place of origin: whether it was brought in the Balkan area from known jade deposits (and if so from where) or there was a jade deposit in the Balkan area, now exhausted.

The main goal was to demonstrate we have a device that can be used with great success when analyzing archaeological samples. Through this study of Neolithic adornments (earrings, beads, pendants) we can say we have a powerful tool for studying such archaeological samples. Surely, on some samples we can use just the SEM-EDS, but for other ones other methods must be added: XRF, PIXE, ICPMS.

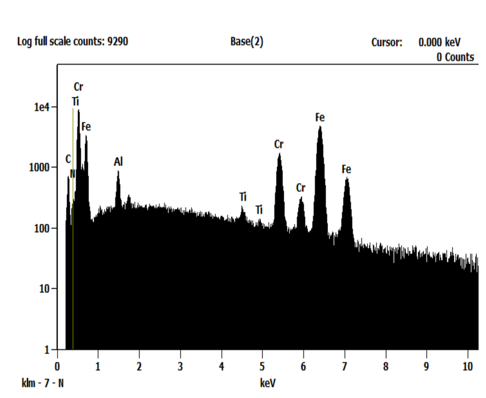
Further information

Other analysis that can emphasize how we can use the SEM-EDS system we performed on a stainless steel sample coated with a thin layer of TiN. This is important as Ti and N are very close on the X-ray spectrum. We analyzed two different in thickness TiN samples. We were able to observe a noticeable difference in TiN between the thick and the thin one.



Element	Net Counts	Weight %	Weight % Error	Atom %	Atom % Error
C	6439	3.98	± 0.13	11.89	± 0.76
N	28016	11.26	± 0.35	28.86	± 1.78
Al	2190	0.20	± 0.01	0.26	± 0.04
Si	4529	0.34	± 0.01	0.43	± 0.03
Ti	361920	37.77	± 0.11	28.32	± 0.16
Cr	73750	9.77	± 0.07	6.75	± 0.10
Mn	3929	0.64	± 0.08	0.42	± 0.10
Fe	182851	32.60	± 0.15	20.96	± 0.19
Ni	14095	3.45	± 0.11	2.11	± 0.13

Figure 11. Thick TiN layer deposited on Ti alloy substrate



Element	Net Counts	Weight %	Weight % Error	Atom %	Atom % Error
C	8867	25.59	± 0.27	55.33	± 1.17
N	1597	6.22	± 0.66	11.53	± 2.44
Al	5035	2.03	± 0.07	1.95	± 0.13
Ti	956	0.39	± 0.07	0.21	± 0.08
Cr	24902	11.21	± 0.13	5.60	± 0.13
Fe	78009	54.55	± 0.33	25.37	± 0.31

Figure 12. Thin TiN layer deposited on steel alloy substrate

References

[1] Principles and Practices of Variable Pressure/Environmental Scanning Electron Microscope (VP-ESEM), Debbie J. Stokes,2008, John Wiley & Sons, Ltd. ISBN: 978-0-470-06540-2;
[2] Energy Dispersive Spectroscopy, 2015 John Wiley & Sons Ltd, T, Microscopy EKB Series Editor: Dr Julian Heath, Spectroscopy and Separations EKB Series Editor: Nick Taylor;
[3] Scanning Electron Microscopy and X-Ray Microanalysis, J. I. Goldstein, 2003 Kluwer Academic/ Plenum Publishers, ISBN: 0-306-47292-9;
[4] Backscattered Scanning Electron Microscopy and Image Analysis of Sediments and Sedimentary Rocks, Krinsley D., 1998 Cambridge: Cambridge University Press. doi:10.1017/CBO9780511628894;
[5] Zeiss EVO series Scanning Electron Microscope Instruction Manual;
[6] Ultra Dry Silicon Drift X-ray Detector Manual;
[7] K. Kanaya, S. Okayama, J. Phys. D., J. Appl. Phys. 1972, 5, 43;
[8] Studiul unor podoabe neolitice din jad folosind microscopul electronic prevazut cu analizor de raze X, Bogdan Constantinescu, Paul Mereuta, Daniela Stan, Done Serbanescu, Institutul de Arheologie "Vasile Parvan", 28 martie 2018;
[9] JADE 2, Objets-signes et interprétations sociales des jades alpins dans l'Europe néolithique, cap. 19. Des Alpes à la Mer Noire (Bulgarie, Roumanie et Ukraine), Pierre Pétrequin, Done Şerbănescu, et al., 2017 – ISBN : 978-2-84867-575-6 – 1468.

Acknowledgments

We gratefully acknowledge funding from the PN 18 09 02 01 *"Cercetari interdisciplinare de fizica nucleara aplicata"* grant program and the PCCDI 52 *"Platformă pluridisciplinară complexă de cercetare integrativă și sistematică a identităților și patrimoniului cultural tangibil și non-tangibil din România (PATCULT#RO)"* PN-III-P1-1.2-PCCDI-2017-0686 grant agreement.