Day 1 (27 May)

14:00-15:30 lectures
Session III -Analytical aspects of obsidian studies

14:00-14:20
Kasztovszky, Zs. - Szilágyi, V. - Maróti, B. - Harsányi, I. - Len, A. - Gméling, K.: Neutron studies in the obsidian research - performed at the Budapest Neutron Centre

14:20-14:40
Donato, P. - Barba, L. - Crocco, M. C. - De Rosa, R. - Donato, S. - Filosa, R. - Lanzafame, G. - Niceforo, G. -Pastrana, A. - Crisci, G. M.: Microtomography of the vesiculated obsidians of Sierra Las Navajas (Hidalgo, Mexico)

14:40-15:00
Mashima, H. - Suto, T.: Linking WD-XRF and ED-XRF for obsidian sourcing: a case study for the Paleolithic Omegura sites at Nagawa town, Nagano prefecture, Japan

15:00-15:20
Stevenson, Ch. M. - Rogers, A. - Ladefoged, T. N.: A Molecular Model for Water Diffusion in Obsidian

15:20-15:30
General discussion on session III

15:50-17:00: Poster session
Session III - Analytical aspects of obsidian studies
Starnini, E. - Panelli, C. - Le Bourdonnec, F.-X. - Lugliè, C.: New results from sourcing the early Neolithic obsidian artefacts from Pollera Cave (Liguria, NW Italy)
Aghamalyan, N. R. - Kafadaryan, Y. A. - Nersisyan, M. N. - Smbatyan, H. A.: Semitransparent obsidian of dark gray color from Artheni deposit (Armenia)
Kohút, M. - Čižmár, E. - Dekan, J. - Drábik, M. - Hrouda, F. - Jesenák, K. - Kliuikov, A. - Miglierini, M. - Mikuš, T. - Milovská, S. - Šauša, O. - Šurka, J. - Bačo, P.: Physical methods of the Carpathian obsidians study
Petřík, J.-Prokeš, L.-Přichystal, A.-Škrdla, P.-Kaminská, Ľ.-Oliva, M.-Svoboda, J.-Nemergut, A.-Burgert, P.-Kuča, M.:Non-destructive ED-XRF provenance analysis of Palaeolithic obsidian artifacts from the Czech Republic and Slovakia

Neutron studies in the obsidian research - performed at the Budapest Neutron Centre

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Session III - Analytical aspects of obsidian studies
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One important task in the archaeometry of obsidian objects is to determine the provenance of the raw materials. For this task, several analytical methods are used to measure the elemental or isotopic composition of the objects. At the Budapest Neutron Centre, already in the early 2000's we have demonstrated that Prompt Gamma Activation Analysis (PGAA) is able to quantify, non-destructively, the major components and some fingerprinting trace elements of the bulk material. When using an external neutron beam, the analysis of large objects is possible without the need for sampling. In the last few years, we were able to utilize PGAA and NAA methods in a complementary mode, to obtain a wider set of analytical data for provenance studies.
Over the years, we have performed successful case studies on archaeological objects with Hungarian, Croatian, Polish and Romanian places of origin. We have demonstrated that PGAA can be used as effectively in provenance research as other widely used methods.
In one study, we used the combination of PGAA, Mössbauer Spectroscopy, Electron Microscopy and Small Angle Neutron Scattering (SANS) to explain the geochemistry of mahogany obsidian. The possibility to apply SANS for provenancing obsidian is currently being further studied.

During our work we have been co-operating with numerous Hungarian and other European Museums, often with national (OTKA) and European (CHARISMA and IPERION-CH) financial support.

Keywords: neutrons, PGAA, NAA, SANS, non-destructive study, provenance

Microtomography of the vesiculated obsidians of Sierra Las Navajas (Hidalgo, Mexico)

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Session III - Analytical aspects of obsidian studies
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Sierra de las Navajas obsidian, highly exploited by the pre-colonial Mesoamerican people, is unique throughout the world for its green color and gold/silver shine. The surface of these obsidian often shows small vesicles. A study of the three-dimensional morphology and distribution of vesicles, performed by high-resolution X-ray micro-CT on the SYRMEP beamline of the Elettra synchrotron light source (Trieste), allowed to calculate a vesicularity in the order of 2 vol.%, and to verify that vesicles are isolated, elongated and iso-oriented.
A higher number of samples was analyzed by X-rays microtomography at the STAR lab of University of Calabria in order to investigate the influence of vesicularity on the macroscopic aspect. All the selected obsidians are green, but they show different hue: some are homogeneously shining, some have no hue at all and a very smooth surface and some others show bands with variable hue and roughness. The 3D reconstruction of vesicles showed that the opaque samples and the bands with no hue of inhomogeneous obsidians are poorly or not vesiculated. The stronger is the hue, the higher is the number of vesicles. Moreover, the vesicles are always elongated and iso-oriented. This accounts for the different aspect shown by different cuts of the same sample: the highest hue is on the surfaces on which the major axes of the vesicles lay, which generally coincides with the surface of natural fracture, while the orthogonal cuts are opaque.
The preliminary results of this study suggest that microvesiculation strongly influences the hue and the fracture of the obsidians, which in turn are among the main factors determining the use of obsidians as weapons, tools or ritual objects. It was observed, for example, that the pre-hispanic blades were produced with obsidian showing no hue (and no vesicularity), because this allows to produce sharper artifacts.
Keywords: X-ray micro-CT, obsidian fracture, vesiculation

Linking WD-XRF and ED-XRF for obsidian sourcing: a case study for the Paleolithic Omegura sites at Nagawa town, Nagano prefecture, Japan

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Session III - Analytical aspects of obsidian studies
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Non-destructive compositional analyses with an energy dispersive X-ray fluorescence spectrometer (ED-XRF) were carried out for 1,069 pieces of obsidian artifacts excavated from the Paleolithic Omegra sites at Nagawa town in Nagano prefecture, Japan. Eight pieces of obsidian slabs, whose compositions were determined using a flux fuse method with wave dispersive X-ray fluorescence spectrometer (WD-XRF), were used as standards for ED-XRF analyses. Analytical results of the standards using ED-XRF showed good correlations with those using WD-XRF for elements heavier than phosphorus (P). Determinations using bulk fundamental parameter (FP) method, however, did not show a good correlation for Mn which is one of the elements used for the sourcing of law materials of obsidian artifacts in Japan, it is because of the overlap between the high energy-side slop of Mn K-α and the low energy side slop of Fe K-α. Instead, determinations using the empirical calibration curve method, which corrects interference from Fe, showed a good correlation for Mn. The Omegra artifacts were compared with law stones on compositional diagrams. Compositional features indicate that the law materials of the Omegra artifacts would have been collected not only from the Omegra area and the Wada-Takayama area at the Omegura side of the dividing mountain, but from the Hoshigato area the other side of the divide. In addition, chemical compositions of a few artifacts indicate that their law materials would have been collected from the northern Yatsugatake area at the south of Omegura, which means that the prehistoric humans might have migrated in the High land area.

Keywords: WD-XRF, ED-XRF, obsidian, sourcing, non-destructive analysis

A molecular model for water diffusion in obsidian

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The obsidian hydration dating of manufactured obsidian tools and debitage converts the amount of surface diffused molecular water into a calendar age using diffusion coefficients derived from experiments conducted at elevated temperature (140–180^{o}C). The procedures for these accelerated hydration experiments are well developed, but an understanding of water diffusion at the molecular level is not well articulated. We propose that the rate of water diffusion in obsidian is controlled by the number of hydroxyls (OH) in the glass structure that are linked to non-bridging oxygen that form in the glass during the molten phase, and then, structurally frozen in during the cooling. The linked hydroxyls create pathways for the diffusion of molecular water. Larger numbers of bound hydroxyls create more diffusion pathways and faster hydration rates. We quantify this relationship by the correlation of hydroxyl concentration with activation energy values.

Keywords: obsidian, hydration rates, non-bridging oxygen, diffusion

New results from sourcing the early Neolithic obsidian artefacts from Pollera Cave (Liguria, NW Italy)

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The results of a new chemical characterization conducted on early Neolithic obsidian artefacts from the excavations campaign 1971-73 at Pollera Cave are presented. We analysed four artefacts from the Impresso-Cardial deposit (layer III, level XXII), already analysed by means of neutron activation (INAA) at the end of the '70s during Lawrence H. Barfield's pioneering obsidian circulation research in northern Italy.
The new investigations have been undertaken with the aim of resolving some inconsistencies found in previous publications (i.e. 3 artefacts, one of which generically attributed to the Impressed Ware Culture, the second from the XXII level and the last from XVII, published in 1979, whilst another article in 1991 reports 4 artefacts, all from level XXII). This contradictory information did not allow us to identify the individual analysed artefacts and to attribute them to their respective sources identified at that time (Lipari and Sardinia). Moreover, the evidence of imports of Lipari obsidian in upper Tyrrhenian area during the early Neolithic does not agree with the data from the neighbouring Arene Candide Cave. Therefore, the four artefacts have been re-analysed in France using non-destructive methodologies: PIXE at CENBG (AIFIRA platform) and EDXRF at IRAMAT-CRP2A.
The new analyses established that all the four obsidian artefacts found in the Early Neolithic Pollera's horizon (all marked as from level XXII) can be actually ascribed to only two different chemical-compositional groups (SB2, SC) of the Sardinian source of Monte Arci. These new results are in better agreement with the data obtained from Arene Candide and offer new ideas for discussing the dynamics of circulation of this volcanic glass in the Tyrrhenian area during the Neolithization process (VI millennium BCE).
The difference with previous results can be explained considering the pioneering stage of the research during the '70s, when only little comparative data were available for the obsidian source identification, thus possibly biasing the attribution. The occurrence of typing mistakes reporting the information can be another explanation for the aporia. However, this research reveals the importance of checking back with more modern and sensitive analytical methods old determinations, especially when they appear in contradiction with new evidence.

Keywords: obsidian sourcing, PIXE, EDXRF, Early Neolithic, Pollera Cave (Liguria, Italy)

Semitransparent obsidian of dark gray color from Artheni deposit (Armenia)

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Session III - Analytical aspects of obsidian studies
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Obsidian is a natural glass produced when volcanic lava rapidly cools through the glass transition temperature and freezes not permitting sufficient time for crystal growth. Armenia has one of the most obsidian-rich natural landscapes in the world and accordingly has considerable reserves of obsidian. Obsidians are natural alumosilicate glasses composed of $M_2O–Al_2O_3–SiO_2$, (M = Na, K, Ca), and contain different elements present in major (>1 wt%), minor (0.1–1.0 wt%) and trace (<0.1 wt%) amounts incorporated into the silicate network during glass formation. They can contain also significant amounts of water (up to 10–12 wt%) both in the form of OH groups and as molecular water, which affect strongly their physical and chemical properties, and as well as the crystalline inclusions (so-called microlites, up to 1–5 wt%) in the glassy matrix. The color of the glass depends upon the presence of various metals together with the circumstances of its formation, but obsidian is typically black or grey and is sometimes banded. Analysis of obsidian samples were carried out by different methods (scanning electron microscopy–energy dispersive spectroscopy (SEM-EDS), XRD analysis, the absorption, reflection and Raman spectroscopy in the UV, visible and IR ranges, as well as thermo-gravimetric analysis (TGA) measurements for characterization of semitransparent obsidian of gray color from Arteni deposits.

Keywords: obsidian, physical and chemical properties

Physical methods of the Carpathian obsidians study

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Recent study of the Carpathian obsidians have been focused on the origin of obsidians by means of Electron Probe Micro-Analysis (EPMA) of glass + minerals, LA ICP MS from glass spots and WR, fission track dating (FT) of glass, K/Ar dating of WR, Ar/Ar dating of glass + biotite, radiogenic isotopes (Sr, Nd, Pb, Hf) and stable isotopes (O, H, Li, B) see Kohút et al. (2019 – this volume). However, important results in geological and archeological study were obtained by means of the μCT, X-ray spectroscopy, Raman spectroscopy, Mössbauer spectroscopy, Positron annihilation lifetime spectroscopy (PALS), DTA (thermogravimetric analysis), Fourier-transform infrared spectroscopy (FTIR), Magnetic susceptibility + thermomagnetic curves, and Electron (spin) paramagnetic resonance (ESR/EPR) methods as well as. The comprehensive research was realized on the Carpathian obsidians samples from the localities Viničky, Cejkov, Brehov and Hraň. Generally, complex study based on their chemical composition does not support an exact discrimination between samples from studied localities, and it is recommended to classify these obsidians by common label "*Carpathian 1*" only. Naturally, there exist some small mutual differences among samples from these localities; indeed these variations are often statistically overlapped. Noteworthy, there exist peculiar physical differences within some hand specimens in the micro-domains due to presence or absence of oriented flow fabric, presence of various microlites, dominance of the Fe-Ti oxides and/or pyroxenes trichites in nanoscale, their specific gravity etc., albeit glass composition of these obsidians is generally comparable. The trichites magnified up to 500x look like continuous linear alignments (5 - 10 μm in diameter) are actually discontinuous, triaxial, hieroglyphic formations, documenting the rapid quenching of the flowing melt in nano dimension. Besides scarce miarolitic cavities representing *macro-voids* (≥2 mm in size) there were observed *meso-voids* (100 ~ 300 μm), *micro-voids* (10 ~ 30 μm) and *nano-voids* (0.2 ~ 1.6 nm) by means of μCT and PALS.
Keywords: Carpathian obsidians, physical methods, micro- & nanoscale, voids & pores

Non-destructive ED-XRF provenance analysis of Palaeolithic obsidian artifacts from the Czech Republic and Slovakia

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Technological characteristics and surely attractive appearance made volcanic glass obsidian rare but prominent raw material of the Stone Age in East-Central Europe. There is only one source area in continental Europe connected with the acid Tertiary volcanism at the border of Western and Eastern Carpathians. The important point is that individual natural sources of obsidian have slightly different chemical composition which enables to determine provenance of the artifacts based on concentrations of certain elements. However, in the Czech Republic obsidian artifacts are rare among Palaeolithic assemblages, thus it is important to apply non-destructive methods. We have used both portable and bench-top ED-XRF devices for non-destructive provenance analysis of obsidian tools. Calibration based on international reference materials and NAA/ICP MS analyzed natural obsidians were employed to make analyses reliable. Artifacts were analyzed together with samples from natural occurrences from Eastern Carpathians. It is possible to distinguish the main sources known as the Carpathian I, Carpathian II and Carpathian III and even some specific locations within them. The most striking result of analyses is that obsidians used as raw materials for Palaeolithic and Mesolithic artifacts were made of both Carpathian I and Carpathian II sources. Preliminary conclusion shows that while the Carpathian II sources were used during the Szeletian and Aurignacian, the Carpathian I sources prevail since the Gravettian.

Keywords: obsidian artefacts, Paleolithic, provenience, ED-XRF