MINERALOGICAL ANALYSIS OF A HISTORICAL STONE ARTIFACT FROM THE BRATISLAVA CITY MUSEUM COLLECTIONS (REG. NO. VE-73)

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Abstrakt: *Mineralogická analýza historického kamenného artefaktu zo zbierok MMB (REG. Č. VE-73).* Historický kamenný artefakt (evidenčné číslo VE-73), zo zbierok Múzea mesta Bratislavy (MMB, Bratislava, Slovensko), bol analyzovaný v spolupráci so Slovenským Národným Múzeom – Prírodovedným múzeom (Bratislava, Slovensko), s cieľom identifikovať horninu a určiť provenienciu materiálu použitého na výrobu tohto predmetu. Zo získaných výsledkov röntgenovej fluorescenčnej spektrometrie a Ramanovej spektroskopie môžeme konštatovať, že študovaný historický objekt je vytvorený zo sedimentárneho organogénneho vápenca so zvýšeným obsahom organického uhlíka. Na základe našich výsledkov nie je možné odhadnúť, či by skúmaný vápenec mohol pochádzať z ložísk v Palestíne. Na identifikáciu pôvodu horniny by bola potrebná komplexnejšia štúdia.

Key words: mineralogy, XRF, Raman spectroscopy, historical stone artifact

Introduction

A historical stone artifact (registration number VE-73), from the collections of the Bratislava City Museum (BCM, Bratislava, Slovakia) was analyzed in collaboration with the Slovak National Museum – Natural History Museum (Bratislava, Slovakia). The artifact is a black stone, shaped like a small prayer book with a spine, measuring 11.8 × 8.2 × 2 cm (**Fig. 1, A/left**). According to museum records, it was acquired in the second half of the 19th century from Ferdinand Stelczner. Both sides of the book's cover feature an engraved inscription of Psalm 122, written in the Arabic script in the „Middle Arabic" language. The general meaning of this Psalm is: *I rejoiced when they said, „Let us go to the house of the Lord." Our feet are standing in your gates, Jerusalem. Jerusalem is built like a city that is closely compacted together. That is where the tribes go up – the tribes of the Lord – to praise the name of the Lord, according to the statute given to Israel. There stand the thrones for judgment, the thrones of the house of David. Pray for the peace of Jerusalem: „May those who love you be secure. May there be peace within your walls and security within your citadels." For the sake of my family and friends, I will say, „Peace be within you." For the sake of the house of the Lord our God, I will seek your prosperity.*

A similar stone artifact is housed in the collection of the Smithsonian National Museum of Natural History (Washington, D.C., USA) (**Fig. 1, B/right**). The museum records indicate that it was acquired in 1885. The donor, Rev. George Whitefield Samson (1819-1896), served as the fifth rector of Columbian College (later renamed George Washington University) and contributed several objects to the museum, likely obtained during his missionary travels. Like the Bratislava artifact, this stone object also bears an engraved inscription of Psalm 122 (de la Vega Nosek 2025).

In this study, we aimed to analyze historical stone artifact housed at BCM, Bratislava, using a mineralogical approach, as well as we tried to assess the rock's geological origin and provenance.

Fig. 1 – A – historical artifact deposited at BCM (11.8 × 8.2 × 2 cm)**; – B –** historical artifact deposited at the Smithsonian National Museum of Natural History [1].
Obr. 1 – A – historický predmet uložený v MMB (11.8 × 8.2 × 2 cm)**; – B –** historický predmet uložený v Smithsonian National Museum of Natural History [1].

Methods

The concentrations of selected elements were measured using an ARL Quant'X EDXRF spectrometer (Thermo Scientific Inc., USA) at the laboratory of the Slovak National Museum – Natural History Museum in (SNM-NHM, Bratislava, Slovakia). Excitation rays were generated by an air-cooled X-ray tube with Rh anode (maximum power: 40 W, anode voltage: 4-50 kV, anode current: 0.02– 1.98 mA). The emitted X-rays were detected using a Peltier-cooled Si (Li) detector (crystal area: 15 mm^2, crystal depth: 3.5 mm, energy resolution: 155 eV at the 5.9 keV Mn Kα line), along with a pulse processor. Instrument calibration was performed using certified reference materials (NSC DC73043, CRM016-50, BCR-176R, and BCR-320R). All measurements were conducted under vacuum conditions.

The relative concentrations of elements at selected spots, necessary for the interpretation of micro-Raman spectra, were measured by using a micro-XRF spectrometer M6 JETSTREAM (Bruker, Germany) at the laboratory of Slovak National Gallery (SNG, Bratislava, Slovakia). The instrument's measuring head features a 30 W Rh-target microfocus X-ray tube with a maximum voltage of 50 kV and a maximum current of 0.6 mA. The beam is shaped by a polycapillary optic, allowing for variable beam sizes, with a minimum of approximately 40 μm, depending on the distance between the object and the measuring head.

Raman spectra were acquired using a Thermo Scientific DXR3xi Raman imaging microscope at the SNM-NHM. Excitation laser wavelengths of 780 nm and 532 nm were utilized, with a 50 x objective, a 25 μm confocal pinhole, and an EMCCD detector. Spectra were collected at laser power ranging from 0.1 to 15 mW, with acquisition times between 0.2 and 30 s (30 scans per cycle). Spectral processing, including fitting with Voigt functions, was performed using the Thermo Fisher Scientific OMNIC v. 9.11 software package.

Photographic documentation was carried out using a Leica DVM6 digital microscope, deposited at SNM-NHM, Bratislava, and Keyence VHX-7000 digital microscope, deposited at SNG, Bratislava.

Results

Chemical composition

The chemical compositions of two selected areas of the studied artifact are presented (**Tab. 1**). The primary components of the sedimentary rock are carbonates, as indicated by the elevated CaO content, which ranges from 22.25 wt.% to 56,68 wt.%. The lower CaO concentration corresponds to the „black" zones, likely due to an increased organic carbon content. Sulfur concentrations are also significant, reaching up to 9.96 wt.% as SO_3. High sulfur levels in organogenic limestones can result from various factors related to depositional environments, diagenetic processes, and microbial activity associated with organic matter.

The primary sources of sulfur in oceanic sediments include organic matter, pyrite (FeS_2), and sulfate minerals (Goldhaber 2003). The orange pigment observed on the surface of the artifact item (**Fig. 2, right**) is rich in Pb, while the red inclusions are characterized by elevated concentrations of Fe and Zn (**Fig. 3**).

	wt. % (A)	wt. % (B)
Na_2O	1.07	0.53
MgO	0.55	0.28
Al_2O3	1.82	0.83
SiO2	5.22	2.25
P_2O5	3.14	1.37
SO3	9.96	4.24
Cl	0.23	0.12
K_2O	0.41	0.18
CaO	56.68	22.25
TiO2	0.09	0.02
Cr_2O3	0.06	0.02
Fe_2O3	0.74	0.23
CuO	0.03	0.01
ZnO	0.05	0.02
SrO	0.28	0.09

Table 1: Chemical composition of two different areas of the studied artifact.
Tab. 1: Chemické zloženie dvoch rôznych miest študovaného predmetu.

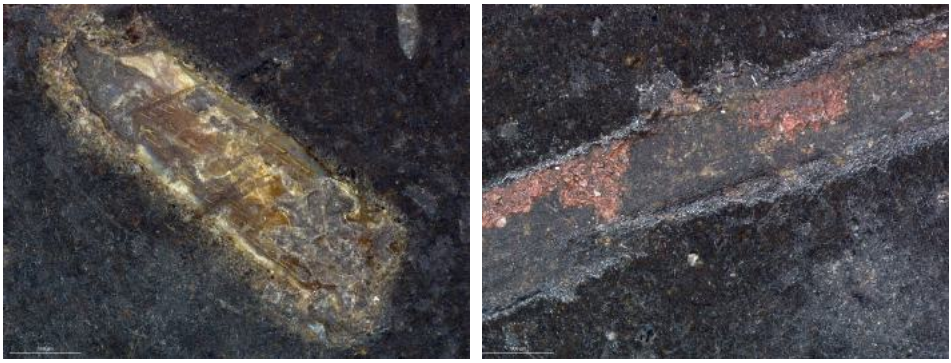

Fig. 2: Belemnite specimen – common component of the limestone studied (left), orange pigment on the surface of the studied item, identified as minium (right).
Obr. 2: Belemnit – často prítomný organizmus v skúmanom vápenci (vľavo), oranžový pigment identifikovaný ako mínium, na povrchu študovaného predmetu (vpravo).

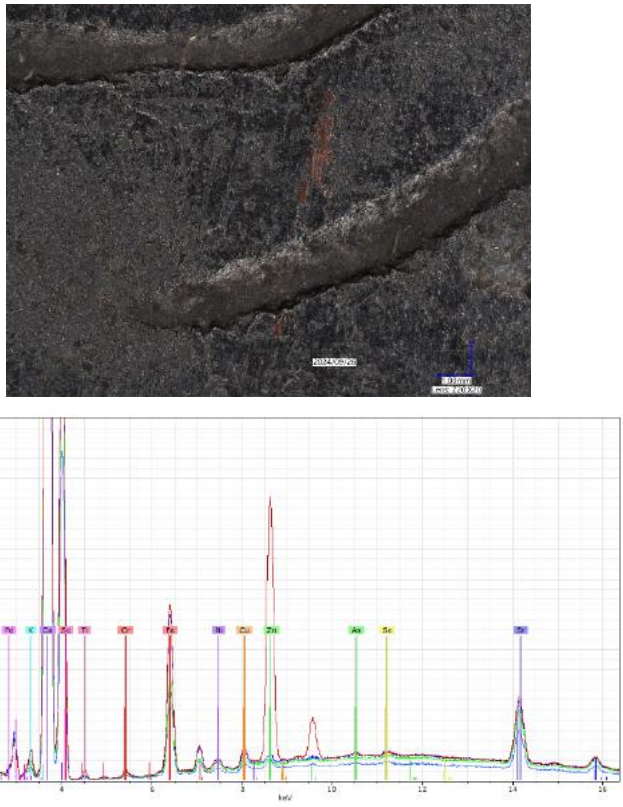

Fig. 3: Red inclusion in studied limestone (above) and its relative chemical composition (below).
Obr. 3: Červená inklúzia v skúmanom vápenci (hore) a jeho relatívne chemické zloženie (dole).

Mineralogical composition

The mineralogical composition aligns well with the chemical data. Optical microscopy and Raman spectroscopy identified calcite [$CaCO_3$] as the primary mineral (**Fig. 4**). Very small secondary gypsum crystals (2-5 μm) were detected exclusively through optical methods. Raman spectroscopy confirmed that the Pb-rich orange pigment present on the stone book is minium [Pb_3O_4] (**Fig. 5**), with Raman band positions matching those reported by Marucci et al. (2018). The red inclusions contain abundant Fe oxides.

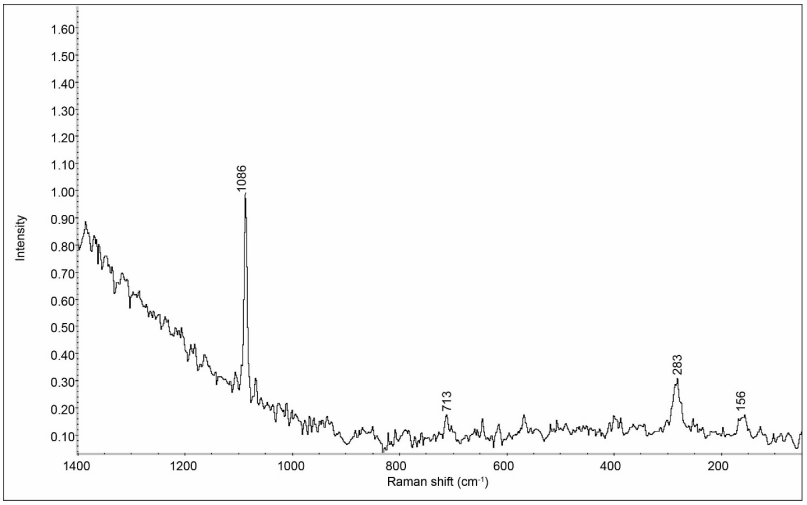

Fig. 4: Raman spectrum of calcite (532 nm).
Obr. 4: Ramanovo spektrum kalcitu (532 nm).

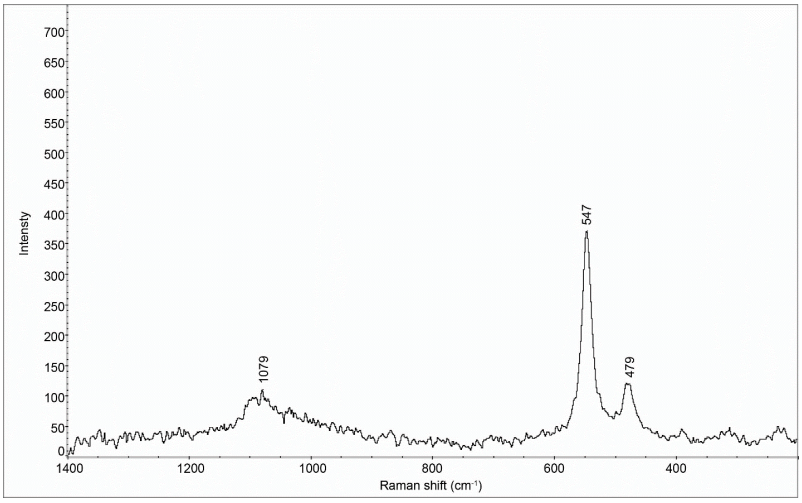

Fig. 5: Raman spectrum of minium (532 nm).
Obr. 5: Ramanovo spektrum mínia (532 nm).

Discussion

Material analysis of the investigated stone book artifact indicates it is a sedimentary organogenic limestone with an elevated carbon content, classifying it as bituminous limestone. Bituminous limestones typically contain minerals such as calcite, quartz, and dolomite, as well as aragonite derived from crushed seashells (Connan et al. 2024). They also have a high organic matter content (e.g. steranes and terpanes) (Connan et al. 2022). Due to its sedimentary nature, this type of rock can contain skeletal fragments of marine organisms such as corals, foraminifera, and mollusks (Salem 2021). The studied rock is primarily composed of calcite, confirming its limestone classification. Additionally, its chemical composition and the presence of fossils – such as belemnite (**Fig. 2, left**) – support its organogenic and marine origin. The dark coloration of the limestone, along with optical microscopy observations, further suggest presence of organic carbon. Additionally, minium, a lead-based pigment identified on the surface of the rock, is a material historically used in artworks (Aze et al. 2008).

A similar artifact – a stone book housed at the Smithsonian National Museum of Natural History – was also identified as bituminous limestone [1]. The chemical and mineralogical composition of our studied item aligns with that of the Smithsonian artifact. The latter's origin has been attributed to Palestine (de la Vega Nosek 2025), where bituminous limestone deposits are found in regions such as Nabi Musa, the Yarmouk Valley, Bethlehem, and Wadi al-Quneitra. At Nabi Musa, near Jericho, a well known deposit of black bituminous limestone – often referred to as „Moses stone" or „Dead Sea stone" – occurs. This rock weathers to a light grey but appears brown in less bituminous varieties and jet black in highly bituminous layers. Below these bituminous limestone beds, a brown limestone layer composed mainly of fish remains and foraminifera is present [2]. However, whether the limestone studied in this research originates from these Palestinian deposits remains uncertain.

Conclusions

Material analysis of the examined artifact concluded that it is a sedimentary organogenic limestone with an elevated organic carbon content, classifying it bituminous limestone. The observed chemical and mineralogical composition closely aligns with that of the Smithsonian item. Limestone is primarily composed of calcite, and a presence of fossils supports its organogenic/marine origin. The dark coloration of the limestone, along with optical microscopy findings, indicate the presence of carbonaceous material. Based on mineralogical and geochemical results, we conclude that the studied object is composed of sedimentary organogenic limestone with a high carbon content. However, it is not possible to determine whether the limestone originates from Palestinian deposits. A more comprehensive study would be required to accurately identify the geological source and establish the provenance of the artifact.

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Acknowledgements

This work was supported by the project APVV-21-0212.

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