

## Vrednotenje modelirnih mas za restavriranje Peračiškega tufa

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Na področju konserviranja in restavriranja spomenikov iz naravnega kamna težimo k uporabi materialov, ki naj bi bili čim bolj kompatibilni z originalnim materialom. Na Gorenjskem se je v preteklosti kot gradbeni material veliko uporabljal andezitni tuf. Njegova uporaba sega že v čas Rimljanov, kar dokazujejo najdbe v arheološkem najdišču Mošnje. Tuf so predvsem uporabljali za gradnjo stopnic, vogalnih stebrov na objektih, okenskih okvirjev in portalov. Večina različkov tufa ni dovolj odporna na dejavnike okolja, zato močno propadajo. Na mestih, kjer so izdelki močno poškodovani, jih je potrebno utrditi, nadomestiti z ustrežno modelirno maso ali svežo kamnino. Namen raziskave je bil razviti recepturo ustrežne kompatibilne modelirne mase, ki bi imela lastnosti čim bolj podobne dvema različkoma tufa. Najprej so bile določene lastnosti dveh litotipov tufa iz okolice Peračice, drobnozrnatega ter debelozrnatega tufa iz Bogatajevega kamnoloma in kamnoloma Črnivec. Petrografska analiza je bila izvedena z metodo optične mikroskopije. Fizikalne in mehanske lastnosti so bile določene s plinsko sorpcijo, absorpcijo vode zaradi kapilarnega dviga, vpijanem vode pri atmosferskem tlaku, tlačno trdnostjo, odprto poroznostjo ter odpornostjo na kristalizacijo soli. Da bi razvili ustrežno modelirno maso, smo pripravili mešanice drobljenega tufa ter kremenca z različno zrnastostjo in masnimi razmerji. Za vezivo smo uporabili etil silikat. Izmed mešanic smo izbrali šest vizualno najustrežnejših za nadaljnje preiskave. Na teh vzorcih so bile izvedene preiskave fizikalno-mehanskih lastnosti, torej sama absorpcija vode zaradi kapilarnega dviga, vpijanje vode pri atmosferskem tlaku, tlačna trdnost, odprta poroznost ter odpornost na kristalizacijo soli. Preliminarni rezultati so pokazali, da je z ustrežno kombinacijo kremenca, tufa in etil silikata možno izdelati kompatibilne nadomestne modelirne mase, ki imajo primerljive lastnosti kot primarna različka tufa, tako v vizualnem pogledu kot v fizikalno-mehanskih lastnostih. Seveda bo potrebno skozi restavratorske posege te materiale evaluirati tudi na mestu vgradnje samem, tako s stališča vgradljivost kot njihove dolgoročne obstojnosti.

## Moonmilk stalactites: mainly water, some microfibrillar calcite – what holds them together?

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Moonmilk is a generic term for soft, fragile, microcrystalline aggregate speleothems with high porosity and variable, generally

carbonate mineralogy. Hydrated moonmilk has a distinctive pasty and plastic texture with water content typically ranging from 40 to 85%, whereas dry moonmilk is characterized by powdery and crumbly texture. The most common and abundant moonmilk deposits are composed of calcite (>90% of their solid part) and occur in several morphological varieties of speleothems: isolated patches or extensive veils (mm to dm thick) coating the cave walls, ceilings and floors; flowstones; stalactites; and subaqueous spherical aggregates in cave ponds ("cottonballs"). Calcite moonmilk microfabric normally consists of microcrystalline aggregates of needle fiber calcite (NFC) and calcite nanofibers. The origin of moonmilk is controversial since the fibrous calcite morphologies have been attributed to either (microbial) biomineralization or purely physicochemical processes.

We present a distinctive type of calcite moonmilk, forming large, cylindrical and club-shaped stalactites of soft consistency. They have been studied in two caves in Slovenia, both known for their moonmilk speleothems: Brezno za hramom Cave (Mt. Hrušica, ~10 km NW of Postojna; altitude 650 m a.s.l.), and Snežna jama Cave (Mt. Raduha in the Kamnik-Savinja Alps; cave altitude between 1500 and 1600 m a.s.l.). Water temperature, pH, and conductivity were measured in situ from drips collected under the stalactites. Moonmilk deposits were sampled with small box cores, in-situ fixed with glutaraldehyde, dehydrated using different techniques, and examined with SEM and XRD. In selected unprocessed samples, the water content was determined by weighting fresh and dehydrated material.

The stalactites hang from the walls and ceilings coated with moonmilk veils, generally aligned along joints and at isolated point sources of seepage water. They are cylindrical, bell-shaped, club-shaped or bulbous, yet all the shapes are characterized by a flat (cut-off) base. The stalactites are up to 1 m long and up to 0.5 m in diameter. They are white or brownish due to clay impurities. XRD analysis shows that they are composed of almost pure low-Mg calcite. Mineral fabric of the stalactite moonmilk, observed under SEM, consists of irregular, sponge-like 3-dimensional mesh of monocrystalline NFC (0.5-2 µm wide and up to 500 µm long), polycrystalline NFC, flexible calcite nanofibers (50-100 nm wide), tubular structures (2-10 µm in diameter), and mineralized microbes. The studied stalactites were all entirely waterlogged, containing 80-94% of water.

In general, two textural types of moonmilk can be distinguished in the stalactites. NFC-dominated moonmilk appears as aggregates of microfibrils with no preferred orientation. NFC crystals are mostly uncemented or only weakly cemented by interwoven rhombohedral overgrowths or intertwined nanofibers, apparently giving very limited structural support for the stalactite growth. The second type consists of patches, built almost entirely of interlaced calcite nanofibers, exhibiting dense structure and a high potential of water retention. Similarly, this second type provides no stable structural basis since nanofibers tend to collapse instantly upon dehydration. However, films of mucilaginous substances remaining after simple air-drying of samples indicate relatively large amounts of organic material, presumably extracellular polymeric substances secreted by microorganisms in moonmilk.

Many studies have shown positive association between calcite moonmilk deposits and the presence of microbes. Apart from microbial involvement in the nucleation of crystal growth and

biologically induced mineralization, microbially produced organic substances can act as cohesive and adhesive agents in soft, structurally metastable speleothems such as moonmilk

## Preliminarne raziskave izvora naravnega kamna iz arheološkega najdišča Mošnje

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Arheološko najdišče Mošnje leži na savski terasi med naseljema Mošnje in Globoko. Odkrito je bilo ob nadzoru gradbenih del na trasi takrat bodočega avtocestnega odseka Vrba–Peračica. Najdišče predstavlja rimsko podeželsko vilo, ki jo je sestavljalo pet zidanih objektov v celoto povezanih z opornim zidom, potisnjenim v ježo zgornje terase. Pri zidavi vile so za nekatere elemente (stopnice, zid, pragovi, ognjišča) uporabili različne kamnine. Iz naravnega kamna so tudi številne druge najdbe kot so sončna ura, možnarji, žrmlje in mozaične kocke.

Glavni namen raziskave je določiti vrsto in različke naravnega kamna uporabljenega v Mošnjah ter ugotoviti njihovo izvorno lokacijo. Arheološke artefakte smo makroskopsko pregledali in sistematsko razdelili v osnovne skupine kamnin. Kjer je bilo potrebno in možno smo izdelali tudi zbruske, posneli rentgenske difraktogramе in vzorce pregledali pod SEM/EDS.

Na arheološkem najdišču se kot gradbena surovina najpogosteje pojavlja naravni kamen, ki so ga uporabljali kot osnovni gradbeni material za izdelavo vogalov zidov, tlakov in ognjišč. Manjši predmeti so bili izdelani iz kremenovega peščenjaka in keratofirja (žrmlje), delno tudi iz kremenovega konglomerata.

Provenienco kamnin, ki so služile kot naravni kamen za zidavo vile in izdelavo različnih predmetov, smo skušali ugotoviti s primerjavo arheološkega materiala s kamninami iz opušenih in delujočih kamnolomov v oddaljenosti približno 20 km od najdišča. Poiskali smo lokacije kamnolomov na tem območju ter odvzeli vzorce kamnin za primerjalno analizo. Pregledali smo tudi prodišča Save v bližnji okolici, ki jih bomo še natančno opisali (velikost blokov, litološka raznolikost). Glede na možnost enostavnega transporta kamnitega materiala od prodišča, obstaja verjetnost, da je del sedimentnega materiala prinesen z najbližjih savskih teras.

Največji delujoči kamnolom na tem območju je v bližini Kamne Gorice v vzhodnem pobočju Jelovice, s starim poimenovanjem »Fajfa«. V njegovem spodnjem delu pridobivajo triasne keratofirje kot tehnični kamen za obrabne plasti cestnišč (slednji so močno sekundarno spremenjeni) ter triasne apnenice in dolomite, ki ležijo v naravnem kontaktu nad keratofirji.

Oligocenske piroklastite (tufe), so in se delno še vedno, pridobivajo v Bogatajevem, Pernuševem in Klinarjevem kamnolo-

mu. Bogatajev kamnolom je največji in v njem so pred kratkim potekale raziskave za ugotovitev količine zaloga in ekonomske upravičenosti ponovnega odprtja. V njem smo našli sledove pridobivanja kamninskih blokov s klesanjem (tool marks). Ostali kamnolomi so manjši in namenjeni predvsem lokalni uporabi.

Z mineraloškim in petrološkim analizami bomo skušali potrditi lokalni izvor keratofirja, tufov in sedimentnih kamnin. Pridobljeni podatki bodo pripomogli k boljšemu razumevanju pridobivanja in uporabe gradbenega materiala v rimskem obdobju na slovenskih tleh, predvsem pa pri razreševanju vprašanja, ali so za gradnjo zadostovala ležišča kamnin v okolici objekta oz. so bile surovine mogoče uvožene (pripeljane iz bolj oddaljenih nahajališč). Podatki bodo pripomogli tudi pri vzpostavitvi baze o uporabi različnih kamnin ter njihovem izvoru na slovenskih tleh glede na različna arheološka obdobja ter geografsko lego.

## Mercury emissions due to tectonic activity and its accompanying phenomena

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Physical-chemical properties and transformation ability of mercury and its compounds under natural conditions are responsible that this element is present at various concentrations in all environmental compartments in the world. At room temperature elemental mercury is volatile and can therefore be subjected to long range transport and it is also considered as a global pollutant, particularly when its emissions are related to human activities. Beside anthropogenic it can be also of natural origin. Natural sources are evaporation from land and waters, forest fires, ores that are enriched by Hg, tectonic, seismic and volcanic activity. The portion of naturally emitted mercury into the global atmosphere is relatively high in comparison to anthropogenic emissions. It is estimated that natural emissions are between 2.000 and 5.220 tones per year. Naturally enriched areas with Hg are mostly connected to tectonic plate margins and can be divided into three Hg enriched planetary belts: Pacific, Mediterranean and Asian. Mediterranean region has several Hg deposits, among them there are also three biggest word mercury mines including former mercury mine in Idrija. Tectonic activity with its accompanying phenomena and geologic sources can importantly contribute to local and global Hg emissions and influence its cycle in the environment. Technologically enhanced mercury emissions in areas with elevated natural mercury represent specific problems as the levels of mercury frequently exceed legally accepted limits.

Degassing thru active faults zone are consequence of complex radiogenetic, thermal and geodynamic processes in Earth crust. Due to increased stone permeability and porosity, active tectonic faults act as drainage from Earth crust thru which gasses (CO<sub>2</sub>, CH<sub>4</sub>, H<sub>2</sub>S, H<sub>2</sub>, NH<sub>4</sub>, Rn, He, Ne, Ar in Hg) and underground water are trickled thru surface. Tectonic tensions influence water and gasses pore pressure and with that on migration processes towards the surface. Most important emitted gas from bed rock is CO<sub>2</sub> accompanied with other gasses such as N<sub>2</sub>, CH<sub>4</sub> and H<sub>2</sub>, that