

PROCESS OF TUFA PRECIPITATION IN KARST AREA AND GEOCHRONOLOGY OF THE PLITVICE LAKES

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CONTENT:

What is tufa

- Process of tufa formation:
 - a) Physico-chemical conditions
 - b) Biological role of tufa growth
- Case study Plitvice Lakes, Croatia

Dating of tufa deposits - palaeoclimatic conditions



The initial tufa accumulation are extremely porous on a micro- and macro-scale and, with time , the porosity is occluded and the sediment lithified. Tufa is terestrial microbial carbonates that form under open-air conditions from ambient temperature waters in areas of carbonate bed-rock (karst)

The water flows over and percolates through active barriers.



Process of tufa precipitation/formation Geochemical cycle of carbon in the karst environment



The actively growing barriers are situated at the downstream end of each lake.

The role of plants in the precipitation of tufa:

1) Biota remove CO₂ which increases the level of saturation of the water by carbonates.

- 2) Act as a convenient substrate for precipitation.
- 3) Trap and bind calcite seed crystals within their EPS (extracellural polymeric secretions.



Biological role of tufa growth

SEM photograph of the initial phase of agglomeration of calcite crystals deposits on moss thaluses.

SEM photograph of diatom aggregations on moss thaluses. Epiphytic diatoms settling upon fresh moss surface are attached to the moss by muceous strands. Scale bar is 10 μ m.

SEM photograph of diatoms and calcite crystals, glued on the surface of mosses. Pennate diatoms and filamentous cyanobacteria form a dense and sticky mat on the moss, which retains micritic calcite particles in this mat due to a "glue-on" effect of mucus. Scale bar is 30 µm.









Sl. (Fig.) 3

Tufa barriers in the Plitvice Lakes area. Active barriers are very often coverd by vegetation, porous and soft structure.

Active barriers form dams, behind which the lakes are situated.



Passive tufa deposits from Holocene ¹⁴C age: 15200 ± 130 yr B.P. Hard, compact, partly poros

Old/fosil tufa deposits





<u>Plitvice Lakes National Park</u> - protected area

Situated in the Dinaric Karst region very sensitive to any pollution in global and local level

Plitvice Lakes consist of a series of 16 lakes of different size interconnected by waterfalls. The lakes are characterized by intense calcium carbonate precipitation from the water forming tufa barriers and fine-grained lake sediments.



Total distance from springs to Korana River ~ 12 km

Water sampling

Sampling:

- > 3 main springs
- > 5 lakes
- > 3 tributaries
- Korana River, outflow from Plitvice Lakes

Total distance of ~12 km



Bijela Rijeka Spring
 Crna Rijeka Spring
 Plitvice Spring
 Matica Stream
 Prošće Lake
 Gradinsko Lake
 Burgetići Lake
 Kozjak Lake 1
 Kozjak Lake 2
 Novakovića Brod Lake
 Korana River
 Sušanj Stream
 Rječica Stream
 Sartuk Stream



<u>Water analyses</u>:

- Physico-chemical conditions for calcite precipitation (tufa, lake sediment) in waters of Plitvice lakes Measured parameters: T, pH, conductivity, oxygen, alkalinity, Ca²⁺, Mg²⁺
- Possible contamination of water and its influence to the process of tufa precipitation Measured parameters: NH4⁺, NO3⁻, NO2⁻, HPO4²⁻, DOC (dissolved organic carbon)



Temperature in downstream direction

pH in downstream direction





Saturation index of $CaCO_3$ (calculated)



Process of tufa precipitation is very sensitive to any pollution in global and local level.

Possible sources of pollution:

- Anthropogenic waste water, numerous turists, local population
- Global contamination climate change, pollution by air or precipitation
- Influence of the environmental change to the processes in the water

How to control the pollution:

- Water analyses - to control the present conditions in the water

- Sediment analyses - to follow the changes in the environment from the past to present

Concentration values of the nutrients (amonium and nitrates) in the water of Plitvice Lakes - downstream







4 Conslusions for conditions of tufa precipitation

- ✤ The water of Plitvice Lakes where the process of tufa precipitation (CaCO₃) is very intensive is supersaturated with CaCO₃ (I_{sat} values are 4 10). Significant changes between springs, lakes and tributories as well as in the downstream flow of I_{sat} and other factors responsible for tufa precipitation (T, pH, alkalinity), are obvious.
- The water analyses show that the waters of Plitvice Lakes are clear and oligotrophic with no sign of any significant anthropogenic pollution. The concentration of dissolved nutrient salts in the water is very low at most of the sampling points. It has been observed that some contribution of nutrient salts to the lakes had been made by percolating waters from the woods' area.
- Concentration of DOC is higher in the lake waters with a significant eutrophication process (1 - 2 mg/L) then in the non-eutrophicated water (0.3-0.5 mg/L). The process of tufa precipitation can be inhibited by higher concentration of DOC. No systematic difference in concentration of nutrients between "clear" and eutrophicated waters has been observed.

Dating of tufa deposits - palaeoclimatic conditions

Two methods were used for dating of tufa deposite:
1) Radiocarbon dating (¹⁴C) - up to 40 000 yr BP
2) Uranium- thorium dating (²³⁰Th /²³⁴U) - up to 450 000 yr BP

Dating of tufa

Locations of tufa retrieving

1) Recent tufa barriers between lakes Radiocarbon dating method

2) Old tufa:
A - Smolčića pećina
B - Gradina
C - Plitvički Ljeskovac
U-Th dating



Results of ¹⁴C dating of tufa and lake sediments



¹⁴C age of speleothems and tufa in the Dinaric Karst



¹⁴C ages of lake sediments (Prošće Lake) and peat (Plitvički Ljeskovac)

Histogram U-Th ages of speleothems and tufa from the Dinaric Karst area, comparison with palaeoclimatic $\delta^{18}O$ stages



#Conclusions

¹⁴C and ²³⁰Th/²³⁴U dating of tufa in the Dinaric karst showed that tufa growth is restricted to the warm periods of global climate and was interrupted during glacial, stadial and interstadial periods.

Examples/sites of tufa deposits





Plitvice Lakes, Croatia

Plitvice Lakes



Tufa cascade, Una River, Bosnia and Herzegovina



Una River





Tufa cascade, Piva River, Jajce, Bosnia and Herzegovina



Tufa cascade, Sakizcilar, Denizli province, Turkey

AN ANY





LSC, Quantulus 1220 for ¹⁴C dating

Vacuum line for benzene synthesis for LSC measurement



Vacuum line for graphite synthesis for AMS measurement

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AMS for ¹⁴C dating

