FLOWSTONE DEPOSITION IN THE SLOVENIAN CAVES

ODLAGANJE SIGE V SLOVENSKIH JAMAH

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Kogovšek, Janja: Flowstone Deposition in the slovenian Caves

In the underground the flowstones of various colours and forms are frequently met. The question arises how quickly they grow, how intensively they are deposited from the percolated water and what is their age. The flowstone deposits out of infiltrated water, carbonate solution respectively with various alloys and by diverse intensity. Our flowstone studies in the slovenian caves have shown that from one liter of percolated water on about 10 m long distance up to 180 mg $CaCO_3$ could be deposited. The rate of deposition mostly depends on the input hardness of over-saturated water and on the conditions in the cave. But the quantity of deposited flowstone is mostly dependent on the quantity of the percolated water. Thus small trickles in Postojnska jama deposit in one year 0.5 kg of flowstone, while the quantity is at least ten times bigger at the abundant trickles in Škocjanske jame, according to our estimation.

Key words: Slovenia, flowstone deposition, cave mineral

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Kogovšek, Janja: Odlaganje sige v slovenskih jamah

Siga se iz prenikle vode, oz. raztopine karbonatov in številnih primesi, izloča različno intenzivno. Naše raziskave sig v slovenskih jamah so pokazale, da se iz enega litra prenikle vode na do 10 m dolgi poti izloči do 180 mg$CaCO_3$. Ta stopnja izločanja pa zavisi predvsem od izhodne trdote prenasičene prenikle vode in pogojev v jamskem prostoru. Vendar pa količina odložene sige zavisi predvsem od količine pretekle vode. Tako se pri kapljanjih v Postojnski jami odloži v enem letu do 0.5 kg sige, pri izdatnih curkih v Škocjanskih jamah pa po naši oceni vsaj 10 krat več.

Ključne besede: Slovenija, odlaganje sige, jamski mineral

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INTRODUCTION

Deposited flowstone contains besides the main component $CaCO_3$ various alloys which either originate in the percolated water or these particles are transported and cemented in the flowstone during the deposition of dissolved matters. Primary röntgen micro-analysis, the method with electronic micro-sound has shown rather big heterogeneity of flowstones in the distance of some ten micrometers already. Emmission spectrography and flame atomic absorption spectometry have shown that the flowstones contain Al, Fe, Mg, Na, and also Pb, Mn, Ni, Cr, Zn and Cu. Intensive gray and orange coloured flowstones contain considerably more iron and aluminium (up to 0.650 mg Fe g^{-1} and up to 1.300 mg Al g^{-1}) as the others white, or slightly coloured flowstones.

The intensity of the flowstone growth in Postojnska jama was observed by GAMS (1968a) during one year from 1963 to 1964. He stated that from one liter of percolated water up to 102 mg $CaCO_3$ were deposited. In one year there was on the observed sites from 0.3 to 2 kg of flowstone deposited. Gravimetric definition of the deposited flowstone on the glass stripes hanging off the ceiling has given considerably lower values.

OUR MEASUREMENTS OF FLOWSTONE DEPOSITION

Our observation of the flowstone deposition were based on long lasting frequent measurements of percolated water hardness before deposition and later after defined way of deposition. Parallelly we measured the discharge. The deposition was followed in Pisani rov of Postojnska jama, in Škocjanske jame in Paradiž and in Velika dvorana, in Taborska jama and in Planinska jama.

In Pisani rov (KOGOVŠEK, 1982) we measured the deposition from small trickles up to 100 ml min^{-1} with relatively small oscillations and on the distance of deposition up to 2.7 m. From one liter of percolated water up to 90 mg $CaCO_3$ were deposited. During smaller discharges the carbonates were deposited in higher degree than during bigger ones, but the quantity of deposited flowstone mostly depends on the quantity of the percolated water. The flowstone deposition was more abundant in autumn and in winter during small discharges than in other part of the year which shows irregular flowstone growth over one year already.

Trickle 1 in Planinska jama is more abundant. Its discharge oscillates from 30 ml min^{-1} to over 100 l min^{-1} and it reacts extremely quickly to the rainwater. The deposition was followed on 10 m long way (KOGOVŠEK & HABIČ, 1981). At the discharge of about 100 ml min^{-1} from one liter up to 55 mg $CaCO_3$ were deposited. At the discharges of more 1 min^{-1} no deposition was registered. Minimal deposition effect obviously covers the effect of dilution.

In Škocjanske jame (KOGOVŠEK, 1984) from the trickles in Paradiž out of 1 l of water up to 60 mg $CaCO_3$ were deposited, in one year there was 0.6 kg of flowstone deposited. Similar was stated for the trickles in Pisani rov of Postojnska jama. The trickle in the Big Chamber where the discharge considerably oscillates (to 5 l min^{-1}) as well as the hardnesses from 1 l of water on 10 m long distance on the stalagmite Orjak from 37 to 170 mg of dripstone were deposited which means 23 to 65 % of all the carbonates in the percolated water. It is interesting that here the highest hardnesses and the highest degree of dripstone deposition occur during bigger discharges with the exception of extremely high discharges only. Thus both decisive influences coincide which means the maximal possible deposition which is higher than in already mentioned cases in Planinska jama and Postojnska jama. The negative effect is presented by unstability of the trickle only as during summer drought it could be dry for 4 months even. Unfortunately the discharge measurements during the whole year were not frequent enough to make the calculation of annual quantity of the deposited dripstone. Bigger amount of dripstone deposition thus occur in Hankejev kanal where the trickles never dry up.

Dripstone deposition was monitored in Taborska jama, Dolenjska too (KOGOVŠEK, 1990). During lower discharges, up to 200 ml min^{-1} the trickle in Zadnja dvorana deposited after 6 m long trickling down 90 to 180 mg $CaCO_3$ from one liter of percolated water. During maximal discharges only up to 25 mg $CaCO_3$ l^{-1} were deposited. The measurement results are gathered in Table 1.

Table 1

Cave observation site	distance of trickling down	min.-max. deposition flowstone	annual quantity of deposited water	annual quantity of deposited flowstone
	m	mg $CaCO_3$/l	m^3	g
Post.j.-Pisani rov				
23	2.7	8 - 110	14	550
24	1.8	8 - 88	8.6	200
25	0.5	15 - 75	2.4	4
29	1.8	20 - 80	2.7	100
Planinska j.				
curek I	10	0 - 55	2000	-
Škocjanske jame				
Paradiž	1.0	15 - 60	16	600
Vel.dvorana	10	37 - 170	-	-
Taborska j.				
Zadnja dvorana	6	25 - 180	-	-

THE COMPOSITION OF THE DEPOSITED FLOWSTONE

In the underground caves the flowstone in form of calcite, which is the most stable crystal form of $CaCO_3$ and rarely less stable aragonite, are usually met. During the deposition of the calcium carbonate from percolated water which is the solution of several other alloys they are deposited as well, depending on conditions. Small solid particles transported by the water could occur in the dripstone as well. The evaporation in most of the caves does not contribute to the flowstone formation as the cave air is usually saturated by humidity. It plays more important role in dry caves only. The flowstone deposited in such a way is less pure as all the dissolved particles are admixed.

The coposition of various flowstone samples of Postojna cave was presented by GAMS (1968b) where he inferred that the flowstone is composed from 99.14 to 100 % of $CaCO_3$.

We've chosen visually different flowstones and we analysed them regarding the carbonate contents gravimetrically by weighing the adsorbed CO_2 after decompositon by acid and manometrically by measurement of CO_2 pressure after acidic decomposition, by measurement of ignition loss and by differential thermic analysis. Calcium and magnesium were titrimetrically defined. Qualitative emmission spectrographic analysis (semi-quantitative method according to Krooner-Valder) has shown which metals are present in our samples. Quantitative presence of them was defined by flame atomic absorption spectometry (KOGOVŠEK, 1981).

Unhomogeneties in dripstone, being the result of its slow and irregular growth, changing of percolated water and conditions respectively, are frequently discernible by eye. These unhomogenities were researched in detail by primary röntgen microanalysis - the method with electronic microsound. The line and point analyses in cross section of speleothems were done and distribution of elements defined: Ni, Fe, Zn, K, Ca, Na, Al, Ti and Mn.

Analysed samples of flowstone mostly contained CaO and CO_2, MgO most of them below 0.3%. The exception is flowstone below the trickle 1 in Planinska jama with 0,8% MgO contents which is deposited from the percolated water with Ca/Mg=3. The solubility of $MgCO_3$ is bigger than that of $CaCO_3$ this is why Mg appears in flowstone in considerably lesser degree as well all the others more soluble components.

Qualitative emmission spectographic analysis of samples has shown the presence of Fe, Al, Mg, Pb, Cr, Sn, Ni, Na, and Cu which were later quantitatively defined by atomic absorption spectrometry. We analysed ground, homogenised samples and particular particles which were directly dissolved. The differences in the results reflect unhomogeneous structure of dripstone. The samples contained low concentrations (up to 2 ug g^{-1}) of Cu, Zn, Mn, Cr and Ni; Pb up to 40 ug g^{-1}, a little more Na (up to 180 ug g^{-1}) and the most they differ regarding the contents of Fe and Al. In sequence from light, white flowstone up to slightly coloured or intensively orange flowstones have augmented the contents of iron and aluminium too. Intensively gray and orange flowstone contained up to 600 ug g^{-1} of Fe and up to 1400 ug g^{-1} of Al.

All these chemical analyses have given the average flowstne composition, it means of the taken part of the flowstone. But as the flowstones are extremely unhomogeneous we have analysed some samples by primary röntgen microanalysis, by point and line analyses. Point analyses gives us quick information on present elements on the surface of 1 um^2 and the line analyses gives the composition of chosen line which is being researched. Such detailed analysis is very suitable for flowstone materials study as it gives the possibility to analyse thin layers and various inclusions in flowstone samples.

Line analysis in radial direction after cross-section of solid speleothem with light brown-ray concentric layers has shown that Ca is present in high concentrations accompanied by Fe with local enrichments which correspond to slight decrease of Ca contents. Point analyses have shown higher contents of Si and S.

Similar result was obtained by the stalagmite with almost white, solid interior with visible crystallonomic planes which differs by sight from the above mentioned speleothem. The sample contained more K and Fe, local enrichments of Fe are extremely expressed. By point analyses of the external layers of the speleothem we have defined Ca mostly, while in nucleus bigger concentrations of Si and Al were present and slightly smaller ones of K and Fe.

CONCLUSION

Recent flowstone deposition in the slovenian karst caves is rather intensive. The quantity of deposited flowstone depends mostly on the quantity of percolated water and, obviously on initial concentration of dissolved carbonates, cave atmosphere and the length of the way. In Taborska jama and in Škocjanske jame the way of deposition was such that maximal deposition was possible and from one liter of percolated water up to 180 mg $CaCO_3$ were deposited. In Postojnska jama and Planinska jama the way was shorter and up to 90 mg $CaCO_3$ l^{-1} were deposited, 0.5 kg of flowstone during one year period respectively. The oscillations of the flowstone deposition during the year were stated.

Chemical analyses give us average composition of taken sample. Intensively coloured flowstones contained more iron and aluminium mostly. Primary röntgen microanalysis enables the analyses on such short distances and is suitable for flowstone analyses as it is deposited slowly over a long period and because of various reasons the composition of percolated water changes. For younger flowstone, deposited in a recent past, the events in nature and the conditions are rather well known and this is why this method enables their mutual dependence.

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ODLAGANJE SIGE V SLOVENSKIH JAMAH

Povzetek

Recentno odlaganje sige v slovenskih kraških jamah je dokaj intenzivno. Količina odložene sige je odvisna predvsem od količine pretekle vode, seveda pa tudi od izhodne koncentracije raztopljenih karbonatov, jamske atmosfere in dolžine poti. V Taborski jami in Škocjanskih jamah je bila pot izločanja tolikšna, da je možno tudi maksimalno izločanje in se iz 1 litra prenikle vode izloča do 180 mg $CaCO_3$. V Postojnski in Planinski jami se je na krajši poti izločalo do 90 mg $CaCO_3$, oziroma se je iz kapljanj v enem letu odložilo do 0.5 kg sige. Ugotovili smo tudi nihanje izločanja sige preko leta.

Izločena siga poleg glavne komponente $CaCO_3$ vsebuje še številne primesi, ki se izločijo iz prenikajoče vode, ali pa jih ta prinese kot drobne delce in se zacementirajo v sigo ob izločanju raztopljenih snovi. Primarna rentgenska mikroanaliza, metoda z elektronsko mikrosondo, je pokazala na veliko heterogenost sig že na razdalji nekaj deset mikrometrov. Emisijska spektrografija in plamenska atomska absorbcijska spektrometrija sta pokazali, da sige vsebujejo še Al, Fe, Mg, Na, pa tudi Pb, Mn, Ni, Cr, Zn in Cu. Intenzivno siva in oranžna siga vsebujeta opazno več železa in aluminija (do 0.650 mg Fe g^{-1} in do 1.300 mg Al g^{-1}) kot ostale bele, oz. lahno obarvane sige.

Kemijske analize podajajo povprečno sestavo vzetega vzorca. Intenzivneje obarvane sige so vsebovale predvsem več železa in aluminija. Primarna rentgenska mikroanaliza omogoča analizo na tako majhnih razdaljah, da je primerna za analizo sige, ki se izloča počasi v daljših obdobjih, ko se je zaradi različnih vzrokov spreminjala sestava prenikajoče vode. Za mlajšo sigo, ki se je izločila v bližnji preteklosti, za katero so nam pogoji in dogajanja v naravi dokaj dobro poznani, bi nam ta metoda omogočila spoznati njuno medsebojno odvisnost.