ESR DATING OF POSTOJNA CAVE STALACTITE

(WITH 5 FIGURES)

DATIRANJE STALAKTITA IZ POSTOJNSKE JAME Z ESR METODO

(S 5 SLIKAMI)

MOTOJI IKEYA*
TOSHIKATSU MIKI**
RADO GOSPODARIČ***

* Technical College, Yamaguchi University, Ube, Japan.
** Physikalisches Institut der Universität Stuttgart, BRD.
*** Inštitut za raziskovanje krasa ZRC SAZU, Postojna, YU.

SPREJETO NA SEJI
RAZREDA ZA NARAVOSLOVNE VEDE
SLOVENSKE AKADEMIJE ZNANOSTI IN UMETNOSTI
DNE 25. NOVEMBRA 1982

CONTENT — VSEBINA

Abstract UDC 551.442.4.001.5(497.12—14)

Ikeya Motoji, Toshikatsu Miki, Rado Gospodarič: ESR Dating of Postojna Cave Stalactite.

Acta carsologica, 11 (1982), 117—130, Ljubljana, 1983, Lit. 9.

The growth rate (3—4 mm/100 years) and the age (about 190.000 years) of the initial stalactite layers by the ESR method is estimated. Some physico-chemical dating problems of the achieved results from Postojna Cave compared with those from Akyoshi Cave in Japan are discussed. The geochronological commentary ranged the stalactite growth beginning at the end of Mindel — Riss Interglacial, the upper seven sinter layers belonging to the Riss Glacial, Riss-Wüum Interglacial and Würm Glacial. The high flood, expressed by the loam among some sinter layers had interrupted the stalactite growth in the Riss Glacial.

Izvleček UDK 551.442.4.001.5(497.12—14)

Ikeya Motoji, Toshikatsu Miki, Rado Gospodarič: Datiranje stalaktita iz Postojnske jame z ESR metodo.

Acta carsologica, 11 (1982), 117—130, Ljubljana, 1983, lit. 9.

Z ESR metodo je ugotovljena stopnja rasti (3—4 mm/100 let) in starost (okrog 190.000 let) sige v notranji plasti stalaktita. Fizikalno-kemični problemi datiranja pri dobljenih rezultatih iz Postojnske jame so primerjani s podobnimi problemi v japonski jami Akyoshi. Geokronološka razlaga uvršča začetno rast stalaktita v konec mindel-riškega interglaciala, sedem nadaljnjih plasti stalaktita pa v riški glacial, riss-würmski interglacial in würmski glacial. Med dvema plastema sige ohranjena poplavna ilovica odraža visoko poplavo v riškem glacialu.

INTRODUCTION

Electron spin resonance (ESR) is a method of analysis in physics and chemistry utilizing the microwave absorption under the magnetic field. It can detect the unpaired electron with a magnetic moment. Natural radiation of α, β and γ rays, from the radionuclides (such as uranium and thorium) and their decay products, produces radiation damage in rocks, minerals and archaeological materials (J. M. Aitken, 1974; S. Feming, 1976). Radiation damage have been utilized to measure the radiation dose.

Thermoluminiscence is a well known technique, which can be used like ESR to measure the concentration of defects. The thermoluminiscent dosimetry (TLD) of $CaSO_4$ (Tm) is generally used to monitor the radiation exposure of personel at nuclear reactor facilities. It is also used as a method of dating pottery and ceramics in archaeology.

We introduced ESR dating similar to TL dating of cave deposits. We used the presence of radicals with unpaired electrons in stalactites, stalagmites and cave pearls (M. Ikeya, 1975) as well as in bones and tooth animal (M. Ikeya, 1978) excavated by anthropologists. One can estimate the total exposed dose of material due to natural radiation from its content of radicals by standarized the observed enhancement of radicals content using artifical irradiation (M. Ikeya, 1975). The total dose of natural radiation, sometimes called the archaeological dose (AD) can be used to estimate the age of the material if the annual radiation dose is known. Thus, a method of dating using radiation damage produced by natural radiation has been established. Details of ESR dating have been published elsewhere (M. Ikeya, 1975, 1978).

This report covers ESR dating of a Postojna Cave stalactites and its natural radiation dose measured with the TLD of $CaSO_4$ (TM). Throughout this paper we denote the radiation dose with the unit of Rad, i.e. the unit of absorbed radiation energy, 100 erg. per gram of material.

EXPERIMENTAL PROCEDURES

The ESR spectrum of the stalactite was measured with a 100 kHz field modulation and 4 gauss amplitude at room temperature before and after γ-ray irradiation. The thermoluminiscence glow curve of the stalactite was also measured at the rate of the temperature increase of about 1,5 °C/min after the powder carbonate had been washed with acetic acid to remove defects created by the milling and grinding procedure. Details of the ESR and TL dating have been described in earlier works (M. Ikeya, 1978; T. Miki, M. Ikeya, 1978).

γ-ray irradiation was made using ^{60}Co al the source at Katherin Hospital in Stuttgart, Nagoya University and Reactor Institute of Kyoto University.

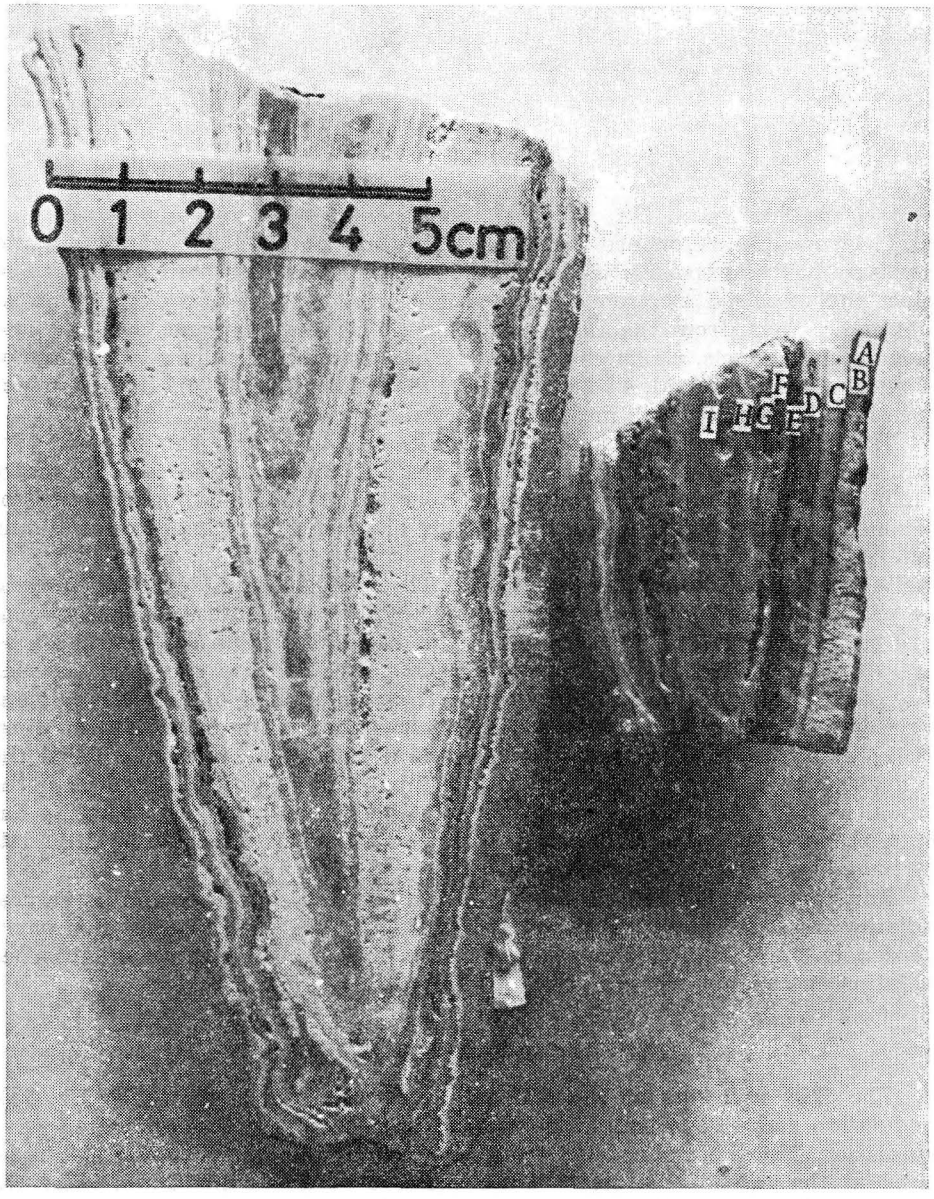

Fig. 1. Photo of Postojna Cave stalactite and its cross section. The pattern of the dark loam sediment between white sinter layers indicate the growth conditions. The longitudinal growth has recently almost stopped

Sl. 1. Prerezan stalaktit iz Postojnske jame. Vzorec temnejšega ilovnatega sedimenta med sigovimi plastmi nakazuje razmere med rastjo. Vzdolžna rast se je danes skoraj ustavila

The total natural radiation dose received by the stalactite was obtained by assuming a linear relation between the concentration of defects and the radiation dose. No further studies like the radioactive elements determination have been performed for the Postojna Cave stalactites.

RESULTS AND DISCUSSION

Fig. 1 is a photo of the Postojna Cave stalactite obtained during the author's visit in 1977. The cross section shows the brown sediment which indicate that the stalactite took some impurities during its growth in the past. We suggest (M. Ikeya, 1978) that the main brown sediment were formed about the same time as the high water levels. The shape of the brown sediment clearly indicates that the growth direction was shifted presumably because of tilting ob the cave floor or because of the relative shift of the ceiling from where the water is supplied. The longitudinal growth seemed to have essentially stopped for the large stalactite (I) while the small ones were still

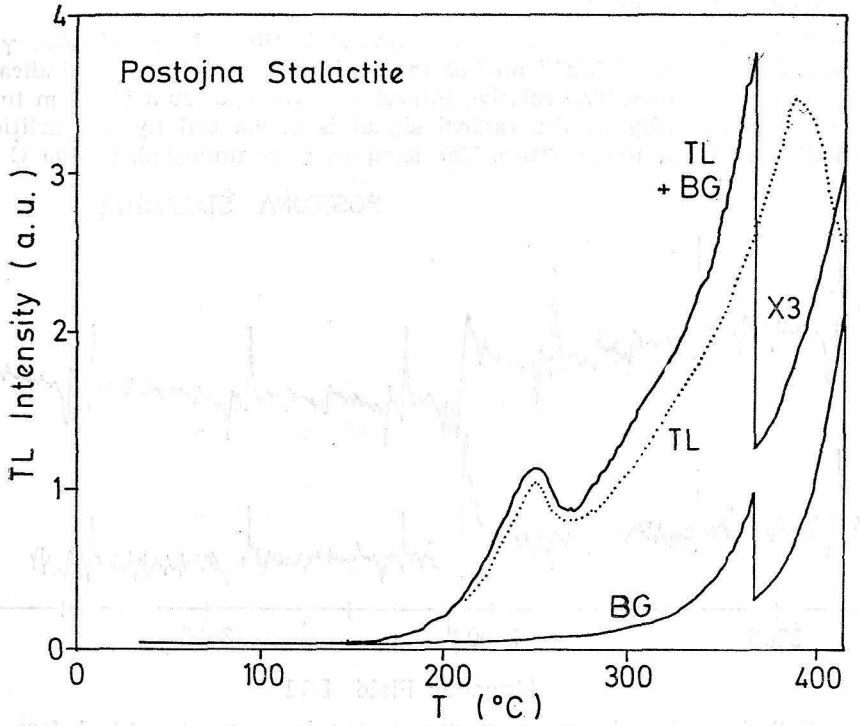

Fig. 2. Thermolumniscence (TL) curve of Postojna Cave stalactite. The TL peaks at 510 and 620 K was observed. The background termal glow due to the heating is also shown

Sl. 2. Termoluminiscenčna krivulja (TL) stalaktita iz Postojnske jame. Opazne so TL konice pri 510 K in 620 K. Razvidno je tudi ozadno termalno žarenje zaradi segrevanja

growing. The growth might come from the splashing of dropping water since the radial growth in one specific direction is dominant.

Thermoluminiscence

Fig. 2 shows the TL glow curve of the Postojna stalactite. The TL peaks at 510 and 620 K have been observed for Petralona stalagmites. The peak height at 510 K is enchanced by an artificial γ-irradiation. The peak at 320 K was formed by γ-irradiation but is unstable. One can determine the AD with TL as has been done for Akiyoshi stalactite (T. Miki, M. Ikeya, 1978). However, precautions must be taken to reduce the tribothermoluminiscence due to the grinding. Samples must be mixed well to obtain the AD with the TL method, since the locally high concentrations of impurities cause a fluctation in the data. We had not studied the Postojna stalactite further with TL because of the complicated procedure for sample preparation but tried to date it with ESR.

Electron spin resonance

Fig. 3 shows ESR spectra of the Postojna stalactite before and after γ-irradiation. The spectra of Mn^{++} and of the radical were detected as indicated by the lines and arrows. The relative intensity of the spectrum is taken to be arbitrary. The intensity of the radical signal is enchanced by the artificial γ-irradiation at room temperature. The samples were annealed, at 100 °C for

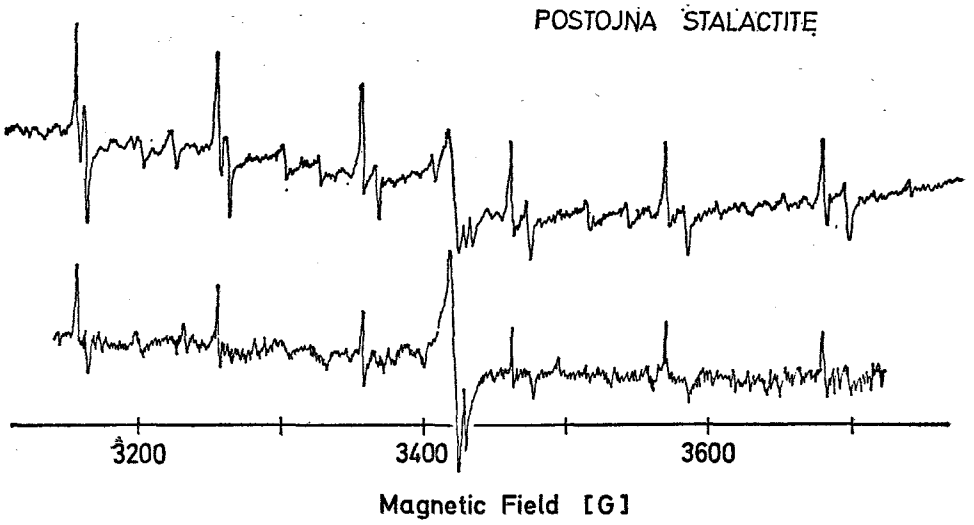

Fig. 3. ESR derivative absorption spectra of Postojna Cave stalactite before and after the artificial γ-irradiation from ^{60}Co. The radical signal at the central position is enhanced by the irradiation. The other signals are associated with Mn^{++} and Ca^{++} sites in the carbonate

Sl. 3. ESR absorbcijski spektri stalaktita iz Postojnske jame pred in po umetnem γ obsevanju s ^{60}Co. Osnovni signal na osrednjem mestu je povečan zaradi obsevanja. Ostali signali se nanašajo na gnezda Mn^{++} in Ca^{++} v karbonatu

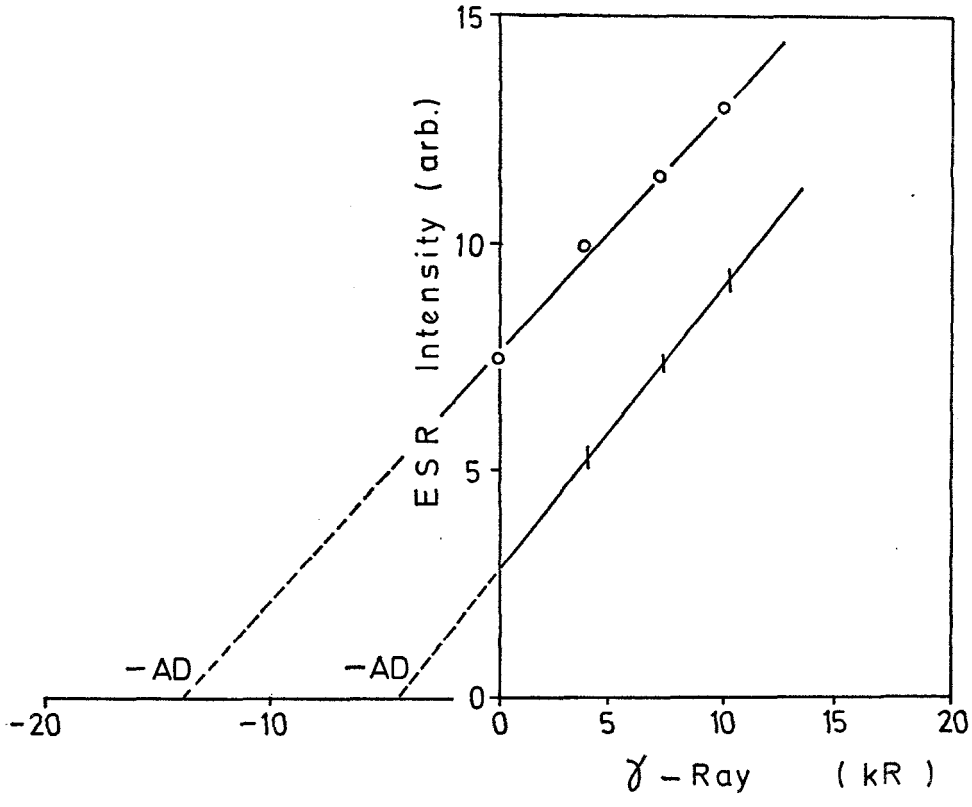

Fig. 4. The enchancement of radical signal intensity as a function of the radiation dose of γ-rays from ^{60}Co. The archaeological dose (AD) has been obtained by extrapolating the linear growth

Sl. 4. Povečanje intenzivnosti osnovnega signala kot funkcija obsevalne doze γ-žarčenja ^{60}Co. Arheološko dozo smo dobili z ekstrapoliranjem linearne rasti

10 minutes, to remove the unstable radical soon after γ-irradiation. The typical enchancement of the signal intensity by the γ-irradiation is shown in Fig. 3. The linear extrapolation of the signal intensity versus dose gives the AD.

Fig. 4 shows the obtained AD as a function of the position from the surface. The AD at the surface of the stalactite is somewhat larger than the AD at the position close to the surface. Naturally AD increased in the old inside position until close to the central position. The maximum AD, obtained for this stalactite was (38±3) kRad. Neglecting the surface data point which sometimes gives a large AD for unknown reasons, one can roughly obtain the growth velocity of (2.2±0.2) μm/Rad for the old inside of the stalactite.

The AD obtained for the other stalactites ranges in the some order of magnitude. In this case, the porous stalactite sometimes gives small AD, presumably because of recrystalization.

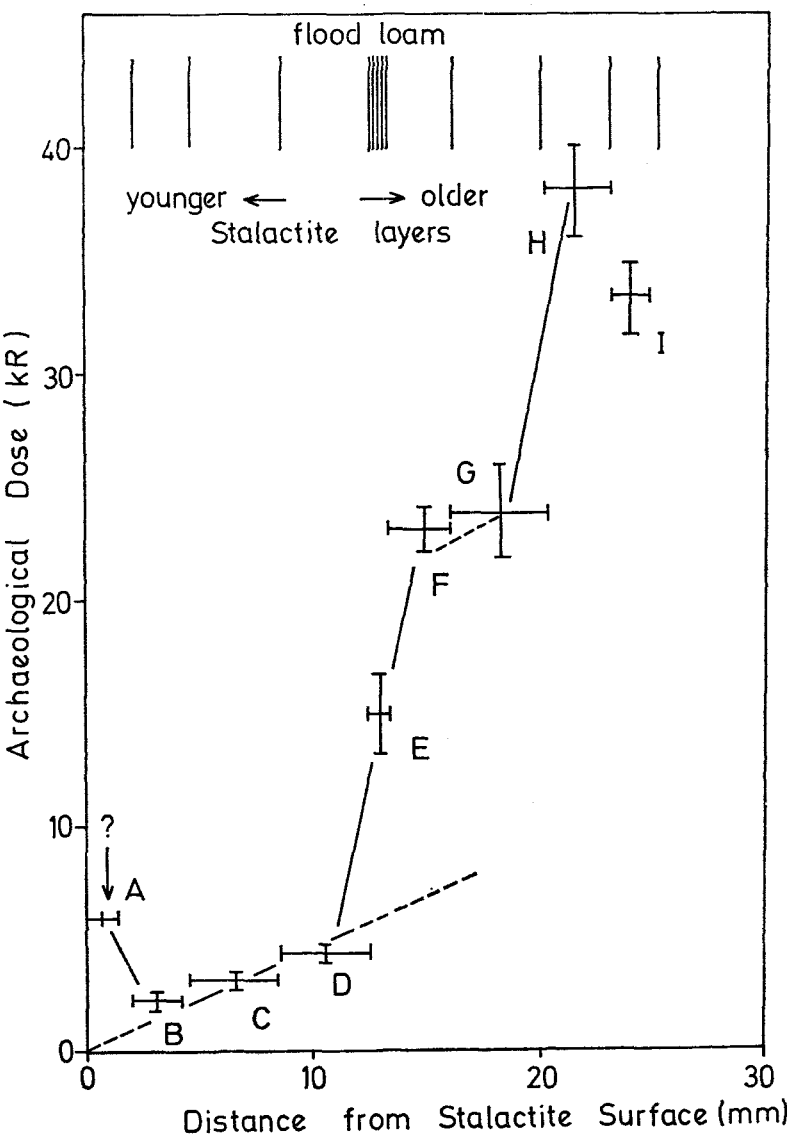

Fig. 5. The archaeological dose (AD) in kRad of Postojna Cave stalactite as a function of a distance from the surface. The reason for the large AD at the surface is not known. The growth velocity per Rad has been obtained. The growth is rapid in recent years

Sl. 5. Arheološka doza (AD) stalaktita iz Postojnske jame kot funkcija oddaljenosti od površja, izražena v kRad. Vzrok velikih vrednosti AD na površju ni znan. Dobili smo podatke o hitrosti rasti na Rad. Ta je velika v zadnjih letih

The Age and Growth Velocity

Unfortunately measurements of the radioactive elements in Postojna Cave deposits have not been done. We have measured the natural γ-ray radiation outside and inside the Postojna Cave with the thermoluminiscence dosimeter (TLD) of $CaSO_4$ (TM) (National TLD-110S). The annual dose was 98 ± 4 mR/yr outside the cave and 38 ± 2 mR/yr inside the cave. The amount inside the cave is highter than 20 mR in the Akiyoshi Cave, the largest cave in Japan. The terra rossa or the soils flown as well as a high concentration of atmospheric radioactivities accumulated in the cave may cause this high results. Recent study of atmospheric radioactivity in the Akiyoshi cave indicates o high concentration of 3 pCi/l. (T. Miki, M. Ikeya, 1979) The concentration may reach one working level (WL) measure used in uranium mines, 100 pCi/l) for along cave like Postojna Cave.

The annual dose rate used to convert the AD into real age in years is not the γ-ray dose rate obtained by the TLD measurement. It involves the radiation of α, β and γ-rays from inside the stalactite. The contents of the radioactivities in ^{238}U, ^{232} Th series and ^{40}K are not known at present. We simply assume the annual radiation dose of 0.1—0.2 Rad/yr. Considering the relatively high γ-rays dose rate determined with TLD, the dose rate around 0.2 R/yr might be appropriated. The ages and the growth velocities are thus calculated from the AD (Fig. 5).

The age and the position close to the center is 1.9×10^5 yrs. The recent radial growth rate is thus (0.44 ± 0.04) μm/yr. The average growth velocity in the past before about 5.0×10^4 yrs, is (0.06 ± 0.02) μm/yr. It is interesting to note that the radial growth rate of Akiyoshi stalactite is recently 0.45 μm/yr as compared to the value 0.045 μm/yr estimated for older periods before 7.0×10^4 years. The radial growth rates coincide roughly.

The estimated age of the stalactite in the present work exceeds the previously expected. Our ESR dating of flowstones indicates a very young formation and a fast growth rate. However, the pattern of brown sediment of the present stalactite suggests that longitudinal growth had been stopped in the past. We have cross checked the age of some stalagmites with U/Th method and ^{14}C dating and could show a reasonable agreement. Thus, it would not be doubtful that we have picked up a very old stalactite that had stopped in the longitudinal growth. The ESR dating of the stalagmite in Grotta Castellana gave an AD of 6.8 k Rad and a radial growth velocity of 6 μm/rad: corresponding to $3.4 \cdot 10^4$ yrs and the 1.2 μm/yr. The longitudinal growth rate was estimated as 35 ± 5 μm/yr. This value corresponds to growth rates of 3—4 mm in one hundred years and agrees with the rates reported by ^{14}C dating for stalagmites in the postglacial period.

The assumption of 0.2 Rad/yr may not be appropriate because there may be a high concentration of radioactive elements in the stalaktite. We are not certain on this point. A high AD at the surface is sometimes observed. It would not be due to radioactivity from ^{222}Rn and its daughters. The atmospheric radioactivity from the decay of ^{222}Rn and its daughter emanating from cracks and fissures in the cave will certainly produce γ and α-rays. But the inner parts have once represented the surface of the stalactite. Therefore, unless

some drastic change in the cave environment has occured recently, the surface damage must not be observed so high. It is also hard to consider that the damage was caused by nuclear bomb tests. Our investigation indicates the presence of ^{137}Cs in the bottom soil of doline but not in the cave so far as Japanese cave Akiyoshi is concerned. The effect of some biological species is suspected. Thus, the large AD at the surface is a question open to further research in nuclear archaeo-speleology.

GEOCHRONOLOGICAL DISCUSSION

One of the most interesting tasks of the speleology is the study of relative and absolute sinter age. The caves of Classical Karst around Postojna are richly concretioned therefore the studies and testing of the research methods, originating here and abroad, are the most brought forward. Till now in the Postojna Cave System the relative dating methods have been successfully used and some data about the radiometric sinter age have been obtained by ^{14}C and U/Th methods.

The additional dating experiment about the absolute sinter age from Postojna Cave has been made by M. Ikeya with ESR method, as it is evident from this contribution. We try to give some explanations to this article concerning the analysed sample and the geochronological interpretation of the obtained results.

In the last years we studied the sinter and its age in Pisani rov (The Coloured Gallery) of the Postojna Cave. We studied the recent sinter growth by chemical methods and we distinguished the generations of stalactites and stalagmites of various shapes by geological methods. In Pisani rov we know at least three sinter generations which growth was several times interrupted because of changeable Pleistocene climate and because of flooded channel. Taking in account the brown loams on the sinter and on the rocky channel walls it is possible to conclude that the muddy flood water several times reached the channel and at least once reached so high (up to 540 m above the sea level, it means 30 m higher as lies actual entrance to the cave) that the channel was flooded up to the ceiling. In this period the sinter could not be deposited, the percolating water simply melted together with flood water. On the older stalactites the brown loam coming from ponor flysch hinterland was deposited. Such layer of brown loam (layer E) is preserved in analysed stalactite. A lot of different coloured layers on the stalactite, distinguished among them (Fig. 1) prove, that the sinter growth on the ceiling was several times interrupted, the last time in the period when the analysed stalactite was broken from the ceiling and has fallen to the gallery's floor. There it was namely found and chosen for the analysis.

The ESR method of dating fixes the origin of stalactite nucleus to 190.000 years b.p. thus we can conclude that the sinter growth phase occurred at the end of Riss-Mindel Interglacial, while the highest flood period was in Riss Glacial. The next sinter layer on the stalactite above the loam could be from the Upper Riss Glacial and Riss-Würm Interglacial. The upper layers can be ranged in Würm Interstadials, because the Holocene age could not be taken into account, becaues the chosen stalactite group had been already broken from

the ceiling in this time. Several other cases in Pisani rov namely show that Pleistocene collapsed sinters are already thickly covered by Holocene white sinter (R. Gospodarič, 1976).

The recent physico-chemical methods of absolute sinter dations, among them the ESR method, complete the stratigraphic rangement of autochtonous and allochthonous cave sediments. Thus they give a contribution to knowledge of Quaternary geology in karst caves and on karst in general.

ACKNOWLEDGEMENT

The authors wish to thank to Institute for Karst Research SAZU at Postojna for the help by sampling of stalactite and settling the TLD capsules. Presented laboratory work has been made first at II. Physikalisches Institut in Stuttgart as a research fellow of Alexander von Humbolt Foundation and then at Reactor Institute of Kyoto University as a Joint Use of University Reactor.

REFERENCES

Aitken, J. M.: Physics and Archaeology, 2nd edition, Clarendon Press, Oxford (1974).
Fleming, S.: Dating in Archaeology, J. M. Dent & Sons, London (1976).
Gospodarič, R.: Acta carsologica, 7, Slovenska akademija znanosti in umetnosti, Ljubljana (1976), 5—135.
Gospodarič, R.: Acta carsologica, 9, Slovenska akademija znanosti in umetnosti, Ljubljana (1981), 87—100.
Ikeya, M.: Nature, **255** (1975), 48—50.
Ikeya, M.: Archaeomoetry, **20** (1978), 147—158.
Ikeya, M.: Naturwissenschaften, **65** (1978), 489.
Miki, T., M. Ikeya: Japan J. Appl. Phys., **17** (1978), 1703—1904.
Miki, T., M. Ikeya: Article submitted to Health Phys. (1979).

DATIRANJE STALAKTITA IZ POSTOJNSKE JAME Z ERS METODO

Povzetek

Preučevanje relativne in radiometrične starosti sige sodi med najbolj zanimive naloge speleologije. Ker so jame klasičnega krasa okrog Postojne bogato zasigane, je razumljivo, da je prav tod možno uveljaviti in preizkusiti ustrezne raziskovalne metode, ki se porajajo doma in v svetu. V Postojnskem jamskem sistemu so bile doslej koristno uveljavljene relativne metode datiranja (R. Gospodarič, 1976), nekaj podatkov o radiometrični starosti sige pa smo dobili tudi z 14 C in U/Th metodama (R. Gospodarič, 1981).

Nadaljnji poskus datiranja sige iz Postojnske jame sta izpeljala Motoji Ikeya in Toshikatsu Miki z ESR metodo, kar je razvidno in pojasnjeno v pričujočem prispevku. Za boljše razumevanje teh analitičnih podatkov pa je treba dodati še nekaj geokronoloških pojasnil.

V preteklih nekaj letih smo preučevali sige in njeno starost v Pisanem rovu Postojnske jame. S kemičnimi metodami smo ugotavljali recentno rast sige, z geološkimi metodami pa razlikovali generacije oblikovno pestrih stalaktitov in stalagmitov. V Pisanem rovu poznamo vsaj tri generacije sige, katerih rast je bila večkrat prekinjena zaradi spremenljive pleistocenske klime in zaradi poplavljenega rova. Po rjavi ilovici na sigi in skalnih stenah rova je možno sklepati, da je kalna poplavna voda večkrat zašla v rov, vsaj enkrat tako visoko (do 540 m nadmorske višine, to je 10 m više kot je današnji turistični vhod v jamo), da ga je zalila do stropa. Tedaj se siga ni mogla odlagati, ker se je prenikla voda preprosto zlila s poplavno vodo. Ta je na starejše stalaktite odložila rjavo alohtono ilovico, kakršna je ohranjena v analiziranem stalaktitu (plast E). Več raznobarvnih, med seboj ločenih plasti stalaktita (sl. 1) pa nadalje govorijo, da je bila rast sige na stropu še večkrat prekinjena, nazadnje tedaj, ko se je analizirani stalaktit odlomil od stropa in padel na tla. Tam smo ga namreč našli in izbrali za analizo.

Ker je ESR metoda datiranja pokazala, da je jedro stalaktita staro 190.000 let b. p., je možno sklepati na sigotvorno fazo ob koncu riško-mindelskega interglaciala, na omenjeno najvišjo poplavno dobo pa v riškem glacialu. Naslednja plast sige na stalaktitu (nad ilovico) je lahko iz mlajšega riškega glaciala in interglaciala riss-würm, nadalje krovne plasti pa je možno uvrstiti v würmske interstadiale, saj holocenska starost ne pride več v poštev, ker se je v našem primeru izbrana stalaktitna skupina tedaj že odlomila od stropa.

Novejše fizikalno-kemične metode radiometričnega datiranja sige, med njimi tudi ESR metoda, dopolnjujejo stratigrafsko uvrščanje avtohtonih in alohtonih jamskih sedimentov. S tem prispevajo k poznavanju kvartarne geologije kraških jam in krasa nasploh.