Zanesljivost datacij z uranovim nizom v Divjih babah I
Vpliv sedimentacijskih vrzeli na koncentracije urana v sedimentih in na datacije uranovega niza

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Izvleček

V prispevku so obravnavane štiri datacije U-niza ($^{230}Th/^{234}U$) iz najdišča Divje babe I v povezavi z geokemičnimi in drugimi analizami. S kombinacijo podatkov vseh analiz skušamo razložiti razlike med datacijami U-niza in drugimi radiometričnimi datacijami (^{14}C AMS in ESR), ki se nanašajo na iste vzorce ali plasti.

Odlaganje U v kosteh in sedimentih Divjih bab I predstavlja odprt sistem. Njegova vezava ni potekala linearno, niti ni do nje prišlo kmalu ali pozno po odložitvi kosti, kot to predvidevajo modeli, ampak imamo dejansko opraviti s kombinacijo vseh treh možnosti. Na remobilizacijo in odlaganje U so močno vplivali daljši zastoji v sedimentaciji, kar je domnevno glavni vzrok za nepravilnosti in netočnosti v določanju starosti z metodo U-niza, posredno pa tudi z metodo ESR.

Abstract

The contribution deals with four U series ($^{230}Th/^{234}U$) dates from the Divje babe I site in connection with geochemical and other analyses of sediments. We attempt with a combination of data of all analyses to explain the difference between U series and other radiometric ages (^{14}C AMS and ESR), relating to the same samples or layers.

Absorption of U in bones and sediments of Divje babe I took place in an open system. Its binding did not take place linearly, nor was there early or late uptake after deposition of the bones as models envisage, but we are actually dealing with a combination of all three possibilities. Extended gaps in sedimentation greatly influenced mobilisation and absorption of U. They lead to remobilisation of U, which is the suspected cause of irregularities and inaccuracies in determining age by the U series method, and indirectly also the ESR method.

V obdobju po uvedbi radiometričnih metod za neodvisno določanje absolutne starosti je postalo jasno, da litostratigrafskih, biostratigrafskih in arheoloških stratigrafskih enot ne gre enostavno enačiti s kronostratigrafskimi enotami. Če to počnemo, obstaja nevarnost krožnega argumentiranja. Ker kronostratigrafijo pogosto enačimo s kronometrijo, je treba z določeno mero previdnosti obravnavati tudi izsledke radiometričnih metod za določanje starosti, ki jim ne smemo slepo zaupati.

V Divjih babah I smo poleg sedimentoloških, paleontoloških in arheoloških podatkov pridobili tudi več kot 70 različnih radiometričnih datumov (radiokarbonskih z metodo akceleratorske masne spektrometrije - ^{14}C AMS, uranovega niza - ^{230}Th in elektronske spinske rezonance - ESR). Pomembno je, da so bile z različnimi metodami datirane iste plasti, v primeru ^{14}C in ^{230}Th celo isti vzorci. Vse radiometrične datacije so naredili vrhunski strokovnjaki za posamezne metode: Erle E. Nelson (1997), Teh-Lung Ku (1997), Henry P. Schwarcz in Bonnie A. B. Blackwell (Lau et al. 1997; Turk et al. 2001; Yu et al. 2001). Kljub temu je prišlo do velikega neskladja med rezultati, pridobljenimi z različnimi metodami za radiometrično določanje starosti (*tab. 1*).

Znano je, da vsaka metoda temelji na določenih predpostavkah in modelih, ki pojasnjujejo vnos radioaktivnih elementov v snov, ki jo želimo datirati. Te predpostavke so lahko v nekaterih primerih, zaradi

Tab. 1: Primerjava datacij U-niza z drugimi radiometričnimi datacijami v najdišču Divje babe I.
Table 1: Comparison of U series dates with other radiometric dates at Divje babe I site.

Plast Layer 1986 (1997)	Starost ^{230}Th Age ^{230}Th* ka	Starost ^{14}C Age ^{14}C** ka	Starost ESR Age ESR*** ka	Razlika ESR – ^{14}C, ^{230}Th Difference ESR – ^{14}C, ^{230}Th ka
2 (2)	26,2	35,3	–	9,7
13 (11-12)	24,5	50,4	77,5 - 85,1	53,0 - 60,6
17a (17a$_3$)	83,7	39,9	101,1	18,4
20 (19/20)	80,3	>54	114,7	34,2

* Ku 1997.
** Nelson 1997.
*** Turk et al. 2001; YU 2001.

določenih okoliščin, napačne, modeli pa preveč poenostavljeni in posplošeni ter zato neustrezni.

Da ta trditev drži, bomo poskusili pokazati na primeru datacij z uranovim nizom (odslej U-niz) v Divjih babah I. Vanje smo podvomili, ker so te datacije inverzne in v primerjavi z drugimi meritvami starosti premlade (*tab. 1*). Zato bolj zaupamo nekaterim ^{14}C AMS datacijam in ESR datacijam. Večja zanesljivost meritev starosti v najdišču z uporabo metode ^{14}C AMS za plasti 2 - 8 in metode ESR za starejše plasti je podprta z litostratigrafijo, biostratigrafijo in arheološko stratigrafijo (Turk et al. 2001, 2002; Šercelj, Culiberg 1991; Toškan 2002; Turk 1997, 2002). S kombinacijo vseh naštetih metod, izvzemši ^{230}Th, je bila določena meja med kisikovo izotopsko stopnjo (OIS) 5 in OIS 4 ter med srednjim in mlajšim paleolitikom v OIS 3 (Turk et al. 2001, 2002; Yu et al. 2001).

Metoda datiranja z izotopoma ^{234}U in ^{230}Th temelji na predpostavki, da se v predmetu, ki ga želimo datirati, kmalu po odložitvi naberejo uranovi (U) izotopi, kemično manj aktivni torijevi (Th) pa ne. Razpadna U-veriga do ^{230}Th obsega tri dolgožive izotope: $^{238}\text{U} \rightarrow \ldots \rightarrow {}^{234}\text{U} \rightarrow {}^{230}\text{Th}$. Razpolovni čas ^{238}U je 4,5 milijarde let in je veliko daljši od razpolovnega časa ^{234}U (245 ka) in ^{230}Th (75,4 ka). Število atomov ^{238}U v predmetu se zato praktično ne spreminja s časom, tako da je aktivnost ^{238}U (število razpadov na sekundo) ves čas enaka. V radiacijskem ravnovesju je aktivnost ^{234}U enaka aktivnosti ^{238}U, vendar pa pri absorpciji U v predmetu pogosto pride do izotopske obogatitve, ki poruši radiacijsko ravnovesje.

Število atomov ^{230}Th ob odložitvi (t = 0) je nič, po dovolj dolgem času pa se vzpostavi radiacijsko ravnovesje z U. Če sta U-izotopa ob odložitvi v ravnovesju, sama odložitev pa se zgodi ob trenutku t = 0, se aktivnost ^{230}Th eksponentno približuje aktivnosti U-izotopov:

$$A_{230} = A_{234}(1 - \exp(-t/\tau_{230})) \quad . \qquad (1)$$

Pri tem smo z A označili obe aktivnosti, τ_{230} pa je razpadni čas ^{230}Th. Zaradi različnih procesov, kot so radiacijske poškodbe in izotopska frakcinacija v kemičnih procesih, U-zotopa navadno nista v radiacijskem ravnovesju. V praksi je zato potrebno meriti aktivnosti obeh U-izotopov, in če se ti znatno razlikujeta, izračunamo čas odložitve t po nekoliko popravljeni enačbi 1 (Geyh, Schleicher 1990). Časi, ki jih lahko merimo z metodo U/Th, so lahko nekajkrat večji od τ_{230} = 75,4 ka / ln 2 $\approx$ 100ka.

Metoda datiranja z U in Th izotopi velja le v zaprtih sistemih, ko se število atomov ^{238}U po vnosu ob t = 0 ne spreminja več. Če med odložitvijo predmeta prihaja do izluženja U, je ocenjena starost predmeta prevelika, če pa se po odložitvi v predmetu absorbira dodatni delež U, predmetu pripišemo premajhno starost. Starosti, ki so bile določene z metodo U/Th v najdišču Divje babe I, so očitno premajhne, zato lahko domnevamo, da se je del U v vzorcih vezal kasneje.

Vnos U bomo ponazorili z enostavnim modelom, da se je del U nabral v predmetu zelo hitro ob času t = 0, drugi del pa se je vezal diagenetsko počasneje, približno linearno s časom:

$$A_{234} = A_0 + at \quad . \qquad (2)$$

Nadalje bomo privzeli, da sta uranova izotopa v radiacijskem ravnovesju. Kot vidimo v *tab. 1*, se aktivnosti uranovih izotopov razlikujeta največ za 8 %. Če popravka ne upoštevamo in računamo starost po enačbi 1, naredimo napako največ 0,9 ka (v plasti 17 a$_3$), ki je nepomembna v primerjavi z drugimi razlikami v *tab. 1*.

Z zvezo (2) dobimo za razmerje aktivnosti ^{230}Th in ^{234}U:

$$\frac{A_{230}}{A_{234}} = \frac{gt/\tau_{230} + (1 - g)(1 - \exp(-t/\tau_{230}))}{1 + gt/\tau_{230}} \quad . \qquad (3)$$

Pri tem smo uvedli nov brezdimenzijski parameter $g = a\ \tau_{230} / A_0$, ki je merilo za odprtost sistema. V povsem zaprtih sistemih je g = 0 in enačba 3 preide

v enačbo 1. V povsem odprtih sistemih pa je prispevek $A_0 = 0$, tako da dobimo razmerje A_{230} / A_{234} v limiti $g \rightarrow \infty$. Parameter g za vse štiri datirane plasti ocenimo iz starosti, ki so bile izmerjene z drugimi metodami. Za plasti 2 in 11 - 12 uporabimo starosti z metodo ^{14}C AMS, za plasti 17 a_3 in 20 pa starosti po metodi ESR. Kot vidimo v *tab. 2*, je najbolj odprt sistem plast 11 - 12: vrednost *g* presega 100, tako da je bila koncentracija U ob $t = 0$ približno dva odstotka končne vrednosti. V limiti $g \rightarrow \infty$ dobimo za plast 11 - 12 starost 51,1 ka. To je največja starost, ki jo še lahko dobimo z linearnim modelom po enačbi 2. Če je starost plasti 11 - 12 večja (bližja starosti, določeni z metodo ESR), je vnos U v mlajših obdobjih potekal bolj intenzivno kot linearno s časom (Grün et al. 1988). Odvisnost U aktivnosti v vzorcu lahko tedaj opišemo s funkcijo t^{p+1}; $p = -1$ ustreza modelu, ko se je ves U absorbiral v času $t = 0$, pri $p = 0$ pa absorpcija poteka linerno s časom. Vrednosti $p > 0$ pomenijo intenzivnejšo absorpcijo U v mlajših obdobjih. Razmerja Th in U aktivnosti pri necelem *p* ni mogoče podati analitično. Za numerično računanje smo izpeljali prikladen razvoj v vrsto:

$$\frac{A_{230}}{A_{234}} = \frac{t}{\tau_{230}} \exp\left(-\frac{t}{\tau_{230}}\right) \sum_{i=0} \frac{(t/\tau_{230}))^{i}}{(p+2+i)i!} \quad . \quad (4)$$

Če za plast 11 - 12 privzamemo povprečno starost 81,3 ka, iz enačbe (4) izračunamo p = 1,11. Tako velika vrednost *p* pomeni, da se je polovica U absorbirala v zadnjih 16 ka. Med vsemi štirimi plastmi je najbolj zaprt sistem plast 17 a_3; absorpcija U v času odlaganja prispeva 25 % k celotni vsebnosti U (zadnji stolpec v *tab. 2*).

Vrednosti *g* in parametra $gt / (\tau+gt)$, ki kaže delež absorpcije U v času odlaganja, se v grobem spreminjajo podobno kot razmerje Th/U v najdrobnejši frakciji sedimentov Divjih bab I (*sl. 6 a*). To razumemo tako, da velika vrednost Th/U pomeni malo razpoložljivega U za vnos v vzorec. Koncentracija U v vzorcu tako ni dosegla nasičenja ob času $t = 0$, ampak se je v vzorcu večala postopoma.

V zvezi z vprašljivimi datacijami U-niza v najdišču Divje babe I smo analizirali Th in U v sedimentih, ločenih v tri frakcije (*tab. 3*). Istočasno kot Th in U smo analizirali tudi druge kemične elemente, ki jih bomo podrobno obravnavali na drugem mestu, tukaj pa samo toliko, da v grobem pojasnimo kemične procese v sedimentih. Analizirane frakcije so:

1.) frakcija pod 0,5 mm (osnova),
2.) frakcija od 0,5 do 3 mm (osnova, ki vsebuje poleg avtohtonih klastov še autigene agregate in alohtone kostne drobce) in
3.) frakcija od 40 do 60 mm (matična dolomitna kamenina - najbolj avtohtona frakcija).

Na variabilnost Th in U v profilu (*sl. 1:* a,b) vpliva:

1.) variabilnost kemične sestave matičnega dolomita (Th in U), ki je zastopan vsaj z dvema različicama: večinskim zelo svetlo sivim, debelozrnatim dolomitom (nekateri drobci vsebujejo dolomitne žilice) in manjšinskim srednje sivim, drobnozrnatim dolomitom,
2.) razlika v mobilnosti Th in U in razlika v njunem odlaganju ter
3.) prisotnost alohtonih kostnih drobcev, katerih količina se spreminja v profilu (*sl. 2*) približno tako, kot se spreminja količina vseh fosilnih ostankov (glej Turk et al. 2002, sl. 7).

Variabilnost pod točko 2 je bila najvplivnejša, medtem ko variabilnost Th in U v matičnih kamninah in variabilnost kostnih drobcev nista imeli večjega vpliva, zaradi sorazmerno homogene zastopanosti obeh različkov dolomita v sedimentu in majhnih masnih deležev kostnih drobcev v njem.

Bistvo problema je torej v tem, da so se nekateri kemični elementi postsedimentno premeščali in

Tab. 2: Odprtost-zaprtost sistema U/Th v izbranih plasteh najdišča Divje babe I, kot jo podaja parameter *g* (glej tekst). Krepko so označene starosti, ki smo jih uporabili pri računanju *g*. Z δt smo označili napako, ki jo naredimo pri računanju starosti v zaprtih sistemih, če ne upoštevamo različnih aktivnosti ^{238}U in ^{234}U. Zadnji stolpec podaja delež U, ki se v predmetu absorbira v času odložitve.

Table 2: How open or closed the U/Th system is in selected layers of the Divje babe I site as indicated by parameter *g* (see text). Ages used in calculating *g* appear in bold. δt is the error made in calculating ages in closed systems if the different activities of ^{238}U and ^{234}U were not taken into account. In the last column the amount of U absorbed by the object during the time of deposition.

Plast/Layer 1986 (1997)	Starost ^{14}C(ka) Age ^{14}C (ka)	Starost ESR (ka) Age ESR (ka)	δt (ka)	g	gt/(τ+gt)
2 (2)	**35,3**	–	–	2,78	0,47
13 (11-12)	**50,4**	77,5 - 85,1	–	156	0,98
17a (17a_3)	39,9	**101,1**	0,9	0,359	0,25
20 (19/20)	>54	**114,7**	0,7	0,815	0,46

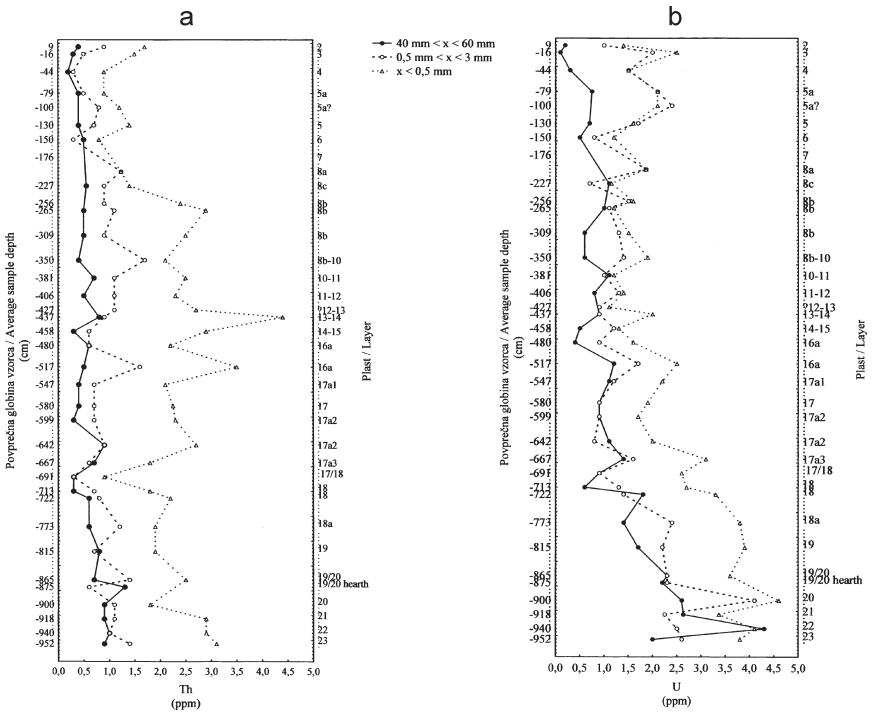
Tab. 3: Th in U (ppm) v različnih frakcijah sedimenta v plasteh Divjih bab I.
Table 3: Th and U (ppm) contents in various sediment fractions at Divje babe I.

Plast	Globina	Th	U	Th	U	Th	U
Layer	Depth	x < 0,5 mm		0,5 mm < x < 3 mm		40 mm < x < 60 mm	
2	9	1,7	1,4	0,9	1	0,4	0,2
3	-16	1,5	2,5	0,5	2	0,3	0,1
4	-44	0,9	1,5	0,3	1,5	0,2	0,3
5a upper	-79	0,9	2,1	0,5	2,1	0,4	0,6
5a lower	-100	1,2	2,1	0,8	2,4	0,4	0,9
5	-130	1,4	1,6	0,7	1,7	0,4	0,7
6	-150	0,8	1,2	0,3	0,8	0,5	0,5
7	-176	_	_	_	_	_	_
8a (breccia)		_	_	_	_	_	_
8c	-227	1,4	1,15	0,9	0,7	0,6	1,1
8b upper	-258	2,4	1,6	0,9	1,5	_	_
8b middle	-265	2,9	1,2	1,1	1,1	0,5	1
8b lower	-309	2,5	1,5	0,9	1,3	0,5	0,6
8b-10	-350	2,1	1,9	1,7	1,4	0,4	0,6
10-11	-381	2,5	1,2	1,1	1	0,7	1,1
11-12	-406	2,3	1,4	1,1	1,3	0,8	0,9
?12-13	-427	2,7	1,1	1,1	0,9	0,3	0,5
13-14	-437	4,4	2	0,9	0,9	0,6	0,4
14-15	-458	2,9	1,3	0,6	1,2	0,5	1,2
16a upper	-480	2,2	1,6	0,6	0,9	0,4	1,1
16a lower	-517	3,5	2,5	1,6	1,7	0,3	0,8
17a1	-547	2,1	2,2	0,7	1,2	0,5	1
17	-580	2,3	1,9	0,7	0,9	0,3	0,9
17a2 upper	-599	2,3	1,7	0,7	0,9	0,9	1,1
17a2 lower	-642	2,7	2	0,9	0,8	0,7	1,4
17a3	-667	1,8	3,1	0,6	1,6	0,3	0,9
17-18	-691	0,9	2,6	0,3	0,9	0,3	0,6
18 upper	-713	1,8	2,7	0,7	1,3	0,6	1,8
18 lower	-722	2,2	3,3	0,8	1,4	0,6	1,4
18a	-773	1,9	3,8	1,2	2,4	0,8	1,7
19	-815	1,9	3,9	0,7	2,2	0,7	2,3
19/20	-865	2,5	3,6	1,4	2,3	1,3	2,2
19/20 hearth	-875	_	_	0,6	2,3	0,9	2,6
20	-900	1,8	4,6	1,1	4,1	0,8	2,5
21	-918	2,9	3,4	1,1	2,3	1,1	2,7
22	-940	2,9	4,1	1	2,5	0,8	2,7
23	-952	3,1	3,8	1,4	2,6	1	4,3

Povprečna globina v cm.
Averrage depth in cm.

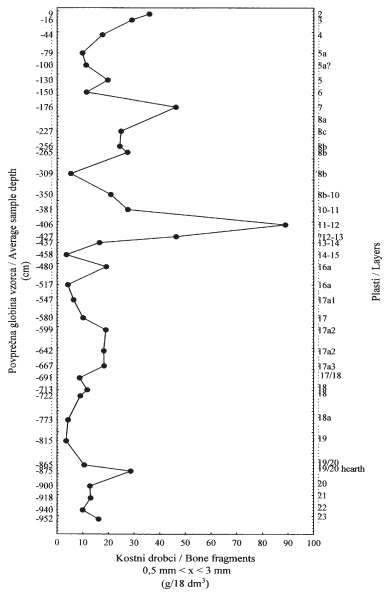
so se domnevno vezali predvsem v cemente. Zato je poznavanje procesa cementacije izredno pomembno za geokemijo sedimentov v Divjih babah I. Ta proces zelo dobro predstavljajo autigeni agregati (Turk et al. 2002). Ti so nastali najprej v najdrobnejši frakciji, potem pa so se postopno večali vse do strnjenih cementiranih sedimentov (breč) na velikih površinah (Turk, Bastiani 2000). Proces ni bil reverzibilen, vendar se je lahko zgodilo, da so manjši agregati v pogojih permafrosta razpadli (Williams, Smith 1989), pri čemer se je proces vrnil na začetek.

V frakciji, manjši od 0,5 mm, lahko pričakujemo agregate v vseh sedimentih Divjih bab I, ker se proces cementiranja začne v tej frakciji. V večjih frakcijah je ta proces v različnih nivojih in mikrookoljih, odvisno od razmer, napredoval različno daleč. Ker agregati rastejo z dotokom novega cementa in njegovim izločanjem na kristalizacijskih jedrih



Sl. 1: Porazdelitev Th (a) in U (b) v treh sedimentnih frakcijah profila Divjih bab I.
Fig. 1: Distribution of Th (a) and U (b) in three sediment fractions in the profile of Divje babe I.

manjših agregatov, s čemer se lahko ti združujejo, lahko pričakujemo, da bo manj manjših agregatov tam, kjer je več večjih agregatov.



Sl. 2: Porazdelitev kostnih drobcev velikosti 0,5 mm < x < 3 mm v profilu Divjih bab I.
Fig. 2: Distribution of bone detritus of 0.5 mm < x < 3 mm size in the Divje babe I profile .

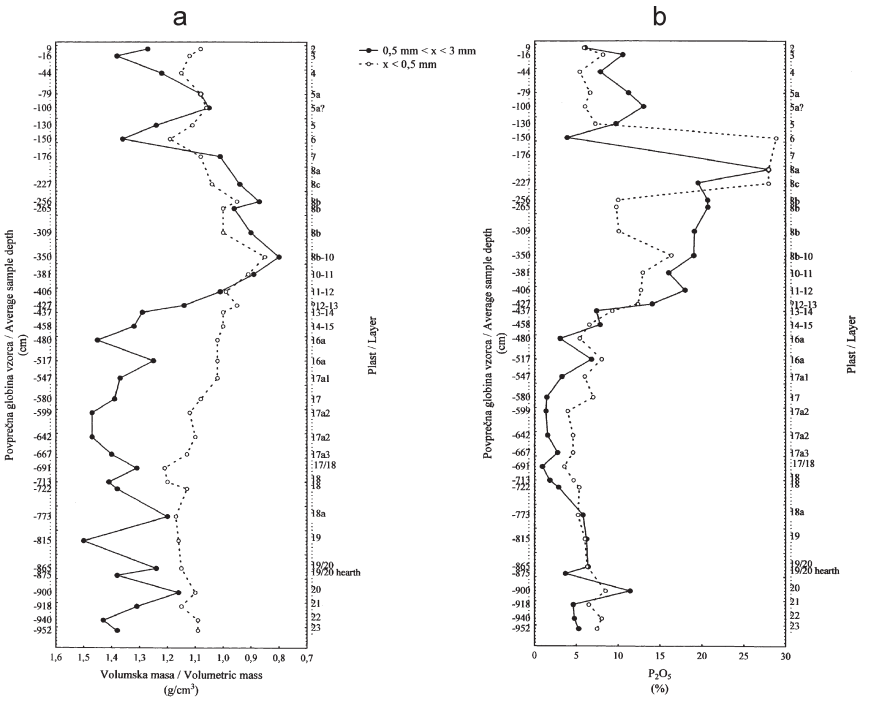
Če primerjamo porazdelitev kemičnih elementov (geokemijo[1]) in agregatov (sedimentologijo) v profilu (*sl. 3:* a,b), ugotovimo naslednje:

1.) Vsaj 90 % agregatov v frakciji, večji od 0,5 mm in manjši od 3 mm (odslej frakcija, večja od 0,5 mm), ima fosfatni cement. Izjema so agregati v plasti 17/18, kjer je cement kalcit. V plasteh 5 a in 7 do 8b - 10, kjer je proces "agregatizacije" in cementacije močno napredoval (veliko agregatov, večji sprimki, breče), prevladujejo fosfatni agregati v frakciji, večji od 0,5 mm, nad fosfatnimi agregati v frakciji, manjši od 0,5 mm (*sl. 3: a*). Zastopanost fosfatnih agregatov smo ocenili z volumensko maso. Prisotnost agregatov zmanjša volumensko maso sedimenta. V večini ostalih plasti, kjer v frakciji, manjši od 0,5 mm, ni korelacije med agregati (volumensko maso) in P, domnevamo, da je v tej frakciji manj fosfatnih agregatov in da se je proces agregatizacije ustavil.

2.) Sedemindvajset od 31 analiziranih elementov je v večji ali manjši korelaciji z agregati v eni od analiziranih frakcij.

3.) Korelacija je odvisna od tega, v kateri fazi procesa agregatizacije, ki je trajal od tisoč do več tisoč let, so se vezali posamezni elementi. Pri tem

[1] Vse geokemčne analize je opravil Acme Analytical Laboratories Ltd. Vancouver, BC, Canada.



Sl. 3: Porazdelitev agregatov, izražena z volumensko maso (a) in porazdelitev fosforja (b) v dveh drobnejših sedimentnih frakcijah v profilu Divjih bab I.
Fig. 3: Distribution of aggregates, expressed by volumetric mass (a) and distribution of phosphorus (b) in the two finer sediment fractions in the profile of Divje babe I.

je treba poudariti, da so agregati v drobnejših frakcijah (do velikosti nekaj mm) nastali dejansko v zelo zgodnji diagenezi, kar potrjuje vzročna zveza med agregati, večjimi od 0,5 mm, in fosilnimi ostanki jamskega medveda (glej Turk v tem letniku *Arh. vest.*).

Pri razlagi datacij U-niza nas ne zanima izvor kemičnih elementov, ampak nas zanimajo diagenetski in kemični procesi, ki so potekali v sedimentih Divjih bab I. V povezavi s temi procesi lahko razdelimo vse analizirane elemente v dve večji in eno manjšo skupino.

Elementi obeh večjih skupin (Na, K, Rb, Y, La in ostali lantanidi, Th, Zr, Fe, Al in Si, kot prva večja skupina in Ca, Sr, Ba, Cu, Zn in P kot druga večja skupina) so v profilu porazdeljeni podobno kot agregati oziroma volumenska masa v frakciji, manjši od 0,5 mm, ali kot agregati v frakciji, večji od 0,5 mm. To ne pomeni, da so v statističnem smislu vsi elementi v vseh primerih v značilni in veliki korelaciji z agregati. Zaradi metodoloških problemov, povezanih s kvantificiranjem agregatov v frakciji, manjši od 0,5 mm, so izračunani, statistično značilni korelacijski koeficienti (R) med agregati in kemičnimi elementi v tej frakciji nekoliko manjši, kot v frakciji, večji od 0,5 mm. V treh od 54 primerov pa je R, kljub podobni porazdelitvi, tako majhen in neznačilen, da statistično vzeto, korelacije ni.

Elementi prve večje skupine: Na, K, Rb, Y, lantanidi (redke zemlje), Th, Zr, Fe, Al, in Si imajo v frakciji, manjši od 0,5 mm, v profilu podobno porazdelitev kot agregati (volumenska masa) te iste frakcije (R = od - $0,35_{Y}$ do - $0,79_{Na}$, $p < 0,05$, $N = 34$, vsi R so statistično značilni). Po drugi strani imajo vsi našteti elementi v frakciji, večji od 0,5 mm, podobno porazdelitev kot agregati te iste frakcije (R = od - $0,38_{Th}$ do - $0,85_{Na}$, $p < 0,05$, $N = 34$, vsi R so statistično značilni). Vseh naštetih elementov je količinsko veliko več v frakciji, manjši od 0,5 mm, kot v frakciji, večji od 0,5 mm. Če so večji agregati nastali iz manjših, bi morali biti elementi v obeh frakcijah količinsko izenačeni. Ker razen v plasti 8a (breča) in 8b - 10 niso izenačeni, lahko sklepamo, da so prisotni predvsem v delcih, manjših od 0,5 mm.

Elementi druge večje skupine: Ca, Sr, Ba, Cu, Zn in P imajo v obeh frakcijah v profilu podobno porazdelitev kot agregati v frakciji, večji od 0,5 mm (R = od - $0,38_{\text{Sr, v frakciji manjši od 0,5 mm}}$ do - $0,92_{\text{P, v frakciji večji od 0,5 mm}}$, $p <= 0,05$, $N = 34$, vsi R, razen pri Ca, Ba, Zn v frakciji, manjši od 0,5 mm, so statistično značilni). Vsi ti elementi so bolj ali manj uravnoteženi v obeh analiziranih frakcijah, kar pomeni, da so vezani predvsem na fosfatni cement agregatov. Statistično značilni korelaciji med P in agregati, večjimi od 0,5 mm (R = - 0,92, $p < 0,05$,

N = 34) na eni strani in agregati, večjimi od 0,5 mm, ter stratigrafsko stabilnimi fosilnimi ostanki (R = - 0,76, p < 0,05, N = 33) na drugi strani, dokazujeta, da so določeni kemični procesi potekali v zgodnji diagenezi v obdobju največ nekaj tisoč let po odložitvi fosilnih ostankov. Fosfatne spojine kot rezultat teh procesov so se nespremenjene ohranile vse do danes.

Vezni člen med prvo in drugo skupino je Na, ki je v obeh frakcijah v statistično značilni korelaciji s P ($R = 0,66_{\text{frakcija, manjša od 0,5 mm}}$, p < 0,05, N = 33, $R = 0,91_{\text{frakcija, večja od 0,5 mm}}$, p < 0,05, N = 36).

Elementi tretje skupine (U, Co, Ni in Pb) so v profilu porazdeljeni bistveno drugače od vseh ostalih elementov in agregatov. U je tako element, ki ima v Divjih babah I drugačno zgodovino kot drugi analizirani elementi.

Ker je Th zelo nemobilen element, in ker kost, naj bo sveža ali fosilna, vsebuje zelo malo Th (Schwarcz, Blackwell 1992), medtem ko so v sedimentih Divjih bab I koncentracije Th povprečno 20-krat večje kot v kosteh (*tab. 4*), Th ne more biti vzrok za napake pri datiranju z U-nizom. Vzrok je U, ki se absorbira v kosti v procesu fosilizacije. Zato najbolj preperele kosti v Divjih babah I vsebujejo več U (1,1 ppm) kot najmanj preperele kosti (0,2 ppm). V primerjavi z nekaterimi najdišči so to nizke vrednosti (glej Blackwell, Blickstein 2000, tab. 1), vendar še vedno v mejah običajnega razpona (Schwarz, Blackwell 1992). V sedimentih Divjih bab I je U nekajkrat več kot v kosteh (*tab. 1*), vendar še vedno malo v primerjavi z drugimi najdišči (glej prav tam). Treba je opozoriti, da se koncentracija U v preperelem apnencu (in dolomitu?) zmanjšuje (Zupan Hajna 2003, 56), medtem ko se v prepereli kosti povečuje (Schwarz, Blackwell 1992, 8, sl. 12.5).

Medtem ko je Th slabo topen in ne migrira z vodo, velja za U ravno obratno. Zato predvidevamo, da je prišlo do določene migracije in preporazdelitve U v profilu sedimentov Divjih bab I. To je razvidno iz primerjave porazdelitve obeh elementov v profilu (*sl. 1:* a,b).

Th in U sta v dolomitnih klastih v profilu v statistično značilni korelaciji (R = 0,75, p < 0,05, N = 32). Klasti predstavljajo dolomitno kamnino, iz katere je s preperevanjem nastal večinski del sedimentov v najdišču Divje babe I. Sedimenti so se nedvomno obogatili z alohtonim U in Th, tako da se je vsebnost obeh elementov v primerjavi z matičnim dolomitom večkrat povečala (*sl. 4*). Proces obogatitve Th in U, kot ga vidimo danes, ni potekal linearno s časom.

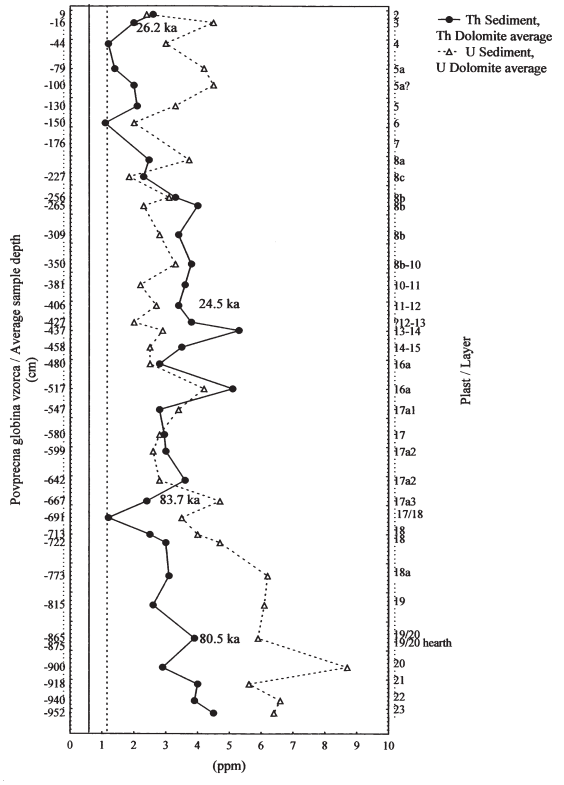
Med U v sedimentih in U v matičnem dolomitu je v profilu statistično značilna korelacija (R = 0,74, p < 0,05, N = 31). Med Th v sedimentih in Th v matičnem dolomitu v profilu je manjša, a še statistično značilna korelacija (R = 0,52, p < 0,05, N = 31). U se je v sedimentu odlagal zelo neenakomerno. Plasti 2 - 4 so se v zadnjih 35.000 letih, neznano kdaj, izredno obogatile z U (*sl. 5*). Pri Th posameznih tako velikih odstopanj ni opaziti (*sl. 5*). U ima v profilu še eno posebnost, ki jo Th in drugi elementi v Th skupini (Na, K, Rb, Y, lantanidi, Zr, Fe, Al in Si) nimajo. V plasteh 2 do 12 - 13 so vrednosti U v frakciji, manjši od 0,5 mm, in frakciji, večji od 0,5 mm, precej izenačene. V ostalih plasteh pa so, razen dveh izjem, vrednosti U v frakciji, manjši od 0,5 mm, precej večje kot v frakciji, večji od 0,5 mm (*sl. 1:* b). Posebnost lahko razložimo bodisi z manjšo prisotnostjo U v delcih, manjših od 0,5 mm, v plasteh 2 do 12 - 13, bodisi z različnimi kemičnimi procesi (absorbcijo? U v sedimentih plasti 2 do 12 - 13 in adsorbcijo? U v sedimentih večine plasti spodnjega dela profila).

Predel profila (plasti 8 c - 17 a_2), ki je obogaten s Th, ima najmanj U, celo manj kot Th. Razen v plasti 2 je nad tem predelom in pod njim U bistveno več kot Th. Uran pa nad plastmi 8 c - 17 a_2 in pod njimi tudi bolj odstopa kot Th od povprečja v dolomitu, ki ga predstavljajo vse vrednosti frakcije 40 mm < x < 60 mm (*sl. 4*). Edina smiselna razlaga je ta, da so se sedimenti nad tem predelom in pod njim diagenetsko obogatili z U. Vprašanje je, kaj se je dogajalo v plasteh 8 c - 17 a_2.

Plasti 7 do 11 - 12, za katere so značilni agregati, korodirani klasti in korodirane kosti, predstavljajo najvlažnejšo fazo v času odlaganja sedimentov v Divjih babah I (Turk et al. 2002). V tej fazi je nastala

Tab. 4: Povprečje Th in U (ppm) v vseh analiziranih plasteh (N = 31), v cementu breč v plasti 8 a (N = 7) in v kosteh iz različnih plasti (N = 4).
Table 4: Average Th and U contents (ppm) in layers (N = 31), in cements of breccia from Layer 8 a (N = 7) and in bones from various layers (N = 4).

	Frakcije/Fractions				Kosti
	x < 0,5 mm	0,5 mm < x < 3 mm	40 mm < x < 60 mm	Breccia	Bones
Th	2,1	0,9	0,6	1,2	< 0,1
U	2,3	1,6	1,2	1,9	0,8



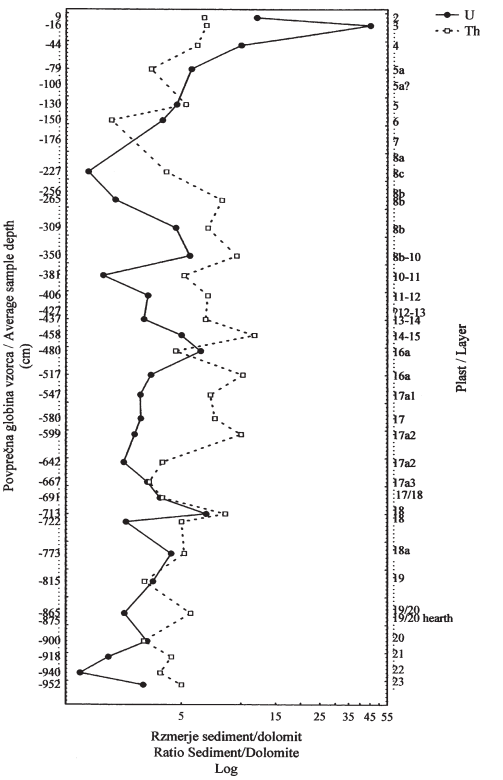
Sl. 4: Porazdelitev Th in U v sedimentu, ki jo predstavljata združeni vrednosti za frakcijo x < 0,5 mm in frakciji 0,5 mm < x < 3 mm. Dodano je povprečje Th in U v profilu za dolomitno kamnino, ki jo predstavlja frakcija 40 mm < x < 60 mm. Na ustreznih mestih so izpisane tudi Th/U-datacije vzorcev kosti.
Fig. 4: Distribution of Th and U in sediments, which represent a combined values for the x < 0.5 mm fraction and the 0.5 mm < x < 3 mm fraction. The average Th and U for dolomite bedrock represented by the values of 40 mm < x < 60 mm fraction is added. Four Th/U dates of bone samples are plotted in appropriate places.

večina autigenih agregatov, ki so vzročno povezani z masovnimi fosilnimi ostanki jamskega medveda. Po tem in predvsem pred tem je agregatov bistveno manj, ker je znatno manj tudi fosilnih ostankov (*sl. 2* in *3:* a). Dejansko se je vlažna faza lahko začela že veliko prej, v plasti 17 a_2, ko se v frakciji, manjši od 0,5 mm, poveča vsebnost elementov Th-skupine (Na, K, Rb, Y, lantanidi, Zr, Fe, Al in Si) in ostane povečana vse do plasti 7. V tej vlažni fazi, ki je, sodeč po ESR datacijah, imela časovni razpon več deset tisoč let, se je veliko U iz plasti 8 c - 17 a_2 zanesljivo postopno spralo v nižje ležeče plasti. Proces mobilizacije in odlaganja U je bil lahko enakomeren in stalen, ali pa so se vrstila posamezna obdobja s povečanim izluževanjem in odlaganjem U z daljšimi vmesnimi prekinitvami. Na ta način so kosti v sedimentih dobivale vedno nove in vedno mlajše količine U, ki so vplivale na določitev njihove starosti z U-nizom in tudi z metodo ESR.

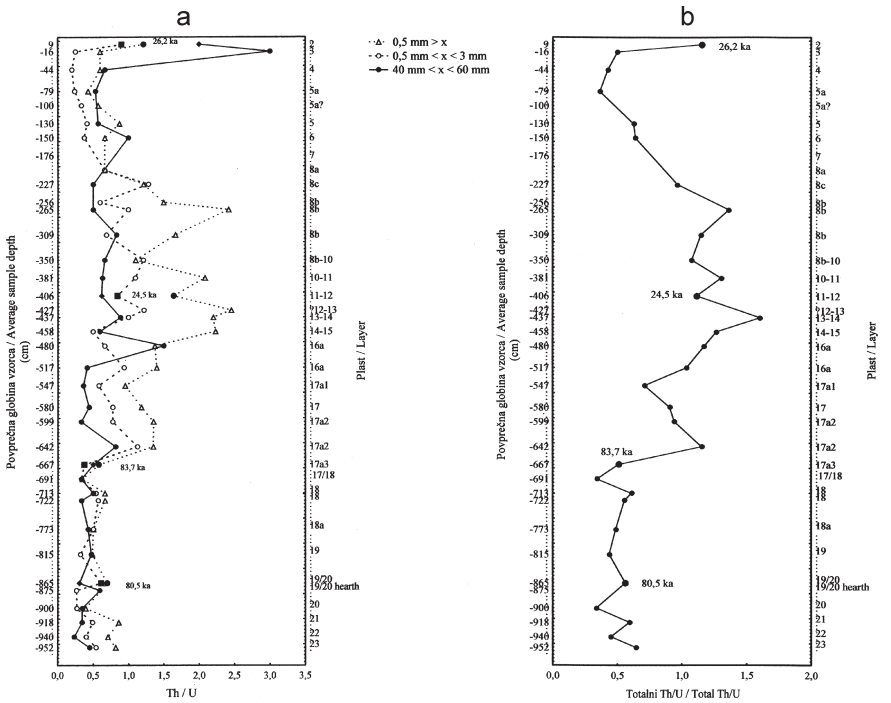
Če izhajamo iz dejstva, da je Th slabo topen in predpostavljamo, da se ni premeščal, lahko s pomočjo Th grobo ocenimo prvotne količine U v profilu.

V profilu se spreminja predvsem Th v frakciji, manjši od 0,5 mm (*sl. 1:* a), ki popolnoma obvladuje razmerja med Th in U v posameznih frakcijah in v celotnem sedimentu (*sl. 6:* a,b). Domnevamo, da je bila količina sinsedimentnega U podobno porazdeljena v profilu, kot je porazdeljena današnja količina Th v frakciji, manjši od 0,5 mm, ali kot je porazdeljeno razmerje med celokupnim Th in U. Ker je U v matičnem dolomitu približno dvakrat več kot Th, so bile vse sinsedimentne vrednosti U domnevno večje od današnjih vrednosti Th. To domnevno pomeni naslednje za plasti, datirane z U-nizom (glej *sl. 4*):

Plasti 2 in 11 - 12 sta danes, zgodovinsko-razvojno gledano, osiromašeni z U, plast 11 - 12 bistveno bolj kot plast 2. Pri procesu mobilizacije U so se občasno v kosti adsorbirale večje količine U, ki so pomladile njihovo starost, določeno na podlagi



Sl. 5: Razmerje U v sedimentu, ki ga predstavljata združeni vrednosti za frakcijo x < 0,5 mm in frakciji 0,5 mm < x < 3 mm in dolomitni kamnini, ki jo predstavlja frakcija 40 mm < x < 60 mm ter razmerje Th v sedimentu in dolomitni kamnini, določeno na enak način.
Fig. 5: Ratio of U in sediment represented by combined values for the x < 0.5 mm fraction and the 0.5 mm < x < 3 mm fraction and dolomite represented by the 40 mm < x < 60 mm fraction, and the ratio of Th in the sediment and dolomite determined in the same way.



Sl. 6: Razmerje Th/U v treh sedimentnih frakcijah (a) in to isto razmerje v vseh treh frakcijah skupaj (b). Na ustreznih mestih so izpisane Th/U-datacije vzorcev kosti.
Fig. 6: Th/U ratio in three sediment fractions (a) and the same ratio in all three fractions together (b). Th/U dates of bone samples are plotted in appropriate places.

U-niza. Plast 11 - 12 je glede na svojo odložitev sprejela dodatno količino U mnogo kasneje kot plast 2, domnevno v času izpiranja plasti 8 c, glede na različno radiometrično določeno starost pa v zadnjih 16 ka. Razen tega je lahko že pred tem dobila več dodatnih količin U.

Plasti 17 a_3 in 19/20 imata danes vrednosti U, ki so bistveno večje od vrednosti Th, kar je pričakovano. Obe plasti sta sprejeli v preteklosti dodatno količino U kot posledico izpiranja višje ležečih plasti, ki so danes osiromašene z U. Uran, ki bi se izpral denimo iz plasti 17 a_2, bi bolj pomladil plast 19/20 kot plast 17 a_3.

V zvezi s takšno razlago se postavlja še nekaj vprašanj.

Prvič, kako je lahko izprana plast 11 - 12 postsedimentno sprejela večjo količino U, ne da bi se ta količina U vsaj delno zadržala v sedimentu do danes, kot se je zadržala v plasti 17 a_3 in 19/20. Drugič, zakaj se U v kosti iz plasti 11 - 12 ni izlužil, kar bi imelo za posledico večjo starost kosti.

Možen je naslednji odgovor: U, ki se je vezal v kost, je v njej tudi ostal, U v sedimentu plasti 11 - 12 pa se je kasneje izpral. Takšna razlaga je podprta z ugotovitvami, da se koncentracija U v prepereli kamnini zmanjšuje, v prepereli kosti pa povečuje.

Obe vprašanji si upravičeno postavimo tudi za kost v plasti 2, kjer se morda ponuja rešitev celotne uganke. V plasti 2 je namreč vsaj en kazalec za dejansko povečanje vsebnosti U, in sicer je to veliko odstopanje U v sedimentu od povprečja dolomita v frakciji 40 mm < x < 60 mm (*sl. 5*). V ostalih plasteh, razen v plasti 3 in 4, je to odstopanje bistveno manjše. Veliko odstopanje v plasteh 2 - 4 je lahko povezano z dolgo prekinitvijo sedimentacije. Ker drugod v profilu, kljub litološko dokazljivim prekinitvam v sedimentaciji (glej Turk et al. 2001; 2002), ni tako velikih odstopanj, domnevamo, da se je lahko z odlaganjem novih sedimentov tako akumuliran U izpral in porazdelil v globlje plasti.

Večje prekinitve v sedimentaciji domnevamo tudi na meji plasti 6 in 7 tik pod plastjo 11 - 12 ter na meji plasti 17 a_1 in 17, in sicer neodvisno od radiometričnih datacij, ki lahko prav tako pokažejo prekinitev v sedimentaciji (Turk et al. 2001). Te prekinitve bi lahko vplivale na datacije kosti z U-nizom v plasteh 11 - 12, 17 a_3 in 19/20, če so se plasti 7 - 8 c, 12 - 15 in 17 - 17 a_2, ki so bile v času brez sedimentacije od 0 do 50 cm pod površjem, bogatile z U in če se je ta U v času po ponovni vzpostavitvi sedimentacije spral v nižje plasti. Daljše so bile prekinitve v sedimentaciji, večji je bil domnevno učinek na premeščanje U in tako na datacije U-niza. To pa lahko vpliva tudi na datacije z metodo ESR, pri kateri je pomembna doza žarčenja,

ki je odvisna od koncentracije U v sedimentu.

Odlaganje U v kosteh in sedimentih Divjih bab I predstavlja odprt sistem. Njegova vezava ni potekala linearno, niti ni do nje prišlo kmalu ali pozno po odložitvi kosti, kot to predvidevajo modeli (Grün et al. 1988; Blackwell, Blickstein 2000), ampak imamo dejansko opraviti s kombinacijo vseh treh možnosti. Na remobilizacijo in odlaganje U so močno vplivali daljši zastoji v sedimentaciji, kar je domnevno glavni vzrok za nepravilnosti v določanju starosti z metodo U-niza, posredno pa tudi z metodo ESR. Neobčutljivi na takšne motnje so fosfatni cementi v Divjih babah I, ki bi bili v čisti obliki najprimernejša snov za datiranje z metodo U-niza (Schwarcz, Blackwell 1992, 6).

Zahvale

Avtorji se zahvaljujemo prof. dr. Simonu Pircu za popravke v angleškem tekstu

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Reliability of Uranium Series Dating in Divje babe I
Effect of sedimentation gaps on uranium concentrations in sediments and on uranium series dating

Translation

Since the introduction of radiometric methods for independent determination of absolute age, it has become clear that lithostratigraphic, biostratigraphic and archaeological stratigraphic units cannot be simply equated with chronostratigraphic units. If we do this, there is the danger of circular argumentation. Since chronostratigraphy is often equated with chronometry, we cannot blindly trust the results of radiometric methods for determining age, but must consider them with a certain amount of care.

In Divje babe I, in addition to sedimentological, paleontological and archaeological data, we also performed more than 70 different radiometric dates (radiocarbon by the accelerated mass spectometry method - ^{14}C AMS, uranium series - ^{230}Th, and electronic spin resonance - ESR). It is important that the same layers were dated by various methods, and in the case of ^{14}C and ^{230}Th, even the same samples. All the radiometric dates were made by top experts for individual methods: Erle E. Nelson (1997), Teh-Lung Ku (1997), Henry P. Schwarcz and Bonnie A. B. Blackwell (Lau et al. 1997; Turk et al. 2001; Yu et al. 2001). However, there was great discordance between the results obtained by the different methods for radiometric determination of age (*Table 1*).

It is known that each method is based on specific assumptions and models that explain the uptake of radioactive elements in the substance that we wish to date. In some cases, because of specific circumstances, these assumptions can be mistaken, and models oversimplified and generalised, and therefore unsuitable.

We will attempt to show that this claim holds in the case of uranium series (hereinafter U series) dating in Divje babe I. We doubted them because these ages are inverse and in comparison with other measurements of age, too young (*Table 1*). We therefore have more confidence in some ^{14}C AMS and ESR dates. The greater reliability of age measurements at the site by means of the ^{14}C AMS method for Layers 2 - 8 and the ESR method for older layers is supported by lithostratigraphy, biostratigraphy and archaeological stratigraphy (Turk et al. 2001, 2002; Šercelj, Culiberg 1991; Toškan 2002; Turk 1997, 2002). By a combination of all the enumerated methods, except for ^{230}Th, the boundary between oxygen isotope stage (OIS) 5 and OIS 4 was determined, and between the Middle and Upper Paleolithic in OIS 3 (Turk et al. 2001; 2002; Yu et al. 2001).

The method of ^{234}U and ^{230}Th isotope dating is based on the premise that soon after deposition, uranium (U) isotopes concentrate in the object that we wish to date, but the less active thorium (Th) does not. The U-decay chain to ^{230}Th embraces three daughter isotopes: $^{238}\text{U} \longrightarrow \ldots \longrightarrow {}^{234}\text{U} \longrightarrow {}^{230}\text{Th}$. The half-life of ^{238}U is 4.5 billion years and is a great deal longer than the half-life of ^{234}U (245 ka) and ^{230}Th (75.4 ka). The number of atoms of ^{238}U in an object, therefore, is practically unchanged with time, so that the activity of ^{238}U (decay rate) is the same throughout. In secular radioactive equilibrium, the activity of ^{234}U is the same as the activity of ^{238}U, but with the absorption of U in the object, isotope enrichment often occurs, which destroys the secular radioactive equilibrium.

The number of atoms of ^{230}Th on deposition ($t = 0$) is zero, but after a sufficiently long time, it achieves radioactive equilibrium with U. If the U isotopes are in equilibrium at the time of deposition, and deposition itself occurs at the moment $t = 0$, the activity of ^{230}Th exponentially approaches the activity of the U isotopes:

$$A_{230} = A_{234}(1 - \exp(-t/\tau_{230})) \quad . \qquad (1)$$

whereby we marked the two activities by A, and τ_{230} is the lifetime of ^{230}Th. Because of different processes, such as radioactive damage and isotope fractionation in chemical processes, the U isotopes are not normally in secular radioactive equilibrium. In practice, therefore, the activities of both U isotopes must be measured, and if they differ significantly, the time of deposition t is calculated by a slightly modified equation 1 (Geyh, Schleicher 1990). Ages that can be measured by the U/Th method can be several times greater than τ_{230} = 75.4 ka / ln 2 $\approx$ 100ka.

The method of dating with U and Th isotopes only applies to closed systems, when the number of atoms of ^{238}U no longer changes after uptake at $t = 0$. If leaching of U occurs during deposition of the object, the age assessment of the object is too large, and if an additional amount of U is absorbed in the object after deposition, too low an age is ascribed to the object. Ages that have been determined by the U/Th method at the Divje babe I site are clearly too low, so it can be presumed that U absorption took place some time after deposition.

We will illustrate U uptake with a simple model assuming that part of the U absorbed in the object was very fast at time $t = 0$, and the other part took place more slowly, approximately linearly with time:

$$A_{234} = A_0 + at \quad . \qquad (2)$$

We will further assume that the uranium isotopes are in secular radioactive equilibrium. As can be seen in Table 1, the activity of the uranium isotopes differs by a maximum of 8%. If we do not take the correction into account and calculate the age by equation 1, we make an error of a maximum 0.9 ka (in Layer 17 a_3), which is insignificant in comparison with other differences in *Table 1*.

In relation to (2) we obtain for the ratio of activities of ^{230}Th and ^{234}U:

$$\frac{A_{230}}{A_{234}} = \frac{gt/\tau_{230} + (1-g)(1 - \exp(-t/\tau_{230}))}{1 + gt/\tau_{230}} \quad . \qquad (3)$$

We have here introduced a new non-dimensional parameter $g = a\ \tau_{230} / A_0$, which is a measure for the openness of the system. In completely closed systems, $g = 0$ and equation 3 transforms into equation 1. In completely open systems, the initial contribution is $A_0 = 0$, so that the ratio A_{230} / A_{234} is obtained in the limit $g \longrightarrow \infty$. We assess parameter g for all four dated layers from the ages that were measured by other methods. For Layers 2 and 11 - 12 we use the age from the ^{14}C AMS method, and for Layers 17 a_3 and 20 ages by the ESR method. As can be seen in *Table 2*, Layer 11 - 12 is the most open system: the value of g exceeds 100, so that the concentration of U at $t = 0$ was approximately two percent of the final value. At the limit $g \longrightarrow \infty$ for Layer 11 - 12 we get an age of 51.1 ka. This is the maximum age that can be obtained with the linear model by equation 2. If the age of Layer 11 - 12 is greater (closer to the age determined by the ESR method), the uptake of U in later periods took place more intensively than linearly with time (Grün et al. 1988). The dependence of U activity in the sample can now be described by the function t^{p+1}; p = - 1

corresponds to the model when all U was absorbed at time $t = 0$, and at $p = 0$ absorption takes place linearly with time. Values of $p > 0$ mean more intensive U absorption in later periods. The relation of Th and U activity at non-integer p cannot be given analytically. For a numerical calculation, we derived suitable power series

$$\frac{A_{230}}{A_{234}} = \frac{t}{\tau_{230}} \exp(-\frac{t}{\tau_{230}}) \sum_{i=0} \frac{(t/\tau_{230}))^{i}}{(p+2+i)i!} \quad . \qquad (4)$$

If we assume an average age of 81.3 ka for Layer 11 - 12, from equation (4) we calculate p = 1.11. Such a large p value means that about half of the U has been absorbed in the last 16 ka. Among all four layers, Layer 17 a_3 is the most closed system; U absorption during the time of deposition contributes 25% to the total U content (last column in *Table 2*).

Values of g and of parameter $g\tau$ / (τ+$g\tau$), which shows the amount of U absorption during the time of deposition, change roughly the same as the relation Th/U in the smallest fractions of sediments of Divje babe I (*Fig. 6:* a). We understand this in such a way that a large value of Th/U means little available U for uptake into the sample. The concentration of U in a sample did not reach saturation at the time $t = 0$, but increased gradually with time.

In connection with the questionable U series dating at the Divje babe I site, we analysed the Th and U in sediments separately in three fractions (*Table 3*). At the same time as Th and U, we also analysed other chemical elements, which will be discussed in detail elsewhere, and here only sufficiently to explain the chemical processes in the sediments. The analysed fractions are:

1.) fraction below 0.5 mm (matrix),

2.) fraction from 0.5 to 3 mm (matrix containing in addition to autochthonous clasts also authigenic aggregates and allochthonous bone fragments) and

3.) fraction from 40 to 60 mm (dolomite bedrock - the most autochthonous fraction).

The following affect the variability of Th and U in the profile (*Fig. 1:* a,b):

1.) variability of the chemical composition of the dolomite bedrock (Th and U), which appears in at least two types: mainly very light grey, coarse grained dolomite (some fragments contain dolomite veins) and suborinately medium grey, fine grained dolomite,

2.) differences in the mobility of Th and U and differences in its deposition, and

3.) presence of allochthonous bone fragments, the amount of which changes in the profile (*Fig. 2)* approximately in the same manner as the amount of all fossil remains (see Turk et al. 2002, Fig. 7).

The variability under point 2 was the most influential, while the variability of Th and U in the bedrock and the variability of bone fragments did not have major influence because of the relatively homogenous representation of the two types of dolomite in the sediment and the small mass share of bone fragments.

The essential problem therefore is that some chemical elements were postdepositionally mobilised and some of them were presumably bound mainly in cement. So recognition of the process of cementation is extremely important for the geochemistry of sediments in Divje babe I. Authigenic phosphate aggregates very well represent this process. These were first formed in the smallest fractions, and then gradually increased right up to contiguous cemented sediments (breccia) in large areas (Turk, Bastiani 2000). The process was in fact not reversible, although it could happen that smaller aggregates disintegrated in permafrost conditions (Williams, Smith 1989), by which the process returned to the beginning.

We can expect aggregates in all sediments of Divje babe I in the fraction smaller than 0.5 mm, since the cementation process began in this fraction. In the larger fractions, this process at various levels and microenvironments, depending on conditions, advanced variously far. Since aggregates increase with supply of new cement and its segregation into crystallisation nuclei of smaller aggregates, by which these could unite, we can expect that there will be fewer smaller aggregates in areas of larger aggregates.

If we compare the distribution of the chemical elements (geochemistry[1]) and aggregates (sedimentology) in the profile (*Fig. 3:* a,b), we find the following:

1.) At least 90% of the aggregates in the fraction larger than 0.5 mm and smaller than 3 mm (hereinafter: fraction larger than 0.5 mm) have phosphate cement. The aggregates in Layer 17/18 are an exception, since the cement is calcite. In Layers 5 a and 7 to 8 b - 10, where the process of "aggregatisation" and cementation was greatly advanced (many aggregates, partially cemented sediment, breccia), phosphate aggregates predominate in the fraction larger than 0.5 mm over phosphate aggregates in the fraction smaller than 0.5 mm (*Fig. 3:* a). We assessed the representation of phosphate aggregates by volumetric mass. The presence of aggregates reduces the volumetric mass of the sediment. In the majority of layers, where there is no correlation between aggregates (volumetric mass) and P in the fraction smaller than 0.5 mm, we assume that there are fewer phosphate aggregates in this fraction because the process of aggregatisation was halted.

2.) Twenty seven of 31 analysed chemical elements are more or less correlated with the aggregates in one of the analysed fractions.

3.) The correlation depends on the phase of the process of aggregatisation, which lasted from a thousand to several thousand years, during which the individual elements were bound. It must be stressed in this that aggregates in the smallest fractions (up to a size of a few mm) were actually created during very early diagenesis, which confirms the causal link between aggregates greater than 0.5 mm and fossil remains of cave bear (see Turk in this issue of *Arh. vest.*).

In explaining the U series dates, we are not interested in the origin of the chemical elements but in the chemical and diagenetic processes that took place in the sediments of Divje babe I. In connection with these processes, we can separate all analysed elements into two larger groups and one smaller one.

The elements of both larger groups (Na, K, Rb, Y, La and other lanthanides, Th, Zr, Fe, Al and Si, as the first larger group, and Ca, Sr, Ba, Cu, Zn and P as the second larger group) are distributed in profile similarly as aggregates or the volumetric mass in the fraction smaller than 0.5 mm, or as aggregates in the fraction larger than 0.5 mm. This does not mean that in the statistical sense all elements are in all cases in significant and strong correlation with aggregates. Because of methodological problems connected with the quantification of aggregates in the fraction smaller than 0.5 mm, the calculated, statistically significant correlation coefficients between aggregates and chemical elements in this fraction are somewhat lower than in the fraction larger than 0.5 mm. In three of 54 cases, R is small and insignificant, despite a similar distribution, and there is no correlation.

The first group elements: Na, K, Rb, Y, lanthanides (rare earths), Th, Zr, Fe, Al and Si, in the fraction smaller than 0.5 mm have a similar distribution in profile as the aggregates (volumetric mass) of the same fraction (R = from - 0.35_{Y} to - 0.79_{Na}, $p < 0.05$, N = 34, all R are statistically significant). On the other hand, all the enumerated elements in the fraction

[1] All geochemical analyses were performed by Acme Analytical Laboratories Ltd. Vancouver, BC, Canada.

larger than 0.5 mm have a similar distribution as the aggregates of the same fraction (R = from - 0.38_{Th} to - 0.85_{Na}, $p < 0.05$, N = 34, all R are statistically significant). There are a great deal more of all the enumerated elements in the fraction smaller than 0.5 mm than in the fraction larger than 0.5 mm. If the larger aggregates were formed from smaller ones, the elements in the two fractions should be the same in quantitative terms. Since they are not the same, except in Layers 8a (breccia) and 8b - 10, we can conclude that they are mainly present in fragments smaller than 0.5 mm.

The second group elements: Ca, Sr, Ba, Cu, Zn and P have a similar distribution in both fractions in the profile as aggregates in the fraction larger than 0.5 mm (R = from - $0.38_{Sr,\ in\ the\ fraction\ smaller\ than\ 0.5\ mm}$ to - $0.92_{P,\ in\ the\ fraction\ larger\ than\ 0.5\ mm}$, $p <= 0.05$, N = 34, all R, except Ca, Ba, Zn in the fraction smaller than 0.5 mm are statistically significant). All these elements are more or less in equilibrium in both analysed fractions, which means that they are characteristic especially for phosphate cement of aggregates. A statistically significant correlation between P and aggregates larger than 0.5 mm (R = - 0.92, $p < 0.05$, N = 34) on the one hand, and aggregates larger than 0.5 mm and stratigraphically stable fossil remains (R = - 0.76, $p < 0.05$, N = 33), on the other, shows that specific chemical processes took place in early diagenesis in the period of a maximum of a thousand years after deposition of the fossil remains. Phosphate compounds, as a result of these processes, have been preserved unchanged right up to present.

The link between the first and second group is Na, which is in statistically significant correlation with P in both fractions (R = $0.66_{\text{fraction smaller than 0.5 mm}}$, $p < 0.05$, N = 33, R = $0.91_{\text{fraction larger than 0.5 mm}}$, $p < 0.05$, N = 36).

Elements of the third group (U, Co, Ni and Pb) are distributed in profile in an essentially different way than all other elements and aggregates. U is thus an element that has a different history in Divje babe I than other analysed elements.

Since Th is of very low mobility and since bone, whether fresh or fossil, contains very little Th (Schwarcz, Blackwell 1992), while the concentrations of Th in the sediments in Divje babe I were in average 20-times higher than in bones (*Table 4*), Th cannot be the cause of the error in U series dating. The cause is U, which is absorbed in bones in the process of fossilisation. So the most weathered bones in Divje babe I contain more U (1.1 ppm) than the least weathered bones (0.2 ppm). In comparison with some sites, these values are low (see Blackwell, Blickstein 2000, Table 1), but still within the limits of the normal range (Schwarz, Blackwell 1992). There is several times more U in the sediments of Divje babe I than in bones (*Table 1*), but still little in comparison with other sites (see ibid). It must be pointed out that in weathered limestone (and dolomite?) clasts U concentration decreases (Zupan Hajna 2003, 56) while in weathered bones U concentration increases (Schwarz, Blackwell 1992, p. 8, Fig. 12.5).

While Th is poorly soluble and practically does not migrate with water, the reverse is the case with U. We assume a certain migration and redistribution of U in the profile of sediments in Divje babe I. This is clear from comparison of the distribution of the two elements in the profile (*Fig. 1:* a,b).

Th and U in dolomite clasts in the profile are in statistically significant correlation (R = 0.75, $p < 0.05$, N = 32). Clasts represent dolomite bedrock from which pressumingly the majority of the sediments in Divje babe I were formed by weathering. The sediments are undoubtedly enriched with allochthonous U and Th, so that the content of the two elements in comparison with the dolomite bedrock is increased by several times (*Fig. 4*). The process of enrichment of Th and U to the present levels did not take place linearly with time.

Between U in the sediments and U in the dolomite bedrock is a statistically significant correlation in the profile (R = 0.74, $p < 0.05$, N = 31). Between the Th in the sediments and the Th in the dolomite bedrock there is a smaller, but still statistically significant correlation in the profile (R = 0.52, $p < 0.05$, N = 31). The U is deposited in the sediment somewhat unevenly. Layers 2 - 4 were extremely enriched with U at some unknown time in the last 35,000 years (*Fig. 5*). There are not such large deviations observable for Th in individual layers (*Fig. 5*). The U in profile has a further particularity, in contrast to Th and the other elements in the Th group (Na, K, Rb, Y, lanthanides, Zr, Fe, Al and Si). In Layers 2 to 12 - 13, the values of U in the fraction smaller than 0.5 mm and in the fraction larger than 0.5 mm are fairly equal. In other layers, with two exceptions, the values of U in the fraction smaller than 0.5 mm are considerably higher than in the fraction larger than 0.5 mm (*Fig. 1:* b). We can explain the particularity either by a smaller presence of U in particles smaller than 0.5 mm in Layers 2 to 12 - 13, or with different processes (absorption? of U in the sediments of Layers 2 to 12-13 and adsorption? of U in the sediments for the majority of layers of the lower part of the profile).

The part of the profile (Layers 8 c - 17 a_2) that is enriched with Th, has lowest U, even lower than Th. Except in Layer 2, there is essentially more U than Th above and below this part of profile. The U above and below layers 8 c - 17 a_2 also deviates more than Th from the average contents of U and Th in the dolomite which were calculated from the values of fraction 40 mm < x < 60 mm (*Fig. 4*). The only sensible explanation is that the sediments above and below this part of the profile were diagenetically enriched with U. The question is what took place in Layers 8 c - 17 a_2?

Layers 7 to 11 - 12, for which aggregates, cavernously corroded dolomite clasts and bones are characteristic, represent the most humid phase in the time of deposition of sediments in Divje babe I (Turk et al. 2002). The majority of authigenic aggregates, which are causally connected with mass fossil remains of cave bear, grew in this phase. Below, and especially above this part of the profile, there are essentially fewer aggregates because there are also essentially fewer fossil remains (*Fig. 2* and *3:* a). In fact, the humid phase could have started a great deal earlier, in Layer 17 a_2, when the content of elements of the Th group (Na, K, Rb, Y, lanthanides, Zr, Fe, Al and Si) increases in the fraction smaller than 0.5 mm and remains high right up to Layer 7. In this humid phase, which could be placed within a time span of several tens of thousands of years judging from ESR dating, much of the U from Layers 8 c - 17 a_2 was gradually leached and moved to lower layers. The process of leaching and deposition of U may have been uniform and constant, or individual periods with increased leaching and deposition of U may have been followed by extended intermediate periods with normal leaching and deposition of U. In this way, the bones in the sediments received ever new and ever younger amounts of U, which affected the determination of their age with U series and also by the ESR method.

If we start from the fact that Th is very poorly soluble and presume that it was not mobilized, we can roughly estimate the original amount of U in the profile with respect to Th.

In profile, Th variation in the fraction smaller than 0.5 mm (*Fig. 1:* a), completely dominates the relation between Th and U in individual fractions and in the entire sediment (*Fig. 6:* a,b). We suspect that U was distributed similarly in the profile as at present Th in the fraction smaller than 0.5 mm, or as the ratio between the total Th and U. Since there is approximately twice as much U in the dolomite bedrock as Th, all synsedimentary values of U were presumably larger than the present values of Th. This presumably means the following for the layers dated by U series (see *Fig. 4*):

Layers 2 and 11 - 12 are presently presumably depleted with U, Layer 11-12 more than Layer 2. In the process of mobilisation of U, much U was occasionally absorbed in bones, which rejuvenated their age determined on the basis of U series. Layer 11-12 received additional U much later in relation to its deposition

than Layer 2, presumably at the time of leaching of Layer 8 c, and in view of the different radiometrically determined ages, in the last 16 ka. Besides, it could have already before this received additional U.

Layers 17 a_3 and 19/20 contain at present essentially larger U than Th, which is to be expected. Both layers in the past received additional U as a result of the leaching of higher lying layers, in which now U is depleted. The uranium that was leached, for instance from Layer 17 a_2, would rejuvenate Layer 19/20 more than Layer 17 a_3.

In connection with this explanation, a number of questions arise.

Firstly, how could Layer 11-12 postsedimentarily receive major U without this quantity of U at least partially remaining absorbed in the sediment until today, as it remained in Layers 17 a_3 and 19/20? Secondly, why was the U in bones of Layer 11 - 12 not leached, which would result in a greater (apparent) age of the bones?

The following answer is possible: the U that was absorbed in the bones also remained in them, but the U in the sediment of Layer 11 - 12 was later leached. Different increases-decreases of U concentration in the weathering of rock and bone corroborates such an explanation.

Both questions can also be justifiably raised for the bones in Layer 2, where perhaps a solution to the issue is offered. In Layer 2, there is at least one indicator of an actual increase in the content of U, since the U in the sediment greatly deviates from the average dolomite in the fraction 40 mm < x < 60 mm (*Fig. 5*). In other layers, except in Layers 3 and 4, this deviation is essentially smaller. The great deviation in Layers 2 - 4 could be linked to the long interruption in sedimentation. Since elsewhere in the profile, despite the lithologically demonstrated gaps in sedimentation (see Turk et al. 2001; 2002), such large deviations do not occur, we suspect that with the deposition of new sediments, the accumulated U could have been leached and redistributed to deeper layers.

We suspect major gaps in sedimentation also on the boundary of Layers 6 and 7, below layer 11 - 12 and on the boundary of Layers 17 a_1 and 17, independently of radiometric dating which could similarly show sedimentation gaps (Turk et al. 2001). These interruptions could have influenced the U series dating of bones in Layers 11 - 12, 17 a_3 and 19/20, if Layers 7 - 8 c, 12 - 15 and 17 - 17 a_2, which at the time without sedimentation were located from 0 to 50 cm below the surface. They were enriched with uranium if this U in the period after reestablishment of sedimentation was leached and redeposited in lower layers. The longer the interruption in sedimentation, the greater was the presumed effect on migration of U, and thus on the U series dating. This could also affect dating by the ESR method, in which the radiation dose is important, which is dependent on the concentration of U in all sediment components.

Deposition of U in bones and sediments of Divje babe I occurred in an open system. Its absorption did not take place linearly, nor did it occur early or late after deposition of the bones as the models envisage (Grün et al. 1988; Blackwell, Blickstein 2000), but was most probably controlled by a combination of all three possibilities. Long lasting interruptions in sedimentation also strongly affected the remobilisation and deposition of U, and are presumably the main cause for the irregularities in determining the age with the U series method, and indirectly also with the ESR method. Phosphate cements in Divje babe I, which in pure form would have been a more suitable substance for U series dating, were insensitive to such disturbances (Schwarcz, Blackwell 1992, 6).

Acknowledgement

We thank Prof. Dr. Simon Pirc for useful comments on English version of our paper.

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