

Chemical composition of a Pliocene large mammal (mastodont ?) bone fragment from alluvial deposits at Grad, Northeastern Slovenia

Kemična sestava odlomka kosti velikega pliocenskega sesalca (mastodonta?) iz rečnih sedimentov pri Gradu v severovzhodni Sloveniji

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Abstract

Upper Pliocene alluvial deposits outcropping at Grad, Northeastern Slovenia, contain bone fragments which very possibly belong to a mastodont. The bones are altered to apatite with outstanding abundance of As, Sr, Be, U, Y and Hg. Normalised REE abundance shows a consistent decrease of LREE to Eu, and then an increase of HREE, with almost equal normalised La_N and Yb_N values.

Kratka vsebina

Zgornjepliocenski rečni sedimenti pri Gradu vsebujejo odlomke kosti, ki najverjetneje pripadajo mastodontu in so spremenjene v apatit. V kemični sestavi močno izstopajo sorazmerno visoke vsebnosti As, Sr, Be, U, Y in Hg. Normirane vsebnosti lantanidov kažejo padanje od La do Eu in nato ponoven porast do Yb tako, da sta normirani vsebnosti La_N in Yb_N približno enaki.

Introduction

Apatite (fluorapatite, hydroxyapatite and carbonate apatite) is the most commonly occurring phosphate group in the nature. Phosphate minerals can precipitate in low temperature environments, very commonly by the aid of microorganisms (O'Brien et al. 1981). Apatite precipitated by macroorganisms include bones (hydroxylapatite, carbonate apatite) and teeth (fluorapatite). Crystal structure of apatite enables incorporation of many trace elements (Finlay et al. 1999; Cathcart & Gulbrandsen 1971), particularly uranium and yttrium. But many secondary phosphate minerals enrich-

ed with REE and other trace elements, like rhabdophane and florencite, may crystallise on etched surface of apatite during initial stage of weathering (Taunton et al. 2000).

Upper Pliocene through-cross bedded fluvial pebbly sands outcrop at Grad, close to basaltic volcanoclastic complex. Bone fragments are not rare, but very poorly preserved and well rounded owing to transportation in a very dynamical environment of braided rivers (Kralj 2001). Their precise determination is not possible (Vida Pohar, pers. comm.), but very probably, they belong to a mastodont. This contribution deals with alteration mineralogy and chemical composition of a bone fragments analysed during

the author's Ph.D. studies of volcanoclastic rocks and their depositional environment (Kralj 1995).

Geological setting outline

Goričko is a hilly district in Northeastern Slovenia characterised by widespread surface occurrence of Upper Pliocene clastic sediments (Fig. 1). Goričko forms a part of the Mura basin, the southwesternmost of several in the Tertiary system of Pannonian basins. Intensive subsidence of this area is closely related to the activity of deep-seated Raba fault, and it was followed by rapid sedimentation, directed from northwest to the southeast. Coarse-grained material was sedimented in the environment of alluvial fan which evolved in time and space into the environment of braided rivers. Sandy gravels and gravelly sands were dominating deposits. The pebbles are well rounded and mainly of quartzite composition.

Contemporaneously with sedimentation of alluvial fan deposits, alkali basaltic volca-

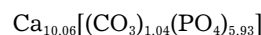
nism occurred. The main style of eruptions was explosive, hydrovolcanic, and it mainly produced wet pyroclastic surge deposits. Fluvial currents rapidly redistributed pyroclastic deposits and resedimented them together with non-volcanic fluvial sediment. Mixed volcanogenic-fluvial deposits infilled the crater and its vicinity. In the final stage of volcanic activity, large debris flows were produced by hydrovolcanic explosions devastating the crater surroundings.

Braided rivers occurred after cessation of volcanic activity. They rapidly infilled lower parts of the existing paleorelief and flattened the area. Braided river deposits do not contain any traces of volcanic material. Mastodont bone fragments occur as a channel lag deposit.

Mineralogical and chemical composition of the bone fragments

The bone fragments were studied by the means of polarising microscope, X-ray diffraction and chemical analysis. Chemical analysis was performed in X-RAL Laboratories in Ann Arbor, the United States of America. It comprises abundance determination of 14 major oxides and 56 trace elements by wet chemical method, XRF (X-Ray Fluorescence), ICP (Inductively Coupled Plasma Source) and MS (Mass Spectroscopy).

Under the microscope, apatite replacing hard tissues of the bone shows very low – light to dark grey birefringence colors, and microcrystalline texture. X-ray diffraction patterns indicate that the mastodont bone has been replaced by carbonate apatite and some limonite. Ideal stoichiometric formula of carbonate apatite is $\text{Ca}_{10}[\text{CO}_3(\text{PO}_4)_6]$ or $\text{CaCO}_3 \text{Ca}_9(\text{PO}_4)_6$, although its crystal structure may accommodate a number of other ions and trace elements, too. Calculation, based on chemical analysis (Tab. 1), however, has shown that the real composition is very close to ideal.



Apatite, which replaces the studied mastodont bone is particularly rich in arsenic, uranium, quick silver and yttrium. Distribution of rare earth elements (REE), normalised to chondrite values after Nakamu-

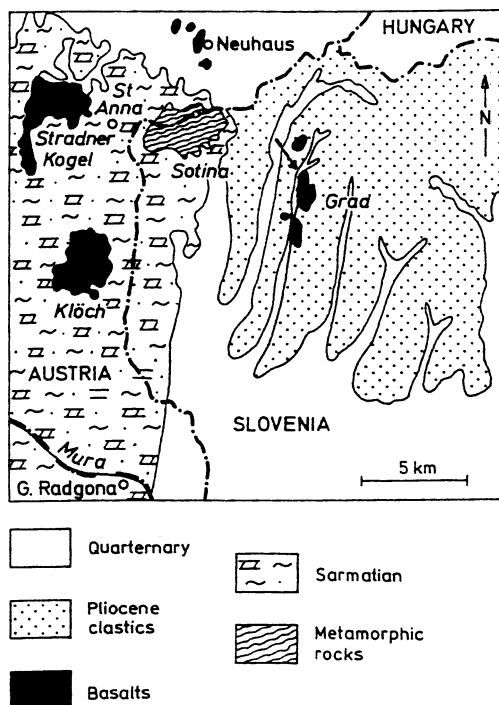


Fig. 1. Simplified geological map of Western Goričko (after Pleničar, 1968)

ra (1966) shows a decreasing trend of light rare earth elements (LREE) reaching the lowermost point at Eu, and then normalised values of heavy rare earth elements (HREE) increase, so that Yb reaches almost the same normalised value as La (Fig. 2). Comparison with the composition of bulk Earth shows

extremely low abundance of Ba and Zr, and high for Cs, La, Sr, Y and Yb (Fig. 3).

Conclusions

The bone fragments, found in Upper Pliocene alluvial sediments at Grad consist of

Table 1: Chemical composition of the bone fragment from alluvial gravelly sands at Grad

Oxide/Element	Unit	Sample GG07	Oxide/Element	Unit	Sample GG07
SiO ₂	wt. %	0,96	Pd	ppm	2
TiO ₂	wt. %	0,01	Ag	ppm	<0,5
Al ₂ O ₃	wt. %	0,55	Cd	ppm	0,7
Fe ₂ O ₃	wt. %	3,78	In	ppm	<0,5
FeO	wt. %	0,1	Sn	ppm	13
MnO	wt. %	0,12	Sb	ppm	6,1
CaO	wt. %	45,3			
MgO	wt. %	0,20	Cs	ppm	<1
Na ₂ O	wt. %	0,25	Ba	ppm	<10
K ₂ O	wt. %	0,01			
P ₂ O ₅	wt. %	33,4	La	ppm	15,5
			Ce	ppm	26,6
L.O.I.	wt. %	14,0	Pr	ppm	3,4
H ₂ O ⁺	wt. %	3,5	Nd	ppm	16,3
H ₂ O ⁻	wt. %	6,8	Sm	ppm	3,2
CO ₂	wt. %	3,6	Eu	ppm	0,99
			Gd	ppm	5,6
Li	ppm	2	Tb	ppm	0,9
Be	ppm	16	Dy	ppm	8,9
B	ppm	<10	Ho	ppm	2,66
S	ppm	<50	Er	ppm	9,3
Cl	ppm	<100	Tm	ppm	1,5
Sc	ppm	5,02	Yb	ppm	10,6
			Lu	ppm	1,89
V	ppm	29			
Cr	ppm	<10	Hf	ppm	<0,5
Co	ppm	3	Ta	ppm	<0,1
Ni	ppm	4	W	ppm	<1
Cu	ppm	11,9	Pt	ppm	<10
Zn	ppm	130	Au	ppm	3
Ga	ppm	2,0	Hg	ppm	350
Ge	ppm	20	Tl	ppm	<0,1
As	ppm	190	Pb	ppm	2
Se	ppm	<0,5	Bi	ppm	<1
Rb	ppm	8	Th	ppm	0,6
Br	ppm	2	U	ppm	110

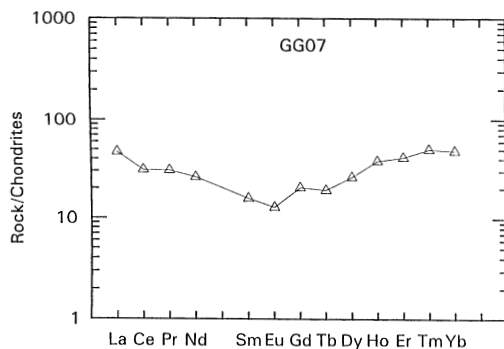


Fig. 2. Normalised REE abundance for the analysed bone fragment (sample GG07)

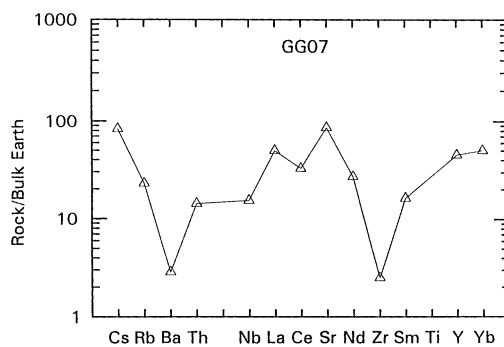


Fig. 3. Rock/Bulk Earth abundance for the analysed bone fragment (sample GG07)

carbonate apatite and some amorphous iron oxides and hydroxides. Chemical formula, derived from chemical analysis, confirmed X-ray analysis, and has shown, that carbonate apatite has nearly stoichiometric com-

position. It is hard to believe that such high concentrations of uranium, yttrium, arsenic and quick silver have been precipitated in the bone of a living organism. They could be related to later recrystallisation of apatite and its geochemical tendency to accommodate many trace elements from the environment into its crystal structure.

References

- Cathcart, J. B. & Gulbrandsen, R. A. 1973: Phosphate deposits. In: D.A. Brobst & W. P. Pratt (eds.): United States Mineral Resources. - U.S. Geol. Surv. Profess. Papers 820, 265 pp, Boulder.
- Finlay, J.A., Allan, V. J. M., Conner, A., Callow, M. E., Basnakova, G. & Macaskie, L.E. 1999: Phosphate release and heavy metal accumulation by biofilm-immobilised and chemically coupled cells of a *Cytrobacter* sp. pre-grown in continuous culture. - *Bio-technol. Bioeng.* 63, 87-97.
- Kralj, P. 1995: Litofacijesi pliocenskog fluvijalnog i vulkanklastičnog kompleksa područja Grada u sjeveroistočnoj Sloveniji. - Disertacija Sveučilišta u Zagrebu. 128 pp, Zagreb.
- Kralj, P. 2001: Pliocene clastic sediments in western Goričko, Northeastern Slovenia. - *Geologija* 44/1, 73-79, Ljubljana.
- Nakamura, N. 1974: Determination of REE, Ba, Fe, Mg, Na and K in carbonaceous and ordinary chondrites. - *Geochim. Cosmochim. Acta* 38, 757-775, Amsterdam.
- O'Brien, G.W., Harris, J.R., Milnes, A.R. & Veeh, H.H. 1981: Bacterial origin of East Australian continental margin phosphorites. - *Nature* 294, 442-444
- Pleničar, M. 1968: Osnovna geološka karta SFRJ 1:100.000, List Goričko in Leibnitz. - Zvezni geološki zavod Beograd.
- Taunton, A.E., Welch, S.A. & Banfield, J.F. 2000: Microbial controls on phosphate and lanthanide distributions during granite weathering and soil formation. - *Chem. Geol.* 169, 371-382, Amsterdam.