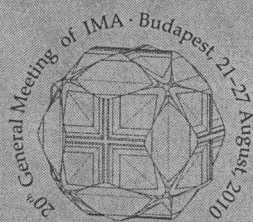




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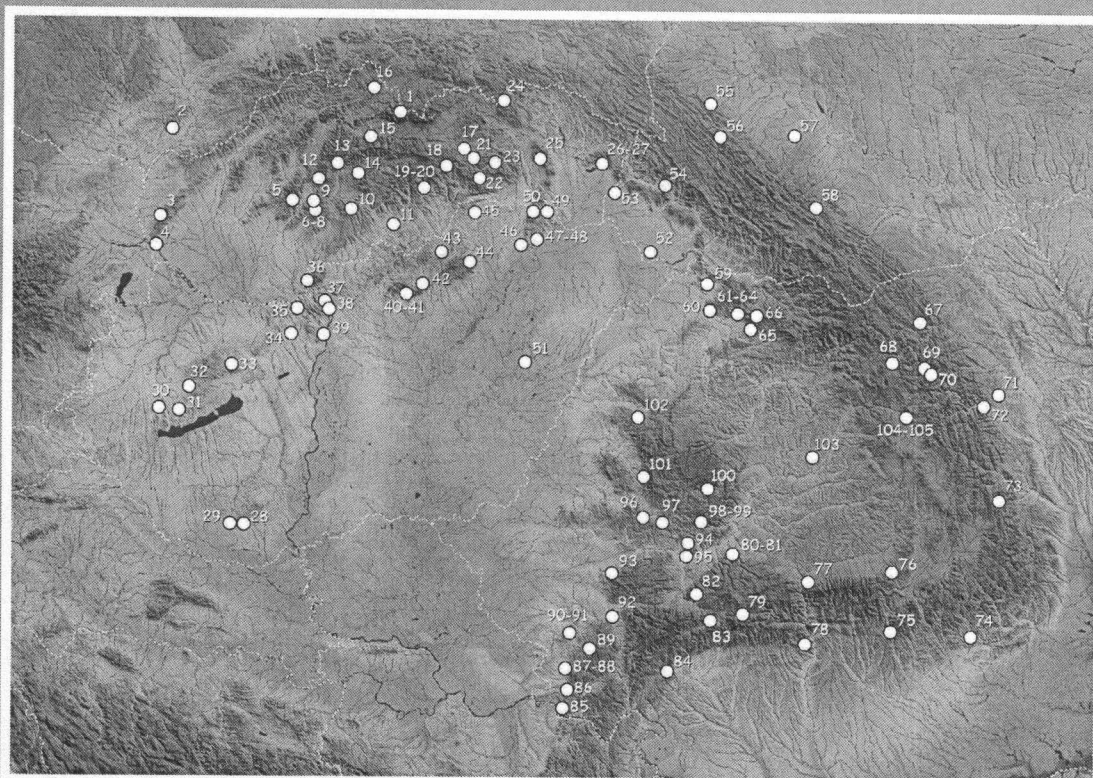
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On the cover: Map of the Carpathian region with type localities of new mineral species, rocks, fossil resins and hydrocarbons discovered in (first described from) the area, including both valid and discredited species. See the last page for the locality names corresponding to numbers. Map plotted by Ferenc Márai from the data of Gábor Papp for the exhibition of the Hungarian Natural History Museum, entitled "There is something new under the earth", organised on the occasion of IMA2010.

Calcium oxalates in renal stones

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Urolithiasis is a rather widespread disease. However till now there are no reliable methods of preventive maintenance of this illness, despite of significant efforts made in the past. Moreover, it is not completely clear, how renal stones are forming.

The majority of renal stones consist of the calcium oxalate hydrates whewellite $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ and weddellite $\text{CaC}_2\text{O}_4 \cdot (2+x)\text{H}_2\text{O}$. Origin and growth kinetics, area of stability and the phase transitions of calcium oxalate crystals were studied in details for a long time. However, the comparison of experimental data shows strong differences suggesting that some additional factors may influence formation and stability of calcium oxalate phases.

The main purpose of this work is to research the factors that raise the weddellite stability: temperature, pH, proportion of calcium and oxalate ions, organic and inorganic components of physiological solution, amount of micromycetes and bacterial-viral associates, and time of crystallization. Special attention has been devoted to study the variability of the water content in the structure of weddellite and its influence on the dehydration and phase transitions in renal stones. Besides, another purpose of the work was to reveal correlations between x and weddellite unit cell parameters and to offer on this basis an express way to estimate the amount of zeolitic water present.

The influence of crystallization conditions on the formation of calcium oxalates was investigated by simulation experiments according to a physiological medium. To estimate the variation of the amount of zeolitic water in the structure of weddellite and to reveal the ratio of x and unit cell parameters the crystal structures were refined by single crystal x-ray diffraction of nine weddellite crystals from different renal stones.

The results showed that the factors increasing the weddellite stability are supersaturation, pH, concentration of stabilizing impurities (for example CO_3^{2-} or Mg^{2+}), and the amount of protein substance. Since it was found that weddellite transforms into whewellite with time, the stability of the former presumably depends on the amount of structural water.

In the weddellite crystal structure (S.G. $I4/m$) [1] Ca atoms are coordinated in slightly distorted square antiprisms linked by a common edge to two adjacent ones to form chains along the c axis. These chains are connected to each other by common oxalate groups and hydrogen bonding of water molecules. Capolyhedra chains form channels occupied by "zeolitic" water molecules.

Our investigation showed that the amount of "zeolitic" water indeed causes a variation of the unit cell parameters, especially the a parameter (12.336 – 12.371 Å) as well as the interatomic spacing. For example, the distance between W1 water molecules, adjacent to the "zeolitic" water of one layer parallel to (001) varies from 3.211 – 3.287 Å.

According to the limiting values of the a unit cell parameter our result allows to estimate the variation of the x values (0.13 – 0.37 at. u.) in the weddellite crystals of renal stones. Thus in most cases x is close to the upper limit.

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[1] Tazzoli, V. & Domeneghetti, C. (1980) *Am. Mineral.*, **65**, 327-334.

Quaternary mammalian bones and teeth diagenesis in karst cavities of Middle and Northern Urals, Russia: implications of thermal, elemental and spectroscopy data

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Chemical composition and microstructure of Quaternary mammalian bones and teeth remains have been investigated by means of scanning electron and atomic force microscopy, electron probe microanalysis, trace element inductively coupled plasma mass-spectrometry, thermal and thermokinetic analysis, infrared, Raman and electron spin resonance spectroscopy.

Samples of bones and teeth remains represented 11 various sites of Middle and Northern Urals, Russia. They included Holocene and Pleistocene ornithogenic and zoogenic rodent remains from the earth surface, rock-shelters, grottoes and karst cavities [1].

The hydrolytic degradation of the organic component of bone tissue and the conversion of the inorganic constituents of bone have been registered on SEM images, e.g. porosity increase, peeling, bacterial attack, rotting, initial structure decomposition and secondary mineral formation [2].

The dynamics of elemental composition of bone have been investigated and geochemical indices were calculated. The rare earth elements (La-Lu) and high field strength elements (Y, Zr, Hf, Ta, Th, U) appear to be promising indicators of relative age estimation by tissue accumulation degree.

After thermal analysis (20-800°C) estimates of organic content determined as mass loss at 200-650°C in bone remains series have been used to reveal different age admixtures and chronological ranging.

Ion-radicals induced by thermo-chemical transformations of organic constituent in the temperature range of 200-650°C have been observed in bone (tooth) tissues. The line shape and width parameters of ion radicals have been analyzed and their age variations examined.

Phase transformation during fossilization has been examined by infrared and Raman spectroscopy in four spectrum ranges attributed to inorganic phase structural fragment vibrations (PO_4^{3-} , H_2O and OH^- , CO_3^{2-} in A and B-positions). From this, bone apatite crystallinity, degree of apatite P-O bond ionicity-covalency, carbonate-ion relative concentration and its inter-positional distribution, and alterations in bone surface micro- and nanostructure were deduced.

Several types of fossilization distinguished by correlations of organic components of bone and trace elements content have been assigned. The results obtained were used to evaluate the relative age of bone. Some questions about the degree of synchronism were discussed for the investigated series of fossil and sub-fossil rodent bone remains representing various sites in the Urals.

[1] Smirnov, N. et al. (2009) *Physical and chemical characteristics of mammal fossil bone remains and the problem of their relative age estimation. Part I. Thermal analysis and trace element mass-spectrometry*. Goshchitzky, Ekaterinburg (in Russian). [2] Votyakov, S. et al. (2009) *Physical and chemical characteristics of mammal fossil bone remains and the problem of their relative age estimation. Part II. Infrared and radio-spectroscopy, microscopy*. Goshchitzky, Ekaterinburg (in Russian).