

Hydrothermal genesis of metatyuyamunite, $\text{Ca}(\text{UO}_2)_2(\text{VO}_4)_2 \cdot 3\text{-}5\text{H}_2\text{O}$ in the Valea Rea Cave, Romania

Bogdan P. ONAC

University of Cluj, Department of Mineralogy, Kogalniceanu 1, and Speleological Institute "Emil Racovita", Clinicilor 5, 3400 Cluj, Romania (bonac@bioge.ubbcluj.ro)

Joe KEARNS

Materials Research Laboratory, The Pennsylvania State University, University Park PA, 16802-4801, U.S.A.

P. DAMM

Speleological Institute "Emil Racovita", Clinicilor 5, 3400 Cluj, Romania

William B. WHITE

Materials Research Laboratory and Department of Geosciences, The Pennsylvania State University, University Park PA, 16802-4801, U.S.A.

Sandor MATYASI

Geo Prospect, Cuza Voda 9, 3638 Stei, Bihor, Romania.

ABSTRACT. Metatyuyamunite, $\text{Ca}(\text{UO}_2)_2(\text{VO}_4)_2 \cdot 3\text{-}5\text{H}_2\text{O}$, a new mineral for Romania, occurs as canary yellow sub-millimeter-size plate-like crystals in Valea Rea Cave (Bihor Mountains). This unusual mineral has precipitated on, and in between delicate needle-like aragonite crystals. X-ray diffraction, optical and scanning microscope (including EDS), and luminescence were used to identify metatyuyamunite. The X-ray diffraction pattern can be indexed with the orthorhombic cell $a = 10.77$; $b = 8.53$; $c = 17.62$ of metatyuyamunite. From a genetic point of view it seems that tyuyamunite was first precipitated from hydrothermal solutions and in a later stage it dehydrated to metatyuyamunite.

Introduction

During the course of mineralogical sampling undertaken in Valea Rea Cave, an unidentified yellow mineral growing over a white crust was collected from a side passage. X-ray powder patterns indicate the presence of metatyuyamunite, a hydrated uranyl vanadate.

This is the first reported occurrence of metatyuyamunite in Romania. Furthermore, it is the third such occurrence in a cave environment worldwide. The two other known cave occurrences are Spider Cave (New Mexico, USA) (POLYAK & MOSCH, 1996) and Caverns of Sonora (Texas, USA) (ONAC et al., 2001). In the outside environment, metatyuyamunite is rather a common mineral, associated with uranium and vanadium deposits (LANGMUIR, 1997).

The presence of metatyuyamunite in Valea Rea Cave adds one more species to cave mineral association described by ONAC et al. (1995), GHERGARI et al. (1997), and GHERGARI & TAMAS (1999).

Geographic and geological setting

Valea Rea Cave is located on the upper part of Rea Valley, just below the top of Cărligati (Bihor Mts., Romania) (Fig. 1) (DAMM et al., 1996). Since its discovery on 1986, over 18 km of passages have been mapped to a total depth of 360 m. The main axis of the cave, the Colectorului (Collector) Gallery, is an active stream passage (20-25 l/s) approximately 3.5 km in length. Two other fossil galleries are located above the active one at 20 m and 50 to 70 m's respectively. Typically, large chambers or labyrinth passages are to be found where all three galleries interconnect.

Due to a large variety of rocks that occur in the Valea Rea - Cornu Muntilor region, one can consider it a petrographic mosaic. All geological deposits occur as narrow stripes oriented NE-SW. Three compartments are evident starting from the north and going to the south (Fig. 2) (BLEAHU et al., 1985):

- *The North Compartment* consists of andesites (bearing pyroxenes and hornblende) formed during the 1st cycle of banatitic eruptive activity (Maastrichtian – Paleogene) (STEFAN et al., 1988).

- *The Central Compartment* includes a Permian to Triassic sedimentary formation belonging to the Upper Sebisel Member of the Finis - Ferice Nappe (BORDEA & BORDEA 1972; BALINTONI, 1997).

The geological succession begins with purplish-red color quartzite sandstone, conglomerates, and shales on Verrucano facies. Locally, within some of these horizons, important concentrations of uranium were found during mining prospecting.

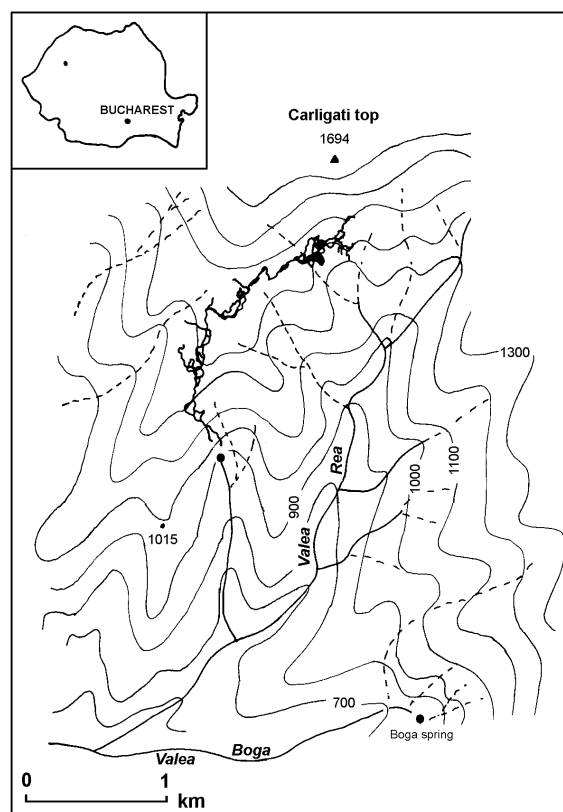


Fig. 1. Location of Valea Rea Cave.

The unit above consists of white conglomerates and quartzite sandstone of Lower Triassic age, covered by a series of 600-m thick black dolomites (\pm chert), shales and limestone breccia. Valea Rea Cave is developed mainly within the dolomite horizon of Anisian (Middle Triassic) age.

- *The South Compartment* consists mainly of granodiorite formed during the IInd cycle of the banatitic activity. Dykes of granites and microgranites having a SE-NW orientation cut through the sedimentary rocks.

The metallogenesis in Bihor Mountains is associated with the IInd cycle, characterized by bodies of intrusive, hypabyssal and plutonic rocks. Mineralizations are of pyrometasmatic and hydrothermal origin. The main paragenesis assemblages are V-Ni-Co; Zr-Ti-Cr; Cu-Mn, and Pb-Zn. Uranium was originally concentrated syngenetically in a fluvial environment. At later stage, it was mobilized by hydrothermal solutions and redeposit along fault lines in organic rich gray sandstones of Permian age (MATYASI, 1998). Hydrothermal ore minerals build up mainly in veins and hydrometasmatic bodies; locally there are impregnation bodies or simple nests (STEFAN et al., 1988).

Geochemical studies of banatitic magmatites from the northern Apuseni Mountains show values of 3.4 to 6.6 ppm for uranium, while the vanadium content range between 6 and 170 ppm (exceptionally) (STEFAN et al., 1992). The uranium concentration recorded in the Permian rocks occurring just below the cave shows values up to 1% (MATYASI, 1998).

Occurrence of metatyuyamunite

Metatyuyamunite forms yellow patches that cover white delicate crystals on both walls of a narrow-side passage (20 m in length), 300 m downstream from Ventilator Waterfall (in the upper third of the cave system) (Fig. 2). Each of these yellow patches is a few square centimeters, but altogether are spread over several square meters.

The cave temperature in the close vicinity of sample location is about 9°C whereas the relative humidity is 99-100%.

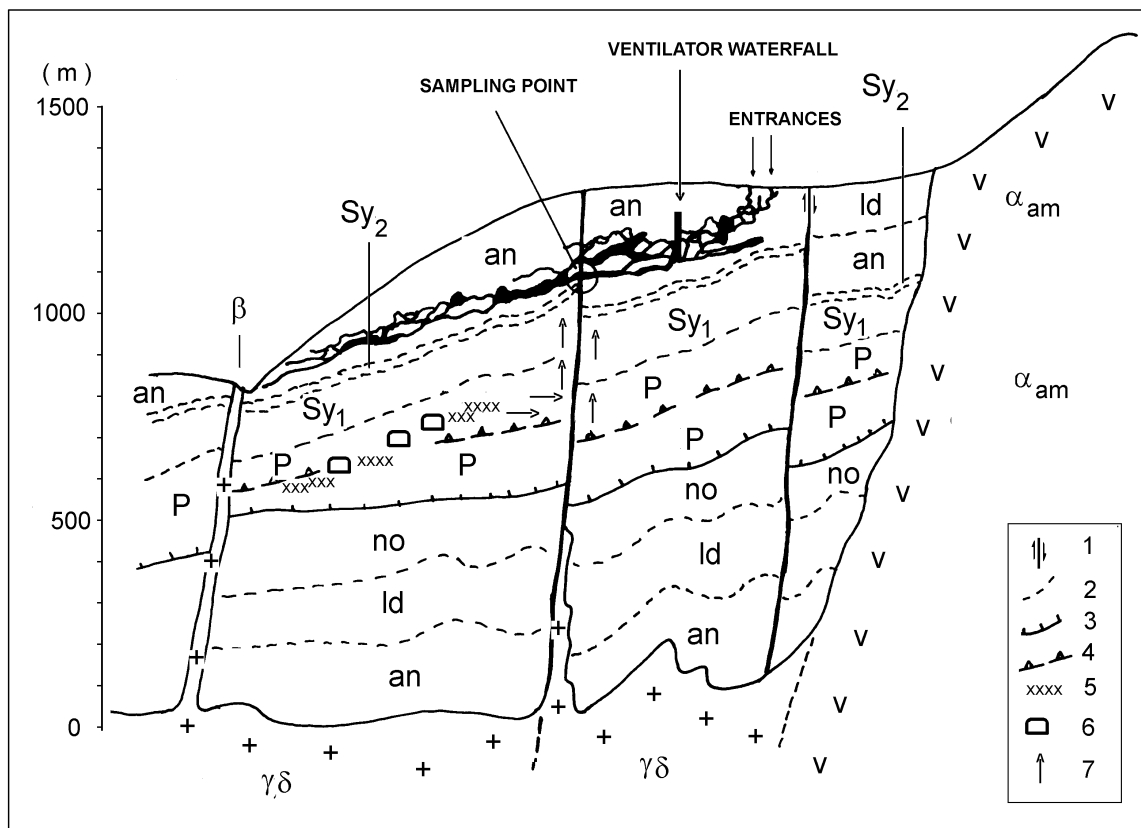


Fig. 2. Geological cross-section along Valea Rea Cave showing the lithology, tectonic features and the cave network.
1: faults; 2: geologic boundaries; 3: nappe overthrusts; 4: reverse faults; 5: mineralization zones; 6: mining galleries;
7: ascending geothermal solutions; α_{ap} : andesite; $\gamma\delta$: granodiorite; β : basalt; P: permian; Sy₁: Lower Scitian;
Sy₂: Upper Scitian; an: Anisian; ld: Ladinian; no: Norian.

Analytical methods

X-ray diffraction data

The X-ray diffraction powder pattern for metatyuyamunite was obtained on a Scintag V Pad diffractometer, (Cu-K α), using quartz as an internal standard. The scanning was continuous at a speed of 1° 2 θ /min and a time constant of 2.5 seconds. The diffractometer was operated at 45 kV and 40 mA within the 2 θ range of 5 to 80°, and refined between 8 and 33°. The X-ray

pattern shows a number of lines, all well-marked and sharp. The strongest five lines 8.32 (90), 4.16 (40), 3.25 (55), 2.36 (26), 2.10 (40) are presented in Fig. 3. Since the X-ray diffraction pattern comprises only 8 lines, the indexing of these reflections may look uncertain, but nevertheless gave a clear orthorhombic cell having, $a = 10.77$, $b = 8.53$, $c = 17.62$. These values are close to those from ICDD file 8-287 and to those obtained by POLYAK & MOSCH (1996) or ONAC et al. (2001).

The X-ray diffraction pattern for the white crust on which metatyuyamunite was precipitated is almost identical to that of synthetic aragonite (ICDD file 5-453).

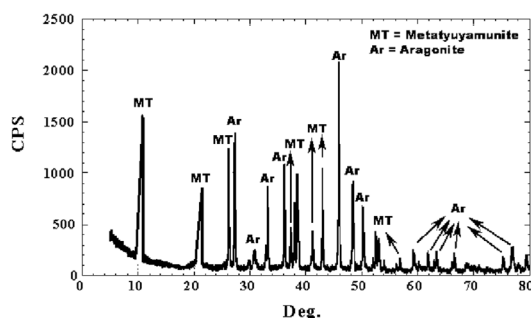


Fig. 3. X-ray diffraction pattern of metatyuyamunite.

Optical and scanning electron microscope analyses

Observations made on a Stemi 2000-C (Zeiss) binocular (50x magnification) revealed that bladed crystals of metatyuyamunite (0.1-0.3 mm in size) are sprinkled over millimeter-size, transparent to translucent, colorless to white acicular crystals and radial aggregates of aragonite. Metatyuyamunite crystals have a canary yellow color and adamantine luster.

In thin section, metatyuyamunite is colorless to pale yellow; the extinction is parallel and shows perfect rectangular cleavage.

The scanning electron microscope (SEM) investigation was conducted on a Hitachi S-3500N device. The SEM images revealed euhedral to subhedral decimicron platy-like crystals of metatyuyamunite (Fig. 4) as well as acicular crystals of aragonite. Some of the aragonite crystals are twinned.

Several crystals of metatyuyamunite were examined by means of electron probe microanalysis using an energy dispersive spectroscopy (EDS) detector attached to the SEM. The semi-quantitative elemental analysis provided by EDS confirmed the presence in all samples of uranium (~67%), vanadium (~21%), calcium (~6.5%), and oxygen.

Luminescence

A Hitachi (model 4010) spectrofluorophotometer was used to investigate the luminescence of the metatyuyamunite. Under short wave UV, the yellow crystals luminesce bright green.

Measurements of the excitation and emission spectra show the characteristic emission of the uranyl ion (Fig. 5). The sharp lines at 504, 525, and 547 nm are characteristic of the uranyl ion and in good agreement with the results obtained on the Sonora specimen by ONAC et al. (2000). The broad band centered at 450 nm is not part of the uranyl spectrum and likely arises from fulvic acid and related organic compounds incorporated into the co-existing aragonite.

Results and discussion

Hydrothermal solutions are responsible for the origin and development of Valea Rea Cave. Diagnostic features supporting this origin include exotic mineral deposits (celestine, barite, dickite, nacrite, quartz etc.), tree-form effluent chimneys, multi-story mazes, and highly corroded wall crusts (ONAC et al., 1995; GHERGARI et al., 1997).

Eh, the concentration of vanadium, and the amount of carbon dioxide mostly control the geochemical behavior of uranium (LANGMUIR, 1978; MAYNARD, 1983). Carnotite and all other uranyl minerals are soluble at low CO₂ pressures similar to those found in a cave environment. The following features are sufficient for a general understanding of the behavior of uranium in natural waters: it is soluble under oxidizing conditions unless

vanadium is present, and is insoluble under reducing conditions (DREVER, 1997).

We believe uranium and vanadium were mobilized by hydrothermal solutions moving upward through the Permian sandstones occurring below the cave. After development of cave and under subsequent vadose evolution of the cavity, uranium was transported as highly soluble uranyl carbonate complexes in neutral to alkaline, oxidizing waters. The presence of even small amounts of vanadium in solution led to immobilization of uranium as carnotite, tyuyamunite or other uranyl minerals. Uranium could also have been precipitated under reducing conditions, created by a reducing zone in the dolomite due to rich organic matter and/or sulfide minerals such as pyrite (LANGMUIR, 1997).

The problem in interpreting the presence of metatyuyamunite in Valea Rea Cave is whether it is primary or of secondary mineralization (i.e. formed by dehydration of tyuyamunite). STERN et al. (1956) determined the number of moles of water was a function of the partial pressure of water vapor. Plateaus on the dehydration curve were found at values of 5 and 8.5 moles of water per moles of Ca(UO₂)₂(VO₄)₂. Considering the wide range of water vapor partial pressure (relative humidity) recorded in cave environments the two minerals can theoretically co-exist. Our analytical investigation revealed only the presence of metatyuyamunite, which was successfully rehydrated to tyuyamunite by placing it in a moist atmosphere (the rehydrated mineral was confirmed by X-ray diffraction). Therefore, the problem mentioned above is still an open question.

Regarding the precipitation of the mineral association, the following succession is suggested. Either metatyuyamunite or tyuyamunite (dehydrated in one step to metatyuyamunite in a later stage) or both could have been precipitated where CO₂-rich groundwater equilibrated with cave atmospheric CO₂ levels. This succession would only occur after aragonite was first deposited as wall crust from a uranyl-rich carbonate complex. The presence of metatyuyamunite crystals, randomly disposed between or over aragonite crystals, may be evidence to support our theory.

The presence of uranium-vanadium compounds in Valea Rea Cave add new insight into the hydrothermal interpretation of its speleogenesis, regardless of which of the two minerals were precipitated first.

Acknowledgements: We thank Hassan Juwhari for measuring the luminescence spectra. This research was funded by CNCSIS grant 69/382 to Bogdan P. Onac.

References

- BALINTONI, I. 1997. Geology of Romanian metamorphic terrains. Carpatica, Cluj, 176 p.
- BLEAHU, M., BORDEA, S., BORDEA, J., MANTEA, G., POPESCU, A., MARINESCU, F., CIOFLICA, G., STEFAN, A. 1985. Geological map of Romania, Pietroasa sheet (1:50.000), IGG Bucuresti.
- BORDEA, S & BORDEA, J. 1972. New stratigraphic and structural data from north-western Bihor Mountains. D. S. Inst. Geol. Geof. LIX, 5: 5-13 (Romanian)
- DAMM, P., PERENYI, K., POP, C., SZUCS, S., ZIH, J. 1996. Considerations on Valea Rea Cave (Bihor Mountains). Cerc. Speol., 4: 21-23 (Romanian).
- DREVER, J. I. 1997. The Geochemistry of Natural Waters. Surface and Groundwater Environments. Prentice Hall, New Jersey (3rd ed.), 436 p.
- GHERGARI, L., TAMAS, T., DAMM, P., FORRAY, F. 1997. Hydrothermal paleokarst in Pesteria din Valea Rea (Bihor Mountains, Romania). Theor. Appl. Karst., 10: 115-125

GHERGARI, L. & TAMAS, T. 1999. Huntite - mineral formed in supergene conditions (Valea Rea Cave, Bihor Mountains). *Rom. J. Mineral.*, 79: 151-158

LANGMUIR, D. 1978. Uranium solution-mineral equilibria at low temperatures with applications to sedimentary ore deposits. *Geochim Cosmochim Acta* 42: 547-569

LANGMUIR, D. 1997. Aqueous environmental geochemistry. Prentice Hall, New Jersey, 486-511 p.

MATYASI, S. 1998. Mineralogical, geochemical and genetic study of uranium mineralizations from NW part of Bihor Mountains. Unpublished Ph.D. Thesis, University of Bucharest, pp 146 (Romanian)

MAYNARD, J. B. 1983. Geochemistry of sedimentary ore deposits. Springer Verlag, New York, 147-180

ONAC, B. P., BENGHEANU, M., BOTEZ, M., ZIH, J. 1995. Preliminary report on the mineralogy of Valea Rea Cave (Bihor Mountains, Romania). *Theor. Appl. Karst.*, 8: 75-79.

ONAC, B. P., VENI, G., WHITE, W. B. 2001. Depositional environment for metatyuyamunite and related minerals from Caverns of Sonora, Texas (USA). *Eur. J. of Miner.* 13

POLYAK, V. & MOSCH, C. J. 1996. Metatyuyamunite from Spider Cave, Carlsbad Caverns National Park, New Mexico. *NSS Bull.* 57: 85-90

STERN, T.W., STIEFF, L. R., GIRHARD, M.N., MEYROWITZ, R. 1956. The occurrence and properties of metatyuyamunite, $\text{Ca}(\text{UO}_2)_2(\text{VO}_4)_2 \cdot 3-5\text{H}_2\text{O}$. *The American Mineralogist*, 41(3-4): 187-201.

STEFAN, A., LAZAR, C., BERBELEAC, I., UDUBASA, G. 1988. Evolution of magmatism in the Apuseni Mountains and associated metallogenesis. *D. S. Inst. Geol. Geof.* 72-73(2): 195-213

STEFAN, A., ROSU, E., ANDAR, A., ROBU, L., ROBU, N., BRATOSIN, I., GRABARI, G., STOIAN, M., VÂSDEA, E. 1992. Petrological and geochemical features of the banatitite magmatites in northern Apuseni Mountains. *Rom. J. Petrology*, 75: 97-115