

Estratto da:

Per. Mineral. (1991), 60, 15-20

Kutnahorite from Caverna Pocala Soil (Trieste Karst, Italy)

Graziano Cancian
and
Francesco Princivalle

ETÀ ALPINA DELLE GIULIE
ONE DI TRIESTE DEL C.A.I.

MISC

0314

1883

IBLIOTEC A



Kutnahorite from Caverna Pocala Soil (Trieste Karst, Italy)

G. CANCIAN (*) and F. PRINCIVALLE (**)

(*) Società di Studi Carsici «A. F. Lindner», 34070 Fogliano, Gorizia, Italy

(**) Istituto di Mineralogia e Petrografia, Università di Trieste, P.le Europa 1, 34100 Trieste, Italy

ABSTRACT. — A detailed X-ray mineralogical research was carried out on the soil of Caverna Pocala (Trieste Karst), a cave well known for the rich bone deposit of Pleistocene fauna.

In a thin layer Ca-kutnahorite, kutnahorite, hydroxyl-apatite and aragonite are present in addition to calcite, quartz, feldspars and clay minerals. The appearance of both Ca-kutnahorite and kutnahorite is very interesting, as up to now they had never been found in caves. Moreover, these two Ca-Mn carbonates are always associated with hydroxyl-apatite and aragonite. Notable is also the presence of gypsum.

The origin of kutnahorites, hydroxyl-apatite and aragonite may be related both to decomposition of the bone deposit and to pedogenetic factors, occurred in a reductant environment.

In this framework the calcium carbonate may precipitate also as aragonite, because of the presence of strontium derived from bones decomposition. The origin of gypsum may be related to organic factors that occur in this reductant environment.

RIASSUNTO. — Sul suolo della caverna Pocala (Carso Triestino), grotta molto nota per il ricco deposito di ossa di fauna pleistocenica, sono state fatte ricerche mineralogiche per mezzo di diffrattometria a Raggi X.

In un sottile strato sono stati riconosciuti oltre a calcite, quarzo, feldspati e minerali argillosi calcio-kutnahorite, kutnahorite, idrossiapatite e aragonite. Di particolare importanza è stato il rinvenimento di calcio-kutnahorite e kutnahorite, dato che finora non erano mai state segnalati nelle grotte. Inoltre questi due Ca-Mn carbonati sono sempre associati a idrossiapatite e aragonite. Un'altro fatto interessante è infine costituito dalla presenza di gesso sotto forma di noduli e incrostazioni.

L'origine di Ca-kutnahorite, kutnahorite, idrossiapatite e aragonite può essere relazionata alle particolari condizioni della grotta. Infatti l'idrossiapatite può trarre origine dalla decomposizione del ric-

co deposito di ossa presente, mentre la Ca-kutnahorite e la kutnahorite si possono essere originate in seguito a fenomeni pedogenetici avvenuti in ambiente riducente.

Inoltre, per la presenza di stronzio (di derivazione ossea) il carbonato di calcio ha potuto precipitare anche sotto forma di aragonite.

L'origine del gesso può essere ricondotta a fenomeni di natura organica, avvenuti nell'ambiente riducente sopra descritto.

KEY WORD: Kutnahorite, soil, Karst, Caverna Pocala (Trieste, Italy).

INTRODUCTION

The Caverna Pocala (91VG), entirely developed in carbonates (Borgo Grotta Gigante member: Cucchi *et al.*, 1987), is a well-known cave of Trieste Karst. The cave is fairly long (about 137m) and reaches the maximal width of 37m at the bottom. The soil is mainly composed of loam, often with calcareous debris and numerous bones of Pleistocene fauna, in particular «Ursus Spelaeus». As a result of a large number of successful excavations, about one thousand bone remains and several paleolithic and eneolithic human handwork (Gherlizza and Halupca, 1988) have been found.

A thin gray layer, with carbonaceous debris at the contact, was found in the pale-brown loam. The X-Ray diffraction analysis of this layer shows a presence of two carbonates, namely Ca-kutnahorite and kutnahorite, not very common in caves. These carbonates are

always associated with hydroxyl-apatite and aragonite.

The kutnahorite is a Ca-Mn carbonate of dolomite group, discovered by Bukowsky (1901) at Kutná-Hora in Czechoslovakia. The ideal formulas for kutnahorite is $\text{CaMn}(\text{CO}_3)_2$. Ca-kutnahorite is a Ca-rich type, whose formula as reported by Gabrielson and Sundius, (1966) is $\text{Ca}_{1.48}\text{Mn}_{0.38}\text{Mg}_{0.14}(\text{CO}_3)_2$. They are usually associated with metamorphic Mn-rich deposits. Winter et al. (1981) found these minerals in metamorphic Mn-carbonates (Bald-Knob, North-Carolina, USA), and reported as formation temperature $575 \pm 40^\circ\text{C}$. In Italy, Cortesogno et al. (1979) found Ca-kutnahorite in «diaspri» of Ligurian ophiolites. Bini and Menchetti (1985) found kutnahorite as spherules intergrown with aragonite needles in the Limi di Terranuova Formation,

near Levane in the Upper Valdarno (Italy). The latter discovery is remarkable as the kutnahorite is formed in a sedimentary environment and is associated with aragonite. Their formation seems to appear due to «pedogenetic phenomena mainly related to variation in the water table level» (Bini and Menchetti, 1985).

EXPERIMENTAL PROCEDURES AND STUDIED MATERIALS

Fig. 1, shows profile and map of the Caverna Pocala, and sample location.

1 — Sample: thin white encrustation on the soil.

— Mineralogy: very abundant calcite, scarce aragonite, and rare quartz.

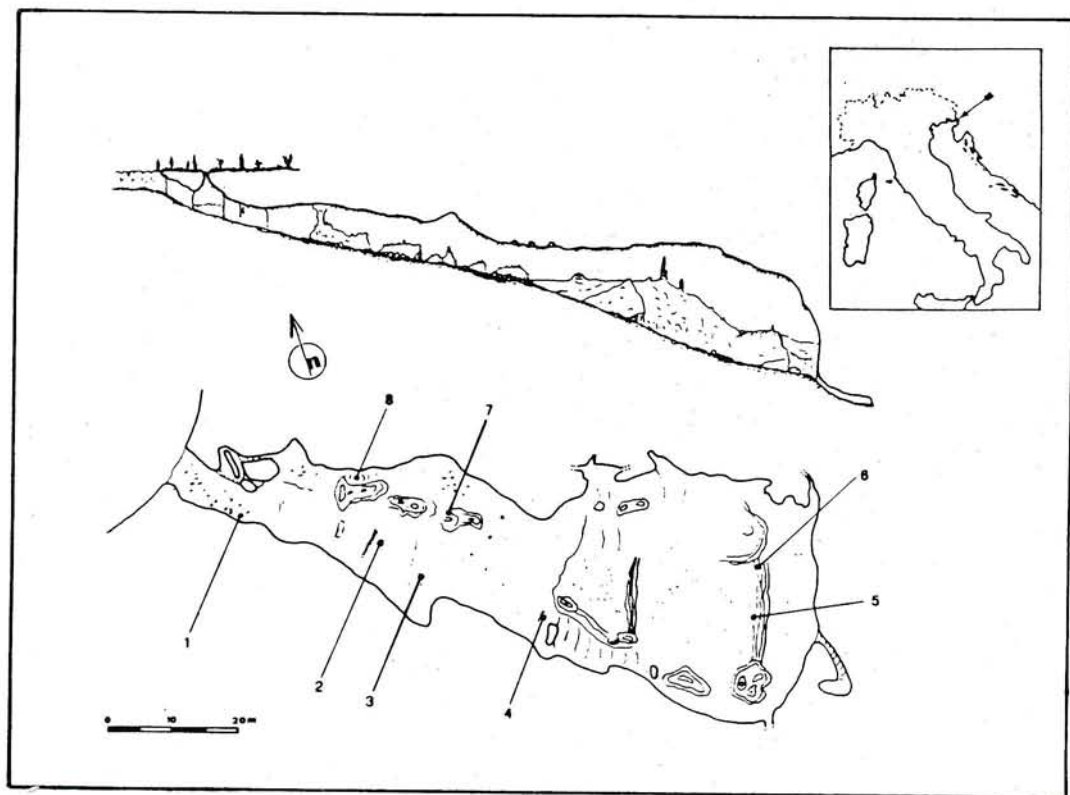


Fig. 1. - Map and profile of Caverna Pocala (Trieste Karst). The sample locations are reported in the map.

2 — *Sample*: gray layer (thickness 5-8 cm.) sometimes with thin (1-5 mm.) bleu-green layering.

— *Mineralogy*: The large number of analysed samples shows the presence of abundant Ca-kutnahorite, calcite and quartz, minor amount of aragonite, hydroxyl-apatite, kutnahorite and scarce diasporo and Fe-oxides. Ca-kutnahorite is more abundant towards the center of the layer, whereas towards the borders calcite and organic substances prevail. Ca-kutnahorite and hydroxyl-apatite are always associated; the other minerals are present in variable amounts. The thin blue-green layer shows the same paragenesis, with calcite being the dominant mineral.

— *Sample*: dark loam on the top and the bottom of the gray layer.

— *Mineralogy*: organic substances with carbonaceous debris, calcite, quartz, hydroxyl-apatite. Aragonite and kutnahorite are rare.

— *Sample*: soil over and under the gray layer.

— *Mineralogy*: clay, quartz, feldspar, calcite, dolomite, hydroxyl-apatite and diasporo. Clay is mainly composed of illite and subordinate clorite, kaolinite and smectite.

3 — *Sample*: tender white encrustations on the soil.

— *Mineralogy*: abundant calcite with scarce aragonite.

4 — *Sample*: thin tender layer similar to that of point 2, but darker.

— *Mineralogy*: abundant calcite and quartz with minor amount of hydroxylapatite, Ca-kutnahorite, kutnahorite, aragonite and rare feldspars and illite.

5 — *Sample*: pale-red layer (thickness 10-15 cm.).

— *Mineralogy*: clay and quartz are very abundant, calcite, hydroxyl-apatite and gibbsite are present in moderate amounts, whereas feldspar is rare. Clay is composed of illite, that prevail over clorite, kaolinite and smectite.

— *Sample*: dark encrustations often covering calcareous debris.

— *Mineralogy*: hydroxyl-apatite.

6 — *Sample*: little tender nodule of white-ivory color.

— *Mineralogy*: gypsum. The gypsum reflections are often similar to those of brushite, that is, a common phosphate in the caves (Cancian, 1987). In order to confirm the presence of gypsum, all the samples were heated. As a result reflections of bassanite or anidrite were obtained, proving the presence of gypsum.

7 — *Sample*: tender white-ivory encrustation of 1-2 cm thick.

— *Mineralogy*: gypsum.

8 — *Sample*: bone fragment included in small white-ivory mass.

— *Mineralogy*: hydroxyl-apatite and gypsum.

Seven samples collected from the gray layer of point 2 were accurately analyzed in order to determine lattice constant of Ca-kutnahorite and hydroxyl-apatite. The X-ray diffraction analyses were carried out using SIEMENS D500 powder diffractometer under the following conditions: radiation $\text{CuK}\alpha$ (40 kW, 20 mA) Ni filtered, speed 0.5° 2 θ /min., slits 1° . The a_0 and c_0 cell parameters were computed by means of least squares method using 10 indexed reflections. The data are reported in Table 1.

Moreover, these 7 samples were prepared for microprobe analysis with a CAMECA/CAMEBAX system equipped with four WDS spectrometers operating at 15kV and 5nA. The CAMECA-PAP program was used to convert elemental X-ray counts into weight % oxides. Unfortunately, as a consequence of the intergrown grains it was impossible to perform accurate analyses on each mineral. As an example we report the following analysis: $\text{CaO}=18.47\%$, $\text{MnO}=8.28\%$, $\text{MgO}=2.87\%$, $\text{FeO}=0.53\%$, $\text{SiO}_2=10.87\%$, $\text{Al}_2\text{O}_3=2.73$, $\text{K}_2\text{O}=1.45\%$, $\text{Sum}=45.20$, that suggests the presence of both Ca-kutnahorite and Kutnahorite, with quartz and clay.

TABLE 1

Cell parameters of Ca-kutnahorite and hydroxyl-apatite of 7 samples collected from the gray layer of the second sampling station. Standard deviation in parentheses refer to last digit.

Sample	Ca-kutnahorite		hydroxyl-apatite	
	a_o (Å)	c_o (Å)	a_o (Å)	c_o (Å)
1)	4.910 (5)	16.82 (11)	9.434 (9)	6.915 (14)
2)	4.914 (3)	16.71 (3)	9.430 (10)	6.894 (13)
3)	4.909 (7)	16.74 (9)	9.414 (9)	6.891 (9)
4)	4.920 (7)	16.63 (9)	9.457 (16)	6.862 (16)
5)	4.916 (8)	16.68 (11)	9.458 (15)	6.881 (25)
6)	4.922 (5)	16.71 (7)	9.459 (9)	6.891 (6)
7)	4.914 (7)	16.82 (10)	9.453 (15)	6.890 (17)
Mean	4.915 (6)	16.73 (9)	9.444 (12)	6.889 (14)

TABLE 2

Cell parameters of Ca-kutnahorite from literature and present paper.

	a_o (Å)	c_o (Å)
Bini & Menchetti, 1985	4.910	16.552
Gabrielson & Sundius, 1966	4.91	16.60
Present paper	4.915	16.73

DISCUSSION

Two interesting Ca-Mn carbonates, kutnahorite and Ca-kutnahorite associated with hydroxyl-apatite, calcite, quartz, and aragonite are present in a thin layer of the soil of Caverna Pocala.

As considered Ca-kutnahorite, the mean values of a_o and c_o cell parameters are 4.915 Å and 16.73 Å, respectively. These values are slightly higher with respect to those reported by other authors (Table 2). This may be due to small changes of composition (e.g. Ca content variations). The cell parameters of Ca-Mn carbonate increase with Ca content increasing, vice-versa decrease with Mn content increasing (Table 3). Thus, our Ca-kutnahorite samples probably contain more Ca than those reported by other authors (Table 2), even if the

effect of other cations as Fe^{2+} and Mg is not valuable.

Kutnahorite was identified only in two samples. The calculation of their cell parameters ($a_o=4.85$ Å and $c_o=16.47$ Å) was very problematic, due to overlapping of peaks of kutnahorite and Ca-kutnahorite. The obtained values are comparable with those reported by Bini and Menchetti (1985) ($a_o=4.897$ Å and $c_o=16.47$ Å).

The mean a_o and c_o values of hydroxyl-apatite are 9.44 Å and 6.89 Å respectively. These values are comparable with those reported by Sudarsanan and Young (1969; $a_o=9.424$ Å, $c_o=6.879$ Å). Some of the investigated samples present a_o and c_o cell parameters slightly higher with respect to those of Sudarsanan and Young (1969). This could be related to small chlorine content

TABLE 3

Variation of cell parameter of Ca-Mn carbonates with Ca content increase. a), d) rhodochrosite and calcite respectively by Effemberger *et al.*, 1981; b) kutnahorite by Peacor *et al.*, 1987; c) Ca-kutnahorite by Bini and Menchetti, 1985.

					a_o (Å)	c_o (Å)
a)		Mn _{0.930}	Mg _{0.010}	Fe _{0.060} CO ₃	4.768	15.635
b)	Ca _{0.49}	Mn _{0.496}	Mg _{0.011}	Fe _{0.003} CO ₃	4.873	16.349
c)	Ca _{0.67}	Mn _{0.260}	Mg _{0.065}	Fe _{0.005} CO ₃	4.910	16.565
d)	Ca _{0.99}		Mg _{0.010}	CO ₃	4.990	17.061

(Chlorapatite: $a_o=9.52\text{Å}$ and $c_o=6.85\text{Å}$; Mackie *et al.*, 1972).

The presence of hydroxyl-apatite may be related to bone decomposition, while as regards the presence of Kutnahorites, these may be related to pedogenetic processes occurred in a reducent environment, as those described by Bini and Menchetti (1985). This is testified by the presence of dark loam at the top of the layer, caused by the decomposition of organic substances in stagnant water.

Finally we found aragonite and gypsum, unusual to find in Karst caves. Aragonite is probably related to the presence of Sr, coming out of the bone decomposition, and occurs both in thin layer associated with kutnahorites and hydroxyl-apatite and in encrustations associated with calcite.

Gypsum is present in nodules and encrustations. It's formation may be influenced by organic factors. It is notable that in other caves (Hill and Forti, 1986) gypsum and phosphates are associated with guano deposits. Balenzano *et al.* (1984), identified ardealite, a very rare Ca phosphate-sulphate, associated with guano in a calcareous cave of Puglia (Italy). Moreover, the decomposition of organic substances in reducent environment can origin H_2S , and later, with variation of water level, oxidize to H_2SO_4 . The following reaction of H_2SO_4 with carbonates can produce gypsum (Forti and Rossi, 1987). We believe that analogous processes as described above were responsible for the gypsum formation in the Caverna Pocala.

In the summary, the decomposition of bones could allow the formation of hydroxyl-apatite and aragonite, and, pedogenetic processes under reducent conditions would be responsible for the genesis of kutnahorites and gypsum.

ACKNOWLEDGMENTS

Many thanks are due to the «Società di Studi Carsici A.F. Lindner», for sample collection, to prof. E.M. Piccirillo and prof. S. Menchetti for their critical review of the manuscript. The financial support of the C.N.R. «Centro di Studio per l'Orogeno delle Alpi Orientali (Padova)» and of the «Ministero dell'Università e della Ricerca Scientifica e Tecnologica» (MURST 40% and 60%) is gratefully acknowledged.

REFERENCES

- BALENZANO F., DELL'ANNA L., DI PIERRO M. and FIORE S. (1984) — *Ardealite* $CaHPO_4 \cdot CaSO_4 \cdot 4H_2O$: a new occurrence and new data. «Neues Jb. Mineral. Mh.», **10**, 461-467.
- BINI B. and MENCHETTI S. (1985) — *Kutnahorite from Levante Upper Valdarno (Italy)*. «Per. Mineral.», **54**, 61-66.
- BUKOWSKY A. (1901) — *Kuttenberger mangan-mineralien*. Anz. der III Congr. Bohm. Naturforsch. und Ärzte. Prague, 293, Abstracted in «Jb. Min.», **2**, 238, (1903).
- CANCIAN G. (1987) — *Ricerche mineralogiche sui fosfati delle grotte del Carso Goriziano e Triestino*. Atti VII conv. Reg. di Speleologia del Friuli Venezia Giulia. Gorizia.
- CORTESOGNO L., LUCCHETTI G., and PENCO A.M. (1979) — *Le mineralizzazioni a maganese nei diaspri delle*

- ofioliti liguri: mineralogia e genesi. «Rend. Soc. It. Mineral. e Petrol.», **35**, 151-197.
- CUCCHI F., PIRINI RADDRIZZANI C. and PUGLIESE N. (1987) — *The carbonate stratigraphic sequence of the Karst of Trieste (Italy)*. «Mem. Soc. Geol. It.» XL-1987, 33-44.
- EFFEMBERG H., MEREITER K. and ZEMANN J. (1981) — *Crystal structure refinements of magnesite, calcite, rhodochrosite, siderite, smithsonite and dolomite, with discussion of some aspects of the stereochemistry of calcite-type carbonates*. «Z. Kristallogr.», **156**, 233-243.
- FORTI P. and ROSSI A. (1987) — *Le concrezioni poliminerali della grotta di S. Ninfa (Trapani): un esempio evidente dell'influenza degli equilibri solfuri-solfati sulla minerogenesi carsica*. «Atti e Mem. Comm. grotte Boegan», **26**, 47-64, Trieste.
- GABRIELSON O. and SUNDIUS N. (1966) — *Ca-rich kutnahorite from Langban, Sweden*. «Arkiv. Min. Geol. Stockholm», **4**, 287-290.
- GHERLIZZA F. and HALUPCA E. (1988) — *Spelaeus*. C.A.T., Gruppo Grotte, Trieste.
- HILL A.C. and FORTI P. (1986) — *Cave minerals of the world*. «Nat. Spel. Soc. Cava Avenue», Huntsville, Alabama, USA.
- MACKIE P.E., ELLIOT J.C., and YOUNG R.A. (1972) — *Monoclinic structure of synthetic $\text{Ca}_3(\text{PO}_4)_2\text{Cl}$, Clorapatite*. «Acta Cryst.», **B28**, 1840-1848.
- PEACOR D.R., ESSENE E.J., GAINES A.M. (1987) — *Petrologic and crystal-chemical implications of cation order-disorder in kutnahorite $[\text{CaMn}(\text{CO}_3)_2]$* . «Am. Mineral.», **72**, 319-328.
- POSSNER S.A., BLUMENTHAL C.N. and BETTS F. (1984) — *Chemistry and structure of precipitated hydroxyl-apatite*. In Nriagu J.O., «Phosphate minerals», Moore P.B. ed., Springer Verlag, Berlin, New York.
- SUDARSANAN K. and YOUNG R.A. (1969) — *Significant precision in crystal structural details: Holly Springs hydroxyl-apatite*. «Acta Cryst.», **B25**, 1534-1543.
- WINTER G.A., ESSENE E.J. and PEACOR D.R. (1981) — *Carbonates and pyroxenoids from the manganese deposit near Bald Knob, North Carolina*. «Am. Mineral.», **66**, 278-289.

