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REGULAR RHOMBOHEDRIC CALCITE CRYSTALS INTERGROWTHS IN THE CAVE „PEȘTERA CRISTALELOR DIN VALEA REA" (RODNEI MOUNTAINS, ROMANIA)

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ABSTRACT

In a small cave carved in the metamorphic limestones of Piatra Rea, a whole section of the passage walls and ceiling, about 13 m long, is covered with quasi-parallel calcite crystals, up to 10-12 cm long and 2 cm thick. Crystallographic, microscopic, DTA, X-ray and spectral quantitative investigations strongly suggest a vug-type genesis. The last crystallization sequences display temporary air-rich episodes and, finally, seepage and dripping crusts witness for full-air conditions. The paragenesis which resulted from this last stage of crystallization (calcite, aragonite, strontianite, dolomite, pyrite) suggests a special chemistry of the solutions (also confirmed by the spectral analyses) and probably, a higher temperature. Calcite crystals intergrowths developed under specific conditions, which had evolved from a closed space to an aerial environment during long periods of time, in which changes of the solutions chemical composition and temperature had occurred.

Key words: regular intergrowths, calcite, aragonite, strontianite, dolomite, pyrite, paragenesis.

LES CONCRESCENCES RÉGULIÈRES DE CRISTAUX RHOMBOÉDRIQUES DE CALCITE DANS LA GROTTE „PEȘTERA CRISTALELOR DIN VALEA REA" (MONTS DE RODNA, ROUMANIE)

RÉSUMÉ

Dans une petite grotte de Piatra Rea, développée dans des calcaires cristallins, a été identifié un secteur d'environ 13 m en longueur, dont les parois et le plafond sont tapissés presque intégralement par une couche de cristaux quasi-parallèles de calcite, dont la longueur atteint 10-12 cm, pour une épaisseur de 2 cm. Les déterminations cristallographiques, microscopiques, thermogravimétriques, diffractométriques et spectrales quantitatives suggèrent la formation des agrégats de cristaux dans un espace de type géode. Les dernières étapes de cristallisation se sont déroulées dans des conditions d'aération partielle, tandis que les croûtes d'égouttement et de percolation sont apparues dans des conditions d'aération complète de l'espace. La paragenèse apparue dans cette dernière étape de cristallisation (calcite, aragonite, strontianite, dolomite, pyrite) suggère une composition chimique particulière des solutions (qui a été aussi confirmée par les analyses spectrales) et une température plus élevée. Les concrescences des cristaux de calcite se sont formées dans des conditions qui ont évolué de l'espace clos aux conditions d'aération complète, pendant un intervalle de temps assez long, dans lequel se sont produites des variations de la composition chimique et de la température des solutions.

Mots clés: *concrescences régulières, paragenèse, calcite, aragonite, strontianite, dolomite, pyrite.*

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1. GENERAL GEOLOGICAL AND KARSTOLOGICAL DATA

The metamorphic limestones from Piatra Rea are situated within Rodnei Mountains, in the Fântâna Valley. They are known as "Fântâna limestones" and occur as interbeddings in the sericite-chlorite schists with layers of black quartzite and green schists, designated as the Fântâna Formation, which belongs to the Repedea series, of Silurian age (KRÄUTNER *et al.*, 1983) (see Fig. 1)

The horizontal setting of the metamorphic limestones is ellipsoidal, their thickness exceeds 600 m, and they display a rough topography, with rocky steps, ledges and isolated cliffs.

The most characteristic endokarstic phenomena are the potholes, usually developed on tectonic fractures, and sometimes conditioned by gravitational sliding. Two of them are more than 50 m deep, with a maximum of -62 m reached in the pothole from Podul Cailor. Horizontal cavities, generally of small extent (less than 100 m), rich in speleothems and with abundant, characteristic, moon-milk deposits, developed along cracks or bedding planes.

All the cavities identified in Piatra Rea are fossil, but the massif is also known to include an underground drainage, proven by tracer tests (Adrian IURKIEWICZ *personal communication*) performed between the Știol swallets and the Fântâna spring (3.5 km straight line distance).

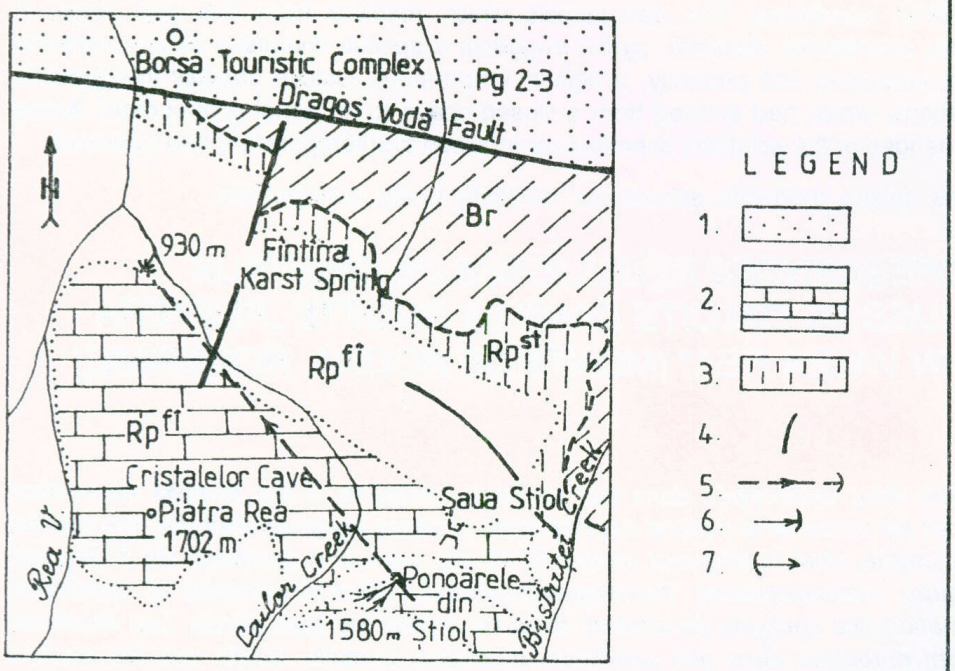

Fig.1 - Schematic geological map of the Piatra Rea area (Rodnei Mountains).1 - Paleogene (sandstones, conglomerates) Pg 2-3; 2 - Fântâna Formation Rp fi; a) - Fântâna limestones; 3 - Știol formation Rp st; 2+3 - Repedea Series; 4 - fault; 5 - underground drainage; 6 - swallet; 7 - karstic spring. *Carte géologique simplifiée de la zone Piatra Rea (Montagnes Rodnei). 1 - Paléogène (grès, conglomérats) Pg 2-3; 2 - La formation de Fântâna Rp fi; a) - calcaires de Fântâna; 3 - La formation de Știol Rp st; 2+3 La série de Repedea; 4 - faille; 5 - drainage souterrain; 6 - ponor; 7 - source karstique.*

2. DESCRIPTION OF THE CAVE

Pestera Cristalelor din Valea Rea is situated on one of the ledges of the rocky spur called Cătînul Izvorului, located on the left bank of Izvorul Cailor Creek, 400 m downstream of Cascada Cailor falls. It has been discovered by Speo-Montana Baia Sprie Club in 1989. It consists of a single ascending passage, usually fossil, still preserving traces of a temporary water course. The passage is developed along a crack striking SSE-S. The cave has a total length of 21 m and a depth of 1.5 m (Fig. 2).

Four meters after the entrance, a sudden lowering of the ceiling is followed by a 13 m long section, where the walls and the ceiling are almost entirely covered with a

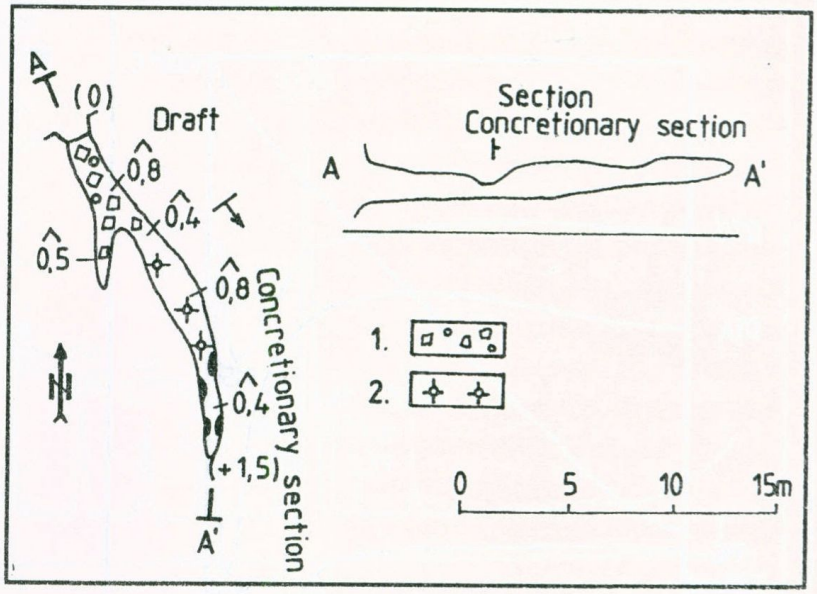

Fig.2

Crystals Cave: draft and section. 1 - incasion gravels; 2 - calcite intergrowths crystals.

Grotte des Cristaux: plan et section. 1 - gravier d'incazion; 2 - groupement des cristaux de calcite.

crystallized carbonate crust, 10-12 m thick, with points of crystals partly smoothed by dripstone deposits. Close to the end of the passage, the floor is decorated too, but only with dripstone.

3. DESCRIPTION OF THE CALCITE RHOMBOHEDRONS INTERGROWTHS

A cross-section through the crystallized calcite layer indicates the presence of three sequences, with distinct features.

The bottom layer is 2-3 cm thick and consists of prismatic bodies, with thicknesses of 5-6 mm, covered by iron oxide-hydroxides films on the crystallographic surfaces.

A median, 6-8 cm thick section follows. It is white, locally translucent, and includes rhombohedral crystals prolonging those of the bottom layer, although with increased thickness (up to 2 cm), so that a single crystal of the median layer encloses two or three crystals of the bottom layer, yet strictly preserving the initial orientation. The outer section, up to 5 cm thick, consists of alternating, sub-centimetric sequences of either transparent or opaque, white, grey or yellowish calcite, moulding the crystallographic surfaces of the median layer, which are delineated in this way. The terminal section displays protuberances covered by a thin crust, under which the extremities of the crystals, consisting of an association of micro-rhombohedrons, are visible.

The remarkable feature of the entire crystalline aggregate is the preservation of the orientation of the crystallographic axes, continuously, starting from the bottom and up to the extremities of the crystals. Characteristic for the concretionary layer as a whole is the presence of the parallel intergrowths of rhombohedral crystals.

4. ANALYSIS DATA

Both crystallographic observations, and microscopic, DTA, X-ray and quantitative spectral analyses have been performed.

- The crystallographic observations indicate the presence of the rhombohedral planes (1011), the growth of the crystals having taken place along a definite direction, with the A3 axis of the rhombohedral prism parallel to the substratum and to the growth surfaces (where the supply with solutions occurred).
- The microscopic analyses performed over the three sections indicate a remarkable homogeneity. In the outer, striped section, no impurities have been noticed. The appearance is solid, with frequent twinnings, which outline the rhombohedral crystals. The splitting angle is about 75°, while the refraction indexes are highly variable as a function

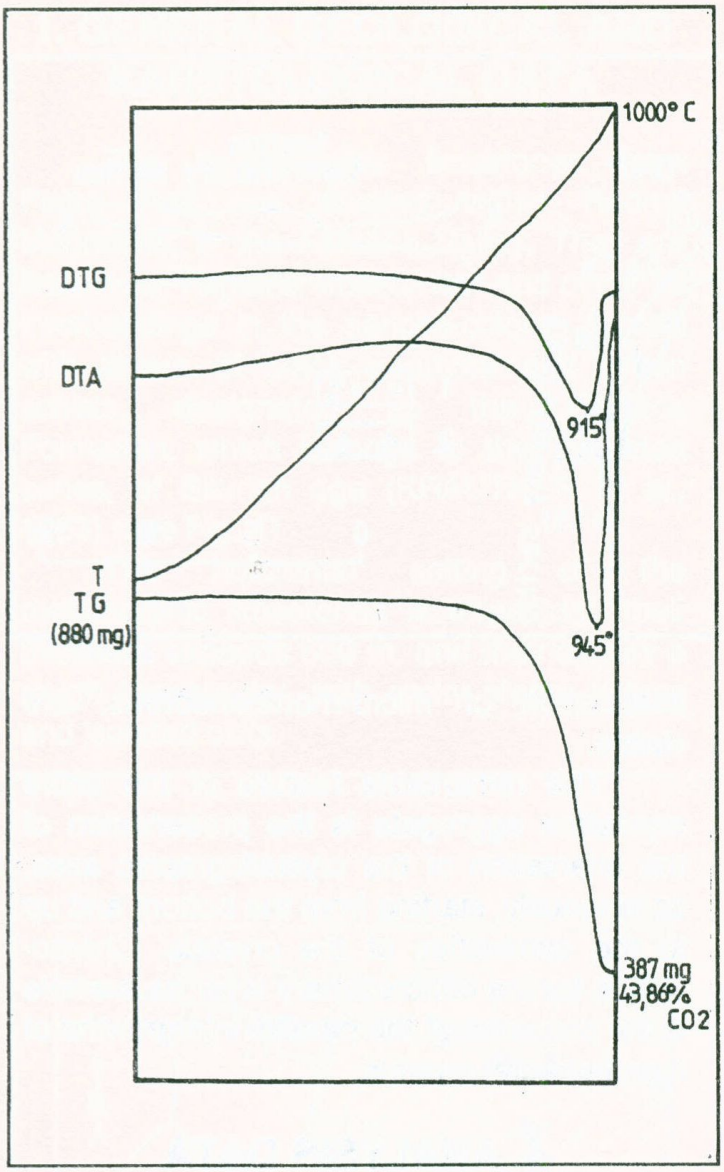

Fig.3
DTA analysis of the calcite from Crystals Cave.
L'anayse DTA de calcite de la Grotte de Cristaux.

of direction, which is a characteristic of pure calcite (relief pleocroism).

- The DTA analyses performed on samples from the median and the outer sections indicate the presence of pure calcite (Fig. 3). A single peak occurs, both on the DTG and on the DTA curves, at 915°C and at 945°C respectively, which is a characteristic of pure calcite. The high temperature at which CO_2 is lost is also indicative of the presence of pure calcite, the thermal effect being a consequence of the calcite decomposition and of CO_2 elimination.
  According to the DTG diagram, the thermal effect is accompanied by a loss of weight of 43.86%, which compared to the theoretical content of 43.97% of the calcite is demonstrating the purity of the rock.
- X-ray analyses have been performed on two samples from the outer section. Calcite is indicated by the d=3.05 Å line (the maximum intensity line for this mineral), while other very net and characteristic calcite diffraction lines are recorded at d=2.50 Å; 2.29 Å; 2.08 Å; 1.90 Å; 1.87 Å (Fig. 4). Also visible is a low intensity reflection of d = 3.39 Å, corresponding to the maximum reflection of the aragonite, traces of which exist within the sample, probably as remnants of the original aragonite, which has been substituted by the calcite through recrystallization processes. Other weak reflections, with d = 3.15 - 3.19 Å, point out that very small amounts of strontianite exist as well.
  The reflection with d = 2.85 Å is indicative of the presence of dolomite, the amount of which exceeds those of aragonite and of strontianite.
  The analysis performed on reddish calcite identified also pyrite, with d = 2.71 Å. This sample includes also iron oxide-hydroxides, which are responsible for the reddish colour. Still they could not be identified on the diffraction diagrams, because of their low degree of crystallinity.
- Four quantitative spectral analyses have been performed, as follows: nos. 1 and 2 on samples from the bottom layer, no. 3 on a sample from the median section and no. 4 on a sample from the outer section of the calcite intergrowths (Tab.1). The distinction between the sample from the outer section and the other samples is quite obvious, as indicated by the significant amounts of Ba 810 (ppm), Pb (14.5 ppm), Ni (6.3 ppm), Sc (14 ppm). It is worth noticing that Sr has been identified in all four samples.

5. DATA INTERPRETATION

The data previously discussed suggest that the parallel rhombohedric calcite crystals intergrowths started their evolution in a vug-type space, which was completely flooded. These conditions were due to the

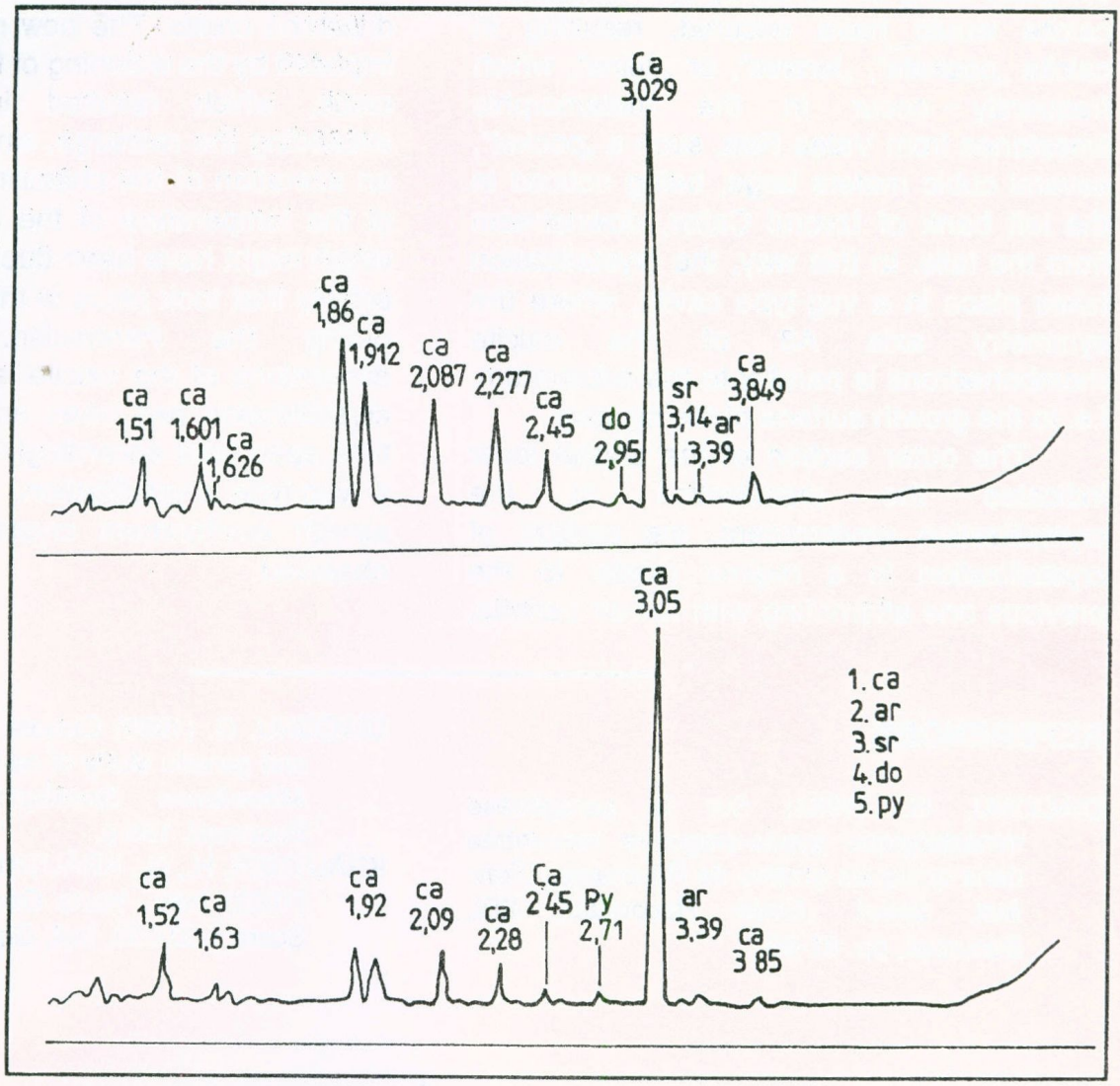

Fig.4

X - ray analysis of the upper part of the crystal intergrowths.
1 - calcite;
2 - aragonite;
3 - strontianite;
4 - dolomite;
5 - pyrite.

Les analyses de la partie supérieure des groupements des cristaux
1 - calcite;
2 - aragonite;
3 - strontianite;
4 - dolomite;
5 - pirite.

Table 1: Quantitative spectral analysis. ***Analyses spectrales quantitatives.***

Nr.	Pb	Cu	Ga	Sn	Ni	Co	Cr	V	Sc	Y	Be	Zn	Ba	Sr	Li
1	4	3	3	3	bld	bld	bld	9.5	bld	bld	3	bld	42	455	bld
2	3	bld	bld	bld	bld	bld	bld	8.7	bld	bld	bld	bld	bld	740	bld
3	3.8	bld	bld	bld	bld	bld	bld	6.5	bld	3	bld	bld	11	463	bld
4	14.5	3	bld	bld	6.3	bld	bld	10.2	14	4	bld	bld	810	625	bld
Detection limit	3	3	3	3	3	3	10	3	10	3	3	10	10	10	30

Note: bld = below detection limit

preexistence of a cavity, generated along a crack, into which crystallization was active for a long time period. The large amounts of Sr, Ba, Pb and Mg, indicated by the spectral and X-ray analyses, suggest that the abundance of these elements in the solutions of the final stage of crystallization favoured the precipitation of the calcium carbonate in an aragonitic (orthorombic) network. The processes responsible for such a behaviour are analogous to those described by DIACONU (1983, 1990), i.e. the generation of hydronium - H_3O - molecules, which impose on the virtually stagnant generating solutions specific organizations, compatible with the crystallization of the calcium carbonate in the aragonitic network.

The fact that only traces of aragonite occur, would suggest that such structures of the generating solutions have been only incipient. Since the crystals are parallel, the solutions must have been virtually stagnant, but if such circumstances had been maintained for a longer period of time, a

complete filling of the cavity with crystallized calcite would have occured, resulting in calcite „pockets", „lenses", or „veins", which frequently occur in the metamorphic limestones from Valea Rea, such a „pocket", several cubic meters large, being noticed in the left bank of Izvorul Cailor, downstream from the falls. In this way, the crystallization takes place in a vug-type cavity, where the symmetry axis A3 of the calcite rhombohedrons is parallel to the substratum, i.e. to the growth surface of the crystals.

The outer section of the crystal layer indicates the modification of the crystallization environment, the periods of crystallization in a regime similar to the previous one alternating with full air periods, outlined by precipitation of oxides and of dripstone crusts. The new regime has been imposed by the widening of the outflow of the crack, which resulted in a discharge exceeding the recharge, simultaneously with an alteration of the chemistry and, perhaps, of the temperature of the solutions, events which might have been due to the magmatic activity that took place in the neighbourhood during the Pannonian. The overall dimensions of the calcite layer indicate that crystallization has been active over a long time span, and accordingly the shifting from a vug-type crystallization, to a temporarily air-rich environment crystallization can be observed.

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