Geological Quarterly, Vol. 39, No. 1, 1995, p. 75–94

Tomasz DURAKIEWICZ, Stanisław HAŁAS, Zdzisław M. MIGASZEWSKI, Jan URBAN

Origin of the “calcite groats” in the Chelosiowa Cave near Kielce (Holy Cross Mts.) inferred from petrographic and isotopic investigations

The curious calcite grains (“groats”) in the Chelosiowa Cave in the Holy Cross Mts. were examined petrographically and isotopically. A model of rapid CO_2 degassing due to dehermetization of the cave interior was invoked to explain extremely negative $\delta^{18}O$ values (–11 to –21‰ vs PDB) and enrichment in ^{13}C, up to –4‰ vs PDB. The results of petrographic and geologic investigations precluded a hydrothermal origin of the “calcite groats”.

INTRODUCTION

During the geologic exploration of the Chelosiowa Cave in the Holy Cross Mts., small isolated patches of loosely-packed composite and simple calcite grains were found (J. Urban, Z. Złonkiewicz, 1989; J. Urban, 1992). The origin of these curious forms called “calcite groats” has remained unsolved so far. Similar occurrences have not been described in other reports. Isotopically similar calcite forms have been discovered in the Stratena Cave, Carpathian Mts., and Buml Cave in Bohemian Karst most recently by Dr. K. Žak (personal communication). The term “calcite groats” should not be used as a synonym of “popcorn” (J. Thailkill, 1971) or “cryogenic calcite powder” (I. D. Clark, B. Lauriol, 1992) due to different formation mechanisms.

On the basis of the conclusions derived from all the relevant data, the so-called “soda water” model is the most likely. In addition, coupled geologic, petrographic and isotopic investigations indicated that the exceptionally negative values of $\delta^{18}O$, even below –20‰ vs PDB, are not connected with hydrothermal activity, but with very fast crystallization of calcite from cold water substantially enriched in ^{16}O.

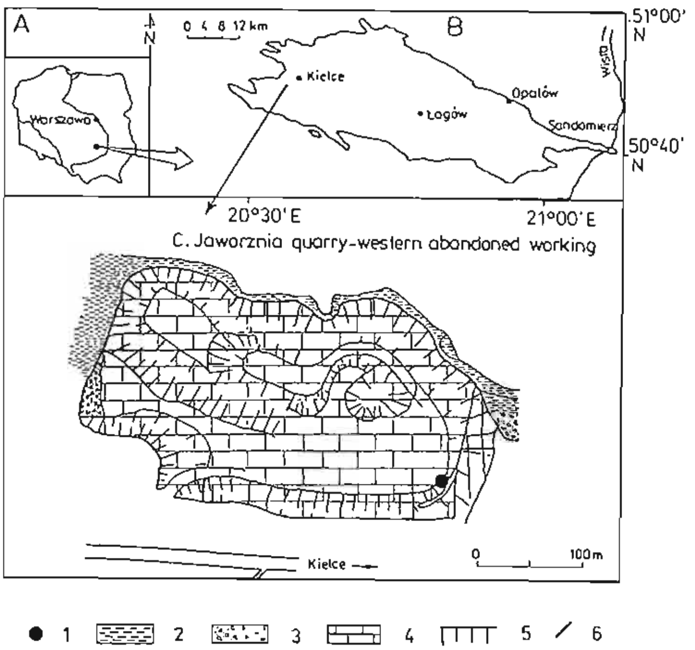


Fig.1. Location sketch of the Chelosiowa Cave (after J. Głazek, A. Romanek, 1976)

1 — cave entrance, 2 — sandstones and siltstones (Lower Triassic), 3 — conglomerates (lowermost Triassic), 4 — limestones (Middle/Upper Devonian), 5 — rock scarps, 6 — faults

Lokalizacja Chelosiowej Jamy (według J. Głazka, A. Romanka, 1976)

1 — wejście do jaskini, 2 — piaskowce i mułowce (trias dolny), 3 — zlepieńce (trias najniższy), 4 — wapienie (dewon środkowy i górny), 5 — osuwiska i ściany, 6 — uskoki

The mechanism described here might explain similar isotopic ranges encountered in calcites from other sites in the world.

GEOLOGIC SETTING

The entrance to the Chelosiowa Cave is located in the eastern face of the western abandoned quarry of Jaworznia, close to the southwestern boundary of the city of Kielce (Fig.1). The site belongs to the southern limb of the Kielce Syncline. The geologic column of this quarry consists of uppermost Givetian and lowermost Frasnian coral-stromatoporoid limestones overlain discordantly by Lower Triassic terrigenous deposits.

The limestones are medium- and thick-bedded, massive and grey. The average strike and dip values are 110/30° NNE. The nearly horizontal, overlying Permian/Triassic deposits (dipping 5–10°) are composed of fine- and medium-grained, thin- and medium-bedded sandstones, with brown-red elayey siltstone interbeds (A. Romanek, 1974; J. Głazek, A. Romanek, 1976).

Breccias consisting of limestone pebbles, cobbles and boulders cemented by Triassic material are exposed in some places, including the direct neighbourhood of the cave. According to M. Kuleta (unpublished data) these are the sediments of numerous alluvial fans, accumulated along a morphological scarp that may have been shaped as a result of tectonic movements and/or karstic phenomena.

The main cave occurs within the Devonian bedrock and comprises numerous chambers, vaulted rooms, and narrow passages reaching at least 2.5 km. It is the longest cave in the area of extra-Carpathian Poland. The cave is developed horizontally; the differences between the bottom levels of individual chambers span 30 m. The lowermost site, a karstic well, reaches the Devonian aquifer. The oldest traces of underground karst formation in this bedrock originated in Triassic time, as evidenced by a palaeomagnetic investigation (J. Nawrocki, personal communication). By far, most of the preserved cave originated in the Pliocene. Beginning from South-Polish Glaciation time (Mindel, Elsterian) the cave was cut off from the surface (L. Lindner, 1977). Therefore the cave could have been isolated from the atmosphere for a long time. The whole cave, or at least its major portion, was located above the aquifer from (at least) the Eemian Interglacial. The present-day entrance of the cave was exposed by open excavation of the bedrock (a deep quarry) in the sixties and seventies of this century.

Many unique and morphologically diversified speleothems and related deposits, as well as erosional forms are exposed here. At least two generations of speleothems may be distinguished: (1) the older represented by large-size calcite varnish with stalactites and stalagmites yelding a radial crystallization structure; all these forms have signs of meehanical and strong chemical corrosion; (2) the younger characterized by small, but coarse-crystalline stalactites, commonly having nongravitational forms. These stalactites apparently formed very slowly under conditions of total cave isolation from the surface.

Aside from the vadose calcite described above, the cave walls are cut by white and pink hydrothermal calcite veins (this calcite will be referred to as "różanka").

ANALYTICAL PROCEDURES

The "calcite groat" samples were examined by petrographic and isotopic methods. Microscopic examination was performed with a *MST 131 PZO PL* Warszawa stereoscopic microscope and an *Amplival Carl Zeiss Jena* optical microscope. To identify carbonate minerals, combined organic and inorganic stains were applied (G. M. Friedman, 1971). In addition, X-ray diffraction analysis with a *DRON-2.5* diffractometer using Fe-filtered CuKα radiation was performed. Spectrum analysis with a *PGS-2* reticular emission spectrometer was carried out to identify trace elements in selected calcite samples. The content of MgO in the "calcite groats" was determined with an *PYE UNICAM SP-1900* atomic absorption spectrometer.

Stable carbon and oxygen determinations were performed with a modified *MI-1305* mass spectrometer on CO_2 produced according to J. M. McCrea (1950). A 15 g portion of "calcite groats" was subjected to ^{14}C analysis at the Silesian Technical University using a counter filled with CO_2 produced from the calcite grains.

The results of trace element determination in the "calcite groats",

Sample	Cu	Zn	Pb	Ag	Ni
"Calcite groats"	24	–	190	0.1	6
	10	30	110	0.1	1
	9	25	100	0.1	2
	8	10	50	0.1	1
	5	10	15	0.2	–
	155	350	920	3	–
Hydrothermal calcites	17	–	7	0.1	2
	65	–	870	–	4
	45	20	20	0.1	1
Vadose	87	–	10	–	5
	25	–	50	–	2
	100	–	9	–	3
	95	840	990	–	3
Limestone	37	–	200	–	1

RESULTS

SUMMARY OF FIELD INVESTIGATIONS

The following key-points may be drawn from the performed field work:

1. "Calcite groats" occur on surfaces of different deposits, i.e., boulders, bottom muds, calcite sediments and wall crusts at various levels. Only in one site is a patch of "calcite groats" covered by a 1.5 cm-thick silty layer. Aside from the bottom muds, the surfaces of these deposits are locally steep. The grains of "calcite groats" are not cemented to the ground.
2. "Calcite groats" occur as scattered grains within isolated patches up to several metres in diameter. The largest patch also has the greatest thickness, about 5 cm.
3. Small patches contain simple morphological forms of the "calcite groats", i.e., pins, needles and isometric grains as opposed to the larger patches, which are primarily made up of more complex forms of aggregates.
4. There is no genetic connection in occurrence of "calcite groats" and other calcite deposits, i.e.: veined calcites, calcite sediments and wall crusts. Only in a few places can "calcite groats" under calcite veins or speleothems be observed. The "calcite groats" were also found in limestone chambers devoid of any calcite precipitates. The locations of "calcite groat" accumulations have no relationship with recent sites of water penetration into the cave, as with locally occurring pools.
5. No traces of partial or total inundation of the cave during crystallization of the "calcite groats", i.e., the presence of bottom sediment remnants or high water marks on the walls, have been detected.

Table 1

calcites and limestones in ppm (A. Szczecińska, M. Kozłowska)

Co	V	Cr	Mo	Ba	Sr	Sn	Mn
7	10	2	–	630	200	–	≈ 10
–	1	1	–	150	120	–	≈ 50
–	2	2	–	370	160	–	≈ 100
–	1	1	–	360	180	–	≈ 50
–	–	–	–	200	200	–	≈ 50
–		40	0.1	10	1	–	≈ 100
2	10	–	–	15	430	–	≈ 100
7	10	–	–	40	370	–	≈ 500
6	10	1	–	20	320	–	≈ 100
6	10	4	–	80	250	–	≈ 100
3	10	–	–	230	30	–	≈ 10
4	10	–	–	500	50	–	≈ 10
8	10	–	–	760	40	–	≈ 10
1	18	1	–	25	190	–	≈ 50

6. The position of the "calcite groats" among the cave deposits attests to a relatively young age, which was confirmed radiometrically (25,000 years BP, see below).

7. In numerous sites, the "calcite groats" accumulations resemble thin-bedded layers formed by sowing grains from a certain height, i.e., their amount rapidly decreases in niches, vugs and under boulders, but simultaneously increases close to steep cave walls where they form mini fans.

PETROGRAPHY

X-ray analysis revealed that low-Mg calcite is the only carbonate mineral making up the "calcite groat" grains. This was confirmed by the chemical analysis (MgO content ranges from 0.07 to 0.20%). Aragonite was not found. Petrographic investigations of the "calcite-groats" revealed two basic morphological types:

Type I, aggradational (aggregate), is composed of the following varieties:

1. Pin- and fan-shaped, and grainy concretions with sharp edges ("hedgehogs", "roses", "wreaths" and "twigs").

2. Pin- and fan-shaped, and grainy concretions smoothed at surfaces ("brambles", "cauliflowers" and "grape bunches").

Type II, degradational (corrosive), includes:

1. Isometric grains (scalenohedrons and rhombohedrons) revealing various degree of structural degradation:

a — grains slightly altered by corrosion (insignificant edge rounding and small amounts of micropores),

b — skeletal forms of a scalenohedral- or rhombohedral-shape.

2. Plates (including "plane trusses").

3. Pins and needles, commonly with microknobs, resembling "harpoons", "fish-bones" and "combs".

The most important morphological forms are depicted in Plates I–IV. The diameter of particular grains varies from tenths of millimetres through a few centimetres. The corrosive grains are generally smaller — the smallest are the pins and needles averaging 1–2 mm in length. Microscopic examination reveals that crystallization was exceptionally fast. In thin sections, the concretions showed no sign of hydrothermal gaseous-liquid inclusions. Non-hydrothermal inclusions are chaotically arranged, showing no zonation.

The corrosive forms are the result of selective dissolution of the concretions. They constitute the majority of "calcite groats" (about 80%). Some are similar to those encountered at surfaces of hydrothermal and vadose calcites. The latter two differ distinctly in their isotopic composition from the "calcite groats". In the speleologic literature similar forms have not been described so far. Only N. P. Palmer and M. V. Palmer (1989) mentioned deposits composed of corroded calcite crystals which originated by subaerial weathering of ceilings and walls of the caves in the Black Hills (South Dakota). According to these authors, corrosion had extended over at least several million years.

TRACE ELEMENT GEOCHEMISTRY

Trace element concentrations were determined for the "calcite groats" and for comparison purposes for the hydrothermal and vadose calcites, as well as limestones. The results are shown in Table 1. Aside from local variations in abundance of heavy metals, as also found in other calcites, the "calcite groats" contain excessive amounts of Ba and Sr. It should be emphasized that hydrothermal calcites have much higher Sr concentrations than their vadose counterparts, whereas the opposite is true for Ba.

Considering these irregularities of trace element abundances, there was no common source which could be responsible for the origin of the "calcite groats". Water in which the "calcite groats" were formed, had previously percolated through pores and fissures of the cave host rock. While dissolving calcite the water incorporated trace elements from the genetically-diversified deposits, described above.

ISOTOPE GEOCHEMISTRY

Carbon and oxygen stable isotope measurements were performed on 64 samples of the "calcite groats". The results are depicted in Figures 2 and 3. The values of $\delta^{13}C$ range from –9.89 to –3.67‰, whereas $\delta^{18}O$ (relative to PDB) ranges from –20.98 to –10.85‰. To compare the variation of $\delta^{13}C$ and $\delta^{18}O$ in different calcite deposits, 19 additional samples of hydrothermal and vadose calcites (including those scraped from the walls) from the Chelosiowa Cave were measured isotopically (Fig. 2).

In general, the "calcite groats" differ significantly from other calcites because of their extremely negative $\delta^{18}O$ values, locally exceeding –20‰. Their totally different oxygen isotope composition, as compared to those of the corrosive forms on surfaces of the hydrothermal and vadose calcites, precludes their genetic relationship. The aforementioned corrosive forms reveal only small isotopic shifts (generally toward enrichment in the heavy carbon isotope) in relation to their host deposits. Such shifts have been recorded for $\delta^{13}C$

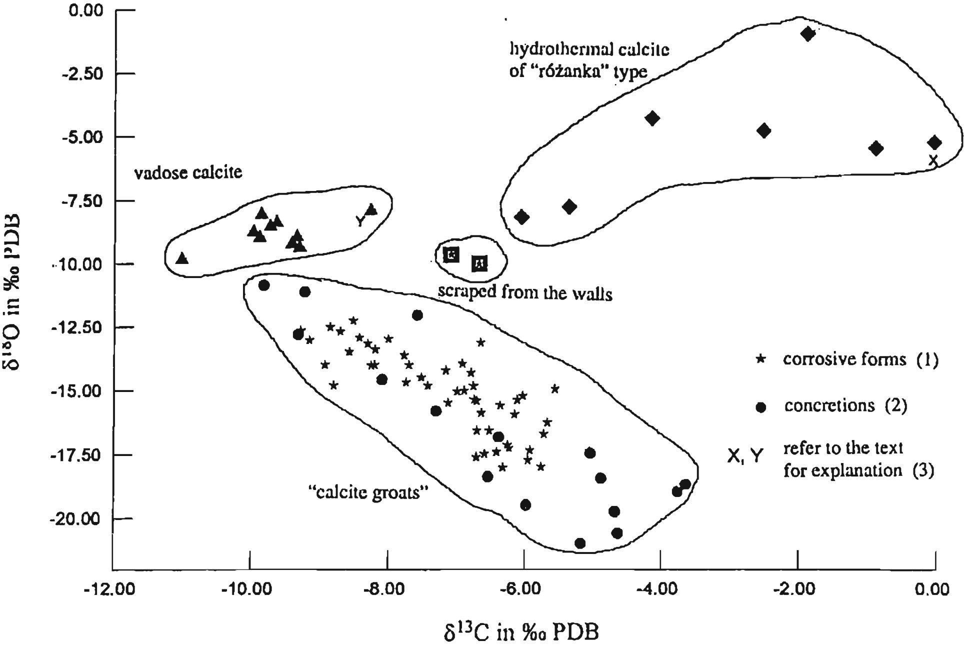


Fig. 2. $\delta^{13}C$ and $\delta^{18}O$ for various types of calcites from the Chelosiowa Cave
Wartości $\delta^{13}C$ i $\delta^{18}O$ dla różnych form kalcytów z Chelosiowej Jamy
1 — formy korozyjne, 2 — konkrecje, 3 — patrz tekst

values in strongly corroded hydrothermal forms (point X in Fig. 2) and in highly disintegrated vadose calcites (point Y in Fig. 2). These values generally fall into the range of their genetic derivatives.

There is a significant negative correlation between the $\delta^{13}C$ and $\delta^{18}O$ in the "calcite groats" (Fig. 3). A large number of concretions have the most negative $\delta^{18}O$ values, whereas the corrosive forms are generally less depleted in ^{18}O (Fig. 3). Different morphological varieties ascribed to the corrosive type of "calcite groats" do not yield substantial variations in the $\delta^{13}C$ and $\delta^{18}O$.

"SODA WATER" MODEL

Based upon the results of the geologic, petrographic, and isotopic investigations, the following model seems to be the most probable.

The model age of the "calcite groats" based solely upon ^{14}C content is 25,000 years BP. However, a more realistic estimation yields a somewhat younger age which may coincide with the Baltic Glaciation period. The cave must have been totally sealed off for a long period of time. Under such conditions, isotopically light water with $\delta^{18}O \approx -15‰$ SMOW infiltrated very slowly through the cave bedrock. Similar low $\delta^{18}O$ values were encountered in deep relict groundwaters under the Baltic Sea bottom (S. Hałas *et al.*, 1993) and, locally, in crystallization water from Miocene gypsum in the Carpathian Foredeep (S. Hałas, H. R. Krouse, 1982). On its way, the water dissolved limestone and calcites, and was finally stored in small and shallow pools. In a closed system, the carbon dioxide reached the saturation level. The pools must have been partly covered by an ice sheet. The ice formation caused further isotope fractionation, driving off the heavier oxygen isotope from the remaining water. According to J. R. O'Neil and L. H. Adami (1968) this process leads to enrichment of water with a lighter oxygen by 3.0‰ with respect to ice at isotope equilibrium at 0°C. Therefore, we suppose that the primary "calcite groats" acquired $\delta^{18}O$ values below −15‰ PDB.

The specific isolated environment of the cave may have been "frozen" for thousands of years. It resembled a bottle of soda water. "Calcite groats" formed when the cave became suddenly open to the atmosphere. The probable reasons for such an event could be gravitational collapse or forming of cracks brought about by permafrost progress or thawing. In the present phase of the investigation, none of these possibilities can be confirmed or categorically excluded.

With the decompression, the carbon dioxide gas was rapidly expelled from the water. Under such conditions, the calcite concretions started to crystallize very fast. The $\delta^{13}C$ value of the fast crystallizing calcite would be almost identical to that of HCO_3^- ions (J. V. Turner, 1982), whereas its $\delta^{18}O$ value would be significantly lower than that corresponding to isotope equilibrium with water (E. Usdowski *et al.*, 1979). The initial precipitate with $\delta^{13}C$ value of about −5‰, reflects the −5‰ value of the $\delta^{13}C$ in HCO_3^-. Taking into account 10.8‰ for the $HCO_3^- - CO_2(g)$ equilibrium fractionation at 0°C (W. G. Mook *et al.*, 1974) we obtain $\delta^{13}C$ in $CO_2(g)$ to be equal to −15.4‰. In addition, there is a significant carbon isotope fractionation between $CO_2(g)$ and $CO_2(aq)$ (7.6‰, after S. Hałas, J. Lis, 1980). Hence $^{13}CO_2$ escapes faster than $^{12}CO_2$, lowering the $\delta^{13}C$ values in both dissolved species $CO_2(aq)$ and HCO_3^-, and subsequently in $CaCO_3$ precipitated during outgassing. This process could have produced a shift in the $\delta^{13}C$ of the "calcite groats" toward lower values.

Simultaneously with the decompression, a portion of degassing water would form an aerosol, which spread a fraction of the precipitate over an extended area of the cave. It promoted crystallization of concretions at a certain distance from the host pools. The walls were probably covered by a thin film of water. If this happened, the amount of calcite that precipitated from water present on the walls could have been rather large, so that the role of the host pools in production of the initial calcite may have been minor.

After crystallization, the "calcite groats" moved gravitationally or by water and redeposited in the places where we find them today. The chain of solution, reprecipitation and recrystallization processes, that have been proceeding up to the present, caused the substantial shift in the stable isotope record of the "calcite groats" toward that of the contemporary vadose calcite. The $\delta^{13}C$ and $\delta^{18}O$ values for many samples lie along a mixing line, which passes through the most shifted values of initially precipitated concretions and those of the vadose calcite. Two samples that were scraped from the cave walls

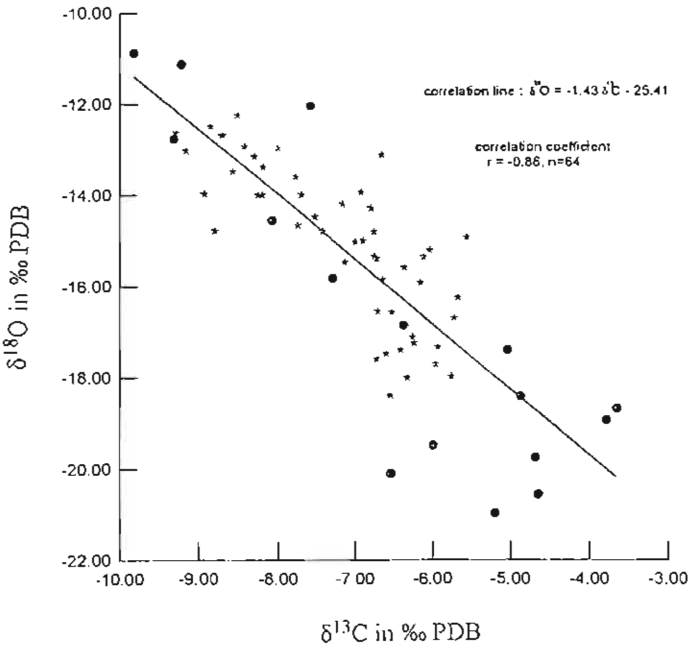


Fig. 3. $\delta^{13}C$ vs and $\delta^{18}O$ for "calcite groats" from the Chelosiowa Cave
Explanations as in Fig 2
Wartości $\delta^{13}C$ i $\delta^{18}O$ dla "kaszki kalcytowej" z Chelosiowej Jamy
Objaśnienia jak na fig. 2

represent a mixture of the "calcite groats", hydrothermal calcite and vadose calcite, as shown in Figure 2.

CONCLUSIONS

The investigation showed that the "calcite groats" were formed under specific vadose conditions apparently at the time of Baltic Glaciation. Furthermore, their very negative $\delta^{18}O$ values were not caused by hydrothermal activity. On the contrary, typical hydrothermal veined calcites in the Holy Cross Mts. area have much less negative $\delta^{18}O$ values (progress report — Z. M. Migaszewski and S. Hałas). The youngest hydrothermal calcite veins encountered in the region might have been connected with the Alpine tectonic movements in the Early Tertiary. The above arguments together with the petrographical evidence, exclude a hydrothermal origin (corrosion of hydrothermal veins) for the "calcite groats", as previously supposed by J. Urban and Z. Złonkiewicz (1989).

The source of the carbon dioxide for "calcite groats" crystallization remains unknown thus far. No calcite deposits derived from CO_2-rich springs have been traced in the Quaternary profile in the Holy Cross Mts. Palaeozoic inlier. In the present author's view the carbon dioxide was primarily a mixture of mantle and organic CO_2. This supposition may be supported by the fact of a small volume of the "calcite groats" in relation to the remaining calcites formed in the Chelosiowa Cave.

Acknowledgements. The authors express thanks to Prof. M. Pazdur of the Silesian Technical University in Gliwice for radiocarbon determination, as well as to A. Szczecińska and M. Kozłowska of the Polish Geological Institute in Kielce for performing spectral emission analysis. We would also like to thank Mr. A. Kasza and Mr. M. Domański for their help in field investigations in the cave. The research was partly supported financially by the Department of Environmental Protection of the Province Office in Kielce (project no. 15/92) and by the State Committee for Scientific Research, Warsaw.

Instytut Fizyki
Uniwersytetu M. Curie-Skłodowskiej
Lublin, Pl. M. Curie-Skłodowskiej 1
Oddział Świętokrzyski
Państwowego Instytutu Geologicznego
Kielce, ul. Zgoda 21
Instytut Ochrony Przyrody
Polskiej Akademii Nauk
Kraków, ul. Lubicz 46
Received: 24.03.1994

REFERENCES

CLARK I. D., LAURIOL B. (1992) — Kinetic enrichment of stable isotopes in cryogenic calcites. Chem. Geol., 102, p. 217–228.

FRIEDMAN G. M. (1971) — Staining. In: Procedures in sedimentary petrology (ed. R. E. Carver), p. 511–530. Wiley.

GŁAZEK J., ROMANEK A. (1976) — Punkt IIIB-4 — Jaworznia. Przew. 48 Zjazdu Pol. Tow. Geol. Starachowice, p. 240–247. Wyd. Geol. Warszawa.

HAŁAS S., KROUSE H. R. (1982) — Isotopic abundances of water of crystallization of gypsum from the Miocene evaporite formation, Carpathian Foredeep, Poland. Geochim. Cosmochim. Acta, 46, p. 293–296.

HAŁAS S., LIS J. (1980) — Carbon isotope fractionation in closed and open systems $CO_2 - H_2CO_3 - HCO_3^- - CO_3^{2-}$: Applications to sampling for studies of derivation of carbon dioxide in mineral waters. Akad. Wiss. DDR, Leipizg, ZFI Mitteilungen, 29, p. 57–68, no. 2a.

HAŁAS S., TREMBACZOWSKI A., SOLTYK W., WALENDZIAK J. (1993) — Sulphur and oxygen isotopes in sulphates in natural waters: (2) Deep-waters from horizons below Baltic sea floor. Isotopenpraxis, 28, p. 229–235.

LINDNER L. (1977) — Pleistocene glaciations in the western part of the Holy Cross Mountains (Central Poland) (in Polish with English summary). Studia Geol. Pol., 53.

McCREA J. M. (1950) — On the isotopic chemistry of carbonates and a paleotemperature scale. J. Chem. Phys., 51, p. 5547–5558.

MOOK W. G., BOMMERSON J. C., STAVERMAN W. H. (1974) — Carbon isotope fractionation between dissolved bicarbonate and gaseous carbon dioxide. Earth Planet. Sc. Lett., 22, p. 169–176.

O'NEIL J. R., ADAMI L. H. (1968) — The oxygen isotope partition function ratio of water and the structure of liquid water. J. Phys. Chem., 73, p. 1553–1558.

PALMER N. P., PALMER M. V. (1989) — Geologic history of the Black Hills caves, South Dakota. NSS Bull., 51, p. 72–99.

ROMANEK A. (1974) — Pozycja stratygraficzna i geneza zlepieńców odsłoniętych w rejonie Jaworzni. Kwart. Geol., **18**, p. 950–951, no. 4.

THAILKILL J. (1971) — Carbonate deposition in Carlsbad Caverns. J. Geol., 79, p. 683–695.

TURNER J. V. (1982) — Kinetics fractionation of carbon-13 during calcium carbonate precipitation. Geochim. Cosmochim. Acta, **46**, p. 1183–1191.

URBAN J. (1992) — Chelosiowa Jama. Jaskinie. Kraków.

URBAN J., ZŁONKIEWICZ Z. (1989) — Wstępne wyniki badań geologicznych jaskini Chelosiowa Jama w Jaworzni koło Kielc. Kwart. Geol., 33, p. 367–369, no. 2.

USDOWSKI E., HOEFS J., MENSCHEL G. (1979) — Relationship between ^{13}C and ^{18}O fractionation and changes in major element composition in a recent calcite-depositing spring — a model of chemical variations with inorganic $CaCO_3$ precipitation. Earth Planet. Sc. Lett., **42**, p. 267–276.

Tomasz DURAKIEWICZ, Stanisław HAŁAS, Zdzisław M. MIGASZEWSKI, Jan URBAN

GENEZA „KASZKI KALCYTOWEJ" Z CHELOSIOWEJ JAMY K. KIELC W ŚWIETLE BADAŃ IZOTOPOWYCH I PETROGRAFICZNYCH

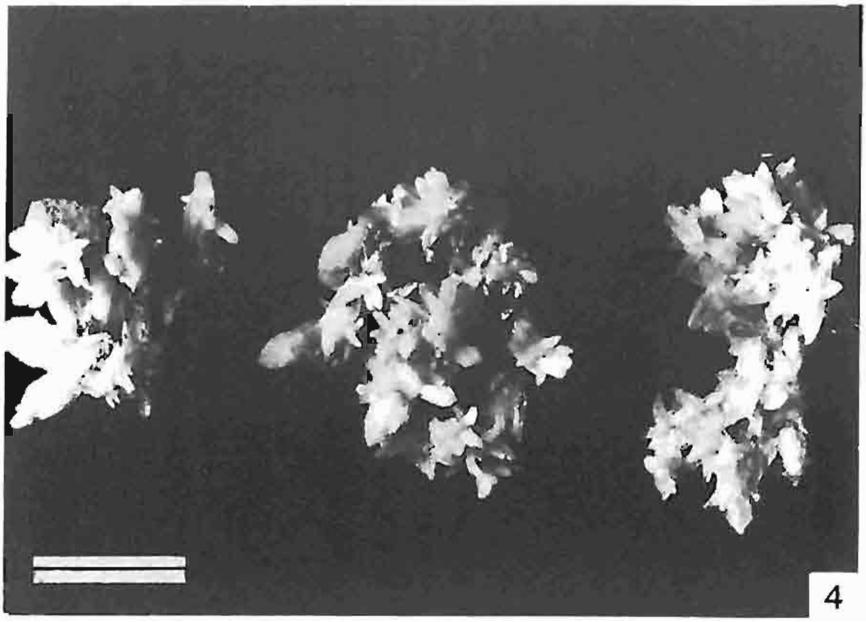
Streszczenie

Badaniom petrograficznym i izotopowym poddano ziarna kalcytowe z Chelosiowej Jamy k. Kielc, nazwane „kaszką kalcytową" (dalej k.k.). Na podstawie przeprowadzonych badań wyjaśniono genezę k.k., a w szczególności wydzielono 2 główne typy i 7 podtypów morfologicznych k.k., zaproponowano model opisujący powstanie k.k. i określono jej wiek na zlodowacenie bałtyckie. Według modelu, opracowanego na podstawie wyników badań izotopowych 64 próbek k.k., silne wzbogacenie kalcytu w lekki izotop tlenu jest wynikiem gwałtownej dehermetyzacji jaskini. Ucieczka CO_2 nagromadzonego w jaskini pod znacznym ciśnieniem cząstkowym spowodowała szybkie wytrącenie kalcytu o $\delta^{13}C \approx -5‰$ PDB, dzięki preferencyjnej ucieczce $^{13}CO_2$ z roztworu w czasie degazacji. Woda o $\delta^{18}O \leq -20‰$ SMOW powstała wskutek wiązania $H_2{}^{18}O$ w lodzie. Stąd $\delta^{18}O$ wytrąconej k.k. jest mniejsza od $-15‰$ PDB. W toku późniejszej rekrystalizacji skład izotopowy k.k. zmieniał się, dążąc do składu izotopowego typowego dla kalcytów naciekowych. Spowodowało to rozrzut wartości $\delta^{13}C$ i $\delta^{18}O$ wzdłuż prostej o równaniu $\delta^{18}O = -1{,}43\delta^{13}C - 25{,}41$.

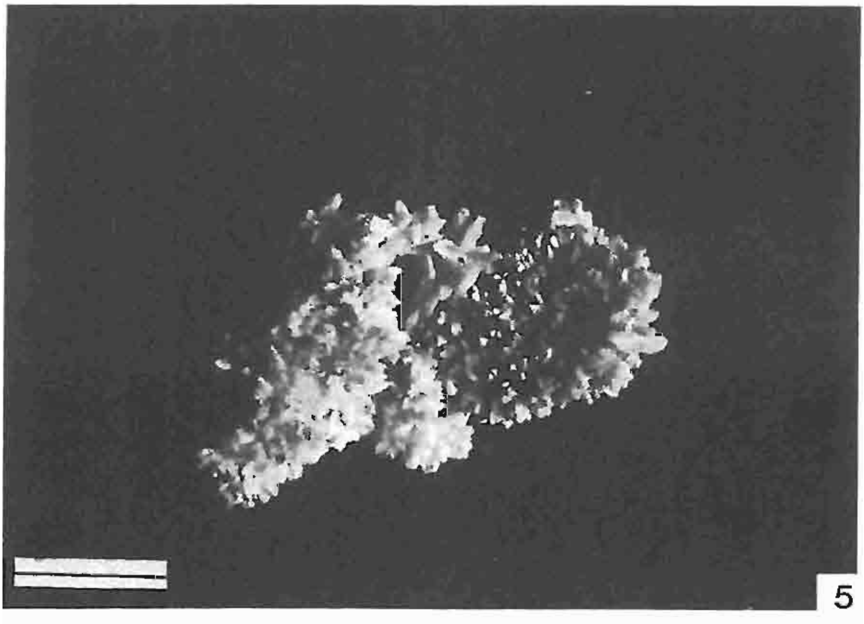
PLATE I

Figs. 4, 5. Various morphological forms of concretions: Fig. 4 — "twigs" and a "wreath", Fig. 5 — "hedgehog"; scale bars are 0.5 cm

Morfologiczne formy konkrecji: fig. 4 — „gałązki" i „wieniec", fig. 5 — „jeżyk"; długość skali 0,5 cm



4



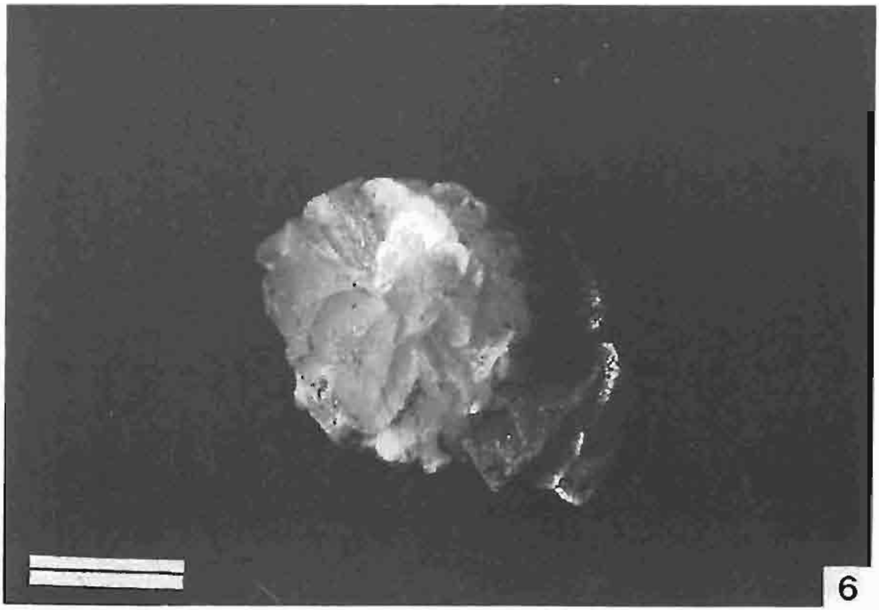
5

Tomasz DURAKIEWICZ, Stanisław HAŁAS, Zdzisław M. MIGASZEWSKI, Jan URBAN — Origin of the "calcite groats" in the Chelosiowa Cave near Kielce (Holy Cross Mts.) inferred from petrographic and isotopic investigations

PLATE II

Figs. 6, 7. Various morphological forms of concretions: Fig. 6 — "rose", Fig. 7 — "grape bunches" and a "bramble"; scale bars are 0.5 cm

Morfologiczne formy konkrecji: fig. 6 — „różyczka", fig. 7 — „winogrona" i „jeżyna"; długość skali 0,5 cm



6

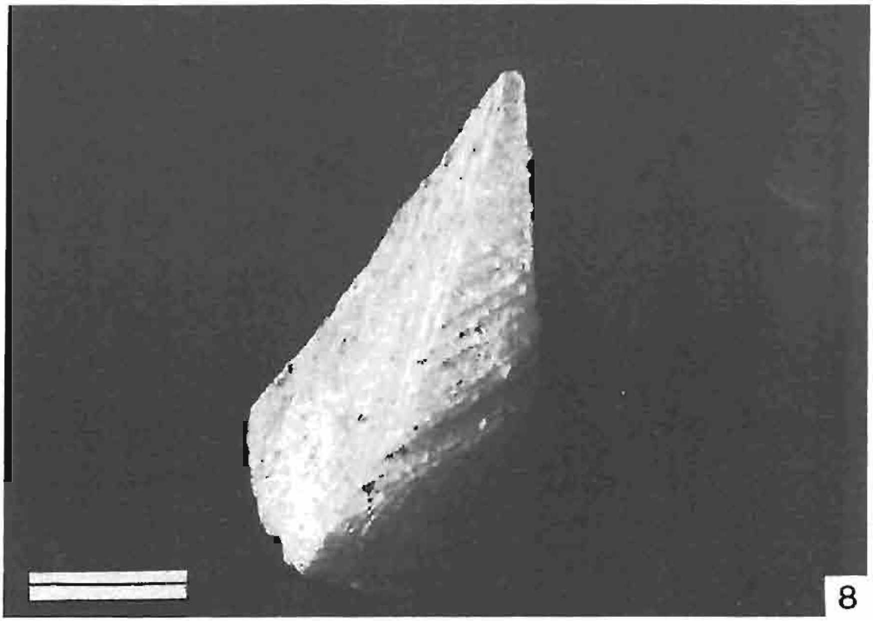
7

Tomasz DURAKIEWICZ, Stanisław HAŁAS, Zdzisław M. MIGASZEWSKI, Jan URBAN — Origin of the "calcite groats" in the Chelosiowa Cave near Kielce (Holy Cross Mts.) inferred from petrographic and isotopic investigations

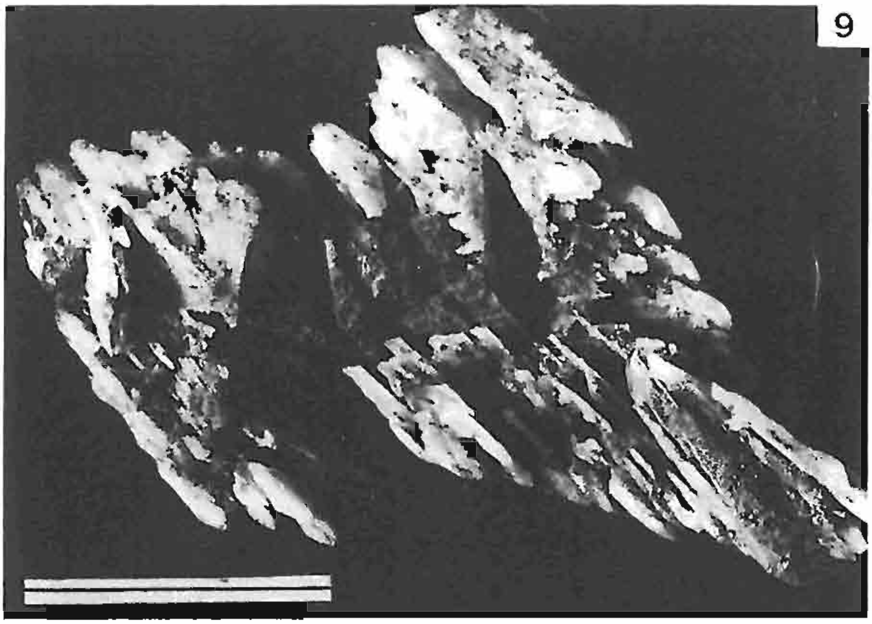
PLATE III

Figs. 8, 9. Various corrosive morphological forms: Fig. 8 — scalenohedral "full" grain slightly corroded, Fig. 9 — scalenohedral thick-walled skeleton; scale bars are 0.5 cm

Morfologiczne formy korozyjne: fig. 8 — skalenoedryczne „pełne" ziarno lekko skorodowane, fig. 9 — skalenoedryczny szkielet cienkościenny; długość skali 0,5 cm



8



9

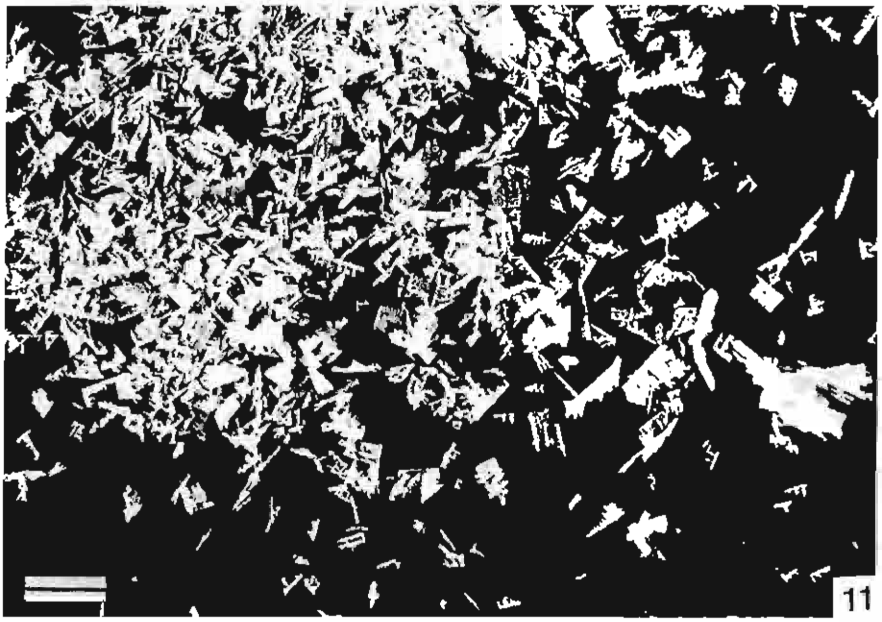
Tomasz DURAKIEWICZ, Stanisław HAŁAS, Zdzisław M. MIGASZEWSKI, Jan URBAN — Origin of the "calcite groats" in the Chelosiowa Cave near Kielce (Holy Cross Mts.) inferred from petrographic and isotopic investigations

PLATE IV

Figs. 10, 11. Various corrosive morphological forms: Fig. 10 — spatial and plane "trusses", "needles" and "pins", scarce "hedgehogs", Fig. 11 — "needles", "pins" and plane "trusses"; scale bars are 0.5 cm

Morfologiczne formy korozyjne: fig. 10 — przestrzenne i płaskie „kratownice", „igły", „szpilki" i rzadkie „jeżyki", fig. 11 — „igły", „szpilki" i płaskie „kratownice"; długość skali 0,5 cm

10



11

Tomasz DURAKIEWICZ, Stanisław HAŁAS, Zdzisław M. MIGASZEWSKI, Jan URBAN — Origin of the "calcite groats" in the Chelosiowa Cave near Kielce (Holy Cross Mts.) inferred from petrographic and isotopic investigations