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Ślady po kryształach halitu w dolomitach dewońskich w kamieniołomie Zachełmie

Casts of halite crystals in the Devonian dolomites of the Zachełmie Quarry

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Abstrakt

Nieczynny kamieniołom w Zachełmiu jest znany z racji odkrycia i opisu śladów najstarszego lądowego kręgowca – tetrapoda. W tym samym kamieniołomie znaleziono dobrze zachowane 3 ślady po pojedynczych kryształach halitu (na 2 próbkach skał). Wielkość śladów po tych kryształach wynosi od 1 do ok. 2,5-3 cm. Przypuszczalnie jeden ślad zostawił kryształ sześcienny, a 2 ślady powstały po kryształach typu *hopper*. Kilkakrotnie szczegółowo przebadane i opisane utwory dolomitowe z tego miejsca wskazują, że środowiskiem ich depozycji była płytka, rozległa laguna odsłaniająca kilkakrotnie dno i okresowo sprzyjająca sedymentacji ewaporatów. W niniejszym artykule autorka rozważa możliwość miejsca oraz czasu krystalizacji halitów, tzn. czy te kryształy wytrąciły się z roztworu w zbiorniku, czy też nieco później, już w obrębie osadu węglanowego, na skutek penetracji sedymentu przez solanki. Oba „miejsca" i czas precypitacji halitu wydają się równie prawdopodobne.

Słowa kluczowe: halit, ślady, dolomity, dewon, Zachełmie

Abstract

The abandoned Zachełmie Quarry has been known for the discovery and descriptions of the trackways of a tetrapod, the oldest land vertebrate animal. Three well-preserved casts of single halite crystals were found on two salt samples collected from the same site. The sizes of the halite traces range from 1 to ca. 2.5-3 cm. Most certainly, they are two casts of hopper and one of cube form crystals. The local dolomite formations, studied and described several times in detail, indicate that a shallow and vast lagoon that had uncovered the sea bottom several times and periodically allowed for the sedimentation of evaporites was the sedimentation environment. In this paper, the author considers possible place and time of halite crystallisation, i.e. whether the crystals were precipitated from the basin's solution or somewhat later, as a result of brine penetration through the carbonate sediment. Either halite "location" and precipitation time seem to be equally probable.

Key words: halite, casts, dolomites, Devonian, Zachełmie

Introduction

Three casts of features representing regular shapes were found at the surface of two small dolomite rock samples (8x9 cm and 10x11 cm each) collected from the abandoned Zachełmie Quarry, located at the feet of the Chełmowa or Chełm Hill, in May 2014. The rock samples were foundin the debris at the feet of the outcrop in the western section of the quarry. We should emphasize that the samples were not cut out directly from the outcrop wall. Nevertheless, the details of the samples clearly indicated that they had originated from that location. The regular shape of the traces proved non-organic origin and constituted rather the remains of the objects that had originally had the form of cubes or similar. The minerals that crystallise in a regular system (cubic class crystals) occur in nature. The most common of them are halite, pyrite, and fluorite.

Study area location and geological framework

The Zachełmie Quarry is located ca. 12 km north of Kielce, in the north-western part of the Holy Cross Mountains (Fig. 1). Devonian rocks that crop out at this at this place,

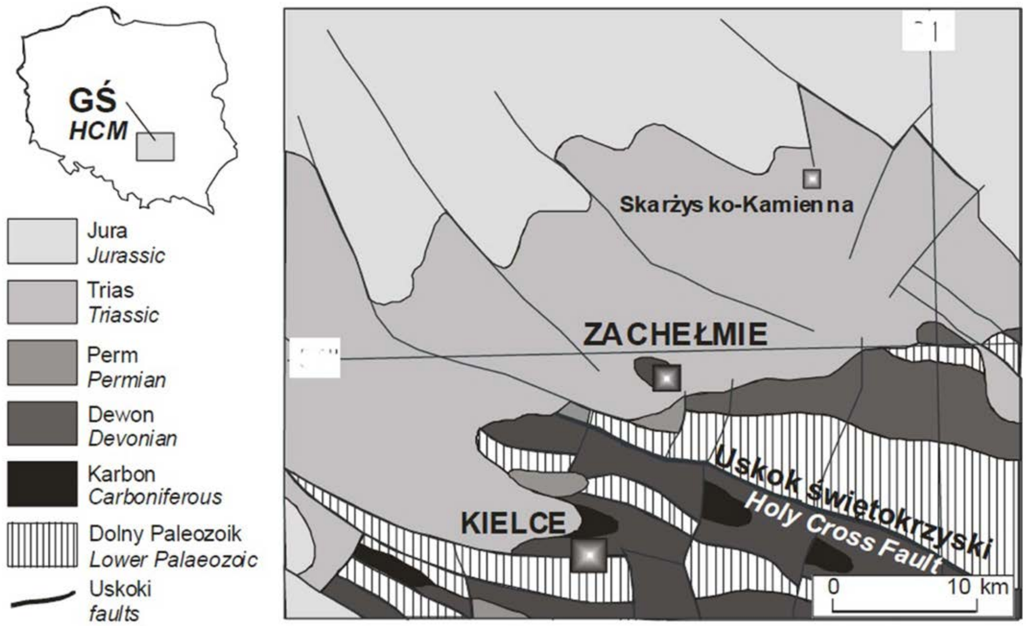

***Fig. 1**. Location of the Zachełmie Quarry o n the backgrand of fragment of geological map of Poland (after Dadlez et al., 2000; simplified)*
HCM – Holy Cross Mountains
Ryc. 1. Położenie kamieniołomu w Zachełmiu na tle fragmentu mapy geologicznej Polski (Dadlez i in., 2000; uproszczone)
GŚ – Góry Świętokrzyskie

make up a Variscan structural unit that is partly overlain by the Buntsandstein sandstone formation (Alpine structural unit). The southern wall of the quarry is built of dolomites assigned to the Wojciechowice Formation. The thickness of dolomites is estimated at ca. 100 m. The beds dip at the angle of 35-45 degrees in the N-NE direction (Fig. 2). The age of those rocks was estimated on the basis of the conodont fauna (*Costatus* level) at Middle Eifelian (Narkiewicz, Narkiewicz, 2010). During the Middle and Late Devonian, the area lay on the southern or south-eastern rim of the so-called Old Red Continent constituting part of Laurussia (Euamerica; Narkiewicz et al., 1998; Belka, Narkiewicz, 2008), including Baltica. That continent bordered a wide shelf of a Devonian basin in the south, where sedimentation, from that characteristic for the open marine environment up to shallow-water sedimentation, developed locally, with a carbonate, or carbonate-terrigenous platform or evaporites (Narkiewicz et al., 2011; Narkiewicz, Retallack, 2014).

The Devonian rocks occurring in the Zachełmie Quarry are generally described as dolomites. In fact, they were shaped as bedded pelitic (micritic) dolomites, dolomitic mudstones, marly dolomites, and dolomitic marls and shales containing changeable admixtures of siltsthat strengthen slight but well-visible parallel lamination (Narkiewicz, Narkiewicz, 2010; Narkiewicz, Retallack, 2014; Niedźwiedzki et al., 2014; Narkiewicz et al., 2015) and foster rock cracking into small plates, with the development of shale separation.

***Fig. 2**. Western part of the Zachełmie Quarry*
Ryc. 2. Zachodnia część kamieniołomu w Zachełmiu

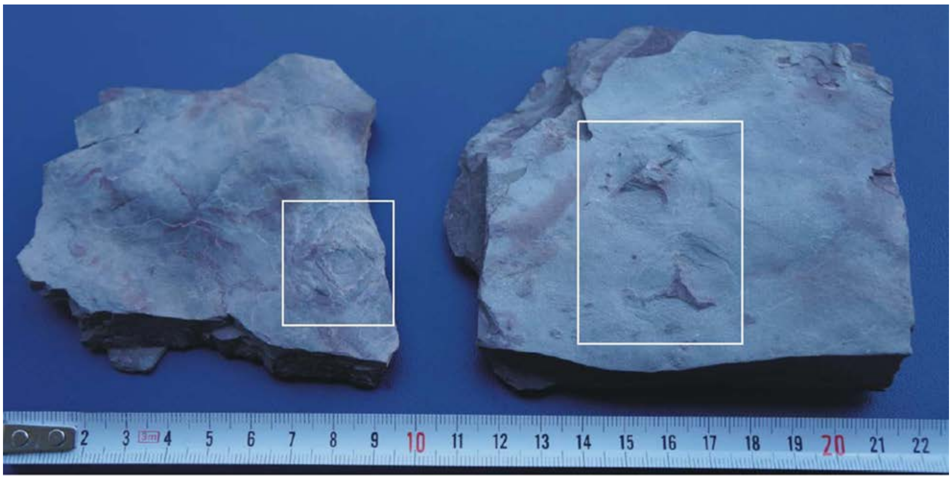

***Fig. 3**. Two fragments of rocks with halite casts*
Ryc. 3. Próbki 2 skał ze śladami po halicie

Sedimentation formation and environment

The environment in which the rocks originated was that of a vast, flat, and shallow-water carbonate platform (Skompski, Szulczewski 1994), or a vast and shallow lagoon, with a record of temporary sea bottom surfacing, as proven by excellently preserved polygonal mud-cracks on bedding planes, rain drop traces or paleosols levels, as well as the tetrapod trackweys that made the quarry famous (Narkiewicz, Narkiewicz, 2010; Niedźwiedzki et al., 2010; Narkiewicz, Retallack, 2014; Niedźwiedzki et al., 2014; Narkiewicz et al., 2015). Besides, the basin presented adequate salinity, at least periodically, for the evaporite sedimentation to develop within some levels. In the lower complex of the Wojciechowice Formation, trace of vanished evaporates – casts of anhydrite – occur, in the form of millimetre-large crystals and nodules, with the diameter of up to 2 cm. Presently, anhydrite has been replaced by quartz and dolomite (Narkiewicz, Retallack, 2014; Narkiewicz et al., 2015). The ancient subtropical climate, the existence of a very shallow and isolated basin periodically showing the sea bottomand increased water salinity enabled fast dolomitisation of the deposited carbonate mud that has built present-day dolomites as syndepositional or eogenetic dolomites (Narkiewicz et al., 2015). That is also confirmed by oxygen and carbon isotope analyses applied to those dolomites, indicating the marine source of dolomitizing fluids.

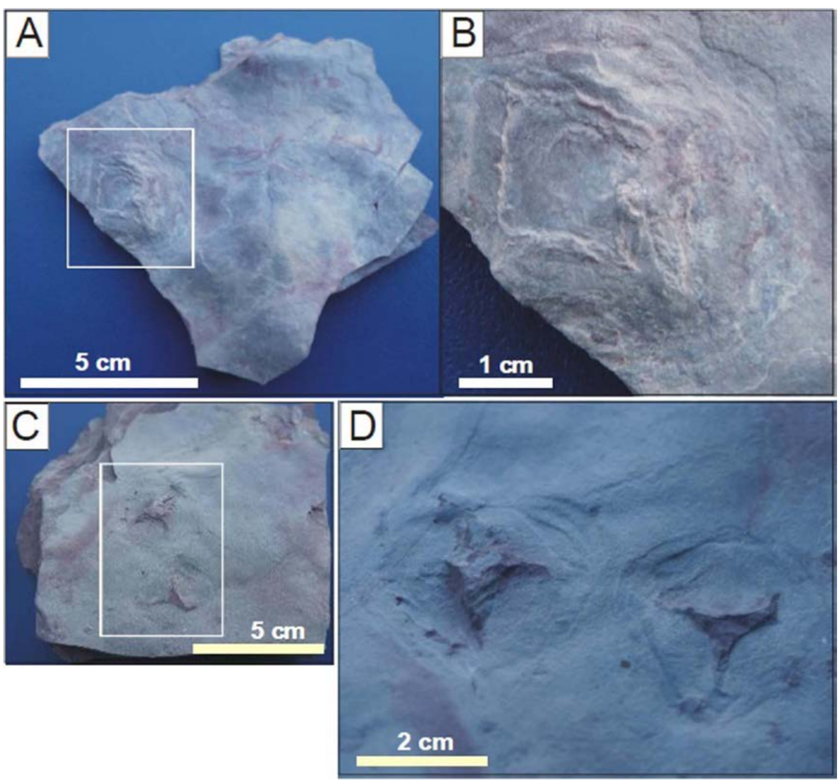

***Fig. 4**. Halite casts: one on Sample 1 (A, B) and two on Sample 2 (C, D)*
Ryc. 4. Ślady po halicie: pojedynczy na próbce 1 (A , B) i podwójny na próbce 2 (C, D)

Besides, the oxygen isotopic data of dolomite corresponds to $\delta^{18}O$ values of the Middle Devonian sea water (Narkiewicz, Retallack, 2014; Narkiewicz et al., 2015).

Besides, the compacted casts of cubical halite crystals have been preserved in dolomitic marly shales, as mentioned by Narkiewicz and Retallack (2014) and Narkiewicz et al. (2015). Such casts were found in the eastern part of the Zachełmie Quarry, within layer EM 38, according to Narkiewicz et al. (2015). The author of this paper found herself two samples (Fig. 3) of rocks with three casts in the western section of the quarry, to be described below, when she studied the issue of the presence of sodium chloride crystals in those formations.

Research material

Sample 1 (Fig. 4 A,B) preserves a casts like a square, with the side length of about 1 cm, surrounded by additional two rows of rolls, up to 1 mm high (poorly formed in some locations), constituting a type of a "halo" around the casts. Such additional lining around a square form, 2-3 mm thick, causes that the whole casts as the size of about 2.5 x 3 cm. The second rock sample (Fig. 4 C,D) shows two clear square casts, with the side length of ca. 1.5 cm and ca. 2 cm each. However, they are slightly different that the previously described specimen. The regular casts of the second rock sample miss such a clear, raised, and supplementary lining in the form of rolls. Still, one can see a subtle profile of lining surrounding the casts when magnified to 2.5 x 2.5 cm and 3 x 3 cm, respectively. Besides, in the central parts of both casts, presenting slight culminations, there are additional elements, in the form of 2-3 distinct arms running from the casts centres to the square angles. The arms are 0.5-0.7 mm long. Each trace may have originally possessed four arms like that, although they have not been preserved until today completely. We can observe additionally that, in each of the three casts, the walls of regular objects lie equally flat, in parallel to the dolomitic marly shale surface.

Interpretation

The casts preserved on the surface of the above described rock samples were probably created as a result of crystallisation followed by dissolution of halite crystals. The appearance of Sample 1 indicates that the crystal had the form of a typical cube, while that of Sample 2 may suggest that the casts were impressed by hopper cube crystals whose faces had the forms of depressed stepped pyramids (hoppers). That shape was a result of the faster growth of the crystal on the edges and corners than in the central sections of the faces (Goldsztaub, Kern, 1953; Gornitz, Schreiber, 1981; Handford, 1991).

The key issues concern the origin of those crystals and the time of the beginning of crystallisation (Fig. 5 A). When considering those aspects, one should notice that, in a classical approach, chlorides crystallise at the end of the evaporation cycle, preceded by sulphate sedimentation. The presence of sulphates in the dolomites of Zachełmie were mentioned here before. In fact, Narkiewicz and Retallack (2014) described only the pseudomorphs anhydrite, in the form of millimetre-large crystals and small nodules. However, the sizes of the casts left by halite described here indicate that the crystals were at least 2-3 cm large and they were preserved only as single mineral specimens. There are two possibilities to explain the presence of those single halite crystals found in carbonate formations:

1. The crystals were formed close to water surface where the top water layer (at the air–brine interface) could reach the

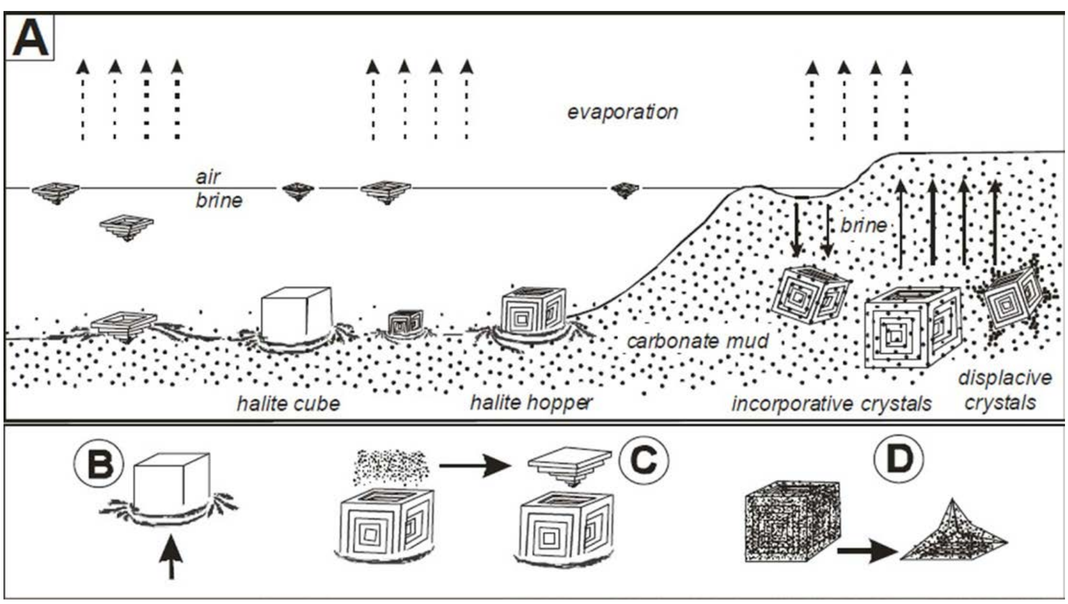

Fig. 5. Origin of halite casts (adapted from: Arthurton, 1973; Gornitz, Schreiber, 1969; Handford, 1991 and modi fied by author)
Ryc. 5. Geneza śladów po halicie (za Arthurton, 1973; Gornitz, Schreiber, 1969; Handford, 1991, zmienione przez autorkę)

concentration allowing for halite precipitation, owing to intense evaporation, as a four-sided, inverted pyramidal hopper / cornet-shaped crystals (halite raft). Sometimes such crystals sink later to the basin's bottom (Fig. 5 C), and continuing to grow on the sea floor (Arthurton, 1973; Gornitz, Schreiber, 1981; Southgate, 1982; Lowenstein, Hardie, 1985; Handford, 1991; Warren, 2016). Otherwise, crystallisation was taking place at the brine pool floor gradually from the beginning, around a crystallisation nucleus (Handford, 1991).

2. The crystals were formed only in the sediment (since they are somewhat younger than the sediment in which they are found), as displacive/incorporative halite hoppers (Fig. 5 A) either as a result of their relocation to the sea bottom, diffusion of dense and warm brine deep into the sediment, or as a result of the ascend of solution to the surface (evaporative pumping mechanism; Hsü, Siegenthaler, 1969) when the sea floor was uncovered and exposed to intense evaporation. During that ascend or descend of brine through the sediment (depending on circumstances, i.e. the fact whether the sea bottom was uncovered or covered by a layer of water, respectively), brine was gradually getting oversaturated, resulting in crystallisation and gradual growth of halite crystals (Gornitz, Schreiber, 1981; Lowenstein, 1982; Lowenstein, Hardie, 1985; Handford, 1991; Warren, 2016). Halite crystallising in the sediment has the form of hopper crystals that incorporate the surrounding material in which they grow. That happens during fast crystallisation of incorporative crystals. In the case of slow precipitation, sediment is subjected to disturbance and relocation: it is pushed away by a gradually growing mineral becoming a displacive crystal. The crystals growing in that way are free of a large quantity of impurities (Gornitz, Schreiber, 1981; Handford, 1981; Southgate, 1982; Handford, 1991).

Present-day halites crystallising within sediments (displacive crystals) were described in detail by Gornitzand, Schreiber (1981). Those crystals originated from the area of the Dead Sea. They are usually found at the depth of 0.6-2.0 m below the sediment surface, and their edges reach the length of even 10 cm. Well preserved fossil casts of such structures occur in Devonian (Frasnian; Rychliński et al., 2014), Silurian (Demicco, Hardie, 1994), Cambrian (Raine, Smith, 2017), and even Archaean (2.58 Ga; Eriksson et al., 2005) formations.

In the case of the sodium chloride crystals of Zachełmie, it is difficult to specify clearly the course of the mineral precipitation process, running either (1) in the solution (brine) in the basin, or (2) in the sediment. Both halite precipitation places seem to be probable and they fit well the image of the Wojciechowice Formation carbonate sedimentation of Zachełmie, presented by the authors mentioned above. Although we can point rather at the first option in the case of the single halite casts on Sample 1, impressed by a ca. 1 cm large crystal which lied and grew on the floor of a basin (Fig. 5 B). The issue remains open in the case of Sample 2. The latter casts have 3D forms, with as lightly convex central section from which elements reminding arms spread, which can suggest that the casts constitute either:

(a) the negative moulds and casts impressed with "concave" – depressed stepped pyramids face of the hopper halite crystals that had been finally formed on the sea floor and became covered with carbonate deposits with time (Fig. 5 C) or

(b) two poorly preserved fragments of casts hopper halite crystals which grew fast in the sediment and enclosed some surrounding sediments during the process (Fig. 5 D).

However, the fact that both casts were impressed by the crystals which were lying similarly flat and in parallel to the dolomitic marly shale surface is striking, although one can expect various arrangements of the crystals growing in sediments, not necessarily on the sediment surface.

Results and conclusions

1. The three casts preserved on two samples of dolomite rocks found in the Zachełmie Quarry, described in this paper, originated from halite crystal growths.
2. The crystal's side edges ranged from 1 to ca. 2.5-3 cm.
3. Most probably, two of those traces were impressed by hopper crystals.
4. Halite crystals occurring in the Zachełmie dolomites could have developed either (a) as a result of NaCl crystallisation in the surface water (air-brain) of a shallow basin and they later fell down to the sea bottom or otherwise crystallised at the shallow basin's sea floor from the beginning, or (b) they developed after carbonate sediment deposition, as a result of vertical travel of solutions whose concentration increased enough for the salt precipitation process to start and that is when the crystallising halite partly caught and trapped the material from the environment of the sediment in which it grew.

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