

Calcite pseudomorphs after evaporites from the Muschelkalk (Middle Triassic) of the Holy Cross Mountains (Poland)

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Abstract: Pseudomorphs after sulphate minerals, together with accompanying phenomena, are the only evidence of evaporites in the Muschelkalk of the Holy Cross Mts. They appear as geodes or full-filled nodules built of coarse-crystalline calcite, and their after-evaporite origin have been interpreted on the ground of lithological, petrographical and geochemical characteristics. Evaporitic conditions of sedimentation are indicated mainly by remnants of sulphate minerals occurring commonly in the geodes, and by remnants of dolomite in the host rocks. Dissolution of sulphates, evidenced by collapse breccias, pseudomorphs, and pervasive calcitization of the geodes-bearing horizons, took place in consequence of fresh water influx, which is suggested by elemental and isotopic data.

Key words: sulphates, carbonates, pseudomorphs, Muschelkalk, Holy Cross Mountains.

1. Introduction

Evaporite minerals, as well as pseudomorphs after them, are well known from the epicontinental Triassic of Europe (Fig. 1), mainly from salinar deposits of the Röt (*e.g.* Bodzioch & Kwiatkowski 1992; Szyperko-Teller *et al.* 1997; Paul 1999), Middle Muschelkalk (*e.g.* Gaertner & Rohling 1993; Gajewska *et al.* 1997a) and Keuper (*e.g.* Gajewska *et al.* 1997b; Beutler *et al.* 1999), but there were no descriptions of such phenomena from the Muschelkalk out-

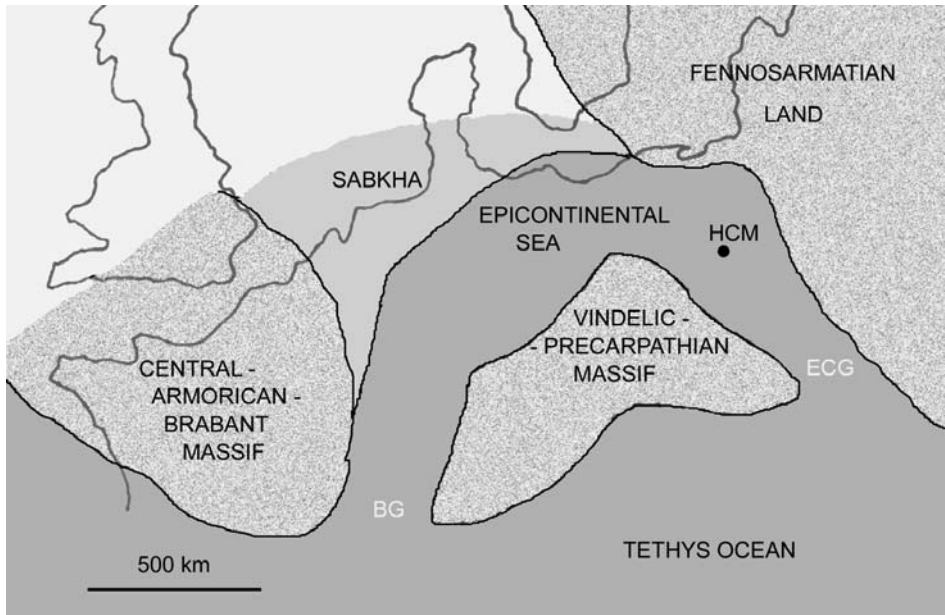


Fig. 1. General paleogeographic position of the Holy Cross Mts. (HCM) in the Middle Triassic times (slightly modified after Beutler & Szulc, 1999). ECG: East Carpathian Gate, BG: Burgundy Gate.

crops surrounding the Holy Cross Mts. Only Szulc (2000, Fig. 26) has marked evaporites in his general lithostratigraphical column of the Muschelkalk from the northern margin of the Holy Cross Mts. without any evidences, however, limestones, dolomites and thin silicoclastic intercalations are exclusively known from this profiles (*e.g.* Rydzewski 1924; Samsonowicz 1929; Senkowiczowa 1956, 1970; Rdzanek 1980; Bodzioch 1984). Therefore, the question of evaporites in the Muschelkalk of the Holy Cross Mts. should be explained.

Lithological, petrographic, cathodoluminescence (CL), elemental (XRF) and isotopic ($\delta^{18}\text{O}$ and $\delta^{13}\text{C}$) data completed for the purpose of this paper uphold three theses:

1. There are no evaporites in outcrops of the Muschelkalk around the Holy Cross Mts. Small, isolated gypsum crystals dispersed in clay occur in the Upper Muschelkalk (Brząkowska 2002) but they are a product of Recent weathering (author's unpublished data).

2. There occur after-evaporite horizons but, of course, "after-evaporite formations" are not the same as "evaporites".

3. After-evaporite horizons are built of carbonates containing calcite pseudomorphs after nodular anhydrite which have been mentioned in the older literature as undefined "calcite clusters" (*e.g.* Samsonowicz 1929; Senkowiczowa 1956).

2. Geological setting

Remnants after evaporites described below occur in the north-eastern margin of the Holy Cross Mts., where the Muschelkalk is best exposed near Nietulisko and Bukowie (Fig. 2).

The Muschelkalk is developed here typically for the whole of the epicontinental basin (Fig. 3), i.e. it is dominated by highly fossiliferous limestones in its lower and upper parts, and by unfossiliferous, dolomitic layers in the middle part. The thickness of the sequence is reduced up to 10 times in comparison with the SW-margin of the Holy Cross Mts. This was interpreted as a strong stratigraphical condensation (Senkowiczowa 1970), however, conodont stratigraphy (Ptaszyński 1981) indicates significant diachronism of the Buntsandstein/Muschelkalk boundary. Most probably, sedimentation of the Muschelkalk had started here much later than in neighboring, south-western areas, and the rate of subsidence was much lower. Remnants after evaporites occur at the base of the Muschelkalk sequence, within thin-layered, gray to yellowish, recrystallized limestone showing a crumpled structure, and in the Middle Muschelkalk, within yellowish, coarse-crystalline limestone.

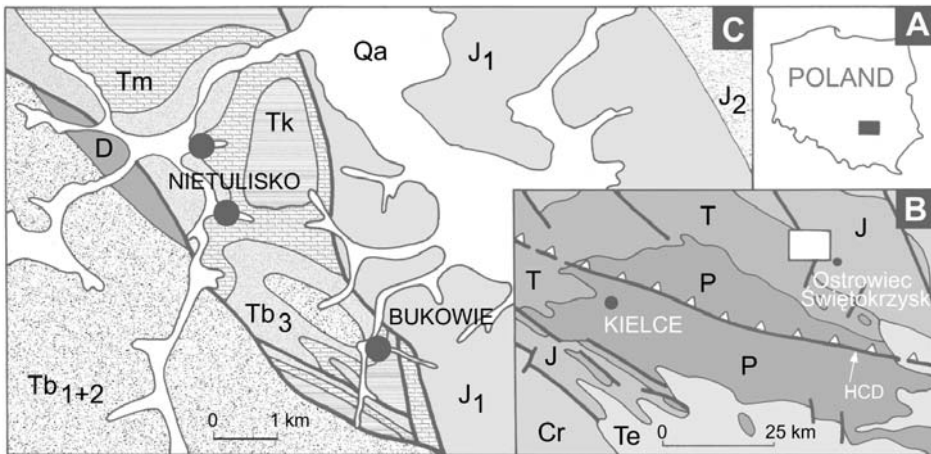


Fig. 2. Location of the Muschelkalk sections discussed. **A:** Geographical position of the Holy Cross Mts. (gray rectangle), **B:** Geological sketch map of the Holy Cross Mts: white rectangle – study area shown in detail in Fig. 2C, P – Paleozoic, T – Triassic, J – Jurassic, Cr – Cretaceous, Te – Tertiary, HCD – Holy Cross Dislocation. **C:** Detail location of the profiles (gray circles) near Nietulisko and Bukowie (the map after Samsonowicz 1929): D – Devonian, Tb₁₊₂ – Lower and Middle Buntsandstein, Tb₃ – Upper Buntsandstein, Tm – Muschelkalk, Tk – Keuper, J₁ – Lower Jurassic, J₂ – Middle Jurassic, Qa – Quaternary alluvial deposits).

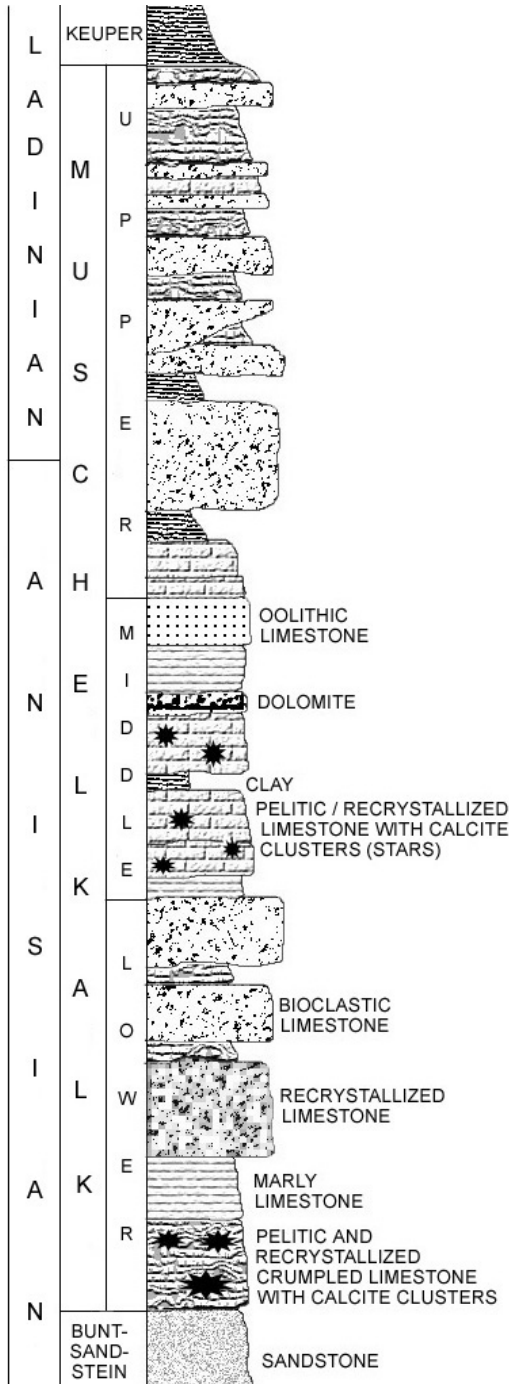


Fig. 3. Lithology and stratigraphy of the Muschelkalk in the Bukowie section. Chronostratigraphical subdivisions after Trammer (1975) and Ptaszyński (1981). Total thickness of the Muschelkalk sequence is 20 meters.

3. Description

In the Lower Muschelkalk, pseudomorphs after evaporites appear as small (1–10 cm in the diameter), oval clusters (geodes) of calcite, which usually are not completely filled (Fig. Pl. I: A). The development of calcite crystals change gradually from the external to internal part of clusters. Close to the host rock, they are milky colored, xenomorphic and small (1–3 mm). Towards the center, they become more clear, more idiomorphic and coarser. The best developed crystals occur in the central part of those clusters that are incompletely filled with calcite. In such cases, large (up to 2 cm), idiomorphic crystals with almost clear peripheral rims predominate. They show the shape of lenticles or very flat pyramids of rhomboidal base, which is not typical for calcite.

In thin sections, the calcite appears as inclusion-rich, very coarse-crystalline, xenomorphic, blocky sparite. Within sparite crystals or between them, there occur a lot of small anhydrite crystals (usually less than 0.2 mm), which sometimes show outlines of subhedral laths (Pl. I: B) and mottled interference colors (yellow and blue) in cross polarized light. Apart from that, they often form linear concentrations creating an angular network, especially in the external part of clusters (Pl. I: C). In other cases, such concentrations can also consist of fine-crystalline, granular sparite enriched in solid inclusions of anhydrite. Boundaries of blocky sparite crosscut this linear concentrations very often, thus individual parts of the network are incorporated into particular calcite crystals (Pl. I: D).

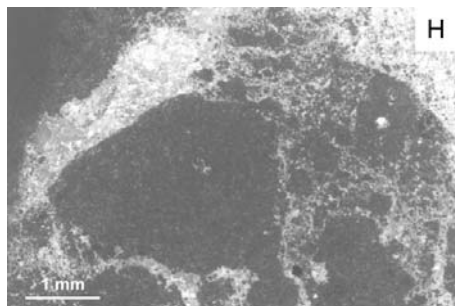
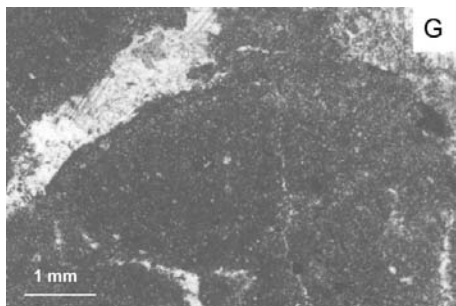
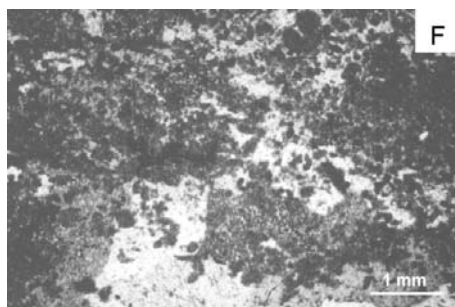
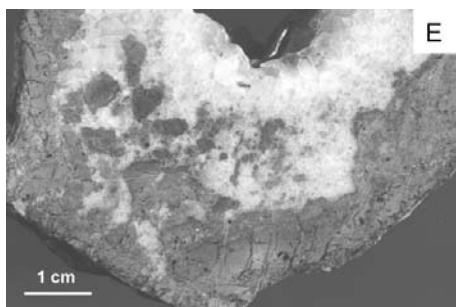
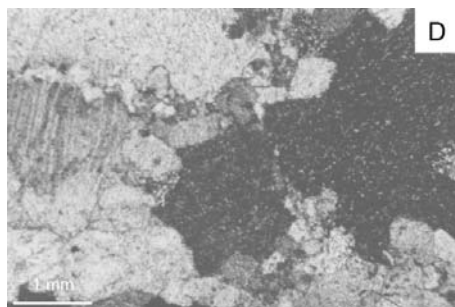
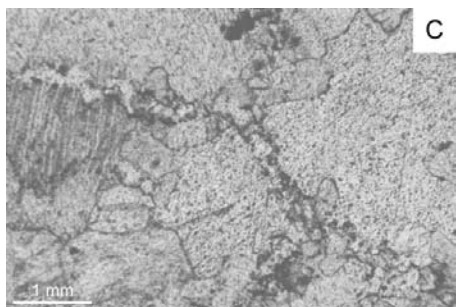
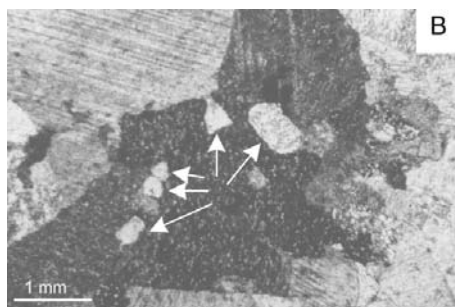
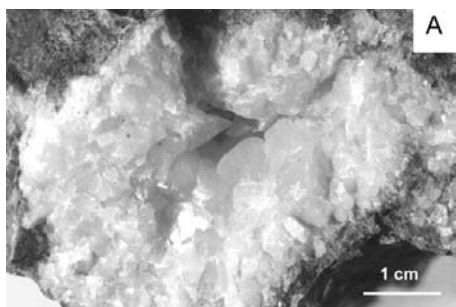
In most cases, a breccia consisting of host rock fragments cemented with calcite occurs at the bottom part of clusters (Pl. I: E). Size and shape of mostly irregular and randomly oriented particles are extremely diversified, and a direct contacts of the particles are rare (i.e. the breccias show a matrix-supported, float-stone structure).

The host rock is built of crystalline limestone containing a lot of carbonate, mainly unrecognizable grains built of micrite (Pl. I: F). Individual, xenomorphic crystals of sparite matrix are large (0.5 to 2 mm) and cloudy, and they crosscut the boundaries of grains or encase them poikilotopically. Near the calcite clusters, the host rock is irregularly cracked, however, some radial pattern of larger cracks can be assumed (Pl. I: E). Largest fissures are opened towards the clusters and filled with calcite crystals which continue into the cluster mosaic. The fissure-filling calcite is built of milky colored, cloudy under microscope, small crystals (1–2 mm), identical in their petrographic features with those of the external part of clusters.

Cathodoluminescence of all types of calcite (i.e. cluster-building, fissure-filling and sparite matrix) is uniform, bright-orange, while micritic components are dull-red or non-luminescent. It is clearly visible that bright-orange luminescent calcite fills a very dense network of fine cracks, and forms a matrix containing particles of primary micritic sediment (Pl. I: G).

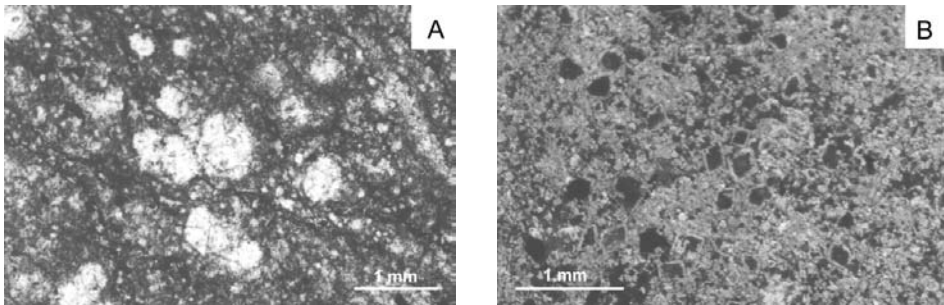
Analysis of element composition shows a difference between the cluster-

Plate I



- A. Hand sample of a calcite cluster (geode). Lowermost Muschelkalk, Bukowie. Discoidal crystals are well visible in the center.
- B. Remnants of anhydrite (arrowed) within inclusion-rich, blocky sparite. Thin section made of the specimen shown in Fig. A, cross polarized light.
- C. Angular network of linear concentrations of fine-crystalline sparite. Another part of the thin section shown in Pl. I: A, plane polarized light.
- D: The same as in Pl. I: C, cross polarized light. Large calcite crystal (black) encases a part of the network consisting of fine-crystalline, granular sparite.
- E. Breccia occurring at the bottom of a calcite cluster. Polished slab made of the specimen shown in Pl. I: A. The system of cracks with some radial pattern is best demonstrated in the lower and left part of the photo.
- F. Thin section of the host rock. Lowermost Muschelkalk, Bukowie, cross-polarized light. Large calcite crystals (white and gray areas) containing micritic grains (black areas) or cross-cutting them are best visible in the bottom left part of the photo.
- G. Calcite filling fissures that surround geodes (white-gray areas), Lowermost Muschelkalk, Bukowie. Thin section, ordinary light.
- H: CL image of the sample shown in Pl. I: G. Bright-orange luminescent calcite is visible as white-gray areas.

Plate II



- A. Small calcite clusters (white areas), Middle Muschelkalk, Bukowie. Thin section, plane-polarised light.
- B. CL image of the Middle Muschelkalk dolomitic limestone containing small calcite clusters, Bukowie. Isolated pseudomorphs after eu- or subhedral dedolomite crystals are well visible (black rhombic areas).

building calcite and host rock, especially in the amount of MgO and MnO. Cluster-building calcite is poor in MgO (less than 1%) and rich in MnO (about 0.4%), while the host rock is enriched in MgO (up to 15%) and depleted in MnO (less than 0.05%). Stable isotope composition of the cluster-building calcite shows negative values for both $\delta^{18}\text{O}$ (-8.17% PDB) and $\delta^{13}\text{C}$ (-2.32% PDB).

Calcite clusters occurring in the Middle Muschelkalk are much smaller than those of the Lower Muschelkalk (in most cases, their diameter does not exceed 2 mm), oval, and built of granular, coarse-crystalline, milky-colored sparite (Pl. II: A). Cathodoluminescent and geochemical characteristics of these clusters are very similar to the geodes described above. The host rock is built of coarse-crystalline, cloudy, ferroan, high-Mg sparite containing eu- to subhedral, rhombic dolomite crystals (Pl. II: B). In all cases, the dolomite crystals are built of high-ferroan dolomicrite surrounded by a zone of clear dolomite. The matrix shows medium-red CL, while dolomite rhombs are non-luminescent in the center and bright-orange in the peripheral parts.

4. Interpretation

All lithological, mineralogical, petrographical and geochemical data presented above support the thesis about after-evaporite origin of the described calcite clusters:

1. The shape of clusters and accompanying cracks strongly resembles anhydrite or gypsum nodules growing within carbonate sediments in sabkha environments (*e.g.* Kinsman 1969).
2. Breccias occurring at the bottom part of calcite clusters represent the dissolution-collapse ones, typical for dissolution of primary minerals and then collapse of a cavity (*e.g.* Blount & Moore 1969; Friedman 1997).
3. Unusual shape of large calcite crystals is typical for discoidal or hemipyramidal forms of sulphate minerals (*e.g.* Arakel 1980).
4. Small crystals of anhydrite dispersed in sparite mosaic are the remnants after larger, dissolved crystals or aggregates.
5. Angular network built of small anhydrite crystals or of fine-crystalline, granular calcite (pseudomorphs after anhydrite) underline outlines of primary minerals. Its origin can be explained by displacive growth of polycrystalline calcite mosaic which replaced anhydrite.
6. Inclusion-rich crystals of cluster-building calcite suggest *in situ* replacement of former minerals (*e.g.* Bausch 1965), while their inclusion-free, external zones could precipitate directly from pore solution.
7. Remnants after dolomite, as well as coarse-crystalline, cloudy texture of host rocks and their enrichment in MgO, indicate calcitization of the original dolomite sediment (*e.g.* Jones *et al.* 1989; Bodzioch & Kwiatkowski 1992; Chatalov 1999).

8. Uniform CL characteristics of all types of calcite, i.e. cluster-building, fissure-filling and sparite matrix (in the case of the Lower Muschelkalk), can indicate the same calcitizing pore solutions. Slightly different CL of the Middle Muschelkalk host rock can be explained by originally higher content of Fe^{2+} ions in dolomite sediment, which reduces the CL effect (e.g. Machel 2000). Bright-orange, peripheral zones of dolomite rhombs can be referred to originally limpid dolomite (Folk & Land 1975) growing under an influence of fresh water.

9. The values of $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ obtained for cluster-building calcite are typical for some meteoric cements (e.g. Moore 1989). Freshwater precipitation of calcite is also marked by high amount of manganese (e.g. Veizer 1983).

The remarks presented above allow to reconstruct the origin of after-evaporite horizons occurring in the NE margin of the Holy Cross Mts. In general, calcite clusters can be explained as a result of replacing of primary anhydrite nodules by secondary calcite, which explains also all associated phenomena (Fig. 4). Subaerial exposure and evaporation of original lime mud led to growth of anhydrite nodules within the sediment and, consequently, to dolomitization of the sediment in the way of increasing Mg/Ca ratio in pore brines (e.g. Butler 1967), and to cracking induced by diminishing volume and drying of the sediment (Fig. 4.1). Large input of fresh waters caused completely or partial dissolution of anhydrite (Fig. 4.2A and 4.3A, respectively) first, and collapse of formed cavities afterwards (Fig. 4.2B and 4.3B). Pervasive calcitization of the sediment appeared in three steps. At first, remnants of anhydrite (if remained) were replaced *in situ* by calcite (Fig. 4.3C), then pure dolomite was replaced in the same way (Fig. 4.2C and 4.3D), and, in the end, clear calcite precipitated in the remaining pore spaces and overgrew the after-anhydrite and after-dolomite crystals (Fig. 4.2D and 4.3E).

The time of calcitization is uncertain. It could take place either during early diagenesis, upon an influence of episodic rains or river floods affecting sedimentation of evaporite units, or during Cenozoic uplift of the Holy Cross Mts., under an influence of ground waters. Uniform CL and geochemical characteristics suggest that there are no late diagenetic cements, therefore, all transformations of minerals can be interpreted as early diagenetic. On the other hand, diagenetic calcitization usually leads to complete reducing the pore space (e.g. Chalov 1999), and absence of mineral generation younger than secondary calcite can suggest even Recent processes (see Back *et al* 1983 for an excellent example). The problem is unsolvable on the ground of the data presented in this paper and needs radiometric dating of pseudomorphic calcite.

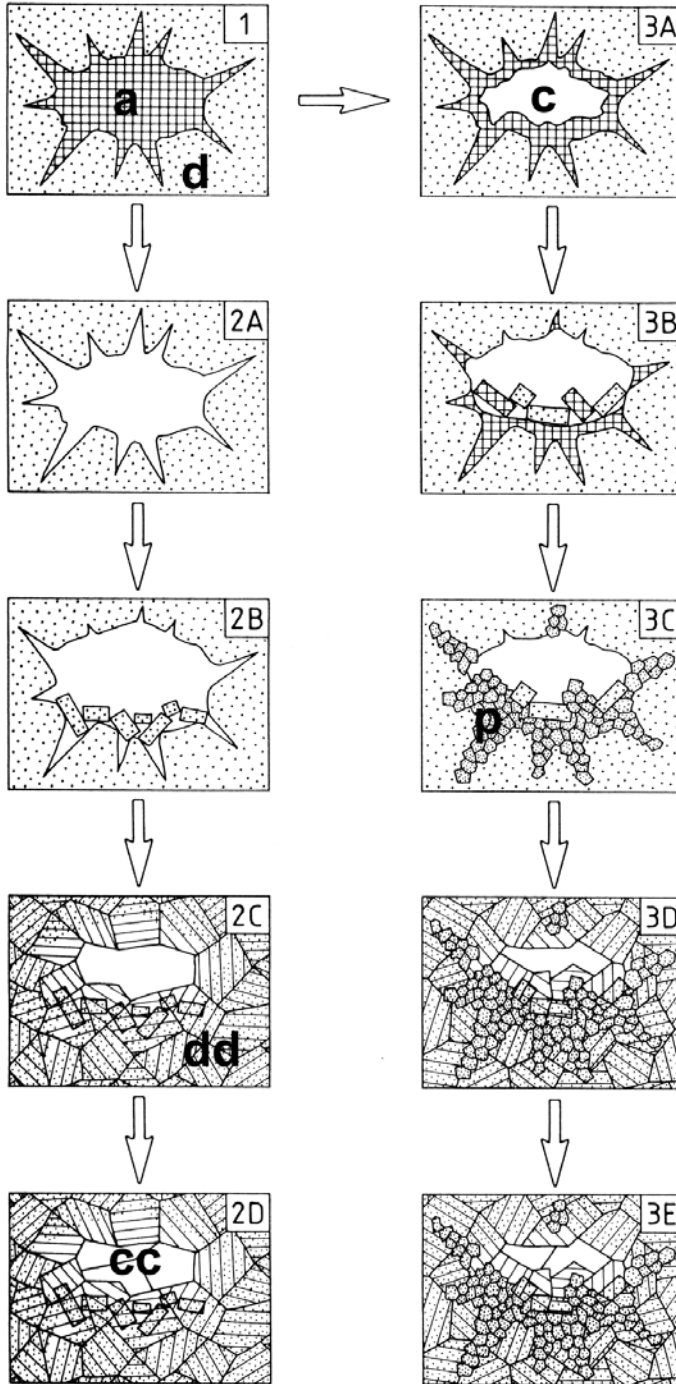


Fig. 4. Interpretation of the origin of calcite clusters from the Muschelkalk of the Holy Cross Mts. a: anhydrite, d: dolomite, c: cavity, p: pseudomorphs after anhydrite, dd: dedolomite, cc: clear calcite. Other explanations in text.

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