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DIAGENESIS OF THE VETERLÍN REEF COMPLEX (MALÉ KARPATY MTS., WESTERN CARPATHIANS): ISOTOPE GEOCHEMISTRY, CATHODOLUMINESCENCE, AND FLUID INCLUSION DATA

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Abstract: The void structures of the Veterlín Limestone are cemented by radiaxial fibrous calcite (RFC), which originated by transformation from the original metastable forms of carbonate. In the transmitted light, the cement of the remaining pores is shaped as blade and blocky pseudospar, while under cathodoluminescence it is structured as zonal luminescent scalenohedral calcite (SHC) and dull euhedral calcite (EHC). Nucleation of neomorphic pseudospar on crystals of predate high-Mg cement occurred in conditions of relatively shallow burial. Saddle dolomite is an another product of the burial diagenesis. Seawater values of $\delta^{18}O$ (-1.2 to -4.5 ‰) and $\delta^{13}C$ (+1.5 to +4.1 ‰) or marine values influenced by mixing (values with a wider distribution of $\delta^{13}C$) are characteristic for isotopic composition of cements in the Veterlín Limestone. The final generation of cements (blocky pseudospar BPS) shows the influence of burial fluids with depletion of $\delta^{18}O$ (-6 to -9 ‰) and preservation of positive values of $\delta^{13}C$ (marine burial trend). The calculated isotopic temperatures from cements ranged between 18 to 60 °C. Homogenization temperatures of fluid inclusions are not consistent with crystallization temperatures of the burial cement, in accordance to their reequilibration under overheating and neomorphism. The Th of the fluid inclusions (155 - 350 °C) probably correspond to the peak-temperature conditions of the Veterlín Limestone, which is also partly the same as that obtained from the CAI of conodonts (110 - 200 °C). The presented diagenetic (cementation) model reflects more really our knowledge about the depositional conditions and also spatial distribution of facies in the Veterlín reef complex.

Key words: diagenesis, reef limestone, cathodoluminescent microscopy, C and O isotope geochemistry, fluid inclusion.

Introduction

The greater part of the Western Carpathian mountain system is built up by thick carbonate masses of the Triassic cycle. A significant part of the Middle and Upper Triassic sedimentary formations in the Western Carpathian region is formed by platform facies of the Wetterstein limestones. Earlier studies of the Wetterstein limestones were devoted mainly to sedimentological investigation and biotic composition (Bystrický 1964, 1982 etc.; Mello 1974, 1975; Hanáček 1976; Jablonský 1973; Gaál 1982; Buček 1988; Michalík et al. 1993), but not yielding a sufficient information about the post-sedimentary development of the limestones. Diagenetic processes changed the sedimentary properties of the rocks with varying intensity. Their identification can explain all depositional conditions which occurred in the Wetterstein carbonate platforms. In the region of the Malé Karpaty Mts., the Wetterstein type limestones named as the Veterlín Limestone form thick carbonate complexes in a tectonically significantly divided as well as reduced area (Plašienka et al. 1991). Different parts of the original sedimentary body of the Veterlín Limestone occur in higher nappe units of the Malé Karpaty Mts. as well as in the neighbouring Vienna Basin basement (Fig. 1). More accurate information on the diagenesis and also the sedimentary development of the Middle to Upper Triassic carbonates is also relevant to the solution of practical geological problems.

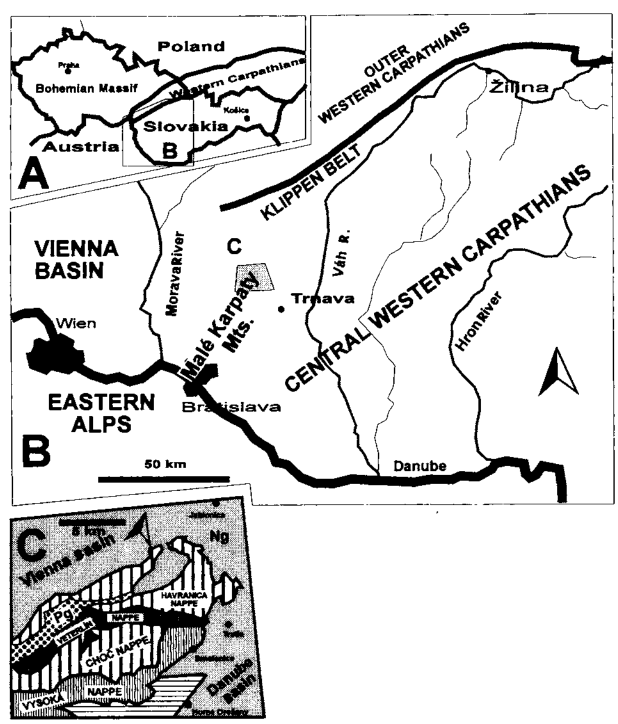


Fig. 1. Location map of the area studied.

In this work we were concerned above all with the study of cements and cavity fillings, with the use of petrographic, cathodoluminescence, isotopic and microthermometry studies. The study of cements as a reflection of the porogenesis and their diagenetic interpretation supplements preceeding results from litho- and biofacial analysis (Michalík et al. 1993; Lintnerová & Hladíková 1992).

Geological setting

The northern part of the Malé Karpaty Mts. (Fig. 1) is formed by carbonate masses of the Veterlín and Havranica Nappes, which are correlated with Göller Nappe of the Northern Limestone Alps (Michalík et al. 1993). The carbonate sequence of the Veterlín Nappe consists of Anisian Gutenstein Dolomite (40 m), Annaberg Limestone (200 - 250 m), Zámostie Formation (30 - 40 m), Ladinian Reifling Formation (40 - 60 m), and Veterlín reef complex formed by platform carbonates.

The Veterlín reef complex consists of a 600 - 1200 m thick sequence of Upper Ladinian to Lower Carnian carbonates, which can be divided into slope mega-breccias and grain flows, fore-reef detritic limestones, reef core bioherm limestone, back-reef and lagoonal limestone. Massive white-grey and cream biolithic limestones (bindstones and bafflestones), spongal-algal limestones and bioclastic limestones with skeletal grains and peloids (grainstones and rudstones) represent the reef facies of the Veterlín complex. The main constructional components of the Veterlín limestones are the calcareous sponges *Sphinctozoa* and *Inozoa*, nodular and dendroidal forms of cyanophytic algae (*Tubiphytes obscurus*), chlorophytic and rhodophytic algae (*Heterotrichella, Pycnoporidium, Solenopora* etc.), incrusting algae (*Thaumatoporella* etc.), colonial and solitary corals and others. The Upper Ladinian to Lower Carnian age of the Veterlín limestones was estimated with the help of foraminifers, dasycladacean algae and conodonts (Buček et al. 1991; Michalík et al. 1993).

Methods

The cements and cavity fillings of the Veterlín Limestone were subjected to thin section, cathodoluminescence and geochemical studies. Methods of fluid inclusions study and colour alteration of conodonts (CAI) were used in addition.

The overall diagenetic fabric of the limestones (22 large thin sections) and the crystallography of the cements (60 small thin sections) were studied by standard petrographic methods. In addition, the usual methods of thin section technique (colouring with alizarine, etching with HCl etc.) were used. Polished and etched (0.2 % formic acid) slides were used for study of the cements with the help of scanning electron microscope (SEM). 35 polished thin sections, with thickness up to 50 μm were prepared for cathodoluminescence study. Cathodoluminescence records were carried out at Geology Department of the Vienna University by a Technosyn 2001 unit operating at 20 kV and 200 - 600 μA. The isotopic analyses were performed in the Isotopic Laboratory of the Czech Geological Survey in Prague, on the Finnigan MAT2 mass spectrometer. Microsamples for isotopic analysis were taken from the polished slides. They were dissolved in 100 % H_3PO_4 at 25 °C. A total of 50 carbon and oxygen isotopic analyses were obtained. The results are given as δ(°/₀₀) and related to the V-PDB standard. The accuracy of measurements is better than + 0.1 °/₀₀ for both measured elements. We estimate the isotopic temperatures by calculation according to Craig's equation (1965) for calcites: $T = 16.9 - 4.21 (\delta_c - \delta_w) + 0.14 (\delta_c - \delta_w)^2$, where δ_c is $\delta^{18}O$ of CO_2 produced from $CaCO_3$ (100 % H_3PO_4, 25 °C) and δ_w is the $\delta^{18}O$ of CO_2 in equilibrium with water at 25 °C, both PDB. We used a value of -1.0 °/₀₀ PDB (Frisia-Bruni et al. 1989) for Mesozoic sea water (δw). The contents of Ca, Mg, Fe, Sr and Na were determined by the standard AAS-method from the separated parts of rock and cement (Geological Institute of the Slovak Academy of Science, Bratislava). The microthermometry results were obtained by measuring the fluid inclusions in doubly polished plates of carbonate with a thickness of 0.2 mm with help of the Linkam freezing-heating stage at the Geological Institute of Slovak Academy of Science, Banská Bystrica. A programme directed the rate of freezing and heating and varied from 100 to 0.2 °C · min^{-1}.

Cement petrography

The most frequent diagenetic phenomena in the limestones of the Veterlín reef complex are cavities, filled by multiple generations of isopachous calcite cements, and cavities with unstratified blocky fillings of pure calcite (Fig. 2). The first type of cavity corresponds to the pore structures named as "evinosponges" (Stoppani 1858; Cosjin 1928; Hofsteenge 1932). Similar cavity structures with multiple generations of fibrous calcite layers were described by German (1971) from the Wetterstein limestones of the Northern Limestone Alps, under the older name of "Grossoolithen". The origin of "evinosponges" and "Grossooliths" in conditions of marine-phreatic and marine-meteoric conditions was proved by studies of crystalline structure, cathodoluminescence and geochemistry by Brandner & Resch (1981), McKenzie & Lister (1983), Henrich & Zenkl (1986), Jadoul & Frisia (1988), Frisia-Bruni et al. (1989), Lobitzer et al. (1990), Mazzullo & Lobitzer (1988) and others.

In the Veterlín Limestone, single or multiple isopachous layers form 10 to 80 % of the evinosponges. They reach a diameter of several centimetres, with the majority isolated or concentrated in small anastomatic groups. Evinospongial cavity structures are best developed in limestones with a growth-constructional porosity. Evinospongial structures in the limestones with vacuole and cavernous types of porosity are developed rarely. The calcite fillings formed by blocky pseudospar there are predominant.

The isopachous cement of cavities in the Veterlín Limestone is formed by brown coloured fibrous (palisade) calcite. The contacts of the evinosponges with the surrounding limestones are usually erosional, influenced by internal dissolution. Stratified isopachous and circumgranular cement is sharply placed on the irregular walls of cavities. More rarely, the walls of cavities are micritized, evidently by algal micritization (Fig. 3 A), or covered by thin laminae of calcilutite (speleothemic microdripstone, Asserto & Folk 1980). Apart from these effects of corrosion and karstification on the walls of cavities, encrustation by pisolithic calcretes were also noted (Fig. 3 B). The calcite of the isopachous cement is formed by polycrystalline aggregates with convergent (radiaxial fibrous calcite - RFC) or more rarely also a divergent (fascicular) optical orientation of the fibrous crystals (Figs. 4 A, B). Precursor ray-crystals and interfibre replacive (cannibalistic) subcrystals are discernible among them. At the contact of the remaining pores, the fibrous crystals of the initial cement are cut down by the effects of dissolution and syntaxial

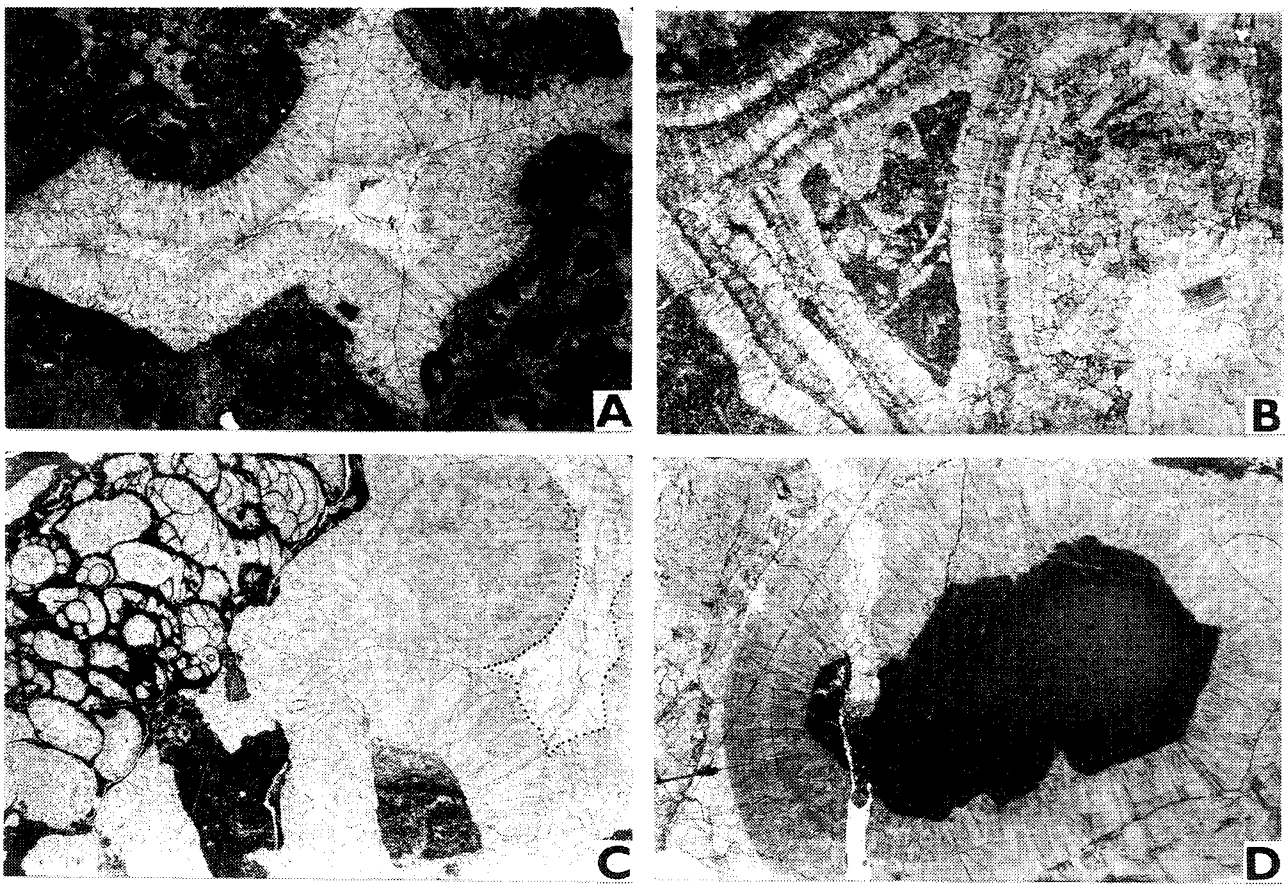


Fig. 2. Void porosity of the Veterlín Limestone and its cements. **A** - Small evinospongia showing irregular dissolutional walls covered with fibrous calcite layer and finally cemented with sparry calcite. Loc. Kršlenica, magnif. 8.5x. **B** - The evinospongia with multiple generations of fibrous calcite layers alternating with dolomite ones. Loc. Vajarská, magnif. 8.5x. **C** - Cavity structures developed between growth skeletons (e.g. sponges) in which the fibrous layers are shaped as hemispheroids. Loc. Kršlenica, magnif. 20x. **D** - Fibrous cement formed evinosponge fringes on the limestone autoclasts. Loc. Kršlenica, magnif. 25x.

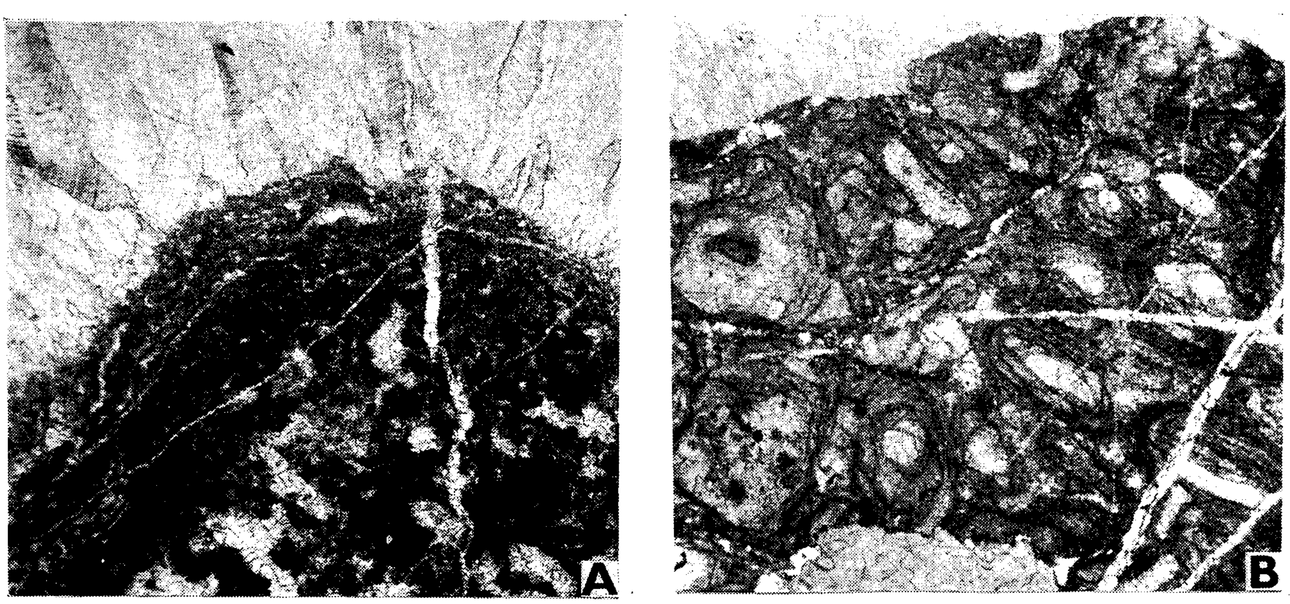


Fig. 3. Coating effects on the cavity walls. **A** - Mamillary crusts originated by algal micritization of the cavity walls. Loc. Kršlenica, magnif. 42x. **B** - Pisolithic crusts originated by calcretization of the cavity walls. Loc. Kršlenica, magnif. 60x.

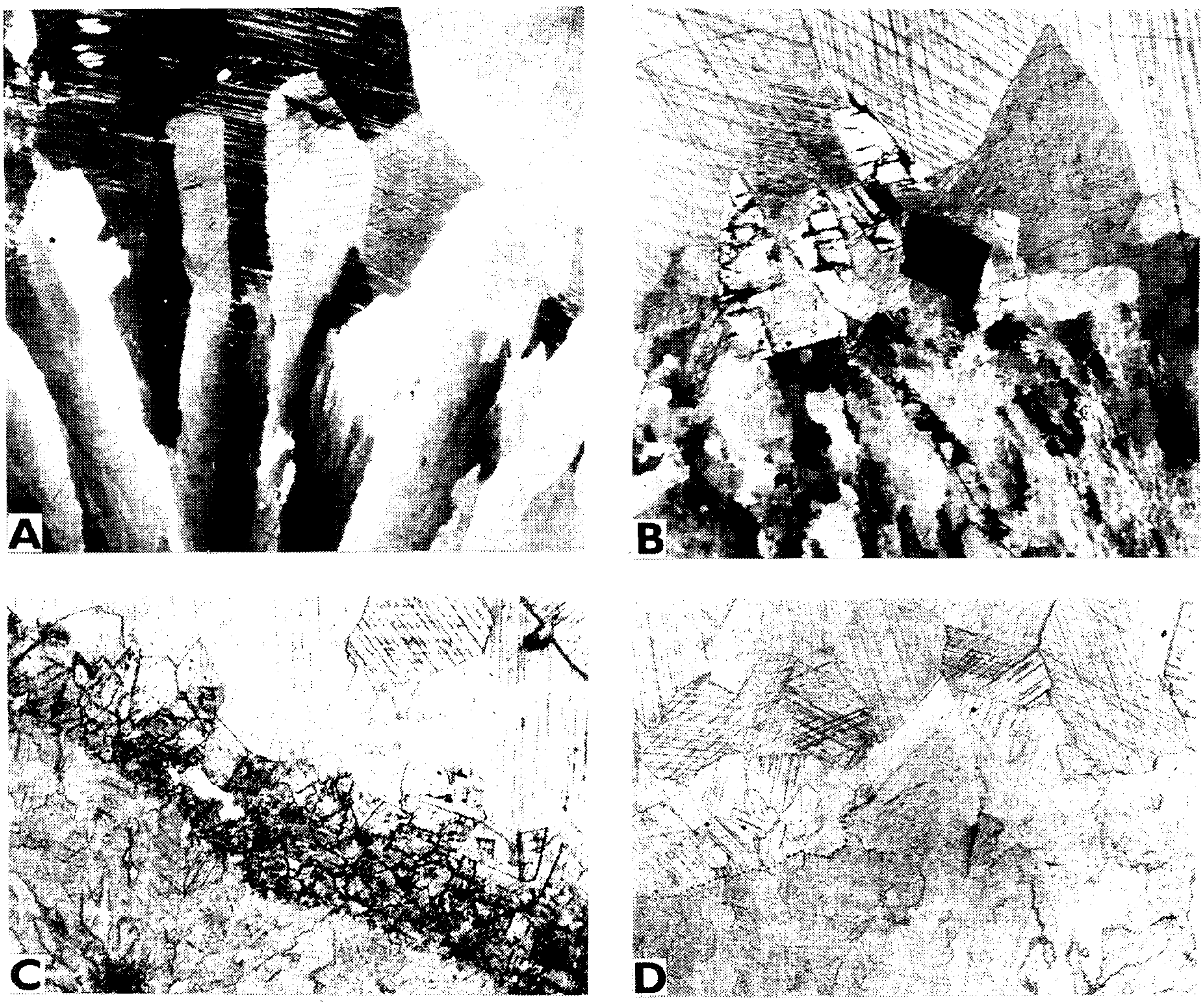


Fig. 4. Crystallographic fabric of the fibrous calcite cements. A - Polycrystalline aggregates of the radiaxial calcite with very distinct elongate subcrystals (cross nicols), Loc. Kršlenica, magnif. 60x. B - Radiaxial cement composed of fibrous subcrystals with strong undulose extinction. Scalenohedral termination on the fibrous calcite represents syntaxial overgrowth (cross nicols). Loc. Vajarská, magnif. 60x. C - Corrosive surface between fibrous layer and blocky calcite cement which is marked by saddled dolomite crystals. Loc. Vajarská, magnif. 42x. D - Radiaxial calcite crystal syntaxially overgrowing by sharp scalenohedral point. Loc. Kršlenica, magnif. 42x.

growth with new points (Fig. 4 B). While the crystals of isopachous cement contain impurities and often exhibit cleavage of twin lamellae, undulations and irregular intercrystalline definition, the points of syntaxial growth are pure and scalenohedrally defined. In cross section, the rays of radiaxial calcite have suture-like intercrystalline surfaces. The contact between two generations of isopachous cement is usually syntaxial, and sometimes marked by small rhombohedrons or subhedral dolomite layers (Figs. 4 C, D). Radiaxial calcite is probably not a primary component of isopachous cement, since the original filling of the evinosponges has little stability and almost always succumbs to paramorphic inversion (Mazzullo 1980). In the case of radiaxial calcite, its crystallographic transformation from the original acicular bundles of high-Mg calcite or aragonite is supposed (Kendal & Tucker 1973; Mazzulo 1980). We noted relics of the primary structure of the radiaxial cement in the form of acicular bundles of calcite ("raggioni" type - cf. Assereto & Folk 1980) in the cavity fillings of the limestones at the Čelo locality.

After the pore margins, the remaining part of the cavities are filled by bladed and in the centres by coarse blocky pseudospar (Figs. 5 A, B). The cavities which were not initially cemented by radiaxial calcite are filled only by bladed and blocky pseudospar (Čelo locality). In other cases the pseudospar phase is not developed, and the crusts of isopachous cement come directly into contact (opposite-radiaxial cement).

As the results of cathodoluminescence study show (see below), the pseudospar fillings were formed by a neomorphism of the predate cement. Bladed pseudospar replaces the scalenohedral drusy calcite at the margins of the remaining pores. The blocky pseudospar originated by nucleation on euhedral crystals of the original cement in the centres of the remaining pores. However, its crystallographic structure is entirely independent at the predate structures (Fig. 6). The cavities filled by the monocrystalline calcite blocks in the Veterlín Limestone of the Kršlenica locality are a special case. These cavities do not have isopachous rims and their contact with the surrounding limestone is uncorrosive. The cavities of these blocks did not

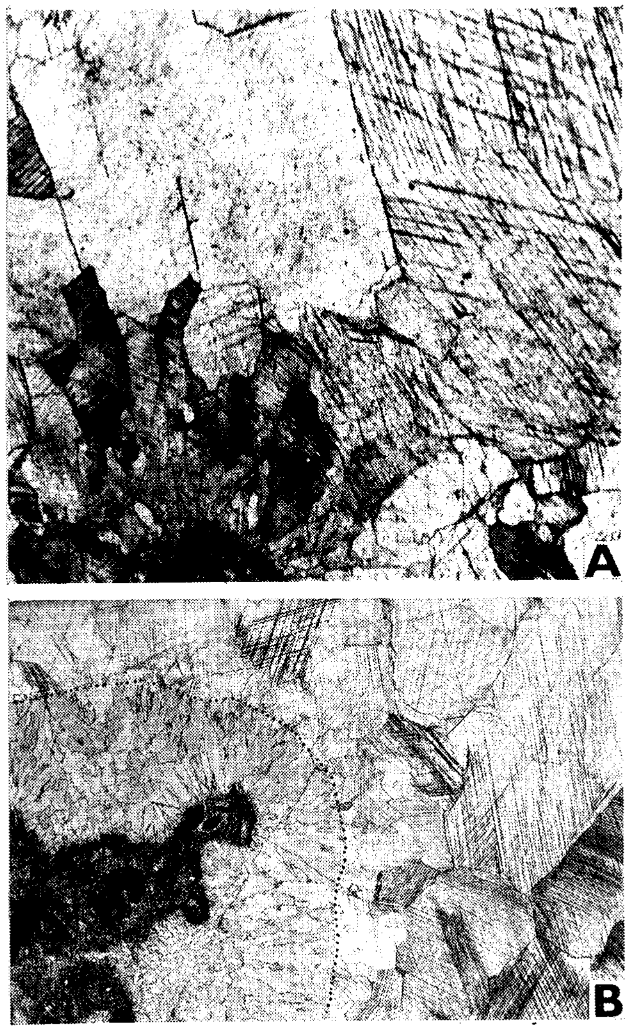


Fig. 5. Crystallographic fabric of the calcite pseudospar in the void-filling cements. **A** - Blade-shaped and blocky crystals of the calcite pseudospar. Coarse blocky calcites have straight cleavage. Loc. Čelo, magnif. 42x. **B** - Initial fibrous cement followed by blocky pseudospar mosaics. Their contact seems to be dissolutional. Loc. Kršlenica, magnif. 25x.

form a connective pump system in the reef, since their walls are not eroded by the circulation of water fluids and are not initially cemented. They are probably isolated, eogenetic and as such could be filled by marine cement. Although blocks of low-Mg calcite may not be precipitated from marine pore waters at lover temperature (Frisia-Bruni et al. 1989), calcite blocks in the Veterlín Limestone are paramorphic filling of the predate cement, or represent burial cement precipitated from the remnants of the undersaturated fluids (Mg penetrated into the surrounding sediment and caused dolomitization).

Cathodoluminescence observation

The cathodoluminescence study enabled us to clarify the cement stratigraphy of the cavity fillings (Fig. 7).

The initial cement of cavities is developed as non-luminescent radiaxial fibrous calcite (RFC). Dissolutional hiatuses on the surfaces of isopachous layers are shown more clearly by the luminescence. The pseudospar of the remaining pores, which in transmitted light has a bladed and blocky habit, is appeared quite differently in the cathodoluminescence light (Figs. 6, 7). The fibrous phase of the initial cementing of the cavities is followed by a scalenohedral calcite (SHC) - Figs. 6 A_1-B_1, A_2-B_2. Scalenohedral crystals with dull or banded luminescence and brightly luminescent haloes on the surface grow into the remaining pore cavities. The centres of the cavities are filled by euhedral sparry calcite (EHC) with dull luminescence, clearer only on the intercrystalline surfaces (Fig. 7). The crystallographic structure of these euhedral calcites is quite different from the structures of replacive calcites occurred in the neomorphic fillings. This points to the nucleation of the crystals of calcite pseudospar on crystals of pre-existing cement. The calcite filling of hair-like microfractures shows the clearest yellow-orange luminescence.

Cement geochemistry

The isotopic composition of cements in the Veterlín Limestone (Tab. 1) was studied at three localities - Kršlenica (22 analyses, comparison of analyses Lintnerová & Hladíková 1992), Vajarská (18 analyses) and Čelo (10 analyses). The contents of Ca, Mg, Mn, Fe, Sr and Na in the blocky calcites were determined (Tab. 2). The following isotopic trends appear in the cements of the Veterlín Limestone, and at the same time there were certain differences between the three localities mentioned (Figs. 9, 10, 11).

1 - *Marine trend* (Vajarská locality: Figs. 9, 11): The contents of $\delta^{18}O$ reach the highest values at the localities compared, and comparable to the values found in recent marine carbonates (Hudson 1977). In the matrix of the rock, as well as in the generations of RFC cement, the values of $\delta^{18}O$ vary from -2.7 to -1.2 ‰ (Tab. 1), which corresponds to the values of $\delta^{18}O$ from limestones of the intra-platform Reifling depression of the Veterlín Unit (Masaryk et al. 1993). The differences in $\delta^{18}O$ and $\delta^{13}C$ between the matrix and the first generation of RFC cement are lowest, in the part of the samples they also have a positive shift towards the cements. In the fillings of the remaining pores, or cavities filled by blocky calcite, $\delta^{18}O$ values reach the range -6.1 to -6.9 ‰ and they have similar depletion as the cements from other localities affected by processes of burial diagenesis.

2 - *Marine trend partly influenced by mixing* (Kršlenica locality: Figs. 8 to 11): The contents of $\delta^{13}C$ vary in the range +2.0 to +4.1 ‰, but in individual samples the differences are smaller. They remain positive, but have a greater range of values, which indicates the partial influence by solutions of meteoric origin. The values of $\delta^{18}O$ are -2.6 to -8.0 ‰ and decline in the direction from the matrix to the inner parts of the cavity filled by pseudospar to blocky calcite (Figs. 8, 10). Such values of $\delta^{18}O$, with a wider dispersion for $\delta^{13}C$ does not exclude the mixing of marine and meteoric waters in a phreatic environment.

3 - *Burial trend* (Čelo locality: Figs. 9, 11): The values of $\delta^{13}C$ are relatively high and vary in a narrow range (+3.1 to +3.5 ‰). They have a negative pair $\delta^{18}O$ values, which show the most significant lightening from the localities studied (-5.9 to -8.6 ‰).

Fluid inclusions microthermometry

The usable fluid inclusions are recorded only in blocky calcite cement. Fluid inclusions in blocky pseudospar (BPS) are circular or elliptical with diameters up to 5μm. In calcite crystals the inclusions are isolated, or arranged along twin lamellae. They

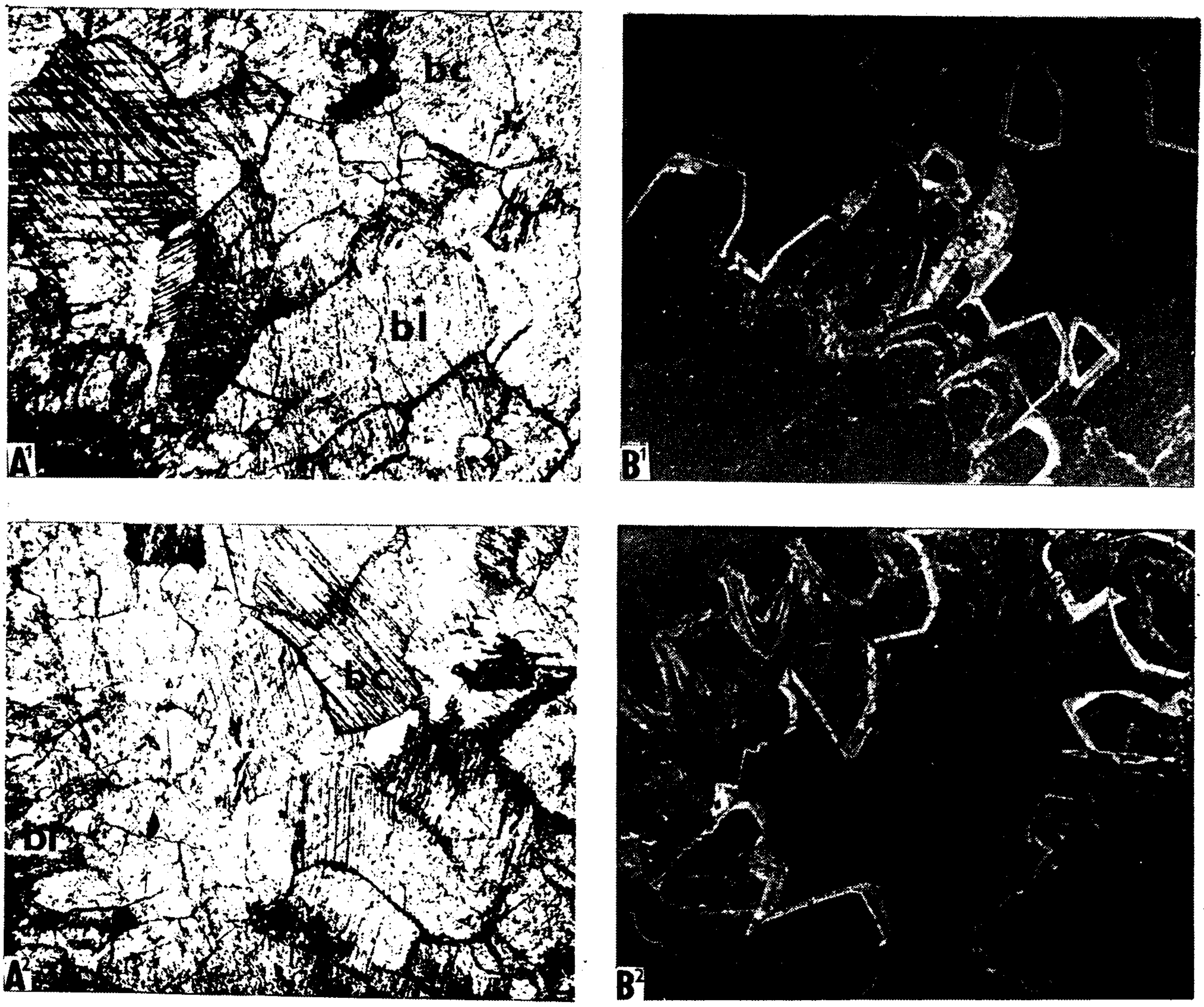


Fig. 6. Calcite cavity fillings in the Veterlín Limestone showing different crystalline structures in transmitted (A^1A^2) and cathodoluminescent (B^1B^2) lights. Locality Čelo, magnif. 42x. A^1A^2 - Neomorphic cavity cement formed by bladed and blocky pseudospar (bl, bc). B^1B^2 - Cavity structures A^1A^2 in cathodoluminescent light. Originally, they were filled by scalenohedral calcite crystals with banded luminescence and bright luminescent haloes.

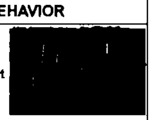
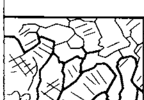
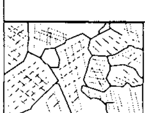
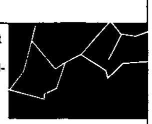
CEMENT TYPE		DIAGENETIC EVENT	CATHODOLUMINISCENCE BEHAVIOR	
	radiaxial calcite	isopachous (circumvoid-circumgranular) layers	non luminescent	
	bladed pseudospar	scalenohedral phase	dull crystals with bright luminescent haloes	
	blocky pseudospar	late mosaic phase	non-luminescent to dull crystals with brightly luminescing intercrystalline boundaries	

Fig. 7. The crystalline structures and cathodoluminescence behaviour of different types of cements in the cavity fillings of the Veterlín Limestone.

are two- or three-phases inclusions consisting of aqueous solution and vapour bubble or aqueous solution, vapour and liquid CO_2. Small quantities of CO_2 have been detected by freezing-point measurements and/or by CO_2 clathrate dissociation temperatures. Upon heating the fuid inclusions in calcite yielded homogenization temperatures (Th) ranging from 155 to 350 °C (Fig. 13 A). The initial melting temperatures (Te = -34 to - 65 °C, Fig. 13 B) suggest the presence of NaCl, $MgCl_2$, $CaCl_2$ (may be also another salts) in the trapped fluids. Ice- or CO_2 clathrate-melting temperatures (Tm) ranged from -17 to 2.0 °C. These Tm values are responsible for fluid salinity range from 0.7 to 20.2 wt. % NaCl. The measured microthermometric data suggest that the CO_2-enriched inclusions yield the higher temperatures of homogenization than H_2O-NaCl inclusions without CO_2 (see discussion).

Table 1: Isotopic analyses of O and C for the part of the reef limestones studied.

Samples	$\delta^{13}C$ [‰]PDB	$\delta^{18}O$ [‰]PDB
Vajarská 2		
matrix	+1.5	-1.6
cement ISP	+2.1	-1.7
calcite BPS	+2.4	-1.8
Vajarská 3		
matrix	+2.2	-1.5
cement ISP I	+2.2	-2.7
cement ISP II	+2.7	-1.4
calcite BPS 1	+2.6	-2.5
calcite BPS 2	+1.8	-6.9
calcite BPS 3	+1.0	-6.1
Vajarská 4		
cement ISP I	+2.5	-2.5
cement ISP II	+2.4	-2.6
calcite BPS	+2.2	-2.4
Vajarská 10		
matrix	+2.3	-2.7
cement ISP II	+2.3	-1.2
cement ISP III	+2.0	-5.6
calcite BPS	+2.4	-3.8

Samples	$\delta^{13}C$ [‰]PDB	$\delta^{18}O$ [‰]PDB
Kršlenica 5		
cement ISP I	+2.8	-3.9
cement CG	+2.6	-4.1
calcite BPS	+3.4	-5.3
Kršlenica 7		
matrix	+3.1	-5.0
cement ISP I	+3.0	-4.6
calcite BPS	+2.5	-8.0
Kršlenica 8		
matrix	+2.8	-4.2
cement ISP I	+2.0	-5.0
calcite BPS	+2.9	-5.7
Kršlenica 40/1		
cement ISP I	+3.1	-4.7
cement ISP II	+3.2	-5.6
calcite BPS	+3.0	-6.1
Kršlenica 40/2		
matrix	+4.1	-2.6
cement ISP I	+3.0	-4.5
cement ISP II	+2.8	-3.9
cement ISP II	+3.1	-4.4
calcite BPS	+2.9	-6.5
crinoid	+3.4	-4.2
Kršlenica 40/6		
matrix	+2.4	-3.8
cement ISP	+3.8	-2.7
calcite BPS	+2.8	-5.0

Samples	$\delta^{13}C$ [‰]PDB	$\delta^{18}O$ [‰]PDB
Čelo 1		
matrix	+3.3	-6.4
cement ISP	+3.3	-6.2
calcite BPS 1	+3.1	-8.6
Čelo 2		
matrix	+3.2	-6.8
cement	+3.2	-6.1
calcite BPS1	+3.4	-6.3
calcite BPS2	+3.5	-5.9
Čelo 3		
matrix	+3.3	-6.4
cement	+3.3	-7.9
calcite BPS	+3.4	-7.3

Colour alteration index of conodonts

Since the colouring of conodonts is controlled by the temperature of the rock environment (Colour Alteration Index - CAI - Harris 1979; Epstein et al. 1977), we also used this criterion for estimating the temperatures of burial. The association of conodonts was extracted from the lowest part of the Veterlín Limestone Formation representing the fore-reef slope, that is the transitional facies into the Reifling depression (Lintnerová & Hladíková 1992; Michalík et al. 1993; Masaryk et al. 1993). In the Veterlín Unit, the platform limestones and basinal sediments pass laterally and stratigraphicaly one another, and so there is no reason to suppose differences in their thermal history.

Conodonts from the Veterlín Limestone show CAI values of 3 (max. 3.5), which would correspond to temperatures around 110 - 200 °C (max. 240 °C). Such values exceed the range of diagenetic temperatures.

Dolomitization

In the Veterlín Limestone, dolomitization has a selective character (fabric-selective dolomitization). Well developed limpid dolomite rhombohedrons are associated especially with the marginal zones of algal nodules, sponge skeletons etc. (Fig. 14 A, D). They reach a size of 0.08 - 0.13 mm, and usually have dull cores. Dolomite rhombohedrons and their aggregates are also especially concentrated in the walls of the evinosponges (Fig. 14 B), and most of all in the limestone extraclasts surrounded by circum-granular RFC cement (Fig. 14 C), which are mostly completely dolomitized. Since the dolomitization structures are still controlled by the depositional structures of the limestones, they probably represent early diagenetic phenomena. It is probably necessary to connect the main phase of dolomitization with fluids liberated from the high-Mg carbonates, which were transformed into low-Mg calcites, at conditions of shallow burial. These dolomitization processes preceded the main phase of calcite cementation of cavities, and interparticle pores, which points to their burial origin. The form of their products, zonal dolomite rhombohedrons with dull cores and pure rims (Fig. 14 B, D), also points to the burial character of this dolomitization (Mattes & Mountjoy 1980). At the same time the dull cores represent replacement dolomite (Amthor & Friedman 1991), already nucleated in an earlier phase of dolomitization. This phase of dolomitization occurred even before the precipitation of RFC cement and is perhaps connected with the mixing of waters in the cavity system of the Veterlín Limestone.

Saddle dolomite crystals relatively often replace the block pseudospar of the remaining pores. It is a younger diagenetic product than the pseudospar, since it cuts into its mineralogical

Table 2: Results of chemical analyses of the matrix and cements of the reef limestones. CaO, IR (insoluble residuum) - classic chemical analysis; MgO, Na, K, Mn, Fe, Zn, Sr - AAS.

Samples	CaO	MgO	IR	Na	K	Mn	Zn	Fe	Sr
	%			ppm					
Vajarská 1									
matrix	51.08	4.33	0.02	264	75	42	21	125	153
cement	52.80	2.60	0.10	134	50	31	6	80	219
calcite	55.39	0.44	0.01	108	50	29	6	70	311
Vajarská 2									
matrix	36.56	16.60	0.14	229	68	33	15	138	62
cement	46.92	7.93	0.12	202	55	29	12	101	105
cement	55.24	0.68	0.03	140	50	32	8	62	247
Vajarská 3									
matrix	55.11	0.93	0.15	141	55	32	4	81	160
cement	55.24	0.62	0.08	122	44	29	3	76	178
cement	55.24	0.59	0.04	145	38	30	4	64	154
Vajarská 4									
matrix	55.11	0.93	0.15	141	55	32	4	81	160
cement	52.61	3.03	0.01	333	62	37	6	94	121
cement	54.97	0.74	0.01	135	57	24	6	73	156
Kršlenica 5									
matrix	55.11	0.93	0.03	112	32	101	11	108	108
cement	55.25	0.35	0.02	104	44	62	6	99	117
Kršlenica 7									
matrix	55.66	0.39	0.02	163	53	49	6	72	130
calcite	55.52	0.27	0.00	195	79	230	5	166	145
Čelo 1									
matrix	55.65	0.26	0.03	113	25	55	7	53	138
calcite	55.79	0.21	0.06	158	55	61	7	49	194
Čelo 2									
matrix	53.13	2.37	0.05	120	25	39	18	79	85
cement	48.64	6.01	0.05	245	33	61	13	66	138
calcite	52.15	3.06	0.18	173	40	69	11	63	161
Čelo 3									
matrix	47.38	7.04	0.23	275	47	71	20	171	99
cement	55.23	0.62	0.09	123	37	39	10	117	92
calcite	55.37	0.33	0.01	158	27	81	10	53	186

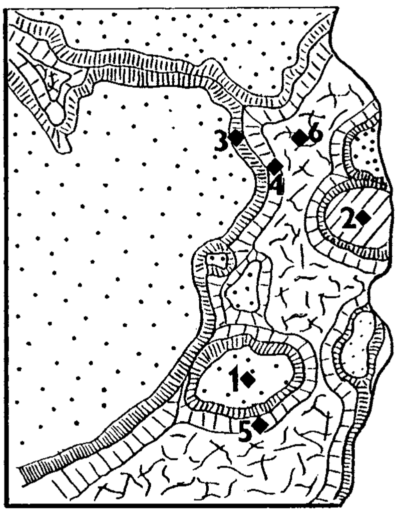
boundaries (Fig. 15). The presence of saddle dolomite suggests the replacement dolomitization of blocky pseudospar by diagenetic fluids in higher temperature condition. Dolomitization process is generally favored by high temperature (60 - 90 °C).

Interpretation and discussion

Cathodoluminescent evidence

Cathodoluminescence study proves the structural redistribution of the cavity fillings in the Veterlín Limestone and their replacing by neomorphic spar. From the cathodoluminescence behaviour of the calcite in cavity fillings, it is possible to consider the conditions of neomorphosis, which may have an eogenetic (transformation from metastable carbonates) or mesogenetic character (stabilization in conditions of burial diagenesis). The chief contribution of cathodoluminescence is proof of the zonally luminescent calcite growing into the remaining pore cavities, the scalenohedral habit of which recalls the vadose cement of the "dog tooth" type. The presence of zonally luminescent cement in cavity fillings of the limestones is mostly considered a sign of meteoric-phreatic diagenesis (Meyers 1974, 1978; Grover & Read 1983 etc.). Subzones of clear luminescence in dull crystals could indicate a stagnation of marine influence in the cavity system of the Veterlín Limestone and the alteration of pore fluids by meteoric waters enriched with Mn. On the other hand, the luminescence zonality of calcite is explained by fluctuating changes of redox conditions in marine burial cements (Kerans 1985). According to Scholle & Halley (1985) banded luminescence of burial cements resulted from fluctuating changes in the temperatures of pore waters with the burial depth.

Changes in luminescence are associated with a decline in $\delta^{18}O$. In contrast to the meteoric cement, lack of corrosion phenomena and a shift of isotopic carbon to negative values is characteristic of zonally luminescent calcites of burial cements (Hur-



Kršlenica 2	^{13}C	^{18}O
1 - extraclast of host limestone	4,1	-2,6
2 - crinoidal particle	3,4	-4,2
3 - isopachous cement I.	3,0	-4,5
4 - isopachous cement II.	4,1	-2,6
5 - isopachous cement III.	3,4	-4,2
6 - blocky pseudospar	2,9	-6,5

Fig. 8. Sample Kršlenica-2 showing the isotopic relations between the host rock and the cement generations, and the method of taking material for $\delta^{18}O$ and $\delta^{13}C$ analyses.

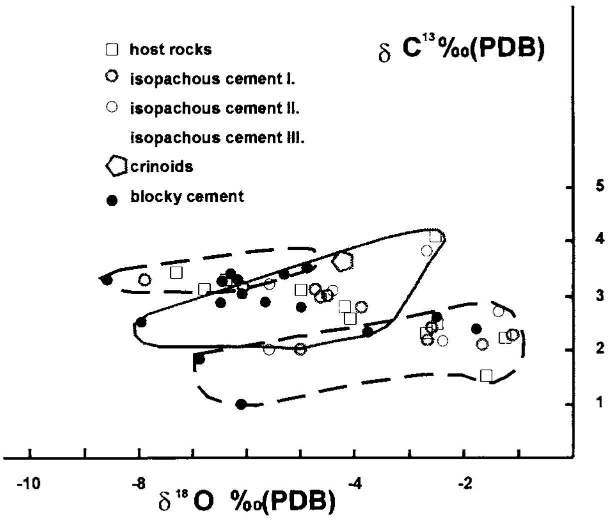


Fig. 9. In the graph of $\delta^{13}C$ vs. $\delta^{18}O$ ploted all samples with differentiation for matrix, isopachous cements and cements of the remaining pores (legend), we can follow the grouping of values from individual localities.

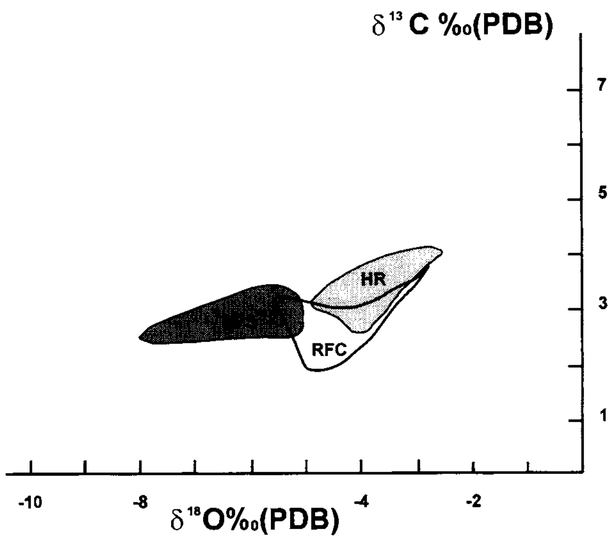


Fig. 10. The isotopic values from the locality Kršlenica most significantly document the depletion of $\delta^{18}O$ from the host rocks (HR) into the younger generation of cement fillings (RFC - BPS).

ley & Lohman 1989). The absence of corrosion effects, chemical composition (e.g. Mn - Tab. 2) and positive values of $\delta^{13}C$ in SHC/EHC-cement fillings of the Veterlín Limestone points rather to their marine-burial origin.

Isotopic evidence

The differences between the limestones and the first isopachous cements are not isotopically very significant. In spite of this, the values of $\delta^{18}O$ in the stratified isopachous cement show a negative shift (Fig. 9, Tab. 1). Partial changes of chemistry also appear (Tab. 2). The dissolution of the walls of cavities before the precipitation of isopachous layers could indicate at least phreatic conditions of diagenesis (Frisia-Bruni et al. 1989). The wider variation of $\delta^{13}C$ recorded at the Kršlenica locality, is probably an isotopic signatures for mixing of pore fluids in the cavity system of the Veterlín Limestone. The dolomitization of the walls of the evinosponges could also be a phenomenon of the percolation of meteoric waters (mixing dolomitization). However, the precipitation of dolomite in the evinosponge walls could also be caused by Mg fluid liberated from high-Mg radial fibrous calcite stabilized on low-Mg calcite in conditions of shallow burial (burial dolomitization). Smaller differences in the contents of $\delta^{18}O$ between the initial cement of the cavities and the surrounding limestones may be explained by the limestones receiving a state of equilibration with isotopically light meteoric water, but more probably with pore fluids whose $\delta^{18}O$ depletion was a result of burial temperature (filling of pores, but also recrystallization of limestones by sparite with light oxygen). Moreover, in several cases the limestones yielded the greater content of light oxygen, comparable to the values measured in Upper Triassic aragonite tests (-2.5 ‰ according to Scherer 1977) and to other marine isotope standards (e.g. -5.0, -4.2 and -3.8 ‰ $\delta^{18}O$ in limestones from the Kršlenica locality, Tab. 1; Figs. 9, 10).

The decrease of $\delta^{18}C$ in younger generations of isopachous cement (RFC) reflects the progressive lightening of pore waters. The most significant differences of isotopic content are between the cement of the isopachous layers and the cement of the remaining pores, which are filled by blocky pseudospar (BPS). The decline in $\delta^{18}O$ content in the cement of the remaining pores reaches values which have already been characteristic for meteoric cements. However, the increase in light oxygen mentioned in the isopachous cement and especially in the cement of the remaining pores is not in accordance with the contents of iso-

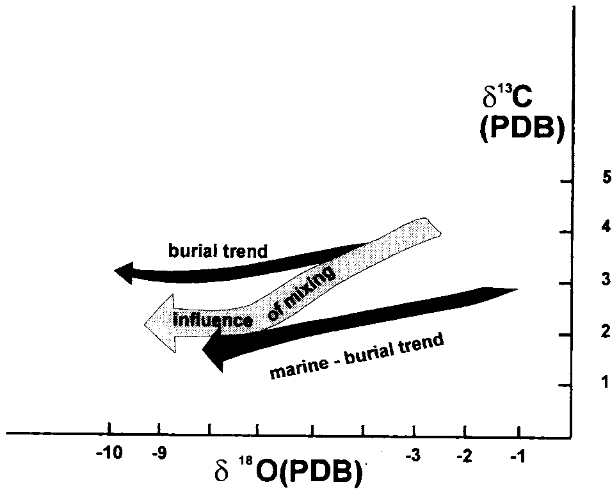


Fig. 11. Isotopic trends appearing in the diagenetic development of the Veterlín Limestone at the localities Vajarská (marine trend), Kršlenica (marine trend partly influenced by mixing), and Čelo (burial trend).

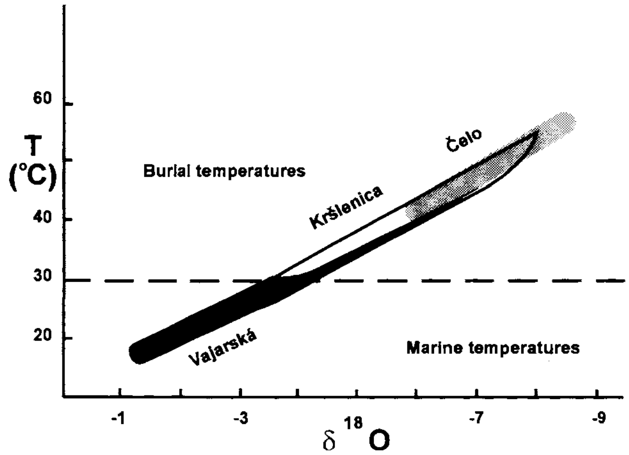


Fig. 12. Diagram of isotopic temperatures T against $\delta^{18}O$, defining the fields of sedimentary and diagenetic cement temperatures of the Veterlín Limestone.

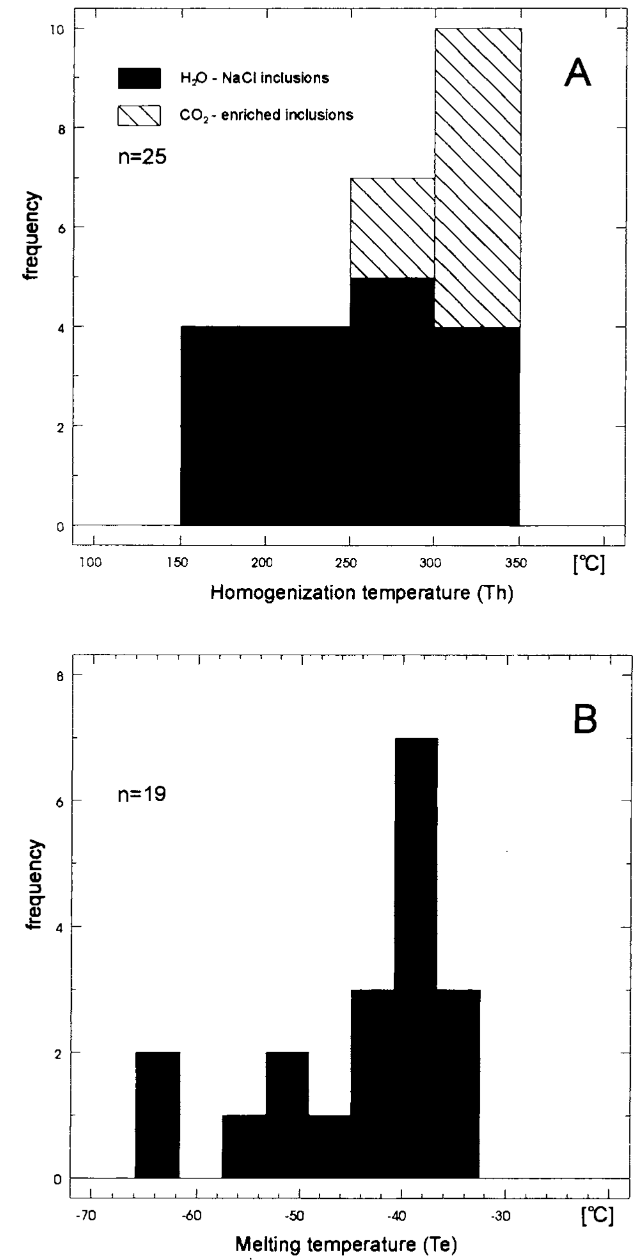


Fig. 13. Fluid inclusion measurements from the blocky calcite cement of the Veterlín Limestone. **A** - Histogram of homogenization temperatures (Th). **B** - Histogram of initial melting temperatures (Te).

topic carbon, which are entirely consistent and never reach negative values (Tab. 2, Fig. 10). However, the positive values of $\delta^{13}C$ in evinosponge cements of the Veterlín Limestone do not exclude the possibility of their meteoric alteration, especially if the range of values is greater. Jadoul & Frisia (1988), Frisia-Bruni et al. (1989), Kantor & Mišík (1992) etc. also mention such values in the evinosponges of Wetterstein limestones or similar limestones, the origin of which clearly reflects conditions of mixed marine-meteoric diagenesis. Therefore, it is possible that, the production of light carbon from soil CO_2 (plant metabolism, bacterial breakdown etc.) in conditions of an extensive Triassic carbonate platform was minimal. Signs of covariant linear trends in the positive values of $\delta^{13}C$, which appear for example in cavity cements at the Kršlenica locality (Figs. 8 to 10), could therefore be considered as a record of meteoric alteration.

On the other hand, the constant contents of carbon isotopes and the decrease in the proportions of oxygen isotopes are often mentioned from burial cements (Walls et al. 1979; Dickson & Coleman 1980; Moldovanyi & Lohmann 1984 etc.). The isotopic composition of burial cements is not controlled only by the composition of pore waters, but chiefly by temperature (Hurley & Lohmann 1989). While the proportions of carbon isotopes are not more significantly influenced by temperature, the contents of light oxygen increase by -2 ‰ for each 10 °C of temperature (Friedman & O'Neil 1977). Such isotopic proportions are also characteristic for cavity fillings in the Veterlín Limestone. Therefore, we interpret the depletion in $\delta^{18}O$ and concominant more or less constant contents of carbon isotopes, as a result of crystallization from warm burial fluids (purely marine, or with meteoric influence as well) and not from isotopically light meteoric waters. Saddle dolomite is also typical for

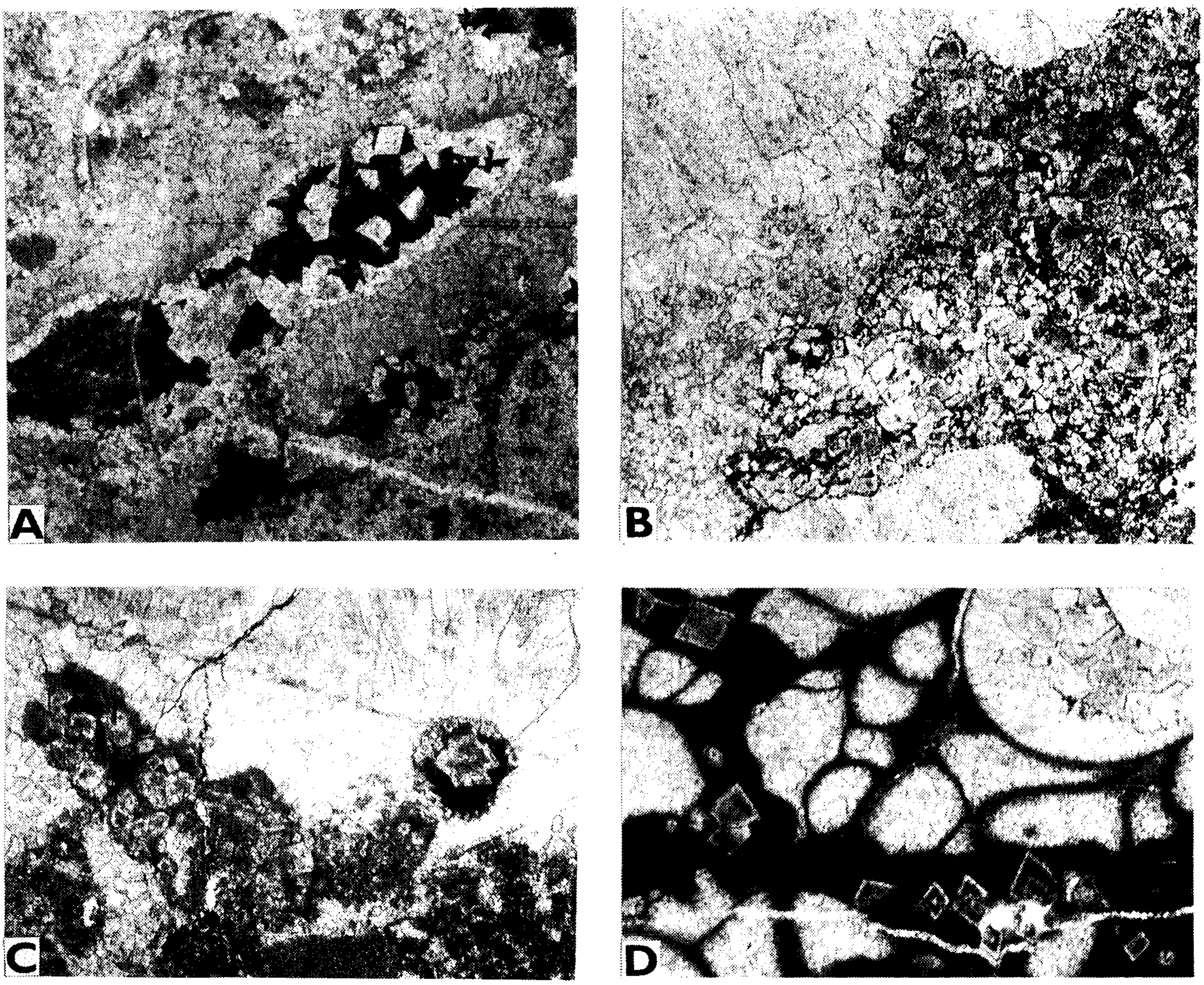


Fig. 14. Textural patterns of the dolomitization in the Veterlín Limestone. **A** - Limpid dolomite rhombohedrons deposited preferentially on the outer margin of the *Tubiphytes*-nodule. Loc. Kršlenica, magnif. 25x. **B, C** - Circumvoid dolomitization of the evinosponge walls. Loc. Kršlenica, magnif. 42x. **D** - Dolomite rhombohedrons exhibiting a cloudy cores and clear rims (some of them showing a zonal structure too). They are deposited in the walls of the sponge skeleton. Loc. Kršlenica, magnif. 60x.

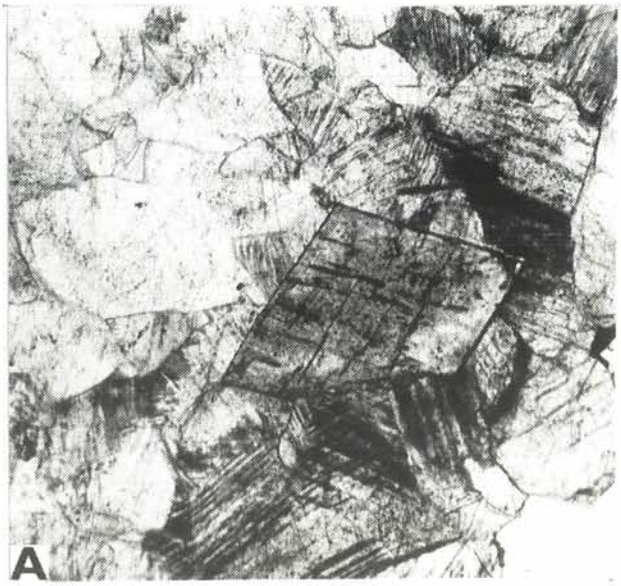
burial cements indicating higher diagenetic temperatures (Radke & Mathis 1980).

The fact that any reliable isotopic evidence for meteoric origin does not exist, even for blocky calcite from the cavity fillings of Veterlín Limestone, is apparently in disagreement with crystallographic habitus. Blocky structure, substrate selectivity, dissolution features, lack of luminescence and covariant trends of oxygen and carbon isotopes, are marks of meteoric-phreatic cements (Walkden & Williams 1991). On the other hand, it is also known that deeply buried cements have similar morphology to some meteoric cements (Saller & Moore 1991). Therefore, blocky calcites may be also originated in conditions of deep burial by change of the chemistry of pore fluids and depletion in ^{18}O, as a result of temperature alteration. However, morphologically homogeneous calcite blocks in the Veterlín Limestone mask the structure of predate cements. Apart from the cathodoluminescence, significant differences of isotopic composition between the marginal and middle parts of calcite blocks have been recorded (e.g. Vajarská 3: margin -2.5 ‰ $\delta^{18}O$, middle -6.1 to -6.9 ‰ $\delta^{18}O$).

Evaluation of temperature

Temperatures comparable to the recent marine conditions were calculated from samples from the Vajarská locality. High $\delta^{18}O$ values (-1.2 to -2.7 ‰) for the matrix, and marine RFC cements with normal marine values for $\delta^{13}C$ (+1.0 to +2.7 ‰), yield temperatures in the range 18 - 25 °C. Frisia- Bruni et al. (1989) calculating from the aragonite-water equation determined for the Upper Triassic marine water, an average temperature of 24 °C, which corresponds to -2.75 ‰ $\delta^{18}O$ (for aragonite values according to Scherer (1977) were used). The values for isotopic proportions and the temperatures corresponding to them, from the Vajarská locality, are comparable to marine conditions creating aragonite/calcite in the Cassian beds, or in recent seas.

The temperatures of the later cements (blocky calcites) from the Vajarská are shifted into the area of diagenetic temperatures 30 - 47 °C (Fig. 12). The range of temperatures calculated from the Kršlenica (24 - 53 °C) partly extend the range of temperatures from the Vajarská. The burial blocky cements with a maximum lowering of $\delta^{18}O$ to -8.6 ‰ from the Čelo locality have



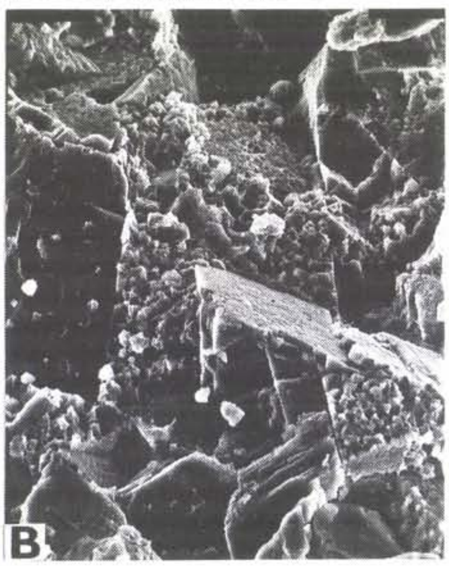


Fig. 15. Saddle dolomite hosted in late mozaic calcite cement (LMC). **A** - Well-formed saddle dolomite crystal which cuts across mineralogical boundaries of LMC and showing sweeping extinction. Loc. Kršlenica, magnif. 107x. **B** - SEM image of saddle dolomite crystal with steps of rhombohedral planes and small faces. Loc. Vajarská, magnif. 100x.

a higher temperature compared to the Vajarská locality (Fig. 12). At such temperatures, low-Mg calcite may be precipitated from purely marine fluids (Frisia-Bruni et al. 1989). However it is possible that meteoric conditions also influenced the most significant negative shift of $\delta^{18}O$, and the more closed or stagnant system in the back-reef environment with buried sediments. This is reflected especially in the isotopic temperatures calculated from the limestones, as well as the cavity cements at the Čelo locality (41 - 57 °C).

The saddle dolomite is also a specific component of the cements which may also define the temperature conditions of the diagenetic system. According to Radke & Mathis (1980), a temperature range of 60 to 150 °C, but especially a temperature close to 90 °C may be characteristic. The saddle dolomite was stratified into the youngest parts of the cement fillings, or the boundaries between the final generations of marine and burial calcite cement.

Isotopic temperatures are characteristic of the conditions of diagenetic stabilization of the matrix and cements. Diagenetic recrystallization of the matrix occurred in a low temperature environment, close to the conditions of sedimentation. Burial cements with temperatures not exceeding 60 °C correspond to relatively shallow burial (according to the geothermal gradient).

The results of the fluid inclusion study are not in accordance with other paleothermometric data. Disagreement between homogenization and isotopic temperatures is quoted relatively frequently (Moore 1985; Coniglio & Williams-Jones 1992, etc.). Oxygen depletion at the measured Th temperatures could result in more negative values of $\delta^{18}O$. Other authors also mentioned similar isotopic values from cements showing high homogenization temperatures for inclusions (e.g. Liu & Rigby 1992, Th 170 - 200 °C; $\delta^{18}O$ -5.3 to -8.7 ‰; $\delta^{13}C$ +1.8 to +4.19 ‰). The melting temperatures of inclusions (Tm) reflecting the mixture of the meteoric-briny waters, while the carbon isotopic ratios are derived from marine-burial waters.

The wide range of homogenization temperatures (Th = 155 - 350 °C and variable salt composition (0.7 to 20.2 wt. % NaCl) characterizes the fluid inclusions which have undergone to post-entrapment reeqilibration (Goldstein 1986). The reequilibration of the fluid inclusions studied can be also supported by the presence of CO_2, at the same time no organic carbon has been recorded in the isotopic composition of the cements. The presence of CO_2 in the fluid inclusions can be explained by stability variations of the carbonates in the co-ordinates temperature - CO_2 fugacity under the conditions of recrystallization and neomorphism. The variability in the CO_2-contents can be explained also by the liberation of H_2O from the inclusions which were reequilibrated through the hydrofracturation of the calcite under burial heating (Bakker & Jansen 1991; Goldstein l.c.). Overheating of the inclusions caused plastic deformations of the inclusion walls (stretching or leakage) as well as the enlargement of the inclusion bulks. As a result of these effects, the inclusions yielded higher temperatures of homogenization (Bodnar & Bethke 1984). From the wide range of Th, variable fluid salinity and CO_2-enriched composition, we assume that the fluid inclusions actually preserve none the crystallization temperatures of the cements. Therefore, the original inclusions were clearly overprinted by the processes of reequilibration, neomorphism and overheating. Perhaps only the H_2O-NaCl inclusions yielding homogenization temperatures between 155 - 215 °C without CO_2 were inferred by mentioned processes in lesser intensity. Therefore, they are closer to the temperatures of burial diagenesis. Similar temperatures were also derived by the fluid inclusion study of Walter et al. (1993) from the blocky calcite cements of the Wetterstein limestones in the Northern Calcareous Alps (200 - 250 °C).

The temperatures determined by the colour of conodonts and the homogenization temperatures of the fluid inclusions overlap each other and essentially reflect the highest temperatures in the burial and tectonic history of the Veterlín Unit.

Model of diagenesis

Syndepositional porogenesis occurred in the reef complex of the Veterlín Limestone. The cavity structures began to develop from primary vacuole, cavernous and growth-constructed porosity (Fig. 16). The cavity system of the Veterlín Limestone,

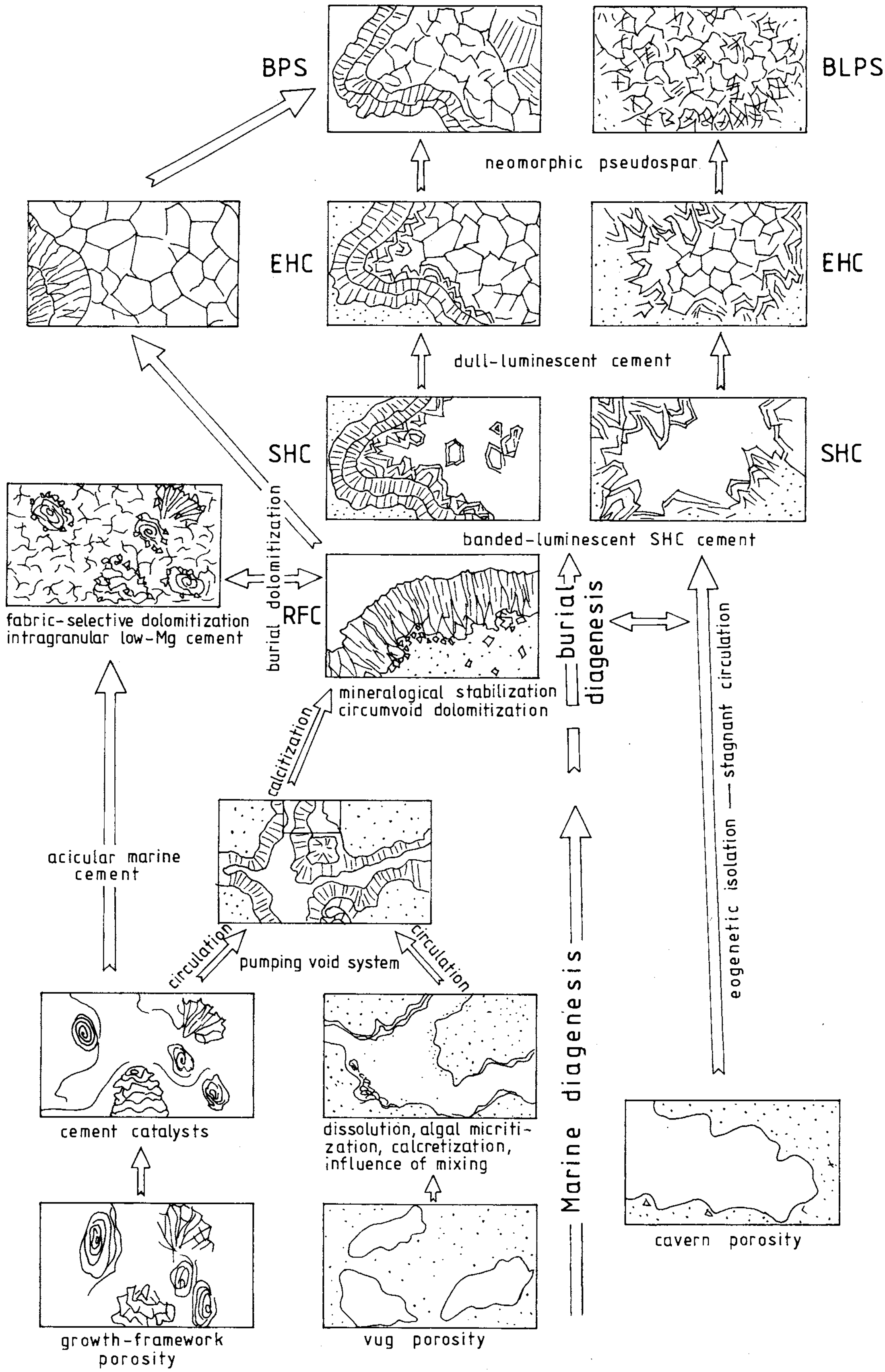


Fig. 16. Reconstruction of the diagenetic development of the Veterlín Limestone, including the processes of porogenesis, internal dissolution, marine cementation, burial diagenesis and neomorphism. Explanations of the abbreviations see in the text.

formed in this way, in the early period of diagenesis was partly exhumed and opened to meteoric waters. The substrate selectivity of the cavity fillings show that the system was exposed to internal dissolution, probably by marine-meteoric waters, when still in a precementational stage of diagenesis. In periods of stagnation to subaerial exposure, the walls of the cavities were micritized, covered with calcretes and karstified. In the isotopic stratification of cavity fillings, this meteoric event is perhaps shown only by the oxygen isotopic reeqilibrium between the carbonates and isotopically lighter pore waters (recrystallization of limestones by sparite with an isotopically lighter composition). The first phase of incomplete dolomitization is probably also connected with the mixing of pore fluids in the cavity system.

In the stage of initial cementation, the cavity system of the Veterlín Limestone was closed and pumped by marine water. Isopachous layers, originally formed by acicular bundles of calcite or aragonite (metastable cavity filling), were precipitated from the circulating marine fluids. As cement catalysts, to the precipitation of the isopachous calcite evidently also contributed the calcareous sponges *Sphinctozoa*, small nodules of *Tubiphytes*, corals and other constructing organisms (compare Jadoul & Frisia 1988). In the course of mineralogical stabilization, this cement underwent a paramorphic transformation into radiaxial fibrous calcite, in the stage of shallow burial. RFC is notable for its marine isotopic composition as well as for the lack of luminescence. Fluids liberated from the high-Mg carbonates, when they were transformed into low-Mg calcites, also caused the main phase of burial dolomitization.

After the precipitation of the isopachous layers, the cavity system of the Veterlín Limestone was starved. The dissolutional hiatuses were accompanied by erosion of the crystals of radiaxial fibrous cement and nucleation of rhombic dolomite. The remaining pore-filling cement and blocky calcite cement was probably precipitated from burial fluids. Scalenohedral zonally luminescent and euhedral unluminescent calcite (SHC + EHC) and more rarely also saddle dolomite were formed. The marine - burial origin of these cements is also shown by the more significant depletion of $\delta^{18}O$, with a corresponding temperature from 30 to 57 °C, with preservation of positive values for $\delta^{13}C$. In later diagenetic processes, the predate cement of the remaining pores (SHC + EHC) was homogenized, calcitized and replaced by neomorphic pseudospar (BLPS, BPS).

The diagenetic development outlined was not the same in all facies zones of the Veterlín reef complex. Only the limestones from the Kršlenica show the greatest complexity of cavity fillings, with phenomena of mixing (dolo-moldic porosity, a wider dispersion of $\delta^{13}C$), active circulation (RFC) and burial precipitation. Their diagenesis occurred in a marine phreatic environment of a reef platform, where processes of mixing and meteoric alteration took place episodically. In the atypical reef development of the Kršlenica sequences (lower intervals) poronecrosis culminated in eo/mesogenetic isolation of the cavities and in precipitation of burial cement in the form of blocky calcite. A more developed anastomatic system of cavities was observed in the cavities at the Vajarská. It was created by active circulation of marine waters in porous body of the reef edge. The cavity fillings from the Vajarská show characteristics of more open marine cement; - a multilayered structure of RFC, marine isotopic proportion in the matrix and RFC, and a smaller negative shift of $\delta^{18}O$ in BPS, a lack of luminescence, etc. The limestones from the Čelo area probably represent the back reef facies in the Veterlín reef complex. Their cavity fillings bear the more distinct records of stagnant circulation (lack of RFC), percolation of lagoonal waters (dolomite layers in the evinosponge cement) and thermal alteration of probably already meteorically lightened burial fluids (the greatest depletion of $\delta^{18}O$, the development of zonally luminescent SHC). The system of facies zones of the Veterlín Unit also including the dolomitized lagoonal limestones with communities of miliolid foraminifers and dasycladacean algae, and the fore reef and slope sediments (breccias, megabreccias, calciturbidites, etc.).

Conclusions

1 - A model of porosity infilling of the Veterlín Limestone was created by detailed petrographic study. Cathodoluminescence study enabled us to describe the missing diagenetic stages and understand the progress of cementation.

2 - Isotopic study confirmed the petrographic stratification of the cements and allowed us to move the final phases of cements precipitation to the burial diagenesis stage. The morphology of calcite crystals is not an adequate criterion for this process.

3 - The marine character of the cements is partly influenced by the meteoric-mixing processes. This is reflected in the wider range of $\delta^{13}C$, as well as in morphological features of the cements or the development of the pore systems.

4 - The calculated isotopic temperatures varied in the interval 18 to 60 °C, at which the higher belong to the burial cements (30 - 60 °C). The homogenization temperatures of fluid inclusions do not provide as information about the crystallization temperatures of the cements. They probably correspond to the highest temperatures of alteration of the rocks, which is also partly the same as that obtained from the CAI of conodonts.

5 - On the basis of the petrographic and isotopic stratification of the cements, we were able to propose a diagenetic model, and at the same time to clarify the conditions of sedimentation, as well as to make a spatial reconstruction of the reef bodies in the tectonic unit studied.

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