

DISTRIBUTION OF STABLE O AND C ISOTOPES AND MICROELEMENTS IN TRIASSIC LIMESTONES OF THE VETERLÍN UNIT, THE MALÉ KARPATY MTS.: THEIR DIAGENETIC INTERPRETATION

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Abstract: The authors compared the distribution of stable O and C isotopes and elements Sr, Mn, Ca and Na in Triassic platform carbonates of the Veterlín Unit in the Malé Karpaty Mts., with the aim of characterizing the conditions of post-sedimentary evolution as well as their importance for the characterization of sedimentation conditions. The results have shown that solutions of meteoric origin did not affect to a more important extent the development of the studied limestone sequences. The values of $\delta^{13}\text{C}$ are predominantly positive (-0.7 to +3.6 ‰ PDB). $\delta^{18}\text{O}$ are in the whole set shifted towards negative values reflecting thus a temperature increase of diagenetic solutions in buried sediment. The highest $\delta^{13}\text{C}$ values have been determined in limestones of depressions (-2.5 to -2.2 ‰ PDB), with a shift towards more negative values in inner platform limestones as well as in reef margin limestones. In a part of the studied samples, high $\delta^{13}\text{C}$ have been preserved, indicating, together with high Sr contents and the presence of aragonite relic in calcites, aragonite mineralogy of the original sediment. Since the influence of meteoric solutions in the (early)diagenetic process was not marked, the distribution of microelements (Sr) reflects gradual changes of the sedimentation environment conditions.

Key words: platform limestones, Triassic, microelements, stable isotopes of O and C, diagenesis, sedimentation environment.

Introduction

In the presented paper we compare the microelement and isotopic composition of the Triassic limestones of the Veterlín Unit in the Malé Karpaty Mts., with the aim of evaluating the effects of post-sedimentary evolution on the properties of carbonate platform sediments. The work is a continuation of papers on Triassic carbonate rocks from nappe units of the Malé Karpaty Mts. (Lintnerová et al. 1988, 1990) dealing with facial and geochemical characteristics of lithostratigraphic units. It has been proved that the observed changes in the microelement contents are related to changes of sedimentation conditions, or facies (Veizer & Demovič 1974) and they can be one of the criteria characterizing the conditions of the studied formations. In the presented work we would like to add more information on the origin and probable composition of (early)diagenetic solutions and thus also to complement the conception of the sedimentation process itself (emergence - changes in the composition of solutions).

The petrographic methods we added the study of micrite limestones with help of a scanning electron microscope. No special attention has been given to dolomites (conditions of their formation), in the presented paper we only bring more accurate chemical composition of dolomite samples.

Geology

The studied region is formed by Alpine nappes - Choč, Veterlín and Havranica (Masaryk 1990). The succession of beds in the Veterlín Nappe comprises a clastic beds of the Lower Triassic and a carbonate complex of the Middle and Upper Triassic. It outcrops at the surface in the southern part of the Biele hory Mts. (between the villages Sološnica and Smolenice), near Dechtice and on the southern (Dobrá Voda) side of the Brezová structure (Fig. 1). The following formations can be identified in the a vertical profile above the clastic Lower Triassic Benkov and Šuňava Formations (Masaryk 1990; Buček et al. 1991):

- 1 - Gutenstein Formation (cca 40 m, Lower Anisian).
- 2 - Annaberg Formation (cca 150 - 200 m, Lower Anisian - Pelsonian).
- 3 - Záměstie Formation (cca 10 m, Upper Pelsonian - Lower Illyrian).
- 4 - Reifling Formation (cca 70 m, Illyrian - Longobardian/Cordevolian).
- 5 - Raming Formation (cca 70 - 100 m Longobardian/Cordevolian).
- 6 - Veterlín Formation (cca 400 - 600 m, Cordevolian - Julian).
- 7 - Lunz Formation (cca 10 - 20 m, Julian).

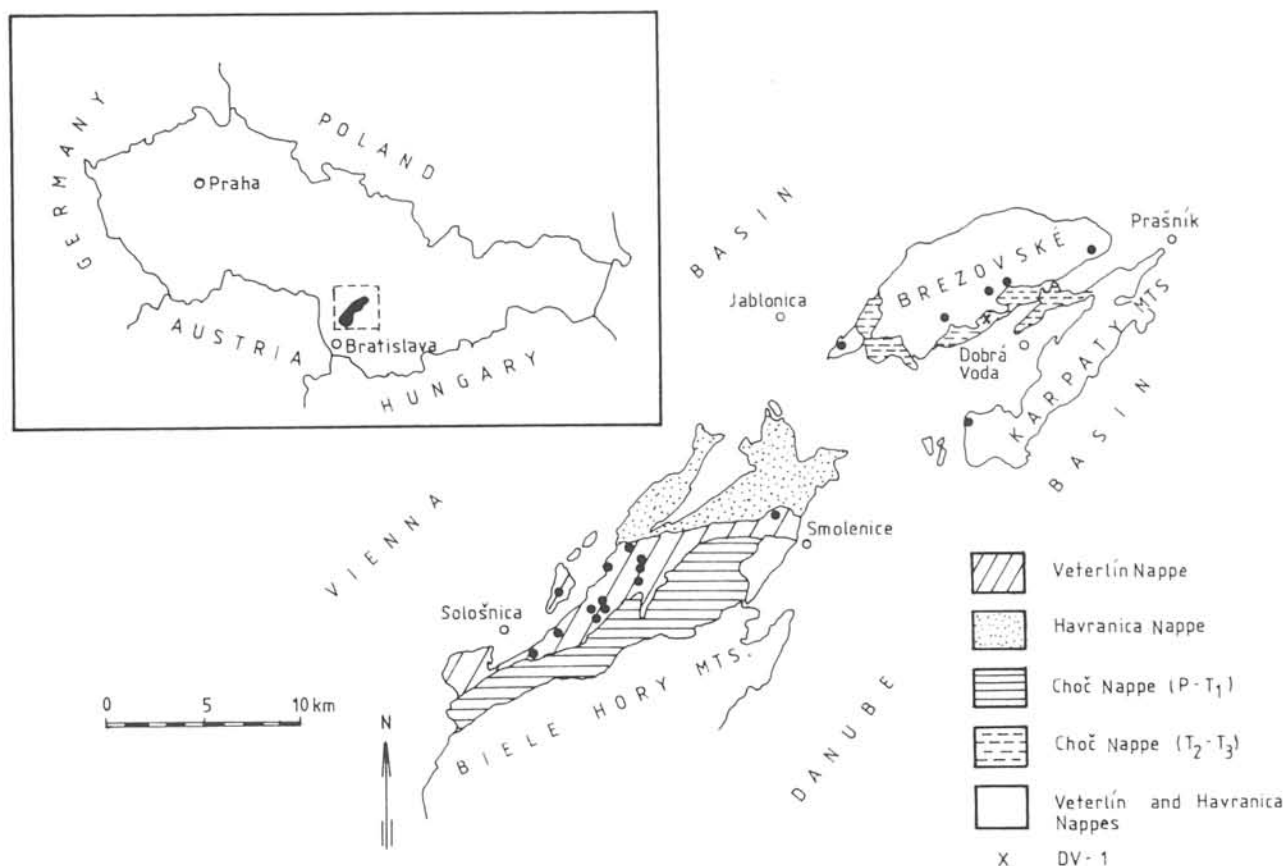


Fig. 1. Map of studied region and location of the profiles - full circle.

8 - Oponitz Formation (cca 10 - 15 m, Tuválian).

9 - Hauptdolomite Formation (cca 20 - 30 m, Norian).

The last three formations are found only in isolated outcrops and their classification with the units has not been confirmed. The relationship of the Veterlín Nappe to the underlying Permian volcano-sedimentary complex (Malužiná Formation) and to the Lower Triassic sequence has not been fully explained yet.

The Havranica Nappe is facially monotonous (Middle as well as Upper Triassic) and it is formed predominantly by shallow-water limestones (Lintnerová et al. 1990; Masaryk 1990).

In the Dobrá Voda 1 (DV-1) borehole a succession of beds has been identified coinciding with the Choč (Biely Váh) succession (Michalík et al. 1992). Basin Reifling limestones form the predominant part of the carbonate sequence (Illyrian - Tuválian) and below them there are Anisian Gutenstein limestones and dolomites.

Description of studied formations and samples

As it follows from the above lithostratigraphic overview, the Veterlín Unit is a more or less continuous sequence and this is reflected also in the unsharp transition between the distinguished lithostratigraphic units (Fig. 2). We can describe several evolution stages in the sedimentary record, which cannot always be defined by the above mentioned units. The first stage of undifferentiated, protected platform is represented by dark, microcrystalline (mudstone) Annaberg and Gutenstein limestones. The Gutenstein Formation is in the Biely hory Mts. represented by dolomites, in the Brezovské Karpaty Mts. also by limestones.

Zámotie Formation limestones with high content of organic remnants (Michalík et al. 1992; Buček et al. 1991), partly also of allochthonous character are lying above them. The limestone gradually acquired features of a more open and deeper sedimentation. The increase of organic detritus quantity has been described also in the upper part of Annaberg limestones (Lintnerová et al. 1990; Masaryk 1990). The second stage - sedimentation in intraplatform depression - is represented by Reifling limestones. They are predominantly dark, brownish grey limestones with cherts and nodular limestones (RKL) and greyish brown thin-bedded limestone (RBL), both types containing conodont microfauna (Masaryk et al. 1984; Buček et al. 1991). It is not possible to divide sharply the light- to dark-grey limestone of Raming Formation from the uppermost parts of Reifling limestones. The predominant part of the Raming limestones belongs already to the next evolution stage of the platform, represented by the platform margin. They consist of partly resedimented slope material. Small reef bodies formed by organodetrital and organogenic (Wetterstein type) limestone (abundant algae and sponges, less coral) have been found above them. Material of these bodies can be found also in forereef - slope breccias to megabreccias in upper parts (Fig. 2) of the Raming Formation. The sediment was at least partly lithified at the place of its sedimentation - on the reef, and it was only later transported in the form of separated blocks to forereef space. We consider them to belong to one stage - the stage of reef complex development, together with the Wetterstein type dolomites. These form the uppermost, continuously observable part of the sequence and they represent predominantly backreef (lagoon) development.

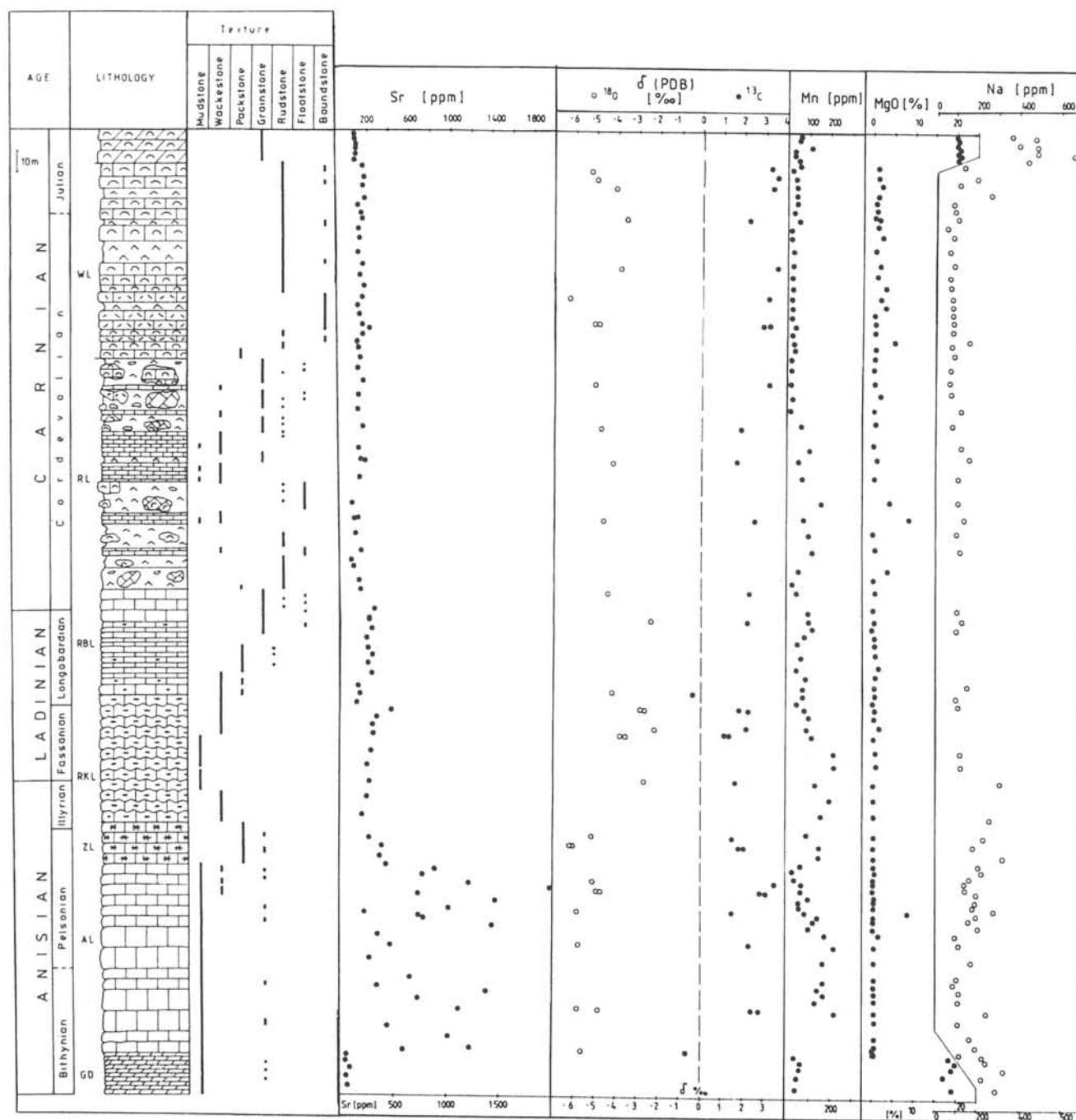


Fig. 2. Idealized profile of the Veterlín Unit. GD - Gutenstein Dolomit, AL - Annaberg Limestone, ZL - Záměstie Limestone, RKL, RBL - Reifling Limestone (RBK - Bankalk, RKL - Knolenkalk, for more details see Lintnerová et al. 1990), RL - Raming Limestone, WL - Veterlín Limestone (limestone of Wetterstein type), in the uppermost part dolomite (WD).

Samples were collected from partial profiles (Lintnerová et al. 1988, 1990) and their classification with the described carbonate types is marked in the profile on Fig. 2. Tab. 1 lists the samples with isotopic analyses.

Applied methods

Chemical analyses of rock sample were carried out by standard X-ray fluorescence method (Philips PN 1410/2p) and mic-

roelement contents were analysed by the AAS method (Perkin-Elmer 2380) after dissolution of sample in HCl. Mineral composition of rock sample was studied by X-ray diffraction method (Philips 1050, CuK α). For dolomite samples we used the method of Goldsmith & Graf (1958) and Lumsden (1979), with NaCl as the internal standard. In a part of sample CaO, MgO and IR (insoluble residue) contents were determined by classical chemical analysis (Tab. 1). Total organic carbon contents were determined by infrared spectroscopy after pyrolytic decomposition of sample (Laboratory of Czech Institute of Geology in Brno).

Table 1: Chemical analyses of samples on which isotopic analyses have been carried out.

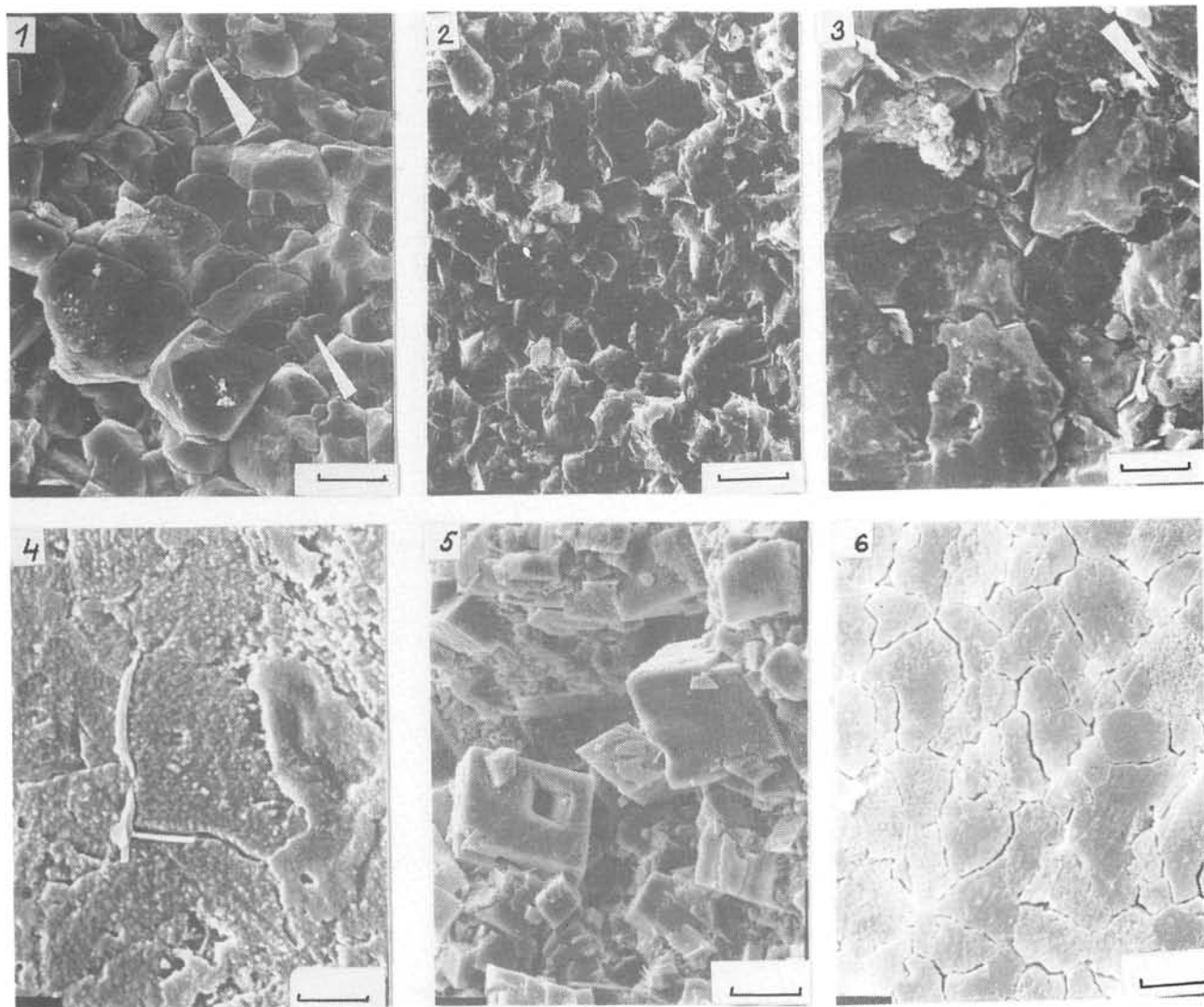
	CaO	MgO	IR	Sr	Sr/Ca	Na	Mn	$\delta^{13}\text{C}$	$\delta^{18}\text{O}$
	wt. %				ppm	ppm		‰PDB	
1	54.67	0.68	0.87	578	1.48	125	0	-0.7	-5.6
2	55.22	0.72	2.93	1105	2.81	240	230	2.4	-4.6
								2.7	-4.8
3	55.61	0.86	2.10	435	1.10	110	220	2.3	-5.8
4	44.04	9.55	2.35	210	0.67	255	85	1.5	-5.9
5	53.77	0.94	2.07	718	1.88	195	102	3.1	-4.9
								2.9	-4.8
6	54.87	0.55	0.75	1278	3.28	155	66	3.5	-5.1
7	55.62	0.54	0.72	378	0.95	170	150	2.0	-6.2
								1.9	-6.2
8	54.58	0.69	2.20	265	0.68	230	80	1.6	-5.2
9	50.94	0.65	10.80	248	0.68	320	130	1.6	-2.6
10	55.02	1.04	1.96	173	0.44	120	70	-0.5	-4.3
11	51.39	0.90	7.84	302	0.82	0	120	1.2	-3.8
								1.1	-3.7
12	51.76	2.09	9.42	282	0.76	0	94	2.1	-2.2
13	41.82	0.65	25.03	460	1.54	0	85	2.2	-2.9
								1.9	-2.8
14	55.83	1.08	0.19	152	0.38	0	43	2.2	-4.5
15	53.29	0.71	4.29	223	0.58	133	105	2.2	-2.4
16	45.94	8.89	0.66	99	0.30	103	82	2.5	-4.7
17	53.54	1.29	1.83	158	0.41	158	51	1.7	-4.2
18	54.86	0.60	0.89	163	0.41	110	58	1.8	-4.8
19	54.59	0.69	0.65	161	0.41	74	15	3.1	-5.1
20	54.90	0.76	1.11	146	0.37	78	27	2.9	-5.1
								3.1	-4.7
21	53.68	2.24	0.90	156	0.40	80	23	3.1	-6.3
22	54.10	0.96	1.24	188	0.66	89	18	3.5	-3.8
23	55.12	0.73	1.05	141	0.36	101	25	2.3	-3.6
24	55.52	0.02	0.90	168	0.42	140	37	3.3	-4.1
25	55.40	0.12	0.81	185	0.47	190	32	3.5	-5.1
26	55.45	0.24	0.31	150	0.38	140	27	3.2	-5.3
27	54.25	1.23	2.36	453	1.17	125	48	3.6	-6.7
28	51.37	1.22	4.57	1015	2.78	145	90	3.6	-4.7
29	53.23	0.39	4.99	768	2.03	170	136	1.3	-3.3
								1.4	-3.9
30	46.56	2.07	16.90	283	0.85	220	94	1.8	-3.9
31	38.64	2.09	30.68	173	0.63	205	204	1.6	-3.9

Samples 1 to 6 - Annaberg limestones; 7 and 8 - Záměstie limestones; 9 to 13 and 15 Reifling limestones; 14, 16 to 22 Raming limestones; 23 to 26 - Veterlín limestones; 27 to 31 - Reifling limestones from DV-1, Sr/Ca = 1000 Sr/Ca, S - Samples No..

O and C isotopic analyses were carried out on microsamples drilled from rock plates. The sample were decomposed in vacuum at 25 °C by 100% H₃PO₄ (McCrea 1950), CO₂ was measured by mass spectrometer Finnigan MAT 2 (Czech Institute of Geology Prague). The results are given as δ (‰) and related to the international standard V-PDB. The accuracy of measurements is better than +0.1 ‰ for both measured elements.

For the study of samples by scanning microscope (Tesla BS

300) we used rock fragments, polished thin section and polished rock slabs. Polished slabs were etched by 0.2% formic acid and dolomite also by 1% HCl, from 20 seconds to 10 minutes (Lasek & Sandberg 1984). The study complemented the already published petrographic data (Lintnerová et al. 1988, 1990; Masaryk 1990; Michálek et al. 1992). The summary profile (Fig. 2) includes some quantitative data (Masaryk in Lintnerová et al. 1990) on microfacial analysis of samples from the Veterlín Unit.



Figs. 3. and 4. Microcrystalline Gutenstein and Annaberg limestones and dolomites.

Fig. 3.1. Recrystallized mudstone with interlocking relic structures (nanostructures). Anhedral micritic grain (arrows) are sometimes enclosed by microspar to spar subhedral crystals. (Scale bar $16\ \mu\text{m}$, etching 20 s in 0.2 formic acid).

Fig. 3.2. Subhedral restricted, packed grains of dolomite. (Scale bar $14\ \mu\text{m}$, etching 120 s in 0.2 formic acid).

Fig. 3.3. Slight etching (20 s 0.2 formic acid) of the fractured surface setting off small flaky particles of detrital clay minerals on the grain boundaries of calcite. See also the aggregate of anhedral micritic grains (scale bar $4\ \mu\text{m}$) in the upper part and between spar grain (arrows).

Fig. 3.4. Polished and etched (20 s, 0.2 % formic acid) surface of a slab of microcrystalline limestone with the particles of detrital clay minerals. Scale bar $2\ \mu\text{m}$.

Fig. 3.5. Dolomite microsparite to sparite rhombs (scale bar $13\ \mu\text{m}$). Micrite dolomite matrix can be distinguished in its surroundings.

Fig. 3.6. Matrix of microcrystalline dolomite (scale bar $7\ \mu\text{m}$), after etching of a polished rock slab (60 s, 0.1 % HCl).

Results

Mineral and chemical composition of rocks

The Veterlín sequence is a complex of pure limestones and dolomites. An exception is a part of the Reifling limestone with higher content of silica (sometimes larger cherts) and clays. Clay material concentrated in thin beds and stylolites consists predominantly of illite. In other limestones it is dispersed, it forms flaky particles on the boundaries of grains (Figs. 3.2, 3.3). Accessory amounts of sulphides, predominantly pyrite, were determined in IR from dark microsparite limestones of the lower part of the Gutenstein and Annaberg Formation (Lintnerová et al. 1988; Michálek et al. 1992).

Beside Gutenstein and Veterlín (Wetterstein) dolomite (Fig. 2), dolomite intercalation also occurs in limestones. Rhombohedral grains of dolomite have been frequently observed in fissures and stylolites (Masaryk 1990). The dolomitization grade is reflected in MgO contents (Fig. 2). In limestone samples they vary from 0 to 0.5%, i.e. dolomitization does not exceed 20%, which has been confirmed by X-ray diffraction analysis. Mol. % of CaCO_3 in dolomite samples from both formations varied from 50.3 to 52% and it so far did not allow to distinguish more precisely the dolomite in relation to the observed difference in petrographic properties (the assumed differences in the conditions and time of dolomitization). Petrographic differences are only partly reflected in microelement distribution (Tab. 1). The dolomites differ in their grain-size and colour. Not very marked-

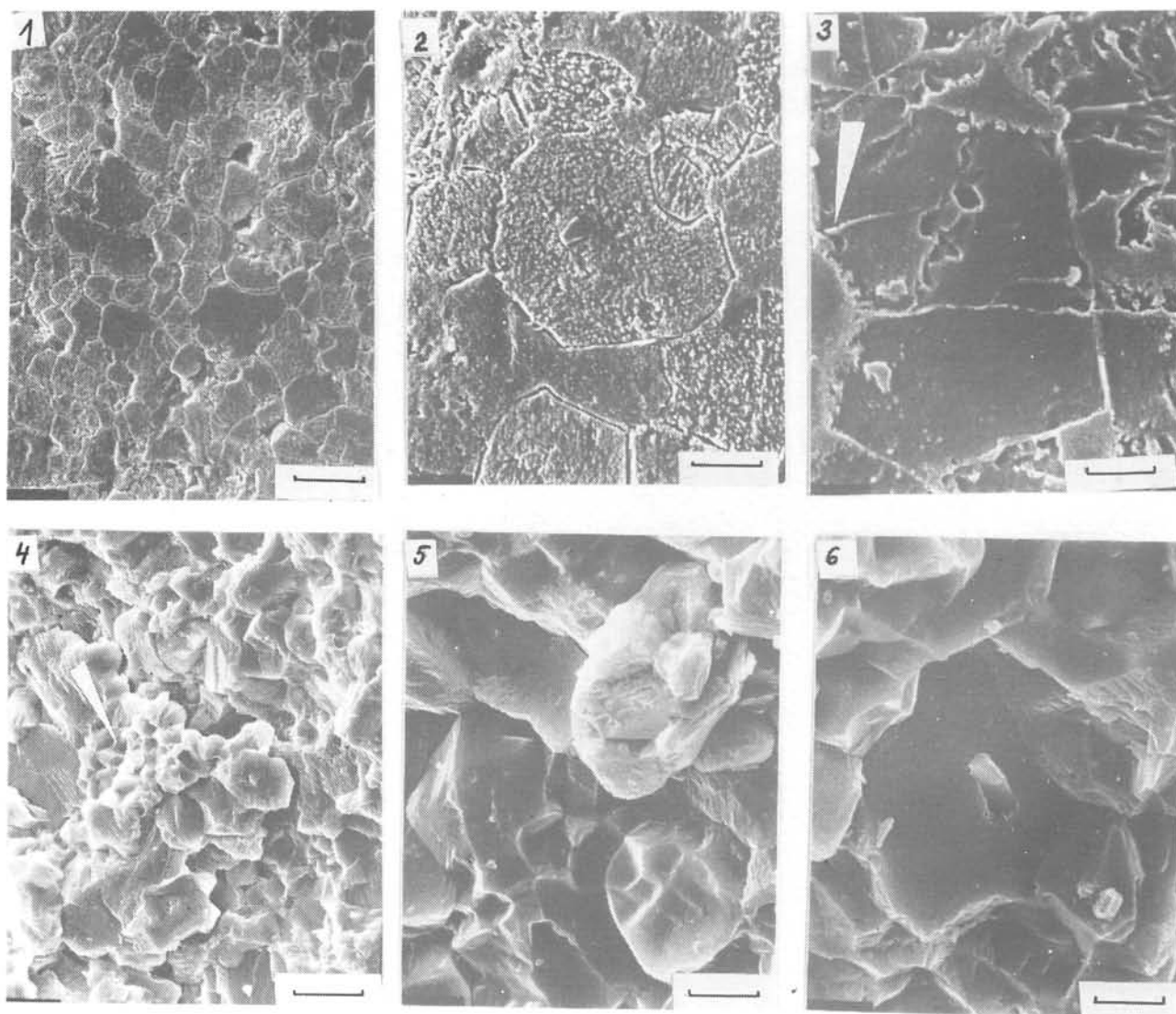


Fig. 4.1. Microsparite limestone consists of anhedral, 1 to 8 μm large grains (scale bar 7 μm). Note also the micrite grains enclosed by spar. Etching of polished rock slab - 20 s in 0.2 % formic acid (the same etching in Figs. 4.2 to 4.6).

Fig. 4.2. Greater magnification allows to document the relic structures in the microcrystalline limestones. Micrite grain (scale bar 3 μm) engulfed in a sparite one.

Fig. 4.3. On a small number of calcite crystal some pits could be observed, which by their shape remind of aragonite needle crystals. Etching made also more prominent elongated (arrows), rib-like crystals on the margins as well as inside the crystals (scale bar 2 μm).

Fig. 4.4. Microcrystalline limestones with aggregates of micrite grains (scale bar 19 μm).

Figs. 4.5. and 4.6. Details of a grain from Fig. 4.4. Several types of nanostructures and (scale bar 7 μm) mud/aragonite relics.

ly bedded, even massive Veterlín (Wetterstein) dolomites are coarse-crystalline, predominantly light-grey, with weakly preserved sedimentary structures (grainstone). Dark Gutenstein microcrystalline (mudstone, Fig. 3.5, 3.6) dolomite are sometime laminated and oolitic and predominantly clearly bedded (Lintnerová et al. 1990, Fig. 2.).

Micritic and microsparitic limestones were studied by scanning microscope (Lasemi & Sandberg 1984) and we selected samples with high Sr contents (over 1000 ppm). Beside real grain size and their differentiation we also studied the presence of

aragonite relics in calcite crystals (Figs. 3 and 4). Recrystallization made more prominent grains 4 - 10 μm large (from the measured 200 grains in the samples), regularly distributed, without marked crystalline faces or preferential orientation (Fig. 4.1, 4.2). Besides the clay mineral particles on grain boundaries already mentioned (Fig. 3.3, 3.4) we also observed on the limited number of grains (Figs. 3.1, 4.3 to 4.6) the "nanostructures" (Negra & Loreau 1988). This traces of mud origin of sediment can to help better understand diageneses of micrite carbonate and alteration of former mineralogy of sediment.

Total organic carbon

Total organic carbon (T.O.C.) has been determined in 25 limestone samples selected according to their facies type and colour differences. The values did not exceed 0.1% in any of the samples, i.e. we could not determine relative differences or signs of the presence of higher T.O.C. either in dark, muddy limestones, or in light-coloured organodetritic limestones. The assumption of possible accumulation of organic carbon in dark muddy limestones has not been confirmed and dark colour is probably caused rather by grain size than by organic pigment, even though its presence cannot be wholly excluded. The contents of clay mineral particles is not of substantial importance, as it has been documented by SEM photographs (Fig. 3).

Microelements

The contents of Sr (Fig. 2) were differentiated according to the distinguished evolution stages of carbonate sedimentation and their relative differences can be interpreted in the sense of sedimentation condition changes (Veizer & Demović 1974; Brand & Veizer 1980; Lintnerová et al. 1988). High Sr contents (up to 2000 ppm) have been determined in dark muddy limestones of undifferentiated platform, in comparison with light-coloured organodetritic limestones of reef platform margin (100 - 200 ppm Sr). The range of Sr values in limestones of depressions and re-sedimented slope limestones was 100 to 400 ppm. Sr contents in light-coloured organodetritic limestone blocks in megabreccias are similar to those in overlying limestones. Tab. 1 lists also Sr contents in five limestone samples from the borehole DV-1: they vary in a wide range from 173 to 1015 ppm. They represent a more typical development of deeper-water sediment (Reifling facies) with rich fauna of conodonts and foraminifers (Michálek et al. 1992) and with traces of gradual deepening and shallowing of sediment. The lowest Sr values (40 - 110 ppm) were measured in samples from both dolomite formations (Fig. 2); they cannot be distinguished on the basis of Sr. However, dolomites from backreef region had high contents of Na (up to 600 ppm) and they could signalize increased salinity of the environment (Veizer et al. 1978) or a hypersaline character of the dolomitizing solutions (Land & Hoopes 1973). The range of Na values in limestones was lower, while the increase of Na contents cannot be always connected with dolomitization. The values of Mn contents vary in the range of 15 to 230 ppm and there are relative differences between the described facies zones. Higher contents were determined in dark (Annaberg and Reifling) limestones (Fig. 2), Mn contents in light-coloured organodetritic limestones of platform margin were minimal. Fig. 5 shows the relation between Mn and 1000 Sr/Ca for samples from partial profiles from the studied unit of the Biele hory Mts.. The diagram (Brand & Veizer 1980) shows a shift of Mn and Sr contents caused by recrystallization in the diagenetic development in relation to the primary mineralogy of sediment. Most samples fall into the space corresponding to high-Mg calcite composition of primary sediment, or to CaCO₃ with relatively very low Mn content.

O and C isotopes

Isotopic analyses of O and C were carried out on 26 samples limestones selected according to petrographic description and Sr content differentiation (Fig. 2). Dolomite were not included in the set.

The values of $\delta^{13}\text{C}$ in samples of dark microsparite (mudstone) limestones varied in the range of +1.5 to +3.5 ‰, only one sample had a lower value: -0.7 ‰. The value of $\delta^{18}\text{O}$ vary in the range of -6.2 to -4.9 ‰, i.e. they are markedly shifted towards negative values in comparison with recent limestone. A-

nalyses from different spots of one sample (Tab. 1) did not differ (also not in other limestone types, Tab. 1), which indicated isotopic homogeneity of the samples. We included into this set also samples No. 7 and 8 (Tab. 1) from the Záměstie Formation, which represent certain transition to intraplatform depression limestones.

Isotopic composition of limestone samples from this depression is in part different from the previously mentioned ones. For the $\delta^{13}\text{C}$, values from -0.5 to +2.2 ‰ were determined, and for $\delta^{18}\text{O}$ they are -4.3 to -2.2 ‰. Limestones of this facies from the borehole DV-1 have more negative $\delta^{18}\text{O}$ and a wide range of $\delta^{13}\text{C}$ values. This part is also formed by microsparite rocks (mudstone, wackstone) with variable contents of organic detritus and pellets. Sediments of the depression gradually pass into slope and fore reef facies. Slope limestones have lower value of $\delta^{13}\text{C}$ and higher $\delta^{18}\text{O}$ than reef limestones. The predominance of material with clear relationship to reef body, as well as in the reef limestones themselves, is reflected in the values of $\delta^{13}\text{C}$, which are markedly increased - +2.3 to +3.5 ‰. On the contrary, $\delta^{18}\text{O}$ is shifted towards negative values - -6.3 to -3.8 ‰ — which could be a reflection of differences in the primary rock porosity and of the penetration of solutions and formation of marine and diagenetic cements.

Discussion

In the Triassic sequence studied, the most marked changes are those of Sr contents and they can be related to rock type, its primary properties derived from the sedimentation environment in the sense of Veizer & Demović (1974), Veizer (1983). High Sr contents in a part of the micritic limestones indicate aragonite mineralogy of the precursor sediment (Brand & Veizer, 1980) and partly anorganic character (increased salinity?) of the aragonite ooze. In samples with high Sr contents and grain size of 1 to 12 μm (Figs. 3, 4) we did not observe the presence of diagenetic cements, and thus they can be considered to be the result of neomorphic recrystallization of precursor mineral (aragonite) to (micro)spar calcite. The source of high Sr was

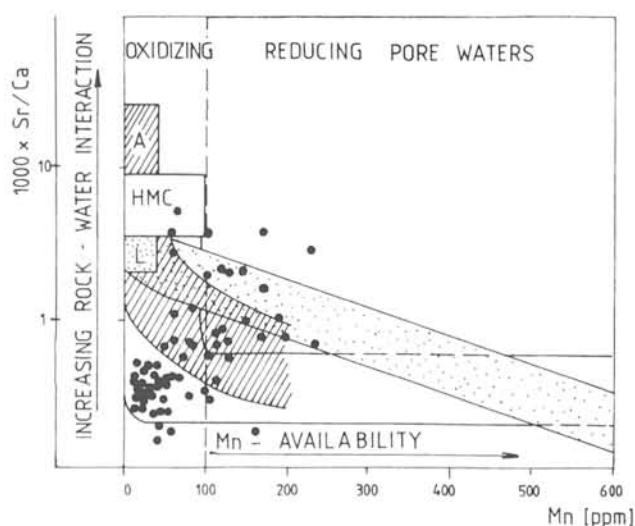


Fig. 5. The relation between Sr (expressed as 1000 Sr/Ca) and Mn for samples from the studied partial profiles. A - aragonite, HMC - high-Mg calcite, L - low-Mg calcite. Diagram after Brand & Veizer (1980) and adjusted after Lohmann (1988).

primary aragonite. Neomorphic calcite from modern sediments of platforms contain aragonite relics (Folk 1965; Steinen 1982; Sandberg 1983; Lasemi & Sandberg 1984). One of the criteria of set of criteria for the recognition of original mineralogy of grains and/or cement (Sandberg 1983) is the common occurrence of original aragonite as relics in the enclosing coarse calcite mosaics (Moore 1989). This relic has been also described from ancient limestones (Sandberg & Hudson 1983; Louks & Folk 1976). Negra & Lorea (1988) suggested that the micropar had clearly a double origin (cement and neomorphism) and series of punctate, close-grained, interlocking and coalescing "nanostructures" are interpreted as degrees of diagenetic evolution. Meteoric diagenesis led to rapid dissolution of aragonite (commonly needle-like) particles and no traces of their existence have been preserved. The possibility of their preservation in the "closed" diagenetic environment (marine pore fluids, water nearly saturated with respect to CaCO_3) is - together with inherited chemical and isotopic composition - greater.

The decrease of Sr contents in samples of these limestones is in our opinion connected with the higher grade of recrystallization, dolomitization and maybe also by the increase of the amount of organodetritic material. We assume that they contain more high-Mg calcite (possible source of Mg for partial dolomitization, Sperberg et al. 1984) and partly also a different regime (open) of the diagenetic process.

It is known that calcite has $\delta^{13}\text{C}$ values lower by 1.8 ‰ than aragonite originating in the same conditions (Hoefs 1980). The values of $\delta^{13}\text{C}$ in the samples are similar to values obtained from modern environments, which is quite usual for marine carbonates (Veizer 1977; Walls et al. 1979; Tucker & Wright 1990). E.g. $\delta^{13}\text{C}$ values in aragonite ooids or cements have been found to lie in the range of +3 to +5 ‰ (PDB), with an average of +4 ‰ (Tucker & Wright 1990). Some increased $\delta^{13}\text{C}$ values of our set of samples could indicate aragonite composition.

$\delta^{18}\text{O}$ is in ancient limestones frequently shifted towards more

negative values in comparison with modern aragonite and high-Mg calcite marine sediments (Hudson 1977; James & Choquette 1983; Moore 1989), which are approaching 0 ‰ (PDB).

The trend of $\delta^{18}\text{O}$ decrease in carbonates in relation to increasing age has been well documented (Veizer & Hoefs 1976). Three possible causes of this have been described: diagenetic equilibrium with meteoric waters, higher temperature of marine water during geological history (this trend is not significant in the Mesozoic, but it is in the Paleozoic and Precambrian), and changes of the conditions (temperature) of diagenetic processes in the buried sediment.

Veizer (1977) assumed that δO^{18} in primarily aragonite and high-Mg calcite sediment is negatively shifted in comparison with low-Mg calcite sediments, which has been tested in relation to Sr. However, we did not observe a negative covariant relationship between the contents of Sr (1000 Sr/Ca) and $\delta^{18}\text{O}$ in the studied set of samples (this would have indicated meteoric diagenesis in an open system). Only a part of the samples with higher Sr contents (above 0.8 1000 Sr/Ca) have more negative $\delta^{18}\text{O}$. According to Veizer (1977) their distribution is influenced by other (facial) factors and diagenetic stabilization took place in partly isolated environment, due to migration (mixing) of solutions. At the same time it reflects different mineral composition of the sediment.

The process of diagenetic stabilization and the origin of diagenetic solutions can be evaluated on the basis of cross diagram $\delta^{18}\text{O}$ vs $\delta^{13}\text{C}$ (Fig. 6). According to Lohman (1988), a covariant trend of $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ is manifested in the direction of decrease of the values during diagenesis in the conditions of meteoric water influence (inverse J). A second one is the trend of $\delta^{18}\text{O}$ decrease in buried sediment caused by increase of pore water temperature with buffering effect on the composition of $\delta^{13}\text{C}$ in cement (Moore & Druckman 1981; Choquette & James 1987; Moore 1989). It is more probable, the set of samples studied behaves according to the second trend. Practically all $\delta^{13}\text{C}$ values are positive and they vary in a rather wide range, however,

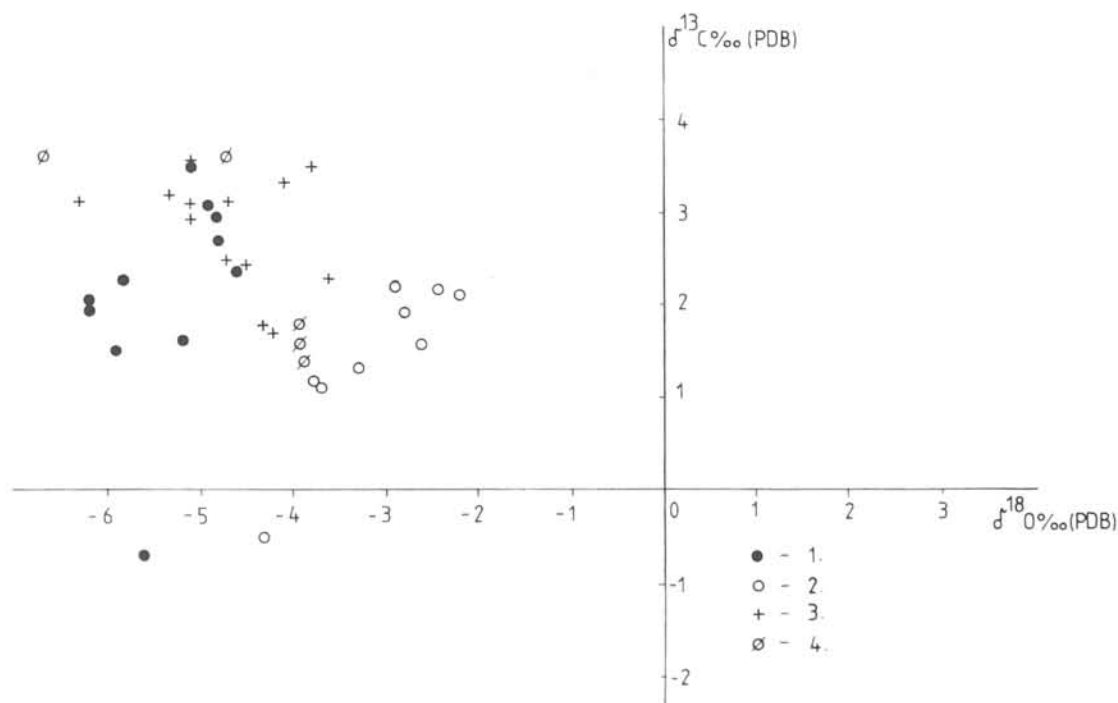


Fig. 6. Cross diagram of $\delta^{13}\text{C}$ vs $\delta^{18}\text{O}$ (PDB) according to Lohmann (1988) for samples of the studied limestones.

Full circle - first evolution stage (Annaberg, Gutenstein and Zámotie limestones). Empty circle - second evolution stage (Reifling limestones). Cross - third evolution stage (Raming and Veterlín limestones). Crossed circle - DV-1 (Reifling limestones).

they absolutely do not exclude partial (slight) influence of meteoric water (interruption of sedimentation). Differences in isotopic ratios determined in carbonates of the described parts of platform (evolution stages) can be affected by this to various extent, theoretically most in limestones of the reef body.

Light-coloured organodetritic and organogenic limestones are characterized by coarse grain-size, the presence of cements and fillings with reflect the primary porosity of sediments. Aragonite cement has been described to occur frequently in Upper Paleozoic and Lower Triassic reef complexes (Louks & Folk 1976; Given & Lohmann 1985; Tucker & Wright 1990). Given & Lohmann (1985) mentioned for reef calcites without luminescence the values of $\delta^{13}\text{C}$ of +5.3 ‰ and for $\delta^{18}\text{O}$ -2.8 ‰ (PDB) as the result of early diagenesis in a closed system. The values for luminescent calcite are markedly negative - $\delta^{13}\text{C}$ -3.0 ‰ and $\delta^{18}\text{O}$ -8.2 ‰. The values of $\delta^{13}\text{C}$ in our set are only positive: +2.3 to +3.6 ‰ and $\delta^{18}\text{O}$ varies in range of -6.3 to -3.6 ‰ (Tab. 1). In comparison with the rest of the samples the shift of the values is not very significant and the cement (not only aragonite) probably also had marine character.

The highest $\delta^{18}\text{O}$ values have been determined in limestones of depression. The samples 12, 13 and 15 (Tab. 1) have the highest $\delta^{18}\text{O}$ values from the whole set (-2.2 to -2.4 ‰), but they are considerably lower than those mentioned by Hudson (1977) for modern pelagic oozes (-0.5 to +2.0 ‰ PDB for $\delta^{13}\text{C}$ as well as $\delta^{18}\text{O}$). The values of -2.2 ‰ (PDB) corresponds in marine conditions to crystallization at 22 °C (Savin 1977), i.e. to the temperature of reef region environment. However, the values of $\delta^{18}\text{O}$ in the rest of the samples are lower, giving unrealistic temperatures of the sedimentary environment.

The material of the platform margin sedimented in the drowned part of the platform and it was complemented by skeletons of planktonic organisms. Periplatform oozes are in modern environments composed of aragonite as well as calcite (Schlager & James 1978; Mullis et al. 1984) and the composition of sediment changes with the distance from platform margin (depth). In deep-water conditions, low-Mg calcite should predominate (Veizer 1983) and Sr can maintain a high level of values (up to 1000 ppm). We do not consider the Veterlín sequence to be of markedly deep-water character, but pelagic limestones from the borehole DV-1 we do (Tab. 1 - high Sr).

The "openness" of the diagenetic system is frequently tested according to the ratio Mn-Sr/Ca (Brand & Veizer 1980). From the adjusted diagrams after Lohmann (1988) on Fig. 5 it follows that Mn increase in diagenetic calcite is possible if there is a Mn source in an open system with reduction pore water. The parts of the sequence described have different mineralogy and several Mn values are significantly shifted. They are values for dark organodetritic limestones with microsparite matrix from deepening depression with resedimented (locally reduction environment) material. These samples also displayed high Na contents. We could accept increased salinity in comparison with marine water for dark microsparite limestones without organic remnant contents. On the contrary, increased Na contents in dark limestone on the boundary with limestone of the depression with a rich community of organisms (partial resediment) rather corresponds to migration of saline solutions during diagenetic processes, or even in buried sediment.

Conclusions

1 - The isotopic composition of the studied limestones generally does not differ from the composition of marine sediments. The predominantly positive and increased $\delta^{13}\text{C}$ values more or less exclude meteoric diagenetic recrystallization, which is generally consistent with the conception of development of carbonate sedimentation and climatic conditions in the studied region.

2 - Micritic to microsparitic limestones partly formed from aragonite mud which was transformed into stable calcite in a closed diagenetic system. This follows from the high Sr values, high $\delta^{13}\text{C}$ values, grain size and the character of recrystallization, as well as the presence of relic structures.

3 - The highest $\delta^{18}\text{O}$ values have been determined in limestones of the depression (Reifling limestone) which we consider to have been composed already immediately after sedimentation of low Mg-calcite and to have formed in cooler conditions.

4 - Neither in light-coloured organogenic and organodetritic limestones could we identify a shift in isotope distribution which would indicate significant influence of meteoric water in (early) diagenetic development. This indicates that it was not a case of emerged platform margin (reef). This assumption should be tested by a study of cements.

5 - The general shift of $\delta^{18}\text{O}$ towards negative values probably corresponds to changes in the temperature of pore solutions in post-sedimentary development of the rocks.

6 - Assuming that meteoric diagenesis did not affect to a greater extent the post-sedimentary development of the studied formation, the distribution of microelements reflects relatively well the sedimentation conditions. This is especially true of Sr, which has already been stated in earlier papers. The composition of solutions did not change considerably in the post-sedimentary development and thus the relative element contents did not change well, even though a general decrease occurred.

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