GEOLOGICKY ZBORNIK — GEOLOGICA CARPATHICA, 39, 3, BRATISLAVA, JUNE 1988, Pp. 301—322

OTÍLIA LINTNEROVÁ* — PETER MASARYK* — EDUARD MARTINY*

TRACE ELEMENTS DISTRIBUTION IN TRIASSIC CARBONATES FROM THE VETERNÍK AND HAVRANICA NAPPES (THE MALÉ KARPATY MTS.)

(Figs. 9, Tabs. 2)

Abstract: Trace elements contents (Sr, Na, Mn, Zn) were observed in the Gutenstein dolomites, Annaberg, Reifling, Wetterstein and Dachstein limestones representing the most significant and the most represented facial types of carbonates from the higher Central Carpathians nappes of the Malé Karpaty Mts. Trace elements were determined by AAS method.

Observation of trace elements contents in carbonates enabled us to establish the conditions of their origin and diagenesis, as well as relation between the facies and trace elements contents (Sr, Mn). The study proved that Na content may be applied to orientation determination of palaeosalinity. Further on, changes of facies in the studied sequence were examined. It was proved that there are transitional facies between the Reifling and Wetterstein limestones and a continuous sequence of strata is preserved.

Резюме: Были изучены содержания рассеянных элементов (Sr, Na, Mn, Zn) в гутенштайнских доломитах, аннабергских, райфлингских, веттерштайнских и дахштайнских известняках, представляющих наиболее значительные и представительные фациальные типы карбонатов высших центральных покровов Малых Карпат. Рассеянные элементы были определены методом ААС.

Изучение содержаний рассеянных элементов в карбонатах позволило определить условия их образования и диагенеза и взаимное отношение между фациями и содержаниями рассеянных элементов (Sr, Mn). Исследование подтвердило, что содержание Na можно использовать для ориентировочного определения палеосолености. Затем были исследованы изменения фаций в изучаемой толще. Было подтверждено, что между райфлингскими и веттерштайнскими известняками существуют переходные фации и сохранена непрерывная последовательность пластов.

Introduction

Triassic carbonate rocks from the Malé Karpaty Mts. are studied in the paper. Limestones and dolomites from the selected lithostratigraphic sections are geochemically characterized. The sections were studied complexly in order to solve obscurities in determination and position of nappe units in the studied region. Trace elements contents (especially Sr and Na) were geochemically examined in relation to major elements — Mg, Ca from the selected, lithofacially and biostratigraphically treated sections through the Gutenstein dolomites, Annaberg, Wetterstein, Reifling and Dachstein limestones.

Geochemical study of limestones and dolomites of the Western Carpathians

* RNDr. O. Lintnerová, RNDr. P. Masaryk, Ing. E. Martiny, CSc., Geological Institute of the Centre of Geoscience Research, Slovak Academy of Sciences, Dúbravská cesta 9, 814 73 Bratislava.

was systematically dealt with by Veizer (1970), Veizer — Demovič (1969, 1973, 1974), Veizer et al. (1971), Hanáček (1969).

Veizer — Demovič (1974) generalized the results of their study in this region and they explained utilization of Sr as indicator of ancient limestones and dolomites formation conditions. They distinguished high-Sr (deep-sea and hypersaline) and low-Sr limestones (shallow-water organogenic and organodetrital). They found out that early diagenetic dolomites contain higher Sr concentrations than the late diagenetic ones. Later Veizer specified this theory and it became a basis of several works on geochemistry, as well as a subject of discussions (Veizer et al., 1978; Brand — Veizer, 1980; Yudovich et al., 1980; Wiggins, 1986; Morrow — Mayers, 1978).

Kinsman (1969) stated that Sr content in diagenetically stabilized limestones indicated mechanism of diagenesis (open and closed systems). Resulting Sr concentration ranges from 700 to 10 000 ppm after the first phase of diagenetic recrystallization of typical aragonite sediment, whereas calcites with much lower Sr content (below 350 ppm) are result of later diagenetic recrystallizations. Morrow — Mayers (1978) simulated diagenetic process in limestones. Decrease of Sr concentration in ancient limestones to 100—200 ppm level could be caused only by late diagenetic process. Early diagenesis does not lower Sr content in majority of limestones below 400 ppm. During late diagenesis Sr concentration is controlled by changes in porosity, acidity of underground waters and residence time in porous solutions. Facially controlled porosity changes might enable to determine range of values observed in several ancient limestones (Veizer, 1978; Morrow — Mayers, 1978 a).

Possibilities of Na use for determination of salinity of environment of carbonates formation or diagenesis were discussed in several works. These works, similarly as in Sr, are based on the fact that recent carbonates have quite higher Na content (e.g. Tokuyama et al., 1972: 1900—4400 ppm Na for aragonites; Busenberg — Plummer, 1985: 1290—5190 ppm Mg for calcites and 2750—5890 ppm Na for aragonites) than ancient limestones and dolomites (Veizer et al., 1978: 100—900 ppm for limestones and dolomites; Badiozamani, 1973:100—300 ppm for limestones; Fritz — Katz, 1972: 100—600 ppm Na for dolomites). Land — Hoops (1973) recommend to use Na as indicator of salinity of diagenetic solutions and dolomitization solutions. Similarly, Fritz — Katz (1972) presuppose that Na content is in relation to diagenetic history of dolomite crystals. They assume that Na comes from 3 sources: NaCl from dolomitization brines, Na bound in dolomite structure, Na bound to clay minerals inhereted from original $CaCO_3$ sediment. Na in the dolomite lattice is in relation to salinity of dolomitization solutions. Fine-grained, supratidal dolomites have higher Na content than coarse-grained, late diagenetic and hydrothermal dolomites. Sass — Katz (1982) applied Na (Na/Ca — Sr/Ca — Mg/Ca and O and C isotopes) to the solution of platform dolomites genesis. Na/Ca ratio together with ^{18}O in the process of (penecontemporaneos) dolomitization were conditioned by salinity of surrounding water; Mg/Ca and Sr/Ca ratios correspond to chemism changes of interstitial solutions. Veizer et al. (1977, 1978) established the value of 230 ppm Na for the ancient limestones and dolomites as a boundary for the carbonates formed from the solutions close to normal sea water and from hypersaline solutions or they were dolomitized by them. Jaffrezo — Renard (1979) also used Na as indicator of palaeosalinity and they included it into salinity index together with K, Mg, Sr.

Experimental study of Na coprecipitation in calcites, aragonites and dolomites, as well as comparison of Na contents in natural and synthetic calcites and aragonites (White, 1977, 1978; Kitamo et al., 1975; Busenberg — Plummer, 1985) cleared up a form of Na occurrence and distribution in the structure of $CaCO_3$ minerals and Na effect on properties of minerals. Busenberg — Plummer (1985) proved that significant amount of SO_4^{2-} and Na^+ occurs in calcites precipitated from the sea (or synthetic sea) water. SO_4^{2-} and Na^+ amount in solid solution with calcite is in direct proportion to log of crystals growth rate. If SO_4^{2-} content in solid solution raises to 3 mol %, solubility of calcite will be the same as solubility of aragonite. Na has only very little effect on solubility product of calcite. Incorporation of Na in calcite is controlled by the Freundlich isotherm (Busenberg — Plummer, 1985). Distribution coefficients determined experimentally from the various studies are different, their value changes by 1 order. Amount of Na bound in calcite may be to a certain extent dependent on number of crystal defects in the calcite lattice.

Brief survey of geological structure

The NE part of the Malé Karpaty Mts. is built up from tectonic units composed mainly of Triassic carbonate rocks. The region is noted for complicated tectonic structure and relatively bad exposure what was a reason of various classifications and views on tectonic structure in the past. Views of many authors working in the mentioned region (Andrusov, 1936; Peržel, 1966; Mahel', 1967; Bystrický — Mahel', 1970; Biely et al., 1980) differed especially in the tectonic interpretations or in classification to the certain tectonic units of the Western Carpathians or the Eastern Alps. Mahel's paper (1987) represents a survey of the latest information on geological structure of the Malé Karpaty Mts. The author presents this classical core mountain range as a transitional segment between the Alps and the Carpathians with a numerous group of peculiarities and differences in geological structure.

New complex revaluation of lithological content and stratigraphy (Michalík et al., 1986) was necessary regarding the possibilities of direct correlation with the units in the basement of the Vienna basin Neogene filling. Detailed lithofacial and biostratigraphic research cleared up many of doubtful questions and it shifted the possibilities of correlation with the Vienna basin basement from theoretical to practical level.

Three higher nappes — Veterník, Havranica and Jablonica — occur in the overlying strata of the Krížna (Vysoká) Nappe. Their mutual relation, lithological content and stratigraphy are evident from the geological section (Fig. 1) and stratigraphic column (Tab. 1). Determination of stratigraphic range of the Reifling limestones (Illyrian — Cordevolian) and their gradual facial transition to limestones of fore-reef and reef Wetterstein type (Masaryk et al., 1984; Michalík et al., 1986) represented a significant change when compared with the older data.

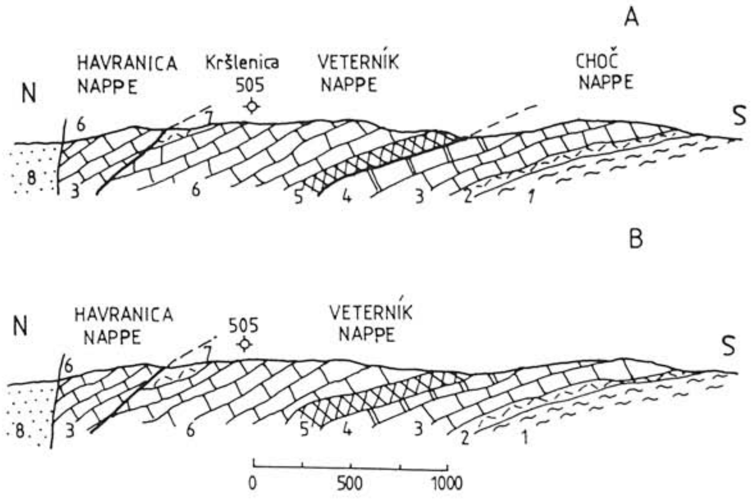


Fig. 1. Schematic geological section south of Plavecký Mikuláš. A. According to Bystrický — Mahel (1970), adapted partly according to Biely et al. (1980). B. Adapted by the authors according to Michalík et al. (1986).
Explanatory notes: 1 — Benkov (Campilian) Formation; 2 — Gutenstein dolomites; 3 — Annaberg limestones; 4 — Reifling limestones; 5 — Raming limestones; 6 — Wetterstein limestones; 7 — Wetterstein dolomites; 8 — Palaeogene.

In our opinion, the mentioned nappes — Veterník, Havranica and Jablonica — represent the equivalents of higher nappes than the Choč Nappe and they may be spatially and facially correlated with the Göller Nappe group established in boreholes under the Neogene filling of the Vienna basin. Jiříček (1984) arrived at the same conclusion in correlation of the Alpine and Carpathian units.

Geochemical study of the carbonate sequences completes lithofacial and stratigraphic data making them more accurate. The samples were taken from the same sections as for lithofacial-stratigraphic research.

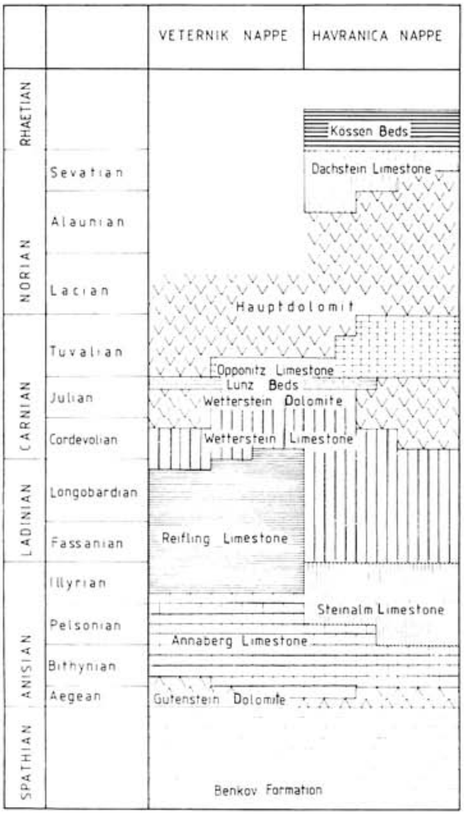
Lithofacial characteristics of the sections

Section Čertova dolina valley: Gutenstein Dolomite

The section is situated S of the village Plavecké Podhradie (Fig. 2). Gutenstein dolomites represent basal member of carbonate sedimentation of the Veterník Nappe in the overlying strata of the Permian—Triassic volcanic-detrital sequence (Malužiná, Šuňava and Benkov Formation). Grey to grey-brown platy and thin-bedded dolomites prevail. Thickness of the sequence varies from several metres to 35—40 m. Dolomites do not contain stratigraphically significant fossils and their age was determined as the Lower Anisian (Aegean — Bithynian) only on the basis of their position in the sequence.

Table 1

Stratigraphic table of the Triassic of the Havranica and Veterník Nappes



From the structures, dolosparites and microdolosparites with indistinct relics after original structure prevail. Parallel lamination, relics of stromatolitic structures, autoclastic breccias, pseudomorphs after evaporites and beds of highly porous dolomites to rauhwackes are its characteristic features. Two beds formed by oolitic dolomite are very distinct. In facial relations, it is a shallow-water supratidal sediment. Frequent pseudomorphs after gypsum and minimum fossil or organic detritus contents indicate hypersaline environment.

Sections Sološnica and Suchá dolina valley: Annaberg Limestone

The section Sološnica is situated in the quarry at the SE margin of the village Sološnica, the section Suchá dolina valley (IVb) lies SE of the village Plavecké Podhradie (Fig. 2). Annaberg Limestone occurs in direct overlying strata of the Gutenstein dolomites and it represents a thick complex (200—250 m) of bedded and heavy-bedded dark grey to brown-grey limestones. Limestones contain the Pelsonian species of foraminifers and dasycladaceans

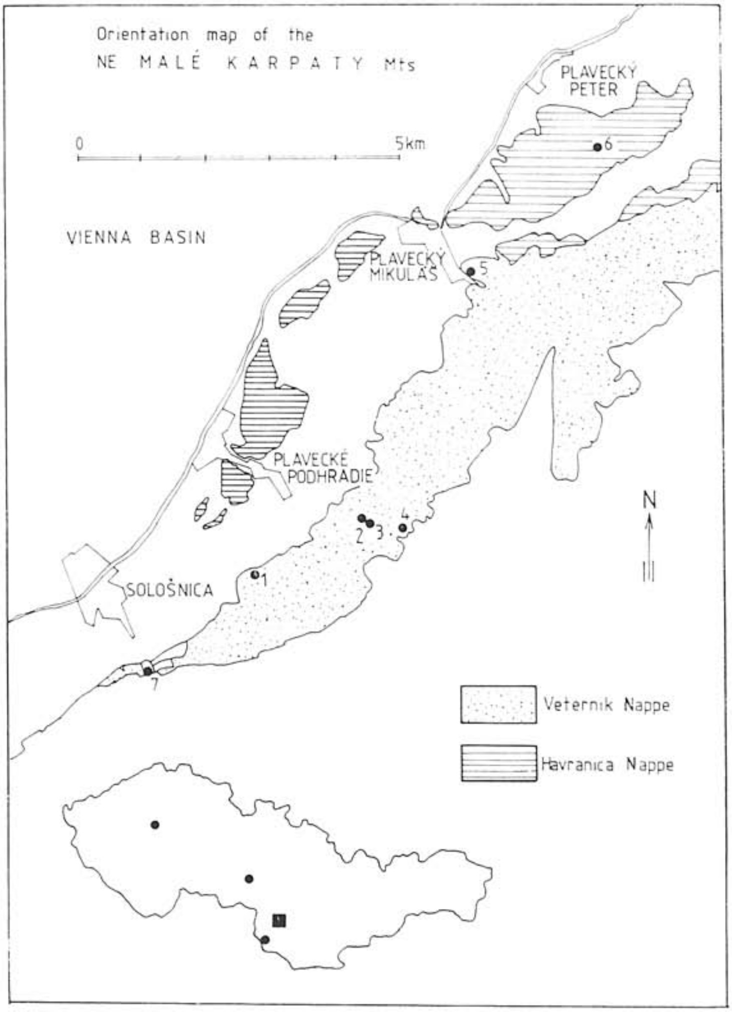


Fig. 2. Orientation map of the studied region with denotation of the Veterník and Havranica Nappes and with localization of geochemically treated sections. *Explanatory notes:* 1 — Čertova dolina; 2 — Rajtárka; 3 — Červenica; 4 — Suchá dolina IVb; 5 — Kršlenica; 6 — Plavecký Peter II/83; 7 — Sološnica.

mainly in the central and higher parts of the sequence. The section Sološnica comprises basal, relatively monotonous part of the sequence. Muddy micrites almost without fossils and sporadic crinoids prevail there. Limestones underwent a slight recrystallization and local dolomitization. Higher part of the sequence is represented in the section Suchá dolina valley (IVb). Dark grey and grey-brown heavy-bedded, mostly micritic and microsparitic limestones with sporadic beds of organic detritus pass gradually upwards to thin-bedded muddy micritic limestones. The Annaberg limestones represent a sediment of shallow shelf with low dynamics of environment (lagoon with restricted circulation). Quiet sedimentation of muddy, slightly detrital limestones is only sporadically interrupted by thin beds of organodetrital limestones with dasycladaceans, ostracods, crinoids and foraminifers. Weak, irregular diagenetic dolomitization is quite frequent, continuous dolomite beds are rare.

Sections Rajtárka and Červenica: Reifling Limestone

The sections are situated SE of the village Plavecké Podhradie (Fig. 2). Reifling limestones occur in the overlying strata of the Annaberg limestones and they represent a marked lithological horizon in the Veterník Nappe. Their age was determined as Illyrian—Cordevolian by conodonts study (Masaryk et al., 1984). The Reifling limestones are mostly dark grey to brown-grey, nodular with numerous silicites. Upwards they pass to thin-bedded and platy organodetrital limestones without cherts.

Limestones are mostly micritic, microsparitic with quite fine organic detritus (filaments, spicules of sponges, crinoids, radiolarians, ostracods and foraminifers). In the higher horizons there are also limestones with pelmicritic structure and beds of laminated and gradationally bedded biosparitic and biointrasparitic limestones. The highest horizons contain detritus of reef-forming organisms (bryozoans, solenopores, sphinctozoans).

Reifling limestones represent deep-water sediment probably of large intraplatform depression. The highest horizons with beds of detrital, gradationally bedded limestones correspond to slope and fore-reef zones.

Section Kršlenica: Wetterstein Limestone, Raming Limestone

The section is situated on the SW slopes of Kršlenica hill and it starts directly in the village Plavecký Mikuláš. Wetterstein limestones occur in the overlying strata of the Reifling limestones. Limestones are usually massive, only sporadically bedded. From facial zones, fore-reef limestones, mostly coarse-clastic breccia sediments with large blocks of reef limestones, then organogenic limestones of reef margin (mostly coral-sphinctozoan facies) are present. The sequence of bedded to platy detrital, quite dark limestones (Raming Limestone) representing the sediments of reef slope to reef core is recorded in the section Kršlenica (Biely et al., 1980).

Bedded limestones from the reef slope have mostly biomicritic, biopelmicritic (packstone — wackestone) character with appearances of weak recrystallization and dolomitization. Upwards they gradually pass to breccia-like organogenic limestones in coral-sphinctozoan facies.

Stratigraphic range of the Raming and Wetterstein limestones is not explicitly proved. Foraminiferal fauna of the lower horizons is identical with the uppermost horizons of the Reifling limestones (Upper Ladinian — Lower Carnian, Jendrejáková, 1986 in Michalík et al., 1986). Probable stratigraphic range is the Lower to Middle Carnian.

Section Plavecký Peter: Dachstein Limestone

Dachstein limestones occur in the overlying strata of Hauptdolomit (Norian) in the Havranica Nappe. They were studied from the section near Plavecký Peter (quarry), for localization see Fig. 2. Limestones are light grey-brown, mostly bedded, beds of nodular limestones and greenish shales are rare. Organic detritus content is low especially in the lower horizons where diagenetic dolomitization is distinictly manifested. Upwards organic detritus and fossil contents are increasing. The highest beds are typical by frequent stromatolitic structures and lumachelle beds. The age was determined as the Upper Norian—Rhaetian on the basis of foraminifers (Kullmanová, 1980 in Biely et al., 1980; Jendrejáková, 1986 in Michalík et al., 1986).

The Dachstein limestones of the Havranica Nappe represent sediments of shallow-water flat shelf and adjacent lagoon with open circulation.

Methods of analytical-geochemical and mineralogical research

Macrocomponents content (SiO_2, Al_2O_3, CaO and MgO) in the carbonate rocks was determined by X-ray fluorescence analysis after melting of samples with $Li_2B_4O_7$ in 1 : 4 ratio. X-ray spectrometer Philips PW — 1410/20 was used.

Method of atomic absorption spectrometry was used for determination of trace elements contents (Cu, Mn, Na, Sr and Zn) in the portion dissolvable in HCl (1 : 1). Sodium content was determined also in water leach (Sass — Katz, 1982). Both data (Na_{HCl}; $Na_{HCl} - Na_{H_2O} = \Delta Na$) were used for interpretation of Na contents. Sodium contents in HCl portion were used especially for comparison with data presented by Veizer et al. (1978). Atomic absorption spectrometer Perkin-Elmer 2380, hollow cathode lamps and acetylene--air flame were applied. Sr was determined at presence of additive La-oxine solution. Individual elements were determined at the most sensitive resonance lines, secondary resonance lines were used at higher concentrations. Accuracy of determinations was checked by standard reference materials: limestone KH (ZGI Berlin), limestone GFS-401 (G. F. Smith, U.S.A.). Precision of results of analyses was checked by repeated measurements.

Calcite, dolomite and non-carbonate contents were determined by manometric method (Turan — Vančová, 1972). Accuracy of the results was verified by chelatometric determination of CaO and MgO.

Mineral composition of non-carbonate portion was established partly by X-ray diffraction (CuK_α), partly by recalculation from the chemical analyses according to Yudovich (1981).

Results and discussion

Results of chemical analyses for individual sections are listed in Figs. 3—7 and Tab. 2. The results obtained from 80 samples from 7 sections are presented. Sections length and density of taken samples were adapted to thickness of the

Table 2

Ca, Mg, Sr, Na contents and 1000 Sr/Ca ratio in the studied carbonate rocks

Rocks	Number of samples	Arithmetic mean ± standard deviation				
		Ca	Mg	Sr	Na	1000 Sr/Ca
Gutenstein Dolomite	5	23.52 ± 1.23	11.24 ± 0.92	66 ± 16	262 ± 41	0.27 ± 0.06
Annaberg Limestone	15	37.78 ± 2.10	0.42 ± 0.09	977 ± 430	178 ± 37	2.57 ± 0.97
Reifling Limestone	15	37.23 ± 1.72	0.75 ± 0.88	148 ± 64	119 ± 15	0.40 ± 0.17
Wetterstein Limestone	26	38.25 ± 1.27	0.95 ± 0.72	130 ± 23	92 ± 28	0.33 ± 0.59
Dachstein Limestone	26	31.36 ± 4.28	6.06 ± 4.10	186 ± 67	313 ± 174	0.61 ± 0.19

sequence and to the local conditions, such as exposure of the field and tectonic dislocation of the studied sequence. (Thickness of geochemically studied part of the sequence is marked out in individual sections — Figs. 3—7).

Short section (only 5 samples) through basal dolomites does not enable to make serious conclusions on genesis of dolomite. The results may be compared with data of Veizer et al. (1971), Veizer — Demovič (1974), Mišík (1968) who referred to early diagenetic origin of the Middle Triassic dolomites or to aridity of climate with evaporization features. Sr content in the studied Gutenstein dolomites is much lower (44—94 ppm Sr, 1000 Sr/Ca: 0.19—0.41) than that presented by Veizer — Demovič (1974) for this type of dolomite (100—600 ppm, 1000 Sr/Ca: over 0.5). Microstructural characteristics (autoclastic breccia, pseudomorphs after gypsum, lack of fossils, micritic character and fine lamination), as well as Na content: 200—300 ppm are typical of early diagenetic origin of dolomite in the environment with raised salinity in comparison with the sea water. Low Mn contents prove aridity of environment (Yudovich, 1981); Bencini — Turi (1974) stated that dolomitization does not change Mn content. Increased Zn content is interesting: 30—71 ppm (cf. e. g. Morrow — Mayers, 1978; Brand — Veizer, 1980; Pingitore, 1978). Original aragonite sediment probably did not contain raised Zn concentrations; little insoluble residue mostly of silicate composition (chlorite — illite) is not considered as a sufficient source in diagenetic process. The source is represented probably by postdiagenetic solutions which might also affect Sr, Na and Mg contents. Formation of "cellular" dolomite and grade of recrystallization support this fact. Dolomite content ranges from 92 to 99 %.

Geochemical characteristics of the Annaberg, Reifling (pseudo-Reifling) and Wetterstein limestones are plotted in Figs. 4, 5, 6. These are pure limestones, insoluble residue content is raised by cherts in the Reifling limestones (Fig. 5). IR of limestones has clayey character of illite-chlorite composition, grains of authigene quartz and feldspar are rare. Fe-minerals are more frequent, usu-

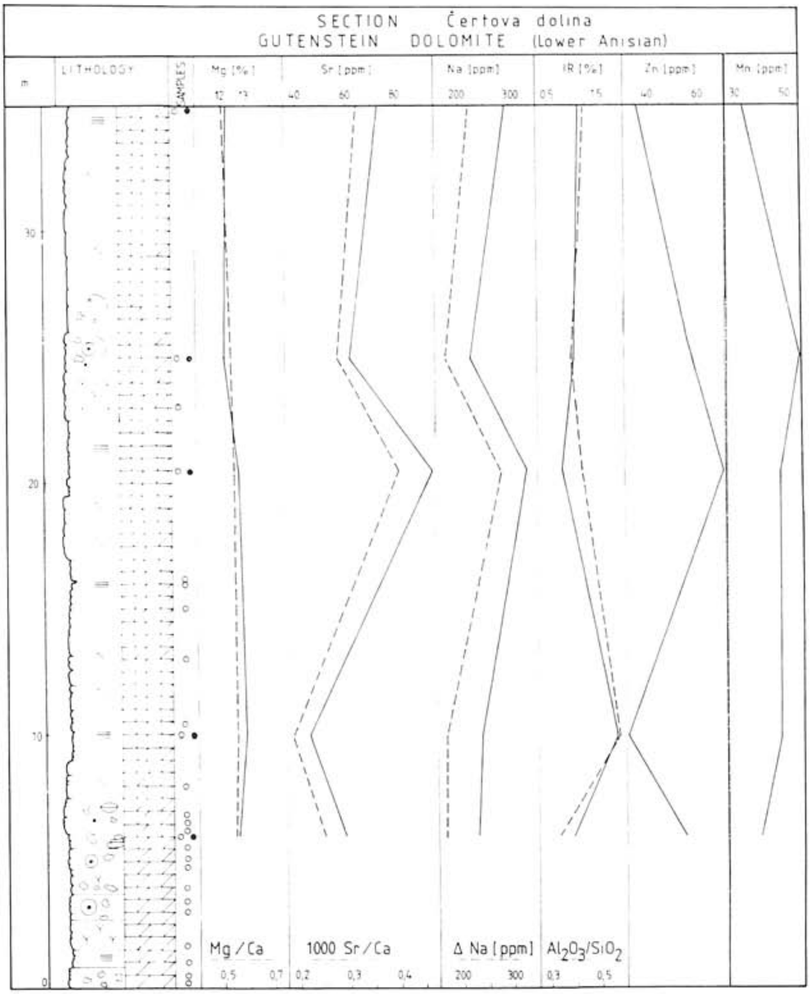
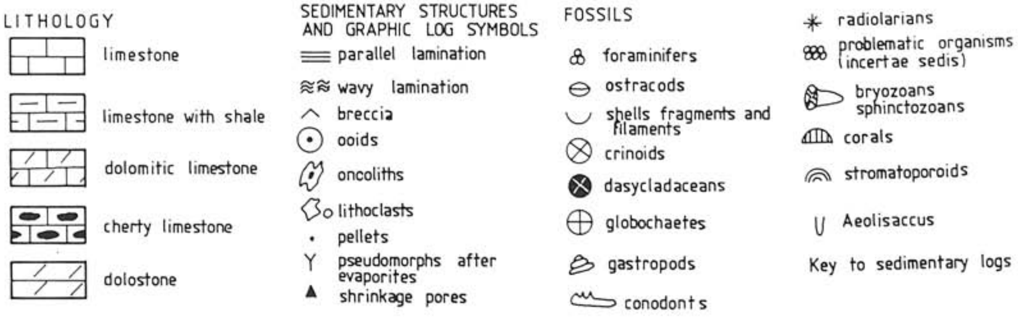


Fig. 3. Vertical distribution of IR, elements and oxides in the section Čertova dolina valley, Gutenstein Dolomite (Δ Na = Na_{HCl} — NaH_2O, valid also for Figs. 4—7).



Key to sedimentary logs

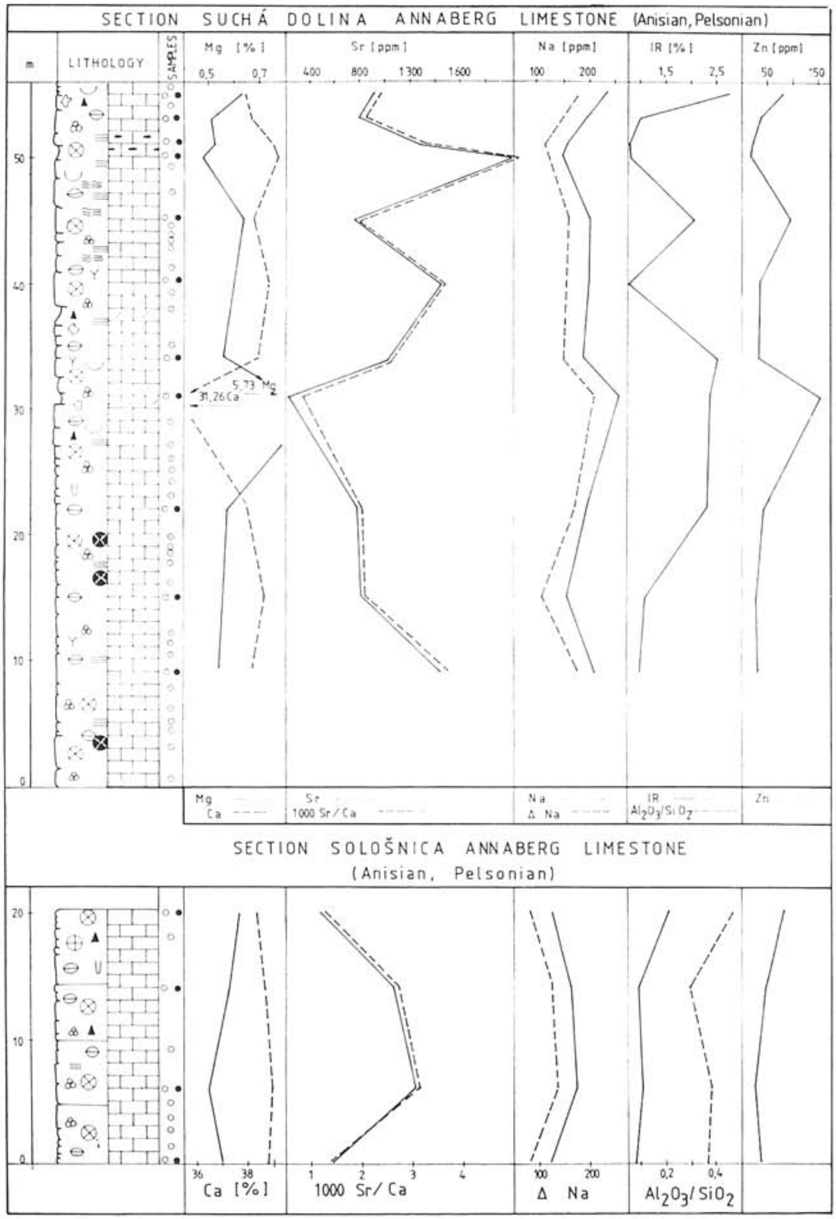


Fig. 4. Vertical distribution of IR, elements and oxides in the sections Sološnica and Suchá dolina valley IVb, Annaberg limestones.

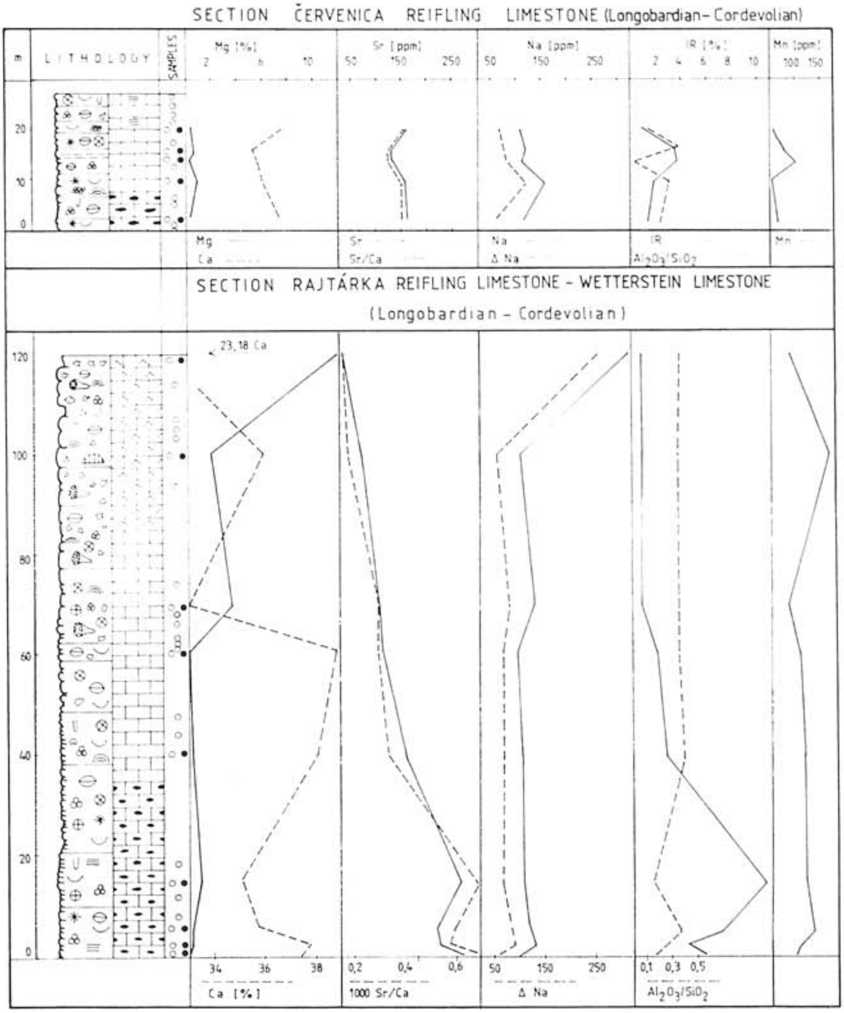


Fig. 5. Vertical distribution of IR, elements and oxides in the sections Rajtárka and Červenica, Reifling limestones.

ally in form of pigment, coatings and microveins (limonite) and authigene pyrite. Anhydrite in form of sporadic grains was identified in the Annaberg limestones. Al_2O_3/SiO_2 ratios are plotted in the graphs (Figs. 3—7) in order to make more detailed characteristics of insoluble residue (Y u d o v i c h, 1981). Their values range from 0.1 to 0.4. Values below 0.1 are typical of quartzy IR, over 0.3 of IR formed by hydrolysis products — clays genetically connected with weathering crusts (Y u d o v i c h, 1981). Cherty Reifling limestones have low values of ratio. Ratio values completed well mineralogical characteristics. IR contents of the studied limestones have low values, they

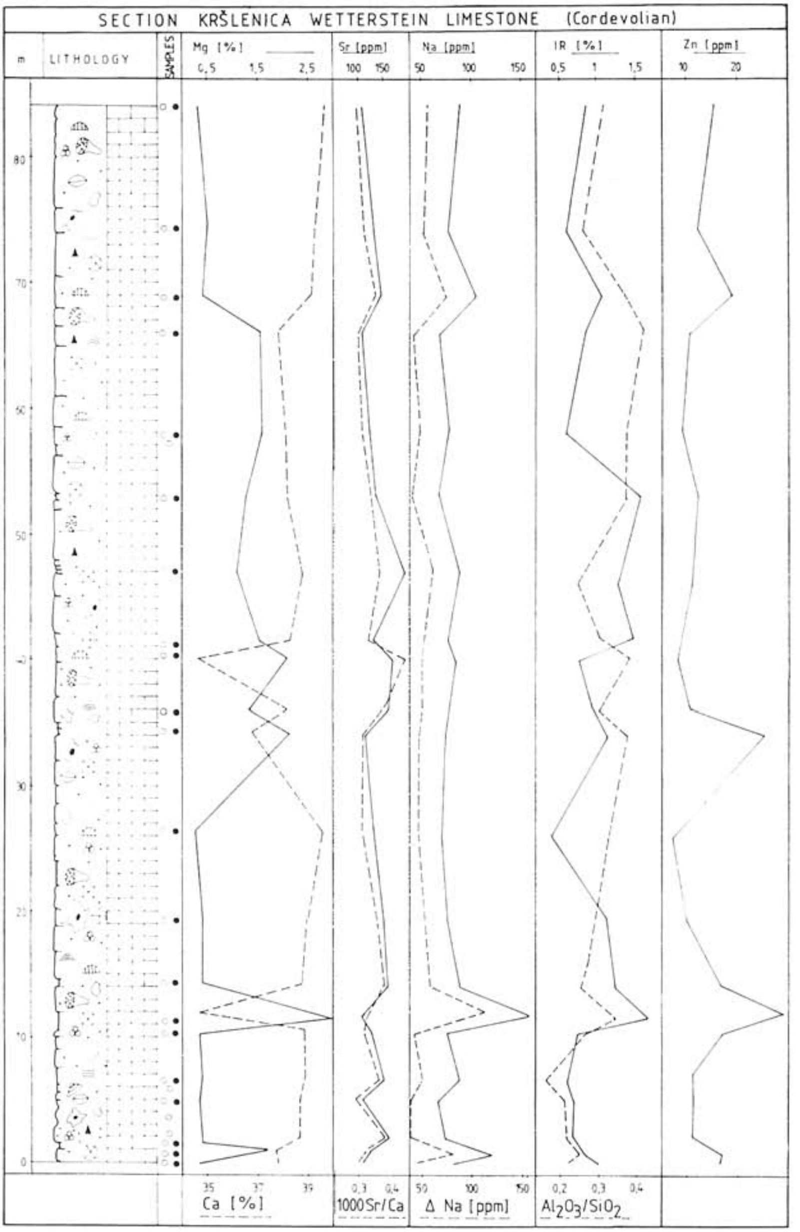


Fig. 6. Vertical distribution of IR, elements and oxides in the section Kršlenica, Wetterstein Limestone.

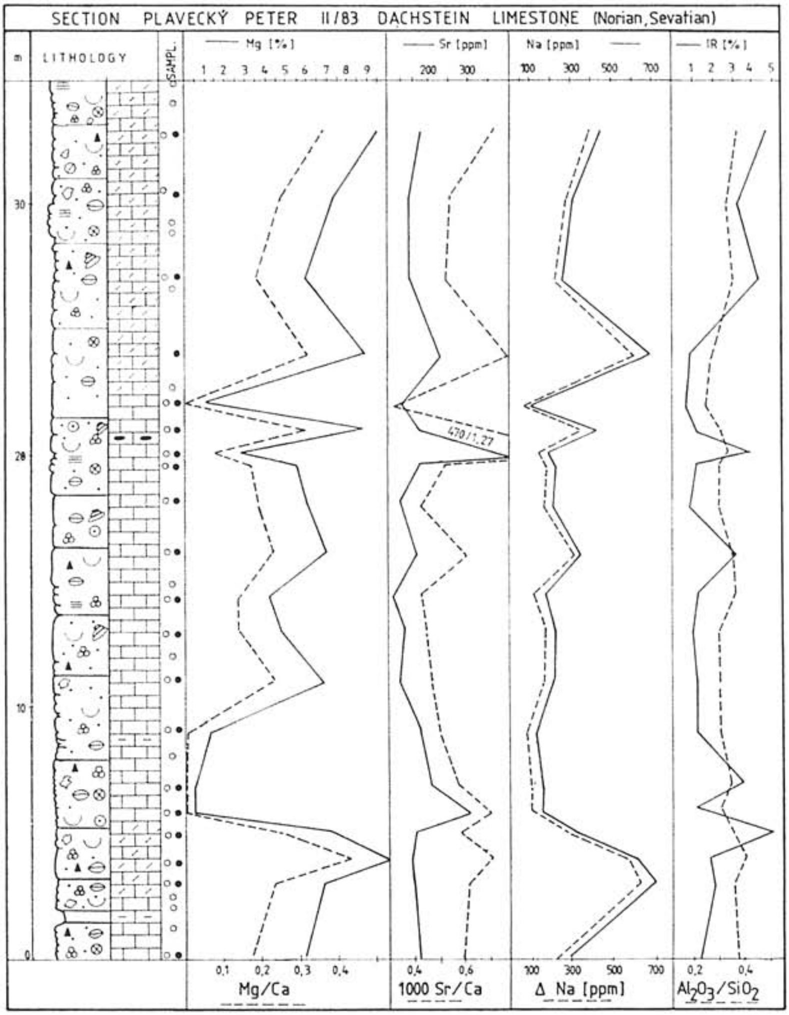


Fig. 7. Vertical distribution of IR, elements and oxides in the section Plavecký Peter II/83, Dachstein Limestone.

represent silty mineral transported to the sedimentary area from distant sources.

The Annaberg limestones are sediments of shallow shelf with low dynamics of environment (lagoon). Sr content is markedly lowered in places with increased dolomite content (Fig. 4). Sr content is quite high (480—2000 ppm) and it can be compared with high-Sr group of limestones distinguished by Veizer — Demovič (1974): lagoonal limestones, originally biochemically precipitated aragonite sediment with low supply of detrital material. Raised salinity of environment was reflected also in Na values: 125—255 ppm. According to Veizer et al. (1978), the Annaberg limestones belong to transient group of facies ranging from normal salinity environment and hypersaline environment (boundary 230 ppm Na). It is supported by pseudomorphs after gypsum or anhydrite in IR (section Sološnica). Zn content (Fig. 4) in the Annaberg limestones varies within a wide interval of values (28—154 ppm) with the highest concentration in dolomite. Negative correlation with CaO —0.85 and Sr —0.69 is remarkable. Zn content raised in diagenetic process (Milliman, 1974 gives 20 ppm Zn for recent carbonate skeletal (shell) material) and on the basis of relation to the other components it is connected with dolomitization. Meteoric water which is, in comparison with the sea water, enriched in Zn (Mn, Fe) may be the Zn source. Owing to high Zn distribution coefficient for calcite (Crocket — Winchester, 1966 give values ranging from 5.2 to 5.5), enrichment of calcite in Zn may occur in diagenetic (open) system (Pingitore, 1978; Brand — Veizer, 1978). In the Annaberg limestones where partly isolated diagenetic system (high Sr content or Sr/Ca ratio) is presupposed just as in the Gutenstein dolomites, postdiagenetic enrichment of limestones in Zn is assumed. Mn content is low (38—148 ppm) and according to Bencini — Turi (1974) low Mn content in shallow-water limestones reflects original composition of the sediment, mostly aragonite one.

The Reifling limestones represent pelagic sediments which was formed under the conditions of normal salinity "pseudo-reifling" limestone represents a facial transition from the pelagic facies to the sediments of fore-reef and reef facies represented by a complex of the Wetterstein and Raming limestones. Sections Rajtárka and Červenica document the transient facies (Upper Ladinian — Lower Carnian). Diagenetic stabilization of the limestones took place in the open system; strontium was removed from recrystallization environment of original, mostly aragonite sediment. Sr content in the typical Reifling limestones is higher than in the transient (lower part of the section Červenica, Fig. 5) limestones without cherts. Relatively low differences in Sr contents of the Reifling and Wetterstein limestones and 1000 Sr/Ca ratios are well observable in the histograms (Fig. 8). They demonstrate well the decrease of Sr content towards the reef limestones or dolomites. Sodium content in these limestones varies within an interval typical of limestones formed in the normal sea water (Veizer et al., 1978): 103—153 ppm Na.

Average Ca, Mg, Sr and Na contents for individual types of limestones are listed in Tab. 2. Mn contents in the Reifling limestones are plotted in the graphs (Fig. 5). Values characterizing shallow-water oxidation environment without Mn supply from the other sources are quite low: 50—170 ppm Mn (Yudovich, 1981; Bencini — Turi, 1974). However, slight Mn content increase in the basinal limestones is observed when compared with the Wetterstein limestones (13—34 ppm). It is caused probably by different dynamics of the sedimentary environment. Brand — Veizer (1980) studied the changes of Mn content in the diagenetic environment. Mn content should be raised in the diagenetic process, it results from the value of Mn distribution coefficient for calcite which is higher than 1.

The Wetterstein and Raming limestones represent fore-reef and reef facies. Sr content is low: 100—200 ppm. Sr decrease in the ancient limestones to such low level is explained by late diagenetic (repeated) effect of solutions of meteoric origin (Kinsman, 1969; Morrow — Mayers, 1978; Bat-

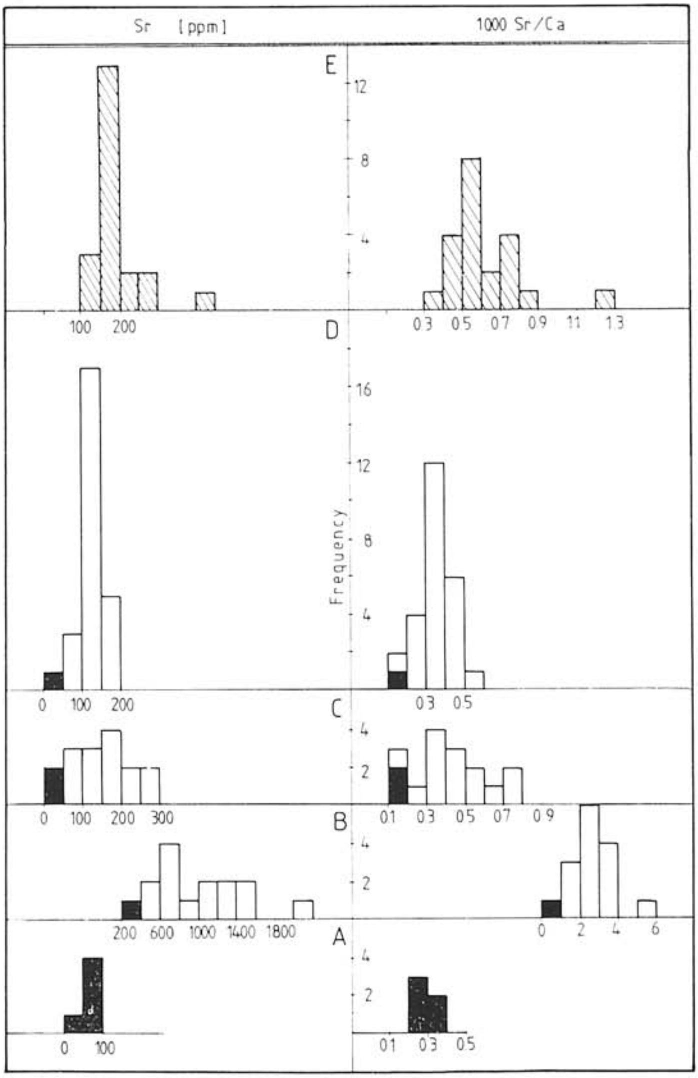


Fig. 8. Histograms of Sr contents and 1000 Sr/Ca ratios in the studied types of limestones and dolomites.
Explanatory notes: A — Gutenstein Dolomite, B — Annaberg Limestone, C — Reifling Limestone; D — Wetterstein Limestone; E — Dachstein Limestone. White — limestones, black — dolomites, lined — dolomitic limestones (valid also for Fig. 9).

hurst, 1971). Veizer— Demovič (1973, 1974) included them to low--strontium group of limestones (below 300 ppm) which comprises mostly limestones organodetritally stabilized in the open system. Diagenetic processes in carbonates are still discussed problem in the works on geochemistry. Morrow — Mayers (1978) consider "bimodal classification" of carbonates according to Sr content corresponding to original conditions of origin (mineralogy, climate, salinity) (Veizer — Demovič, 1974) rather as a result of diagenetic processes. Residence time of solutions flowing through unstable phases (aragonite, high-Mg calcite), porosity of solutions and acidity of underground waters control Sr content in diagenetic limestones (low-Mg calcite). Diagenetic solution causes different degree of Sr removal during late diagenesis in relation to genetic porosity of the sediment (Cameron, 1969). Carbonates of shelf margin of the grainstone type must be more leached (150 ppm Sr, reef) than their lagoonal equivalents of the mudstone type (300 ppm Sr). Contents of back-reef limestones presented by Veizer — Demovič (1974) are higher, they are close to the values obtained by the present study (977 ppm Sr for the Annaberg limestones — see Tab. 2). Brand — Veizer (1980) explain diagenetic process by equilibrium and disequilibrium ways of recrystallization of metastable carbonate minerals (Veizer, 1978; Morrow — Mayers, 1978 a). On the basis of survey of literary data and regional-geochemical study of strontium in the Palaeozoic carbonates from the Western Urals (1400 samples), Yudovich et al. (1980) supported anomalous depletion of the ancient reef carbonates (50—100 ppm Sr) in comparison with the recent ones (see e. g. Matthews, 1968; Milliman, 1967; Lowenstam, 1961; Amiel et al., 1973). Decrease of Sr content was caused by underground water of meteoric origin. Sr content in carbonate rocks, particularly in economically significant reef complexes is inevitably connected with the facial conditions of sedimentation. In addition, mostly afacial factors must be studied: closed diagenetic systems, epigenetic dolomitization, epigenetic Sr supply (Yudovich et al., 1981).

Differences in Sr contents of the described types of limestones plotted in the histograms (Fig. 8) may be interpreted in the sense of facial dependence worked out by Veizer — Demovič (1973, 1974). Porosity of original sediment must be also regarded as facial characteristics (see also Veizer, 1978; Morrow — Mayers, 1978 a).

Sodium contents in the Wetterstein limestones range from 65 to 122 ppm and they correspond to normal salinity of the sea water (Veizer et al., 1978). Effect of diagenesis on Na values is described also by Brand — Veizer (1980). Diagenetic effect of meteoric water decreases Na, Sr and Mg contents. It follows theoretically from low Sr and Na distribution coefficients for calcite and lower Sr and Na (Mg) contents in the meteoric water.

The Dachstein dolomites, dolomitic limestones and limestones (Fig. 7) document dolomitization effect on Sr and Na contents. The Dachstein limestones are just little marly, silicate phase content does not exceed 5 %. There was a clayey bed in the lower part of the section, carbonate content reaches there only 33.5 % (6.5—6.7 m — unmarked bed in Fig. 7). Only illite with very little of chlorite admixture (up to 5 %) was determined in it by X-ray diffraction. IR of carbonates has a similar illite composition with low chlorite, quartz and feldspar contents (diagenetic minerals). Irregular dolomitization was established in the whole section. Mg content varies within a wide interval: 0—11 % (Fig. 7). Organodetrital limestones of the central part are least affected by dolomitization. Sr content reaches low values in dolomitized beds: 100—200 ppm, 1000 Sr/Ca ratio is over 0.5. Dolomitization of this type of shallow-

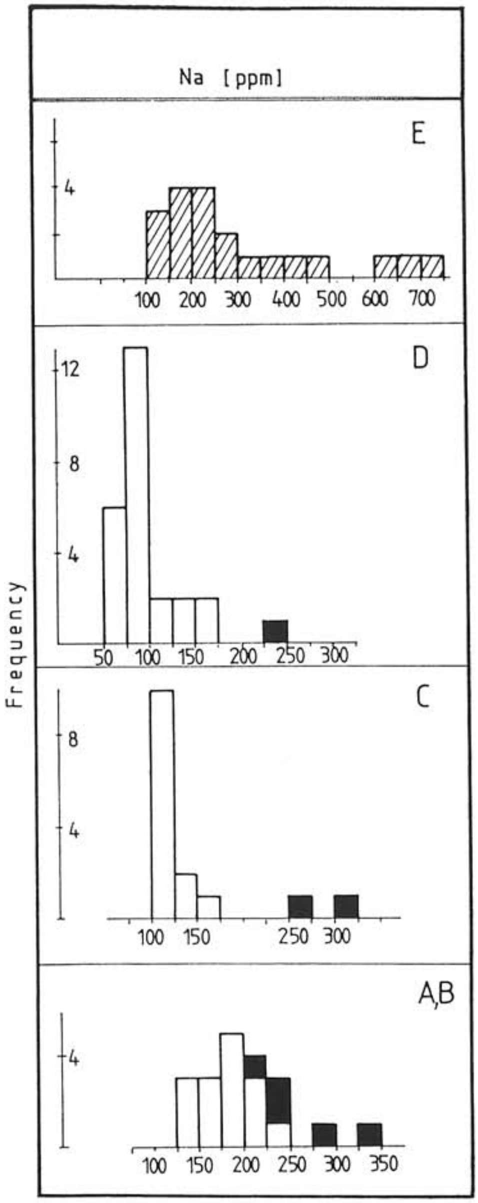


Fig. 9. Histograms of Na (Na_{HCl}) contents in the studied types of limestones and dolomites.
For explanatory notes see Fig. 8.

-water sediment with cyclic sedimentation features (lagoonal to supratidal) took place due to solutions with increased salinity. Increased Na contents: 200—700 ppm (Figs. 7 and 9) correspond to this fact. Na content is distinctly correlated with MgO or CaO contents (correlation coefficients +0.78 or —0.78 are considered to be of orientation character in the sense of Busenberg — Plummer, 1985). Sodium characterizes here salinity of dolomitization solutions (Land — Hoops, 1973; Fritz — Katz, 1972). Na contents in the studied carbonates are plotted in the histograms (Fig. 9). Distribution of Na values for the individual facial types of limestones or dolomites is shown. Na values calculated from Na_{HCl} — Na_{H_2O} (Sass — Katz, 1982) are plotted in Figs. 3—7. From the values it is evident that Na content is systematically lower (by 40—50 ppm), but relative relations between the individual samples are not changed in any section, they copy Na_{HCl} values.

Results of Na contents obtained by the study of the Triassic carbonates from the Biele pohorie Mts. in the Malé Karpaty Mts. support competence of Na application to orientation determination of palaeosalinity. Effect of diagenesis on Na contents in carbonates is more complicated than in interpretation of Sr values. It results mainly from the way of Na occurrence in the lattice of carbonate minerals (Busenberg — Plummer, 1985; White, 1977, 1978). Na values should be interpreted mainly in connection with the other trace elements (Sr, Mn), as well as with the results of oxygen and carbon isotopic composition study (Veizer et al., 1977, 1978; Brand — Veizer, 1980; Sass — Katz, 1982). It is necessary to work with large enough and suitable set of samples.

Conclusions

The Gutenstein dolomites, Annaberg, Reifling, Wetterstein and Dachstein limestones of the Veterník and Havranica Nappes of the Malé Karpaty Mts. are characterized in the present work. Results of the mentioned carbonate types are given in Tab. 2.

Significance of trace elements for geochemical study of carbonates was dealt with. Sr, Na, Mn and Zn were chosen as indicator elements for the study of their formation and diagenesis conditions. Comparison of Sr and Na contents provides the most significant information, in spite of dissension of views on application of Na as a palaeosalinity indicator.

Results of our work support dependence of Na content on salinity of the sedimentary environment, though effect of diagenesis on Na content is not univocally solved.

Mn is also an important indicator of carbonates formation and diagenesis conditions, in spite it is not so widely applied as Sr.

Trace elements study of the carbonate rocks was used as one of the methods in reconstruction or modelling of the sedimentary environment.

In the present work we directed our attention at the study of facial changes of the lithostratigraphic units in the Havranica and Veterník Nappes. Geochemical methods proved that there are transient facies between the Reifling and Wetterstein limestones and continuous sequence of strata is preserved.

Translated by O. Mišániová

REFERENCES

AMIEL, A. J. — FRIEDMAN, G. M. — MILLER, D. S., 1973: Distribution and nature incorporation of trace elements into modern aragonite corals. Sedimentology (Amsterdam), 20, 1, pp. 47—64.

ANDRUSOV, D., 1936: Subtatranské příkrovy Západních Karpat. Carpatica (Praha), 1, pp. 1—36.
BADIOZAMANI, K., 1973: The dorag dolomitization model — application to the middle Ordovician of Wisconsion. J. sed. Petrology (Tulsa), 43, pp. 965—984.
BATHURST, R. G., 1971: Carbonate sediments and their diagenesis. Elsevier, Amsterdam — Oxford — New York, 620 pp.
BENCINI, A. — TURI, A., 1974: Mn distribution in the Mesosoic carbonate rocks from Lima Valley, Northern Apennines. J. sed. Petrology (Tulsa), 44, pp. 774—782.
BIELY, A. — BYSTRICKÝ, J. — MELLO, J., 1980: Problematika hronika a „gemerika" v Malých Karpatoch a vo Viedenskej panve. Materiály XXIII. celoštátnej geologickej konferencie slovenskej geologickej spoločnosti. Geol. Inst. D. Štúr (Bratislava), pp. 17—30.
BRAND, U. — VEIZER, J., 1980: Chemical diagenesis of multicomponent carbonate systems — 1: Trace elements. J. sed. Petrology (Tulsa), 50, pp. 1219—1236.
BUSENBERG, E. — PLUMMER, L. N., 1985: Kinetic and termodynamic factors controlling the distribution of SO_4^{2-} and Na^+ in calcites and selected aragonites. Geochim. cosmochim. Acta (London), 49, pp. 713—725.
BYSTRICKÝ, J. — MAHEĽ, M., 1970: Beitrag zur Stratigraphie der Trias der Kleinen Karpaten. Geol. Zbor. Geol. carpath. (Bratislava), XXI, 1, pp. 191—198.
CAMERON, E. M., 1968: A geochemical profile of the Swan Hills Reef. Can. J. Earth Sci. (Ottawa), 5, pp. 287—309.
CROCKET, J. H. — WINCHESTER, J. W., 1966: Coprecipitation of zinc with calcium carbonate. Geochim. cosmochim. Acta (London), 30, pp. 1093—1109.
FRITZ, P. — KATZ, A., 1972: The sodium distribution of dolomite crystals. Chem. Geol. (Amsterdam), 10, pp. 237—244.
HANÁČEK, J., 1969: K problému geochémie vápencov triasu Malých Karpát. Geol. Práce, Spr. (Bratislava), 49, pp. 123—139.
JAFFREZO, M. — RENARD, M., 1979: Éléments en traces de calcaires a dasycladales et charophytes. Bull. Cent. Rech. Explor. — Prod. Elf-Aquitaine (Pau), 3, 2, pp. 640—649.
JIŘÍČEK, R., 1984: Korelace severních vápencových Alp a Západních Karpat v podloží Vídenské pánve. Zem. Plyn Nafta (Hodonín), 29, 2, pp. 117—203.
KINSMAN, D. J. J., 1969: Interpretation of Sr^{2+} concentration in carbonate minerals and rocks. J. sed. Petrology (Tulsa), 39, pp. 486—508.
KITAMO, Y. — OKUMUDA, M. — IDOGAKI, M., 1975: Incorporation of sodium, chloride and sulfate with calcium carbonate. Geochem. J. (Tokyo), 84, pp. 75—84.
LAND, L. S. — HOOPS, G. K., 1973: Sodium in carbonates and rocks: A possible index to the salinity of diagenetic solution. J. sed. Petrology (Tulsa), 43, 3, pp. 614—617.
LOWENSTAM, H. A., 1961: Mineralogy, O^{18}/O^{19} ratios, and strontium and magnesium contents of recent and fossil brachiopods and their bearing on the history of the oceans. J. Geol. (Chicago), 69, pp. 241—260.
MAHEĽ, M., 1967: Regionální geologie ČSSR II., Západné Karpaty 1. Academia, Praha.
MAHEĽ, M., 1987: The Malé Karpaty Mts. — constituent of the transitional segment between the Carpathians and Alps; important tectonic window of the Alpides. Miner. slov. (Bratislava), 19, 1, pp. 1—27.
MASARYK, P. — PUŠKÁROVÁ, K. — BUČEK, S., 1984: Contribution to stratigraphy of Reifling limestones of the Malé Karpaty Mts. (West Carpathians). Geol. Zbor. Geol. carpath. (Bratislava), 35, 2, pp. 242—258.
MATTHEWS, R. K., 1968: Carbonate diagenesis: Equilibrium of sedimentary mineralogy to the subaerial environments: Coral Cap of Barbados, West Indies. J. sed. Petrology (Tulsa), 38, 4, pp. 1110—1119.
MICHALÍK, J. — BORZA, K. — BUČEK, S. — MASARYK, P. — JENDREJÁKOVÁ, O. — BYSTRICKÝ, J. — KÖHLER, E., 1986: Stratigrafia a stavba príkrovov Malých Karpát s ohľadom na vyjasnenie štruktúrnych anomalít v podloží Viedenskej panvy. Geol. Inst. of Slovak Acad. Sci., Bratislava, Manuscript, 377 pp.
MILLIMAN, J. D., 1967: Carbonate sedimentation of Hogsty Reef, a Bahamian atoll. J. sed. Petrology (Tulsa), 37, pp. 658—676.
MILLIMAN, J. D., 1974: Marine carbonates — Part I. Recent sedimentary carbonates. Springer-Verlag, New York, 375 pp.

MIŠÍK, M., 1968: Traces of submarine slumping and evidence of hypersaline environment in the Triassic of the West Carpathian Core Mts. Geol. Zbor. Geol. carpath. (Bratislava), 19, pp. 205—224.
MORROW, D. W. — MAYERS, I. R., 1978: Simulation of limestone diagenesis — a model based on strontium depletion. Can. J. Earth Sci (Ottawa), 15, pp. 376—396.
MORROW, D. W. — MAYERS, I. R., 1978a: Simulation of limestone diagenesis — a model based on strontium depletion: Reply. Can. J. Earth Sci. (Ottawa), 15, pp. 1685—1687.
PERŽEL, M., 1966: Stratigraphie der Trias der Choč — Decke des Biele pohorie der Malé Karpaty. Geol. sbor. Geol. carpath. (Bratislava), 17, 1, pp. 157—166.
PINGITORE, N. E. Jr., 1978: The behaviour of Zn^{2+} and Mn^{2+} during carbonate diagenesis: Theory and application. J. sed. Petrology (Tulsa), 48, pp. 799—814.
SASS, E. — KATZ, A., 1982: The origin of platform dolomites: New evidence. Amer. J. Sci. (New Haven), 282, pp. 1184—1213.
TOKUYAMA, A. — KITANO, Y. — KANESHIMA, K., 1972: Geochemical behaviour of chemical species in the processes of limestones in the Tyukyu Islands. Geochim. J. (Tokyo), 6, pp. 83—92.
TURAN, J. — VANČOVÁ, L., 1972: Nutzung der Manometrischen Methode bei der Bestimmung von Karbonaten. Geol. Zbor. Geol. carpath. (Bratislava), 23, 1, pp. 99—114.
VEIZER, J., 1970: Zonal arrangement of the Triassic rocks of the Western Carpathians: A contribution to the dolomite problem. J. sed. Petrology (Tulsa), 40, pp. 1287—1301.
VEIZER, J., 1978: Simulation of limestone diagenesis — a model based on strontium depletion: Discussion. Can. Earth. Sci. (Ottawa), 15, pp. 1063—1685.
VEIZER, J. — DEMOVIČ, R., 1969: Geochemistry of sedimentary carbonate rocks (Mantle Series of High Tatra Mts. and Middle Triassic of Slovak Karst Region). Geol. Zbor. Geol. carpath. (Bratislava), 20, pp. 303—332.
VEIZER, J. — DEMOVIČ, R., 1973: Environmental and climatic controled fractionation of elements in the Mesozoic carbonate sequences of the Western Carpathians. J. sed. Petrology (Tulsa), 43, 1, pp. 258—271.
VEIZER, J. — DEMOVIČ, R., 1974: Strontium as a tool in facies analysis. J. sed. Petrology (Tulsa), 44, pp. 93—115.
VEIZER, J. — DEMOVIČ, R. — TURAN, J., 1971: Possible use of strontium in sedimentary carbonate rocks as a paleoenvironmental indicator. Sed. Geology (Amsterdam), 5, pp. 5—22.
VEIZER, J. — LEMIEUX, J. — JONES, B. — GIBLING, M. R. — SAVELLE, J., 1977: Sodium: Paleosalinity indicator in ancient carbonate rocks. Geology (Assoc. Teachers Geol. Cardiff), 5, pp. 117—179.
VEIZER, J. — LEMIEUX, J. — JONES, B. — GIBLING, M. R. — SAVELLE, J., 1978: Paleosalinity and dolomitization of Lower Paleozoic carbonate sequence, Somerset and Prince of Wales Island, Arctic Canada. Can. J. Earth Sci. (Ottawa), 15, pp. 1448—1461.
WHITE, A. F., 1977: Sodium and potassium coprecipitation in aragonite. Geochim. cosmochim Acta, (London), 41, pp. 613—625.
WHITE, A. F., 1978: Sodium coprecipitation in calcite and dolomite. Chem. Geol. (Amsterdam), 28, pp. 65—72.
WIGGINS, W. D., 1986: Geochemical signatures in carbonates matrix and their relation to deposition and diagenesis, Pensylvanian marble falls limestones, Central Texas. J. sed. Petrology (Tulsa), 56, pp. 771—783.
YUDOVICH, J. E., 1981: Regional geochemistry of sedimentary beds. Nauka, Leningrad, 276 pp., (in Russian).
YUDOVICH, J. E. — MAIDL, T. V. — IVANOVA, T. I., 1980: Geochemistry of Sr in carbonate sediments. Nauka, Leningrad, 150 pp. (in Russian).

Manuscript received July 7, 1987.