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EMPLOYING OF SEMIQUANTITATIVE SPECTRAL ANALYSIS FOR STRATIGRAPHIC AND LITHOFACIAL INVESTIGATION IN LIMESTONES FROM THE MANTLE SERIES OF THE HIGH TATRA MTS.

(Text-figs. 1—7, Pl. I—II)

Abstract: Example of application of semiquantitative spectral analysis in Malmian — Urgonian carbonate complex. Possibility of employing of the method.

Introduction

The chemical composition of a sedimentary carbonate rock is the reflection of conditions that predominated in the sedimentary environment and only to a small degree it was influenced by the time (geological period) of rock forming. It means that rocks formed with analogous facies conditions also in different periods would have analogous chemical composition. The change of chemical composition (besides few exceptions) can be applied for stratigraphic investigations only when simultaneously facies conditions changed.

The chemical composition of sedimentary carbonate rocks is determined by two groups of elements. Those bound to carbonates (Ca, Mg, Sr, partly Ba, Mn or other but in small quantity) and other bound mainly to insoluble remnant (Si, Al, Fe and other). The character of the chemical composition of sedimentary carbonate rocks depends on the ratio of these both constituents.

Rocks with small content of insoluble remnant form in regions with fast biogenic, chemical or biochemical sedimentation, much more vigorous in contrast to the supply of elements of insoluble remnant. They are prevailingly sediments of the shallow water zone. The elements dominating in this group are Ca, Mg and Sr. Their contents depends as mentioned, on physical-chemical and biogenic factors. Increased Mg contents themselves are an indicator of shallower environment. The content of $MgCO_3$ present as solid solution in calcite skeletons of calcareous algae reaches to 28,75 weight per cent (K. E. Chave 1954). Dolomites need for their rise increased salinity (over 14 ‰) and their formation is supported by increased temperature, pH and increased partial pressure of CO_2 (N. M. Strachov 1958). These are conditions attainable rather in lagoon and shallow sea than in deep sea environment. Sr is bound predominately to aragonite constituent of biogenic or chemically precipitated limestones. With diagenetic alteration of unstable aragonite to calcite Sr disperses and disappears. The changes of Mg and Sr content are also partial indicator of relative age of rock forming time.

Employing of semiquantitative spectral analysis for their division is unsuitable because these elements are represented in amounts over or about 1 % which are shown by the analysis only as 1—100 %.

The second group of carbonate sedimentary rocks includes rocks with considerable content of insoluble remnant. It was caused either by strong supply of elements of insoluble residue characteristic of littoral or shallow neritic areas (with unpeneplaned coast or built of carbonate rocks) or by very slow increase in carbonate constituent

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characteristic of pelagic areas on the contrary. Attention is needed to be called to the fact that this division is very schematic, valid only in general and many exceptions to it exist there.

The insoluble residue of pelagic carbonate rocks in contrast to near-shore is formed of well sorted clay fraction with prevailing alumosilicates and their related elements. K. H. Wedepohl (1960) proves also increased contents of some elements in deep sea pelagic clay of the Atlantic and Pacific Ocean in contrast to shallow water clay as of Mn, Co, Ni, Cu, Zn, Mo, Pb in the Atlantic and also Sc, Y and Ba in the Pacific. He explains it by the fact that because of very slow supply of terrigenous constiuent and rate of sedimentation, which is 3.4 times slower in the Pacific than in the Atlantic, in the transportation of these elements volcanic gases and partly cosmic dust started to become important.

The content and ratio of elements in the insoluble residue depend on the rate and the character of supply, granulometric and mineralogic composition and to a smaller degree on physical-chemical and biological factors. This may serve indirectly as an indicator of the age of rock. E. g. if in change of the character of material transported from land the time corresponding to this change is ascertained, the change of chemical composition can be connected with belonging period. It is, however, rather accidental ascertaining than lawful and the character of insoluble residue also was influenced in pelagic environment only in few cases by such changes.

The employing of semiquantitative spectral analysis for the division of such rocks is more promising but with little accuracy and considerable subjective mistakes also quite questionable.

Certain results, can be reached by this method with comparison of carbonate rock groups with small content of insoluble residue(predominately neritic) to those with increased content of the residue (pelagic or near-shore). The content and the ratio of the main elements (Ca, Mg, Si, Al, Fe and other) will not show greater differences because of inaccuracy and subjectiveness of the method. Quite different is the situation at elements accompanying them. Some of these will lack in purer limestones. The change of chemical composition may be considered as evaluable and reliable for semiquantitative spectral analysis only when there some elements are missing in one group of carbonate rocks in contrast to their presence in other group.

Such criteria can have certain importance for the classification of carbonate rock masses in areas, where there are no other criteria, e. g. in decrystalised or strongly diagenetically altered rocks, although during recrystalisation and diagenesis also considerable change of chemical composition took place.

Lithofacial Description

In the mantle ceries of the High Tatra Mts. a sequence of grey to greyishpink massive limestones appear in the Malmian—Aptian. The limestones are macroscopically all very similar and their distinguishing in survey is prevailingly conventional. On the basis of microfacies two members are distinguishable (text-figs. 4, 5, 6, 7): Malmian—Neocomian (Hauterivian) and Barremian—Aptian. The sequence is available for solving of chemical alternation between both environments because of good possibility of stratigraphical classification and paleogeographical reconstruction.

Malmian—Neocomian: there are grey to light pink compact limestones. Microscopically they have mostly muddy texture with considerable contents of pellets of various size. In biomicrofacies they are characterized by association of Foraminifera (mainly

Protoglobigerina), Saccocoma, Filaments, *Globochaete alpina* Lombard, Ostracoda and very sporadic crinoid and Lamellibranchiate fragments (text-figs. 4, 5, 6, 7 and pl. I, fig. 1, 2).

According to the classification of R. L. Folk (1959) they can be designated pellmicrites. According to their lithological character and biofacies we can them perhaps compare with recent pellet mud which originates under hemipelagic paleogeographic conditions, e. i. in depth of about 1000 m and in a distance of some tens to 500 km from the continent (Z. Kukal 1964).

Barremian—Aptian: there are grey compact limestones with muddy to organodetrital texture. Among quite rare organic textures fragments of Brachiopods, of thick shell Lamellibranchiata, Bryozoa, crinoid segments and echinoid spines are found there. This type of limestones can be denoted micrites with organic remains or biomicrites. They represent untypical strongly tectonically effected Urgonian facies (pl. II, fig. 1, 2).

Their areas of sedimentation is neritic. They are reef and reef-like sediments, also having been tectonically effected already during the time of sedimentation.

Differences in Chemical Composition of Deep-Sea and Shallow-Water Sediments

The main differences are made dependent upon the content and the character of insoluble residue. The supposition is incorrect that in pelagic sediments there would be greater supply of insoluble residue but it was caused by smaller rate of sedimentation of biogenic constituent. In our case it is also confirmed by the fact that the sequences of Barremien—Aptian are only a bit thinner than those of Malmian—Neocomian, although their sedimentation lasted much shorter time. The content of trace elements in pelagic sediments possibly was also influenced by the factors mentioned by K. H. Wedepohl (1960).

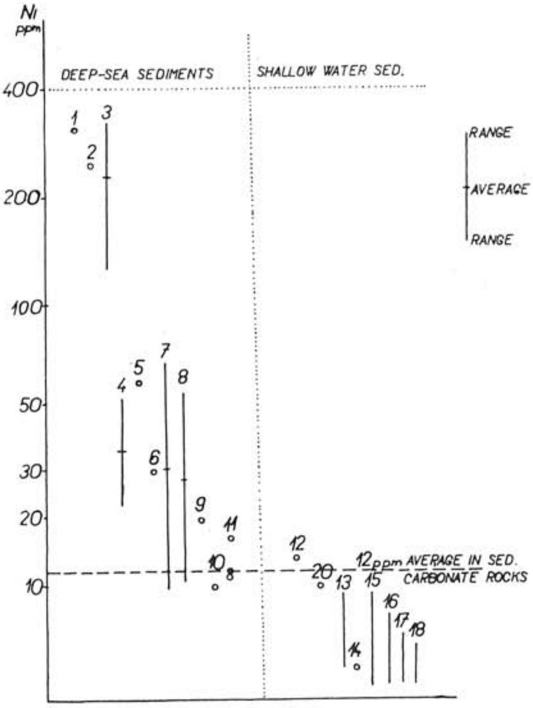
For illustration of changes of the content of trace elements in pelagic and shallow-water environment we compiled from data in literature diagrams for these trace elements which in our case appeared to be decisive. They are Ti, Ni, Bo (text-figs. 1, 2, 3). We took into consideration only types of recent and earlier rocks and organic remains the environment of sedimentation they had originated in was discernible.

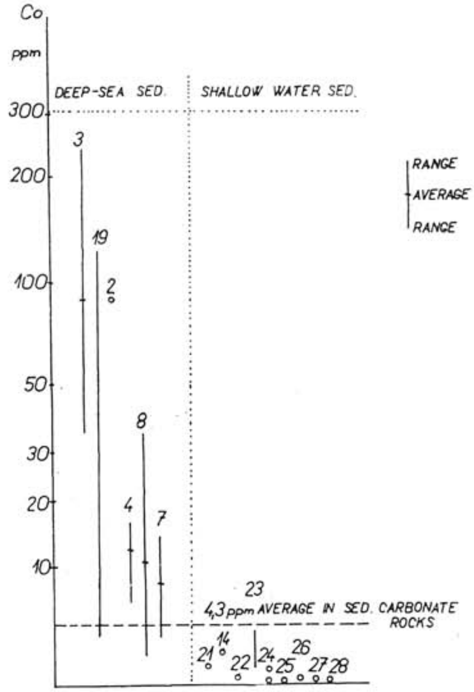
Pelagic sediments are then characterized by increased content of Al, Fe, Mn, Ti, Co, Ni, Cu, etc. (G. Arrhenius 1963). The accumulation of elements bound to clay fraction was also supported by more reductional environment of deep-sea basins. Mn is mainly bound to Mn nodules. A considerable amount of Fe and elements of Fe group is also bound to them. Increased Ni contents are frequent in areas with increased organic activity (G. Arrhenius 1963). Such an area was the environment of sedimentation, in which pellet mud originated, as evidenced by great content of fecal pellets. The presented diagrams show clearly increased content of trace elements in pelagic environment of sedimentation, although a sharp boundary between their content in various environments cannot be drawn because of their large variation.

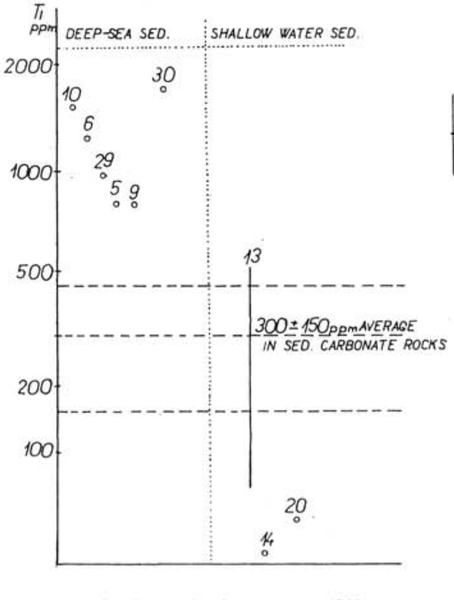
Comparison of Microfacies and Chemical Profiles

In the area of the Tichá dolina Valley Western Tatra Mts. four profiles were drawn through the named sequence, along which microfacies investigation as well as semiquantitative spectral analysis were carried out. Following elements were determined: Ca, Mg, Sr, Ba, Na, K, Si, Al, Ti, Fe, Mn, Cr, Co, Ni, Au, Ag, Zn, Pb (table 1).

In graphs (text-figs. 4, 5, 6, 7) in horizontal direction in lower part of the graph







Text-fig. 1, 2, 3. In paranthesis number of analyses is given. In the case of only 1 indicated analyses it is marked out with small circle in the graph. In the case of greater number of analyses their extent is marked out with small circle in the graph. In the case of greater number of analyses their extent is marked out with line and the average is indicated.

In M. H. Carr and K. K. Turekian 1961: 1 — E. D. Goldberg and G. Arrhenius 1958, Pacific pelagic mud; 2 — E. J. Young 1954, pelagic mud; 19 — A. A. Smales 1957, carbonate pelagic mud; 21 — D. J. Stanton 1944, pure limestones with $CaCO_3$ (over 90 %). N. Zealand (5); 23 — D. J. Stanton 1944, shallow-water limestones. N. Zealand (48);

In D. L. Graf 1960: 4 — D. P. Maljuga 1949, calcareous sediments of deeper part of the Black sea (4); 5 — K. H. Wedepohl 1955, Globigerina mud (1); 6 — K. H. Wedepohl 1955, Globigerina mud (1); 7 — K. Kullenberg 1957 (in A. A. Smales 1957), carbonate pelagic sediments (9); 8 — dtto (15); 9 — K. H. Wedepohl 1955, Globigerina sand (1); 10 — K. H. Wedepohl 1955, Globigerina (1); 11 — K. K. Turekian 1958, eupelagic mud of equatorial Atlantic (3); 13 — H. L. Cannon 1955, Lockport dolomite; 14 — I. Noddack and W. Noddack 1939, *Brissopsis lyrifera* (1); 20 — M. Blumer and H. Erlenmayer 1950, *Encrinus* (1); 29 — K. H. Wedepohl 1955, Globigerina (1); 30 — C. Correns 1941, average of deep-sea carbonate rocks with $CaCO_3$ content over 50 %. Meteor expedition (178).

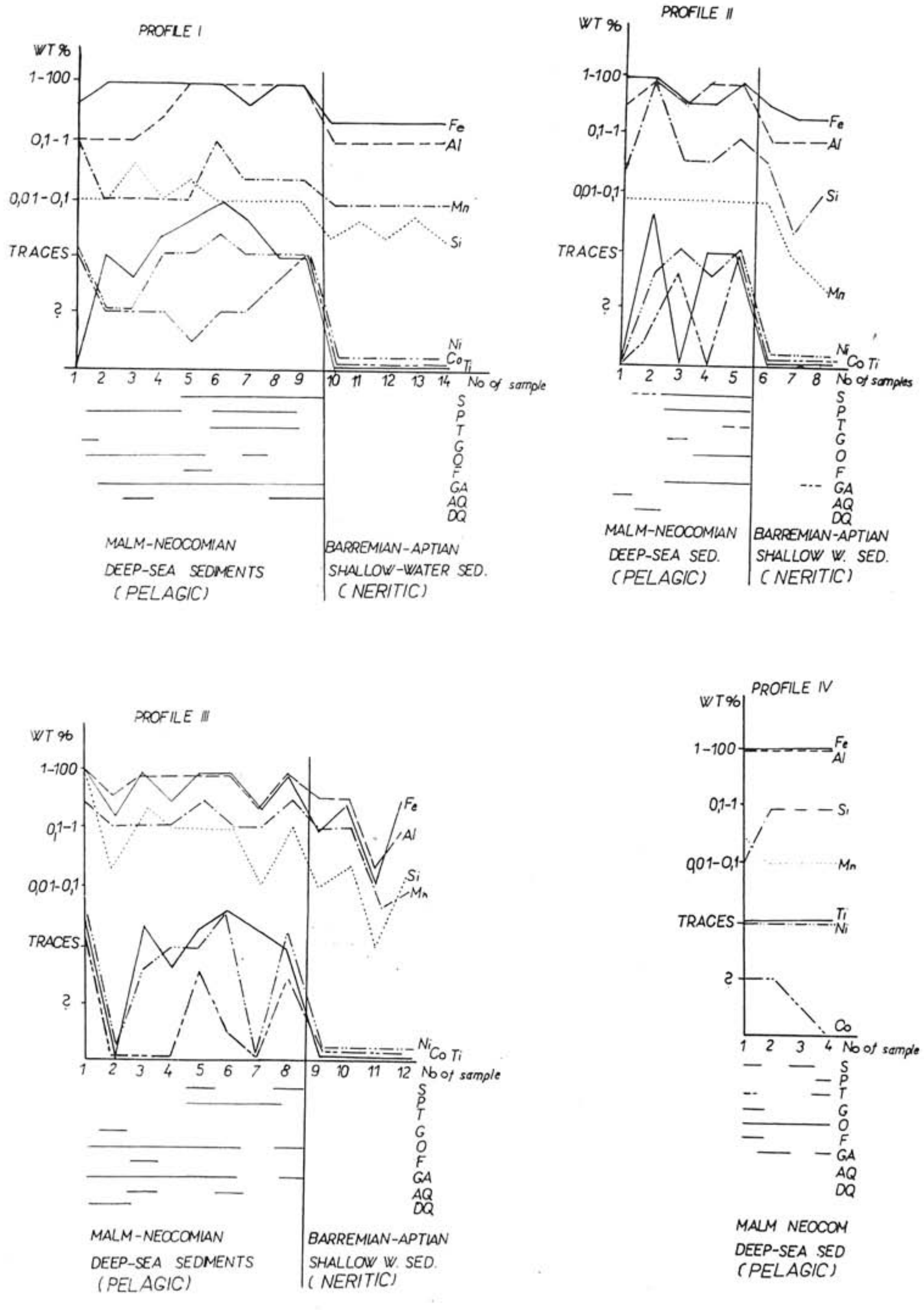
3 — S. K. El. Wekeel and J. P. Riley 1961, deep-sea carbonate mud (10); 15 — J. Hanáček 1962, light Noric limestones, Hranovnica (10); 16 — K. Hanáček 1962, light Ladinian limestones, Hranovnica (10), 17 — J. Hanáček 1962, light Upper Anisian limestones, Hranovnica (19); 18 — J. Hanáček 1962, dark Anisian limestones, Hranovnica (3); 22 — M. H. Carr and K. K. Turekian 1959, dolomite from the Office for Standards of USA (1); 24 — M. H. Carr and K. K. Turekian 1961, calcareous dolomites (2); 25 — M. H. Carr and K. K. Turekian 1961, carbonate shells; 26 — M. H. Carr and K. K. Turekian 1961, corals (3); 27 — M. H. Carr and K. K. Turekian 1961, Pelecypoda (8); 28 — M. H. Carr and K. K. Turekian 1961, Gastropoda (3).

Table 1

	Profile I														Profile II							
	Malm—Neocomian									Barremian—Aptian					Malm-Neocomian					Barr.-Aptian		
Si	3	3	2—3	3	3—2	3	3	3	3	4—3	3—4	4—3	3—4	4—3	3—2	1	2—3	2—3	2	2—3	4—3	3
Pb	4	5	5	4	5	4	4	4	4—3	4	4	3	4	0	4	4	4	5	4—3	4	4—3	4
Mg	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
Mn	2	3	3	3	3	2	3—2	3—2	3—2	3	3	3	3	3	2	2	2	2	2	2	3—4	3
Al	2	2	2—1	1	1	1	1	1	1	2	2	2	2	2	2—1	1	1—2	1	1	2	2	2
Ti	0	4	4—5	4—3	3—4	3	3—4	4	4	0	0	0	0	0	0	3—4	0	4	4	0	0	0
Fe	1—2	1	1	1	1	1	1—2	1	1	2—1	2—1	2—1	2—1	2—1	1	1	1—2	1—2	1	1—2	2—1	2—1
Cu	4—3	4	4—3	4—3	4—3	4—3	4—3	3—4	4—3	4	4—3	4	4	4	4—3	3	3—4	4	3	3	4	4—3
Ag	4	0	0	4—5	5	4	4	4	4	4	4	4	4	5—4	0	4—5	4—5	4—5	4—5	5	4—5	0
Na	3	3	3	3—2	3—2	2	3—2	3—2	2—3	3—2	3	3—2	3	3—2	2	1	2	2	1	2	3	3
Zn	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Ni	4	5	5	4	4	4—3	4	4	4	0	0	0	0	0	0	4—5	4	4—5	4	0	0	0
Co	4	5	5	5	0	5	5	4—5	4	0	0	0	0	0	0	0	4—5	0	4	0	0	0
K	—	—	—	—	—	1	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Ca	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
Cr	4	4	4—5	4	4—3	3—4	4	4	4	4	4	4—5	4	5	4	4	5	5	4	4	4	4
Ba	3	4	4	4	4—3	3—2	4	4—3	3—4	4—3	3	4—3	3—2	4—3	2	2—1	2	2—3	2—3	2	4	4
Sr	2—1	1—2	1—2	1—2	1—2	1	1—2	1—2	1—2	1—2	1—2	1—2	1—2	1—2	1	1	1—2	1—2	1	1	1—2	1—2

	Profile III												Profile IV			
	Malm—Neocomian								Barrem—Aptian				Malm—Neocomian			
Si	1	3—2	2—1	2	2	2	3	2	3	3—2	4	3—2	3	2	2	2
Pb	3	4	4	4—5	4	4	5	4	4—5	4	4	4	4—3	4	4—5	4—5
Mg	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
Mn	2—1	2	2	2	2—1	2	2	2—1	2	2	3—4	3	3—2	3	3	3
Al	1	1—2	1	1—2	1	1	2—1	1	1—2	1—2	3—2	2	1	1	1	1
Ti	3—4	0	4—3	4—5	4—3	3—4	0	4	0	0	0	0	4	4	4	4
Fe	1	2—1	1	1	1	1	2—1	1	2	2—1	3	2—1	1	1	1	1
Cu	3	3—4	4—3	3—4	3	3—4	4—3	3	4—3	3—4	4—3	4	4—3	4—3	3—4	4—3
Ag	4—5	5	0	5	4—5	5—4	4—5	5—4	4—5	4—5	4—5	4—5	5	5	4	4
Na	1	2	1	1	1	1	2	1	2	2	3—2	3	2	2—3	2—1	2—1
Zn	—	—	—	—	—	—	—	—	—	—	5	—	—	—	—	—
Ni	3	0	4—5	4	4	3—4	0	4—3	0	0	0	0	4	4	4	4
Co	3	0	4—5	4	4	3—4	0	4—3	0	0	0	0	5	5	0	0
K	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Ca	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
Cr	4	4	4	4	4	4	4—5	5	5	5	5	5—4	—	—	—	—
Ba	1—2	2—3	2—3	2—3	3—2	2—3	3—2	3—2	3—2	3—2	2—3	2—3	3	3	3	3
Sr	2	1	2—1	1—2	1—2	1	1—2	1	1—2	1—2	1	1—2	2	2	2—1	2—1

Explanations: 1 — 1—100 %, 2 — 0,1—1 %, 3 — 0,001—0,1 %, 4 — Traces, 5 — Questioned



Text-figs. 4, 5, 6, 7. S — Saccocoma., P — pellets., T — Tintinidae; G — *Protoglobigerina;* O — Ostracoda; F — filaments; GA — *Globochaete alpina* Lombard; AQ — authigenic quartz; DQ — detrital quartz.

elements found by microfacies analysis are marked. A line indicates their presence in thin section the number of which is marked on horizontal line. The results of semiquantitative spectral analysis are marked in vertical direction.

The comparison of microfacies and semiquantitative spectral analysis makes evident that limestone of the Malmian—Neocomian which deposited in pelagic area differ from Barremian—Aptian shelf limestones in increased content of Al, Si, Fe or also of Mn and mainly in the presence of Ti. Na and Co, lacking completely in Barremian—Aptian limestones. Ti, Ni and Co probably are bound to clayey or organic part of fecal pellets.

In the comparison of content of other trace elements above discussed dependencies have not been ascertained.

Conclusion

The results of semiquantitative spectral analysis in lithology and stratigraphy of sedimentary carbonate rocks may be considered as reliable only in cases when some elements are absent in certain facies of carbonate rocks in contrast to their presence in other compared facies. This is possible in comparison of carbonate rocks having increased content of insoluble residue (predominately pelagic or near-shore) to pure, predominately neritic carbonate rocks.

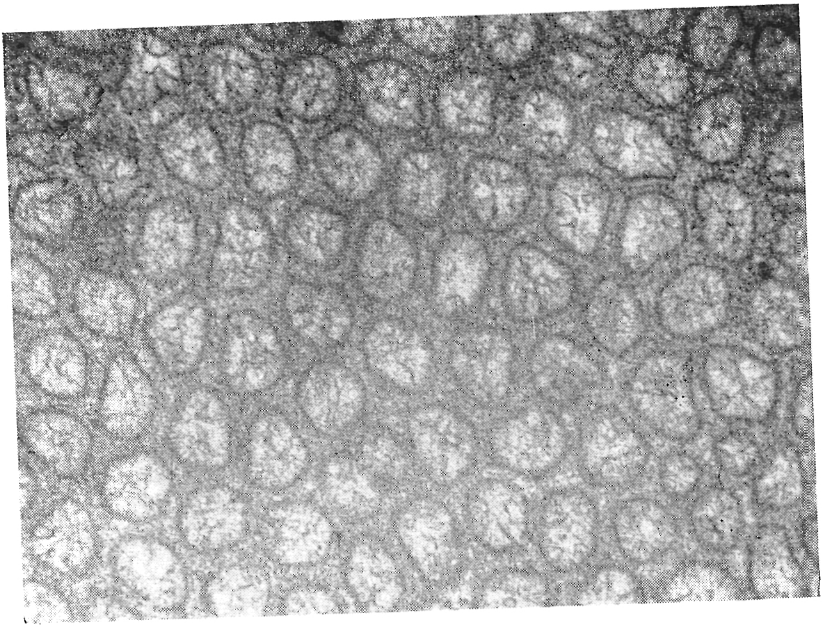
In the mantle series of the High Tatra Mts. on the basis of absence of Ti, Ni and Co clear distinguishing of Barremian—Aptian shelf limestones and Malmian—Neocomian pelagic limestones was made possible.

Translated by J. Pevný.

REFERENCES

Arrhenius G., 1963: Pelagic sediments. The Sea, ideas and observations on the progress in the study of the seas. Vol. 3. New York. — Carr M. H., Turekian K. K., 1961: The geochemistry of Co. Geoch. et Cosmochim. Acta 23, 1—2. — Folk R. L., 1959: Practical petrographic classification of limestones. Bull. Amer. Assoc. Petrol. Geol. 43, 1. — Graf D. L., 1960: Geochemistry of carbonate sediments and sedimentary carbonate rocks. Part III. Minor element distribution. Division of the Illinios state geol. surv., circular 301. — Hanáček J., 1962: Ročná zpráva o geologickom výskume na liste Hranovnica. Geofond, Bratislava. — Hill J. W. and coll., 1963: The sea, ideas and observations on progress in the study of the seas. Vol. 3. The earth beneath the sea, history. New York. — Chave K. E., 1954: Aspects of the biogeochemistry of Mg: Calcareous marine organisms. Journ. Geol. 62. — Kukal Z., 1964: Geologie recentních sedimentů. Praha. — Strachov N. M., 1958: Fakty i gipotezy ob obrazovanii dolom. porod. Izv. AN SSSR, Ser. geol. 6, Moskva. — Veizer J., 1964: Geologicko-petrografické pomery územia medzi Tichou a Kamenistou dolinou v Západných Tatrách. Kat. geol. PF UK, Bratislava. — Wakeel S. K., Riley J. P., 1961: Chemistry and mineralogical studies of deep-sea sediments. Geoch. et Cosmochim. Acta 25, 2. — Wedepohl K. H., 1960: Spurenanalytische Untersuchungen an Tiefseetonen aus dem Atlantik. Ein Beitrag zur Deutung der Geochemischen Sonderstellung von pelagischen Tonen. Geoch. et Cosmoch. Acta 18, 3—4.

Review by B. Cambel.



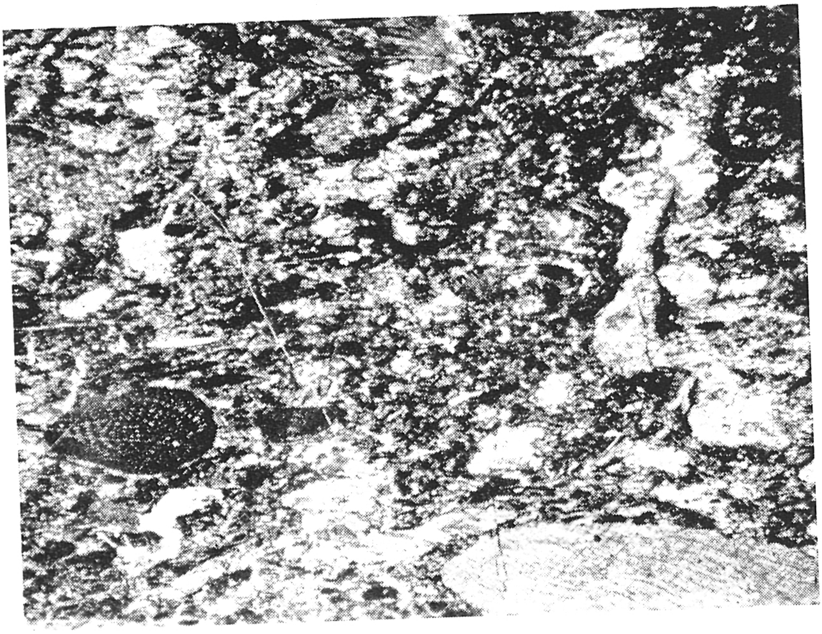
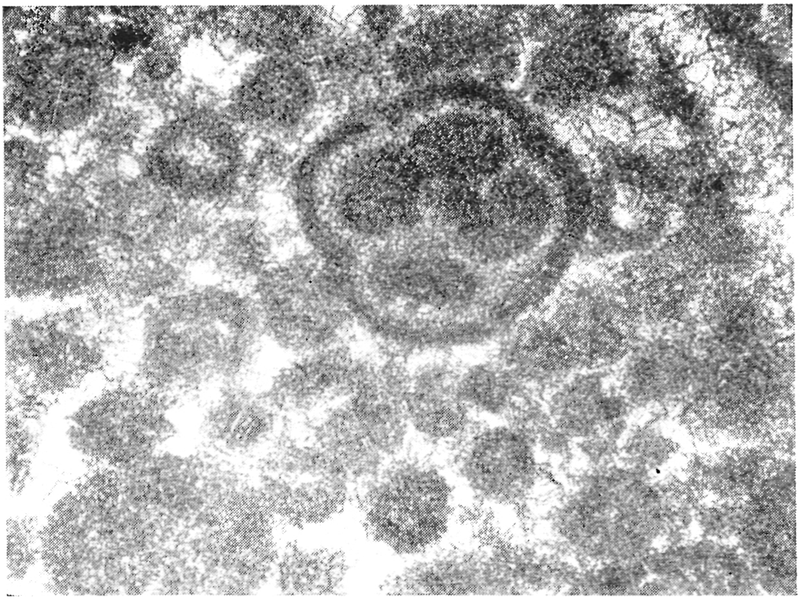


Fig. 1. Pseudoolitic (pellet) limestone. In the core of the pellet there is a *Protoglobigerina*. Malmian probably Oxfordian. Magn. 136×. Rozpadlý Grúň. — Fig. 2. Saccocoma microfacies. Cross section through secunbranchialium of Saccocoma. Pink muddy limestone. Malmian (Kimmeridgian). Magn. 45×. Western slope of the Tichá dolina Valley. Photo L. Osvald.



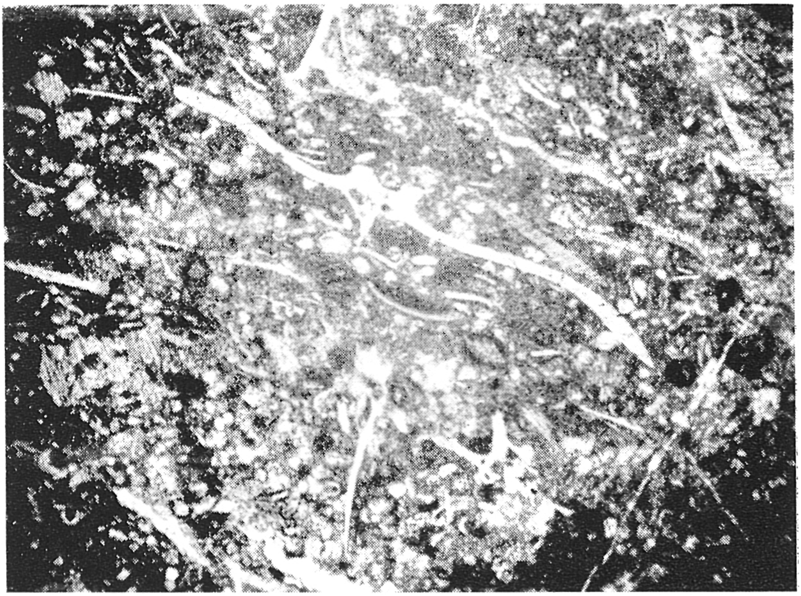


Fig. 1. Tangential section through a Bryozoon. Grey gravel limestone. Barremian-Aptian (Urgonian). Magn. 55×. Western slope of the Tichá dolina Valley. — Fig. 2. Organodetrital, strongly tectonically effected limestone. Cross sections through thick shell Lamellibranchiata and through a Bryozoon. Grey gravel limestone. Barremian—Aptian (Urgonian). Magn. 11×. Western slope of the Tichá dolina Valley. Photo L. Osvald.