

Stable Isotope record in Miocene Fossils and Sediments from Rohožník (Vienna Basin, Slovakia)

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Abstract: Results of stable isotope analyses of Miocene (Badenian, Sarmatian) molluscs and sediments from the localities Rohožník - Vajarská and Rohožník - Konopiská are presented and used for interpretations of Miocene depositional as well as diagenetic conditions in this part of the Vienna Basin.

Key words: Miocene, Vienna Basin, Molluscs, Stable Isotopes

1. Geological setting, Regional Geology and Palaeontology

The locality Rohožník is situated (Fig. 1, 2) in the eastern part of the Vienna Basin and on the western edge of Malé Karpaty Mts., 14 km NE. from the town of Malacky (Slovakia).

The pre-Neogene basement in this area is represented by Triassic megabreccia of Wetterstein-type limestones belonging to the uppermost tectonic units (tyrolicum) of the Northern Calcareous Alps.

In the wider surroundings of Rohožník the Miocene sedimentation began in Badenian by faunistic sterile *block and coarse grained conglomerates*. It is a continental facies of debris cones with material from the pre-Neogene basement, e. g. of the Malé Karpaty Mts. provenience. The penetration of the (Upper) Badenian marine transgression is documented by basal conglomerates and sandstones. The petrographic composition of their pebble material corresponds also to the basement, indicating their local origin. The matrix of the conglomerates consists mainly of the organodetritic sandy limestone (detritus of molluscs, algae, moss animals, worms and foraminifers). The matrix as well as the pebbles often bear the boring traces of the bivalves *Lithophaga* sp. and *Gastrochaena* sp. and sponges *Cliona* sp. The sandstones are mostly calcareous, with a changing composition, with abundant molluscs and red algae. The sediments originated in the littoral zone, in the depressions of the underlying rocks, in a good aerated and lighted sea with a high dynamics. In the direction of the depth the amount of organic rests is increasing to the detriment of the terrigenous material.

In the direction of the top the basal clastic sediments are passing into *Leitha (algal) limestones* forming a

typical reef complex (Fig. 3). The origin of reefs was related to a tectonically active coastal line influenced by the transtension tectonics of Leitha faults of the NNE-SSW direction with a markedly normal character (Marko et al., 1990). Other algal bioherms were formed also on the basement elevations on the SE margin of the basin in the depths to about 40 m, in the sea with the normal salinity. They are very rich in flora and fauna (red algae, moss animals, corals, foraminifers, worms, echinoids, molluscs). These sediments were accessible until recently in the quarry Rohožník - Vajarská and their detailed paleontological research was made for example by Schaleková (1973, 1978), Mišík (1976), Benejová (1985). Baráth (1992) distinguished 6 microfacial limestone types related to the sedimentation in different hydrodynamic conditions. The facies of algal limestones was relatively stable and it yielded the material also for other laterally substituting facies. The sediments of these facies are accessible at the locality Rohožník- Konopiská, nowadays already an unexploited deposit of the correction clays for the production of portland cement, situated about 1.5 km SW. of the quarry Rohožník - Vajarská. The forereef detritic carbonate facies, which originated as a result of the wave activity, accumulated in the form of reef talus cones on the submerged slopes of the Malé Karpaty Mts. before the frontal part of the reef complex. It has the character of the *coarse-grained breccias* consisting of the detritus of reef limestones, red algae and molluscs. In the direction into the basin, these sediments are finger-like or in the form of lens-like bodies, layers and films of variable thickness reaching - often to a considerable distance - the sediments of the basinal pelitic facies. Hladilová, 1991 found out 15 species of bivalves, 19 species of gastropods and 1 species of scaphopods in

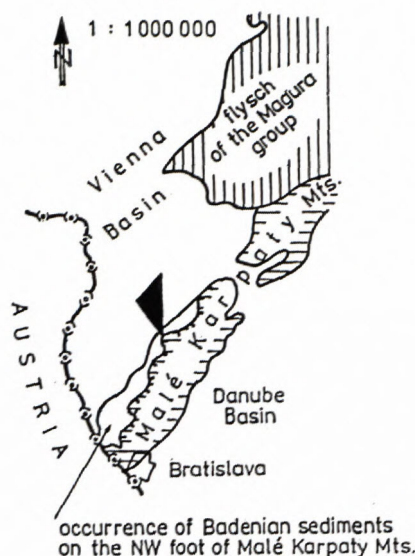


Fig. 1: Simplified geological map of the wider surroundings of Rohožník

these layers. Thick-walled types, considerably damaged (broken, rolled), are prevailing.

The sediments of the basinal facies are represented by the greenish to bluish dark-grey *calcareous clays* with changing contents of organic matter and pyrite. Clays are mostly homogeneous, only in places a slight lamination characteristic for an anoxic environment without bioturbation can be observed. In places, calcareous and gypsum concretions appear in these sediments. In clays, rich assemblages of foraminifers, ostracods, calcareous nannoplankton and fish otoliths were found out (Čierna, 1973, Kučerová, 1982, 1984, 1986, Pachón Duarte, 1989, Horák, 1985, Holec, 1973, 1975, 1978). The molluscan community (Hladilová, 1991) is poor in species and rich in individuals, with a significant predominance of the species *Corbula gibba* and *Hinia illovensis*. Fossil traces *Oichnus paraboloides* and *Entobia ichnosp.* can be often found on the molluscan shells (Pek, Mikuláš & Lysáková, 1997). Together with the sediment character it bears witness of occasional worsening of the environmental conditions near to the bottom of the basin, probably as a result of the lowering of water dynamics and O₂ contents (episodically worse aeration).

The upper part of the profile at the locality Rohožník-Konopiská is formed of *sandy clays to sands* with frequent oblique, cross and ripple-drift bedding (Upper Badenian/Sarmatian). In these sediments abundant fossils of molluscs with prevailing pirenells and ervilias were found out (Hladilová, 1991). Except of molluscs benthic foraminifers and poor assemblages of calcareous nannoplankton occur in sands (Šutovská, oral communication, 1988). Paleontological analyses indicate a salinity decrease as well as the growing of water dynamics of the marine environment, e. g. an isolation and a significant shallowing of the basin with a mixing of the elements from the phytal and aphytal infra- and circalittoral. The shells often carry signs of transport and rolling, some fossils are redeposited from older sediments.

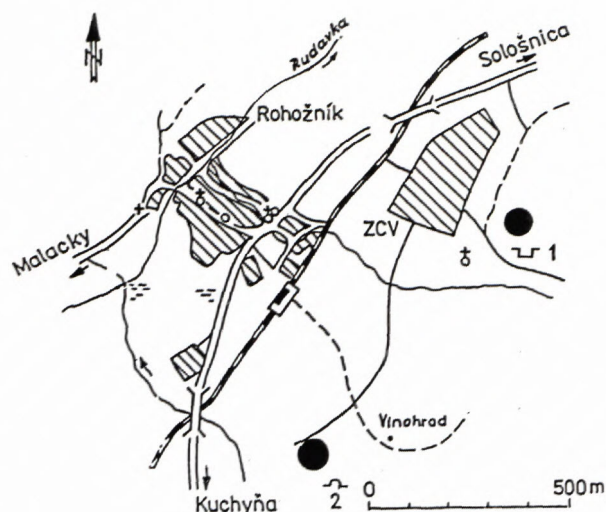


Fig. 2: Sketch map of the vicinity of Rohožník
1 - Rohožník - Vajarská, 2 - Rohožník - Konopiská

2. Methods

2.1 Sampling

For stable isotope analyses following components were collected from the site Rohožník - Konopiská and Rohožník - Vajarská:

- A) fossil shells of molluscs from various facies:
 - facies of algal limestones - *Venus* sp. (locality Rohožník - Vajarská)
 - facies of coarse-grained forereef sands - *Ostrea digitalina*, *Glycymeris* sp., *Lunatia catena helicina*, *Ancilla glandiformis*, *Venus multilamella*, *Turritella* cf. *erronea*, *Conus dujardini* (locality Rohožník - Konopiská)
 - facies of calcareous clays - *Corbula gibba*, *Lunatia catena helicina*, *Vermetus intortus* (locality Rohožník - Konopiská)
 - facies of sandy clays to sands - *Corbula gibba*, *Clithon pictus*, *Pirenella picta*, *Vermetus intortus*, *Lunatia catena helicina*, *Turritella* cf. *erronea*, *Conus* sp., *Bittium reticulatum*, *Acteocina lajonkairieana*, *Cerithium* cf. *politoanei* (locality Rohožník - Konopiská)

- B) sediments containing carbonate and organic matter:
 - algal limestones (Rohožník - Vajarská, pebbles of the algal limestones from the coarse-grained forereef sands - Rohožník - Konopiská)
 - calcareous clays - Rohožník - Konopiská
 - sandy clays to sands - Rohožník - Konopiská

- C) carbonate concretions from the calcareous clays (Rohožník - Konopiská):

- gypsum concretion („gypsum rose“) from the calcareous clays (Rohožník - Konopiská)

2.2 Isotopic methods

2.2.1 Isotopic analysis of carbonate

For carbon and oxygen isotopic analysis calcium carbonate samples were decomposed in vacuum by 100 %

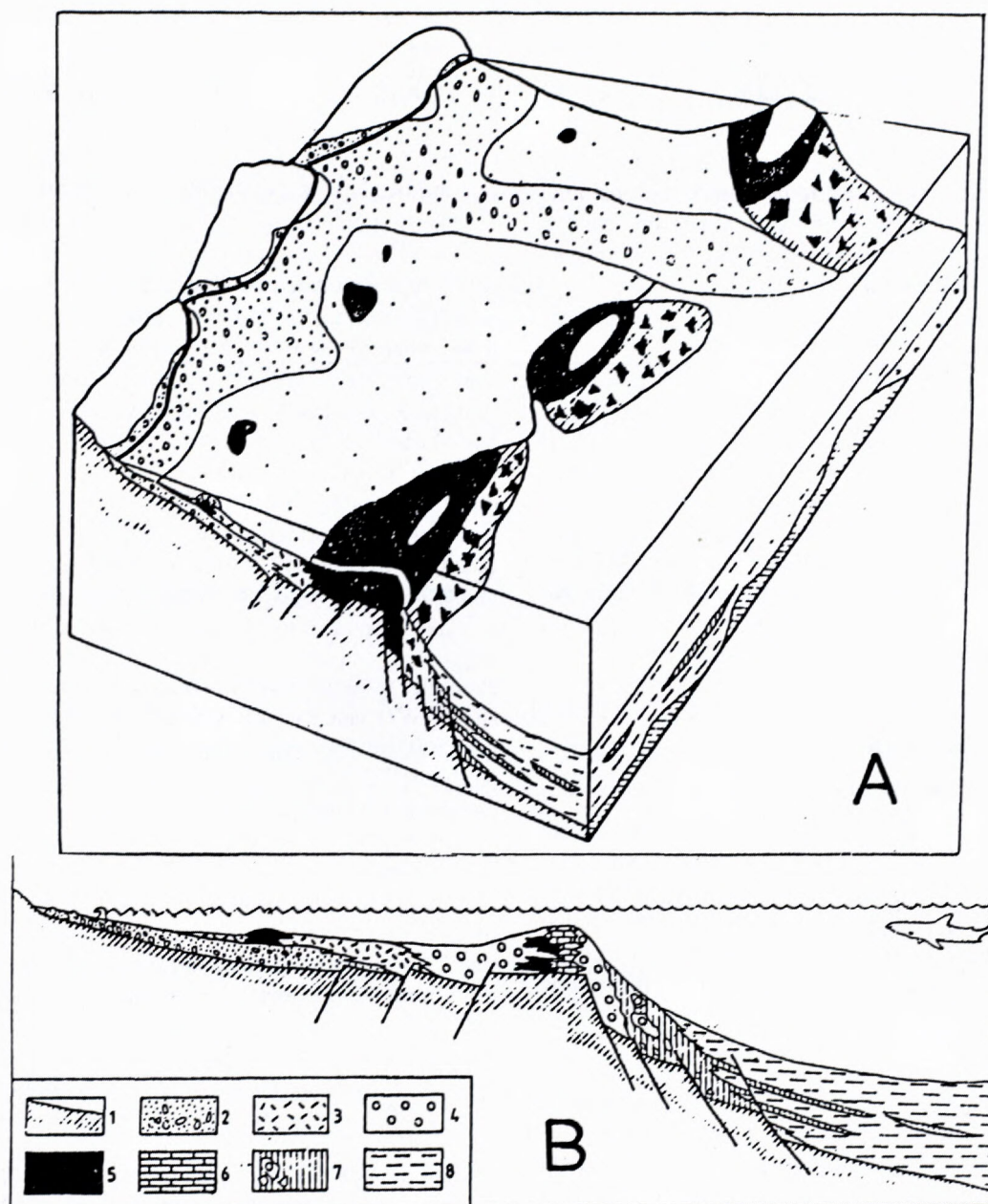


Fig. 3: A - Rohožník - reconstruction of the reef complex (after Baráth, 1992)

B - Rohožník - a schematic profile through the reef complex. 1 - pre-Neogene basement, 2 - basal rudstone, 3 - algal - foraminiferal wackestone, 4 - rhodolith bafflestone, 5 - algal - bryozoan and algal - coral bindstone, 6 - biotrititic rudstone, 7 - forereef coarse-detrital rudstone to grainstone, 8 - basinal mud facies. After Kováč et al., 1991 and Baráth, 1992.

H_3PO_4 at 25 °C (McCrea, 1950). Released CO_2 was analysed on the Finnigan MAT 251 mass - spectrometer. The results are reported in per mil deviation from V-PDB standard using δ notation. The precision of both carbon and oxygen isotope analyses is better than ± 0.1 ‰. Corrections for aragonite were carried out.

2.2.2 Isotopic analysis of organic carbon

For mass-spectrometric analyses carbonates from samples were removed by hot diluted phosphoric acid. The residue after washing and drying was oxidized in flow of oxygen at 950 °C. Formed carbon monoxide was

decomposed by CuO at 900 °C, compounds of chlorine and sulphur were reacted with silver wool, water formed during oxidation was frozen. Nitrogen oxides which were very often formed were reduced by hot copper to N_2 . Isotope measurements of pure carbon dioxide were performed by mass - spectrometer Finnigan MAT 251. The δ values were defined as the per mil deviation from V-PDB standard. The reproducibility was ± 0.1 ‰.

2.2.3 Isotopic composition of sulphur in sulphate

Gypsum was dissolved in hot distilled water and precipitated from water as BaSO_4 . For isotopic measurement

BaSO₄ was converted to SO₂ in a vacuum line using the method of Yanagisawa & Sakai, 1983. BaSO₄ was mixed with V₂O₅ and SiO₂ (weight ratio of 1:10:10), heated to 980 °C over a period of 10 min and kept for another 10 min. SO₂ was trapped in a glass ampoule by liquid nitrogen and sealed. All $\delta^{34}\text{S}$ analyses were performed on a Finnigan MAT 251 mass spectrometer with reproducibility of 0.2 ‰. The results were expressed in the usual δ notation as a per mil deviation of the $^{34}\text{S}/^{32}\text{S}$ ratio in sample from the CDT standard.

2.2.4 Isotopic composition of oxygen in sulphate

BaSO₄ with pure graphite in platinum foil was decomposed in vacuum line at about 1000 °C. Carbon monoxide which was produced during reaction was converted to carbon dioxide by a high voltage transformer connected to platinum electrodes (Šmejkal & Hladíková, 1987). CO₂ was trapped by liquid nitrogen and its isotopic composition was measured on a Finnigan MAT 251 mass spectrometer with reproducibility of 0.2 ‰. The results were expressed in the usual δ notation as a per mil deviation of the $^{18}\text{O}/^{16}\text{O}$ ratio in sample from the V-SMOW standard.

3. Results and discussion

3.1 Fossil shells of molluscs

The list and isotopic compositions of bivalves and gastropods selected for isotopic studies are in Table 1. All studied molluscs secreted aragonite shells, only shells of *Ostrea digitalina* are formed by calcite. It was found that the studied shells preserved their primary mineralogy. According to Brand, 1981 the preservation of metastable aragonite has been used to infer that the isotopic composition of the component must be also primary. In addition, gastropods precipitate shell carbonate in isotopic equilibrium with their ambient seawater and exert only minimal „vital effects“ (Milliman, 1974). For these reasons isotopic composition of studied aragonite shells can reflect the isotopic composition of the Neogene seawater.

According to paleontological studies the molluscs lived under different conditions - in a deeper seawater, in a shallower seawater and in a brackish water. Oxygen isotopic compositions of their shells should reflect these different environments.

Molluscs living under normal marine conditions in shallow water (from coarse-grained forereef sands) show $\delta^{13}\text{C}$ values from -1.0 to 1.2 ‰ and $\delta^{18}\text{O}$ values from -1.0 to 2.3 ‰ and average $\delta^{18}\text{O}$ value makes 0.4 ‰ (Table 1, facies 1). According to Savin, 1977 the Miocene ocean water was depleted in $\delta^{18}\text{O}$ in comparison with present ocean water. Assuming that the seawater had $\delta^{18}\text{O}$ value -1 ‰ in this area and using Craig's, 1965 paleotemperature equation we obtained the average temperature of 11 °C as a temperature of water in which this group of molluscs lived. It is necessary to mean that the highest isotopic temperature (17 °C) was calculated for *Conus dujardini* and the lowest isotopic temperature (about 2 °C) was calculated for *Lunatia catena helicina*

(sample 3). However, according to palynology, subtropical climate existed during Lower and Middle Badenian in the mentioned area, therefore temperatures of about 11 °C (even 2 °C) are too low. In addition, the difference 15 °C between the highest and the lowest temperatures is too big for subtropical climate. There are at least two possibilities how to explain the mentioned discrepancies.

The first one: the $\delta^{18}\text{O}$ value of water in the Badenian sea could be higher than -1 ‰ SMOW, i.e. the $\delta^{18}\text{O}$ value which was postulated by Savin, 1977 for ocean water. It is well known, that $\delta^{18}\text{O}$ value of the recent ocean water is 0 ‰, whereas the $\delta^{18}\text{O}$ value of water in the Mediterranean Sea is +1 ‰, the $\delta^{18}\text{O}$ value of water with higher salinity in Red Sea is 2 ‰ and $\delta^{18}\text{O}$ value of water in Black Sea is about -3 ‰ (Anati & Gat, 1989). If we substitute higher $\delta^{18}\text{O}$ value for seawater into the paleotemperature equation, then for measured $\delta^{18}\text{O}$ values of fossils we obtain higher temperatures. For example, if we take into account the average $\delta^{18}\text{O}$ value of fossil shells, i.e. 0.4 ‰ and 0 ‰ for sea water, we obtain temperature of 15 °C.

The second possibility explaining discrepancies in calculated temperatures is the redeposition of shells. For example *Lunatia catena helicina* (Table 1, sample 3) shows $\delta^{18}\text{O}$ value which is typical for shells found in facies 2. If this shell was redeposited the difference between the highest and the lowest isotopic temperature calculated for facies 1 would decrease.

The molluscs from the facies 2 (calcareous clays) lived in seawater at a greater depth. They show $\delta^{13}\text{C}$ values from -2.7 to -0.6 ‰ (average -1.9 ‰), and $\delta^{18}\text{O}$ values from 0.7 to 2.5 ‰ (average 1.9 ‰) (Table 1, facies 2). It is evident that $\delta^{18}\text{O}$ values of shells from this group are higher than those from the previous group. If we assume the same $\delta^{18}\text{O}$ values of sea water for both marine environments then the molluscs from facies 2 were formed under lower temperature, e. g. in cooler water reflecting the greater depth. The low $\delta^{13}\text{C}$ values of fossils from facies 2 demonstrate that molluscs built up CO₂ rich in ^{12}C into their shells. Carbon dioxide rich in ^{12}C is produced during oxidation of organic matter and the consequence of the greater consumption of oxygen for oxidation of organic matter is the lowering of O₂ content in water. The lowering of O₂ content resulted also from the paleontological studies.

The third group of studied molluscs (from sandy clays and sands) lived in brackish environment. In comparison with normal sea water the brackish water is characterized by lower $\delta^{18}\text{O}$ values. The $\delta^{18}\text{O}$ values of molluscs from facies 3 (Table 1) which are from -3.0 to 0.8 ‰ reflect lower $\delta^{18}\text{O}$ values of the brackish water. The $\delta^{13}\text{C}$ values of shells from this group are comparable with $\delta^{13}\text{C}$ values found for shells formed in normal marine environment. The correlation between $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values of molluscs from brackish environment was not found and therefore it is possible to assume that external contribution of organic matter did not exist.

We also compared $\delta^{18}\text{O}$ values of species living in two different environments (for example *Lunatia catena helicina*, *Corbula gibba* and *Vermetus intortus* from fa-

Table 1: Carbon and oxygen isotopic composition of molluscs from Rohožník

sample I.D.	facies	species	carbonate mineralogy	$\delta^{13}\text{C}$ (‰ PDB)	$\delta^{18}\text{O}$ (‰ PDB)	
14	1	<i>Ostrea digitalina</i>	calcite	0,3	-0,4	Bivalvia
2b	1	<i>Venus multilamella</i>	aragonite	-1,0	1,0	Bivalvia
2c	1	<i>Glycymeris</i> sp.	aragonite	0,4	0,0	Bivalvia
7	1	<i>Turritella</i> cf. <i>erronea</i>	aragonite	1,2	0,4	Gastropoda
9	1	<i>Conus dujardini</i>	aragonite	0,9	-1,0	Gastropoda
2a	1	<i>Ancilla glandiformis</i>	aragonite	0,2	0,3	Gastropoda
3	1	<i>Lunatia catena helicina</i>	aragonite	-0,7	2,3	Gastropoda
1b	2	<i>Corbula gibba</i>	aragonite	-2,2	1,9	Bivalvia
13	2	<i>Corbula gibba</i>	aragonite	-2,7	2	Bivalvia
13/1	2	<i>Corbula gibba</i>	aragonite	-1,5	2,5	Bivalvia
13/2	2	<i>Corbula gibba</i>	aragonite	-2,5	1,9	Bivalvia
13/3	2	<i>Corbula gibba</i>	aragonite	-2,8	2,4	Bivalvia
4	2	<i>Vermetus intortus</i>	aragonite	-0,6	0,7	Gastropoda
1c	2	<i>Lunatia catena helicina</i>	aragonite	-1,2	2,1	Gastropoda
1	2	<i>Lunatia catena helicina</i>	aragonite	-1,3	1,9	Gastropoda
15	3	<i>Corbula gibba</i>	aragonite	-1,1	0,8	Bivalvia
3a	3	<i>Clithon pictus</i>	aragonite	1,1	-2,2	Gastropoda
3b	3	<i>Pirenella picta</i>	aragonite	-0,5	-3,0	Gastropoda
5	3	<i>Vermetus intortus</i>	aragonite	-1,2	-2,2	Gastropoda
2	3	<i>Lunatia catena helicina</i>	aragonite	-1,3	-2,4	Gastropoda
6	3	<i>Turritella</i> cf. <i>erronea</i>	aragonite	1,3	-0,4	Gastropoda
8	3	<i>Conus</i> sp.	aragonite	0,1	-1,5	Gastropoda
10	3	<i>Bittium reticulatum</i>	aragonite	0,0	-1,3	Gastropoda
11	3	<i>Acteocina lajonkaireana</i>	aragonite	-0,6	-2,4	Gastropoda
12	3	<i>Cerithium</i> cf. <i>politioanei</i>	aragonite	0,1	-1,6	Gastropoda
12/1	3	<i>Cerithium</i> cf. <i>politioanei</i>	aragonite	0,1	-1,7	Gastropoda
12/2	3	<i>Cerithium</i> cf. <i>politioanei</i>	aragonite	-0,1	-2,0	Gastropoda
12/3	3	<i>Cerithium</i> cf. <i>politioanei</i>	aragonite	-0,3	-2,8	Gastropoda

cies 1 and 3, *Turritella* cf. *erronea* from facies 2 and 3 - see Table 1). We can see that their $\delta^{18}\text{O}$ values are different reflecting the trend in oxygen isotopic composition of water. All $\delta^{18}\text{O}$ values of shells from brackish environment are lower than $\delta^{18}\text{O}$ values of shells from marine environments (Fig. 4).

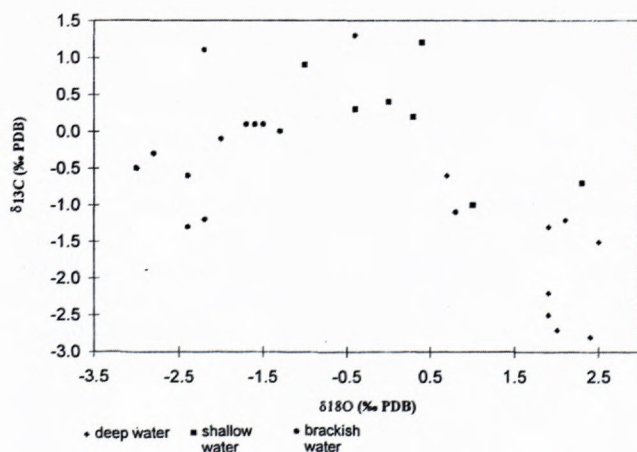


Fig. 4: Carbon and oxygen isotopic composition of molluscs from Rohožník

3.2 Algal limestones

Whole-rock isotopic data clearly reflect all phases of limestone formation. According to Hudson (1977), most calcite cements formed during diagenesis show lower $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values than those of marine carbonate sediments. Carbon and oxygen isotopic data of algal limestones from Rohožník are given in Table 2. It is evident that algal limestones are characterized on one side by very low and on the other side by very high $\delta^{13}\text{C}$ values. The $\delta^{13}\text{C}$ values from 5.1 to 6.1 ‰ are the highest values from the whole data set. They are higher than $\delta^{13}\text{C}$ values given for marine carbonates by Hoefs (1997). The reason for such high $\delta^{13}\text{C}$ values is not entirely clear, but Lloyd (1971) suggested that algal photosynthesis consumed ^{12}C isotope from bicarbonate reservoir and residual dissolved bicarbonate - precursor of calcium carbonate - became rich in ^{13}C isotope. So high $\delta^{13}\text{C}$ values were found also for the forereef of the Devonian reef in the southern Moravia (Hladíková et al. 1997).

The very low $\delta^{13}\text{C}$ values close to -12 ‰ found for algal limestone from Rohožník-Vajarská (Table 2) are typical for carbonates which incorporated oxidized organic carbon.

Table 2: Isotopic composition of sediments

sample I.D.	carbonate $\delta^{13}\text{C}$ (‰ PDB)	carbonate $\delta^{18}\text{O}$ (‰ PDB)	org. matter $\delta^{13}\text{C}$ (‰ PDB)	sulphate $\delta^{34}\text{S}$ (‰ CDT)	sulphate $\delta^{18}\text{O}$ (‰ SMOW)
<i>Rohožník - Vajarská</i>					
algal limestone, sample 1	-12,7	-4,3			
algal limestone sample 2	-11,2	-5,6			
<i>Rohožník - Konopiská</i>					
algal limestone, sample 1a	5,6	-0,3			
algal limestone, sample 1b	5,1	-0,3			
algal limestone, sample 2a	-2,6	-2,6			
algal limestone, sample 2b	-3,7	-2,9			
algal limestone, sample 3	6,1	-2,6			
calcareous clay, sample 1	-0,5	-4,2	-26,4		
calcareous clay, sample 3	-0,6	-5,7	-25,6		
calcareous clay, sample 4	-0,3	-3			
sandy clay, sample 3	-0,9	-6,9			
carbonate concretions					
sample 5a	-44,7	3,1	-30,5		
sample 5b	-49,7	3,4			
gypsum concretion				-7,3	14,2

3.3 Carbonate cements

Isotopic composition of carbonate cements and organic matter from calcareous and sandy clays were determined, results are also in Table 2. The $\delta^{13}\text{C}$ values of carbonate carbon are homogeneous from -0.3 to -0.9 ‰ and $\delta^{18}\text{O}$ values are -3.0 to -6.9 ‰. Such isotopic compositions could reflect the formation of cements during interaction of carbonates with pore waters. Especially, greater range of $\delta^{18}\text{O}$ values can be a result of successive isotopic exchanges between carbonate and water.

The most frequent $\delta^{13}\text{C}$ values of total organic matter are from -20 to -30 ‰ (Hoefs 1997). The main cause for mentioned differences in $\delta^{13}\text{C}$ values of living organisms are different ways of their biosynthesis and different content of biopolymers: lipids, aminoacids, lignin and polysaccharides (Kříbek 1997). A carbon isotopic composition of dissolved bicarbonate in sea water, which is used for photosynthesis, represents another very important factor affecting $\delta^{13}\text{C}$ values of organic matter. Popp et al. (1989) found that the carbon isotopic fractionation between marine carbonates and organic matter from Early to Mid-Cenozoic became lower. It is in accordance with $\delta^{13}\text{C}$ values of total organic matter from Tertiary marine sediments published by Lewan (1986). $\delta^{13}\text{C}$ values for Paleocene - Oligocene are from -32.3 to -25.1 ‰, for Miocene from -21.3 to -23.4 ‰.

From Rohožník we analysed carbon isotopic composition of organic matter from two samples of calcareous clays and one sample from carbonate concretion. The $\delta^{13}\text{C}$ values of total organic matter in calcareous clay are from -25.6 to -26.4 ‰, the $\delta^{13}\text{C}$ value for carbonate concretion is -30.5 ‰ (Table 2). The $\delta^{13}\text{C}$ values of total organic matter from Rohožník area are lower than those

published for Miocene. Regarding the low number of analysed samples and lacks of other supplementary data we can hardly explain why $\delta^{13}\text{C}$ values from Rohožník are lower than published data. The lower $\delta^{13}\text{C}$ values of dissolved bicarbonate in sea-water, which was indicated also by fossils living in deeper marine environment, could be a possible explanation of the lower $\delta^{13}\text{C}$ values of total organic matter.

Extremely low $\delta^{13}\text{C}$ values between -44.7 and -49.7 ‰ were found for carbonate concretions. These very low $\delta^{13}\text{C}$ values are accompanied by relatively high $\delta^{18}\text{O}$ values, i.e. $\delta^{18}\text{O}$ values close to 3 ‰ (Table 2). Such very low $\delta^{13}\text{C}$ values could not be the result of oxidation of organic matter its $\delta^{13}\text{C}$ values being significantly higher (Table 2). We assume that they are the result of oxidation of methane $\delta^{13}\text{C}$ values of which are mainly in the range of -40 to -50 ‰ for Neogene of the Vienna Basin (Buzek et al. 1992). Higher $\delta^{18}\text{O}$ values of these cements give evidence that methane was oxidized near the surface, where it is possible to expect a higher evaporation and consequently higher $\delta^{18}\text{O}$ values of water.

Such reactions are confined to the vicinity of fractured hydrocarbon reservoirs and thus could be a valuable guide to petroleum exploration; but they are not likely to be of great quantitative significance (Hudson 1977). Such studies could provide a valuable tool in petroleum exploration since the Vienna Basin, including the wider surroundings of Rohožník, represents an important oil- and gas-bearing area.

Sulphur and oxygen isotopic compositions of gypsum concretion (so called „gypsum rose“) were determined. The average $\delta^{34}\text{S}$ value of gypsum concretion is -7.3 ‰ CDT and the average $\delta^{18}\text{O}$ value is 14.2 ‰ V-SMOW (Table 2). The $\delta^{34}\text{S}$ values of sulphate dissolved in the

Tertiary sea water which could be the source of sulphur for gypsum concretion were in the range from 21.6 to 21.9 ‰ CDT (Claypool et al. 1980). It is clear that marine sulphate could not be the source of sulphur during formation of „gypsum rose“. The mentioned sulphate was formed during the oxidation of sulphides which are characterized by negative $\delta^{34}\text{S}$ values (Hoefs 1997). The $\delta^{18}\text{O}$ value found for gypsum concretion is rather high. Sulphates, which were formed by oxidation of disseminated sulphides by meteoric water, are characterized by the $\delta^{18}\text{O}$ values from 0 to -5 ‰ V-SMOW (Šmejkal & Dubánek, 1990). It is necessary to mention that during a slow oxidation of disseminated sulphides under low temperatures first of all H_2SO_3 is formed. The fourth oxygen which is needed for formation of H_2SO_4 is obtained from airy O_2 dissolved in water and its $\delta^{18}\text{O}$ value is between 9 and 12 ‰ V-SMOW (Šmejkal & Dubánek, 1990). It is evident that gypsum concretion was formed from water rich in isotope ^{18}O . Waters rich in ^{18}O could be formation waters or strongly evaporated meteoric waters. The $\delta^{18}\text{O}$ values of formation waters in Vienna Basin show the great range of $\delta^{18}\text{O}$ values, but their highest $\delta^{18}\text{O}$ value is 5.6 ‰ V-SMOW (Buzek & Michalíček 1997). Also the positive $\delta^{18}\text{O}$ values found for carbonate concretion (Table 2) give evidence that waters rich in isotope ^{18}O were present in the studied sequence of strata.

4. Conclusions

a) Paleoenvironmental changes in Rohožník (mainly changes of water depths and salinity) documented in sedimentological as well as paleontological records are also reflected in isotopic values of individual organisms. The $\delta^{18}\text{O}$ values of molluscan shells from brackish environment are generally lower than those from marine environments.

b) Algal limestones from Rohožník - Vajarská show $\delta^{13}\text{C}$ values typical for carbonates which incorporated oxidized organic carbon. Some of the $\delta^{13}\text{C}$ values of algal limestones from the coarse-grained forereef sands from the locality Rohožník - Konopiská are higher. This fact is not entirely clear but it can be probably connected with the process of algal photosynthesis.

c) The isotopic compositions of carbonate cements reflect their formation during interactions of carbonates with pore waters (successive isotopic exchanges between carbonate and water).

d) The $\delta^{13}\text{C}$ values of total organic matter from the Rohožník area are lower than values published for Miocene. This fact can be probably explained by the lower $\delta^{13}\text{C}$ values of dissolved bicarbonate in the sea-water in the Rohožník area.

e) Extremely low $\delta^{13}\text{C}$ and higher $\delta^{18}\text{O}$ values of carbonate concretions from calcareous clays (Rohožník - Konopiská) are probably the result of near-surface oxidation of methane. Such reactions are confined to the vicinity of fractured hydrocarbon reservoirs and thus could be a valuable guide to petroleum exploration.

f) The $\delta^{34}\text{S}$ value of gypsum concretion from the calcareous clays (Rohožník - Konopiská) shows that the sulphate representing the source of sulphur for this concretion was formed during the oxidation of sulphides. The positive $\delta^{18}\text{O}$ value found for gypsum concretion reflects its origin from water rich in isotope ^{18}O (formation waters or strongly evaporated meteoric waters).

5. References

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