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Data on chemical and isotope Composition of Carboniferous and Mesozoic Carbonates of Inner Western Carpathians

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Abstract: Carbonate samples were collected from the Lower and Upper Carboniferous of the North Gemeric Unit, including the stratigraphically undated Dúbrava Beds, which are at present considered to be a part of the Bôrka Nappe and the Upper Carboniferous carbonates of the Turňa Nappe. The principal aim of this work was to identify the differences in the bulk chemical composition, the contents of trace and rare earth elements, as well as the isotope composition of C and O in the studied carbonates, and thus to obtain criteria for correlation of problematic horizons and for the interpretation of carbonate genesis and post-deposition alterations.

Besides these completely analysed samples the studied set comprises single isotope analyses of Mesozoic carbonates of the Turňa and Silica Nappes, as well as additional isotope analyses from eastern occurrences of the Bôrka Nappe and from the Košice and Burda magnesite deposits. The presented results helped to distinguish carbonate rocks of different grade of metamorphism, as well as different sedimentary conditions.

Key words: Inner Western Carpathians, Carboniferous and Mesozoic carbonates, bulk chemical composition, trace and rare earth elements, O and C isotopes, TVI decrepitation analysis

Introduction

Stratigraphic and paleogeographic problems of the Upper Paleozoic have been solved using the method of lithogeochemistry and determination of isotope composition of C and O from selected carbonate horizons of the northern Gemericum. The selected samples included carbonates from biostratigraphically documented horizons as well as horizons so far biostratigraphically undocumented.

33 samples were collected in the first stage, with the aim of determining the feasibility of selected methods and to which degree the obtained results may be interpreted in view of the complex geological development of the studied area, above all the multiphase metamorphic development, hydrothermal-metasomatic alterations, changes in lithologic composition, insufficiently uncovered terrane and many others. The analysed set included samples from Lower Carboniferous sequences of the Ochtiná Formation as well as the Črmeľ Group, from the Upper Carboniferous Zlatník Formation as well as the Turiec Formation from the borehole BRU-1, of the same age. Further samples were taken from the so far problematic, as far as its age is concerned, Dúbrava Beds from the Nižná Slaná depression, which are at present considered to be a part of the Bôrka Nappe.

The principal aim of this work was to identify the differences in the proportions of elements, including rare earth elements, as well as the isotope composition of C and O in the studied samples, and thus to obtain criteria for stratigraphic correlation of so far undated horizons. Of course, the aim of the investigation was also maximum use of the obtained data for the interpretation of carbonate genesis and post-deposition alterations, and thus solving the problems of sedimentation environment.

Besides completely analysed samples, the studied set included also additional analyses of isotope composition of Mesozoic carbonates from the Bôrka, Turňa, Silica Nappes, and the Foederata Group as well as from magnesite deposits from the area of Košice and Burda. The presented work contains first analytical results from the above set. We are aware of the fact that more precise interpretation of the data will require further samples. Because of this, we consider the presented interpretation to be preliminary results and data on geochemical and isotope composition of the carbonates as our contribution to the newly established database on the composition of above all Carboniferous carbonates.

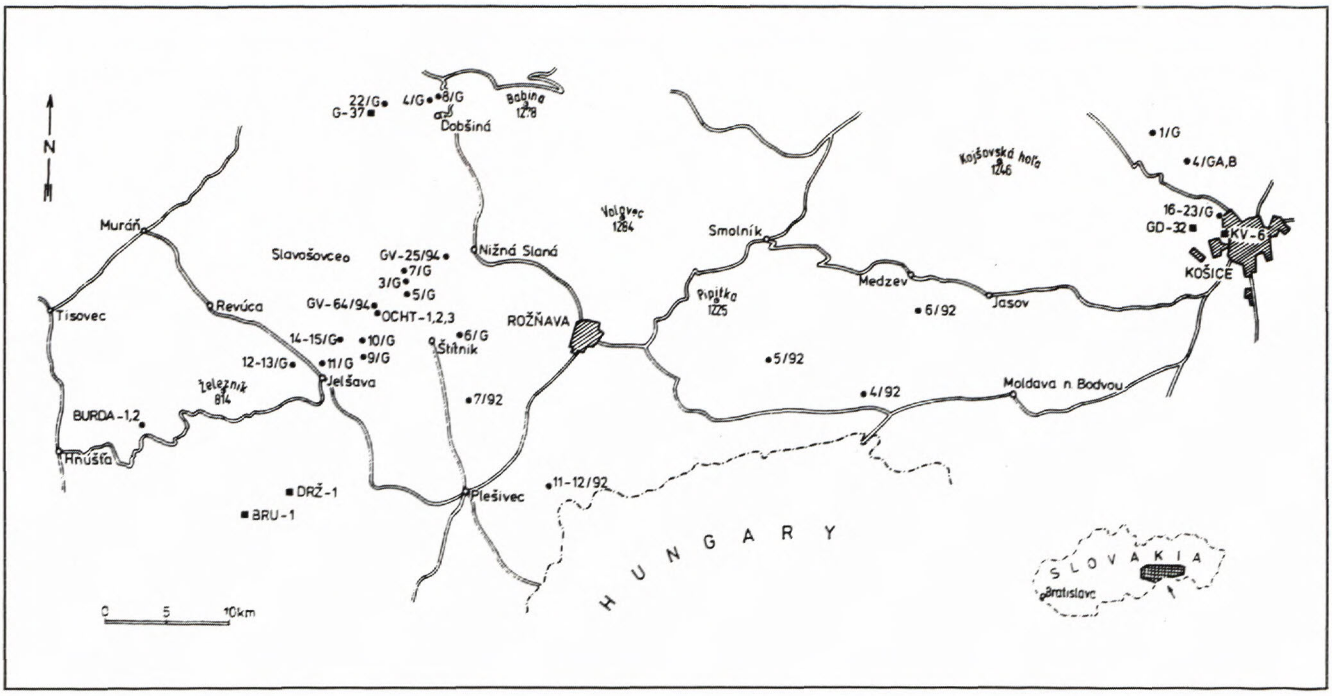


Fig. 1 Location of studied samples.
● – *Samples from surface occurrences and mine adits;* ■ – *samples from boreholes.*

Geological setting and localisation of the samples

Northern Gemericum

Ochtiná Formation - Lower Carboniferous

The upper part of the Ochtiná Formation is characterised by the development of carbonate members, indicating generally in the paleogeographic evolution a stage of shallowing of the original sedimentation basin. 25 samples have been analysed lithogeo-chemically from this sequence, O and C isotope analysis has been made from 16 samples. The material was collected at following localities:

Loc. Ochtiná – the stratigraphic succession starts with black, graphite shales, replaced towards the overlier by heavy-bedded dolomites, in some places with intercalations of dark shales. The dolomites are in their upper part changed into magnesite. 3 samples were taken for isotope study - 1. dolomites; 2. fine-grained limestones with disseminated grains of magnesite; 3. coarse-grained magnesite. The samples are marked as Ocht.-1, Ocht.-2, Ocht.-3. At this locality, the age of the upper part of the Ochtiná Formation was originally biostratigraphically documented on the basis of trilobite, brachiopod fauna, as Namurian B-C (BOUČEK and PŘIBYL, 1960). Later on, this age was stratigraphically re-evaluated and on the basis of conodonts the whole formation was reclassified as Upper Visean - Serpukhovian (KOZUR, MOCK and MOSTLER, 1976).

Loc. S of Markuška – a small lens of grey, fine-crystalline, finely laminated limestones of the Ochtiná Formation. It is found below the main magnesite horizon in the part of the Ochtiná Formation where clastic metasediments with admixture of basic volcanic material are predominant. The sample is marked 7/G.

Loc. Hrádok – a dolomite lens from the underlier of the main magnesite horizon, in the continuation of the Miková-Dúbrava belt. The carbonates are dark-grey in colour, recrystallized, irregularly grained. The sample was taken in the area of the elev. p. 707 and marked 10/G. Sporomorphs of Visean age have been found in the underlier of this carbonate lens (BAJANÍK and PLANDEROVÁ, 1985).

Loc. Burda – a phyllite complex with subordinate metasandstone intercalations, in which there are beds of grey, finely lamelled crystalline limestones. On the geological map of the Slovenské rudohorie Mts. - eastern part (BAJANÍK et al. 1984) they have been included into the Zlatník Formation, however, without biostratigraphic evidence. This has been based on the fact that below the horizon there are in places thin layers of fine-grained metaconglomerates. It is however very probable that they are a part of the Ochtiná Formation, or its youngest members, which have been otherwise reduced. A marginal possibility is that it belongs to younger sequences, equivalent to the Dúbrava beds. This stratigraphic classification is thus still problematic. Samples from this locality have been marked Burda-2, Burda-3.

Loc. Dúbrava-Miková - they belong to the upper part of the Ochtiná Formation, to the main magnesite horizon. They are considered to be equivalent to magnesites from Ochtiná. Samples were taken from the mine Miková (provided by workers of Geological Survey Spišská Nová Ves, Division Rožňava). They are representing dolomites associated with magnesites directly at the deposit. Sample 14/G corresponds to heavy-bedded, dark-grey dolomite and 15/G is fine-grained, massive dark-grey dolomite.

Loc. Bankov-Košice - magnesite layers associated with dark shales and metasandstones. On the geological map of Slovenské rudohorie Mts. - eastern part (BAJANÍK et al., 1984) the whole sequence has been included into the Zlatník Formation, without any biostratigraphic evidence. Litho-logically it is however absolutely identical with the sediments of the magnesite horizon of the Ochtiná Formation. A total number of 7 samples was taken from the deposit Bankov, from different magnesite grain-size varieties: 16/G - fine-grained magnesite, 17/G - coarse-grained magnesite, 18/G - medium-grained magnesite, 19/G - fine-grained magnesite, 20/G - medium-grained magnesite, 21/G - fine-grained magnesite. Sample 23/G was taken from the borehole KV-6, located in the deposit area of Bankov (material provided by dr. Varga).

Besides these further magnesite samples were taken into isotope analysis from magnesite deposits of Burda and Košice only (borehole GD-32).

Črmeľ Group – Lower Carboniferous

Loc. Črmeľ Valley - grey, crystalline limestones form only a few thin lenses among predominant clastic metasediments associated with basic volcanics and volcanoclastics. The age of this lithostratigraphic unit was determined on the basis of sporomorphs as Upper Tournaisian - Visean (SNOPKOVÁ in BAJANÍK, SNOPKOVÁ and VOZÁROVÁ, 1986). The sample from the Črmeľ Group limestones is marked 1/G.

Loc. Kavečany - small magnesite lenses are a part of the uppermost Črmeľ Group. They were correlated with the first magnesite horizon from Ochtiná (ABONYI, 1971). 2 samples were taken from an abandoned quarry: 4/G - nodular magnesite; 4/G-B - coarse-grained magnesite.

Zlatník Formation – Upper Carboniferous

Its lithologic development represents a volcano-sedimentary formation composed mostly of clastic, less of carbonate lithofacies, which on the majority of occurrences is characterised by the presence of basic volcanic and volcano-clastic rocks. Organodetritic limestones form lenticular bodies in the lower part of the Zlatník Formation, associated here with dark shales and lithic graywackes.

Loc. Dobšiná - the carbonates are captured in several tectonic blocks among rocks of the Early Paleozoic Klátov Group. They were to a considerable extent metasomatically altered into siderites. In the past they were economically exploited. These carbonate horizons provided a lot of biostratigraphic information. According to macrofauna, identified for the first time by RAKUSZ (1932) and later re-evaluated by BOUČEK and PŘIBYL (1960), this horizon belongs to the Westphalian B-C. The found flora was classified as Westphalian A-B (NĚMEJC, 1946; 1953), similarly as conodont fauna (KOZUR and MOCK, 1977). Dark-grey organodetritic limestones, irregularly-grained, with an admixture of originally clayey substance, were taken from 3 localities - 1. north-western margin of Dobšiná, loc. Jeruzalemberg, sample 2/G; 2. northern margin of Dobšiná, in the continuation of Kúpeľná Street, sample 8/G; 3. Dobšinská Maša - tectonic contact of the Hámor Formation and Rakovec Group, sample 22/G.

Turňa Nappe

Borehole BRU-1, Turiec Formation - Upper Carboniferous

The borehole has been situated into the Brusník anticline, with the aim of investigating its geological structure. Two tectonic units were reached by the borehole profile: 1. olistostrome formation of Upper Carboniferous age - the Turiec Formation (VOZÁROVÁ, 1992), correlated with the formation of Szendro phyllites from Szendro Mts. (depth 0-598.8 m) and classed with the tectonic unit of Turnaicum; 2. olistostrome and pelagic formations of Jurassic age, compared with the Meliaticum Jurassic (Vozárová and VOZÁR, 1992). For isotope study, carbonates were taken from the Upper Carboniferous formation, from the olistholith horizon, in the interval 75-116 m. They are light-grey, some with clayey admixture, or weakly silicified. The carbonates, predominantly limestones, less dolomites, are irregularly recrystallized, with an admixture of organodetritic material. Conodont fauna, identified by Ebner (EBNER et al., 1990) indicates mixed character. Olistoliths from carbonates from the interval 114-116 m contain conodont fauna of Namurian B - Westphalian A age and in the interval 136-146 m of the span Emsian-Turnaisian and Namurian B - C.

From the borehole BRU-1, 5 samples were taken from depths 76.0m, 86.0m, 95.8 m,111.5 m,114.0 m.

The Mesozoic sequences of the Turňa Nappe (Turnaicum) are represented by basin facies of limestones and dark shales in the Middle and Upper Triassic and variegated sediments of evaporite formations associated with "red-beds" in the Permo-Triassic (ex MELLO et al., 1992). The following samples were taken from these sequences:

4/92 - Dvorníky; 6/G - Honce quarry; 9-10/92 - Jelšavská Teplica; the borehole DRŽ-1 from depths 179.1m, 236.6 m, 418.5 m, 443.6 m, 1183.7 m, 1203.8 m.

Bôrka Nappe

Dúbrava Beds

This group includes white crystalline limestone, classified originally by FUSAN (1959), SNOPKO (1966) as Carboniferous and described under the name of Dúbrava Beds. They are associated with metabasalt tuffs, dark shales and metasandstones. The only subordinate lithologic member are here layers of fine-grained metaconglomerates and redeposited rhyolitic material. On the geological map of the Slovenské rudohorie Mts. - eastern part, MELLO (in BAJANÍK et al., 1984) classed a part of the Dúbrava Beds occurrences with the Middle to Upper Triassic of the Meliata Group s.l., based on lithologic similarity with paleontologically documented occurrences. A part of the occurrences - the area of the elev.p. Hrádok, N of Jelšava and S of the village Chyžné - remained classified as Carboniferous, as the equivalent of the Zlatník Formation. This solution however does not correspond to reality, since lithologically as well as by the degree of alteration these occurrences are completely identical with sequences included into the Meliata Group s.l. The Dúbrava Beds are typical not only as far as their lithologic development is concerned, but also by the transitional, medium- to high-pressure type of regional metamorphism in temperature conditions of greenschist facies (VOZÁROVÁ, 1993). In the last time, when compiling the geological map of the Slovenský Kras (Slovak Karst) area, 1 : 50 000 (MELLO et al., 1992), sequences with manifestations of high-pressure metamorphism were distinguished in Meliaticum and defined as a separate unit - the Bôrka Nappe.

A characteristic feature of the Dúbrava Beds from the Nižná Slaná depression, which are also included into the Bôrka Nappe and from which were taken most of samples studied in this work, is the simultaneous occurrence of glaucophanites with green schists. The latter contain actinolites with high Na content in M4 position, which corresponds to medium- to high-pressure conditions (VOZÁROVÁ, l.c.).

From white crystalline carbonates were taken the following samples: dolomites → 3/G - quarry S of Markuška; 9/G - NW of the forester's cottage Hrádok; limestones → 5/G - abandoned quarry N of Ochtiná; 11/G - Jordán Valley, N of Jelšava; 12/G - abandoned quarry S of Chyžné; 13/G - loc. as 12/G; GV-25/94 - W of elev. p. Ždiar; GV-64/94 - NW of Ochtiná village; 5/92 - N of Bôrka village; 6/92 - Šugov valley, S of Medzev.

Bôrka Nappe - eastern part

The dominant member of the eastern part of the Bôrka Nappe are white marbles (samples 5-6/92) which are very closely associated with glaucophanites, and smaller amount of metasediments.

Silica nappe

Non-metamorphosed Mesozoic sequences in the stratigraphic range Lower Triassic to Lower Jurassic (GAÁL - MELLO, in BAJANÍK et al. 1983, MELLO in MELLO et al., 1992). The Lower Triassic is represented by variegated sandy-shaly sediments, yellow and grey carbonate shales and graywackes. In the Middle Triassic, mainly in the Anisian, epiplatform carbonates and dolomites are predominant, replaced in the Ladinian and mainly in the Upper Triassic by sediments of an unstable shelf, alternating with zones of hemipelagic sedimentation (cherty limestones). The Lower Jurassic sequence, preserved rudimentary only, is formed by red nodular and crinoidal limestones, dark biomicrite limestones and radiolarites (Dogger). Mainly the Middle-Upper Triassic limestones were taken into isotope analysis: 7/92 - Ostrý vrch; 11-12/92 Silická Brezová.

Southern Veporicum - Foederata Group

The Foederata Group was defined as Mesozoic part of the cover of the south-Veporic crystalline basement. Carbonate sediments correspond mainly to the Middle and Upper Triassic stratigraphic horizon. Samples for isotope analysis were taken from the borehole G-37 - loc. Dobšiná - Hámor.

Petrographic Characterisation and Degree of Alteration

Northern Gemericum

Lower Carboniferous

Dolomites have in thin sections generally irregularly grained, granoblastic texture, in relics sparite-micrite, rarely with preserved intraclasts of micrite carbonates and with relics of recrystallized tests of crinoids, sometimes foraminifers. In intergranular spaces there is finely dispersed graphite pigment and flakes of metamorphic minerals (sericite, less chlorite and talc). In variable quantities there are oval grains or fine-crystalline aggregates of quartz. Plan-parallel, horizontal lamination has been preserved in crystalline limestones of the Ochtiná Group (loc. Burda and south of Markuška), as well as of the Črmeľ Group, in the form of concentrations of graphite substance and sericite flakes, or pyrite grains. Magnesites are fine- to coarse-sparite, massive, mostly oriented, with marked pseudo-absorption. This sparite aggregate contains finely dispersed graphitic pigment. Besides this, pure, coarse-crystalline magnesite is found in secondary veins. Dolomites are associated with magnesites in one sequence, while the latter, in contrast to bedded dolomites,usually form massive, irregularly restricted bodies. A component of the whole sequence are interlayers of dolomite and graphitic shales and in the underlier of the dolo-magnesite horizon an important layer of basic magmatic rocks. Basic volcanoclastics associated with black shales, metasandstones, mataconglomerates and sporadic bodies of serpentinised ultrabasics complement the lithostratigraphic succession below the magnesite horizon.

Lower Carboniferous sequences in the Gemericum have undergone regional metamorphism reaching PT conditions of the lower part of greenschist facies of low-pressure type. This alteration grade is in carbonates documented by the mineral assemblages: Dol(Mgs)+Tlc; Dol+Qtz; Dol(Mgs)+ +Tlc+Cc+Qtz.Pressure character of metamorphism has been determined from b_0 values of muscovite from associated metapelites (SASSI and VOZÁROVÁ, 1987). Temperature was estimated in the range 350-370 °C, at pressure of 2-3 kbar and relatively high geothermal gradient of 40 °C/km. Recrystallization temperatures corresponding to the epizone have been determined also from illite crystallinity (KI = 0.27-0.35 2 theta, ŠUCHA and VOZÁROVÁ, in press).

Upper Carboniferous

Limestones of the Zlatník Formation have irregularly-grained, biosparite texture, with intraclasts of biomicrite and microsparite texture, with relics of recrystallized tests of crinoids, brachiopods, ostracods, foraminifers. Frequent are secondary veinlets with calcite filling. Metamorphic grade of the Zlatník Formation carbonates corresponds to early stages of epimetamorphism, or the transition between anchi- and epizone. In the more distant associated metapelites (area of Mlynky), corrected illite crystallinities correspond to the value of 0.23 2 theta (ŠUCHA and VOZÁROVÁ, l.c.). In carbonates is the under these conditions stable calcite, along with quartz, associated with small amount of illite and paragonite.

Turňa Nappe

Limestone olistoliths from the Turiec Formation have in the borehole BRU-1 massive, finely lamelled and in some parts also strongly pressure-oriented structure. Their texture is biosparite, in some places microstylolith. In this texture there are chaotically distributed recrystallized fragments of crinoid, ostracod and bivalvian tests. Sporadically, oval bodies with cross-extinction inside have been found, which, according to dr. BOOROVÁ (pers. comm.), correspond to zoospores - *Globochaete* sp. In the crystalline aggregate of calcite there are rhombi of newly-formed dolomite and oval grains and aggregates of quartz. In fine sedimentary laminae, as well as in foliation planes in schistose varieties, there are concentrated besides graphitic substance and pyrite grains also fine phyllosilicate flakes. Fine-crystalline dolomites have also organodetritic textures preserved in relics. The grade of regional metamorphism did not exceed the conditions of lower part of the greenschist facies, which is documented by critical mineral assemblage Ms+Ab in the associated metapelites. Pressure character of the metamorphism has been determined on the basis of b_0 values of muscovites (MAZZOLI and VOZÁROVÁ, 1989). The derived temperatures correspond to values abut 350 °C, at the pressure 2-3 kbar and geothermal gradient of approx. 40 °C/km.

Mesozoic sequence of the Turňa Nappe: Generally the grade of metamorphism of the Mesozoic Turňa Nappe rock sequences reaches anchizone P-T conditions.IC - averages maximally correspond to the boundary of anchi- and epizone (about 300 - 350 °C; ARKAI in ARKAI & KOVÁCS, 1986 from the loc. Zádielske Dvorníky). These results are in accordance with the chlorite-chloritoid metamorphic assemblage, which was ascertained in metasediments associated with the carbonate horizon (loc. Honce; VOZÁROVÁ unpubl. inf.).

Bôrka Nappe

Carbonates of the Dúbrava Beds have in general strongly pressure-oriented textures and according to their recrystallization grade and composition they belong to calcite and calcite-dolomite marbles. In the granoblastic, strongly oriented aggregate with pressure twin lamellae, besides calcite there has been sporadically preserved also aragonite, which is the critical metamorphic mineral of the high-pressure assemblage. Besides quartz, there are in small amounts associated chlorites, phengite and rarely also glaucophane and in dolomites also talc. No relics of organic remnants have been found in them. This mineral assemblage, as well as critical metamorphic mineral assemblages in metabasalt volcanics, occurring together with carbonates in one horizon, allow to interpret PT conditions of the formation of the Dúbrava Beds as greenschist facies of medium- to high-pressure type (T=400-450 °C, P = about 8-10 kbar, geothermal gradient 15 °C/km; VOZÁROVÁ, 1993; FARYAD, 1995).

Silica Nappe

The carbonatic sequence of the Silica Nappe has undergone diagenetic effect only.

Foederata Group

The Alpine metamorphism corresponds to the higher pressure range of greenschist facies. Pressure conditions were estimated by means of b_0 values of muscovites (MAZZOLI et al., 1992).

Lithogeochemical characterisation

Methods

For lithogeochemical study, fresh samples were collected from surface outcrops, mines and borehole profiles, weighing 1 to 5 kg. Complete silicate analysis has been made from the samples, as well as the determination of selected trace elements and a part of lanthanoid-group elements (Tab. 1, 2, 3). The same group of samples was subjected to C and O isotope analysis. Chemical analysis of oxides was made in the laboratory of Dionýz Štúr Institute of Geology (GÚDŠ) and trace elements were analysed in laboratories of E.L., spol. s r.o., Spišská Nová Ves, using AAS and ICP. The elements of the group of lathanoids were determined in laboratories of Geoindustria š.p., Praha-Černošice, using INNA.

Interpretation of results

An important and relatively strongly varying component is SiO_2, the carriers of which are above all allotriomorphic aggregates of low-metamorphic quartz and in dolomites and magnesites to a limited extent also talc, which is a side-product of low-grade metamorphism. The value of Al_2O_3/SiO_2 was used to characterise the silici-clastic admixture in carbonates, especially for expressing the relative proportion of quartz and phyllosilicates (sericite, paragonite, chlorite). Numerical values of this ratio vary in the range of 0.01 to 0.48, while in the majority of samples they are below 0.1, supporting thus our original assumption. Values above 0.3 indicate, according to YUDOVIČ (1981), predominance of originally clayey substance in the insoluble residue, i.e. in the metamorphic stage of phyllosilicates.

From Tab. 3 it follows that these values are higher only in four of the total number of samples, and thus in these samples we may assume more significant admixture of originally clayey substance. Based on this we may assume that in the majority of samples the trace elements as well as rare earths and Na, K, Mn are associated largely with the carbonate component.

P_2O_5 quantities vary in all carbonate groups approximately in the same way. They are derived from phosphatic carbonates formed from fossil phosphatic tests of organisms.

The distribution of indicative elements, as well as C and O isotopes in carbonates is shown in Tab. 3 and on Fig. 1, 2. The value of Mg/Ca in Lower Carboniferous dolomites varies in the range 0.90-0.95, which is somewhat lower than in ideal dolomite stoichiometry. A little greater differences were recorded in dolomites of the Bôrka Nappe (0.88-0.99). According to FOLK and LAND (1975), Ca surplus in dolomites is controlled mainly by the original salinity. In the sense of this hypothesis, salinity is

TAB.1 Abundances of main oxides in the Lower-, Upper Carboniferous and Dúbrava Beds carbonates (in %)

	14/G	15/G	10/G	Ocht-1	7/G	1/G	Burd-2	Ocht-2	16/G	17/G	19/G	20/G	21/G	4/G-A	4/G-B
SiO_2	21.06	4.49	7.28	8.08	2.29	21.45	1.72	13.40	10.02	12.40	5.04	6.82	4.46	12.38	7.15
TiO_2	0.05	0.01	0.05	0.04	0.03	0.17	0.00	0.07	0.02	0.09	0.06	0.04	0.01	0.03	0.03
Al_2O_3	1.24	0.44	0.43	0.98	0.15	2.93	0.82	1.05	0.89	1.40	0.38	0.89	0.76	0.59	0.50
Fe_2O_3	1.59	1.53	0.88	0.75	0.12	0.13	0.26	1.40	1.28	2.13	1.30	0.85	1.61	0.32	0.53
FeO		0.12	0.18			0.56			0.70	0.73	0.75	0.90	0.49	0.37	0.11
MnO	0.17	0.15	0.18	0.16	0.03	0.03	0.03	0.47	0.12	0.19	0.16	0.14	0.09	0.05	0.05
MgO	16.33	19.12	18.02	18.82	0.66	0.56	0.62	0.66	36.36	33.51	41.68	39.47	41.92	39.56	41.91
CaO	24.10	28.06	27.90	29.34	55.28	41.16	55.35	42.47	0.70	0.65	0.44	0.40	0.47	0.97	1.25
Na_2O	0.03	0.03	0.02	0.03	0.02	0.84	0.07	0.03	0.30	0.31	0.18	0.39	0.28	0.08	0.06
K_2O	0.02	0.07	0.06	0.05	0.03	0.69	0.10	0.25	0.08	0.06	0.05	0.10	0.08	0.02	0.01
P_2O_5	0.24	0.20	0.52	0.07	0.08	0.15	0.16	0.16	0.15	0.06	0.08	0.49	0.16	0.21	0.16
H_2O^-	0.03	0.08	0.01	0.00	0.01	0.02	0.02	0.02	0.03	0.02	0.04	0.03	0.03	0.02	0.01
H_2O^+	35.16	45.21	44.42	41.73	41.40	31.43	40.91	40.12	49.70	48.57	49.75	49.64	49.84	45.57	47.85
CO_2															
SO_3	0.25	0.35													
Σ	**100.27**	**99.86**	**99.95**	**100.05**	**100.10**	**100.12**	**100.06**	**100.10**	**100.35**	**100.12**	**99.91**	**100.16**	**100.20**	**100.17**	**99.62**

	2/G	8/G	Bru-1	Bru-1	Bru-1	Bru-1	Bru-1	3/G	9/G	11/G	6/G	5/G	12/G	13/G	GV-25/94	GV-64/94
			95.80	76.00	111.50	86.00	114.00									
SiO_2	3.57	3.32	3.96	18.62	4.39	7.49	5.11	8.33	13.70	6.39	2.28	4.94	7.78	4.48	0.37	4.30
TiO_2	0.05	0.01	0.05	0.22	0.06	0.15	0.12	0.00	0.01	0.00	0.00	0.01	0.04	0.00	0.01	
Al_2O_3	0.25	0.19	0.87	7.50	1.64	1.32	1.87	0.11	1.41	0.05	0.11	1.11	0.05	0.16	0.03	0.30
Fe_2O_3	0.26	0.17	0.65	2.31	1.47	0.72	1.57	0.37	0.89	0.04	0.09	0.14	0.06	0.03	0.11	0.12
FeO	0.22	0.18		0.19	0.13	0.11		0.12	0.31	0.20		0.20		0.04	0.09	0.07
MnO	0.10	0.09	0.18	0.15	0.48	0.20	0.16	0.03	0.05	0.02	0.03	0.02	0.01	0.01	0.04	0.01
MgO	0.51	0.86	0.85	1.17	0.62	0.68	31.62	19.24	17.26	19.69	2.53	1.03	0.75	1.07	0.38	0.58
CaO	53.69	53.14	53.18	36.67	51.32	52.36	18.99	28.48	24.29	31.36	53.79	51.87	53.72	54.55	54.57	52.46
Na_2O	0.01	0.33	0.03	0.13	0.03	0.06	0.07	0.02	0.27	0.01	0.02	0.06	0.01	0.01	0.02	0.01
K_2O	0.06	0.04	0.22	2.01	0.37	0.91	0.21	0.03	0.25	0.02	0.03	0.21	0.02	0.04	0.03	0.03
P_2O_5	0.20	0.15	0.16	0.18	0.14	0.06	0.16	0.03	0.10	0.09	0.11	0.70	0.20	0.23	0.01	0.04
H_2O^-	0.05	0.04	0.00	0.01	0.00	0.01	0.02	0.01	0.02	0.02	0.02	0.00	0.01	0.01	0.03	0.10
H_2O^+	41.23	41.58	39.75	30.66	38.68	35.86	40.91	43.44	41.50	42.24	40.89	39.89	37.16	39.29	0.11	0.01
CO_2															43.56	41.75
SO_3					0.55										0.16	
Σ	**100.20**	**100.10**	**99.90**	**99.82**	**99.88**	**99.93**	**100.81**	**100.21**	**100.60**	**100.13**	**99.90**	**100.18**	**99.81**	**99.92**	**99.51**	**99.77**

$^*H_2O^+$ loss on ignition (at 900 °C), contained are mainly the abundances of CO_2 to a lesser extent the organic matter and rare $(OH)^-$

TAB. 2 Trace elements contents for the Lower-, Upper Carboniferous and Dúbrava Beds carbonates (ppm)

	14/G	15/G	10/G	Ocht-1	7/G	1/G	Burd-2	Ocht-2	16/G	17/G	19/G	20/G	21/G	4/G-A	4/G-B
As	18.30	1.70	6.10	4.40	5.40	3.00	0.50	5.80	0.40	1.50	0.60	2.60	1.60	0.20	0.30
Ba	17.00	21.00	18.00	24.00	31.00	190.00	25.00	24.00	6.00	15.00	22.00	26.000	18.00	8.00	3.00
Cu	9.00	3.00	3.00	6.00	4.00	6.00	4.00	6.00	4.00	2.00	4.00	2.000	3.00	2.00	2.00
Li	15.00	14.00	12.00	11.00	18.00	32.00	20.00	12.00	10.00	6.00	7.00	7.000	7.00	3.00	1.00
Ni	14.00	2.00	5.00	7.00	6.00	5.00	2.00	13.00	8.00	6.00	8.00	6.000	5.00	5.00	3.00
Pb	4.50	2.30	2.10	2.20	1.50	2.50	1.80	3.00	1.00	2.20	1.70	1.600	1.10	0.20	1.00
Rb	2.00	1.00	3.00	1.00	0.50	10.00	0.50	3.00	2.00	2.00	1.00	0.050	2.00	2.00	1.00
Sb	3.50	0.30	0.40	1.40	1.30	0.40	0.20	2.70	0.90	0.40	0.50	0.005	0.60	0.20	0.30
Sr	34.00	38.00	124.00	29.00	414.00	3395.00	275.00	36.00	2.00	10.00	12.00	7.000	3.00	1.00	1.00
V	20.00	7.00	8.00	0.50	27.00	12.00	5.00	10.00	16.00	10.00	8.00	3.000	7.00	23.00	6.00
Y	12.00	4.00	3.00	8.00	5.00	6.00	7.00	9.00	5.00	8.00	6.00	4.000	4.00	4.00	4.00
Zn	3.00	1.00	5.00	0.50	3.00	6.00	2.00	0.50	3.00	6.00	6.00	3.000	2.00	3.00	1.00
Zr	10.00	7.00	6.00	1.50	5.00	68.00	6.00	7.00	16.00	8.00	9.00	7.000	10.00	22.00	7.00
U	0.90	1.60	0.30	1.30	3.90	1.30	0.60	3.90	1.00	2.50	0.60	0.500	0.30	0.50	0.30
Th	1.20	0.40	0.40	4.10	0.20	1.90	0.90	0.40	0.60	1.00	0.30	0.400	0.40	0.70	0.30
Sc	2.53	0.97	0.74	5.24	0.66	2.76	1.31	1.39	1.41	2.21	0.69	1.180	1.11	1.82	1.50

	2/G	8/G	Bru-1	Bru-1	Bru-1	Bru-1	3/G	9/G	11/G	6/G	12/G	13/G	GV-25/94	GV-63/94
			95.8	76.0	111.5	86.0								
As	2.70	1.30	3.40	2.60	2.30	11.20	0.40	0.50	0.30	0.50	0.30	1.00	0.50	5.70
Ba	46.00	32.00	118.00	170.00	92.00	146.00	28.00	66.00	11.00	25.00	28.00	36.00	30.00	5.00
Cu	9.00	5.00	7.00	9.00	5.00	16.00	3.00	7.00	2.00	3.00	3.00	4.00	14.00	6.00
Li	17.00	17.00	18.00	16.00	18.00	16.00	11.00	13.00	11.00	17.00	17.00	16.00		2.00
Ni	2.00	1.00	6.00	9.00	9.00	6.00	1.00	4.00	1.00	0.50	3.00	1.00	2.00	6.00
Pb	3.70	2.30	4.40	4.80	4.80	5.00	2.50	9.60	0.20	1.00	0.20	0.60	7.00	2.00
Rb	0.50	0.50	7.00	24.00	7.00	18.00	99.00	3.00	1.00	0.50	0.50	0.50	2.00	3.00
Sb	0.60	0.30	0.70	1.00	0.40	2.40	0.50	2.70	0.10	0.20	0.05	0.10	0.10	1.00
Sr	235.00	234.00	187.00	170.00	288.00	172.00	143.00	355.00	124.00	197.00	154.00	211.00	194.00	40.00
V	3.00	5.00	9.00	16.00	14.00	18.00	14.00	19.00	8.00	2.00	2.00	1.00	2.00	2.00
Y	6.00	6.00	14.00	13.00	16.00	14.00	1.00	6.00	1.00	1.00	0.50	1.00	2.00	2.00
Zn	1.00	2.00	11.00	7.00	6.00	5.00	3.00	36.00	0.50	5.00	0.50	0.50		2.00
Zr	5.00	4.00	14.00	38.00	16.00	25.00	5.00	12.00	6.00	1.50	5.00	6.00	5.00	2.00
U	1.90	1.40	0.20	0.90	0.30	0.40	1.20	2.00	0.50	0.30	0.70	0.30		
Th	0.20	0.30	1.20	9.30	0.30	1.90	0.20	0.80	0.20	0.10	0.05	0.10		
Sc	0.70	0.59	1.87	8.63	0.73	2.81	0.41	1.96	0.26	0.17	0.22	0.29		

TAB. 3 Geochemical and isotopic data for the Lower-, Upper Carboniferous and Dúbrava Beds carbonates

		Al_2O_3/SiO_2	Ca (%)	Mg (%)	Mn (ppm)	Na (ppm)	Sr (ppm)	Zn (ppm)	K (%)	U (ppm)	Th (ppm)	$(Sr/Ca)10^3$	$(Na/Ca)10^3$	Mg/Ca	$\delta^{18}O_{PDB}$	$\delta^{13}C_{PDB}$	$\delta^{18}O_{SMOW}$
Lower Carboniferous Northern Gemericum												MOLAR	MOLAR	MOLAR			
	14/G	0.06	17.25	9.92	1318.00	222.00	34.00	3.00	0.016	0.09	1.20	0.20	2.24	0.950	-12.31	1.39	19.38
	15/G	0.10	20.08	11.62	1154.00	225.00	38.00	1.00	0.058	1.60	0.40	0.19	1.95	0.950	-17.99	0.80	13.63
dolomites	10/G	0.06	19.97	10.95	1374.00	148.00	124.00	5.00	0.050	0.30	0.40	0.62	1.29	0.900	-17.42	-0.06	14.12
	Ocht-1	0.12	21.00	11.43	1264.00	222.00	29.00	1.00	0.041	1.20	4.10	0.14	1.85	0.910	-15.96	2.39	15.62
	7/G	0.06	39.57	0.23	219.00	148.00	414.00	3.00	0.025	3.90	0.20	1.05	0.65	0.009	-7.49	2.28	23.14
	1/G	0.14	29.46	0.19	219.00	6157.00	3395.00	6.00	0.570	1.30	1.90	11.50	36.44	0.010	-13.72	-3.87	16.71
limestones	Burda-2	0.48	39.62	0.21	219.00	519.00	275.00	2.00	0.083	0.60	0.80	0.69	2.28	0.009	-5.90	1.10	24.78
	Ocht-2	0.08	30.40	0.23	3626.00	222.00	36.00	1.00	0.207	0.40	0.90	0.12	1.27	0.012	-16.34	2.21	15.23
	16/G	0.09	0.50	22.10	934.00	2225.00	2.00	3.00	0.066	1.00	0.60	0.40	0.44	0,02*	-16.37	0.36	14.91
	17/G	0.11	0.46	20.36	1483.00	2300.00	10.00	6.00	0.050	2.50	1.00	2.17	0.50	0,02*	-16.86	-1.20	14.41
	19/G	0.07	0.32	24.89	1264.00	1335.00	12.00	6.00	0.041	0.60	0.30	3.75	0.42	0,01*	-16.05	-0.93	15.24
magnesites	20/G	0.13	0.28	23.97	1099.00	2893.00	7.00	3.00	0.083	0.50	0.40	2.50	1.03	0,01*	-15.30	1.21	16.02
	21/G	0.17	0.34	25.48	714.00	2077.00	3.00	2.00	0.066	0.30	0.40	0.88	0.61	0,01*	-16.29	-0.16	14.99
	4/G-A	0.05	0.69	24.04	385.00	593.00	1.00	3.00	0.017	0.50	0.70	0.14	0.08	0,03*	-19.64	-4.03	11.54
	4/G-B	0.07	0.89	25.47	385.00	445.00	1.00	1.00	0.008	0.30	0.30	0.11	0.05	0,03*	-19.63	-3.90	11.55
														*Ca/Ca+Mg			
Upper Carboniferous Northern Gemericum																	
	2/G	0.07	38.43	0.29	769.00	74.00	235.00	1.00	0.050	1.90	0.20	0.61	0.33	0.012	-13.02	0.89	18.03
limestones	8/G	0.06	38.04	0.17	714.00	2448.00	234.00	2.00	0.032	1.40	0.30	0.61	11.22	0.007	-12.64	0.35	18.62
Borehole Bru-1 Upper Carboniferous - Turnaicum																	
	95,8 m	0.22	38.06	0.51	1373.00	222.00	187.00	11.00	0.183	0.20	1.20	0.49	1.02	0.022	-10.66	-0.29	19.88
	76,8 m	0.40	26.18	0.71	1154.00	964.00	170.00	7.00	1.670	0.90	9.30	0.65	6.42	0.045	-9.93	1.37	20.63
	111,5 m	0.37	36.74	0.37	3736.00	222.00	288.00	6.00	0.307	0.30	0.30	0.78	1.05	0.017	-11.52	-1.07	18.99
	86,0 m	0.18	37.48	0.41	1538.00	445.00	172.00	5.00	0.755	0.40	1.90	0.46	2.07	0.018	-11.38	0.20	19.13
dol.	114,0 m	0.36	22.63	11.54	1264.00	297.00			0.174	0.05	1.30		2.29	0.840	-11.40	-1.37	19.11
?Upper Triassic - ?Jurassic Bôrka Nappe																	
	3/G	0.01	20.38	11.69	220.00	148.00	143.00	3.00	0.025	1.20	0.20	0.70	1.27	0.950	-12.03	0.80	18.46
dolomites	9/G	0.10	17.39	10.49	385.00	2003.00	355.00	36.00	0.207	2.00	0.30	2.04	20.07	0.990	-17.94	-5.59	13.58
	11/G	0.01	22.45	11.96	165.00	74.00	124.00	1.00	0.016	0.50	0.20	0.55	0.57	0.880	-12.19	-0.92	19.51
	6/G	0.05	38.50	1.54	220.00	148.00	197.00	5.00	0.025	0.30	0.10	0.51	0.67	0.066	-4.95	1.94	25.76
	5/G	0.22	37.13	0.62	165.00	445.00			0.174	0.20	0.40		2.09	0.027	-10.08	0.41	20.47
	12/G	0.01	38.45	0.45	55.00	74.00	154.00	1.00	0.016	0.70	0.05	0.40	0.33	0.018	-7.41	0.03	23.23
limestones	13/G	0.03	39.05	0.65	55.00	74.00	211.00	1.00	0.033	0.30	0.10	0.54	0.33	0.027	-6.73	0.90	23.93
	GV-25/94	0.08	39.13	0.23	22.00	148.00	194.00		0.025			0.49	0.66	0.009			
	GV-64/94	0.07	37.55	0.20	54.00	74.00	141.00	5.00	0.025			0.37	0.34	0.009			

TAB. 4 Contents of REE (ppm) in the Lower-, Upper Carboniferous and Dúbrava Beds carbonates (chondrite values used for normalization after Boynton, 1984)

	LOWER CARBONIFEROUS														
	14/G	15/G	10/G	Ocht-1	7/G	1/G	Burd-2	Ocht-2	16/G	17/G	19/G	20/G	21/G	4/G-A	4/G-B
La	6.80	1.50	1.60	16.50	2.00	9.20	3.80	4.40	0.90	0.90	0.90	1.70	1.30	2.70	2.30
Ce	11.30	3.70	3.00	33.80	4.20	19.40	5.70	8.20	3.90	2.70	2.60	2.70	2.60	3.40	6.30
Nd	5.00	3.00	2.00	13.00	2.00	8.00	3.00	4.00	2.00	2.00	2.00	1.00	2.00	1.00	3.00
Sm	0.72	0.56	0.24	2.36	0.46	0.63	0.50	0.77	0.44	0.70	0.20	0.24	0.26	0.54	0.48
Eu	0.31	0.04	0.13	0.84	0.09	0.32	0.13	0.30	0.19	0.29	0.09	0.09	0.11	0.21	0.21
Tb	0.20	0.10	0.05	0.60	0.10	0.05	0.20	0.20	0.10	0.30	0.05	0.10	0.05	0.10	0.20
Yb	1.00	0.30	0.30	1.60	0.40	0.60	0.60	0.70	0.60	1.00	0.30	0.50	0.40	0.30	0.30
Lu	0.16	0.04	0.05	0.22	0.07	0.13	0.10	0.10	0.09	0.16	0.05	0.08	0.06	0.04	0.04
La_{cn}	21.94	4.84	5.16	53.23	6.45	29.68	12.26	14.19	2.90	2.90	2.90	5.48	4.19	8.71	7.42
Ce_{cn}	13.99	4.58	3.71	41.83	5.20	24.01	7.05	10.15	4.83	3.34	3.22	3.34	3.22	4.21	7.80
Nd_{cn}	8.33	5.00	3.33	21.67	3.33	13.33	5.00	6.67	3.33	3.33	3.33	1.67	3.33	1.67	5.00
Sm_{cn}	3.69	2.87	1.23	12.10	2.36	3.23	2.56	3.95	2.26	3.59	1.03	1.23	1.33	2.77	2.46
Eu_{cn}	4.22	0.54	1.77	11.43	1.22	4.35	1.77	4.08	2.59	3.95	1.22	1.22	1.50	2.86	2.86
Tb_{cn}	4.22	2.11	1.05	12.66	2.11	1.05	4.22	4.22	2.11	6.33	1.05	2.11	1.05	2.11	4.22
Yb_{cn}	4.78	1.44	1.44	7.66	1.91	2.87	2.87	3.35	2.87	4.78	1.44	2.39	1.91	1.44	1.44
Lu_{cn}	4.97	1.24	1.55	6.83	2.17	4.04	3.11	3.11	2.80	4.97	1.55	2.48	1.86	1.24	1.24
$(La/Yb)_{cn}$	4.58	3.36	3.32	6.95	3.38	10.34	4.27	4.23	1.03	0.61	2.01	2.29	2.19	6.05	5.15
$(La/Lu)_{cn}$	4.41	3.90	3.32	7.79	2.97	7.35	3.94	4.56	1.04	0.58	1.87	2.21	2.25	7.02	5.98
$(Eu/Sm)_{cn}$	1.14	0.19	1.44	0.94	0.52	1.35	0.69	1.03	1.15	1.10	1.18	0.99	1.13	1.03	1.16
$(Ce/La)_{cn}$	0.63	0.95	0.72	0.78	0.81	0.81	0.57	0.71	1.66	1.15	1.11	0.61	0.77	0.48	1.05

	UPPER CARBONIFEROUS							DÚBRAVA BEDS						
	2/G	8/G	Bru-1	Bru-1	Bru-1	Bru-1	Bru-1	3/G	9/G	11/G	6/G	5/G	12/G	13/G
			95.80	76.00	111.50	86.00	114.00							
La	3.40	2.20	8.80	27.00	2.70	15.60	13.40	0.70	3.40	0.80	0.60	1.80	0.300	0.50
Ce	5.10	3.50	15.40	55.80	4.80	44.10	35.40	2.10	9.90	1.70	0.90	6.40	0.900	1.10
Nd	3.00	1.00	7.00	18.00	3.00	12.00	11.00	1.00	4.00	1.00	0.50	3.00	0.500	1.00
Sm	0.48	0.38	1.27	2.51	0.46	2.02	1.81	0.37	0.77	0.12	0.06	0.37	0.060	0.06
Eu	0.40	0.22	0.49	0.71	0.20	0.68	0.60	0.10	0.33	0.01	0.03	0.14	0.020	0.02
Tb	0.10	0.10	0.30	0.40	0.10	0.50	0.40	0.10	0.20	0.05	0.05	0.10	0.050	0.05
Yb	0.50	0.40	1.10	1.40	0.60	1.50	1.40	0.20	0.50	0.10	0.05	0.30	0.050	0.05
Lu	0.06	0.06	0.14	0.22	0.08	0.21	0.23	0.02	0.07	0.01	0.01	0.04	0.005	0.01
La_{cn}	10.97	7.10	28.39	87.10	8.71	50.32	43.23	2.26	10.97	2.58	1.94	5.81	0.970	1.61
Ce_{cn}	6.31	4.33	19.06	69.06	5.94	54.58	43.81	2.60	12.25	2.10	1.11	7.92	1.110	1.36
Nd_{cn}	5.00	1.67	11.67	30.00	5.00	20.00	18.33	1.67	6.67	1.67	0.83	5.00	0.830	1.67
Sm_{cn}	2.46	1.95	6.51	12.87	2.36	10.36	9.28	1.90	3.95	0.62	0.31	1.90	0.310	0.31
Eu_{cn}	5.44	2.99	6.67	9.66	2.72	9.25	8.16	1.36	4.49	0.14	0.41	1.90	0.270	0.27
Tb_{cn}	2.11	2.11	6.33	8.44	2.11	10.55	8.44	2.11	4.22	1.05	1.05	2.11	1.050	1.05
Yb_{cn}	2.39	1.91	5.26	6.70	2.87	7.18	6.70	0.96	2.39	0.48	0.24	1.44	0.240	0.24
Lu_{cn}	1.86	1.86	4.35	6.83	2.48	6.52	7.14	0.62	2.17	0.31	0.31	1.24	0.160	0.31
$(La/Yb)_{cn}$	4.59	3.72	5.40	13.00	3.03	7.01	6.45	2.35	5.05	5.37	8.08	4.03	4.040	6.70
$(La/Lu)_{cn}$	5.90	2.33	6.53	12.75	3.51	7.72	6.05	3.64	5.05	8.32	6.26	4.68	6.060	5.19
$(Eu/Sm)_{cn}$	2.21	1.53	1.02	0.75	1.15	0.89	0.88	0.71	1.14	0.23	1.32	1.00	0.870	0.87
$(Ce/La)_{cn}$	0.57	0.61	0.67	0.79	0.68	1.08	1.01	1.15	1.12	0.81	0.57	1.36	1.140	0.84

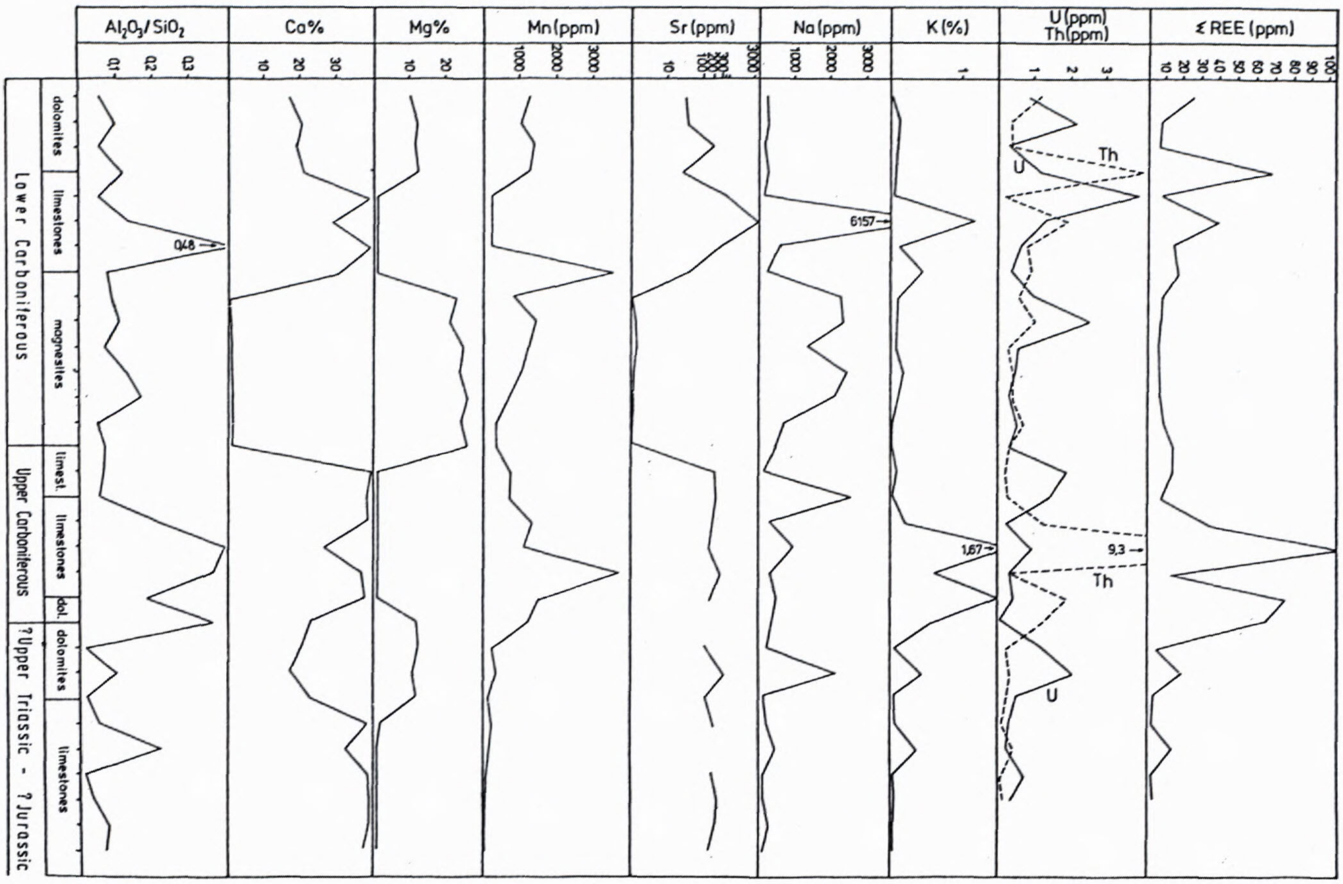


Fig. 2 Distribution of Al_2O_3/SiO_2, Ca, Mg, Mn, Sr, Na, K, U, Th and rare earth elements in carbonates of the Lower and Upper Carboniferous and in the Dúbrava Beds.

reduced due to mixing with meteoric water, leading to increasing Mg/Ca values in dolomite in spite of their decrease in solutions. Mg/Ca values in limestones are low, varying generally within 0.01-0.04. In our case we must assume mixing of the solutions and migration of their salinity in diagenetic as well as later on in the metamorphic processes. However, in spite of approximately same temperature conditions of metamorphism of Lower Carboniferous and ?Mesozoic carbonates significant differences may be observed in their Mn and Sr/Ca values, considered generally the indicators of open diagenetic system.

Mn contents in Carboniferous rocks vary in the order of thousands (dolomites and limestones of the Lower Carboniferous - 1174 ppm, n = 8; dolomites and limestones of the Upper Carboniferous - 1507 ppm, n = 7), while in ?Mesozoic carbonates of the Dúbrava Beds only in tens of ppm (149 ppm, n = 9). Mn contents in magnesites are approximately identical with other types of Lower Carboniferous carbonates (895 ppm, n = 7). Extreme increase of Mn in Carboniferous carbonates may be explained by Mn source in migrating reduction pore water in an open system, during complex post-sedimentary alterations.

Sr contents in Lower Carboniferous carbonates are considerably higher than in associated dolomites and magnesites (limestones = 36-3395 ppm; dolomites = 29-124 ppm; magnesites = 1-36 ppm), due to their greater capacity to substitute Sr for Ca (Fig.2, 3). Upper Carboniferous limestones have relatively levelled Sr contents, in the range of 170-288 ppm, but generally lower than average values presented in literature. Similar Sr contents have been determined also in carbonates of the Dúbrava Beds, while there are no greater differences between dolomites and limestones (limestones = 141-211 ppm; dolomites = 124-355 ppm).

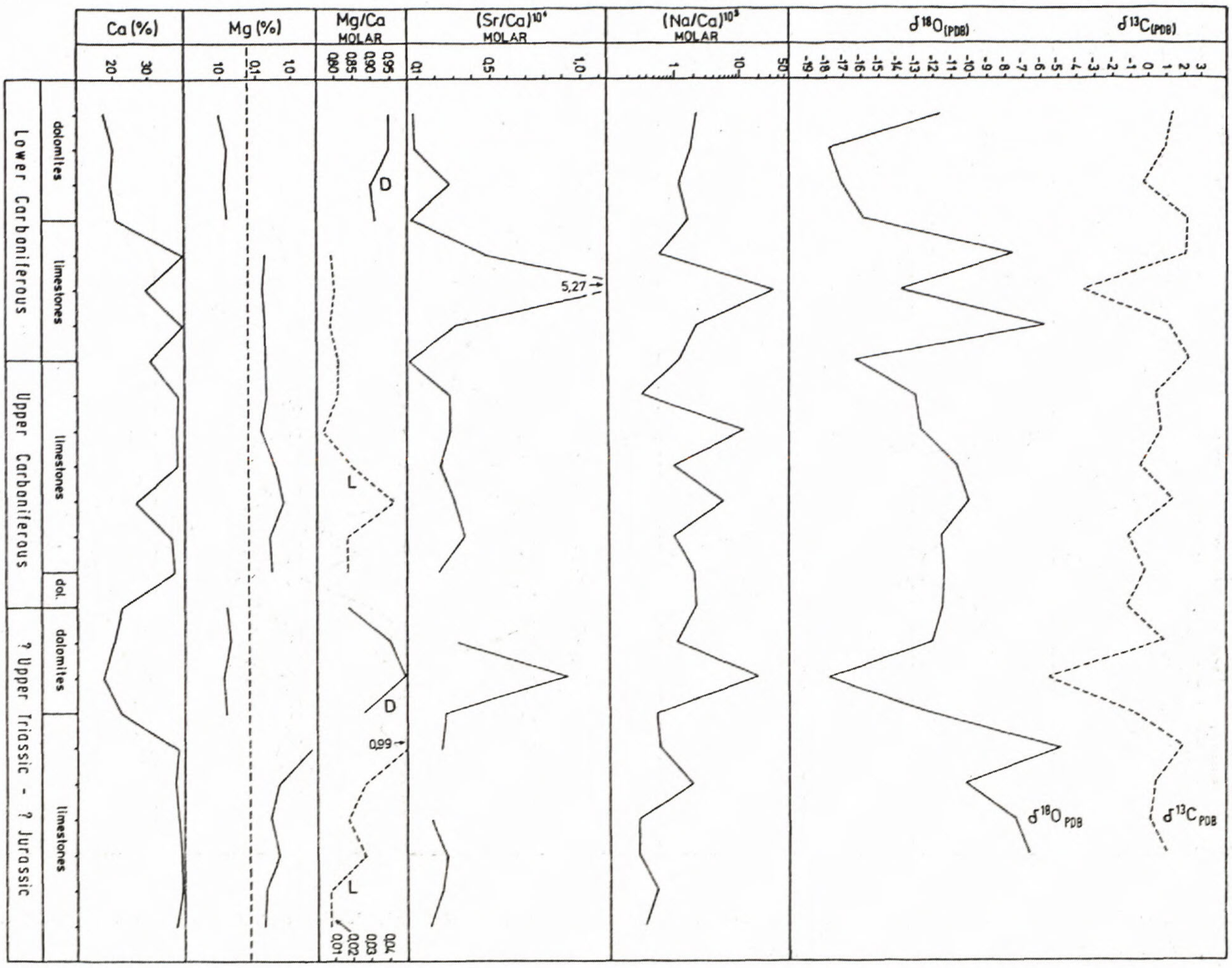


Fig. 3 Relationship of Mg, Sr, Na to Ca and isotopes of oxygen and carbon in dolomites and limestones of the Lower and Upper Carboniferous and in the Dúbrava Beds.

The relationship between Sr (expressed as 1000·Sr/Ca) and Mn (in ppm) provides information on the original sedimentation environment and diagenetic conditions (BRAND and VEIZER, 1980). In the analysed set of limestone samples, a marked division may be observed in the Sr as well as Mn contents (Fig. 4). Limestones of the Dúbrava Beds have relatively low Sr/Ca as well as Mn. On the Sr/Ca vs. Mn (Fig. 4) diagram they are all lying in a relatively narrow interval, in the high-Mg-calcite zone, within Mn values not exceeding $x \pm s$, and thus also the degree of openness of the diagenetic system. It must be assumed that during the complex post-diagenetic alterations of these limestones Sr was strongly depleted. It is probable that the original composition corresponded to HMC, with normal Mn values. Almost all Carboniferous limestones display increased Sr/Ca values as well as Mn, in the major part of them they are extremely high. In a part of them Mn values do not indicate exceeding of the degree of system openness, while Sr was depleted less than in the previous group. This may indicate than at least a part of the carbonate in original samples was open low-Mg calcite (original sparite cement) and/or aragonite. A substantial part of the Carboniferous limestones is depleted in Sr and at the same time enriched in Mn. This means that the whole diagenetic system was open and considerably influenced by meteoric water and, later on, also by chemistry of metamorphic fluids.

Na contents are generally higher in carbonates of the Carboniferous than in the Dúbrava Beds. This applies to limestones as well as dolomites. Generally highest average Na values are in magnesites. Considering that Na contents and values of Mg/Ca, Sr/Ca and Na/Ca may be indicators of salinity in the sedimentation environment (LAND and HOOPS, 1973; SASS and KATZ, 1982), Carboniferous and Dúbrava Beds carbonates formed in different sedimentation environment. Carboniferous carbonates formed probably in generally shallow, subtidal environment, not excluding alternation with higher-salinity conditions. This suggests dolomite formation as the result of early diagenetic alteration of aragonite sediment. This would be indicated by positive correlation between Sr/Ca and Na/Ca and antipathetic covariance with Mg/Ca. Distribution of δO^{18} and δC^{13} shows in dolomites and limestone negative correlation with Sr/Ca and Na/Ca (Fig.3). Some extreme Na contents are probably connected with enrichment during metamorphic processes and it is thus not possible to interpret them from the viewpoint of sedimentation environment.

Marked dependence between Th, K and Al_2O_3 concentration was determined only in limestones of the Upper Carboniferous Turiec Formation. In other sample sets the contents of K, Th,U do not correlate positively with maximums of Al_2O_3/SiO_2. This means that they may be boded also in carbonates. In general, anomalous U and Th contents have not been determined in any of the samples. However, Th quantities show good positive correlation with rare earths.

The carbonate sets display certain differences in the distribution, but above all in total REE contents (Fig. 1; 5a,b,c,d). This is a reflection of their mineralogical composition and probably, to a certain extent, of their different paleo-setting. A common feature of all three sets is their strong enrichment with LREE with approximately same steepness of the distribution curve, as well as identical trend of REE enrichment depending on the chemical composition of carbonates. In all three sets the highest REE contents were determined in dolomites. There are substantial differences in REE totals and the character of Eu anomaly (Tab. 4).

Average REE contents in the set of Lower Carboniferous carbonates are following: dolomites ® x = 27.75 ppm (s.d. = 28.62; v. = 819.3; n = 4); lime-

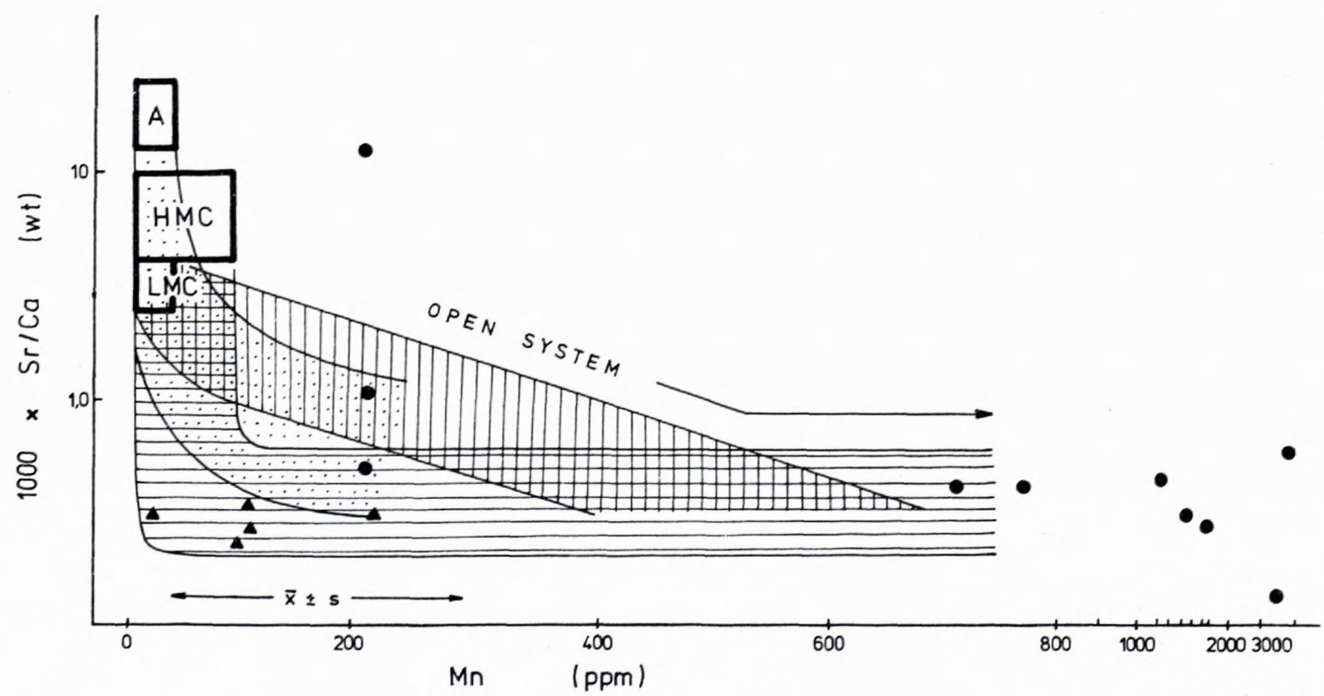


Fig. 4 Relationship between Sr (expressed as 1000 Sr/Ca) and Mn, studied in samples of the Lower and Upper Carboniferous and in the Dúbrava Beds. Diagram after BRAND-VEIZER (1980).

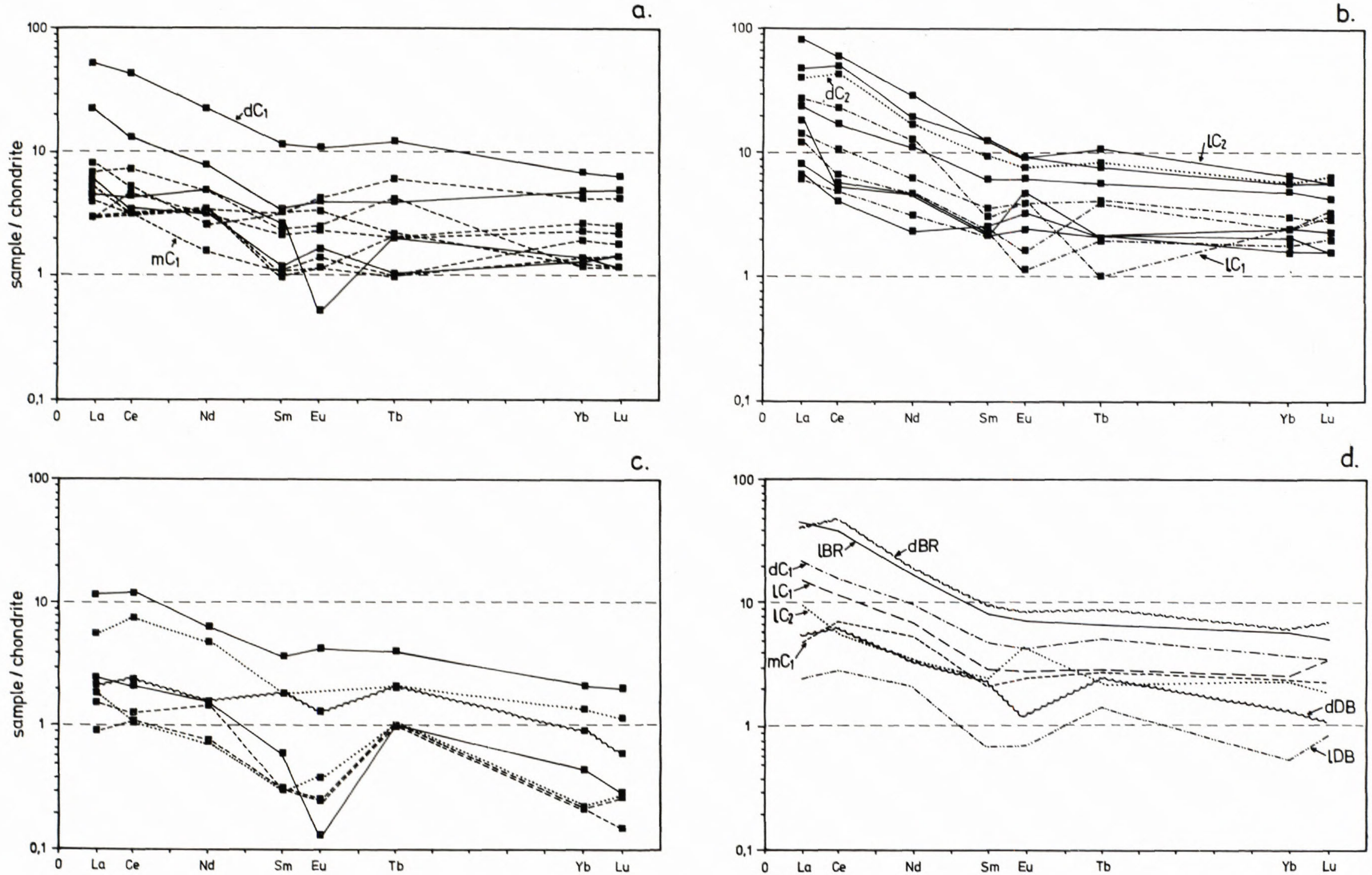


Fig. 5 Chondrite-normalized distribution curves of rare earth elements. a) dolomites (dC1) and magnesites (mC1) of the Lower Carboniferous, b) limestones of the Lower Carboniferous (lC1), limestones (lC2) and dolomites (dC2) of the Upper Carboniferous, c) limestones (dashed and dotted line) and dolomites (full and undulating line) of the Bôrka Nappe, d) average distribution curves for limestones (lC1), dolomites (dC1), and magnesites (mC1) of the Ochtiná Formation, limestones of the Zlatník Formation (lC2), limestones (lBr) and dolomites (dBr) of the Turiec Formation from the borehole BRU-1 (Turňa Nappe), limestones (lDb) and dolomites (dDb) of Dúbrava Beds, Bôrka Nappe. All values normalised after BOYNTON *(1984).*

stones ® x = 20.06 ppm (s.d. = 12.75; v. = 162.6; n = 4); magnesites ® x=8.11 ppm (s.d. = 2.26; v.= 5.11; n = 8). Dolomites and limestones have approximately the same course of the distribution curve, with average contents of $(Eu/Sm)_{cn}$ = 0.90-0.94 and $(La/Lu)_{cn}$ = 5.84-5.03. Slightly positive Eu anomalies are displayed by samples with higher contents of Na, Mn and in the case of limestones also Sr. The distribution curve in magnesites is relatively the flattest, with slightly positive Eu anomaly, correlating with their higher Na and Mn contents ($(Eu/Sm)_{cn}$ = 1.10; $(La/Lu)_{cn}$ = 2.14).

Upper Carboniferous limestones display considerable differences in the total REE contents. In the Northern Gemericum unit, in the Zlatník Formation, average REE content is 10.45 ppm (s.d.= 3.66; v. = 13.4; n = 2) and in the Turňa Nappe, in the Turiec Formation, average REE contents reach as much as 57.27 ppm (s.d. = 42.1; v. = 1775.4; n = 4). This trend is preserved also in the dolomite sample (REE = 64.01). High REE contents are directly depending on increased quantity of the originally clayey admixture in these rocks, which was enriched in organic substance. Distribution curves of the Turiec Formation carbonates have more marked LREE and HREE fractionation, with corresponding average $(La/Lu)_{cn}$ = 8.64 values in the Turiec and 4.85 in the Zlatník Formation. While limestones of the Zlatník Formation display slight positive Eu anomaly (average value $(Eu/Sm)_{cn}$ = 1.13), in the Turiec Formation they have negative Eu anomaly - (Eu/Sm) = 0.88.

Carbonates of the Dúbrava Beds are characterized by the lowest REE contents from the studied sets. The same trend is preserved here as well, i.e. higher quantities in dolomites (x=8.66 ppm; s.d.=8.66; v.=74.9; n=3) than in limestones (x = 4.75 ppm; s.d.= 4.94; v = 24.4; n = 4). Moreover, dolomites are depleted in Eu (average value $(Eu/Sm)_{cn}$ = 0.50), while the average chondrite-normalized Eu/Sm value in limestones is 1. LREE vs. HREE fractionation is in both carbonate types approximately the same.

From the above analysis it follows that rare earth distribution and their total contents are associated with i) phyllosilicates, thus in pre-metamorphic state clayey component, and ii) substitution with Ca, Th, Mn, Na and Sr. Fig. 6 shows relationships of REE contents and their LREE enrichment to CaO and Al_2O_3. Carbonates of the Dúbrava Beds are in comparison with other sets significantly depleted in REE and, at the same time, on the chondrite-normalized curve they display relatively higher HREE enrichment in relation to LREE, in comparison with carbonate sets of the Lower and Upper Carboniferous (Fig. 5d). This means that their composition was less affected by terrigenous source and, to the contrary, the source of HREE enrichment was most probably synsedimentary volcanism. They formed in an area more distant from the continent, in deeper sedimentation environment, and, on the contrary, carbonates of the Lower and Upper Carboniferous of Gemericum formed in a shallow basin situated near the continent. The latter is supported by lithological characteristics as well as the character of found fauna communities.

REE contents in Lower and Upper Carboniferous carbonates of Gemericum as well as Turnaicum are similar to typical REE curves presented by RONOV et al. (1974) for sedimentary carbonates as well as for sparite-magnesite deposits of the Eastern Alps (MORTEANI et al., 1982). Dolomites and limestones of the Dúbrava Beds, on the contrary, with their low REE contents, negative Eu anomaly and relative HREE enrichment in relation to LREE, remind of the isotope composition of oceanic water (HOGDAHL et al., 1968). Generally it may be stated that Carboniferous sets enriched in rare earth elements display positive Eu anomaly, or at least a very flat course of the normalized curve. To the contrary, decrease of the bulk rare earth contents in carbonates of the Dúbrava Beds is directly proportional to the negative Eu anomaly (Fig. 5d). In the majority of Lower Carboniferous samples there is a slightly negative Ce anomaly. According to MORTEANI et al. (1982), this anomaly indicates marine sedimentation environment. However, it was also documented that the clay component may mask this anomaly.

Generally, we may observe a depletion of LREE in magnesites in comparison with associated limestones and dolomites. This may be evidence that magnesites formed by Mg-metasomatism of pre-existing carbonates. This may have been caused by the fact that Mg^{+} ion has a radius more similar to HREE and thus LREE are during Mg-metasomatism substituted along with Ca^{+}. MORTEANI et al. (1982), KIESL et al. (1990) as well as MORTEANI and NEUGEBAUER (1990) explain this process by Mg-metasomatism of pre-existing dolomites, either by higher-temperature fluids generated in the process of low-grade regional metamorphism, or by irregular increase of geothermal gradient caused by thrusting. The theory of Mg-metasomatic origin of magnesites is supported also by enrichment in Ni, Co, Cr and Sc in Lower Carboniferous dolomites and magnesites, while these con-

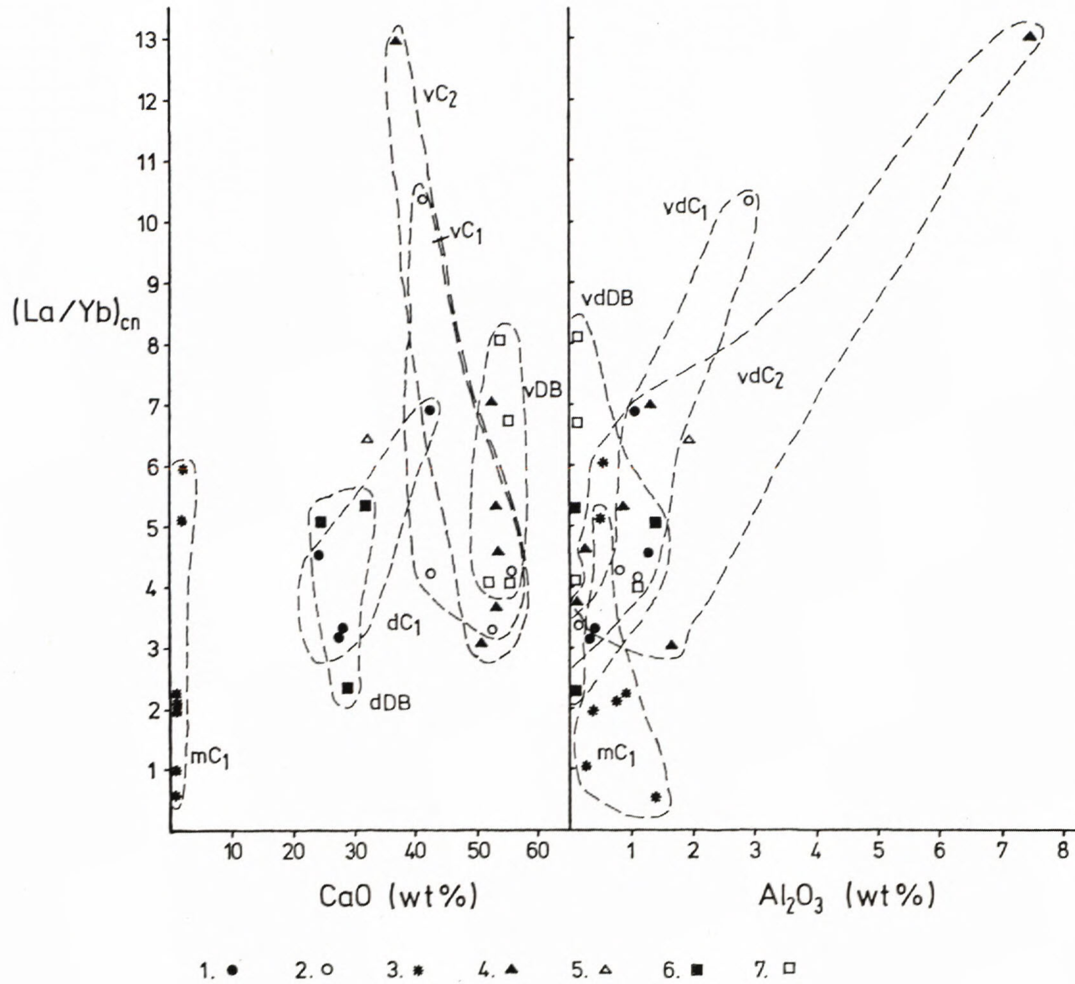


Fig. 6 The relationship of (La/Yb)cn to CaO (wt.%) and Al_2O_3 (wt.%). Explanations: carbonates of the Lower Carboniferous - 1– dolomite dC1 (full circle); .2– limestone vC1 (empty circle); 3– magnesite mC1 (asterisk); carbonates of the Upper Carboniferous - 4 – limestone vC2 (full triangle); 5 – dolomite dC2 (empty triangle); Mesozoic carbonates of the Bôrka Nappe - 6 – limestone vDB (empty square); 7–. dolomite dDB (full square).

tents evidently do not correlate with increased Al (in contrast to carbonates from the borehole BRU-1).

From other micro-elements, there have been determined the contents of B, Ba, Co, Cr, Cu, Li, Ni, Pb, Rb, V, Y, Zn and Zr. From them, B, Ni, Cr, Co, Cu, Y, Sc and in a limited number of samples also U and Th exceed average values for carbonates (Tab. 2).

Isotope Composition of Oxygen and Carbon

Data on isotope composition of carbonates from the Western Carpathian area are available in the works of DEMOVIČ et al. (1972), VEIZER et al. (1976), KANTOR et al. (1981-1993), HLADÍKOVÁ et al. (1987), LINTEROVÁ et al. (1992). They brought information predominantly on isotope composition of limestones and dolomites of Mesozoic and younger age.

Into this work we included, besides Carboniferous carbonates of Gemericum, Turnaicum and Dúbrava beds, for comparison also samples of carbonates of the Silica Nappe, from further occurrences of the Bôrka Nappe, from the Foederata Group of the Southern Veporicum envelope, from Turnaicum in the borehole DRŽ-1 as well as further samples from the magnesite deposit Bankov near Košice (samples from the collection of dr. Ďurkovičová and from the depository of the Department of Isotope Geology at GÚDŠ, Tab. 5).

Methods

For analyses of isotope composition of oxygen and carbon we selected 73 bulk samples of limestones, dolomites and magnesites. In some samples we analyzed also secondary veins. The homogeneity and mineral composition of the samples were checked radiometrically. 20-30 mg of a sample were used for the analysis, the samples were crushed in agate mortar, heated in vacuum at 470 °C for 30 min. to remove organic carbon. CO_2 was released by a reaction with 100 % H_3PO_4 at 25 °C for calcites and 100 °C for magnesites and dolomites. Gaseous CO_2 samples were measured by standard method on a mass spectrometer MAT 250.

The isotope ratios of $^{18}O/^{16}O$ and $^{13}C/^{12}C$ were investigated in carbonate minerals, presented as d per mil, in relation to international standards in PDB or SMOW. The results of isotope analyses are listed in Tabs. 5, 6 and shown on Figs. 7-9.

Interpretation of results

The Črmeľ Group

3 samples were analysed - 2 magnesites from Kavečany, with different structure (coarse-grained and nodular) and laminated limestone from the Črmeľ Valley.

All samples are characterised by high contents of the light carbon isotope - with values of $\delta^{13}C_{PDB}$ of -3.87 to -4.03 ‰ - different from other magnesite samples. Due to limited number of analyses it is now difficult to comment the low values of $\delta\ ^{13}C_{PDB}$, however, the high Sr/Ca and Na/Ca ratios allow to assume that these rocks sedimented originally in shallow marine environment. It is not possible to exclude yet an influence of interstitial solution chemistry in the post-diagenetic processes resulting from genetic relationship with basic rocks. A more precise answer to this problem requires analyses of a greater number of samples.

The Ochtiná Formation

This formation contains the largest number of analysed samples (31). Mineralogically they are limestones, dolomites and predominantly magnesites.

Data on isotope composition indicate evident smaller variance of the values of $\delta\ ^{13}C_{PDB}$ and great differences of the isotope composition of oxygen. The lowest light oxygen isotope contents yield limestone samples from the localities of Burda and Markuška. The values of $\delta\ ^{18}O_{PDB}$ and $\delta\ ^{13}C_{PDB}$ approach values for marine unaltered Carboniferous sediments from the Gobler Formation in the Sacramento Mts. (ALGEO et al., 1992). MARGARITZ et al. (1°990) studied isotope composition of marine limestones of Upper Carboniferous age in North America and the determined the values of $\delta\ ^{13}C_{PDB}$ are in the range of +2 to +4‰ and $^{18}O_{PDB}$ -9.6 to -3.8‰. MEYERS and LOHMAN (1985) mentioned for marine limestones of Mississipian age $\delta\ ^{13}C_{PDB}$ of +4‰ and $^{18}O_{PDB}$ -1.5‰.

Isotope composition of least altered carbonate rocks of the Ochtiná Formation is consistent with the range mentioned by Veizer et al. (l.c.) for Carboniferous limestones and dolomites. For the sample with the lowest content of light oxygen isotope we calculated the value of sea water paleotemperature in the Carboniferous (Tab.7), it however yielded an unrealistic value, which confirms opinions on increasing light oxygen isotope contents during geological stages by gradual equilibration of marine limestones with isotopically lighter meteoric water. The decrease of the values in our samples represents for $\delta\ ^{18}O_{PDB}$ 3 to 4‰.

Another group of samples distinguished in the Ochtiná Formation on the basis of isotope composition of oxygen consists of limestones and dolomites from the borehole KV-6 (Košice-Bankov) and dolomite from Dúbrava (mine Miková), with mean values of $^{18}O_{PDB}$ -12.31 to -10.50‰. Isotope composition of oxygen in the rest of dolomite and magnesite samples is relatively homogenous, in the range of -17.99 to .14.99‰. Isotope composition of carbon for all 3 distinguished sample groups indicates marine origin of carbonate sediments altered into magnesites. An exception is only a magnesite sample from secondary vein the $\delta\ ^{13}C_{PDB}$ of which, -5.51‰, indicates probable presence of meteoric water during its formation. Isotope composition of carbon in the studied magnesites in the range of -1.55 to +2.37‰ leads to the assumption that alteration of limestones into dolomites and magnesites was caused by solutions not very different from marine water, at increased temperatures.

. KRALIK et al. (1989) summarised the results of isotope analyses of magnesites and classified them in 3 groups:

1. Cryptocrystalline to fine-grained magnesites genetically associated with ultrabasic rocks have carbonisotope composition in the range of $\delta\ ^{13}C_{PDB}$ -6 to -18‰ and the values of $\delta\ ^{18}O_{SMOW}$ +22 to +29‰.

2. Fine-grained Qarternary to recent magnesites forming in evaporite environment are characterised by high contents of heavy carbon as well as oxygen isotopes ($\delta\ ^{13}C_{PDB}$ +1.7 to +4.6‰ and $^{18}O_{SMOW}$ +32 to +38‰). Older magnesites of this type forming

extensive stratiform deposits have δ $^{13}C_{PDB}$ +2 to +3‰ and $^{18}O_{SMOW}$ +25 to +37‰. Smaller unconnected layers and concretions have δ $^{13}C_{PDB}$ -2 to -6‰ and $^{18}O_{SMOW}$ +18 to +22‰. To this group have been assigned also magnesites of Eastern Alps and Western Carpathians (sedimentary magnesites genetically connected with evaporites of Upper Permian - Lower Triassic age, Smižany, Nov. Huta).

3. Coarse-grained magnesites having a wide range of δ $^{13}C_{PDB}$, -7.5 to +4‰ as well as $^{18}O_{SMOW}$ values - +13 to +17‰.

The analytical results of Lower Carboniferous magnesites show rather that the majority of samples belongs to group No.3. On the basis of isotope analyses of C, O and rare earth element, as well as of selected elements contents we may consider that the genesis of the Lower Carboniferous magnesites was complicated, polygenetic. Relatively high Na contents in magnesites as well as Sr contents in some associated samples of limestones and dolomites, as well as the distribution of Sr/Ca and Mn, in spite of their low-metamorphic alteration, is evidence of their probable formation in shallow-marine, in some places not excluding even evaporite environment. REE contents, which are higher than in typical sedimentary magnesites, as well as the course of normalised REE curve and marked Mn-enrichment signalise Mg input by metasomatic processes. The assumed Mg source may be derived from the associated basic and ultrabasic rocks as well as intraformational crinoid detritus, with high MgCO3 contents (Bathurst, 1975, Neugebauer, 1978). Estimated temperatures of low-metamorphic solutions attained 300-350 °C, and thus we may assume that magnesite formed at temperature increase and almost constant Ca/Ca+Mg (Cc+Dol + +Mgs equilibrium reaction according to T-X diagram of Johannes, 1970).

Zlatník Formation

We analysed 3 samples from rocks of this formation, collected in the surroundings of Dobšiná. In two of them (2/G, 8/G) there were abundant secondary veinlets, which were subjected to analysis as well. Isotope composition of oxygen as well as carbon of these samples is very similar and comparable with values determined in the borehole BRU-1, in its upper parts. Isotope composition of the secondary veinlets is also not very different. The third sample, Dobšiná-Hámor (22/G) has substantially different isotope composition. The grade of alteration recorded in petrographic description as well as geological setting - a scale on the contact of the Hámor Formation and Rakovec Group - indicate the possibility of higher-grade metamorphism, which is reflected in the oxygen isotope composition similar to values characteristic for dolomites and magnesites of the Ochtiná Formation. Isotope composition of carbon in this sample indicates that it formed in marine environment and its metamorphism occurred at higher temperatures without participation of light carbon of organogenic origin.

Turiec Formation - borehole BRU-1

Differences in the isotope composition of oxygen are not significant, they vary within δ $^{18}O_{PDB}$ -11.85 to -9.93 ‰. More marked are differences in the isotope composition of carbon. Towards greater depth the values become more negative - lighter isotope content increases. Differences in isotope composition of carbon may have been caused by the inhomogeneity of the original sediment (olistoliths of shallow- as well as deep-water carbonates mixed within one horizon). Decrease of $\delta^{13}C_{PDB}$ values may have been affected by CO_2, released by decomposition of organic substance abundant in the rocks. Isotope analyses of secondary veinlets separated from limestones of three deeper levels indicate higher contents of light C isotope than in the original sediment.

Dúbrava Beds

Unclear stratigraphic classification of some localities of the Dúbrava Beds initiated the investigation of isotope composition of carbonate rocks in this area. Five of the studied 6 samples occupy on the O/C diagram (Fig. 7) a field with $\delta^{13}C_{PDB}$ = -0.92 to 0.80 ‰ and $\delta^{18}O_{PDB}$ = -12.19 to -6.73 ‰. An exception is the sample from the locality Hrádok, having substantially different oxygen ($\delta^{18}O_{PDB}$ = -17.94 ‰) as well as carbon ($\delta^{13}C_{PDB}$ = -5.59 ‰) isotope composition, enriched substantially in light isotopes of both elements. At the first five samples (Chyžné 12/G, 13/G, Ochtiná 5/G, Markuška 3/G and Jelšava 5/G) the differences in carbon isotope composition are small, they vary in the range of -1 to +1 ‰. They are similar to marine shallow-water sediments, at the diagenesis of which meteoric water played an important role. Differences in the

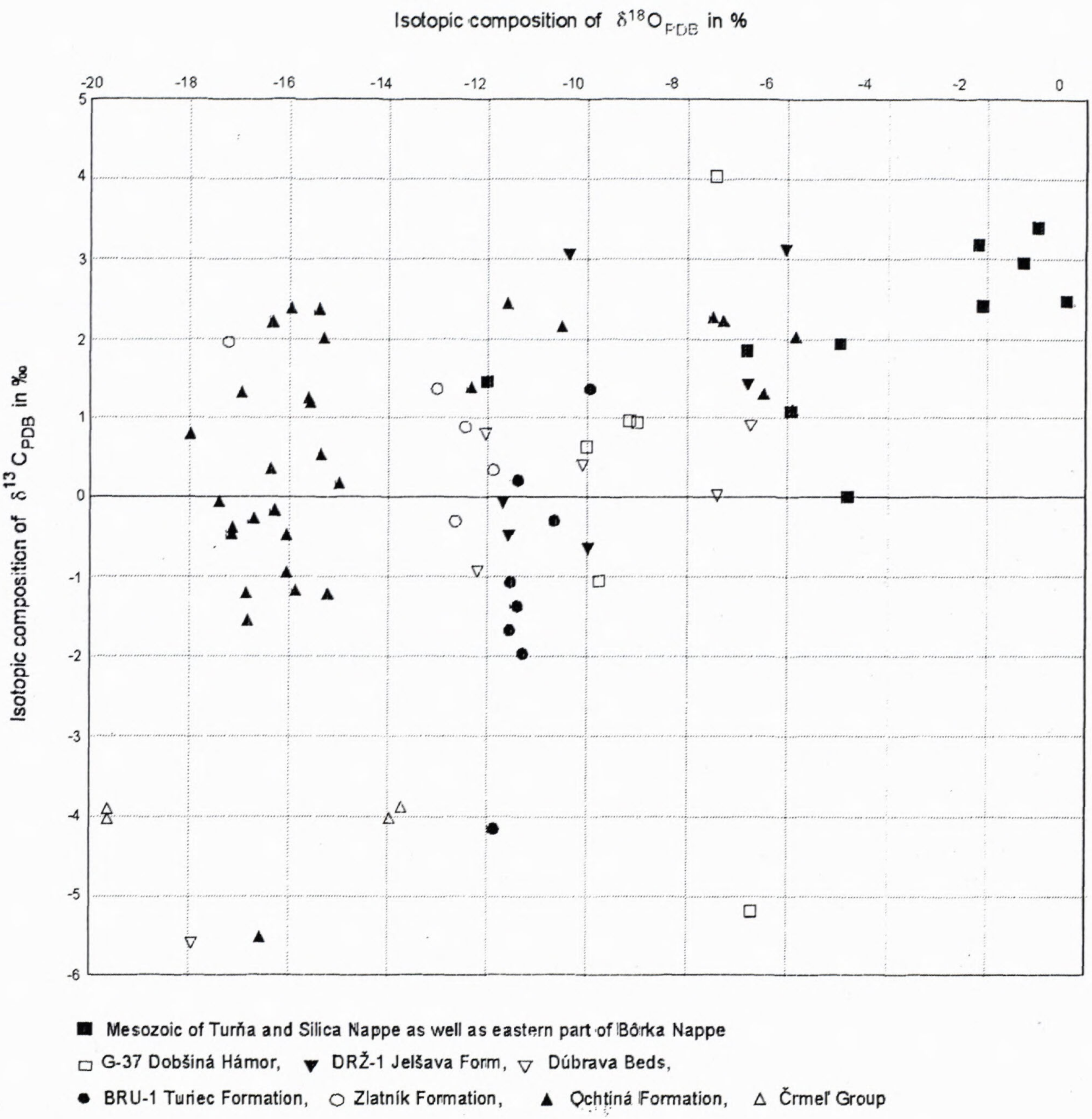
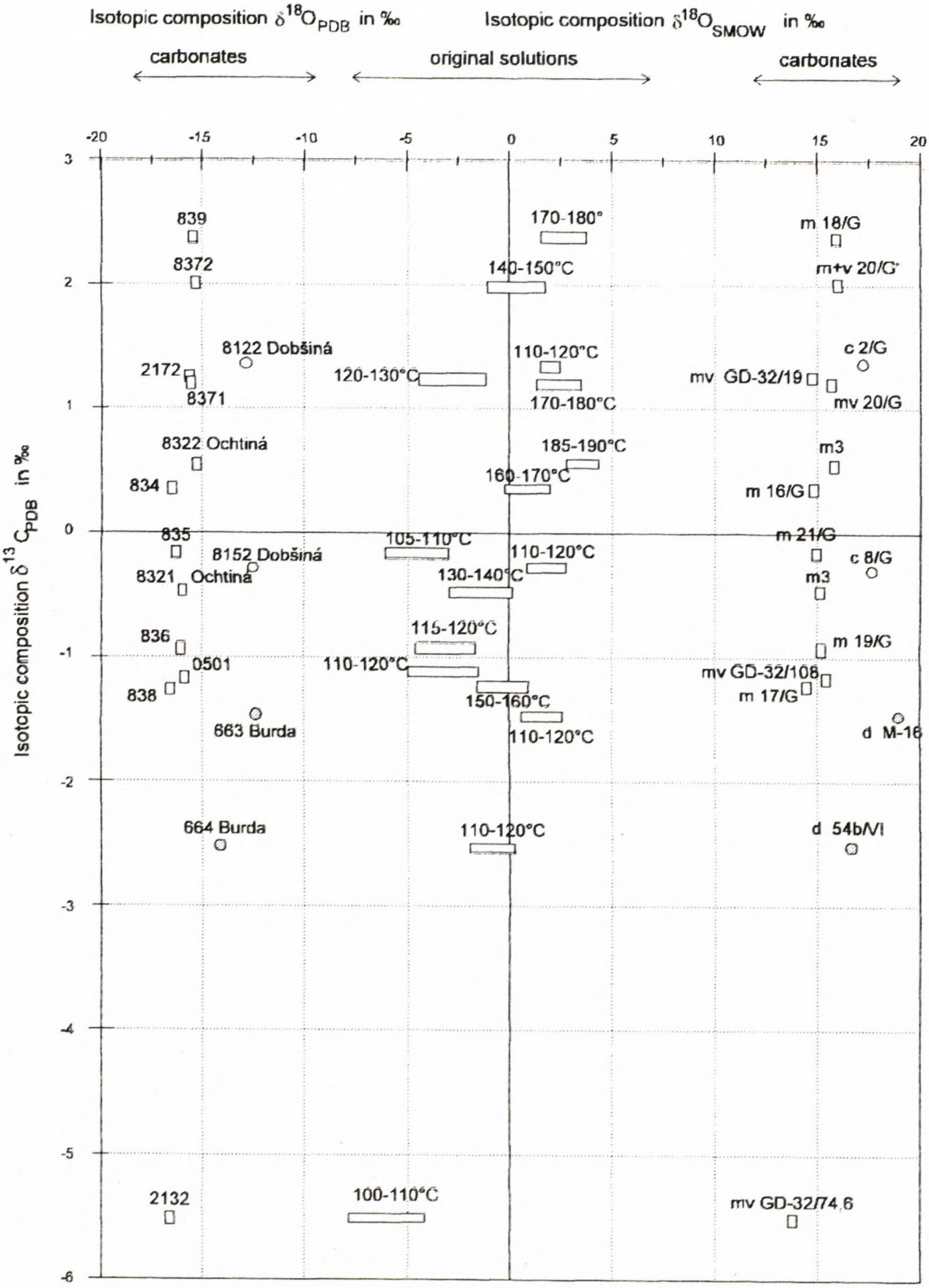


Fig. 7 Isotope composition of oxygen and carbon in the studied carbonates.

isotope composition of oxygen are more significant. Samples of Chyžné 12/G, 13/G have $\delta^{18}O_{PDB}$ values near to -7 ‰, similarly as higher-metamorphosed Mesozoic limestones. The other 3 samples (limestones from Ochtiná and dolomite from Jelšava) approach by their isotope composition of $\delta^{18}O_{PDB}$ = -12.19 to -10.08 ‰ the composition of carbonates from the Zlatník Formation, Brusník anticline as well as the borehole G-37. Very marked is the distribution of projection points on the graph of O/C isotope relationship (Fig. 7). Metamorphic manifestations and pressure effects of the same character have been recorded in petrographic description of samples of these rocks. It is evident that isotope composition of C and O in the described set of carbonates had been influenced primarily by metamorphic solutions. The relationship of Sr/Ca to Mn, the generally low REE contents and relative enrichment in LREE indicate, in controversy with isotope composition, rather deep-water environment of origin.



c - calcite, d - dolomite, m - magnesite, v - vein or veinlet

xxxx - laboratory number (on the left side of the Fig.) xxXX - geological number (on the right side of the Fig.)

xxx-xxx°C - TVI decrepitation temperatures

▭ - assumpionaly range of the isotopic compositioin of the original solutions

Fig. 8 Isotope composition of carbonates and their source solutions with TVI temperatures.

tab. 5

Laboratory number	Carbonate	*Zones of metamorphism	Geological number	Lokality	Occurrence	Formation	Age	Measured isotopic composition of carbonates in permil δ 13CPDB	δ 18OPDB	δ 18OSMOW
O1_623	limestone			Dobšiná	ice cave		Senonian	0.01	-4.79	25.92
O1 891	limestone	ANC	5/92	Bôrka		Bôrka Nappe	Jurassic?	1.46	-12.00	18.50
O1 885	limestone	DIA	7/92	Ostrý vrch		Silica Nappe	Norian	2.96	-1.26	29.57
O1 890	limestone	DIA	11/92	Silická Brezová	quarry	Silica Nappe	Norian	2.47	-0.40	30.46
O1 887	limestone	DIA	12/92	Silická Brezová	quarry	Silica Nappe	Middle Norian	3.41	-0.99	29.84
O1 883	limestone	ANC	4/92	Dvorníky		Turňa Nappe	Karnian	1.08	-5.93	24.75
O1 892	limestone	UPGSF	6/92	Medzev		Bôrka Nappe	Karnian	1.85	-6.81	23.85
O1 888	limestone	ANC	10/92	Jelšavská Teplica		Turňa Nappe	Karnian	3.18	-2.17	28.63
O1 886	limestone	ANC	9/92	Jelšavská Teplica		Turňa Nappe	Anisian	2.42	-2.09	28.71
O1 810	limestone	ANC-GSF	6/G	Honce	quarry	Turňa Nappe	Middle-Late Triassic	1.94	-4.95	25.76
O1 825	dolomite	UPGSF	11/G	Jelšava	old quarry	Dúbrava Beds	Jurassic?	-0.92	-12.19	19.51
O1 829	limestone	UPGSF	13/G	Chyžné	quarry, S from the Chyžné	Dúbrava Beds	Jurassic?	0.90	-6.73	23.93
O1 820	limestone	UPGSF	12/G	Chyžné	quarry, S from the Chyžné	Dúbrava Beds	Jurassic?	0.03	-7.41	23.23
O1 809	limestone	UPGSF	5/G	Ochtiná	quarry	Dúbrava Beds	Jurassic?	0.41	-10.08	20.47
O1 811	limestone	UPGSF	3/G	Markuška	quarry	Dúbrava Beds	Jurassic?	0.80	-12.03	18.46
O1 824	dolomite	UPGSF	9/G	Hrádok	exposure	Dúbrava Beds	Jurassic?	-5.59	-17.94	13.58
O1 494	limestone	GSF		Dobšiná-Hámor	borehole G-37/652,5	Foederata Group	Triassic	0.64	-10.01	20.54
O1 490	limestone	GSF		Dobšiná-Hámor	borehole G-37/850,5	Foederata Group	Triassic	-1.05	-9.75	20.81
O1 492	limestone	GSF		Dobšiná-Hámor	borehole G-37/879,0	Foederata Group	Triassic	4.05	-7.44	23.20
O1 4912	dolomite	GSF		Dobšiná-Hámor	borehole G-37/882,0	Foederata Group	Triassic	0.97	-9.16	21.42
O1 4911	limestone	GSF		Dobšiná-Hámor	borehole G-37/882,0	Foederata Group	Triassic	-5.19	-6.69	23.97
O1 489	limestone	GSF		Dobšiná-Hámor	borehole G-37/898,0	Foederata Group	Triassic	0.95	-9.00	21.59
O1 914	calcite	DIA-ANC		Držkovce	borehole DRŽ-1/179,1-4	Jelšava Formation	Lower Triassic	3.06	-10.37	20.18
O1 913	limestone	DIA-ANC		Držkovce	borehole DRŽ-1/236,6-237	Jelšava Formation	Lower Triassic	-0.65	-9.96	20.60
O1 915	limestone	DIA-ANC		Držkovce	borehole DRŽ-1/418,5-8	Jelšava Formation	Lower Triassic	-0.48	-11.56	18.95
O1 912	limestone	DIA-ANC		Držkovce	borehole DRŽ-1/443,6-444	Jelšava Formation	Lower Triassic	-0.07	-11.68	18.83
O1 916	dolomite	DIA-ANC		Držkovce	borehole DRŽ-1/1183,7	Perkupa Formation	U. Permian - L. Triassic	1.43	-6.79	25.08
O1 908	dolomite	DIA-ANC		Držkovce	borehole DRŽ-1/1203,8	Perkupa Formation	U. Permian - L. Triassic	3.12	-6.05	24.62
O1_791	limestone	LPGSF		Brusník	borehole BRU-1/76	Turiec Formation	Upper Carboniferous	1.37	-9.93	20.63
O1 795	limestone	LPGSF		Brusník	borehole BRU-1/86	Turiec Formation	Upper Carboniferous	0.20	-11.38	19.13
O1 7921	limestone	LPGSF		Brusník	borehole BRU-1/95,8	Turiec Formation	Upper Carboniferous	-0.29	-10.66	19.88
O1 7922	calcite veinlet			Brusník	borehole BRU-1/95,8	Turiec Formation	Upper Carboniferous	-4.15	-11.85	18.64
O1 7931	limestone	LPGSF		Brusník	borehole BRU-1/111,5	Turiec Formation	Upper Carboniferous	-1.07	-11.52	18.99
O1 7932	calcite veinlet			Brusník	borehole BRU-1/111,5	Turiec Formation	Upper Carboniferous	-1.67	-11.54	18.97
O1 7981	limestone	LPGSF		Brusník	borehole BRU-1/114	Turiec Formation	Upper Carboniferous	-1.37	-11.40	19.11
O1 7982	calcite veinlet			Brusník	borehole BRU-1/114	Turiec Formation	Upper Carboniferous	-1.96	-11.28	19.24
O1 8121	limestone	ANC	2/G	Dobšiná	exposure	Zlatník Formation	Upper Carboniferous	0.89	-12.45	18.03
O1 8122	calcite veinlet		2/G	Dobšiná	exposure	Zlatník Formation	Upper Carboniferous	1.37	-13.02	17.44
O1 8151	limestone	ANC	8/G	Dobšiná	quarry behind the asbestos quarry	Zlatník Formation	Upper Carboniferous	0.35	-11.88	18.62
O1 8152	calcite veinlet		8/G	Dobšiná	quarry behind the asbestos quarry	Zlatník Formation	Upper Carboniferous	-0.30	-12.64	17.84
O1 830	limestone	ANC-GSF	22/G	Dobšinská Maša	exposure	Zlatník Formation	Upper Carboniferous	1.95	-17.23	13.11
O1 666	calcite	LPGSF	1/M	Burda	mine	Ochtiná Formation	Lower Carboniferous	1.31	-6.47	24.20
O1_822	limestone	LPGSF	3	Burda	left site of cuarry	Ochtiná Formation	Lower Carboniferous	2.03	-5.85	24.81
O1_823	limestone	LPGSF	2	Burda	right site of quarry	Ochtiná Formation	Lower Carboniferous	1.10	-5.90	24.78
O1 8412b	dolomite	LPGSF		Košice	borehole KV-6/290	Ochtiná Formation	Lower Carboniferous	2.45	-11.58	20.14
O1 8412a	limestone	LPGSF		Košice	borehole KV-6/290	Ochtiná Formation	Lower Carboniferous	2.17	-10.50	20.04
O1 8411	calcite veinlet			Košice	borehole KV-6/290	Ochtiná Formation	Lower Carboniferous	-1.20	-15.21	15.18
O1 816	calcite	LPGSF	7/G	Markuška	cut in the brook	Ochtiná Formation	Lower Carboniferous	2.28	-7.49	23.14
O1 816 C.	calcite(control.a.)	LPGSF	7/G	Markuška		Ochtiná Formation	Lower Carboniferous	2.23	-7.28	23.36
O1 826	dolomite	GSF	10/G	Hrádok	exposure	Ochtiná Formation	Lower Carboniferous	-0.06	-17.42	14.12
O1_828	dolomite	LPGSF	14/G	Dúbrava	mine Miková	Ochtiná Formation	Lower Carboniferous	1.39	-12.31	19.38
O1 831	dolomite	LPGSF	1	Ochtiná	lower part of quarry	Ochtiná Formation	Lower Carboniferous	2.39	-15.96	15.62
O1 827	dolomite	LPGSF	15/G	Dúbrava	mine Miková	Ochtiná Formation	Lower Carboniferous	0.80	-17.99	13.53
O1 833	dolomite	LPGSF	2	Ochtiná	lower part of quarry	Ochtiná Formation	Lower Carboniferous	2.21	-16.34	15.23
O1 2171	magnesite	LPGSF		Košice	borehole GD-32/19	Ochtiná Formation	Lower Carboniferous	1.32	-16.96	14.30
O1 2172	magnesite	LPGSF		Košice	borehole GD-32/19	Ochtiná Formation	Lower Carboniferous	1.26	-15.61	14.77
O1 2121	magnesite	LPGSF		Košice	borehole GD-32/66,5	Ochtiná Formation	Lower Carboniferous	-1.55	-16.82	14.45
O1 2132	magnesite	LPGSF		Košice	borehole GD-32/74,6	Ochtiná Formation	Lower Carboniferous	-5.51	-16.57	13.78
O1_0501	magnesite	LPGSF		Košice	borehole GD-32/108	Ochtiná Formation	Lower Carboniferous	-1.16	-15.87	15.43
O1 0502	magnesite	LPGSF		Košice	borehole GD-32/108	Ochtiná Formation	Lower Carboniferous	0.18	-14.99	16.34
O1 834	magnesite	LPGSF	16/G	Košice	mine	Ochtiná Formation	Lower Carboniferous	0.36	-16.37	14.91
O1 579	magnesite	LPGSF		Košice		Ochtiná Formation	Lower Carboniferous	-0.45	-17.16	13.18
O1 577	magnesite	LPGSF		Košice		Ochtiná Formation	Lower Carboniferous	-0.26	-16.71	13.63
O1 8322	magnesite	LPGSF	3	Ochtiná	back part of quarry	Ochtiná Formation	Lower Carboniferous	0.54	-15.35	15.96
O1 8321	magnesite	LPGSF	3	Ochtiná	back part of quarry	Ochtiná Formation	Lower Carboniferous	-0.47	-16.06	15.24
O1 578	magnesite	LPGSF		Košice		Ochtiná Formation	Lower Carboniferous	-0.38	-17.14	13.19
O1_838	magnesite	LPGSF	17/G	Košice	mine V-601	Ochtiná Formation	Lower Carboniferous	-1.20	-16.86	14.41
O1 8371	magnesite	LPGSF	20/G	Košice	mine PB-05-01	Ochtiná Formation	Lower Carboniferous	1.21	-15.58	15.73
O1 8372	magnesite		20/G	Košice	mine PB-05-01	Ochtiná Formation	Lower Carboniferous	2.01	-15.30	16.02
O1 835	magnesite	LPGSF	21/G	Košice	mine PB-05-02	Ochtiná Formation	Lower Carboniferous	-0.16	-16.29	14.99
O1 836	magnesite	LPGSF	19/G	Košice	mine PB-05-03	Ochtiná Formation	Lower Carboniferous	-0.93	-16.05	15.24
O1 839	magnesite	LPGSF	18/G	Košice	mine SB-05-2	Ochtiná Formation	Lower Carboniferous	2.37	-15.40	15.91
O1 813	limestone	GSF	1/G	Črmeľ údolie	exposure	Črmeľ Group	Early Carboniferous	-3.87	-13.72	16.71
O1_813	limestone	GSF	1/G	Črmeľ údolie	exposure	Črmeľ Group	Early Carboniferous	-4.01	-13.96	16.48
O1 840	magnesite	GSF	4/GB	Kavečany	quarry SE from altitude H. bok	Črmeľ Group	Early Carboniferous	-3.90	-19.63	11.55
O1 842	magnesite	GSF	4/GA	Kavečany	quarry SE from altitude H. bok	Črmeľ Group	Early Carboniferous	-4.03	-19.64	11.54

*Zones of Metamorphism: DIA-ANC = zone of diagenesis - zone of anchimetamorphosis; ANC = zone of anchimetamorphosis; ANC-GSF = zone of anchimetamorphosis - green schist facies; UPGSF = upper part green schist facies; GSF = green schist facies; LPGSF = lower part green schist facies

Isotopic composition of O & C of some carbonates from the Ochtiná and Zlatník Formation, their TVI decrepitation temperature and probable isotopic composition of original solutions
[calculated according to Aharon1988]

Laboratory number	Carbonates	Notice	Geol. number	Locality	Occurrence	Formation	Age*	Measured isotopic composition of carbonates in ‰			TVI	TVI	Calculated isotopic composition of original solutions with M1, D1 in ‰		Calculated isotopic composition of original solutions with M2, D2 in ‰	
								δ 13CPDB	δ 18OPDB	δ 18OSMOW	in °C from	in °C to	δ 18OSMOW from	δ 18OSMOW to	δ 18OSMOW from	δ 18OSMOW to
8152	calcite	secondary veinlet	8/G	Dobšiná	quarry behind the asbestos quarry	Zlatník Formation	U.C.	-0.295	-12.638	17.835	100	120	0.77	2.75		
8122	calcite	secondary veinlet	2/G	Dobšiná	exposure	Zlatník Formation	U.C.	1.368	-13.020	17.441	110	120	1.40	2.35		
864	dolomite		54b/VI	Burda	mine, O. level	Ochtiná Formation	L.C.	-2.538	-14.824	16.792	110	120	-0.81	0.23	-1.92	-0.82
863	dolomite		M-16	Burda	mine, I. level	Ochtiná Formation	L.C.	-1.480	-12.544	19.146	110	120	1.55	2.59	0.44	1.54
8321	magnesite	coarse-crystalline	3	Ochtiná	back part of quarry	Ochtiná Formation	L.C.	-0.471	-16.056	15.236	130	140	-0.75	0.12	-2.90	-1.86
8322	magnesite	fine-grained	3	Ochtiná	back part of quarry	Ochtiná Formation	L.C.	0.539	-15.352	15.962	185	190	4.06	4.37	2.72	3.08
2132	magnesite	veinlet		Košice	borehole GD-32/74,6	Ochtiná Formation	L.C.	-5.514	-16.568	13.784	100	110	-5.25	-4.15	-7.99	-6.69
835	magnesite	fine-grained	21/G	Košice	mine PB-05-02	Ochtiná Formation	L.C.	-0.158	-16.292	14.992	105	110	-3.46	-2.94	-6.13	-5.48
0501	magnesite	veinlet		Košice	borehole GD-32/108	Ochtiná Formation	L.C.	-1.161	-15.869	15.429	110	120	-2.50	-1.50	-5.04	-3.83
836	magnesite	fine-grained	19/G	Košice	mine PB-05-03	Ochtiná Formation	L.C.	-0.934	-16.048	15.244	115	120	-2.19	-1.69	-4.62	-4.02
2172	magnesite	veinlet		Košice	borehole GD-32/19	Ochtiná Formation	L.C.	1.260	-15.614	14.767	120	130	-2.16	-1.22	-4.49	-3.37
8371	magnesite	vein of white magnesite	20/G	Košice	mine PB-05-01	Ochtiná Formation	L.C.	1.207	-15.578	15.729	170	180	2.87	3.52	1.33	2.12
8372	magnesite	veinlets in the white magnesite	20/G	Košice	mine PB-05-01	Ochtiná Formation	L.C.	2.008	-15.299	16.017	140	150	0.90	1.70	-1.08	-0.11
838	magnesite	coarse-grained	17/G	Košice	mine V-601	Ochtiná Formation	L.C.	-1.198	-16.858	14.408	150	160	0.09	0.85	-1.72	-0.82
834	magnesite	medium-grained	16/G	Košice	mine	Ochtiná Formation	L.C.	0.357	-16.373	14.909	160	170	1.35	2.05	-0.32	0.51
839	magnesite	medium-grained	18/G	Košice	mine SB-05-2	Ochtiná Formation	L.C.	2.374	-15.403	15.909	170	180	3.05	3.70	1.51	2.30

Age*: U.C. - the Upper Carboniferous, L.C. - the Lower Carboniferous

The very different isotope composition of dolomite from the locality Hrádok (9/G) may have been influenced by meteoric water penetrating along the Hrádok thrust line near which the sample was collected.

Mesozoic carbonates of the Silica and Turňa Nappes

Mesozoic limestones of the Silica Nappe are the least metamorphosed carbonate sediments from the studied set. They formed in marine neritic environment. Data on isotope composition of oxygen - $\delta^{18}O_{PDB}$ = -17 to -0.40 ‰ show that their diagenesis took place in marine environment as well. The $\delta^{13}C_{PDB}$ values of these limestone vary from 2.42 to 3.41 ‰. Similar data from limestones of this type have been presented by KANTOR et al. (1992) and FABRÍCIUS et al. (1970) from brachiopod and mollusc tests from Hallstatt limestones of Eastern Alps. The authors calculated from these data water environment temperature with values of 16.7 to 29.7 °C. From data of our analyses we calculated paleotemperatures according to EPSTEIN et al. (1953), varying in the range of 18.2 - 25.6 °C, if we consider the $\delta^{18}O_{SMOW}$ value of marine water 0 ‰. The results of these calculation are listed in Tab. 7. For a comparison there is included the paleotemperature calculation for two samples of the Turňa Nappe (Dvorníky, Honce, Jelšavská Teplica), a sample from the eastern occurrences of the Bôrka Nappe (Medzev, Bôrka) and of the lowest-metamorphic Carboniferous limestone. For these four samples, disproportionally high temperatures have been obtained, even at water environment value of -1 ‰. The data indicate higher metamorphic grade of these samples.

Table 7

Sample No.	Locality	$\delta^{18}O_{PDB}$‰	t°C at	
			dw=-1	dw=0
887	Silická Brezová	-0.99	16.5	20.9
890	Silická Brezová	-0.40	14.0	18.2
885	Ostrý vrch	-1.26	17.6	22.1
886	Jelšavská Teplica	-2.09	21.4	26.1
888	Jelšavská Teplica	-2.17	21.7	26.5
883	Dvorníky	-5.93	41.1	46.9
810	Honce	-4.95	35.7	41.2
892	Medzev	-6.81	46.2	52.3
823	Burda 2	-5.90	40.9	46.0

Bôrka Nappe (eastern part)

The second group of samples of Mesozoic age consists of Triassic and Jurassic (?) limestones of the eastern part of the Bôrka Nappe. In comparison with the previous group, its isotope composition is different - higher contents of light oxygen as well as carbon isotopes ($\delta^{13}C_{PDB}$ 1.09 to 1.85 ‰, $\delta^{18}O_{PDB}$ - 12 to -4.95 ‰). The results indicate higher metamorphic grade, documented also by the calculated paleotemperatures (Fig. 8). Metamorphism has been proved also in the sample from Medzev - Šugov Valley, where crystalline limestones occur in association with glaucophanites. Exceptionally high light oxygen isotope contents are in the sample from Bôrka, indicating the highest metamorphic grade from the sample group studied.

KANTOR and MIŠÍK (l.c.) presented in their work $\delta^{13}C_{PDB}$ values for different limestone and dolomite types of Mesozoic age from the Western Carpathians ranging from 0.68 to 3.58 ‰, $\delta^{18}O_{PDB}$ -8.01 to - 0.48 ‰, and LINTNEROVÁ et al. (l.c.) from the Veterlín Series of the Malé Karpaty Mts. $\delta^{13}C_{PDB}$ of 0.5 to 3.6 ‰ and $\delta^{18}O_{PDB}$ of -6.3 to -2.2 ‰. The isotope composition of limestones from the Malé Karpaty Mts. has been interpreted by these authors as influenced by meteoric water during diagenesis of a part of the studied limestones. This problem has been studied in greater detail by LINTNEROVÁ in MICHALÍK et al. (1993).

We extended the original sample material to include also samples from the borehole DRŽ-1 (Držkovce), which was complexly lithologically as well as stratigraphically evaluated in the final report of MELLO et al. (1994). We analysed four limestone samples from the Jelšava Beds (Lower Triassic) and two dolomite samples from the Perkupa Formation (Upper Permian-Lower Triassic). Both lithostratigraphic sequences belong to the Turňa Nappe (Turnaicum).

On the basis of data on isotope composition of carbon it may be stated that limestone from the depth 179.1 m formed in deeper-marine environment ($\delta^{13}C_{PDB}$ = 3.06 ‰). Isotope composition of oxygen ($\delta^{18}O_{PDB}$ = -10.37 ‰) would indicate higher temperature at deep burial of the sediments during diagenetic alterations, without the participation of meteoric water. The rest of limestone samples (from depths of 236, 418 and 443 m) indicate shallow-water environment ($\delta^{13}C_{PDB}$ = -0.05 to -0.07 ‰) and the presence of surface water in diagenetic processes.

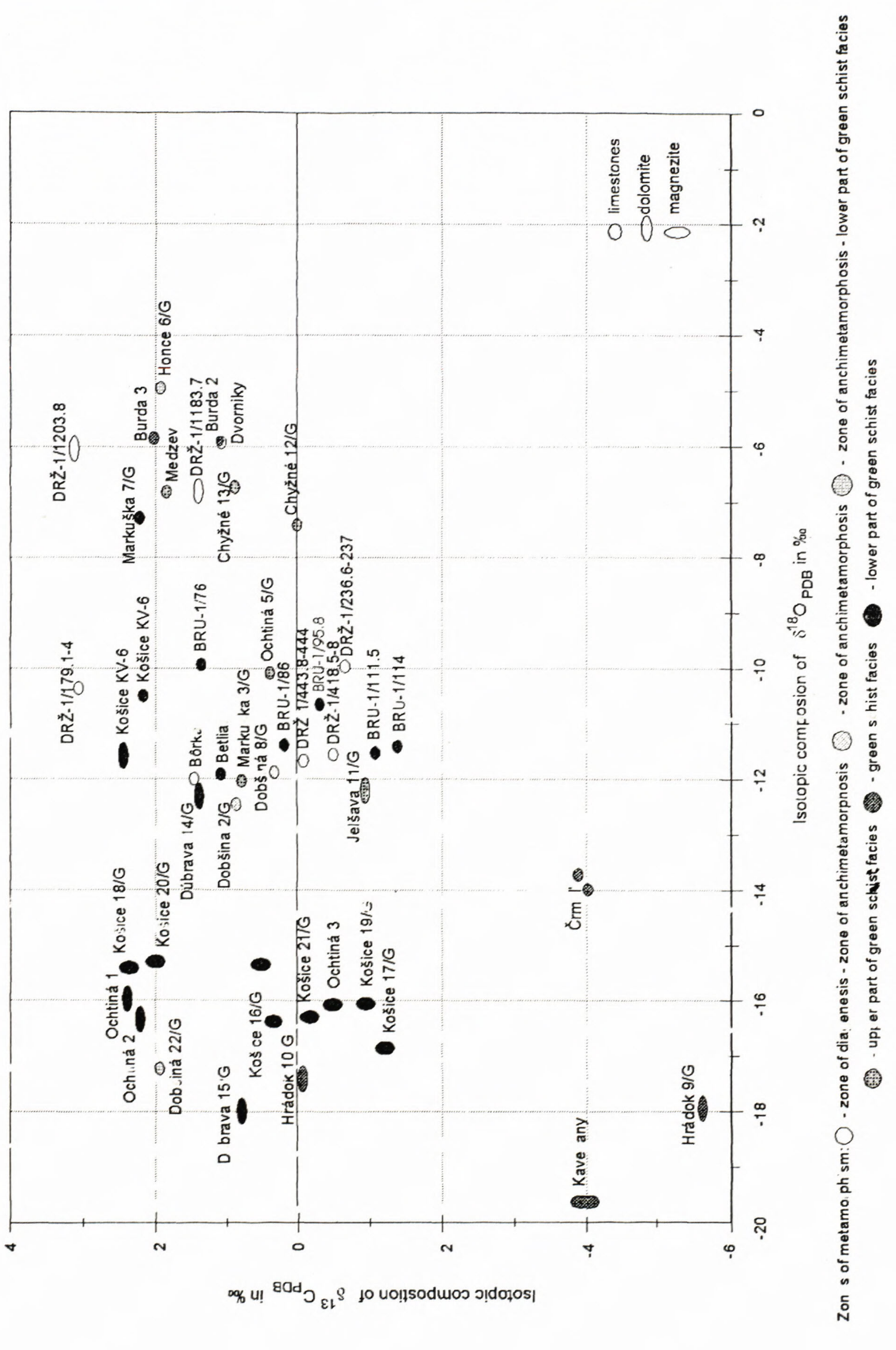


Fig 9 Relationship of the isotope composition of O and C in carbonates depending on the grade of regional metamorphism.

Dolomites from the lower part of the evaporite formation (from depths of 1183, 1203 m) contain more heavy oxygen as well as carbon isotope than limestones from the upper part of the formation. Since at these samples we must also assume alterations in greater depths, we must consider the isotope composition (enrichment in heavy O, C isotopes) to be a product of hypersaline environment, similar to "sebkhas" of the Persian Gulf. The presence of a several 100 m thick evaporite layer supports the probability of the formation of the studied dolomites in this way. Dolomites of such origin have not been so far isotopically recorded in the Western Carpathians.

KANTOR and MIŠÍK (1992) proved on the basis of their isotope composition the formation of the dolomites in schisohaline environment.

Foederata Group of Veporicum

Sample material comes from the borehole G-37 (Dobšiná-Hámor),from which there are not sufficient data on its stratigraphic classification. Material from the borehole has not been evaluated in detail - according to present knowledge the rocks from the depth 625 - 989 m, the analyses of which are presented, should belong to the Mesozoic metamorphic complex of the Foederata Group, which is a part of the Veporicum crystalline complexes. In this levels of the borehole, there occurred also evaporite sediments (850 - 868 m), which, on the basis of the isotope composition of sulphur, were classified by Kantor (KANTOR et al., 1982) as Middle to Upper Triassic.

Isotope composition of carbon and oxygen in 4 limestone and 1 dolomite sample are characterised by considerable variability. We assume that the great variability in the isotope composition of carbon indicates frequent changes of sedimentation environment during the formation of carbonate shallow-water rocks (from depths of 625.5, 850.5 and 898 m) having $\delta^{13}C_{PDB}$ of -1 to +1 ‰ and hypersaline ones from the depth of 879 m ($\delta^{3}C_{PDB}$ = 4.05 ‰).

Isotope composition of oxygen in all samples indicates higher grade of pressure reworking which underwent rocks in the lower part of the borehole G-37. This is indicated also by the distribution of gypsum and anhydrite, which, except for a continuous layer, occurs in the carbonate rocks in the form of an irregular network of fine veinlets (Tab. 5, Fig. 7).

For a comparison, the sample of the Senonnian freshwater limestone from the Dobšiná ice cave has, consistently with its origin, the lowest content of heavy carbon isotope, approaching zero value.

Application of thermometric study and isotope analyses in determination of possible isotope composition of source solutions of the studied carbonates

From the studied set of carbonate samples, suitable ones were selected for thermometric investigations. Decrepitation TVI analysis yielded values in the range of 100 to 190 °C measured on sixteen samples, which could be evaluated (Tab.6). These temperatures are more or less consistent also with the relationship of the liquid and gaseous phase observed at microscopic study of the carbonates.

Results of TVI decrepitation analyses and isotope analyses of oxygen - $\delta^{18}O_{SMOW}$ of the studied carbonates have been used to calculate estimated isotope composition of the source solutions. The relation of fractionation alpha factors between the carbonates and water has the following general form:

$$1000 \ln a_{carbonate-water} = \delta_{carbonate} - \delta_{water} = A.10^6.T^{-2} + B,$$

where T is absolute temperature and A and B are constants. In our case, we used constants applied by AHARON (1988):

	A	B
for $CaCO_3$	2.78	-2.89
for $dolomite_1$	3.06	-3.24
for $dolomite_2$	3.23	-3.29
for $magnesite_1$	2.95	-2.16
for $magnesite_2$	3.53	-3.58

Estimated values of oxygen isotope composition in source solutions of the carbonates studied, based on measured TVI decrepitation temperatures and oxygen isotope composition in SMOW, are listed in Tab. 6. We used for calcites one set of constants, for dolomites and magnesites both (above). These data are in the graph on Fig. 8. We consider here values calculated using constants for $magnesite_2$ and $dolomite_2$.

TVI decrepitation temperature of secondary carbonate veinlets varies from 100 to 130 °C. Estimated isotope composition of oxygen in source solutions is different for various carbonates, the TVI decrepitation temperatures of which vary from 100 to 130 °C.

E.g., for magnesite from the sample 01_2132 (Košice borehole GD-32) it is as much as -7.99 ‰ d18OSMOW, which suggests enrichment of source solutions by meteoric water. Interesting is the value of d13CPDB in this sample - -5.51 ‰. It is practically the isotopically lightest carbon in the whole set studied. Lower values of isotope composition of oxygen in source solutions are obtained also from magnesite veinlets of the same borehole, from the depth 108 and 190 m. $\delta^{13}C_{PDB}$ in these two samples is near to zero ($\pm$ 1 ‰).

Low TVI decrepitation temperatures (105 to 120 °C) were measured in samples 19/G and 21/G with $\delta^{18}O_{SMOW}$ +15.1 $\pm$0.1 ‰. They are fine-grained magnesites for which we estimate isotope composition of oxygen in the source solutions between $\delta^{18}O_{SMOW}$ -5 and -6 ‰.

On the basis of thermometric and isotope studies we can assume that magnesite veinlets in the borehole GD-32 from the depth 19 and 108 m formed under the same conditions and from similar source as fine-grained magnesites of the samples 19/G and 21/G.

Another group consists of coarse-grained to medium-grained magnesites of the samples 16/G, 17/G, 18/G and 20/G from Košice, for which TVI decrepitation temperatures have been determined in the range of 140 to 180 °C. Isotope composition of these magnesites is $\delta^{13}C_{PDB}$ from -1.2 to +2.4 ‰, $\delta^{18}O_{PDB}$ from -16.85 to -15.4 and $\delta^{18}O_{SMOW}$ from +14.4 to +16.1 ‰. Similar data on isotope composition of magnesites from Košice have been presented by GUILLOU and LETOLLE (1986). These data allow to assume common origin for this group of magnesites. This is supported also by the calculated isotope composition of oxygen in source solution, varying in the range of $\delta^{18}O_{SMOW}$ -1.7 to +1.5 ‰. Such isotope composition of oxygen in source solution is near to isotope composition of oxygen in marine water.

We are confronted with a noteworthy situation concerning the magnesite sample from Ochtiná 3 (Fig. 8). In this sample, coarse-grained magnesite (01_8321) is intersected by younger fine-grained magnesite (01_8322). For the coarse-grained magnesite, TVI decrepitation temperature of 130-140 °C has been measured. From these data, $\delta^{18}O_{SMOW}$ of -2.9 ‰ has been calculated for the source solution.

TVI decrepitation temperature for fine-grained magnesite is 185-190 °C, with $\delta^{18}O_{SMOW}$ of +2.42 ‰ for the source solution. In contrast to Košice, a higher TVI decrepitation temperature has been measured here for the more fine-grained type, and thus also a different oxygen isotope composition for the source solution. This means that fine-grained magnesite in Ochtiná formed at different conditions than in Košice.

For two dolomite samples from the mine Burda (01_663 and 01664) with the values of $\delta^{13}C_{PDB}$ -1.48 and -2.54 ‰, $\delta^{18}O_{PDB}$ -12.54 and -14.82 ‰, $\delta^{18}O_{SMOW}$ +10.15 and +16.79 ‰, respectively, TVI decrepitation temperatures have been measured for both samples in the range 110-120 °C. From this, values of oxygen isotope composition in source solution were estimated at $\delta^{18}O_{SMOW}$ +0.44 and -1.92 ‰. On the basis of these data it may be assumed that marine water participated in their formation.

At last, we shall mention isotope composition of two secondary calcite veinlets in limestones of the Zlatník Formation from Dobšiná (8/G and 2/G): $\delta^{13}C_{PDB}$ -0.29 and +1.37 ‰, $\delta^{18}O_{PDB}$ -12.64 and -13.02 ‰, $\delta^{18}O_{SMOW}$ +17.84 and +17.44 ‰. TVI decrepitation temperatures measured for these calcites were from 100 to 120 °C. From these values we may estimate the isotope composition of oxygen in source solution - $\delta^{18}O_{SMOW}$ +0.75 and +1.40 ‰. The source of oxygen in these solutions may have been in marine water (buried one as well).

Conclusions

Significantly higher concentrations of Mn, Sr, Na, U, Th and rare earth elements have been found in Carboniferous carbonates, as compared with carbonates with the Dúbrava Beds. With the exception of carbonates from the borehole BRU-1, no direct dependence of these elements on Al contents could be observed. These differences result from different sedimentation conditions (shallow-water, in places with increased salinity, vs. deep-water), as well as different interaction grade in the diagenetic system, influence of meteoric water, or chemical composition of metamorphic fluids.

REE contents as well as the course of normalised curve in Carboniferous carbonates are similar to values mentioned for sedimentary carbonates and magnesite deposits in the Eastern Alps. Dolomites and limestones of the Dúbrava Beds, to the contrary, approach by their low REE contents, more marked negative Eu anomaly as well as relative HREE enrichment in relation to LREE, the isotope composition of oceanic water.

Considerable depletion in REE occurred in magnesites, as well as relative enrichment of HREE in relation to LREE, in comparison with associated limestones and dolomites. We explain this by Mg-metasomatism of pre-existing dolomites, solutions enriched in Mg from the associated basic and ultrabasic rocks, although intraformational source (crinoid detritus) has been considered as well. This is indicated by general REE decrease, characteristic of basic and ultrabasic rocks, as well as enrichment in Cr, Ni, Co, Sc in some of the samples.

When evaluating the distribution of oxygen and carbon isotopes in carbonates of the sets studied we must bear in mind several standpoints, above all the sedimentation environment, age classification and grade of metamorphism (Fig. 9). Since geological structure of Gemericum is complex, the development of each rock group, or even of separate samples, was complicated, affected by polyphase processes.

The oldest, Lower Carboniferous carbonates belong to two sets - the Ochtiná Formation and the Črmeľ Group. Their extent of study, as far as isotope composition is concerned, is not the same. In the Ochtiná Formation significant differences may be observed in the isotope composition of oxygen, in the direction limestones - dolomites - magnesites. With advancing alteration, the proportion of the light oxygen isotope, and to a lesser extent also of carbon, increases. Rocks of the Ochtiná Formation are metamorphosed in conditions of the greenschist facies, values of their isotope composition correspond to the grade of metamorphism, age of the sediment as well as shallow-water sedimentation environment.

On the basis of isotope composition of magnesite from this formation we assume that alteration of limestones to magnesites occurred at the presence of solutions similar to marine water. This has been confirmed also by results of a detailed isotope and paleothermometric study, which has shown that two solution types participated in the formation of magnesites:

a) solutions, where $\delta^{18}O_{SMOW}$ of -1.7 to +1.5‰ is similar to the composition of marine water. These values have been calculated for coarse-grained magnesites with decrepitation temperature of 140-180 °C.

b) solutions with isotope composition of $\delta^{18}O_{SMOW}$ of -8 to -4.5‰, determined in magnesites with decrepitation temperatures of 100-130°C, in which influence of meteoric water is evident.

Isotope composition of carbon from carbonates of the Ochtiná Formation corresponds to marine carbonates.

Different isotope composition of carbon - higher content of the light isotope - has been recorded in rocks of the Črmeľ Group. In view of the small number of analysed samples we cannot consider it sufficiently representative. It could indicate the influence of freshwater environment at their formation, or diagenesis, or a connection with basic rocks associated with them in the Črmeľ Group.

The set of rocks from the borehole BRU-1 comes from a carbonate olistostrome of Upper Carboniferous age. The grade of metamorphism corresponds to the boundary anchizone - epizone. This is reflected in small differences in the isotope composition of oxygen and its higher values in relation to the Ochtiná Formation.

Approximately the same values of $\delta^{18}O$ and $\delta^{13}C$ are in samples from the Zlatník Formation, which are, as far as age is concerned, comparable with carbonates from the borehole BRU-1. They represent shallow-water organodetritic limestones, changed only to a very low metamorphic grade. Different values of $\delta^{18}O$ are in the sample from Dobšiná (22/G), the isotope composition of which has been affected by water circulating along the fault, near which the sample was located.

A separate group of samples are limestones from the Dúbrava Beds. Isotope composition of oxygen varies in them in the range of $\delta^{18}O_{PDB}$ -12 to -6‰, at small differences in the isotope composition of carbon. They are rocks metamorphosed in the upper part of the greenschist facies. Their isotope composition of oxygen has however higher values than in the weakly metamorphosed rocks of the Zlatník Formation, the equivalent of which it has been considered by a part of geologists (Fig. 8). To the contrary, the measured isotope composition of oxygen in some samples approaches values of metamorphic Mesozoic complexes of the Bôrka Nappe (Medzev - Šugov, Bôrka).

From this, affinity of the Dúbrava Beds to the metamorphic Mesozoic in the eastern occurrences of the Bôrka Nappe may be derived, as assumed in the geological map of Slovenské rudohorie - eastern part (BAJANÍK et al., 1984), Slovenský kras

(MELLO et al., 1992), as well as on the basis of petrographic analysis metabasaltic rocks of the Dúbrava Beds sequence.

Exceptionally different isotope composition (high content of the light carbon as well as oxygen isotope) displays the dolomite sample from Hrádok, originally also included into Dúbrava Beds. Its composition, however, reminds rather of carbonates of Lower Carboniferous age, enriched in light carbon. Similar values of isotope composition of carbon reach, besides samples from the Črmeľ Group, only secondary carbonate veinlets, in which we assume the participation of surface water in their formation.

Another problematic group are samples marked Burda 2,3. In the geological map of Slovenské rudohorie Mts. (l.c.), they were included into the Zlatník Formation. ABONYI (1971) correlated them with the Dúbrava Beds. During field investigation, even their classification with the Ochtiná Formation has not been omitted. However, their isotope composition trends to the Dúbrava Beds as well as limestones of the Ochtiná Formation from the underlier of the magnesite horizon. However, it is not possible to solve this problem unequivocally, due to the small number of analysed samples from this horizon.

We could distinguish in the Mesozoic rocks very well rocks of different grade of metamorphism (Silica, Turňa and Bôrka Nappes, Foederata Group), as well as different sedimentation conditions.

The results of the study of carbonate sediments of the Carboniferous to Mesozoic showed the possibility of application of this method and helped to solve some controversial problems. They may be used to parallelize rocks and to gain further, independent data on the condition of their formation, as well as subsequent processes. They also showed the necessity of a detailed knowledge of the studied rocks for correct interpretation of the results of isotope analyses.

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References

ABONYI A., 1971: Magnezitové ložiská Slovenska. In: Zborn. o nerudných surovinách Slovenska. Mineralia slovaca, (Bratislava), 3, 12–13, 319–342.

AHARON P., 1988: A stable isotope study of magnesite from the Rum Jungle Uranium field, Australia: Implications for the origin of strata-bound massive magnesites. Chem. Geol., 69, 127–145.

ALGEO T. J., WILKINSON, B.H., LOHMANN K.C., 1992: Meteoric-burial diagenesis of Middle Pennsylvanian limestones in the Orogrande Basin, New Mexico: Water/rock interactions and basin geothermics. J. Sed. Petrology, 62, 4, 652-670.

ARKAI P., KOVÁCS S., 1986: Diagenesis and regional metamorphism of the Mesozoic of Agtelek-Rudabanya Mountains (Northeast Hungary. Acta Geol. Hung., 26 (3-4), Budapest, 349-373.

BAJANÍK Š, IVANIČKA J., MELLO J., PRISTAŠ J., REICHWALDER P., VOZÁR J. & VOZÁROVÁ, A., 1984: Geologická mapa Slovenského rudohoria - východ, 1 : 50 000. Geol. Úst. D. Štúra, Bratislava.

BAJANÍK Š., PLANDEROVÁ E., 1985: Stratigrafická pozícia spodnej časti ochtinského súvrstvia gemerika medzi Magnezitovcami a Magurou. Geol. Práce, (Bratislava), Spr. 82, 67-76.

BAJANÍK Š., SNOPKOVÁ P. & VOZÁROVÁ, A., 1986: Litostratigrafia črmeľskej skupiny. Reg. geol. Záp. Karpát, Správy o geol.výskumoch, Geol. Úst. D. Štúra, Bratislava, 21, 65-68.

BATHURST R.G.C.,1975: Carbonate sediments and their diagenesis (2nd.ed.). Elsevier, Amsterdam, 620 p.

BOUČEK B., PŘIBYL A., 1960: Revision der Trilobiten aus dem Slovakischen Oberkarbon. Geol. Práce, (Bratislava), Spr. 20, 5-50.

BOYNTON W.V., 1984: Cosmochemistry of the rare earth elements: meteorite studies. In: Rare earth elements. Ed. Henderson P. Development in geochemistry 2, Elsevier.

BRAND U., VEIZER J.,1980: Chemical diagenesis of multicomponent carbonate system. 1.Trace elements. J. Sed. Petrol., 50, 1219-1236.

DEMOVIČ R., HOEFS J. & WEDEPOHL K. H., 1972: Geochemische Untersuchung an Travertinen. Contr. Mineral. Petrology, (Berlin-New York), 37, 15-28.

EBNER F., VOZÁROVÁ A., STRAKA P. & VOZÁR J., 1990: Carboniferous conodonts from Brusník Anticline (South Slovakia). In: Thirty years of geological cooperation between Austria and Czechoslovakia, D. Minaříková - H. Lobitzer (eds.),Vienna-Prague, 249-252.

EPSTEIN S., BUCHSBAUM R., LOWENSTAM H. A. & UREY, H.C., 1953: Revised carbonate-water temperature scale. Bull. Geol. Soc. Am., 64, 1315-1326.

FABRICIUS F., FRIEDRICHSEN H. & JACOBSHAGEN, V., 1970: Paläotemperaturen und Paläoklima in Obertrias und Lias der Alpen. Geol. Rdsch., (Stuttgart), 59, 2, 805-826.

FOLK R. L., LAND L. S., 1975: Mg/Ca ratio and salinity: two controls over crystallization of dolomite. Am. Assoc. Petroleum Geologists Bull., v.59, 60-68.

FUSÁN O., 1959: Poznámky k mladšiemu paleozoiku gemeríd. Geol. Práce, (Bratislava), Zoš. 55, 171-181.

GUILLOU J. J., LETOLLE R., 1986: Origine mixte chemique des dépots de magnésite antérieurs au Jurassique en milieu marin confiné, marginal-littoral. C. R. Acad. Sc. Paris, 303, Série II, 207- 212.

HLADÍKOVÁ J., ELIÁŠOVÁ, H. & ELIÁŠ, M., 1987: Podmínky sedimentace diageneze štramberských vápenců. Conditions of sedimentation and diagenesis of the Štramberk Limestone. Čas. Mineral. Geol., (Praha), 32, 3, 271-285.

JOHANNES W., 1970: Zum Enstehung von Magnesitvorkommen. N. Jb. Min. Abh., 113(3), 274-325.

KANTOR J., RYBÁR M., ELIÁŠ, K., ĎURKOVIČOVÁ, J.& GARAJ M., 1981: Metodika izotopovej paleotermometrie a paleoekológie podľa vápnitých schránok fosílií. Manuskript - Geofond, Bratislava.

KANTOR J., ĎURKOVIČOVÁ J., ELIÁŠ K., RYBÁR M., GARAJ M. & FERENČÍKOVÁ, E., 1982: Genetická charakteristika evaporitov Západných Karpát podľa izotopov síry. Manuskript - Geofond, Bratislava.

KANTOR J., HARČOVÁ E. & ĎURKOVIČOVÁ J., 1986: Použitie izotopov v schránkach organizmov, sedimentoch a sádrovcoch pre charakteristiku vodného prostredia a genézy na príklade panónu z Pezinka, bádenu z Devína - Dev. N. Vsi. a jury -kriedy od Kostolca. Manuskript - Geofond, Bratislava.

KANTOR J., HARČOVÁ E. & ŠÚTOVSKÁ, K., 1990: Izotopové zloženie foraminifér ako indikátor podmienok sedimentácie sečianskych vrstiev karpatu (vrt LKŠ-1, asi 15 km jz. od Lučenca). Manuskript - Geofond, Bratislava.

KANTOR J., FORDINÁL K & HARČOVÁ E., 1992: Izotopové zloženie bádenských mäkkýšov z vrtu HGP-3 od Stupavy. Manuskript - Geofond, Bratislava.

KANTOR J, MIŠÍK M., 1992: Isotopic compositions of oxygen and carbon in selected Mesozoic and Tertiary limestones and dolomites in Slovakia. Západ. Karpaty, Sér. Mineralógia, petrografia, geochémia, metalogenéza, (Geol. Úst. D. Štúra, Bratislava), 15, 7-27.

KANTOR J., HARČOVÁ E., FORDINÁL K.. & ŠÚTOVSKÁ K., 1993: Oxygen and carbon isotopic composition of foraminiferal and moluscan tests from Westcarpathian Neogene. Proc. 8th Meeting of the Ass. Europ. Geol. Soc., Budapest.

KIESL W., KOEBERL CH. & KORNER W., 1990: Geochemistry of magnesites and dolomites at the Oberdorf/Laming (Austria) deposit and implication for their origin. Geologische Rundschau, 79/2, Stuttgart, 327-335.

KOZUR H., MOCK R. & MOSTLER H., 1976: Stratigraphische Neueinstufung der Karbonatgesteine der unteren Schichtenfolge von Ochtiná (Slovakei) in das oberste Vise -Serpukhovian (Namur A). Geol. Pal. Mitt., (Insbruck), 6, 1, 1-29.

KOZUR H., MOCK R., 1977: Erster Nachweis von - Conodonten im Paläozoikum (Karbon) der Westkarpaten. Čas. pro min. a geol., (Praha), 22, 3, 299-305.

KRALIK M., AHARON P., SCHROLL E.., ZACHMANN D., 1989: Carbon and oxygen isotope systematics of magnesites: A review. Monograph Series on Mineral Deposits, Gebrüder Borntraeger, (Berlin-Stuttgart), 28, 197-223.

LAND L. S., HOOPS C. K.,1973: Sodium in carbonate sediments and rocks: a possible index to the salinity of diagenetic solutions. J.Sed.Petrol., 43, 614-616.

LINTNEROVÁ O., HLADÍKOVÁ J., 1992: Distribution of stable O and C isotopes and microelements in Triassic limestones of the Veterlín Unit the Malé Karpaty Mts.: Their diagenetic interpretation. Geol. carpath., (Bratislava), 43, 4, 203-212.

MAGARITZ M., HOLSER W.T., 1990: Carbon isotope shifts in Pennsylvanian seas. Amer. J. Sci., 290, 977-994.

MAZZOLI G., VOZÁROVÁ A., 1989: Further data concerning the pressure character of the Hercynian metamorphism in the West Carpathians (Czechoslovakia). Rend. Soc. Ital. Min. Petr., (Milano), 43, 3, 635-642.

MAZZOLI C., SASSI R., VOZÁROVÁ, A., 1992: The pressure character of the Alpine metamorphism in the Central and Inner Western Carpathians (Czecho-Slovakia). In: Vozár, J. ed.: Special. Vol. IGCP Pr. No. 276, D. Štúr Inst. Geol., Bratislava, 109-117.

MELLO J., ELEČKO M. ,PRISTAŠ J., SNOPKO L., VOZÁROVÁ A., HANZEL V., 1992: Vysvetlivky ku geologickej mape Slovenského rudohoria, 1 : 50 000. Archív Geol. Úst. D. Štúra, Bratislava.

MELLO J., VOZÁROVÁ A., VOZÁR J., GARGULÁK M., HANZEL V., KÁČER Š., KAROLI S., MOLÁK B., ŠUCHA V. & ŠIRÁŇOVÁ V., 1994: Vyhodnotenie štruktúrneho vrtu DRŽ-1 (Držkovce). Manuskript, Archív GÚDŠ, Bratislava.

MEYERS W. J., LOHMANN K. C., 1985: Isotope geochemistry of regionally extensive calcite cement zones and marine components in Mississippian Limestones, New Mexico. In: Carbonate Cements (Ed. by N. Schneidermann and P. H. Harris), Spec. Publ. Soc. Econ. Paleont. Miner., 36, 223-239.

MICHALÍK J., MASARYK P., LINTNEROVÁ O., SOTÁK, J., JENDREJÁKOVÁ O., PAPŠOVÁ J. & BUČEK, S., 1993: Facies, paleogeography and diagenetic evolution of the Ladinian/Carnian Veterlín reef complex, Malé Karpaty Mts. (West Carpathians). Geol. carpath., (Bratislava), 44, 1, 17-34.

MORTEANI G., MOLLER P., SCHLEY F.,1982: The rare earths element contents and the origin of the sparry magnesite mineralizations of Tux-Lanerbachs, Entachen Alm, Spiessnägel, and Hochfilzen, Austria, and the lacustrine magnesite deposits of Aiani-Kozani, Greece, and Bela Stena, Yugoslavia. Economic Geology, 77, 617-631.

MORTEANI G., NEUGEBAUER H., 1990: Chemical and tectonic control on the formation of sparry magnesite deposits - the deposits of the northern Greywacke Zone (Austria). Geologische Rundschau, 79/2, Stuttgart, 337-344.

NĚMEJC F., 1946: Příspěvek k poznání rostlinných nálezů a stratigrafických poměrů na Slovensku. Rozpr. ČAVU, (Praha), Tř.II., 56, 15, 1-34.

NĚMEJC F., 1953: Úvod do floristické stratigrafie kamenouhelných oblastí v ČSR. ČSAV, Praha, 1-173.

NEUGEBAUR J., 1978: Micritization of crinoids by diagenetic dissolution. Sedimentology, 25, 267-283.

RAKUSZ GY., 1932: Die oberkarbonischen Fossilien von Dobšina und Nagyvisnyo. Geolog. Hung., Sér. Palaeont., (Budapest), 8, tab.9, 1-123.

RONOV A.B., BALASHOV Y. A., GIRIN Y. P., BARTISHKO R.K. & KASAKOV G. A., 1974: Regularities of rare earths elements distribution in the sedimentary shell and in the crust of the earth. Sedimentology, 21, 171-193.

SASSI F.P., VOZÁROVÁ A., 1987: The pressure character of the Hercynian metamorphism in the Gemericum (West Carpathians, Czechoslovakia). Rend. Soc. Ital. Min. Petrol., (Roma), 42, 73-81.

SASS E., KATZ A.,1982: The origin of platform dolomites: new evidence. Amer.Journ.Science, (New Haven), 282, 1184-1213.

SNOPKO L., 1966: Stratigrafické začlenenie vrchného karbónu SGR. Manuskript - Archív Geol. Úst. D. Štúra, Bratislava.

TUCKER M. E., WRIGHT V. P., 1990: Carbonate sedimentology, Oxford, Vyd. Blackwell, 482 s.

VEIZER J., HOEFS J., 1976: The nature of $^{18}O/^{16}O$ and $^{13}C/^{12}C$ secular trends in sedimetary carbonate rocks. Geochim. Cosmochim. Acta, (Oxford-NewYork), 40, 1387-1395.

VOZÁROVÁ A., 1992: Nové litostratigrafické jednotky v brusníckej antiklinále. Geol. Práce, (Bratislava), Spr. 96, 25-31.

VOZÁROVÁ A., 1993: Stupeň premeny dúbravských vrstiev. In: Zborn. Geodynamický model a hlbinná stavba Západných Karpát, M. Rakús - J. Vozár (eds.). Geol. Úst. D. Štúra, Bratislava, 227-231.

VOZÁROVÁ A., VOZÁR J., 1992: Tornaicum and Meliatikum in borehole Brusník BRU-1, southern Slovakia. Acta Geolog. Hung., (Budapest), 35/2, 97-116.

YUDOVICH J.E., 1981: Regional geochemistry of sedimentary beds. Nauka (Leningrad), p.276.