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DIAGENESIS AND POROSITY OF THE UPPER TRIASSIC CARBONATES OF THE PRE-NEOGENE VIENNA BASIN BASEMENT

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Abstract: The Upper Triassic carbonates of the Opponitz Formation and Hauptdolomit Formation represent reservoir rocks of gas deposits in the basement of the Vienna Basin Neogene fill. During study of the reservoir rock properties of dolomites in the well Kuklov-3 (K-3) significant variations in porosity as a result of late diagenesis processes in buried sediment were found. On the basis of petrographical, SEM and mineralogical-geochemical methods, we identified neomorphic calcite layers, also found in the Kuklov-4 (K-4) well. Coarse crystallized calcite crystals are idiomorphic (e.g. ditrigonal scalenohedron). They have a relatively high content of Sr, Fe and Na, and decreased isotopic ratio of O (δ^{18}O: –6 to –9 ‰) or also C (δ^{13}C: –0.7 up to +1.8 ‰) in comparison with values in dolomites (δ^{18}O: –4.8 up to;1.3 or also δ^{13}C: 0.1 to +4.1 ‰) or also in limestones (mostly δ^{18}O: –3.9 to –3.6 ‰). Microstructural analysis indicates that they substitute dolomites as a result of dedolomitization under conditions of deep burial. Diagenesis under conditions of deep burial results in forming of new minerals such as kaolinite, pyrite and illite. The observed changes (increasing) of reservoir rocks porosity of dolomites both in the well K-3 and K-4 (at the depth of 3660 to 3830 m) were caused by diagenetic processes taking place in the deep burial environment and these processes were probably limited to a layer of (originally dolomitic) breccias.

Key words: Upper Triassic, carbonate reservoir, chemical and mineralogical composition, SEM, dedolomitization, stable isotopes of O and C.

Introduction

The presented paper is aimed at the question of whether the observed change in Upper Triassic dolomites of wells Kuklov-3 (K-3) and Kuklov-4 (K-4) in the basement of the Neogene fill of the Vienna Basin (Fig. 1) is a result of late-diagenetic processes. Upper Triassic carbonates (Opponitz Limestone Formation and Hauptdolomite Formation) represent reservoir rocks of gas deposits in the Slovak part of the basin. The present burial depth of the Triassic sequence in the Vienna Basin is predominantly more than 3000 m (in an interval of 2000 to 3000 m, except near basin rims). The porosity values of the carbonate rocks are frequently below the lower limit referred to good carbonate reservoir rocks (< 6 %). The porosity record of the dolomite sequence in the well K-3 shows that the usual porosity reduction with increasing depth reversed. We observed abnormal increased porosity values (above 15 %) in this part of the well. Study of reservoir rocks properties of dolomites was carried out in the framework of the state research project „Evaluation of prospectivity of searching for hydrocarbon in selected areas of the Western Carpathians“ (Masaryk 1996 in: Janků et al. 1996). Preceding results (Borza et al. 1985; Masaryk et al. 1988; Ostrolucký & Jiříček 1986; Ostrolucký 1994) were supplied with other petrographical, mineralogical and geochemical results (Lintnerová 1988; Masaryk 1990, 1996). It is becoming evident that late-diagenetic alteration of a carbonate sequence affected mostly parts built up by breccias and significantly influenced their reservoir rock properties.

Geological and reservoir setting

Both, in the Austrian and the Slovak part of the Vienna Basin, three nappe zones (Bajuvaricum, Tirolicum and Juvavicum) were interpreted separated from each other by Upper Cretaceous and Paleogene sediments of the Gosau type (Wessely 1983, 1988; Jiříček 1984). The most external, thrusted over the Klippen Belt are the Bajuvaric nappes (Frankenfelds and Lunz nappes). The Upper Cretaceous and Paleogene sediments of the Giesshübel Syncline have been deposited on these nappes in a transgressive position. According to Wessely (1983, 1988), Jiříček & Tomek (1981), Jiříček (1980, 1984), Sauer et al. (1992) the Bajuvaric nappes are extended in the belt Aderklaa–Schönkirchen–Prottes–Borský Jur–Kuklov-Šaštín–Senica and are submerged under the Upper Cretaceous and Paleogene sediments of the Myjavská pahorkatina Upland. They appear at the surface in form of isolated structures southwards of the Klippen Belt between Podbranč and Lubina.

Well exploration into pre-Neogene basement of the Vienna Basin was aimed at elevation structures (Šaštín, Závod, Studienka, Borský Jur, Kuklov, Senica) with a mean depth of the Neogene basement in the interval of 3000 to 4000 m. In the Slovak part of the basin two gas deposits — Borský Jur and Závod were discovered in Upper Triassic dolomite sequences of the Opponitz Limestone and Hauptdolomite Formations. Both wells K-3 and K-4 were drilled into the marginal zone of the Borský Jur reservoir (Fig. 1). The well K-3 is considered to have one of the most complete sections through the Lunz Nappe sequence (the interval of 2700 to 5200 m). Be-

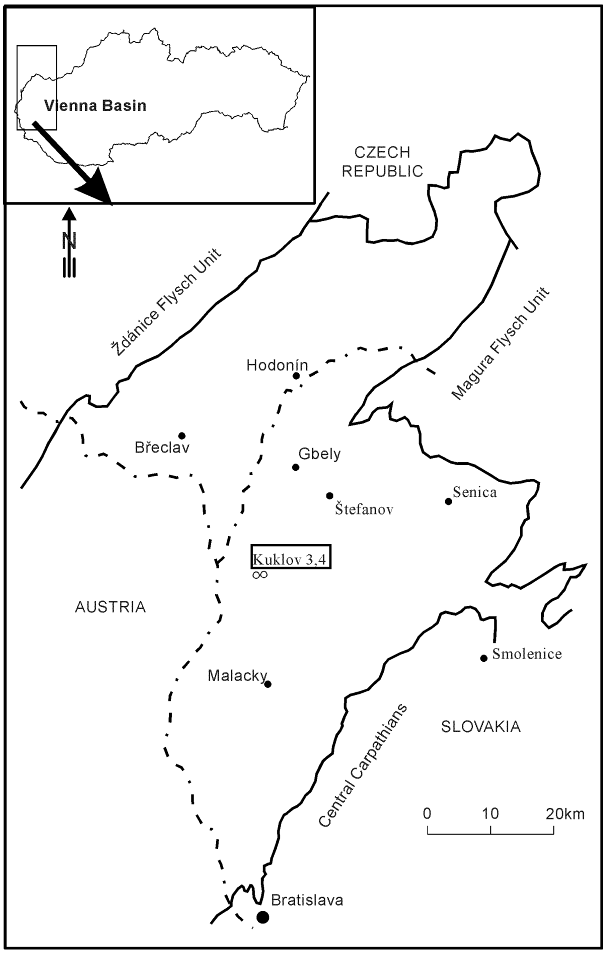

Fig. 1. Localization map of the Kuklov 3 (K-3) and Kuklov 4 (K-4) boreholes.

sides the Upper Triassic dolomites (2700 to 3832 m), the well also penetrated the Lunz-Reingraben Formation (up to 4758 m) and a part of the Reifling Formation (up to 5200 m). The lithological nature and changes in reservoir rocks were checked in logs (Figs. 2–3). Biostratigraphical subdivision of the carbonate sequences was problematical because of the lack of fossils.

The Uppermost layers of the Upper Triassic dolomites contain foramifers Uppermost Norian to Rhaetian (Borza et al. 1985). It is possible to accept the lithofacial subdivision of the Hauptdolomite Formation proposed by Scherreiks (1971) and later made more precise by Fruth & Scherreiks (1982, 1984, 1985) also for sequences of the Vienna Basin basement. On the basis of this subdivision, the well K-3 drilled through the middle and basal part of the Hauptdolomit Formation and Opponitz Limestone Formation (Fig. 3). The Opponitz Limestone Formation was also found in the well K-4, but the Mesozoic sequences were drilled in an inverted arrangement (Masaryk et al. 1988).

Methods

150 thin-sections were studied from the wells K-3 and K-4. Some of them were coloured with alizarine red. The porosity of well core rocks was evaluated by methods of triple scaling, Hg-porosimetry and optical coloured porosimetry. We also utilized the results of processed logs of the well K-3 (processed by computer). For all methods of porosity measurements in details see Masaryk (1996). We studied the fracture surfaces of dolomite and also etched and polished rocks thin plates (0.5% formic and 1% hydrochloric acid, 15 sec. to 1 min.) under a scanning electron microscope (SEM). The mineral composition of rock samples was studied by X-ray diffraction analysis (CuKα). The dolomite stechiometry (mole calcite- dolomite ratios) and the dolomite crystal ordering have been evaluated by methods of Lumsden (1979). The calcium and magnesium content of the carbonate parts of rock samples (HCl dissolved) were checked by chemical analysis. The calcite and dolomite contents were corrected on the basis of insoluble residue (IR) gravimetrical determination (Table 3). The elements listed in Table 2 were determined by the AAS method in the sample portions soluble in hydrochloric acid. The 67 whole-rock analyses from both wells were done by the X-ray fluo-

Table 1: The results of porosity measurement by four methods.

WELL	DEPTH (m)	P HG (%)	P HG >20 nm (%)	TOP (%)	VP(%)	LITHOLOGY	AGE
Kuklov 3	2708–3013	1.50	0.39	3.05	2.03	Grey-brown loferitic and brecciated dolomites	Norian
Kuklov 3	3089–3238	1.33	0.45	2.10	0.64	Grey-brown laminated dolomite with anhydrite	Norian
Kuklov 3	3390–3665	0.91	0.32	0.00	1.07	Grey-brown massive limestone	Carnian
Kuklov 3	3676–3832	2.03	0.37	8.77	3.35	Grey-brown limy dolomite and dedolomite	Carnian
Kuklov 4	3329–3573	0.30	0.10	0.00	0.40	Grey-brown massive limestone	Carnian
Kuklov 4	3641–3644	10.42	6.72	13.00	11.75	Grey-brown porous dolomite	Carnian
Kuklov 4	3697–3734	2.95	1.55	3.50	3.07	Grey-brown carbonate breccia	Carnian

P HG (%)— average of the total porosity measured by Porosimetro 2000, (Hg-porosimetry)
P HG >20 nm (%)— average of the effective porosity measured by Porosimetro 2000
TOP(%)— average of the total optical porosity (colour optical porosimetry)
VP (%)— average of the total volume porosity (triple weight)

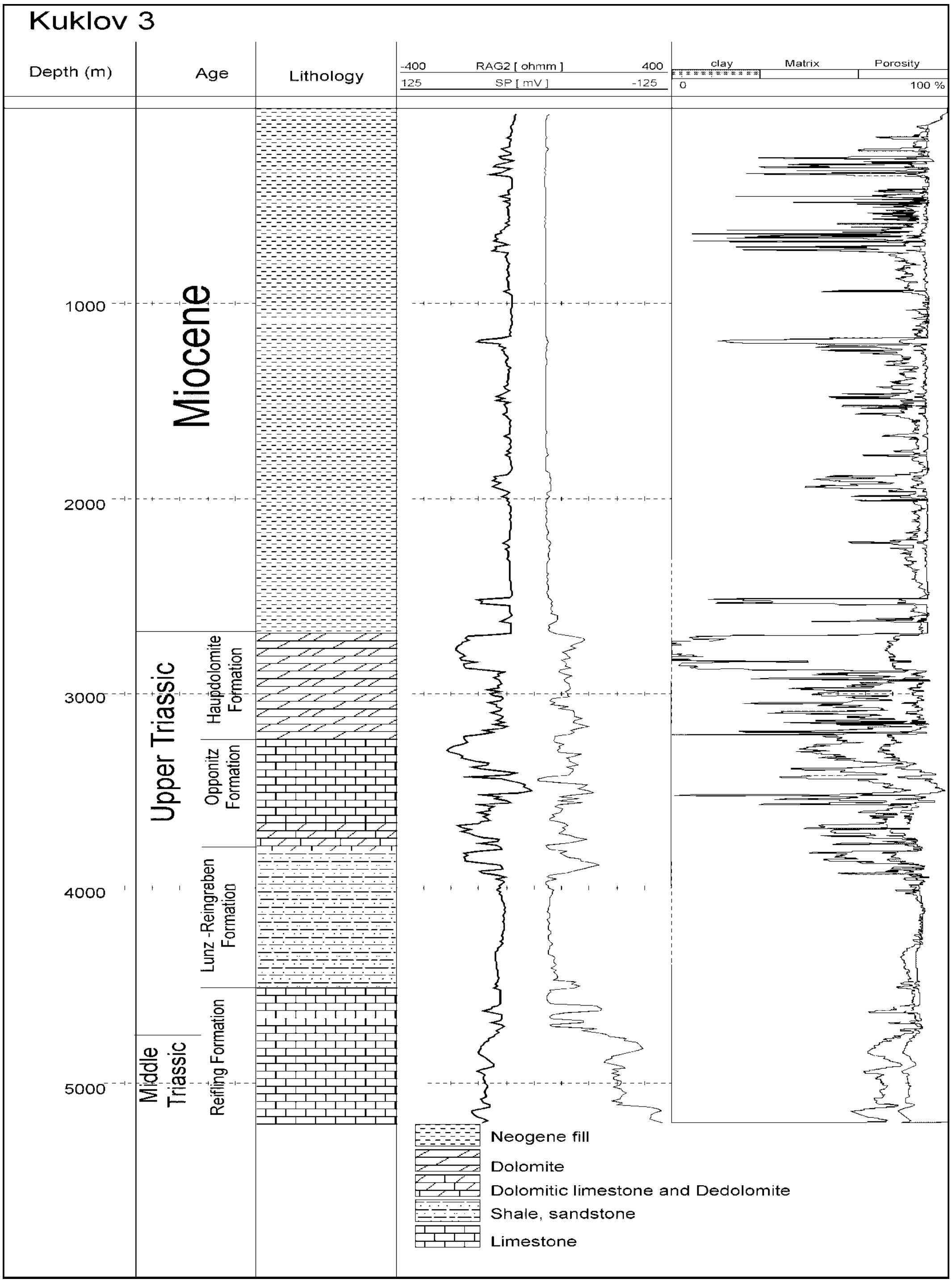

Fig. 2. Borehole K-3: Lithological section and the values of log porosity.

rescence method. Some of them are listed in Table 2, but the complete analyses are unpublished (Borza et al. 1985; Lintnerová 1988).

Powder specimens for isotopic analysis from analysed cores were prepared. Samples were dissolved by the standard method (McCrea 1950), i.e. in 100% phosphoric acid in vacuum at 25 °C. In samples containing calcites and dolomites, carbon dioxide has been separated step by step, according to reaction time. The values of the isotopic ratio were corrected (decreased by 0.8 ‰) in respect to a different fractional factor of oxygen in reaction with the acid. The quoted way of separation is favourable for samples with the content of one component over 10 %. Results were quoted as an isotopic ratio δ in per mile, related to the PDB standard for both elements. The accuracy of the assurements is better than 0.1 ‰ for both $\delta^{13}C$ and $\delta^{18}O$.

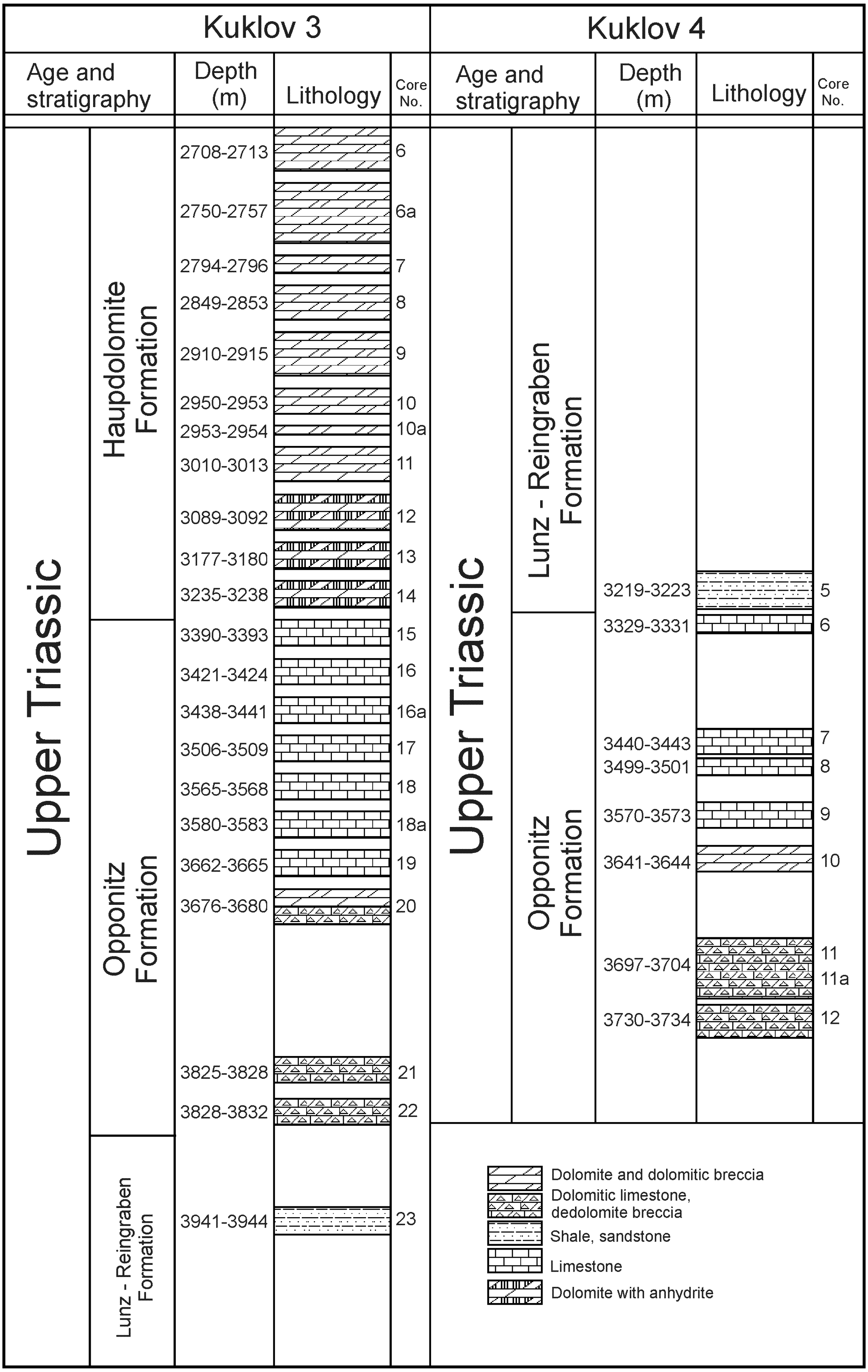

Fig. 3. Upper Triassic carbonate cores in boreholes Kuklov 3 and Kuklov 4.

Results

Petrographic characteristics of the specimens

Well Kuklov-3 (K-3)

The Upper Triassic carbonate rocks of the well K-3 were subdivided into three lithological types (Figs. 2–3). The dolomites of cores 6–11 represent the middle part of the Hauptdolomit Formation sequence, while cores 12 to 14 were taken from the basal dolomitic-anhydritic complex (after Scherreiks 1971; Fruth & Scherreiks 1982, 1984, 1985). The limestones and dolomites of cores 15 to 22 (Fig. 3) belong to the Opponitz Limestone Formation.

Cores 6 to 11 are formed by grey-brown tectonized loferite dolomites (Fig. 4: 1–2). The uppermost part of the dolomites (cores 6,6a) are formed primarily by dolosparite (grain size 200–250 μm,) and sporadically by microsparite. In other cores recrystallization is not so intensive, and fine-grained dolomitic matrix (5–25 μm in size) is partly recrystallized into microsparite (30–100 μm in size). Initial sedimentary textures and structures were almost completely wiped away and are preserved only in the form of indistinct ghosts (Fig. 4: 1). Fossil fragments (ostracods, foraminifers, crinoids) occurred only rarely (Fig. 4: 2). The primary stromatolite structure is the most typical phenomenon in this part of the sequence (Fig. 4: 3–4, 7). The dolomites were relatively intensively fractured and the secondary joints are filled primarily by calcite, less by dolomite and rarely by anhydrite crystal aggregates. The open jointed network in tectonized layers (tectonic breccia) wholly increase communication of pore spaces. Locally, the rocks have the nature of pseudorudite and are formed by lighter dolomicrosparitic clasts enclosed by dark dolomitic matrix.

Table 2: Chemical composition of the rock samples. Sample 6/2708 it is: 6-core number, 2708 = 2708 m in the borehole.

Sample	CaO	MgO	CO_2	Fe	Mn	Na	Sr
		wt. %			ppm		
K3							
6/2708	31.62	20.58	46.69	250	36	250	81
6a/2757	32.09	20.19	46.90	380	61	330	81
7/2704	32.19	19.92	46.93	300	44	460	75
8/2851	31.80	20.42	46.87	310	39	450	690
8/2853	32.29	19.83	47.07	290	39	440	71
10/2951	28.09	20.40	42.70	1550	74	650	96
10/2952	32.33	20.75	45.44	920	87	580	94
10/2953	24.66	16.58	36.36	2770	87	1050	94
11/3011	28.33	20.36	42.18		55	575	116
12/3090	3.72	2.51	5.66		108	738	995
13/3177	9.01	6.47	14.12		63	295	2218
14/3237	32.11	20.82	45.11		91	373	839
15/3391	53.64	1.31	42.54		20	330	800
15/3392	53.48	1.21	42.87		23	310	755
16/3421	51.84	2.70	42.45	910		195	701
17/3566	54.56	0.72	43.82	870		150	500
19/3663	42.45	4.43	37.48		328	475	443
20/3676	32.84	19.73	47.16		28	375	103
20/3677	32.41	19.60	47.03		32	388	100
21/3825	34.36	18.07	47.05	210	17	580	93
21/3826	55.48	0.59	43.09	455	10	128	378
21/3827	55.46	0.68	42.29	1330	14	113	228
22/3828	53.69	2.07	43.51	420	19	125	393
22/3829	50.00	4.71	44.48	420	22	125	231
22/3830	52.57	2.81	43.98	385	17	148	280
34/4902	48.72	0.95	41.17		29		890
K4							
11/3699	53.42	1.21	42.59		80	260	325
11/cl	54.96	2.60		570	77	160	295
11/ce	53.14	0.15		760	82	310	309
11a/cl	52.57	1.61		580	45	190	305
11a/ce	38.27	0.71		1880	64	700	250
12/3732	46.83	1.41			68	450	230
12/cl	36.95	0.71		960	140	730	248
12/ce	38.55	0.50		690	55	720	203

cl — clast, ce — cement

Cores 12 to 14 (Fig. 3) contain grey-brown brecciated dolomites with anhydrite. The dominant breccias have clasts formed by laminated loferite dolomites (Fig. 4: 3–4, 7–8) and matrix formed by laminated anhydrites with dolomite intercalations (Fig. 4: 5). The anhydrite of these layers is coarse grained and tabular or needle-shaped crystal forms are characteristic. The dolomite laminae are micritic, frequently with a clay admixture. The dolomite clasts in the breccia are formed by the same types of dolomites as described from cores 6 to 11.

Cores 15 to 19 (Fig. 3) are formed by grey-brown laminated limestones. The matrix of the limestones is micritic with an inexpressive fine lamination. The limestones (limy mudstones) are poor in organic remnants and other allochems. Sporadic pellets, ostracods, crinoids, globochaetes and foraminifers are most frequently concentrated into thin laminae. The matrix includes a finely dispersed clayey-silty admixture (approx. 5 to 10 %) concentrated into stylolite surfaces that represent a result of pressure dissolution. The limestones were fractured by a relatively dense net of joints or veinlets which were formed by secondary sparry calcite, seldom by dolomite. Diagenetic dolomitization affected these limestones only indiscernibly. Besides sporadic small rhombs in the matrix of these limestones there are more abundant authigenic pyrites and clay minerals. These limestone types with a relatively high clayey-silty admixture also include more intensively dolomitized limestones.

The rocks of cores 20 and 21 (Fig. 3) are formed by pale-brown brecciated dolomite to dolomitic limestone. The matrix is microsparitic to sparitic with relics of sporadically recrystalized foraminifers, ostracods, ooid relics and intraclasts (Fig. 5: 1–2). The detritus content in dolomites reaches up to 10 % (wackestone type). The matrix has the typical granular nature of dolomites, but locally with an increased calcite content, fairly visible in thin sections coloured by alizarin red and also according to the changes in size of crystals. Irregular islands of dolomite (Fig. 5: 3) and relics of dolomite (dolomitic ash) between and inside large calcite grains indicate processes of a diagenetic alteration — dedolomitization. The original laminated structure of dolomite is visible in hand specimens but completely disappears in thin sections. Dolomites were also strongly fractured and brecciated. A primary part of joints and pores is filled by neomorphic sparry calcite, but part of the pores is free. This is very important for reservoir rock properties (the increasing of the permeability).

We noticed a significant increase of calcite content in the lower part of core 21 and in core 22, and although specimens resembled dolomite by their appearance they are actually formed by neomorphic calcite. The calcite crystals are sparitic (Fig. 5: 3–8) with relics of dolomicritic matrix. Relics of dolomicritic grains with their rims partially rhombohedrally boundered as well as in form of large rhombohedral grains were typical. Some core parts are formed by a carbonate breccia with angular clasts with sizes of 0.1 mm to 4 cm. Clasts were of a different nature, resembling the described compact dolomites or limestones. The cement of these breccias is formed by coarse-grained neomorphic calcite (Fig. 4: 6–7) and micritic parts (matrix), which are also calcitic. Ghosts, remnants of tests probably from foraminifers and ostracods, appear locally.

Well Kuklov-4 (K-4)

The cores 11, 11a and 12 (Fig. 3) are formed by grey-brown carbonate limestone breccias. Dolomites are present only in core 10 (Fig. 3). The appearance and texture properties of them are very similar to those from well K-3, core 20.

The matrix of the limestone breccias is formed by microsparitic to sparitic calcite with a clayey admixture. The matrix is relatively homogeneous without allochems. Besides the matrix, a syntaxial calcitic cement is found at the rims of some clasts. The clasts are dominantly angular to subrounded with signs of corrosion. The contacts between clasts and matrix are frequently obscured and rather resemble to gradual transition. The breccia is distinctively polymodal, clast sizes vary between 0.5 to 10 cm. Sporadically the clasts show sedimentary structures, e.g. lamination, fenestral porosity, loferite structure which are typical for (the described) dolomites. They are formed by neomorphic calcite sparite with small inclusions (relics) of dolomite. Micritic aggregate grains with ghosts of a pseudo-oolitic texture can be observed locally. In the sparite mosaic some grains thicken towards rims, which are formed by completely pellucid rhombohedral calcite grains. Generally recrystallization is manifested by the presence of numerous inclusions and authigenic minerals, e.g. pyrite. The breccias studied in the well K-4 were gradually formed by leaching/dissolution and neomorphic calcite grains substituted the original dolomitic material.

Properties of the dolomite porosity

The comparison of measurement results gained by a few methods (Table 1, Fig. 2) confirms a significant variability in the dolomite porosity in the wells K-3 and K-4 or confirms some increase of porosity towards depth. This increase at the depth below 3600 m (Fig. 2) is connected with dolomites or dedolomitized breccias, which is documented by porosity based on logs processing of the well K-3 (Fig. 2). On this basis, it is impossible to make any statement as to the absolute values of porosity, but the relative changes of reservoir rock properties provide valuable information which shows that segments with an increased porosity coincide with intervals of (late) diagenetic alteration. Apart from significantly (fracture) porous and permeable dolomites in the beds directly underlying the Neogene, which represent the old erosional surface of the Triassic dolomites, and are associated with two known deposits in the Slovak part of the Vienna Basin, it is possible to identify further important reservoir horizons. In both wells, K-3 and K-4, reservoir rocks did not contain gas, but were filled with salt water. For comparison Ostrolucký (1994) gives mean porosities for the Opponitz Limestone Formation (K-3) of up to 7.33 % and a permeability of 3.56 mD, simultaneously he gives a mean value for the porosity of all the dolomites (reservoir rocks) of this well of 1.3 % and a permeability of 0.2 mD.

From the viewpoint of reservoir rock properties we can classify the petrographic types as follows:

1. The coarse-grained dolosparites of a sugary appearance are characterized by a predominantly planar polymodal coarse crystalline mosaic with sizes of crystals above 100 μm (mean 250 μm in size). The extensive dolomitization resulted in a total destruction of the original rock and therefore we cannot observe any primary sedimentary textures and structures. Porosity values (Table 1) reach an average of 2.5 % (the interval 0–7.5 %), scanty communication — permeability of intercrystalline porosity represents a certain insufficiency.

2. The laminated muddy dolomites and dolomitic limestones of mudstone type with anhydrite are characterized by predominance of micritic, microsparitic types of the matrix with sizes of dolomite crystals of up to 50 μm generally without clasts or other allochems. The anhydrite formed synsedimentary laminae, but was secondarily mobilized and represents fill of veinlets, stylolites and fractures. The original sedimentary structural-textural elements are well preserved. The values of the total porosity (Table 1) are low — 1 to 2 % ± 2 %, the rocks are, with exception of breccia layers, nearly impermeable.

The calcarenites of dolograinstone type with irregular clast recrystallization and dolosparitic cement are characterized by various stages of original sedimentary texture and structure preservation. Clasts are predominantly formed by pellets, bio and lithoclasts. Dedolomitization results in a brecciated to microsparitic nature with ghosts of clasts. The porosity values of the original dolomites were low — 0–5 %, but dedolomitized layers (Table 1) have higher porosity values — 5–12 % with a relatively good microfracture porosity. These layers are some of the best reservoir rocks within the whole carbonate complex.

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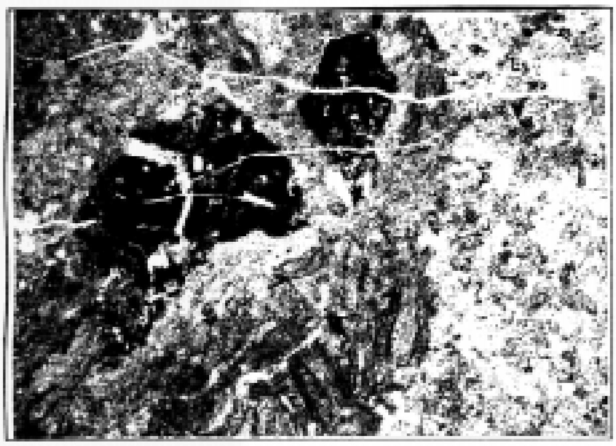
Fig. 4. Thin section photos of dolomites from well K-3 (cores 8 to 14). **1** — Coarse- to fine-grained dolosparite with relics of the dolomicrite in the pseudoclastic structure (2910 m, magnification 7×). **2** — Dolosparite with ghosts of bioclasts (ostracods, foraminifers) and dolomicrite relics (2849 m, magnification 9×). **3–4** — Dolomite with stromatolitic (loferite) structure (3091.8 m & 3235.5 m, magnification 7×). **5** — Laminated finecrystalline anhydrite with thin laminae of dolomicrite (3178.3 m, magnification 7×). **6** — Coarse crystalline anhydrite with dolomite relics (3089 m, magnification 7×). **7–8** — Dolomitic breccia with a stromatolitic structure in the clast (3237.4 m & 3012 m, magnification 7×).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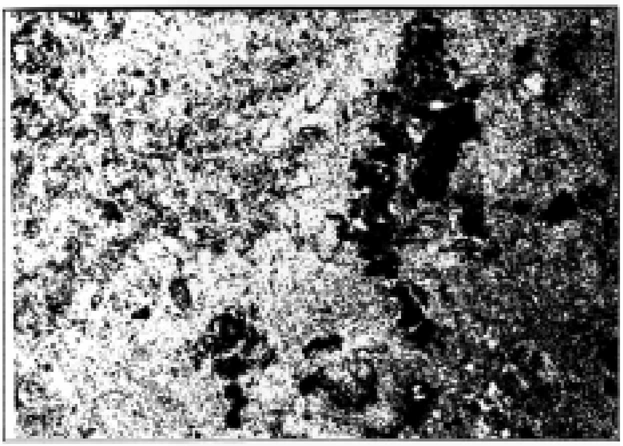
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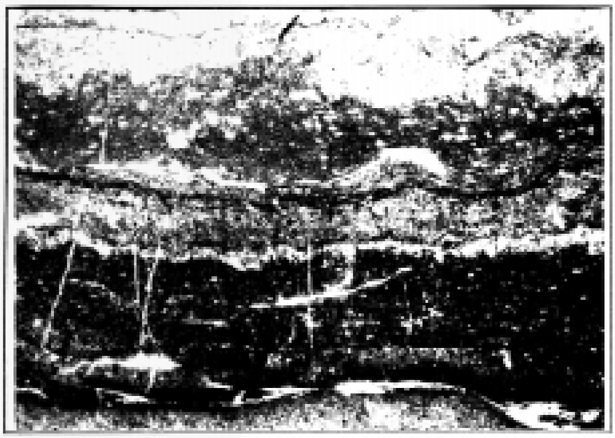
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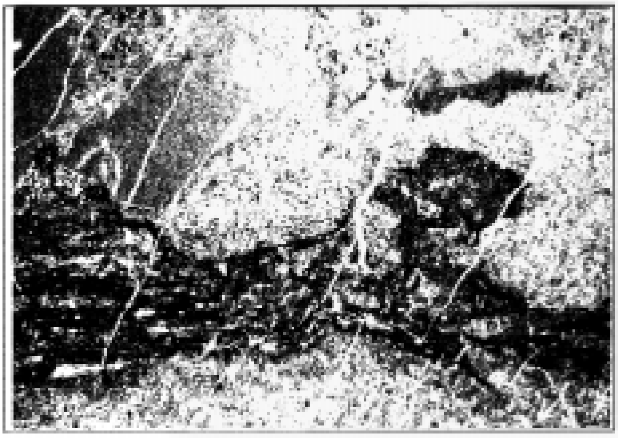
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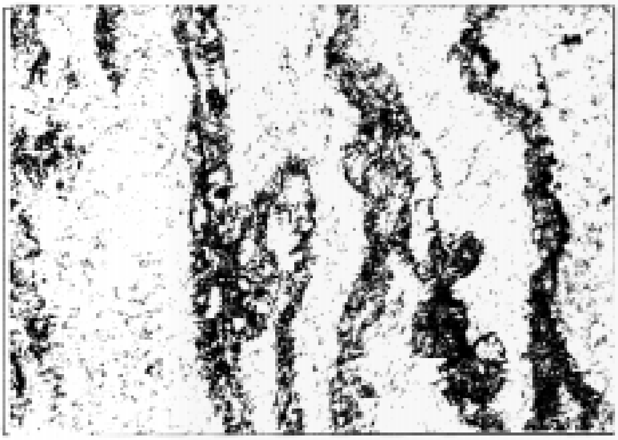
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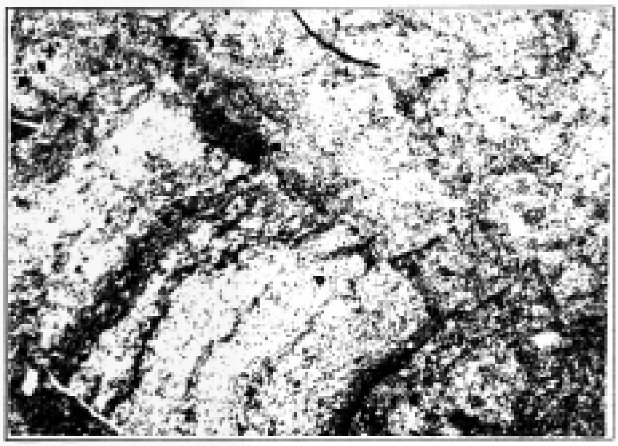
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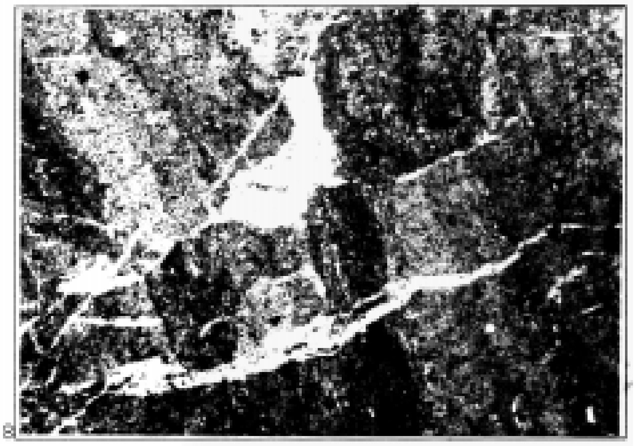
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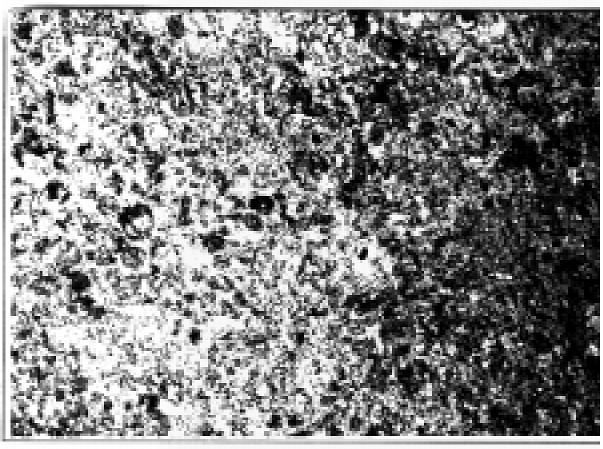

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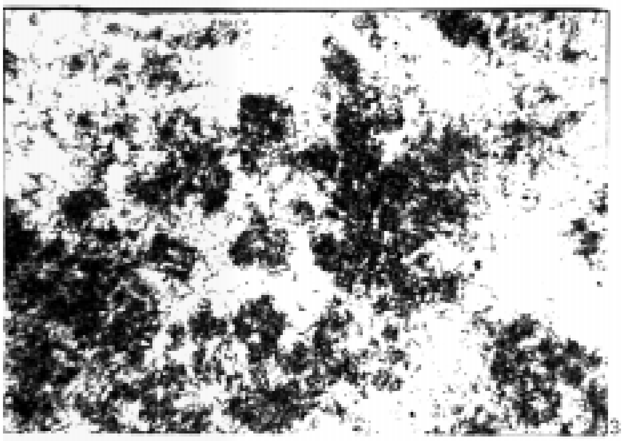

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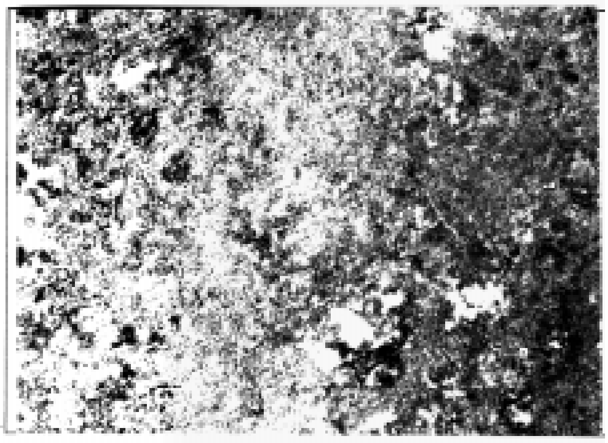

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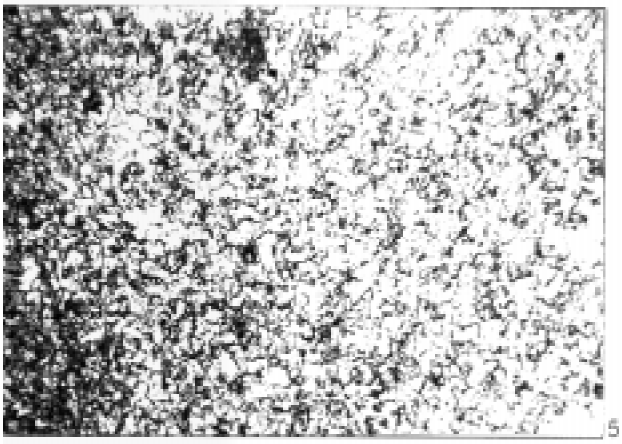

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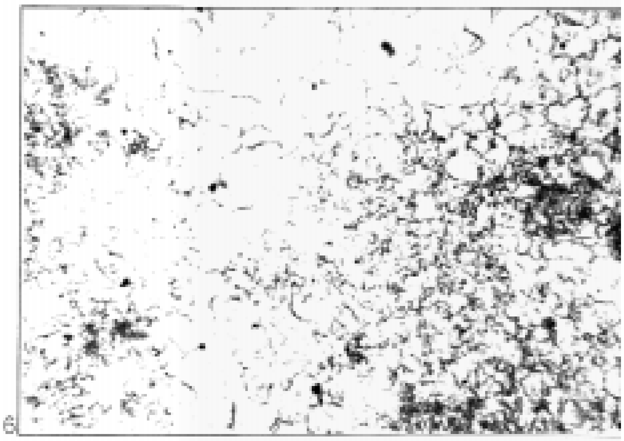

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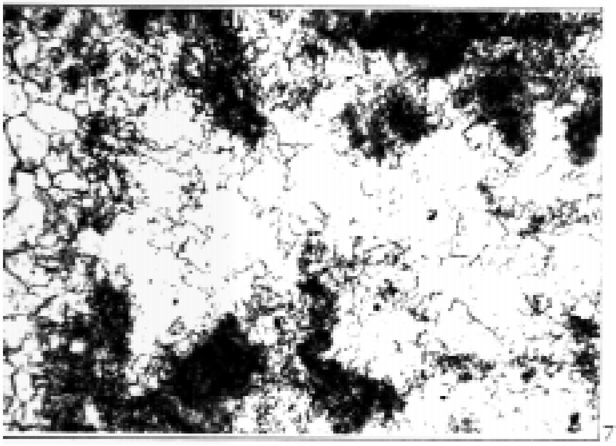

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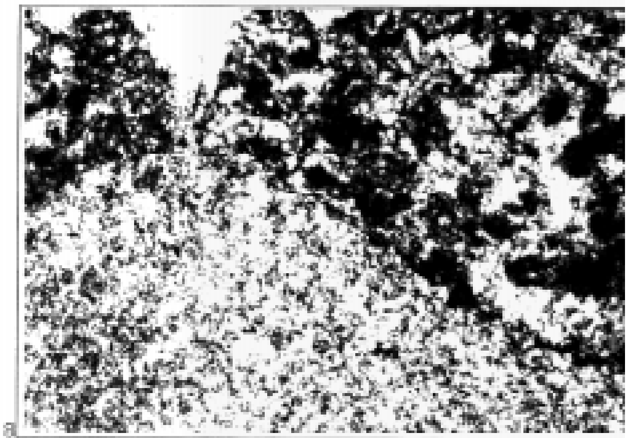

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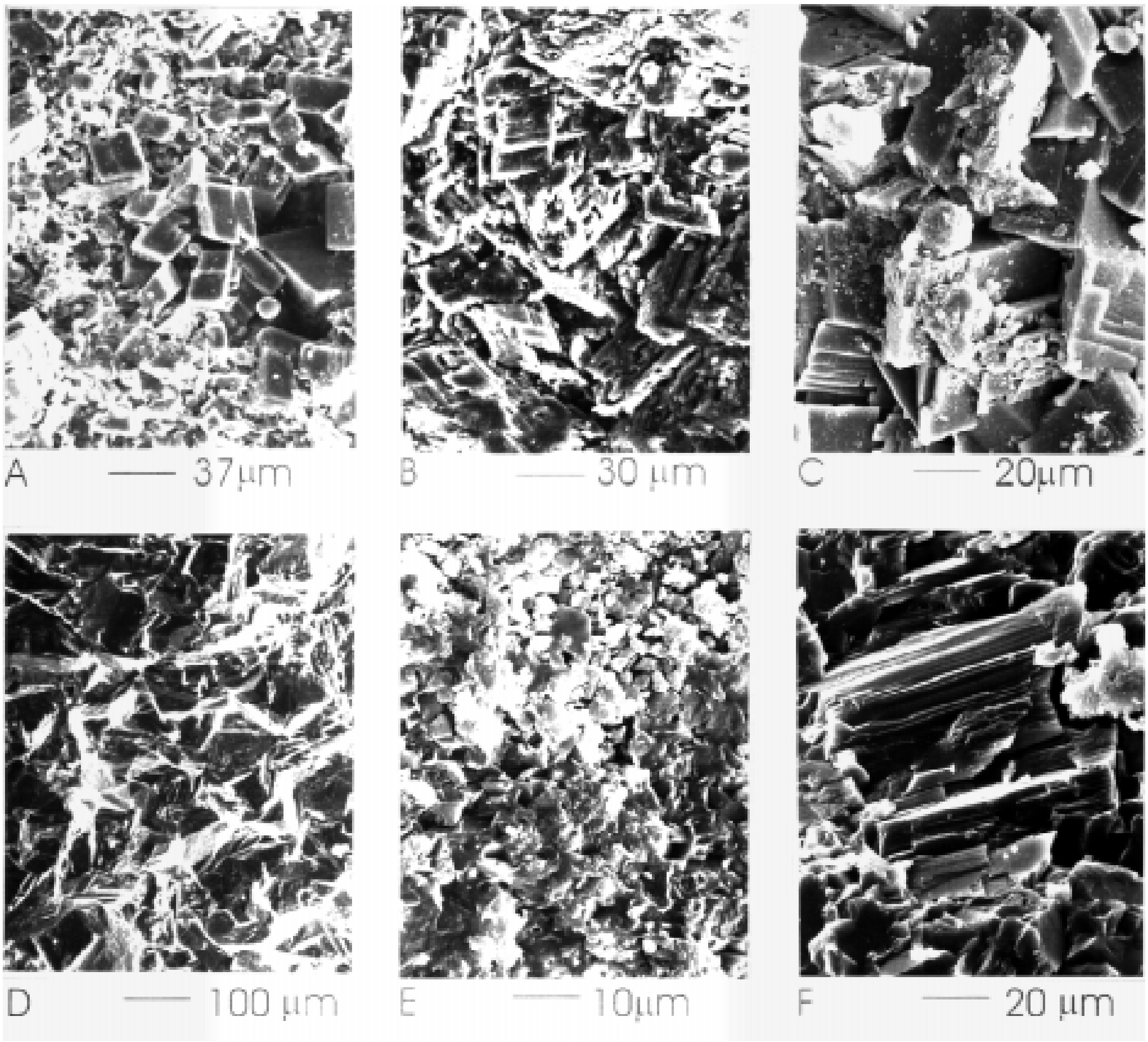

Fig. 6. Microphotographs (SEM) of the dolomites in K-3, cores 6 to 13. **A** — Microsparitic dolomite rhombs in the matrix replaced by dolosparite rhombs. **B** — Large dolomite grains were dissolved and the new intragranular porosity was formed. **C** — Framboidal pyrite aggregates were grown among dolosparite crystals. Dolomite grains were also partly dissolved. **D** — Sparry calcite grains were formed in the pore space and also calcite filled fine veins. **E** — Dolomite matrix with siliclastic mineral coating (mica, illite), often on the stylolites. **F** — Large crystal aggregates of anhydrite in dolomite.

SEM

A total of 15 samples from the dolomite intervals (Fig. 3) separated by limestone layers were selected from the well K-3 for SEM study. The first layer was caught by cores 6 to 14 (the interval 2708 to 3240 m), and the second one by cores 20–21 (the depth 3676 to 3830 m).

In the SEM micrographs it is possible to distinguish two grain size classes in fine-grained dolomites (Fig. 6A–B). The dolomite matrix is formed by grains below 10 µm in size and a coarser grained crystalline phase, above 10 to 100 µm in size. The grains reach in average around 50 µm in size and are of typical rhombohedral morphology. These rhombs grow partly into opened pores, partly replace matrix (Fig. 6A–B). Their presence generally increases intergranular pore spaces most expressed in specimens of cores 6, 6a (Fig. 6B). On rhombohedrons' surfaces we can see intracrystalline pores and fractures, which were a result of proper recrystallization of the dolomite. Diagenetic dissolution by

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Fig. 5. Thin section photos of dedolomites from well K-3 (cores 20 to 22). **1–2** — Oolite dolograinstone with preserved interparticle and intercrystalline porosity (3676 m, magnification 86×, 7×). **3–4** — Neomorphic sparry calcite replacing dolomicrite matrix with vuggy macroporosity (3829 m, magnification 86×, 7×). **5** — Pseudomorphic dolomitic texture of sparry calcite (3829.5 m, magnification 86×). **6–7** — Neomorhic sparry calcite with relics of dolomite (3827 m, 3831.5 m, magnification 86×). **8** — Pseudomorphose after dolosparite (the lower part) and neomorphic calcite with relics of dolomicrite (the upper part), (3829.5 m, magnification 45×).

pore solutions was indicated by disturbed rhombohedral grains (Fig. 6B–C) and in places even by irregular residual grains that were paler. The new phases in dolomites are represented by calcites (Fig. 6D) in joints as well as framboidal pyrites (Fig. 6C) studied in specimens of cores 6 to 8. Anhydrites reduced by organic substances were probably the source of the sulphur (Fig. 6F). The dolomite grains near the framboidal pyrites were also (slightly) corroded (Fig. 6C). The calcite crystals closely fill joints and are massive without surface disturbance (Fig. 6D). Clastic minerals can be seen at grain boundaries in typical laminae, deformed after formation of carbonate grain. They were represented by mica or chlorite grains pressed out by the dolomitization, but also by (successive) pressure dissolution. Tiny dispersed particles at grain surfaces (Fig. 6E) are probably authigenic illites.

The dolomite matrix of the core 20 is microsparitic and it forms idiomorphic rhombic grains larger than 10 µm, in average 20 to 40 µm in size (Fig. 7A–C). SEM study showed that specimens of the lower part of core 21 and in core 22 were formed by predominantly well crystallized, perfectly limited crystals. We can recognize typical crystalline forms of calcite, e.g. ditrigonal scalenohedral (Fig. 7C–F). We did not notice rhombohedral neomorphic crystals. Neomorphic crystals did not bear any signs of surface disturbance but were strewn with residual (pale-dissolved) irregularly limited grains or dust (Fig. 7E–G). Grains frequently bear growth defects or inclusions of smaller crystals. These crystals do not fill only cavities but seem to substitute the essential (large) volume of specimens. Locally grains were closely crammed (Fig. 7D) but as a whole specimens seem to be relatively loose, porous (Fig. 7E–G) for example in comparison with calcitic cement in joints (Fig. 6B). We found authigenic kaolinite in etched surfaces (Fig. 7H–I) and from these parts of cores fluorite was also described (Mišík 1986). Kaolinite forms platy pseudohexagonally limited crystals. We also sporadically observed grains of grown feldspar or quartz, again in etched surfaces.

From the well K-4 we took 5 specimens from cores 10 to 12, depth interval of 3641 to 3734 m (Fig. 3). Dolomites were found only in core 10 and they had increased calcite content (Table 2). Calcite forms predominantly the fill of cavities, pores and joints (Fig. 8A). Dolomitic micritic to microsparitic grains (up to 10 µm in size) bear quite apparent traces of dissolution (Fig. 8B). Cores 11, 11A and 12 have the appearance of a dolomitic breccia but they were proven by chemical analysis to be actually limestones (Table 2). These limestones displayed higher variability of grain size, intercrystal porosity as well as of the surfaces disturbance and presence of relic grains of the preceding phases. The most important for us seemed to be the presence of „fresh diagenetic“ calcite grains (Fig. 8C–E) and crystals of clay minerals (Fig. 8E–F). These calcite grains were similar after their morphology to grains studied in the core 22 of the well K-3 (Fig. 7D–G). Crystals are without a surface dissolution disturbance but they contain growth's defects — pores, frequently with crystalline negative morphology. Small relic grains of the original phase are also present on the surface of grains and in intercrystal spaces. Some of them have partly rhombohedral limitation, similar to dolomite grains from the core 10. Authigenic clay minerals, probably illites in their typical fine grained form (Fig. 8F) cover the surfaces of calcite grains and fill pore spaces between crystals. In specimens from cores 11A and 12 distinctive signs of recrystallization and traces of dissolution were also observed (Fig. 8H–I). On fracture surfaces we could observe preserved isles of the original phase — fine-grained dolomite which seems to be displaced towards crystal rims or into the intercrystal spaces of neomorphic calcites (Fig. 8H–I). According to relations between grains, we can see that neomorphic clay minerals were probably crystallized simultaneously with the calcite grains formation (Fig. 8H) or later and grow into free intercrystal spaces (Fig. 8F).

Geochemical-mineralogical analysis of specimens

We want to document by chemical analyses of specimens that in cores 21 and 22 (Fig. 3) alteration of the chemical and mineral composition of the rock arose. In one core (21) the dolomite or dolomite breccia, has been altered into limestone (limestone breccia) although the rock is of a dolomitic appearance. The neomorphic limestones are „pure“ and contain hardly any aluminosilicate minerals. The limestone layers continue into core 22 which also has a brecciated appearance. Dolomite content slightly increased in specimens of core 22 (Table 3). By analogy the breccia from K-4 was formed by calcites (Table 3), but had an increased or more variable content of clayey material, as well as of authigenic material as it was documented also by SEM microphotography. Their content in original clasts changed. Mineral composition was studied by X-ray diffraction. X-ray records were assessed by a semi-quantitative method and the obtained assessments correspond well to the mineral composition calculated from chemical analyses of rock specimens or from the calcium and magnesium content determined by classical chemical analysis (Tables 2–3).

Finer-grained, less crystallized dolomites from the well K-3 were close to stechiometric composition (50.5 to 52 mol. % of $CaCO_3$), coarse-grained (sparitic) reveal a slight content of lime (53 to 56 mol. % of $CaCO_3$). However, referred variability could reflect alteration processes either in the topmost part (disturbed rhombohedrons — core 6,6A and relatively little of calcite cement) or in the lower part in cores 20 and 21. The stechiometry differences were not clearly manifested in differentiation of dolomite crystal ordering. The ratios of reflection intensities 221 and 101 (Lumsden 1979; Hardy & Tucker 1988) were relatively high in both dolomite grain size groups and

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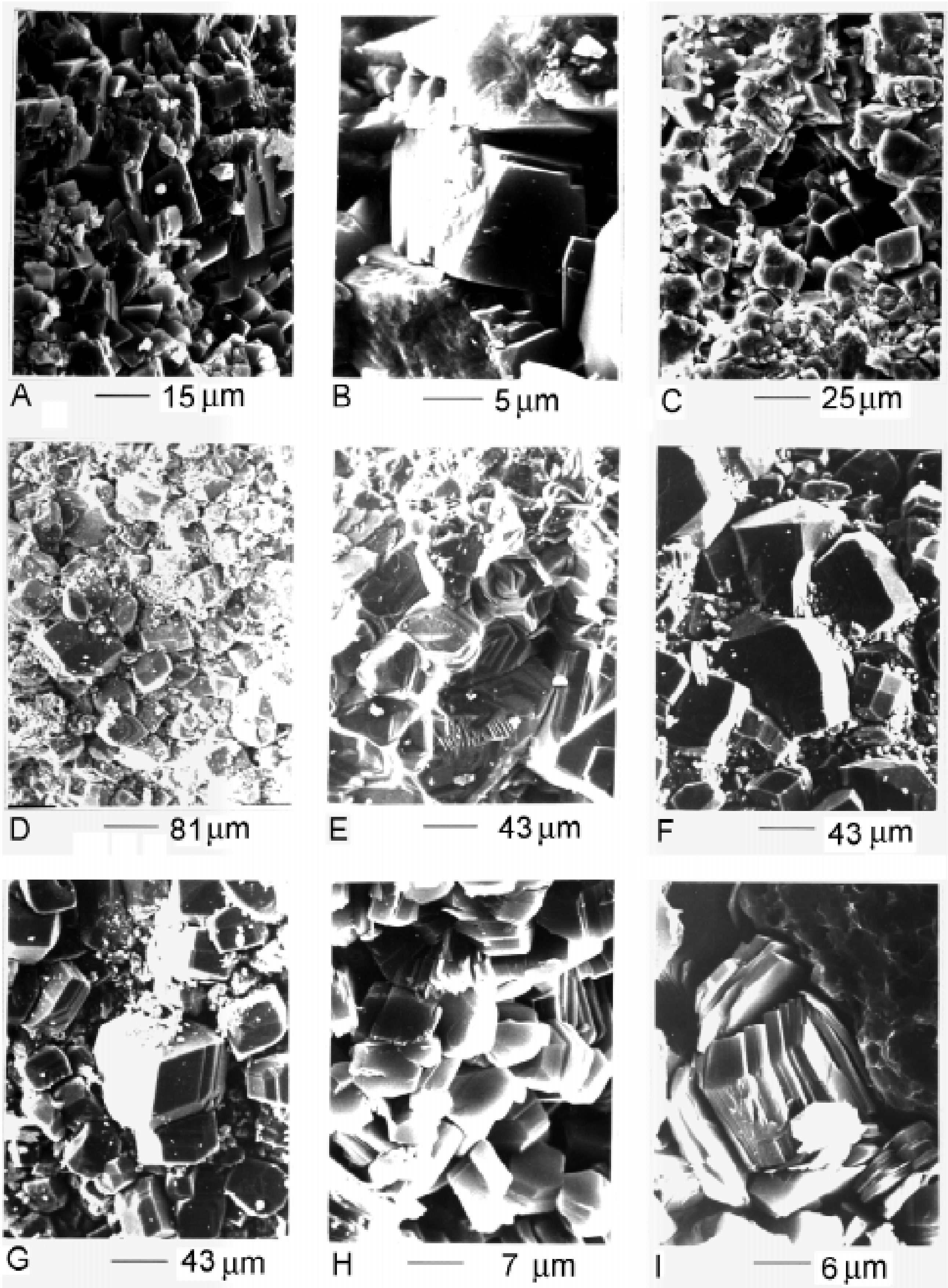
Fig. 7. Microphotographs (SEM) of the dolomites and calcites (dedolomites) in the K-3, cores 20 to 22. **A–B** — Dolomite microsparitic to sparitic matrix formed by idiomorphic rhombs. **C** — Leaching or partly dissolved dolomite rhombs on both grain generations. **D** — Large neomorphic idiomorphic calcite crystals covered with dolomite ash. **E** — Neomorphic calcite in some part of sample filling the space completely. **F–G** — Calcite crystals (dedolomite) with „open“ intercrystalline pores with residual dolomite grains. **H–I** — Neomorphic platy kaolinite crystal on the calcite surface (etched by acid).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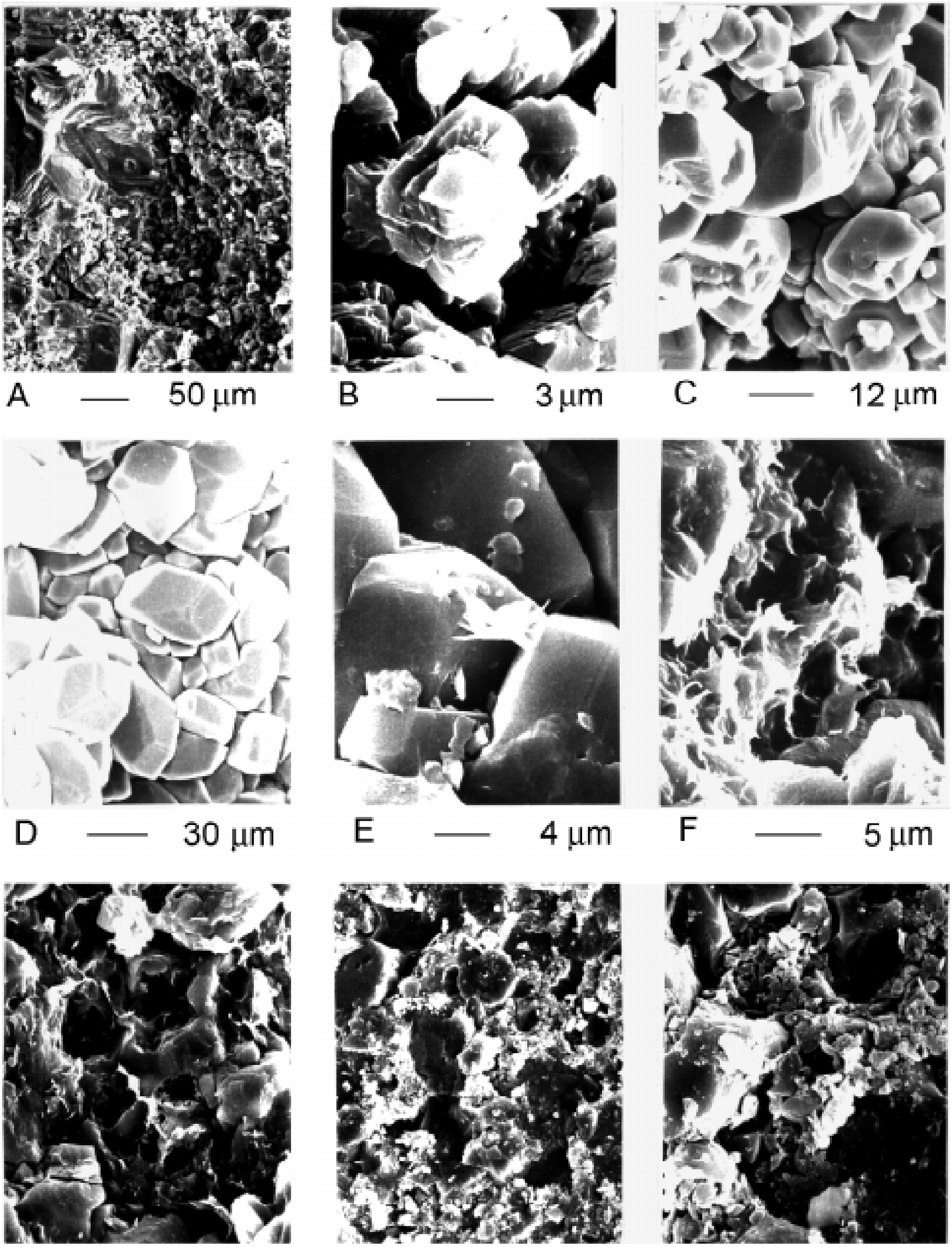
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Table 3: Mineralogical composition and isotope analyses of the rock samples.

Sample	calcite	dolomite	IR	calcite		dolomite	
		wt. %		per. mil PDB			
				$\delta^{13}O$	$\delta^{18}O$	$\delta^{13}C$	$\delta^{18}O$
K3							
6/2708	6.67	91.67	1.66			0.1	-2.1
7/2704	8.15	90.80	1.05			3.0	1.3
8/2851	8.19	91.06	0.85	2.1	0.2	2.4	0.5
10/2952	12.05	84.08	3.78	1.2	0.6	1.4	0.9
11/3011	5.18	83.58	11.24			2.3	0.2
12/3090	0.39	11.50	88.11			0.5	-0.1
13/3177		29.58	70.11			1.8	-0.3
14/3237	14.30	79.22	6.48			2.9	-2.0
15/3391	94.72	1.88	3.23	3.8	-3.7		
15/3392	93.43	3.73	2.67	3.7	-3.6		
19/3663	66.32	17.41	16.27	2.5	-4.3	2.7	-4.8
20/3676	9.94	89.63	0.56	3.3	-2.1	4.1	-1.6
20/3677	8.71	90.50	0.46			3.9	-1.4
21/3825.5	81.20	17.75	1.05	1.5	-7.6		
21/3825.8	90.32	8.86	0.92	1.4	-8.6		
21/3826	95.11	4.68	0.21	1.5	-9.0		
22/3827	90.11	9.47	0.42	3.5	-4.6		
22/3827.5	85.92	12.90	2.18	2.0	-8.6		
22/3828	92.73	5.71	1.56	1.8	-7.7		
34/4902	86.96	3.42	9.16	1.7	-3.9		
K4							
11/3697	92.36	5.51	2.18	-0.7	-7.4		
12/3730cl	90.26	5.00	4.74	1.1	-6.4		
12/3730ce	90.26		21.68	1.4	-8.2		
12/3732	80.08	6.43	10.87				
12/3732cl	60.10		29.90	1.2	-8.0		
12/3732ce	63.40		26.60	1.2	-8.2		

cl — clast, ce — cement

were in the range 0.6 to 1.0. Dolomites with evaporates and specimens with quartz (cores 11 to 13) were not assessed by this method. Contents of microelements in rock specimens (Table 2) documented relative differences in composition of dolomite/limestone layers. Analyses of separated parts of breccias (Table 2), clasts and matrix/cements show partly comparably high quantities of observed elements (Sr, Fe, Mg or Na) in the observed parts, and also comparably higher concentrations than in the limestones. The neomorphic calcites have a higher content of observed elements than the overlying dolomites. Thus, if they originated by substituting dolomites, then these alterations indicate buried diagenesis in a buried sediment and the operation of diagenetic solutions. On the other hand fluids with a sufficient concentration of calcium or brines could be obtained by dissolution of evaporite layers or cements (Fig. 3; the well K-3, cores 12 to 14), although the fluids could be originally of a meteoric origin (e.g. buried together with sediment below the Neogene fill, or descending to depth along faults during different time periods). High contents of Na could indicate the presence of sea water pore solutions or rock brines in the recrystallization process.

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Fig. 8. Microphotographs (SEM) of the dolomite and the calcite in the K-4, cores 10 to 12. **A** — Micrite to microsparite dolomite matrix with large calcite grains in the join. **B** — Microsparite dolomite rhombs were dissolved/leached (detail from A). **C–D** — New generation of the idiomorphic calcites, with the characteristic calcite crystal-morphology. **E–F** — Neomorphic illite particles covering calcite surface and also filling the open pore spaces between grains. **G** — Siliclastic minerals mainly accumulated in the stylolite were altered and form new mineral phases. **H–I** — Dissolution and substitution of dolomite crystals by calcites. Small residual dolomite rhombs were accumulated among large calcite grain.

Isotopic analysis

We can interpret two basic trends in the distribution of data in both fields of isotopic data (Fig. 9) which reflect on the one side preserved sedimentary or early diagenetic dolomitization distribution of values of isotopic ratios and on the second later or deep burial diagenetic influences on isotopic ratios of O and C. The specimens from the Hauptdolomite Formation (cores 6 to 14, Fig. 9, field 1) have more positive values of $\delta^{18}O$ than dolomites or calcites from the Opponitz Limestone Formation and indicate the evaporitic type of dolomitizing solutions, probably the sabkha type of dolomitization in strata overlying an evaporite sequence. The values of $\delta^{13}C$ for these specimens were in the range of normal sea values (0 to 4 ‰), however, they were slightly decreased (Table 3). The specimen from core 6 is fairly shifted to lower values both for $\delta^{13}C$ (+0.1 ‰) and $\delta^{18}O$ (–2.0 ‰). The dolomites of this core were most tectonically disturbed, but calcite content was low here. The values of couples calcite-dolomite were close though they were lower in younger calcites. The calcites had to be formed in joints from pore solutions which did not significantly differ in the origin of C and O, but they could be formed at higher temperatures. However, it could even be a case of mixing of (meteoric) solutions/water dissoluing dolomites in surface (pre-Neogene) conditions and calcites were formed from them. Limestones and dolomites of the Opponitz Limestone Formation form the second field (Fig. 9, field 2) and indicate a different sedimentation or also a dolomitization environment. The values of $\delta^{18}O$ were predominantly lower and $\delta^{13}C$ were predominantly higher than for the Hauptdolomite Formation specimens. In dolomites (only 3 analyses) values of $\delta^{18}O$ were considerably variable in comparison to limestones. The limestones have preserved balanced original (sedimentary) high values $\delta^{13}C$ which do not follow smaller variations in the values for $\delta^{18}O$ in the set. In comparison of the couple calcite-dolomite from core 20 we can see that dolomite has higher ratios of C and also O than the neomorphic calcite (Table 3) which indicates a (late) diagenetic origin of the calcite (Fig. 9, field 2′). In the value set for the Opponitz Limestone Formation specimens we can follow a more distinctive diagenetic trend towards the basement (Table 3). The most significant is the decrease of the $\delta^{18}O$ ratio and also a slight decrease of the $\delta^{13}C$ ratio in the calcites. Changes of the same nature were manifested in both ratios, but $\delta^{13}C$ remained relatively small. An exception is represented by a calcite specimen from the well K-4 (core 11) which has a more significantly decreased carbon ratio (Fig. 9). The two specimens were partly enriched in C^{12}, and in both cases this could be also the influence of carbon of an organic origin, for example as a result of the decay of organic matter (reduction of sulphates) as well as the influence of mixing of different solutions. Our set also includes a specimen of the Reifling Limestone Formation from a depth of 4902 m (i.e. approx. 100 m deeper). This limestone has no apparent signs of diagenetic alteration, (Masaryk et al. 1993) as with limestones from core 15. It differed rather by isotopic ratio of C than O and the decreased ratio could be a reflection of an originally deeper sedimentary environment.

Discussion

Taking into account microstructural properties as well as changes of the chemical composition of dolomites or calcites, from wells K-3 and K-4, we judged that dolomites were also diagenetically altered under conditions of deep (present) burial (Fig. 3). We described a diagenetic stratum characterized by the presence of a new generation of coarse grained, well crystallized calcites (Figs. 7–8) in the Opponitz Limestone Formation at a depth of approximately 3660 to 3830 m with an observed significant increase of porosity. These calcites substituted partially or totally the original sedimentary dolomite breccia in wells K-3 and K-4. In both wells this layer is situated at an equivalent depth which itself indicates that it was created under conditions of the deep (present) burial, especially since we know that in spite of the close position of these wells (Fig. 1), they did not penetrate the same lithological succession. In well K-4 the Opponitz Limestone Formation is in a reversed position indicating the tectonic complications in the basin basement. Diagenetically altered beds are joined rather to layers of original dolomite, and or dolomitized breccias. As a matter of course, there was a disadvantage in this comparison caused by the fact that we could study only separated segments of sequence from the well cores and the missing segments were much longer than the available cores.

Based on our results we assume that the neomorphic calcites were the result of the dedolomitization process in a deeply buried sediment. Dedolomitization was originally described as a close subsurface process, but later on also for different conditions and depths (DeGroot 1967; Back et al. 1983; Land & Prezbindowski 1981; Stoessel et al. 1987; Kastner 1982; Budai et al. 1984; Loucks & Elmore 1986 and others). We noticed the disturbed, mostly dolosparitic grains in the dolomites of the highest part of the basement (e.g. cores 6, 6A, 8, Fig. 6). However calcite fills have mainly tectonic joints (Figs. 4, 6D). The disturbance/dissolution of dolomites has a similar nature in a deeper part of the well sections (cores 20 to 21), but the neomorphic calcites are entirely different. According to our observation, calcites crystallized not only in joints, but they substituted a greater volume of the dolomite or dolomitic breccia. A style of dolomite rhombohedrons substitution is characteristic for the dedolomitization (Rao 1969; Mišík 1988; Holail et al. 1988) and can virtually be considered as a primary proof. We used a SEM for the study of microstructures as well as an optical microscope. The SEM microphotographs illustrated relations between the new and preceding grains well. The neomorphic calcites are different from calcites in joints and their morphology is quite similar to laboratory evolved dedolomite crystals (Stoessel et al. 1987). It is also possible to see the presence of other mineral phases and judge the relative (temporal) succession of the origin of phases. We could see the presence of post-dedolomitization phases — illite, kaolinite, pyrite or fluorite. Fluorite was described together with celestine by Mišík (1986) in well K-3. The coexistance of these phases documents the efficiency of diagenesis and the extent of deep burial conditions. Neomorphic illites spreading to the free spaces between calcites (Fig. 8) could be a good indicator of such a process. Kaolinite with a platy-morphology (Osborne et al. 1994) is also characteristic product of diagenesis in deep burial basin conditions (at least 2000 m).

Large, idiomorphic calcite crystals evidently needed a sufficiently long time for their formation. The presence of impermeable beds (e.g. the Lunz Formation, Fig. 3) as well as the actual depth (below 3 km) favours the lateral flow of the solutions. However, it is impossible to exclude the role of tectonic joints as ways for dedolomitizing solutions. In the highest part of dolomites almost exclusively tectonic joints are filled by calcite. It is evident that also in a dedolomitized layer some calcites crystallized into free space (tectonic fractures?). However, proper calcitized parts were frequently packed, which was indicated by measured porosity data. The first (principal) increase in porosity was attached to partly substituted dolomites where there are many partially dissolved grains. The porosity was also decreased by a subsequent illite formation (mostly K-4, Fig. 8). The affect of solutions rich in calcium and sulphates/chlorides was considered in the interpretation of dolomite alteration. We assume that, for example, dissolved anhydrite layers could serve as the source of calcium. A sufficient amount of Ca^{2+} is a critical factor for the process of dedolomitization (Kastner 1982; Back et al. 1983; Stoessell et al. 1987), and not a high content of sulphates (Katz 1968; Land & Prezbindowski 1981; and others). However, the composition of the solutions is still not clear (Land & Prezbindowski 1981; Stoessell et Moore 1985).

Dedolomites created under conditions of deep burial (Budai et al. 1984) differ from close subsurface ones by having a relatively high content of elements such as Sr, Fe, but also Na. Na indicates non-meteoric origin of solutions (of water) leading to the formation of the neomorphic calcites. It is typical for Fe that it is joined to the carbonate and oxide or hydroxide minerals. Comparing the content of observed elements in dolomites, limestones and diagenetic calcites, we can see that neomorphic, coarse grained calcites have relatively high content of the above mentioned elements, higher than dolomites.

The isotopic ratios of O and C in the neomorphic calcites significantly decreased, especially that of $\delta^{18}O$. The $\delta^{13}C$ is shifted only relatively, and still represents values of marine carbonates and such values Budai et al. (1984) mentioned for a joint type of dedolomites. The isotope values of the studied rock specimens are in general comparable with the previously studied Triassic carbonates (Lintnerová & Hladíková 1992; Soták & Lintnerová 1994), and with some ancient sabkha facies (Tucker 1990). Calcites forming fill of joints in tectonized dolomites have also relatively high isotopic ratios, although relatively lower then adjacent dolomites. It is impossible simply to identify these conditions only as a reflection of the thermal differentiation of isotopes in respect to an evaporite environment and enrichment of oxygen ratio in a

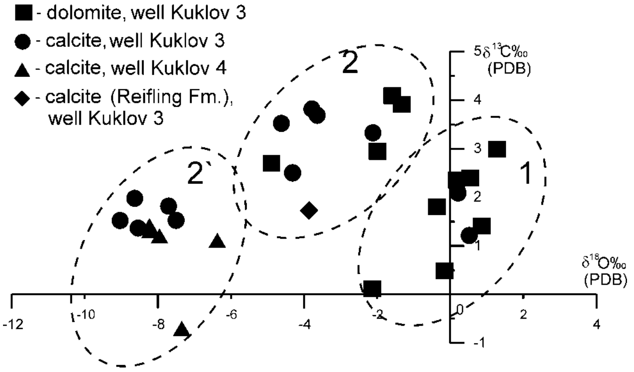

Fig. 9. Isotopic results in graph documenting the diagenetic trend in both groups of carbonate. Squares — dolomite K-3, circles — calcite K-3, triangle — calcite K-4, rhombs — sample of Reifling Limestones.

heavier isotope connected with that. This process can also be considered for late diagenetic (dedolomitization) fluids, although in a longer transport (higher amount of water) this effect could become less important. The Vienna Basin is regarded as a „cold basin“ and the interpolated temperatures at the depth of 3000 to 4000 m are 107 to 127 °C (max. 150 °C: Franko et al. 1995). From diagenetic alteration of the organic matter of the Lunz Formation (3940 to 4550 m) a temperature range of 100 to 120 °C was deduced (Borza et al. 1985). The process of dedolomitization could quite well operate at such temperatures (Stoessell et al. 1987).

Conclusions

1. Diagenetic post-sedimentation processes influenced the properties of the dolomite rocks to a different extent. Most extensively the breccia layers in the depth of 3660 to 3830 m were altered, so that significant values of secondary porosity (locally up to 15 %) appeared.

2. The top parts of the dolomite sequences forming the erosive surface of the Mesozoic basement to a certain extent preserved their properties since they were formed by dolomitization in a sabkha environment. This is indicated by their relatively high (evaporitic) isotopic ratio of O and C. Values of isotopic ratios of calcitic and dolomitic cements (tectonic breccia) were at least lowered, which could have been affected precisely by the evaporite participation in the sequence.

The porosity changes are found in the calcitic dolomite to limestone layers where sparitic, idiomorphic calcites with remains of preceding dolomite can be observed. The microstructural and also geochemical properties of these calcites indicate their late-diagenetic origin in the buried sediment. The $\delta^{18}O$ was significantly decreased, but the content of microelements as well as values of $\delta^{13}C$ remained relatively high.

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