

## 7. Petrographic characteristic of studied sections

In addition to the microfacies analysis, a detailed petrographic evaluation of these sediments was undertaken. The results are in agreement with previously published data, and also reveal some specific details concerning the diagenetic changes these carbonates underwent. The results are summarized in tab. 9.

The unrecrystallized micritic matrix of these limestones is probably the result of the mechanical decomposition of the bioclastic material (KUKAL 1964). This is supported by the lack of relict fibrous structures (such as phantom crystals of aragonite). These limestones are relatively rich in insoluble residues (clay), and some of them possess nodular textures. Organic remains are also abundant. These observations repudiate a diagenetic origin for the micrite (see KUKAL 1964).

The microsparite which is especially common in the Radotín Limestone facies (Lochkov Formation, Černá rokle) seems to have resulted from the recrystallization of a micritic matrix. This is verified by the local displacement of clay and organic matter into crystal interspaces, whereas the original matrix should have contained an amount of insoluble residue. In some cases the microsparite is pure and composed of larger crystals, without clay or any admixture of organic matter. Common transitions from microsparite to sparite confirm an analogous origin for the sparite.

Sparite cement is common in bioclastic crinoidal limestones. The analysis of the sedimentary environment of these limestones shows the influence of waves in littoral or sublittoral zones, which sorted the organic debris. Sparite cement crystallized in the voids between bioclasts, either immediately after sedimentation or after the washing out of micrite. Syntaxial sparite overgrowths around crinoid stems are a very common feature. In a deeper basin below wave base the organic debris was not thoroughly flushed out or reworked, and relics of the micritic matrix often recrystallized into microsparite. Such relics are especially common in SMF 5 where they can occur within sparite cement, bioclast interspaces, or as fillings in shells.

The amount of insoluble residue (clay with some organic matter) is highly variable. It is well known that organic matter and clay suppresses the recrystallization of micritic matrices. The nodular Dvorce-Prokop Limestone, in which the original matrix is preserved due to its higher clay content, is a good example of this phenomenon. According to KUKAL (1964, 1975) nodular structures form mainly in limestones that contain 15–25 % insoluble residue.

KUKAL (1964) also found a relation between organic matter and clay content. Organic carbon is often bound to the clayey component. In some cases, however, organic matter accumulates even in clay-poor microsparitic limestones, as in the Radotín Limestone (Černá rokle).

The migration of organic matter as a result of warming during the Variscan orogeny, or due to the deeper burial of these sediments (as presumed by SUCHÝ et al. 1996), are

both possible. The Radotín Limestone is richer in organic matter. Considering that some organic matter migration is to be expected, the higher proportion of insoluble residue in the Dvorce-Prokop Limestone must have hindered such movement. By contrast, the clay-poor Radotín Limestone served as a favorable medium for such migration.

Clastic quartz usually occurs as sharp-edged, fine or sand sized grains of silt in most of the thin-sections. According to KUKAL (1964) it may be of eolian origin. This interpretation is supported by the uniform size of these grains, which is distinct from the grain size of limestones. Bioclastic limestones of shallow-water origin have relatively minor proportions of clastic quartz, much less than in micritic and biomicritic limestones.

Authigenic minerals are represented mainly by pyrite, dolomite, and a localized silica component.

The pyrite does not show any correlation to the grain size of the limestones. It is present as idiomorphic crystals or small aggregates of pyrite crystals of different sizes, sharply delimited from the matrix or cement. It is generally agreed that the pyrite is of an early diagenetic origin, formed by bacterial reduction of sulphates in the sea water (BERNER 1969, 1981), though additional accretion during late diagenesis is also possible.

Dolomite is present in several types of different origins. The first is a fine-grained mosaic of poorly developed dolomite rhombohedra (such as the Radotín Limestone in Černá rokle or the Přídolí Limestone in the Radotín section). The origin of this type is connected with the lithification of sediment during the early stages of diagenesis (KUKAL 1955b). Early diagenetic dolomitization on a larger scale is evident in the Marble quarry (beds X/8 and 8/9) and in Požáry quarry (bed 159). These dolomites form beds up to 1 m in thickness (with biomicritic limestone lenses in the Marble quarry). Crystals of dolomite are equally sized (size between 0.03 and 0.2 mm), without preferential orientation or zonal fabric (pl. 8 – figs. 1 and 3). Insoluble residue has been displaced into the spaces between the dolomite rhombohedra.

The dolomite of a second type is characterized by individual idiomorphic crystals or their aggregates (pl. 8 – fig. 4). The origin of this dolomite is late diagenetic (or epigenetic, according to KUKAL 1955b, 1964). Zoned dolomite crystals are present in the Cikánka and Požáry quarries. The crystal nuclei are usually ochre-coloured and overgrown by sharply delimited rhombohedra of pure dolomite. The late diagenetic concentration of pre-existing, early diagenetic dolomite is possible, but it is difficult to date these phases. The Variscan thermal event could also have caused such an episodic overgrowths. However, weathering could also have been involved in creating this texture.

Dolomite crystals often appear along microstylolites where Mg-ions concentrated during high-pressure dissolution (pl. 8 – fig. 2). These sutures could also serve as zones for the secondary migration of Mg-ions, especially when these structures became slightly crushed.

The problems of dolomitization and source of the Mg-ions have been frequently discussed (for example, see

Table 9. Petrography of limestones in the studied boundary intervals

SILURIAN				SILURIAN	DEVONIAN				DEVONIAN			
Upper Ludlow		Lower Přídolí	Upper Přídolí	Upper Přídolí	Lower Lochkovian			Upper Lochkovian	Lower Pragian			
"BcF"	"MF"		Rad.		Kosoř	Kotýs	"scyph."		Rad.	Kosoř	Kotýs	Dv.-Pr.
Bioclasts	K	●	●	●	●	X	●	●	X	X	●	X
	MI	●	●	●	X	●	X	VCh	●	X	●	X
	Po	●	●	●	●	X	●	Cik		●		●
Micrite	K	/	●	●	●	X	●	●	●	X	●	X
	MI	●	●	●	X	/	X	VCh	●	X	●	X
	Po	●	●	●	●	X	●	Cik		●		●
Sparite	K	/	●	/	/	X	/	●	●	X	/	X
	MI	●	●	●	●	X	X	VCh	●	X	/	X
	Po	●	●	●	/	X	●	Cik		●		●
Clay	K	X	●	●	●	X	/	●	●	X	●	X
	MI	/	●	/	/	X	X	VCh	●	X	●	X
	Po	/	●	●	●	X	X	Cik		/		●
Clastic quartz	K	X	●	/	/	X	/	●	●	X	/	X
	MI	/	X	/	/	X	X	VCh	●	X	●	X
	Po	X	X	/	/	X	/	Cik		●		/
Chitinous and phosphatic remains	K	X	/	X	X	X	X	●	●	X	●	X
	MI	/	X	X	X	/	X	VCh	●	X	●	X
	Po	/	/	/	/	X	/	Cik		●		/
Dolomite	K	●	X	●	●	X	●	●	●	X	/	X
	MI	●	X	●	X	X	X	VCh	●	X	●	X
	Po	/	X	●	●	X	●	Cik		●		●
Silicification	K	X	●	X	X	X	X	●	●	X	/	X
	MI	X	/	X	X	X	X	VCh	●	X	/	X
	Po	X	/	X	X	X	X	Cik		●		/
Pyrite	K	/	●	/	/	X	X	●	●	X	●	X
	MI	●	●	●	X	X	X	VCh	/	X	●	X
	Po	/	●	●	X	X	X	Cik		/		●

Localities: K – Kosov quarry, MI – Marble quarry, Po – Požáry quarry, R – Radotín, Pd – Podolí, Čr – Černá rokle, VCh – Velká Chuchle, Cik – Cikánka; Facies: Rad. – Radotín Limestone, Kosoř – Kosoř Limestone, Kotýs – Kotýs Limestone, Dv.-Pr. – Dvorce-Prokop Limestone, Sliv. – Slivenec Limestone, "BcF" – bioclastic facies, "MF" – micritic facies, "scyp." – coarse-grained crinoidal and cephalopod limestones of so-called "Seyphocrinites horizon"; relative content of components: ● – abundant, ● – common, / – rare, / – sporadic, X – component is not present, [X] – facies is not present at locality, [ ] – facies is present out of studied interval.

KUKAL 1986, and SUCHÝ et al. 1996). According to PETRÁNEK (1951b) the crinoid stems were the source of the Mg, which is supported by the common crystallization centres in their axial canals observed in coarse-grained crinoidal limestones (Cikánka, Velká Chuchle, Požáry). The original crinoid skeleton was composed of low-Mg calcite (PETR et al. 1997). NÁPRSTEK's theory (1954) of stagnant water with a high concentration of Mg-ions is highly improbable. Micritic to biomicritic limestones of deeper-water origin contain mainly early diagenetic dolomite. The source of Mg-ions could thus have been the sea water, the micritic matrix, and/or organic matter.

Several types of silicification have been observed, although it occurs infrequently. One type is represented by microscopic nodules of chalcedonic quartz (Velká Chuchle, Kosov, Požáry) as described by SVOBODA et al. (1957). These nodules probably originated by the local replacement of sparite or micrite by radial fibres of chalcedony (pl. 7 – fig. 3). Fracture fills can also serve as centers of silicification.

Another type of silicification is represented by silicified bioclasts in coarse-grained bioclastic limestones (Cikánka, Kosov; pl. 7 – figs. 1 and 2). Crystals of early diagenetic dolomite invading silicified crinoid stems show that silicification preceded dolomitization. This is in agreement with PETRÁNEK (1951b), NÁPRSTEK (1954), and KUKAL (1955b), all of whom considered silicification in the Barrandian limestones to have been of an early diagenetic origin. Quartz fillings of fractures in the biomicritic limestone of the Požáry quarry (Lower Přídolí) show that late diagenetic silicification also occurred. The fractures are filled by first generation calcite and by second generation chalcedonic quartz.

A third type of silicification resulted in the nodular cherts that occur in the fine-grained Kosoř Limestone in the Radotín section (pl. 7 – fig. 4), in which sponge spicules are frequently preserved. The presence of idiomorphic dolomite crystals in the siliceous substance demonstrates that this silicification preceded dolomitization.

According to PETRÁNEK (1951b), PETRÁNEK and ŠTENGLOVÁ (1953), and KUKAL (1964) the sources of the silica were siliceous shells and sponge spicules. Other siliceous organisms reported from some Barrandian limestones, such as radiolarians by PETRÁNEK (1951a, b, c), were not found.

## 8. Geochemistry

Although the study of the chemical composition of carbonates in selected sections is not the main objective of this paper, we can compare some of our results with previously published data (such as SVOBODA et al. 1957, KUKAL 1964, PETR et al. 1997). Only rough data based on a limited number of analyses are presented here, for which FeO, MgO, and insoluble residues were analyzed in the main types of carbonates.

All the three plots show the positive correlation of the three components: FeO, MgO, and insoluble residue. This trend is especially pronounced in the micritic and biomicritic limestones.

By contrast, such correlations are not evident in shallow-water bioclastic (crinoidal) limestones. This can be explained by the observation that bioclastic limestones lack the micrite which contains clay and minute quartz grains.

The oxidation of Fe ions into Fe<sub>2</sub>O<sub>3</sub> in a basinal dysoxic and/or anoxic environment is less probable than in well oxygenated, shallow-water zones (such as the Cikánka or Lower Lochkovian in the Požáry quarry). The shallow marine facies of the Lower Devonian (e. g. the Kotýs, Slivenec, and Řeporyje Limestones) are often red or pink-coloured due to the presence of Fe-pigment. It is well known that Fe ions are often fixed in a bivalent form in dolomite, and sometimes in clay.

Most of the MgO is bound to dolomite, and only small amount to clay minerals. In micritic limestones the early diagenetic dolomite predominates, but in bioclastic lime-

Table 10. Results of chemical analyses

	layer	FeO [%]	MgO [%]	insoluble residue [%]	type of limestone
Lochkovian – Pragian	Čr-87	0.58	0.99	19.52	micritic or biomicritic
	Čr-70	0.46	0.99	8.7	micritic or biomicritic
	VCh-2	0.11	0.65	3.36	biosparitic
	VCh-22	0.24	0.82	4.52	micritic or biomicritic
	Cik-4	0.19	0.69	1.06	biosparitic
	Cik-16	0.11	1.5	2	biosparitic
Přídolí – Lochkovian	R-3	0.34	1	13.3	micritic or biomicritic
	R-12	0.13	0.8	11.18	biosparitic
	Po-161	0.24	1.92	1.7	biosparitic
Ludlow – Přídolí	K-3	0.1	0.41	2.02	biosparitic
	MI-3	0.11	0.68	2.12	biosparitic
	MI-8	0.21	0.75	7.98	micritic or biomicritic
	Po-96	0.03	2.52	4.82	micritic or biomicritic
	Po-98	0.06	0.74	2.46	biosparitic

Čr – Černá rokle near Kosoř, VCh – Homolka near Velká Chuchle, Cik – Cikánka near Praha-Slivenec, R – Praha-Radotín, Po – Požáry quarry near Praha-Řeporyje, K – Kosov quarry near Beroun, MI – Marble quarry near Praha-Lochkov. Analysed in the chemical laboratories of the Czech Geological Survey by H. Hanušová, J. Šíkl and M. Mikšovský.