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Zechstein (Ca1) limestone-marl alternations from the North-Sudetic Basin, Poland: depositional or diagenetic rhythms?

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Limestone-marl alternations constitute a characteristic rock facies within the Zechstein Limestone (Ca1) deposits of the North-Sudetic Basin, Poland. Rhythmites of this type are exposed in a 10-metres section at Nowy Kościół, which from the beginning of the last century has been considered representative for this part of the Zechstein basin, and were formerly interpreted as calcareous storm sediments alternating with marls deposited during more quiet conditions. Our results of sedimentological, petrographical and chemical studies suggest that the Nowy Kościół section is a record of distal storm deposits, but that the present-day layering does not precisely reflect the depositional rhythm. Post-depositional changes have overprinted and blurred the original pattern. We propose a model of diagenetic alteration in which dissolution and reprecipitation of calcium carbonate in the shallow subsurface formed new layer boundaries; subsequent modifications during deeper burial followed these early diagenetic changes.

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INTRODUCTION

Limestone-marl alternations, a common component of many carbonate sections throughout the geological record, have been the subject of long-lasting controversy (e.g. Bathurst, 1971; Hallam, 1986; Einsele and Ricken, 1991). They have been interpreted as reflecting cyclic depositional changes or, conversely, being solely of diagenetic origin.

The former interpretation assumes that each individual layer carries an environmental signal and — as a whole — the section is a geological record of temporal environmental changes, such as orbitally forced climatic fluctuations. Since the pioneering work of Hays *et al*. (1976), who recognized a record of Milankovitch cycles in Pleistocene deep-sea sediments, many authors have attempted to find such trends in older sediments. For example, orbitally-induced palaeoclimatic variations have been deduced from studies of Lower Carboniferous (Elrick *et al*., 1991), Lower Jurassic (Weedon and Jenkyns, 1999) or Cretaceous (Bellanca *et al*., 1996) limestone-marl sequences. All of these examples concerned deep-water sediments. Four main types of mechanism forming pelagic calcareous rhythmites have been recognized (Einsele and Ricken, 1991; and references therein): (a) productivity cycles reflecting a variable supply of carbonate biogenic material, (b) dilution cycles predicated upon periodic fluctuation of supply of fine terrigenous sediments, (c) dissolution cycles related to periodic dissolution of carbonate and (d) calcareous redox cycles indicating fluctuations of bottom water oxygenation. Among the environmental changes which may cause alternating sediment cycles, sea level fluctuations, humidity-aridity variations, current variations and so on have been proposed. The role of diagenesis in these “depositional models” has not been ignored, although it has been assumed that the environmental signal is not entirely blurred by subsequent modification.

Opposing these models, diagenetic scenarios describe limestone-marl couplets as products of unmixing of homogenous or nearly homogenous precursor sediment. This hypothesis has been postulated on the basis of differential diagenesis between limestone and marl layers: limestones usually undergoing cementation during early diagenesis, whereas marls were subject to dissolution processes (Bathurst, 1971). Frequently, limestone layers contain well preserved delicate fossils and undeformed or only slightly deformed trace fossils, whereas in marls fossils are flattened, deformed or even dissolved away (e.g. Munnecke and Samtleben, 1996; Westphal *et al*., 2000). A lack of distinct differences in the composition of diagenetically stable components (such as palynomorphs or diagenetically inert chemical compounds) between limestones and marls is a further premise in this argument (Munnecke *et al*., 2001; Westphal *et al*., 2004). The calcium carbonate necessary to the cement limestone layers was said to derive from dissolution of calcite in adjacent marls (Ricken, 1986; Hallam, 1986). Recently, an aragonite-based model has been developed (Munnecke and Samtleben, 1996; Westphal *et al*., 2000; Munnecke *et al*., 2001; Böhm *et al*., 2003). This model proposes that dissolution of metastable aragonite during early marine burial diagenesis is a driving mechanism for further differentiation. The dissolved calcium carbonate is diffusively transported upwards through the sediment column to reprecipitate as stable calcite in the cementation zone. The cemented layer, due to tight cementation, does not undergo dissolution. This model is applicable to shallow-marine and hemipelagic sediments, analogous to those from modern aragonite sedimentation areas (Westphal and Munnecke, 2003). However, the diagenetic model alone does not explain large lateral extent, of the order of kilometres, of the limestone and marl layers. Ricken (1986) and Ricken and Eder (1991) suggested that diagenesis enhances minor initial differences in the precursor sediment. Also, Böhm *et al*. (2003), who provided a computer simulation of the aragonite-based model, came to the conclusion that a very limited external trigger is necessary to obtain laterally extensive limestone-marl alternations.

Our study concerns the lower Zechstein limestone-marl sequence which crops out in the abandoned quarry at Nowy Kościół in the North-Sudetic Basin, SW Poland. Alternating marls and limestones, constituting a *ca*. 10 m thick section, have been interpreted as distal tempestites deposited in a vast lagoon, where limestone layers were formed by a storm-generated supply of calcareous material from neighbouring shoals, and marl layers were deposited from suspension during quiet weather conditions (Raczyński, 1996, 1997). Analogous rocks that crop out nearby in the vicinity of Leszczyna were interpreted either as distal storm deposits or as sediments reflecting cyclic flooding on the neighbouring land (Śliwiński, 1988). Generally, this lithofacies association is widespread in the eastern part of the North-Sudetic Basin, and the Nowy Kościół section has been regarded for a long time as typical of the Zechstein Limestone in that area (e.g. Riedel, 1917; Scupin, 1931; Niśkiewicz, 1967; Peryt, 1978*a*). The limestone-marl sequence passes into the copper-bearing Kupferschiefer to the north (Eisentraut, 1939), and small-scale lithological variations within the Kupferschiefer have been interpreted as oxygenation cycles caused by wavebase fluctuations (Oszczepalski, 1988); consequently, sea level changes during the Kupferschiefer deposition have been suggested (*op. cit*.). The aim of this study was to investigate whether the limestone and marl layers at Nowy Kościół are closely related to cyclic depositional changes, and thus represent signals of environmental changes such as sea level oscillations or climate fluctuations in the Late Permian, or if they reflect postdepositional alteration. In other words, we consider the role of diagenesis in the formation of the layering seen today.

GEOLOGICAL SETTING AND LITHOSTRATIGRAPHY

The North-Sudetic Basin (Fig. 1) is a remnant of a Late Palaeozoic intramontane trough formed as a result of the Variscan orogeny. The area studied was located in the south-eastern, marginal part of the European Zechstein Sea Basin (Fig. 1A). At present, the Zechstein outcrops form a relatively narrow zone in the outer part of the North-Sudetic Basin. The Nowy Kościół section, studied here, is situated in the eastern part of the basin, in the Leszczyna Syncline, a minor tectonic unit formed during Late Cretaceous tectonism.

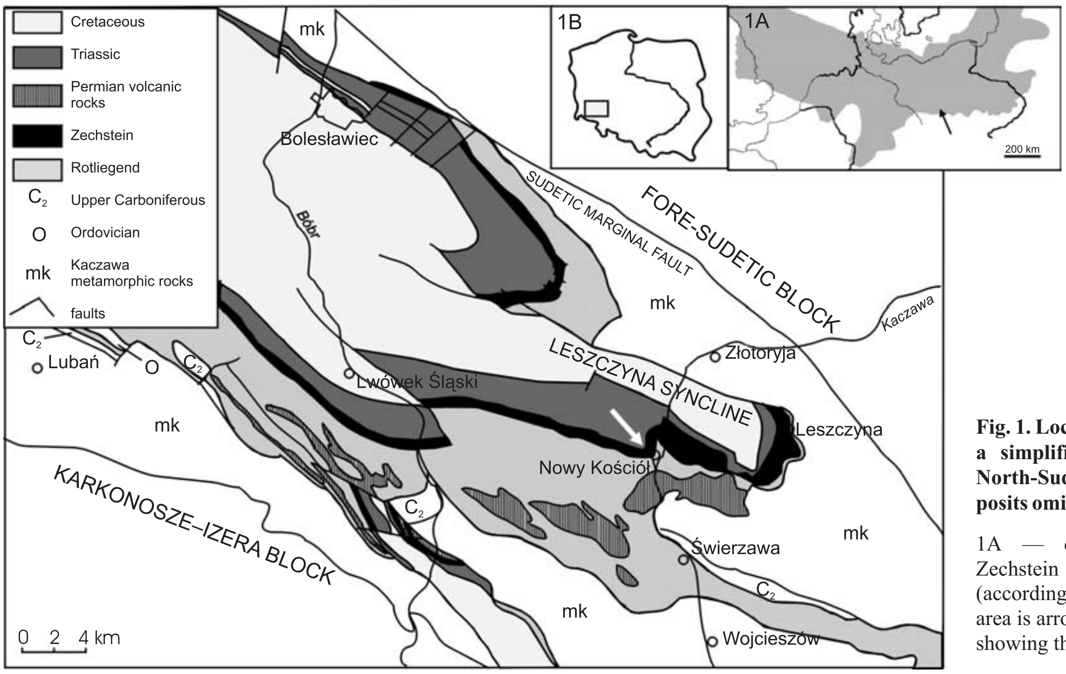

Fig. 1. Location of study section within a simplified geological map of the North-Sudetic Basin; superficial deposits omitted (after Sawicki ed., 1965)

1A — depositional limits of the Zechstein Limestone (Ca1) in Europe (according to Scholle *et al*., 1995), study area is arrowed; 1B — outline of Poland showing the North-Sudetic Basin

A pronounced dominance of siliciclastics and carbonates over evaporates, and a reduced thickness of the succession constitute distinctive features of the North-Sudetic Basin sediments in comparison with those of the central part of the Zechstein Basin. Therefore, direct application of the Zechstein cyclothem lithostratigraphy has turned out to be problematic, although many such attempts have been undertaken (e.g. Gunia, 1962; Peryt, 1978*a*; Raczyński, 1997). The old local division proposed by Scupin (1931) is still in use. According to this division, the limestone-marl association is subdivided into three subunits: Spotted Marls, Copper-bearing Marls and Lead-bearing Marls (Fig. 2). In the following, we refer to this division although it does not reflect sedimentological features but is based on the imprecise criterion of ore content (Fe, Cu and Pb).

The limestone-marl alternations, together with the underlying micritic limestones (Basal Limestone according to Scupin, 1931) and overlying micro-oncolitic limestones (middle Zechstein of Scupin, *op. cit.*), are regarded as equivalent to the Zechstein Limestone (Ca1; Peryt, 1978*a*; Raczyński, 1997), that is, carbonate rocks of the first evaporatic cyclothem. The limestone-marl sequence, at least in its lower part, is also a near-shore equivalent of the copper-bearing Kupferschiefer shale (Eisentraut, 1939; Peryt, 1984; Oszczepalski, 1988), as the latter and the Zechstein Limestone overlap in the peripheral part of the basin. The time interval represented by the Kupferschiefer has been estimated from ten to a hundred thousand years (Wedepohl, 1994), and the duration of sedimentation of the entire first evaporatic cyclothem did not exceed two million years (Menning, 1995).

The Zechstein rocks, containing copper, sulphate and carbonate deposits, have been intensively studied since the second half of the nineteenth century. As a consequence, the palaeogeography and depositional environments of the North-Sudetic Basin are relatively well reconstructed for the Late Permian (e.g. Gunia, 1962; Piątkowski, 1966; Śliwiński, 1988; Oszczepalski, 1988; Raczyński, 1997). The limestone-marl association was deposited in a narrow (20–30 km) and long (~100 km), WNW–ESE stretching bay (lagoon). Along the southern shorelines of this bay, extensive oolitic-oncolitic barriers formed.

METHODS

This study is based on macroscopic observations of exposures and on results of microscopic and chemical analyses. The entire section which crops out at Nowy Kościół, not only the limestone-marl alternations, was sampled and examined for the following two reasons: (1) the lack of distinct erosive boundaries and (2) the assumption that the entire section constitutes the equivalent of the Zechstein Limestone (Ca1). However, the main investigations focused on the limestone-marl alternation.

Thin sections were prepared from 40 samples. Cathodoluminescence observations were conducted using *CCL2 mk3* equipment with cathode voltage of 15 kV and beam current of 500 mA.

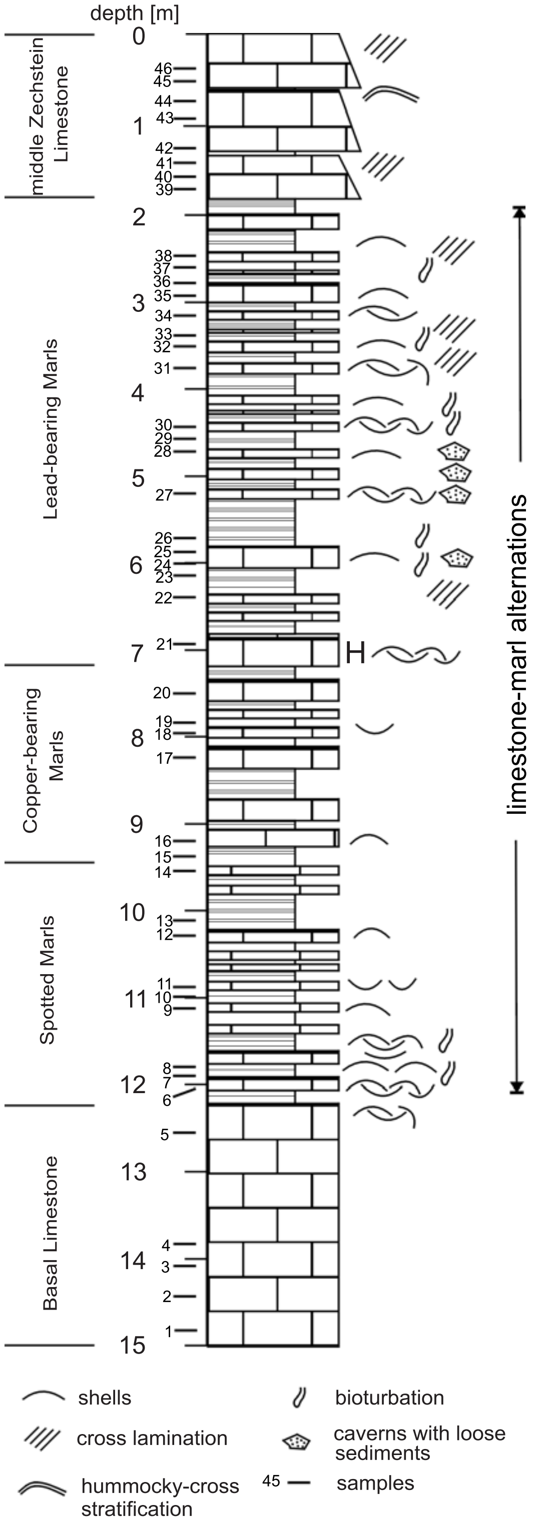

Fig. 2. Section of limestone-marl rocks exposed at Nowy Kościół Scupin's (1931) local division of the Zechstein is shown

Major and trace elements were determined by X-ray fluorescence spectrometry (XRF) at the Institute of Geology, Poznań. An *S4 Explorer* wavelength-dispersive spectrometer system with a Rh tube was used. Twenty-eight whole-rock samples were crushed and powdered, ignited to 1000°C for 1h and subsequently melted with lithium tetraborate (at 1:5 proportions). Four samples were taken from the Basal Limestone, five from the middle Zechstein Limestone and nineteen from marls and limestones of the Spotted, Copper- and Lead-bearing Marls. Ten

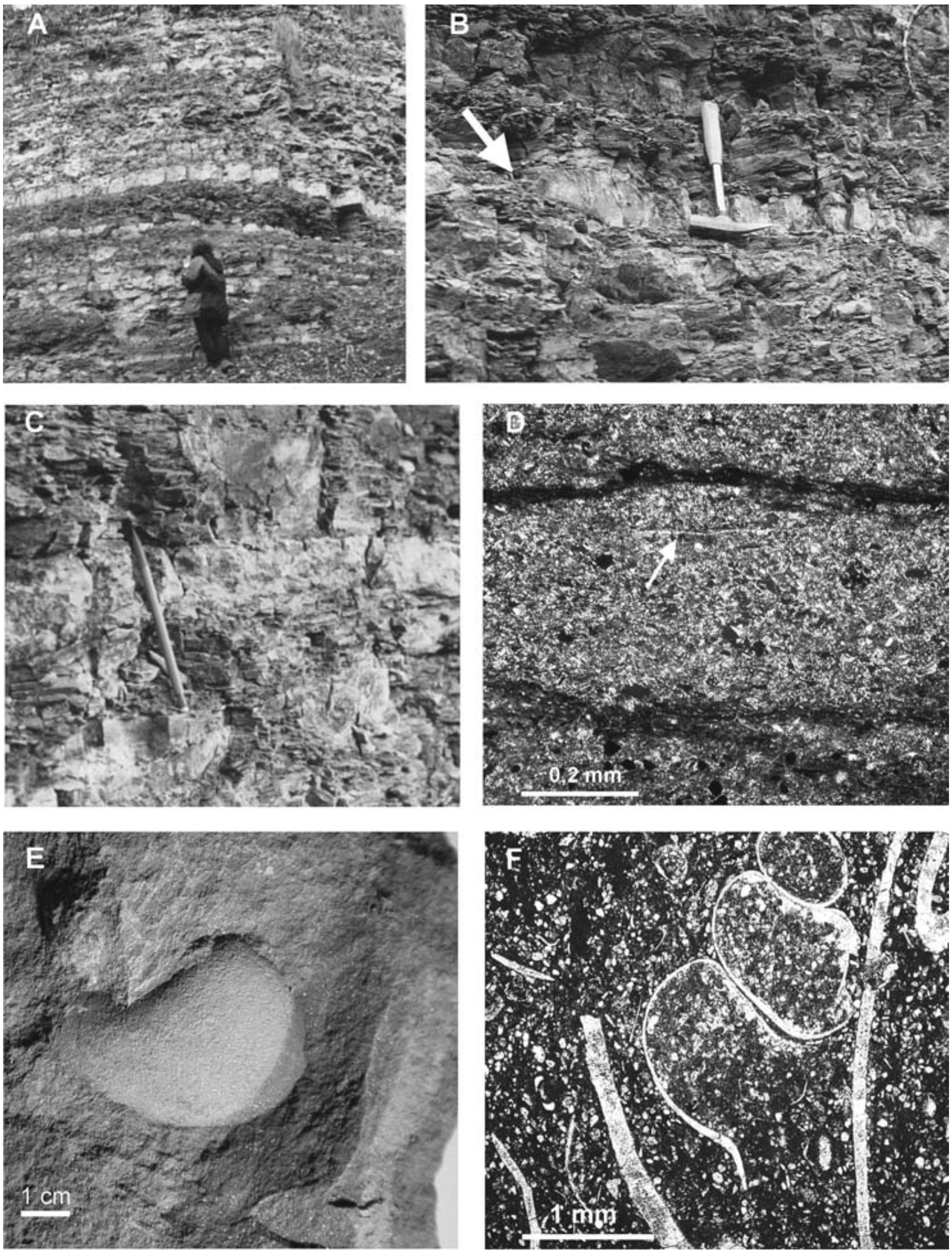

Fig. 3. Limestone-marl alternations from the lowermost Zechstein of the North-Sudetic Basin (Nowy Kościół abandoned quarry)

A — Copper- and Lead-bearing Marls, in the middle is the thickest limestone bed ("H limestone"); **B** — close-up of limestone bed showing its discontinuous character (arrow) and variable thickness, Lead-bearing Marls; **C** — close-up of limestone-marl alternations with slightly gradational boundaries, Lead-bearing Marls; **D** — photomicrograph of marl showing thin anastomosing laminae of iron compounds and organic matter, a thin *Aviculopinna* shell is arrowed, Lead-bearing Marls; **E** — internal cast of bivalve shell (*Schizodus* sp.) in marl from the Spotted Marls; **F** — photomicrograph of bivalve and gastropod shell accumulation from the lower part of a limestone bed; abundant, oval-shaped, small spar concentrations are visible in the micritic background, Lead-bearing Marls, plane-polarized light

marls and nine limestones were analysed; samples being taken from adjacent beds. Loss on ignition (LOI) was determined by heating the dried samples to 1000°C for 1h. Both major and trace elements were measured on fused pellets. The accuracy of determination was checked using certified reference materials. The precision of determinations was < 2% for major and < 10% for minor and trace elements. The carbonate content (expressed as % $CaCO_3$) was obtained by converting the CaO concentrations measured by XRF.

LITHOLOGICAL AND MICROSCOPIC OBSERVATIONS

RESULTS

During field observations we used the terms "marl" and "limestone" in a descriptive sense, i.e. more massive and hard layers were classified as limestones, whereas shaly and fissile ones were classified as marls. There is no distinct difference in colour between these rock types; after drying, limestones are usually slightly paler. Further analyses indicated that the macroscopic distinction did not always correspond to the definition of limestones (>75% $CaCO_3$) and marls (25–75% $CaCO_3$; Barth *et al*., 1939 *vide* Pettijohn, 1975), although limestones always contained higher amounts of calcium carbonate.

Individual marl and limestone layers are on average between 10 and 15 cm thick, but their thickness differs along the section in an irregular way (Fig. 2). A few marl beds are 40 cm thick, and the thickest limestone bed, the "H limestone" (or *Leitbank*, Eisentraut, 1939) is up to 30 cm thick (Fig. 3A). Adjacent limestones and marls are of similar thickness with few exceptions, where thick marls are associated with thin limestone layers or thin marls are intercalated between thick limestones (Fig. 2). The thickness of marl and limestone layers decreases in the upper part of the section where it averages at 7 cm. Limestone layers are not always continuous — some pass laterally into marls (Fig. 3B). Moreover, bed thickness also varies laterally by a few centimetres. Bed bases and tops are gradational to sharp (Fig. 3C). No erosional structures were observed. Lenticular and small-scale cross-bedding occurs in the upper part of the section, especially in the limestone layers, although it is present also in the marls. Limestones range from mudstones to packstones whose principal allochems are bivalve shells and foraminifers. In some layers a transition from packstone through wackstone to mudstone occurs within several centimetres, while an upward-fining trend in skeletal grain-size within many individual limestone beds has also been observed.

Marls largely are foraminiferal mudstones to wackstones rich in clay minerals. In addition to the clay minerals, small quartz, feldspar and mica grains are common. Both limestones and marls contain framboidal pyrite, which are locally abundant, as in the Copper-bearing Marls.

Fossil content and taxonomic diversity vary along the section and are highest in the limestones from the basal parts of the Spotted Marls; they contain shells of bivalves, ostracods, gastropods, foraminifers, articulated and inarticulated brachiopods, bryozoan and echinoderm fragments, sponge spicules and fish debris. The Copper-bearing Marls are relatively fossil-poor, whereas abundant shells occur in the overlying Lead-bearing Marls.

Generally, the limestone beds are richer in the skeletal material, even though not each limestone layer is enriched in it. Some are even entirely devoid of skeletal remains. Fossil remains form discontinuous horizons, and locally lenticular shell accumulations; in some cases, several shell horizons are present within one limestone layer (e.g. in the "H limestone"). The skeletal material does not occur in growth position; in particular, bivalve shells are disarticulated and randomly oriented (Figs. 3F and 4A). In many cases, shell accumulations are present several centimetres above bed bases, overlying bioturbated, fossil-poor limestones (Fig. 4A). Notably, preservation of fossils in the limestone and marl layers are distinctly different along the entire section. In limestones, abundant bivalve and gastropod shells are preserved as cement-filled moulds (Figs. 3F and 4C). In addition to skeletal fossil remains, the limestone beds — especially from the Lead-bearing Marls — contain trace fossils. Indistinct U-shaped burrows locally disturb lamination and show few (no?) traces of compaction (Fig. 4B; vertical burrows are often slightly laterally flattened).

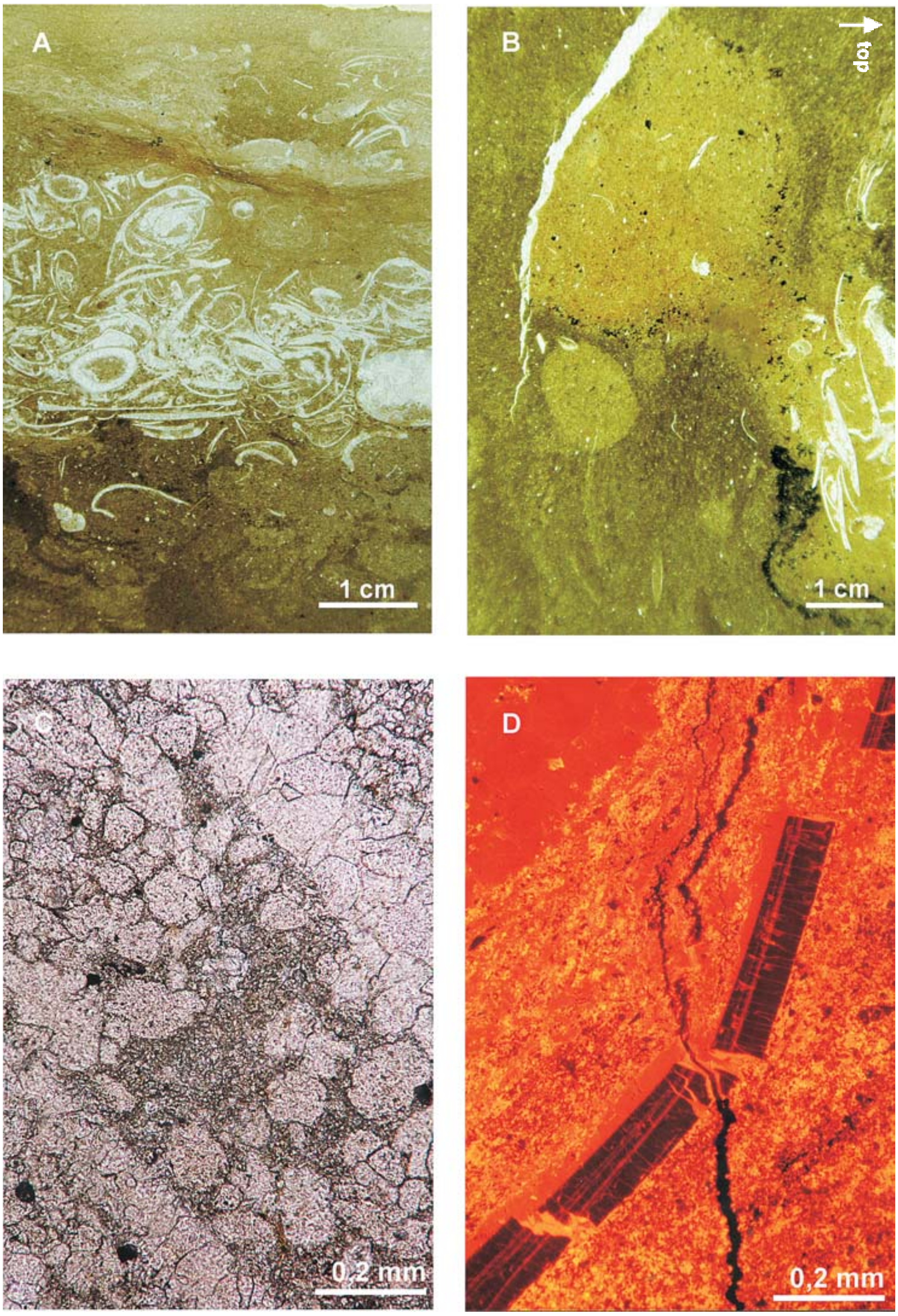

Fig. 4. Features of limestones from the Zechstein limestone-marl alternations, Nowy Kościół abandoned quarry, North-Sudetic Basin

A — bivalve shell accumulation inside limestone bed, with bioturbated micritic limestone below and above, Lead-bearing Marls; **B** — burrows with a circular cross-section in limestone, the larger one is cut by a sparite-filled fissure, top to the right, Lead-bearing Marls; **C** — photomicrograph of neomorphic spar replacing bivalve shells and micritic background sediment, plane-polarized light, Lead-bearing Marls; **D** — cathodoluminescence photomicrograph of broken *Aviculopinna* shell from the upper part of the "H limestone"

Compared to the limestones, the marl interlayers are usually impoverished in fossils with regard to quantity (Fig. 3D). However, the most striking feature of marls in comparison with limestones is that formerly aragonitic shells are preserved exclusively as internal casts or imprints (Fig. 3E). Moreover, in some marls from the Spotted and Lead-bearing Marls such internal casts of randomly oriented single bivalve shells form accumulations similar to those in the limestone beds. In addition, the internal casts of bivalves in life positions occur in some marl layers in the lower part of the Spotted Marls. However, because of lack of shell material they are not conspicuous and easy to overlook. Originally calcitic skeletal material (foraminifers, ostracods, echinoderms and calcitic bivalves) in the majority of cases is well preserved. Marls adjacent to bioturbated limestones are also bioturbated, although, because of compaction, this is evident only in microscopic studies. Furthermore, outlines of almost totally compacted burrows occur on bedding planes of marls from the Lead-bearing Marls. They are distinguishable by colour and by ostracod shell accumulations (the latter being probably excrement consumers). Another type of burrow, from the marls of the Lead-bearing Marls, is extremely rare. These burrows, 2 × 3 cm in diameter, are infilled with limestone material.

The preservation of the elongated calcitic bivalve *Aviculopinna prisca* (Geinitz) is distinctive. Where found in vertical growth position, the upper two thirds of the bivalve occur in the lower part of a limestone, whereas the lower thirds with the apex is missing from the underlying marl. Furthermore, individual redeposited *Aviculopinna* shells in the limestone layers of the Copper- and Lead-bearing Marls are broken (Fig. 4D).

The micritic matrix of the limestones has been almost totally replaced by microspar and, locally, pseudospar (Fig. 4C). Diverse crystal size, patchy distribution of coarse mosaic and, locally, poikilotopic texture with larger crystals enclosing micrite/microsparite suggest common neomorphic/cementation processes. Bivalve and gastropod shells are completely infilled with clear, coarse drusy sparite, in some cases with large, single calcite crystals. The arrangement of the infilling crystals often indicates a two-step process of infilling — calcite surrounding shell moulds crystallized first, followed by the infilling calcite. Limestones from the Lead-bearing Marls contain numerous circular or oval-shaped bioclasts, 50–100 μm in diameter, that also are infilled with sparite. In addition, sparite crystals infill primary porosity inside paired valves. The microspar and the neomorphic spar replacing fossils usually show orange cathodoluminescence. By contrast, the majority of originally calcitic fossils, such as brachiopods, *Aviculopinna*, some ostracod and foraminifer shells, are non-luminescent (Fig. 4D). Locally, dissolution seams occur in the limestones. They are, however, more conspicuous in the Basal Limestone and in the middle Zechstein Limestone than in the thin limestone layers of the limestone-marl alternation.

By contrast, the marls are composed mainly of clay minerals and distinctly lower amounts of microspar/spar. Carbonate cement is concentrated inside foraminiferal and paired ostracod shells. Additionally, circular to lenticular, *ca*. 0.5–2 mm accumulations of microspar are scattered in the matrix. Clay minerals are oriented parallel to bedding. Presumable dissolution seams are common and emphasized by accumulations of clay minerals, iron compounds and organic matter (Fig. 3D). In thin sections, only originally calcitic fossils have been observed, such as foraminifers, ostracods, *Aviculopinna* and echinoderms, whereas originally aragonitic ones are absent. Locally, calcitic shells are concentrated along the dissolution seams and show signs of dissolution. Elongated *Aviculopinna* shells are always oriented parallel to bedding, and are usually thinner than in the limestone layers.

A summary of the characteristic features of the limestone and marl layers are presented in Table 1.

The limestone-marl sequence is underlain by the Basal Limestone, generally fossil-poor micritic limestones. Micro-oncolitic/oolitic limestones of the middle Zechstein, that overlie the limestone-marl alternation, are thick-bedded grainstones, locally interbedded with thin marly shales. They show distinct hummocky-cross and ripple stratification and an upwards decrease grain-size.

Table 1

Summary of characteristic features of limestone and marl layers from the limestone-marl succession exposed at Nowy Kościół

Features		Limestones	Marls
Sedimentary structures		locally: lamination, small lenticular bedding, upward decrease of fossil size and abundance	small scale cross-bedding in the Lead-bearing Marls
Trace fossils		abundant (especially in the Lead-bearing Marls)	abundant
Burrow compaction		weak	strong
Fauna	shell accumulations	common in the Spotted and Lead-bearing Marls	locally in the Spotted and Lead-bearing Marls (internal casts)
	preservation of primarily aragonitic shells	common calcitization (neomorphism)	only imprints and internal casts of shells
	Aviculopinna shells at limestone/marl contact	well preserved original prismatic structure	missing (dissolved?) lower part
Microspar/neospar		abundant	less abundant
Microstylolites		rare	common
Chemical composition	Al_2O_3/TiO_2	19–21, mean: 20	19–22, mean: 20
	Al_2O_3/SiO_2	0.3	0.3
	Al_2O_3/K_2O	mean: 3.0	mean: 2.9
	Sr [ppm]	174–875	111–346

INTERPRETATION

The limestone layers from the Nowy Kościół limestone-marl sequence have been interpreted as distal storm deposits that originated from shallow-water-derived calcareous mud transported basinwards, diluting marly-clayey background sedimentation (Raczyński, 1996, 1997). This interpretation is supported by (1) the abundant shell accumulations in some limestone beds, (2) the upward transition from packstones to mudstones and shell size gradation in individual limestone beds, (3) the lack of sedimentary structures that indicate reworking of sediments by waves or currents. The occurrence of ripple lamination in the upper part of the interbedded succession, and the occurrence of conformably overlying coarse-grained grainstones with hummocky-cross and ripple stratification (i.e. proximal storm deposits) suggest that the sequence repre-

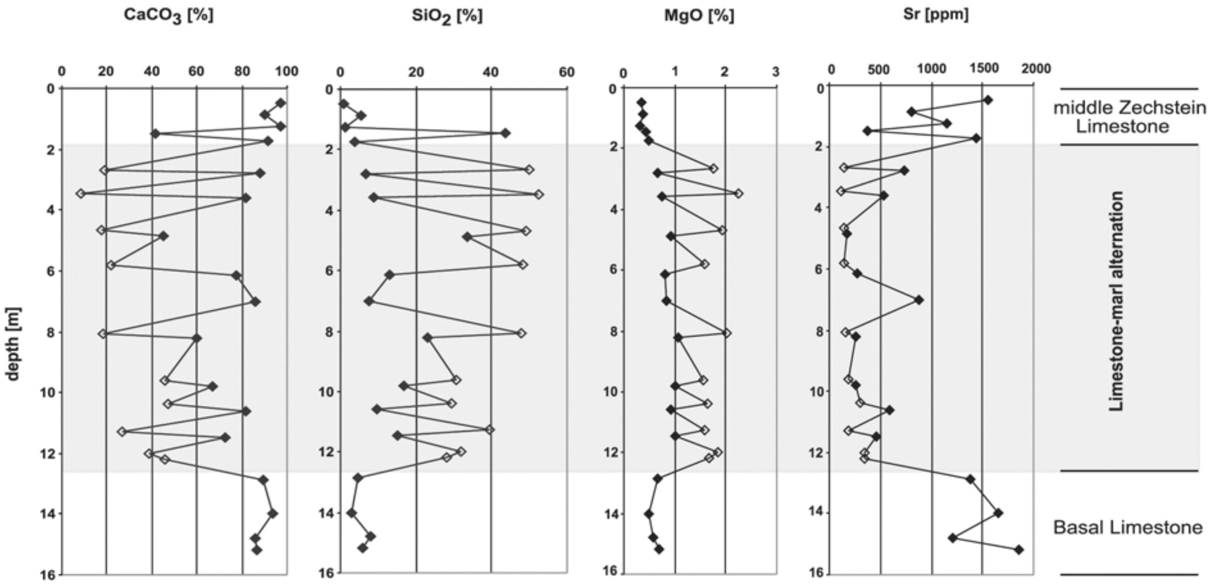

Fig. 5. Diagrams showing variation of selected major and trace constituents ($CaCO_3$, SiO_2, MgO, Sr) with depth for the Zechstein rocks from Nowy Kościół

Black diamonds — limestones, white diamonds — marls

sents a shallowing-up trend. Some thick limestone layers (e.g. the "H limestone") have been interpreted as amalgamated sequences of erosively bounded storm deposits without intervening marl layers. Although some limestone layers from the Spotted Marls and Copper-bearing Marls do not contain shell remains and are composed of micrite without grain-size gradation, they have been, by analogy, interpreted as muddy tempestites. A model of productivity or dissolution cycles cannot be applied to these shallow-water Permian rhythmites because of a lack of pelagic calcareous nannoplankton and the shallow-water depth. Small-scale oxygenation cycles, proposed as a cause of the lithological diversity of the Kupferschiefer (Oszczepalski, 1988), are difficult to verify in this case because either both limestones and marl interlayers are bioturbated (as in the Lead-bearing Marls) or neither show bioturbation (as in the Copper-bearing Marls). Besides, both limestones and marls contain framboidal pyrite.

However, several macroscopic observations do not fit the simple tempestite model. The limestone beds are locally discontinuous, nodular, and show gradational lower boundaries. Both chaotic shell accumulations (preserved as internal casts) and ripple lamination occur also in the marl interlayers. The accumulations of bivalve internal casts were first described by Riedel (1917), who proposed the term "bivalve beds" for the Spotted Marls. Also Piątkowski (1966) noticed that some marls contain abundant *Aviculopinna* fragments. The shell accumulations in the limestone layers, i.e. the coarsest material settling from storm currents, do not occur at bed bases; the shells were encountered several centimetres above the bases, overlying bioturbated micritic limestones. No thickening-upward trend exists, both limestone and marl beds are thin in the upper part of the interbedded succession. Typical storm deposits show erosive bases, grain-size gradation with coarsest material at the bottom, wave ripples at the top, and, in the case of overall shallowing, the entire sequence coarsens and thickens upwards (e.g. Seilacher and Aigner, 1991). Therefore, a rhythmic storm-quiet weather origin alone for the limestone-marl couplets is not a sufficient explanation. Our suggestion is post-depositional, diagenetic reorganization of the succession in the section studied. Below, we present arguments for this hypothesis.

The alternating limestone and marl layers are visible in the quarry due to their different resistance to weathering: the rocks weather either as hard limestone beds or as less resistant, fissile marls. This, in turn, depends on their calcium carbonate content and cementation. It was documented on the base of investigations of many rhythmic sequences that there is a certain threshold value of $CaCO_3$, above and below which rocks weather in a different way (Einsele and Ricken, 1991). This "weathering boundary" depends on the duration and intensity of weathering processes, and usually falls in the range between 65 and 85% (*op. cit.*). In the case studied the boundary fluctuates around 50–60% $CaCO_3$ (Fig. 5).

However, the present-day differences in the $CaCO_3$ content have been modified by diagenesis. Limestone beds were passively enriched in calcium carbonate during diagenesis which is explicitly shown by spar cementing pore space inside paired shells of bivalves, ostracods, gastropods and foraminifers, and implicitly by well preserved burrows that are almost circular in cross-section. Modern lime muds have an average of 70% porosity (Enos and Sawatsky, 1981). At least part of original porosity must have been filled early with cement, otherwise burrows would have been compressed and elongated shells broken. Individual broken *Aviculopinna* shells are a good example of the local lack of cementation. Summing up, during diagenesis, limestone beds acted as calcium carbonate absorbers. By contrast, marls are compacted as evidenced by strongly oriented clay minerals and flattened burrows. This implies that the marl intervals were not sufficiently cemented during early diagenesis. Moreover, the aragonitic shells were dissolved and calcium carbonate was exported. In addition, part of the calcium carbonate was removed as an effect of pressure solution. Undulating thin clay seams correspond to microstylolites in Wanless's (1979) terminology, and mark pathways along which dissolved carbonate was removed. Parts of the calcitic shells were dissolved under pressure, which is well exemplified by the systematic lack of the apical part of *Aviculopinna* in the marls. Thus, the marls either retained the original amount of calcium carbonate or, which is more probable, lost part of it. In the latter case they would have been calcium carbonate donors. Macroscopic observations suggest that zones of calcium carbonate enrichment and impoverishment do not precisely follow primary bedding, i.e. the diagenetic rhythm does not correspond to the sedimentary rhythm.

Common recrystallization of limestones, revealed by the occurrence of microsparitic and pseudosparitic matrix and spar crystals inside formerly aragonitic shells, indicate that precursor sediment was partly composed of metastable phases, such as aragonite and high-Mg calcite. Lasemi and Sandberg (1993) found that larger neomorphic calcite crystals (4–9 µm) indicate aragonite-dominated mud precursors. Low-Mg calcite-dominated sediments show low diagenetic potential and should preserve their original texture. Observations of cathodoluminescence validated the assumption that originally calcitic material remained unaltered to a high degree. Thus, an abundant originally aragonitic fauna and microfabric clues indicate the primary occurrence of aragonitic components.

MAJOR AND TRACE ELEMENT GEOCHEMISTRY

RESULTS

Chemical data for the samples from the Nowy Kościół section are listed in Table 2 and illustrated in Figures 5–7. Results from the underlying Basal Limestone and the overlying middle Zechstein Limestone samples are also shown for comparison.

The calcium carbonate content fluctuates between 9 and 88% in the limestone-marl sequence (Fig. 5). According to the Barth's *et al.* (1939) classification (*vide* Pettijohn, 1975), the "limestones" correspond to the range of marly limestones, limey marls and marls, whereas "marls" have turned out to be marls, clayey marls and calcareous shales (especially in the upper part of the Nowy Kościół section). The average content of $CaCO_3$ in the Spotted, Copper- and Lead-bearing Marls amounts to 67, 63 and 75% for the limestone layers and 38, 32 and 17% for the marl layers, respectively. In comparison with the underlying couplets, there is an increase in calcium carbonate in the limestones of the Lead-bearing Marls, accompanied by a decrease in the marl interlayers.

Silica is the second main constituent of the rocks. Its content in the limestone-marl association ranges from 7 to 52%. There is a strong negative correlation between $CaCO_3$ and SiO_2 concentrations (correlation coefficient = –0.99). The Al_2O_3 and K_2O concentrations exhibit similar distribution patterns to SiO_2. The Al_2O_3/SiO_2 (Fig. 6) and Al_2O_3/K_2O ratios are extremely stable throughout the entire limestone-marl sequence. Also, the Al_2O_3/TiO_2 ratios are very stable along the limestone-marl association, and the P_2O_5/SiO_2 ratios do not show significant fluctuations (Fig. 6). There is a strong positive correlation between the TiO_2, K_2O, SiO_2 and Al_2O_3 concentrations (Fig. 7A–C) and between the P_2O_5 and $CaCO_3$ concentrations (Fig. 7D).

The MgO content is low and varies between 0.67 and 2.24% in the limestone-marl sequence (Fig. 5). Generally, samples with a lower amount of $CaCO_3$ exhibit a higher amount of MgO. This, and the fact that dolomite was not observed microscopically in the limestone-marl association, suggests that MgO is largely included in the silicate minerals.

Strontium content fluctuates between 111 and 875 ppm (Fig. 5). However, the strontium content in the underlying Basal Limestone and overlying middle Zechstein Limestone is significantly higher and reaches 1863 and 1551 ppm, respec-

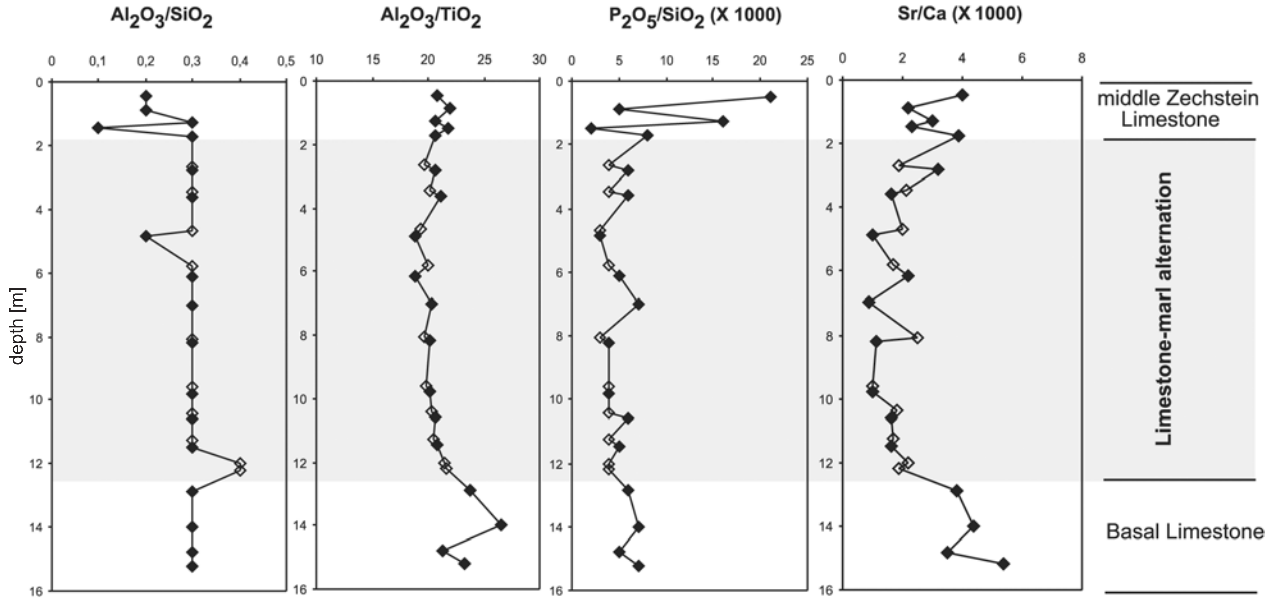

Fig. 6. Diagrams showing depth-variation of ratios of some relatively immobile compounds (Al_2O_3/SiO_2, Al_2O_3/TiO_2, P_2O_5/SiO_2) for the Zechstein rocks from Nowy Kościół; Sr/Ca fluctuations are also shown

Other explanations as on Figure 5

Table 2

Major and trace element concentrations for the Zechstein rocks from Nowy Kościół

Sample	CaO [%]	MgO [%]	SiO_2 [%]	Al_2O_3 [%]	K_2O [%]	TiO_2 [%]	P_2O_5 [%]	SO_3 [%]	Sr [ppm]	Zn [ppm]
45 (MZL)	54.48	0.36	0.96	0.23	0.07	0.011	0.02	0.09	1551	21
43 (MZL)	50.37	0.38	5.57	1.10	0.46	0.050	0.03	0.01	806	31
42 (MZL)	54.29	0.31	1.28	0.35	0.12	0.017	0.02	0.02	1147	14
41 (MZL)	23.32	0.43	43.62	6.32	2.64	0.290	0.10	–	378	19
39 (MZL)	51.41	0.50	3.66	1.11	0.40	0.054	0.03	0.04	1439	26
37 (L-bM)	10.62	1.75	49.93	14.32	5.07	0.730	0.21	–	147	41
36 (L-bM)	49.42	0.67	6.88	2.23	0.71	0.108	0.04	0.08	737	28
33 (L-bM)	4.80	2.24	52.47	17.49	5.97	0.870	0.19	–	111	119
32 (L-bM)	45.79	0.74	8.97	2.84	1.01	0.134	0.05	0.16	532	32
29 (L-bM)	9.98	1.93	49.20	14.53	5.12	0.750	0.16	–	140	22
28 (L-bM)	25.14	0.93	33.51	7.55	2.63	0.400	0.10	0.31	174	46
26 (L-bM)	12.27	1.59	48.23	12.37	4.33	0.620	0.17	–	147	262
24 (L-bM)	43.33	0.81	12.94	3.33	1.14	0.176	0.06	0.16	279	104
21 (L-bM)	48.20	0.83	7.43	2.29	0.65	0.113	0.05	0.09	875	47
19 (C-bM)	10.44	2.03	47.72	14.34	4.94	0.730	0.16	–	164	0
18 (C-bM)	33.58	1.07	23.04	6.36	2.20	0.316	0.09	0.34	263	50
15 (C-bM)	25.51	1.55	30.77	9.76	3.32	0.490	0.12	0.13	191	72
14 (C-bM)	37.47	1.00	16.71	5.06	1.76	0.252	0.07	0.15	260	45
13 (SM)	26.57	1.63	29.30	10.13	3.53	0.497	0.13	0.07	307	60
12 (SM)	45.73	0.93	9.51	3.18	1.06	0.154	0.06	0.11	597	34
10 (SM)	15.06	1.58	39.32	11.57	3.97	0.565	0.14	0.06	184	73
9 (SM)	40.75	1.02	15.31	4.44	1.49	0.213	0.07	0.11	461	42
7 (SM)	21.75	1.85	32.01	11.67	4.02	0.545	0.14	0.08	346	84
6 (SM)	25.46	1.66	28.25	10.22	3.57	0.472	0.12	0.08	346	74
5 (BL)	50.11	0.66	4.66	1.59	0.55	0.067	0.03	0.05	1377	25
4 (BL)	52.50	0.49	2.86	0.85	0.28	0.032	0.02	0.03	1656	26
2 (BL)	48.06	0.57	7.84	2.38	0.84	0.112	0.04	0.03	1214	59
1 (BL)	48.68	0.70	5.88	1.98	0.67	0.085	0.04	0.04	1863	60

MZL — middle Zechstein Limestone, L-bM — Lead-bearing Marls, C-bM — Copper-bearing Marls, SM — Spotted Marls, BL — Basal Limestone; marl samples are marked by a gray background

tively. Sr/Ca ratios are either similar for limestones and their marl interlayers (especially in the Spotted Marls) or different; in several cases Sr/Ca ratios are higher in marls than in the adjacent limestones (Fig. 6). Sr/Ca ratios in the rocks of the Basal and middle Zechstein Limestones are *ca*. two times greater then in the limestone-marl sequence. A weak negative correlation exists between the Sr and SO_3 content (Fig. 7F).

INTERPRETATION

The most noticeable feature of the limestone-marl sequence is a strong positive correlation between metal oxides which are not included in carbonate structures, such as SiO_2, Al_2O_3, TiO_2, K_2O (Fig. 7A–C). The silicate minerals occurring in the rocks studied belong to one of three groups: (a) clay minerals, mica and biotite, (b) quartz and (c) feldspars. The very stable ratios between chemically inert compounds (Al_2O_3/TiO_2, Al_2O_3/SiO_2, in the case studied also Al_2O_3/K_2O) suggest that, as far as siliciclastic material is considered, no primary differences exist between the limestones and their marl interlayers. Moreover, the ratio of P_2O_5/SiO_2 is also relatively stable throughout the limestone-marl sequence although the P_2O_5 concentrations reflect the content of fish debris and organo-phosphatic inarticulate brachiopods. The almost linear negative relationship between the P_2O_5 and $CaCO_3$ concentrations also suggests that phosphorus-bearing components are evenly scattered among the silicate background. The observed

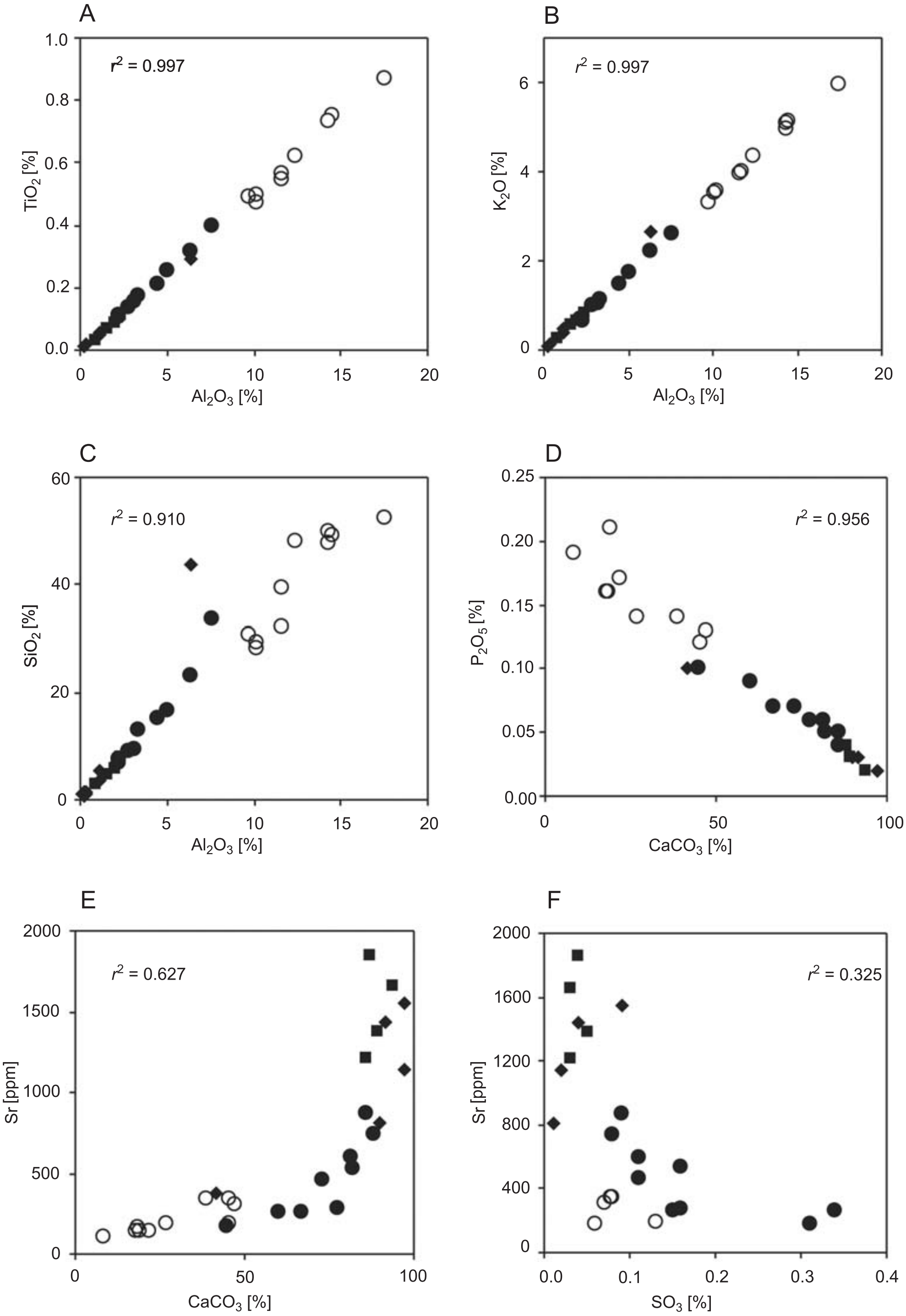

Fig. 7. Bivariate diagrams for the Zechstein rocks from Nowy Kościół; a strong correlation between different chemical compounds shows that there are no differences between limestones and marl interlayers with regard to the composition and ratios of minerals containing these elements

Black circles — limestones, white circles — marls from the limestone-marl sequence, black squares — samples from the Basal Limestone, black diamonds — samples from the middle Zechstein Limestone; *r* — correlation coefficient

relationships between various chemical compounds may be explained in two ways: either as the result of steady background deposition of siliciclastics associated with temporal variations in the supply of carbonate material, or as the result of diagenetic redistribution of calcium carbonate in an originally more or less uniform precursor sediment.

The diversity of strontium content in the section of the Zechstein Limestone (Ca1) studied is also remarkable. The concentrations of strontium in the limestone-marl sequence are low (111–875 ppm) and typical for most ancient limestones (several hundred ppm Sr — e.g. Kinsman, 1969; Veizer, 1983); under- and overlying rocks are enriched in strontium (>1100 ppm in the majority of samples). Different Sr/Ca ratios suggest that the observed difference cannot be simply explained by the lower calcium carbonate content in the limestone-marl sequence in relation to the under- and overlying limestones (i.e. a diluting effect of clay minerals). High concentrations of strontium in carbonate rocks from the peripheral parts of the Polish Zechstein basin were interpreted as the result of recrystallization in sulphate-bearing pore-fluids and the presence of sulphates themselves (Ważny, 1969; mean 1320 ppm for 450 samples). However, sulphates have been observed neither in the limestone-marl sequence nor in the Basal and middle Zechstein Limestones. Moreover, a negative correlation exists between the Sr and SO_3 concentrations. Therefore, the present-day strontium content diversity may reflect a diversity of initial mineralogy.

Modern aragonite precipitated from seawater has up to 10 000 ppm Sr, whereas calcite has around 1000 ppm (e.g. Veizer, 1983). This is consistent with the high distribution coefficient for strontium in aragonite (= 1.14) as compared to that in calcite ($D^{Sr}_{calcite}$ = 0.14; Kinsman, 1969), where the distribution coefficient describes the partition of trace element between the crystallizing mineral and solution. Any neomorphic processes such as aragonite calcitization or calcite recrystallization lower the original Sr content due to the low $D^{Sr}_{calcite}$ and dilution of Sr concentration in pore solutions impoverished in this element, such as, for example, meteoric water (Veizer, 1983). This is the reason for significantly lower strontium concentrations in most ancient limestones as compared to present-day carbonate sediments. As was shown by Kinsman (1969), an idealized transformation of aragonite containing 9800 ppm Sr into calcite in a closed system would result in 1400 ppm Sr in the latter crystal. It is widely accepted, therefore, that a high strontium content in limestones may indicate their originally aragonitic composition (e.g. Veizer, 1983; Tucker, 1985; Brand, 1989; Lasemi and Sandberg, 1993).

It may be concluded, based on the high concentrations of strontium, that the original sediments of the Basal and middle Zechstein Limestones were probably aragonitic in composition, i.e. at least partly composed of aragonitic muds and/or grains. Additionally, this is consistent with the model of dominating abiotic aragonite sedimentation in Permian seas (Sandberg, 1983; Hardie, 1996). The lower strontium content in the limestone-marl sequence may indicate its original calcitic composition. However, this is in contradiction to the microfabric clues of precursor sediment mineralogy, as discussed above. Unquestionably, primary aragonitic material also occurred in the limestone-marl interval for example bivalves and gastropods built their shells from the aragonite. Furthermore, the strontium concentrations in some limestone layers are in a range consistent with an aragonite precursor (600–800 ppm). Therefore, mixed calcite-aragonite precursor sediments which were deposited and underwent diagenesis in an environment of slightly lower salinity than the under- and overlying rocks are most probable. The abundant siliciclastic material was probably delivered from the adjacent land by rivers, that might have caused a lower salinity. In summary, the Sr content range suggests that the mineralogy of the lime muds might have changed during deposition of the Zechstein Limestone (Ca1).

DISCUSSION

Diagenetic modification of calcium carbonate content may exert a twofold effect, it may enhance or obliterate/shift primary bedding. There exist strong and convincing arguments for original layering in some limestone-marl/shale rhythmites, such as differences in structure, composition and fossil content which cannot be an effect of diagenesis. For example, Bellanca *et al.* (1996) noted differences in sedimentary structures, content of calcareous nannofossils, organic mater, pyrite, radiolarians, Si/Al and K/Al ratios between limestones and marlstones. Burrows crosscutting a limestone/marl boundary and infilled with a material from over- or underlying beds are also an indication of a primary bedding (Elrick *et al.*, 1991; Weedon and Jenkyns, 1999). The classic work of Hays *et al.* (1976) is based on differences in ^{18}O of planktonic foraminifers and statistical analyses of radiolarian assemblages between successive sediment portions. However, in our studied case such unambiguous arguments are lacking. Neither the macroscopic and microscopic observations nor the chemical analyses support sedimentation changes recorded in a one-to-one pattern. The systematic differences between limestones and marls, consisting in different calcium carbonate and shelly fossil content, especially of originally aragonitic composition, may be an effect of diagenesis. Cherns and Wright (2000) showed that in certain limestone beds significant amounts of skeletal material may be dissolved causing a bias in the palaeontological record. We suggest that the present-day bedding in the Nowy Kościół quarry is a combined result of primary and diagenetic mechanisms. Diagenetic processes shifted primary layer boundaries and enhanced depositional differences.

Diagenetic modification of calcareous sediments containing metastable carbonates has been known from many case studies. For example, Aigner (1985) in his work devoted to tempestites noticed that storm layers in the German Muschelkalk are “mummified” by micritic over- and underbeds. On the other hand, the origin of diagenetic bedding, i.e. laterally extensive alternating zones of cementation and dissolution, is more problematic. Melim *et al.* (2001) suggested so-called “halo-effects” around the skeletal layers due to increased fluid flow in the most permeable beds. In the case studied, however, shells are embedded in micrite and there is no indication of greater permeability. Therefore, the shell accumulations did not exclusively determine the locus of cementation processes. This is also supported by the occurrence of accumulations of internal shell casts in the marl layers, i.e. in the presumable dissolution layers. Also, there are no cementation aureoles around nest accumulations of shells, which are situated in the continuous limestone beds. Furthermore, some limestone layers lack any shelly fossils. Hence, another explanation is required.

Recent geochemical investigations of modern shallow-water tropical platforms (e.g. the South Florida Platform or Great Bahama Bank) indicate intensive diagenetic alterations of shallow-buried sediments (e.g. Walter and Burton, 1990; Patterson and Walter, 1994; Malone *et al.*, 2001). It was documented that, in spite of a high supersaturation of seawater with respect to aragonite and high Mg-calcite, sediment pore-waters are undersaturated with respect to these minerals (*op. cit*). This is caused by aerobic oxidation of organic matter and production of excess dissolved CO_2, anaerobic sulphate reduction producing acidic, sulphide-rich pore-waters and oxidation of dissolved sulphide to sulphuric acid (e.g. Walter and Burton, 1990; Ku *et al.*, 1999). As a result, dissolution of aragonite and high Mg-calcite is a common feature of carbonate sediments in the shallow subsurface. Walter and Burton (1990) investigated the upper metre of bioturbated sediments, whereas Malone *et al.* (2001) stated that pore-waters become undersaturated with aragonite within the upper 10 m of Great Bahama Bank slope sediments. Dix and Mullins (1992), examining deep-water carbonates of the northern Bahamas, observed a drastic fall in aragonite content in the first 20–40 m of burial. On the other hand, dissolution of aragonite and an increased degree of sulphate reduction elevate the alkalinity of pore-waters, promoting rapid precipitation of stable low-Mg calcite (e.g. Patterson and Walter, 1994; Malone *et al.*, 2001). For the study of limestone-marl alternations, interesting evidence comes from the work of Melim *et al.* (1995, 2001), who documented two contrasting styles of shallow subsurface diagenesis depending on the permeability of the surrounding sediments. Highly permeable sections showed aragonite dissolution, whereas weakly permeable ones are extensively cemented with calcite. Furthermore, Westphal *et al.* (2000) described alternating cemented and uncemented fine-grained layers from Pliocene periplatform carbonates of the Great Bahama Bank. In this case, however, the trigger for diagenetic differentiation has not been determined. Summing up, modern tropical platform metastable carbonates undergo strong dissolution and reprecipitation processes in the shallow subsurface.

The above observations are a starting point to interpret the Nowy Kościół limestone-marl rhythmites. Cementation processes in the limestone beds must have acted in the shallow subsurface, as sedimentary structures, such as burrows with circular cross-sections, are preserved without noticeable deformation. Cement precipitation required a source of calcium carbonate. On the other hand, the limestone layers do not posses features typical of hardgrounds, i.e. sea-floor cemented sediments associated with intervals of reduced deposition/nondeposition, or current-swept seaways. They lack borings, encrusting organisms, and manganese concretions. The preserved fauna is dominated by soft sediment dwellers. The alternating cemented and uncemented beds may be, therefore, attributed to redestribution of calcium carbonate driven by chemical gradients, in accordance with the model of aragonite dissolution-calcite precipitation in the marine burial realm (Munnecke and Samtleben, 1996; Westphal *et al*., 2000; Böhm *et al*., 2003). The key assumption for this explanation is the occurrence of metastable aragonite and/or high Mg-calcite as well as organic matter during deposition of the sediments. As previously discussed, several lines of evidence suggest that the aragonite was a primary component of the sediments. Remnants of organic matter are present up to now in the form of coalified plant fragments. Apart from the latter, microbes could significantly add to the organic matter production. The C_{org} content in the equivalent mergelkalk from the Konrad mine (*ca*. 20 km further to the north) is up to 2% (Sun *et al*., 1995). Thus, the metastable carbonates were dissolving as sediments passed successively through a zone of aragonite undersaturation. The dissolution started with the least stable, aragonite mud particles, possessing the largest reactive surfaces, before affecting coarser skeletal material. Dissolved Ca^{2+} and CO_3^{2-} ions with CO_3^{2-} ions produced by sulphate reduction processes locally must have caused an increase in alkalinity sufficient for carbonate precipitation. Once new carbonate (calcite) crystals precipitated, the alkalinity dropped. This, in turn, could have caused a gradient in CO_3^{2-} concentrations between precipitation and surrounding zones high enough for activation of diffusive supply of Ca^{2+} and CO_3^{2-} ions. If we assume original layer distribution of key components in the sediments, which is probable, we would expect a layered redistribution, i.e. growth similar to concretion growth leading to the origin of beds rather than spheres or nodules. Macroscopic and microscopic observations suggest that cementation and dissolution zones not only do not reflect original bedding, but also differentiate genetically similar beds, e.g. tempestites. As a consequence, in the shallow burial realm, incipient new layering could form, which overprinted the depositional bedding. Dissolution of aragonitic shells in the limestone beds took place when the matrix was cemented enough to preserve the mold space against collapse; the molds were subsequently filled with cement. However, the cementation was not completed, as is indicated by some broken *Aviculopinna* shells. In the marl interlayers, cement was precipitated only locally, most often in the protected microenvironments such as the inner parts of shells. This is probably the cause of preservation of internal casts of aragonitic shells.

The early diagenetic differentiation influenced later, burial alteration. The whole succession was buried to at least several hundred metres as shown by microstylolites in the limestone-marl sequence and stylolites occurring in the overlying micro-oncolitic limestones. The apical parts of *Aviculopinna* shells, rooted in the marl layers, were probably dissolved under pressure. This bivalve, originally composed of stable low Mg-calcite, should have been stable during early diagenesis.

Munnecke *et al.* (2001) developed a numerical model in which, from the present-day carbonate content of marls and limestones, and ratio of thickness of these rocks, they calculated the primary composition of sediment. According to their model, precursor sediments of the Lead-bearing Marls would have been slightly enriched in aragonite by comparison with the underlying beds. A slightly higher strontium concentration in limestones of the Lead-bearing Marls is in accordance with this result.

Raiswell (1988) proposed a model for the origin of limestone-shale rhythmites in which anaerobic methane oxidation is a driving force for early cementation. Carbonates precipitated in this particular geochemical zone have very distinct carbon isotope signatures. Following his conclusions we suggest that stable isotope analyses of carbonates and organic matter could verify the proposed model as diagenetic carbonates formed during burial of organic-rich sediments can be distinguished by their carbon isotope composition (Irwin *et al*., 1977). Bechtel and Püttmann (1997), studying the Kupferschiefer from the Lower Rhine Basin, Germany, provided evidence for generation of carbonates from isotopically light CO_2, originated from degradation of organic matter.

This paper describes one of the rare examples Permian limestone-marl alternations. Westphal and Munnecke (2003) compiled all published data for the Permian rhythmites and found only a few records. One important belt of such rhythmic limestone-marl deposits is the shallow-water Zechstein Sea succession of the Fore-Sudetic Monocline (Peryt, 1978*b*) and along the present-day Lithuanian-Latvian boundary (Kurss and Savvaitova, 1986; Kadunas, 2001). In terms of cyclostratigraphy, these successions should be interpreted with caution, because they may partly reflect postdepositional changes. We suggest that, by analogy, Zechstein nodular limestones occurring in the marly matrix in the eastern part of the North-Sudetic Basin (Śliwiński, 1988) may not constitute a separate depositional facies but may be diagenetic in origin.

CONCLUSIONS

The Zechstein limestone-marl alternations from the Nowy Kościół section are interpreted to be neither purely depositional nor entirely diagenetic in origin. Diagenesis caused calcium carbonate redistribution within the primary calcareous sediments, at least partly of storm origin, transposing and obliterating primary bedding. Therefore, the limestone-marl couplets do not reflect rhythmic depositional signals in a one-to-one pattern. In other words, the diagenetic rhythm did not follow the rhythm of sedimentation.

Probably, the original sediments were less differentiated with regard to calcium carbonate content than are present-day deposits. Limestone layers were passively enriched in $CaCO_3$, whereas marl intervals lost part of original carbonate component. In limestones, aragonite skeletal material was replaced by calcite, whereas in marls it was dissolved and removed. Only internal casts of shells are preserved.

The foundations of the present-day layering were formed during early diagenesis in the shallow subsurface and were stimulated by reactions involving metastable carbonate grains. Later processes in deeper burial followed the newly-formed differentiation. These conclusions are consistent with the aragonite model of limestone-marl alternations.

The present study is a contribution to the problem of origin of the Zechstein limestone-marl alternations. Such a lithofacies association may occur in the peripheral part of the Zechstein sea basin. The obtained results suggest that simple reconstruction of environmental changes may be misleading. Moreover, this example supports the hypothesis that carbonate sediments of the Permian, a period of aragonite seas, may have been especially prone to diagenetic modifications.

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