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EDTA-insoluble residues from the Zechstein Ca-2 unit (Late Permian), the Løgumkloster-1 Well, Denmark

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Abstract

EDTA-insoluble residues of carbonate rock samples from the Upper Permian Ca-2 unit of the Løgumkloster-1 well have been investigated by X-ray diffraction, scanning electron microscopy, instrumental neutron activation analysis, and magnetic measurements. The sediments have undergone severe diagenesis including dolomitization and anhydrite mineralization. Two original facies types have been recognized, an oolitic shoal facies, and a lagoonal carbonate facies. The mineralogy of the inorganic insoluble residue reflects the facies type division: the lagoonal facies contains muscovite, feldspar and quartz; the shoal facies contains a non-crystalline silicate phase, quartz, and mica. It is thought that the muscovite in the lagoonal facies is derived from weathering of exposed basement highs. The non -crystalline silicate phase in the shoal facies is thought to be a diagenetic phase precipitated at a rather late stage in the diagenetic history.

Introduction

Aim of study

Little effort has been directed towards the description and understanding of the EDTA-insoluble residue of the almost pure carbonate intervals in the North European Zechstein Basins. In the present work we investigate the occurrences, mineralogy, and geochemistry of the EDTA-insoluble residues from the Ca-2 interval in the Løgumkloster-1 well core. The analytical results are discussed with respect to origin, transport mechanisms, and diagenetic alterations. These results add important information to the interpretation of the sedimentary environments, diagenetic history, and regional geological history of the Zechstein Basins.

Geological setting of the Southern Permian Basin

The Løgumkloster-1 well is located in Southern Jylland, Denmark (Fig. 1). During Late Permian this area was situated on the southern slope of the Ringkøbing-Fyn High, which formed the northern margin of the North German Zechstein Basin (Fig. 1; Baartman in Rasmussen 1978). This basin extended from the east coast of Mid-England to the Polish-Russian border. It was bounded southward by the eroded Variscan mountains. The basin was

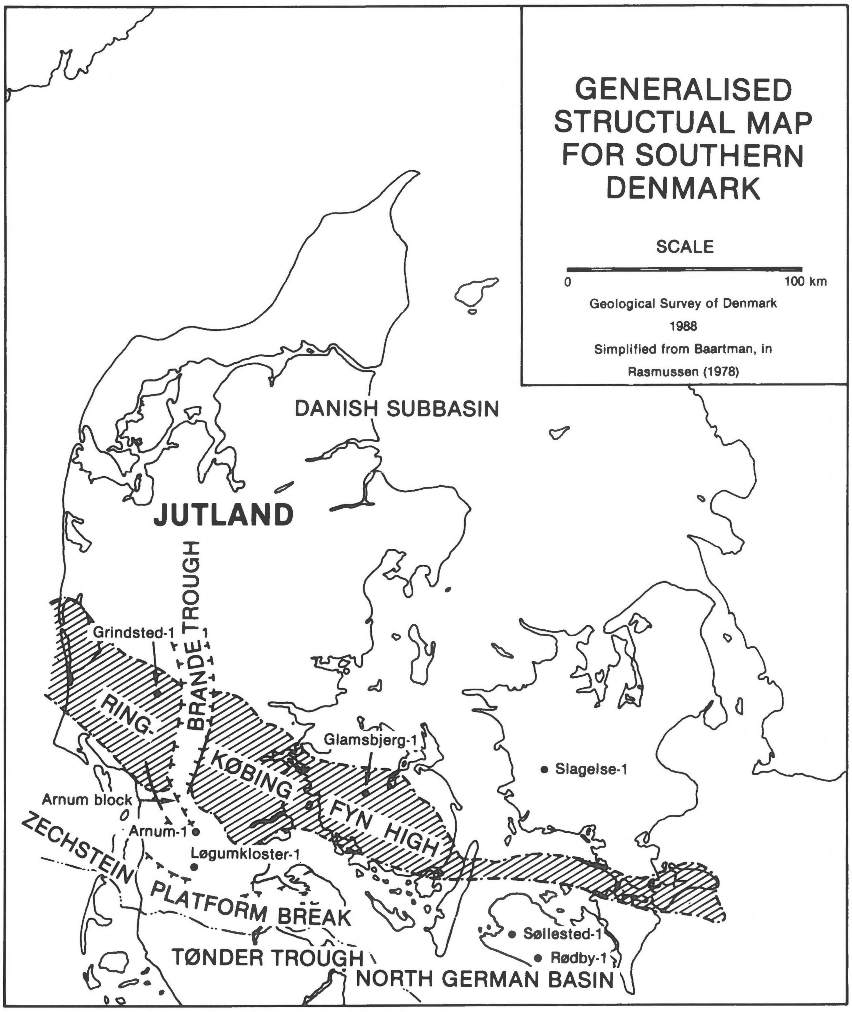

Fig. 1. Location map. The samples in the present study are from the Løgumkloster-1 well in Southern Jylland, Denmark.

the result of a continued intracratonic subsidence initiated in early Permian. When the Zechstein sea invaded the basin, probably from the north via the troughs of the Mid North Sea and Ringkøbing-Fyn Highs (the Central Trough, the Horn Trough, and the Brande Trough), the floor of the basin lay at least 200 m below sea level (Smith 1979, Glennie & Buller 1983, Glennie 1986). Because of the hot and arid climate in the Zechstein basin area there was a very low rate of sediment influx from the exposed, marginal desert areas (Glennie & Buller 1983). Sedimentation was initially dominated by shallow marine carbonates around the margins. The sedimentary setting is comparable to the arid tidal flat model with supratidal sabkha development (e.g. Shinn 1983). Detrital material transported by water was probably only supplied to this setting by periodic flash-floods from the basement highs. As the Zechstein inland sea became progressively more saline, deposition of gypsum and anhydrite was concentrated along the basin margin, and halite was precipitated basin-wards. This sedimentary sequence is repeated in the characteristic Zechstein cycles, of which at least four can be recognized in the North German Basin (Richter-Bernburg 1955). The cyclicity of the Zechstein Deposits is believed partly to have been controlled by eustatic changes

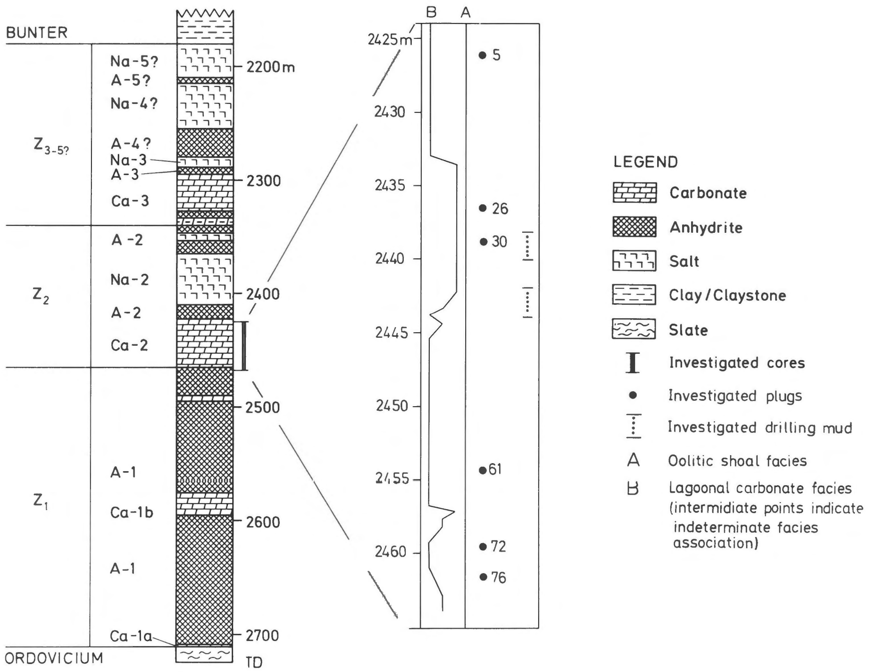

Fig. 2. Lithology and stratigraphy of the Zechstein sequence in the Løgumkloster-1 well based on mud and wireline logs. The classification of Richter-Bernburg (1955) is used. The facies types of the Ca-2 sequence and the distribution of samples are shown to the right.

of ocean level caused by Permian glaciations (Pöhlig 1986).

During the Permian the area north of the Variscan mountains was most likely situated in the northern hemisphere between palaeolatitudes of ca. 10° N and 30° N in the trade wind belt having prevailing palaeowinds from a northeasterly direction. This has been deduced from the shape of the Rotliegendes sand dunes and from palaeomagnetic data (Glennie 1972).

During deposition of the shallow water Ca-2 carbonates the area around the Løgumkloster-1 well was most likely partly sheltered by the Ringkøbing-Fyn High and off-shore winds would have dominated this part of the basin.

In connection with the Variscan orogeny widespread volcanic activity occurred during the Early Permian. Known volcanic areas include the Oslo Graben, eastern North Sea, West Baltic and the northern and eastern parts of Holland, West Germany, and DDR (Dixon & Fitton 1981). Erosion products such as conglomerates and conglomeratic sandstones derived from porphyries, lavas, and tuffs are also widespread, especially in Central Germany (the Thüringerwald area). Volcanic material occurring in the Rotliegendes clastic sediments has been detected in wells in South Denmark, south of the Ringkøbing-Fyn High, e.g. in the Rødby-2 well (Sorgenfrei & Buch 1964) and in the Søllested-1 well (Pedersen 1983).

Previous work

The Zechstein Group in the Løgumkloster-1 well is 531 m thick. The ca. 41 m thick Ca-2 carbonate unit (ca. 2424 m – ca. 2465 m b.KB) studied in this work (Fig. 2), corresponds to the Hauptdolomit of the Z2 carbonate (Stassfurt-Serie) of Germany (Richter-Bernburg 1955). A detailed account of the geological history and the geochemistry of the Ca-2 carbonate of Løgumkloster-1 is given in Stentoft (1990), Stentoft et al. (1990) and references therein. There are two general facies types in the interval, an oolitic shoal facies (type A), and a lagoonal carbonate facies (type B). See Fig. 2.

The primary mineralogy of the Ca-2 sediments was most likely dominated by aragonite or high-Mg calcite (Botz & Müller 1981). Since deposition the Ca-2 sediments have experienced a complex diagenetic history which is described in Stentoft (1990). The most important diagenetic events were as follows: (1) a phase of early dolomitization. (2) a phase of leaching with formation of inter- and intra-grain porosity. (3) a phase of stylolitization with associated fracturing. (4) a second phase of leaching resulting in a widening of preexisting pores and fractures. (5) late anhydritization. From fractures the anhydrite was spread in all directions, partly replacing the dolomite and partly filling the pores and cavities. After anhydritization, the rock was cemented by scattered sub- to euhedral quartz crystals, which have partly replaced the anhydrite and enclosed many dolomite grains during their growth. Ultimately oil was introduced, and visible oilstaining of the core has been observed in the interval between 2437.5 m and 2455 m b.KB. Below ca. 2455 m, scattered droplets of oil were found in isolated pores and in stylolites. Above 2437.5 m only very few small, scattered pitch-like fillings of oil are seen in the pores.

Investigations on the German Zechstein units have shown that small amounts of acid insoluble residues are present (Füchtbauer 1958, Füchtbauer & Goldschmidt 1959, Smykatz-Kloss 1966, Pundeer 1969, Braitsch 1971, Pöhlig 1986, Huttel 1989). The dominant minerals reported in the insoluble residues are muscovite (and illite), quartz, feldspar, chlorite and fluorite.

In the present investigation we have characterized the residue by analyzing the EDTA-insoluble residues of 5 carbonate rock samples by Instrumental Neutron Activation Analysis (INAA), X-ray diffraction (XRD), electron microscopical examination (SEM-ED), and palaeomagnetic measurements. The aim of this study is to characterize the insoluble residue and to find clues to its origin. In many works on Zechstein carbonates the insoluble residue is treated as a sort of dust bin, to which most unexplained chemical and mineralogical components are ascribed at convenience. In this work we try to analyze what components are really in the dust bin of insoluble residues, and from where they originated.

Sample preparation and analytical procedures

Sampling

The Ca-2 interval is ca. 41 metres long in the Løgumkloster-1 well, and most of it is preserved as full core. Quite large samples were obtained from 5 stratigraphical levels. They were carefully selected to be typical of the lithofacies association A and B respectively. One sample of the drilling mud was included as well in order to demonstrate if contamination from the drilling mud into the core or onto the samples took place. Samples were obtained from vertical plugs as ca. 200 gram pieces. The contamination on the core surface was avoided by sampling the interior of the core only. The carbonate, sulphate, and salt minerals were dissolved by repeatedly treating the powdered plugs with an alkaline EDTA solution (Bodine & Fernalld 1973). The samples were finally washed with water and weighed following drying at 60° C at 40% RH for 24 hrs. Chemicals and water were of analytical grade. A batch of the drilling mud was treated similarly with EDTA.

Sub-samples of some of these samples were also investigated following heating to 110, 300 and 550° C.

INAA

4 of the 5 samples have been subjected to INAA analysis. In treating one sample ca. 200 grams of rock were crushed in an agate mortar. Batches of ca. 50 grams were subjected to analytical grade EDTA dissolved in de-ionized water, and the residues subsequently combined and mixed to a common sample. Ca. 50 mg of residue was transferred to polyethylene irradiation vials and irradiated for 4 hours in the heavy water reactor DR-3 at Risø, Denmark. The thermal neutron flux at the sample position was $4 \cdot 10^{13}$ neutrons cm^{-2} sec^{-1}. Samples

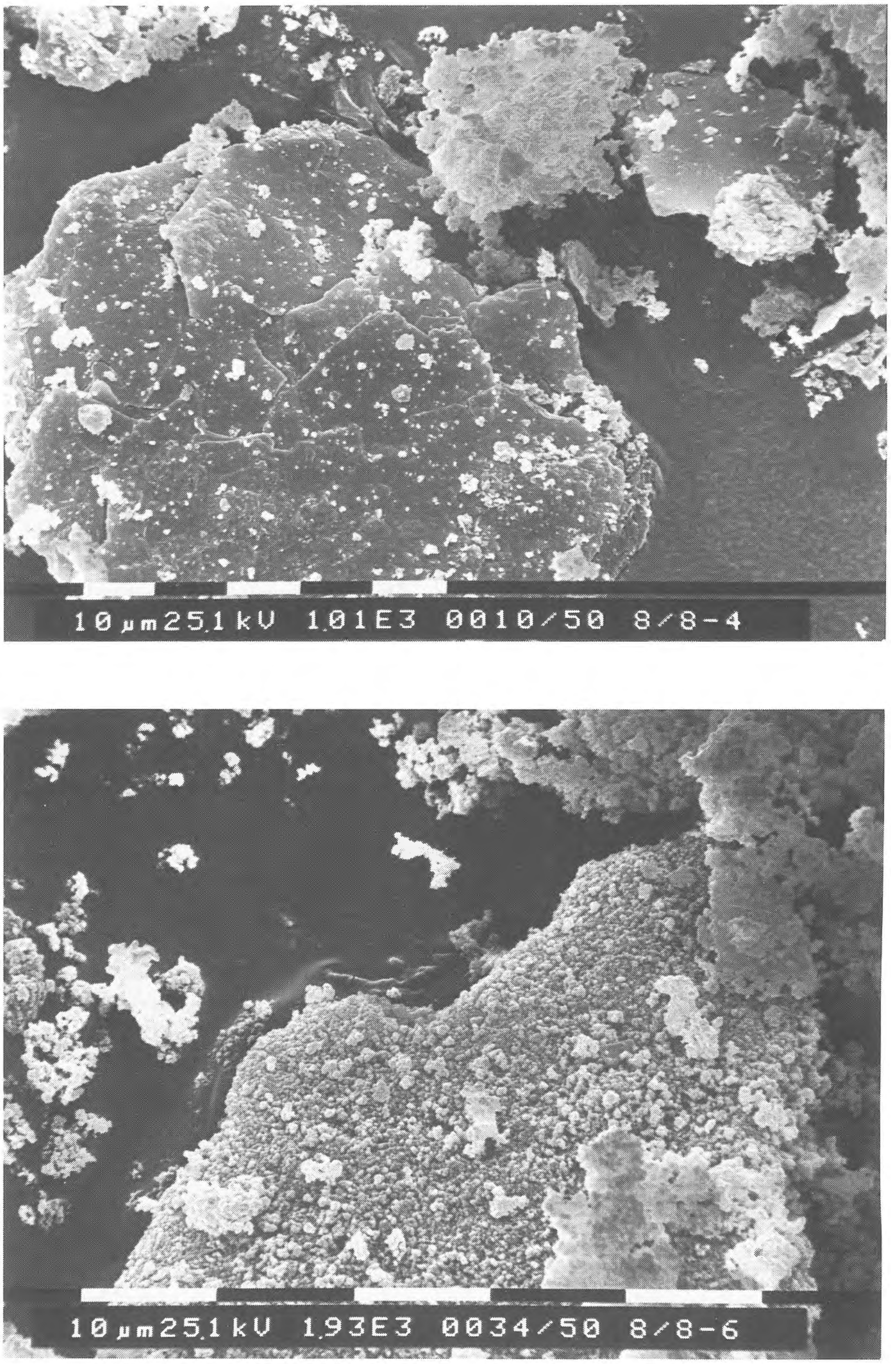

Fig. 3. a (top). SEM micrograph of the insoluble residue from sample 61 showing flaky muscovite-like grains. b (bottom). SEM micrograph of aggregated insoluble residue from sample 26, mostly consisting of apparently non-crystalline material.

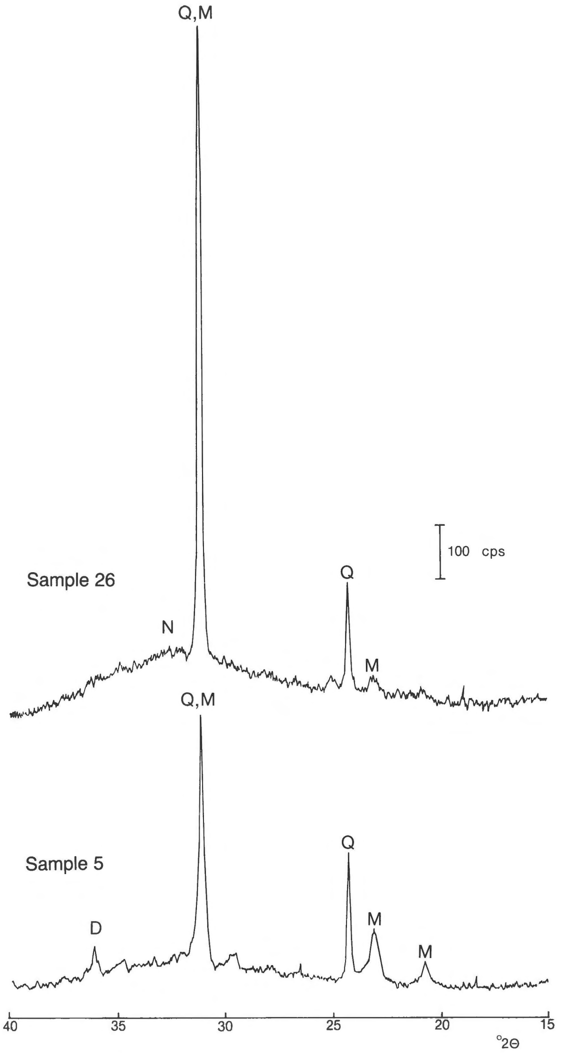

Fig. 4. X-Ray diffraction spectra of samples 26 and 5 (unoriented powder samples). The identified minerals are indicated on the diffractograms, N: non-crystalline component, M: muscovite, Q: quartz, D: dolomite.

were irradiated together with iron oxide (Fe_2O_3) as an internal standard.

The measurements were carried out on a high-purity germanium detector with an efficiency of 13.8%, with 1.91 keV as full width half maximum at the 1332 keV line of Eu. A Nuclear Data 4096 multichannel pulseheight analyzer was used to collect the data. Samples were measured for 30 minutes in the first count after 7–9 days, and for 5–12 hours in the second count after 20–30 days.

The spectra were analyzed for 38 elements, among which generally 20 elements occurred in amounts above the detection threshold. The elements for which concentrations were achieved are: Na, K, Ca, Sc, Cr, Fe, Co, Zn, As, Se, Br, Rb, Sr, Sb, Cs, Ba, La, Ce, Nd, Sm, Eu, Tb, Yb, Lu, Hf, Ta, Ir, Au, Hg, Th, and U. The uncertainty was generally better than ±10% (one standard deviation), but some variation in the uncertainty was encountered depending on the bulk chemistry of the sample.

X-ray diffraction

XRD was carried out on powdered samples of whole rock samples, as well as on EDTA insoluble residues. The XRD analysis was carried out on a Phillips X-ray 1050 vertical diffractometer equipment, using Co-K_α radiation. The samples were investigated as unoriented (Na-saturated) and oriented samples (Mg-saturated, Mg-saturated + Ethyleneglycol).

Magnetic measurements

The palaeomagnetic measurements were carried out on a United Scientific SCT-A-100 helium cooled SQUID-magnetometer (Superconducting QUantum Interfering Device). All 5 samples of insoluble residue were measured for NRM (Natural Remanent Magnetization). The susceptibility of the samples were measured on a KLY-2 Kappabridge.

Results and discussion

SEM examination of the residue samples reveals a pronounced difference in appearance between the two facies types. Figure 3 shows a typical micrograph from each facies type. The residue samples of the lagoonal facies type are characterized by the occurrence of many large (50–200 μm) flaky muscovite-like mineral grains. The residue samples of the oolitic shoal facies are characterized by a ubiquitous and apparently non-crystalline assemblage.

Each lump in the assemblage is quite small, typically 0.1–1 μm.

X-ray diffractograms of a sample from each facies are shown in Fig. 4, and the mineralogy of the samples is reported in Table 1. The presence of a non-crystalline component characterized by a very broad peak with maximum at 0.32 nm is noted in samples from the oolitic shoal facies (lithofacies A), whereas crystalline minerals dominate in the lagoonal facies (lithofacies B). A faint rise of the background at the same position can be recognized in the XRD spectrum of the lagoonal facies sample. The presence of muscovite is detected by the peak at 0.44 nm, and large muscovite-like flakes (50–200 μ) are seen in the SEM (see Fig. 3). The occurrence of illite cannot be excluded but is considered minor compared to muscovite. Two of the well defined peaks in the XRD spectra of samples 26, 30 and 61 cannot be assigned with certainty (0.414 nm and 0.314 nm). The peak at 0.314 nm is possibly due to the presence of fluorite. Swelling minerals (e.g. smectites) were not identified in the diffractograms of the oriented samples.

The presence of four abundant minerals in the drilling mud (plagioclase, smectite, kaolinite, and analcime, see Table 1), which are not identified in the insoluble residues, indicates that contamination from the drilling mud is negligible.

The results of the INAA analysis are listed in Table 2. Only concentrations above the detection thresholds are given in Table 2. Also given in Table 2 is the trace element concentration of nearby bulk samples (from Stentoft et al. 1990).

Table 3 lists the results of the magnetic measurements. It should be noted that the palaeointensities of the residues are measured on powdered samples, and therefore only the order of magnitude is of relevance.

From the INAA analysis EDTA-insoluble residue and bulk sample composition has been compared. The average of the ratios of the residue/bulk composition for the oolitic shoal facies as determined by INAA is shown in Fig. 5. A similar plot for the lagoonal facies is shown in Fig. 6.

It is apparent from both these plots that the heavy REE are less concentrated in the EDTA insoluble residue than the light REE. This is probably caused by a differential and easier dissolution of the heavy REE than of the light REE. Preferential dissolution of heavy REE by EDTA was also observed by Spirn (1965), Roaldset & Rosenqvist (1971a, 1971b), and Piper (1974); see also McLennan (1989). The even-odd effect reported by Roaldset & Rosenqvist (1971a, 1971b) was not observed in the present data set. A fair agreement exists between the average amount of residue which can be estimated from the INAA results, ca. 0.5–2%, and those found by the dissolution experiments, ca. 0.5% (cf. Figs 5 and 6, and Table 1).

Figure 7 shows the abundance ratios of the averages of the residues from the samples of the lagoonal facies divided by those of the samples of the oolitic shoal facies. It should be noted that the reason for apparent enrichments in the lagoonal facies type probably is due to a larger amount of muscovite in these samples. Judging from the con-

Table 1. Sample codes, Facies type, A: oolitic shoal, B: lagoonal. Depth of samples (below KB). Weight of sample prior to EDTA treatment. Percentage of EDTA-insoluble residues. Mineralogy from XRD, *: dominant phase in residue; small amounts of unidentified phases occur in samples 26, 30, and 61

Samp no.	Facies type	Weight g	Depth m.b.KB	Residue %	Mineralogy
5	B	170	2425.9	0.55	quartz*, muscovite, trace of dolomite
26	A	170	2436.5	0.38	non-crystalline*, quartz, mica
30	A	200	2438.8	0.47	non-crystalline*, quartz, mica
61	B	200	2454.3	0.37	quartz*, muscovite, K-feldspar
72/76	B	877	2460–62	0.63	quartz*, muscovite, K-feldspar, trace of pyrite
	Drilling mud	–	2438–40 2442–44	–	quartz, plagioclase, mica, smectite, kaolinite, analcime

tents of Fe, Cr, Zn, and light REE, there is about twice as much muscovite in the lagoonal facies type samples as compared to the oolitic shoal facies (the dashed line in Fig. 7). Keeping this fact in mind, the lagoonal facies type samples are enriched in K, Rb, and Cs, in Sc and heavy REE, and in Ta, W and Th. This enrichment is in accordance with a higher content of clay minerals (muscovite) present in the

Table 2. Results of the INAA analysis

Depth	Sample	Na µg/g	K µg/g	Ca µg/g	Sc µg/g	Cr µg/g	Fe µg/g	Co µg/g	Zn µg/g
2425.8	5	38100	9600	13300	3.76	142	5180	1.65	473
2436.5	26	69400		1270	0.681	87.5	2240	2.15	534
2438.8	30	66400		977	0.493	48.6	1880	0.906	209
2454.3	61	43600	20000		3.94	107	4430	2.24	1490
2425.8	Bulk-5	450		232000	0.0846	2.140	134.0	0.1720	6.98
2436.5	Bulk-26	278		73000	0.0150	0.718	16.5	0.0863	14.70
2438.8	Bulk-30	273		84700	0.0148	0.705	18.9	0.0292	5.44
2454.3	Bulk-61	406	181	266000	0.0530	1.070	95.3	0.1180	15.70

As µg/g	Se µg/g	Br µg/g	Rb µg/g	Sr µg/g	Ag µg/g	Sb µg/g	Cs µg/g	Ba µg/g	La µg/g
4.21	1.75	3.44	52.9	732	2.18	1.95	2.71		15.4
	0.658	6.15	7.03	701	3.94	2.77	0.525		4.51
	0.848	7.02	5.73	2470	1.39	1.86	0.384		3.21
4.51	1.15	5.28	59.4	1660	4.35	3.17	2.67		10.1
0.287	0.110	5.90		7510			0.0326	24.9	0.346
0.081		6.10		548		0.0135			0.691
0.170		6.26		6320		0.0122		42.6	0.963
0.352	0.131	7.77		8330			0.0178	39.9	0.107

Ce µg/g	Nd µg/g	Sm µg/g	Eu µg/g	Tb µg/g	Yb µg/g	Lu µg/g	Hf µg/g	Ta µg/g	W µg/g
80	65.9		0.196	0.192	1		10.9	0.846	41.8
29.5	28.9		0.0374		0.0144		11.3	0.236	9.85
25	23.4		0.0311		0.0371		10.1	0.157	12.3
57.8	52.9		0.114		0.123		14.2	0.853	30.5
1.420	1.440	0.023	0.0247	0.0249	0.0775		0.0585		
0.746	1.050		0.0032		0.0159	0.0023			
1.110	1.550	0.113	0.0046		0.0133	0.0056			
0.690	0.796		0.0063				0.0449		

Ir ng/g	Au ng/g	Hg µg/g	Th µg/g	U µg/g
1.3	16.6		6.05	
1.8	20.8		0.368	
0.86	7.5		0.35	
1.8	20.6		3.86	
		2.160	0.0892	2.65
		0.491	0.0151	2.03
		0.482	0.0137	3.36
		0.201	0.0443	

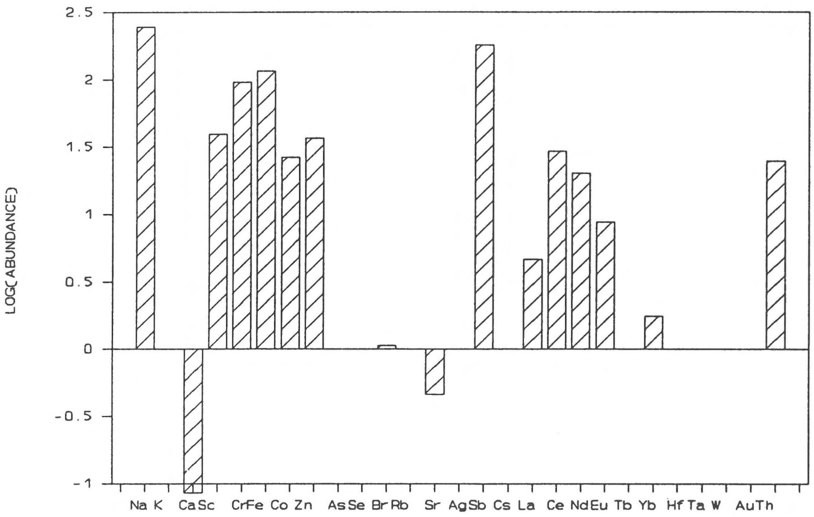

Fig. 5. The oolitic shoal facies. Abundance ratios between the EDTA residual and the bulk rock from the INAA determinations.

lagoonal facies than in the oolitic shoal facies. This is compatible with the geological setting of the two environments as discussed below. The pronounced enrichment of the heavy REE indicates that the muscovite has experienced extended contact with sea water.

It is noteworthy that the lagoonal facies samples are enriched in Ca, but depleted in Sr. This may be caused by tiny amounts of anhydrite still remaining undissolved in the lagoonal facies samples, although this mineral has not been detected by other means.

The lagoonal facies samples are depleted relative to the oolitic shoal facies in the typical halite elements Na and Br. It is, however, unlikely that any salt remains in any of the samples after the thorough EDTA dissolution. Bromine could also be attributed to organic matter, e.g. residual oil or kerogen (Fuge 1974), but it is unclear why the lagoonal facies should be depleted in organic matter relative to the oolitic shoal facies. The reason for these depletions remains obscure.

Table 3. The magnetic measurements

Sample	Facies type	Specific susceptibility 10-6 SI	Specific intensity 10-8 emu/g
5	lagoonal	9.1	230
26	oolitic	(− 11)	710
30	oolitic	10	2100
61	lagoonal	13	210

The lagoonal samples are also slightly depleted in Sb, whereas Se is neither depleted nor enriched in accordance with the Fe, Cr, Zn and light REE normalization mentioned above (the dashed line in Fig. 7). This relationship also seems somewhat obscure, because the calcophile elements Se and Sb could occur in tiny amounts of sulphides, which would have been suspected to occur mainly in the lagoonal facies. Our findings, however, do not support this interpretation, and another explanation for where Se and Sb is situated is called for.

Both the very low palaeomagnetic intensity of the residues and the very low magnetic susceptibility points to the possible presence of clay minerals, and certainly excludes the occurrence of major or even moderate amounts of ferromagnetic minerals, such as magnetite, ilmenite or haematite (Telford et al. 1976, Collinson 1983). This is evidence against an airborne deposition of the insoluble residue, because such a transport mechanism would almost certainly have brought in small (e.g. <2–$3\,\mu$) particles of ferromagnetic minerals. Transport by water, on the other hand, would allow the heavy

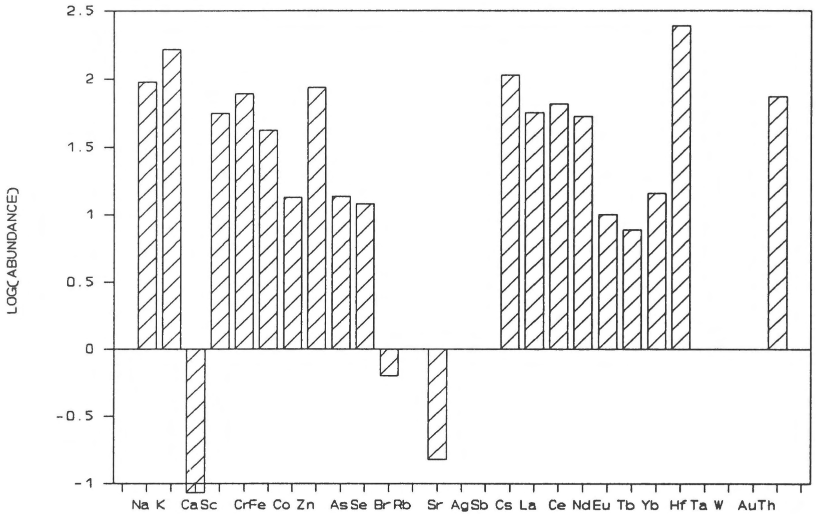

Fig. 6. The lagoonal facies. Abundance ratios between the EDTA residual and the bulk rock from the INAA determinations.

ferromagnetic minerals to drop out of suspension before reaching the present depositional area, and would therefore be in accordance with the observed lack of such minerals.

The magnetite spherules reported by Elmore et al. (1987) in other types of carbonate reservoirs have not been observed in the present material neither by SEM nor optically.

The non-crystalline material mentioned could possibly be interpreted as a glass phase, i.e. volcanically derived glass. This is, however, considered unlikely as no typical alteration products of volcanic glasses (e.g. smectite) are identified, and morphological characteristics of volcanic material like glass shards have not been noted in the SEM investigation. Furthermore it is considered unlikely that volcanic glasses could be preserved at all in the present geological setting. We know of no occurrence of fresh glass of this age.

Non-crystalline silica could also originate from mechanical degradation of opaline sponge-spicules. Sponge-spicules have, however, not been identified in the present material during petrographic description, and this origin is therefore considered unlikely.

Diagenetic replacement of anhydrite by silica occurs in hypersaline environments, and syn-sedimentary formation is possible in the concentrated water of the isolated sea basins (Grimm 1962, Milliken 1979). The replacement is facilitated by freshwater influx, and this could have led to preferential formation of non-crystalline silica in the shoal facies, as these sediments could have been emergent periodically. This is in accordance with our findings. Early diagenetic anhydrite formed by de-watering of gypsum has not been observed in thin sections but syn-sedimentary gypsum may have been present, as dolomite pseudomorphs of gypsum crystals are common in the Ca-2 sequence (Stentoft 1990).

The significant amounts of quartz in the residue is interpreted to originate from diagenetic processes. All the quartz observed in this sections occurs as sub- to eu-hedral crystrals which have partly replaced a late diagenetic anhydrite (Pöhlig 1986, Huttel 1989, Stentoft 1990).

Potential source areas for clastic material in the Ca-2

In the area around the Løgumkloster-1 well the nearest exposures during sedimentation of the Ca-2 was the Ringkøbing-Fyn High and possibly also the Arnum block (Fig. 1). The latter is interpreted to have been an emergent area of non-

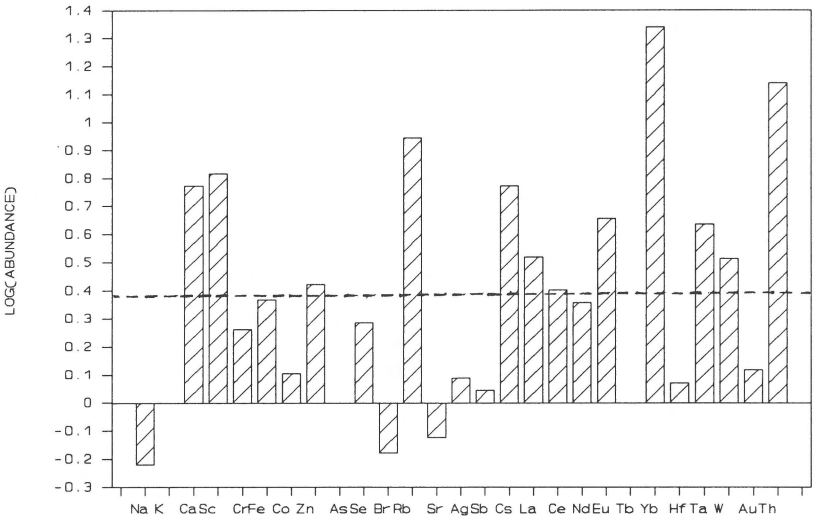

Fig. 7. The ratio of the averages of the abundances of the lagoonal facies (samples 5 and 61) and averages of the abundances of the oolitic shoal facies (samples 26 and 30). The dashed line represents the average difference in the amounts of muscovite present in the two facies based on Fe, Cr, Zn and light REE. Depletions or enrichments relative to this line represents differences in the composition of the insoluble residue.

deposition; most likely it had an erosional surface, at least during the Z-1 cycle. The Arnum block was flooded and evaporite deposition was apparently initiated during the Z-2 cycle (Stemmerik & Frykman 1989). The exposed basement rocks of these areas, which have probably been eroded during Ca-2 times, have been investigated in three wells: Arnum-1, Grindsted-1, and Glamsbjerg-1 (Fig. 1; Noe-Nygaard 1963). They all comprise various types of gneisses of Precambrian age.

In the Arnum-1 well the cores may represent a fanglomeratic deposit rather than a weathered basement surface. The rocks consist of angular fragments of gneisses, including biotite-hornblende gneiss and garnet-hornblende gneiss, which are embedded in a red arkosic sedimentary rock. In the Grindsted-1 well the basement rock is a biotite gneiss, with main constituents of quartz, potassium feldspar, oligoclase, biotite, some amphibole and a little epidote. The basement rock of the Glamsbjerg-1 well is a granodioritic hornblende gneiss with light quartz-feldspar bands. The uppermost part of the basement rock sequence of the Glamsbjerg-1 well is somewhat weathered.

It seems that these continental source areas had the potential to supply a variety of fine grained detrital material including both smectites and non-swelling clays like kaolinite and illite. Both wind and water could at least theoretically have been responsible for the long distance transport necessarily involved in the present geologic setting.

When discussing the possible origin of the fine grained material it is conceivable that some fine-grained particles, i.e. the clay and silt fractions, from the degrading basement rocks have been transported by the off-shore trade wind to the area around the Løgumkloster-1 well, and eventually have been incorporated in the shallow marine carbonate sediments of the Ca-2 interval. Comparable transport processes have been investigated in present day environments. Windblown Sahara dust accumulating on the island of Crete in the Mediterranean has been investigated by Nihlén & Solyom (1989), and was found mostly to consist of kaolinite. Other investigations have indicated also illite and chlorite as dominant phases in windblown material derived from Africa (Chester et al. 1972, 1977, 1984).

The clay minerals could also be water transported. In the Permian Southern Denmark setting the weathered feldspar-rich basement most certainly supplied clay-size material to the marine environment by periodic flash-floods. This material would be expected to settle in the sheltered lagoonal areas. That no clays like kaolinite have been detected in the Ca-2 material is somewhat odd, and may indicate that a diagenetic process has been active destroying these phases at a later time. The fairly long transport distances involved make it likely that a thorough sorting of minerals and grain sizes took place during transport.

It is also possible that pyroclastic grains of the clay fraction from volcanoes further away might account for the presence of some of the non-carbonate fines in the Ca-2 sequence. Two different volcano fields could have delivered airborne dust particles, namely the volcanoes in the Oslo Graben far to the north of the Løgumkloster-1 well area, and the volcanoes in the Polish-Dobrugea Trough south-east of the area. No magmatic activity took, however, place in North-western Europe, north of the Variscan mountains during Zechstein times according to Ziegler (1978) and Dixon & Fitton (1981). Several radiometric age determinations by K/Ar- and Rb/Sr-methods on igneous rocks of the Oslo Graben area, however, make it reasonable to assume that some magmatic activity took place in the Oslo Graben area throughout the whole of the Permian period (Ramberg & Larsen 1978, Sundvoll 1978a, 1978b, Ziegler 1988). A granodioritic agglomerate ca. 6 cm in diameter interpreted to be a volcanic bomb, was found within a clayish dolomite sequence from Late Permian Z-2 in the Slagelse-1 well, situated north-east of the Ringkøbing-Fyn High (Fig. 1). This alleged volcanic bomb is a singular and very exotic occurrence, but it may indicate proximity of older volcanic deposits or even contemporary explosive volcanism (Jacobsen 1984). Despite these indications no grains of definite pyroclastic origin have been detected in the samples investigated in the Ca-2 interval.

Conclusion

The distribution of the insoluble residue, some of which is considered to be primary sedimentary material, varies in accordance with the facies types. The lagoonal facies has formed a sheltered environment where clays and micas could settle. An interpretation that this was water-born material is preferred based on the enrichments in the heavy REE and on the lack of occurrences of ferromagnetic minerals. It seems most likely that the fine grained fractions are derived from weathering of exposed basement highs.

Grains of definite pyroclastic origin have not been detected, and ferromagnetic minerals are not present in substantial amounts based on the magnetic investigations. A volcanic origin of the insoluble material is therefore not supported.

The distribution of the muscovite, preferentially occurring in the lagoonal facies, is compatible with sorting induced by the hydrodynamic process working in the different environments. The high-energy oolitic facies kept the fine grained fractions suspended in the water, and these fractions were trapped mostly in the more quiet and sheltered lagoonal facies.

That no other layer-silicate phases are present is somewhat puzzling, since such phases are common as alteration products in most similar geological settings. Their absence is ascribed to one of the many diagenetic dissolution processes that the formation was subjected to. Most of the quartz present is interpreted to be a diagenetic phase precipitated in the formation at a late stage in the diagenetic history. The non-crystalline silicate phase observed primarily in the oolitic shoal facies is also considered to be a product of diagenesis and its detailed origin remains obscure.

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