# Dolomite and dedolomitization in Danian bryozoan limestone from Fakse, Denmark

NIELS OLUF JØRGENSEN



Jørgensen, N. O.: Dolomite and dedolomitization in Danian bryozoan limestone from Fakse, Denmark. *Bull. geol. Soc. Denmark*, vol. 37, pp. 63–74, Copenhagen, October 14th, 1988. https://doi.org/10.37570/bgsd-1988-37-06

The bryozoan limestones in the middle Danian (Lower Paleocene) carbonate rock complex of Fakse Quarry, Denmark, includes small intraformational bodies of dolomite that occur in three different ways: 1) completely dolomitized bryozoan limestones; 2) partially dolomitized bryozoan limestones in which the larger skeletons have resisted total dolomitization, and 3) concretionary dolomite. Furthermore, scattered secondary rhombohedral porosity is observed in bryozoan limestones indicating former occurrences of

dolomite. The dolomites are calcian with an elemental composition of approximately (Ca<sub>.55</sub>, Mg<sub>.45</sub>)Co<sub>3</sub>. The Sr content averages 500 ppm Sr, whereas the Mn and Fe contents are relatively low, c. 200 ppm Mn and 2000–4000 ppm total Fe respectively. The oxygen and carbon isotope values (-2.3% to -3.9%  $\delta^{18}$ O; +1.9% to +4.6%  $\delta^{13}$ C) are close to the field of early diagenetic dolomite replacing marine limestones. The carbon isotopes are enriched by approximately 2% in comparison to the host sediment, which suggests that dolomitization most likely took place in a zone of methanogenesis. Crystal chemistry and geochemistry indicate a common genetic origin for these dolomites. The dolomite formation was probably an early diagenetic event in which the sequence from occurrences of individual dolomite rhombohedra, concretionary dolomite and partially dolomitized bryozoan limestones, to completely dolomitized bryozoan limestones is interpreted to represent progressive dolomitization.

Dedolomitization is most pronounced in the dolomite concretions and to lesser extent in the dolom-itized bryozoan limestone beds. The isotopes of the replacive calcite suggests that dedolomitization took place under the influence of meteoric water. The progressive dedolomitization appears to be governed by the access of meteoric water along cleavage traces spreading to the entire dolomite crystals. Therefore, cleavage traces probably control dedolomitization under suitable physicochemical conditions.

N. O. Jørgensen, Institute of Historical Geology and Palaeontology, Øster Voldgade 10, 1350 Copenhagen K, Denmark. April 7th 1988.

# Introduction

The Fakse Linestone Quarry, situated to the east of the small town of Fakse in southern Sealand, Denmark, constitutes together with the nearby Stevns Klint the type localities of the Danian Stage (fig. 1). Fakse is located in the southeastern part of the Danish sub-basin in a middle Danian (lower Paleocene) depositional environment of biogenic carbonates dominated by bryozoan limestones which in northwesterly direction give way to coccolith limestones (Håkansson and Thomsen 1979). The carbonate rocks in the Fakse Quarry are located on the marginal part of the basin, close to the Ringkøbing-Fyn High, and have never been exposed to deep burial diagenesis.

The section exposed in the quarry is of the Tylocidaris bruenichi Zone, middle Danian, and belong to nannoplankton zone NP 3 (Asgaard 1979, Perch-Nielsen 1979). The quarry displays a

sequence of bryozoan limestones, which primarily occur as a complex of mounds, intercalated by mounds or lenses of coral limestones, which have arisen through extensive growth of ahermatypic corals. The carbonate sequence have been glacially eroded and covered by Quaternary glacial deposits. The carbonate rocks are highly fossiliferous and the fauna and the lithofacies have been described among others by Rosenkrantz (1938), Rosenkrantz and Rasmussen (1960), Asgaard (1968), Cheetham (1971) and Floris (1979, 1980).

The bryozoan limestones and the coral limestones show a wide range of subfacies and variations in diagenesis. The bryozoan limestone facies varies from mud-supported, chalk-like uncemented rock, through wackestone and packstone, cemented to various degrees. The bryozoan limestone locally contain greyish to brownish flint, either as nodules or continuous flint layers. The coral limestone is an early lithi-



Fig. 1. Location of Fakse Quarry, Sealand, Denmark.

fied rock showing a wide variety of diagenetic alteration and micritic infilling (Floris 1979). The corals are preserved only as cement filled voids.

Dolomite is generally rare in the Fakse

Quarry. It has so far only been found in association with bryozoan limestones as a replacement of individual limestone beds and as concretionary dolomite. Generally the dolomite shows evidence



Fig. 2. Quarry face showing completely to partially dolomitized bryozoan limestone bed (dol.) in a section of bryozoan limestones (br. lms.) and a flank of a coral mound (c. lms.). The middle Danian limestones are covered by Quaternary glacial deposits (qu.).



Fig. 3. Scanning electron micrograph of completly dolomitized bryozoan limestones showing idiotopic-subhedral to sucrosic texture. Fracture surface. Bar scale 200 µm.

of extensive and progressive dedolomitization. The objective of this paper is to elucidate the inferred processes of dolomitization and dedolomitization on the basis of textures, fabrics and geochemical properties of the dolomites.

# Material and methods

Fabrics and textures were studied by means of thin sections under the optical microscope and details of crystal habits and textures were examined in the scanning electron microscope (SEM) on fractured specimens and polished and etched sections. Cathodoluminescence petrography was applied to detect any possible zoning of dolomite crystals and to reveal former dolomite texture in dedolomitized limestones.

The elemental composition of individual crystals of dolomite and adjacent calcite was studied with an electron microprobe, whereas the elemental composition of pure, unconsolidated dolomite sand was determined by use of atomic absorption spectrophotometry. Unit-cell parameters were determined by least-squares analyses of X-ray powder data obtained with a Guinier camera.

Stable isotope analyses were limited to bulk samples because the grain size of the carbonate rocks studied is too small to permit separation by physical methods. A chemical procedure, based on the different reaction rates with acid, was applied to analyse the calcite-dolomite mixture (see Degens and Epstein 1964, Clayton et al. 1968). The <sup>13</sup>C/<sup>12</sup>C and <sup>18</sup>O/<sup>16</sup>O ratios were determined with a Variant MAT 250 mass spectrometer. The dolomite data are corrected for the fractionation in phosphoric acid reaction according to the results given by Sharma and Clayton (1965).

# Dolomite distribution and petrography

The dolomites studied are entirely associated with bryozoan limestones in which they occur as small intraformational bodies either as a replacement of bryozoan limestone beds or as concretionary dolomite. The dolomite textures are classified using the scheme proposed by Gregg and Sibley (1984).

The largest exposure of dolomitized bryozoan limestones seen in the quarry to day has a lateral extension of approximatel 40 meter and a thickness of about 1.5 meter. The dolomitized beds are laterally limited by Quaternary glacial deposits and a flank of a coral mound (fig. 2). From below they are limited by a flint layer whereas they upwards give way to non-dolomitized bryozoan limestones beds. The dolomite occurs in two different ways:

1) Completely dolomitized bryozoan limestone, yellow to brownish in colour, and showing fossil moldic porosity. The dolomite occurs as relatively uniform sized rhombohedra with the longest diameter within the range of 100–150 microns (fig. 3). The texture varies from massive idiotopic-subhedral to crystal-supported sucrosic texture, in which the intercrystalline area is only occasionally filled with micritic calcite. Straight



Fig. 4. Scanning electron micrograph of dolomite sand. Note that the sediment almost exclusively consists of dolomite rhombohedra. Bar scale 200  $\mu$ m.



Fig. 5. Scanning electron micrograph of polished and etched section of partially dolomitized bryozoan limestone showing idiotopic-euhedral texture. The intercrystalline area is primarily filled by secondary calcite cement. Note dedolomitization along cleavage traces in the individual dolomite rhombohedra. Bar scale 100 um.



Fig. 7. Scanning electron micrograph of polished and etched section showing sharp contact between partially dolomitized bryozoan limestone (right) and completely dolomitized bryozoan limestone (left). Bar scale 200 µm.

compromise boundaries are common and many crystals have crystal-face junctions.

In places the completely dolomitized bryozoan limestones disintegrate into individual dolomite rhombohedra or minor aggregates forming an unconsolidated dolomite sand with a characteristic mealy consistency (fig. 4).

2) Massive but only partially dolomitized bryozoan limestone, yellow to brownish in colour. The dolomite rhombohedra have relatively uniform size with the longest diameter in the range of 100–150 microns (fig. 5). The dolomite texture is idiotopic-euhedral to idiotopic-porphyritic. Most individual dolomite rhombohedra are partially dedolomitized and have a mosaic of neo-



Fig. 6. Scanning electron micrograph; polished and etched specimen of partially dolomitized bryozoan limestone showing neomorphic microspar due to dedolomitization in cleavage of dolomite crystal. Bar scale 10 μm.

morphic microspar which primarily occurs along cleavage traces (fig. 6). The intercrystalline area is filled by micron-sized equicrystalline secondary calcite and coarse anhedral calcite spar. Skeletal debris, particularly bryozoan stems, are frequently observed and may be partially dolom-



Fig. 8. Dolomite concretion (c) in an old quarry face of bryozoan limestones. The concretion is approximately 1 meter in diameter.

Bulletin of the Geological Society of Denmark



Fig. 9. Section of dolomite concretion from Fakse Quarry. Note the irregular outline and the outermost black rim which indicates iron oxides.

itized. The partially dolomitized bryozoan limestones generally have a low porosity and fossil moldic porosity is less frequent than in the completely dolomitized beds.

The two types of dolomite occur side by side showing a sharp contact (fig. 7).

Concretionary dolomite occurs in a few places in the quarry. The concretions are yellow to reddish brown in colour and may be up to 1 meter in diameter (fig. 8). The concretions are subspherical and contain extensive irregular cavities filled with slightly indurated bryozoan limestone (fig. 9).

The concretions exhibit a characteristic zoning. The majority of the concretion consists of a core, generally with a idiotopic-euhedral to idiotopicporphyritic texture similar to that observed in the massive, partially dolomitized bryozoan limestones. The progress of dedolomitization varies within the individual dolomite crystals from initial calcification along cleavage traces to a final stage where the entire crystal has been replaced by neomorphic microspar (fig. 9). Extensive areas in the center of the concretions are almost free of dolomite and contain coarse, anhedral sparry calcite, equicrystalline microspar and patches of skeletal debris and lime mud. However, cathodoluminescence petrography reveals numerous ghosts of rhombohedra, particularly in the microspar, indicating the former occurrences of dolomite crystals and the neomorphic origin of the calcite fabrics (fig. 11).

The core passes gradationally into a narrow outer rim of approximately 1 cm (fig. 9). The dolomites in the rim zone are extensively dedolomitized. Dolomite decreases in the outer part



Fig. 10. Scanning electron micrograph of polished and etched specimen from the central part of a dolomite concretion showing variable dedolomitization in dolomite in dolomite rhombohedra. The intercrystalline area is filled by secondary calcite cement. Bar scale 100  $\mu$ m.



Fig. 11. Dolomite recognition in neomorphosed dolomite concretion. A) Thin-section photomicrograph of central part of dolomite concretion showing skeletal debris in a matrix consisting principially of secondary microspar. Plane-polarized light. B) Cathodoluminescence photomicrograph of the same specimen as in A showing numerous dolomite rhombohedra not apparent under plane-polarized light confirming the neomorphic origin of the microspar. Bar scale 500 µm in each photograph.



Fig. 12. Scanning electron micrograph of polished and etched specimen from the margin of a dolomite concretion. The dolomite rhombohedra (left) have been intensively dedolomitized and subsequent leaching has resulted in moldic rhombohedral porosity in the outside margin (right) Bar scale 300 µm.

of the rim which is dominated by coarse sparry calcite and neomorphic microspar. This zone is highly porous due to considerable moldic rhombohedral porosity (fig. 12). The individual rhombic pores are generally divided by calcite 'wings' into a regular boxwork (fig. 13).

The outer part of the rim is stained intensively reddish brown of iron oxides which partially fill in the secondary moldic rhombohedral porosity. The iron oxides do not show crystal forms under the SEM, but X-ray diffractometry indicates that they are goethite.

A third type of carbonate consists of slightly indurated bryozoan limestone with numerous skeletal debris in a matrix of lime mud containing scattered secondary moldic rhombohedral porosity indicating the former occurrences of dolomite crystals (fig. 14). This type of carbonate is found in close proximity to the dolomitized bryozoan limestones and in the bryozoan limestone elsewhere in the quarry. The dolomite texture was idiotopic-porphyritic of matrix-supported individual rhombohedra. The lime mud has been dolomitized and a large number of the skeletal debris are also replaced by dolomite (fig. 14).

## Geochemistry

The three different dolomites have a rather uniform crystal chemistry. The X-ray powder diffraction patterns of the dolomites show well-de-



Fig. 13. Scanning electron micrograph of fractured specimen from the margin of a dolomite concretion showing extensive moldic rhombohedral porosity with characteristic calcite 'wings' within the rhombic pores parallel to the cleavage traces of the dolomite crystal. Bar scale 200 µm.

fined lines, including ordering reflections, which can be indexed using a hexagonal unit-cell. The hexagonal unit-cell parameters a and c (in Å) range within 4.82–4.83 and 16.13–16.14, respectively. The calculated unit-cell dimensions indicate a Mg/Ca ratio of approximately 45/55 corresponding to an elemental composition of Ca<sub>.55</sub>, Mg<sub>.45</sub>CO<sub>3</sub> (see Goldsmith et al. 1961, Land 1980). This corresponds to a large number of magnesium determinations using electron microprobe and atomic absorption spectrophotometry, which indicate a range within 43–48 mol% MgCO<sub>3</sub>.

The elemental distributions of Mg, Sr, Mn and Fe in dolomites, associated calcite fabrics and the bryozoan limestones are shown in table 1. The dolomites have a rather uniform elemental com-



Fig. 14. Thin-section photomicrograph of bryozoan limestone showing considerable moldic rhombohedral porosity indicating the former occurrece of dolomite. Crossed nichols. Bar scale 300 µm.

	Mg wt% (ppm) Mg/Ca			Sr ppm	Mn ppm	Fe ppm
Completely dol. beds Dolomite N = 108	х s	11.78 0.27	45/55	480 92	175 67	2240 476
Partially dol. beds Dolomite N = 75	х́ s	11.71 0.30	45/55	475 108	190 71	2170 346
Neomorph. calc. Microspar, N = 38	x s	18360 14560		310 96	125 78	1980 355
Calc. microspar $N = 55$	х s	2730 2040		260 92	115 66	1870 387
Calc. spar $N = 28$	х s	1100 210		210 92	110 66	565 387
Dolomite concretions Dolomite N = 49	x s	11.51 0.33	44/56	505 134	175 115	3295 978
Neomorph. calc. Miccrospar, N = 58	x s	22610 22649		195 60	170 119	3150 967
Calc. microspar N = 29	S	10170 4976		200 92	155 128	2940 892
Calc. spar $N = 84$	х s	1080 227		195 88	130 72	615 418
Bryozoan limestone N = 6	x s	3320 528		630 89	390 111	1120 438

Table 1. Geochemistry of dolomites, associated calcite fabrics and bryozoan limestone from Fakse Quarry, Denmark.

position. However, the concretionary dolomite on average is slightly more calcian, i.e. Mg/Ca  $\sim$ 44/56, than the dolomitized beds (Mg/Ca  $\sim$  45/ 55). On the other hand, the iron content is significantly higher, i.e. approximately 3300 ppm total Fe, in the concretionary dolomite compared to the c. 2200 ppm total Fe obtained from the other dolomites. The Sr and Mn contents are relatively constant in all dolomites studied with approximately 500 ppm Sr and 175 ppm Mn, respectively.

The neomorphic microspar within the dolomite crystals reveals a very high and varying Mg content, and the associated neomorphic microspar in the matrix also shows a high Mg content, particularly in the concretions. The Mn and Fe contents in the neomorphic microspars are about the same or slightly lower than in the dolomites. In contrast, the Sr contents are significantly lower in the two microspar fabrics studied than obtained from the dolomites. The calcite spar is characterized by relatively low contents of all the elements studied (table 1). The dolomite-free, slightly indurated bryozoan limestone shows and elemental composition which is similar to those generally obtained from Danian bryozoan limestones in the Danish subbasin (Jørgensen 1975 and 1981).

The stable isotope values of the host sediment, the bryozoan limestones, are within the range of -1.6% to -2.9%  $\delta^{18}$ O and +0.8% to +1.8% $\delta^{13}$ C (fig. 15). The oxygen isotope values for the dolomites lie between -2.3% and -3.9%  $\delta^{18}$ O, which represent a minor depletion in <sup>18</sup>O relatively to the host sediment. In contrast, the dolomites are more enriched in <sup>13</sup>C showing values from +1.9% to +4.6%  $\delta^{13}$ C. There are no significant differences in the oxygen isotopic signature between the different dolomites studied.

The coexisting secondary neomorphic microspar and calcite spar reveal a strong depletion in <sup>18</sup>O and <sup>13</sup>C to both dolomite and the bryozoan limestones. The  $\delta^{18}$ O values vary from -5.1‰ to -7.8‰  $\delta^{18}$ O whereas the  $\delta^{13}$ C values show a wide range from -2.2‰ to -7.0‰  $\delta^{13}$ C. The stable isotopic determinations for the coexisting second-



Fig. 15. Cross plot of  $\delta^{13}$ C versus  $\delta^{18}$ O obtained from dolomites, associated calcite fabrics and bryozoan limestones from Fakse Quarry. Values obtained from dolomite-calcite mixtures are indicated by circles. Infilled circles: dolomite, open circles: coexisting calcite. Infilled squares: pure dolomite from the completly dolomitized beds and dolomite sand, open squares: secondary calcite cement from dolomite concretions. Triangles: bryozoan limestones.

ary calcites were limited to bulk analyses, since the grain size and textural configuration do not permit a physical separation of the different fabrics. However, samples which consist of mixtures of dolomite and calcite are dominated by neomorphic microspar, whereas the almost dolomite-free samples from the center of the concretions are dominated by coarse calcite spar. No significant differences exist between those two sample populations (fig. 15).

## Interpretation and discussion

#### **Dolomite formation**

The petrographic evidence shows that the Fakse dolomites were formed by replacement of the bryozoan limestones and the almost identical crystal chemistry and geochemistry indicate that the dolomites studied have a common genetic origin. The different distribution and occurrences of the dolomites most likely reflect stages in progressive dolomitization. The following phases in the process of dolomitization are suggested on the basis of petrographic evidence.

- The initial dolomitization appears as scattered occurrences of individual replacive dolomite rhombohedra in the lime mud of the bryozoan limestones forming a matrix-supported idiotypic-porphyritic texture. This stage is represented by the slightly indurated bryozoan limestones containing scattered secondary moldic rhombohedral porosity.
- 2) The dolomitization proceeded into the formation of a idiotypic-euhedral texture in which the lime mud as well as skeletal fragments may be partially dolomitized. This stage led to the formation of dolomite concretions and partially dolomitized bryozoan limestone beds.
- 3) The final phase of dolomitization led to an idiotopic-subhedral to sucrosic texture in which any trace of the pre-existing biogenic constituents is destroyed and where larger skeletal fragments have been dissolved leaving a fossil moldic porosity.

The low-Mg calcitic bryozoan limestones were most likely not the primary source of magnesium, but probably connate waters and dissolution of metastable high-Mg calcitic skeletons within the coral-bryozoan mound complex.

The Sr content in the Fakse dolomites of approximately 500 ppm Sr is relatively high in comparison to most ancient dolomites (Mattes and Mountjoy 1980). The strontium content of dolomite is inherited from the Sr<sup>2+</sup>/Ca<sup>2+</sup> ratio of the solution from which the dolomite precipitated and the distribution coefficient of strontium in dolomite. Estimates of the low-temperature distribution coefficient are unsatisfactory (Veizer et al. 1978, Land 1980). However, the varying strontium content of ancient dolomite is most likely the result of changing pore water  $Sr^{2+}/Ca^{2+}$ ratios due to subsequent diagenetic processes (see Pingitore 1982, Baker and Burns 1985). Obviously, there is no knowledge of the pore water chemistry in the Fakse bryozoan limestones at the time of dolomitization. Most likely the Sr<sup>2+</sup>/Ca<sup>2+</sup> ratios in the pore water were significantly higher than the sea water due to extensive early diagenetic dissolution of aragonitic skeletons (primarily corals) within the rock complex. Thus, although the distribution coefficient is unknown, the Sr content in the Fakse dolomites was probably governed by a relatively high  $Sr^{2+}/Ca^{2+}$ ratio in the precipitating solution.

The manganese and iron contents are relatively uniform in the different modes of dolomites. It was previously predicted that the process of diagenetic partition leads to enrichment of both Mn and Fe in the solid carbonate phase (Pingitore 1978, Brand and Veizer 1980, Mattes and Mountjoy 1980). However, the contents of manganese in the dolomites are lower and the iron content significantly higher than found in the host rock, the bryozoan limestones. It is therefore believed that the concentrations of Mn and Fe reflect the quantity of these ions delivered to the site of dolomitization rather than subsequent diagenesis.

The carbon and oxygen isotope values for the bryozoan limestones show a relatively broad range of values (-1.0% to -3.0%  $\delta^{18}$ O, +0.5% to +1.8%  $\delta^{13}$ C). However, the bulk samples of the bryozoan limestones constitute a mixture of original skeletal matter, recrystallized skeletons, carbonate mud and secondary precipitated calcite and the scatter in the values obtained is most likely the result of increasing diagenesis.

The stable isotopic signatures of the dolomites come close to values obtained from a variety of early diagenetic dolomites that replace marine limestones (see Mattes and Mountjoy 1980). The oxygen isotope composition is practical identical or slightly depleted in comparison to the host rock. However, most carbon isotope compositions obtained are enriched by approximately 2‰  $\delta^{13}$ C in comparison to the bryozoan limestones. The formation of isotopically heavy CO<sub>2</sub> is generally attributed to decay of organic matter by methanogenesis, producing light CH4 and enriching the remaining  $CO_2$  in <sup>13</sup>C (Nissenbaum et al. 1972, Pisciotto and Mahoney 1981, Baker and Burns 1985). Most likely the organich-rich bryozoan-coral mound complex promoted methane production leading to the formation of heavier carbon carbonates.

The timing of the dolomitization is rather speculative. The isotopic signature indicates an early diagenetic event. Metastable biogenic carbonate constituents in the bryozoan-coral mound complex were most likely the major source of magnesium and strontium and, apparently, dissolution and lithification of these carbonates was a very early process (Floris 1979). Therefore, the dolomitization was probably an early diagenetic event which took place contemporaneously and as a result of extensive early diagenesis of metastable carbonates in the bryozoan-coral mound complex. The rather uniform geochemistry of all types of dolomites indicates that the stability of the dolomites was retained until the beginning of dedolomitization.

#### Dedolomitization

All the Fakse dolomites show evidence of varying degrees of dedolomitization. Dedolomitization is minor in the completely dolomitized bryozoan limestones. The process is widespread in the partially dolomitized beds and extensive dedolomitization has taken place in the concretionary dolomites.

The resistance to dedolomitization is related most likely to crystal chemistry and order/disorder properties (Katz 1968, Lippman 1973, Folk and Land 1975). Thus selective dedolomitization and dedolomitization of rhombohedral zones are attributed to variations in the physicochemical conditions during the process of crystallization (Frank 1981). However, unit-cell parameters and the Mg/Ca ratios obtained indicate that all dolomites have a similar crystal chemistry and ordering and this should mean equal resistance to dedolomitization. Furthermore, geochemistry and cathodoluminescence petrography did not reveal any significant zoning in the Fakse dolomites. However, it can not be excluded that the extensive dedolomitization which has taken place in the concretions may be related to the relatively high iron content in these dolomites.

Dedolomitization in the Fakse dolomites apparently begins as a replacement by neomorphic Mg-rich microspar along cleavage traces from where it spreads to the entire dolomite crystals. Subsequently the Mg-rich microspar may recrystallize to low-Mg calcite. The variable stability of the different carbonates is significantly demonstrated by the formation of the characteristic calcite 'wings' in the rhombohedral pores as a result of selective leaching. The occurrence of three solid carbonate phases, i.e. dolomite, high-Mg calcite and low-Mg calcite, within the individual rhombohedra is believed to reflect progressive phases in dedolomitization.

Dedolomitization along cleavage traces was described by Frank (1981) in Upper Cambrian dolomites from southeast Missouri. He observed calcite walls which divided the dolomite crystals into a three-dimensional boxwork of almost equal-sized rhombohedra. The phenomenon has much in common texturally with the calcite 'wings' observed in the Fakse dolomites. Thus, the geochemical and petrographic data suggest that cleavage traces may control the areas of dedolomitization in relatively stable and chemical homogeneous dolomites.

The oxygen isotopic signatures of the later replacive calcite in the range of -2.2% to -7.0% $\delta^{18}$ O indicate that the process of dedolomitization took place under the influence of meteoric water and, therefore, the intensity of dedolomitization is governed by the access of meteoric water. The trend in the stable isotope values for the replacive calcite points in the direction of the dolomite field (fig. 15) and probably reflects micture in various degrees of the isotopically relatively heavy dolomites and light isotopic composition of the meteoric water. Furthermore, the trend indicates that the precipitation of the secondary replacive calcite was most likely closely related to the process of dedolomitization. Groot (1967) emphasized the importance of high rate of water flow to generate effective dedolomitization. Therefore, porosity and permeability in the partially dolomitized bryozoan limestones were most likely relatively high prior to dedolomitization than in the case of the completely dolomitized beds. The rather low porous and massive habit of the partially dolomitized beds which are observed today is probably due to the precipitation of large amount of secondary calcite cement in connection with the dedolomitization.

In places, the process of dedolomitization led to secondary porosity, most likely by subsequent leaching of the metastable phase of neomorphic high-Mg calcite leaving a rhombohedral porosity (Evamy 1967). The selective dissolution resulted in the rhombohedral pores in the outer rim of the dolomite concretions. So far, rhombohedral porosity has only been observed in the outermost rim of the concretionary dolomites and the slightly dolomitized but high porous bryozoan limestones, probably because these particular sites have been exposed to considerable fresh water due to their high porosity.

Goethite is an important pore filling material in the outermost rim of the dolomite concretions. Iron oxides are often associated with dedolomitization reflecting weathering and oxidation of ferroan dolomite (among others Al-hashemi and Hemmingway 1973, Evamy 1963 and Frank 1981). However, the Fakse dolomites are not particularly ferroan, and so far iron oxides have not been recorded within the dedolomitized cleavage traces, as was noted by Frank (1981). Therefore, the diagenetic features at the concretion surfaces probably resulted from late stage diagenetic aggressive meteoric waters that dissolved the neomorphic Mg-rich microspar.

# Conclusions

The Fakse dolomites are limited to intraformational bodies in bryozoan limestones; their crystal chemistry and geochemistry indicate that they have a common genetic origin. The dolomite formation was most likely an early diagenetic event which took place in the zone of methanogenesis and resulted in equicrystalline and compositionally rather homogeneous but slightly calcian dolomites. The major source of magnesium was supplied most likely to the site of the dolomitization by large scale dissolution and recrystallization of biogenic high-Mg calcite within the carbonate rock complex. The geochemistry and the petrographic evidence suggest that the different occurrences of dolomite reflect stages of progressive dolomitization. The dolomitization apparently was initiated in the micritic matrix of the bryozoan limestones and continued into the larger skeletal debris. The advancing dolomitization led to the formation of dolomite concretions and partially dolomitized bryozoan limestones, ending with complete dolomitization in which any trace of the pre-existing biogenic constituents was destroyed by a replacive mosaic of idiomorphic dolomite.

The Fakse dolomites are influenced by dedolomitization to varying degrees. The completely dolomitized limestones show little dedolomitization, whereas extensive dedolomitization has tak-

en place in the concretionary dolomite and in the partially dolomitized bryozoan limestones. The dedolomitization appears to be initiated by formation of neomorphic Mg-rich microspar along cleavage traces. From here, the process spreads to entire crystal bodies, and subsequently the metastable Mg-rich neomorphic microspar may recrystallize to low-Mg calcite. It is therefore proposed that cleavage traces may control areas of dedolomitization under the proper physicochemical conditions. The oxygen isotopic signature of the replacive calcite suggests that the dedolomitization took place under the influence of meteoric water, and probably the variable distribution of dedolomitization is the result of intensity of water flow due to local variations in porosity and permeability. High rates of water flow probably result in dissolution of the metastable Mg-rich neomorphic microspar leading to secondary rhombohedral porosity as observed at the surface of the concretions and the slightly dolomitized, but highly porous, bryozoan limestones.

Acknowledgements. The instruments utilizied, Jeol 733/Superprobe and Varian MAT 250 mass spectrometer, are funded by the Danish Natural Research Council. H. Egelund prepared the graphs and J. Bailey improved the English text.

## Dansk sammendrag

Karbonatbjergartskomplekset i Fakse Kalkbrud (mellem Danian) indeholder mindre forekomster af dolomit. Dolomiterne er begrænset til bryozokalk facies og kan forekomme som komplet dolomitiserede bænke af bryozokalk, delvis dolomitiserede bænke af bryozokalk samt som spredte konkretioner. Dolomiterne er svagt Ca-rige Ca.55, Mg.45CO3, og er karakteriseret af en ensartet geokemisk sammensætning, som tyder på en fælles genetisk oprindelse. De forskellige petrografiske typer af dolomit tolkes derfor som repræsenterende stadier af fremadskridende dolomitisering.

Dolomiterne i Fakse Kalkbrud er stærkt påvirket af dedolomitisering. Dedolomitiseringen tager sin begyndelse i zoner parallelt med spalteplanerne i de enkelte dolomitkrystaller og breder sig herfra til hele krystallen. Sammensætningen af de stabile iltisotoper i den replacive calcit tyder på, at dedolomitiseringen fandt sted under påvirkning af meteorisk vand. Dedolomitiseringen fører stedvis til en sekundær rhombisk porøsitet i bjergarten i tilfælde af, at den replacerende metastabile Mg-rige calcit opløses under vedvarende påvirkning af meteorisk vand.

## References

- Al-Hashimi, W. S. and Hemingway, J. E. 1973: Recent dedolomitization and the origin of the rusty crusts of Northumberland. Jour. Sed. Petrology, 43, 82–91.
- Asgaard, U. 1968: Brachiopod palaeoecology in Midlle Danian Limestones at Fakse, Denmark. Lethaia, 1, 103–121.

- Baker, P. A. and Burns, S. J. 1985: Occurrence and formation of dolomite in organic-rich continental margin sediments. Am. Assoc. Petroleum Geologists Bull., 69, 1917-1930.
- Cheetham, A. H. 1971: Functional morphology and biofacies distribution of Cheilostome bryozoa in the Danian Stage (Paleocene) of southern Scandinavia. Smiths. Contr. Paleobiol., 6, 87 pp.
- Clayton, R. N., Jones, B. F. and Berner, R. A. 1968: Isotope studies of dolomite formation under sedimentary conditions. Geochim. et Cosmochim. Acta, 32, 415–432.
- Degens, E. T. and Epstein, S. 1964: Oxygen and carbon isotope ratios in coexisting calcites and dolomites from recent and ancient sediments. *Geochim. et Cosmochim. Acta*, 28, 23-44.
- Evamy, B. D. 1967: Dedolomitization and the development of rhombohedral pores in limestones. *Journ. Sed. Petrology*, 37, 1204–1215.
- Floris, S. 1979: Guide to Fakse Limestone Quarry. In Birkelund, T. and Bromley, R. G., (eds.), Cretaceous-Tertiary Boundary Events. I. The Maastrichtian and Danian of Denmark, University of Copenhagen, 1979, 152-163.
- Floris, S. 1980: The coral banks of the Danian of Denmark. Acta Palaeontologica Polonica, 25, 531-540.
- Folk, R. L. and Land, L. S. 1975: Mg/Ca ratio and salinity: Two controls over crystallization of dolomite. Am. Assoc. Petroleum Geologists Bull. 59, 60-68.
- Frank, J. R. 1981: Dedolomitization in the Taum Sauk Limestone (Upper Cambrian), Southeast Missouri. Journ. Sed. Petrology, 51, 7–18.
- Goldsmith, J. R. and Heard, H. C. 1961: Lattice constants of the calcium-magnesium carbonates. Am. Mineralogist, 46, 453–457.
- Gregg, J. M. and Sibley, D. F. 1984: Epigenetic dolomitization and the origin fo xenotopic dolomite texture. *Journ. Sed. Petrology*, 54, 908–931.
- Groot, K. de 1967: Experimental dedolomitization. Journ. Sed. Petrology, 37, 1216–1220.
- Håkansson, E. and Thomsen, E. 1979: Distribution and types of bryozoan communities at the boundary in Denmark. In Birkelund, T. and Bromley, R. G., (eds.), Cretaceous-Tertiary Boundary Events. I. The Maastrichtian and Danian of Denmark, University of Copenhagen, 1979, 78–91.
- Jørgensen, N. O. 1975: Mg/Sr distribution and diagenesis of Maastrichtian white chalk and Danian bryozoan limestone from Jylland, Denmark. Bull. geol. Soc. Denmark, 24, 299-325.
- Jørgensen, N. O. 1981: Mg and Sr distribution in carbonate rocks from the Maastrichtian/Danian boundary of the Danish Subbasin and the North Sea Central Graben. Sedimentary Geology, 30, 311-325.
- Katz, A. 1968: Calcian dolomites and dedolomitization. Nature, 217, 439–440.
- Land, L. S. 1980: The isotopic and trace element geochemistry of dolomite: the state of the art. *In* Zenger, D. H., Dunham, J. B., and Ethington, R. L., (eds.), Concepts and Models of dolomitization. *Soc. Econ. Paleontologists Min*eralogists Spec. Publication No 28, 87-110.
- Lippman, F. 1973: Sedimentary carbonate minerals. Berlin, Heidelberg, New York, Springer-Verlag, 229 pp.
- Mattes, B. W. and Mountjoy, E. W. 1980: Burial dolomitization of the Upper Devonian Miette Buildup, Jasper National Park, Alberta. In Zenger, D. H., Dunham, J. B. and Ethington, R. L. (eds.), Concepts and models of dolomitization: Soc. Econ. Paleontologists Mineralogists Spec. Publication No 28, 259-297.

- Nissenbaum, A., Presley, B. J. and Kaplan, I. R. 1972: Early diagenesis in a reducing fjord, Saanich Inlet, British Columbia – I. Chemical and isotopic changes in major components of interstial water. *Geochim. et Cosmochim. Acta*, 36, 1007–1027.
- Perch-Nielsen, K. 1979: Calcareous nannofossil zonation at the Cretaceous/Tertiary boundary in Denmark. In Birkelund, T. and Bromley, R. G., (eds.), Cretaceous-Tertiary Boundary Events. I. The Maastrichtian and Danian of Denmark, University of Copenhagen, 1979, p. 115–135.
- Pingitore, N. E. 1982: The role of diffusion during carbonate diagenesis. Journal of Sedimentary Petrology, 52, 27-39.
- Pisciotto, K. A. 1981: Review of secondary carbonates in the Monterey Formation, California. *In* Garrison, R. E., Douglas, R. G., Pisciotto, K. A., Isaacs, C. M. and Ingle, J. C., (eds.), The Monterey Formation and related siliceous rocks of california. *Soc. Econ. Paleontologists Mineralogists Pacific Section Spec. Publication*, 15, 273–283.

Pisciotto, K. A. and Mahoney, J. J. 1981: Isotopic survey of

diagenetic carbonates, DSDP Leg 63. In Yeats, R. S., Haq, B. U. et al. Initial Reports of the Deep Sea Drilling Project, 63, 595-609. Washington, U.S. Government Printing Office.

- Rosenkrantz, A. 1938: Bemærkninger om det østsjællandske Daniens Stratigrafi og Tektonik. Meddr dansk geol. Foren. 9, 199-212.
- Rosenkrantz, A. and Rasmussen, H. W. 1960: South-eastern Sjælland and Møn, Denmark. Guide to excursions nos A42 and C37. Int. geol. Congr. 21, 17 pp.
- Sharma, T. and Clayton, R. N. 1965: Measurement of O<sup>18</sup>/O<sup>16</sup> ratios of total oxygen of carbonates. *Geochim. Cosmochim. Acta*, 29, 1347–1353.
- Veizer, J., Lemieux, J., Jones, B., Gibling, M. R. and Savelle, J. 1978: Paleosalinity and dolomitization of Lower Paleozoic carbonate sequence, Somerset and Prince of Wales Island, Arctic Canada. *Canadian Jour. Earth Sci.*, 15, 1448-1461.