Late Permian carbonate concretions in the marine siliciclastic sediments of the Ravnefjeld Formation, East Greenland

Jesper Kresten Nielsen and Nils-Martin Hanken

This investigation of carbonate concretions from the Late Permian Ravnefjeld Formation in East Greenland forms part of the multi-disciplinary research project *Resources of the sedimentary basins of North and East Greenland* (*TUPOLAR*; Stemmerik *et al.* 1996, 1999). The *TUPOLAR* project focuses on investigations and evaluation of potential hydrocarbon and mineral resources of the Upper Permian – Mesozoic sedimentary basins. In this context, the Upper Permian Ravnefjeld Formation occupies a pivotal position because it contains local mineralisations and has source rock potential for hydrocarbons adjacent to potential carbonate reservoir rocks of the partly time-equivalent Wegener Halvø Formation (Harpøth *et al.* 1986; Surlyk *et al.* 1986; Stemmerik *et al.* 1998; Pedersen & Stendal 2000). A better understanding of the sedimentary facies and diagenesis of the Ravnefjeld Formation is therefore crucial for an evaluation of the economic potential of East Greenland.

The original field work was carried out in 1998, when sampling was undertaken of representative carbonate concretions and surrounding beds from a limited number of well-exposed sections in the Ravnefjeld Formation. The sampled material was subsequently investigated by a combination of petrography and stable isotope chemistry to decipher the relationships between the diagenetic development of the carbonate concretions and the mineralisation in the sequence. The sequential precipitation of the cement generations was analysed in cement-filled primary voids in gastropods because these showed the most complete development of the different cement generations. The geochemistry of stable isotopes ($\delta^{13}C$, $\delta^{18}O$ and $\delta^{34}S$) was also studied (Nielsen 2001). During the petrographic work, we became aware of a hitherto unrecognised biota dominated by calcispheres. The well-developed cement generations in primary cavities in skeletal material were used to elucidate the diagenesis.

Geology and carbonate concretions

The East Greenland Basin was formed through a combination of Late Carboniferous rifting and Early Permian subsidence related to thermal contraction of the crust (Surlyk *et al.* 1986). A major transgression in the Upper Permian brought a change from continental to marginal marine deposition characterised by the formation of fluvio-marine conglomerates, hypersaline algae-laminated carbonates and evaporites. After a new regressive phase with the development of karstified palaeosurfaces (Surlyk *et al.* 1984, 1986), a eustatic sea-level rise led to the establishment of marine conditions under which the muddy sediments of the Ravnefjeld Formation were deposited in a partially restricted basin with euxinic (super-anoxic) bottom water (Fig. 1; Piasecki & Stemmerik 1991; Nielsen 2001). Contemporaneously, the open marine carbonate platforms and bryozoan buildups of the Wegener Halvø Formation were formed along the basin margins and on submarine structural highs, leading to a partially closed basin which was at least 400 km long and 80 km wide (Surlyk *et al.* 1986).

In the Kap Stosch area (Fig. 1), the Ravnefjeld Formation comprises calcareous and micaceous shales and bioturbated siltstones subdivided into two laminated (L1 and L2) and three bioturbated (B1, B2 and B3) intervals (Figs 2, 3). This subdivision is similar to that described elsewhere in the basin (Piasecki 1990; Piasecki & Stemmerik 1991). The thickness of the laminated intervals, including the intercalated bioturbated interval (B2), is remarkably uniform in the exposed parts of the basin and usually amounts to 12 to 15 m, whereas the lower and upper bioturbated intervals (B1 and B3) vary significantly in thickness due to the palaeotopography of the underlying karstified palaeosurfaces and structural elements (Piasecki & Stemmerik 1991).

Compilation and lithostratigraphic correlation of profiles along the coastline of Kap Stosch indicate a sub-basin about 25–30 km wide in an east–west direction, connected by a seaway with the southern part of the East Greenland Basin (Piasecki 1990; Piasecki & Stemmerik 1991). Deposition of the basinal, shale-dominated Ravnefjeld Formation was confined to the sub-basin centre, enclosed by partly time-equivalent carbonate buildups of the Wegener Halvø Formation to the west along the post-Devonian main fault, the Stauning Alper fault, and at the Clavering Ø high north-east of Kap Stosch (Fig. 1; Christiansen *et al.* 1993).

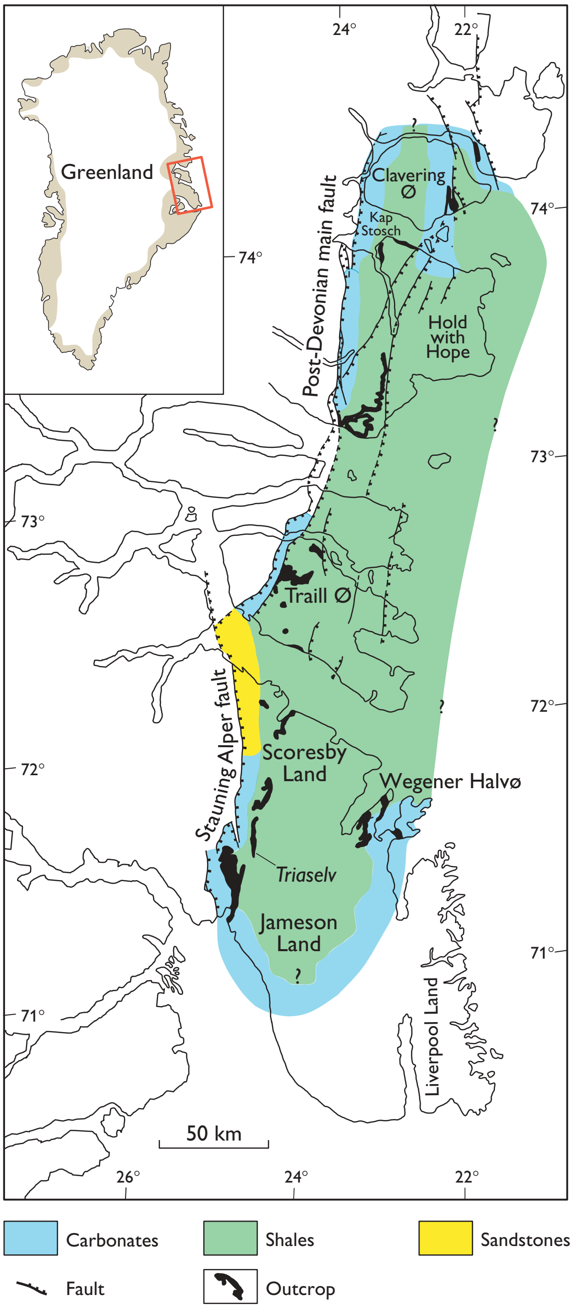

Fig. 1. Map of central East Greenland showing the distribution and extent of the Upper Permian outcrops, the shale, sandstone and carbonate facies of the East Greenland Basin and structural lineaments. Modified from Christiansen *et al.* (1993).

Carbonate concretions occur in the laminated intervals (L1 and L2) of the Ravnefjeld Formation at Kap Stosch and in the similarly developed sequence at Triaselv to the south (Fig. 1). These concretions are typically distributed in distinct horizons that are traceable throughout the outcrops in the Kap Stosch and Triaselv areas. Carbonate concretions are more frequent in the bioturbated intervals (B1 and B3) at Kap Stosch than in other parts of the basin. The concretions are

Fig. 2. The Upper Permian – Lower Triassic succession on the Kap Stosch peninsula on Hold with Hope. The Ravnefjeld Formation (*c.* 25 m shown) in the lower part of the photograph is unconformably overlain by the lowermost Triassic sediments of the Wordie Creek Formation. Dark screes are Palaeogene basalt blocks derived from about 1300 m above sea level.

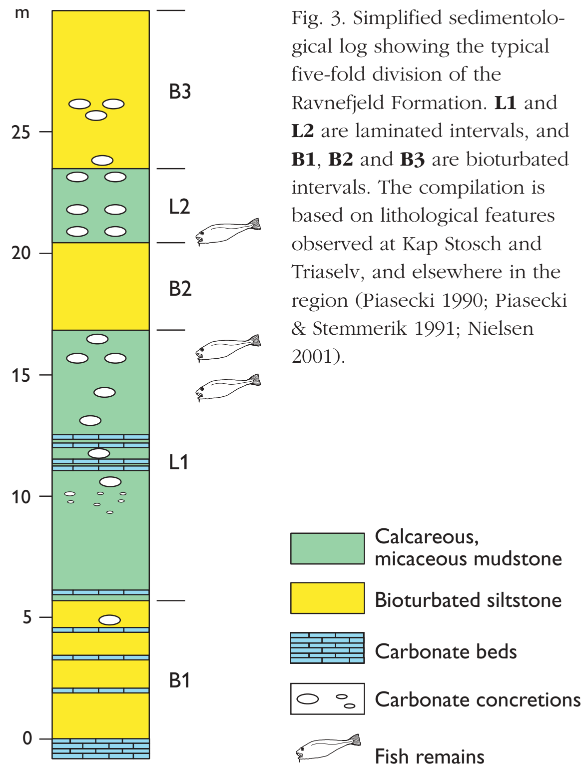

Fig. 3. Simplified sedimentological log showing the typical five-fold division of the Ravnefjeld Formation. **L1** and **L2** are laminated intervals, and **B1**, **B2** and **B3** are bioturbated intervals. The compilation is based on lithological features observed at Kap Stosch and Triaselv, and elsewhere in the region (Piasecki 1990; Piasecki & Stemmerik 1991; Nielsen 2001).

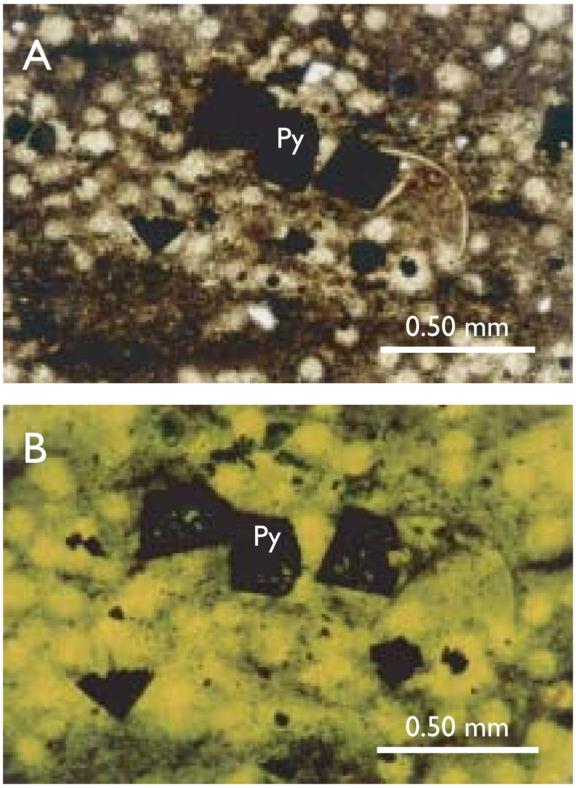

Fig. 4. Micrographs of the abundant calcispheres, partially replaced by euhedral pyrite (**Py**) as viewed in transmitted light (**A**) and ultraviolet fluorescence (**B**) (sample GGU 446352). The pyrite contains fluorescent calcite inclusions.

slightly elliptical and range from a few centimetres to more than three metres in diameter. Their long axes are parallel to the bedding, but they show no sign of parallel orientation. Although fish remains have been found both in the concretions and in the surrounding sediments since the late 1920s (e.g. Bendix-Almgreen 1993), knowledge of the nature of concretion formation was very limited prior to initiation of the present project.

The Ravnefjeld Formation comprises most of the former *Posidonia* (originally *Posidonomya*) Shale (Newell 1955; Maync 1961) considered to be of Kazanian age, which is roughly equivalent to the European Zechstein cycle 1 (Piasecki 1984; Rasmussen *et al.* 1990; Utting & Piasecki 1995); it is of latest Wuchiapingian age, based on the conodont fauna (Stemmerik *et al.* 2001).

Biological constituents of the carbonate concretions

Both pellets and trace fossils are very common in the carbonate concretions. The pellets show signs of bedding-parallel, compactional deformation, indicating loading due to overburden before cementation.

Some carbonate concretions contain a rich skeletal fauna consisting mostly of small fragments due to mechanical breakage before final deposition. No systematic investigation of the skeletal fauna has been undertaken, but some aspects that are important for the facies analysis and diagenesis of the Ravnefjeld Formation are pointed out.

Calcispheres (calcareous, hollow, spherical bodies about 75–200 microns in diameter) are very abundant in the laminated concretions from the L1 and L2 intervals (Fig. 4A, B). The origin of calcispheres has been a matter of debate, but most are believed to represent reproductive cysts of green algae belonging to the family Dasycladaceae (Wray 1977). Upper Palaeozoic calcispheres are often encountered in shallow-water deposits (especially in restricted or back-reef environments), and as such they provide a useful palaeoenvironmental indicator. This interpretation is in good agreement with Piasecki & Stemmerik (1991) and Nielsen

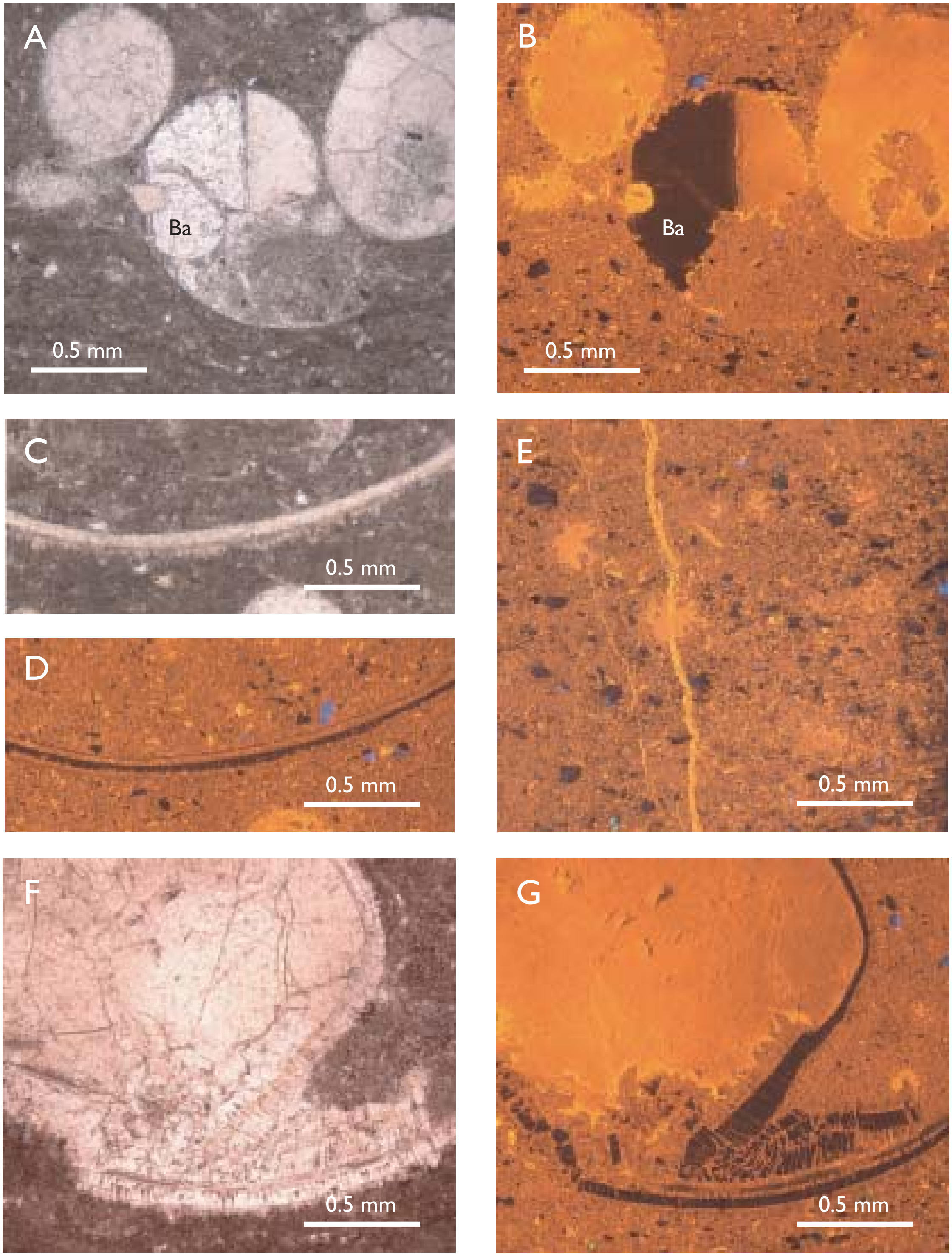

Fig. 5. Micrographs of the millimetre-sized gastropods containing authigenic calcite and baryte (**Ba**) viewed in transmitted light (**A**) and cathodoluminescence (**B**); compaction has not affected these shells. Bivalve shell in transmitted light (**C**) and cathodoluminescence view (**D**) is affected by micritisation and authigenic calcite crystals. The youngest calcite generation (**E**) is confined to veins and displays orange luminescence. Weak disintegration and displacement of the prismatic crystals of a thin-shelled fossil (**F**, **G**) followed by calcite cementation of the cavity (sample GGU 446370-2).

(2001), who pointed out the restricted nature of the basin during deposition of the sediments in the Ravnefjeld Formation.

Disarticulated bivalves of *Posidonia permica* are common in carbonate concretions from intervals L1 and L2. The bivalves have two distinct shell layers: an outer layer that has retained the original, normal prismatic microstructure, and an inner layer preserved as drusy sparite, indicating that this part of the shell was originally composed of aragonite which dissolved during early diagenesis leaving a void that was later filled with sparry calcite. The outline of the aragonitic layer has often been preserved as a dark micritic envelope (Fig. 5C, D). Such envelopes are usually produced by endolithic cyanobacteria which bore into the skeletal debris. Micritic envelopes due to endolithic cyanobacteria can be used as a depth criterion, indicating deposition within the photic zone (less than 100–200 m); this is in good agreement with the facies analysis of the Ravnefjeld Formation carried out by Christiansen *et al.* (1993).

Small gastropods occasionally occur in the carbonate concretions of the L1 and L2 intervals. Their original wall structure is preserved as drusy sparite, indicating that the shell was originally composed of aragonite that dissolved leaving a void filled with sparry calcite at a later diagenetic stage. Many specimens have a muddy geopetal fill in the lower part of the cavity, with sparry calcite filling the upper part (Fig. 5A, B).

Diagenesis of the carbonate concretions

An investigation of the cement generations in the primary cavities of gastropods has been undertaken. Since these cavities are the largest encountered in the carbonate concretions, the various cement generations are best developed here. A cathodoluminescence study of these cavities has shown a distinct pattern of zoning, representing a series of cement generations or phases of crystal growth. Each zone represents the precipitation of calcite from pore waters with different chemical compositions (Meyers 1991; Machel 2000). Four distinct calcite generations have been detected (Fig. 5B, E, G). The initial carbonate cement shows dark brown luminescence and the second generation bright yellow; both these generations are volumetrically small. The third calcite generation displays brownish luminescence and is volumetrically dominant, while the fourth and youngest calcite generation shows orange luminescence and is limited to veins cutting through all the other cement generations.

The cathodoluminescence colours in calcite cements depend upon the concentration of Mn^{2+} and/or Fe^{2+} ions (e.g. Smith & Dorobek 1993), and normally the earliest is black, precipitated from shallow oxic water, followed by yellow and brownish generations that reflect gradually more reducing conditions due to increased burial. The lack of non-luminescent carbonate cement in the concretions implies that all the carbonate cement was precipitated from reducing pore water. Prior to calcite cementation, there had also been sufficient overburden to cause incipient compaction of both pellets and thin-shelled fossils (Fig. 5F, G).

Authigenic baryte crystals are present in primary voids in some gastropods (Fig. 5A, B). Petrographic investigations show that the baryte crystals were precipitated on the yellow luminescent calcite generation, and overgrown by the brownish, indicating an early diagenetic precipitation of baryte. Baryte seems to be limited to concretions which contain a high concentration of originally aragonitic skeletal material. As shown by Turekian & Armstrong (1960) the concentration of barium in recent aragonitic gastropods and bivalves can be fairly high. If this was also the case in Upper Palaeozoic time, the early diagenetic dissolution of aragonite may have provided a local barium source for precipitation of baryte.

Both pyrite framboids and euhedral pyrite crystals are common. A combination of stable isotope analyses and a study of the size distributions of small pyrite framboids indicates that these formed within the euxinic parts of the water column while the laminated sediments were being deposited (Nielsen 2001). When they reached

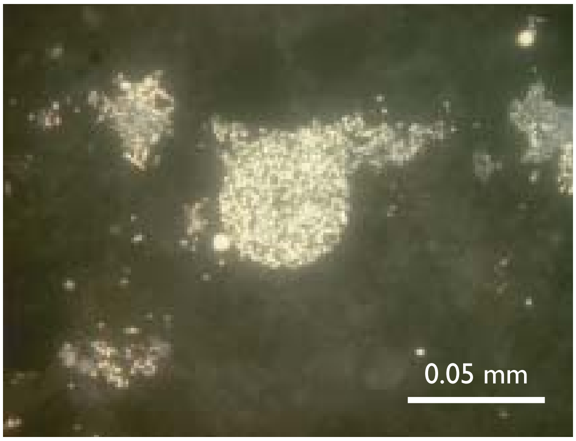

Fig. 6. Micrograph of a pyrite framboid in the bioturbated sediments (B3 interval) of the Ravnefjeld Formation (sample GGU 446358).

a maximum size of about 10 microns, they became hydrodynamically unstable and sank to the sea floor where they were incorporated in the bottom sediments (Wilkin & Barnes 1997; Cutter & Kluckholm 1999). Larger authigenic pyrite framboids are commonly found within and around burrows (Fig. 6). This association is well known from recent deposits where it results from the sharp redox transition between the burrow and the surrounding sediments arising from the decay of organic matter in the burrows during bacterial sulphate reduction (Berner & Westrich 1985). In addition to these early diagenetic pyrite framboids, later diagenetic euhedral pyrite partly replaces both the calcareous matrix and calcite cements, leaving calcareous inclusions in the euhedral pyrite (Fig. 4B; Nielsen 2001).

Chalcedonic quartz, with its characteristic bundles of thin fibres, is only known as sporadic infill in calcispheres and articulated ostracods. The silica most likely originated from the dissolution of opaline sponge spicules, which have been identified in thin sections. There is no sign of calcite cement together with chalcedonic quartz which indicates that precipitation of quartz was prior to calcite precipitation.

Rhombohedral microdolomite crystals (< 20 microns) are disseminated throughout the calcareous matrix, often associated with fecal pellets. Mesodolomite crystals (> 20 microns) occur only sparsely. As shown by Nielsen (2001), the dolomite is characterised by a depletion in ^{18}O, which indicates that the partial dolomitisation might be due to meteoric water invasion at a shallow burial depth.

Timing of the carbonate concretion formation

The investigations in the Kap Stosch area have revealed a succession of five laminated and bioturbated intervals, with several distinct horizons of carbonate concretions. The concretions studied from the bioturbated intervals B1 and B3 show well-preserved bioturbation, and this indicates that concretion formation was initiated subsequent to the infaunal activity. Compactional deformation such as deflected laminae and very thin beds at the outermost rims of the studied concretions, which are distinctive for the concretions in the L1 and L2 intervals, points to formation after some compaction. This view is also supported by the finds of slightly deformed pellets and thin-shelled fossils, which clearly indicate that some compaction of the soft, fine-grained sediment had occurred before carbonate precipitation took place.

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Authors' addresses

J.K.N., *Geological Institute, University of Copenhagen, Øster Voldgade 10, DK-1350 Copenhagen K, Denmark.* Present address: *Department of Geology, University of Tromsø, Dramsveien 201, N-9037 Tromsø, Norway*. E-mail: *jesper.kresten.nielsen@ibg.uit.no*

N.-M.H., *Department of Geology, University of Tromsø, Dramsveien 201, N-9037 Tromsø, Norway*.