Hydrothermal activity in the Upper Permian Ravnefjeld Formation of central East Greenland – a study of sulphide morphotypes

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Bituminous shales of the Ravnefjeld Formation were deposited in the subsiding East Greenland basin during the Upper Permian. The shales are exposed from Jameson Land in the south (71°N; Fig. 1) to Clavering Ø in the north (74°20′N) and have attracted considerable attention due to their high potential as hydrocarbon source rocks (Piasecki & Stemmerik 1991; Scholle *et al.* 1991; Christiansen *et al.* 1992, 1993a, b). Furthermore, enrichment of lead, zinc and copper has been known in the Ravnefjeld Formation on Wegener Halvø since 1968 (Lehnert-Thiel 1968; Fig. 1). This mineralisation was assumed to be of primary or early diagenetic origin due to similarities with the central European Kupferschiefer (Harpøth *et al.* 1986). Later studies, however, suggested base metal mineralisation in the immediately underlying carbonate reefs to be Tertiary in age (Stemmerik 1991). Due to geographical coincidence between the two types of mineralisation, a common history is a likely assumption, but a timing paradox exists. A part of the TUPOLAR project on the 'Resources of the sedimentary basins of North and East Greenland' has been dedicated to re-investigation of the mineralisation in the Ravnefjeld Formation in order to determine the genesis of the mineralisation and whether or not primary or early diagenetic base metal enrichment has taken place on Wegener Halvø, possibly in relation to an early period of hydrothermal activity. One approach to this is to study the various sulphides in the Ravnefjeld Formation; this is carried out in close co-operation with a current Ph.D. project at the University of Copenhagen, Denmark.

Diagenetically formed pyrite is a common constituent of marine shales and the study of pyrite morphotypes has previously been successful from thermalli immature parts of elucidating depositional environment and thermal effects in the Alum Shale Formation of Scandinavia (Nielsen 1996; Nielsen *et al.* 1998). The present paper describes the preliminary results of a similar study on pyrite from thermally immature parts of the Ravnefjeld Formation which, combined with the study of textures of base metal
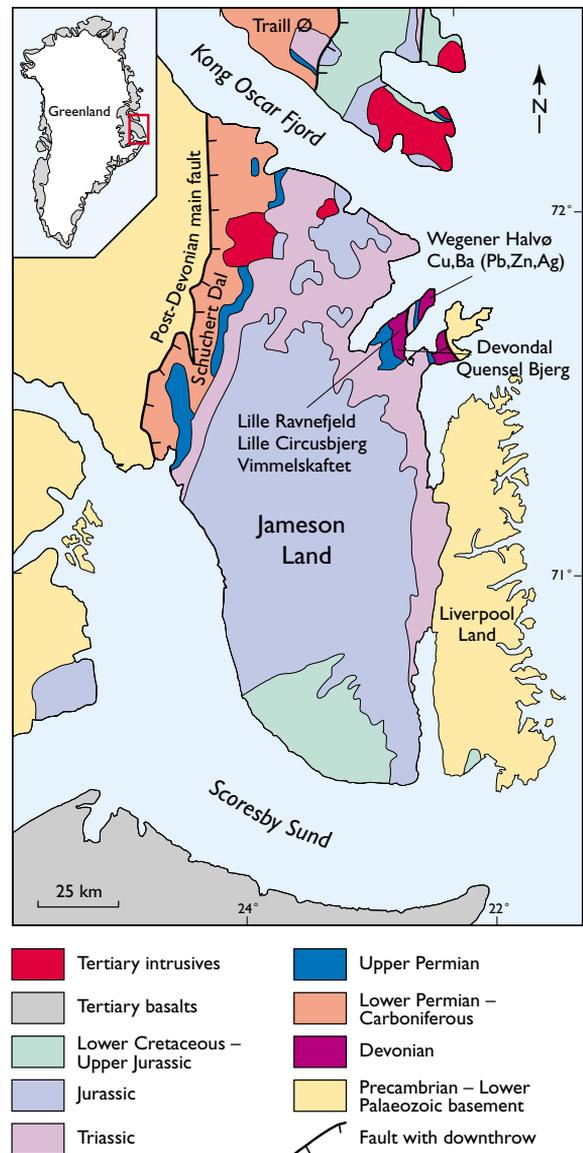
Fig. 1. Simplified geological map of the Jameson Land region in central East Greenland based on Survey maps.

sulphides in the Wegener Halvø area (Fig. 1), may provide an important step in the evaluation of the presence or absence of early thermal activity on (or below) the Upper Permian sea floor.

Geology and mineralisation

The Ravnefjeld Formation forms part of the Upper Permian Foldvik Creek Group, which marks the first marine transgression in East Greenland since the Caledonian orogeny. The bituminous shales of the Ravnefjeld Formation are time equivalent with the carbonates of the Wegener Halvø Formation that forms reef structures along the eastern margin of the basin (Surlyk *et al.* 1986); the Ravnefjeld Formation partly interfingers with and partly overlies the reef structures on Wegener Halvø. The Ravnefjeld Formation is up to 60 m thick and can generally be divided into three bioturbated and two laminated units (Piasecki & Stemmerik 1991). Along the eastern basin margin, the formation is dominated by bituminous siltstones which in inter-reef depressions are interlayered with numerous packstone and grainstone layers; more sandy lithologies are found in some areas along the western basin margin.

Mineralisation with lead, zinc and copper sulphides in the Ravnefjeld Formation is so far only known from Wegener Halvø. The base metal enrichment in this area is, however, widespread and within an area of almost 50 km² ore minerals can be found at nearly all localities (Pedersen 1997). Base metal enrichment is present only in the lowermost few metres of the shale formation, except for a locality on Lille Ravnefjeld where abundant sphalerite and galena are found over a considerable vertical section. Heavily mineralised blocks in this area were first recorded in 1979 (Thomassen & Svensson 1980). Field work in 1996 (Pedersen 1997) confined the zone of strongest mineralisation to an inter-reef basin, coinciding with a N–S trending lineament. The lineament follows the southern continuation of the valley of Vimmelskaftet and is, hence, termed the Vimmelskaftet lineament. No vertical faulting is apparent along the lineament during or after the deposition of the shales, but the coincidence of the lineament with the axis of the shale basin both on Lille Ravnefjeld, and further south on Quensel Bjerg and in Devondal, suggests that it had acted as a zone of weakness already in Upper Permian time, leading to erosion during subaerial exposure of the carbonates prior to onset of shale deposition. The lineament is obvious in the field because it is intruded along its entire length by a Tertiary dolerite dyke. The intensity of mineralisation around the lineament, both in the shales on Lille Ravnefjeld and also in the carbonate reefs at Quensel Bjerg, suggests that the lineament has been an important zone of hydrothermal activity during one or more events (Pedersen 1997).

Morphology of primary pyrite

Primary sulphides have been examined in a drill core from the Schuchert Dal area in the western part of the basin where the shales are thermally immature and no signs of secondary metal enrichment exist. Pyrite is the main sulphide phase in this area. Based on analysis of the total sulphur, a higher degree of sulphidation is found in the two thick units of laminated organic-rich, calcareous shales, whereas a lower degree is found in the three thin bioturbated units (Piasecki & Stemmerik 1991). The sulphide phase consists of finely disseminated micrometre-sized grains within amorphous kerogen and can be divided into a number of morphotypes.

Clusters (up to 30 µm)

This morphotype is a non-spherical aggregate of euhedral to subhedral microcrystals. The microcrystals are normally arranged in a disordered way (Fig. 2A).

Framboids (up to 20 µm)

Two types of framboids have been recognised. One comprises anhedral grains, probably tiny framboids, and the other type consists of euhedral to subhedral grains. The grains in the two types are mostly arranged in a concentric pattern. The outer form of the framboids is always spherical.

Facing page:
Fig. 2. Backscatter photomicrographs showing the morphotypic features of primary diagenetic pyrite. Note the small scale. **A**: The cluster shown consists of tiny dispersed microcrystals. **B** and **C**: The end-members of a gradual transition from an ordinary framboid, via semi-massive to a totally massive morphotype. **D**: Large and well-organised cubic morphotype of smaller cubes. **E**: A concretionary outline of euhedral to subhedral pyrite surrounded by carbonate and quartz. **F**: Fragment of microfossil bryozoa which has become pyritised at apertures in the skeletal structure by anhedral to subhedral and massive framboidal pyrite. **G**: Pyritisation follows the layer structure of phyllosilicates. Note also the pyritisation and non-elastic property of pre-existing silicate minerals in (B) and (C). **H**: Combined type of cluster, massive framboids and euhedral grains have a nearly spherical outline.
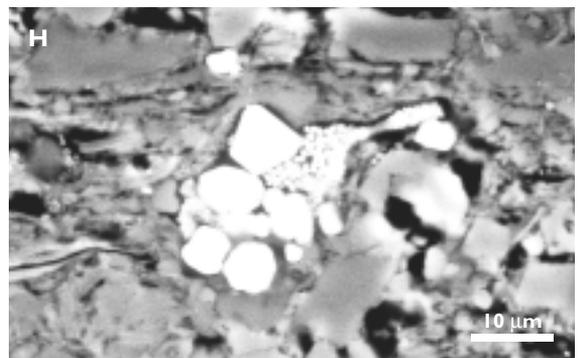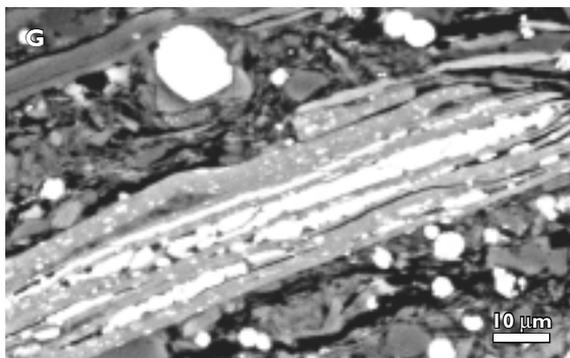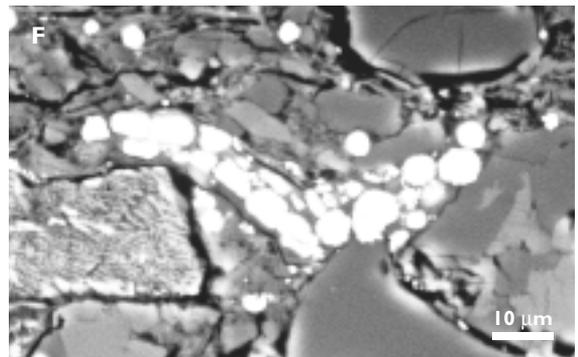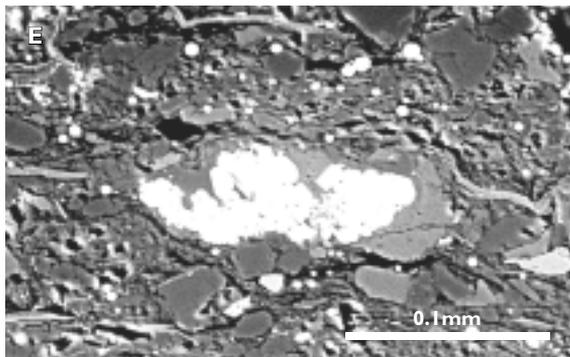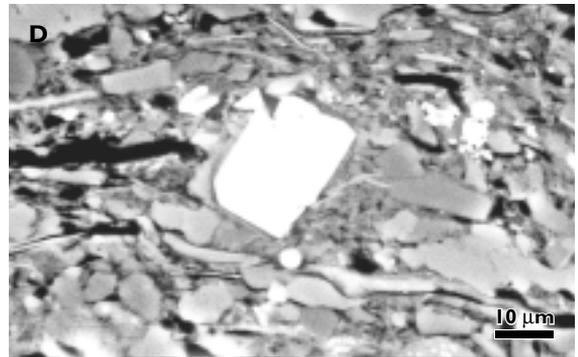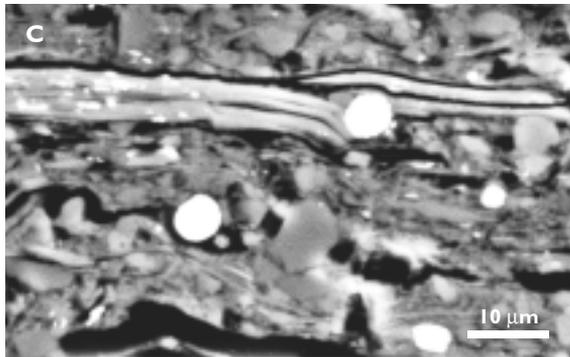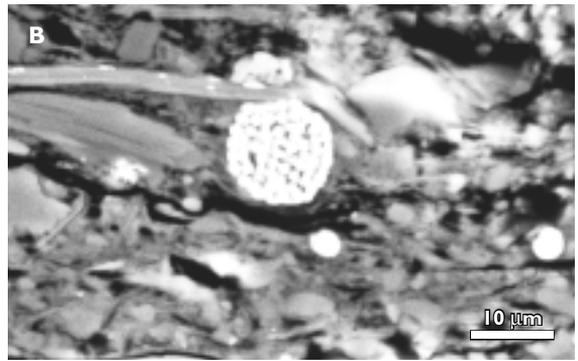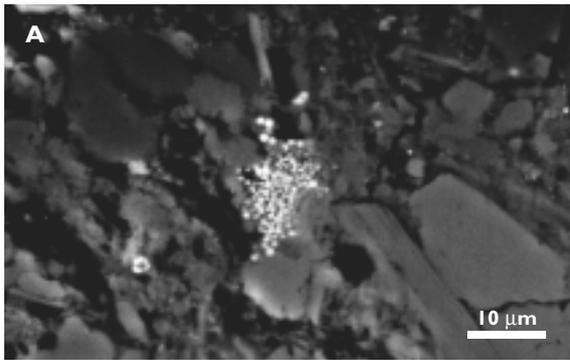
The framboids and the above mentioned clusters can be found as ordinary (Fig. 2B) and semi-massive and massive (Fig. 2C) types occasionally with some overgrowth. These morphotypes mark the gradual transition from a cluster or framboid to a more massive form and finally to euhedral form. This is in good agreement with morphotypical and genetic models by Raiswell (1982) and Sawlowicz (1993).

Euhedral to subhedral (up to 500 µm)

Morphotypes of euhedral to subhedral cubes (few to tens of micrometres) are often found as individuals, some with remnant structures after clusters and framboids in their interior. Larger cubes may comprise a more composed and complex structure of numerous smaller cubes (Fig. 2D). Euhedral forms are also found in composite aggregates with an irregular and concretionary outline surrounded by large carbonate and quartz grains (Fig. 2E).

Anhedral (up to 100 µm)

In immature shales anhedral pyrite occurs as solitary and widely dispersed grains. These grains are often rich in inclusions. In some cases anhedral grains without larger inclusions occur as pyritic fill in fossils and replacing silicates (see below).

Pyritisation of fossils (up to 200 µm)

Pyritic fill is mainly found in apertures in fragmentary bryozoans (Fig. 2F); they are probably derived from time-equivalent bryozoan mounds of the Wegener Halvø Formation. Pyritisation of trace fossils has also been recognised in the bioturbated units of the Ravnefjeld Formation.

Sulphidation of silicates (up to 200 µm)

Subhedral to anhedral forms of pyrite have been observed in Fe-Ti-rich phyllosilicates (Fig. 2G). It is likely that the sulphidation has affected the interlayer cations between the layers in the phyllosilicate structure.

Combined forms (up to 200 µm)

Relatively large spherical to non-spherical aggregates of clusters, framboids and euhedral to anhedral grains have been found in small numbers (Fig. 2H). Clusters and framboids in this case can also be ordinary to massive. Up to a few hundred grains are estimated to construct the aggregates. The overall orientation of their two length-axes is parallel to the lamination of the calcareous shales.

The presence of these pyritic morphotypes indicates a very early sulphide formation by precipitation in a low-oxygen bottom water and porewater regime in a non-consolidated substrate (Canfield & Raiswell 1991). Certain morphotypes are preferentially found in the laminated units (clusters, framboids, pyritisation of fossils and sulphidation of silicates) and others in the bioturbated units (aggregates of euhedral-subhedral morphotypes). This distribution of the morphotypes could have been controlled by the properties of the substrate and its biological reworking, which also influenced the diffusion rates and availability of iron, sulphate and metabolic organic matter for bacterial sulphate reducers (BSR). Hydrogen sulphide produced by the BSR reacted with iron through monosulphide and polysulphide to form pyrite (Raiswell 1982). Preliminary S-isotope analysis supports the suggested formation pathway.

Morphology of base metal sulphides

Base metal sulphides in the mineralised horizons on Wegener Halvø mainly occur as disseminated, anhedral to subhedral grains or aggregates, varying in size from a few hundred micrometres to several centimetres. Continuous massive sulphide layers (2–3 cm in thickness) are found in the highly mineralised zone around the Vimmelskaftet lineament on Lille Ravnefjeld. Sulphide aggregates are occasionally monomineralic, but more often polymineralic assemblages are found.

Sphalerite and galena are by far the most abundant base metal sulphides in the Ravnefjeld Formation with chalcopyrite becoming increasingly important towards the north-west on Wegener Halvø. The base metal sulphides, in contrast to most pyrite, never show framboidal forms but always replace earlier minerals, sometimes with the original grain contours preserved as 'ghosts' in the sulphide grains.

Low-Fe calcite (commonly as shell fragments of smaller fossils) is the mineral that is most often replaced, but where the calcite is silicified, sulphides can replace both calcite and quartz with no tendency to favour either phase.

High-Fe calcite is not common in the samples studied, but where present usually occurs in association with base metal sulphides. Dolomite is a relatively com-
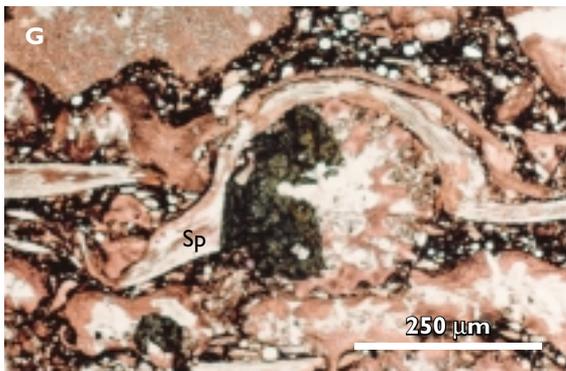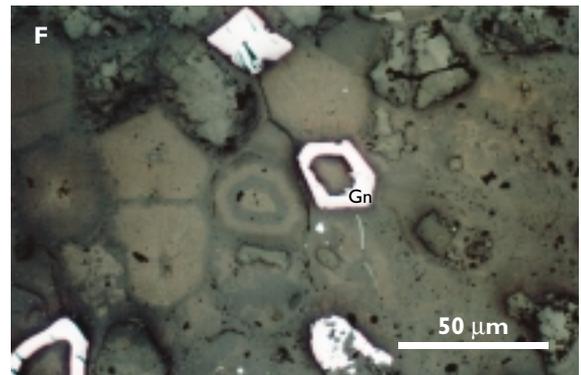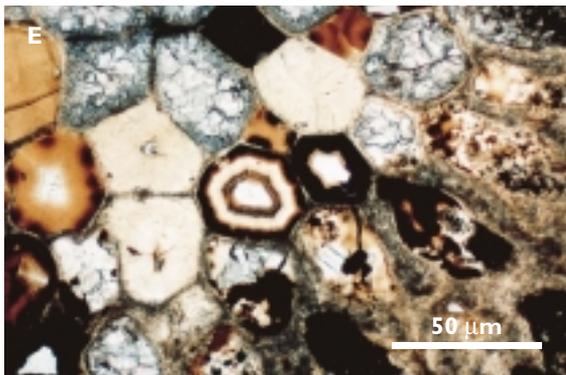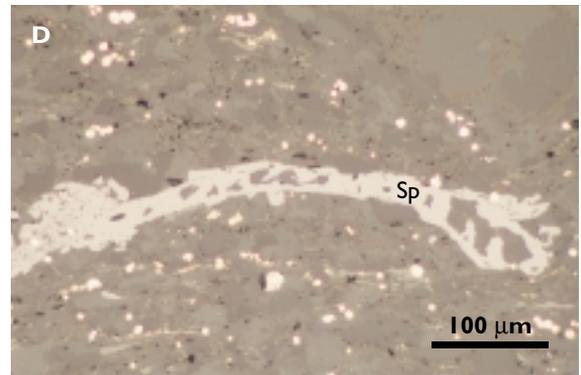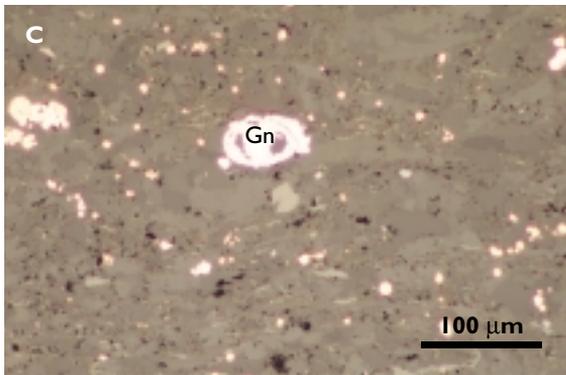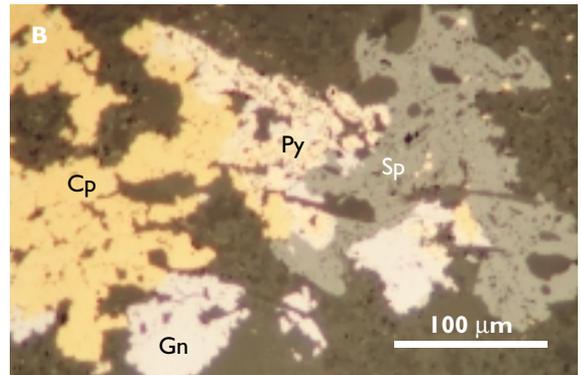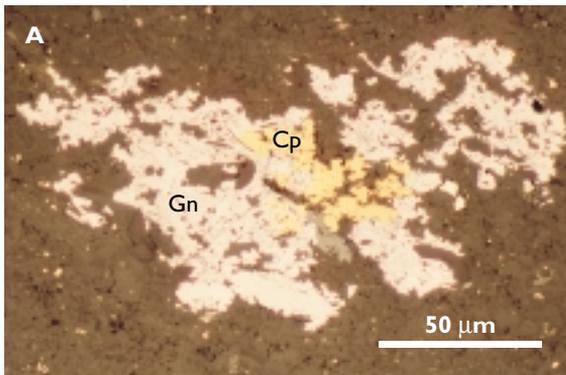
Fig. 3. **A, B**: Galena (Gn)-chalcopyrite (Cp)-sphalerite (Sp)-pyrite (Py) nodule in a concretionary shale lens from Lille Circusbjerg with (B) showing the internal relationships between the sulphide phases. **C**: Microfossil (*c*. 50 µm) replaced by galena (Gn) in almost unlithified shale. **D**: Shell fragment replaced by sphalerite (Sp) in the same sample as in (C). **E**: Different types of cavity fillings in fossil from packstone (transmitted light). Both coarse crystalline quartz and fine-grained, zoned quartz can be seen. **F**: Same as (E), but in reflected light, showing the distribution of galena (Gn) in the sample. **G**: Stained section showing post-compactional sphalerite (Sp) replacing low-Fe calcite.

mon phase in many mineralised samples, forming dispersed crystals which are obviously later than all other carbonates, although earlier than the introduction of base metal sulphides.

Base metal sulphides are always later than the diagnostic pyrite morphotypes, but have never been observed to replace them. Primary pyrite usually occurs in the organic-rich parts of the samples, whereas galena and sphalerite are concentrated in the carbonate-rich layers. In some cases, however, pyrite and base metal sulphides occur together, and sphalerite and galena can then be found to embrace framboids without imposing any effect on them. Occasionally, cubic pyrite crystals are found in zones of mineralisation. They may be either newly formed grains or derived by recrystallisation of framboidal pyrite during hydrothermal activity.

In general, four types of mineralised lithologies can be discerned (listed in order of importance):

1. Packstone layers;
2. Concretionary shale layers (cemented by calcite or quartz, or both);
3. Concretionary shale lenses (cemented by calcite);
4. Non-lithified shales.

The relative timing of mineral introduction into the sediments can be difficult to deduce. The discussion of primary or early diagenetic versus epigenetic mineralisation, however, can be eased if the sulphides can be related to a pre- or post-compactional stage. Composite nodules < 0.5 cm in size of galena, sphalerite, chalcopyrite and pyrite (Fig. 3A, B; in rare cases pure pyrite) are found finely disseminated throughout some concretionary lenses. Such shale lenses have obviously been cemented prior to compaction of the surrounding shales and can be assumed to have acted as impermeable lithologies into which post-compactional introduction of metals has been impeded. In some concretionary lenses, however, sulphides are clearly related to a few microscopic fractures (< 1 mm) from which metals can be seen to have diffused several centimetres into the surrounding rock.

In all the mineralised lithologies (except for the concretionary shale lenses), microfossils can be observed to be replaced by either galena (Fig. 3C) or sphalerite (Fig. 3D). In the mineralised packstone layers, all kinds of shell fragments, microfossils and cement can be replaced. Cavities within larger fossils may be filled with zoned quartz. The inner zone in some cavities consists of black quartz (Fig. 3E), the colour of which is assumed to stem from organic material. In these cases

base metal sulphides have clearly crystallised after the quartz precipitation and have preferentially replaced the black quartz (Fig. 3F). The exact timing of this type of mineralisation is difficult to determine, but a relatively late period of mineralisation is indicated.

Only in a few cases is there evidence of clearly post-compactional crystallisation of base metal sulphides. One example is shown in Fig. 3G where a shell fragment can be seen to have bent around another fossil during compaction of the sediment. In this case, sphalerite has overprinted the compactional structures and is obviously post-compactional. This, however, is not certain evidence for late introduction of the metals into the sediments. The sphalerite could also be the result of recrystallisation of primary zinc-minerals during a thermal event, e.g. in the Tertiary.

It must be concluded that the timing and genesis of the base metal enrichment in the Ravnefjeld Formation on Wegener Halvø is still ambiguous and that further work is needed. We consider that sulphur isotope analysis of the various sulphides, and a detailed study of textures and geochemistry of the primary pyrite in the mineralised areas compared to unmineralised areas, may provide a way to determine the possible presence of an Upper Permian thermal event in the Wegener Halvø area.

Acknowledgement

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