New evidence for a large Palaeoproterozoic impact: spherules in a dolomite layer in the Ketilidian orogen, South Greenland

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Abstract: An unconformable sedimentary succession deposited between c. 2130–1848 Ma on Archaean gneisses of the foreland of the Palaeoproterozoic Ketilidian orogen includes a layer with coarse sand-sized spherules. The layer is c. 1 m thick and consists mainly of coarse diagenetic dolomite. In addition to c. 18% spherules, the layer also contains 3% well-sorted, very fine quartzose sand and 6% larger intracherts of chert and carbonate. The spherules were previously interpreted as microfossils (Vallenia sp.) because of their spheroidal shapes and inclusions of carbonaceous matter. The spherules are reinterpreted as replaced impact ejecta because they have shapes typical of splash-form microtektites, some contain possible examples of replaced skeletal spinel crystals, perlitic cracks and devitrification spherulites, and non-spherical particles with shapes and textures of typical glassy and scoriaceous volcanic ash are absent. The carbonaceous matter is attributed to hydrocarbons that migrated into the spherule layer from elsewhere in the sedimentary succession. The spherules were reworked after deposition, probably as a result of turbidity currents or storm- or impact-induced waves. Analysis of one spherule-bearing sample revealed only 0.02 ppb iridium, a value comparable with low iridium abundances in distal layers of other terrestrial impact ejecta. The spherules in South Greenland are the first distal impact ejecta recognized in mid-Precambrian strata. They represent a major impact because their aggregate thickness exceeds the thickest spherule accumulations reported from the Cretaceous-Tertiary boundary layer. Given their loosely constrained age and the implied scale of the impact, the Ketilidian spherules could be distal ejecta from either the Vredefort, South Africa, (c. 2025 Ma) or Sudbury, Canada, (c. 1850 Ma) impacts.

Keywords: Palaeoproterozoic, South Greenland, spherules, impacts, ejecta.

The size and age of lunar impact structures and astronomical observations of asteroids and comets point to numerous large bolide impacts early in Earth history (Glikson 1999), but geological evidence for these impacts is rare and controversial. The most commonly cited evidence of early Precambrian impacts are layers rich in sand-sized spherules of former silicate melt, for example in Early Archaean volcanic rocks (Lowe & Byerly 1989; Byerly & Lowe 1994). Interpretation of these spherules as impact-related has been challenged (Koeberl 1998; Reimold et al. 2000), but is supported by petrographic contrasts with volcanic ejecta, iridium and related siderophile anomalies (Lowe et al. 1989; Kyte et al. 1992). Ni-rich spinels (Byerly & Lowe 1994) and chromium isotopes (Shukolyukov et al. 2000). Layers rich in similar spherules have also been reported from Late Archaean–Early Palaeoproterozoic sedimentary successions in Western Australia and South Africa (Simonson 1992; Simonson et al. 1999, 2000a; Hassler & Simonson 2001), likewise supported by iridium and siderophile anomalies (Simonson et al. 1998; Simonson et al. 2000b). However, no shocked minerals have been reported from any of the early Precambrian spherule layers. In this paper we present textural evidence suggesting that sand-sized spherules in a dolomite layer on the margin of the foreland of the Ketilidian orogen (Fig. 1) which were previously interpreted as microfossils (Vallenia sp., Bondesen et al. 1967) are more likely the result of a Late Palaeoproterozoic bolide impact.

Geological setting

The Ketilidian orogen was the result of oblique convergence c.1800 Ma ago (Chadwick & Garde 1996) which gave rise to the Julianeåhåb batholith and associated intra- and forearc basins (Psammite and Pelite Zones) that accreted against a foreland of Archaean gneisses in the north (Fig. 1). Adjacent to the batholith the foreland gneisses in the Ketilidian Border Zone (Fig. 1b) are unconformably overlain by Palaeoproterozoic low-grade metasedimentary rocks of the Vallen Group (Bondesen 1970; Higgins 1970). The spherules described in this paper are from a dolomite-rich layer in the upper part of the group. The Vallen Group is tectonically overlain by the Sortis Group of metabasalts, subvolcanic metagabbros and turbidites (Bondesen 1970; Higgins 1970) which were thrust from the NNE during Ketilidian deformation (Garde et al. 1998). The unconformity and primary depositional and volcanic structures are well preserved in Midternæs and Grænseland (Fig. 1c), but masked or obliterated further south by more intense Ketilidian deformation and higher grade metamorphism.

According to Bondesen et al. (1967), a spherule-bearing dolomite layer crops out at two localities in Grænseland and one in NE Midternæs ‘at the same stratigraphic position in the sequence at each of the three localities’ (see also Bondesen et al., table 2). Lam & Raunsgaard Pedersen (1968) reported one more locality of the spherule-bearing layer between the two original outcrops in Grænseland. They confirmed that the spherules occur in the same stratigraphic position in the
sequence in Grønland and Midtøerne, and Bondesen (1970) remarked that ‘it is thus possible to establish “biostratigraphic” correlations of the upper Grønness Formation over a considerable area’. The Midtøerne locality is c. 26 km from the furthest site in Grønland (Fig. 1c). Bondesen et al. (1967) noted that at each locality the spherules are limited to a thickness of c. 1 m. They have comparable shapes, sizes and abundances. In NE Midtøerne, the spherules appear to be restricted to a thickness of c. 1 m in a dolomite which is part of a mixed succession c. 30 m thick of dolomites and purple shales that include black and grey cherts: the layer of spherules is c. 1 m thick in the Grønness Formation in Grønland. Lam & Raunsgaard Pedersen (1968) reported that the Grønness Formation ‘has many other dolomitic layers, but in spite of exhaustive searching Vallenia has only been found in this uppermost dolomite layer’. Bondesen et al. (1967) described Vallenia sp. as globular structures about 0.5 mm in diameter. Individual Vallenia sp. are separated usually by a few millimetres, but are not normally in contact (Lam & Raunsgaard Pedersen 1968). Dark material forming a thin skin or outer spherical layer c. 3–5 µm thick, an inner layer 30–120 µm thick, and black-brown or opaque cores with irregular limits was reported by Bondesen et al. (1967) as carbonaceous with δ13C values within the range for carbon produced by photosynthesis. Bondesen et al. (1967) drew attention to a cellular structure with irregular radiating narrow sectors divided by transverse walls or thickenings in the outer parts of some of the dark cores. They noted that carbonate grains in the dolomite groundmass extend across the outer layers or into the cores, rows of quartz grains occur just inside some of the outer spherical layers, and common cracks in the cores of the type specimens are filled with carbonate and quartz. Locally abundant grains of quartz (possibly clastic), scattered laths of colourless mica, grains of plagioclase (albite) and rounded crystals of zircon were also noted in the rock matrix of granoblastic dolomite with subordinate calcite.

Bondesen and his co-workers acknowledged that the phylogenetic affinity of Vallenia sp. was uncertain because it has no counterpart in any fossil or living group, but they were persuaded of its organic affinity by the carbon isotope composition which is close to that of freshwater green algae, though lighter than that of modern marine algae. On the grounds of carbon compounds in whole rock analyses, they suggested that Vallenia sp. may be a plant. They believed that spherule distribution and lack of contacts may have been due to a planktonic mode of life. Additional analyses of carbon compounds in whole rock samples containing Vallenia sp. in NE Midtøerne and Grønland by Lam & Raunsgaard Pedersen (1968) were used to strengthen the view that the spherules were organic.

Bondesen et al. (1967) also reported small ‘spore-like’ spherules <20 µm in diameter in quartzites lower in the Vallen Group and in a ‘coal layer’ low in the Sortis Group.
in Grønland. On the basis of its carbon compounds, Raunsgaard Pedersen & Lam (1968, 1970) concluded that the ‘coal layer’ was the result of a large-scale accumulation of organic material 1800–2000 Ma ago. Lam & Raunsgaard Pedersen (1972) also extracted organic carbon compounds from a dolomitic shale in the Vallen Group and a graphitic dolomite in the Rendesten Formation of the Sortis Group in Grønland.

Irregular concentrations of carbonaceous material, some with cellular or filamentous structures, found not only with Vallenia sp. but also in cherty quartzites elsewhere in the Vallen Group were interpreted as parts of unspecified, but larger, organic entities (Bondesen et al. 1967). Bondesen and his colleagues also reported loose blocks with stromatolitic structures near the localities of Vallenia sp. and coarse spherical structures c. 1 cm in diameter of unknown origin in loose blocks of a disintegrated quartzite in dolomite close to the unconformity in Grønland.

**Spherules and associated sediments in NE Midternæs**

Sample GGU 71380 consists primarily of spherules, chert fragments and quartzose sand set in a groundmass of coarsely crystalline dolomitic carbonate (Fig. 2). Based on a count of 1835 points on a single large thin section, the relative abundances of these constituents are approximately 73% dolomite, 18% spherules, 6% cherty fragments, and 3% epiclastic sand (excluding veins and fracture fills). These abundances are consistent with the bulk composition of the sample as determined by XRF (Table 1). A small subsample of GGU 71380 was also analyzed in bulk for platinum group elements (Table 2).

The dolomite matrix making up the bulk of the sample is grey when fresh but pale brown on weathered surfaces. It consists of a generally equigranular mosaic of crystals 0.5–1.0 mm in size (Fig. 2). They are completely intergrown and lack detrital outlines. Cathodoluminescence revealed finely zoned euhedral cores in the middle of many of the carbonate crystals. We therefore interpret these as replacive crystals that grew during diagenesis.

The epiclastic sand is well sorted and restricted to very fine and fine sand size grades. It consists largely of monocristalline quartz and is dispersed throughout the sample in varying abundance (Fig. 2a). Most quartz grains are subangular to subrounded, with uniform or undulatory extinction and trains of minute inclusions, some of which are two-phase fluid inclusions. No shock deformation textures were seen. Many epiclastic sand grains luminesce in colours ranging from very faint to bright blue. The epiclastic sand includes a sizeable minority of feldspar grains, including microcline, based on twinning observed in polarized light, medium-bright blue luminescence of some grains, and SEM observations. Colourless mica, chlorite, Na-plagioclase and rounded grains of zircon are also found with the Grønland spherules (Bondesen et al. 1967).

The cherty fragments range in size up to c. 4 mm long, and in colour from clear to dark (presumably with organic matter). Some contain minor amounts of quartzose silt to very fine sand, either disseminated or in the form of thin laminations. This internal detritus luminesces in colours comparable to those of the epiclastic sand grains disseminated in the dolomite. Their tabular angular form (Fig. 2c) and close petrographic resemblance to cherts elsewhere in the sedimentary succession show that the chert fragments are almost certainly intraclasts derived by local scour rather than lithic detritus eroded from distant sources. Margins and interiors of many chert clasts are irregularly replaced by coarse carbonate crystals. Although they are diverse texturally, all of the chert fragments are made up of minute, randomly oriented quartz

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**Fig. 2.** Photomicrographs of typical spherules in matrix of coarsely crystalline dolomite (GGU 71380). (a) Spherules consisting of crystals (white and grey) and carbonaceous matter (black) in plane polarized light. Note botryoidal growths lined with carbonaceous matter in centre of spherule in lower right and fine quartzose sand (white) scattered throughout matrix. Arrow indicates spherule with spinel-like inclusions (shown at higher magnification in Fig. 5a). (b) A similar field of view between crossed polarizers. Spherules contain coarser, equigranular quartz crystals (black arrows), radial-fibrous aggregates (black-on-white arrows), and/or carbonaceous material (black material). (c) Several spherules and a tabular chert clast in plane polarized light. Dark spherule in lower right contains spinel-like inclusions. Note concentration of quartzose sand just above chert clast. Scale bars are 1 mm.
Table 1. Major and trace element composition of a sub-sample of GGU 71380 (see text) from the Palaeoproterozoic Ketilidian orogen, South Greenland.

<table>
<thead>
<tr>
<th>Element</th>
<th>wt%</th>
<th>ppm</th>
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<tbody>
<tr>
<td>SiO₂</td>
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<td></td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.11</td>
<td></td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>2.79</td>
<td></td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>2.98</td>
<td></td>
</tr>
<tr>
<td>MnO</td>
<td>0.06</td>
<td></td>
</tr>
<tr>
<td>MgO</td>
<td>12.5</td>
<td></td>
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<tr>
<td>CaO</td>
<td>23.3</td>
<td></td>
</tr>
<tr>
<td>Na₂O</td>
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</tr>
<tr>
<td>K₂O</td>
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<td>P₂O₅</td>
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<td>LOI</td>
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</tr>
<tr>
<td>Total</td>
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<tr>
<td>Ba</td>
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</tr>
<tr>
<td>Ce</td>
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</tr>
<tr>
<td>Co</td>
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</tr>
<tr>
<td>Cr</td>
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</tr>
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<td>Cu</td>
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<td>Mo</td>
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<td>Nb</td>
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<tr>
<td>Ni</td>
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<tr>
<td>Pb</td>
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<tr>
<td>Rb</td>
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</tr>
<tr>
<td>Zn</td>
<td>&lt;30</td>
<td></td>
</tr>
<tr>
<td>Zr</td>
<td>65</td>
<td></td>
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</tbody>
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Determined by XRF on an automated SIEMENS SRS 3000 using 10 gm of pulverized and homogenized sample material. Major and trace elements in wt% and ppm, respectively.

Table 2. PGE analysis of 20 gm from sample GGU 71380 from the Palaeoproterozoic Ketilidian orogen, South Greenland.

<table>
<thead>
<tr>
<th>Element</th>
<th>ppm</th>
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<tbody>
<tr>
<td>Ru</td>
<td>0.93</td>
</tr>
<tr>
<td>Rh</td>
<td>0.73</td>
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<tr>
<td>Pd</td>
<td>2.07</td>
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<tr>
<td>Re</td>
<td>0.02</td>
</tr>
<tr>
<td>Os</td>
<td>0.00</td>
</tr>
<tr>
<td>Ir</td>
<td>0.02</td>
</tr>
<tr>
<td>Pt</td>
<td>0.12</td>
</tr>
<tr>
<td>Au</td>
<td>0.25</td>
</tr>
</tbody>
</table>


of the non-spherical shapes appear to be products of tectonic deformation: no preferred dimensional elongation of the spherules is evident, and where they are cross-cut by fractures and veinlets, they are separated into slivers which show no internal deformation. Some spherules were affected by pressure solution at points of impingement with other silicate grains or stylolite seams, but the effects of such deformation are very local and easily identifiable.

The internal textures of the spherules are diverse, but consist of two main elements, namely, radial-fibrous aggregates of chalcedony, sericite and/or K-feldspar (Fig. 3a, b) and blocky quartz crystals c.100 µm in diameter associated with felted to locally radial-fibrous sericite (Fig. 3c, d). Crystals in the fibrous aggregates are uniformly length-slow, radiate inwards towards the centres of the spherules and meet along planar to smoothly curved contacts (Fig. 3b). The fans are tan in transmitted light, but dark material in the spherules is less common and more irregular compared with descriptions by Bondesen et al. (1967). In contrast, the blocky quartz crystals and associated sericite have no preferred orientation, except where sericite locally forms coarser radial-fibrous aggregates. Unlike the chalcedonic fans, radial sericite fabrics are not oriented inward but instead form isolated or interlocking fans or rosettes (Fig. 3d). Growth of randomly oriented blocky quartz crystals and associated sericite led to local disruption of the radiating texture of the chalcedonic fans. Relict radiating texture is preserved in the quartz grains as undulatory extinction with a radial or sector structure. Relative proportions of the two main textural components vary widely from one spherule to another. Irrespective of their internal textures, many spherules are replaced by invasive carbonate, commonly in a thin marginal zone of uneven thickness. In many cases, a dark line or selvedge that is probably organic matter is found along the contact between the invading carbonate and the silicates in the cores of the spherules (Fig. 3a). The dark selvedge was reported by Hansen (1978) to be a mixture of quartz and presumed phlogopite. He proposed that a double-layered wall forming the boundary of spherules described by Bondesen et al. (1967) was an effect of diagenetic shrinkage. Hansen (1978) also concluded that a microbanding similar to cellular structures reported by Bondesen et al. (1967) is not organic but an optical effect related to twinning in phlogopite.

In addition to the dominant textures described above, a minority of the spherules contain unusual textures relevant to their interpretation as impact ejecta. One consists of families of dark parallel lines in patterns ranging from orthogonal grids to feathery or cruciform individuals (Fig. 5). These patterns occur in c. 6% of the spherules and are strikingly similar to skeletal spinels grown from natural (Byerly & Lowe 1994, fig. 4D) and synthetic (Gayraud et al. 1996, fig. 3D) silicate melts, as well as skeletal spinels in spherules from the K–T boundary (Fig. 5d). Orthogonal networks fill the interiors of some spherules completely (Fig. 5a), whereas the networks are confined to the edges of other spherules (Fig. 5b, c). The spherules that contain these networks consist of fine-grained polygonal quartz and sericite, but we were unable to detect any X-ray signal from the dark material itself. We therefore assume the lines consist of carbonaceous matter that has replaced spinel. Less frequently, dark lines of organic matter(? in spherules largely occupied by chalcedonic fans form arcuate patterns that resemble perlitic cracks (Fig. 6a). Rarest of all are spherules with what appear to be sprays of acicular crystals radiating inwards from their margins (Fig. 6b). These sprays resemble devitrification spherulites, but again the lines are unoriented.
pseudomorphs rather than actual crystals. Among all the textures observed, we saw no candidates for replaced or infilled vesicles.

Reinterpretation of *Vallenia* sp.

*Spherules as melt droplets*

The belief that the Grønland spherules had a biological origin hinged primarily on their spheroidal shapes and the presence of carbonaceous matter with δC\(^{13}\) compatible with photosynthetic carbon. These lines of evidence are no longer persuasive in the light of subsequent advances. For example, it is now known that Palaeoproterozoic cocoidal microfossils are much smaller than the spherules: spheroidal acritarchs with diameters >1 mm only occur in Mesoproterozoic and younger strata. In their comprehensive compilation of Proterozoic microfossil occurrences, Mendelson & Schopf (1992, p. 870) therefore interpreted *Vallenia erlingi* Raunsgaard Pedersen as recrystallized ooliths or spherulites and placed them in a table of ‘micropseudofossils.’ The presence of highly elongated grains is also inconsistent with the interpretation of the spherules as organic.

Moreover, in the light of hydrocarbon migration in sedimentary successions much older than those of the Vallen Group (Gray *et al.* 1998; Dutkiewicz *et al.* 1999), the presence of carbonaceous matter in the Midternaes and Grønland spherules can no longer be used as incontrovertible evidence of a biological origin. Carbonaceous matter, including graphite, is common in black shales in the lower part of the Grønland Formation and the underlying Bláis Formation (Bondesen 1970). Specifically, Bondesen (1970) showed that the spherule-bearing dolomite layer in Grønland is interbedded with carbonaceous pelites, and locally underlain by carbonaceous black pelites of the Bláis Formation. Whereas the spherule-bearing dolomite layer in Midternaes is also interbedded with, and underlain by, shales, Higgins (1970) makes no specific reference to carbonaceous material apart from a conspicuous...
graphitic shale in the Bläis Formation and abundant carbonaceous material in a thin section of black pelitic shale in the Grønset Formation in the west of Midternaes. Carbonaceous sediments in the Bläis and Grønset Formations represent potential sources of fluid hydrocarbons that could have migrated into the spherule layer during diagenesis. Another potential source may have been microbial mats in banded iron formations within finely grained sediments, but they differ in several ways from the spherules described here. Concretions are larger, they have cross-sections that are not as uniformly circular, internally they are homogeneously finely crystalline, and they are usually encased in finer grained sediment (see for example Jackson & Raiswell 1991, fig. 10).

In contrast, the external shapes and internal textures of the Midternaes spherules are fully in accord with those of droplets of silicate melt. Both spheroidal and dumbbell shapes are typical of splash-form microtektites (Glass 1990) and droplets of magma quenched during volcanic eruption (Heiken & Wohletz 1985). Highly elongated shapes also occur in impact droplets (Fig. 4b) and are much more abundant than spheroids among volcanic droplets (Heiken & Wohletz 1985). The possible presence of skeletal spinel crystals, perlitic cracks and devitrification spherulites inside some spherules is likewise consistent with the spherules originating as silicate melt droplets. Finally, radial-fibrous aggregates are commonly found in both altered volcanic glasses (Dimroth & Lichtblau 1979) and altered impact spherules (Bohor & Glass 1995). Such aggregates can form by several mechanisms including direct crystallization in cooling glass and total dissolution and subsequent infilling of spherical voids. Cross-cutting relationships in the Midternaes spherules show that the blocky quartz and felted sericite post-date the radial-fibrous aggregates. Fibrous phases were commonly replaced by coarser, more equant crystals later in diagenesis.

**Impact melt, not volcanic**

Volcanic melt spherules are most commonly generated by lava fountaining, but it is unlikely the Midternaes spherules were generated this way. Most particles formed during fountaining of basaltic magma are highly vesicular and show extreme shape variation from true spherules to strands of Pele’s hair (Heiken & Wohletz 1985). Moreover, since these particles are deposited close to the vent, they are unlikely to form thin layers in sedimentary successions. Lava fountains which generate pyroclasts that travel farther tend to be associated with ‘highly evolved basalts and basaltic andesite magmas’ and create ‘scoriaceous ash’ (Sparks et al. 1997, p. 260) rather than glassy spherules. For example, tholeiitic spherules in a single site in a Tertiary deep-sea sediment are dispersed through 15 m of strata and associated with ubiquitous stony and glassy fragments that are irregular and vesicular (Von der Borch 1971). In contrast, the Midternaes spherules appear to be concentrated in a single layer that lacks typical pyroclastic...
detritus. Moreover, the layer apparently persists, albeit with recent erosional breaks, for >26 km, which is too far for ballistic transport of pyroclasts from a fire fountain. The lack of any typical volcaniclastic detritus in the layer is also at variance with reworking of glassy droplets that were originally part of a volcanic edifice.

In contrast, a number of layers rich in sand-size spherules of former melt have been interpreted as distal impact ejecta. These include parts of the Cretaceous–Tertiary (K–T) boundary layer (Bohor & Glass 1995; Smit 1999), three Cenozoic strewn fields of microtektites (Glass 1990), a Late Eocene layer of microkrystites (Glass et al. 1985) and microtektite-like spherules in Late Devonian strata (Claeys & Casier 1994; Claeyrs et al. 1996). As noted above, layers rich in sand-sized spherules interpreted as impact ejecta also occur in Early Archaean volcanic successions (Lowe et al. 1989; Byerly & Lowe 1994) and Late Archaean to Early Palaeoproterozoic sedimentary successions (Simonson 1992; Simonson et al. 1999, 2000a). The dominant textures inside the Midternæs spherules are unlike any reported from Cenozoic microtektites or microkrystites. They have aspects in common with some altered, pre-Cenozoic impact spherules, but few if any of these older spherules are a close textural match with the Midternæs spherules. The unusual textures inside the Midternæs spherules also have possible counterparts in impact ejecta. Skeletal spinel crystals occur in spherules from the K–T boundary layer (Kyte & Smit 1986), Late Eocene impact spherules (Pierrard et al. 1998) and spherules from the late Pliocene Eltanin impact (Margolis et al. 1991). Perlitic cracks have also been reported from tektite glass (Thein 1987), but such reports are uncommon. No vesicles were seen in the Midternæs spherules. They occur in some impact spherules, but their abundance varies widely. For example, the volatile contents of Cenozoic microtektites are low (Glass et al. 1997), but in contrast many spherules in the K–T boundary layer are highly vesicular (Smit 1999).

The absence of any obvious enrichment in iridium in the Midternæs sample does not advance the case that they are...
impact spherules, but it does not rule it out either. Glassy impact spherules such as Cenozoic microtektites (Glass 1990) and spherules in Late Devonian strata (Claeys et al. 1996) show little or no enrichment in iridium or other PGEs. The original composition of individual spherules in GGU 71380 is also uncertain because none of the primary glassy or crystalline phases have survived. However, available evidence, though scanty, suggests the spherules had a wide range of composition. On the one hand, the lack of vesicles and the presence of possible perlitic cracks suggest some were originally high-silica melts. On the other hand, the relict skeletal spinels indicate that others were low-silica mafic melts. Glassy particles from a single volcanic eruption are typically restricted to a narrow range of compositions, in contrast with the wide compositional range of spherules generated by a single impact (e.g. Glass et al. 1985). The wide compositional variation of impact glasses primarily reflects heterogeneity of target rocks. The Ketilidian foreland with its Archaean orthogneisses and interpersed tracts of metasedimentary, metabasaltic and metabasaltic rocks would have provided a very heterogeneous target area for a Palaeoproterozoic impact. However, since impact spherules typically come to rest thousands or even tens of thousands of kilometres from the point of impact (Glass et al. 1997; Smit 1999), the Ketilidian foreland itself may not have been the source for the Midternæs–Grønland spherules.

Reworking of the spherules

Persistence of the Midternæs–Grønland layer for >26 km is consistent with ballistic flight of the spherules during a large impact event. By analogy to airfall tuffs, the spherules should form a single normally graded layer had they been ballistically emplaced and not subsequently disturbed, but this is not the case. The fact that the spherules are thoroughly mixed with well-sorted epiclastic and other detritus clearly indicates reworking during and/or after deposition by waves and/or currents. The spherules and epiclastic sand form two discrete populations that are significantly different in size (Fig. 2a). The epiclastic detritus was derived from a distant continental source area, but it is unlikely that the spherules were brought from a comparably distant source since they are much larger.

The Midternæs dolomite layer lies in the midst of a succession rich in thinly laminated black shales. This setting suggests it was deposited below wave base in a relatively low-energy environment. If so, wave and current activity would have resulted only from events of unusually high energy. The presence of coarse intraclasts of carbonate and chert likewise point to abnormally vigorous substrate scour. By analogy to parts of the K–T boundary layer (Bourgeois et al. 1988; Smit et al. 1996) and Precambrian layers (Wallace et al. 1996; Simonson et al. 1999; Hassler & Simonson 2001), we suggest reworking could have been caused by impact-induced waves and/or currents, but the available data are equally consistent with reworking by non-impact sedimentary processes. For example, deposition of the spherule-rich layer may have resulted from turbidity currents or unusually large storm waves some time after the postulated impact. Further field studies are needed to pinpoint the environmental setting and depositional processes involved in forming the Midternæs spherule layer.

Conclusions

The previous interpretation of silicate spherules in a single dolomitic layer c. 1 m thick in the foreland of the Palaeoproterozoic Ketilidian orogen as microfossils is no longer tenable. In the first instance, they are too large to be Palaeoproterozoic acritarchs. Secondly, the wide variations in organic carbon abundance from one spherule to another are better explained as the result of hydrocarbon migration from carbonaceous sediments elsewhere in the succession. The splash form shapes and internal textures shown by the Midternæs spherules indicate they were originally molten. Based on the preponderance of spheroidal shapes and the absence of features typical of normal volcanic ash such as vesicles and tricuspate shapes, we interpret the spherules as distal impact ejecta rather than volcanic ash. Skeletal spinel crystals and perlitic cracks, albeit pseudomorphed, in the Midternæs spherules are similar to those reported from both impact and igneous melts. Whereas the absence of an iridium anomaly and shocked mineral grains does not further the impact interpretation, it does not negate it either, because...
some Phanerozoic layers lack clear enrichment in iridium, and none of the early Precambrian spherule layers have yielded any shocked mineral grains to date.

The original melt composition of the Midternæs spherules is uncertain because of secondary replacement, but available evidence suggests they had a wide range of basic to acid melt compositions. The Archaean basement of the Ketilidian foreland would have provided a suitably heterogeneous target area, but given the dimensions of Phanerozoic strewn fields and the global deposition of a layer of spherules 2–3 mm thick by the K–T impact (Smit 1999), the postulated impact could have taken place well beyond the Ketilidian Border Zone in South Greenland. The Midternæs spherule layer shows some similarities with Phanerozoic and Precambrian spherule layers and other ejecta that were reworked by impact-induced waves and currents, but we cannot rule out the possibility that the spherules were simply reworked by more normal sedimentary processes.

In spite of reworking, the volume of spherules in the Midternæs layer shows that they were the result of a large impact. Since the spherules make up c. 18% of the layer, which is c. 1 m thick, their estimated total thickness is c. 18 cm. This exceeds the thickest accumulations reported to date from any Phanerozoic layer of impact spherules. The thickest known are two sites where the K–T boundary layer consists largely of replaced spherules and is 6–10 cm thick (Olsson et al. 1997; Norris et al. 1999). These sites were c. 2000 and 3000 km from their source, the Chixculub structure, at the time of impact (Smit 1999). Moreover, the total thickness of spherules in the Midternæs layer exceeds all but the thickest accumulations from early Precambrian layers (Simonson & Harnik 2000).

Glikson (1999) estimated that c. 400 terrestrial impact structures with diameters of 100 km or more should have formed since 3800 Ma, yet candidates for distal impact ejecta layers are few and far between. Moreover, no candidates for distal impact ejecta layers have been reported in the almost 2 billion years between the formation of a spherule layer in Western Australia at 2490 Ma (Simonson et al. 1999) and deposition of ejecta from the Acraman structure of South Australia at 590 Ma (Wallace et al. 1996). We believe the Midternæs spherules are the first occurrence of distal impact ejecta to be recognized in this 1.9 billion year-long gap. The two largest impact structures on Earth formed during this interval, i.e. Vredefort in South Africa at c. 2025 Ma and Sudbury in Canada at c. 1850 Ma (Grieve 1998). Since both have diameters significantly larger than the Chixculub structure formed at the K–T boundary (Grieve 1998), it is highly likely that both impacts gave rise to global ejecta blankets. The age of the Midternæs–Grønland spherules is only loosely constrained to c. 2130–1848 Ma, but the possibility that they are distal ejecta from one of these impacts warrants detailed searches for similar spherules in low-grade, low-strain Palaeoproterozoic sediments in Greenland and elsewhere.

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