Palaeogene glendonites from Denmark

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Pristinely preserved mineral pseudomorphs called glendonites, up to 1.6 m long, from the Palaeogene strata of Denmark allow detailed crystallographic characterisation and add to the understanding of the transformation of the precursor mineral, ikaite ($CaCO_3{\cdot}6H_2O$), to calcite, which constitutes the glendonite. We describe Danish pseudomorphs after ikaite from two localities and formations: the Early Eocene Fur Formation and the Late Oligocene Brejning Formation. This detailed study highlights that key aspects such as morphology and mode of occurrence of these ancient glendonites are identical to those of their parent mineral ikaite, when it grows in marine sediments. Systematic distortion of the angles in glendonite and marine sedimentary ikaite relative to the ideal ikaite symmetry may arise due to the incorporation of organic matter into the crystal structure, and we demonstrate the similarity between modern and ancient ikaite formation zones in the marine sedimentary realm with respect to organic matter.

Keywords: Glendonite, ikaite, morphology, distorted symmetry, Fur Formation, Brejning Formation.

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Mineral pseudomorphs called glendonites have been described and studied from many different geological sites that span the Precambrian to Recent (e.g. Kemper 1987; De Lurio & Frakes 1999; McLachlan *et al*. 2001; Selleck *et al*. 2007; Grasby *et al*. 2017; Rogov *et al*. 2017; Wang *et al*. 2017; Vickers *et al*. 2018; Popov *et al*. 2019). These pseudomorphs were thought to be associated with cold climates, even before the precursor mineral to these pseudomorphs was identified, as they were often found in sediments associated with other cold-climate indicators (e.g. Kemper 1987). These early studies speculated that minerals such as gaylussite, glauberite, thenardite, gypsum or aragonite might have been the parent minerals, although none of the proposed precursor minerals could satisfactorily match the structure of glendonite. For example, glendonite appears to be crystallographically similar to gypsum but differs in key aspects of symmetry. The early names given to these pseudomorphs reflect their uncertain origins and often refer to the locality in which they were found, or their physical appearance, e.g. jarrowite, fundylite, gennoishi, hedgehogs, barley corns, White Sea hornlets, chrysanthemum stones (e.g. Kaplan 1979; Huggett *et al*. 2005 and references therein; Greinert & Derkachev 2004; Kemper & Schmitz 1975 and references therein; Brooks 2016).

Ikaite (calcium carbonate hexahydrate, $CaCO_3{\cdot}6H_2O$), was only proposed as the parent mineral to such pseudomorphs in 1982, long after its discovery in nature in the Ikka fjord, Greenland (Pauly 1963). This is because the ikaite in the Ikka fjord grows as tufa towers and superficially looks very different from the glendonite pseudomorphs. However, with the discovery of euhedral ikaite from the sea floor of the Bransfield

Strait, Antarctica (Suess *et al*. 1982), the similarity in morphology to glendonite was striking, and further study of the chemistry, mineralogy, and stable isotope composition of this ikaite led to the conclusion that euhedral ikaite was indeed the precursor mineral to glendonite (Suess *et al*. 1982). Since then, several papers have elaborated on the relationship between precursor ikaite and its pseudomorph glendonite, e.g. Greinert & Derkachev (2004); Huggett *et al*. (2005); Frank *et al*. (2008); Vickers *et al.* (2018). The name glendonite was first given to the stellate calcite nodules found in the Permian of Australia, in Glendon, New South Wales (Dana 1849; David *et al.* 1905), and is now used to describe all pseudomorphs after ikaite (Palache *et al.* 1951). Such pseudomorphs are commonly composed of calcite, but other minerals, such as quartz or opal (De Lurio & Frakes 1999; Wang *et al*. 2017) are known to replace ikaite in rare cases.

Ikaite is a metastable mineral that precipitates under cold conditions and specific geochemical regimes (e.g. Marland 1975; Bischoff *et al.* 1993; De Lurio & Frakes 1999). Ikaite spontaneously starts to dehydrate at temperatures above 4°C or possibly up to 15°C, a temperature that may be variable and dependent on the chemistry of the fluid in which the ikaite grew (Marland 1975; Zhou *et al.* 2015; Purgstaller *et al.* 2017; Stockmann *et al.* 2018). Since the discovery from Bransfield Strait (Suess *et al.* 1982), many euhedral ikaite crystals have been retrieved from marine sediments, but most have recrystallised rapidly once taken to the surface, preventing crystallographic studies (Bell *et al.* 2016; Zabel & Schultz 2001). The decomposition of ikaite to calcite within the sediment produces a characteristic fabric of primary sand-sized calcite grains that account for *c*. 31.4 % by volume of the original ikaite, due to the loss of crystal water (De Lurio & Frakes 1999; Larsen 1994, Vickers *et al*. 2018). This temperature dependency of ikaite fits with the observation of ancient glendonites occurring in association with other cold-climate indicators (e.g. Kemper & Schmitz 1975). However, glendonite is also found in a number of sediments where cold depositional environments cannot be assumed (e.g. Huggett *et al.* 2005; Spielhagen & Tripati 2009; Vickers *et al.* 2019; Popov *et al.* 2019), and these have remained enigmatic occurrences despite the progress made in recent years. Several papers have described the characteristic petrography of glendonite and related it to the transformation process from ikaite (Shearman & Smith 1985; Greinert & Derkachev 2004; Huggett *et al*. 2005, Vickers *et al*. 2018), yet this process is still not fully understood.

As ikaite decomposes to calcite faster than it can be examined, and as glendonite has too much variation and distortion to yield systematic measurements of the habit and growth, gypsum may give a suggestion to understanding ikaite/glendonite growth. Gypsum has the same symmetry class as ikaite, being monoclinic (2/m), and sediment-grown gypsum even resembles glendonite to some extent. In this study, we describe the glendonites from the Danish Palaeogene deposits and discuss the possible use of lenticular gypsum as a model for interpretation of glendonite, with an explanation of the apparent symmetry that for many years has baffled crystallographers. We argue that the distortion observed in marine sedimentary ikaite and ancient glendonites likely arises from the interaction with and dependence on organic matter when ikaite grows in marine sediments. The Danish Eocene outcrops viewed in context with recent observations of ikaite are consistent with mineralogical interaction with catalysing agents being responsible for the rarity of ikaite precipitation in most sediments, and their abundance at specific sites.

Glendonite 'crystals' mentioned in the following are of course pseudomorphs.

Geological setting

In Denmark, glendonites are found in Palaeogene deposits of the Fur and Brejning Formations, which are exposed in the western Limfjord area (Fig. 1). The two glendonite-bearing formations differ in age and lithology. The early Eocene Fur Formation is a *c.* 55 Ma old marine diatomite, and the late Oligocene Brejning Formation is a marine micaceous silt-clay with an estimated age of 25 Ma (Figs 2, 3).

Fur Formation

The Fur Formation is a 60 m thick marine diatomite of early Eocene age (Fig. 3). It shows an alternation between laminated and structureless, bioturbated diatomite, interpreted as due to deposition during anoxic and weakly oxic conditions (Pedersen 1981). The formation contains *c*. 200 numbered layers of volcanic ash (Bøggild 1918), which originated from the North Atlantic Igneous Province (Larsen *et al.* 2003). The Fur Formation is divided into the Knudeklint Member (ash layers -35 to -1) and the Silstrup Member (ash layers +1 to + 140) (Pedersen & Surlyk 1983; Heilmann-Clausen *et al*. 1985; Schiøler *et al*. 2007). The volcanic ash layers have yielded reliable radiometric ages. In combination with orbital forcing they have dated the PETM (Storey *et al.* 2007; Westerhold *et al.* 2009; Charles *et al.* 2011). The Fur Formation is a Konservat-Lagerstätte, containing pristinely preserved vertebrate, invertebrate and plant fossils (e.g. Bonde 1979; Rust & Andersen 1999; Collins *et al*. 2005; Waterhouse *et al.* 2008; Lindgren *et*

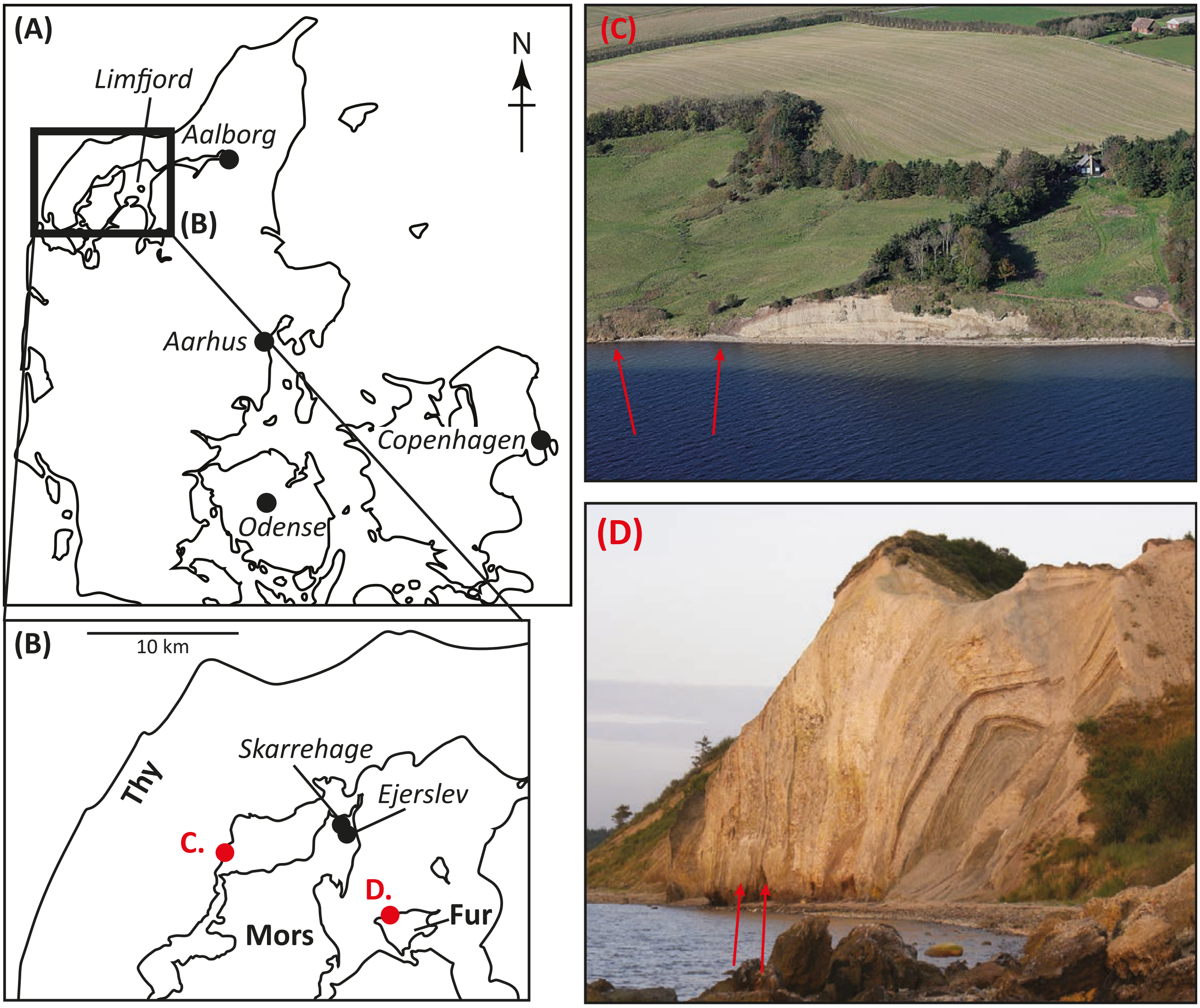

Fig. 1. Palaeogene glendonite-bearing outcrops in the Limfjord region of Denmark. **A**: Map of Denmark, with **B:** the Limfjord region in pop-out. **C:** Sea-cliff Silstrup Sydklint in Thy, at the right arrow exposing brownish Upper Oligocene Brejning Formation overlying whitish Fur Formation. At the left arrow, Skadedal with landslides of strata from higher levels of the Brejning Formation, carrying glendonites. **D:** Knudeklint on the island of Fur, with eroded sea cliff exposing the early Eocene Fur Formation. Red arrows indicate locations where glendonites are found.

al. 2012, 2014). The Fur Formation overlies the Stolle Klint Clay of the Ølst Formation and is overlain by the Røsnæs Clay Formation (Fig. 3; Schiøler *et al*. 2007). The Stolle Klint Clay was deposited during the Paleocene–Eocene Thermal Maximum (PETM) event (Schoon *et al*. 2013). The Røsnæs Clay Formation correlates to the Early Eocene Climate Optimum (EECO; Schmitz *et al*. 2004).

The glendonites in the Fur Formation are generally confined to certain stratigraphic levels that could be interpreted as palaeo-ikaite formation zones (IFZs). Zone 1 is the interval between ash layers +3 to +15, with the largest number found in the interval +9 to +15. Zone 2 starts with sporadic glendonites upwards from ash layer +48 to +50, more above this level, and the major concentration occurring just below, within and between the two distinct, 6–13 cm thick, closely spaced ash layers +60 and +62 (Fig. 3; Pedersen *et al*. 2012, fig. 33). Moreover, glendonites are more frequent at some localities than at others, and if glendonite is present in zone 1 at a locality, it is usually also present in zone 2. The major glendonite localities are on Fur at Knudeklint and on Mors at Ejerslev and Skarrehage (Fig. 1).

Brejning Formation

The late Oligocene Brejning Formation is a greenish to brown, glaucony-rich clay with scattered pebbles. In the upper part there is an increased content of organic matter, silt and sand. The formation is normally 2–4 m thick but may be more than 20 m thick. The Brejning Formation contains a marine fossil fauna consisting of invertebrates and marine mammals, along with terrestrial driftwood often broken down by teredinids. When undisturbed, the Brejning Formation is 27 m thick in the Limfjord region (*Śliwińska et al.* 2014). The formation is of late Chattian to early Aquitanian (latest Late Oligocene to earliest Early Miocene) age (Rasmussen *et al.* 2010). The Brejning Formation includes the Sydklint Member, which is a diatomite layer up to 28 cm thick, that occurs in the coastal cliff of

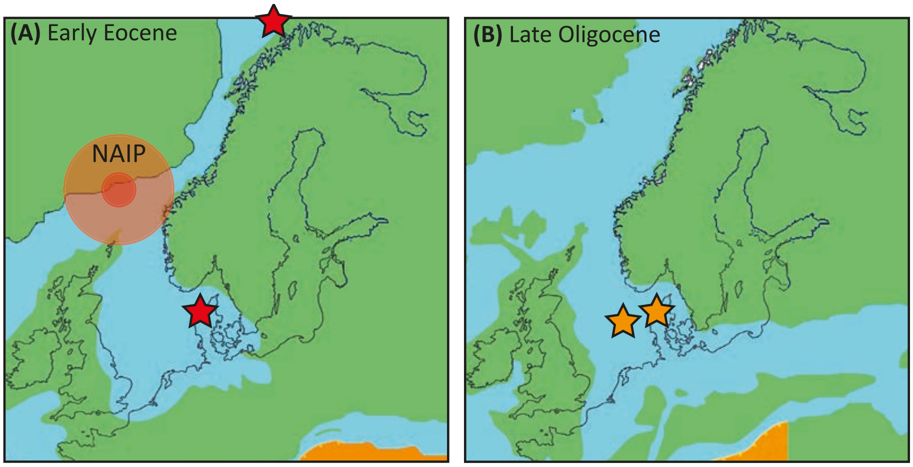

Fig. 2. Palaeogeographic reconstructions of the North Atlantic realm (Gravesen 1993), showing the context of the Limfjord region during **A**: the Early Eocene, and **B**: the Late Oligocene. NAIP = North Atlantic Igneous Province. Stars in the North Sea and north of Norway (Svalbard) indicate other glendonite occurrences mentioned in the text.

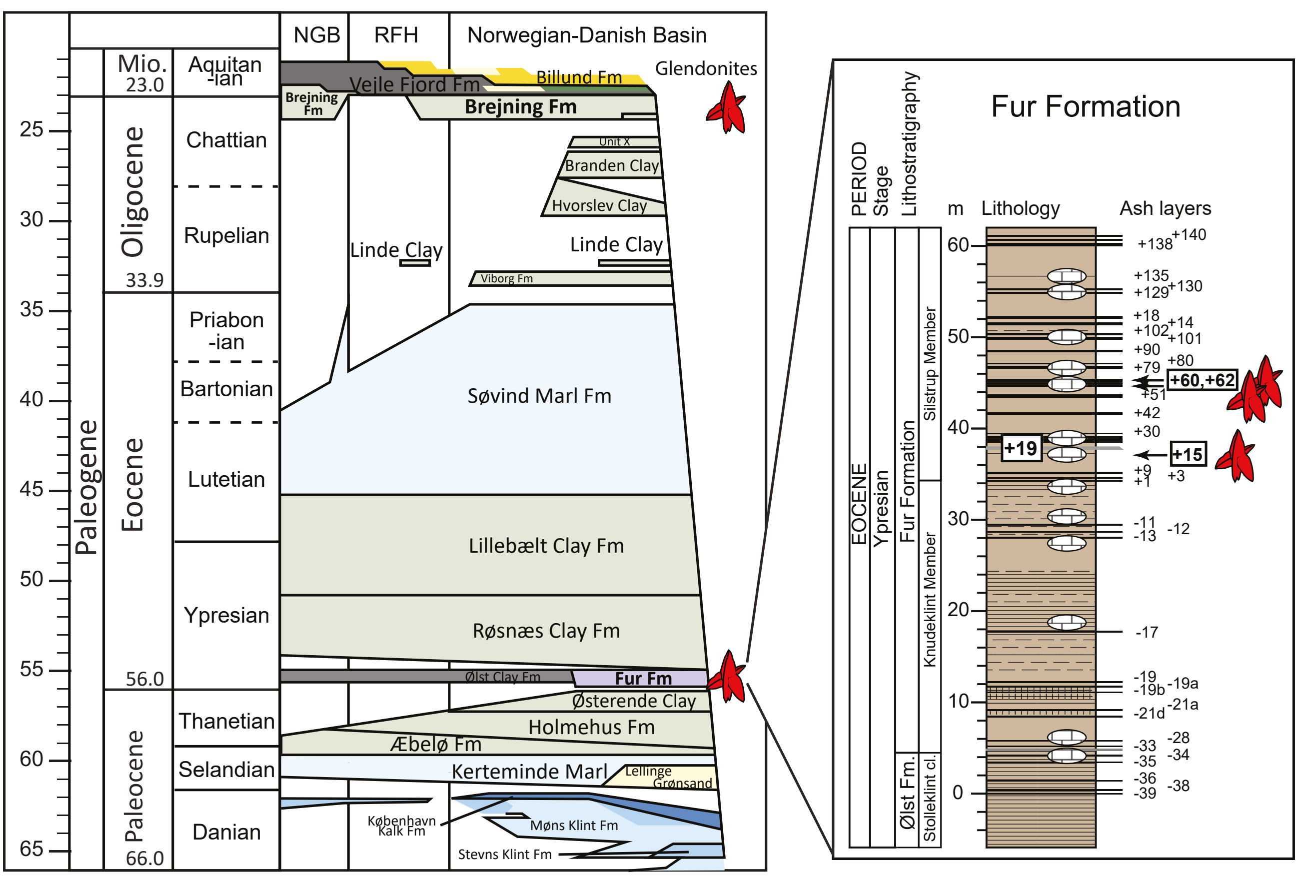

Fig. 3. Stratigraphic scheme showing the position of the Fur and Brejning Formations. The expansion shows the Fur Formation with the two glendonite horizons indicated by small crystal images. Palaeogene scheme from Sanderson *et al.* (2014); Fur Formation schematic log after Rasmussen *et al.* (2016).

Silstrup Sydklint (Heilmann-Clausen 1997; Rasmussen *et al*. 2010). About 2 m of the Brejning Formation is exposed in Silstrup Sydklint (Fig. 1). The Sydklint Member unconformably overlies the Fur Formation (Heilmann-Clausen 1997; Rasmussen *et al*. 2010,fig. 12).

No glendonites have been found in the exposed part of the Brejning Formation in Silstrup Sydklint. At Skadedal immediately south-west of Silstrup Sydklint (Fig. 1), numerous small glendonites have been collected on the beach in front of landslides of micaceous clay. In this study, the glendonite-bearing slipped strata at Skadedal are dated to the latest Oligocene, see below. They may thus be referred to the Brejning Formation, presumably a higher level than exposed in Silstrup Sydklint.

Interestingly, presumed glendonites have been found in the broadly coeval Oligocene part of the Lark Formation in a North Sea sediment drillcore (J. Hovikoski, personal communication 2019).

Sample collection

Glendonites from the Fur and Brejning Formations have been collected over 30 years by staff of Museum Mors and Museum Salling, along with private collectors, making this sample set of exceptional scientific value as it is one of the largest glendonite sample sets from a single region.

Today more than 500 specimens from the Fur Formation have been noted or retrieved. The type sample is National History Museum of Denmark number SNM DK 56 (Statens Naturhistoriske Museum, Danekræ number 56) (Fig. 4E), see Bonde *et al*. (2008). The large Eocene glendonites enable observations to be made not only of the morphology but, more importantly, features of the growth form not easily observed on very small (centimetre size) or poorly preserved pseudomorphs.

A large number of glendonites have been found over a period of 25 years on the beach at Skadedal (Fig. 1). A biostratigraphic analysis (dinoflagellate cysts) has been made of a clean sample of black micaceous clay with glendonite, taken 400 m south-west of Silstrup Sydklint. The sample includes a dinoflagellate cyst assemblage with common (10–20%) *Deflandrea phosphoritica*, fairly common *Homotryblium plectilum* and other species typical for the late Chattian *Deflandrea phosphoritica* Zone of Dybkjær & Piasecki (2010). The glendonites from Skadedal can hence be referred to the Brejning Formation. They are much smaller than glendonites from the Fur Formation. The type sample is SNM DK 873 (Fig. 4J).

Glendonites that are enclosed in younger concretions are often perfectly preserved both with regard to external morphologies and interior pseudomorphic minerals. Diagenetic pyrite often occurs at the interface between glendonite and concretion, and where the pyrite is weathered (oxidised to gypsum and iron oxides), the glendonite can relatively easily be separated mechanically from the concretion. In contrast, exposed, unprotected glendonites may be weathered so that only imprints are left.

Methods

Goniometric measurements and 3D scanning

Due to the limitation of sample size for scanning (<10 × 10 × 20 cm), traditional goniometric work was performed by casting the samples and cutting the cast into segments that could be measured mechanically with a digital protractor.

The 3D scanning was performed using an ATOS Core 80 sensor at Zebicon, Billund, Denmark. Pictures and angles were extracted by using the GOM Inspect 2017 program. The precision of the instrument exceeds the preservation of the sample detail. The 3D scans are most accurate for dull faces, so glendonites with rough surfaces yield the most reliable data.

Results

Glendonite size and morphology

The sizes of the glendonites vary from centimetre to metre scale. The largest specimen from the Fur Formation is a cluster named the Lynghøj crystal; it measures 1.65 m across and consists of 16 individual blades, with a single blade measuring 80 × 15 × 6 cm. The entire cluster is estimated to weigh over 50 kg. The average mass of the Eocene specimens is 10 kg, and the average size is 50 × 40 × 30 cm, which is the approximate size of the type specimen SNM DK 56 (Fig. 4E). In contrast, the average weight of the Oligocene specimens is 10 g, and the average diameter is 1.5 cm. Despite the difference in size, all recorded morphological groups of glendonite have been found amongst both Eocene and Oligocene specimens.

Typical glendonites throughout geological time are very distinct in morphology and growth. All individuals display an overall monoclinic affinity, regardless of location, environment or age, which implies that it must be a feature of the ikaite habit. In the Palaeogene glendonites of Denmark, all three glendonite morphologies identified by Frank *et al*. (2008), plus variants thereof, are observed (Fig 4).

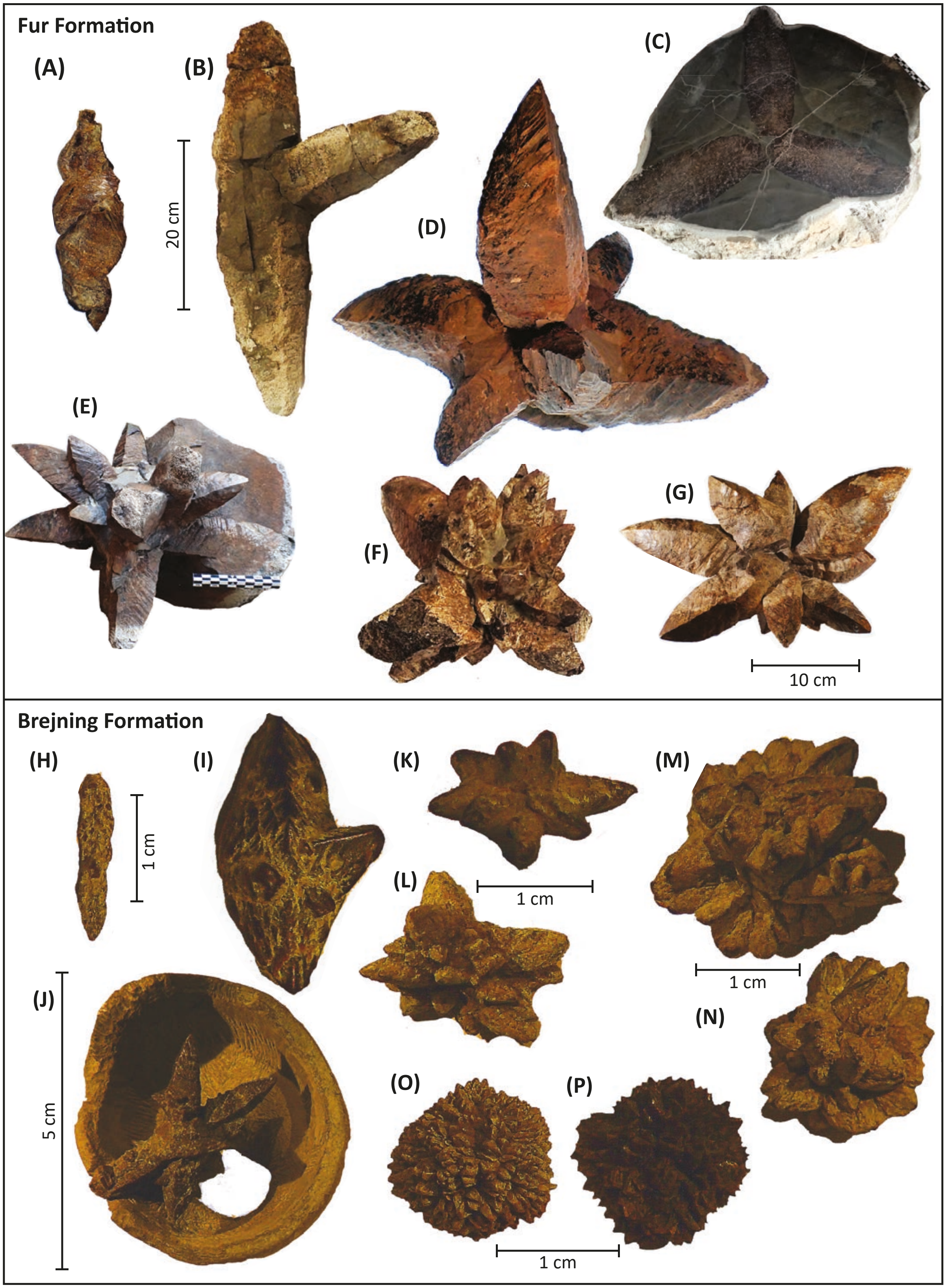

Fig. 4. Glendonites from the Fur and Brejning formations, examples of morphologies. **A**: Blade Type 2. **B**: Blade Type 1. **C**: Stellate cluster Type 1 in concretion, cut and polished, 69 cm diameter. **D**: Stellate cluster Type 1, 42 cm largest diameter, specimen SNM DK 56. **E**: Stellate cluster Type 2, partly in concretion, 37 cm diameter. **F** and **G**: Stellate cluster Type 2, both *c*. 20 cm diameter. **H**: Blade Type 2. **I**: Blade Type 1. **J**: Stellate cluster Type 1 in concretion, specimen SNM DK 873. **K** and **L**: Stellate clusters Type 2. **M** and **N**: Rosettes Type 1, with dozens of small blades in a radial pattern. **O** and **P**: Rosettes Type 2, with hundreds of small blades in a radial pattern giving a spherical appearance.

Blades: The bladed glendonites are elongate single crystals that taper at each end and have lozenge-shaped cross sections. They can vary from bodies with no distinct surface texture to a growth form very typical of glendonite in both surfaces and edges. We subdivide the blades into two types. Type 1 has an intersecting blade growing at an angle of 56° or 87° to the main one (Fig. 4B, I). Type 2 blades are long and slender with a flattened cross section, or shorter and thicker with a lozenge-shaped cross section (Fig. 4A, H).

Stellate clusters: These can also be subdivided into a Type 1 and a Type 2. Both types consist of a cluster of individual blades, with discrete blades extending from a common nucleation point. The number of blades ranges from a minimum of three up to a dozen; they may be up to 70 cm long but are usually much smaller. Type 1 stellate clusters have angles between the relatively few individual blades fixed at either 56° or 87° (Fig. 4C, E, J). Type 2 stellate clusters have more blades that cluster with random angles between them, but still with a common nucleation point (Fig. 4D, F, G, K, L). Hybrid specimens with both randomly angled blades and blades at fixed angles of 56° or 87° also occur. Both Eocene and Oligocene stellate glendonites can be subdivided into Type 1 and Type 2.

Rosettes: Rosettes are composed of more than 12 small, slender blades that have grown in a radial pattern and together constitute almost spherical bodies. Type 1 rosettes have dozens of individual blades with more clearly defined terminations than Type 2 (Fig. 4M, N). Type 2 rosettes are composed of hundreds of blades and have a rough surface due to just slightly protruding terminations of each crystal (Fig. 4O, P).

Glendonite in the Fur Formation

In the Fur Formation, stellate clusters are predominant and bladed specimens uncommon. Only a few rosettes have been found. The stellate clusters often have a nucleation point in the centre, but penetration growth clusters also occur. The latter have recognisable angles between the cluster arms, whereas the non-penetration types are aggregates of individual bodies at random angles. When split, the cluster aggregates show a hollow nucleation point from which the individual crystal ends are slightly retracted and do not touch. In penetration clusters no hollow centre is seen.

In this study, the external morphology of the best preserved specimens was investigated, particularly the type sample SNM DK 56. The examined rough surfaces of SNM DK 56 are covered by orange iron oxide and sometimes dendrites of iron oxide or manganese oxide, along with tiny millimetre-sized gypsum crystals. These features are visible to the naked eye. The 3D scans confirmed that these features are secondary, and that the roughness of the surface is not a feature of the precursor mineral. The surfaces display the growth form characteristic of glendonite, with numerous pinacoid and prism faces in competitive growth. This growth form results in characteristic triangular 'arrowhead' patterns on the surfaces as seen in Fig. 5, particularly in Fig. 5A. The glendonite itself consists of red-brown calcite with a distinct texture described by Huggett *et al*. (2005).

Glendonite in the Brejning Formation

In the Brejning Formation, the most frequent morphology is Type 1 rosettes, with lesser numbers of Type 2 rosettes. Diameters range from millimetres to centimetres, with 1.5 cm being the average size and 5 cm the maximum. The samples consist of dark red-brown calcite, some of which is encased in concretionary calcite. Some glendonites have grown inside calcium-carbonate cemented, elongated burrows, a phenomenon also observed by Greinert & Derkachev (2004) in the Sea of Okhotsk. The freely grown samples retrieved from the beach are mechanically weathered. Those in concretions do not split easily and only two have been prepared, of which the best preserved is the stellate cluster SNM DK 873 (Fig. 4J). This has therefore been selected as the 'type sample' for this site. The morphological characteristic of glendonites from the Fur Formation is also recognised on the largest specimens from the Brejning Formation.

3D scanning and crystallographic angle measurements

Glendonites in general, and the Danish glendonites in particular, are visually characterised by having an apparent mirror plane along the length of a crystal, with characteristic recognisable convex and concave faces situated in pairs on either side of the mirror plane (Fig. 5). The individual faces display a distinct growth form of repeated pinacoid and prism faces, leading to a surface pattern of growth lines resembling arrowheads, most prominent on the convex faces (Cv, Fig. 5A, B). This is most readily observed on clusters, but all single-body individuals have this feature as well, regardless of the type of morphology. The feature is not easily identified if preservation is poor or samples are small. Concave sides (Cn) have as their main characteristic a staircase-like development of repeating prism faces (Fig. 5C). Concave sides can have structures of converging arrowheads similar to those of the convex but much less distinct.

A general observation of all glendonites is that the symmetry is distorted, resulting in variations in the facial angles along the length of the crystal. Angles vary along the growth direction, and only near the terminations do measurements of different angles become more consistent between crystals. The terminations are elongated edges rather than tips (Fig. 5D), a feature most easily observed on stellate clusters. The visual symmetries are referred to as having monoclinic affinities, as they are not truly symmetrical.

Measurements during this study of the facial angles of 39 glendonites from occurrences worldwide show a considerable range (Table 1). The most obtuse angles are those between the convex and concave faces, i.e. the flattened forms are flattened parallel to the apparent mirror plane (vertical plane in Fig. 5D). Notably, the sum of the four average facial angles around the periphery (Cv1/Cv2 + Cn1/Cn2 + 2×Cv/Cn, see Fig. 5D) of the 39 crystals in Table 1 is 367°, close to the 360° of a crystal with flat faces. If this is not simply coincidence, there seems to be a statistical balance between convexity and concavity in the measured crystal population.

Table 1. Measurements of facial angles of 39 glendonites

Angle	Cv1/Cv2	Cn1/Cn2	Cv/Cn
Range	45–99°	56–97°	66–125°
Average	77°	82°	104°
1 sd	12°	10°	13°

Cv1/Cv2: The angle between the two convex faces (see Fig. 5)
Cn1/Cn2: The angle between the two concave faces
Cv/Cn: The angle between the convex and concave faces

Discussion

Understanding the elusive glendonite habit

Many crystallographers have attempted, without success, to find a mechanism by which other monoclinic minerals could be the glendonite precursor, e.g. gypsum ($CaSO_4{\cdot}2H_2O$), gaylussite ($Na_2Ca(CO_3)_2{\cdot}5H_2O$),

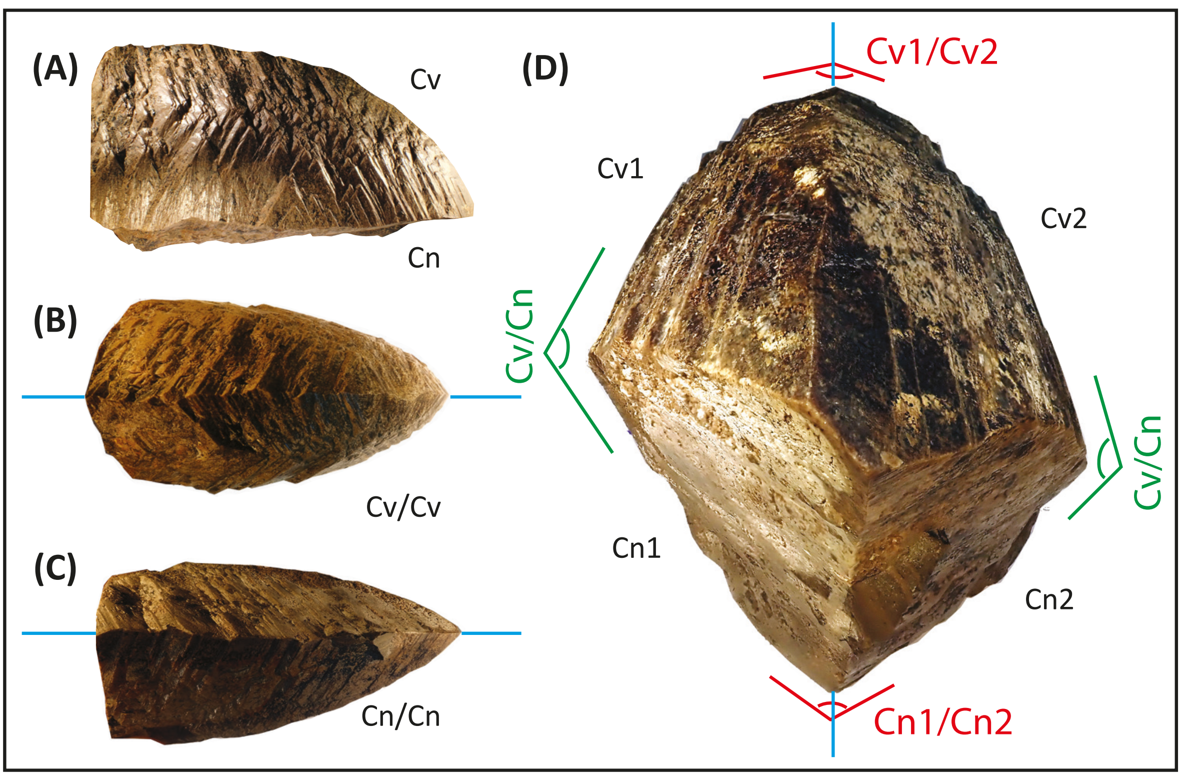

Fig. 5. Typical morphology of glendonite from the Fur Formation. Cv is the convex side and Cn is the concave side. Blue lines show the trace of the mirror plane on the paper. **A**: 'Lateral' view with the mirror plane parallel to the paper, showing both a convex side with 'arrowhead' pattern and a (barely visible) concave side. **B**: View with the mirror plane running left-to-right perpendicular to the paper, showing the two convex sides with opposing arrowhead patterns. **C**: View from the opposite side to that in B, showing the two concave sides with similar visual symmetry with a stepped pattern. **D**: Glendonite viewed from the end, with the distorted mirror plane oriented vertically towards the viewer, showing the distortion of the plane and the resulting edge at the end. The opposing faces near the end are displaced by the angle and length of the endpoint edge. Key angles measured from samples of well characterised glendonite (Table 1) are indicated.

thenardite (Na_2SO_4) and mirabilite ($Na_2SO_4·10H_2O$). Gypsum has been particularly favoured as an alternative to ikaite as the parent mineral due to the morphological similarities between gypsum and glendonite (Warren 2016). Gypsum may occur as single crystals, intergrown clusters and random clusters along with the more compact rosette form known as desert roses (Aref 1998; Rubbo *et al*. 2012). Comparison of our glendonite data with that of Rubbo *et al*. (2012) for swallowtail gypsum shows similarities in twinning and interfacial angles, but in contrast to gypsum, the glendonite displays a large variation in angles and none are direct matches for gypsum. Furthermore, the elongation of the faces of one crystallographic form is also a feature the glendonites have in common with gypsum. Viola (1897) described how gypsum can grow an elongated 001 face. Observing the same growth form in the two minerals does not prove a genetic link, yet is worth considering.

Not only is the morphology of glendonite much more similar to marine sedimentary ikaite than to gypsum, but there is also no plausible mechanism proposed for a regular replacement of gypsum by calcite in the geological record. This would need to account for the fact that the primary calcite phase observed in ancient glendonites constitutes only *c*. 1/3 of their volume (Huggett *et al.* 2005), and also for the loss of sulphur from the structure in favour of carbonate. A simple replacement of gypsum by $CaCO_3$ would normally result in a calcite spar, consisting of homogenous, randomly oriented crystallites. In comparison, the fill of glendonite crystals is multiphase (e.g. Huggett *et al.* 2005), consistent with the ikaite to calcite transition proposed by Vickers *et al.* (2018). The breakdown of ikaite to calcite produces a characteristic fabric of primary sand-sized calcite grains which account for approximately 1/3 by volume of the original ikaite, due to the loss of crystal water (de Lurio & Frakes 1999; Larsen 1994). Concurrently a thin outer crust forms to preserve the original outline of the ikaite crystal (Greinert & Derkachev 2004; Huggett *et al.* 2005; Sanchez-Pastor *et al.* 2016). A full preservation of the ikaite shape requires a diagenetic fill of the remnant porosity. This additional calcite has to have a different source to the primary calcite sourced from dissolving ikaite, because the ikaite supplies insufficient Ca^{2+} to cement the entire structure.

Although gypsum has been convincingly shown not to be the parent mineral of glendonite, gypsum may be useful as an analogue for understanding the distortion observed in marine sedimentary ikaite and in glendonite. Initial visual observations of glendonite shapes suggest that the glendonite samples display a normal monoclinic (010) mirror plane with symmetric pinacoid and prism faces. However, upon closer observation (using 3D scanning and a visual study of the crystal tip) it is evident that what appears to be a normal monoclinic mirror plane is not so (Fig. 5D). Glendonite derived from marine sedimentary ikaite shows distortion from the 'ideal' monoclinic prismatic 2/m ikaite symmetry as calculated by Lin *et al*. (2013) and as observed in non-sedimentary ikaites, i.e. from sea-ice grown ikaite or ikaite tufas (Buchardt *et al*. 1997; Dieckmann *et al*. 2008, Rysgaard 2012; Sekkal & Zaoui 2013).

Cody & Cody (1988) demonstrated a link between gypsum morphologies, temperature and organic content, and it may be a similar story for ikaite. Indeed, several studies have suggested that interaction with organic compounds causes structural distortion in ikaite/glendonite (e.g. Chave 1965; Suess 1970; Swainson & Hammond 2001; Rodríguez-Ruiz *et al.* 2014). It is possible that ikaite/glendonite morphology is controlled by more factors than is gypsum, as a single environment can contain a wider range of morphologies of ikaite/glendonite than is observed for gypsum.

Ikaite Formation zones in relation to size, morphology and organic matter

Ikaite Formation Zone (IFZ) is the term used where, in recent marine settings, ikaite occurs in distinct horizons and only seldom in the rest of the associated sediment, as at Firth of Tay (Lu *et al.* 2012), Bransfield strait (Suess *et al.* 1982) and Kara Sea (Kodina *et al.* 2003). It is therefore of interest to compare these modern IFZs to the sediment horizons in which large numbers of glendonites are found, i.e. presumed ancient IFZs. There does not appear to be a clear link between sediment type and morphology/form/type of either ancient glendonites or modern marine sedimentary ikaite, because glendonite/ikaite of different types occur in a range of sediment types (e.g., Kemper 1975; Suess *et al.* 1982; Zabel & Schultz 2001; Blais-Stevens *et al.* 2001; Kodina *et al.* 2003; Frank *et al.* 2008; Lu *et al.* 2012; Krylov *et al.* 2015; Grasby *et al.* 2017; Rogov *et al.* 2017). Recent studies suggest that direct microbial anaerobic oxidation of methane (AOM) from cold seeps provides a carbon source for ikaite (e.g. Greinert & Derkachev 2004; Morales *et al.* 2017) as well as other carbonate phases. These are characterized by extreme $\delta^{13}C$ depletion (<< -30 ‰) arising from methane. Another carbon source for marine ikaite growth is sedimentary organic matter that also undergoes oxidation via sulfate reduction. Hereby methane is produced from dissolved carbonate by methanotrophs after sulfate reduction and then oxidized via AOM, resulting in a variety of carbonate phases including ikaite. These carbonates are characterized by lesser $\delta^{13}C$ depletion (< -30 ‰) arising from sedimentary organic matter

(Suess *et al*. 1982). The sediments of the two IFZs in the Fur Formation show no obvious signs of fluid seepage; they do however show slightly more soft sediment bioturbation than non-glendonite-bearing levels, indicative of higher organic matter. To date, however, no catalyst, organic or otherwise, has been unequivocally identified as being the sole trigger for ikaite precipitation.

Conclusions

The study provides an overview of the Danish Palaeogene glendonites, illustrating the wide range of growth forms present. Careful study, utilising 3D scanning, has enabled observation and interpretation of the glendonite structure. The assumed monoclinic symmetry of the pseudomorphs is demonstrated to be distorted from the perfect monoclinic crystal structure, likely due to incorporation of organic matter (a likely catalyst for ikaite precipitation) into the original parent ikaite. Specific glendonite-bearing horizons are interpreted as ancient analogues of modern Ikaite Formation Zones, and comparison with glendonites worldwide suggests that sediment type is not a control on ikaite/glendonite habit.

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