



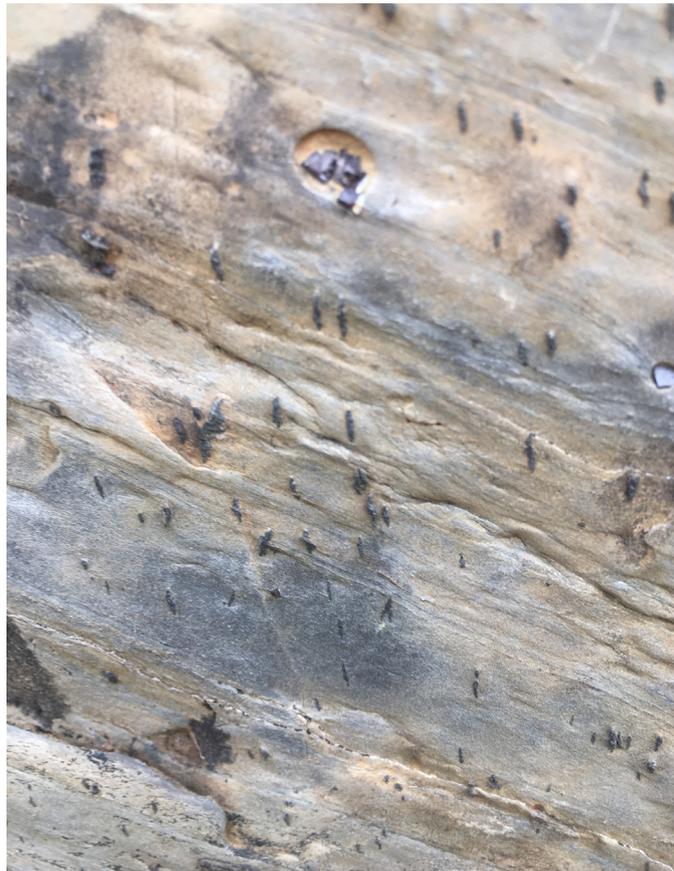
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A structural study of the occurrence of ikaite pseudomorphs in Neoproterozoic metalimestones on Islay, Scotland

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Abstract: Aligned ikaite porphyroblasts have been replaced by calcite with a maximum volume decrease of ~88% in Neoproterozoic Dalradian metalimestone exposed near Ballygrant on Islay, Scotland. Microscopic and structural analyses reveal that the ikaite minerals formed before deformation, at a time when Scotland was located at the lower latitudes, thus indicating a cold climate at the time of formation. The Ballygrant metalimestone underlies a ~900 meter thick glacial deposit that has previously been linked to the ‘Snowball Earth’ hypothesis. The discovery of these ikaite pseudomorphs below the glacial deposit points toward a relatively slow cooling of the climate near the equator reflecting a transition toward a ‘normal’ glacial period and thus refutes a suggested ‘Snowball Earth’ event, which is reported to reflect a more abrupt switch over from warm to cold climate in the sediment record.

Introduction

Large ice sheets have accumulated and retreated on the continents in the Northern Hemisphere at several occasions in the past, events we refer to as “glacial” and “interglacial” periods, respectively. During the last 11,500 years, the Northern Hemisphere has been in an interglacial period (i.e. without large ice sheets), whereas the last glacial period began ~120,000 years ago (Ncdc.noaa.gov, n.d.). It has been proposed, based on paleomagnetic evidence, that during Neoproterozoic time (1000 Ma to 542 Ma,) global ice sheets reached sea level at lower latitudes, close to the equator, and were thus much more extensive than during Quaternary glacial periods (Hoffman et al. 1998). These global glaciations have been referred to as “Snowball Earth” events and several authors have contemplated that a cluster of continents at the lower latitudes, making up a supercontinent called Rodinia, contributed to these glacial events by creating favorable conditions for rapid weathering and CO₂ drawdown to the extent that ice began to accumulate, followed by a positive feedback of the resulting increased albedo (Hoffman et al. 1998 and Hoffman and Schrag 2002).

Fairchild and Kennedy (2007) compare Neoproterozoic glacial deposits with Quaternary glacial deposits and suggest that a “Snowball Earth” glaciation would leave an abrupt change in the stratigraphic succession before and after the glacial period due to the positive albedo feedback that would accelerate the ice growth, whereas a “normal” glaciation as seen in Quaternary sediments would produce “repeated alternations of glacial and non-glacial facies” in the sediment record. This difference in stratigraphy between “Snowball Earth” glaciations and “normal” glaciations can be seen in the Marinoan glacial deposits in China and Namibia, but is absent in other Neoproterozoic formations, which results in a controversy involving the Snowball Earth theory (Fairchild and Kennedy 2007). Thus a “Slushball Earth” hypothesis has been proposed to account for the Neoproterozoic low-latitude glacial deposits (Fairchild and Kennedy 2007).

According to Hoffman and Schrag (2002), Neoproterozoic glacial deposits typically have a “close association with large (> 10‰) negative δ¹³C shifts in seawater proxies,” and

are often followed by carbonate layers, referred to as 'cap carbonates,' and large sedimentary iron formations. Hoffman and Schrag explain these features as follows:

A Snowball Event [...], should begin and end abruptly, particularly at lower latitudes. It should last for millions of years, because outgassing must amass an intense greenhouse in order to overcome the ice albedo. A largely ice-covered ocean should become anoxic and reduced iron should be widely transported in solution and precipitated as iron formation wherever oxygenic photosynthesis occurred, or upon deglaciation. The intense greenhouse ensures a transient post-glacial regime of enhanced carbonate and silicate weathering, which should drive a flux of alkalinity that could quantitatively account for the world-wide occurrence of cap carbonates. The resulting high rates of carbonate sedimentation, coupled with the kinetic isotope effect of transferring the CO₂ burden to the ocean, should drive down the δ¹³C of seawater, as is observed (2002).

The Port Askaig Tillite formation, exposed on Islay in Scotland, is of relevance to the Snowball Earth hypothesis, and consists of 'mixtites' (defined by Spencer (1971) as "unsorted and usually unstratified till-like beds") interbedded with stratified siltstone, sandstone, conglomerate, and dolomite. Several authors have agreed upon a Neoproterozoic glacial origin of the Port Askaig deposits, but have conflicting interpretations on the ice-sheet dynamics and subglacial deformation of the sediment (Fairchild and Kennedy 2007). Spencer (1971) interpret the 'mixtites' within the Port Askaig formation to have been deposited during melting of grounded ice sheets, and interbedded with shallow water sediments deposited in a shelf sea (Spencer 1985), whereas others argue for glaciomarine deposition, followed by partly reworking from tidal currents that the Port Askaig Tillite records (Tanner et al. 2013). Not only the depositional process, but also the direction of the ice movement is disputed. Spencer (1971) proposes SE-NW movement of the ice and Eyles (1988) suggests a movement in the opposite direction.

The mineral ikaite, classified as a hydrous calcium carbonate, is associated with cold climate deposits because the mineral has only been observed in its natural state in temperature conditions between -1.9°C and 7°C (Huggett et al. 2005). Ikaite was identified as a mineral in 1963 by Pauly (1963), who discovered the mineral in the Ikka Fjord in Greenland, hence the name ikaite (Huggett et al. 2005). The mineral, previously only found in experiments, has since then been discovered in a range of environments including: glacial environments; coastal waters, such as the Fjord where it was first found in nature; marine environments, such as deep-sea and continental shelf sediments; and non-marine settings, such as groundwater discharge sites in lakes (Papadimitriou et al. 2013), but requires special conditions to be met in order to form. Marland (1975) investigated the relationships between the three minerals ikaite, calcite and aragonite (where calcite and aragonite are polymorphs with the same chemical formula) in a phase diagram and concluded that ikaite can only be stable at very high pressures, whereas an invariant point between the three phases is located at ca 3kbar and 2°C (Figure 2). Thus, Sherman and Smith (1985) argued that during deposition and diagenesis of sedimentary deposits these temperature and pressure conditions cannot 'prevail,'

which results in a metastable state of ikaite in sedimentary rocks. Furthermore, due to this metastable state of the mineral at higher temperatures, Ikaite typically transforms, through dehydration processes, into calcite and water as temperature rises above $\sim 4^{\circ}\text{C}$ at atmospheric pressures (Boch et al. 2015; Brooks 2016; Fairchild et al. 2016; Oehlerich et al. 2013). Additionally, the transformation from ikaite to calcite ($\text{CaCO}_3 \cdot 6\text{H}_2\text{O} \rightleftharpoons \text{CaCO}_3 + 6\text{H}_2\text{O}$, from Marland (1972)) should, according to Sherman and Smith (1985), result in a volume decrease of 68.6% if this occurs in a closed system, i.e. no ions are lost or added. If the ikaite to calcite transformation results in a preservation of the original mineral shape, calcite would become the 'pseudomorph mineral' to ikaite (Stephenson et al. 2013) (See Figure 1 for examples of these types of pseudomorphs).

A pseudomorph is defined by Stephenson et al. (2013) as “a replacement product, usually crystalline and consisting of one or more minerals, that retains the distinctive original shape of the parent crystal.” Moreover, because aragonite is also a high pressure mineral and is unstable below 0°C , Sherman and Smith (1985) suggested that a metastable phase of ikaite would precipitate from seawater at ‘normal’ pressures and low temperatures if sodium hexametaphosphate and magnesium ions together with other inhibitors would be present and therefore favor ikaite precipitation and block calcite precipitation, respectively. Hu et al. (2014), on the other hand, report in their study that phosphate concentrations do not influence the precipitation of ikaite and argue that the controlling factor of ikaite precipitation in artificial sea ice is pH (due to its strong influence on CO_3^{2-} concentrations).

The great interest in the dynamics of the mineral is due to ikaite’s potential as a proxy for reconstructing past climates and glacial conditions, along with the salinity of oceanic deep waters (Oehlerich et al. 2013; Papadimitriou et al. 2013; Sánchez-Pastor et al. 2016). It is therefore of high interest to many geoscientists to study the pseudomorphs left behind in the sedimentary record as “fossils” of the mineral.

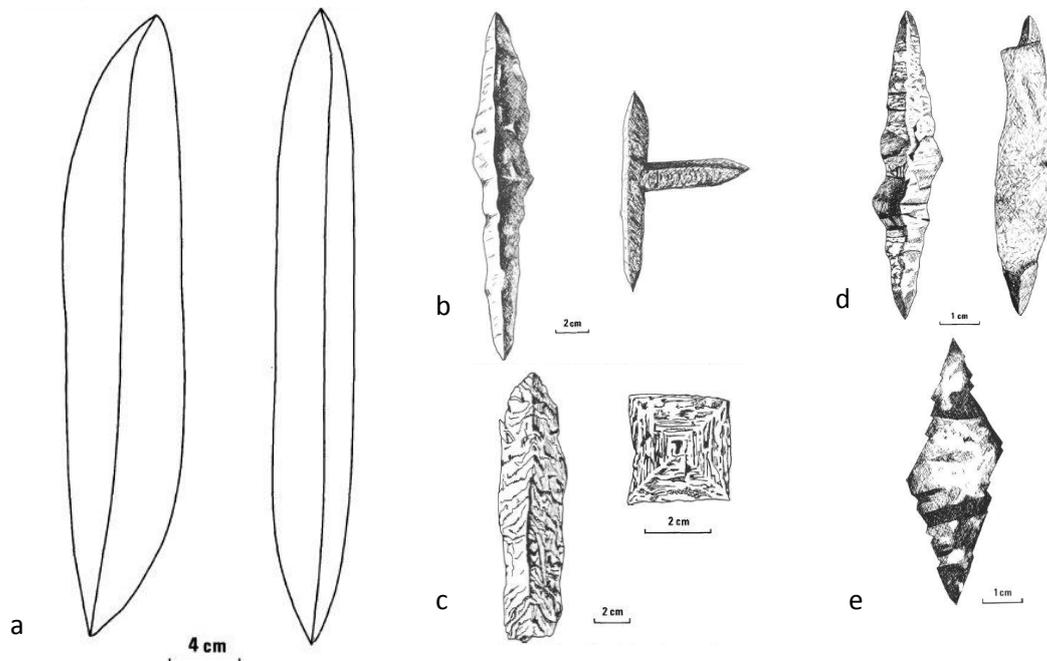


Figure 1. Drawings illustrating how ikaite-pseudomorphs can look like, from Sherman and Smith (1985). (a) “Glendonite pseudomorph from Permian of New South Wales.” (b) “Pseudomorphs from Quaternary muds near Cardross, River Clyde, Scotland.” (c) “Thinolite pseudomorphs from Quaternary tufas, Pyramid Lake Nevada. Left, vertical elevation; right, basal cross-section.” (d) “Fundylites from Quaternary tidal flat muds of the Bay of Fundy, New Brunswick, Canada. The specimen on the right is partly encased in a calcareous concretion.” (e) “Ikaite crystal from recent marine sediments of Bransfield Strait, Antarctica.”

Hugget et al. (2005) describes three types of ikaite pseudomorphs: ‘Type A’, single crystals, twins and ‘interpenetrant’ forms of pseudomorphs, which occur in tufas believed to have grown up into overlying water over bicarbonate springs. These are referred to as thinolites; ‘Type B’ pseudomorphs, defined by Hugget et al. (2005) as “hemispherical fist-sized clusters of twinned and interpenetrant crystals with flat bases” that have been discovered on bedding surfaces, indicating that the precursor mineral grew up into overlying water from the sediment-water interface, alternatively within the sediment; and ‘Type C’ pseudomorphs, which occur as double terminated “single crystals or clusters embedded in fine-grained sediments rich in organic matter,” indicating that they grew under isostatic pressure in unconsolidated sediment. Furthermore, Hugget et al. (2005) gives pseudogaylussite, fundylite and glendonite as examples of these types of pseudomorphs.

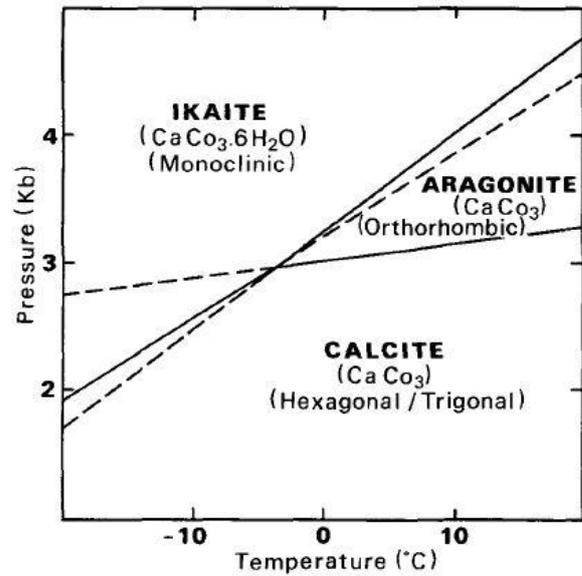


Figure 2. “Stability relations of ikaite with respect to temperature and pressure” (Sherman and Smith 1985).

As we can infer from the descriptions of the ikaite-pseudomorphs, ikaite is typically formed through precipitation from supersaturated aqueous solutions (Boch et al. 2015). However, in laboratory studies elevated pressure (>3kbar), has also been suggested to facilitate ikaite formation at temperatures of 25°C (Boch et al. 2015). In Marland’s (1975) laboratory study including synthetic ikaite, calcite and aragonite it was concluded that ikaite is stable at

pressures above 6-7 kb at 25°C, thus also confirming that ikaite is metastable at the Earth’s surface (Figure 2). Marland (1975) states that “even in the deepest ocean basins, pressures are only one-third of that required to reach the ikaite stability field.”

Alternatively, inferred ikaite pseudomorphs discovered on Kerrera, Scotland, have, in a study conducted by Dempster and Jess (2015), been interpreted as metamorphic ikaite porphyroblasts within the slates of the Dalradian Argyll Group. In studies involving rocks that have undergone metamorphic deformation, Eskola’s (1920) classification of metamorphic facies is used to determine the P-T conditions at which a rock has been metamorphosed. Figure 3 illustrates pressures and temperatures possible on Earth, together with metamorphic

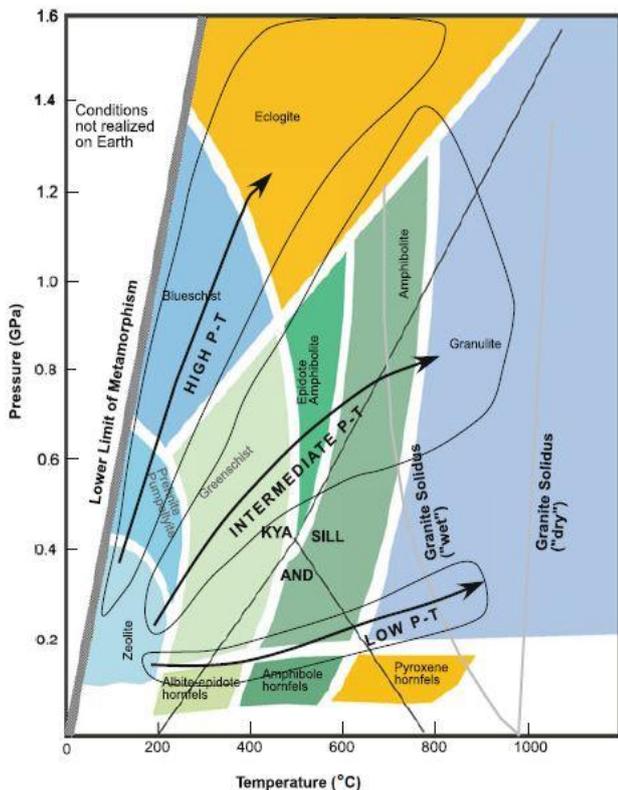


Figure 3. ” Metamorphic facies series, facies, and tectonic associations” (Sen 2014).

facies and their tectonic association. Because ikaite is a high pressure mineral its formation during metamorphism would plot in the section of a P-T diagram where the pressure and temperature conditions are “not recognized on Earth”. Dempster and Jess (2015) explained in their study involving ikaite-pseudomorphs – that the precursor mineral to the pseudomorphs were of ultra-low temperature metamorphic origin linked to deep penetration of permafrost. Dempster and Jess (2015) argue that the only way to lower metamorphic temperatures at depth, which would result in a lowering of the geothermal gradient, is a combination of extremely cold air temperatures at the surface; long time scales; and lack of ice cover acting as a thermal blanket. However, ikaite stability needs to be extended to higher temperatures together with “a pre-existing low geothermal gradient” and extreme cold conditions in order to be formed metamorphically (Figure 4). Thus, Dempster and Jess (2015) argue that this type of extreme lowering of surface temperatures following initial ductile deformation and crustal thickening could account for the existence of ikaite in the Esdale slates (graphitic meta-mudstones and –limestones located stratigraphically above the Port Askaig Tillite formation and was deposited in a deep-water basin ~600 Ma (Anderton 1975, and Dempster and Jess 2015)).

Pseudomorphs have been discovered in the metalimestone succession of the Ballygrant Formation in the Dalradian sequence on Islay, Scotland and are located stratigraphically below the Esdale slates and Post Askaig formation. These pseudomorphs appear as small, ~5 mm elongate structures in a finer grained metalimestone, which all are lying in an angle to the bedding in which they are located in and are similar in appearance to the pseudomorphs described by Dempster and Jess (2015). Additionally, other aligned pseudomorphs have also been found in the Bonahaven Dolomite Formation on North Islay, and are thus located stratigraphically above the Port Askaig Formation. This study will, through field analysis, structural- and petrographic studies, determine the timing of formation of the Ballygrant pseudomorphs, if the precursor mineral might be Ikaite, and if their alignment is related to the alignment of the Bonahaven pseudomorphs.

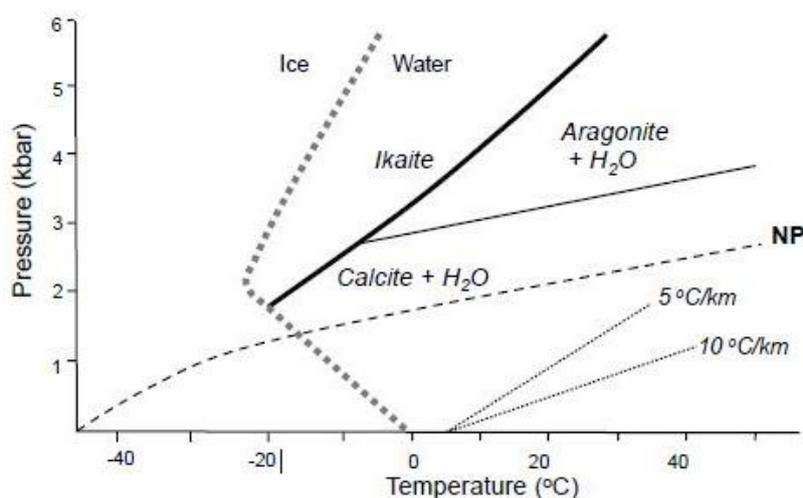


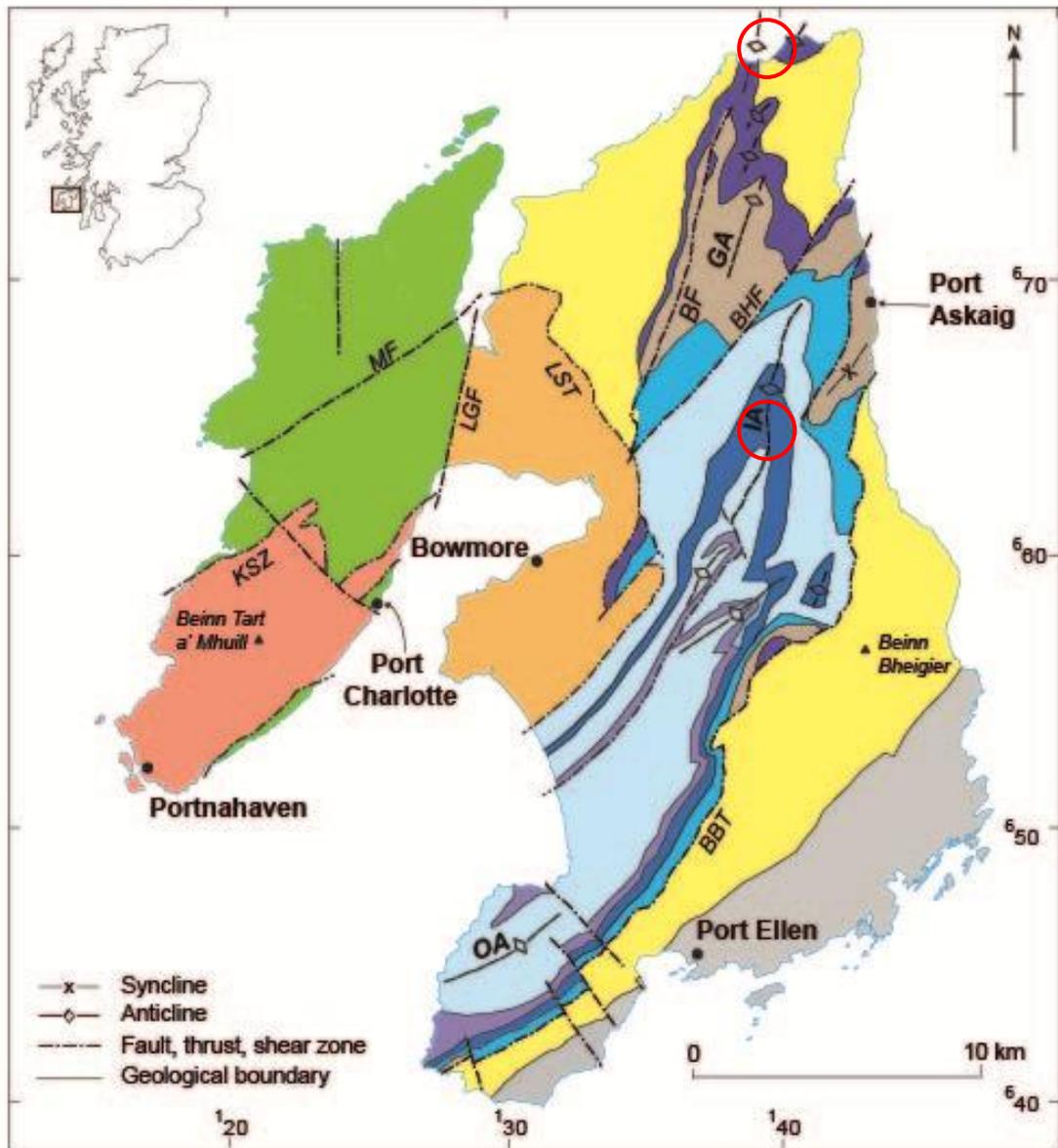
Figure 4. “P-T phase diagram showing stability field of ikaite [...], with reference lines of example geothermal gradients and (NP) estimated Neoproterozoic geothermal gradient; based on 10 °C km⁻¹ initial geotherm, 50°C fall in surface temperature for 10 Ma, and thermal diffusivity of *c.* 10⁻⁶ m² s⁻¹ with an increased rate of heat transfer in cold crust [...].It should be noted that even with these extreme conditions some expansion of the stability field of ikaite towards higher temperature is required” (Dempster and Jess 2015).

Geological Background

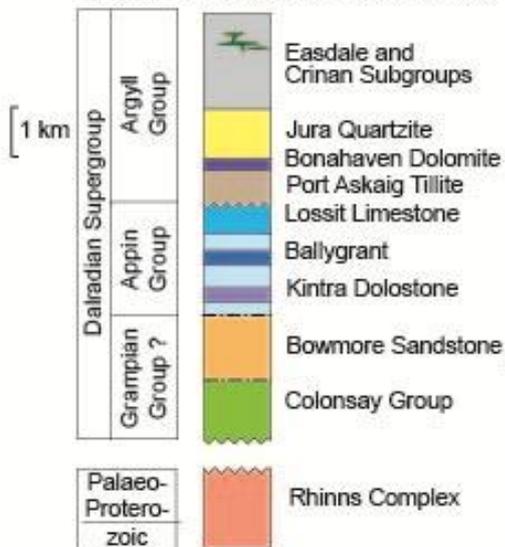
The Dalradian Supergroup, which makes up the bedrock of the Grampian Highlands of Scotland and extends south-west towards the northern parts of Ireland, is for the most part a clastic sedimentary rock sequence with subordinate limestones and volcanoclastic layers, formed during the mid-Neoproterozoic to early Paleozoic (Stephenson et al. 2013). Brasier and Shields (2000) described the Dalradian Supergroup as one of the thickest and possibly most complete rock sequence from Neoproterozoic-Cambrian time to be found anywhere, and is believed to “record protracted rifting associated with the breakup of Rodinia” (Arnaud 2004). The sequence was deformed and metamorphosed to greenschist and upper amphibolite facies during the Grampian Event of the Caledonian Orogeny at mid-Ordovician times (Stephenson et al. 2013 and Fettes et al. 2001). Three groups constitute the Dalradian Supergroup — Grampian Group, Appin Group and Argyll Group (from oldest to youngest) (Figure 5). The rocks in the Appin Group are interpreted to be of shallow marine origin, followed by a marked change from shelf sedimentation to deep water sedimentation in the overlying Argyll Group (Anderton, 1985 and Glover et al. 1995)

The Appin and part of the Argyll Groups are well exposed on Islay, owing to erosion of the Islay anticline. Figure 5 illustrates an excellent stratigraphic column of the Appin and Argyll groups seen on Islay. Here the Kintra dolostone, Ballyrant formation and Lossit Limestone (Islay Limestone) constitute the Appin group. The Lossit Limestone, defined by Tanner et al. (2013) as a banded unit composed ooidal and stromatolitic, thin-bedded metamorphosed limestones, lies unconformably below the ~900 meter thick Port Askaig Tillite Formation (Arnaud and Eyles 2002) that marks the base of the Argyll Group. The Port Askaig Formation, suggested to be of Sturtian age (Prave et al. 2009, McCay et al. 2006, and Sawaki et al. 2010), is overlain by the Bonahaven Dolomite formation that displays negative $\delta^{13}\text{C}$ composition at its lower parts (Brasier and Shields 2000) and is believed to represent a ‘cap carbonate’ with high contents of clastic material compared to other cap carbonates of Marinoan age (Halverson et al. 2005). The Bonahaven Dolomite is overlain by the Jura Quartzite and Esdale and Crinan Subgroups, which are exposed near Port Ellen on Islay.

The Ballygrant Formation, exposed at Cnoc nan Uan on Islay, belongs to the Appin Group and is described by Tanner et al. 2013 as a “dark grey, slaty and phyllitic graphitic metamudstones, followed by a bluish grey metalimestone.” Samples taken from the Ballygrant Limestone in a previous study revealed that the dominant minerals at an outcrop in Cill Bhraenan are calcite, quartz and muscovite (Skelton et al. 2015). The Ballygrant Limestone was correlated by Rast and Litherland (1970) with the Lismore Limestone because of the identical appearance to one another. Additionally, the Fordyce Formation, located on the north coast of Scotland has also been correlated with the Ballygrant formation (Prave et al. 2009). According to Prave et al. (2009), the Ballygrant limestone and the other limestones belonging to the Appin group are characteristic of “development of a prograding carbonate shelf off which material was shed into a deeper basin.”



Generalised stratigraphic column for Islay



Schematic cross sections along lines A-A' and B'B'

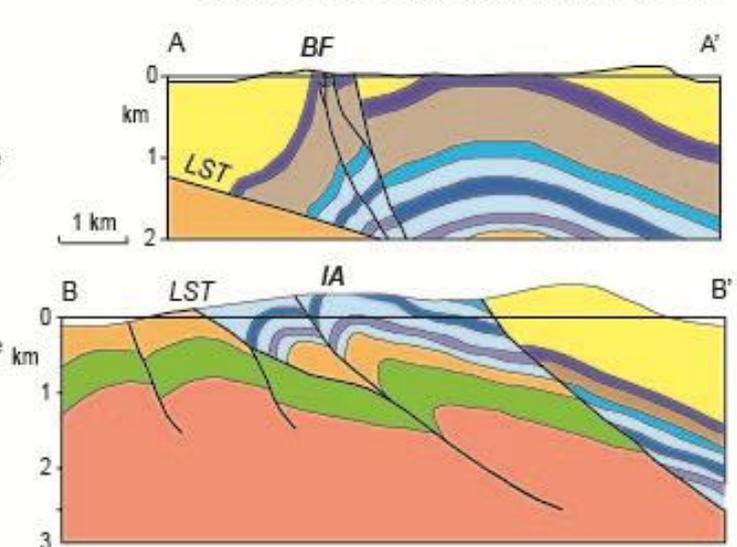


Figure 5. *Top.* Geological map of Islay, Scotland. *Left.* Stratigraphic column. *Right.* Schematic cross-sections. The red circles show the study areas (Skelton et al. 2015).

Methods

The fieldwork was conducted at Cnoc nan Uan located on central Islay (GPS point N55°74,008' W006°10,584'), and at Port An T-sruthain located on north Islay (N55°55.533' W006°10.878'), where pseudomorph-bearing samples from the outcrops of the Ballygrant limestone and Bonahaven Dolomite were collected for petrographic analysis. The outcrop at Cnoc nan Uan was divided into 4 parts in order to more easily sort the data (Figure 6). Then the samples were described in the field and photographed. Dip and dip direction of the pseudomorphs, bedding planes and foliation were measured with a compass-clinometer at both locations. Thereafter stereograms were used to determine spatial relationships between the pseudomorphs lineation, bedding planes and foliation planes. The alignment of the pseudomorphs in the Bonahaven Dolomite was then compared to the Ballygrant pseudomorphs.

In order to test if the parent mineral to the pseudomorphs in the Ballygrant limestone was ikaite or some other syn-sedimentary mineral (e.g. gypsum), three characteristics were studied: first, the shape of the porphyroblasts; second, the composition of the porphyroblasts; and third, evidence of volume change was calculated by measuring the volume percentage of the pseudomorph occupied by the mineral within the core. This was then compared with the expected volume change for transformation of ikaite to calcite based on molecular weight and density, in accordance with the review by Dempster and Jess (2015).

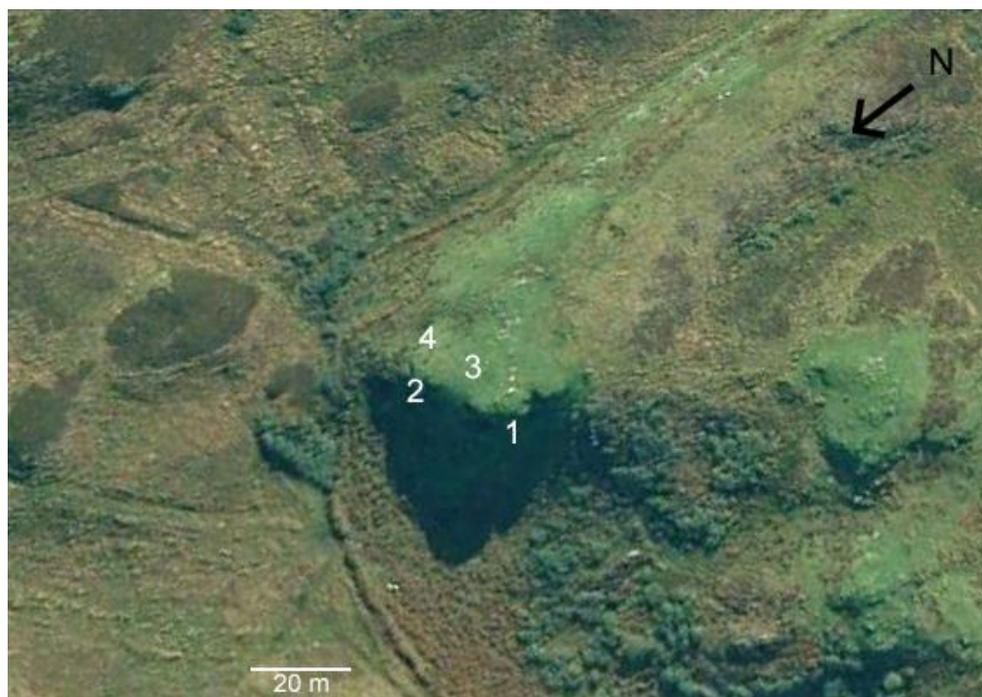


Figure 6. A Google Earth image showing the study area. The numbers reflects the four parts that the outcrop was divided into.

The samples were taken to Stockholm University where selected rocks were cut along their β -surface (parallel to lineation and perpendicular to foliation) with a diamond blade saw into 20x35x12 mm blocks. The blocks were then polished on a grinding wheel combined with powdered SiC (grain size 78 μm), before they were glued onto thin sections slides with epoxy

for microscope analysis. Microscope analysis of the thin sections was then carried out to determine the timing of pseudomorph-formation by looking for inclusion trails, pressure shadows and the pseudomorphs' relationship to foliation.

Mineral chemistry was determined by, Scanning Electron Microscopy (SEM) to identify the minerals in the thin sections. One thin section (Figure 7 and 8) was placed on a tray in the SEM and then pumped to low vacuum. Thereafter backscatter detector Oxford X-max was used to analyze the pseudomorphs, where heavy and light minerals appeared in light and dark colors, respectively. Lastly, points were marked out within the pseudomorphs as targets for the SEM where the elements within the points were analyzed in Aztac Software.

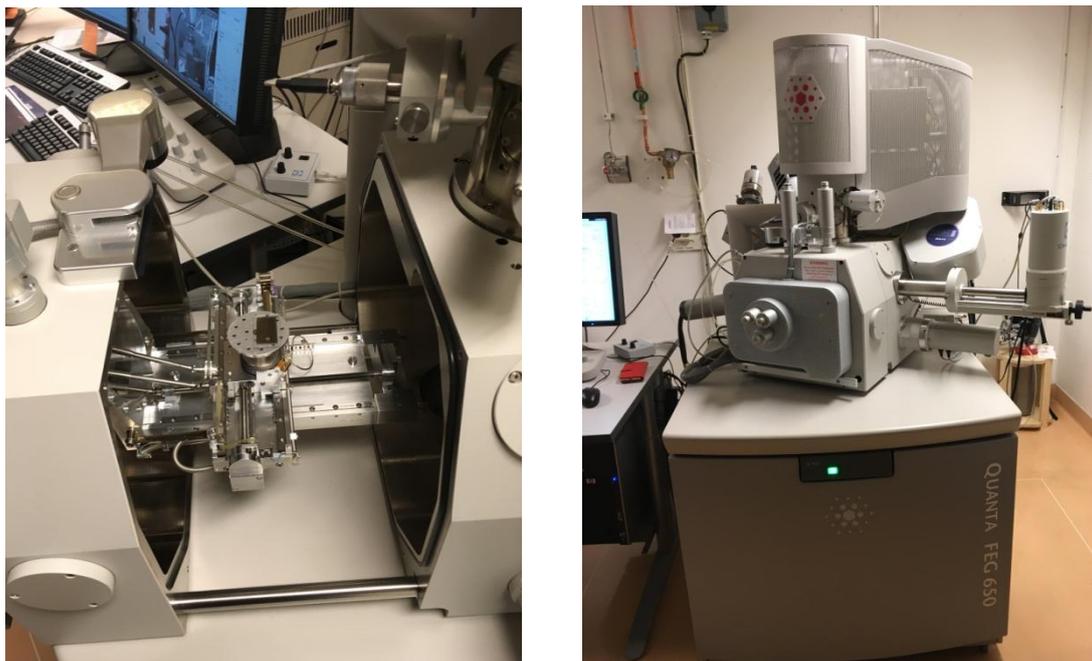


Figure 7: a) Thin section placed on the tray within the SEM. b) SEM of brand "Fey" and model "Quanta Feg 650."

After completing the SEM analysis the thin section was carbon coated for 9 seconds and brought to Uppsala University for Electron Probe Microanalysis (EPMA). EPMA revealed a more specific chemistry and higher resolution images of the minerals making up the pseudomorphs. For the EPMA JXA-8530F JEOL SuperProbe was used to determine the chemistry of the minerals within the pseudomorphs. First an energy dispersive X-ray spectrometer (EDS) was used to perform a fast check of the minerals within the pseudomorphs. This was done by marking out targets on the different minerals and shooting with a voltage of 15 kV, probe current of 5 nA, and beam sizes 3 μm and 10 μm (depending on mineral sizes). Thereafter a more quantitative elemental analysis was done with wavelength dispersive X-ray spectrometers (WDS).

In order to determine the change in volume of the Ballygrant pseudomorphs, Adobe Photoshop was used to visually count the pixels within highlighted areas of the pseudomorphs (Figure 9). Two layers were made on top of an image of a pseudomorph in Photoshop, with the rim highlighted blue in the middle layer and the core highlighted red in the top layer. A histogram showed the amount of pixels in each layer, which was divided into percentages (pixels in core layer divided by pixels in the rim layer). The surface area change calculated in

Photoshop was then used to calculate an approximate volume change by using a mathematical formula for a prolate spheroid.

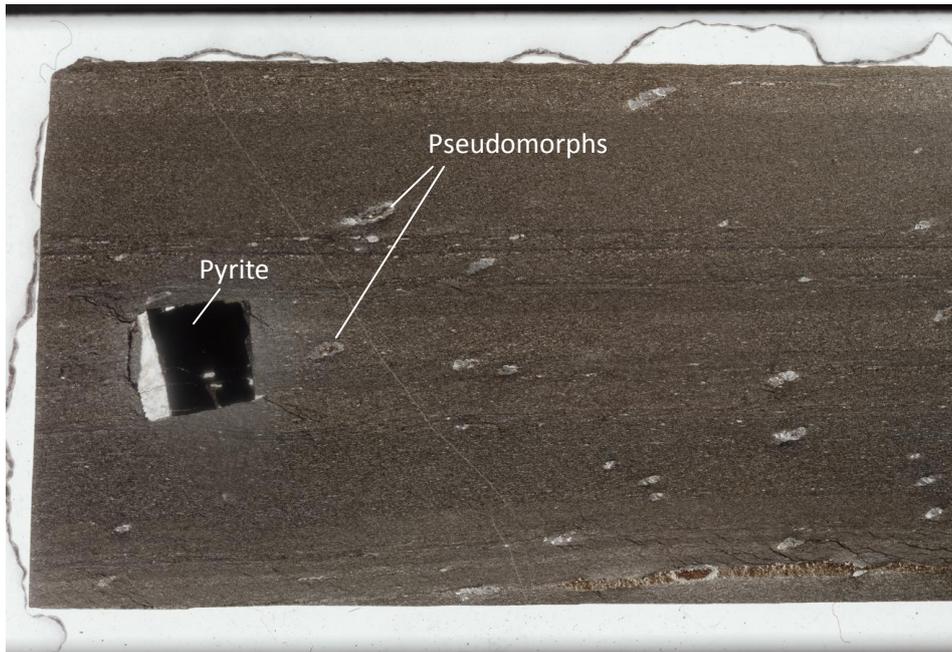


Figure 8. Thin section used in microscope analysis, SEM and EPMA. Note the relatively large euhedral Pyrite crystal with a white pressure shadow along its left margin and the smaller pseudomorphs aligned in the matrix. The thin section slide is from a sample of the Ballygrant metalimestone.

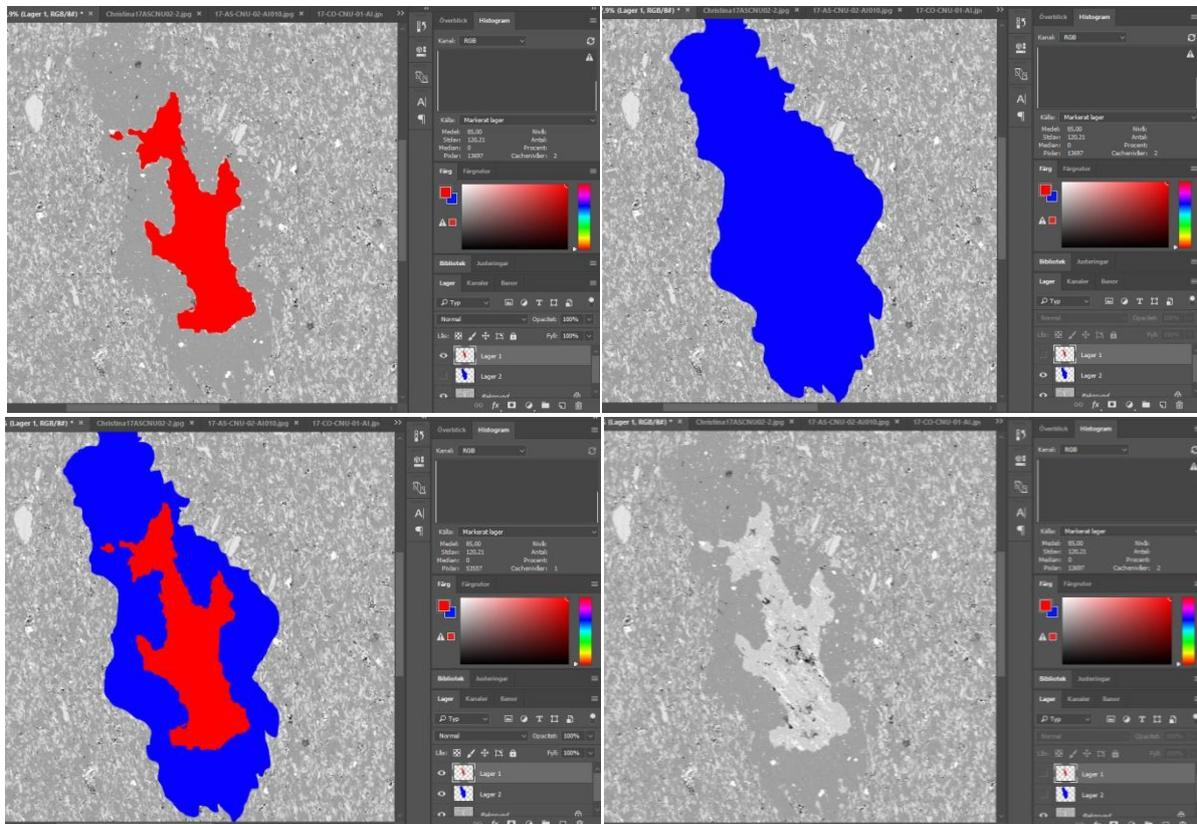


Figure 9. The image is illustrating how Adobe Photoshop was used in order to determine the surface area change of the pseudomorphs by counting pixels within the red and blue areas and then divide them with each other.

Results

Several beds of the Ballygrant formation exposed at Cnoc nan Uan contain ~5 mm large elongated pseudomorphs embedded in a fine grained, brown and dark blue-grey interlaminated matrix of metamorphosed limestone (Figure 10). All the pseudomorphs appear to be aligned in similar direction, which is oblique to the bedding plane. Additionally, euhedral pyrite crystals (~1-7 mm large) stand out from the weathered surface of the metalimestone, and leave voids in some areas where crystals have fallen out.

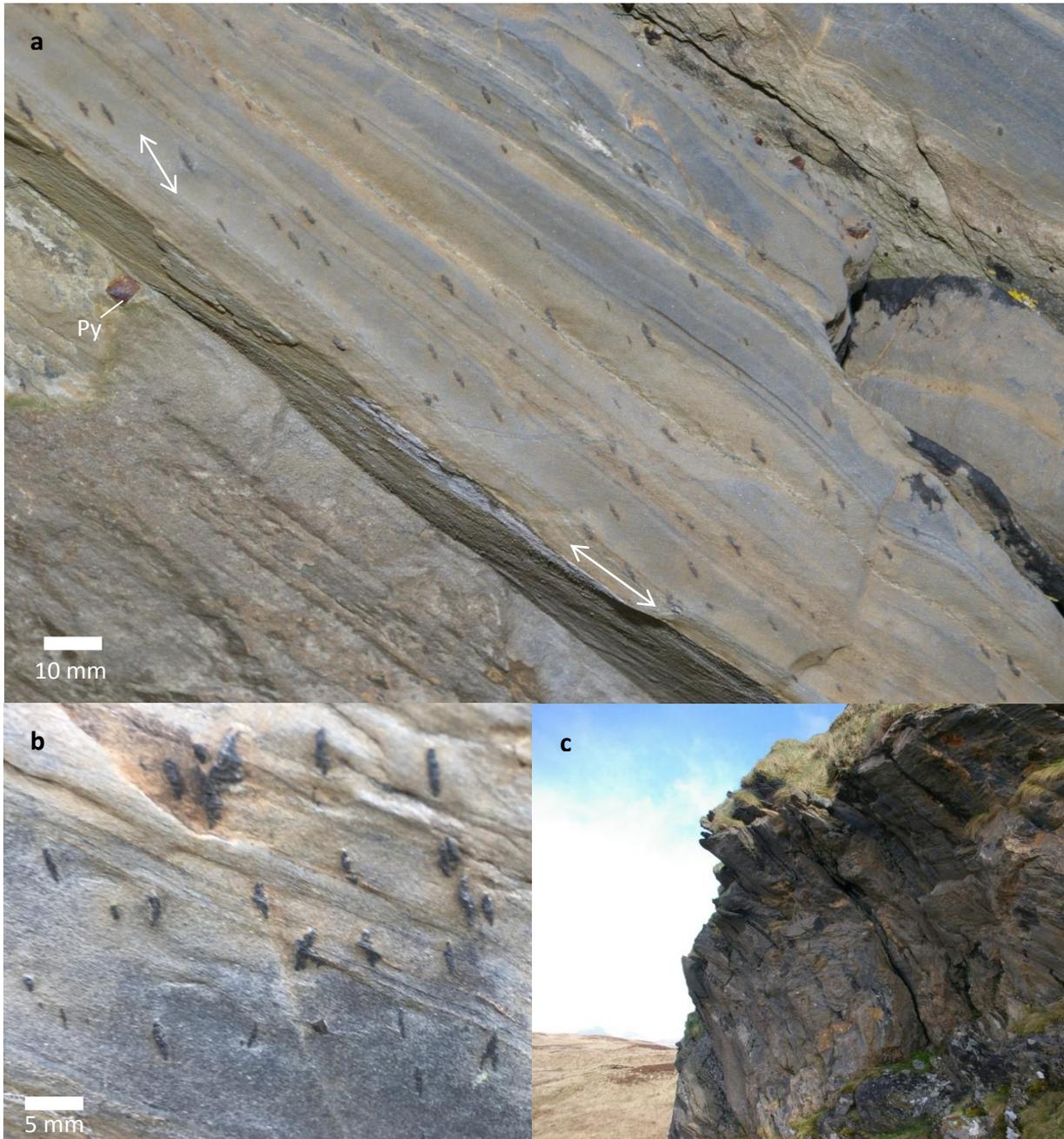


Figure 10. (a) Pseudomorphs embedded in interlaminated blue-gray and brown metalimestone at Cnoc nan Uan (N55°47,008' W006°10,584). The top left arrow illustrates the pseudomorph lineation and lower right arrow shows the bedding plane. (b) Close-up of the pseudomorphs. (c) Outcrop ('part 1') of Ballygrant metalimestone at Cnoc nan Uan.

Stereogram

Stereograms were used to compare the orientation of the pseudomorph lineation with bedding and foliation planes (See Figures 11-13). There is no overlap between pseudomorph lineation and the bedding planes (Figure 11), but some overlap between pseudomorphs lineation and foliation planes (Figure 12). The poles to bedding (imaginary lines perpendicular to bedding) and foliation are not in the same orientation as the pseudomorph lineation, which means the pseudomorphs do not align perpendicular to neither bedding nor foliation (Figure 13). Also, the pseudomorphs are not aligned parallel to the fold hinges at Cnoc nan Uan (Figure 14). Stereogram analysis of the pseudomorphs located in the Bonahaven Dolomite on North Islay reveals a similar alignment to the Ballygrant pseudomorphs when unfolding the bed (Figure 15).

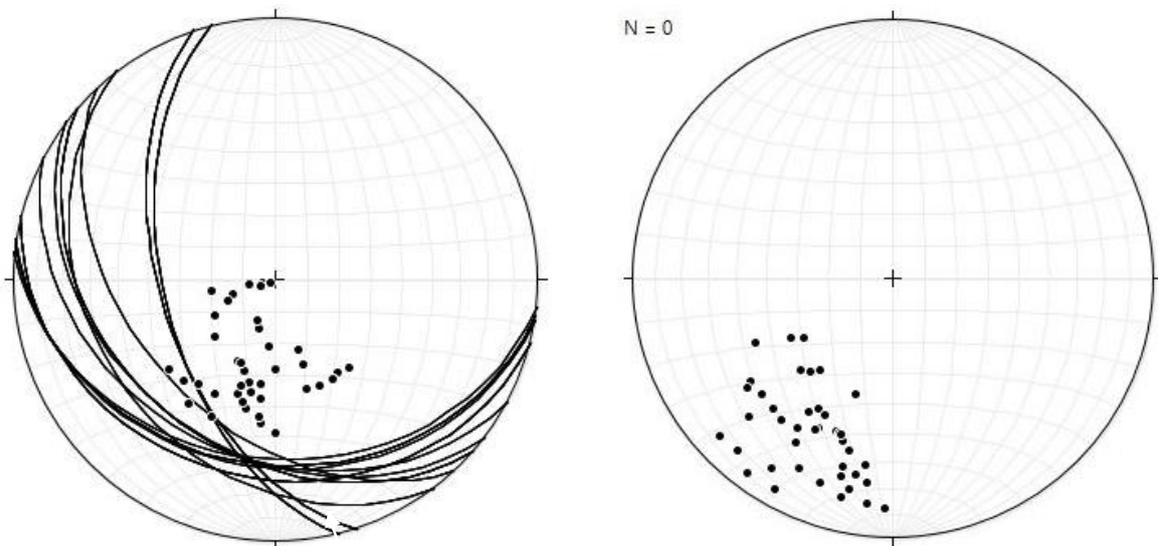


Figure 11. Pseudomorphs and bedding planes plotted in stereograms with North at the top of the stereograms. *Left:* Pseudomorph lineation (dots) and bedding planes (lines). *Right:* Pseudomorphs lineation in unfolded beds (lineation before deformation).

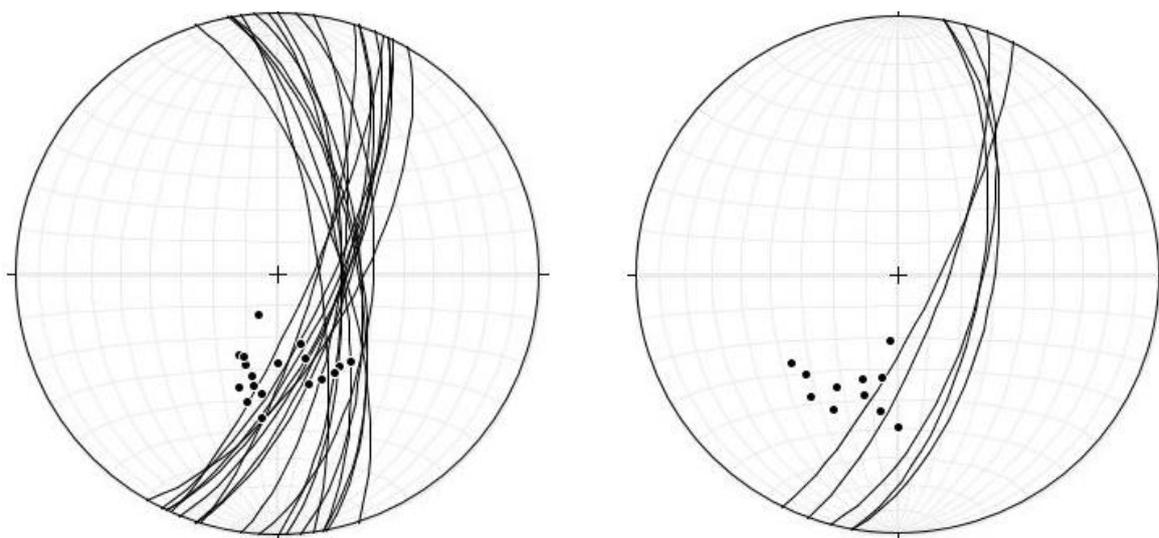


Figure 12. Pseudomorphs and foliation planes plotted in stereograms. *Left:* Pseudomorph lineation (dots) and foliation planes (lines) in unit 2. *Right:* Pseudomorphs lineation and foliation planes in unit 3.

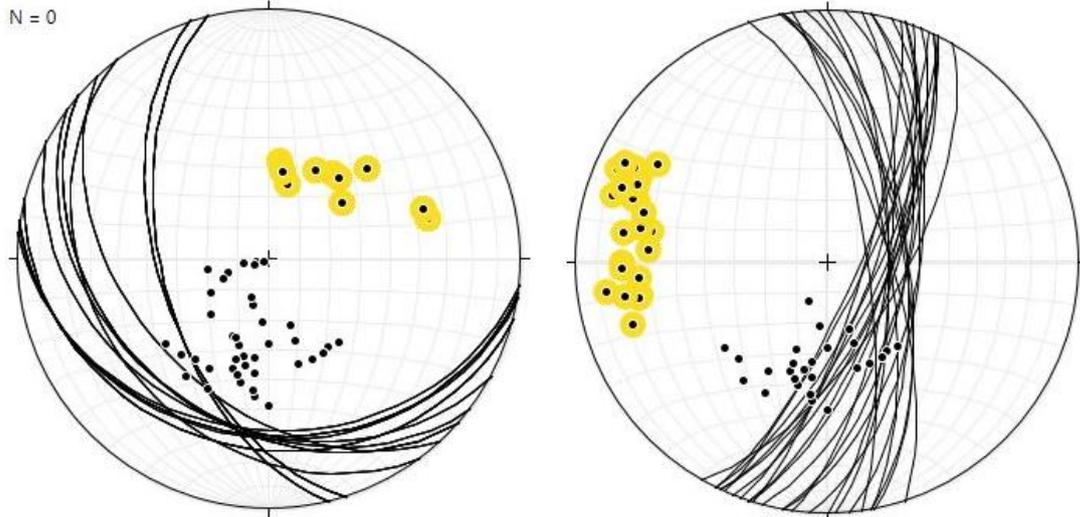


Figure 13. *Left*: Pseudomorph lineation (black dots) plotted together with bedding planes (lines) and poles to bedding (yellow dots). *Right*: Pseudomorph lineation (black dots) plotted together with foliation planes (lines) and poles to foliation (yellow dots).

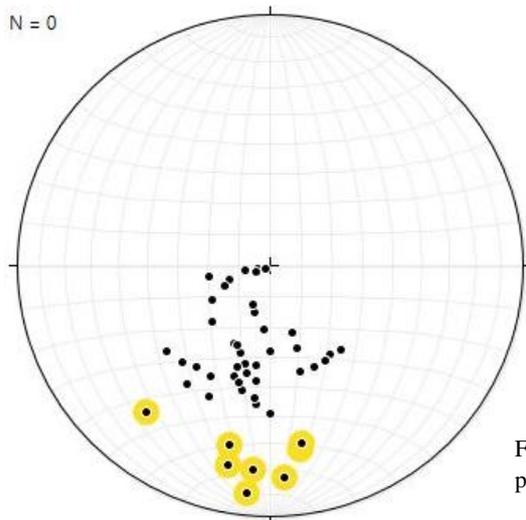


Figure 14. Pseudomorph lineation (black dots) plotted together with fold hinges (yellow dots).

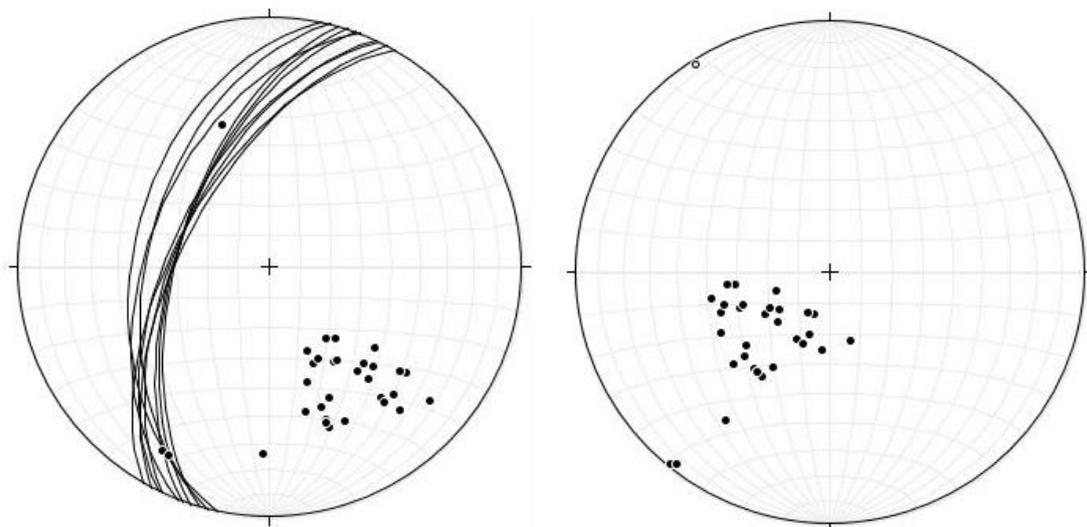


Figure 15. Stereograms showing the relationship between pseudomorphs and bedding planes in the Bonahaven formation on North Islay. *Left*: Pseudomorph lineation (dots) and bedding planes (lines). *Right*: Pseudomorph lineation in unfolded beds. Here an average bedding plane was used when unfolding.

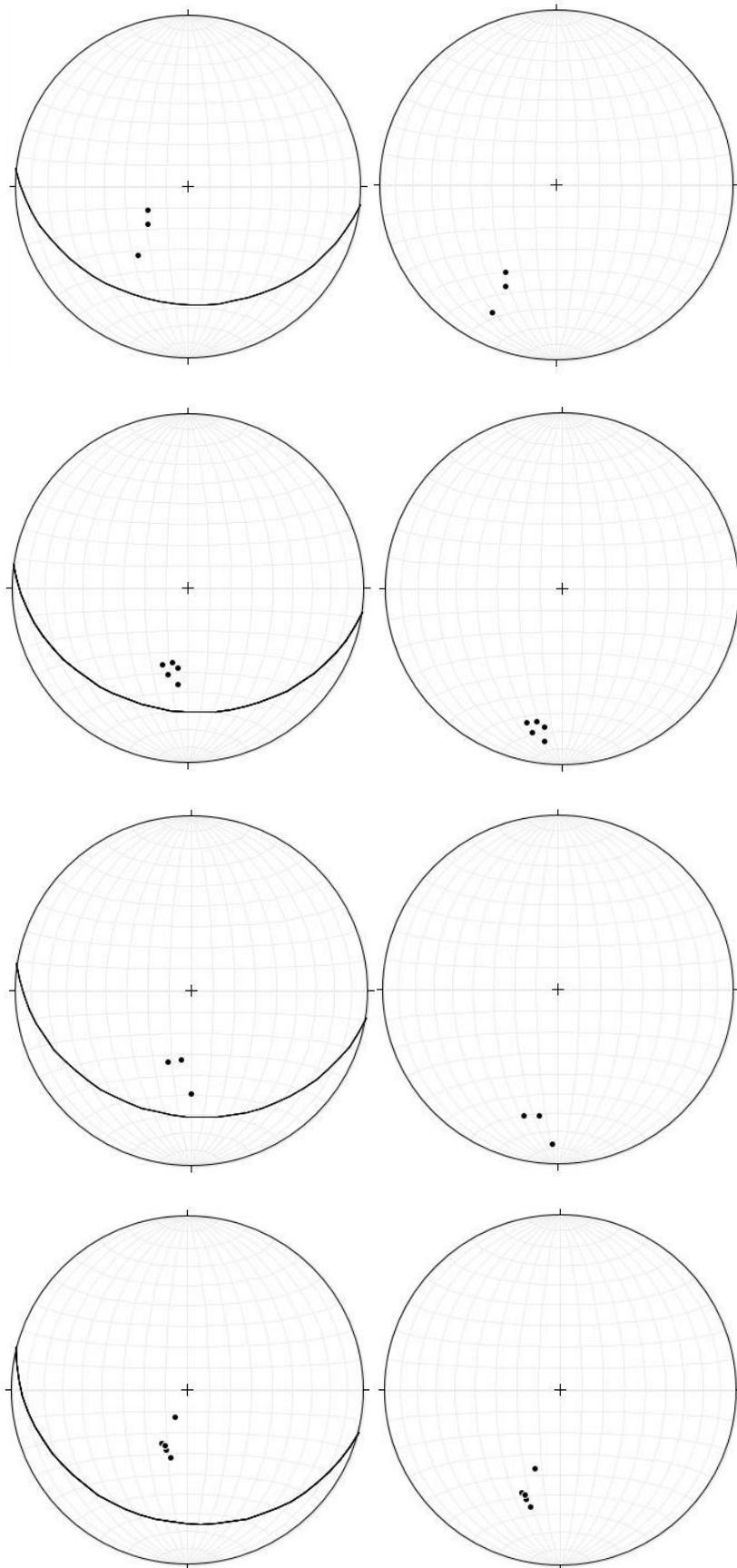


Figure 16. Stereograms showing pseudomorph lineation within differently oriented beds at Cnoc nan Uan. *Left.* Pseudomorph lineation (dots) with bedding plane (line). *Right.* Pseudomorph lineation in unfolded bed.

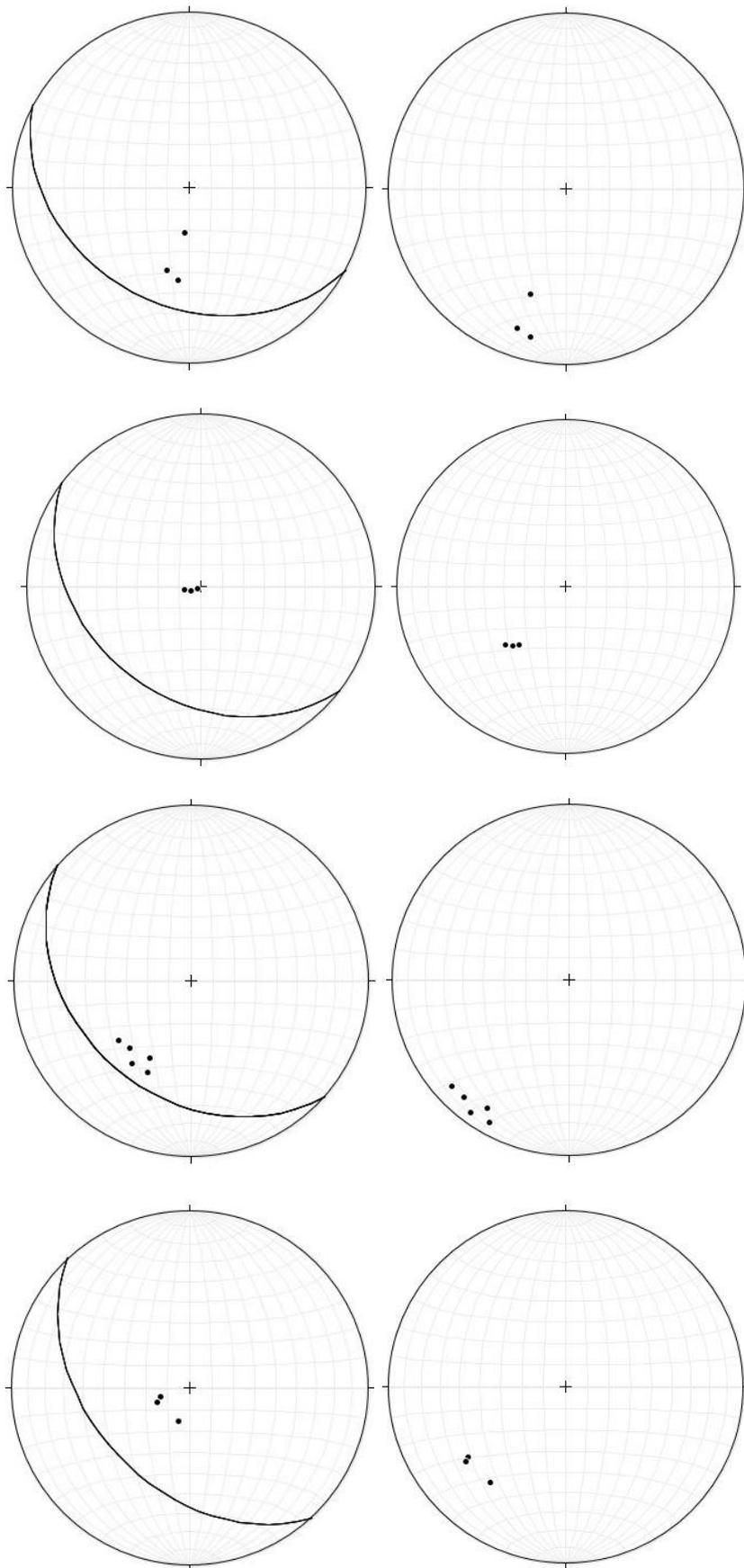


Figure 16. cont.

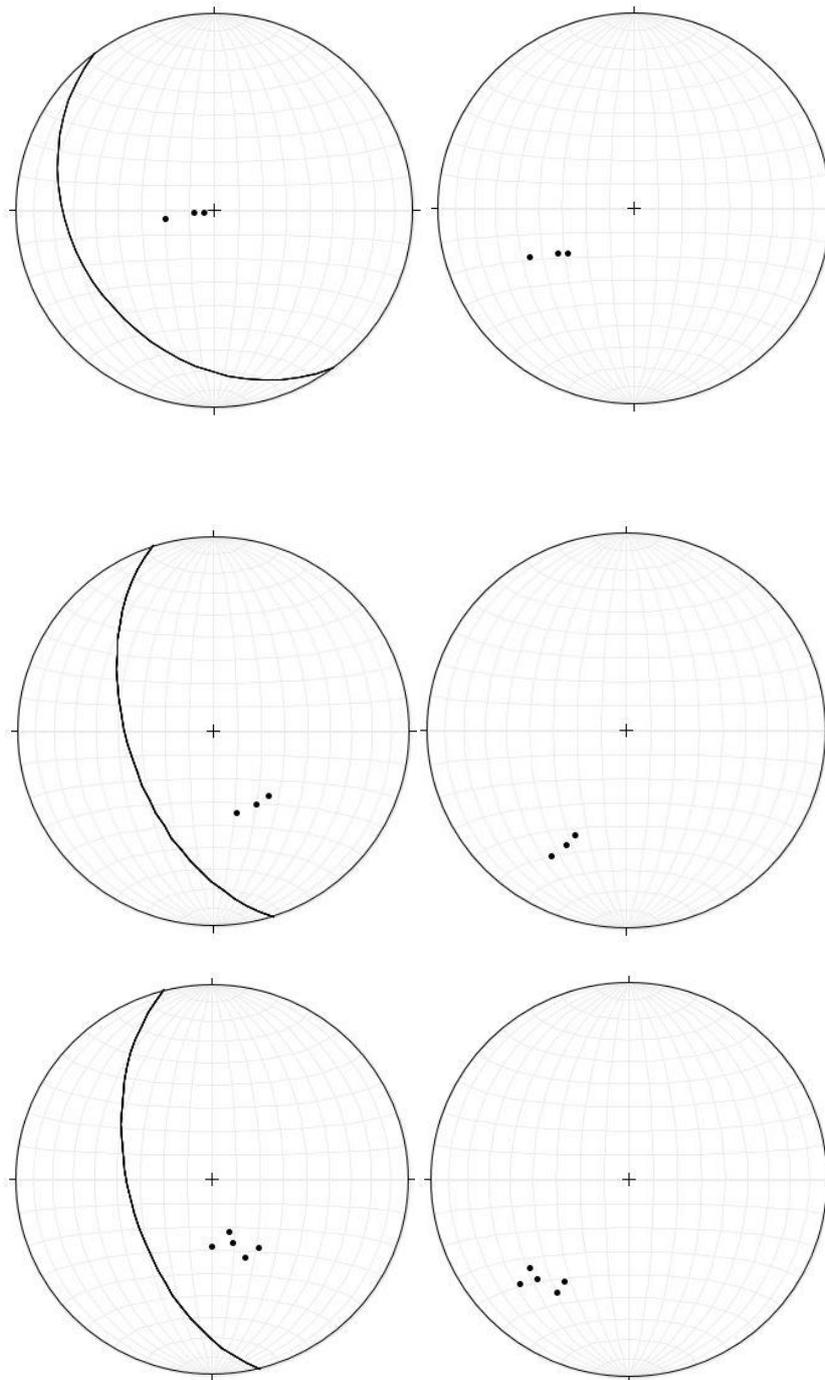


Figure 16. cont.

Microscope:

Mineral assemblage: SEM and Microprobe analysis confirm that the major minerals constituting the pseudomorphs are quartz, calcite and iron oxide with minor amounts of pyrite, apatite, chlorite, titanite, and K-feldspar (Figure 17). One pseudomorph analyzed in the microprobe contains a relatively large void within the calcite core, with needle-like crystals of heavier minerals growing inside (Figure 17b). The mineral needles in the void lack alignment and grow freely into the empty space. However, heavy minerals within the calcite core of other pseudomorphs are aligned (Figure 18).

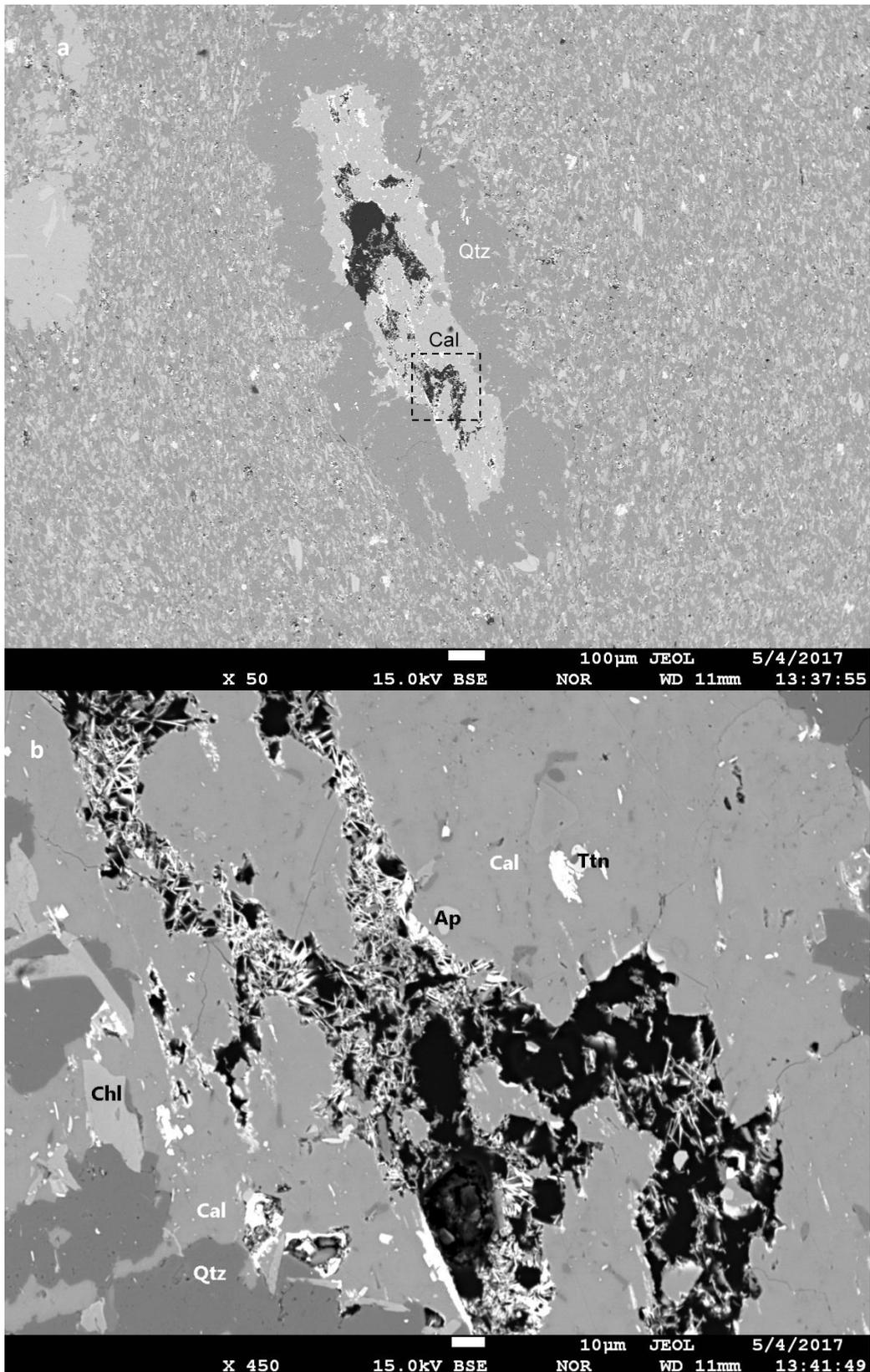


Figure 17. (a) Microprobe image of a pseudomorph with a light gray colored calcite core and darker gray colored quartz rim. Box shows the location of (b). (b) A close up of the void within the calcite core. Note the white needle like crystals of heavier minerals growing into the void.

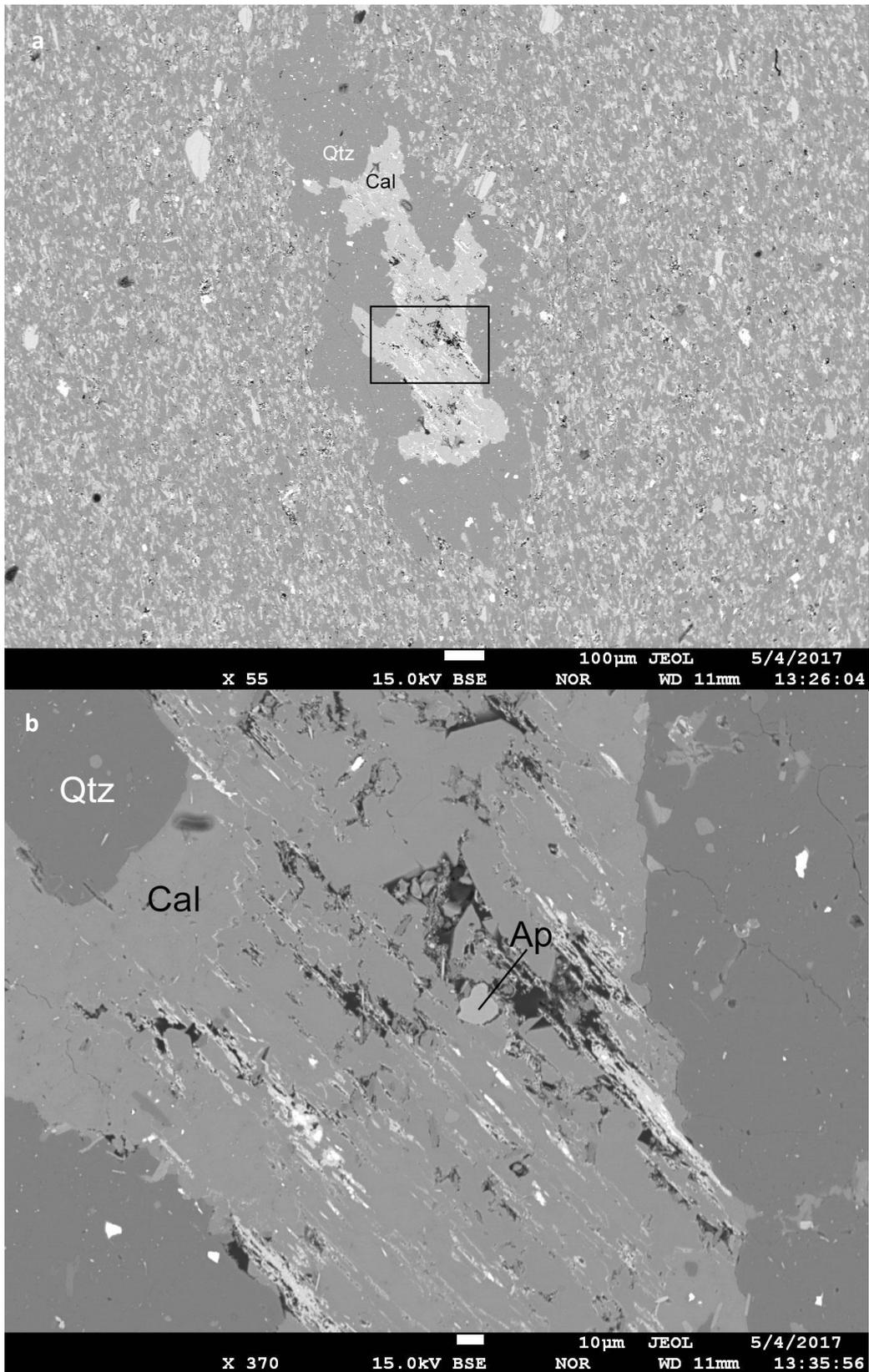


Figure 18. (a) Microprobe image of a pseudomorph with a light gray colored calcite core and darker gray colored quartz rim. Box shows the location of (b). (b) A close up of the lineated white colored heavy minerals within the calcite core.

Appearance: The calcite cores of the pseudomorphs show dark brown birefringence in a petrographic microscope and the quartz rims show first order birefringence colors (Figure 19). Cleavage planes of the calcite are hard to distinguish in the microscope due to the small size of the minerals, but it is possible that the heavy minerals lining up within the calcite cores are parallel to cleavage planes. Also, pressure shadows seem to appear as long ‘tails’ at some of the pseudomorphs’ edges. Specifically, one pseudomorph in the thin section illustrated in Figure 8 shows a white colored ‘tail’ on one side of a pseudomorph corresponding to the direction of the pyrite’s pressure shadow (Figure 20).

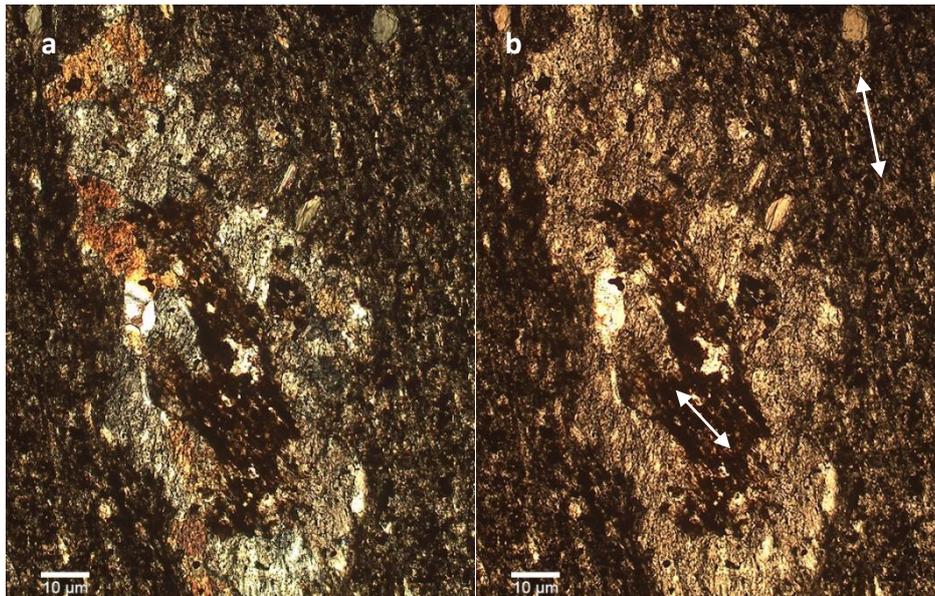


Figure 19. A microscopic photo of a pseudomorph with a brown calcite core and a yellow-brown quartz rim. The top arrow in (b) shows the foliation direction and the lower arrow shows the alignment of heavy minerals within the calcite.



Figure 20. A close-up of the thin section slide in Figure 8 showing a pressure shadow (ps) along the Pyrite left margin having similar direction as the long white ‘tail’ of the pseudomorph in the upper right corner.

Relation to foliation: Some of the pseudomorphs appear in the microscope to be aligned in the similar direction as the foliation (Figure 21), and others lay with an angle to the foliation (Figure 21c), which is consistent with the results of the stereograms. The linedated inclusions within the calcite cores are not aligned with the foliation.

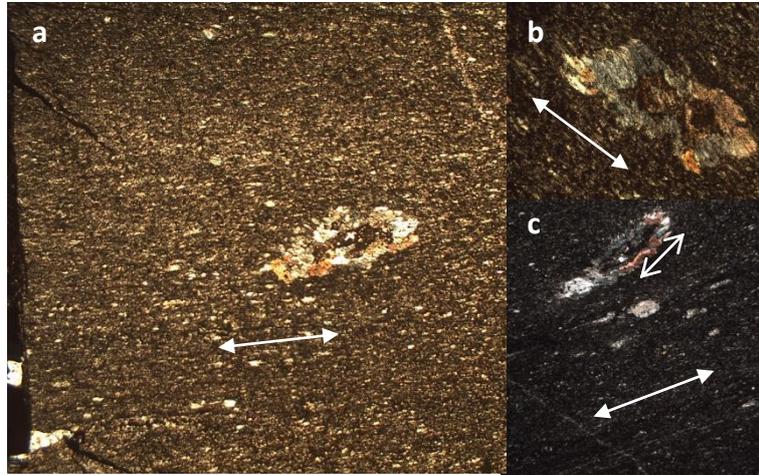


Figure 21. (a) and (b) pseudomorph laying in a similar direction as the foliation (white arrow in matrix). (c) Pseudomorph laying with an angle to the foliation. The top arrow illustrates the direction of the pseudomorph, while the bottom arrow shows the direction of foliation. Not the pressure shadow in (c) that has the same orientation as the foliation and not the pseudomorph.

Volume change: The estimated average surface area of the core relative to the original mineral, calculated from 5 pseudomorphs, is $\sim 26.0 \pm 2.3\%$ (i.e. the surface area change is $\sim 74\%$). This value was used when calculating the estimated volume change of the pseudomorphs by using the following formula:

$$A = \pi r^2$$

$$V = \frac{4}{3}\pi r^3$$

$$\frac{A_c}{A_p} = \frac{\pi r^2}{\pi R^2} = \frac{r^2}{R^2}$$

$$\frac{V_c}{V_p} = \frac{\frac{4}{3}\pi r^3}{\frac{4}{3}\pi R^3} = \frac{r^3}{R^3}$$

R = short radius of the pseudomorph

r = short radius of the core

$$\frac{V_{c/p}}{A_{c/p}} = \frac{\left(\frac{r}{R}\right)^3}{\left(\frac{r}{R}\right)^2} = \frac{r}{R}$$

$$V_{c/p} = A_{c/p} \left(\frac{r}{R}\right)$$

Example:

$$V_{c/p} = 26.9 \left(\frac{1.1}{2.4}\right)$$

$$V_{c/p} = 12.3\%$$

The estimated average volume change of all 5 pseudomorphs is $\sim 88.0 \pm 1.67\%$ (see Table 1 for more details). This value is the maximum volume change because we cannot be certain that the pseudomorphs were cut exactly through their centers. Also, the calculations assume a prolate shape of the pseudomorphs and do not take the void within one of the pseudomorphs into consideration.

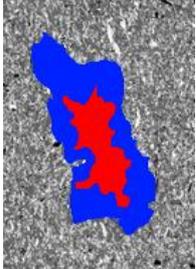
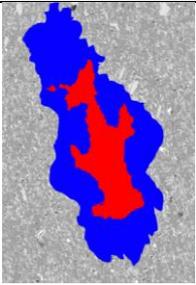
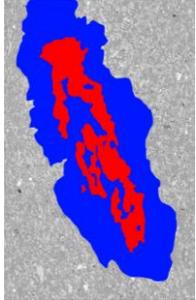
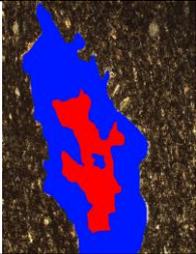
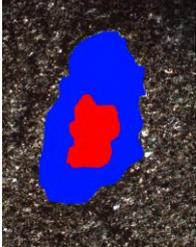
| Pseudomorphs | Surface Area % (core px./pseudo. px.) | Volume % |
|---|---------------------------------------|---|
|  | $\frac{1904}{6766} (100) = 28.1$ | $28.1 \left(\frac{0.65}{1.8}\right) = 10.1 \%$ |
|  | $\frac{13697}{49392} (100) = 27.7$ | $27.7 \left(\frac{2.5}{4.5}\right) = 15.4 \%$ |
|  | $\frac{15238}{56548} (100) = 26.9$ | $26.9 \left(\frac{1.1}{2.4}\right) = 12.3 \%$ |
|  | $\frac{18523}{71931} (100) = 25.8$ | $25.8 \left(\frac{1.75}{4.05}\right) = 11.1 \%$ |
|  | $\frac{11455}{52667} (100) = 21.7$ | $21.7 \left(\frac{1.8}{3.5}\right) = 11.2\%$ |
| <i>Average:</i> | <i>26.04</i> | <i>12.02%</i> |
| $SD = \sqrt{\frac{\sum x-x^- ^2}{n}}$ | $SD = \sqrt{\frac{26.64}{5}} = 2.3$ | $SD = \sqrt{\frac{16.71}{5}} = 1.83$ |

Table 1. The Table is showing how surface area and volume were calculated for each measured pseudomorph (including standard deviation (SD)).

Discussion

In the following discussion, I consider the origin of the pseudomorphs in the Ballygrant metalimestone on Islay and the timing of their formation.

Pseudomorph Origin: The elongated shape of the pseudomorphs and the mineral assemblage, which are concentrically arranged within, are the first evidence suggesting ikaite as the parent mineral. The pseudomorphs' mineral assemblage with calcite core and quartz rim are very similar to the ikaite pseudomorphs described by Dempster and Jess (2015), where the quartz rim surrounding the calcite core was interpreted to have formed from a Si-saturated fluid that filled the voids formed when volume decrease took place during the initial replacement reaction (Dempster and Jess 2015). Also, the cavity within the calcite core is strong evidence of a volume decrease during transformation (Frondel 1935). Gypsum, alternatively, can have a similar shape to ikaite (Figure 22) and has been reported as pseudomorphs in other parts of the Dalradian rock sequence on Islay (Anderton 1975). Also, gypsum calcitisation (a process involving calcite replacement of calcium sulphate salts) can preserve the original morphology and internal structure of gypsum (or anhydrite) and consequently produce calcite-pseudomorphs (Warren 2016 and Alonso-Zarza & Tanner 2010). However, the expected volume decrease for gypsum/anhydrite transition is ~38% (Kendall 1975), which is significantly smaller than the ~88% volume decrease of the pseudomorphs in the Ballygrant metalimestone. The volume decrease of the Ballygrant pseudomorphs is, on the other hand, larger than the volume decrease expected to occur during an ikaite-calcite transition. This large volume decrease can be explained if sections were not through the centers of the pseudomorphs. Another explanation could be if ions were added/lost during the ikaite/calcite transformation at Ballygrant, because Sherman and Smith's (1985) reported that a volume decrease of 68.6% is expected to result from a transition occurring within a closed system (this is however also possible for a gypsum/anhydrite transition, but with more elemental loss). Assuming the first explanation (i.e. how the section was cut) the volume decrease could also be evidence pointing to ikaite as the precursor mineral.

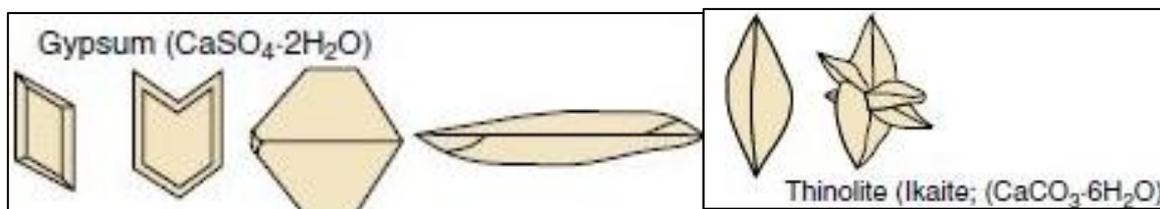


Figure 22. Modified sketches from Warren (2016) showing different appearances of gypsum compared to Ikaite.

Timing of growth: The minerals preserved as needles in the cavity within one of the calcite cores is not only a key evidence of a volume decrease, but also imply that the cavity survived the deformation at the hinge of the Islay anticline, assuming the pseudomorphs were formed before deformation. Similar mineral crystals are seen as inclusions in other calcite cores that follow the minerals cleavage planes.

The Pressure shadows appearing as long ‘tails’ adjacent to some of the pseudomorphs appear to be similar to pressure shadows of the gypsum pseudomorphs discovered in the Argyll group reported by Anderton (1975) who described the appearance of some gypsum pseudomorphs as “ragged” with small tails that was added by “the 'sweating out' of quartz along incipient cleavage planes” (Anderton 1975). Figure 23 illustrates development of these pseudomorphs from Anderton’s (1975) study. The occurrences of pressure shadows therefore rules out a post-deformational origin of the pseudomorphs in the Ballygrant metalimestone. Also, the stereogram analysis of the pseudomorphs lineation in relation to bedding and foliation planes imply that some pseudomorphs seem to lie in the foliation plane and could therefore have been aligned during deformation of the rock, but since foliation is caused by folding we would expect the pseudomorphs to also align parallel with the fold hinges, which is not observed. I therefore infer that the pseudomorphs are not directly related to the folding. Moreover, the stereogram with unfolded beds implies that the pseudomorphs (measured in parts 1, 2, 3) within different beds of the Ballygrant Formation had the same orientation before folding, but that they were not perpendicular to the bedding (the same goes for the pseudomorphs in the Bonahaven Dolomite) (see Figures 11-16). These results entail that the pseudomorphs in the two formations replaced a mineral that was formed before folding.

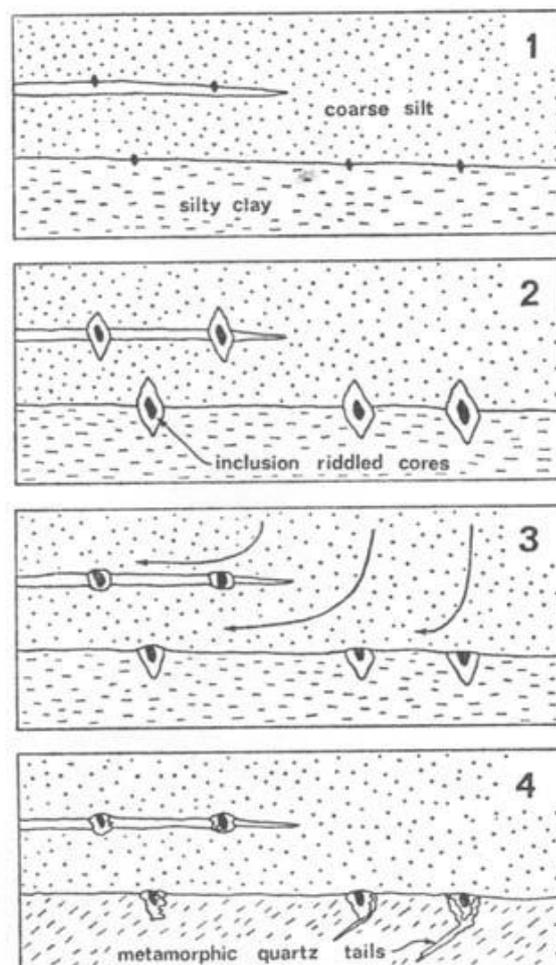


Figure 23. A modified schematic sketch suggesting the evolution of gypsum-pseudomorphs and the development of pressure shadow ‘tails’ (Anderton 1975).

The alignment of the pseudomorphs is likely caused by another process occurring before the Grampian Event, which raises the question as to what process caused the lineation of the pseudomorphs. The pseudomorphs alignment can perhaps be related to a metamorphic event pre-Grampian as suggested by Dempster and Jess (2015), but it might also be possible that glaciotectionic processes might have deformed the Appin limestones on Islay during a Neoproterozoic ice age. If that is the case, this might explain a relationship between pseudomorphs' lineation and the interpreted SE-NW ice movement (suggested by Spencer (1971)) during deposition of the Port Askaig Formation.

According to Fleming, Stevenson & Petronis (2013) glacial stress can form structures such as fold, faults, boudins and fabrics in unlithified or weakly lithified sediments. Thus, if the Ballygrant pseudomorph lineation is caused by a glaciotectionic process it is possible that the ikaite transformed into calcite after alignment (when temperatures increased and glaciers regressed), which would explain the preservation of the cavity within the calcite core. Fleming, Stevenson and Petronis (2013) also state that "variation in lithology and the dynamic nature of subglacial conditions means that earlier deformation structures can be overprinted," which might account for the lack of other pre-Grampian deformation structures in the Ballygrant Formation. However, if the alignment of the pseudomorphs in the Bonahaven dolomite, which is located stratigraphically above the Port Askaig Tillite formation, is related to the Ballygrant pseudomorphs (Figure 25) the timing of alignment would be younger than the Sturtian glaciation. This would then suggest that the force causing the pseudomorph alignment must have penetrated through the ~900 meter thick Port Askaig succession in order to affect the pseudomorphs in the Ballygrant formation. The similar alignment of the Bonahaven and Ballygrant pseudomorphs might also be accounted for by an unknown metamorphic event as proposed by Dempster and Jess (2015). However, co-alignment of pseudomorphs in two formations might also merely be a coincidence.

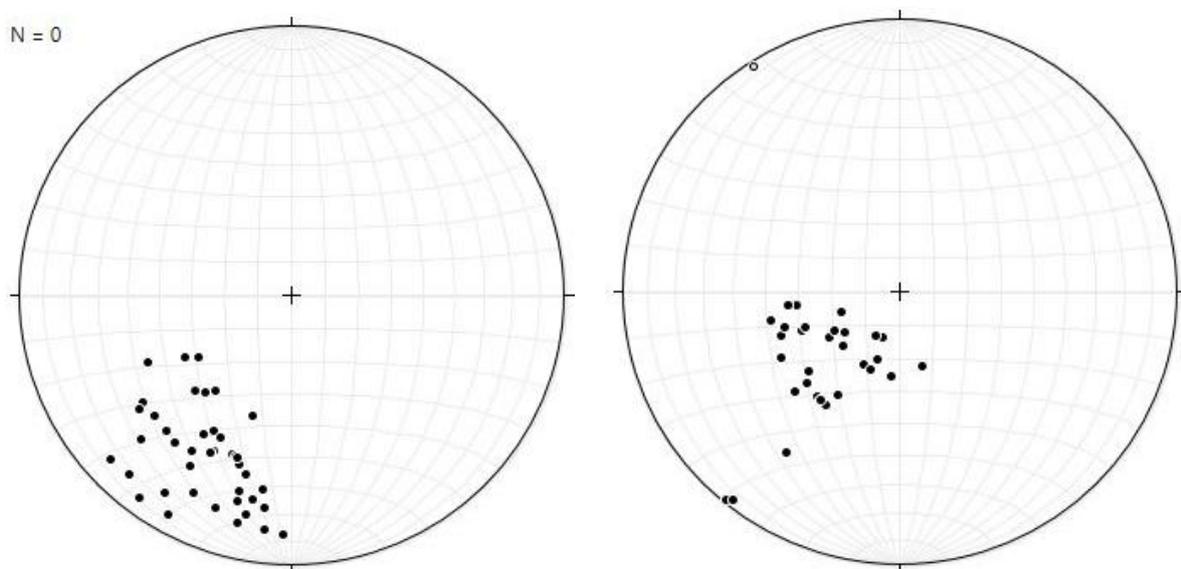


Figure 25. Stereograms showing a possible relationship between pseudomorph lineation in unfolded beds of the Ballygrant metalimestone (left) and the Bonahaven Dolomite (right) owing to the similar alignment after unfolding all the beds.

Conclusion

The aligned pseudomorphs within the Ballygrant metalimestone on Islay have been interpreted to originate as possibly ikaite before transitioning into calcite, owing to their concentrically arranged mineral assemblage of mostly quartz (rim) and calcite (core) and a volume decrease of ~88%. Microstructures such as pressure shadows and the pseudomorphs' oblique alignment to the foliation suggest that ikaite originate as pre-deformational porphyroblasts, which indicates a cold climate at the time of formation. This finding could suggest a less rapid 'switch over' to glacial conditions as expected by a snowball earth event, and might therefore refute the hypothesis and instead account as evidence of a 'normal' glacial period. Stereogram analyses imply that the alignment of the pseudomorphs occurred before the Grampian deformation of the limestone. Also, other pseudomorphs, located in the Bonahaven Dolomite, appear to co-align with the pseudomorphs in the Ballygrant metalimestone. The process owing to the pseudomorph alignment in the Ballygrant metalimestone (and possible co-alignment with the pseudomorphs in the Bonahaven Dolomite) is, however, unknown but this study suggests glaciotectonic or metamorphic processes as two possibilities.

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