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Ikaite pseudomorphs in Neoproterozoic Dalradian slates record Earth's coldest metamorphism

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Abstract: Calcite pseudomorphs have replaced euhedral ikaite ($CaCO_3.6H_2O$) porphyroblasts in Dalradian calcareous slates and metadolostones of western Scotland, with a volume decrease of at least 47%. Porphyroblast-fabric relationships indicate that the initial growth of ikaite post-dates a penetrative tectonic fabric developed during upright folding. This is the first reported occurrence of metamorphic ikaite porphyroblasts and points towards growth within the slates during an ultra-low temperature metamorphism with an exceptionally low geothermal gradient. This event is associated with the penetration of long-lived and extreme permafrost deep into sub-aerially exposed bedrock during Neoproterozoic glaciation. The presence of the well-preserved pseudomorphs within the Easdale slates of the Argyll group implies that a Neoproterozoic orogenic unconformity exists above the stratigraphic position of these rocks.

The Neoproterozoic era was a time of global climatic change, linked to periodic extensive glaciations, with characteristic sequences of tillites, cap carbonates and associated fluctuations in seawater isotopic ratios (Hoffman & Schrag 2002; Fairchild & Kennedy 2007). A series of glacial events occurred at ca. 580 Ma (Bowring *et al*. 2007), 635 Ma (Hoffmann *et al*. 2004) and 717-662 Ma (Rooney *et al*. 2013), which are controversial in the suggested intensity, cause, effects, timing and longevity (Fairchild & Kennedy 2007). The Neoproterozoic Dalradian metasedimentary succession in Scotland was initially deposited during rifting and break-up of the Rodinia supercontinent (Soper 1994; Dempster & Bluck 1995; Strachan & Holdsworth 2000) and contains many of the characteristics of the global glacial events, including a widely recognized tillite horizon with a proposed cap carbonate sequence, and significant fluctuations in carbon isotope ratios (Brasier & Shields 2000; McCay *et al*. 2006; Prave *et al*. 2009). The stratigraphy is complicated by local excision of parts of the sequence and later orogenesis and this together with the lack of reliable age constraints means there is some uncertainty in the correlation of the succession with global Neoproterozoic events. In this study, we present evidence that extreme surface temperatures during a prolonged glacial period penetrated deep into the bedrock and influenced conditions in the metamorphic realm.

Geological setting

The Dalradian metasedimentary rocks on the island of Kerrera in western Scotland are believed to be members of the Easdale subgroup within the Argyll Group (Harris *et al*. 1994). They were deposited prior to 600 Ma (Dempster *et al*. 2002) as graphitic mudstones and limestones with occasional poorly graded turbidites in a deep water basin (Anderton 1979; Anderton 1985; Harris *et al*. 1994) and post date a suggested "Snowball Earth" horizon marked by the Port Askaig tillite (Spencer 1971). This tillite is widely correlated through Scotland (Brasier & Shields 2000) and linked to the Marinoan event at ca 635 Ma (Rooney *et al*. 2011), although others have associated it with Sturtian glaciation (Prave *et al*. 2009). A variety of other local glaciogenic horizons have been identified from within the Dalradian succession (e.g. McCay *et al*. 2006) although their significance with respect to the timing of global events is uncertain. The Dalradian rocks have experienced polyphase deformation and greenschist facies regional metamorphism during the Grampian orogeny (Soper *et al*. 1999). Based on ages determined in the higher grade metamorphic rocks towards the north-east, the timing of peak metamorphism is ca. 470 Ma (Oliver *et al*. 2000; Baxter *et al*. 2002). However the possibility of Precambrian orogenesis affecting parts or all of the succession has also been widely proposed (Dempster & Bluck 1995; Dempster *et al*. 2002; Hutton & Alsop 2004). A reliable age framework for the deposition, early deformation and metamorphism has yet to be established due to the lack of stratigraphic horizons that can be readily dated. The Dalradian rocks are locally unconformably overlain by conglomerates and sandstones of latest Silurian and earliest Devonian age (Trewin *et al*. 2012).

Petrography and structures

The Easdale slates are fine grained (10-20 μm), grey, graphite-rich, variably calcareous, and interbedded with <50 cm beds of metacarbonates (Fig. 1A). The rocks have experience polyphase deformation with early upright folds associated with an axial planer cleavage. The slates contain muscovite, albite, quartz, chlorite, graphite, Fe-oxides, apatite and zircon with variable amounts of dolomite and locally contain 5 mm euhedral pyrite porphyroblasts. Quartz and albite both show a strong shape fabric (Fig. 2E, I, J) with typical aspect ratio of between 2 and 3 in thin sections. This together with strongly aligned muscovite and chlorite define a penetrative slaty cleavage. Minor beards of white mica perpendicular to σ_1 are occasionally developed in the margins of some quartz grains. A crenulation cleavage is present in the phyllosilicate-rich slates oriented at a high angle to the slaty cleavage (Fig. 1A). The calcareous slates contain lower proportions of phyllosilicates, and more dolomite; which has a fine grained granoblastic texture and is typically zoned with an Fe-rich rim. No talc has been observed in these rocks. Generally the southwest Highlands appears to be characterised by low temperature and perhaps high pressure greenschist facies metamorphism (Graham *et al*. 1983; Dempster 1992), in contrast to the higher temperature Barrovian metamorphism that dominates the areas to the northeast (Barrow 1893).

At Eilean Orasaig (NM79400 26600) the calcareous slates and metadolostones contain abundant brown elongate porphyroblasts up to 3 cm long that stand proud on weathered surfaces (Fig. 1). The porphyroblasts occur widely on the tidal island and also locally on the main island of Kerrera. Similar elongate porphyroblasts have also been observed on the mainland in the Easdale slates near Oban and on the island of Seil. They have straight or gently curving edges and elongate pyramidal terminations and hexagonal or square cross sections (Fig. 1D, E). Internal parts of the porphyroblasts are commonly partially dissolved on weathered surfaces (Fig. 1E). The porphyroblasts vary from small (ca. 2 mm) evenly dispersed grains in phyllosilicate-rich calcareous slates (Fig. 1B, C), to fewer larger crystals in the metadolostones (Fig. 1A). Elongate porphyroblasts commonly show a slight central offset in the alignment of the long axis of the crystal with double terminations or oppositely canted pyramidal terminations (Fig. 1D, E). Elongate porphyroblasts are typically aligned, especially the smaller grains, plunging at between 30-70^{o} towards the NE within the plane of the early upright cleavage (Fig. 1A-C). This alignment contrasts with bedding-cleavage intersection and crenulation lineations that plunge at shallow angles to the NE and SW respectively (Fig. 1A). Neither alignment or abundance of the porphyroblasts is linked to bedding structures. At Eilean Orasaig, the penetrative cleavage is typically near vertical, strikes towards the NE and is oriented at a high angle to bedding. Upright close-tight gently plunging parallel minor folds are associated with the axial planer cleavage. These have ca. 0.5-1 m scale wavelengths and are widely developed throughout Kerrera and are parasitic to larger folds with wavelengths of 10's of metres. Locally the minor folds are curvilinear. All elements of the deformation history of the Dalradian rocks on Kerrera may be correlated with the history reported from elsewhere within the Easdale slates and more widely with Dalradian rocks through the rest of the Scottish Highlands (e.g. Roberts & Treagus 1977).

Porphyroblast structure and relationship to fabric

The porphyroblasts are pseudomorphs with a concentric structure typically with a ca 100-500μm outer selvage of quartz and a core of calcite ± quartz ± pyrite or quartz ± pyrite (Fig. 2A, C, D). The outer rim of inclusion-free quartz tends to be wider (up to 500μm) at the pyramidal terminations (Fig. 2D). Such quartz is commonly fibrous and fibres may be intergrown with sparse chlorite and show curved morphology with a rotational symmetry (Fig. 2B). Other rims of clear quartz are coarser grained, especially those around cores dominated by either inclusion-rich quartz or pyrite. The pseudomorphs have sharp contacts with the matrix and typically there is no discernable disturbance of the fabric in the matrix near the porphyroblasts (Fig. 2E, I). Locally around the pyramidal terminations of a few porphyroblasts, the fabric is both intensified and is slightly bent in towards the apex of the porphyroblast (Fig. 2H). No pressure shadows are developed adjacent to the porphyroblasts and the fabric in the matrix does not wrap around the porphyroblasts. Calcite in the centre of the pseudomorphs is granular and commonly contains graphite and Fe-oxide inclusions and more rarely chlorite, muscovite and tourmaline (Fig. 2G). The boundary between the calcite and inclusion-free quartz fibres is often marked by inclusion-rich subhedral quartz, which may be in optical continuity with some individual fibres of quartz in the outer rim. Inclusion trails in calcite, quartz and pyrite all show an internal fabric, defined by metamorphic minerals (Fig. 2 E-I), that aligns with the cleavage in the matrix or shows small up to ca. 10^o rotation that matches the sense of rotation implied by the curvature of the quartz fibres. Finer grained calcite and quartz in the central areas of some pseudomorphs typically lack abundant inclusions, instead graphite and Fe-oxides are concentrated on calcite grain boundaries (Fig. 2D, E). Some porphyroblasts, especially the smaller ones, are dominated by inclusion-rich quartz and lack a central calcite core. Pyrite is associated with calcite in the core of some pseudomorphs and also forms in a rough concentric structure around calcite (Fig. 2C). It shows a replacement texture with the calcite and quartz that is similar to that between the early formed calcite and the later inclusion-rich quartz. Samples commonly contain both pyrite cubes and replacement pyrite.

Origin of the porphyroblasts

No relicts of original porphyroblast minerals are preserved, although they are likely to be chemically similar to calcite, the first phase of replacement. The quartz fringes that surround the pseudomorphs are interpreted as a growth from a Si-saturated fluid that fills the cavities formed during a volume decrease associated with the initial replacement reaction. On the basis of 18 measured pseudomorphs, the solid volume loss is 47±9%. This is likely to be a minimum, due to many of the porphyroblasts being cut across the long axis and some minor tightening of the fabric near the ends of the porphyroblasts (Fig. 2H). Coupled to the distinctive elongate shape with scalenohedral terminations (Fig. 1E); the initial replacement by calcite (Fig. 2A); and their presence in organic-rich calcareous slates allow the original mineralogy to be inferred. These elements all point towards the porphyroblast being glendonite (Fig. 1F), a pseudomorph of hydrated calcium carbonate, ikaite (Swainson & Hammond 2001). The pseudomorphs are typically small in comparison to modern examples of glendonite, but bear a remarkable similarity in crystal morphology to those from recent sediments (Fig. 1F), although interpenetrating and stellate forms commonly present in the latter (James *et al*. 2005) have not been observed. Ikaite is replaced by calcite with a volume change of ca 67% (Swainson & Hammond 2001) and fibrous quartz grows into the resulting cavities. Locally minor warping of the external fabric occurs associated with this volume reduction around the ends of the porphyroblast. The inclusion-rich calcite is then replaced, or partially replaced, firstly by quartz and then by pyrite. Some recrystallisation of relict calcite may result in the granular texture and concentrate original inclusions along grain boundaries.

Pseudomorphs after both ikaite and gypsum in various states of preservation are reported in other Dalradian rocks (Spencer 1971; Anderton 1975; Johnston 1995; Hutton & Alsop 1996), although all are interpreted as syn-sedimentary. Gypsum is unlikely to be the parent porphyroblast as the well-preserved crystal habit is not bladed, lenticular or tabular. A solid volume reduction of 38% occurs associated with replacement of gypsum by anhydrite at higher temperatures (Robie *et al*. 1978), below the minimum recorded in the initial replacement reaction.

Interpretation

Porphyroblast-matrix microstructural evidence from the inclusion trails indicate that the precursor porphyroblast grew after the slaty cleavage was formed (Fig. 2E, I); a cleavage which is axial planer to the typically tight upright folds. Folds and associated fabrics may develop in sedimentary successions during slumping (Woodcock 1976; Alsop & Marco 2014) and later mimetic growth may be superimposed on such alignment. However, the following evidence indicates that the fabrics and folds are not syn-sedimentary. Porphyroblast growth occurs within lithified rocks; inclusions of metamorphic minerals occur within the porphyroblasts; structures appear to be part of an established regional sequence developed throughout the Dalradian succession (Roberts & Treagus 1977); and there is no evidence of early localised deformation on Kerrera that predates this history. In addition fabrics associated with slump folds are unlikely to be consistently upright across a large area. Hence the fabric, which is linked to strong shape development in both quartz and plagioclase (Fig. 2J), is tectonic rather than diagenetic, compaction- or slump-related (cf. Alsop & Marco 2014). Porphyroblast alignment (Fig. 1A-C) also points to a metamorphic origin that is associated with active deformation events. The alignment does not reflect a later reorientation of existing grains because of the lack of structural disturbance of the porphyroblasts themselves; the lack of pressure shadows adjacent to the porphyroblasts; and, the lack of any wrapping of the tectonic fabrics around porphyroblasts. Their subsequent replacement was also associated with active deformation as evidence of rotation is preserved in the quartz fibres (Fig. 2B). Thus both original growth of the ikaite porphyroblasts and their subsequent alteration/replacement are metamorphic features linked to ductile deformation. Ikaite psuedomorphs have not previously been reported as a metamorphic porphyroblast. Syn-sedimentary ikaite pseudomorphs in the geological record are typically well preserved (e.g. Fig. 1F), but examples within metamorphic rocks, such those reported from Dalradian rocks in Ireland by Johnston (1995), rarely survive metamorphic events. In contrast the pseudomorphs from the Easdale slates are well preserved, due to the porphyroblast growth occurring within lithified metamorphic rock and development of a protective quartz-rim during the initial volume change. Although a series of replacement reactions have occurred, the lack of subsequent major recrystallisation of the slates in a higher grade metamorphism also favoured their preservation.

Conditions of growth and cause of metamorphism

Ikaite is stable at very low temperatures (Marland 1975) at, or just below, the sediment-water interface (Pauly 1965; Suess *et al*. 1982) and glendonite has been used as a palaeoenvironmental indicator of near freezing surface conditions (Swainson & Hammond 2001; James *et al*. 2005; Selleck *et al*. 2007). Ikaite may grow within sea ice brines (Dieckmann *et al*. 2008) and during shallow diagenesis within organic-rich sediments (Suess *et al*. 1982), but all examples from the geological record are replaced by aggregates of calcite (Huggett *et al*. 2005). Ikaite is also stable at higher pressures (Shahar *et al*. 2005) (Fig. 3) and appears to be favoured by anoxic conditions, low P_{CO2} (Bischoff *et al*. 1993) and high pH and salinity (Hu *et al*. 2014). The growth of large euhedral ikaite porphyroblasts within bedrock slate would probably be favoured by the presence of liquid water, required to counter the kinetic paralysis associated with low temperatures. This together with evidence for growth post-dating ductile deformation argues that growth in slate is most likely to occur at depth in the crust (Fig. 3). This is a unique occurrence of ikaite and suggests that an unusual set of circumstances is responsible for its growth.

The slope of the ikaite-out reaction in P-T space is <4^{o}C/km (Shahar *et al*. 2005) (Fig. 3) and so, assuming average surface conditions, a geothermal gradient of substantially less than this is required to pass through the stability field of ikaite at depth (<1.5^{o}C/km). Geothermal gradients of ca. 15^{o}C/km have been proposed for adjacent areas (Graham *et al*. 1983) but are an order of magnitude greater than those capable of forming ikaite at depth. Indeed the gradients necessary to pass through the ikaite stability field are outside the range of equilibrium geotherms typical on Earth (Syracuse *et al*. 2010). Hence the geothermal gradient is likely to represent a transient and extreme state. There appear two possibilities for generating such conditions:

i) Low temperature, high pressure conditions can be temporarily generated during orogenesis as a consequence of slow thermal readjustments directly after thickening (England & Thompson 1984). Should ikaite stability at depth be associated with this scenario then it would require that the original Neoproterozoic sedimentary rocks were at, or close to, the Earth's surface immediately prior to thickening. This implies that the thickening event also occurred during the Neoproterozoic. Ikaite growth post-dates fabric development, so cold surface rocks must be carried to depth and low temperatures maintained during ductile deformation. This seems unlikely and the model also implies that ikaite growth should be a common feature of the early stages of any crustal thickening event. This is not the case and this explanation is rejected.

ii) An extreme lowering of the surface temperatures after initial ductile deformation and during orogenesis may explain the presence of ikaite. Permafrost conditions are known to extend into the crust to depths of up to 1 km during glacial events lasting ca. 1 Ma, with thermal disturbance to several kilometres depth associated with Holocene glaciation (Safanda *et al*. 2004). However a "normal" glaciation is incapable of influencing temperatures in the metamorphic realm (Lachenbruch & Marshall 1986). The dominant Barrovian metamorphism experienced by Dalradian rocks in the northeast and central Scottish Highlands occurred in the Ordovician (Dempster *et al*. 2002; Oliver *et al*. 2000; Baxter *et al*. 2002) whilst the Laurentian margin was at tropical latitudes (Cocks & Torsvik 2011). Mountain glaciers may have formed on the Grampian orogen after this crustal thickening event, however it is unlikely that the surface conditions would have been cold, or prolonged, enough to allow ikaite formation at depth. The Neoproterozoic was a time of extreme glaciation with lower temperatures at the Earth's surface, perhaps as low as -50°C (Hoffman & Schrag 2002). In addition, the Sturtian event may have lasted up to 50 Ma (Rooney *et al*. 2013), thus significantly increasing the depth to which subsurface freezing conditions may penetrate. Only the combination of extreme very cold surface air temperatures, long timescales and an absence of thermally-blanketing ice cover are capable of lowering metamorphic temperatures at depth (Fig. 3). The low temperatures may also favour more rapid rates of heat transfer in the shallow crust (Robertson 1988; Dempster & Persano 2006) and hence a lower geothermal gradient (Fig. 3). Even with such extreme conditions, a pre-existing low geothermal gradient and ikaite stability extended to higher temperatures are required (Fig. 3). This model also points towards Neoproterozoic thickening in the Dalradian rocks (Dempster & Bluck 1995; Alsop *et al*. 2000; Dempster *et al*. 2002; Hutton & Alsop 2004; Prave *et al*. 2009) and an ultra-low temperature metamorphism, linked to penetration of cold conditions below a Neoproterozoic orogenic unconformity somewhere in the succession above the Kerrera slates.

Timing of ultra-low temperature metamorphism.

Orogenesis during the Neoproterozoic may account for the patchy sedimentary record of glacial activity in the Dalradian basin, and hence the difficulty in correlating with the global stratigraphy (Prave *et al*. 2009). If the ultra-low temperature metamorphic event is linked to Gaskiers glaciation at ca. 580 Ma (Bowring *et al*. 2007), then orogenesis would likely post-date Southern Highland Group deposition (Dempster *et al*. 2002). However the Gaskiers glaciation appears to be a relatively short-lived localised event (Hebert *et al*. 2010), and consequently may have limited influence on temperatures at depth. If ikaite growth is associated with either the Marinoan glaciation at 635 Ma

(Hoffmann *et al*. 2004) or the long-lived Sturtian event at 662-717 Ma (Rooney *et al*. 2013), then a further implication is that the published stratigraphic position (Harris *et al*. 1994) of the Ballachulish slates (Rooney *et al*. 2010), and perhaps also the Kerrera/Easdale slates, requires a significant revision relative to the Port Askaig Tillite. In addition, an orogenic unconformity must be present between the deposition of the Easdale slates and the emplacement of the Tayvallich volcanics. The proposed depositional age of 659±9 Ma for the Ballachulish slates (Rooney *et al*. 2010) suggests that the Port Askaig Tillite is most likely associated with Marinoan glaciation. Hence the published stratigraphy would be incompatible with either a pre-Marinoan or pre-Sturtian metamorphism in rocks younger than the tillite. Irrespective of the exact timing of the Neoproterozoic ultra-low temperature metamorphism in these Dalradian slates, then early fold structures in the SW Highlands must also be of Precambrian age. This confirms evidence for Precambrian deformation from elsewhere in the belt (e.g. Rogers *et al*. 1989; Alsop *et al*. 2000; Hutton & Alsop 2004), and implies that suggested structural correlations between the older parts of the Dalradian succession and both the Palaeozoic rocks at the Highland Border (cf. Tanner 1995) and potentially the youngest part of the Dalradian succession must be re-examined. The extent of Precambrian metamorphism in the Dalradian rocks is unclear as below the distinctive permafrost layer, typical assemblages associated with crustal thickening may be difficult to distinguish from Ordovician assemblages.

These scenarios invoke extreme metamorphic conditions associated with orogenesis during a Neoproterozoic glacial event and extend the range of geothermal gradients that are possible in the Earth's crust. Ultra-low temperature metamorphism will be rare, only occurring during the most severe climatic events within sub-aerial successions, which lack the thermal blanketing effect of either glacial ice or sea-ice

(Rahmstorf 2002). Hence metamorphic ikaite will be unlikely to develop at depth below characteristic Neoproterozoic glacial sequences that form in marine basins. The evidence of ultra-low temperature metamorphism will also be readily lost from orogenic settings with sub-aerial exposure, either overprinted by prograde post-glaciation heating events or destroyed by subsequent erosion of the crustal rocks effected by the permafrost. Consequently the imprint of this unusual Neoproterozoic metamorphism will be difficult to recognize. The extent of ultra-low temperature metamorphism in Scotland is unclear, it is only due to the unusually low grades of the subsequent Ordovician regional metamorphism in the SW Highlands that the evidence survives. The development of ikaite at depth may be an important indicator of the intensity and longevity of glacial events and whilst long timescales are required to develop deep bedrock permafrost within the exposed crust, equally long timescales will be needed for the thaw of the permafrost layer to take place.

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References

ALSOP, G.I. & MARCO, S. 2014. Fold and fabric relationships in temporally and spatially evolving slump systems: A multi-cell flow model. *Journal of Structural Geology*, **63**, 27-49.

ALSOP, G.I., PRAVE, A.R., CONDON, D.J. & PHILLIPS, C.A. 2000. Cleaved clasts in Dalradian conglomerates: possible evidence for Neoproterozoic compressional tectonism in Scotland and Ireland? *Geological Journal* **35**, 87-98.

ANDERTON, R. 1975. Tidal flat and shallow marine sediments from the Craignish Phyllites, middle Dalradian, Argyll, Scotland. *Geological Magazine*, **112**, 337-348.

ANDERTON, R. 1979. Slopes, submarine fans and syn-depositional sedimentology of parts of the Middle and Upper Dalradian in the S.W. Highlands of Scotland. *In*: HARRIS, A.L., HOLLAND, C.H., & LEAKE, B.E. (Eds.), *The British Caledonides – Reviewed*, Special Publication of the Geological Society, London 8, p. 483-488.

ANDERTON, R. 1985. Sedimentation and tectonics in the Scottish Dalradian. *Scottish Journal of Geology 21*, 407-436.

BARROW, G. 1893. On an intrusion of muscovite-biotite gneiss in the south-east Highlands of Scotland and its accompanying metamorphism . *Quarterly Journal of the Geological Society of London*, **49**, 330-358

BAXTER, E.F., AGUE, J.J., & DEPAOLO, D.J. 2002. Prograde temperature-time evolution in the Barrovian type-locality constrained by precise Sm/Nd garnet ages from Glen Clova, Scotland. *Journal of the Geological Society, London*, **159**, 71-82.

BISCHOFF, J.L., FITZPATRICK, J.A. & ROSENBAUER, R.J. 1993. The solubility and stabilization of ikaite ($CaCO_3.6H_2O$) from 0^o to 25^oC: Environmental and paleoclimatic implications for thinolite tufa. *Journal of Geology*, **101**, 21-33.

BOWRING, S.A., GROTZINGER, J., CONDON, D.J., RAMEZANI, J. & NEWALL, M. 2007. Geochronologic constraints on the chronostratigraphic framework of the Neoproterozoic Huqf Supergroup, Sultanate of Oman. *American Journal of Science,* **307**, 1097-1145.

Brasier, M.D. & Shields, G. 2000. Neoproterozoic chemostratigraphy and correlation of the Port Askaig glaciation, Dalradian Supergroup of Scotland. *Journal of the Geological Society London* **157**, 909-914.

Cocks, L.R.M. & Torsvik, T.H. 2011. The Palaeozoic geography of Laurentia and western Laurussia: A stable craton with mobile margins. *Earth Science Reviews*, **106**, 1-51.

Dieckmann, G.S., Nehrke, G., Papadimitriou, S., Göttlicher, J., Steininger, R., Kennedy, H., Wolf-Gladrow, D. & Thomas, D.N. 2008. Calcium carbonate as ikaite crystals in Antarctic sea ice. *Geophysical Research Letters*, **35**, L08501.

Dempster, T.J. 1992, Zoning and recrystallization of phengitic micas: implications for metamorphic equilibration. *Contributions to Mineralogy and Petrology*, **109**, 526-537.

Dempster, T.J. & Bluck, B.J. 1995. Regional metamorphism in transform zones during supercontinent breakup: late Proterozoic events of the Scottish Highlands. *Geology* **23**, 991-994.

Dempster, T.J. & Persano, C. 2006. Low temperature thermochronology: Resolving geotherm shapes or denudation histories? *Geology* **34**, 73-76.

Dempster, T.J., Rogers, G., Tanner, P.W.G., Bluck, B.J., Muir, R.J., Redwood, S.D., Ireland, T.R. & Paterson, B.A. 2002. Timing of deposition, orogenesis and glaciation within the Dalradian rocks of Scotland: constraints from U-Pb zircon ages. *Journal of the Geological Society, London.* **159**, 83-94.

Dickens, B. & Brown, W.E. 1970. The crystal structure of calcium carbonate hexahydrate at ~120°C. *Inorganic Chemistry*, **9**, 480–486.

England, P.C. & Thompson, A.B. 1984. Pressure-Temperature-Time paths of regional metamorphism I. Heat transfer during the evolution of regions of thickened continental crust. *Journal of Petrology*. **25**, 894-928.

FAIRCHILD, I. & KENNEDY, M.J. 2007. Neoproterozoic glaciation in the Earth System. *Journal of the Geological Society, London*. **164**, 895-921.

GRAHAM, C.M., GREIG, K.M., SHEPPARD, S.M. & TURI, B. 1983. Genesis and mobility of the CO_2-H_2O fluid phase during regional greenschist and amphibolite facies metamorphism: a petrological and stable isotope study in the Scottish Dalradian. *Journal of the Geological Society, London.* **140**, 577-599.

HARRIS, A.L., HASELOCK, P.J., KENNEDY, M.J. & MENDUM, J.R. 1994. The Dalradian Supergroup in Scotland, Shetland and Ireland. *In*: GIBBONS, W. & HARRIS, A.L. (eds) *A revised correlation of Precambrian rocks in the British Isles*. Geological Society of London Special Report **22**. 33-53.

HEBERT, C.L., KAUFMAN, A.J., PENNISTON-DORLAND, S.C. & MARTIN, A.J. 2010. Radiometric and stratigraphic constraints on terminal Ediacaran (post-Gaskiers) glaciation and metazoan evolution. *Precambrian Research*.**182**, 402-412.

HOFFMAN, P.F. & SCHRAG, D.P. 2002. The snowball Earth hypothesis: Testing the limits of global change. *Terra Nova* **14**, 129-155.

HOFFMANN, K.H., CONDON, D.J., BOWRING, S.A. & CROWLEY, J.L. 2004. A U-Pb zircon date from the Neoproterozoic Ghaub formation, Namibia: constraints on Marinoan glaciation. *Geology* **32**, 817-820.

HU Y.-B., WOLF-GLADROW, D.A., DIECKMANN, G.S., VÖLKER, C. & NEHRKE, G. 2014. A laboratory study of ikaite ($CaCO_3.6H_2O$) precipitation as a function of pH, salinity, temperature and phosphate concentration. *Marine Chemistry*, **162**, 10-18.

HUGGETT, J.M., SCHULTZ, B.P., SHEARMAN, D.J. & SMITH, A.J. 2005. The petrology of ikaite pseudomorphs and their diagenesis. *Proceedings of the Geological Association.* **116**, 207-220.

HUTTON, D.H.W. & ALSOP, G.I. 1996. The Swilly Slide: A major synmetamorphic, extensional, ductile fault in the Dalradian of Donegal. *Irish Journal of Earth Sciences.* **15**, 41-57.

HUTTON, D.H.W. & ALSOP, G.I. 2004. Evidence for a major Neoproterozoic orogenic unconformity within the Dalradian Supergroup of NW Ireland. *Journal of the Geological Society, London.* **161**, 629-640.

JAMES, N.P., NARBONNE, G.M., DALRYMPLE, R.W. & KYSER, T.K. 2005. Glendonites in Neoproterozoic low-latitude, interglacial, sedimentary rocks, northwest Canada: Insights into the Cryogenian ocean and Precambrian cold-water carbonates. *Geology* **33**, 9-12.

JOHNSTON, J.D. 1995. Pseudomorphs after ikaite in a glaciomarine sequence in the Dalradian of Donegal, Ireland. *Scottish Journal of Geology.* **31**, 3-9.

LACHENBRUCH, A.H. & MARSHALL, B.V. 1986. Changing climate: Geothermal evidence from permafrost in the Alaskan Arctic. *Science* **234**, 689-696.

LUI, M. & YUND, R.A. 1993. Transformation kinetics of polycrystalline aragonite to calcite: new experimental data, modelling and implications. *Contributions of Mineralogy and Petrology* **114**, 465-478.

MARLAND, G. 1975. The stability of $CaCO_3.6H_2O$ (ikaite). *Geochimica et Cosmochimica Acta* **39**, 83-91.

MCCAY, G.A., PRAVE, A.R., ALSOP, G.I. & FALLICK, A.E. 2006. Glacial trinity: Neoproterozoic Earth history within the British-Irish Caledonides. *Geology* **34**, 909-912.

OLIVER, G.J.H., CHEN, F., BUCHWALDT, R. & HEGNER, E. 2000. Fast tectonometamorphism and exhumation in the type area of Barrovian and Buchan zones. *Geology* **28**, 459-462.

PAULY, H. 1963. “Ikaite”, a new mineral from Greenland. *Arctic*, 16, 263–264.

PRAVE, A.R., FALLICK, A.E., THOMAS, C.W. & GRAHAM, C.M. 2009. A composite C-isotope profile for the Neoproterozoic Dalradian Supergroup of Scotland and Ireland. *Journal of the Geological Society, London*. **166**, 845-857.

RAHMSTORF, S. 2002. Ocean circulation and climate during the past 120,000 years. *Nature*, **419**, 207-214.

ROBERTS, J.L. & TREAGUS, J.E. 1977. Polyphase generation of nappe structures in the Dalradian rocks of the southwest Highlands of Scotland. *Scottish Journal of Geology*, **13**, 237-254.

ROBERTSON, E.C. 1988. Thermal properties of rocks. *U.S. Geological Survey Open file Report*. 88-441.

ROBIE, R.A., HEMMINGWAY, B.S. & FISHER, J.R. 1978. Thermodynamic properties of minerals and related substances at 298.15K and 1 Bar (10^5 Pascals) pressure and at higher temperatures. *U.S. Geological Survey Bulletin*. **1452**.

ROGERS, G., DEMPSTER, T.J., BLUCK, B.J. & TANNER, P.W.G. 1989. A high precision U-Pb age for the Ben Vuirich granite: implications for the evolution of the Scottish Dalradian Supergroup. *Journal of the Geological Society, London*, **146**, 789-798.

ROONEY, A.D., CHEW, D.M. & SELBY, D. 2011. Re-Os geochronology of the Neoproterozoic-Cambrian Dalradian Supergroup of Scotland and Ireland: Implications for Neoproterozoic stratigraphy, glaciation and Re-Os systematics. *Precambrian Research*. **185**, 202-214.

ROONEY, A.D., MACDONALD, F.A., STRAUSS, J.V., DUDÁS, F.Ö., HALLMANN, C. & SELBY, D. 2013. Re-Os geochronology and coupled Os-Sr isotope constraints on the Sturtian snowball Earth. *Proceedings of the National Academy Science.* doi:10.1073/pnas.1317266110.

Safanda, J., Szewczyk, J. & Majorowicz, J. 2004. Geothermal evidence of very low glacial temperatures on the rim of the Fennoscandian ice sheet. *Geophysical Reearch Letters*. **31**, L07211.

Selleck, B.W., Carr, P.F. & Jones, B.G. 2007. A review and synthesis of glendonites (pseudomorphs after ikaite) with new data assessing applicability as recorders of ancient coldwater conditions. *Journal of Sedimentary Research*. **77**, 980-991.

Shahar, A., Bassett, W.A., Mao, H-K., Chou, I-M. & Mao, W. 2005. The stability and Raman spectra of ikaite, $CaCO_3.6H_2O$, at high pressure and temperature. *American Mineralogy* **90**, 1835-1839.

Soper, N.J. 1994. Neoproterozoic sedimentation on the northeast margin of Laurentia and the opening of Iapetus. *Geological Magazine* **131**, 291-299.

Soper, N.J., Ryan, P.D. & Dewey, J.F. 1999. Age of the Grampian orogeny in Scotland and Ireland. *Journal of the Geological Society, London*, **156**, 1231-1236.

Spencer, A.M. 1971. Late Pre-Cambrian Glaciation in Scotland. *Memoir of the Geological Society of London* **6**.

Strachan, R.A. & Holdsworth, R.E. 2000. Late Neoproterozoic (<750 Ma) to Early Ordovician passive margin sedimentation along the Laurentian margin of Iapetus. *In*: Woodcock, N.H. & Strachan, R.A. (eds) *Geological History of Britain and Ireland*. Blackwell Science Ltd. Oxford, 73-87.

Suess, E., Balzer, W., Hesse, K.-F., Muller, P.J., Ungerer, C.A. & Wefer, G. 1982. Calcium carbonate hexahydrate from organic rich sediments of the Antarctic shelf: precursors of glendonites. *Science* **216**, 1128–1131.

Swainson, I.P. & Hammond, R.P. 2001. Ikaite, $CaCO_3.6H_2O$: Cold comfort for glendonites as paleothermometers. *American Mineralogist.* **86**, 1530-1533.

SYRACUSE, E.M., VAN KEKEN, P.E. & ABERS, G.A. 2010. The global range of subduction zone thermal models. *Physics of the Earth and Planetary Interiors.* **183**, 73-90.

TANNER, P.W.G. 1995. New evidence that the Lower Cambrian Leny Limestone at Callander, Perthshire, belongs to the Dalradian Supergroup, and a reassessment of the 'exotic' status of the Highland Border Complex. *Geological Magazine* **132**, 473-483.

TREWIN, N.H., GURR, P.R., JONES, R.B. & GAVIN, P. 2012. The biota, depositional environment and age of the Old Red Sandstone of the island of Kerrera, Scotland. *Scottish Journal of Geology* **48**, 77-90.

WOODCOCK, N.H. 1976. Structural style in slump sheets: Ludlow series, Powys, Wales. *Journal of the Geological Society, London* 132, 399-415.

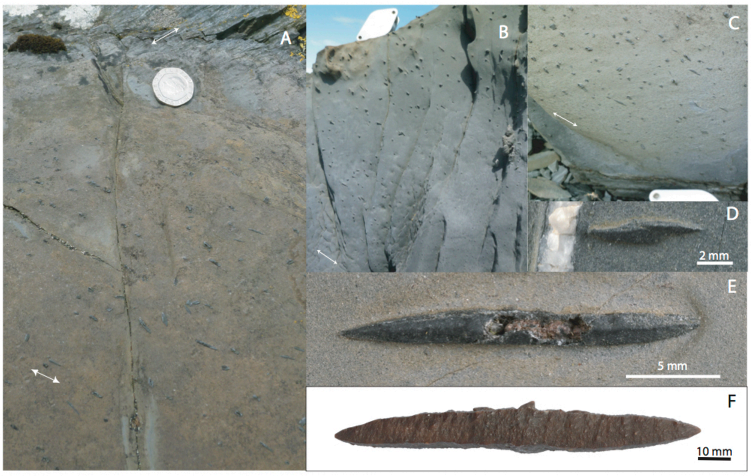
Figure Captions.

Figure 1. Kerrera Slates. A: Bed of metadolostone with aligned ikaite pseudomorphs plunging (lower arrow) in the plane of the cleavage towards the NE, crenulation lineation in the slates is marked by upper arrow (Coin is 2 cm diameter); B: Aligned ikaite pseudomorphs in calcareous slate steeply plunging (arrow) to the NE. Pseudomorph size decreases towards lower part of exposure (Hand lens is 5 cm long); C: Aligned ikaite pseudomorphs in calcareous slates, arrow shows alignment of elongate grains (Hand lens for scale); D and E: Large elongate ikaite pseudomorphs with pyramidal terminations from the Easdale Slates; F: Specimen of ikaite pseudomorph dredged from River Clyde near Cardross (Calcite after Ikaite, courtesy of Glasgow Museums Collections, G1988-50).

Figure 2. Thin section photomicrographs of ikaite pseudomorphs, plane polarized light unless stated otherwise. A: Clear quartz rim around inclusion-rich calcite core, with minor replacement of calcite by inclusion rich quartz; B: Crossed polarized light view of (A) showing quartz fibres and rotational symmetry; C: Ikaite pseudomorph with calcite (Cal) core, pyrite (Py) mantle and quartz (Qtz) rim, clear quartz rim surrounds inclusion rich quartz (Qtz(i)); d: Pseudomorph with clear quartz rim and calcite and inclusion-rich quartz core with concentration of Fe-oxides on grain boundaries between Cal and Qtz. Box shows location of figure 2E; E: High magnification image of pseudomorph edge showing similar alignment of inclusions within quartz (central arrow) and alignment within matrix (lower right arrow); F: Backscattered electron (BSE) image showing aligned inclusions (arrow) within pyrite; G: BSE image of pseudomorph in dolomite-rich slate showing aligned inclusions (arrow) of Fe-oxides (bright) and phyllosilicates (grey) within calcite core; H: Pseudomorph edge showing alignment of inclusions within quartz (left arrow) is the same as mineral alignment in the matrix (right arrow); I: Crossed polarized light view of pseudomorph edge showing identical alignment of matrix minerals (left arrow) and inclusions within quartz (right arrow). Alignment in matrix (lower left of image) is defined by a combination of phyllosilicates and quartz with a shape fabric (above and to the right of the arrow); J: Crossed polarized light view of matrix of Easdale slate showing strong preferred alignment of muscovite laths and parallel well developed shape fabric of quartz and plagioclase.

Figure 3. P-T phase diagram showing stability field of ikaite (Bischoff *et al*. 1993; Shahar *et al*. 2005), with reference lines of example geothermal gradients and (NP) estimated Neoroterozoic geothermal gradient; based on 10^{o}C/km initial geotherm, 50^{o}C fall in surface temperature for 10 Ma, thermal diffusivity of ca. 10^{-6} m^2sec^{-1} with an increased rate of heat transfer in cold crust (Robertson 1988). Conditions for calcite –

Aragonite transformation from Lui & Yund (1993). Note: even with these extreme conditions some expansion of the stability field of ikaite towards higher temperature is required.


A
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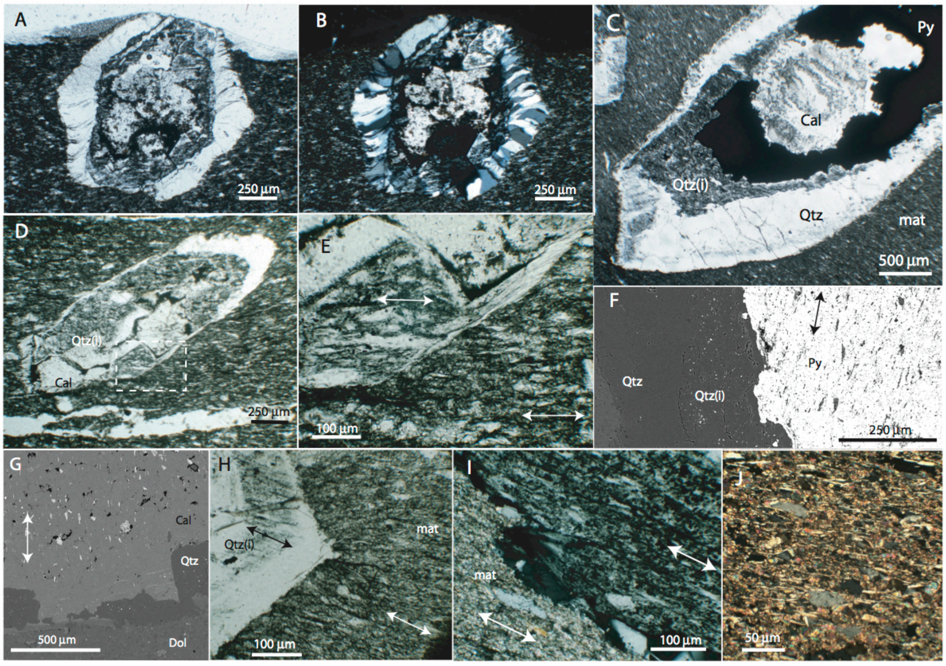
A
250 µm
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Cal
250 µm
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mat
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I
mat
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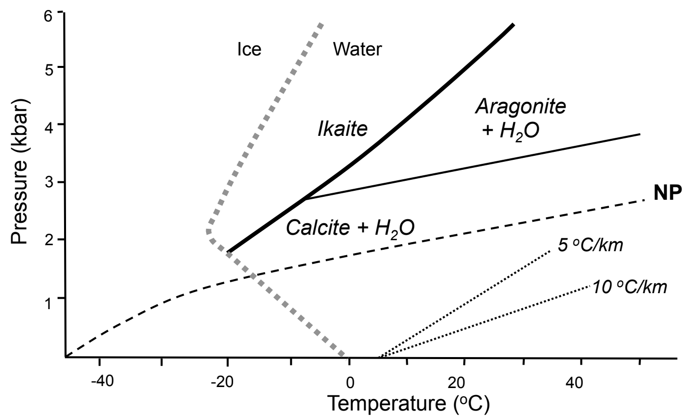
50 µm



Ice
Water
Ikaite
Aragonite
+ H_2O
NP
Calcite + H_2O
5 °C/km
10 °C/km
Pressure (kbar)
6
5
4
3
2
1
-40
-20
0
20
40
Temperature (°C)