



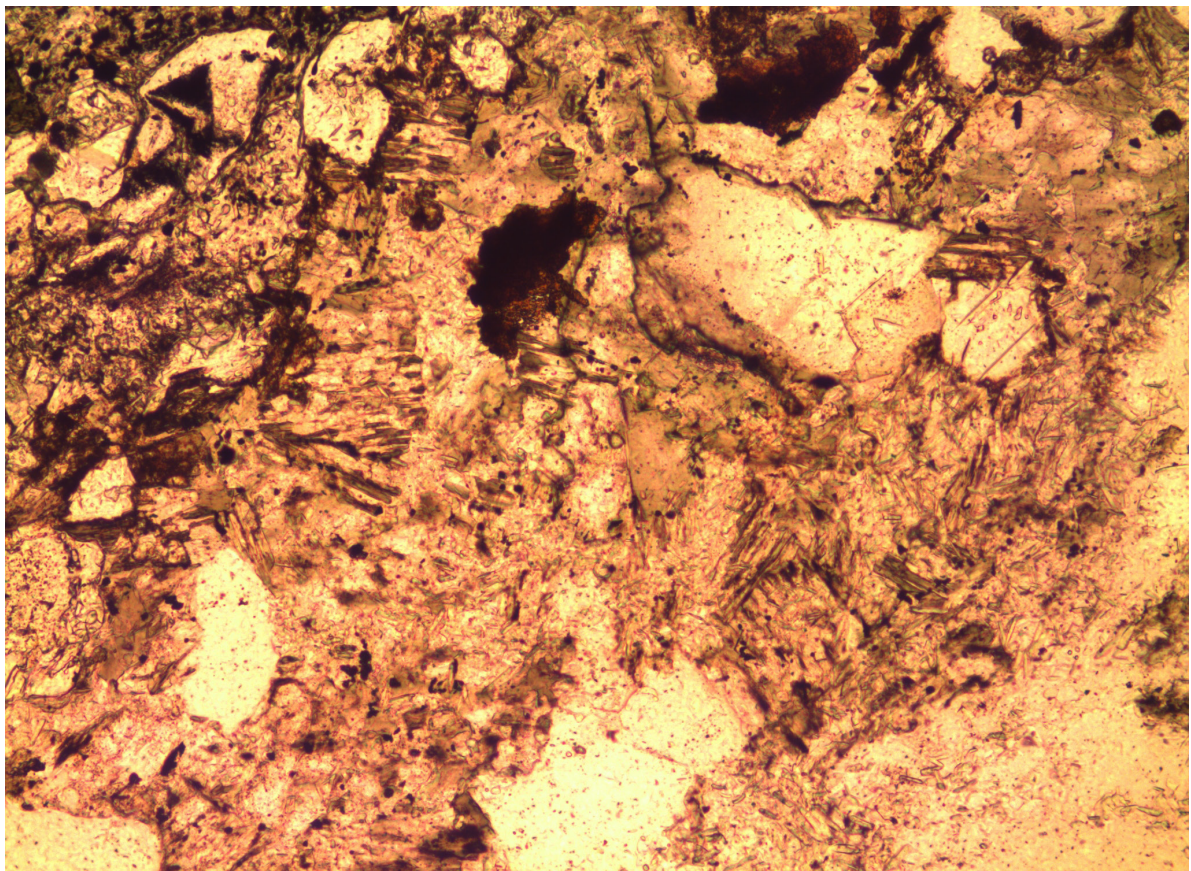
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Investigation of the mineralogy and composition of the Fe-oxide-rich layers of the Neoproterozoic Snowball Earth sequence on Islay and Garvallach Island

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Abstract

The aim of this study is to describe and classify the Fe-oxide-rich layers on Islay and Garvellach, Scotland that are deposited in the Neoproterozoic Snowball Earth sequence on the islands.. Records of glacial deposition on the islands is the Port Askaig Tillite overlaying the Islay Limestone and underling the Bonahaven Dolomite this indicates a rapid change in climate from warm to glaciation and rapid back to tropical climate. The Fe-oxide layers on the both islands appear in the Port Askaig Tillite and are estimated to be roughly the same age, but they differ in their character. Petrographic microscopy and Scanning Electron Microscopy (SEM) where used for this study. The Islay rock sample show clastic metasedimentary rock metamorphosed to biotite grade. With mineral abundant of quartz and the Fe-oxides constitutes 15-30% of the sample. The Garvellach sample is fine-grained that constitutes 50-90% Fe-oxide in the form of hematite blended with fine-grain quartz and should most likely be classified as a banded iron formation (BIF). The relationship between the Islay and Garvellach samples is unclear.

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Introduction

The Snowball Earth is a theory suggesting global glaciation in the Neoproterozoic era that was first put forward by Kirschvink in 1989. The development of the theory began when one of Kirschvink's students was given a rock sample from the Elatina formation in South Australia to analyse for her senior thesis. The rock was a glacially deposited siltstone but palaeomagnetic evidence suggested that the rock had been deposited close to the equator. The article describes investigation of 16 different Neoproterozoic-aged glacially produced rock units from around the world with paleomagnetic evidence indicating deposition at latitudes of between 10° and 60°. The Neoproterozoic glacial deposits occur on all continents and most are overlain by "cap" dolostone suggesting a rapid change back to warm climate after the glaciation. In the article Kirschvink put forward the idea that extensive equatorial ice cover caused a runaway albedo feedback that created the global ice cover by covering the ocean with an ice sheet and the continent with irregular thin covers of ice (Hoffman & Schrag, 2002).

A classical snowball earth rock sequence would consist of limestone deposited in a relatively warm climate overlain by tillite which is lithified glacial till indicating a cold climate which in turn is overlain with cap carbonate rock that are usually depleted in $\delta^{13}\text{C}$ and an indicator on a switch back to warm climate (Hoffman, et al., 1998; Stern, et al., 2006; Hoffman & Schrag, 2002). Banded Iron formation (BIF) is also present in the sequence and it is believed to be the result of ice cover sealing the ocean from the atmospheric O making the water anoxic and rich in dissolved Fe^{3+} that could later precipitate as BIF which are not otherwise observed in the sedimentary records since around 2 Ga (Hoffman, et al., 1998; Fairchild & Kennedy, 2007).

One of the most extensive and best-studied Neoproterozoic glacial rock sequences occurs on the islands of Islay and the Garvellachs on the west coast of Scotland. The Neoproterozoic snowball sequence on the Islands lies within the Argyll Group within the Dalradian Supergroup and is best exposed in the North East on Islay. Here the glacially deposited Port Askaig Tillite formation occurs between the underlying Islay Limestone and overlying Bonahaven Dolomite. Paleomagnetic evidence of the position of Islay at the time is not reliable due to later metamorphic processes that have remagnetization and distortion of the magnetic indicating minerals. However high latitude glaciation can be ruled out (Urrutia-Fucugauchi & Tarling, 1983). An Fe-oxide unit occurs within a within the Port Askaig Tillite on Islay and at the top of the tillite on the Garvellachs. The Fe-oxide layers on the both islands are estimated to be roughly the same age, but they differ in their physical appearance where the unit on Garvellach appears more as a BIF layer whereas the unit on Islay is more of an Fe-oxide bearing sedimentary rock. The glacial units on Islay and Garvellachs have been investigated in numerous articles but there has been as yet no systematic focus on the Fe-oxide units.

This study investigates the mineralogy and composition of the two Fe-oxide-rich layers of the Snowball Earth sequences on Islay and the Garvellach islands in the Inner Hebrides of Scotland. Petrographic microscopy and Scanning Electron Microscopy (SEM) are used to describe the mineralogy, mineral textures and qualitative chemical compositions of the minerals in the samples collected. The aims of the study are to:

- 1) Characterise and classify the Fe oxide layers on Islay and Garvellachs and to interpret the environmental conditions under which they formed.
- 2) Constrain the relationship between the two Fe-oxide units.

Key questions this thesis hopes to address is whether the Garvellach samples classify as real BIF based on the mineralogy and whether the Islay samples were formed by the same process or for example represent deposition of an eroded and reworked BIF.



Figure 1 image map of island of Islay location (from Google)

Snowball Earth

The background and the theory of Snowball Earth

Snowball Earth is a theory suggesting that in the Neoproterozoic and early Paleoproterozoic era (Hoffman, et al., 2017) a series of global-scale glacial events occurred that covered the whole or most of the earth's surface with ice. These events were each followed by rapid and extreme warming of the Earth (Stern, et al., 2006) with global mean surface temperature over 40 °C (Hoffman & Schrag, 2002). Three major groupings of glaciations occurred in this time, Sturtian 740-647 ma, Marinoan 660-635 ma and Gaskiers c. 580 ma (Fairchild & Kennedy, 2007). The Port Askaig formation on Islay, Scotland is one of the best exposed "snowball earth sequences" of rock record associated with both the Sturtian and Marinoan where the boundary between the two episodes is not clear (Fairchild, et al., 2017).

At the time of development of the Snowball Earth events, the landmasses were located near the equator with no landmasses close to the polar regions. With all the land located in subtropical regions the rate of silica weathering would have been high and increase consumption of atmospheric CO₂ leading to lower levels of atmospheric pCO₂ with an effect of cooling the global air temperature and eventually a cold planet (Marshall, et al., 1988; Fairchild & Kennedy, 2007). This cooling generated extensive glaciations on the continents located in equatorial regions which due to a positive albedo feedback (reflection of the sun's light and warmth) caused the ice sheets to grow bigger (Hoffman & Schrag, 2002). When the ice reached the critical latitude of 30° a Snowball Earth was inevitable due to the runaway albedo effect (Fairchild & Kennedy, 2007).

The ending of global Neoproterozoic glaciations is thought to be due to high levels of greenhouse gases generated from volcanoes still active under the ice cover and at some point, released out to the atmosphere out competing the ice albedo and causing warming and the start of ice melt (Stern, et al., 2006). The effect of this release of so much greenhouse gases were that was that the global mean

surface temperature rapidly increased and reached mean temperatures of c. 40°C (Hoffman & Schrag, 2002).

The rock types associated with Snowball Earth

For the rock types of a Snowball Earth event Stern (Stern, et al., 2006) list the following rocks as which when they occur in a sequence at low latitudes, provides evidence for the Snowball Earth. The origin of these rocks is associated with glacial deposition and later precipitation of carbonates and iron due to the extreme warm climate that followed the glacial period and the production of oxygen from the phytoplankton.

Dropstones

A dropstone is an isolated, angular (when not deformed) clast of rock hosted in sedimentary rock. The composition of the clast is commonly unrelated to that of the hosting sediment. The dropstone texture is a series of deformed layers in the surrounding sediment caused by the clast falling into the wet sediment on the lake or seafloor. The interpretation is that the rock clast must have been transported on the sea or lake surface by ice and then deposited when the ice starts to melt (Stern, et al., 2006).

Diamictites

Diamictites are a non-calcareous lithified terrigenous sedimentary rock that occur as poorly sorted polymictic conglomerates and breccias. They can form from many different procedures not necessary just from glaciers. Clasts with angular shape are usually more abundant in the Diamictites and similarities to modern day glacial moraines is an indicator of glacial origin. Identification of scratch marks or striations on the clasts is the best way to determine if the Diamictites are of glacial origin (Stern, et al., 2006)

Cap carbonates

These are thick layers (up to tens of meters) (Hoffman & Schrag, 2002) of pure dolostone and limestone that overlies the glacially deposited rock units and are an indicator of a rapid change in climate from glacial to tropical (Stern, et al., 2006). The Cap carbonates are thought to be much more rapidly deposited (tens of thousands up to $> 10^5$ - 10^6 years) than glacially deposited rock units that formed over millions of years (Stern, et al., 2006). What is distinctive about the Cap carbonates is that they are depleted in $\delta^{13}\text{C}$ in relation to Neoproterozoic carbonates (Hoffman & Schrag, 2002). It has also been reported that they commonly show lamination (cm-scale), hummocky cross-laminated, reverse and normal graded bedding (Stern, et al., 2006).

Banded Iron formation (BIF)

Banded Iron Formation (BIF) is a fine-grained sedimentary rock type with an iron content > 15 wt. % (Hoffman, et al., 2017), that are commonly light brown to red colour due to the presence of haematite and are commonly laminated or interbedded with chert (Konhauser, et al., 2017; Nichols, 2009). BIF deposition was common in Late Archean and Paleoproterozoic when the atmosphere was almost oxygen free and CO_2 levels much higher but have vanished when oxygen levels increased in the atmosphere and oceans until the Snowball Earth event when they are present again. The high levels of partial pressure of CO_2 lowered the pH of the ocean. The low pH water is a great reservoir for iron. To change the oxidation state for iron is dependent on Eh and pH. With rising concentrations of oxygen in oceans due to photosynthetic organisms the soluble Fe^{2+} got oxidized to insoluble Fe^{3+} and preceded to form the iron beds. There are two main BIF types. The Superior-type that were deposited in the Paleoproterozoic era and forms wide spread beds. It needs a change in water chemistry to precipitate the iron. Source of iron comes from continental weathering and transport to oceans by rivers. The iron accumulated in the deeper anoxic waters and with underwater currents transported up to the shallow oxygen water and precipitated out on the stable shelves. The other type is the Algoma-

type that were deposited in the Late Archean and are associated with weathering of volcanic lava and ash, hydrothermal activities and locally sources for the iron and deposition (Stern, et al., 2006; Nichols, 2009). BIF do not occur in the sedimentary records after 1.85 Ga until the Snowball Earth events (Hoffman, et al., 2017). Snowball Earth BIFs are suggested to have formed in a similar way to Superior type BIFs through oxidation of Fe²⁺ rich oceans. It is suggested that when the ice sheet was covering all the oceans surfaces that the water got anoxic and the Fe input from hydrothermal vents remained as dissolved Fe²⁺. The concentrations of Fe²⁺ could increase without interference from oxygen. When the ice started to melt and the oxygen levels in the oceans water increased the Fe²⁺ precipitated to non-soluble Fe³⁺ forming the iron formation (Stern, et al., 2006).

Simplified description of the geology on Islay

The geology of Islay (Figure 2) comprises the Dalradian supergroup exposed in the eastern part of the island and the Rhinns Complex exposed on the west. The Rhinns rocks are that consist of metamorphosed calc-alkaline igneous rocks are the oldest rocks on the island with ages around 1.8 Ga (Webster, et al., 2015). On the east of Islay, the Dalradian is exposed as of a series of Neoproterozoic sedimentary rocks that have been metamorphosed to greenschist facies (Skelton, et al., 2015). The Dalradian rocks on Islay belong to the Appin and Argyll subgroups of the Dalradian metasedimentary sequence. The Appin Group that is exposed in central Islay and contains a > 4 km-thick sequence of carbonates, mudstones and sandstones that have been deposited in shallow waters. The top of the Appin Group comprises of two units of carbonates that are separated by a metapelite. The lower unit is the Storakaig Limestone a blue-grey stratified micritic, oolitic and intraclastic limestone and the uppermost is the Lossit Limestone it contains of oolites and stromatolitic dolomite. The Appin is overlain by the Port Askaig Tillite which is part of the lowermost Argyll Group metasedimentary rocks. It is best exposed in northern Islay and contains of a c. 1 km-thick layer of glacially deposited rock. The Port Askaig Tillite is a diamictite rock containing dolomitic pebbles, cobbles and boulders in the lower part of the unit and with granites and other more exotic rocks in the top part. This reflects erosion from many ice advances were sediments from below the Tillite in the Dalradian being eroded until the basement of igneous and metaphoric rocks is reached. On top of the Port Askaig Tillite sits the Bonahaven Dolomite an indicator on warm climate. This dolomite unit contains features consistent with tropical shallow water to coastal deposition including wave-ripple lamination and stromatolites. On top of the Bonahaven Dolomite lies the Jura Quartzite which vary in thickness from about 5 km to the east and 1.5 km to the south-west (Webster, et al., 2015; Fairchild, et al., 2017).

The sequence from the Lossit Limestone through the Port Askaig Tillite to the Bonahaven Dolomite is interpreted as one of the worlds classic "Snowball Earth" sequences (Webster et al. 2015). Both limestone units contain stromatolites indicative of a warm climate whereas the tillite indicates abundant glacial events. The Lossit Limestone are dated to c. 635 ma. which would link the age of the Port Askaig Tillite to the Marinoan glaciation (Webster, et al., 2015) but ⁸⁷Sr/⁸⁶Sr values for limestone under the Port Askaig show similarities with rocks deposited pre-Sturtian. This would mean the Port Askaig Tillite correlates to the Sturian glaciation (Fairchild, et al., 2017). The Bonahaven Dolomite is the cap carbonate that followed the glaciation. (Webster, et al., 2015). Both the Lossit Limestone and the Bonahaven Dolomite are depleted in δ¹³C.

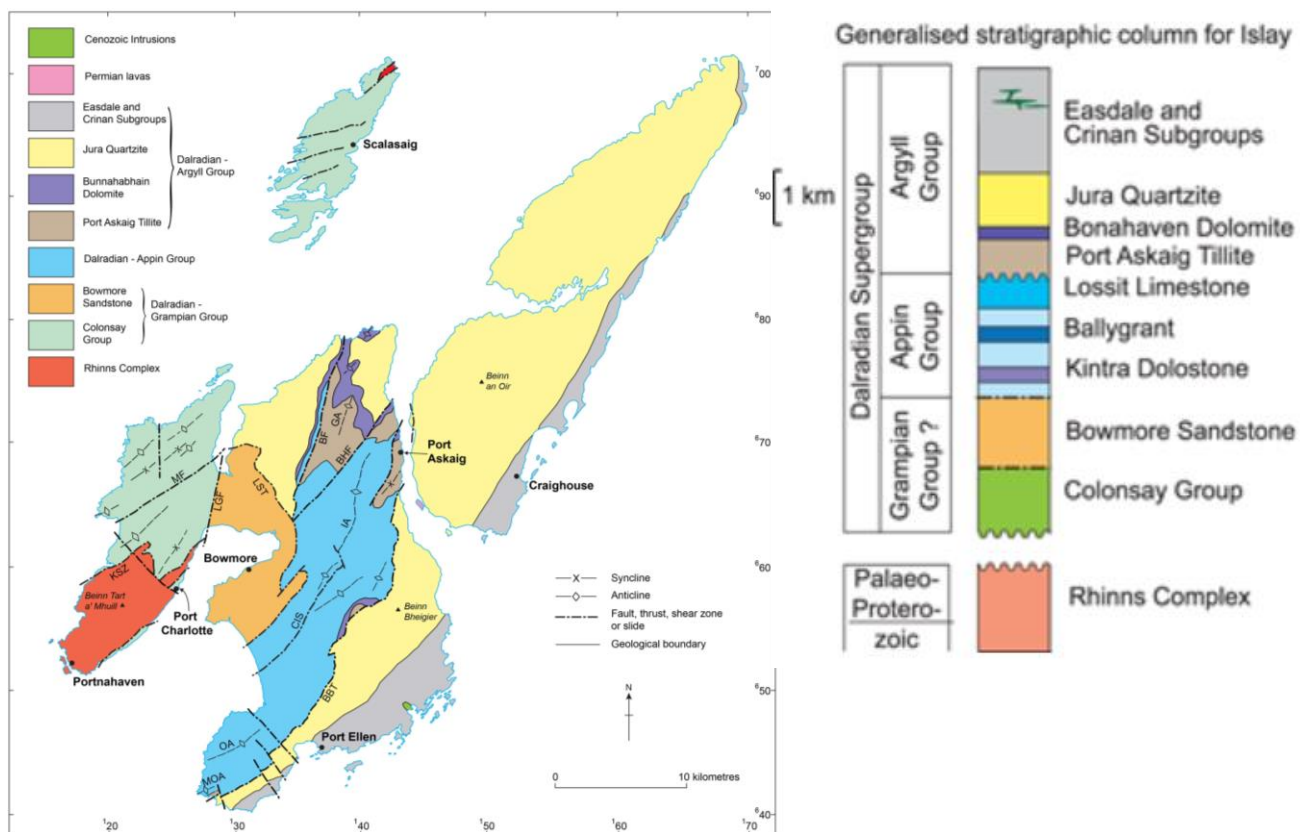


Figure 2 Simplified geological map of Islay and stratigraphic column. (Taken from: Webster, et al., 2015; Skelton, et al., 2015.)

Island of Garvellachs

The Garbh Eileach Formation is a part of the Appin Group and consists of a 70 m thick exposed carbonate rock unit, where the lower unit consists of a mixed limestone-dolomite and an upper section of dolomite with increasing quantity of siliciclastic sand. On top of the Garbh Eileach Formation Lays the Port Askaig Formation (Fairchild, et al., 2017).

Locations and sampling

The samples from Islay were collected from an outcrop near the summit of Beinnan Bhuidhe, on the eastern side of Loch Lossit in central Islay (Fig. 3). The sample was collected from the lower of the two light grey layers visible in the outcrop photo shown in figure 4. The sample from the Garvellach Islands the sample was collected on the southern end of Eilean Naomh (Fig. 5) from an outcrop exposed by a NW-SE striking fault (Fig. 6). Both samples are collected from a specific layer in the stratigraphy referred to as the “disrupted beds”, which occur within the lower part of the Port Askaig tillite unit (Figs. 3 and 6). The Fe-oxide bearing beds occur in roughly the same stratigraphic setting on Islay and the Garvellachs but show distinctly different size and form.

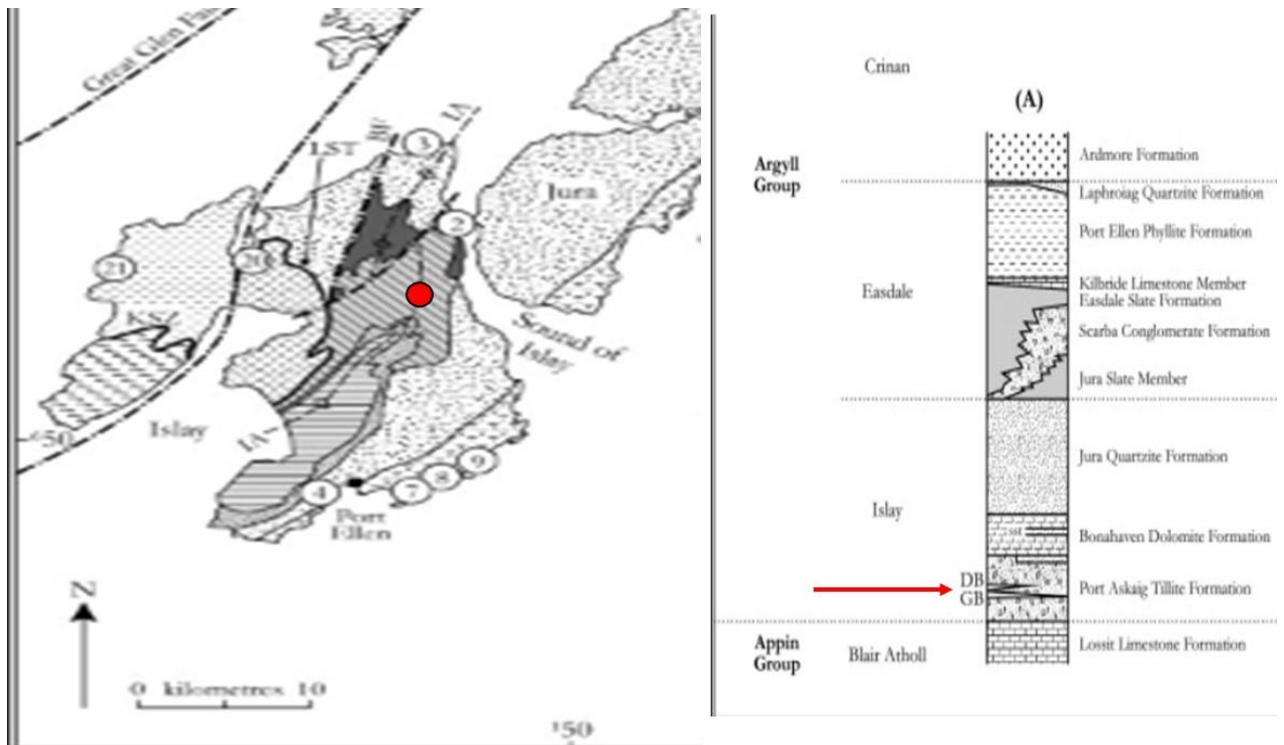


Figure 3 map of Islay showing the location (red dot) from whom the sample was collected. The red arrow point on where in the stratigraphy the sample occur. modified map from: Geoff Tanner, et al., 2013



Figure 4. Photograph of the disrupted beds on Islay where the sample was taken from. photo: private, Alasdair Skelton.

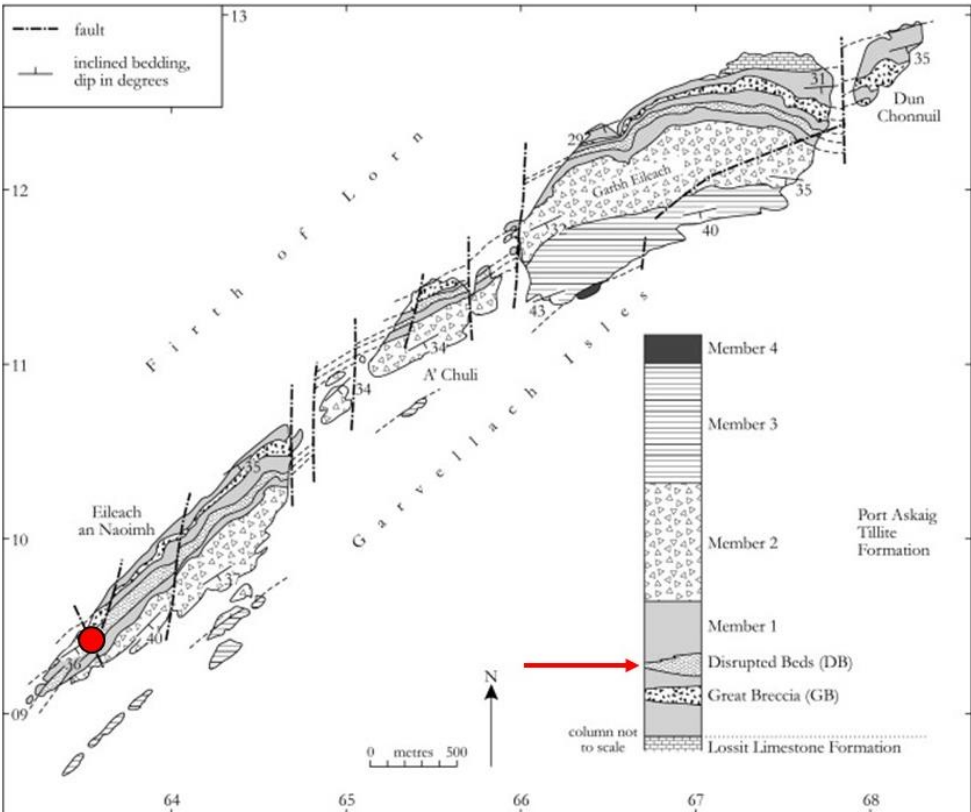


Figure 5 map of Garvellachs showing the location (red dot) from whom the sample was collected. The red arrow point on where in the stratigraphy the sample occur. modified map from: Geoff Tanner, et al., 2013



Figure 6 Photograph of the disrupted beds at Eilean Naoimh on Garvellachs where the sample was taken from. photo: private, Alasdair Skelton.

Methods

Optical microscopy

Four pieces of the rock sample from Islay was cut out to represent the important features of the rock (Fig. 7). The pieces were polished to thin sections (Southampton, U.K). The four thin sections and one from Garvellach were analysed by microscopy (Nikon eclipse 50i pol) both in transmitted light and by reflected light.

Mineral chemistry

The samples were investigated by Scanning Electron Microscope (SEM) in order to observe greater detail in mineral textures and constrain *qualitatively* the chemical composition of different mineral grains. Prior to analyses samples were carbon coated. The samples were investigated using the FEI Quanta FEG 650 SEM with Oxford instruments, X-MAX 80 mm² energy dispersive spectroscopy (EDS) detector. Chamber pressure was set to 0.10 mbar, working distance was 10 mm, spot 4.5 and voltage 20.00 kV. The instrument is calibrated using a Co metal standard to which all elemental spectra are matched. As only one standard is used and as it is not matrix –matched to the minerals being analysed, the values from the chemical analysis are not fully but are accurate enough to be used to identify the general composition of the minerals being analysed.



Figure 7 Photograph of the four pieces that were polished to thin sections and their part of the tranche from where they were cut. Top left represent thin section number 11, right top 12, the middle 13 and bottom 14.

Results

The results in this project are the sample and mineralogical description which are listed below. Combined descriptions using information from both the optical microscopy and SEM are presented and the qualitative composition of some minerals is also presented in tabulated form.

Sample: Garvellachs 1

Mineralogy: Hematite, Dolomite, Apatite, Baryte and Quartz

Mineralogical and textural description:

The rock sample is a fine grained with mesoband layering and veins zick-zacking through the sample. The layers are blackish and dark red colour as seen in fig 8. The sample consists mainly of hematite, dolomite and quartz with minor apatite and barite. The sample shows a laminated texture with large scale brecciation and veining also apparent. The opaque mineral hematite dominates the sample occurring as individual grains up to 50 microns in width and aggregates of anhedral grains. The shape of the hematite crystals varies from euhedral needles to more sub- to anhedral rounded and, angular to sub-angular grains. The proportion of hematite varies in the sample from layer with over 90% to around 50% in layers where hematite is blended with quartz in a matrix like texture (Figure 9). In the parts of the sample where dolomite is more abundant, the content of hematite decreases. The hematite mainly occurs as big interconnected aggregate which indicates it is a precipitate. The veins consist mainly of quartz and dolomite (Fig. 10). The carbonate and quartz in the veins show interlocking grain texture indicative of being precipitated from a fluid.

An interesting feature in the sample is the occurrence of large angular blocks and rounded with distinct rims (Fig. 11). The blocks are composed of intergrown hematite and dolomite and have a rim of dolomite and more minor baryte crystals surrounding them. The round circle is composed of dolomite and quartz with a rim of apatite and hematite.



Figure 8 Photograph of the Garvellach rock sample displaying the overall texture of the sample

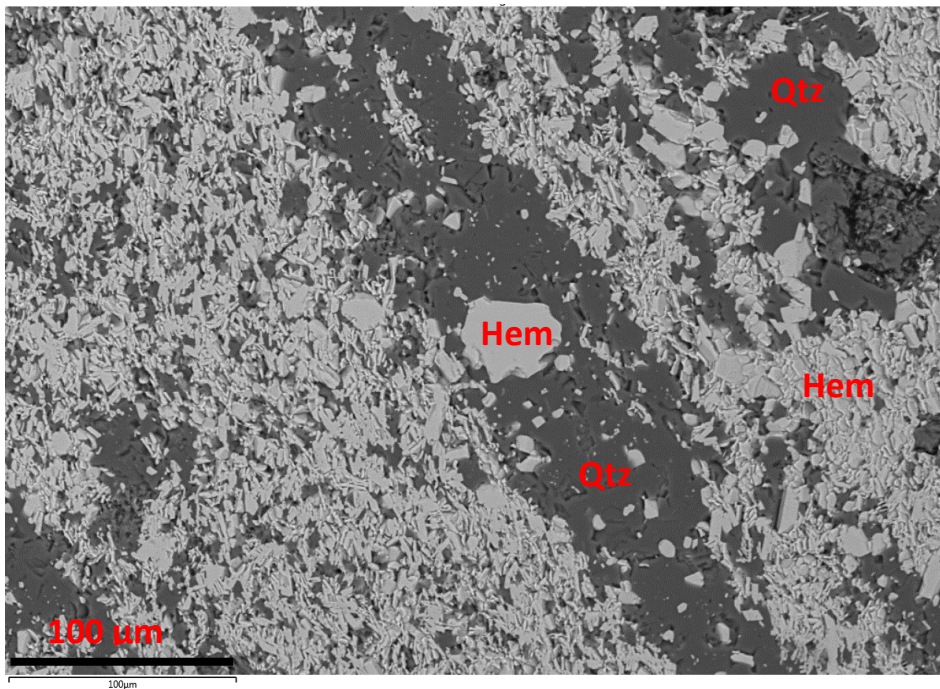


Figure 9 SEM backscatter image over a part of the Garvellach thin section sample showing the typical texture of the minerals present in the sample. Hem = Hematite, Qtz = Quartz

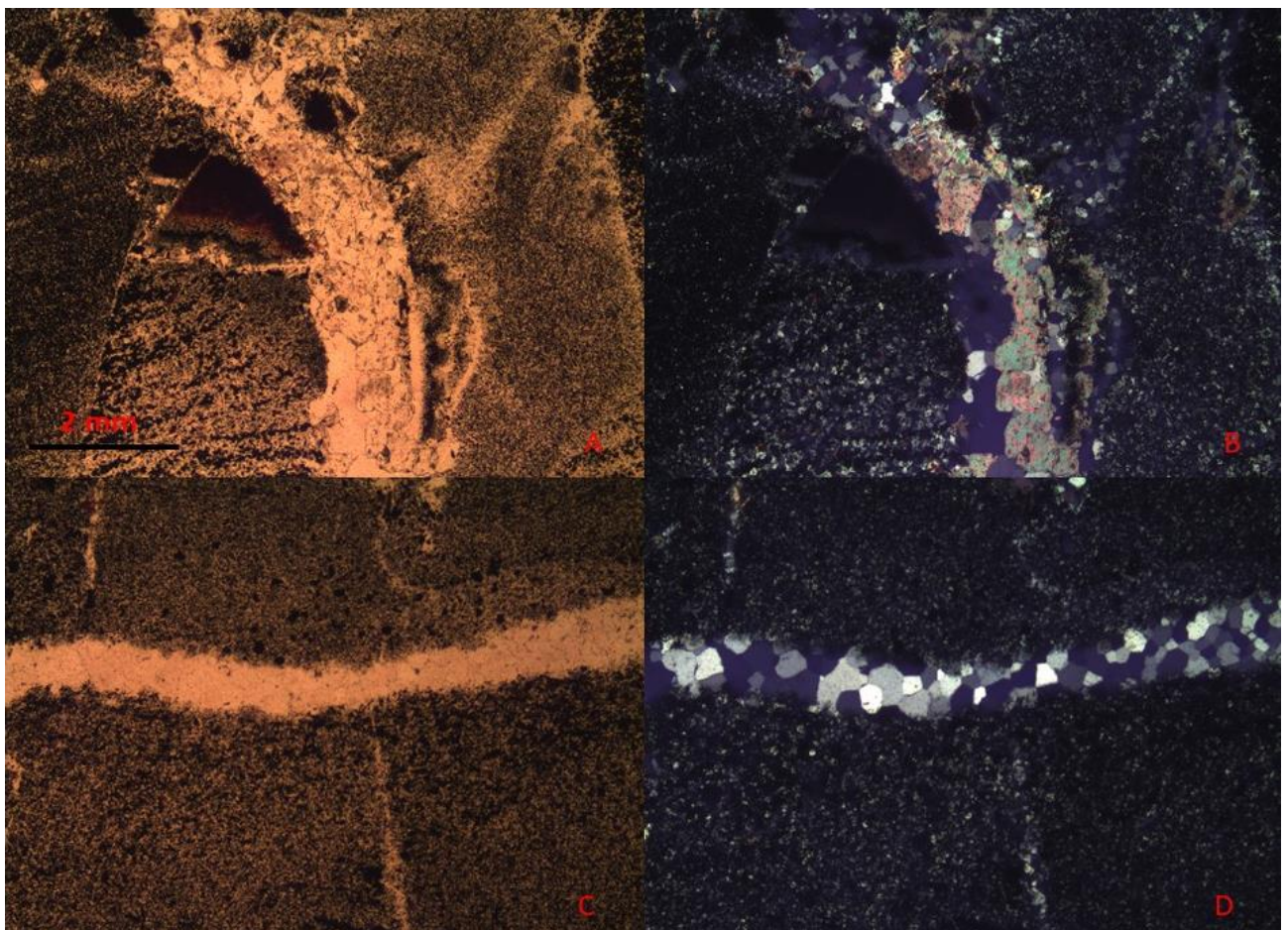


Figure 10 microscope photograph of the Garvellach thin section sample where A (upper left) shows the big vein in ppl that runs throughout the sample. B (upper right) shows the same vein but in xpl. C (down left) shows the pure quartz vein that runs through the matrix texture of hematite and quartz in ppl. D (down right) shows the same vein but in xpl.

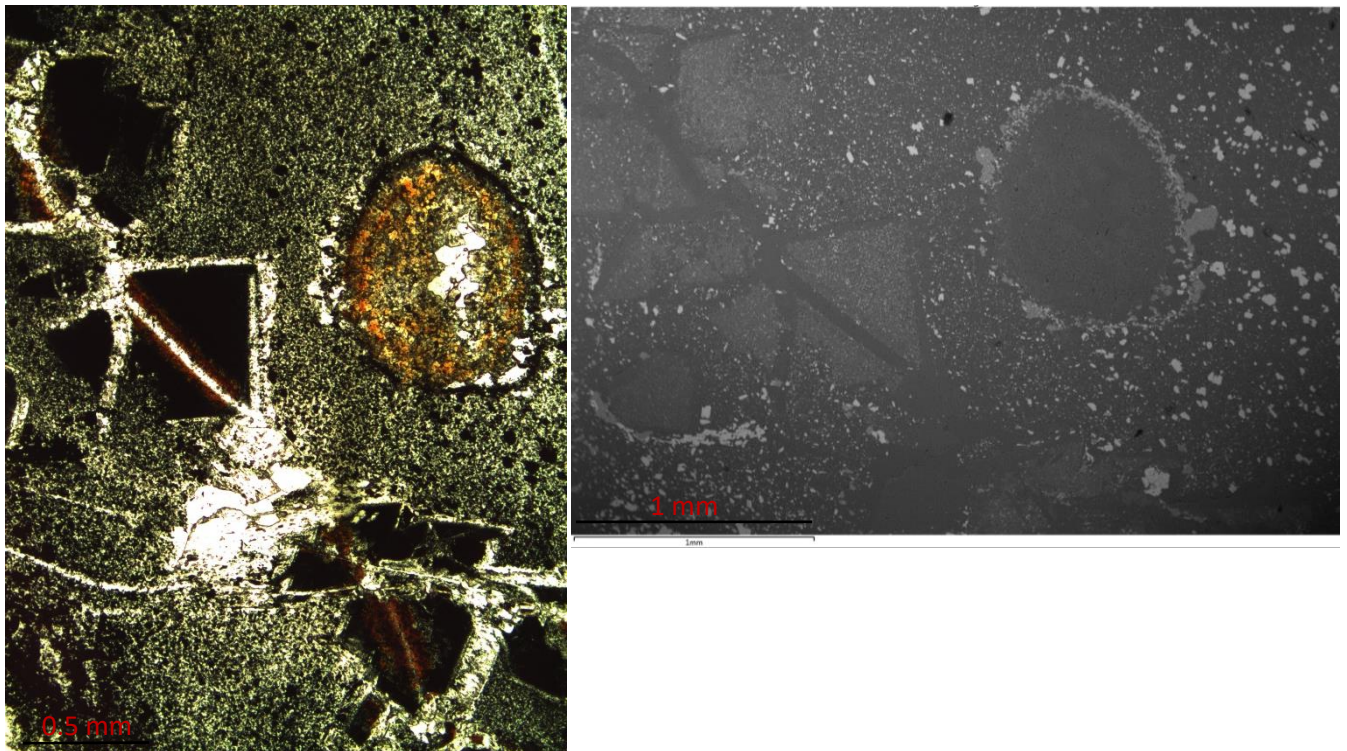


Figure 11 microscope photograph of the microscope over the Garvellach thin section sample viewing the breccia texture that are present in the sample. The left-hand side a photograph in ppl. Right-hand side a SEM backscatter image over the same texture.

The Islay rock sample.

The rock sample from Islay is a layered rock with coarser grained light-coloured layers with visible quartz clasts and darker coloured smoother finer grained layers. The black layers are more abundant in one part of the sample and are represented in samples I1 and I2 (fig. 7). In sample I4 the lighter layers with visible quartz clasts are more abundant.

Sample: Islay 4

Mineralogy: Quartz, Dolomite, Kaolinite, Biotite, Goethite, Hematite, plagioclase and Apatite.

Mineralogical and textural description:

The sample consists mainly of quartz, biotite, kaolinite, goethite, hematite, plagioclase and dolomite with minor apatite. The sample shows clastic texture and is relatively poorly sorted with fine-grained matrix. Quartz is the most abundant mineral together with dolomite and kaolinite and biotite that make up most of the matrix in the sample. The quartz clasts show large variation in size from 100 μm to 0.05 mm and varies from rounded to subangular. Goethite exists as anhedral grains throughout the sample and is the most abundant Fe-oxide. The crystals of hematite make up less than 10 % of the sample and are evenly distributed throughout the sample with grains sizes up to tens of microns and crystals shape that are angular to sub-angular and elongated to sub-round. Patches of fine grained quartz and plagioclase and some elongated biotite grains occur locally throughout the sample, and these patches are usually surrounded by the dolomite and opaque mineral matrix.

The sample contains a circular feature that consists of fine grained dolomite and some euhedral biotite and quartz grains. The circle has a rim of quartz and minor plagioclase grains (Figure 12) and biotite

occurs proximal to this as randomly orientated elongated grains up to 0.05 mm that appear to be being replaced by kaolinite.

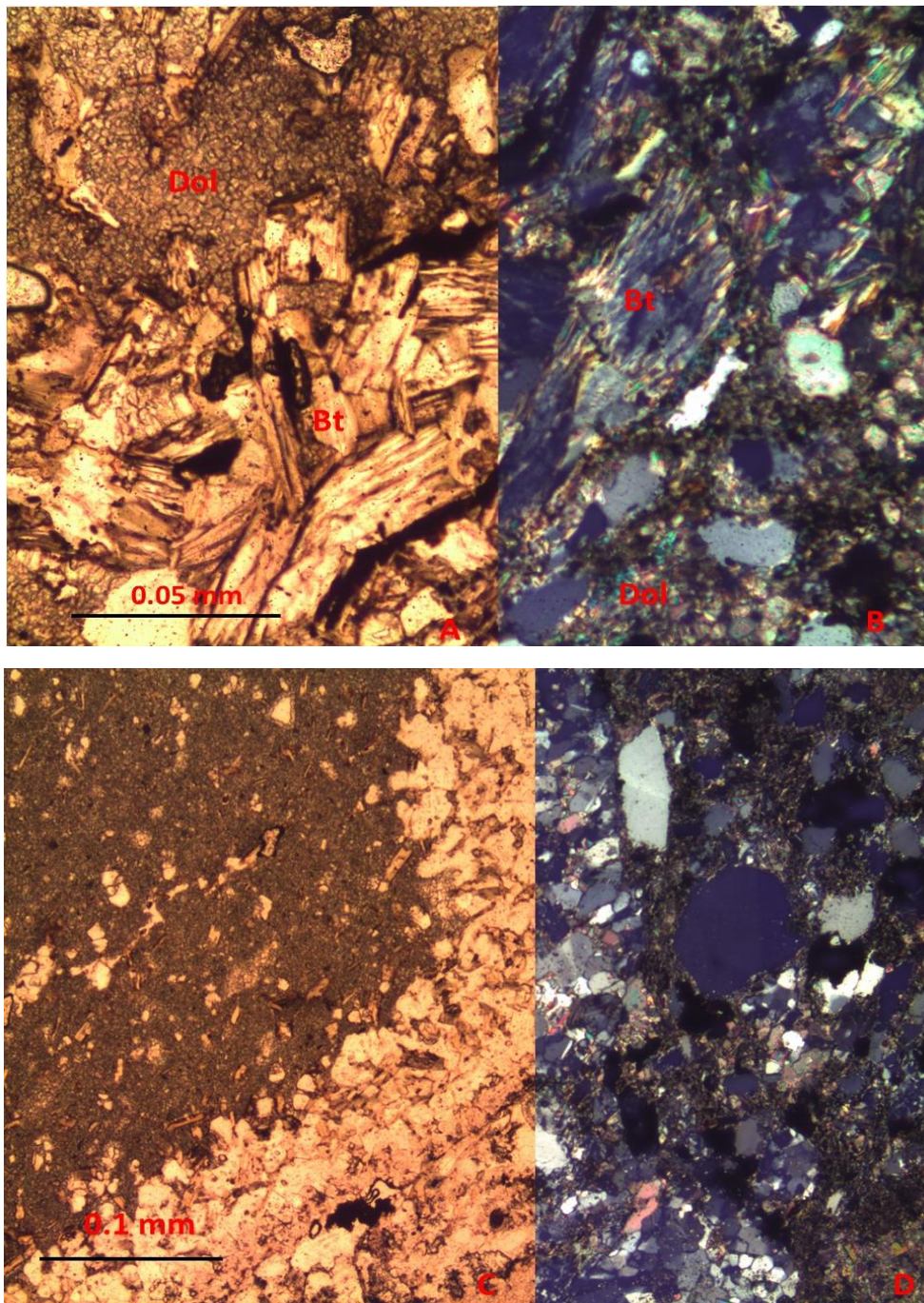


Figure 12 microscope photograph of the Islay thin section sample I4 there A (upper left) show the patch of biotite that are present on the outside of the circle. B (upper right) the same photo but in xpl. C (down left) a corner part of the circle which displays fine-grained dolomite and some elongated biotite with the white rim of quartz and plagioclase and the right-hand side (D) show in xpl. the general texture of the sample with its mineralogy. Bt = Biotite, Dol = Dolomite.

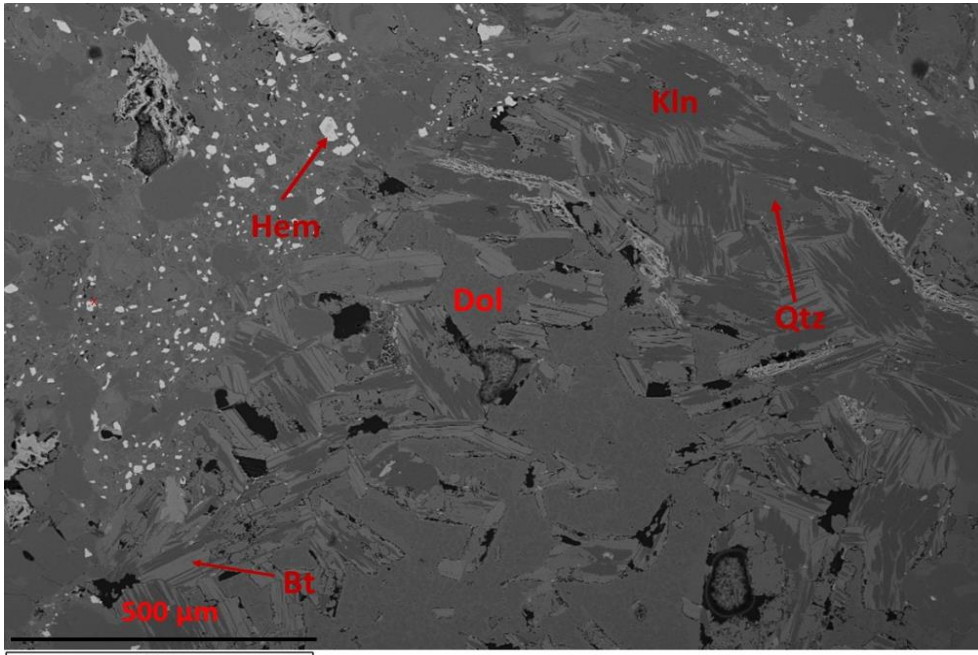


Figure 13 SEM backscatter image showing the mineral texture in the thin section I4. Qtz = Quartz, Dol = Dolomite, Bt = Biotite, Hem = Hematite, Kln = Kaolinite

Sample: Islay 3

Mineralogy: Quartz, Dolomite, Goethite, Hematite, Kaolinite, Biotite, Baryte and Tourmaline.

Mineralogical and textural description:

The sample consists mainly of quartz, dolomite, goethite, kaolinite, biotite and hematite with minor baryte, florencite, zircon and xenotime-(Y). The sample shows fine-grain matrix with clasts of quartz and opaque minerals. The sample contains clasts of quartz up to 0.02 mm in size with elongated, sub-angular to sub-rounded grain shapes. Quartz is the most abundant mineral in the sample. The fine-grained matrix in the sample consists mainly of dolomite, biotite and kaolinite. The hematite makes up around 5-15% in the sample occurring as isolated grains up to 40 microns that are euhedral to subrounded in shape. Patches of anhedral goethite occur in places. In the sample euhedral green-coloured biotite is seen and also weathered biotite to form kaolinite. Couple of euhedral tourmalines are also present (fig. 14).

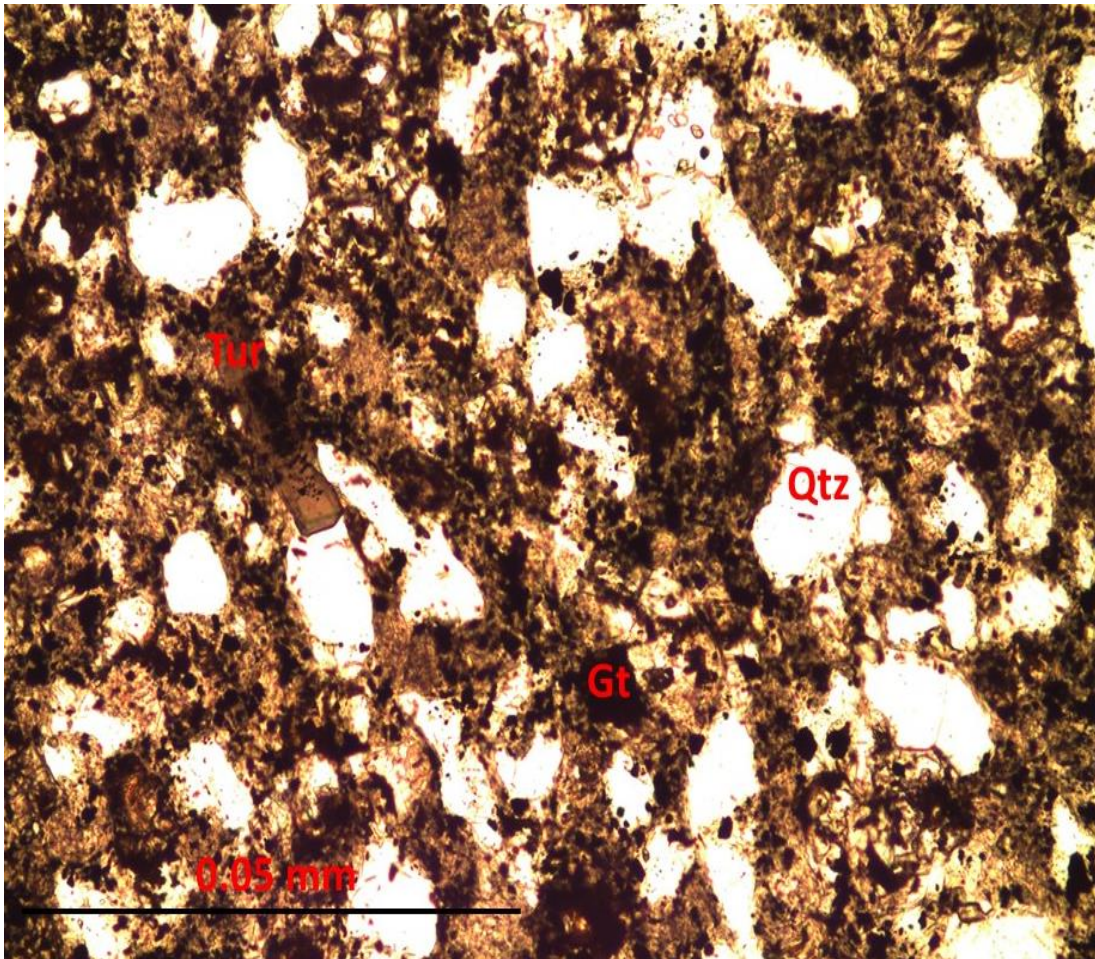


Figure 14 microscope photograph of sample 13 viewing the average composition of the sample. image in ppl over a part of the sample. Qtz = Quartz, Gt = Goethite, Tur = Tourmaline

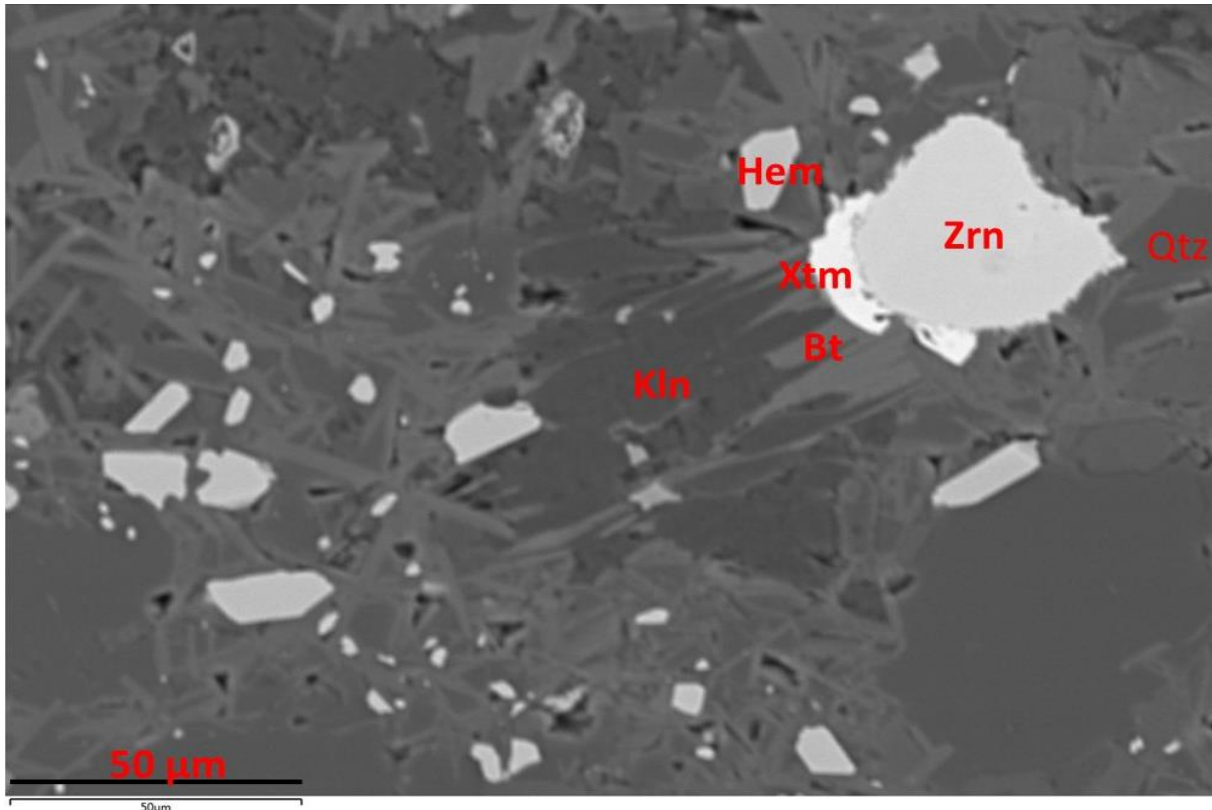


Figure 15 SEM backscatter image of the sample I3 showing i.a. the replacement texture of biotite to form kaolinite and some bizarre minerals. Hem = Hematite, Qtz = Quartz, Kln = Kaolinite, Bt = Biotite, Zrn = Zircon, Xtm = Xenotime-(Y)

Sample: Islay 2

Mineralogy: Quartz, Dolomite, Goethite, Hematite, Biotite, Kaolinite, Apatite and Tourmaline.

Mineralogical and textural description:

The sample consists mainly of quartz, dolomite, kaolinite, goethite and hematite with minor tourmaline and apatite. The sample is layered (fig. 16) with one lighter layer dominated by quartz clasts and anhedral grains of goethite and a darker layer that have less quartz and more of the dolomitic matrix, but clasts of quartz are also present. The quartz clasts are sub-angular to sub-rounded in shape and sits among finer grain matrix of dolomite with biotite and kaolinite in places. Patches of an-hedral goethite are present in the matrix. The opaque minerals are more abounded then in I3 and I4. The opaque minerals c. 20-25 % in the sample. It consists of hematite and goethite. Hematite occurring as individual grains up to 100 microns and are spread out through the whole sample and the crystals are angular to sub angular and euhedral to an-hedral. Euhedral tourmaline grains occur elongated parallel to the layers.

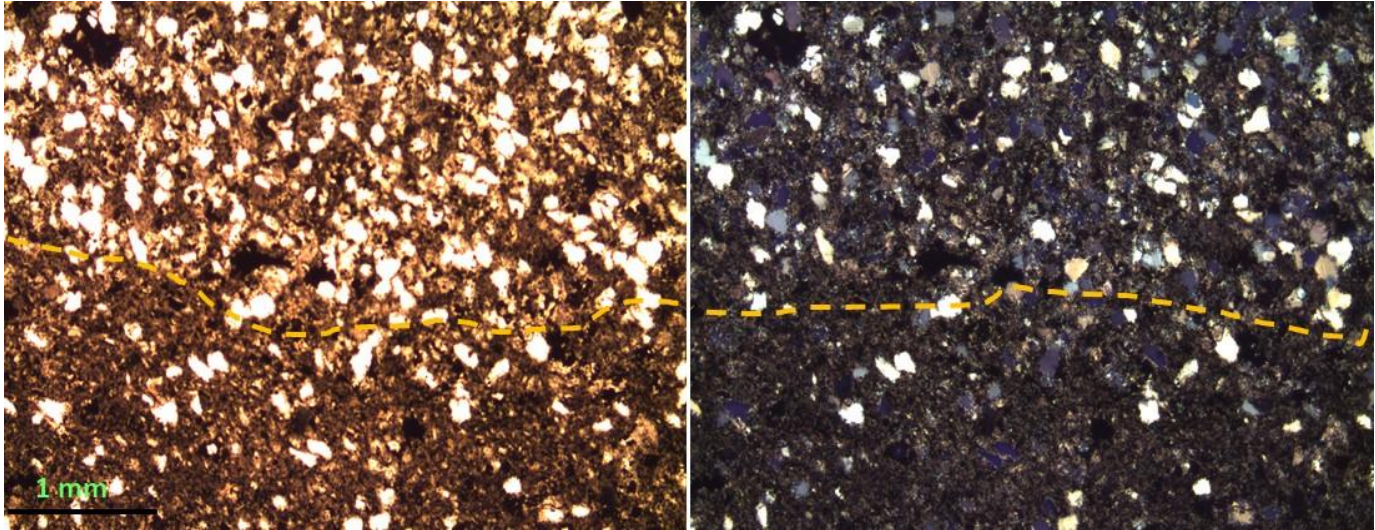


Figure 16 microscope photograph of sample I2 it displays the boundary between the layers in the sample (the yellow dotted line in the middle is where the boundary occur between the layers) left-hand side photo in ppl and right-hand side photo in xpl.

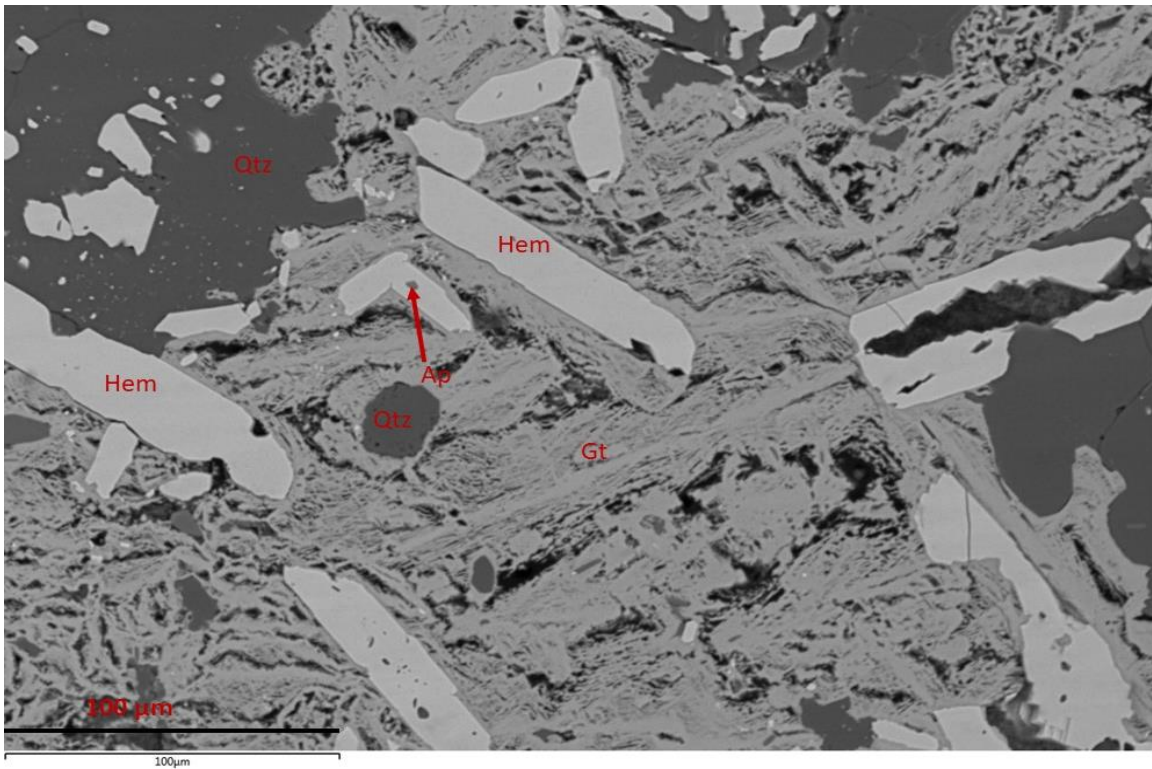


Figure 17 SEM backscatter image of sample I2 showing some of the mineralogy and mineral shapes and texture in the sample. Qtz = Quartz, Hem = Hematite, Gt = Goethite, Ap = Apatite.

Sample: Islay 1

Mineralogy: Quartz, Dolomite, Goethite, Hematite, Kaolinite, Biotite and Tourmaline.

Mineralogical and textural description:

The sample consists mainly of quartz, dolomite, goethite, hematite and kaolinite, biotite with minor tourmaline. The sample shows layering (fig. 18, A) with a paler quartz clast dominated layer and a fine-grained matrix dominated with opaque minerals. The lighter quartz clast dominated layer contains quartz and dark reddish anhedral goethite and euhedral tourmaline grains in a matrix of dolomite, biotite, kaolinite and quartz and some hematite crystals. The matrix dominated layer contains grains

of goethite and hematite grains in the dolomite and kaolinite dominated matrix, quartz clasts are also present but not as abundant as in the other layer. Quartz is the most abundant mineral in the sample and the clasts differ between the layers from grains 0.01 mm up to 0.05 mm in size, angular to more rounded clasts. The opaque mineralogy consists of goethite and hematite and occurs in the entire sample but are more concentrated to the darker layer. The sample contains about 20-30 % oxide minerals where anhedral goethite grains are the most abundant. The concentration of hematite is higher in the matrix layer and the crystals are up to 100 microns in size and euhedral to sub-hedral in shape. The tourmaline is spread out through the entire sample and show elongated shape (fig. 18, B).

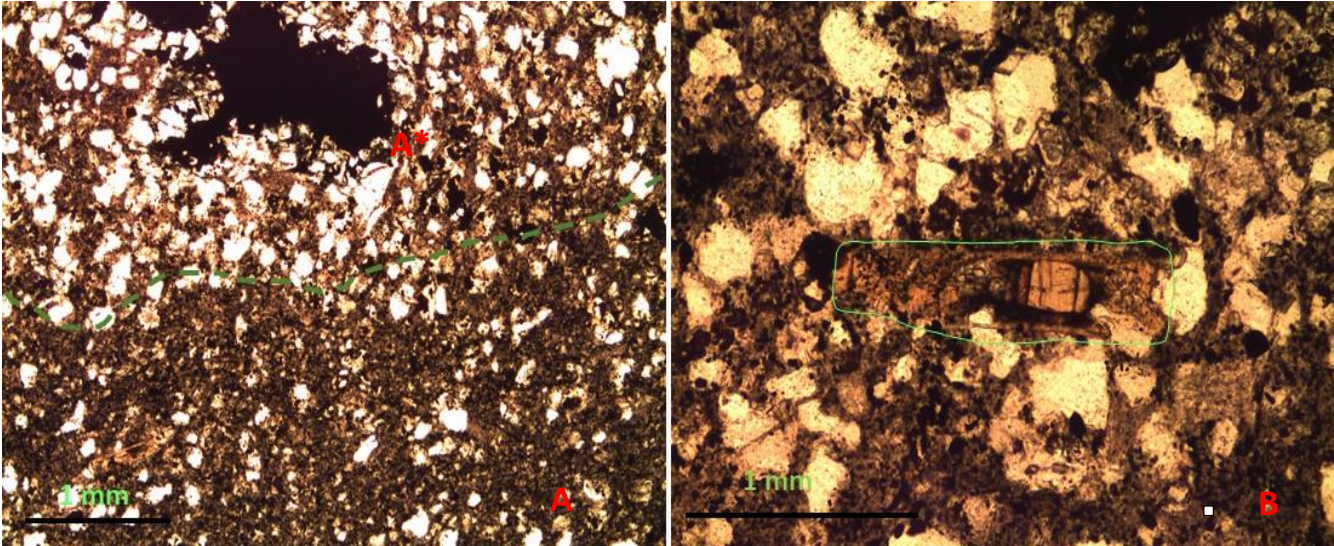


Figure 18 microscope photograph of sample I1 showing on the left-hand side the boundary between the two types of layers that are present in the sample (separated by the green dotted line) and on the right-hand side i.e. a typical grain of tourmaline that are present in the sample.

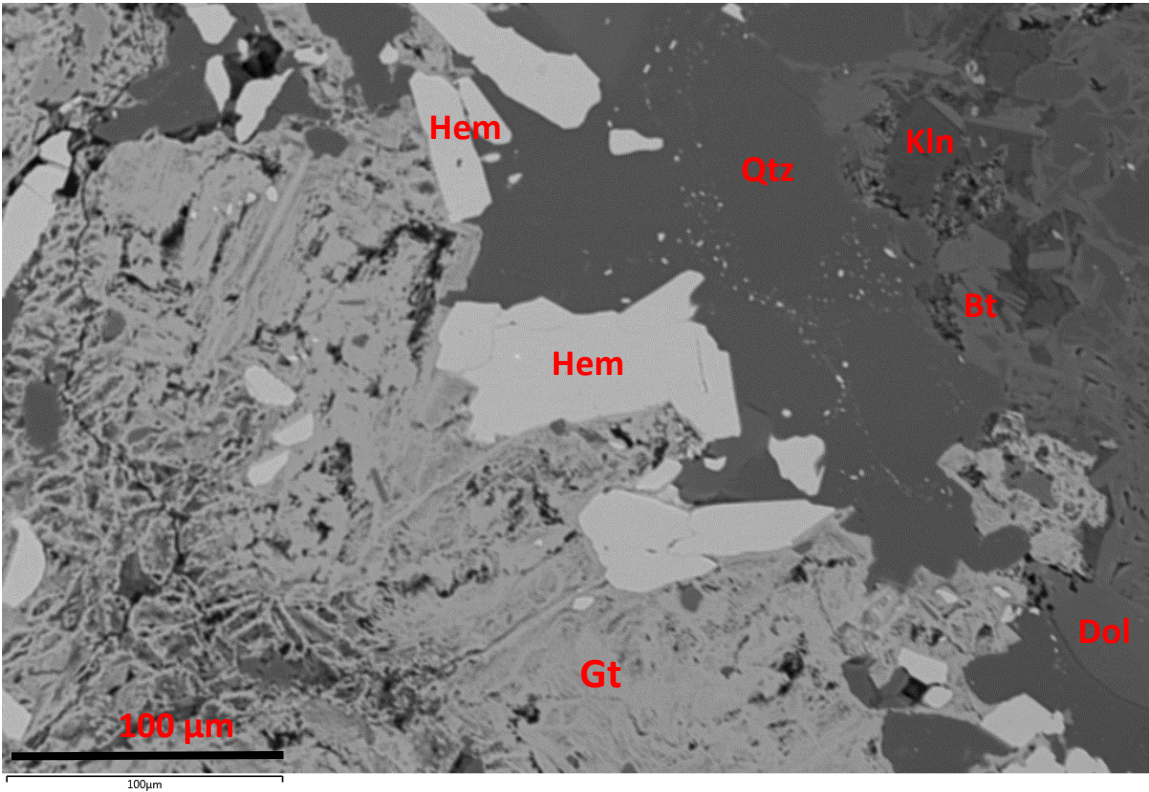


Figure 19 SEM backscatter image showing how the mineralogy and sample texture looks like close to point A* in figure 18 of the sample. Qtz = Quartz, Hem = Hematite, Kln = Kaolinite, Gt = Goethite, Bt = Biotite, Dol = Dolomite

Table 1: Composition of hematite in the samples from this study given in atomic %. The data are from EDS analyses and are therefore not fully quantitative. Ti values under 2 at. % have been removed from the table. Red coloured figures are significantly different from the average values.

n	Garvellach		I1			I2			I3			I4		
	Fe	O	Fe	O	Ti	Fe	O	Ti	Fe	O	Ti	Fe	O	Ti
1	40.7	58.9	41.1	58.7	2.0	39.8	57.4	2.6	40.4	57.4	2.1	39.6	58.1	2.3
2	37.7	61.9	41.9	57.9		39.9	56.9	2.9	39.1	58.7	2.0	39.5	58.3	2.0
3	41.7	58.1	41.5	58.5		31.1	60.9		38.8	59.0	2.2	39.6	57.5	2.3
4	38.2	61.4	38.5	59.0		43.5	56.5		37.6	60.2	2.0	32.8	61.6	5.7
5	41.3	58.5	40.2	59.2		44.4	55.2		39.3	58.3	2.2	34.7	59.2	3.2
6	41.4	58.4	40.6	58.3		42.7	57.0		40.2	57.4	2.2	39.5	58.0	2.5
7	40.3	59.5	38.0	59.4	2.4	43.3	56.7		39.2	58.5	2.2	38.9	59.2	2.0
8	36.9	62.9	34.7	63.4		40.3	58.6		38.7	59.1	2.1	37.6	60.1	2.1
9	41.0	58.7	38.3	59.5		43.5	56.5		39.3	58.4	2.1	37.7	59.7	2.1
10	39.3	60.4				44.2	55.3		40.0	57.9	2.1			
Average	39.9	59.9	39.4	59.3	2.2	41.3	57.1	2.8	39.3	58.5	2.1	37.8	59.1	2.7
σ	1.7	1.7	2.3	1.6		4.0	8.2		0.8	0.8	0.1	2.5	1.3	1.2

Discussion

Classification of Banded Iron Formation

Banded Iron Formations are generally classified either as Algoma or Superior type, Algoma-type iron-formations are deposited in submarine volcanic settings like hydrothermal vents at ocean ridges with small extension as chemical and biogenic precipitated sediments interbedded with volcanic rock and other clastic sedimentary rocks (Taylor, et al., 2015). Superior-type iron-formation are from iron-rich water brought from the deep ocean by upwelling and precipitated on the continental shelf and where individual layers can be traced for hundreds of kilometres. The textures of the sediments changing with age as younger deposits show more often occurrence of Granular Iron Formation (GIF, clastic sedimentary rock) and tidally cross-bedded quartz arenites and stromatolitic dolomites this are suggestive of shallow water depositions where is the older deposits show less occurrence of GIF and are believed to be the result of deposition in deep shelf to upper continental slope. The main difference between the two are the depositional environments and the main mineralogy and trace elements that are expected to be associated with them, but the content of silica, iron and aluminium oxide is roughly the same. Because of the characteristics and the deposition environment for the samples collected one can assume that if they are BIF samples then they would be superior type, so these are the focus of this discussion. The superior type BIF contains 40-55 % silica and 20-35 % Fe and <2 wt.% aluminium oxide (Sciuba, 2013; Guilbert & Park, 1986). The rock types commonly associated with the superior type BIFs are carbonates, quartz arenite and black shale and dolomite, conglomerate and argillite with minor amounts of volcanic rock (Sciuba, 2013; Gross, 1980; Gross, 1983). Chemical precipitates in shallow marine environments on the continental shelf and laminates with chert forming bands of chert-hematite where fine-grained hematite occurs as 5- to 40- μm spheroids (Bekker, et al., 2010). That alternate between the Fe rich bands at a variety of scales where each band is reminding of varve and it thought of as a result of variation in the access of oxygen but if the band is due to seasonal oscillation in ocean chemistry or to other cycles is uncertain. The original minerals in BIF that where formed during deposition or early diagenesis are considered to be: fine-grained ferric oxyhydroxides, siderite, and precursor clays to stilpnomelane and chlorite. The concentration of ferrous iron in the seawater where less than 100 μmol that precepted to form the iron formations. They due however occur on all continents with outcrops in western Australia, southern and western Africa, North and

South America and Asia. They form large bodies up to 100 meters thick and extensions up to 100 kilometres. Also, to be noted is that the Neoproterozoic iron formations are enriched in phosphorus compared to the older ones (Sciuba, 2013; Gross, 1980; Gross, 1983; Guilbert & Park, 1986; Taylor, et al., 2015; Bekker, et al., 2010)

Sample classification

Islay

The Islay samples are sedimentary rock that has been metamorphosed to biotite grade. The samples are dominated by quartz clasts (the amount of quartz in the sample is c. 40%) and dolomite matrix and with immature sorting which is an indicator of deposition of glacial or fluvial transported sediment in a shallow marine environment. The sample contains c. 15-30% iron oxides where both goethite and hematite make up the iron oxides that are present in the sample. Goethite has anhedral grain shape and smears it could be an indicator that is formed due to weathering of other iron oxides by oxidation and hydration and not being a primary mineral. The quartz grains clearly show a clastic texture but the dolomitic matrix that contains the subhedral Fe-oxide grains indicates some sort of precipitation either directly from a shallow marine environment or during diagenesis. A superior type BIF is considered to contain about 20 to 35 % Fe and the Islay sample contains from a visual estimation about 15-30 % Fe-oxides but it lacks lamination texture that are typically associated with BIF.

Garvellach

The Garvellach sample has a high abundance of hematite (> 50 %) which mainly shows an interconnected aggregate texture indicating it formed through precipitation. The sample also shows mesoband layering and fine-grain quartz mixed with the hematite grains. Veins of dolomite and silica indicate late stage fluid flow either during diagenesis or metamorphism. A high-grade hematite (HIF) contains c. 56-68% iron as is the result of BIF transforming by natural process of silica destruction and oxidation of magnetite. This process involves hypogene hydrothermal fluids and supergene weathering (Taylor, et al., 2015). This sample according to texture and mineralogy are more likely to be part of a banded iron formation than the rock collected at Islay.

The relationship between the Garvellach and Islay samples

The samples from Islay and the Garvellachs show significant differences in their texture and composition. The Garvellach sample has much higher Fe content in the form of hematite and the texture indicates it could classify as a BIF. The Islay samples are more Fe-poor and occur in the form of clastic sedimentary rock with some Fe-oxide and carbonate precipitate. In these samples the hematite crystals occur as individual isolated grains while in the Garvellach sample they occur as an interconnected aggregate and in patches. As seen in table 2 the average composition of the hematite crystals varies with the samples from Islay especially I3 and I4 containing abundant Ti. Goethite is heavily represented Fe-oxide in Islay alongside hematite while it is absent in Garvellach sample.

The samples come from within the same stratigraphy in the lower part of the Port Askaig Tillite layer and the main mineralogy is similar even if the abundances and texture vary considerably. It could be that the samples have formed from the same process but that the Fe-oxide precipitation in the Garvellach samples is more dominant. This could be due to for example deeper versus shallower water allowing a greater abundance of Fe-oxide to precipitate and the clastic sedimentary present in the Islay layer could mean it been deposited higher up on the shelf than the fine-grained Garvellach. Another alternative is that the Islay samples represent a reworked layer of the Garvellach material but there is no stratigraphic basis for this argument.

The occurs of Fe-oxide layers in the Snowball Earth sequence in Islay and the Garvellachs

The banded iron formation of a snowball earth sequence is deposited as a layer on top of the glacial deposited rock layers when the ocean gained oxygen again after the sealed of ice (Kirschvink, 1992). But it has been shown that is not always the case as many Neoproterozoic glaciation sequences lack the BIF layer on top of the glacial deposited layer and furthermore, if the BIF layer does exist then it occurs within or below the glacial deposited rock than above the unit (Eyles & Januszczak, 2004; Williams & Schmidt, 2000). As described above, the samples of Islay and Garvellachs were taken from within the lower part of the Port Askaig tillite unit. An explanation for this could be that the glacial sediment that forms the tillite may start to be deposited when the ice cover starts to recede. Therefore, the ocean should be open to some form of oxygenation and be therefore prone to BIF precipitation at the beginning of the period of warming and melting.

Conclusion

This study shows indeed that the disrupted beds in the Port Askaig Tillite on Islay and Garvellach contain Fe-oxide-rich layer.

The Fe-oxide-rich layer on Garvellach has a very high concentration of hematite but it is still unclear if it should be classified as a BIF. For classification as a banded iron formation or even a HIF (high-grade hematite) is harder to determine. It shows the interconnected aggregate texture of the hematite and also mesobanded layering even if they are weak and far from the clear bands seen from other BIF outcrops around the world. It is possible that the sample represents a real BIF. The high amount of hematite in certain part of the rock could point on a HIF but if other parameters are met for HIF are left to be determined.

For the Islay sample does not have enough Fe oxide to classify as a BIF but it is an iron rich sedimentary rocks. The relationship to the Garvellach sample is unclear.

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