
Article:

Dodd, MS, Papineau, D, Grenne, T et al. (5 more authors) (2017) Evidence for early life in Earth's oldest hydrothermal vent precipitates. Nature, 543 (7643). pp. 60-64. ISSN 0028-0836

https://doi.org/10.1038/nature21377

Methods

1.1 Optical microscopy

Standard 30 µm thick, polished and doubly-polished thin sections and 3mm thick polished slabs were prepared with a final polishing step using Al2O3 0.5µm powder for investigation using transmitted and reflected light microscopy. An Olympus BX51 microscope, with 5X, 10X, 20X, 50X and 100X objectives not using immersion oil and CCD camera was used to map petrographic features in thin section. Depth reconstruction images were formed from multiple images taken at 2 micron intervals through thin sections and recombined utilising the Z-project function in the ImageJ software.

1.2 Confocal Raman spectroscopy

Micro-Raman microscopy was conducted on petrographic targets within the polished thin sections using a WiTec alpha300 confocal Raman imaging microscope with a 532nm wavelength laser and operating at a power between 0.1 and 6mW depending on the target. Raman spectra and hyperspectral scans were performed at variable magnification of 20X to 100X and hence variable spatial resolutions of up to 360nm and a spectral resolutions of 4 cm^{-1} were achieved using a 600 lines/ mm grating. Hyperspectral images were created for specific mineral phases using peak intensity mapping for characteristic peaks of each individual minerals in a scan. Average spectra were calculated by creating a mask on homogeneous pixels of individual phases and had their backgrounds fitted to a polynomial function and subtracted. Large area scans (>100µmx100µm) were completed using the same process outlined previously, with spatial resolutions no lower than 10µm. Peak parameters were calculated from a Lorenz function modelled for each selected peak. Cosmic ray reduction was applied to all Raman spectra.

1.3 Scanning electron microscopy

Scanning electron microscopy (SEM) in back scattered electron (BSE) and secondary electron (SE) imaging modes was used to characterise the morphology and composition of selected targets, which were also characterised by energy dispersive x-ray spectroscopy (EDS). Analyses were carried out in the Department of Earth sciences at University College London using a JEOL JSM-6480L SEM. Standard operating conditions for SEM imaging and EDS analysis were a 15kV accelerating voltage, working distance of 10mm and an electron beam current of 1nA. Samples were always coated with a few nanometres of Au prior to analysis.

1.4 Electron probe micro-analyser (EPMA)

Major element mineral analyses were obtained using a JEOL8100 Superprobe (WDS) at Birkbeck. Analysis was carried out using an accelerating voltage of 15kV, current 1nA and a beam spot diameter of 1µm. The analyses were calibrated against standards of natural silicates, oxides and Specpure® metals with the data corrected using a ZAF program.

1.5 Focused Ion Beam nano-fabrication

Focused ion beam (FIB) trench milling was performed using a Zeiss 1540 XB FIB-SEM. Targets located by secondary electrons were protected by a 1-mm thick W shield deposited on the thin section surface. FIB foils were prepared using a focused beam of Ga ions starting with currents of 5nA going down to 200 to 100pA for the final steps to expose subsurface minerals, before secondary electron images were acquired. Detailed description of the FIB nano-fabrication procedures can be found elsewhere [53,54].

1.6 ICP-MS

Analyses were performed by Activation Laboratories Ltd. 41 Bittern Street, Ancaster, Ontario, L9G 4V5, Canada, using a Varian Vista 735 ICP. All major elements had a detection limit of 0.01 wt% or better, Yttrium was measured to a detection limit of 2ppm and all other REE had detection limits of 0.1ppm and better.

1.7 LA-ICP-MS

Analyses were conducted at the London Geochronology Centre (LGC), in the Department of Earth Sciences, UCL, utilising an ESI NWR193 laser ablation system coupled to an Agilent 7700x ICPMS. Instrument parameters are given in tab. 1 and tab. 2. LA-ICPMS procedures followed [55], with Madagascar Apatite (ID-TIMS age 473.5 0.7 Ma; [56]) as an external age standard for corrections of mass bias and fractionation. Isotopes measured and dwell times are listed in table 3 and table 4. Glitter 4.4 (Griffin et al., 2008) was used for data reduction, ages were calculated following Ludwig (2008), where the calculated 206Pb/238U age was used for grains younger than 1100 Ma, and the 207Pb/206Pb age for older grains, rejecting analyses exhibiting more than +5/-15% discordance. Trace element concentrations were calculated using NIST SRM 612 and 610 glass (Reed, 1992; Jochum et al., 2011) as external standard; 44Ca was used as internal standard, assuming stoichiometric concentration for apatite.

LA-ICP-MS instrument parameters

RF power 1340 W
Ar Carrier Gas flow 1.04 l/min
He gas flow 950 ml/min
Sweep Time 400 / 900 ms (U-Pb / trace elements)

Table.S1 Laser Ablation parameters

	Typical
Wavelength	193 nm
Pulse duration	20 ns
Energy fluency	2.5 J/cm2
Ablation spot size	25 µm
Pulse repetition rate	10 Hz
Ablation time / spot	25 / 30 s (U-Pb / trace elements)

Table.S4 Acquired masses for U-Pb dating. 235U was ommitted, natural 238U/235U ratio of 137.88 is assumed.

Mass	Element	Dwell time
29	Si	5ms
43	Ca	5ms
44	Ca	5ms
206	Pb	100ms
207	Pb	200ms
208	Pb	100ms
221	bkg	5ms
232	Th	100ms
238	U	100ms

Table.S5 Acquired masses for trace elements.

Mass	Element	Dwell time
23	Na	5ms
27	Al	5ms
29	Si	5ms
43	Ca	5ms
44	Ca	5ms
55	Mn	10ms
88	Sr	50ms
89	Y	50ms
137	Ba	50ms
139	La	50ms
140	Ce	50ms
141	Pr	50ms
146	Nd	50ms
147	Sm	50ms
153	Eu	50ms
157	Gd	50ms
159	Tb	50ms
163	Dy	50ms
165	Ho	50ms
166	Er	50ms
169	Tm	50ms
172	Yb	50ms
175	Lu	50ms
221	background	5ms

Jaspers of the Løkken ophiolite

Jaspers are typically bedded cherts (silica-rich, microcrystalline rocks) rich in haematite ± magnetite ± Fe-silicate minerals. Stratiform occurrences of jasper with pillow basalts and volcanogenic massive sulphide deposits imply an origin from lithified hydrothermal precipitates[20,26,28], formed in submarine settings analogous to modern mid-ocean ridges or back-arc sea floor spreading centres, intra-plate seamounts, or flanks and calderas of arc volcanoes[21,22,25]. Si-Fe colloidal-gel protoliths of jaspers can be attributed to several processes, including in situ precipitation from low-temperature (20-100°C[mills]) fluid flow through oceanic crust[alt], material derived from low-temperature (2-50°C) vent chimneys[alt], and proximal or distal sedimentation from hydrothermal plumes[mill2].

The Early Ordovician (Tremadoc) Løkken ophiolite was deformed and emplaced during the Caledonian orogeny, reaching metamorphic grades of lower greenschist facies; the original setting was dominated by back-arc rifting in a marginal basin (Grenne and Slack, 2003a). The ophiolite contains laterally extensive jaspilitic beds that cluster at stratigraphic levels associated with the Løkken and Høydal volcanogenic massive sulphide (VMS) deposits and are in places intimately associated with the Fe-Cu-Zn sulphide ore. The jasper, formed originally as sea-floor gels, displays myriads of exceptionally well preserved primary textures, including hematitized bacteria remains, hematitic tubes, and a variety of textures attributed to gel maturation and more advanced diagenetic changes (Grenne and Slack, 2003a). The gel was deposited by particle fallout from hydrothermal plumes, in which silica flocculation and rapid settling of colloidal particles was promoted by the bridging effect of Fe oxyhydroxide (Grenne and Slack, 2003b). Fe was sourced from white smoker-type vents with high Fe/S ratios (Grenne and Slack, 2005), while silica is thought to be primarily of ambient seawater origin based on the interpretation of silica saturation or supersaturation in pre-Late Cretaceous oceans (Grenne and Slack, 2003b). Trace element variations in the gel precursor were controlled by coprecipitation and/or adsorption by Fe oxyhydroxide particles within the plume(s), REE patterns (positive Eu and negative Ce anomalies) reflect mixing of hydrothermal solutions with seawater at dilution ratios of ~10^2 to 10^4.

The Nuvvuagittuq Supracrustal belt (NSB)

The NSB is located in the Northeastern Superior Province, in northern Québec, Canada. It is surrounded and intruded by multiple generations of Eoarchean to Paleoarchean tonalite-trondhjemite-granodiorite (TTG) gneisses dated at 3760 Myr, 3660 Myr, 3500 Myr and 3350 Myr (O'Neil et al., 2013; David et al., 2009) and form a core enclave within the Neoarchean TTG gneisses of the Inukjuak domain. The NSB is dominated by mafic amphibolites composed of cummingtonite-plagioclase-biotite±garnet (O'Neil et al. 2007).

The amphibolite unit has been interpreted to represent mafic volcanic deposits, with compositions ranging from basaltic to basaltic andesite (O'Neil et al., 2011). In some locations pillow lava structures are preserved within the amphibolite (O'Neil et al., 2011). These amphibolites are divided into 3 geochemical groups displaying distinct Al/Ti ratios and following a chemo-stratigraphy within the NSB (O'Neil et al. 2011). The base of the sequence is characterized by low Al/Ti metabasaltic rocks with tholeiitic affinities. They exhibit relatively flat trace element profiles and their chemistry is consistent with derivation from an undepleted mantle source and fractionation under relatively dry conditions (O'Neil et al. 2011). The top of the stratigraphy comprises amphibolites having geochemical compositions consistent with derivation from a re-enriched depleted mantle and fractionation under elevated water pressure (O'Neil et al. 2011). They comprise high Al/Ti basaltic amphibolite relatively depleted in incompatible trace elements and displaying characteristic concave-up REE profiles reminiscent of modern boninites. They are overlaid by intermediate Al/Ti amphibolite of basaltic to andesitic compositions with calc-alkaline affinities displaying LREE-enrichments and flat HREE profiles. Chemical sedimentary rocks (BIF and chert-like silica rocks) mark the transition in the stratigraphy between the low Al/Ti tholeiitic amphibolite and the higher Al/Ti boninitic and calc-alkaline amphibolite. This transition and chemo-stratigraphy have led Turner et al. (2014) to suggest that the NSB metavolcanic rocks were formed in subduction initiation settings similar to modern convergent tectonic settings. Locally, the NSB amphibolite is composed of a cordierite-orthoamphibole mineral assemblage and is characterized by high Mg and K concentrations with depleted Ca, Na and Si. This mineralogical assemblage and geochemical variations are consistent with seawater hydrothermal alteration of the oceanic crust (e.g. Franklin et al., 2005). Along with the presence of pillow lavas and BIF, this suggests that the NSB was formed through submarine volcanism with important hydrothermal activity.

On the basis of mineralogy, two broad types of BIF lithologies are recognized from the NSB, including quartz + magnetite + ferrous silicates (banded silicate formation (BSF)) and quartz + magnetite + Ca-Mg-Fe silicates (BIF) (Mloszewska et al., 2012). Other minor lithologies that have been identified in the belt include: jasper-quartz-carbonate, quartz-biotite schists (with possible meta-conglomerates) and chromite-bearing silica rock (Cates and Mojzsis, 2007; Cates et al., 2013; Dauphas et al., 2007; Mloszewska et al., 2013).

Outcrops of BIF vary from 5 to 30m in thickness, with the jasper forming thinner beds of 1 m thickness and less, which are typically interbedded with layers of amphibolite. In places small veins, typically a few cm wide of jasper are seen infiltrating the amphibolite (Mloszewska et al., 2013), suggesting Fe-Si gels infilled networks in the (interpreted) pyroclastics during deposition. The depositional depth of the NSB jaspers is uncertain from the associated lithologies or textures in rocks of the belt; however, the occurrence of fine-scale, iron-oxide lamination (Fig. S2A) is similar to that in other jaspers and IFs suggestive of a calm depositional environment below wave-base.

The NSB was mostly metamorphosed to upper amphibolite facies with temperatures reaching 650°C and 4-5 Kbars (Cates and Mojzsis, 2009; O'Neil et al, 2007). Sm-Nd isotopic compositions of garnets in the NSB amphibolites suggests that the peak metamorphic event occurred in the Neoarchean (O'Neil et al., 2012) contemporaneous with the intrusion of pegmatites dated at 2688 ± 2 Myr (David et al., 2009). This is also consistent with the regional metamorphism occurring at 2705 – 2680 Myr (Boily et al. 2009). The amphibolites to the southwest and southeast corners of the NSB are characterized by lower metamorphic grade assemblages of chlorite-epidote-Actinolite. To the southeast, chlorite preserves the shape of what appears to have been garnet crystals, suggesting that the lower greenschist assemblage is retrograde (O'Neil et al. 2007). No evidence of retrogressed garnet are observed in the lower grade facies to the SW which may never have reached the upper amphibolite facies. Very local layers in Fe-cherts preserve primary chert, calcite rhombohedra and well-formed minnesotaite needles in jasper, suggesting some rare layers escaped severe recrystallization during peak metamorphism. Furthermore, the crystallisation temperatures estimated for graphitic carbon in rocks from the southwest corner of the NSB do not exceed 550°C (Table S6-8), suggesting the metamorphic facies did not exceed much past greenschist facies.

The geochronology of the NSB is highly debated and two ages have been proposed for the NSB metavolcanic rocks: an Eoarchean age of ~3750 Myr (e.g. Cates and Mojzsis, 2007) and a Hadean age of ~4280 Myr (e.g. O'Neil et al. 2008). Here we will present an overview of this geochronological debate.

One of the challenges in precisely dating the formation of the NSB is the quasi absence of zircon-bearing felsic rocks and their equivocal relationship to the metavolcanic rocks. Rare bands of felsic rocks with trondhjemitic composition have yielded zircons dated by U-Pb between 3750 and 3770 Myr (Cates and Mojzsis, 2007; David et al. 2009; O'Neil et al. 2013; Darling et al. 2013; Augland and David 2015). These trondjhemitic rocks consist of thin discontinuous bands 25-40 cm in width found only to the southern edge of the NSB (O'Neil et al. 2007). Cates and Mojzsis (2007) have interpreted these rocks as felsic intrusions due to cross-cutting relationships observed in the field, giving a minimum age for the NSB. Other field evidence such as felsic intrusions within gabbro sills have led O'Neil et al. (2012; 2013) to the same conclusion about their intrusive nature. Augland and David (2015) have however interpreted these rocks as felsic volcanites giving the actual age for the NSB. This is however not consistent with the cross-cutting relationships observed by Cates and Mojzsis (2007). A fuchsitic quartz-rich rock interpreted by Cates et al. (2013) as a detrital quartzite has yielded 13 zircons with 207Pb/206Pb ages ranging from 3718 Myr to 3780 Myr. They therefore put a maximum age for the NSB at 3780 Myr. This is however not consistent with the principle of inclusion and the maximum age for the detrital quartzite should be constrained by the youngest 3718 Myr detrital zircon. This however would be in contradiction with the minimum age of 3770 Myr for the NSB supported by the cross-cutting felsic rocks (Cates and Mojzsis, 2007). Darling et al. (2013) have obtained a similar U-pb age of 3794 ± 16 Myr for the fuchsitic rocks they conversely interpreted as metasomatically altered felsic orthogneiss of intrusive origin providing a minimum age for the NSB.

A Hadean age for the NSB is supported by the ^{142}Nd isotopic composition of the mafic amphibolites. ^{142}Nd is the daughter product of ^{146}Sm and because the parent isotope has a short half-life of 103 Myr, any deviation in ^{142}Nd compared to modern terrestrial standards implies Sm-Nd fractionation before ca. 4000 Myr, prior to extinction of ^{146}Sm. A significant number of NSB amphibolites exhibit anomalous ^{142}Nd compositions compared to modern terrestrial standards. The correlation between the ^{142}Nd/^{144}Nd and Sm/Nd ratios for all 3 groups of NSB amphibolite is interpreted by O'Neil et al. (2008; 2012) to represent an isochron giving an igneous age of ca. 4280 Myr for the NSB metavolcanic rocks. This Hadean age has been challenged by Roth et al. (2013) interpreting the ^{142}Nd/^{144}Nd vs. Sm/Nd correlation to be produced by mixing with a Hadean enriched reservoir. However, this correlation is preserved between the mafic amphibolite and their ultramafic co-genetic cumulates, which can be used to argue against mixing as a cause of the ^{142}Nd/^{144}Nd vs. Sm/Nd correlation (O'Neil et al., 2012). The composition of these ultramafic rocks is controlled by olivine fractionation and they are interpreted to be co-genetic cumulates to the mafic amphibolites (O'Neil et al 2011). The ^{142}Nd/^{144}Nd vs. Sm/Nd correlation between the mafic liquids and ultramafic cumulates can only be produced if the igneous fractionation occurs while ^{146}Sm was still decaying, i.e. prior to 4000 Myr. The Hadean age of the NSB is also supported by the ^{147}Sm-^{144}Nd isotopic composition of intruding gabbro sills yielding and isochron age of ca. 4100 ± 100 Myr, which would give a minimum age for the NSB metavolcanic rocks (O'Neil et al. 2012).

There is still no consensus on the exact age of the NSB, but nonetheless, it is at least 3770 Ma and possibly as old as 4280 Myr, which makes the NSB BIF among the oldest, if not the oldest, chemical sedimentary rocks on Earth.

Jaspers and BIFs metamorphosed at the upper greenschist/ lower amphibolite facies

Eoarchean supracrustal belts are generally metamorphosed to at least upper amphibolite facies. The metamorphic mineral assemblages of BIFs are well-documented (Figure.10 in Klein, 2005). The petrographic and quantitative analysis of elements in Fe-silicate minerals in BIFs can be used to constrain a metamorphic facies. In the NSB BIFs, the highest grade samples exhibit extensive recrystallization and dissemination of coarse magnetite layers and they contain fayalite and pyroxene that indicate amphibolite to granulite facies (Fig. S3A). With decreasing grades, the BIFs no longer have fayalite and instead have minor pyroxene, amphiboles (dominantly grunerite-cummingtonite), and retrograde phyllosilicates (clinochlore). The low grade BIFs have patches of chert and patches of recrystallized larger quartz grains. In the very lowest grade BIFs, there is acicular stilpnomelane, minnesotaite and rhombohedral ferroan calcite (Fig. S3D). The stilpnomelane in lower grade BIF is likely prograde as this mineral does not form massive pseudomorphs after higher grade minerals but rather fine laths. An upper stability field of 430-470°C and 5-6 Kbar is proposed for stilpnomelane (Miyano and Klein, 1989). Furthermore, the presence of chert suggests that these prograde stilpnomelane - bearing samples did not exceed much past upper greenschist facies.

Null hypothesis and abiotic formation of haematite tubes and filaments

The null hypothesis in the context of early life studies requires one to asses the likelihood of abiotic explanations for observations purporting to support a biological phenomena. If all plausible abiotic explanations are considered and assessed to be significantly unlikely then one can reject the null hypothesis leaving a biological conclusion for the observed features. Below we consider the possible abiogenic mechanisms that could have created haematite tubes and filaments akin to those documented in the NSB.

First, the NSB tubes rarely branch, are commonly straight, and exhibit parallel orientation that may reflect preferred mineral growth. If iron was remobilised along crystal boundaries of acicular minerals as they grew during diagenesis and metamorphism, tube-like structures of haematite could have formed. However, if the precursor was not opal then the mineral would need to have been replaced completely, because only quartz is found inside the tubes. Secondly, acicular mineral growth in rocks is not uniform in shape, in contrast to the consistent morphology of the tubes.

Likewise, metamorphic processes may elongate quartz-hosted haematite to produce aligned, tubular structures like the tubes in the NSB, through fluctuating volume change in the rock during silica remobilisation or metamorphic stretching. Such a process would lead to the structures and minerals in the local environment being preferentially and consistently aligned, yet the orientation of ribbons and tubes of nanoscopic haematite (Fig. 1C) in the NSB jasper is highly variable over scales from hundreds of microns to millimetres. However, 500 µm gaps in iron-oxide layers (Fig. E3B) showing strong alignment of tubes and ribbons of haematite raises the possibility that during metamorphism elevated strain pressure pried apart these iron-oxide layers, which subsequently were infilled with silica and haematite that nucleated on the iron-oxide layers and were elongated during continued layer separation. In addition, layers and pre-existing amorphous structures of haematite may have, under pressure, undergone a process similar to neurulation, whereby layers of haematite are pressed together to form tubes. The two mechanisms above could, in theory, form consistently sized tubes in the range of 16-30 µm by reaching a critical size limit, but it is highly unlikely that such mechanisms can facilitate the growth of multiple tubes from a single haematite knob at varying angles (Fig. 1A, E4), both horizontally and vertically during prograde metamorphism, together with the formation of internal filaments and similarly coiled, branched, and twisted filaments (Fig. E4) with haematite envelopes (Fig. 1C). In addition, their association with carbonate and graphite (Fig. E5D) is most compelling and consistent with a biogenic origin for these tubes and filaments.

Because formation of the NSB tubes via the above metamorphic processes fails to fully explain the NSB tubular structures as metamorphic products, a primary origin of the tubular structures is considered more probable. Nonetheless, there still exist exotic processes that may produce pseudo-microfossils under certain conditions[38]. However, these known exotic processes form filaments of silica and barium carbonate and form under very alkaline conditions, which are unlikely to be relevant for the sea-floor environment of deposition of the NSB jaspers (which lack barite) and formation of the contained tubes. Similar iron-oxide tubes like those present in the NSB have been synthesised using iron-ammonium-sulphate solutions and electric currents, or via mixing of hydrogen with ammonia bubble streams[39]. Notably, these synthesised tubes are demonstrably different from those in the NSB and younger jaspers. Firstly, the experimental tubes have solid walls of iron oxide and consist of a complex mixture of Fe minerals that vary depending on the nature of the bubble solution, whereas the NSB tube walls are composed only of dispersed, individual, nanoscale grains of haematite, consistent with the recrystallization of primary Fe-oxyhydroxide precipitates from seawater. Secondly, the experimental tubes are variable in size, which contrasts with the generally consistent size of the NSB tubes; yet, a number of tubes in the NSB jasper are strongly deformed and display irregular forms and sizes (Fig. 2D). Finally, the synthesised tubes lack internal chains of platy haematite or any other phase, unlike the NSB tubes.

Whereas tubular structures in modern and lithified hydrothermal precipitates are interpreted almost exclusively as microfossils, some branching filaments have been attributed to inorganic, self-organized mineral growth of Fe-oxyhydroxide, controlled by redox fronts in a silica gel[40]. However, such structures are highly branching and are not reported to occur as tubes but instead as solid Fe-oxyhydroxide filaments, and hence are debated in terms of biological origin[30]. Similarly, Fe-oxyhydroxide filaments could form abiogenically in a Fe-Si gel and then be coated subsequently by colloidal silica and Fe-oxyhydroxide to form tubes with internal filaments, like those observed in the NSB. However, this process fails to explain the tubes that lack internal filaments, because silica has never been proven to replace haematite, and fails to explain their associations with carbonate and CM; thus, the tubes unlikely formed via this process. Rather, in our interpretation silica precipitated on and replaced bacterial filaments, which were then coated with nanoscale Fe-oxyhydroxide to form the tubes, while minor amounts of microbial organic matter from the filaments was oxidised to carbonate and are now preserved as carbonate-graphite associations with the filaments (Fig. E5). In summary, the haematite tubes and filaments cannot be explained fully by any known abiotic mechanism and in light of their association with multiple, independent lines of evidence supporting biological activity, the simple uniting explanation is that they represent fossilised microbial remains.

Table. S1 List of samples and their locations and methods used in this study

Formation	Samples	Age	General rock type	Optical microscopy	Raman microscopy	SEM/ EPMA	FIB	LA-ICP-MS	Samples locations	
									Northings	Eastings
Løkken ophiolite, Høydal jaspers, Norway	HO6A, HO7B, TG-82-S6, TG-82-H19	0.485 Ga	Jasper	X	X	X			Mine tailings	
Animike, Mesabi range, Biwabik Iron Formation, USA	MARY-ELLEN1	1.8 Ga	Stromatolitic jasper	X	X				Mine tailings	
Brockman formation, Dales gorge group, Australia	DGH1_38'6'', DGH1_273'1''	2.5 Ga	BIF/ Fe-cherts	X	X	X			DGH1 drill core	
NSB	PC0822, PC0823, PC0824	>3.77 Ga	BIF/ jasper	X	X	X	X	X	58 16 50.9	77 44 14.7
	PC0825								58 17 08.7	77 44 12.2
	PC028/ A								58 17 09.1	77 44 10.8
	PC0844								58 16 53.8	77 44 14.1

Table S2. Iron-oxide tubes and filaments

Locality	**Age**	**Host rock**	**Diameter** **Length**	**Mineralogy**	**Additonal**	**Reference**
Lau hydrothermal basin, Pacific ocean	Present day	Fe-Si hydrothermal vent sediments	0.5-1.5µm 10-100µm	Iron-oxide-silica	Straight, helical and curved varieties. Core of filaments iron-oxide coated by amorphous silica	Li et al., 2012
Chocolate pot hot springs, Yellowstone, USA	Present day	Iron-rich hydrothermal springs	1.5µm >100µm	Ferrihydrite	Very low Total organic carbon present in buried microbial mats	Parenteau and Cady, 2010
Southwest Indian Ridge, Indian Ocean	Present day	Fe-Si oxyhydroxide	2-10µm 10-100µm	Ferrihydrite	Filaments can be curved and intertwining or form bundles of rod-like filaments with the same orientations, diameter and length	Sun et al., 2015
Franklin Seamount, Woodlark Basin, Papua New Guinea	Present day	Fe-Si-Mn oxyhydroxides	0.5-5µm	Iron-oxide-silica	Filaments have hollow structure with walls of iron oxyhydroxide. Filaments branch and some occur as orientated parallel to one another	Boyd and Scott, 2001
Various ophiolites and modern day vent sites	Late Jurassic to present day	Inter-pillow cherts, jasper, Fe-Si seafloor gels and inactive chimney fragments	1-10 µm	Iron-oxide-silica-pyrite-barite		Juniper and Fouquet, 1988
Numerous deposits	490 Ma to Present day	Japsers	1.2-30 µm 20-3000 µm	haematite-iron-oxide	See tables 1, 2 and 3 in Little et al., 2014. Tubes with internal platy haematite chains (Løkken deposit)	Little et al., 2004
Qigebulake Formation, Northwestern Tarim Basin, China	551–541 Ma	Hydrothermal quartz veins	1-5 µm 20-200 µm	Goethite-haematite	No organic carbon detected by Raman	Zhou et al., 2015
Jerome mining district, central Arizona, USA	1738 Ma	Jasper-IF-VMS	1-3 µm 30-50 µm	haematite		Slack et al., 2007
Frere formation, Australia	1880 Ma	Jasper/ IF	Tubes 4-9 µm Filament 0.5-2 µm 100s µm	Nanoscale haematite	Filaments orientated parallel to oncolites	Walter et al., 1976
Gunflint iron-formation, North America	1880 Ma	Jasper/ IF	0.5-8 µm Can exceed 300 µm	Nanoscale haematite	Same filament morphologies in other areas of the formation are preserved by organic matter	Barghoorn and Tyler, 1965; Shapiro and Konhauser, 2015
Kittilä jaspers, Finland	ca. 2000 Ma	Jasper	?	Nanoscale 'dusty' haematite		Kinnunen, 1982
Hamersley BIF, Dales gorge member, Australia	2500 Ma	BIF (haematite + quartz + magnetite + stilpnomelane + ankerite + minnesotaite + riebeckite)	5 µm 100 µm	haematite-dolomite	Filaments preserved as carbonate moulds attached to iron spheres	Karhakis et al., 1976
Nuvvuagittuq supracrustal belt, Canada (filaments)	3750 Ma	Jasper (haematite + quartz + magnetite + ripidolite + chalcopyrite ± calcite ± apatite)	1-7 µm 35-500 µm	Platy-haematite, acicular, grey haematite, moulds in massive nanoscale haematite	Filaments commonly encapsulated by nanoscale haematite. Some have a forked-end. Others exhibit branching	This study
Nuvvuagittuq supracrustal belt, Canada (tubes)	3750 Ma	Jasper (haematite + quartz + magnetite + ripidolite + calcite + chalcopyrite + apatite)	20-30 µm 80-300 µm	Nanoscale haematite	Some contain a central chain of platy haematite	This study

Table S3. Carbonate rosettes in IFs

Locality	Age	Host rock	Diameters	Carbonate	Additional	Reference
Høydal, Norway	480 Ma	Jaspers associated with VMS deposits	100-250 µm	Ankerite	Form circular and rhombohedra rosettes, overgrow haematite filaments; can contain inclusions of CM and associated with apatite	Grenne and Slack, 2003; This study
Gunflint iron-formation, North America	1880 Ma	Jasper/ IF	20-40 µm	Siderite	Associated with CM and sometimes contain cores of apatite	LaBerge, 1973; Winter and Knauth, 1992; Heaney and Veblen, 1991 Carrigan and Cameron, 1991
Hamersley BIF, Dales gorge member, Australia	2500 Ma	BIF (haematite + quartz + magnetite + stilpnomelane + ankerite + minnesotaite + riebeckite)	100-300 µm	Ankerite-siderite	Generally rhombohedral in shape, with poikiloitic textures developing, which form a sphere-shaped centre. Associated with CM layers	This study
			60-80 µm	Dolomite-ankerite	Sometimes have a rosette structure in the middle	Rasmussen et al., 2013
Nuvvuagittuq supracrustal belt, Canada	>3770 Ma	BIF (Calcite + quartz + magnetite + stilpnomelane + haematite + apatite + chalcopyrite)	20-180 µm	Fe-calcite	Poikiolitic, rosettes generally rounded, associated with apatite, can contain inclusions of CM and haematite	This study Mlozsewska et al., 2013

Table S4. Iron-oxide rosettes

Locality	**Age**	**Host rock**	**Diameters**	**Mineralogy**	**Additional**	**Reference**
Lau hydorthermal basin, Pacific ocean	Present day	Fe-Si hydorthermal vent sediments	0.1-2 µm	Si-Ferrihydrite	Associated branching filaments	Sun et al., 2012; Li et al., 2012
Edmond vent field, Indian ocean	Present day	Inner surface of sulphide chimney	1 µm	Non-crystalline silica and acicular iron oxides	Mineralized cells, with cytoplasm preserved	Peng et al., 2010
Milos, Greece	2Ma	Hydrothernal vent iron-formation	30 µm	haematite	Associated filaments, crumpled cores	Chi Fru et al., 2015
Lokken-Hoydal, Norway	480Ma	Jaspers associated with VMS deposits	10-100 µm	haematite-quartz	Forms mm thick layers, large diversity, haematite cores, multi-layered varieties	Grenne and Slack, 2003
Mount Windsor, Australia	ca. 485Ma	Jaspers associated with VMS deposits	100 µm	haematite-quartz	Multi-layered varieties	Duhig et al., 1992
Frere formation, Australia	1850 Ma	Jasper/ IF	20-50 µm	haematite-quartz	haematite cores and associated haematite filaments	This study
Gunflint iron-formation, North America	1880 Ma	Jasper/ IF	3-30 µm	haematite-quartz		Barghoorn and Tyler, 1965; Laberge, 1973
Sokoman formation, Canada	1900 Ma	Jasper	3-25 µm	haematite-quartz		Knoll, 1981; Klein and Fink, 1976; Laberge, 1973
Great Slave group	Paleoproterozoic	IF	10-15 µm	haematite-quartz		This study
Kittilä jaspers, Finland	ca. 2000 Ma	Jasper	?	haematite		Kinnunen, 1982
Boolgeeda formation, Australia	2400 Ma	BIF (haematite + quartz + magnetite + riebeckite + stilpnomelane + goethite + apatite)	10-15 µm	haematite-quartz	Forms mm thick layers	This study
Hamersley BIF, Dales gorge member, Australia	2500 Ma	BIF (haematite + quartz + magnetite + stilpnomelane + ankerite + minnesotaite + riebeckite)	5-20µm	haematite-quartz		Ayres, 1972
				Stilpnomelane and opaque pigments		Rasmussen et al., 2013
Hamersley BIF, Marra Mamba member, Australia	2500 Ma	BIF (haematite + quartz + magnetite + stilpnomelane + ankerite + minnesotaite + riebeckite)	120-200 nm	haematite-quartz		Ahn and Buseck, 1990
Carajás formation, Brazil	2740 Ma	BIF (haematite + quartz + magnetite)	20-30 µm	haematite-quartz-kerogen		Ribeiro da Luz and Crowley, 2012
Nuvvuagittuq supracrustal belt, Canada	>3770 Ma	BIF (haematite + quartz + magnetite + ripidolite + calcite + chalcopyrite + apatite)	15-30 µm 60-100 µm	haematite-quartz	Small and large varieties. Some have haematite cores and concentric layers	This study

Table S5 Wavelength-dispersive spectroscopy (WDS) analysis of various minerals in the NSB BIF and jaspers.

Mineral (Sample*)	**F**	**Cl**	**Na_2O**	**K_2O**	**MgO**	**SiO_2**	**Al_2O_3**	**CaO**	**P_2O_5**	**FeO (Total Fe)**	**MnO**	**ZnO**	**TiO_2**	**Total**
Fluro-apatite (2.E)	1.6	0.1	0.0	0.0	0.0	0.2	0.0	56.2	25.3	0.1	0.0	0.0	0.0	82.9
Fluro-apatite (2.E)	1.4	0.3	0.0	0.0	0.0	0.5	0.0	53.2	26.0	0.2	0.0	0.0	0.0	81.1
Stilpnomelane (2.E)	0.0	0.0	0.0	1.1	4.6	47.9	4.7	0.0	0.0	33.8	0.3	0.0	0.0	92.6
Stilpnomelane (2.E)	0.0	0.0	0.0	1.2	4.5	48.3	4.8	0.0	0.0	34.3	0.3	0.0	0.0	93.4
Magnetite (2.E)	0.0	0.0	0.0	0.0	0.0	0.6	0.1	0.2	0.0	94.3	0.0	0.1	0.0	95.3
Fe-calcite (2.E)	0.0	0.0	0.1	0.0	0.3	0.3	0.3	69.9	0.0	2.8	1.0	0.1	0.0	74.7
Ankerite (2.E)	0.0	0.0	0.0	0.0	0.4	0.0	0.0	69.6	0.0	4.8	1.6	0.0	0.2	76.4
Chamosite (2.B)	0.0	0.0	0.1	0.0	8.9	25.4	18.4	0.0	0.0	35.5	0.2	0.1	0.0	88.5
Chamosite (2.B)	0.0	0.0	0.1	0.0	10.7	25.4	18.8	0.1	0.0	33.7	0.1	0.2	0.0	89.1
Mg-ankerite (2.G)	0.0	0.0	0.0	0.0	16.2	0.2	0.0	30.5	0.0	16.9	1.1	-	-	64.8

*Sample number makes reference to thin sections in Figure E3. Low totals attributed to no analysis for REE, hydroxyl and carbon.

Table S6 Raman graphite parameters of carbonate rosette associated graphite.

Grain No.	**G-band position**	**G-band FWHM**	**D-band position**	**D-band FWHM**	**2D-band position**	**2D-band FWHM**	**D-band area**	**G+D2 band area**	**D/G intensity**	**2D/ G intensity**	**T estimate Beyssac[55] ± 50°C**
G1	1576	9.78	1339	6.25	N.D	N.D	222.69	749.98	1.32	N.D	539
G2	1567	9.80	1341	9.97	2702	5.41	238.21	803.49	0.32	0.23	539
G3	1565	10.57	1350	6.13	2704	4.71	358.58	640.57	0.41	0.48	481
G4	1579	7.31	1345	11.25	2704	5.54	299.53	369.09	0.56	0.11	441
G5	1557	10.61	1337	9.58	2674	7.94	87.27	355.61	0.13	0.2	553
G6	1569	12.04	1334	15.74	2684	9.22	66.72	158.05	0.61	0.36	509
SG1	1584	5.63	1343	5.77	2708	4.46	140.11	672.22	0.08	0.05	564
SG2	1569	8.98	1331	6.60	2680	5.58	160.64	586.33	0.13	0.12	545
SG3	1577	6.91	1343	12.06	2702	5.66	162.30	500.62	0.18	0.14	532
SG4	1577	6.80	1334	7.68	2696	4.67	167.80	515.40	0.56	0.13	532
SG5	1583	5.65	1347	13.18	2702	5.26	284.12	831.28	0.24	0.05	528
SG6	1569	10.56	1344	6.87	2705	4.95	127.96	367.99	0.44	0.44	526
SG7	1570	10.22	1346	9.73	2725	6.82	122.76	278.79	0.34	0.22	505
SG8	1577	6.29	1345	15.36	2700	5.09	365.76	711.13	0.30	0.16	490
SG9	1565	7.64	1342	7.43	2668	5.21	1203.96	2265.20	0.23	0.08	487
SG10	1580	7.19	1349	7.26	2704	4.58	227.73	371.57	0.28	0.21	472
SG11	1570	8.28	1339	6.63	2705	5.06	604.43	937.62	0.29	0.31	467
SG12	1579	7.32	1345	11.30	2704	5.63	322.68	346.98	0.56	0.12	442
SG13	1583	6.17	1344	12.66	2717	6.58	105.02	119.06	0.37	0.20	432
SG14	1581	10.16	1344	14.20	2676	6.20	657.67	537.29	1.10	0.27	396

* Grains starting with G- are from the Raman scan in Fig 3D and grains starting with SG- are from the Raman scan in Fig E6.

Table S7 Graphitic carbon Raman parameters from a jasper sample (Fig. E8D).

G-band position	G-band FWHM	D-band position	D-band FWHM	2D-band position	2D-band FWHM	D-band area	G+D2 band area	D/G intensity	2D/ G intensity	T estimate Beyssac[55] ±50°C
1581	6.18	1359	12.70	2715	9.01	63.77	260.57	0.10	0.24	554
1583	7.29	1348	14.30	2709	10.33	87.76	141.04	0.46	0.51	470
1581	7.03	1346	11.50	2714	12.43	79.70	442.69	0.15	0.25	573

Table S8 Raman poorly crystalline graphite parameters. NR – Not resolvable (Fig. E8E3).

Spectrum No.	**G-band position**	**G-band FWHM**	**D-band position**	**D-band FWHM**	**2D-band position**	**2D-band FWHM**	**D-band area**	**G+D2 band area**	**D/G intensity**	**2D/ G intensity**	**T estimate Beyssac[55] ± 50°C**
1	1585	9.38	1351	8.98	2692	17.55	2614.56	1701.18	1.66	0.45	371
2	1591	7.30	1352	6.15	2701	4.66	1238.30	788.34	2.14	0.14	369
3	1591	7.47	1355	10.10	NR	NR	169.90	87.62	1.91	NR	347