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Geological constraints on detecting the earliest life on Earth: a perspective from the Early Archaean (older than 3.7 Gyr) of southwest Greenland

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At greater than 3.7 Gyr, Earth's oldest known supracrustal rocks, comprised dominantly of mafic igneous with less common sedimentary units including banded iron formation (BIF), are exposed in southwest Greenland. Regionally, they were intruded by younger tonalites, and then both were intensely dynamothermally metamorphosed to granulite facies (the highest pressures and temperatures generally encountered in the Earth's crust during metamorphism) in the Archaean and subsequently at lower grades until about 1500 Myr ago. Claims for the first preserved life on Earth have been based on the occurrence of greater than 3.8 Gyr isotopically light C occurring as graphite inclusions within apatite crystals from a 5 m thick purported BIF on the island of Akilia. Detailed geologic mapping and observations there indicate that the banding, first claimed to be depositional, is clearly deformational in origin. Furthermore, the mineralogy of the supposed BIF, being dominated by pyroxene, amphibole and quartz, is unlike well-known BIF from the Isua Greenstone Belt (IGB), but resembles enclosing mafic and ultramafic igneous rocks modified by metasomatism and repeated metamorphic recrystallization. This scenario parsimoniously links the geology, whole-rock geochemistry, 2.7 Gyr single crystal zircon ages in the unit, an approximately 1500 Myr age for apatites that lack any graphite, non-MIF sulphur isotopes in the unit and an inconclusive Fe isotope signature. Although both putative body fossils and carbon-12 enriched isotopes in graphite described at Isua are better explained by abiotic processes, more fruitful targets for examining the earliest stages in the emergence of life remain within greater than 3.7 Gyr IGB, which preserves BIF and other rocks that unambiguously formed at Earth's surface.

Keywords: Archaean; origin of life; Greenland; geochemistry; isotope geochemistry; geology

1. INTRODUCTION

One of the most exciting discoveries that can be made is a fossil of great antiquity. The importance of each finding exponentially rises as we approach a time near the probable start of sustained life itself at about 3.8 Gyr ago (Ga), at or near the end of the late heavy bombardment (Chyba 1993) of the inner solar system. Such finds yield critical information about the early steps of life's emergence on Earth, and the pathways life followed after its establishment. Consequently, we correctly place tremendous importance on such discoveries.

In the relative comfort of equilibrium conditions at the Earth's surface, where life exists, its signatures are robust and plentiful. For example, it is possible to identify single celled bacteria by their morphology, colonial clustering and even colour (e.g. cyanobacteria). The biochemistry of such organisms also provides distinct clues about their 'biogenicity', whether it be complex organic compounds (Summons *et al*. 1999) or carbon isotope shifts (Horita 2005) generated by metabolic function. In short, it is eminently possible to accurately identify 'life' based on criteria specific to living organisms.

But what might a fossil look like, or have been reduced to, after 3 800 000 000 years? Inevitably, changes will have occurred at the hands of multiple processes. Removed from the nurturing environment of hospitable temperature and pressure and subjected to the disequilibrium forces of Earth's interior, the signals that readily permit identification of life begin to break down: stable organic compounds reduced to graphite (Wopenka & Pasteris 1993) are no longer distinguishable from abiotic matter generated from metamorphosed rocks (e.g. van Zuilen *et al*. 2002*a*; Lepland *et al*. 2003). Even the host sediments or volcanic rocks are prone to exchange their compositional information with percolating fluids and surrounding rocks thus masking original composition and texture (Bridgwater *et al*. 1981; Rosing *et al*. 1996; Fedo & Whitehouse 2002*a*), and biological shapes

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One contribution of 14 to a Discussion Meeting Issue 'Major steps in cell evolution'.

(e.g. Brasier *et al.* 2002) are subject to tremendous change. The changes attendant with *burial and preservation* can be so profound that biotic and abiotic pathways converge to result in objects that may share the same composition, morphology or texture yet have completely different origins.

In all examples of rocks formed during Earth's infancy, the burial process through deposition and/or tectonism is essential in preserving the rocks for subsequent analysis. Without burial, the rocks linger at the surface for a short time only to be eroded and reworked into younger sediments. However, during tectonic burial, rocks may undergo tremendous stresses that result in shape distortions well known from the world of structural geology (e.g. Hatcher 1995), and such deformation is typically accompanied by major increases in temperature and pressure (Yardley 1989). Ironically then, the very events that are critical in preserving the rocks are those that mask the identity of original processes. Considering the potential history *after* formation, perhaps we need to keep the following question foremost in mind: *if it looks like a fossil, can it really be one*?

Using new data and a synthesis of previous work, this paper demonstrates the important role of geology, isotope geology, geochronology and geochemistry for understanding the earliest life in Earth, with a particular focus on the story of the Early Archaean of southwest Greenland. It is in Greenland where the oldest (greater than 3.7 Gyr) supracrustal rocks on Earth are found, yet they have been profoundly changed over time. Specifically, the paper is aimed at detailing the extensive controversy pertaining to the rocks on the island of Akilia, which has been claimed to host the earliest preserved life on Earth in the form of isotopically light (average $\delta^{13}C = -37‰$) graphite (carbon) inclusions in apatite crystals in a distinctive quartz–pyroxene rock (Mojzsis *et al.* 1996). The major purpose of the paper is threefold: (i) before the credibility of the fossils in question can be assessed, it is critical to establish the protolith (the original rock prior to modification by deformation and metamorphism) of the rocks hosting the fossils. This is particularly important in the case under examination, in which the rocks have been metamorphosed to the extent that appreciation of the starting lithology is absolutely essential for testing the veracity of fossil claims; (ii) a claim for the oldest preserved life on Earth requires a solid geochronologic framework to demonstrate the great antiquity. In the case of Akilia, the rocks have been interpreted as being in excess of 3850 Myr (Mojzsis *et al.* 1996), placing them into the critical window coeval with the late heavy bombardment of the inner solar system (Arrhenius & Lepland 2000). If true, this would likely provide the earliest expected glimpse into the first life on Earth. We will address geologic and geochronologic concerns that fail to place a confident age for the rocks and minerals consistent with their respective hosting or being the oldest fossils on Earth and (iii) after assessing the Akilia rocks, we will also explore other evidence for early life from the nearby approximately 3.71 Gyr Isua Greenstone Belt (IGB).

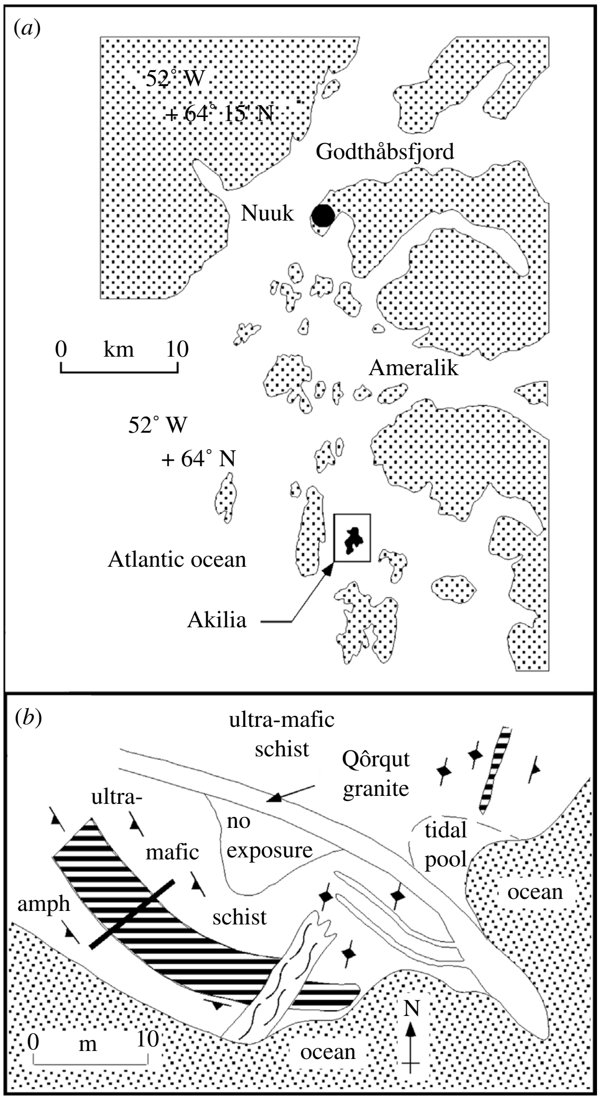

Figure 1. (*a*) Index map showing the location of the outer Godthåbsfjord, southwest Greenland and Akilia. (*b*) Geologic sketch map of the area of interest where the quartz and pyroxene rock (horizontal stripe) is best exposed on the southwest tip of the island. Line crossing the unit demarcates the location of the measured log shown in figure 3.

2. GEOLOGIC FRAMEWORK

In common with other Early Archaean rocks of the outer Godthåbsfjord region (figure 1), two main lithologic assemblages comprise rocks on Akilia and Isua. The most abundant is approximately 3.65–3.85 Gyr composite, banded, tonalitic gneisses (Nutman *et al.* 1996, 1997; Whitehouse *et al.* 1999), historically referred to as the Amîtsoq gneisses. The second assemblage is predominantly comprised of coarse-grained, mafic/ultramafic supracrustal rocks that are generally assumed to be older but only sparse geochronologic evidence exists that substantiates this purported relative chronology. On Akilia, these latter rocks, termed the Akilia association (McGregor & Mason 1977), contain a less common, banded, quartz–pyroxene lithology (figure 2), which has been interpreted as banded iron formation (BIF; e.g. Mojzsis *et al.* 1996; Nutman *et al.* 1997), and claimed to be the host for the reputed fossils. It is the protolith of this banded quartz–pyroxene lithology that has been

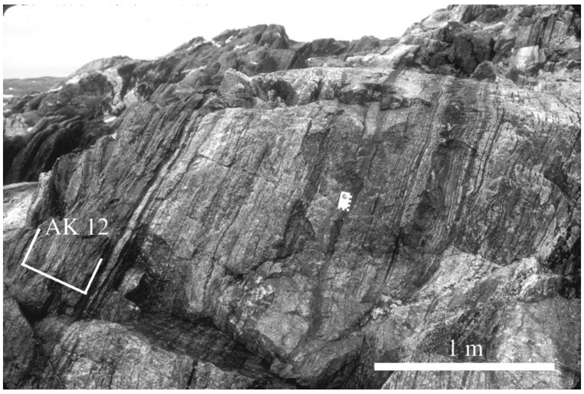

Figure 2. Outcrop photograph showing the best exposed outcrop of the banded quartz and pyroxene rock on Akilia. Note the position of AK 12, which is discussed further in the text.

the centre of great controversy: was it originally BIF, a chemical sedimentary rock precipitated in equilibrium from seawater (Mojzsis *et al.* 1996; Mojzsis & Harrison 2000, 2002*a*; Anbar *et al.* 2001; Friend *et al.* 2002; Nutman *et al.* 2002; Dauphas *et al.* 2004), and thus very suitable for hosting life? Or was it originally a composite, high-temperature, mixed mafic and ultramafic volcanic rock that has been repeatedly metasomatized by silicious and carbonate (and other) hydrothermal systems and metamorphosed at high temperature and pressure (Myers & Crowley 2000; Fedo & Whitehouse 2002*a*,*b*; Whitehouse & Fedo 2003; Bolhar *et al.* 2004), rendering it completely unsuitable as a host for life?

The Amîtsoq gneisses and Akilia association rocks are recognized and distinguished from similar looking Late Archaean rocks in the field on the basis of their intrusion by a suite of dolerites known as Ameralik dykes, which are likely similar in age to approximately 3.5 Gyr intrusions dated in the Isua region (Nutman *et al.* 2004). When considering the geologic and potential biologic history of the rocks on Akilia, and the nature of their protoliths, it is *essential* to appreciate that they have been subjected to multiple episodes of regional metamorphism, including two granulite facies events (at *ca* 3.6 and 2.8 Ga), at temperatures and pressures ranging from approximately 600 to 900 °C and approximately 8–12 kbar, respectively (Griffin *et al.* 1980). These events have imposed a penetrative tectonic fabric (e.g. Myers & Crowley 2000), such that *all lithologies*, including the Ameralik dykes, which only experienced the younger granulite event, are strongly foliated (banded) and have been transposed into parallelism.

3. A SEDIMENTARY ORIGIN FOR ROCKS ON AKILIA?

One of the critical points in establishing the rocks on Akilia as relevant to the earliest life on Earth is demonstrating that the rocks are suitable hosts for potential fossils. In this case, Mojzsis *et al.* (1996) proposed that graphite inclusions in apatite represent relicts of ancient fossils on the basis of their carbon isotopes, and that these minerals comprise part of a rock interpreted as BIF, a chemical sedimentary rock formed in seawater, precisely an environment where life might be expected to be found. We shall discuss specific details of carbon isotope evidence for early life at Isua in §6*b*; for Akilia, the inability of other groups (e.g. Lepland *et al.* 2005; Nutman & Friend in press) to recognize graphite in the original sample from which it was originally claimed renders further discussion which is unnecessary at this point. The rocks have been repeatedly and severely deformed, and so the original iron formation interpretation is quite contentious. This section investigates the details of the rock, whether a sedimentary origin is possible, and, consequently, whether it is suitable as a potential host for life.

(a) *Field relations and petrology*

A great deal of information pertaining to the origin of the quartz–pyroxene rock on Akilia can be discerned from the basic field relations and petrology of the rocks in question. The principal arguments set forth in making the claim for a BIF origin are based on the layered appearance of the rock and its apparent well preserved nature: (i) intense meteorite '…bombardment did not lead to either the extinction of life or the perturbation of the finely laminated >3850 Myr BIF preserved on Akilia island.' (Mojzsis *et al.* 1996); (ii) (They) '…have been interpreted as BIF on the basis of their magnetite layering and by comparison with other units such as in the Isua supracrustal belt…' (Nutman *et al.* 1997); (iii) '…one metachert-BIF is broken up neither by boudinage (segmentation of compositional layers into lens-shaped bodies during ductile deformation) nor minor shearing, nor grossly disrupted by silica mobility. It forms a parallel-sided, approximately 5 m thick unit…' (Nutman *et al.* 1997); (iv) 'the oldest sediment…is a layer approximately 3 m thick of BIF within a body of amphibolite' (Mojzsis & Harrison 2000); (v) 'a 40 m long section of BIF … has escaped boudinage, shearing, or disruption by silica mobility and forms a parallel-sided, approximately 5 m thick outcrop…' (Anbar *et al.* 2001).

To those unfamiliar with the rocks on the island, these statements leave little doubt about the origin of the rocks. Namely, that the fine banding is attributable to sedimentary layering, which in the case of BIF would be by suspension settling in a low-energy water column. Additional comments create an impression that the rocks escaped substantial modification by subsequent geologic processes, even though repeated episodes of high-temperature and high-pressure dynamothermal metamorphism have affected the region. Consequently, we would conclude from the statements in those earlier studies that the protolith of the quartz–pyroxene rocks on Akilia is undisputable BIF with few complications from subsequent deformation events.

In order to appraise these statements that placed such emphasis on prima facie field observation, we undertook repeated trips to Akilia to study the field relationships and log the lithology in detail (figure 3) while also collecting a sample suite representative of all the different variants of the rock unit, which at its thickest part attains about 5 m.

The presence of layering at various scales in the quartz–pyroxene lithology is without question (figure 4). Layers occur from trains of single-crystal-thick pyroxenes

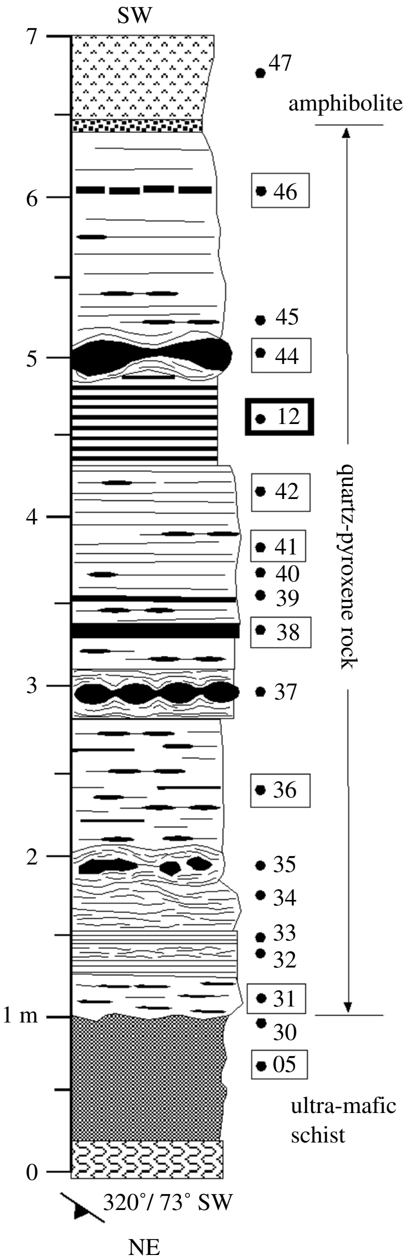

Figure 3. Measured log of the banded quartz and pyroxene rock. Sample numbers shown on the side (All have the AK prefix omitted). Note the common occurrence of boudinage throughout the unit.

(figure 4*a*), to roughly parallel-sided centimetre-thick bands of mixed pyroxene and amphibole (figure 4*b*), to centimetre-thick bands that have segmented into boudins (figure 4*c*). Only rarely are bands of magnetite (a principal component of BIF) present (figure 4*d*), and even then, it comprises less than 5% of the sample. However, layering is a ubiquitous feature of all rocks older than 2.7 Gyr on Akilia, including those of demonstrably igneous origin (figure 5). This type of layering, actually foliation, resulted from intense shearing associated with repeated tectonic events. It is critical to recall that regionally the Amîtsoq gneisses are generally considered younger than rocks of the Akilia association (Nutman *et al.* 1996), and therefore, they would have experienced a deformation history of at least the same if not higher complexity. Furthermore, magnetite not only occurs in the unit under investigation but also in some adjacent ultramafic rocks, rendering its presence non-diagnostic. The unavoidable conclusion is that the foliation observed in rocks of all lithologies on Akilia cannot be used as evidence for 'deposition' of sedimentary layers or to establish a sedimentary protolith for the rock.

In structural association with the penetrative foliation, pinch-and-swell structure and boudinage is common in both the quartz–pyroxene rocks (figures 2, 4*c* and 6*a*) and in the Amîtsoq gneisses (figure 6*b*), contrary to the assertions of Nutman *et al.* (1997) and Anbar *et al.* (2001). As noted in Fedo & Whitehouse (2002*a*), the tails of some boudins are clearly linked to the generation of some of the thin layers seen in the quartz–pyroxene rock. The presence of these deformation structures in association with a penetrative foliation is completely consistent with a high-temperature (i.e. ductile) structural origin for the layering. Such features also argue strongly that the main lithologies have been subjected to intense shearing. The very coarse granoblastic texture that the rocks acquired after their last ductile deformation (Myers & Crowley 2000; Whitehouse & Fedo 2003) renders it difficult to determine whether pure- or simple-shear mechanisms were dominant.

Cross-cutting the main lithologies is a set of N-striking, steeply dipping, apparent right-lateral, centimetre-wide ductile shear zones spaced on a metre scale (figure 7). Displacement of these shear zones is small, on the scale of centimetres, yet they are common on Akilia, which contradicts previous claims. An interesting characteristic of these small ductile structures is that where they intersect the quartz–pyroxene lithology, they are filled with abundant millimetre-scale garnets, whereas they are garnet-free where they cross adjacent mafic and ultramafic rocks. Another interesting set of structures occur as brittle fractures in the quartz–pyroxene rock that filled principally with remobilized pyroxene crystals and less common oxide and sulphide minerals (figure 8). Petrologically, the minerals filling the fractures are in continuity with adjacent layers that define the foliation, suggesting they could be derived from those layers.

Collectively, the abundant small-scale deformational features of the rocks of interest on Akilia, which formed in association with known tectonic events of the outer Godthåbsfjord, are incongruent with the previous descriptions of these rocks being well-preserved metasediments. The observable features documented here and in Fedo & Whitehouse (2002*a*) and Whitehouse & Fedo (2003) all formed long after the inferred time of formation of the rocks and cannot in any way be used to substantiate a sedimentary origin for the rocks on Akilia.

(b) *Geochemical and isotopic data*

Only two petrographic features have ever been used to support a sedimentary origin of the quartz–pyroxene rock on Akilia. As discussed above, neither the 'banding' nor the association of graphite inclusions in apatite have withstood scrutiny, leaving the claim for a sedimentary origin (Mojzsis *et al.* 1996; Nutman *et al.* 1997) unsubstantiated. When considering the geochemical and isotopic data that have been collected for the rocks under question, it is important to note that

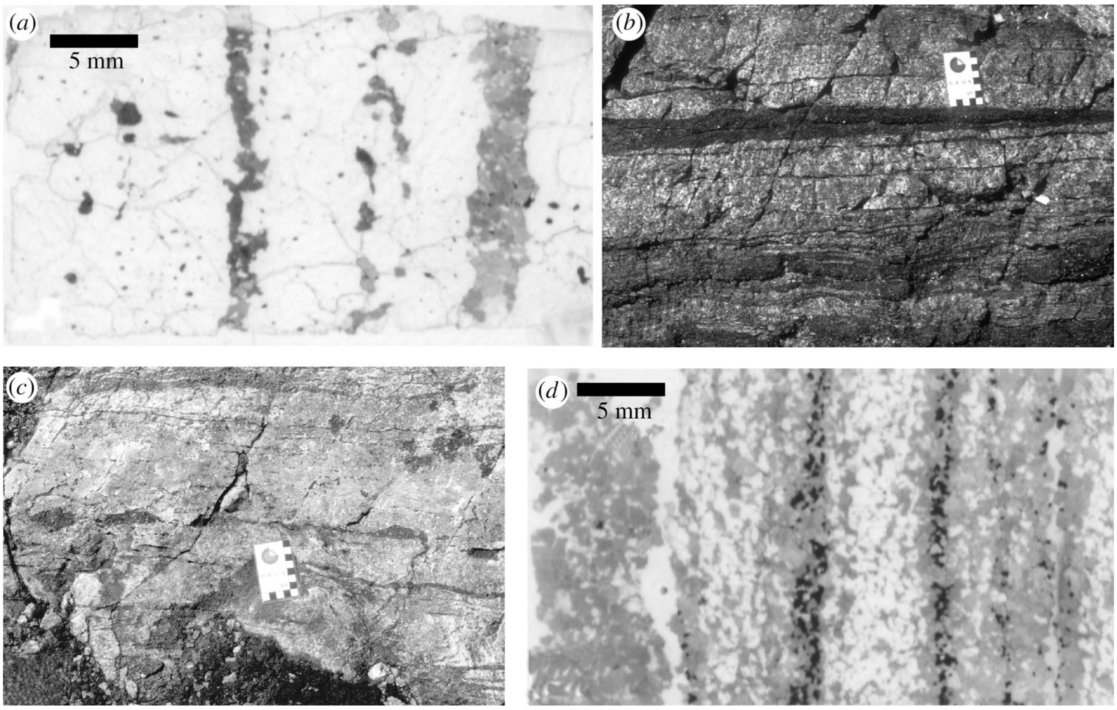

Figure 4. (*a*) Scanned full thin section photomicrograph of finely (millimetre-scale) banded quartz and pyroxene rock (sample AK 34). Dark bands are comprised of pyroxene and the white is quartz. (*b*) Parallel-sided centimetre-thick band of pyroxenite directly below the scale card (in centimetres). (*c*) Directly above the scale card (in centimetres) shows a trail of pyroxenite boudins parallel to main foliation. (*d*) Scanned full thin section photomicrograph showing bands of pyroxene (grey), quartz (white), and magnetite (black). This is sample AK 12, which is shown on figure 2, and also used for U/Pb zircon geochronology.

the burden of positive proof rests with the proponents of a sedimentary origin.

(i) *Geochemistry*

The first geochemical study of the Akilia quartz–pyroxene rocks was inspired by the idea that if the rocks originated as hydrogenous sediments, and were at least 3.85 Gyr old, they could reasonably be expected to yield relatively high concentrations of platinum group elements (PGE). While these elements are very depleted in the silicate Earth, small contributions from chondritic or iron meteorites delivered during the waning stages of the meteorite bombardment should leave discernible fingerprints in sediments that formed at the Earth's surface at 3.85 Ga. The data presented by Anbar *et al.* (2001), however, failed to reveal elevated PGE. This was interpreted as evidence for very high sedimentation rates but does not constitute any proof for a sedimentary origin. For the proponents of a non-sedimentary origin and a younger (3.65–3.7 Gyr) age of the quartz–pyroxene rocks, the failure to find elevated PGE in the quartz–pyroxene rocks (Anbar *et al.* 2001) was a predictable result.

Fedo & Whitehouse (2002*a*) presented the first major and trace element study for the Akilia rocks in an attempt to delineate their origin. These authors argued that the bulk-rock rare earth element (REE) patterns for the quartz–pyroxene rocks differed sufficiently from Isua BIF that they argued against a sedimentary origin. Furthermore, field evidence combined with the similarity of REE patterns between bands of clearly ultramafic origin (thick pyroxenite layers in the unit) with those in the more quartz-rich bands was used to argue that they could be genetically related. Fedo & Whitehouse (2002*a*) concluded that this link would be

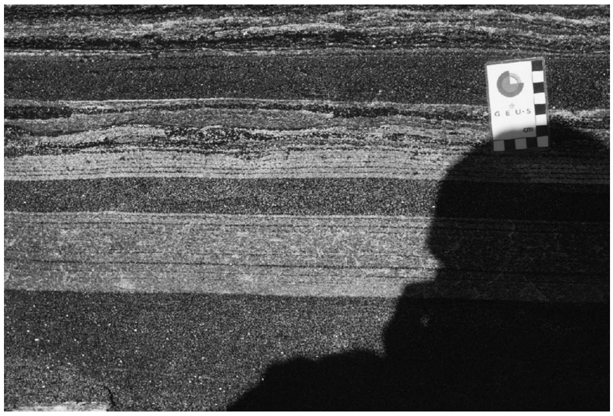

Figure 5. Distinct millimetre-scale banding in Amîtsoq gneisses from Akilia. The protolith of these gneisses is tonalite–trondjhemite–granodiorite (TTG)-suite intrusive igneous rocks. Scale card in centimetres.

consistent with the entire quartz–pyroxene lithology having a mafic to ultramafic volcanic protolith that had been extensively altered by silicious, and probably carbonate, fluids.

In their respective comments pertaining to Fedo & Whitehouse (2002*a*), Friend *et al.* (2002) and Mojzsis & Harrison (2002*a*) presented previously unpublished REE patterns, which they argued were consistent with a BIF origin. The finer details of REE systematics led Fedo & Whitehouse (2002*b*) to conclude that the data presented by Mojzsis & Harrison (2002*a*) were incomplete and inconclusive and that the similarity of the more complete data presented by Friend *et al.* (2002) with hydrogenous sediments was superficial and based on incomplete understanding of the subject. In fact, Friend *et al.*

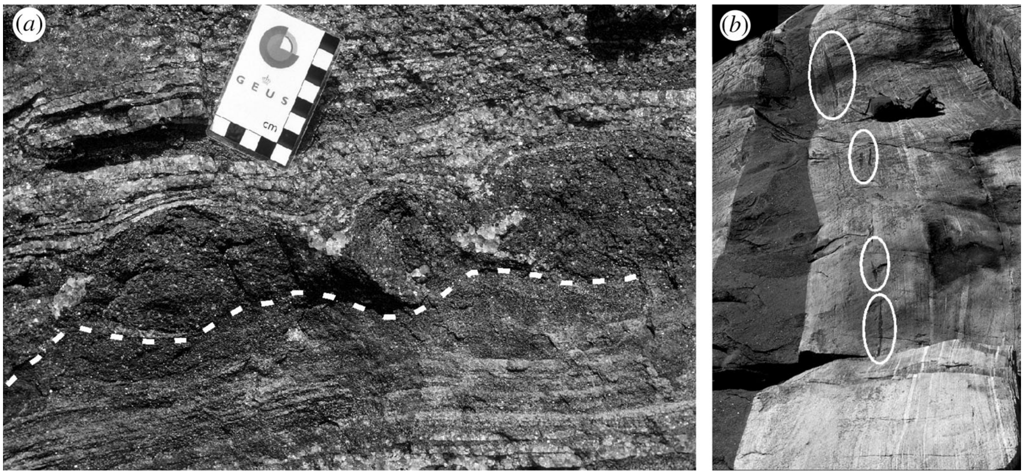

Figure 6. (*a*) Close up showing pinch-and-swell structure at the level equivalent to AK 37 in the measured log. Dashed line shows the bottom of structure. Scale card in centimetres. (*b*) Trail of boudins in Amîtsoq gneisses adjacent to the quartz and pyroxene lithology. Backpack for scale.

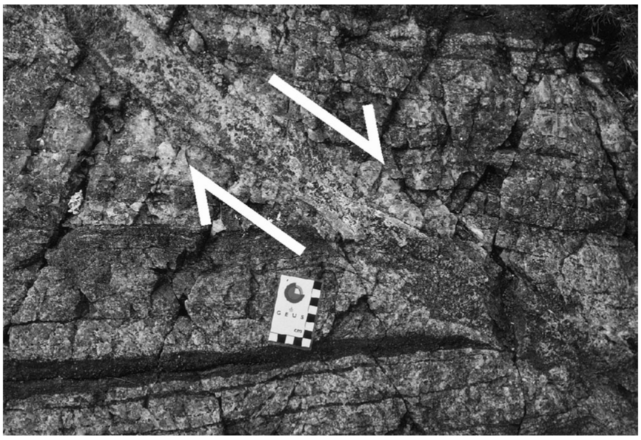

Figure 7. Late-stage apparent right-lateral ductile shear that cross-cuts the quartz and pyroxene banded lithology. The dark spots in the shear zone are garnets. Scale card in centimetres.

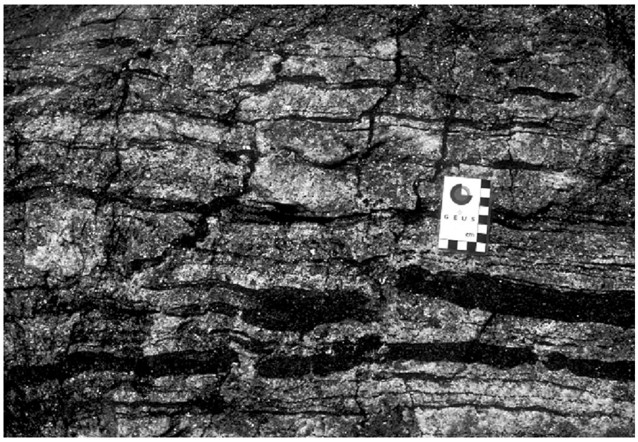

Figure 8. Quartz and pyroxene banded rock with late stage fractures filled with pyroxenite. Scale card in centimetres.

(2002) agreed with the interpretation of Fedo & Whitehouse (2002*a*) with regard to the interpretation of most of the pyroxenite layers and boudins, maintaining only that one sample, G91-26 in which Mojzsis *et al.* (1996) had earlier claimed the presence of biogenic carbon, represented what they called 'best preserved' BIF on the basis of a perceived similarity with the Isua BIF REE pattern. Certainly G91-26 has the most light REE (La to Nd) enriched pattern of all samples so far analysed from the Akilia outcrop (Friend *et al.* 2002) but in our view, except in overall abundance, it is broadly similar to a number of the other quartz–pyroxene rocks (e.g. AK 12, AK 41 and AK 42) and a bounding hornblendite (AK 05), to the extent that its petrogenesis may reasonably be explained within the broad range of processes that have shaped the outcrop as it is seen today.

The issue of REE systematics was revisited by Bolhar *et al.* (2004), who presented the first comprehensive comparison between genuine BIF from the IGB and a variety of quartzose rocks from Akilia and a neighbouring island. Rather than using the normalized REE patterns for comparison with other lithologies like metabasalts, Bolhar *et al.* (2004) specifically examined the patterns for the requisite features that set hydrogenous sediments apart from any other geological material. This approach is based on the work of Bau and co-workers (e.g. Bau & Moeller 1993; Bau 1996). In a series of contributions, Nozaki and co-workers (e.g. Zhang & Nozaki 1998) and Bau and co-workers (e.g. Bau *et al.* 1997) demonstrated that shale-normalized seawater dissolved REE (including Y) patterns are not smooth but have positive anomalies for La, Gd, Y (inserted according to effective ionic radius next to Ho) and Lu. The reason behind these overabundances is the electron configuration of these elements. Since hydrogenous sediments that formed from seawater also show the anomalies (e.g. Bau & Moeller 1993; Kamber & Webb 2001), the seawater REE&Y features are thus diagnostic and, if present in a rock, a strong argument for a sedimentary origin. Bolhar *et al.* (2004) concluded that the REE&Y systematics of the Akilia rocks offered no support for an origin as a hydrogenous sediment, on account of absent La and Gd anomalies. This conclusion is explained below in more detail.

Figure 9*a* compares Archaean turbidite normalized REE&Y patterns for three rocks. The international BIF standard IF-G (data from Dulski 2001) from the 3.71 Gyr IGB, sample 155783, another genuine BIF from the IGB with high-quality data (Bolhar *et al.* 2004) and Akilia quartz–pyroxene rock G91-26 for

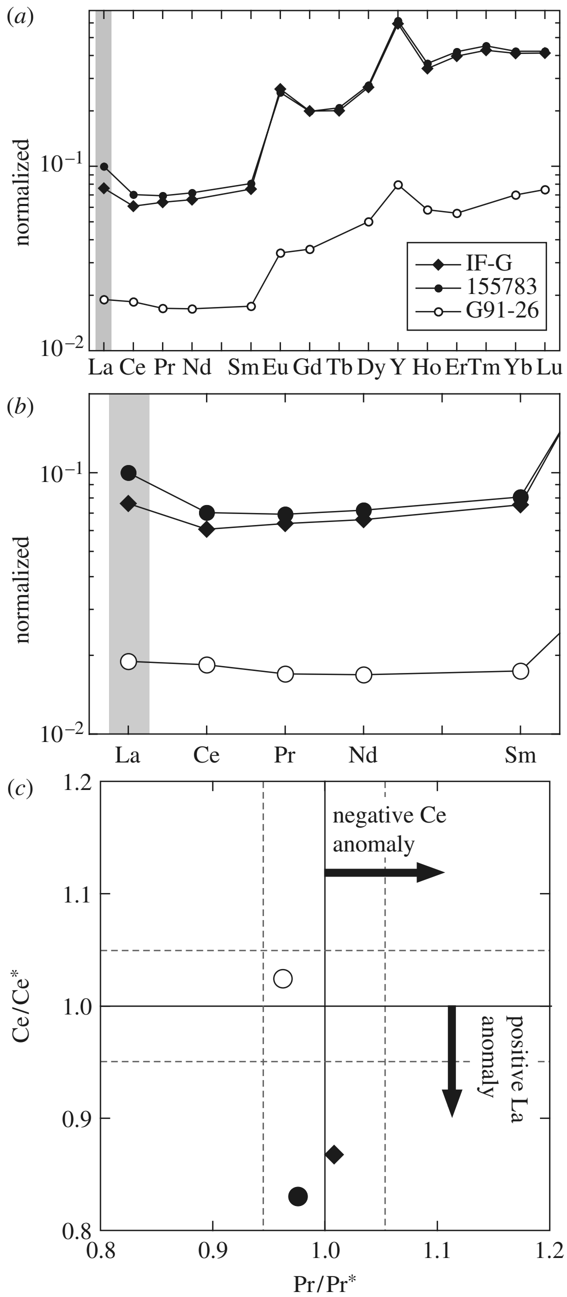

Figure 9. REE&Y systematics of two BIFs and a quartz pyroxene rock from Akilia. (*a*) Shows the Late Archean turbidite (Yamashita & Creaser 1999) normalized REE&Y patterns. (*b*) Detail of (*a*) highlighting light REE systematics. (*c*) Plot of apparent Ce versus apparent Pr anomalies. In Archean chemical sediments a negative apparent Ce anomaly is caused by the real positive La anomaly, while an apparent positive Pr anomaly (absent in these samples) is caused by a negative Ce anomaly.

which Friend *et al.* (2002) have presented a pattern. Notwithstanding the general similarity in REE&Y pattern shape, it is clear that while the two genuine BIFs have positive La spikes, sample G91-26 is flat across the entire light REE, including La. In other words, there is no La overabundance. This is shown in more detail in figure 9*b*, where the two genuine BIFs have straight patterns from Sm to Ce and a distinctive kink upwards to La. By contrast, G91-26, which is also fairly straight from Sm to Ce, simply lacks the kink in La. Archaean chemical sediments (which predate the great oxygenation event) do not have a negative Ce anomaly. Therefore, an apparent negative normalized Ce anomaly, where actual normalized Ce is compared to $(0.5\times\mathrm{La}+0.5\times\mathrm{Pr})$, reflects an overabundance of La. This is shown in figure 9*c*, where only the two genuine IGB BIFs plot at low Ce/Ce*. The coherence of light REE data is demonstrated for all three samples with the lack of an apparent positive Pr anomaly.

The Y/Ho and Zr/Hf ratios comprise yet another set of trace element signatures capable of discriminating a seawater origin. In mafic to intermediate melts, these ratios are very similar to chondritic values, whereas in aqueous solutions these ratios are non-chondritic (Bau 1996). Akilia samples show scatter about the field described by igneous processes, suggesting that they are consistent with a modified mafic to ultramafic igneous origin as proposed by Fedo & Whitehouse (2002*a*) and Whitehouse & Fedo (2003). Sample G91-26 also falls into this group with Y/Ho *ca* 35, while the same genuine IGB BIF samples considered above have consistently super-chondritic Y/Ho ratios (*ca* 43).

(ii) *Sulphur isotopes*

Sulphur provides a stable isotope system potentially capable of tracking whether a rock had interacted with a reservoir that was in contact with the surface of the Earth. Before approximately 2.3 Ga, when free oxygen was released to the atmosphere (the 'Great Oxidation Event'), photochemical reactions in the atmosphere had the capacity to fractionate sulphur isotopes by a mechanism known as mass independent fraction (MIF; Farquhar *et al.* 2000). This stands in contrast to thermodynamic, kinetic and biological processes that produce isotopic fractionation effects based purely on isotopic mass. MIF sulphur can be expressed in terms of Δ^{33}S, which quantifies the displacement of a point from the mass dependent fractionation trend between δ^{33}S and δ^{34}S (Farquhar *et al.* 2000). The basic premise is that a mineral whose original formational age exceeds 2.3 Gyr would incorporate sulphur with a $\Delta^{33}\mathrm{S}\neq 0$ if it is formed at the Earth's surface. Consequently, MIF can serve as a proxy for incorporation of atmospheric sulphur into surficial sulphide completely consistent with it having formed as a sedimentary rock.

In the case of the Early Archaean rocks of southwest Greenland, an apparent MIF S signature in sulphides from the IGB, and from the debated quartz–pyroxene rocks on Akilia were used as evidence that they originated as sedimentary rocks, specifically BIF (Mojzsis *et al.* 2003). Secondary ion mass spectrometry (SIMS) analyses of sulphides from Akilia reported in Mojzsis *et al.* (2003) were interpreted to carry a significant, if small, positive MIF S signature ($\Delta^{33}\mathrm{S}=+0.56\pm 0.15$). This average and standard deviation was, however, determined from about half of the analyses, without a clear explanation of why the remainder were rejected. A compilation of all data presented in Mojzsis *et al.* (2003) points to substantial within-grain scale heterogeneity of S (both in Δ^{33}S and δ^{34}S) and apparent coexistence of both MIF and non-MIF S in the same sample.

In view of the questionable statistics from which the MIF argument of Mojzsis *et al.* (2003) was derived, Whitehouse *et al.* (2005) reinvestigated the sulphur

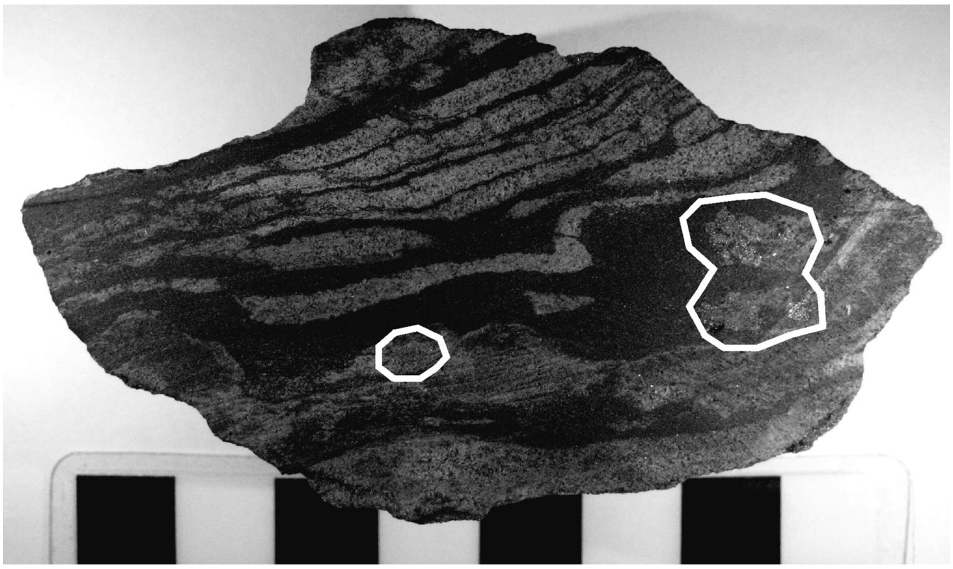

Figure 10. Slabbed hand sample of deformed BIF from the Isua Greenstone Belt (IGB) showing cross-cutting patchwork of pyrite (outlined in white) within the quartz and magnetite bands. This relationship clearly shows that the pyrite is secondary in origin and cannot be related to original depositional environment. Scale in centimetres.

isotopes from sulphides in two samples on Akilia. These samples represent: (i) a pyroxenite boudin and (ii) the *original* rock (G91-26) from which the claim for life was made. In both instances, a total of 42 analyses from pyrrhotite and chalcopyrite show that they are within analytical uncertainty of $\Delta^{33}S=0$. These results indicate that the sulphur reservoir for these minerals did not interact with surface environments, and therefore cannot be used to support a BIF origin for the rocks. In view of the large spread in apparent mass dependent fractionation in the dataset of Mojzsis *et al.* (2003), which was not reproduced in the more comprehensive study of Whitehouse *et al.* (2005), it seems likely that both this spread and the apparent small MIF signature of the former authors was an analytical artefact.

Like with the genuine BIF sample from Isua, Whitehouse *et al.* (2005) stressed that knowing the absolute age of the minerals being analysed is equally crucial for accurately interpreting their history. The sulphides on Akilia, apart from lacking a MIF signature, also contain lead (Pb) that is far too radiogenic if they had formed in the Early Archaean. Rather, the Pb isotope values are clear evidence that these sulphides formed possibly as late as the Middle Proterozoic (*ca* 1.5 Ga), from fluids that sourced relatively radiogenic Pb. Hence, even if these sulphides did carry a MIF sulphur signature, they would not help to distinguish between a hydrothermal or a sedimentary origin.

Genuine BIF with an uncontested sedimentary protolith is well known from the IGB (e.g. Dymek & Klein 1988; Fedo *et al.* 2001). There, BIF occurs in a number of variants, principally dominated by millimetre-scale magnetite and silicate alternations (quartz and much less common amphibole). The report of a MIF S signature in BIF from Isua (Mojzsis *et al.* 2003; Baublys *et al.* 2004; Whitehouse *et al.* 2005) supports the notion that the S isotopic composition is potentially capable of identifying a rock of sedimentary origin, even as far back as 3.71 Ga. However, the finer detail of this argument, as discussed by Whitehouse *et al.* (2005), is that it first needs to be established that the sulphide (or sulphate) mineral now preserved in such rocks is actually of primary or at least sedimentary origin. As illustrated in figure 10, the prominent sulphide minerals shown in the comparatively well-preserved BIF in the IGB accumulated as patchy, secondary, cross-cutting veins in a fold hinge. This implies that they are formed during the folding event, long after the time of deposition. Based partly on the recognition of the secondary nature of the sulphides, the conclusion of Whitehouse *et al.* (2005) is that the S isotopic composition can be recycled into secondary mineral phases, and therefore is not uniquely suited to identifying protolith composition.

(iii) *Iron isotopes*

Iron isotope data from rocks on Akilia have been recently used to propose a BIF origin for the quartz–pyroxene rocks (Dauphas *et al.* 2004). The basic argument stems from a growing, if still very limited, empirical and experimental dataset suggesting that fractionation of iron isotopes in natural systems is a phenomenon apparently restricted to chemically precipitated sediments (e.g. Johnson *et al.* 2003) and biological processes. The wide range of iron isotope fractionation in BIF in particular seems to contrast generally unfractionated igneous rocks and terrigenous clastic sediment. Consequently, the fractionation of Fe isotopes appears capable of identifying relict sedimentary rocks.

Dauphas *et al.* (2004) measured the iron isotopic composition of a number of rocks and minerals on Akilia in order to interpret their origin. Whole rock, magnetite and pyroxene values from the quartz–pyroxene lithology have heavy Fe isotopes, with positive $\delta^{56}Fe$ values that range from about +0.1 to about +1.1‰, values that are similar to those from genuine BIF from the IGB (Dauphas *et al.* 2004). Additionally, mafic and ultramafic volcanic rocks and granitic gneisses were shown to have values very close to zero (Dauphas *et al.* 2004). This led to the conclusion (at the time supported by the apparent presence of MIF S) that the iron isotopes positively established a chemical sedimentary origin for the quartz–pyroxene rocks on Akilia, regardless of the absent trace element fingerprints.

Mid-ocean ridge basalts that are altered are also known to have heavy Fe isotopes in association with loss of Fe (Rouxel *et al.* 2003). Dauphas *et al.* (2004) postulated that if the same process had occurred on Akilia, then the ratio of Fe to Ti, an immobile element under many conditions, should be a key to metasomatic alteration. The samples analysed by Dauphas *et al.* (2004) possess high Fe/Ti ratios (361 to 6962), an observation used by these authors to argue against metasomatic effects. This stands in marked contrast to Fedo & Whitehouse's (2002*a*) sample AK 10, a centimetre-thick pyroxenite boudin considered to be of ultramafic origin (i.e. evidently not BIF), which has a Fe/Ti ratio of 1146 and very high light REE concentrations consistent with metasomatic transport through the rock. This discrepancy is currently unresolved.

Additionally, the reasoning by Dauphas *et al.* (2004) presumes that Ti is an immobile element, although in metamorphic systems Ti is known to be mobile on the scale of metres and even greater distances in deep crustal shear zones (Van Baalen 1993), which the Akilia outcrop could easily be. Consequently, when rocks have been deformed and metasomatized repeatedly like those on Akilia, the Fe/Ti ratio may not be the best, or only, indicator of fluid interaction. Dauphas *et al.* (2004) state specifically that the '…high Fe/Ti ratios observed in the Akilia quartz–pyroxene rocks are most likely primary BIF signatures,' despite the lack of BIF specific chemical features as discussed above and the recognition of the multiple times these rocks have been metamorphosed and potentially exposed to fluid interactions.

Finally, it is worth noting that of the three rocks analysed by Dauphas *et al.* (2004) from the quartz–pyroxene zone, all of which have heavy Fe isotopes, only one, G91-26, corresponds to the sample considered by some other workers (Friend *et al.* 2002) to be a BIF. Inspection of a thin section of SM/GR/97/05 (provided by S. Moorbath), another of the samples studied by Dauphas *et al.* (2004), shows this to be a thoroughly typical magnetite-poor, coarse grained and coarsely layered quartz–pyroxene rock. (A third sample, AK 98 cannot be characterized because Dauphas *et al.* (2004) provide insufficient petrographic description and fail to indicate the position of the sample within the 5 m quartz–pyroxene zone). Thus, the Fe-isotope arguments in favour of a BIF origin partly contradict the interpretation of Friend *et al.* (2002), and with the loss of the MIF S argument (Whitehouse *et al.* 2005), represent the only evidence even partly supporting a BIF origin.

(iv) *Oxygen isotopes*

Little has been published on the oxygen isotopic composition of the debated rocks. In a study of quartz crystals from the quartz–pyroxene rocks from Akilia and from similar rocks on Innersuartuut, a nearby island, van Zuilen *et al.* (2002*b*) reported that the oxygen isotope composition has a consistent $\delta^{18}O_{SMOW} = +12‰$, which is significantly lower than genuine BIF (e.g. Dymek & Klein 1988; Fedo *et al.* 2001) exposed in the IGB (Perry & Ahmad 1977). For example, low-grade metamorphosed BIF from Australia has a $\delta^{18}O_{SMOW}$ *ca* +20‰ (Becker & Clayton 1976). van Zuilen *et al.* (2002*b*) pointed out that the Akilia values are similar to those in granites and pegmatites. In this light, the quartz oxygen isotope data cannot substantiate a sedimentary protolith (e.g. Nutman *et al.* 1997), but support (without being diagnostic of) the idea that the quartz was added metasomatically later (Fedo & Whitehouse 2002*a*).

The isotope data are also congruent with the textural of the quartz on Akilia. Crystals are extremely coarse, in some cases more than 5 mm across, clear and display 120° triple junctions. All these features are hallmarks of the quartz having been strongly recrystallized and reequilibrated during subsequent metamorphic events. An alternative approach to measuring oxygen isotopes in quartz is to use the refractory mineral zircon, which has a well-documented ability to preserve its original $\delta^{18}O$ signature through metamorphic and hydrothermal effects (Valley 2003). Zircon has the added advantage of being a dateable mineral, hence the measured $\delta^{18}O$ might be expected directly to relate to that of the host rock at the time of (re-)crystallization. Sample AK 12 (figures 2 and 3) is comprised of millimetre-wide alternations of pyroxene and quartz with less common bands of magnetite. A 5 kg sample yielded a small number of grains that were selected for an oxygen isotope and U–Pb dating study. Cathodoluminescence (CL) images of anhedral zircon crystals are shown in figure 11*a*. All grains are very dark in CL but some convoluted internal structure may be discerned. As we shall show in §4*a* below, these grains yield an age of (metamorphic) crystallization of approximately 2.7 Gyr. Clearly, any oxygen isotope signature measured can relate only to this time but since it might represent that of the whole rock prevailing prior to this, we have undertaken SIMS analyses of the dated grains and others with identical CL characteristics, data from which are presented in table 1 and figure 11*b*. Eleven out of twelve analyses define a weighted average $\delta^{18}O_{SMOW}$ of $+9.5 \pm 0.5‰$ (95% confidence interval, mean square weighted deviates = 1.7). Like the quartz analyses, this value provides no indication of a BIF-like oxygen isotope signature preserved at 2.7 Ga. Clearly, these results demonstrate that oxygen isotope data cannot be used to determine a sedimentary protolith.

In summary, the current balance of geochemical and isotopic evidence strongly favours a non-BIF protolith of the Akilia quartz-rich rocks. For as long as the presence of C particles as apatite inclusions was not in doubt, it seemed necessary to obtain further geochemical and isotope data to more accurately understand the origin of these rocks. Now that the claim for signs of life has disappeared (Lepland *et al.* 2005) and in view of the fact that the rocks cannot be directly dated (discussed later), the issue has become less critical and future efforts should concentrate on genuine sedimentary rocks from the 3.71 Gyr IGB, which could still yield important discoveries.

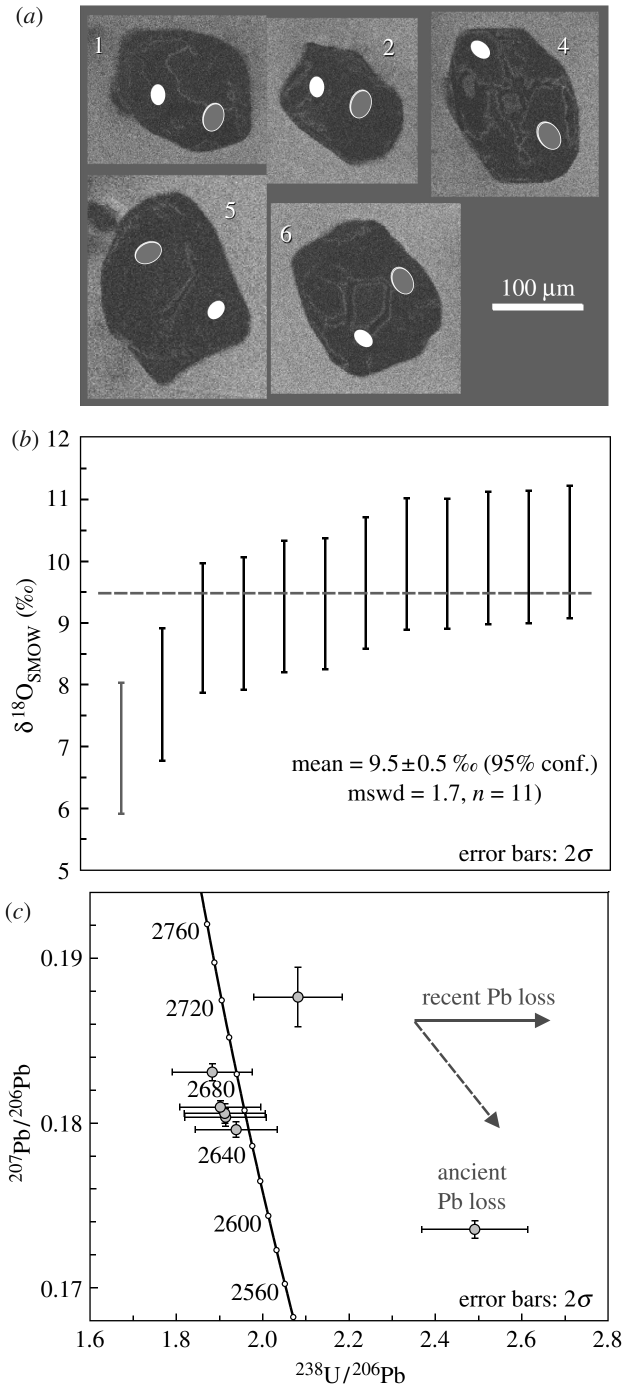

Figure 11. (*a*) Cathodoluminescence (CL) images of selected zircon crystals from finely banded quartz–pyroxene rock AK01-12. Location of SIMS analyses are indicated by ellipses, white to denote O-isotopes, shaded grey to denote U–Th–Pb. (*b*) Zircon O-isotope data with calculated weighted average $\delta^{18}O_{SMOW}$ of $+9.5\pm0.5$‰ (lowest value rejected). (*c*) Zircon U–Pb data plotted in a Tera Wasserburg (inverse) concordia diagram; schematic vectors indicate potential displacements from concordia as a result of recent Pb loss (horizontal line) or ancient Pb loss (angled vector, dashed to indicate that this direction is variable).

4. GEOCHRONOLOGY

Any claim that the Akilia quartz–pyroxene rocks represent the oldest identified water lain sediments on Earth that are actual or potential hosts for hosting the oldest life on Earth, critically older than well-dated 3.71 Gyr sediments at Isua, needs to place the rocks in a rigorous and unambiguous geochronologic framework. There are a number of possible ways to ascertain an absolute age: (i) dating the unit in question; (ii) dating rocks that are clearly interstratified with rocks that otherwise cannot be dated; or (iii) determination of a minimum age by dating an igneous unit that demonstrably cross-cuts the unit in question. The first two methods are highly desirable as they have the potential to very accurately determine the time of formation, whereas the third method gives only the minimum possible age.

(a) *Dating the quartz–pyroxene rock*

The quartz–pyroxene rocks on Akilia, and the Akilia association rocks in general present serious difficulties for direct dating because: (i) their composition is not amenable to providing abundant minerals suitable for geochronology and (ii) well-documented polyphase high-grade metamorphic history of the Godthåbsfjord region has the potential to reset even the most robust geochronometer.

The U–Pb systematics of zircon ($ZrSiO_4$) is one of the most widely applied and robust geochronometers available. Its ubiquitous presence as a recycled detrital mineral in sedimentary rocks is, furthermore, a powerful tool for dating the minimum age of a sediment. Zircon, however, may crystallize or recrystallize in a wide range of geological environments ranging from magmatic through high-grade metamorphic to hydrothermal. Two ion microprobe studies have to date reported single zircon U–Pb ages from quartz–pyroxene lithologies on Akilia. Nutman *et al.* (1997) report analyses from 11 zircon grains yielding ages of approximately 2.7 Gyr from the same sample (G91-26) that has been claimed to host C-isotope evidence for biogenic activity. In an abstract, Mojzsis & Harrison (1999) report an additional seven approximately 2.7 Gyr zircon ages with low Th/U (lower than 0.05) from a possibly equivalent quartz–pyroxene rock, as well as 11 analyses that yielded *ca* 3.5–3.6 Gyr ages and somewhat higher Th/U (0.01–0.4). Both groups of authors favoured a metamorphic crystallization interpretation for these ages, a reasonable interpretation because they closely match documented Early and Late Archaean high-grade metamorphic events in the Godthåbsfjord (Nutman *et al.* 1997; Whitehouse *et al.* 1999; Whitehouse & Kamber 2005). Since neither study presented documentation of the morphology and internal structure of the analysed zircons (nor analytical data in the case of Mojzsis & Harrison 1999), however, their metamorphic interpretation cannot be accepted with complete confidence. While it is probably correct to say that the approximately 3.6 Gyr zircon reported by Mojzsis & Harrison (1999) indicates that the unit was in place at this time and is therefore at least 3.6 Gyr in age, the possibility cannot entirely be dismissed that the older zircons were sourced from elsewhere, either as detritus into a younger (later than 3.6 Gyr) sediment or from an intrusion (e.g. a felsic vein) which has subsequently been deformed and altered beyond all recognition. Presentation of internal structures, e.g. showing that the 3.6 Gyr zircon had 2.7 Gyr overgrowths (a point intriguingly hinted at by Mojzsis & Harrison (1999) in

Table 1. SIMS U–Th–Pb and O isotope data for zircon from Akilia sample AK 12. (U–Th–Pb analyses were performed on a Cameca IMS1270 ion microprobe at the Swedish Museum of Natural History, Stockholm (Nordsims facility) using a method similar to that described by Whitehouse *et al.* (1999) and references therein. Errors on ratios and ages are quoted at the 1σ level.)

analysis[a]	U[b] (p.p.m.)	Pb (p.p.m.)	Th/U[c]	f_{206}[d] (%)	$^{207}Pb/^{206}Pb$	$^{206}Pb/^{238}U$	$^{207}Pb/^{206}Pb$ age (Myr)	$^{206}Pb/^{238}U$ age (Myr)	$\delta^{18}O_{SMOW}$[e] (‰)
1	3300	1600	0.048	0.08	0.1735±0.0003	0.4015±0.0099	2592±3	2176±46	7.8±0.5
2	2600	1600	0.017	0	0.1804±0.0003	0.5224±0.0128	2656±3	2709±55	9.2±0.5
3 (3a, ox)	1500	920	0.019	0.01	0.1796±0.0002	0.5158±0.0127	2649±2	2682±54	6.9±0.5
3 (3b, ox)									9.3±0.5
4	2300	1400	0.050	0.01	0.1831±0.0003	0.5310±0.0131	2681±2	2746±55	10.0±0.5
5	2400	1500	0.031	0.00	0.1810±0.0002	0.5259±0.0129	2662±2	2724±55	8.9±0.5
6	1700	1100	0.021	0.01	0.1806±0.0003	0.5230±0.0128	2658±3	2712±55	10.1±0.5
8	430	250	0.022	0.12	0.1876±0.0009	0.4804±0.0118	2722±8	2529±52	9.9±0.5
9									8.9±0.5
10									9.6±0.5
11									10.0±0.5
12									9.9±0.5

[a] Analysis ID represent grain number on SIMS mount. Oxygen isotope measurements were performed in different locations in the grain.
[b] U concentrations in parentheses have been estimated using measured primary beam, instrument sensitivity, and known concentrations in the 91500 reference zircon.
[c] Th/U ratios presented are those calculated from measured Th and U signals, calibrated to the 91500 zircon reference.
[d] Percentage of ^{206}Pb that is common Pb, calculated from the ^{204}Pb signal assuming a present day Stacey & Kramers (1975) model terrestrial Pb isotope composition.
[e] Oxygen isotope analyses were performed using the Nordsims Cameca IMS1270 operating in multicollector Faraday cup mode following a method similar to that described by Nemchin *et al.* (2006). Errors are the external standard deviation based on nine bracketing and interspersed measurements of the Geostandards 91500 zircon reference, assuming a $\delta^{18}O_{SMOW}$ value of 9.86‰ (Wiedenbeck *et al.* 2004).

a statement referring to 'later growth stages'), might help to address these concerns.

In an attempt to improve zircon U–Pb geochronology from the Akilia quartz–pyroxene unit, we report here the results of new single-crystal U–Pb zircon geochronology by SIMS from sample AK 12, from which we presented oxygen isotope data and CL images in §3*b*(iv). High spatial resolution U–Th–Pb data (table 1) reveals that these zircon grains are very rich in U, with concentrations ranging from 430 to 3300 p.p.m., but poor in Th, with Th/U ratios less than 0.05. In a Tera-Wasserburg concordia diagram (figure 11*c*), four analyses are concordant within analytical error, with $^{207}Pb/^{206}Pb$ ages ranging from 2650 to 2680 Myr, one analysis is slightly discordant with a $^{207}Pb/^{206}Pb$ age of approximately 2720 Myr and another analysis is significantly discordant. We consider that these ages, convoluted internal structure and low Th/U ratios are consistent with metamorphic growth of zircon during the major *ca* 2.7 Gyr tectonothermal event and, hence, that the quartz–pyroxene unit is at least 2.7 Gyr in age. We have been unable to find any zircon older than 2.7 Gyr in our sample, either as discrete grains or as cores within 2.7 Gyr grains.

In addition to zircon U–Pb, several other chronometers have been applied directly to rocks in the quartz–pyroxene unit. Sano *et al.* (1999) used *in situ* ion microprobe U–Pb method to obtain a date of more than 1.5 Gyr for apatite from sample G91-26 that was reported to contain isotopically light carbon in graphite inclusions. This age may represent metamorphic growth or recystallization, however, in either case raising doubt about the significance of any purported biogenic graphite inclusions.

Another example of metamorphic resetting of isotope systematics in the quartz–pyroxene unit is provided by a Pb isotope study of whole rocks and secondary sulphides (Whitehouse *et al.* 2005). The whole rock samples define an *ca* 2.7 Gyr regression line with a low model single-stage initial U/Pb ratio that indicates pre 2.7 Ga residence in a lower crustal setting, probably since the Early Archaean. Individual sulphides analysed by ion microprobe plot within error of the 2.7 Ga regression line, but at relatively radiogenic compositions that are interpreted to represent post 2.7 Ga equilibration with the whole rock Pb, possibly at *ca* 1.5 Ga during the event recorded by the apatite U–Pb system.

Nd isotope systematics have the potential to reveal crustal residence age but surprisingly, to date, no Sm–Nd data have been reported from the quartz–pyroxene unit. Here we report whole-rock Sm–Nd data from sample AK 12 (table 2). These data show that the rock is relatively light-REE enriched, with a $^{147}Sm/^{144}Nd$ ratio of 0.1107 and a present day $^{143}Nd/^{144}Nd$ ratio of 0.51066±0.00003 (2σ; $\varepsilon_{Nd}=-38.6$). A depleted mantle model age (t_{DM}) of 3.63±0.05 Gyr results from these data, consistent with an Early Archaean crustal residence. We caution, however, against over-interpreting this model age with regard to the actual age of the unit because high-grade metamorphism (particularly at granulite facies, e.g. Whitehouse 1988) has the potential to disturb Sm–Nd systematics such that very small changes in the Sm/Nd ratio at 2.7 Gyr (and to a lesser extent 3.65 Gyr) will strongly influence the result.

In summary, direct dating of samples from the quartz–pyroxene unit itself routinely reveals isotope resetting and/or disturbance events at approximately 1.5, 2.7 and 3.6 Ga in accord with well-documented regional events at these times. The very presence of Early Archaean metamorphic zircon (Mojzsis & Harrison 1999), as well as the Early Archaean Nd model age reported here, serves as cryptic evidence that the unit was largely intact (though almost certainly not in its present deformational state) as early as

Table 2. Whole rock Sm–Nd data for Akilia sample AK 12. (Whole rock sample powder was spiked with a mixed ^{149}Sm–^{150}Nd tracer and processed using conventional ion chromatographic methods. Isotope analyses were performed on a Micromass Isoprobe multicollector ICP MS at the Swedish Museum of Natural History, Stockholm, using a sample-standard bracketing method to correct for mass fractionation based on 5 analyses of in-house standard (Nd1) with a ^{143}Nd/^{144}Nd ratio of 0.51214. During the sequence of analyses of which AK 12 was a part, five analyses of the LaJolla Nd standard yielded an average ^{143}Nd/^{144}Nd ratio of 0.511846 ± 0.000038 (2 s.d.). Depleted mantle model age is based on the model of DePaolo *et al.* (1991) and assumes the decay constant for ^{147}Sm of Lugmair & Marti (1978).)

sample	Sm (p.p.m.)	Nd (p.p.m.)	^{147}Sm/^{144}Nd	^{143}Nd/^{144}Nd	2 s.e. (%)	$\varepsilon_{Nd}(0)$	t_{CHUR}	t_{DM}
AK 12	0.374	2.039	0.1107	0.510662	0.006	−38.6	3.48	3.63

approximately 3.6 Ga. However, these attempts fail to establish the age of the precursor to this unit and, critically, to show that Akilia is older than better preserved, unambiguously metasedimentary units at Isua.

(b) *Dating adjacent Akilia association rocks*

An alternative approach to dating the quartz–pyroxene rock itself is to date the adjacent and enclosing mafic/ultramafic rocks of the Akilia association on Akilia. In the context of the protolith discussion surrounding the quartz–pyroxene rock, this may provide a protolith age regardless of whether the quartz–pyroxene unit formed as part of a stratified sequence (Mojzsis *et al.* 1996; Nutman *et al.* 1997) or by modification of the mafic/ultramafic rocks (e.g. Fedo & Whitehouse 2002*a*,*b*). Using analytical data originally presented by Bennett *et al.* (1993) for seven Akilia association gabbroic enclaves from Akilia and the neighbouring island of Innersuartut, Moorbath *et al.* (1997) calculated a Sm–Nd isochron age of 3675 ± 48 Myr. Restricting this calculation to samples from Akilia itself, Kamber *et al.* (1998) reported an isochron age of 3677 ± 37 Myr, which they regarded as closely approximating the age of the gabbroic enclaves as well as associated lithologies including the quartz–pyroxene rock (at that time, still regarded as potential BIF). As with the direct dating approaches, the Sm–Nd isochron age for the Akilia gabbros provides no support for an age greater than that of relevant rocks at Isua.

(c) *Indirect dating of the quartz–pyroxene rock*

In the absence of any direct age constraints on the quartz–pyroxene lithology indicating that it is significantly older than IGB metasediments, proponents of such an older age have relied on U–Pb dating of zircon from a cross-cutting, therefore younger, igneous rock. This is inherently straightforward where rocks are not deformed such that relationships between lithologic contacts are unambiguous. In the case of Akilia, as we discussed above, all lithologies have been severely deformed and metamorphosed such that original contact relationships and, hence, relative age indicators have been thoroughly compromised. The details of these relationships and their implications for determining the age of the quartz–pyroxene rock have been presented by Whitehouse & Fedo (2003) and what follows here is a brief synopsis.

Much of the debate has centred around a single exposure where a supposedly clear example of Amîtsoq gneiss (formerly a quartz diorite) with a presumed age in excess of 3.83 Gyr has been repeatedly claimed to intrude mafic rocks of the Akilia association (Nutman *et al.* 1997, 2002; Mojzsis & Harrison 2002*b*), of which the quartz–pyroxene rock is part. The primary evidence for a supposed cross cutting relationship is the presence of a discordant quartz-diorite sheet passing through layers of mafic schist (illustrated by a simple field sketch, Nutman *et al.* 1997, fig. 2). Detailed observation of the exposure in question, however, revealed that the claimed discordance was an optical illusion created by viewing a three-dimensional outcrop from a specific angle (Myers & Crowley 2000) and that the rocks are not clearly cross-cutting (see Whitehouse & Fedo 2003, fig. 4). Critical to the matter is a structural detail directly in the contact zone between the quartz diorite and the mafic rock in which a centimetre-thick pegmatite band is intensely folded, indicating that the contact is unambiguously tectonic in nature, not intrusive as originally claimed. Hence, regardless of the precise age of the Amîtsoq gneiss sheet, which has itself been the subject of a considerable debate that is beyond the scope of the present paper (see Whitehouse & Kamber 2005), the inability to document an unambiguous cross-cutting relationship renders this approach for dating the Akilia enclave and, by assumed association, the quartz–pyroxene lithology inappropriate and irrelevant.

5. HOW DID THE QUARTZ AND PYROXENE LITHOLOGY FORM?

The geologic, geochemical and isotopic evidence currently points to a complicated origin for the quartz–pyroxene rock (Fedo & Whitehouse 2002*a*; Whitehouse & Fedo 2003). In our preferred scenario, rocks of the Akilia association form as a succession of mafic and ultramafic volcanic rocks (or perhaps shallow intrusive rocks). In the IGB, by area the largest exposure of the Akilia association, these rocks form part of an ocean floor assemblage with no input from continental land masses (Rosing *et al.* 1996; Fedo *et al.* 2001). Lacking specific reasons to exclude them, it is reasonable to extend this interpretation to other smaller fragments of the Akilia association that occur throughout the Godthåbsfjord. Based on observations from the rocks at Isua, the Akilia lithologies were likely strongly infiltrated by fluids that deposited abundant carbonate and quartz (Whitehouse & Fedo 2003, fig. 6). At Isua, metasomatic alteration ranges from little to profound (Rosing *et al.* 1996), so it is expected that original compositions could have been dramatically changed and then diluted by addition of new minerals.

This framework sets the stage for the repeated high-grade dynamothermal metamorphic events that affected the outer Godthåbsfjord, including Akilia (Griffin *et al.* 1980). A consequence of these events is that secondary carbonate could have been transformed to graphite and magnetite by decarbonation (e.g. Perry & Ahmad 1977; van Zuilen *et al.* 2002*a*) or perhaps to pyroxene. Intense deformation associated with these events would have transposed original geologic contacts into parallelism, creating the boudinage common in the lithology. The resulting rock would consist of banded alternations of quartz and geochemically modified mafic and ultramafic rocks. A younger deformation event that generated the small-displacement cross-cutting shear zones appears to be connected with continued fluid/rock interactions because garnet concentrates in the faults only where they deform the quartz–pyroxene rock itself.

6. CLAIMS FOR LIFE IN THE ISUA GREENSTONE BELT

Despite all the excitement, debate and controversy surrounding the Akilia rocks, the first claims for a fossil record are not from there. Rocks of the approximately 3.7 Gyr IGB (also referred to as Isua Supracrustal Belt) have been the centre of attention for some 25 years. Various approaches have been used to seek evidence for life there. Rocks that comprise the belt represent perhaps the largest exposure of what McGregor & Mason (1977) termed the Akilia association. Here, we summarize some of the major claims for a fossil record in rocks of the IGB.

(a) *Isuasphaera*

One of the earliest claims for preserved life comes from putative cell-like body fossils observed in recrystallized chert and named *Isuasphaera isua* sp. (Pflug & Jaeschke-Boyer 1979). The 'fossils,' which range from 20 to 40 μm, occur in different morphologies from spherical to filamentous, single cells and colonies, and even trapped within the state of reproduction compared to that observed in yeast (Pflug & Jaeschke-Boyer 1979). Supporting a biological interpretation for the structures, Pflug & Jaeschke-Boyer (1979) presented chemical data suggesting that there is relict organic material within the cells.

In response to the claims that these spherical objects were unicellular microfossils, Bridgwater *et al.* (1981) examined samples from the same outcrop and drew a substantially different conclusion based on a deeper understanding of the structural and metamorphic events that have profoundly affected the rocks. Rather than seeing a microfossil community, Bridgwater *et al.* (1981) interpreted the features as trails of limonite-stained, inorganic, fluid inclusions formed during episodes of deformation and recrystallization. Such a conclusion fits well with the known upper amphibolite facies metamorphism that has affected the rocks (Nutman *et al.* 1996) and the inconclusive organic geochemistry discussed by Nagy *et al.* (1981). One important parallel with the Akilia story is the presumption that an original protolith is still in a relatively intact state so that an original fossil could be identified. In the case of *Isuasphaera*, rocks were claimed to be 'cherty layers of a quartzite', although we have seen no evidence of primary chert preserved anywhere at Isua. Rather, all cherts have undergone crystal coarsening and now appear as millimetre-scale optically clear crystals.

(b) *Carbon isotope record*

At the time *Isuasphaera* was being discussed, Schidlowski *et al.* (1979) were investigating the potential that carbon isotopes might be a sensitive biomarker for identifying early life in some carbonate rocks in the IGB. Details of this approach have been recently discussed by Horita (2005), but in general terms the idea is that living organisms increase the ^{12}C to ^{13}C ratio by preferentially sequestering ^{12}C during metabolism. The resulting carbon isotope ratio expressed in parts per thousand as $\delta^{13}C$ (relative to Pee Dee belemnite (PDB)) is significant enough to identify organic and inorganic carbon reservoirs, where biologic signatures possess $\delta^{13}C_{PDB}$ values lighter than −10‰, and an average of −27‰ for higher plant Rubisco.

Schidlowski *et al.* (1979) recorded bulk rock $\delta^{13}C_{PDB}$ values ranging from −6 to −25‰ from Isua carbonates as well as approximately −25‰ for reduced carbon, and used these to suggest that life had been established on Earth by 3.7–3.8 Ga. The carbon isotope approach was extended by Mojzsis *et al.* (1996) and Ueno *et al.* (2002), who used high spatial resolution SIMS to measure carbon isotope ratios from individual graphite crystals. Mojzsis *et al.* (1996) looked at a sample of carbonate rock with magnetite, and Ueno *et al.* (2002) collected graphite from a variety of rocks that comprise the IGB. Both studies identified isotopically light carbon in the graphites and concluded that they had a biologic origin. Central to this approach is the assumption that the separation and sequestration of ^{12}C is practically unique to biological processing, or enough so that abiotic pathways could be neglected.

In two detailed studies that assessed the potential 'biomineralic' relationship between apatite and graphite and the carbon isotopic composition for Isua graphite, van Zuilen *et al.* (2002*a*,*b*) and Lepland *et al.* (2003) cast serious doubt on the possible biogenicity of either. The carbonate-rich sample examined by Mojzsis *et al.* (1996) was reinterpreted as a secondary metasomatic rock and not BIF, and therefore was biologically irrelevant (van Zuilen *et al.* 2002*a*,*b*). The graphite formed either from the disproportionation of iron-bearing carbonate or as a younger contaminant. Furthermore, Lepland *et al.* (2003) concluded that graphite was preferentially formed in metasomatic rocks and not in sedimentary rocks like BIF.

Related to such conclusions is the growing body of independent literature that has recently shown that isotopically light hydrocarbon can be produced via several abiotic pathways, from Fischer-Tropsch synthesis at mid-ocean ridges (Holm & Charlou 2001), in crystalline rocks (Sherwood Lollar *et al.* 2002), or experimentally (Horita & Berndt 1999) to the decomposition of siderite (McCollum 2003). Consequently, the notion of graphite enriched in ^{12}C as a unique biosignature has lost credibility in recent years.

(c) *Metaturbidite locality*

There is one other location in the IGB where isotopically light graphite has been discovered and interpreted as the remains of life (Rosing 1999). In this case, the rocks are not carbonates, but clastic sedimentary rocks thought to have formed on the sea floor as turbidite deposits, and they have been dated using a Sm–Nd isochron at 3.78 ± 0.08 Gyr. Rosing's (1999) study showed that the least altered of these rocks had bulk $\delta^{13}C_{PDB}$ values of approximately −19‰, which was interpreted as consistent with a biogenic origin. Subsequently, van Zuilen *et al.* (2002*a*,*b*) carried out experiments that showed that the graphite in this sample, unlike that at many other localities in the IGB, was likely original in nature rather than secondary, strengthening the claim that this locality might preserve Earth's earliest life.

If the light carbon isotopic signature of the turbidite is indeed biogenic, the next question to raise is whether it is possible to infer anything about the metabolic function of the organism(s) responsible. Based on modelling of the Pb isotope composition of the whole rocks, Rosing & Frei (2004) have suggested that this was oxygenic photosynthesis. The results from their model are that: (i) between deposition at *ca* 3.7 Ga and metamorphism at 2.77 Ga, the metasediments had both high U/Pb and (ii) critically, near-zero Th/U ratios. Rosing & Frei (2004) argue that such unusual Th/U ratios can result only from oxidized compartments of the Early Archaean depositional environment that permit solute transport of U but not Th.

Inference of near-zero Th/U (in the following discussion, we use κ_2 and κ_3 to denote the $^{232}Th/^{238}U$ ratio from 3.7 to 2.77 Ga and from 2.77 to 0 Ga, respectively) is based on an assumption that the metasediments have relatively constant κ_3, permitting back projection of a regression line through all the data to the 2.77 Ga $^{206}Pb/^{204}Pb$ ratio (determined from the uranogenic Pb-isotope systematics) in order to constrain the $^{208}Pb/^{204}Pb$ at this time (figure 12). This ratio at 2.77 Ga is essentially the same as that of Stacey & Kramers (1975) model source at 3.7 Ga and thus implies no radiogenic in-growth of ^{208}Pb over this period, hence effectively no Th. However, $\kappa_2 \approx 0$ is neither a unique nor, necessarily, the preferred interpretation of the combined whole-rock and leach data. First, the *a priori* assumption that any suite of whole rock samples has near constant Th/U is not supported by the whole-rock data themselves, which show some degree of scatter (figure 12). Unlike uranogenic Pb isotope systematics where the slope of a regression line in $^{207}Pb/^{204}Pb$ versus $^{206}Pb/^{204}Pb$ space is a function only of age, in the combined uranogenic–thorogenic system represented in $^{208}Pb/^{204}Pb$ versus $^{206}Pb/^{204}Pb$ space, assuming a common age, this slope is a function of Th/U ratio. Thus, each individual data point may be back projected to an initial ratio or, in other words, for a given value of κ_2, a unique κ_3 may be calculated (figure 12, inset). For example, $\kappa_2 = 0$ yields κ_3 values between 4.0 and 4.8, while a typical crustal κ_2 value of 4 yields κ_3 values between 3.2 and 4.3. These latter values require no significant influx of Th at 2.77 Ga to the whole-rock system, as has been proposed by Rosing & Frei (2004).

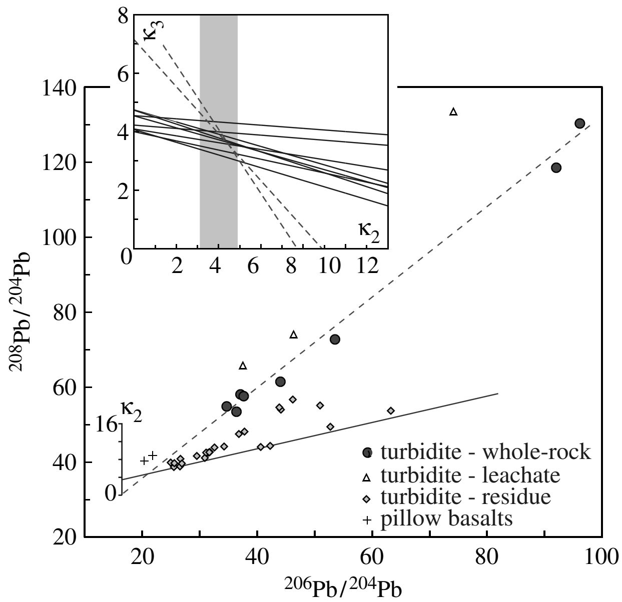

Figure 12. Main diagram: $^{208}Pb/^{204}Pb$ versus $^{206}Pb/^{204}Pb$ plot of the Pb isotope data of Rosing & Frei (2004) from IGB metasediment (turbidite locality). Graduated vertical bar shows the $^{208}Pb/^{204}Pb$ ratios at 2.77 Ga, graduated for values of κ_2 ($= {}^{238}Th/^{204}Pb$ ratio between 3.7 and 2.77 Ga) from 0 to 16. Dashed line is the preferred interpretation of Rosing & Frei (2004) in which a regression through the whole rock points intersects at 2.77 Ga $^{208}Pb/^{204}Pb$ ratio corresponding to $\kappa_2 \approx 0$. Solid line shows an interpretation based on a regression through the least thorogenic residues, intersecting at a value corresponding to $\kappa_2 \approx 4$. Inset diagram: plot of κ_3 ($= {}^{238}Th/^{204}Pb$ ratio from 2.77 Ga to present) versus κ_2 for turbidite whole rocks (solid lines) and adjacent pillow basalt whole rocks (dashed lines). For both rock types, typical crustal values of $\kappa_2 \approx 4$ (broad grey band) correspond to similar values of κ_3, implying that neither significant fraction of Th from U at 2.77 Ga, nor unusually low κ_2 values are required by these data.

Second, in the search for the most likely value of κ_2, the leach residue data appear to provide a more robust constraint than the more radiogenic whole rocks (figure 12). As with the whole rocks, a κ_2 value of zero cannot be ruled out but any value up to approximately 6 (constrained by $\kappa_3 = 0$ for the data point with lowest $^{208}Pb/^{204}Pb$) is permitted. If the leach residues reflect a low but non-zero κ_3 phase(s), then a regression line through the data points with lowest κ_3 may be used to infer a κ_2 value of *ca* 3.5 (figure 12).

In summary, neither the whole rock nor leach residue data require a zero or near-zero κ_2, although this remains a possible, albeit in our view extreme, interpretation. Thus, these data cannot be used unambiguously to infer preferential U solute transport at 3.7 Ga, and by inference operation of oxidative photosynthesis. Despite this reinterpretation, the isotopically light carbon from the 'turbidite' outcrop remains, in our view, a potentially valid indicator of biological activity at approximately 3.7 Ga.

7. CONCLUSIONS

The oldest known supracrustal rocks on Earth are exposed in southwestern Greenland, where they comprise an assemblage of mafic and ultramafic volcanic rocks, BIF and less common clastic sedimentary rocks that formed at approximately 3.7–3.8 Ga. On the island of Akilia, the highly deformed and metamorphosed supracrustal rocks have been at the centre of debate ever since they have been claimed to host the earliest life on Earth (Mojzsis *et al.* 1996). These rocks form part of a distinctive, metre-thick, banded quartz–pyroxene rock originally interpreted to be BIF. A BIF origin is a prerequisite for the graphite to be a potential biomarker because it forms as a chemical sedimentary rock in seawater.

Detailed field observations show that the quartz–pyroxene rock is intensely deformed. The unit is strongly foliated and boudinage is very common. Small scale ductile shears cross-cut the lithology. Such observations indicate that the original character of the rock has been compromised and the present features are a product of deformation and metamorphism, not original deposition of a chemical sediment. Attempts to establish the unit's origin using oxygen, sulphur and iron isotopes have yielded ambiguous results. A number of trace-element geochemical indicators are consistent with the quartz–pyroxene rock having a metasomatized mafic–ultramafic origin (Fedo & Whitehouse 2002*a*,*b*). Attempts at substantiating the great age commensurate with a claim for the oldest life have equally met with significant problems. Direct dates from the unit only provide ages consistent with isotopic resetting during younger metamorphic events. Indirect dating via interpreted cross-cutting relationships has been confounded by the severe tectonic reorganization of lithologic contacts. Despite the wide coverage of this lithology in the popular media and the continued interest in Akilia, it is unavoidable to conclude that the quartz–pyroxene rock is completely unsuitable as a host for life and it cannot even be established to be of an age coeval with the late heavy bombardment of the inner solar system.

Putative body fossils and ^{12}C enriched isotopes in graphite thus far described from the older than 3.7 Gyr IGB are better explained by abiotic processes. However, there remain a number of fruitful targets for examining the earliest stages in the emergence of life there.

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