Evidence for life on Earth before 3,800 million years ago

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It is unknown when life first appeared on Earth. The earliest known microfossils (~3,500 Myr before present) are structurally complex, and if it is assumed that the associated organisms required a long time to develop this degree of complexity, then the existence of life much earlier than this can be argued. But the known examples of crustal rocks older than ~3,500 Myr have experienced intense metamorphism, which would have obliterated any fragile microfossils contained therein. It is therefore necessary to search for geochemical evidence of past biotic activity that has been preserved within minerals that are resistant to metamorphism. Here we report ion-microprobe measurements of the carbon-isotope composition of carbonaceous inclusions within grains of apatite (basic calcium phosphate) from the oldest known sediment sequences—a ~3,800-Myr-old banded iron formation from the Isua supracrustal belt, West Greenland, and a similar formation from the nearby Akilia island that is possibly older than 3,850 Myr (ref. 3). The carbon in
the carbonaceous inclusions is isotopically light, indicative of biological activity; no known abiotic process can explain the data. Unless some unknown abiotic process exists which is able both to create such isotopically light carbon and then selectively incorporate it intoapatite grains, our results provide evidence for the emergence of life on Earth by at least 3,800 Myr before present.

Because of the unique chemical properties of phosphate and its fundamental role in a large variety of biochemical processes, the participation of phosphorus in biogeochemical cycles must be a primitive phenomenon. Authigenic phosphate minerals are a significant sedimentary component of sediments. The principal constituent of modern authigenic phosphate minerals in marine sediments is carbonate (hydroxy)apatite (CHFA), $\text{Ca}_{10} (\text{PO}_4)_{6} (\text{CO}_3)_{2} (\text{OH})_2$. In the marine environment, organisms participate in concentrating organic phosphate from solution and by recycling organic phosphate species from decaying P-rich bioorganic matter. Microorganisms are well known to segregate calcium from magnesium, and actively nucleate CHFA by means of specific oligopeptides. Due to this common formation of authigenic CHFA, microcrystalline aggregates ofapatite in modern as well as ancient sediments characteristically are intergrown with organic matter*. During diagenesis the aggregates recrystallize, eventually forming singleapatite crystals with inclusions of carbonaceous material, which after extensive metamorphism crystallizes to graphite.

Organisms are capable of depositing apatite outside thermodynamic equilibrium in sea water with pH < 8.5 and $[\text{Mg}]:[\text{Ca}] > 0.1$ (refs 10--12), which indicates the potential value of phosphate microminerals and their associated carbonaceous inclusions as indicators of biological activity in ancient sedimentary chemical precipitates, such as chert and banded iron formation. The potential biogenic significance of theapatite alone can only be realized if the range of Mg/Ca ratios and the pH in the source solution can be estimated independently. Even in exceptional cases, BIFs have at most minor fractions of chalcopyrite derived from the weathering of igneous rocks. However, such igneous apatite is free of carbon inclusions and is resistant to dissolution in natural waters; it therefore has minimal interaction with marine biogeochemical cycles and, moreover, is a relatively minor mineral constituent in most igneous rocks and their weathering detritus. But metasedimentary apatite from early Archaean BIFs, if found to contain isotopically light carbonaceous inclusions diagnostic of a bioorganic origin, might be one of the few distinguishable traces of early life in the Earth’s sediments.

Carbon isotopic measurements of carbonaceous matter in sedimentary rocks have provided insights into biogeochemical pathways and the evolution of life with or without the presence of identifiable microfossils. However, conventional methods of mass spectrometry lack the sensitivity to analyse carbon isotopes in individual apatite inclusions which are typically 10$^{-8}$ cm$^2$ and contain 20 pg carbon. The ion microprobe permits the study of isotopic variations at the scale of 10--20 μm spots. To enhance the accuracy of measurements, sputtering of each inclusion was generally continued until a large fraction of the target had been consumed. The required high sensitivity must be maintained at the relatively high mass resolving power ($M/ΔM ≈ 4,000$) necessary to separate interfering $^{13}\text{C}$ ions from $^{12}\text{C}$. We have tested the hypothesis that carbonaceous inclusions contained in apatite from early Archaean sediments are biogenic by using an ion microprobe to perform in situ carbon isotope measurements of such mineral microdomains in cherts and BIFs from Western Australia ($≥ 3,250$ Myr) and from West Greenland ($≥ 3,700$ Myr).

The Pilbara craton of northwestern Western Australia contains well preserved volcano-sedimentary sequences with ages between $> 3,000$ and 3,500 Myr (refs 20, 21). Within the Warrawoona Group, cherts from the Apex Basalt (3,450 ± 16 Myr) contain the oldest microfossils yet identified, some of which resemble extant chemooautotrophic and photoautotrophic prokaryotic morphotypes. Whole-rock carbon isotope ratios of kerogen in the Warrawoona sediments have been interpreted to infer that photosynthesizing, or even cyanobacterium-like, organisms were already active by 3,500 Myr (refs 1, 2, 16--19). The apatite intergrowths with organic matter we report here are from lower greenish facies chert of the (3,250 Myr) Nickel Well unit of the Roebourne belt, west Pilbara Archaean succession (R. Buick, personal communication).

The Isua supracrustal belt in West Greenland contains large volumes of early Archaean BIF and meta-chert. As BIFs are of sedimentary origin, these rocks are at least as old as their metamorphic age of 3,700 Myr. Isua rocks used in this study have been metamorphosed to amphibolite facies; details of the mineralogy and petrographic relationships of the Isua rocks have been given elsewhere.

An early Archaean BIF encompassed within a layered amphi-
bolite and ultramafic complex on Akilia island, southern West Greenland, is cut by a deformed quartz-dioritic sheet dated at 3,860 ± 10 Myr (ref. 3), providing a possible minimum age for the transected sedimentary unit. The sample used in this study (G91-26) comes from a well-preserved layer of BIF consisting of quartz (30%), clinoxyroxene (25%), orthopyroxene (20%), amphibole (15%), magnetite (5%), iron sulphides (<1%) and other minerals (<1%) including apatite, but no observable carbonate. The unit meets the criteria of James (ref. 26) for a silicate facies to low-grade oxide facies BIF. Anhedral olivine to low-grade facies apatite grains, occurring either individually or in groups, and resembling those found in the younger Pilbara cherts and Isua supracrustal belt samples cited above, are typically 10–15 μm in diameter and 30–40 μm in length (Fig. 1) and frequently contain inclusions and envelopes of graphitized carbon. Apatite grains occur in the pyroxenes, quartz, amphibole and (rarely) in magnetite, and when found in groups, are present as trains parallel to banding. In contrast, 3,860–3,870 Myr orthogneiss from the same locality, and transecting and encompassing the supracrustals, contain igneous apatite that are devoid of graphite inclusions, are compositionally distinct, and are associated with common igneous phases such as feldspar not found in chemically precipitated sediments like BIF.

The stable isotopes of carbon are partitioned as a result of both equilibrium exchange reactions and kinetic effects, which are due to metabolic mechanisms as well as inorganic processes such as evaporation, diffusion and condensation. Kinetic isotopic fractionation between organic and inorganic carbon results in marked enrichment of the light isotope in the bioorganic component by several per cent (refs 16, 17). Hence, bioorganic materials, including carbonaceous fossils, are typically characterized by δ13C values of -20 to -35‰ in the case of most photosynthetic bacteria, and can be as light as -50 or -60‰ for products of microbial communities apparently involved in the recycling of methane. In contrast, inorganic carbon is usually heavier than about -10‰, with a typical range between 5 to -5‰ (refs 16, 17).

In situ microprobe measurements of occluded carbon in apatite micrograins from the Akilia island BIF yield a range of δ13C values from -21 (±2)%e to -49 (±7)%e, with a weighted mean of -37 (±3)%e (Fig. 2). Because of the micrometre size of the irregular samples embedded in apatite, the precision and accuracy of individual measurements are typically ±5‰ (1σ) and encompass counting statistics plus an extra component for fluctuation of count-rates during analysis. Isotopic results for carbonaceous inclusions in the Pilbara sediments and Isua BIF yield weighted means of -26 (±3)%e and -30 (±3)%e, respectively. The results for the Pilbara sediments agree with previous whole-rock values obtained by conventional mass-spectrometric techniques for Warrawoona Group sediments. All measured values from our early Archaean apatite inclusions are well resolved from what are generally considered to be inorganic carbon values.

To evaluate the presence of life in the previously oldest known sedimentary rocks, carbon isotope ratios were measured in acid insoluble carbonaceous residues (kerogens) of bulk samples from the 3,700-Myr Isua supracrustal belt BIF. These measurements yielded mean δ13C values of -11 to -15 (±5‰) that have been interpreted as indicating photosynthetic carbon fixation. However, these previous values are close to the range of inorganic carbon δ13C ratios, possibly owing to isotopic exchange with
carbonate carbon present in the Isua rocks during metamorphism, so they have been regarded as ambiguous. Some carbon in igneous rocks is observed to have intermediate isotopic ratios in the range of $-10$ to $-20\%$, but these could reflect biogenic contamination from assimilated sediments. Miller–Urey spark-discharge laboratory experiments, carried out to simulate hypothetical hydrogen-rich primitive Earth atmospheres, yield organic bulk reaction products which are $^{13}$C isotopically heavier than $-10\%$ and that could not have contributed to the carbon in the apatites. We can rule out reduced carbon from carbonaceous meteorites (the richest contain $\sim 3\%$ mass $^{13}$C, as carbon isotope ratios for these generally cluster at $-11$ to $-18\%$) and there is no reason to expect meteoritic carbon to be selectively associated with apatite in BIF. Regardless of the modes of origin for the carbon components in the various materials mentioned above, the $^{13}$C values for the carbon inclusions in apatite are $10$–$15\%$ lighter still than the $^{13}$C values seen in such abiogenic samples, and are characteristic of the range of carbon isotopic compositions for biogenic matter (Fig. 2).

For strongly negative carbon isotope values in metamorphosed sediments to be convincingly interpreted as unaltered products of biogenic fractionation, it is necessary to analyse the magnitude and sign of such effects that could have perturbed an original distribution. Empirical studies have shown that the loss process of CO$_2$ from the oxidation of organic matter is kinetically controlled, and the evolved CO$_2$ is isotopically lighter than the source organic carbon. Hence, loss of volatiles from thermally degrading organic matter leads to the residual organic matter being isotopically enriched in $^{13}$C. However, in order to investigate theoretical scenarios where progressive thermal metamorphism in principle could lead to enrichment of residual carbon in $^{13}$C, we evaluated possible changes in the $^{13}$C value of organic matter included in apatite under both thermodynamically open-system (Rayleigh) and closed-system (single-step) behaviours. Depending on the oxygen fugacity of the system, metamorphism can result in the release from carbonaceous matter of different proportions of CO$_2$ and CH$_4$ fluids, but a loss of methane which partitions the light isotope can never produce isotopic compositions lighter than the starting materials. On the other hand, the escape (during dia-
are not responsible for the association of isotopically light carbonaceous inclusions in metasedimentary apatite.

Together with the intergrowth of carbonaceous matter withapatite in BIF from Akilia island, we conclude that the isotopic results reported here give strong evidence for life on Earth by 3,850 Myr. Although this finding pushes back the horizon for the emergence of life by 300–400 million years, it is not entirely unexpected, given also the apparently evolved nature of lifeforms at ~3,500 Myr. However, the ‘late heavy bombardment’ (>3,800 Myr), documented in the lunar record, has been speculated to place an upper limit on the age of a continuous terrestrial biosphere. The evidence for life presented here overlaps this critical time period and shows that if the accretion models are realistic, such a bombardment did not lead either to the extinction of life or the perturbation of the finely laminated >3,850-Myr BIF preserved on Akilia island.

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