

¹³C-Depleted Carbon Microparticles in >3700-Ma Sea-Floor Sedimentary Rocks from West Greenland

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Turbiditic and pelagic sedimentary rocks from the Isua supracrustal belt in west Greenland [more than 3700 million years ago (Ma)] contain reduced carbon that is likely biogenic. The carbon is present as 2- to 5-micrometer graphite globules and has an isotopic composition of $\delta^{13}\text{C}$ that is about -19 per mil (Pee Dee belemnite standard). These data and the mode of occurrence indicate that the reduced carbon represents biogenic detritus, which was perhaps derived from planktonic organisms.

The oldest known fossils have an age of 3500 million years ago (Ma) and may represent photosynthetic cyanobacteria (1). It can be assumed that a long chain of evolutionary steps preceded the development of these complex organisms. Supracrustal rocks older than 3600 Ma are all metamorphosed at a high grade, and most are strongly deformed; thus, morphological fossils (if originally present) are unlikely to be preserved. Therefore, geochemical evidence for biologic activity coupled with geologic evidence for the habitats of early life may provide better constraints on earlier stages in the evolution of life than fragmented morphological vestiges of the organisms themselves.

Several studies have documented the presence of ¹³C-depleted reduced C in the Isua supracrustal rocks (2–6). Schidlowski *et al.* (2) suggested that the isotopic compositions of carbonate rocks ($\delta^{13}\text{C} \approx -2.5$ per mil) and reduced C ($\delta^{13}\text{C} \approx -5.9$ to -24.9 per mil) were modified by metamorphic reequilibration but still recorded the presence of an early Archean reservoir of ¹³C-depleted C that is comparable to the present sedimentary reservoir of biogenic reduced C. The samples were assumed to be sedimentary in origin, although many lithologies have since been identified as metasomatized orthogneisses and basalts (7). Mojzsis *et al.* reported the occurrence and isotopic composition of graphitic microinclusions in apatites from Isua banded iron formation and in a sample of the correlative Akilia supracrustals and interpreted the association of graphite and apatite as reflecting the decomposition of biogenic sugar phosphates in the sedimentary protolith (6); however, the age of these samples [reported to be ~ 3800 Ma and >3.85 billion

years ago, respectively) and the origin of the apatite are debated (8–11).

The Isua supracrustal rocks represent the metamorphosed and deformed remnants of one or more sequences of sedimentary, volcanic, and intrusive rocks. All rocks at Isua have experienced amphibolite facies metamorphic events (12, 13), and most rocks are deformed (7, 14). Banded iron formation, basaltic volcanic rocks, and peridotite are among the undisputed protoliths; whereas protoliths of felsic gneisses and mica schists are uncertain (7, 15). Carbonate rocks that were assumed to be of sedimentary origin in earlier studies (2, 3) have since been shown to be metasomatic in origin (7, 14). The Isua supracrustal rocks were deposited before 3700 Ma, which is the U-Pb age of igneous zircons from granitic sheets that crosscut the supracrustals (16).

I have studied metamorphic rocks with well-preserved sedimentary structures in a low-strain domain within the metabasaltic Garbenschiefer Formation (7). The rocks are in depositional contact with the basaltic units. The Garbenschiefer amphibolites are derived from dominantly tholeiitic volcanic protoliths (17), and pillow structures are occasionally

preserved (18). The sedimentary rocks can be traced ~ 100 m along strike, and they form a ~ 50 -m-thick succession that is dominated by normally graded beds of clastic sediments, which are 10 to 70 cm thick and have sharp bases (Fig. 1, A and B) that are separated by black slaty units with thicknesses of up to 10 cm. These sequences are intercalated with banded iron formation. Predominant minerals in the graded beds are quartz, mica, chlorite, and graphite.

The black slaty units are finely laminated and consist of varying proportions of quartz, muscovite, biotite, chlorite, pyrrhotite, ilmenite, chalcopyrite, and graphite (Fig. 1C). The dark layers are rich in mica and graphite, whereas the lighter layers are rich in quartz. Packages of such fine layers are interspersed with layers that have thicknesses of up to 1 mm, that are rich in plagioclase, and that lack detectable graphite. These layers are concordant and are continuous over the outcrop. The rocks are cut by 1-mm-wide quartz veins, which lack graphite.

In the least deformed samples, mica and chlorite define a schistosity that is parallel to the sedimentary bedding. In more deformed rocks, all sedimentary structures have been obliterated, and up to 1-cm biotite and garnet porphyroblasts are present. Relics of the sedimentary stratification can be observed as closely spaced planar trails of graphite inclusions in the cores of some biotite and garnet porphyroblasts; graphite is absent from the ground mass here. In samples that have been totally recrystallized to garnet-hornblende-biotite-chlorite schists, the fine sedimentary bedding is totally obliterated, and graphite is absent. These relations indicate that the graphite globules formed before the earliest growth of garnet and biotite and were consumed during progressive metamorphism.

In both graywacke and black slate, graphite is abundantly present as 2- to 5- μm globular grains that are included in the silicate phases. Graphite grains are distributed along the sedimentary bedding, and the graphite grain size does not vary with the abundance

Table 1. Carbon data from the Isua supracrustal belt. Samples 810212, 810213, and 810214 are from sedimentary rocks; samples 930049 and 930055B are from a sedimentologically unconstrained outcrop; and samples 810227 and 810228 are from a discordant graphite vein that crosscuts talc schist. Samples were finely ground in agate and decarbonated in hot HCl. Carbon was converted to CO₂ in an oxygen furnace at 1000°C and analyzed by standard procedures at the Danish Center for Isotope Geology (26). Values of $\delta^{13}\text{C}$ are referenced to the Pee Dee belemnite standard.

Sample	Type	Reduced C (weight %)	$\delta^{13}\text{C}$ (per mil)
810212	Turbidite graywacke	0.1	-19.07
810213	Slate	0.4	-19.11
810214	Mica schist	0.3	-18.77
930049	Garnet-biotite schist	0.9	-14.10
930055B	Micaceous quartzite	0.2	-20.21
810227	Graphite vein	0.4	-12.58
810228	Graphite vein	1.0	-11.40

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of graphite in a layer, except in zones of localized shearing, where C was recrystallized to larger flaky graphite grains that are 10 to 100 μm across.

The identity of the graphite microglobules as the hosts of reduced C in the rocks has been confirmed by backscattered electron images (Fig. 1, E and F) and by reflected light microscopy, which in some cases has shown a strong optical anisotropy, which is characteristic of graphite. The presence of other reduced C components in the globules cannot be excluded, however.

The graywackes have compositions resembling modern arc turbidites (19), indicating that immature volcanic detritus formed an important component in the sediments. Sm-Nd isotopic data from the sediments and the enclosing metabasalts (20) define an isochron of 3779 ± 81 Ma (mean square weighted deviation = 8.76) (Fig. 2).

I have measured the isotopic compositions of reduced C from graywacke and slate and from more strongly recrystallized

slate, which is now represented by mica schist. To constrain the effect of graphite recrystallization in the presence of metamorphic fluids, I sampled fine-grained graphitic and micaceous quartzite and correlative strongly recrystallized garnet-biotite-graphite schist from a sedimentologically unconstrained outcrop. To assess the signature of C in local metamorphic fluids, I analyzed two samples of vein graphite from a different part of the Isua supracrustal belt, as graphite veins are not observed within the meta-sedimentary rocks (Table 1).

The association of graded graywackes and laminated slates can be interpreted in the framework of Bouma sequences (21). The graded units with sharp bases and gradational upper contacts were probably deposited from turbidity currents (22), whereas the laminated slates form pelagic units, which were probably deposited during quiet periods between turbidite pulses.

The turbidites are associated with a 1-m-thick unit of impure banded iron formation, and this sedimentary package occurs in a

succession of basaltic metavolcanic rocks. No terrigenous clastic sediments have been identified in any part of Isua (7), and refractory accessory phases that are typical of terrigenous sources have not been observed in the sedimentary rocks. These observations are consistent with deposition in an oceanic environment in the vicinity of volcanic edifices. The undisturbed nature of the turbidites and pelagic sediments indicates that the water depth was below wave base, probably >100 m. Thus, the sediments were likely deposited below the photic zone. The strong correlation of globule abundance with individual sedimentary strata indicates that the C was deposited as particulate matter during sedimentation of the protolith and was not introduced by secondary processes.

The coarse-grained plagioclase-rich interlayers in the pelagic sediments could have been formed by airborne volcanoclastic sediments that were rapidly deposited. The inverse correlation of graphite abundance to the apparent rate of sedimentation and the absence of C grains from the coarser grained feldspar-rich layers indicate that the C-rich

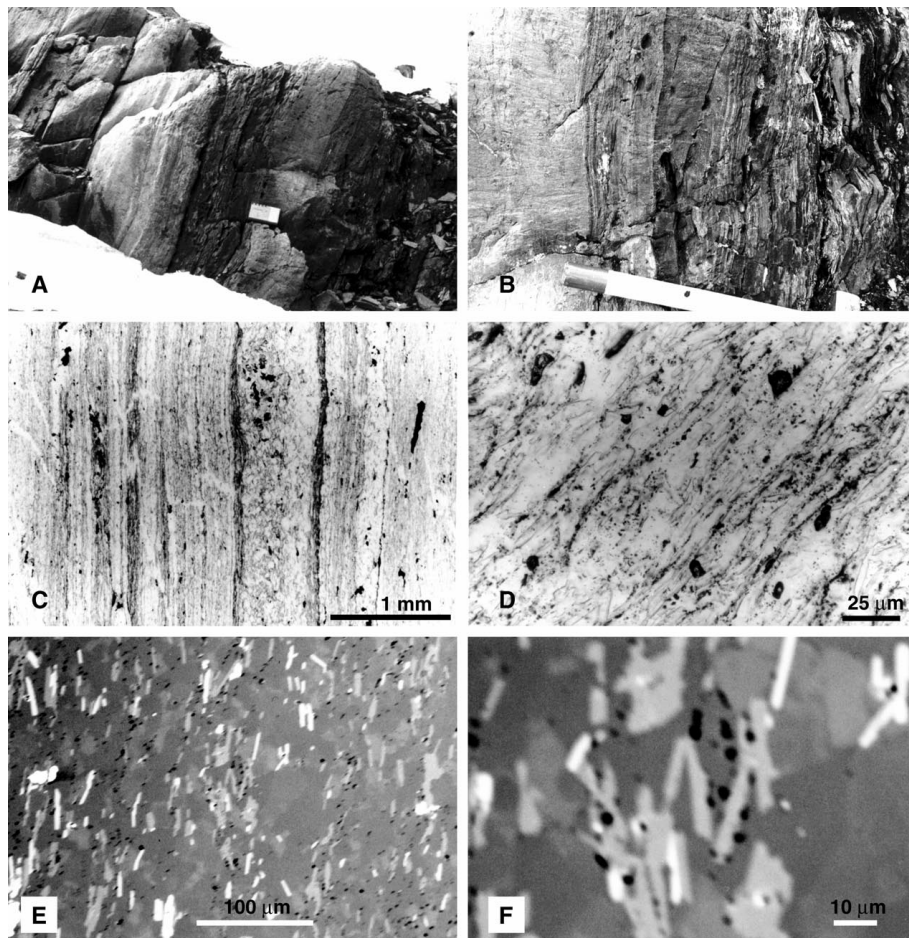


Fig. 1. (A) Turbidite sedimentary rocks from the Isua supracrustal belt, west Greenland. The notebook is 17 cm wide. (B) A close-up of finely laminated slate representing pelagic mud. The hammer is 70 cm long. (C) Photomicrograph of sample 810213, showing finely laminated pelagic mud. The variation in color is mainly due to variations in C abundance. (D) Photomicrograph of C grains arranged along a buckled stringer. (E) Backscattered electron image of a polished surface (sample 810213), showing the distribution of C grains as black areas. (F) Backscattered electron image of a polished surface (sample 810213), showing the rounded shape of C grains (black).

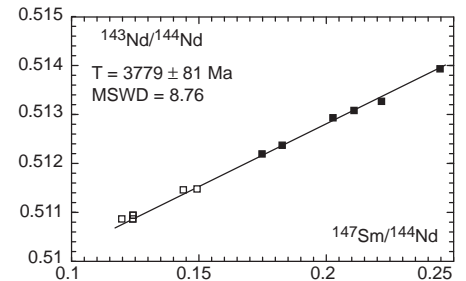


Fig. 2. Sm-Nd isochron diagram showing isotopic data from sediment samples 810196, 810205, 810212, 810214, and 810215 (open squares) and enclosing Garbenschiefer amphibolite (solid squares). Analysis of the sediments was carried out by standard techniques (10), and data for the Garbenschiefer amphibolite are from the least disturbed samples from (20). Analytical errors are within the symbols. T, age; MSWD, mean square weighted deviation.

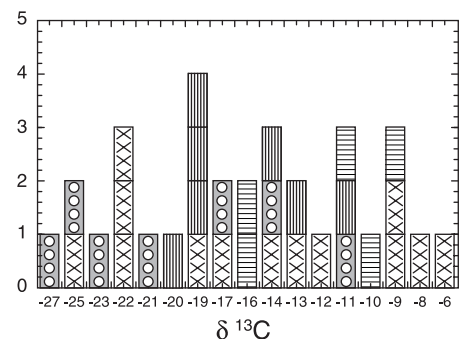


Fig. 3. Distribution of $\delta^{13}\text{C}$ values in classes of one unit of δ for the reduced C of bulk rock from Isua. The bars represent data from (2) (crosses), (3) (open circles), (4) (horizontal lines), and this study (vertical lines).

particles most probably sedimented continuously from suspension at a slow rate and were not derived from an episodic source. The present-day rate of oceanic pelagic sedimentation is <1 cm per 1000 years. The reduced C content of the black slates is comparable to that of modern oceanic pelagic muds, in which the reduced C concentrations are closely correlated with planktonic productivity (23).

Local small-scale redox perturbations may cause a dispersion of the C isotopic composition of graphite that forms during metamorphism (5, 6, 24). The effect of these perturbations is observed as an increase in the range of isotopic compositions as sample volumes decrease. Earlier studies of C isotopic compositions of Isua graphite have shown a general increase in the range of $\delta^{13}\text{C}$ values with a decrease in sample volume (5). Ion microprobe analysis has shown that the variation in one sample can be up to ~40 per mil (within the analytical errors) (6). These results suggest that C isotope compositions are heterogeneous on a grain scale. I thus studied sample volumes that were greater than 5 to 10 cm^3 and analyzed 2-g aliquots of well-mixed sample.

The sedimentary rocks have low $\delta^{13}\text{C}$ values (-18.77 to -19.11 per mil), and the $\delta^{13}\text{C}$ values increase in rocks that are recrystallized and that contain coarse graphite. The ^{13}C values in the least modified samples vary over a narrow range (-19.07 to -19.11 per mil) and show no correlation with the abundance of organic C in the rock. These data suggest that the $\delta^{13}\text{C}$ values in these samples were not greatly disturbed by secondary reaction with transient carbonic fluids, although systematic isotopic modification during the transition from some other reduced C compound to graphite cannot be precluded. The variation in C isotope composition for all Isua reduced C (Fig. 3) could be the result of isotopic dispersion by postdepositional geochemical processes (24), affecting C deposits with primary $\delta^{13}\text{C}$ values close to -19 per mil.

The most voluminous C reservoir in the Isua supracrustal belt is metasomatic carbonate rocks, which have an average $\delta^{13}\text{C}$ of -2.5 ± 1.7 per mil (2). The isotopic composition of these rocks therefore likely reflects the composition of regional carbonic metamorphic fluids; metasomatic veins and strongly deformed rocks also have high $\delta^{13}\text{C}$ values of -11.40 to -14.10 per mil. Thus, the sedimentary reduced C is significantly depleted in ^{13}C , in relation to the hydrothermal and strongly metamorphosed graphite. The increase in ^{13}C in recrystallized samples could thus be caused by a progressive reaction with hydrothermal fluids with a C isotopic composition that is biased by the regional carbonate C composition.

The presumed primary $\delta^{13}\text{C}$ values of about

-19 per mil of the sedimentary graphites are within the range of biologically reduced C and within the range of reduced C compositions of most modern marine sediments (25). The sedimentological and geochemical evidence thus indicates a biogenic origin of the C forming the graphite globules. In analogy to modern oceanic pelagic shales, the precursor organic detritus of the graphite globules could have been derived more or less continuously from planktonic organisms that sedimented from the surface waters. Thus, these organisms could have been photoautotrophic.

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Coordinated Regulation of Iron-Controlling Genes, H-Ferritin and *IRP2*, by c-MYC

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The protein encoded by the c-MYC proto-oncogene is a transcription factor that can both activate and repress the expression of target genes, but few of its transcriptional targets have been identified. Here, c-MYC is shown to repress the expression of the heavy subunit of the protein ferritin (H-ferritin), which sequesters intracellular iron, and to stimulate the expression of the iron regulatory protein-2 (*IRP2*), which increases the intracellular iron pool. Down-regulation of the expression of H-ferritin gene was required for cell transformation by c-MYC. These results indicate that c-MYC coordinately regulates genes controlling intracellular iron concentrations and that this function is essential for the control of cell proliferation and transformation by c-MYC.

The c-MYC proto-oncogene is involved in the control of cell proliferation, differentiation, and apoptosis (1). Structural alterations of the c-MYC locus deregulate c-MYC expression and

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contribute to tumorigenesis by various mechanisms (1). The c-MYC protein is a transcription factor that functions by means of heterodimerization with MAX, a related protein that, like c-MYC, contains basic (b), helix-loop-helix (HLH), and leucine zipper (LZ) domains but lacks the transactivation domain present in the NH₂-terminus of c-MYC (1). MYC-MAX complexes stimulate transcription of target genes containing MYC-MAX binding sites (1). In addition, MYC can act as a transcriptional repressor of genes containing the initiator ele-