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Carbon Isotope Compositions of Graphite and Carbonate in 3.8 x 10^9 Years Old Isua Rocks

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The graphite from the eastern and western belts of the Isua supracrustals showed the $\delta^{13}C$ values in a narrow range from - 8.0 to - 10.9‰, while the contents of the graphite vary in the rocks. Carbonates in the separate rocks gave the values between - 5.0 and - 5.6‰. These values are of the oldest terrestrial materials available.

The oldest traces of life accepted generally are approximately 3.4 x 10^9 y old stromatolites found in Pilbara, Western Australia.[1] The oldest rocks known are Isua metasediments in West Greenland dated about 3.8 x 10^9 y old.[2] An examination claimed the finding of yeast-like microfossils in the Isua rocks,[3] but the reexamination of the putative microfossils showed the objects were not biogenic but inorganic inclusions and post-depositional in origin.[4] An analysis of organic compounds found only those due to biological contamination introduced during geologically much younger periods.[5]

Some of the Isua metasediments include graphite whose origin has been questioned whether it was converted from organic materials of biological origin or from inorganic carbonate during the metamorphism. If an evidence is obtained that the Isua graphite was transformed from biologic organic materials, it, in turn, indicates that life existed as early as 3.8 x 10^9 y ago. In attempts to clarify this origin, the stable carbon isotope compositions($^{13}C/^{12}C$) have been investigated with graphite and carbonate in the Isua rocks.[6] The results reported so far have not been conclusive to either origin and further studies are necessary to obtain information to this question.

The Isua supracrustals, located about 150 km northeast of Godthåb(Nuk), West Greenland, occur in a semicircular belt about 20 km in diameter and approximately 40 km long with max 4 km wide(Fig. 1). Rock samples were collected during the summers of 1978 and 1979 by the expedition party headed by the University of Maryland, U.S.A. From those, seven graphite-bearing and three carbonate-bearing rock samples were used for the carbon isotope composition. In addition, the oxygen isotope compositions($^{18}O/^{16}O$) were obtained for the carbonate samples. The sample localities are shown in Fig. 1. A hand size specimen each of the rock samples was crushed to pieces a few cm in size and apparent contaminants were removed from the surfaces. Thus arranged fresh portions were ground to powder.

For samples containing graphite, the powdered samples were washed by a mixture of benzene and methanol and followed by a series of HF/HCl dissolutions of the inorganic part. The residues were washed by the mixture of benzene and methanol repeatedly until the wash solution became colorless, and the graphite samples were recovered. The samples(ca. 10 to 20 mg) were combusted at 900 °C under O_2 atmosphere.

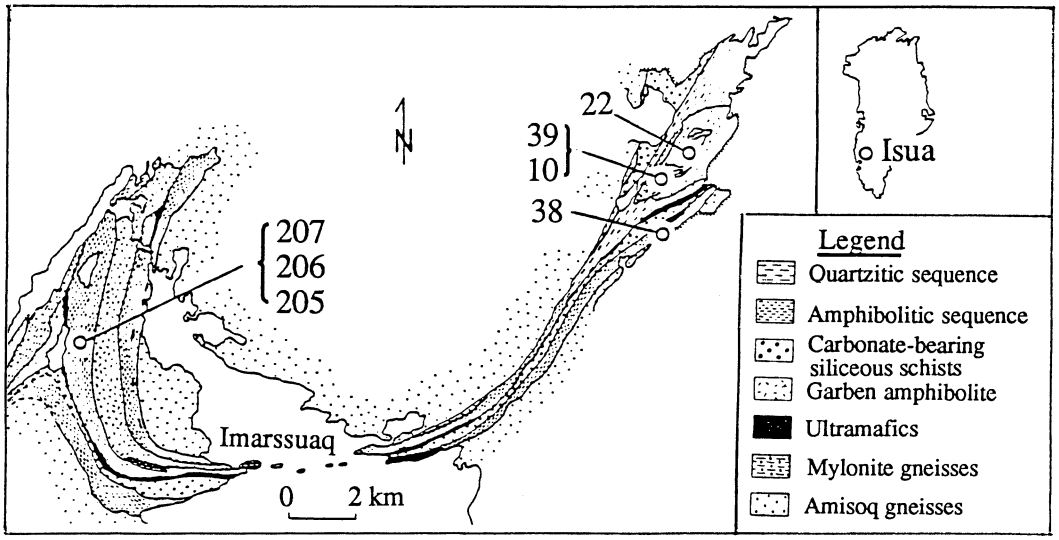

Fig. 1. Geological sketch map of the Isua supracrustal belt [2d] and sample localities of the rocks used in this study. The numbers correspond to those listed in Table 1.

The gases generated were trapped and purified CO_2 was recovered. For samples containing carbonate, the powdered samples(ca. 50 mg) were reacted with 100% phosphoric acid in a 25 °C water bath and CO_2 liberated was collected and purified.

The CO_2 was analyzed on a Varian MAT 250 mass spectrometer and the results are shown by $\delta^{13}C$ per mil deviation from the PDB standard. The carbonate samples also gave the oxygen isotope composition and the results are shown by $\delta^{18}O$ per mil from the SMOW standard. These isotope compositions determined are listed in Table 1 with carbon contents for the seven graphite samples as determined by an ordinary elemental carbon analysis. The carbon contents can be regarded to represent approximate contents of graphite.

The graphite contents vary from 1 to over 4 % in the rock samples. However, their $\delta^{13}C$ values are found in a narrow range between - 8.0 and - 10.9‰. It is unexpected to find such a narrow range for the values of graphite. Although the rock samples are all iron formation, the localities of the rocks are so apart: the two (Nos. 10 and 39) are in the eastern belt and the other three(Nos. 205, 206, and 207) in the western belt, about 25 km apart each other along the belt.

So far, the $\delta^{13}C$ values have been reported on the rocks of only in the eastern belt. The values from - 9.3 to - 16.3 ‰ were obtained for five graphite samples.[6a] These values were considered of graphite formed from carbon released from iron carbonate($FeCO_3$) and isotopically equilibrated at a temperature of more than 400 °C during the Isua metamorphism. Similar values from - 11.3 to - 17.4‰ were reported for three graphite samples together with the values of - 21.4 and - 26.9‰ for the other two graphite samples.[6b] In this study, the latter two values were regarded largely due to contamination by biological organic materials introduced during post-depositional period, since the graphite contents in the rock samples were very small, 56 and 9 ppm, respectively.

The other study obtained the values for reduced("graphitic") carbon from - 5.9 to - 24.9‰ with 13 rock samples of which four are from - 5.9 to - 9.2‰, five from - 12.4 to - 18.7‰ and four from - 21.6 to

- 24.9‰.[6c] The latter four values were interpreted to show the relic of the primary Isua organic material which had been isotopically fractionated by biological mechanisms assumed to be present already at 3.8 x 10^9 y ago, while the other 9 values with higher $\delta^{13}C$ were due to the effect of metamorphism.

Our three carbonate samples show the $\delta^{13}C$ values very similar to each other(Table 1). Similar values were reported for some of the 128 Isua carbonates but the three values are clearly different from their average value(- 2.5‰).[6c] Instead, the three values are apparently very close to the average value(- 5.0 ± 1.5‰) of juvenile mantle carbon.[7]

The $\delta^{18}O$ values of the carbonates are practically the same(Table 1). These values are within the range (+ 7.4 to + 14.1‰) reported for the Isua carbonates,[6b] and are very close to the overall average value (+13.0‰) of the 128 Isua carbonates.[6c]

Although they are not coexisting values in our rock samples, the $\delta^{13}C$ values for graphite are much higher(more ^{13}C) and those for carbonates are notably lower(less ^{13}C) in comparison to the average $\delta^{13}C$ values of organic matter(- 24.7‰) and carbonates(+ 0.9‰), respectively, in Precambrian rocks.[8] The effect of increasing temperature of metamorphism has been known to shift $\delta^{13}C$ values of organic matter to higher and those of inorganic matter to lower.[9] Accordingly, it is possible to speculate that our $\delta^{13}C$ values of

Table 1. Carbon and oxygen isotope compositions of the Isua graphite and carbonate samples and the carbon contents of the graphite-bearing rocks

Univ.of Maryland sample number	Description	C/wt %	$\delta^{13}C$ /‰	$\delta^{18}O$ /‰
10 - 1	Graphite-bearing banded iron formation	3.14	- 10.0	
39 - 2	Graphite-bearing banded iron formation	2.54	- 10.9	
205 - 3	Graphite-bearing banded iron formation	1.62	- 7.8	
206 - 1	Graphite-bearing banded iron formation	2.13	- 8.2	
206 - 3	Graphite-bearing banded iron formation	1.11	- 8.0	
206 - 5	Graphite-bearing banded iron formation	4.38	- 9.4	
207 - 1	Graphite-bearing banded iron formation	2.44	- 8.0	
22 - 6	Carbonate-grunerite ironstone		- 5.2	+ 13.1
38 - 2	Carbonate intercalated in amphibolite		- 5.0	+ 12.3
38 - 3	Carbonate intercalated		- 5.6	+ 12.3

the graphite was shifted from much lower values(i.e., about - 25‰) and those of the carbonates from higher values(i.e., about 0‰) by the Isua metamorphism with a temperature exceeding 400 °C. However, it is also possible to deduce that the graphite was a product of CO_2 released from carbonates by the metamorphism as proposed by the previous study.[6a)]

Our graphite-bearing rocks and carbonate-bearing rocks are fresh and not weathered nor secondary in origin. They show the $\delta^{13}C$ values in the narrow ranges, especially with emphasis on the graphite which occurs not only in the eastern belt but also in the western belt. Therefore, it is reasonable to conclude that no definitive evidence was obtained as to the indication of biological activity, particularly in carbon isotope fractionation. If "graphitic" materials(not well carbonized or poorly crystallized graphite) are found in the Isua rocks, their $\delta^{13}C$ values will provide more usuful clues to the question of the paramount interest as to the existence of life at 3.8×10^9 y ago.

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