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Supplementary Information

Geological Outline

The Saglek-Hebron area is located in the northeastern part of the Labrador Peninsula, northeast Canada (Fig. 1), and comprises a coastal, central part of the early Archean terrane, called the Saglek Block. The block is the western part of the North Atlantic Craton from the northwestern Scotland through the south-central Greenland to the Labrador[1-5] (Fig. 1), and is underlain by the Early to Late Archean suites including orthogneisses, metasedimentary rocks, metavolcanic rocks, ultramafic rocks, mafic dikes and younger granite[1,6-10]. In this region, the orthogneisses are predominant, and account for about 80%[10,11], but supracrustal rocks and mafic to ultramafic mid-Archean dykes, called the Saglek dyke, are also ubiquitously distributed[6]. The orthogneisses, older than the Saglek dyke, are called the Uivak Gneisses whereas the supracrustal rocks are called the Nulliak supracrustal rocks[6,12]. The Nulliak supracrustal rocks contain mafic and ultramafic rocks, gabbroic rocks, chemical sedimentary rocks including carbonate rocks, cherts and banded iron formation (BIF), and clastic sedimentary rocks. Recent reappraisal of the U-Pb dating and detailed Cathodoluminescence observation of zircons from the oldest suite of the Uivak Gneiss (Iqaluk Gneiss) showed that the age of the precursor of the Iqaluk Gneiss is over 3.9 Ga[13]. Thus, the Nulliak supracrustal rocks, intruded by the Uivak-Iqaluk Gneisses, are the oldest supracrustal rocks in the world because the current oldest supracrustal rocks occur in the 3.83 Ga Akilia Island and 3.81 Ga Isua supracrustal belt, southern West Greenland[14-17].

Pelitic rocks occur ubiquitously in the Saglek block and often have preserved bedding planes (Extended Data Fig. 1-2). They are mainly composed of quartz, garnet and biotite with subordinate amounts of plagioclase, zircon, pyrrhotite and graphite, but some also contain sillimanite and cordierite (Extended Data Fig. 2e). Conglomerates at St. John's Harbour East (SJHE) contain pebble- to boulder-sized quartzite clasts (Extended Data Fig. 2b). These clasts are extended parallel to the bedding plane of the matrix and contain no graphite. The matrix is composed of quartz, garnet, biotite, plagioclase, amphibole (mainly cummingtonite), ilmenite, and graphite. Carbonate rocks are also found in SJHE, and have some chert nodules (Extended Data Fig. 2c). They are argillaceous, accompanied with pelitic rocks and cherts. They mainly consist of calcite and dolomite with subordinate amounts of antigorite, apatite, chlorite, magnetite, and graphite. The fine-grained carbonates are calcite, while sparry carbonates are composed of calcite and dolomite. The chert nodules in the carbonate rocks predominantly comprise quartz (Extended Data Fig. 2h).

The supracrustal belts consist of piles of faults-bounded blocks, which are composed of ultramafic rocks, mafic rocks and sedimentary rocks in ascending order, similar to the ocean plate stratigraphy (OPS) of modern ocean plates (Extended Data Fig. 1a). In addition, small-scale duplex structures are found in the studied areas. The geological aspects indicate that the >3.95 Ga Nulliak supracrustal belts originate from an accretionary complex[9]. The abundance and lithostratigraphy of pelitic rocks directly on the mafic rocks suggest that the accreted oceanic crust was so young that pelagic and deep-sea sediments of BIF and chert were not deposited because of short distance from mid-oceanic ridge to subduction zone. Some of carbonate rocks were deposited around, the shallow mid-oceanic ridge because the carbonate rocks underlie the BIF in the Pangertok Inlet area, whereas some carbonate rocks in the St John's Harbour East area and Big Island were deposited in shallow-water environment near a continent because they are intercalated with clastic sedimentary rocks (Extended Data Fig. 1b,d).

The Uivak Gneisses and supracrustal rocks underwent amphibolite to granulite facies metamorphism[8,18]. Some major metamorphisms were estimated at *ca.* 3.89 Ga due to intrusion of a younger suite of the Uivak Gneisses from U-Pb dating of zircons from the Uivak-Iqaluk Gneisses[13], at 3.6 Ga due to intrusion of the Uivak II gneiss[8], and 2.7 Ga from U-Pb dating of zircon overgrowths from supracrustal rocks and the Uivak-Iqaluk Gneisses[11,13] and secondary isochrons of the Uivak Gneiss[19]. Many generations of granitoid were discontinuously intruded into the supracrustal rocks at least *ca.* 3.95, 3.87, 3.6 and 3.3 Ga[8,10,13,20] The most prominent NS-trending fault, the Handy fault (Fig. 1), extends from Handy Island through St John's Harbour to the south[18]. The Early Archean rocks in the western part of the fault suffered from the granulite facies metamorphism whereas those in the eastern part were metamorphosed under the amphibolite facies condition, respectively[18].

Extraction and isotope analysis of organic carbon

We collected 156 sedimentary rocks from the Saglek area, and found graphite in 54 rock samples. We selected 28 samples with a larger amount of the graphite to cover all of lithologies and studied areas for geochemical works. The powdered rock samples were prepared by crushing rock chips. They (1-3 g) were decarbonated by 6 N HCl at 70 °C for 12 hours. The HCl treated samples were further treated with mixed acid of HCl, HF and H_2O (1:4:4 v/v/v in 10 N HCl) at 60 °C for 3 days and repeated 3-4 times, followed by 6 N HCl at 70 °C for 12 hours in order to eliminate the remaining elements which are able to form complex fluorides such as ralstonite ($Na_xMg_xAl_{2-x}(FOH)_6H_2O$) upon drying[21]. All acid reactions were performed in shaking bath to facilitate acid attacks. The acid-treated samples were finally washed with pure water several times and freeze-dried.

The HCl-HF-treated sample powders were placed in an Sn capsule in the range of 1-40 mg and 30-500 µg, respectively, and were combusted with oxygen under He career flow at 1,100 °C in an elemental analyzer (vario MICRO cube, Elementar) connected to mass spectrometer (IsoPrime100, Isoprime), housed at Atmosphere and Ocean Research Institute, The University of Tokyo in order to measure carbon concentration and isotope composition, respectively. Carbon, nitrogen, and sulfur in samples were converted into CO_2, N_2, and SO_2, respectively. Carbon concentrations and isotope compositions of samples were calibrated against an in-house standard material (sulfanilamide), whose carbon concentration and isotope composition were known (41.81 wt.%C, $\delta^{13}C$ = -26.6‰). Based on the replicate analyses of the in-house standard material, analytical reproducibility is within ±0.5‰ (2σ). Results were reported as $\delta^{13}C$ values relative to a VPDB standard (Extended Data Table 1).

Carbon isotope analysis of carbonate

Powdered samples were prepared from several parts of fresh-cut surfaces of rock samples using a micro-drill with a 3 mm-diameter bit. They were analyzed with a Finnigan MAT Delta Plus mass spectrometer interfaced with a Gas Bench II, housed at Atmosphere and Ocean Research Institute, The University of Tokyo. The samples were reacted with purified H_3PO_4 at 70°C in a glass vial preliminary filled with He gas. The results were reported in ‰ relative to VPDB (Extended Data Table 1) using the NBS18 standard ($\delta^{13}C$ = -5.014‰). The analytical reproducibility is within ±0.2‰ (2σ).

In-situ carbon isotope analyses of individual graphite grains

We conducted in-situ analyses of carbon isotope values of individual graphite grains in a pelitic rock (LAF491) and a chert nodule of a carbonate rock (LAA760) with a NanoSIMS 50 instrument installed at the Atmosphere and Ocean Research Institute. The analytical method was described elsewhere[22].

Prior to the carbon isotope analyses, carbon coating on thin sections was completely removed by re-polishing. The samples were then gold coated and baked at *ca.* 100 ºC in the NanoSIMS air-lock for a week. A ~2 pA Cs^+ primary beam with a beam diameter of less than 0.6 μm was rastered over 5 × 5 μm^2 square areas of the graphite gains in the sections. Each analysed area was pre-sputtered with a 200 pA primary beam over the larger raster area (10 × 10 μm) for 240 seconds. We used two magnetic fields with the NanoSIMS multi-collection system: In the magnetic field 1 (B1), secondary ions of $^{12}C^-$ and $^{12}C^{12}C^-$ were detected by electron multiplier EM4 and EM5, with counting time of 3 seconds. Then, the magnetic field was cycled to the second mass (B2). Secondary ions of $^{12}C^-$, $^{13}C^-$, and $^{12}C^{14}N^-$ were detected simultaneously by EM3, EM4, and EM5, respectively. The counting time for B2 was 20s. Total 25 cycles are required for 1 measurement, corresponding to the total counting time of 75s for B1 and 500s for B2, respectively. The carbon isotopic ratios $(^{13}C/^{12}C)_{EM4}$ were calculated from $^{12}C^-$ in B1 and $^{13}C^-$ in B2, using the single detector (EM4). The multi-collection $(^{13}C/^{12}C)_{multi}$ ratios, which used the simultaneous collection of 2 detectors (EM3 and EM4 in B2), were also calculated and compared to the $(^{13}C/^{12}C)_{EM4}$ ratios, to check the stability of the measurement. During the analyses, $^{12}C^{12}C^-/^{12}C^-$ and $^{12}C^{14}N^-/^{12}C^-$ ratios were monitored to check potential contamination.

The carbon isotope compositions were calibrated against an in-house standard material (artificial pure graphite). Its carbon isotope composition was determined as $\delta^{13}C$ = -26.6‰, using the conventional method with the IsoPrime 100 analytical system. Based on the replicate analyses of the standard, analytical reproducibility of NanoSIMS 50 is within ±3‰ (1σ). Results were reported as $\delta^{13}C$ values relative to a VPDB standard (Extended Data Table 2).

Extended Data Fig. 3a shows the carbon isotope values of the individual graphite grains and their host rocks. The graphite grains in the LAF491 range from -19.3 to -30.8‰ in $\delta^{13}C_{org}$ values whereas those in the LAA760 vary from -26.1 to -33.6‰ in $\delta^{13}C_{org}$ values. The formers are consistent with the whole-rock carbon isotope ratio (-28.2‰) but the latter is much lower than the whole-rock value (-10.3‰). Although an exact cause of the large difference in $\delta^{13}C_{org}$ values between the whole-rock and graphite grains in the chert nodule sample is unknown, large grains suitable for the analysis have apparent low $\delta^{13}C_{org}$ values. The large variation of the $\delta^{13}C_{org}$ values of graphite grains both in the pelitic and carbonate rocks is inconsistent with later contamination and secondary formation during the metamorphism, and supports a primary origin.

Whole rock compositions and origin of the carbonate rocks

We analyzed major element and rare earth element compositions of carbonate rocks to determine their origin. The major element compositions were analyzed with X-ray fluorescence spectrometry (XRF: RIGAKU RIX-2100) at the Tokyo Institute of Technology using fused glass beads. The rare earth elements (REEs) were analyzed with an inductively coupled plasma mass spectrometry (ICP-MS: Agilent 7500s) at Komaba, the University of Tokyo. The analytical methods were described elsewhere[23].

Extended Data Figure 3b shows REE patterns of the carbonate rocks with low Y and Zr contents. Because it is well known that a REE pattern, especially Eu anomaly, is significantly influenced by involvement of terrigenous and volcanic materials[24], it is necessary to remove its influence to estimate primary REE patterns of carbonate rocks, precipitated from seawater. We neglected carbonate rocks with high Y (>1.7 ppm) and Zr (>1.2 ppm) contents because they are, generally speaking, quite scarce in seawater and abundant in clastic and volcanic materials.

The REE patterns of carbonate rocks with low Y and Zr contents have distinctive positive La, Eu and Y anomalies, diagnostic of chemical sediments, precipitated from seawater mixed with hydrothermal fluid (Extended Data Figure 3b). The Eu anomalies are apparently correlated with lithostratigraphies and accompanied rocks. The carbonate rocks, which are accompanied with ultramafic and mafic rocks in the SJHS, have large positive Eu anomalies whereas the carbonate rocks in the Big Island and SJHE, which are accompanied with pelitic rocks, have small positive Eu anomalies. And the carbonate rocks in the Pangertok Inlet are accompanied with BIFs. The correlation suggests that the depositional environment of the carbonate rocks changed away from hydrothermal fields as well as they still preserve the primary compositions.

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Estimate of metamorphic grade based on mineral parageneses of metabasalts and garnet-biotite geothermometry

Metamorphic temperatures of host rocks with graphite grains were estimated based on two methods: conventional mineral parageneses of ambient metabasites and geothermometry of garnet-biotite pairs in pelitic rocks. Back-scattered electron images of all the thin sections of pelitic rocks and chemical compositions of minerals were obtained with an electron probe microanalyzer (JEOL-JXA-8800) at the University of Tokyo. The detailed analytical methods were descried elsewhere[30-33]. The analyses were performed on adjacent grains and across the grain boundaries in order to check compositional zonation for each mineral. The metamorphic temperature was estimated from Fe-Mg partitioning between garnet and biotite[34].

Mafic rocks in the St John's Harbour South (SJHS), St John's Harbour East (SJHE) and Big Island have a mineral paragenesis of hornblende (Hbl), plagioclase (Pl) and titanite (Ttn). On the other hand, those in Shuldham Island have a mineral paragenesis of clinopyroxene (Cpx)+Hbl+Pl. Thus, the former underwent the upper amphibolite facies metamorphism whereas metamorphic condition for the latter corresponds to lower granulite facies.

We analyzed chemical compositions of garnets and biotites in order to estimate the metamorphic temperature: their eleven pairs from LAA492 (SJHS), eighteen from LAD961 (SJHE), eleven from LAF002 (Big Island) and five from LAD123 (Shuldham Island), respectively. The representative mineral compositions of the garnets and biotites are listed in Extended Data Table 3. The garnets in LAD123 show zoning in Mg and Fe contents, but the others lack the compositional zonation. The cores of the garnets in LAD123 are more magnesian than their rims. Assuming the metamorphic pressure at 0.5 GPa, temperatures obtained from the garnet rim-biotite core pairs are 653 ± 16 ºC, 691 ± 26 ºC, 585 ± 45 ºC and 518 ± 81 ºC for LAA492, LAD961, LAF002 and LAD123, respectively (errors are 1σ). On the other hand, temperature obtained from garnet core-biotite core pairs is 647 ± 23 ºC at 0.5 GPa for LAD123. The estimated temperatures for LAA492, LAD961 and LAF002 are consistent with upper amphibolite facies condition, but temperature from both garnet rim-biotite core pairs and garnet core-biotite core pairs for LAD123 is lower than those estimated from the mineral paragenesis, lower granulite facies condition. Generally speaking, the estimate from mineral compositions is susceptible to retrogressive metamorphism because of a higher Fe-Mg diffusion rate of biotite. Therefore, metamorphic temperature in Shuldham Island is estimated 700 to 800 ºC based on the mineral paragenesis of the mafic rocks.

Raman microspectroscopy

A Laser Raman micro-spectrometer (JASCO NRS-2000) was used to estimate metamorphic temperature of the graphite. The thin sections were twice exposed to an Ar laser (514.5 nm) for 60 to 80 seconds at a laser power of about 5 mW at the sample surface to obtain Raman spectra in the range of 1,800 to 1,100 cm^{-1} at 1 cm^{-1} resolution. A 100× (NA=0.84) and a 50× (NA=0.80) objective lenses were used, so the spatial resolution of the Raman analysis was about 1-2 µm. We only analyzed the graphite embedded within the rocks below the surface of the thin-section in order to avoid the effect of polishing, which can induce deformation of carbonaceous matter during sample preparation and thus possibly induce artificial modification of the Raman spectroscopic feature[25]. Details of the analytical methods are described elsewhere[26,27].

A Raman spectrum of graphite is composed of first-order and second-order regions, and the first-order region from 1,100 to 1,800 cm^{-1} is often considered[28,29]. In this region, a graphite band (G band) occurs at ~1,580 cm^{-1} whereas poorly ordered carbon displays D1 (~1,350 cm^{-1}), D2 (~1,620 cm^{-1}) and D3 bands (~1,500 cm^{-1}), respectively. The crystallization temperature can be estimated using following spectral parameters[26]:

$$R2 = D1/(G + D1 + D2) \text{ band area ratio} \quad (1).$$

$$T\,(°C) = -455 \times R2 + 641 \quad (2)$$

This equation works in the temperature range of 330 to 650 ºC and the error is estimated ±50 ºC[26]. Peak position, band-area (i.e. integrated area) and band-width (i.e. full width at half maximum, FWHM) were determined (Extended Data Table 4) using a computer program PeakFit 4.12 (SeaSolve Software Inc.).

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