

# Raman and ion microscopic imagery of graphitic inclusions in apatite from older than 3830 Ma Akilia supracrustal rocks, west Greenland

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## ABSTRACT

**Three-dimensional molecular-structural images of apatite grains and associated minerals embedded in a banded quartz-pyroxene-magnetite supracrustal rock from Akilia, southern west Greenland, were constructed by using Raman confocal spectroscopy. The rock sample is the same as that from which apatite-hosted isotopically light graphitic inclusions were reported by Mojzsis and colleagues in 1996; the results were challenged in 2005 by Lepland and colleagues who failed to find carbon-bearing inclusions in this and other Akilia samples. Here we demonstrate that inclusions of graphite wholly contained within apatite occur in this rock. The carbon isotopic composition of one such inclusion, its graphitic composition established by Raman spectroscopy, was measured by secondary ion mass spectrometry to be isotopically light ( $\delta^{13}\text{C} = -29\text{‰} \pm 4\text{‰}$ ), in agreement with earlier analyses. Our results are thus consistent with the hypothesis that graphite-containing apatite grains of the older than 3830 Ma Akilia metasediments may represent chemical fossils of early life.**

**Keywords:** three-dimensional Raman spectroscopy, ion microscope, carbon isotopes, Akilia apatite, early life.

## INTRODUCTION

The search for life's earliest records is complicated by the protracted geologic history of early Archean rocks. For example, the oldest known sedimentary rocks, those of the Isua supracrustal belt of southwestern Greenland (Nutman et al., 1996), have been so metamorphosed that morphological evidence of any microbes then extant was obliterated (Schopf, 2006a). In comparison, isotopic signatures of ancient life are relatively robust. Thus, the presence in the Isua metasediments of isotopically light ( $^{13}\text{C}$  depleted) carbonaceous matter, characteristically a product of isotopic fractionation during autotrophic metabolism, has been invoked as evidence of life (Schidlowski, 1988, 2001; Mojzsis et al., 1996; Rosing, 1999; Ueno et al., 2002). Such evidence, however, can be difficult to interpret, especially in high-grade metamorphic terrains in which original carbon isotopic compositions can be altered by metamorphism (Schidlowski, 1988, 2001) and/or by reactions with carbon-bearing fluids (van Zuilen et al., 2002, 2003).

Of particular significance in the search for evidence of life's roots is the report by Mojzsis et al. (1996) that apatite grains from older than 3830 Ma metasediments at Akilia (island) in southwestern Greenland contain  $^{13}\text{C}$ -depleted microscopic graphitic inclusions (having  $\delta^{13}\text{C}$  values ranging from  $-20\text{‰}$  to  $-50\text{‰}$ ). The apatite-graphite association was interpreted to be a possible biomarker, with the isotopically light carbon preserved despite intense metamorphism by its sequestration within apatite grains (Mojzsis et al., 1996). Among many challenges to this interpretation (Myers and Crowley, 2000; van Zuilen et al., 2002, 2003; Fedo and Whitehouse, 2002; Lepland et al., 2002, 2005), the most pointed is that of

Lepland et al. (2005), who failed to identify apatite-hosted graphitic inclusions in any of the 17 Akilia rock samples they examined.

Here we utilize Raman spectroscopy to demonstrate that inclusions of graphitic carbon, wholly contained within apatite grains, occur in the same quartz-pyroxene-magnetite-bearing Akilia metasediment studied by Mojzsis et al. (1996). Further, we show by use of secondary ion mass spectrometry (SIMS) that such graphite has a carbon isotopic composition consistent with the presence of life. Our results corroborate the most significant observations of Mojzsis et al. (1996), and, in conjunction with other recent studies (Nutman et al., 1997; Rosing, 1999; Ueno et al., 2002; Mojzsis and Harrison, 2002a, 2002b; Mojzsis et al., 2003; Dauphas et al., 2004; Manning et al., 2006), provide new evidence consistent with the presence of carbon-fixing microbes prior to 3800 Ma.

## SAMPLES AND METHODS

The apatite grains analyzed occur in petrographic thin section G92–197B of Akilia field sample G91–26 (catalogued at the Australian National University as sample 92–197), a portion of the same rock studied by Mojzsis et al. (1996). The thin section is composed primarily of quartz and pyroxene with subsidiary magnetite (~10%) present in linear bands; other minerals include amphibole, sulfide, zircon, and quartz-enclosed grains of apatite (Mojzsis et al., 1996, 2003; Lepland et al., 2005). The apatite grains typically range in diameter from ~5 to 50  $\mu\text{m}$ . In this study, our goal was to detect carbonaceous inclusions in grains of apatite and then characterize selected specimens in order to provide data demonstrating the petrography of such occurrences, the crystallographic

order of the carbonaceous matter, and its molecular-structural and isotopic compositions. To this end, we used Raman and SIMS instruments that function as microscopes capable of acquiring in situ chemical or isotopic data at high sensitivity and micron-scale spatial resolution (Castaing and Slodzian, 1981; Schopf et al., 2005; Schopf and Kudryavtsev, 2005). By performing nondestructive Raman analyses first, we are able to correlate molecular-structural and isotopic data on specific targets, a level of detail not achieved in previous analyses of Isua samples (Mojzsis et al., 1996; Rosing, 1999; Ueno et al., 2002).

Apatite grains containing opaque inclusions were identified by optical microscopy. Only opaque inclusion-containing grains situated beneath the surface of the thin section were selected for Raman analyses. Following acquisition of point spectra to identify graphite-bearing inclusions, additional optical images were obtained to document inclusion morphology and their location within apatite grains. To enhance image quality, the thin section was covered by a veneer of fluorescence-free immersion oil (Schopf et al., 2002). The oil was later removed (by ultrasonication) before the sample was ground to expose a selected inclusion at the thin section surface for analysis by SIMS.

Three-dimensional Raman images were obtained for apatite grain #1 (see following) by acquiring a series of two-dimensional Raman confocal maps at sequentially increasing depths and then stacking the images by use of three-dimensional (3-D) rendering software. The Raman images document the distribution of the major minerals (quartz, apatite, and graphite) that compose the analyzed area at a spatial resolution of  $\sim 1.5\text{--}2\ \mu\text{m}$  (see GSA Data Repository<sup>1</sup> supporting materials for details regarding the acquisition of Raman spectra and 3-D images).

Ion microscope images and carbon isotopic measurements of the graphitic inclusion contained in apatite grain #1 were obtained by use of a CAMECA ims1270 ion microprobe. Details regarding sample preparation for SIMS analyses, the acquisition of ion images and carbon isotopic data, and the calibration of instrumental mass fractionation by use of an *Escherichia coli* standard are included in the GSA Data Repository (see footnote 1). On the basis of the information presented there, we consider the systematic uncertainties in the isotopic compositions reported here to be  $<5\%$ .

## RESULTS

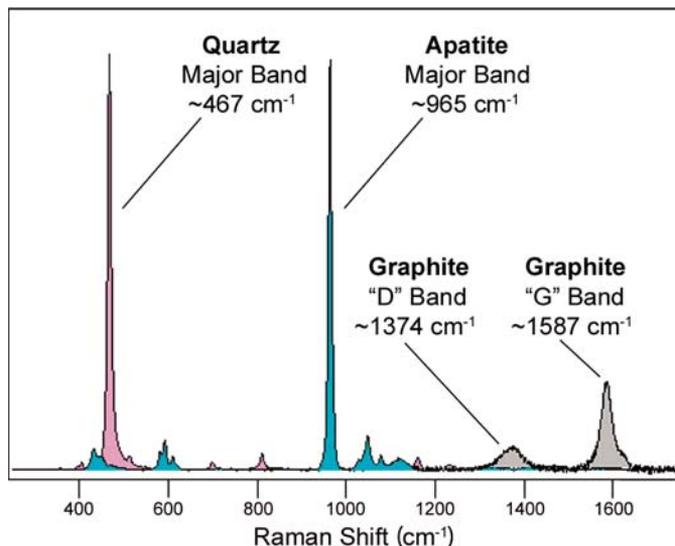
In a survey of  $\sim 4\ \text{cm}^2$  of thin section G92-197B, we identified a few tens of apatite grains that contain optically opaque inclusions. Of these, three specimens, shown by Raman analyses to contain carbonaceous inclusions  $>5\ \mu\text{m}$  encompassed by apatite, were selected for study. While recognizing that this was not a systematic search, we estimate that at least 5%–10% of such apatite-hosted inclusions are carbonaceous.

One such apatite grain (#1) was selected for 3-D Raman mapping and subsequent ion imaging and isotopic analysis. Optical studies showed that this defect-free grain entirely enclosed an opaque inclusion. Prior to polishing, the upper surface of this  $\sim 18\text{-}\mu\text{m}$ -wide  $\times$   $35\text{-}\mu\text{m}$ -high parallelepiped-shaped apatite grain was situated  $\sim 34\ \mu\text{m}$  below the surface of the thin section within a quartz crystal. Contained within the apatite,  $\sim 12\ \mu\text{m}$  below its upper surface, was an elongate opaque inclusion,  $\sim 5\ \mu\text{m}$  across and  $\sim 20\ \mu\text{m}$  long (Figs. 1A–1C), that Raman spectra demonstrated to be graphitic carbon (Figs. 1E–1G; Fig. 2). Three-dimensional Raman mapping showed this inclusion (Figs. 1D, 1H) to be oriented parallel to the long axis of the encompassing apatite grain. Video presentations of the 3-D Raman maps of apatite grain #1 are available in the GSA Data Repository (see footnote 1).

<sup>1</sup>GSA Data Repository item 2007149, experimental methods and animated figure of inclusion in apatite #1, is available online at [www.geosociety.org/pubs/ft2007.htm](http://www.geosociety.org/pubs/ft2007.htm), or on request from [editing@geosociety.org](mailto:editing@geosociety.org) or Documents Secretary, GSA, P.O. Box 9140, Boulder, CO 80301, USA.



**Figure 1.** Optical photomicrographs (A–C) and two-dimensional (E–G) and three-dimensional Raman images (D, H) of quartz-embedded apatite grain #1 that contains graphitic inclusion, in thin section G92-197B of older than 3800 Ma quartz-pyroxene supracrustal rock from Akilia, southwest Greenland; magnification of all parts is shown by scale in D. A–C: Apatite grain at sequentially deeper focal planes; C shows opaque graphitic inclusion. D: Image (viewed from top of specimen, as in A–C) with quadrant of upper surface of apatite grain removed to show graphite inclusion (gray). E–G: Images (from same perspective as in A–D) of plane transecting graphitic inclusion  $\sim 25\ \mu\text{m}$  below upper surface of apatite grain, imaged (E) in major quartz band ( $\sim 467\ \text{cm}^{-1}$ ), showing quartz matrix (white), apatite grain (gray), and space occupied by graphite inclusion (black); imaged (F) in major apatite band ( $\sim 965\ \text{cm}^{-1}$ , white); and imaged (G) in graphite G band ( $\sim 1587\ \text{cm}^{-1}$ , white). H: Image rotated to show elongate graphite inclusion (gray) and parallelepiped-shaped apatite grain viewed from one side.

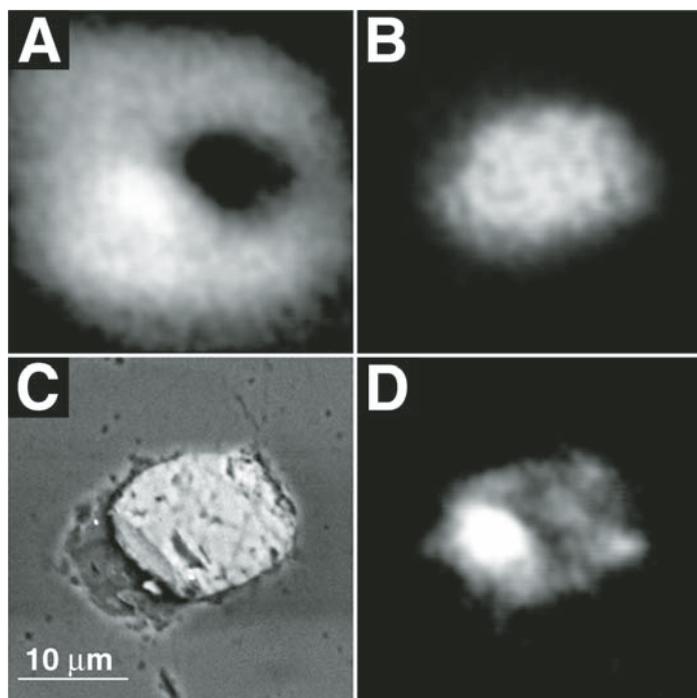


**Figure 2.** Raman spectra of quartz, apatite, and graphite present in Akilia apatite grain #1.

Raman spectroscopy of graphitic material has long been used to characterize the degree of graphitization of carbonaceous matter (e.g., Tuinstra and Koenig, 1970; Nakamizo et al., 1974; Nemanich and Solin, 1979; Lespade et al., 1982). Based on such studies, the Raman spectrum of the inclusion in apatite grain #1 (Fig. 2) shows that it is composed of graphitic carbon, exhibiting the G, D', and D'' bands characteristic of this mineral (at 1587, 1374, and 1621  $\text{cm}^{-1}$ , respectively) as well as a broad second-order band at  $\sim 2730\ \text{cm}^{-1}$  (not shown). These data (in particular, the presence of the D' and D'' bands) suggest that this carbonaceous matter is incompletely graphitized, evidently having a moderately disordered crystal structure. A two-dimensional Raman image acquired at  $\sim 467\ \text{cm}^{-1}$ ,

the major band of quartz, shows a void (Fig. 1E, black) that represents the space within the apatite grain occupied by the graphitic inclusion. It is notable, however, that in a corresponding image acquired at  $\sim 965\text{ cm}^{-1}$ , the major band of apatite (Fig. 1F), no such void is present. We interpret these data to indicate that the inclusion, devoid of quartz, is a mixture of apatite and nanoparticles of graphitic carbon. If the size of graphite crystallites in disordered carbonaceous material is related to the relative intensity of the Raman D' band, as reported by Tuinstra and Koenig (1970), we estimate that the graphitic nanoparticles of the inclusion are  $\sim 10\text{--}15\text{ nm}$ .

After Raman imaging, the thin section was polished to bring the graphitic inclusion of apatite grain #1 near the section surface for isotopic analyses. The grain was located in the ims1270 system by use of a reflected light image, and the inclusion was positioned for analysis by direct ion imaging (Fig. 3). The two isotopic measurements made of the inclusion were preceded by seven analyses of the *E. coli* standard and were followed by a background measurement as well as three additional analyses of the standard. Count rates for  $^{12}\text{C}_2^-$  ranged from  $\sim 1.0$  to  $\sim 2.5 \times 10^5\text{ s}^{-1}$  for both analyses. Because the  $^{12}\text{C}_2^-$  signal measured on quartz a few microns from the apatite grain amounted to only  $\sim 0.5\%\text{--}1\%$  of that from the inclusion, no correction for background carbon was necessary. The carbon isotopic compositions corrected for instrumental mass fractionation are  $\delta^{13}\text{C} = -28.8\% \pm 2.5\%$  and  $\delta^{13}\text{C} = -30.6\% \pm 3.7\%$ , resulting in an average for the graphitic material of  $\delta^{13}\text{C} = -29\% \pm 4\%$  ( $2\sigma$ ).



**Figure 3.** Ion microscope images of apatite grain #1 (A, B, D) and included graphitic particle analyzed for its carbon isotope composition, compared with backscattered electron (BSE) image of same specimen after isotopic analysis (C); scale for all panels shown in C. A: Image in  $^{28}\text{Si}^-$  ions. B: Image in  $^{31}\text{P}^-$  ions. D: Image in  $^{12}\text{C}^-$  ions. Apatite grain and its graphitic inclusion are shown clearly in  $^{31}\text{P}^-$  and  $^{12}\text{C}^-$  images with surrounding quartz shown in  $^{28}\text{Si}^-$  image. Diffuse  $^{12}\text{C}^-$  is associated with phosphorus-bearing apatite (B), but not silica-rich quartz (A). Post-secondary ion mass spectrometry (SIMS) BSE image (C) was made on uncoated sample by use of variable-pressure LEO 1430 VP scanning electron microscope. Crater made by  $\text{Cs}^+$  sputtering during SIMS analysis contains small blebs of carbon-rich material (identified by energy dispersive X-ray analysis), but most of graphitic inclusion was consumed during isotopic measurements.

## DISCUSSION

Because of the significance of the timing and nature of the emergence of living systems on Earth, data relevant to life's earliest history have been (e.g., Moorbath, 2005) and will no doubt continue to be subject to intense scrutiny. In particular, the report by Mojzsis et al. (1996) of the occurrence of apatite-hosted isotopically light graphite inclusions interpreted to be a biomarker of early life in the older than 3800 Ma metasediments at Akilia precipitated a host of challenges (Myers and Crowley, 2000; van Zuilen et al., 2002; Fedo and Whitehouse, 2002; Lepland et al., 2002, 2005). Among these, the potentially most significant is that of Lepland et al. (2005), who used optical and scanning electron microscopy to examine 190 apatite grains from various Akilia samples and failed to find even a single specimen of apatite-hosted graphite. Although some such grains are not relevant to the putative biogenic carbon reported from the Akilia metasediments (i.e., 40 grains examined from an igneous tonalite and 32 grains from ultramafic units), 31 of the apatite grains studied by Lepland et al. (2005) derive from the same unit as the sample studied by Mojzsis et al. (1996). Because only one such graphitic inclusion was illustrated by Mojzsis et al. (1996) and the petrology of SIMS-analyzed specimens reported therein was not precisely documented, the study by Lepland et al. (2005) has cast a pall over the Mojzsis et al. (1996) report, leading some to question the very existence of apatite-hosted graphitic inclusions in the Akilia metasediments.

The data presented here lay such uncertainties to rest. The occurrence of graphitic inclusions within apatite grains of Akilia rocks is demonstrated by 3-D Raman imagery, a technique developed for the study of ancient microscopic fossils (Schopf and Kudryavtsev, 2005) that can be used to address micron-scale mineralogy and petrography. The Raman data suggest that the included graphitic material is moderately disordered and in this respect is similar to the biological carbonaceous matter that composes ancient petrified fossils (Schopf et al., 2005). Though such similarity indicates only that the carbonaceous matter is evidently incompletely graphitized, not that it is necessarily biogenic, carbon isotopic analyses show that the inclusion has  $\delta^{13}\text{C} = -29\% \pm 4\%$ , well within the range of values characteristic of ancient biogenic carbonaceous material (Hayes et al., 1983; Strauss et al., 1992; Schidlowski, 1988, 2001), including that in numerous 3200–3500 Ma microfossil-and/or stromatolite-bearing geologic units (Schopf, 2006a, 2006b).

We do not claim that the data presented here constitute unequivocal evidence of early life. However, our data clearly confirm the most significant observations of Mojzsis et al. (1996), and thus are consistent with the hypothesis that these metasediments hosted early biologic activity. It is noteworthy that despite the controversy regarding these rocks, no plausible mechanisms have been proposed for the abiological production of isotopically light carbonaceous matter and its sequestration in apatite at Akilia. In particular, it was suggested that reduced carbon could have formed by metamorphic disproportionation of carbonate introduced during prior metasomatism, as may have happened in siderite-rich rocks at nearby Isua (van Zuilen et al., 2002, 2003). However, our Raman studies did not detect the signature of any carbonates in the samples studied here, a result in agreement with detailed petrographic, geochemical, and geologic studies (Manning et al., 2006) that show the protolith of the quartz-pyroxene-magnetite banded rocks at Akilia to have been a chemical sediment, not a metasomatized ultramafic (Fedo and Whitehouse, 2002). Moreover, judging from the data of van Zuilen et al. (2003) on graphite in veins of carbonate in Isua rocks, the carbon isotope compositions of the graphitic inclusions of the Akilia apatite are appreciably too depleted in  $^{13}\text{C}$  to have been produced via high-temperature decarbonation reactions.

On the basis of the new data presented here and evidence given in earlier studies of the Isua supracrustal rocks (e.g., Schidlowski, 1988, 2001; Rosing, 1999; Ueno et al., 2002), including those at Akilia (Mojzsis et al., 1996; Manning et al., 2006), it seems likely that the record of life on Earth is as old as the oldest sedimentary rocks now known.

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