

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

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**Allen P. Nutman**

*Institute of Geology, Chinese Academy of Geological Sciences,  
26 Baiwanzhuang Road, Beijing 100037, China*

**Clark R.L. Friend**

*45 Stanway Road, Headington, Oxford OX3 0BP, UK*

Evidence for the age and origin of life is sought in the oldest rocks on Earth, which are ductilely deformed and metamorphosed up to amphibolite or granulite facies (see Schopf [2006] for a review). Consequently, preservation of microstructural or microchemical evidence for life requires some form of mineralogical capsule that can protect that evidence from modification during superimposed metamorphic recrystallization with open system behavior. In their recent study, McKeegan et al. (2007) sought graphite inclusions (as possible biogenic relicts) within apatite grains found in siliceous rock sample G91–26 (ANU catalog 92–197) on the island of Akilia (Greenland). The sample is older than 3600 Ma (probably >3830 Ma). This followed an earlier study with the same approach by Mojzsis et al. (1996; our contribution to which was to provide the sample, its petrography, geological context, and the first dating indicating that Akilia rocks might be very ancient, >3830 Ma).

Mojzsis et al. (1996, p. 57) reported “occluded carbon in apatite micrograins from the Akilia island BIF [banded iron formation]” G91–26 as <sup>13</sup>C-depleted, with carbon isotopic signatures similar to those characterizing some types of microorganisms. These apatites were thought to have grown very early in the rock’s history, thereby leading to the conclusion that this rock contains (the oldest) evidence for life, which had been protected within apatite grains throughout the history of the rock (Mojzsis et al., 1996). Using the same sample, the “frequent” occurrence of these inclusions could not be replicated by Lepland et al. (2005) and Nutman and Friend (2006). Despite a decade having passed since the Mojzsis et al. (1996) paper, neither the actual analytical data nor documentation of the grains analyzed have been presented (not even in the thesis of Mojzsis [1997]), adding to controversy over the results.

McKeegan et al. (2007) try to redress this situation, and we commend them for their very thorough petrographic documentation of a graphite inclusion within a *single* apatite grain. Aside from that grain, there are only two others with graphite “inclusions” shown in Data Repository item 2007149<sup>1</sup>. These however, do not pass petrographic criteria as genuine inclusions, because one comprises a train of graphite flecks traversing an apatite (along an annealed[?] crack), whereas the other is an invagination of graphite into the side of an apatite (see Figure 3 of Nutman and Friend [2006]). Therefore, McKeegan et al. failed to reproduce the observation of Mojzsis et al. (1996) that graphite inclusions in G91–26 apatites were “frequent.”

Regarding the significance of genuine (rare) graphite inclusions in apatites, McKeegan et al. did not draw attention to papers in the past decade that have improved the understanding of the *recrystallization* of phosphates during metamorphism. Even in a simple experimental system consisting of quartz and the phosphate monazite, Ayers et al. (1999) demonstrated that small phosphate grains dissolve and are reprecipitated as larger metamorphic grains with progressive metamorphism. In more complex natural metamorphic systems, the dissolution and regrowth of phosphates with in-

creasing metamorphic grade is also well documented (e.g., Williams, 2001; Wing et al., 2002). Therefore phosphates need not necessarily protect pre-diagenetic material from reaction and isotopic exchange with surrounding media, and there is no reason that apatites in the Akilia rocks behaved otherwise. In a paper not cited by McKeegan et al., we (Nutman and Friend, 2006) demonstrated that G91–26 apatites show marked depletion of the heavy rare earth elements. We interpreted this to result from the presence of garnet (a heavy rare-earth-enriched mineral) in the Akilia rocks, occurring mostly in widely spaced discordant veins, and rarely as disseminated grains. We thus concluded that the G91–26 apatites grew in equilibrium with garnet and therefore must be metamorphic in origin. Consequently, any graphite inclusions cannot a priori be regarded as retaining a pre-metamorphic isotopic signature. This graphite could then be the product of several reactions at different times in the history of the rock—recrystallization of (pre-diagenetic) biogenic material is but one possibility.

We (Nutman and Friend, 2006) demonstrated via infrared absorbance spectroscopy that G91–26 apatites contain carbon in the form of carbonate substituting for phosphate and hydroxyl ions. The well-documented analytical spot shown by McKeegan et al. (their Fig. 3D) contained apatite as well as graphite. Due to the mixed-carbon source in this analysis, the isotopic signature for the G91–26 graphite is still not known with confidence. Furthermore, Tumpene and Peck (2006) observed that carbonate-bearing apatites can be <sup>13</sup>C-depleted, even when a direct biogenic pedigree for such carbon is unlikely. This further complicates the interpretation of McKeegan et al.’s measurement.

The issues we have raised here undermine the conclusion of McKeegan et al. (2007) that their results support evidence for >3830 Ma life in Akilia sample G91–26.

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<sup>1</sup>GSA Data Repository item 2008149 is available online at [www.geosociety.org/pubs/ft2008.htm](http://www.geosociety.org/pubs/ft2008.htm), or on request from [editing@geosociety.org](mailto:editing@geosociety.org) or Documents Secretary, GSA, P.O. Box 9140, Boulder, CO 80301, USA.

**Kevin D. McKeegan**

*Department of Earth and Space Sciences, University of California—Los Angeles, Los Angeles, California 90095-1567, USA*

**Anatoliy B. Kudryavtsev**

*Center for the Study of Evolution and the Origin of Life (Institute of Geophysics and Planetary Physics), University of California—Los Angeles, Los Angeles, California 90095-1567, USA*

**J. William Schopf**

*Department of Earth and Space Sciences, and Center for the Study of Evolution and the Origin of Life (Institute of Geophysics and Planetary Physics), University of California—Los Angeles, Los Angeles, California 90095-1567, USA*

We thank Nutman and Friend (2008) for their interest in our work on the enigmatic Akilia rocks (McKeegan et al., 2007) and for affording us an opportunity to further discuss our results. Contrary to the impression given by Nutman and Friend, the purpose of our study was neither to explicitly seek biogenic remnants nor to quantify the frequency of occurrence of apatite-hosted graphitic inclusions in Akilia sample G91–26. Our intent was also not to elucidate the complex geologic history of the Akilia supracrustals (interested readers should consult Manning et al. [2006]). Rather, our more modest goal was to demonstrate the occurrence of apatite-hosted graphitic inclusions in this rock and to document the morphology, molecular state, and isotopic composition of one such specimen.

Our work was motivated by Lepland et al. (2005) who reported that they had been unable to confirm the presence of graphite in Akilia apatite, a result echoed in a widely circulated opinion piece (Moorbath, 2005). Such contributions cast doubt on the reliability of the carbon isotope data obtained in the University of California—Los Angeles secondary ion mass spectrometry (SIMS) lab, where Mojzsis et al. (1996) carried out the original study, suggesting, for example, that “it remains to be established what objects were analyzed” (Lepland et al., 2005, p. 78). A measure of uncertainty was justified: the original study did not include high-resolution images of the targets analyzed, and the isotopic measurements themselves consumed the sub-nanogram carbon spots uncovered by successive sputtering of the Cs<sup>+</sup> primary ion beam. To resolve such uncertainty, we employed instrumentation that was not available to Mojzsis and colleagues in 1995. Raman imagery enabled us to make a high-resolution three-dimensional map of a quartz-enclosed, apatite-hosted graphite inclusion and to characterize this three-mineral complex in situ, prior to ion microprobe analysis. Isotopically light carbonaceous (graphitic) inclusions demonstrably occur in apatite in this rock. The implications of this finding may be debatable, but the existence of graphitic inclusions in apatite grains of the Akilia sample G91–26 is not.

In their commentary, Nutman and Friend place emphasis on the fact that the Akilia apatite grains are of metamorphic origin, rather than being syngenetic with rock formation. That both the apatite and their graphitic inclusions are metamorphic minerals is not in doubt, but as our work was intended to address the existence of such inclusions, not their geologic history, we saw no need to cite Nutman and Friend (2006) regarding rare-earth element (REE) distributions. In fact, the relevance of an exchange of REE between apatite and a garnet-equilibrated reservoir to the central issue of whether graphite retains an isotope composition of any pre-diagenetic material is not clear. Nevertheless, we agree that the petrogenesis of the graphitic inclusions and the timing of their emplacement are important unresolved issues. Regarding the origin of such carbonaceous matter, Nutman and Friend acknowledge that “recrystallization of ... bio-

genic material is ... one possibility,” a possibility, it should be noted, that is consistent with the measured carbon isotopic composition.

Nutman and Friend also raise uncertainty about the accuracy of the isotopic data, suggesting that they may result from the presence of “a mixed-carbon source” or “carbonate-bearing apatites that are <sup>13</sup>C-depleted.” This concern, based on measurements (Nutman and Friend, 2006) of infrared spectra of seven large (100 μm) apatites separated from G91–26 which showed that up to 0.5 wt% carbonate may substitute for phosphate, is misguided. No evidence of carbonate was detected in the Raman spectrum of the specific apatite grain analyzed. But even if we assume that carbonate was present at 20× the level suggested by Nutman and Friend (2006), it would make no quantitative difference on the carbon isotopic composition measured by SIMS (regardless of its isotopic composition). The reason is well known among SIMS practitioners: under Cs bombardment, the yield of negative carbon ions is ~100× higher from reduced carbon-bearing compounds than from carbonate (for C<sub>2</sub><sup>-</sup>, which we utilized, this factor is close to 2000). Thus, because our analyses were accomplished in situ by focusing the Cs beam onto the specific inclusion imaged by the Raman confocal microscope, any carbon signal coming from beam overlap onto the apatite would have been negligible. Even given the more subtle issue of “matrix effects” on instrumental mass bias, a problem well investigated for SIMS measurements of carbon isotopes both in geologic (McKeegan et al., 1985) and mineral-hosted biologic samples (House et al., 2000; Sangély et al., 2005), we are confident that the isotopic results presented are accurate to the precision stated in our paper.

Our paper firmly establishes the occurrence of isotopically light graphitic carbon included in apatite grains of ~3,830 Ma rocks at Akilia Island. These data are consistent with the existence of life at that remote time in geologic history, but as we state in the paper, “we do not claim [them to be] unequivocal evidence of early life” (McKeegan et al., 2007, p. 593).

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