Origin of life from apatite dating?

Mojzsis *et al.*[1,2] reported the carbon-isotope composition of carbonaceous inclusions in grains of apatite from sediment sequences of Akilia island, southwest Greenland, that are more than 3,850 million years (Myr) old. The δ^{13}C values measured by Mojzsis *et al.*[1] led them to conclude that these carbonaceous materials are evidence of early life 3,850 Myr ago. But if other isotopes (U–Pb and Pb–Pb) are used, the apatites are estimated at just 1,504 ± 336 (2σ) and 1,459 ± 160 (2σ) Myr old. This value is consistent with measurements of 1,600–1,700 Myr for Rb–Sr mineral isochrons on biotites[3] and 1,670 Myr for K–Ar muscovite[4] from Amitsog gneiss in the region. We conclude that, about 1,500 Myr ago, these apatites in Akilia island experienced a metamorphic event of about 600 °C (estimated by the closure temperature of the U–Pb system[5,6]).

Mojzsis *et al.*[1] measured the carbon-isotope composition of graphite inclusions in grains of apatite in banded-iron formations (BIFs) from Akilia island. Their observed δ^{13}C values ranged from −20 per mil (‰) to −50‰, using a PDB standard, indicating a biogenic origin. The BIFs are older than 3,850 Myr (ref. 2), but the age of the apatite housing the graphite material was not determined. Here we present measurements of the U–Pb age of apatites from closely related samples.

We cast the sample chip of the Akilia BIFs (approximately 1 × 1 cm) into epoxy-resin disks with several grains of standard apatite and polished them until they were exposed through their mid-sections. The sample apatites are about 20–30 μm in size and show similar texture to those reported by Mojzsis *et al.*[1]. We focused a primary beam of about 2.5 nA O_2^- to sputter an area of apatites 20 μm in diameter, and extracted the positive secondary ions using 10 kV. We found no isobaric interferences in the mass range over ^{204}Pb and ^{208}Pb at a mass resolution of 5,800. We obtained the ^{238}U/^{206}Pb ratios from the observed $^{238}U^+/^{206}Pb^+$ ratios by calibration using an empirical quadratic relationship between $^{206}Pb^+/^{238}U^+$ and $^{238}U^{16}O^+/^{238}U^+$ ratios of standard. The experimental details of the apatite U–Pb analysis and calibration of data are given elsewhere[7].

Eleven spots on seven individual apatite grains indicate that U concentrations vary significantly from 22.8 to 132 p.p.m. and do not show any correlation with ^{206}Pb/^{204}Pb and ^{207}Pb/^{204}Pb ratios. A correlation diagram of ^{238}U/^{204}Pb and ^{206}Pb/^{204}Pb ratios of the Akilia apatites is shown in Fig. 1. A least-squares fit using the York method gives the ^{238}U–^{206}Pb* isochron ages of 1,504 ± 336 (2σ; mean square of weighted deviates (MSWD) = 6.4). A correlation diagram of ^{204}Pb/^{206}Pb and ^{207}Pb/^{206}Pb ratios yields the ^{206}Pb*–^{207}Pb* isochron ages of 1,459 ± 160 (2σ; MSWD = 1.2). Both ages agree well with each other and are younger than the 3,860 ± 10 Myr of ref. 2 for BIFs. This suggests either that the apatites in the BIFs grew about 1,500 Myr ago, or that they grew earlier than that but were subsequently affected by recrystallization, and/or diffusive exchange with the environment, which reset the U–Pb system of the samples. If the apatites were formed during metamorphism, biogenic carbon could have been introduced during the event.

The Akilia association, including the BIFs and Isua supracrustals, are the oldest known components of the Archaean craton of Greenland and were affected by several metamorphic events after their formation 3,800 Myr ago (ref. 2). The latest event recorded in rock samples is the injection of basic dykes and crustally derived granitic sheets about 1,600 Myr ago, possibly coupled with the anatectic reheating[8]. Biotite from all types of gneisses in the area gives a Rb–Sr isochron age of 1,600–1,700 Myr ago (ref. 3), which is within the error of the isochron ages of the Akilia apatites.

If these apatites were formed 3,800 Myr ago, graphite inclusions within grains of apatites have also experienced a thermal event of around 600 °C about 1,500 Myr ago. The isotope composition of the carbonaceous inclusions might have been altered by the event. It has been suggested[9] that the oxidation of carbonaceous matter during metamorphism could alter the initial ^{13}C value from −10‰ to −35‰ if temperatures are higher than 500 °C and if an oxidizing system is provided. In iron formation, an oxidizing system seems a reasonable suggestion.

The young U–Pb ages on the apatites, indicating closure for Pb in an event as late as 1,500 Myr, and the theoretical possibility that the light signature is a product of fractionation since 3,850 Myr, might in isolation throw doubt on the proposal[1] that the Akilia BIF hosted life when deposited at around 3,850 Myr. However, as stated by Mojzsis *et al.*[1], the petrographic association of the apatite and carbon-rich material is well known from unmetamorphosed BIF with microfossils, and also from modern biological observations. This was considered an equally important line of evidence for biological activity when the Akilia BIF was deposited.

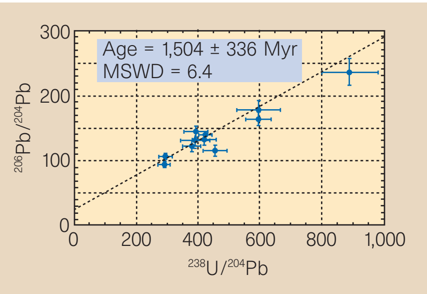

Figure 1 Correlation diagrams of ^{238}U/^{204}Pb and ^{206}Pb/^{204}Pb ratios of Akilia apatites. Errors are shown at the 1σ level. The dotted line shows the best fit by the York method. In the calculation of this ^{238}U/^{204}Pb–^{206}Pb/^{204}Pb diagram, an error correlation of $r = 0.8554$ was used, derived from the correlation coefficient between $\delta(^{238}U/^{204}Pb)/(^{238}U/^{204}Pb)$ and $\delta(^{206}Pb/^{204}Pb)/(^{206}Pb/^{204}Pb)$.

In conclusion, when we seek evidence of the earliest life on Earth, we need to find an apatite with a U–Pb closure age apparently older than 3,500 Myr; with a pattern of rare-earth elements that indicates a biogenic signature; and with carbonaceous inclusions that contain isotopically light carbon.

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Mojzsis et al. *reply* — Sano *et al.* report a ^{207}Pb/^{206}Pb date of 1,459 ± 160 Myr for apatite grains 25 μm in diameter, containing inclusions of isotopically light carbon, from a granulite grade BIF (typically 70% quartz, 10% magnetite, 20% mafic phases and sulphides) from Akilia island, Greenland, that was lithified before 3,850 Myr (refs 1,2). To Sano *et al.*, this suggests either that the apatites "grew about 1,500 Myr ago, or that they grew earlier than that but were subsequently affected by recrystallization, and/or diffusive exchange".

Two lines of evidence support the latter idea. The first is that radiogenic Pb is not quantitatively retained in apatite around 25 μm in diameter[3] at temperatures above 400 °C, during regional slow cooling (1–10 °C per Myr), or during a transient heating event that persists for several million years. It has long been known[4,5] that this region experienced a thermal excursion to temperatures exceeding 400 °C about 1,500 Myr ago. Thus, the Pb–Pb apatite age reported by Sano *et al.* of approximately 1,500 Myr is the expected result.

Second, this rock, which is essentially a quartzite, has no intrinsic capacity to form apatite by metamorphic reactions following diagenesis. Thus, the apatite present in this rock must be original (formed before 3,850 Myr) unless phosphate-bearing fluids were subsequently introduced metasomatically. Although no apatite has been recognized in the BIF that does not contain graphite inclusions, no apatites with graphite inclusions have been found in the immediately adjacent, encompassing gneisses[1,6,7].

Sano *et al.* are concerned that if "the apatites were formed during metamorphism, biogenic carbon could have been introduced". Again, given that the encompassing rocks do not contain graphitic inclusions with isotopically light carbon[1], this could not have occurred after 3,850 Myr.

"If these apatites were formed 3,800 Myr ago," Sano *et al.* allow, "graphite inclusions within grains of apatite have also experienced a thermal event of around 600 °C" (actually 400 °C; see http://oro.ess.ucla.edu/sjm-nature.html) "about 1,500 Myr ago". They posit that the "isotope composition of the carbonaceous inclusions might have been altered by the event". However, the extremely slow self-diffusion rates of carbon in graphite[7] (less than 10^{-39} cm^2 s^{-1} at 600 °C) precludes significant diffusive carbon-isotope exchange.

Could the isotopically light carbon ($\delta^{13}C$; 35‰) in the apatite inclusions[1] be abiogenic? Sano *et al.* seem to prefer a Rayleigh distillation mechanism that was previously[8] raised to illustrate the unlikelihood of such a process occurring. However, such a process has not been documented in the geological record, and Sano *et al.* do not specify how abiogenic carbon of ($\delta^{13}C$ exceeding 10‰; ref. 9) could be fractionated by about 30‰ to mimic a biogenic signature. Under metamorphic conditions, the relevant mineral assemblage (quartz, magnetite, pyroxene, amphibole, pyrrhotite, apatite and graphite) coexists with H_2O-bearing fluid containing both CH_4 and CO_2 (ref. 10). The previous calculations[8] did not consider the participation of CH_4, which mitigates against this type of isotope fractionation because it preferentially partitions ^{12}C, leaving a residue that becomes isotopically heavier with time, not lighter[11]. Thus, the role for Rayleigh fractionation proposed by Sano *et al.* is both improbable and unsupported by their Pb isotope data for apatite. Finally, Sano *et al.* imply that the rare-earth-element signatures of apatites can distinguish between a biogenic and abiogenic origin, but there is no basis for such a suggestion in this context.

In conclusion, the data reported by Sano *et al.* are not pertinent to the formation age of the host apatite and are not relevant to the mode of origin or preservation of the isotopically light carbonaceous inclusions they contain. In our view, the occurrence of this geochemical association in rocks of sedimentary origin is best explained as the product of biological activity[1,12] more than 3,850 Myr ago[1,2].

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Nicotine withdrawal and road accidents

Waters *et al.*[1] suggested that the effects of nicotine withdrawal increase the chances of an accident at work. The second Wednesday of March is 'No Smoking Day' (NSD) in the United Kingdom. If the 'accident effect' is real, increased numbers of other types of accident would be expected on NSD. I have investigated this possibility by using data from the UK national STATS19 accident reporting system[2], which records details of personal injury accidents occurring on public roads in which at least one road vehicle, or a vehicle in collision with a pedestrian, is involved, and which becomes known to the police within 30 days of its occurrence. Damage-only accidents are not included. The date of the accident is also recorded.

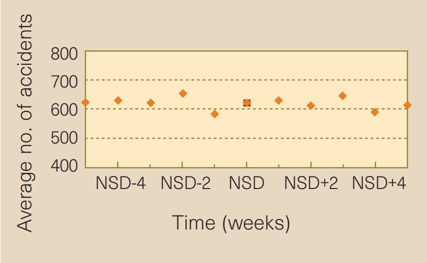

Figure 1 Average number of accidents in 1988–97 on Wednesdays around 'No Smoking Day' (NSD).

I compared the average number of road accidents occurring over the past 10 years (1988–97) on NSD with the average for the Wednesday before and the Wednesday after NSD. Table 1 shows the means and standard deviations of these measures for NSD week and the weeks before and after it. Paired-sample Student's *t*-tests (one-tailed) did not indicate that there were significantly more accidents on NSD than on the previous Wednesday ($t = -1.36$, $P = 0.10$) or the following one ($t = -0.39$, $P = 0.35$).

A visual inspection of the data for the five Wednesdays before and after NSD (Fig. 1) shows no obvious indication that the effects of nicotine withdrawal on NSD led to an increased number of road accidents when compared with the other Wednesdays in February and March. The only feature to stand out is the decrease in accidents between the last Wednesday in February and the first Wednesday in March in 7 of the 10 years examined. No explanation for this effect has been established.

Similar analyses of the severity of accidents and the age and sex of the drivers involved also provide no evidence of an increased number of accidents on NSD.

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Table 1 **Average number of road accidents in 1988 to 1997**

Day	One week before NSD		NSD week		One week after NSD	
	Average no.	s.d.	Average no.	s.d.	Average no.	s.d.
Monday	593.4	63.6	598.8	84.5	627.0	99.0
Tuesday	579.8	122.3	605.6	85.9	606.4	93.3
Wednesday	583.2	98.2	620.7	58.4	628.1	47.8
Thursday	655.3	106.5	605.0	61.5	639.0	85.9
Friday	712.1	70.3	719.0	67.3	781.3	90.0
Saturday	624.3	71.8	649.0	61.4	633.1	103.6
Sunday	453.3	61.7	502.9	60.8	488.3	77.8

s.d., Standard deviation.