

LETTERS

A light carbon reservoir recorded in zircon-hosted diamond from the Jack Hills

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The recent discovery of diamond–graphite inclusions in the Earth's oldest zircon grains (formed up to 4,252 Myr ago) from the Jack Hills metasediments in Western Australia¹ provides a unique opportunity to investigate Earth's earliest known carbon reservoir. Here we report ion microprobe analyses of the carbon isotope composition of these diamond–graphite inclusions. The observed $\delta^{13}\text{C}_{\text{PDB}}$ values (expressed using the PeeDee Belemnite standard) range between -5 per mil and -58 per mil with a median of -31 per mil. This extends beyond typical mantle values of around -6 per mil to values observed in metamorphic and some eclogitic diamonds that are interpreted to reflect deep subduction of low- $\delta^{13}\text{C}_{\text{PDB}}$ biogenic surface carbon. Low $\delta^{13}\text{C}_{\text{PDB}}$ values may also be produced by inorganic chemical reactions², and therefore are not unambiguous evidence for life on Earth as early as 4,250 Myr ago. Regardless, our results suggest that a low- $\delta^{13}\text{C}_{\text{PDB}}$ reservoir may have existed on the early Earth.

Detrital zircon (ZrSiO_4) grains from the $\sim 3,000$ -Myr-old Jack Hills metaconglomerate in Western Australia range in age up to $\sim 4,400$ Myr and currently represent the only direct samples of the Hadean Earth (earlier than $\sim 4,000$ Myr ago). Intense study of these zircons, primarily by microanalytical methods, has yielded an abundance of invaluable data relevant to models of the Earth's earliest tectonic regime. Nonetheless, models for the Hadean eon still range from the uniformitarian, characterized by the generation of voluminous continental crust by subduction-dominated tectonics³ analogous to modern tectonic processes that are thought to have operated since $\sim 3,900$ Myr ago⁴, to a radically different picture of mafic-dominated, potentially long-lived crust, evidence for which largely comes from accessible geochemical and isotopic reservoirs sampled since the Hadean⁵.

The recent discovery of diamond and graphite inclusions in 3,050–4,250-Myr-old zircon grains from the Jack Hills¹ introduces a new dimension to the debate on the early evolution of the Earth. Most profound is the indication of a carbon reservoir and processes capable of crystallizing diamond and graphite. The origin of the carbon and the nature of the carbon reservoir, as well as the process by which microdiamonds can be incorporated in zircon together with 'granitic' inclusions⁶, present problems fundamental to understanding processes active in the early history of the Earth. Carbon isotopes in the diamond and graphite inclusions provide a basic parameter critical for resolving these problems. We report the composition of 22 diamond and graphite inclusions from 18 Jack Hills zircon grains determined by ion microprobe (see Methods).

Diamond and graphite can readily be distinguished by Raman spectroscopy and their contrasting cathodoluminescence intensities (Supplementary Figs 1–3), diamond inclusions being cathodoluminescence bright in comparison with cathodoluminescence-dark

graphite. The inclusions are classified (Table 1), on the basis of Raman and cathodoluminescence response, as being either exclusively diamond (including some polycrystalline aggregates of nanometre- to micrometre-sized diamond) or mixtures of diamond and graphite. Even in inclusions classified as being mainly graphite, the graphite fraction may actually be low, because the strong light absorption of a graphite surface layer only a few nanometres thick would strongly attenuate cathodoluminescence and Raman signals.

Inclusions identified as being mainly graphite exhibit a range of $\delta^{13}\text{C}_{\text{PDB}}$ values between about -51% and -15% , whereas $\delta^{13}\text{C}_{\text{PDB}}$ values in most diamond inclusions (except JH3-189-1) range between about -24% and -5% (Table 1), suggesting a difference in the carbon isotopic composition of diamond and graphite inclusions (Fig. 1). However, diamond inclusion JH3-189-1 does not follow this trend, as it has the lowest $\delta^{13}\text{C}_{\text{PDB}}$ values ($-50.9 \pm 1.3\%$ and $-58.0 \pm 5.2\%$; Table 1). The results of comprehensive tests of potential analytical problems discount the possibility that the observed low $\delta^{13}\text{C}_{\text{PDB}}$ values are analytical artefacts (see Supplementary Information). We further note that it is highly unlikely that an apparent difference of about 20‰ between diamond and graphite is the result of a solid-state phase transition. Consequently, it is not evident on the basis of available data that there is a systematic difference in carbon isotope composition between graphite- and diamond-dominated inclusions. The apparent trend could simply be the result of a statistically small population of analysed inclusions and must be tested in further studies of carbon inclusions in Jack Hills zircons.

There is also no significant correlation between $\delta^{13}\text{C}_{\text{PDB}}$, diamond size, and the age of the host zircon grains (Table 1, Fig. 1). Some zircon grains have more than one diamond–graphite inclusion, and a comparison of the carbon isotope compositions of these inclusions shows no systematic trends. Some grains contain inclusions with similar carbon isotope compositions (for example, two inclusions in zircon JH3-48 have $\delta^{13}\text{C}_{\text{PDB}}$ values of $-34.2 \pm 3.1\%$ and $-34.3 \pm 1.9\%$), whereas other zircons have inclusions with very different $\delta^{13}\text{C}_{\text{PDB}}$ values (for example, two inclusions in the oldest zircon grain, JH3-20, with an age of $4,252 \pm 7$ Myr (ref. 1), show the maximum difference in $\delta^{13}\text{C}_{\text{PDB}}$ values (Table 1)).

Previously¹ we suggested that all diamond inclusions may be older than 4,250 Myr, based on hafnium isotope studies of the Jack Hills zircon population indicating that younger zircon grains may have formed by repeated recycling of a $>4,200$ -Myr-old source⁷. However, regardless of the possibility of several episodes of diamond formation, any given inclusion must be at least as old as its host zircon. The observed large variation in $\delta^{13}\text{C}_{\text{PDB}}$ values in inclusions hosted in the same zircon grain suggests that the carbon inclusions formed from different material and/or under different geological conditions before they were eventually included in the zircon. We

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Table 1 | Analysis of the inclusions

Label	Type†	Zircon growth texture‡	²⁰⁷ Pb/ ²⁰⁶ Pb age (Myr)§	Detection mode	$\delta^{13}\text{C}_{\text{PDB}}$ (‰)
JH15-497-1	dia	oz	3,455±10	7/FC	-18.5±1.0
				7/FC	-13.3±1.2
				2/EM	-18.0±2.6
JH3-20-3	dia	oz	4,252±14	7/FC	-11.8±0.8
				2/EM	-4.8±2.9
				2/EM	-4.9±2.6
JH3-50-4	dia	iz	3,681±10	7/FC	-19.3±1.3
				7/FC	-24.2±1.0
				2/EM	-16.5±3.2
JH11-4-1	dia	oz	3,370±24	7/FC	-20.2±5.1
JH11-250-1	dia*	pz	3,561±16	7/FC	-12.5±1.9
JH15-444-1	dia	oz	3,346±8	7/FC	-17.4±1.5
				2/EM	-17.0±4.7
				2/EM	-50.9±1.3
JH3-189-1	dia*	sz	3,369±12	7/FC	-58.0±5.2
				2/EM	-34.2±3.1
				2/EM	-41.0±5.9
JH3-48-1	dia/gr	cbz	3,454±14	7/FC	-33.6±1.6
JH15-243-1	dia/gr	pz	3,382±12	2/EM	-37.8±3.0
JH15-142-1	dia/gr	rz	3,897±6	7/FC	-28.7±1.4
JH15-82-2	dia/gr	oz	3,225±20	2/EM	-31.8±4.2
				7/FC	-30.5±1.3
				2/EM	-29.4±2.7
JH11-61-16	dia*/gr	sz	3,451±14	7/FC	-23.4±0.9
JH11-267-1	dia/gr	oz	3,377±10	7/FC	-31.0±0.8
JH11-61-15	gr	sz	3,451±14	7/FC	-43.1±1.5
JH15-2-3	gr	oz	3,476±10	7/FC	-36.1±6.4
				2/EM	-35.9±4.5
				2/EM	-40.8±2.0
JH11-13-1	gr	sz	3,600±12	7/FC	-35.6±1.7
JH3-165-1	gr	oz	3,266±14	7/FC	-51.1±1.7
JH3-20-1	gr	oz	4,252±14	2/EM	-40.2±8.5
JH3-48-5	gr	iz	3,454±14	7/FC	-34.3±1.9
				2/EM	-37.9±0.7
				2/EM	-40.3±2.6
JH3-124-3	gr	oz	3,058±14	2/EM	-44.0±3.0
				2/EM	-42.3±2.6
				2/EM	-42.1±3.1
JH3-134-4	gr	oz	3,312±20	2/EM	-47.1±2.9
				7/FC	-28.8±1.6
				2/EM	-24.0±3.5
				2/EM	-30.6±3.7
				2/EM	-26.2±3.2
				2/EM	-15.4±3.5
				2/EM	-27.9±3.7

Mineralogy of the analysed inclusions, textural features of the host zircons, ²⁰⁷Pb/²⁰⁶Pb ages of the inclusion-bearing zircon growth zone, analytical detection mode and $\delta^{13}\text{C}_{\text{PDB}}$ values.

$\delta^{13}\text{C}_{\text{PDB}} = \delta^{13}\text{C}_{\text{measured}} + \delta^{13}\text{C}_{\text{PDB(standard)}} + 10^{-3} \delta^{13}\text{C}_{\text{measured}} \delta^{13}\text{C}_{\text{PDB(standard)}}$, where $\delta^{13}\text{C}_{\text{measured}} = ((^{13}\text{C}/^{12}\text{C})_{\text{sample}} / (^{13}\text{C}/^{12}\text{C})_{\text{standard}} - 1) \times 10^3$.

† dia, mainly diamond; dia/gr, diamond and graphite; gr, mainly graphite; dia*, micrometre-sized, polycrystalline diamond detected by Raman spectroscopy.

‡ oz, oscillatory zoning; iz, irregular zoning; sz, sector zoning; pz, planar zoning; cbz, cross-bedded zoning; rz, re-equilibration zone (see Supplementary Figs 1–3). Late overprint resulting in the formation of homogeneously grey patches in the zircon is not considered in this classification.

§ Data from ref. 1.

|| 7/FC: Multicollector analyses with a 7- μm spot size; 2/EM: Mono-collector analyses using an electron multiplier and a 2- μm spot size.

consider it unlikely that the diamonds post-date their host zircon, perhaps formed from a supercritical COH-rich fluid that infiltrated the host zircon grains along the cracks that are visible in most diamond-bearing zircon grains (Supplementary Figs 1–3), as such a fluid would have had a homogeneous carbon isotope composition inconsistent with the extreme variation in $\delta^{13}\text{C}_{\text{PDB}}$ values observed in different inclusions hosted by the same zircon grain.

In addition, a supercritical COH-rich fluid would have been highly reactive and not in equilibrium with any of the Jack Hills zircons. Thus, such a fluid would probably have reacted with the zircon to form re-equilibration textures⁸ or baddeleyite (monoclinic ZrO_2)⁹. However, no indications of any type of reaction along the cracks have been observed in any of the Jack Hills zircons. We further emphasize that the carbon inclusions occur both in central and outer parts of some host grains, as well as in texturally different parts of complexly

zoned zircon (Table 1, Supplementary Figs 1–3), suggesting that their inclusion into the zircon is not related to any specific process that formed the distinct growth or re-equilibration zones. Some inclusions are located within irregularly zoned parts of zircon grains that have not always been directly dated, leaving open the possibility that these inclusions could be related to processes younger than the dated parts of the grains. Alternatively, these parts can represent zircon with an irregular trace element content, which is a common feature of zircon growth around a foreign object¹⁰.

It has been suggested that carbon was included in zircons of different ages as graphite and then transformed into diamond during a single, high-pressure metamorphic event that occurred less than 3,000 Myr ago¹¹. However, this contradicts the low compressibility of zircon (for example only a ~1.6% density increase at room temperature and 4 GPa)¹² when compared with the very large density increase accompanying the first-order graphite-to-diamond transformation (for example ~44% at room temperature and 4 GPa)¹³, which precludes a graphite inclusion in zircon being transformed into diamond. Therefore, the simplest explanation, and the one which is supported by most observations, is that the diamond formation must pre-date zircon crystallization and, most probably, is not related to zircon formation.

The fact that at least some inclusions are probably as old as 4,250 Myr provides us with the oldest terrestrial carbon reservoir discovered so far¹. We interpret the range of $\delta^{13}\text{C}_{\text{PDB}}$ values observed in these inclusions as a true measure of a potentially heterogeneous early-Earth carbon reservoir. Other than those in the Jack Hills, the oldest terrestrial diamonds found are associated with the kimberlite–lamproite suite of rocks¹³. These diamonds are of peridotite type (P-diamonds), on the basis of their inclusion paragenesis. They are about 3,000 Myr old, or slightly older, and have $\delta^{13}\text{C}_{\text{PDB}}$ values indistinguishable from that of the bulk Earth¹⁴. Light carbon isotope compositions are commonly found in so-called eclogitic diamonds (E-diamonds) showing negative $\delta^{13}\text{C}_{\text{PDB}}$ values (from -0‰ to -40‰), microdiamonds formed in subducted ultrahigh-pressure metamorphic rocks ($\delta^{13}\text{C}_{\text{PDB}}$ from -3‰ to -30‰), impact-related diamonds ($\delta^{13}\text{C}_{\text{PDB}}$ from -8‰ to -22‰) and carbonados ($\delta^{13}\text{C}_{\text{PDB}}$ from -25‰ to -32‰)^{15,16}. Additionally, strongly negative $\delta^{13}\text{C}_{\text{PDB}}$ values (from -15‰ to -40‰) have been observed in sedimentary carbon¹⁵.

These negative values are often taken as indicators of a contribution from a biogenic source which, if applicable to the Jack Hills inclusions, suggests that life might first have appeared on Earth well before the late heavy-meteorite bombardment about 3,900 Myr ago¹⁷. The significance of low $\delta^{13}\text{C}_{\text{PDB}}$ values as a unique biomarker remains controversial², however, particularly when applied to Paleoproterozoic and Eoarchaean rocks from which other evidence for biogenic activity is lacking¹⁸. Experimental work conducted to investigate carbon isotope fractionation effects associated with abiotic organic synthesis^{19,20} has demonstrated that negative $\delta^{13}\text{C}_{\text{PDB}}$ values similar to those observed in the Jack Hills inclusions can also be produced in reactions involving carbon oxides, methane, hydrogen and water, all significant components of both early-atmosphere and volcanic gases.

By analogy with the interpretation of light carbon in <1,500-Myr-old eclogitic and <500-Myr-old metamorphic diamonds⁴, the low $\delta^{13}\text{C}_{\text{PDB}}$ values of >3,000-Myr-old Jack Hills diamond–graphite inclusions, in combination with the observation that their mineralogical characteristics resemble those of modern ultrahigh-pressure metamorphic diamonds¹, could further be interpreted as evidence for an early Archaean and Hadean tectonic regime that was very similar to present day plate tectonics. In contrast, analysis of the consequences of accretion and the giant moon-forming impact^{21,22}, as well as investigation of accessible geochemical and isotopic reservoirs, has been used to conclude that the early history of the Earth was characterized by long-lived mafic to ultramafic crust⁴ and a mantle thermal regime that prevented significant convection⁵. Such a long-lived crust

could accumulate light carbon as a result of interaction with an early-Earth atmosphere that was rich in methane and possibly carbon dioxide (ref. 5). As mantle convection gradually restarted, this crust could have been recycled back into the mantle, introducing light carbon that over time homogenized with mantle.

Possible explanations for very negative $\delta^{13}\text{C}_{\text{PDB}}$ values in mantle-derived materials such as diamonds are not necessarily limited to terrestrial sources. Chondrites have bulk $\delta^{13}\text{C}_{\text{PDB}}$ values between 0‰ and -28‰ (ref. 23), presolar diamonds in primitive carbonaceous chondrites have values as low as -38‰ (refs 24, 25), and extremely low values of $\delta^{13}\text{C}_{\text{PDB}}$ (the majority falling between -20‰ and -50‰) have been reported from some intraplanetary dust particles²⁶. This has led to the suggestion that the variation of carbon isotope composition observed in mantle-derived materials is a primordial feature inherited from the time of accretion¹⁴.

The observations from the Jack Hills carbon inclusions of a $\delta^{13}\text{C}_{\text{PDB}}$ range of about 50‰, with a number extending beyond the lower limits (about -38‰ for the eclogite diamonds¹⁵) established for all other diamonds, clearly distinguishes them from peridotitic diamonds and carbonados, raising the possibility that these features are unique for the early Earth. Even most biogenic carbon²⁷ is heavier than many of the carbon samples from the Jack Hills inclusions, although the organic carbon record includes two $\delta^{13}\text{C}_{\text{PDB}}$ minima, recorded in the Fortescue group (Australia) and in the Francevillian formation of Gabon (Africa), which extend down to values of -50‰ . These minima have been interpreted as evidence of methanogenic carbon fixation²⁷. Mixing of such carbon with mantle-derived carbon may produce the observed variation in $\delta^{13}\text{C}_{\text{PDB}}$. The range of $\delta^{13}\text{C}_{\text{PDB}}$ values observed in carbonaceous chondrites is also different from that of the Jack Hills inclusions. Therefore, if Jack Hills diamonds were formed by impacts (although there is Raman spectroscopic evidence that this is not the case¹), at least some of the carbon required for the formation of these diamonds must have come from impacted terrestrial rocks, where it would still have required a process capable of producing very negative $\delta^{13}\text{C}_{\text{PDB}}$ values. The only extra-terrestrial source of such light carbon is some intraplanetary dust particles and/or presolar grains²⁶. If these were indeed the source of light carbon in the Jack Hills inclusions, a substantial flux would have been required.

All these possible sources of carbon involve accumulation of light carbon near the surface and require a mechanism either to transfer it into the diamond stability field (unless the diamond grew outside its stability field¹⁴) or to transfer impact-produced diamonds at least to the region where zircon is forming. Possible transfer mechanisms

include modern-style plate tectonic subduction and vertical tectonics ('sagduction')²⁸, a process that might have operated in the Archaean. Some inorganic reactions (for example the Fischer–Tropsch process) may produce both diamond and the observed spread in $\delta^{13}\text{C}_{\text{PDB}}$ values² at a variety of depths and conditions, and might obviate the need for additional transfer mechanisms.

We are aware that many of our observations remain unexplained and that conclusions based on them are thus controversial. Specifically, the observed, strongly negative $\delta^{13}\text{C}_{\text{PDB}}$ values in the Jack Hills diamond–graphite inclusions do not indicate a unique source of carbon. We caution that they should not be interpreted as prima-facie evidence for biological activity in the Hadean, although they do not exclude such a possibility. Whatever the process responsible for the formation of light carbon observed in the Jack Hills zircon-hosted inclusions, they most likely predate their respective host grains. Therefore, our data suggest that a light carbon reservoir may have existed from the earliest stages of Earth's history. It is thus conceivable that the low $\delta^{13}\text{C}_{\text{PDB}}$ signature exhibited by many crust- and mantle-derived rocks throughout the Earth's history may in part reflect recycling of this reservoir.

METHODS SUMMARY

Carbon isotope compositions of diamond graphite inclusions were analysed by secondary-ion mass spectrometry using a Cameca IMS1270 instrument (Nordsim facility, Stockholm) operating with instrument parameters typical for light stable isotope analysis (see, for example, ref. 29). Analyses were performed using two different spatial resolutions and secondary-ion detection modes. The first used a nominal 2- μm spot with ^{12}C and ^{13}C signals measured in peak jumping mode on an ion-counting electron multiplier (electronically gated dead time of 44 ns); the second used a nominal 7- μm spot with simultaneous measurement of ^{12}C and ^{13}C on Faraday detectors. In order to eliminate interference of the $^{12}\text{C}^1\text{H}^+$ species on $^{13}\text{C}^+$, all analyses were performed at a nominal mass resolution ($M/\Delta M$) of 4,800. Potential sample-charging effects due to the small size of the inclusions embedded in a non-conducting matrix were minimised using a low-energy, normal-incidence electron flood gun.

Data are reported as $\delta^{13}\text{C}_{\text{PDB}}$ values in parts per thousand (‰), where PDB refers to the carbon isotope composition of the PeeDee Belemnite. A synthetic diamond, SYNAL, with $\delta^{13}\text{C}_{\text{PDB}} = -23.9\text{‰}$ (ref. 30) was used as a reference material. This was mounted in epoxy, coated with gold, and inserted alongside the Jack Hills zircon mounts in the same sample holder to enable bracketing of sample and standard analyses. Each analysis consisted of a 120-s pre-sputter period to remove the gold coating from an area larger than the analytical spot, followed by automated centring of the beam in the field aperture and centring of the magnet field. Multicollector analyses consisted of 16 cycles of 10-s integrations. Mono-collector analyses consisted of 50 cycles through the masses with integration times of 2 s and 6 s on the ^{12}C and ^{13}C peaks, respectively.

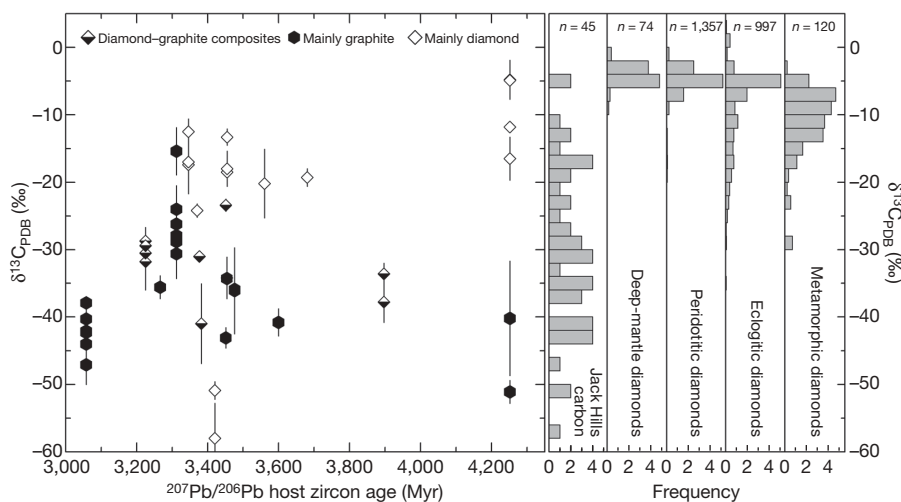


Figure 1 | $\delta^{13}\text{C}_{\text{PDB}}$ values of diamond–graphite inclusions. We plot the values against the age of the Jack Hills host zircons, and provide a comparison of their distribution with $\delta^{13}\text{C}_{\text{PDB}}$ distributions of diamonds

from known geological settings. The $\delta^{13}\text{C}_{\text{PDB}}$ ranges of known diamond sources were redrawn from ref. 15. Error bars, 2 s.d.; n , number of analyses.

Full Methods and any associated references are available in the online version of the paper at www.nature.com/nature.

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Supplementary Information is linked to the online version of the paper at www.nature.com/nature.

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METHODS

Test of diamond–graphite instrumental mass fractionation differences. The complex mineralogical composition of the inclusions, which are mainly represented by mixtures of diamond and graphite in different proportions, raises the possibility of bias in isotope ratios due to different instrumental mass fractionation from the two phases. Although close similarity of instrumental mass fractionation from diamond and graphite has been demonstrated previously³¹, these experiments used extreme energy-filtering methods on a small ion microprobe. Under the analytical conditions used for the present study, which specifically did not utilize energy filtering, we investigated the possibility of matrix influence on the observed carbon isotope compositions, by analysing SYNAL diamond against two pyrolysed graphite samples (pyr-1 and pyr-2). Pyr-1 has a conventionally determined $\delta^{13}\text{C}_{\text{PDB}}$ value of -30.8‰ (G. Layne, personal communication), which was determined using several small subsamples of pyr-1 disk in the Laboratory for Stable Isotope Science at The University of Western Ontario. This value was indistinguishable from the results of a direct $\delta^{13}\text{C}_{\text{PDB}}$ determination using secondary-ion mass spectrometry at the Woods Hole Oceanographic Institution, made by comparing pyr-1 to a pressed pellet of NBS-24 graphite, which yielded an average $\delta^{13}\text{C}_{\text{PDB}}$ value of -30.7‰ .

The results are shown in Supplementary Fig. 4 and Supplementary Table 1 and suggest a $\delta^{13}\text{C}_{\text{PDB}}$ value of $-36.7 \pm 0.5\text{‰}$ (with 95% confidence) for the pyr-2 sample when analysed against the SYNAL diamond and a $\delta^{13}\text{C}_{\text{PDB}}$ value of $-35.7 \pm 0.3\text{‰}$ (with 95% confidence) when analysed against pyr-1 graphite. The errors do not include uncertainties in the 'true' values determined for SYNAL diamond and pyr-1 graphite. The two values are barely outside the errors, suggesting that even if there is a minor matrix effect during the carbon isotope analysis of graphite and diamond, it does not exceed 1‰ and definitely cannot be responsible for the variation in $\delta^{13}\text{C}_{\text{PDB}}$ of about 50‰ observed in the inclusions.

Test of relief effects on instrumental mass fractionation. A second analytical problem is presented by the difficulty of polishing the inclusions well, as a result of significant difference in hardness between the diamond and graphite in the inclusions and between these two minerals and the host zircon. As a consequence, it is impossible to produce a flat, level surface near the inclusions, which raises a concern that some of the isotopic effects observed during the analysis of unknowns may be influenced by changes in the ion optical configuration near the analysed spots, resulting in different sputtering behaviour of ^{13}C and ^{12}C . Although the problem cannot be eliminated completely it was closely monitored during and after the analyses.

Instrumental mass fractionation associated with surface imperfections during an ion probe analysis is commonly accompanied by a decrease in the counting rate of isotopes. Although about 50% of our analyses of inclusions showed an ^{12}C intensity less than 30% of that observed in the standard, and about 35% of the inclusions were found to produce ^{12}C counting rates greater than half of that in the standard, the observed counting rate and $\delta^{13}\text{C}_{\text{PDB}}$ values are not correlated (Supplementary Table 2, Supplementary Fig. 5). Two inclusions that show ^{12}C counting rates similar to the standard have respective $\delta^{13}\text{C}_{\text{PDB}}$ values of $-40.3 \pm 2.6\text{‰}$ and $-4.9 \pm 2.6\text{‰}$. The multicollector measurements, made using the larger (7- μm) spot, generally show smaller counting rates relative to the standard when compared to the signals measured in peak-jumping mono-collector mode, where a smaller (2- μm) spot was used. This systematic difference suggests that the observed decrease in the ^{12}C counting rates during analysis of inclusions is related to the possible overlap of zircon surrounding inclusions by the analytical spot. This overlap is less likely to occur with the smaller spot size used during the mono-collector analysis. The fact that there is no difference visible, within the errors, between the $\delta^{13}\text{C}_{\text{PDB}}$ values obtained using large and small spot sizes (Supplementary Fig. 6) suggests that this partial overlap, if it occurs, does not introduce a significant fractionation between ^{12}C and ^{13}C . It also indicates that there is no major fractionation of isotopes caused by the possible relief within the inclusions, as the analyses with the small spot size are expected to be more sensitive to this relief variation and therefore would produce much larger scatter.

The absence of significant relief effects is further indicated by the two traverses measured in two different inclusions. Although a change in the $\delta^{13}\text{C}_{\text{PDB}}$ values is observed from analytical spots close to the edge of the inclusions (Supplementary Figs 7 and 8), this change is not systematic, as might be expected from the relief-related fractionation effects. In the case of one inclusion, the $\delta^{13}\text{C}_{\text{PDB}}$ values near the edge are increasing, whereas in the second inclusion they are decreasing. In addition, the observed changes near the edges of inclusions are insufficient to change the average $\delta^{13}\text{C}_{\text{PDB}}$ values for these inclusions (Supplementary Figs 3 and 4). Therefore, it is apparent that the very light carbon compositions that are observed in most of the inclusions and are different from the bulk Earth value of about -6‰ cannot be produced by any instrument-related fractionation effects.

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