

SUPPLEMENTARY MATERIALS

SAMPLES PREPARATION

Focused Ion Beam foils, numbered 1160, 1163 (Fig. S1) and 1286, were provided by R. Wirth at GFZ Potsdam. The foils were individually fixed on a perforated organic film on copper grids used for Transmission Electron Microscopy (TEM; Fig. S2). Please refer to Wirth (2009) for a detailed explanation of the FIB and mounting techniques. The grids were gently pressed on the surface of aluminum holders filled with indium prepared at *Équipe de Minéralogie des Intérieurs Planétaires* of the IMPMC-Paris 6 (see details on the technique at <http://www.ed.ac.uk/files/imports/fileManager/IndiumMountPrep.pdf>).

Together with three foil holders, two more holders were charged into the analyzing chamber of the NanoSIMS 50 at AORI, The University of Tokyo: One containing internal standard carbonado GM02 on an epoxy resin and one containing two new diamond standards on pressed indium. The GM02 carbonado was studied in detail by Yokochi *et al.* (2008) and showed a quite homogeneous carbon isotopic signature ($\delta^{13}\text{C} = -29.23 \pm 0.05\%$ vs. PDB) and N content of 85 ± 9 ppm. Because we were concerned whether there is a matrix effect on NanoSIMS when comparing carbon isotope measurements on carbonado and on diamond samples, fragments of the two new diamonds, used as references, were loaded. These are a natural diamond of type Ia (NIa) and a synthetic diamond of type IIa (SIIa) from ALMAX EasyLab[®], which are used for Diamond Anvil cell experiments (Fig. S3). The carbon isotopic analyses at NanoSIMS on these two samples were done blindly and corrected against the GM02. Then precise $\delta^{13}\text{C}$ measurements have been performed on bulk pieces from the two reference samples by mass spectrometry at the *Equipe de Géochimie des Isotopes Stables* (IPGP) to compare. Both FIB-TEM foils and diamond standards were gold coated to dissipate charge during analysis.

NanoSIMS 50 ANALYTICAL CONDITIONS AND COLLECTOR GEOMETRY

The analytical conditions of the CAMECA NanoSIMS 50 at the Atmosphere and Ocean Research Institute of the University of Tokyo are report as below:

Primary beam: Cs^+ with intensity of 0.84 pA (Fig. S4). Actual spot size is less than 0.6 μm .

Accelerating voltage: 16 kV.

Mass resolution power: 3600 (10% peak height).

Magnetic field and geometry of electron multiplier (EM): In the magnetic field 1 (B1), $^{12}\text{C}^-$ was detected using EM4, and $^{12}\text{C}^{12}\text{C}^-$ was detected by EM5. In the

magnetic field 2 (B2), $^{12}\text{C}^-$, $^{13}\text{C}^-$, and $^{12}\text{C}^{14}\text{N}^-$, were detected by EM3, EM4, and EM5 respectively. In the magnetic field 3 (B3), $^{13}\text{C}^-$ was detected by EM3. The counting times are 3s, 5s, and 5s, for B1, B2, and B3, respectively. Waiting time 3s was set before each magnetic field to wait the change of them. Total 22s is required for 1 measurement cycle.

Counting time: Number of cycles ranges from 35 to 80, depending on the thickness of the FIB-TEM foil (always 80 cycles for GM02, NIa and SIIa stds which are thick fragments of diamonds). Variations in thickness did not influence the carbon isotopic measurement or the analytical error. If the ion beam perforates the foil, then the signal quickly degrades and the analysis is stopped. Only data prior of the perforation were used. Total counting times of each magnetic field are 105 to 240 s for B1, and 175 to 400 s for B2 and B3.

Isotope ratios: For the carbon isotope detection mode, to detect $^{12}\text{C}^-$ and $^{13}\text{C}^-$ ions, we used 2 electron multiplier (EM) detectors in different 3 magnetic fields, so we could estimate three $^{13}\text{C}/^{12}\text{C}$ ratios; $(^{13}\text{C}/^{12}\text{C})_{\text{EM3}}$, $(^{13}\text{C}/^{12}\text{C})_{\text{EM4}}$, $(^{13}\text{C}/^{12}\text{C})_{\text{multi}}$. These ratios were calculated considering the difference of counting time. $(^{13}\text{C}/^{12}\text{C})_{\text{EM3}}$ and $(^{13}\text{C}/^{12}\text{C})_{\text{EM4}}$ were measured independently using EM3 and EM4, while $(^{13}\text{C}/^{12}\text{C})_{\text{multi}}$ was measured by simultaneous collection using 2 detectors. $^{12}\text{C}^{12}\text{C}^-$ and $^{12}\text{C}^{14}\text{N}^-$ ions are also collected using EM5 in the same analytical session.

DATA CORRECTIONS

Data were corrected for detector dead time, Quasi Simultaneous Arrival (QSA) effect (Slodzian *et al.*, 2004) and instrumental mass fractionation (IMF). The measured counts are corrected to know the true counts which was lost by the dead time of detector (dead time effect). The dead time of detector equipped in our NanoSIMS 50 is 44E-9s. Quasi-simultaneous arrival effect should be considered when large amount of secondary ions are observed (above 100,000 cps). QSA was originally reported by Slodzian *et al.* (2004) and it takes account the probability that more than one secondary ion per primary impact reaches at the same time the dynode of the electron multiplier (EM) detector. Details on the equations used for the correction of this QSA effect at AORI are reported in Nishizawa *et al.* (2007). Finally IMF effect was calculated for the $^{13}\text{C}/^{12}\text{C}$ ratio on each detector through repeated measurements of std GM02. Analytical uncertainty on carbon isotopic measurements (35–80 cycles) is much smaller (0.15–0.2%) than the total uncertainty reported in Table S1 which includes uncertainties on the single measurement, the QSA and the IMF effect.

Nitrogen concentrations in examined samples are calculated according to the $^{12}\text{C}^{14}\text{N}^-/^{12}\text{C}^{12}\text{C}^-$ ratios and cor-

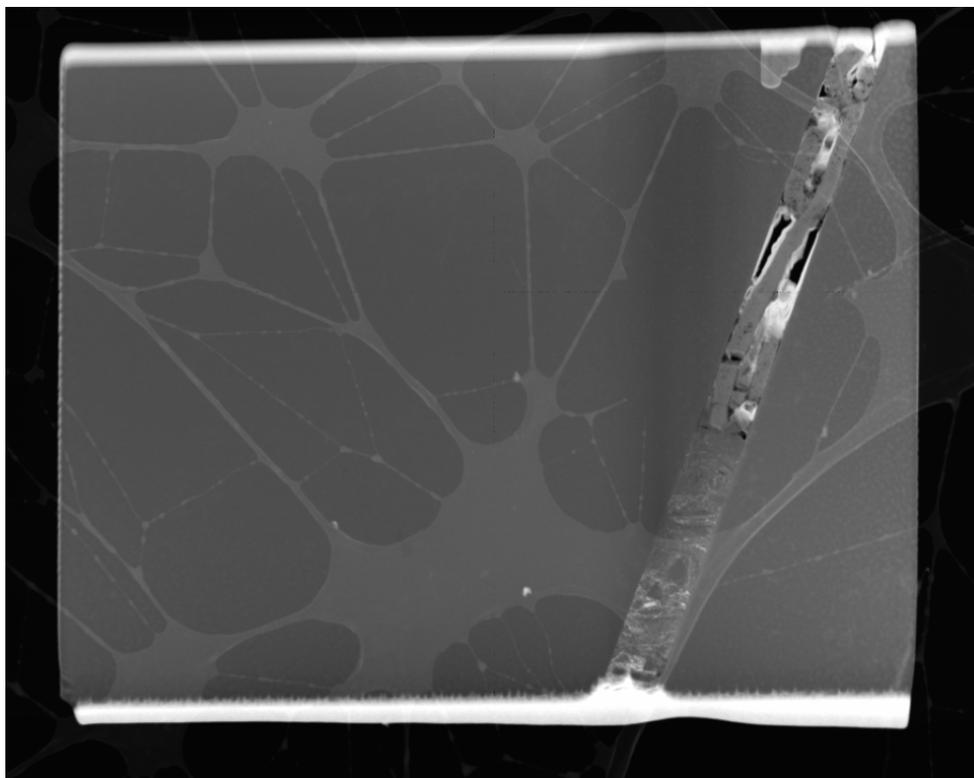


Fig. S1. High-Angle Annular Dark-Field (HAADF) microscopy image of foil 1163 (courtesy of R. Wirth, GFZ Potsdam). The size of the foil is $15 \times 12 \mu\text{m}$.

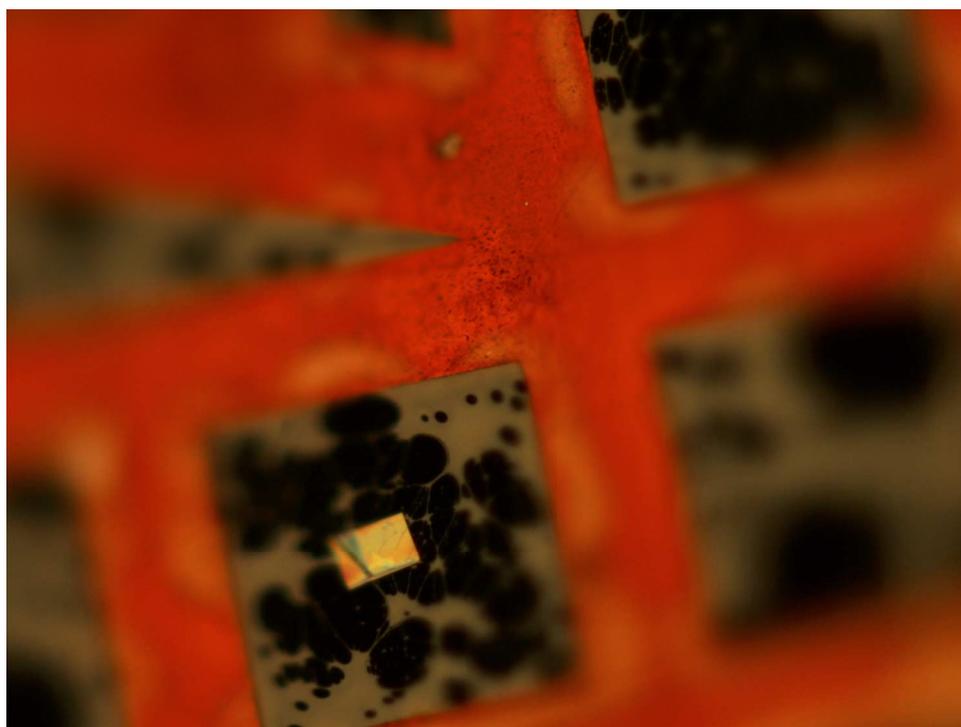


Fig. S2. Optical microscopy image of the TEM grid (in red) with foil 1163 deposited on the organic film (photo A. Ishida, AORI). The size of the foil is $15 \times 12 \mu\text{m}$.

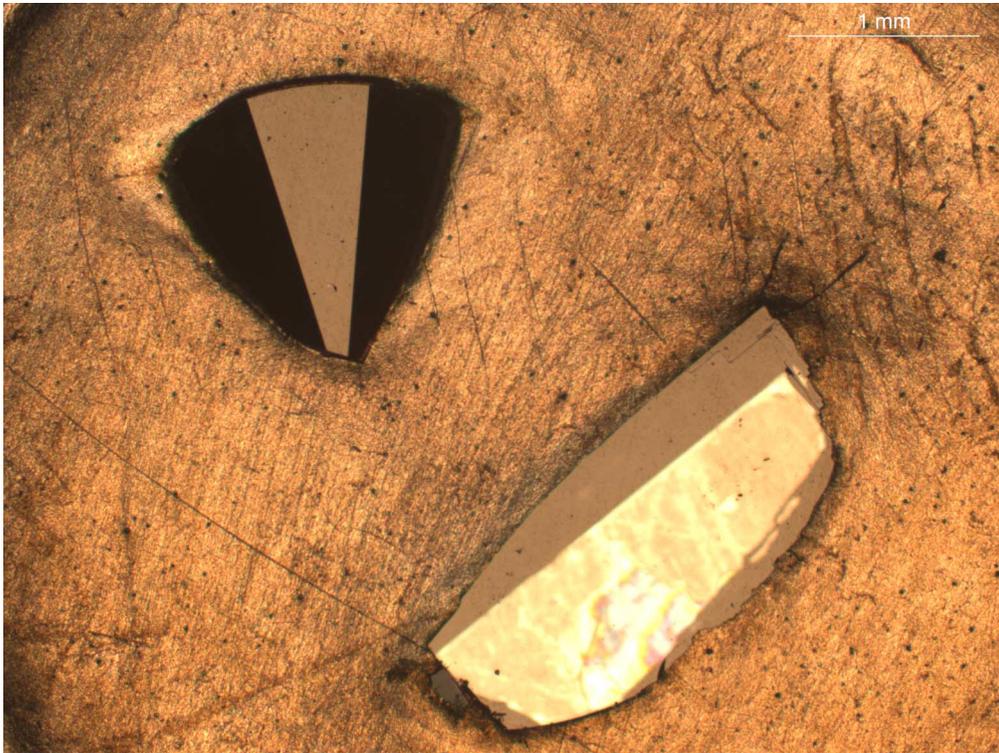


Fig. S3. Optical microscopy image of the NIa (bottom right) and SIa (upper left) diamonds fragments from ALMAX-Easylab[®] pressed in indium.

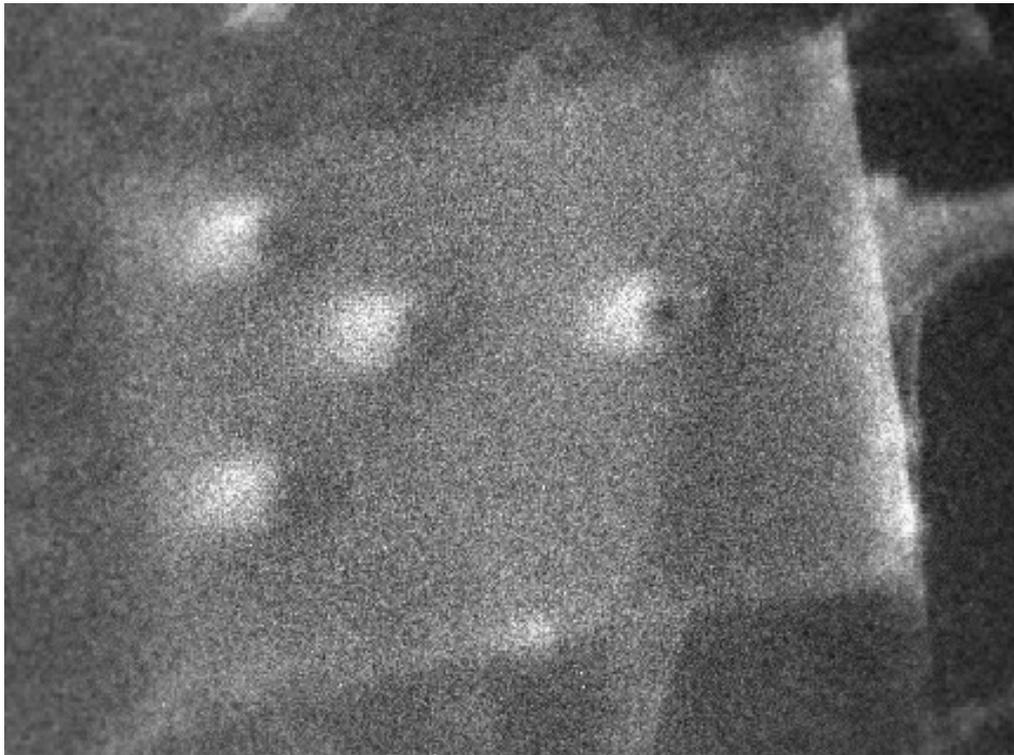


Fig. S4. BSE image of the foil I163 mounted in the NanoSIMS 50 with the craters produced by the Cs+ beam spot where analyses were performed. The size of the foil is 15 × 12 μm.

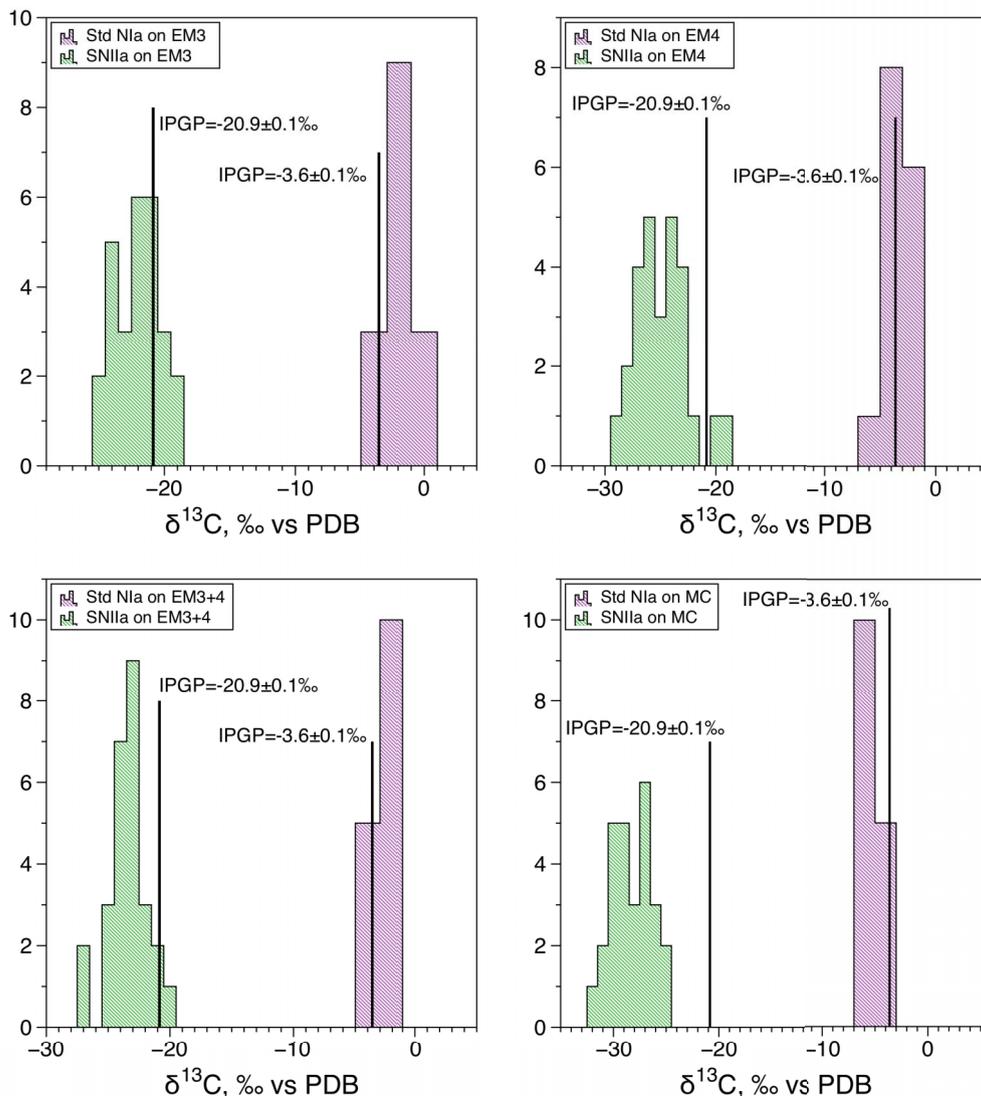


Fig. S5. Histograms representing repeated raster measurements of the $^{13}\text{C}/^{12}\text{C}$ ratios (as $\delta^{13}\text{C}$ values normalized to PDB) for the natural diamond N1a and synthetic S11a from Almax-Easylab compared to the $\delta^{13}\text{C}$ values measured by mass spectrometry at IPGP.

rection factor of nitrogen. The correction factor of nitrogen concentration, 1.5123×10^5 [ppm/ratio], is calculated based on the reported N concentration of GM08 (82 ppm) and the measured average $^{12}\text{C}^{14}\text{N}^-/^{12}\text{C}^{12}\text{C}^-$ ratio of it.

RESULTS OF ANALYSES

Table S1 show the results of the $^{13}\text{C}/^{12}\text{C}$ ratios (corrected for the above-mentioned effects and normalized to the Pee-Dee Belemnite (PBD) value of 0.0112372) measured by single detection mode EM3, EM4, EM3+4 and in multi-collection (MC). $\delta^{13}\text{C}$ results have passed a Grubbs' test, also called the ESD method (Extreme

Studentized Deviate), to determine whether one of the values is a significant outlier from the rest. The outlier is here defined as out of 95% normal distribution (indicated by red font in Table S1). The mean $\delta^{13}\text{C}$ values measured on sample 8/106 on the 3 single mode detector configurations are equal within uncertainties: $\delta^{13}\text{C}_{\text{EM3}} = -6.26 \pm 1.37\%$; $\delta^{13}\text{C}_{\text{EM4}} = -5.00 \pm 2.33\%$; $\delta^{13}\text{C}_{\text{EM3+4}} = -5.98 \pm 1.47\%$, while $\delta^{13}\text{C}$ value measured by MC of $-3.83 \pm 1.76\%$ deviates sensibly from the other values and it is considered an outlier by the Grubbs' test. The EM3 and EM3+4 single detector modes show low precision but high accuracy. Here we assumed the most reliable results those of EM4 that gives the high precision but low accuracy.

Table S1. Results of $\delta^{13}\text{C}$ measurements by NanoSIMS N50 on 8/106, Nia and SIIa diamonds

Sample name	Counting cycles	$\delta^{13}\text{C}$, ‰ vs. PDB	\pm	N ppm						
		EM3		EM4		EM3+4		MC		
8/106	60	-5.0	1.2	-5.2	1.4	-5.1	1.3	-3.1	1.3	108
foil#1160	60	-6.0	1.3	-3.4	1.1	-4.7	1.2	-2.7	1.1	38
	60	-8.2	1.4	-9.5	1.2	-8.9	1.3	-6.0	1.2	108
	45	-5.9	1.4	-10.5	1.4	-8.2	1.4	-9.1	1.4	48
	60	-3.9	1.2	-5.7	1.3	-4.8	1.3	-5.1	1.3	93
8/106	50	-5.5	1.7	-6.5	1.8	-6.0	1.7	-4.3	1.8	84
foil#1163	40	-3.0	1.6	-1.6	2.2	-2.3	1.9	-0.4	2.3	51
	30	-7.2	1.6	-7.4	2.4	-7.3	2.0	-6.5	2.5	52
	40	-7.9	1.7	-6.0	1.8	-7.0	1.8	-4.8	1.9	59
8/106	60	-7.7	1.6	-2.6	1.7	-5.1	1.7	-1.2	1.7	53
foil#1286	60	-7.0	1.4	-6.0	1.9	-6.5	1.6	-3.3	1.9	59
	60	-6.3	1.1	-2.9	1.3	-4.6	1.2	-3.7	1.3	37
	35	-6.7	1.8	-1.9	2.3	-4.3	2.1	-3.3	2.2	44
	60	-4.2	1.4	-6.3	1.4	-5.2	1.4	-5.3	1.5	33
Natural Ia	80	-4.3	1.0	-2.7	1.1	-3.5	1.1	-5.8	1.0	236
	80	-2.9	1.0	-1.2	1.1	-2.1	1.1	-5.5	1.0	215
	80	-2.4	1.2	-5.1	1.0	-3.8	1.1	-6.7	1.0	410
	80	-3.8	1.1	-4.0	1.1	-3.9	1.1	-5.9	1.1	378
	80	-0.1	1.0	-5.0	1.2	-2.6	1.1	-6.7	1.2	483
	80	-2.5	1.1	-3.4	1.1	-2.9	1.1	-5.6	1.1	292
	80	-3.6	1.1	-2.3	1.0	-3.0	1.1	-4.5	1.0	228
	80	-0.3	1.1	-4.3	1.0	-2.3	1.0	-5.8	0.9	426
	80	-2.1	1.0	-1.4	1.2	-1.7	1.1	-3.7	1.2	274
	80	-1.9	1.1	-3.4	1.2	-2.6	1.1	-5.5	1.2	251
	80	-2.4	0.9	-4.3	1.0	-3.4	0.9	-6.5	1.0	260
	80	-0.8	1.0	-3.3	1.1	-2.1	1.1	-4.6	1.1	319
	80	-1.7	1.0	-2.6	0.9	-2.2	1.0	-4.6	0.9	194
	80	-2.1	1.0	-4.6	0.8	-3.4	0.9	-6.4	0.8	269
80	-1.2	1.1	-2.9	1.0	-2.1	1.0	-4.3	1.0	333	
<i>M</i>±<i>SD</i>		-2.0	1.1	-3.5	1.1	-2.7	0.6	-5.6	0.8	305
Synthetic IIa	60	-23.4	1.8	-19.0	2.1	-21.2	2.0	-26.9	2.0	57
	60	-20.4	1.6	-19.9	1.8	-20.1	1.7	-29.2	1.8	34
	60	-22.4	1.6	-25.5	1.5	-24.0	1.6	-31.1	1.6	40
	60	-20.8	1.4	-27.5	1.4	-24.2	1.4	-31.0	1.4	54
	60	-20.0	1.4	-26.5	1.4	-23.3	1.4	-30.1	1.4	38
	60	-23.7	1.4	-29.4	1.1	-26.6	1.3	-31.7	1.1	39
	60	-25.3	1.2	-28.3	1.3	-26.8	1.3	-29.8	1.3	80
	60	-22.1	1.5	-24.2	1.2	-23.2	1.3	-26.9	1.1	41
	60	-24.6	1.5	-26.3	1.4	-25.4	1.4	-29.0	1.4	56
	60	-23.6	1.4	-26.7	1.2	-25.1	1.3	-30.2	1.3	33
	60	-23.6	1.2	-25.3	1.3	-24.5	1.2	-28.4	1.2	43
	60	-21.0	1.3	-26.0	1.5	-23.5	1.4	-29.3	1.5	100
	60	-22.4	1.3	-22.6	1.3	-22.5	1.3	-25.3	1.3	74
	60	-19.2	1.4	-25.0	1.6	-22.1	1.5	-28.2	1.6	38
	60	-24.3	1.3	-23.6	1.2	-23.9	1.3	-27.0	1.2	58
	60	-23.7	1.2	-26.8	1.6	-25.3	1.4	-30.1	1.6	36
	60	-20.5	1.4	-24.2	1.4	-22.4	1.4	-26.8	1.3	48
	60	-19.7	1.5	-21.9	1.2	-20.8	1.3	-25.3	1.2	89
	60	-21.4	1.4	-25.3	1.5	-23.4	1.4	-28.1	1.4	58
	60	-22.1	1.4	-23.2	1.3	-22.6	1.3	-25.9	1.3	62
	60	-21.5	1.5	-24.4	1.6	-23.0	1.5	-26.7	1.6	102
60	-22.0	1.2	-26.3	1.4	-24.2	1.3	-29.2	1.3	48	
60	-20.5	1.5	-22.8	1.5	-21.6	1.5	-26.0	1.5	50	
60	-19.3	1.1	-27.0	1.3	-23.2	1.2	-29.7	1.3	54	
60	-23.4	1.1	-23.0	1.3	-23.2	1.2	-25.8	1.3	123	
60	-21.2	1.5	-26.5	1.5	-23.8	1.5	-29.1	1.5	73	
60	-23.0	1.8	-23.7	1.7	-23.3	1.7	-26.7	1.6	61	
<i>M</i>±<i>SD</i>		-21.9	1.6	-25.1	2.1	-23.3	1.5	-28.1	1.8	59

Red fonts indicate measured values that are considered as outlier as determined through a Grubb's test (extreme studentized deviate); see Supplementray Material's section for details.

COMPARISON OF $\delta^{13}\text{C}$ VALUES MEASURED ON
REFERENCE DIAMONDS BY
MASS SPECTROMETRY AND NanoSIMS 50

Figure S5 shows the histograms of the $\delta^{13}\text{C}$ values measured with the different single detector and multi-collection mode of the natural Ia and synthetic IIa diamond from ALMAX-Easylab, and normalized to internal standard carbonado GM02 and corrected for detector dead time, QSA effect and IMF effect. The results are compared to the $\delta^{13}\text{C}$ values obtained by mass spectrometry at IPGP, following the techniques described in Palot *et al.* (2012). The $\delta^{13}\text{C}$ mean and SD of three measurements of NIa sample and of two measurements on SIIa sample are of $-3.62 \pm 0.11\text{‰}$ and $-20.85 \pm 0.10\text{‰}$, respectively (the above error is external on the measurement and reflects some sample heterogeneity).

The same trends between certainty and accuracy observed for the 8/106 sample are here observed for the measurements of NIa and SIIa (Table S1). The $\delta^{13}\text{C}$ value of NIa measured at EM4 is the closest ($3.51 \pm 1.08\text{‰}$) to the value measured by mass spectrometry at IPGP (Fig. S5). Again the $\delta^{13}\text{C}$ value measured by MC show the largest deviation from the expected values obtained by mass spectrometry for both the NIa and the SIIa sample (Table S1 and Fig. S5).

For the synthetic sample SIIa, the $\delta^{13}\text{C}$ value of $-21.92 \pm 1.59\text{‰}$ measured on the EM3 single detector mode con-

figuration is the closest to the that measured by mass spectrometry, all other detector configuration showing systematically a lighter $\delta^{13}\text{C}$ value with a bias of 2–8‰ compared to the value measured by mass spectrometry. It is still unclear why this bias is so large for the synthetic diamond. Being a synthetic diamond the bias could be related to some sort of matrix effect for which NanoSIMS is particularly sensitive to.

REFERENCES

- Nishizawa, M., Maruyama, S., Urabe, T., Takahata, N. and Sano, Y. (2007) Micro-scale (1.5mm) sulphur isotope analysis of contemporary and early Archean pyrite. *Rap. Comm. Mass Spectrom.* **24**, 1397–1404.
- Palot, M., Cartigny, P., Harris, J. W., Kaminsky, F. V. and Stachel, T. (2012) Evidence for deep mantle convection and primordial heterogeneity from nitrogen and carbon stable isotopes in diamond. *Earth Planet. Sci. Lett.* **357–358**, 179–193.
- Slodzian, G., Hillion, F., Stadermann, F. J. and Zinner, E. (2004) QSA influences on isotopic ratio measurements. *Appl. Surface Sci.* **231–232**, 874–877.
- Wirth, R. (2009) Focused Ion Beam (FIB) combined with SEM and TEM: Advanced analytical tools for studies of chemical composition, microstructure and crystal structure in geomaterials on a nanometre scale. *Chem. Geol.* **261**, 217–229.