1	Revision 1
2	
3	Characterization of carbon phases in Yamato 74123 ureilite to constrain
4	the meteorite shock history
5	word count: 6142
6	
7	ANNA BARBARO ¹ , FABRIZIO NESTOLA ^{2,3} , LIDIA PITTARELLO ⁴ ,
8	LUDOVIC FERRIÈRE⁴, MARA MURRI⁵, KONSTANTIN D. LITASOV ⁶ , OLIVER CHRIST ² ,
9	MATTEO ALVARO ¹ , AND M. CHIARA DOMENEGHETTI ¹
10 11 12 13 14 15 16	 ¹ Department of Earth and Environmental Sciences, University of Pavia, Via A. Ferrata 1, I-27100, Pavia, Italy ² Department of Geosciences, University of Padova, Via Gradenigo 6, 35131, Padova, Italy ³ Geoscience Institute, Goethe-University Frankfurt, Altenhöferallee 1, 60323, Frankfurt, Germany ⁴ Natural History Museum, Department of Mineralogy and Petrography, Burgring 7, 1010, Vienna, Austria ⁵ Department of Earth and Environmental Sciences, University of Milano-Bicocca, I-20126, Milano, Italy ⁶ Vereshchagin Institute for High Pressure Physics RAS, Troitsk, Moscow, 108840, Russia

ABSTRACT

17

The formation and shock history of ureilite meteorites, a relatively abundant type of 18 primitive achondrites, has been debated since decades. For this purpose, the characterization 19 of carbon phases can provide further information on diamond and graphite formation in 20 ureilites, shedding light on the origin and history of this meteorite group. In this work, we 21 present X-ray diffraction and micro-Raman spectroscopy analyses performed on diamond and 22 graphite occurring in the ureilite Yamato 74123 (Y-74123). The results show that nano- and 23 micro-diamonds coexist with nano-graphite aggregates. This, together with the shock-24 25 deformation features observed in olivine, such as mosaicism and planar fractures, suggest that diamond grains formed by a shock event (≥ 15 GPa) on the Ureilitic Parent Body (UPB). Our 26 results on Y-74123 are consistent with those obtained on the NWA 7983 ureilite and further 27 support the hypothesis that the simultaneous formation of nano- and micro-diamonds with the 28 assistance of a Fe-Ni melt catalysis may be related to the heterogeneous propagation and 29 local scattering of the shock wave. Graphite geothermometry revealed an average recorded 30

temperature (T_{max}) of 1314°C (± 120°C) in agreement with previously estimated
crystallization temperatures reported for graphite in Almahata Sitta ureilite.
Key words: carbon phases, diamond, graphite, ureilite meteorites, shock, impact event.
INTRODUCTION
Ureilites represent the second largest group of achondrite meteorites (Goodrich et al.
1992), with about 570 individuals with distinct names but only 6 observed falls (Meteoritical
Bulletin Database 2020). Their formation, origin, and history are still under discussion among
the scientific community. The debate about the formation of carbon phases contained in these
meteorites has been going on for 80 years (see Nestola et al. 2020, and references therein).
As reported by Goodrich et al. (1992), ureilites appear to be fractionated ultramafic
igneous rocks, either magmatic cumulates (Berkley et al. 1980; Goodrich et al. 1987) or

43 partial melt residues (Boynton et al. 1976; Scott et al. 1992) and, thus, the products of planetary differentiation processes. These conclusions were based on mineralogy, textures, 44 fabrics, lithophile element chemistry, and on some aspects of Sm-Nd isotopic systematics 45 (Berkley et al. 1976) observed in these meteorites (Goodrich et al. 1992). Ureilites strongly 46 differ from the other groups of stony meteorites (i.e., due to a high content of carbon phases 47 and distinct oxygen isotopic composition) and, compared to chondrites, they are enriched in 48 Mg, but depleted in metal, troilite, and alkalis. Ureilites typically contain large olivine grains 49 and a few smaller low Ca-clinopyroxene (pigeonite) aggregates in a fine-grained, carbon-50 51 rich, matrix. Minor phases are kamacite (1-3 vol% with the Ni content up to 7.3 %), troilite (1-2%), chromite (1-2%), and carbon material (up to 8.5%) (Cloutis et al. 2010; Goodrich et 52 al. 2015). Carbon is present as diamond, usually with stacking disorder and nanotwins 53

54 (Németh et al. 2014, 2020a, 2020b; Salzmann et al. 2015; Murri et al. 2019), graphite, and
55 organic material (e.g., Sabbah et al. 2010).

The different shock levels observed in ureilites are very important for constraining 56 their history. Shock level determination in meteorites was first proposed by Stöffler et al. 57 (1991, 2018) and is subdivided in six stages of shock for ordinary chondrites, from low (S1) 58 to high (S6) level of shock, based on (i) shock effects in olivine and plagioclase (e.g., 59 extinction, fractures, planar elements) and (ii) the presence of glass and/or of high-pressure 60 silicate phases. Recently, Nakamuta et al. (2016) adapted the shock classification based on 61 62 olivine in chondrites to the observations in ureilites. For this reason, we will apply this classification in this work. 63

The occurrence of diamonds in ureilites poses the question of how this high-pressure 64 mineral formed and whether diamonds in ureilites are similar or not to those formed by shock 65 in terrestrial impact structures (e.g., Masaitis 1998; Hough et al. 1995; Koeberl et al. 1997; 66 Ohfuji et al. 2015; Murri et al. 2019). Three main hypotheses have been proposed for the 67 formation of diamonds in ureilites: (i) static high-pressure conditions in the deep interior of 68 large parent bodies (Urey 1956), (ii) direct transformation from graphite due to shock (e.g., 69 Lipschutz et al. 1964; Bischoff et al. 1999; Grund and Bischoff 1999; Nakamuta et al. 2000, 70 2016; Hezel et al. 2008; Le Guillou et al. 2010; Ross et al. 2011; Lorentz 2019), also strongly 71 supported by De Carli et al. (1995; 2002), and (iii) growth from a dilute gas phase, i.e., at low 72 73 pressure in the solar nebula by a chemical vapor deposition (CVD) process (Fukunaga et al. 1987). The hypothesis of formation under static high-pressure conditions was recently 74 supported by Miyahara et al. (2015) and Nabiei et al. (2018), who concluded that the size of a 75 76 hypothetical Ureilitic Parent Body (UPB) could be comparable to the size of Mars, since static high-pressure conditions would be required for the formation of micrometer-scaled-77 diamond crystallites. The shock hypothesis was instead supported by the results obtained by 78

Nakamuta et al. (2016). Indeed, these authors proposed that diamonds in ureilites could have 79 formed at high-pressure (above 12 GPa) by spontaneous shock transformation from graphite. 80 and at low pressure (6-10 GPa) by a solid-state catalytic transformation from graphite in 81 82 presence of a Fe-Ni melt. Additional support to the shock hypothesis is provided in a recent work by Nestola et al. (2020) on Almahata Sitta samples (AhS 72 and AhS 209b), as well as 83 on NWA 7983. In their study, graphite associated with nano- and (in NWA 7983) micro-84 diamonds was reported, suggesting that the conversion from graphite to diamond was 85 triggered by an impact event and was favored by the catalytic effect of Fe-Ni melts. 86

87 Yamato 74123 (Y-74123) ureilite is a meteorite that was found in Antarctic in 1974 by the Japanese expedition on the Yamato mountains. The first detailed study of Y-74123 88 dates back to 1978, when Hintenberger et al. (1978) measured its noble gases contents as well 89 as several major and minor elements bulk rock abundances. Takeda et al. (1980) have 90 91 reported the petrological description and a chemical characterization of pyroxenes, which revealed Fe-bearing augite compositions (En₇₅Fs₁₈Wo₇) In addition, the magnetic properties 92 of Y-74123 were studied by Nagata (1980). Moreover, Grady et al. (1985) carried out a C-93 isotopic study on Y-74123 reporting values of about $\delta^{13}C_{PDB}$ =-1.7, well inside the range of 94 ureilites. However, the carbon phases of Y-74123 have not been extensively studied yet. 95

In this work, we present the results of a multi-methodological study carried out on diamond and graphite aggregates observed in Yamato 74123, to understand the carbon phases formation in ureilites. In addition, a comparison with similar carbon phases in other meteorites, based on a literature survey, and a discussion on their possible formation hypothesis are also presented.

101

102

METHODS

The fragment of Y-74123 (NHMV-#7636 A) and a corresponding polished thin 103 section (NHMV-L9822) investigated in this study were kindly provided by the Natural 104 History Museum Vienna (Austria). The thin section was investigated by optical and electron 105 microscopy at the Department of Earth and Environmental Science, University of Pavia 106 (Italy). Scanning electron microscopy (SEM) of the uncoated fragment of Y-74123 was 107 performed using a FEI Quanta 200 SEM equipped with an Energy Dispersive X-ray 108 Spectrometry (EDS) in low vacuum mode at the CEASC (Centro di Analisi e Servizi per la 109 Certificazione) of the University of Padova (Italy). Backscattered electron (BSE) images of 110 111 Y-74123 were obtained in low vacuum mode analytical conditions, at the working distance of 10.6 mm, with an emission current of 93 mA, and a voltage of 20 kV, with the aim to identify 112 the graphite beds in which diamonds were probably located. The BSE images collected by 113 SEM were merged and analyzed with ImageJ and MultiSpec software to estimate the relative 114 percentages of each phase of interest observed on the surface of the investigated meteorite 115 fragment. 116

117 Carbon phases were manually extracted from the fragment and mounted on the tip of
118 a 100 µm thick glass fiber (Fig. 1) and investigated using micro-Raman spectroscopy (MRS)
119 followed by X-ray diffraction (XRD).



FIGURE 1. Carbon-bearing subsample of Y-74123 attached at the top of a glass fiber. Micro-Raman spectroscopy and XRD analyses were performed on this subsample.

Micro-Raman spectroscopy analyses were performed on the graphite material 121 occurring in the extracted carbon-bearing subsample of Fig. 1 to estimate the recorded 122 temperature using the geothermometer of Cody et al. (2008), modified by Ross et al. (2011). 123 The analysis of Y-74123 graphite was performed by high-resolution MRS using a Horiba 124 LabRam HR Evolution spectrometer equipped with an Olympus BX41 confocal microscope 125 at the controlled temperature of 20 (±1) °C at the Department of Earth and Environmental 126 Science of the University of Pavia. A 532 nm laser excitation with an operating power of 1-2 127 mW (in order to prevent damage of the graphite), a grating of 600 g/mm, and a magnification 128 129 of 50x was used. The spectrometer was calibrated using the silicon Raman peak at 520.5 cm⁻ ¹. The spectral resolution was 2 cm⁻¹ and the acquisition time for each spectrum was 30 130 seconds with four accumulations. Curve fitting of the spectra was carried out using the 131 OMNICTM software for dispersive Raman (Thermo Fisher Scientific) adopting Gaussian + 132 Lorentzian curves to obtain the best fit. XRD analyses were then performed on the same 133 carbon-bearing subsample (Fig. 1) using a Rigaku-Oxford Diffraction Supernova kappa-134 geometry goniometer with an X-ray Mo micro-source equipped with a Pilatus 200K Dectris 135 detector in transmission mode, controlled by the Crysalis-Pro[™] software at the Department 136 of Earth and Environmental Science in University of Pavia. Line profile analysis fitting of the 137 obtained diffraction pattern was performed using the High Score Plus Software package 138 (Panalytical) to estimate the crystallite size. 139

- 140
- 141

RESULTS

142 Petrographic description and observation by Scanning Electron Microscopy

The investigated polished thin section of Y-74123 consists of aggregates of subhedral to anhedral olivine mineral grains, with varying amounts of interstitial pyroxenes and Si-Al-rich glass. The sample contains coarse-grained olivine and minor pigeonite crystals, ranging from 146 0.1 to 1.5 mm in size, surrounded by a large amount of opaque material (Fig. 2), composed of 147 carbon mixed with different sulfides and metal phases. Pores and small grains of metal and 148 sulfide ($\leq 100 \mu$ m in size) commonly occur in the interstitial space between pyroxene and 149 olivine grains.

150 The shock level of Y-74123 was determined using optical microscope observations on shock microstructures in olivine crystals in transmitted light and following the criteria of 151 Stöffler et al. (1991, 2018) and Nakamuta et al. (2016). Olivine crystals show undulate 152 extinction, planar fractures, and locally, mosaicism. The concurrent observation of undulate 153 154 extinction and mosaicism in olivine indicates a pressure in the range of 15-20 GPa, corresponding to shock level S4 (Stöffler et al. 2018). In addition, both silicates, i.e., olivine 155 and clinopyroxene, show darkening, caused by the dispersion of Fe-Ni metal and sulfides 156 within the grains, which is commonly associated to shock metamorphism (e.g., Rubin 2006). 157 In the investigated sample, even after a careful inspection by optical and electron microscopy, 158 159 high-pressure polymorphs of olivine, such as wadsleyite or ringwoodite, were not found.



FIGURE 2. Yamato 74123 polished thin section (NHMV-L9822) overview in planepolarized light (a) and between crossed polarizers (b); detailed structure of olivine grains in Y-74123 in plane-polarized light (c) and between crossed polarizers (d) are also presented. Note the presence of interstitial opaque material and the size of olivine grains, which dominate the thin section.

160	A fragment of Y-74123, about 8 x 5 x 5 mm in size, was analyzed by SEM. Figure 3a
161	shows a BSE image of a typical carbon aggregate which occurs as interstitial phase in
162	silicates. The size of the carbon phases in Y-74123 is evident in Fig. 3b, where carbon phases
163	are about 10 µm wide.
164	In Fig. 3a, it is possible to see that locally, metal phases, indicated as "Fe-Ni metal",
165	occur next to silicates. These metal phases are extremely fine-grained, partly mixed with the
166	carbon phases.



FIGURE 3. (a) BSE image of a carbon aggregate from which the investigated carbonbearing subsample was extracted. Also note the presence of silicate phases and Fe-Ni metal and alloys (metal + troilite + oxide); (b) detail of (a) in secondary electron (SE). As visible on this image, the aggregates in the carbon phases beds are not larger than 10 μ m in size.

167	The relative abundances, expressed in percentages, of the main mineralogical
168	components present on the surface of the investigated sample of Y-74123 are: 91% of silicate
169	phases (olivine and pyroxene), 7% of carbon phases, and 2% of Fe-Ni metal and alloys,
170	respectively (Fig. 4). The image analysis performed on the surface of the fragment of Y-
171	74123 was important to evidence the best carbon aggregate zone from which to extract the
172	carbon-bearing aggregate to be analyzed by MRS and XRD. The investigated fragment of Y-
173	74123 turned out to be relatively easy to be cut and polished in comparison with many other
174	studied ureilites, indicating a relatively low amount of diamonds.



FIGURE. 4. (a) BSE mosaic of the Yamato 74123 fragment (NHMV-#7636_A) showing the typical texture of the meteorite; (b) image analysis applied to (a) with the percentage referred to silicate phases, carbon phases, Fe-Ni metal, Fe-Ni alloys and Fe-oxides.

176 X-Ray Diffraction

The reconstructed XRD image of the carbon-bearing aggregate of Yamato 74123 and its powder diffraction pattern are shown in Figs. 5a and b. Instead, Fig. 5c clearly shows the presence of spots referred to micrometer sized diamond.

In particular, Fig. 5a shows both rings and spots at *d*-spacing characteristic of cubic 180 diamond (d-spacing at 2.06 Å, 1.26 Å, and 1.07 Å) and hexagonal graphite (highest peak at 181 d-spacing at 3.34 Å, while the peaks at *d*-spacing 2.03 Å and 1.15 Å are overlapped by the 182 diamond peaks). In Fig. 5b the highest peak of diamond (at *d*-spacing 2.06Å) shows an 183 asymmetry. This asymmetry could be ascribed, at higher d-spacing ($d\approx 2.18$ Å), to the 184 presence of cubic and hexagonal sp³ stacked layers or nanotwins (Murri et al. 2019) and, at 185 lower d-spacing ($d\approx 2.02$ Å), to the main peak of Fe metal (which also shows peaks at d-186 spacing 1.42 Å and 1.17 Å). In addition to diamond, graphite, and Fe metal, a few other 187 peaks can be assigned to troilite (d-spacing at 2.99 Å, 2.66 Å, 1.72 Å, and 1.68 Å), and also 188 to minor silicate matrix components. The presence of cubic Ni, common in ureilites, cannot 189 be excluded, as its peaks overlap those of metallic Fe and troilite. 190

To estimate the crystallite size of the carbon phases, we applied line profile analysis fitting to the diffraction pattern reported in Fig. 5b. The integral breadth values, which were obtained by this method, were then inserted into the Scherrer equation (Eq. 1 and 2, Scherrer 194 1918) to estimate the crystallite size, as follows:

195 (1)
$$\beta(2\theta) = \frac{K_{\beta} \times \lambda}{\langle D \rangle_V \cos \theta_{hkl}}$$

196 (2)
$$\frac{D_V}{K_\beta} = \frac{\lambda}{\cos\theta_{hkl} \times \beta(2\theta)}$$

197 Scherrer equation provides a correlation between peaks broadening β , the dimension of 198 diffracted domain, and the crystallite size (D_V) . K is a constant value ranging between 0.5 and

1, describing the contribution of crystallites shape and dependent upon the relative orientationof the scattering vector with respect to the external shape of the crystallite (Scherrer 1918).

For diamond, in order to obtain a reliable estimate of the crystallite size, we only used 201 the two peaks at *d*-spacing 1.26 Å and 1.07 Å, as they do not exhibit any overlap with peaks 202 of other phases within the analyzed carbon fragment . A similar approach was used to 203 estimate the crystallite size of graphite, using the peak at *d*-spacing 3.34 Å (see Table 1). The 204 results are reported in Table 1 along with the unit cell parameters and the space group for the 205 diamond single crystal found in Y-74123. The possibility to estimate the unit-cell parameters 206 for the investigated diamond in Y-74123 implies that micrometer-sized diamonds (i.e., spots 207 in the diffraction image) are present. As it appears from the XRD images (Figs. 5a and c), 208 i.e., on the basis of the presence of spots and rings, we can state that nano-graphite coexists 209 with micro- and nano-diamonds in Y-74123, as also observed by Goodrich et al. (2020) and 210 Nestola et al. (2020) in the NWA 7983 ureilite. 211



FIGURE. 5 X-ray diffraction images of the carbon-bearing subsample from Y-74123. In (a) reconstructed powder diffraction image and in (b) X-ray diffraction pattern of the investigated sample, analyzed by micro X-ray powder diffraction, are shown. The most abundant phases found in the carbon-bearing aggregate are diamond (Dia), graphite (Gr), Fe metal (Fe), and troilite (Tro). In (c) a diffraction image shows the spots corresponding to micrometer-sized diamonds.

Table 1. The unit cell parameters for the micrometer-sized cubic diamond single crystal found in Y-74123. Mo $\lambda \approx 0.71$. 20° positions of the graphite and diamond diffraction peaks, *d* spacings, and the crystallite size (D_v) are reported. The crystallite size was calculated using the most intense peak of graphite at 3.34 Å, and the two peaks of diamond at 1.26 Å and 1.07 Å.

	<i>a</i> = 3.569(1) Å	
	V = 45.46(2) Å ³	
	polycrystalline diamond	
Pos. [2θ°]	d-spacing (Å)	D _v (nm)
32.65	1.26	15
38.50	1.07	11
	polycrystalline graphite	
Pos. [2θ°]	d-spacing (Å)	D _v (nm)
12.10	3.34	8

214 Micro-Raman spectroscopy

We applied the geothermometric approach by Cody et al. (2008) and Ross et al. (2011), following the same procedure as reported in Barbaro et al. (2020a, 2020b) for Almahata Sitta samples (AhS 209b, AhS 72, and AhS A135A), to determine the T_{max} recorded by graphite. The temperature was estimated using Eq. 3, expressed in terms of Raman G-band full width at half maximum (FWHM) (Γ_G):

220 (3)
$$T_{max}(^{\circ}C) = 1594.4 - 20.4\Gamma_{G} - 5.8 \times 10^{-2}\Gamma_{G}^{2}$$

In Table 2, we list the graphite peaks positions (G-band, D-band, and D' band), the relevant Γ_{G} values (G, D, and D' bands FWHM) for Y-74123, as well as the T_{max} estimated using Eq. 3.

In order to compare our Γ_G data with those published by Ross et al. (2011) and Barbaro et al. (2020b), we corrected our data for the instrumental peak broadening using a high-

226	quality gemstone lithospheric diamond (with $\Gamma_G = 5 \text{ cm}^{-1}$), following the same procedure as
227	in Ross et al. (2011) (see Table 2). In Table 2, for each set of acquisition, the values of Γ_G
228	used in Eq. 3 to obtain the $T_{\text{max}},$ are reported. T_{max} values range between 1265 and 1334 (±
229	120) °C. These temperatures are slightly higher than those obtained by Ross et al. (2011) on
230	graphite in AhS #7 ureilitic fragment (T _{max} of 990 \pm 120 °C), whereas they are very similar
231	to those obtained by Barbaro et al. (2020b) on other Almahata Sitta samples (average T_{max} of
232	1266 °C for graphite in AhS 209b, 1242 °C in AhS 72, and 1332 °C in AhS A135A). A
233	comparison between the average temperatures recorded by graphite on the above quoted
234	ureilitic samples is presented in Table 3.

Table 2. Center positions for G, D, and D' bands and FWHM (both in cm⁻¹) of Y-74123. Calculated crystallization temperature, T_{max} , is reported in the last column and was obtained using the Equation 3. The uncertainty on T_{max} is (2 σ) ± 120 °C.

G-band center	G-band FWHM	G-band FWHM correcte d	D-band center	D-band FWHM	D'-band center	D'- band FWHM	T _{max} (°C)
′-74123							
1582	24	15	1356	49	1618	21	1286
1580	22	13	1354	46	1618	19	1310
1579	21	13	1349	37	1611	22	1329
1579	18	11	1356	22	1618	17	1365
1579	20	12	1351	40	1616	23	1334
1581	25	16	1350	50	1617	22	1265

235

Table 3. Comparison among the T_{max} recorded by graphite in different ureilites using the geothermometer by Cody et al. (2008)*.

	AhS #7 (Ross et al.	AhS 209 (Barbaro et al. 2020b)	AhS 72 (Barbaro et al.	AhS A135A (Barbaro et al.	Y-74123 (this work)
	2011)		2020b)	2020b)	
Average T _{max} (°C)	990 ±120	1266 ±120	1242 ±120	1332 ±120	1314 ±120
	graphite in AhS #	al. (2011) for a detailed of 7 sample are after Ross 2020b).			

236

238 **DISCUSSION**

Micro-Raman spectroscopy and XRD analyses in Y-74123 revealed the presence of diamond and graphite aggregates in the interstitial space between silicate grains, as commonly observed in other ureilites (e.g., Hanneman et al. 1967; Vdovykin 1971). Our results from the XRD analysis on Y-74123 confirm the coexistence of nano- and microdiamonds associated with nano-graphite. In the carbon-bearing aggregates, we also detected Fe metal and troilite, which fill the interstitial space between graphite-diamond crystals or occur at the border of the carbon aggregates (Fig. 4).

The observed local differences in size of the newly formed diamonds, i.e., nano- to 246 micro-metric, may result from heterogeneous shock distribution within a heterogeneous 247 sample. The heterogeneous distribution of shock effects is mainly ascribed to shock 248 impedance contrast between contiguous phases. For greater contrast, the shock impedance is 249 amplified (Ogilvie et al. 2011), as in the case of large, "rigid", olivine crystals, separated by 250 251 interstitial, relatively "soft", carbon-bearing matrix. This implies that the shock pressure locally experienced by the carbon phases might have been higher than that recorded by the 252 adjacent olivine crystal, thus, explaining the local occurrence of relatively coarse-grained 253 diamonds. Conversely, for cases of low contrast between phases, the shock impedance would 254 have been suppressed. Furthermore, we cannot exclude that Y-74123 suffered multiple 255 impact events with different P-T conditions. 256

Our study provides further evidence in support of the diamond formation mechanism in ureilites proposed for NWA 7983 ureilite by Nestola et al. (2020). According to this mechanism, the formation of micrometer-sized diamond crystals from graphite observed in Y-74123 is likely due to the combined effect of highly heterogeneous P-T-conditions due to shock wave propagation and immediate penetration of Fe-Ni melt into carbon aggregates,

whereas the formation of nano-diamonds resulted from direct transformation from graphite 262 (i.e., even without the catalytic Fe-Ni melt). The occurrence of Fe compounds, as observed in 263 Y-74123, could explain the formation of diamonds at pressures \geq 15-20 GPa (Nestola et al. 264 2020), which is lower than the pressure of 30-60 GPa estimated for diamonds formed in 265 impact cratering processes on Earth (see, e.g., Koeberl et al. 1997, and references therein). In 266 Nestola et al. (2020) it is clearly reported how the catalyzed formation of diamonds by 267 metallic melts during a shock event can also account for simultaneous formation of micro-268 and nanodiamonds in ureilites. These authors, with the aim to explain this process, reported 269 270 an example of a pulsed heating experiment performed on a graphite-metal charge in a static high-pressure apparatus (Varfolomeeva 1971). This apparatus simulates natural impact 271 processes (De Carli et al. 2002; Bundy et al. 1967) which produced diamonds up to 10-µm-272 sized, found near to the catalyst, and nanodiamonds occurring in other parts of the 273 experimental charge (Nestola et al. 2020 and references therein). 274

The proposed scenario is further supported by the average value of the temperatures 275 determined for Y-74123 graphite $[T_{max}=1314^{\circ}C (\pm 120 {\circ}C)]$, which is similar to the values 276 reported by Barbaro et al. (2020a; 2020b) for Almahata Sitta samples (e.g., AhS 209b, AhS 277 72, and AhS A135A), even though slightly higher than the values reported by Ross et al. 278 (2011) for the AhS #7 sample. As reported by Gillet and El Goresy (2013), the shock peak 279 280 temperature determination for a sample with different mineral composition should also account for the effect of the porosity, grain boundaries, and heterogeneous composition of the 281 rock. In addition, it is important to consider that the shock waves do not propagate at the 282 same speed in all different minerals of a polymineralic rock, as explained above. However, 283 even if it is difficult to estimate the exact peak shock pressure values of the impact event(s), 284 we can argue that the temperature recorded by graphite may correspond to the shock-induced 285 temperature or to a subsequent post-shock thermal event, as hypothesized by Gillet and El 286

Goresy (2013). We exclude that our estimated temperature values could be a pre-shock temperature, because our estimation is determined on newly crystallized nano-graphite. Such nano-graphite cannot be the pristine graphite of the UPB, which should have been micrometer-sized, due to the long residence time spent in the UPB deep interior. Therefore, as reported by Barbaro et al. (2020b) for three AhS ureilitic fragments, nano-graphite formed by shock.

293 Implications

Our study on carbon phases in Yamato 74123 provides hints on the shock history of 294 295 this specific meteorite, and generally, of the UPB. The XRD analysis carried out on Y-74123 showed that nano-diamonds coexist together with micro-diamonds and nano-graphite, in 296 agreement with observations by Nestola et al. (2020) on the NWA 7983 ureilite meteorite. In 297 addition, by means of MRS analyses of graphite, we were able to show that (i) the 298 investigated sample exhibits homogeneous values of G-band centers (between 1579 and 1582 299 cm⁻¹) and D-band centers (between 1349 and 1356 cm⁻¹) and that (ii) the Γ_G of graphite for 300 the G-band range between 11 and 16 cm⁻¹. These values were used to estimate an average 301 T_{max} of 1314°C (±120 °C). 302

Our results support that micrometer-sized diamonds in Y-74123, as also suggested by 303 Nestola et al. (2020) for NWA 7983, formed with the assistance of the catalytic effect of 304 305 metallic melts, without requiring static high-pressures conditions within a large Mars-sized parent body. The formation of micro- and nano-diamonds and nano-graphite is likely to be 306 the result of an impact event or multiple impact events. We assume that the temperature 307 recorded by graphite, close to 1200-1300°C, likely represents the shock-induced temperature 308 excursion or corresponds to a subsequent post-shock temperature. The temperature values 309 obtained in our sample Y-74123, together with further studies on ureilites, using the same 310

approach as presented here, will contribute to widen our knowledge of the graphite resetting 311 temperatures by shock. 312 In conclusion, the results from our combined SEM, XRD, and MRS study in Y-74123 313 suggest that one or multiple shock event(s), with the contribution of metallic melts catalysis, 314 is likely responsible for the formation of diamond, both nano- and micro-diamonds. 315 Moreover, heterogeneity in the peak shock pressure that affected the UPB during the impact 316 event(s) may also explain the coexistence of diamonds with notable different sizes. 317 318 319 Acknowledgements 320 This paper is dedicated to the memory of Heinrich Hintenberger (1910–1990) who donated to 321

the NHM Vienna collection the Yamato 74123 sample used for this study. C.A. Goodrich is acknowledged for interesting discussions. S. Jaret and an anonymous reviewer are thanked for their comments, which greatly contributed improving this manuscript. S. Redfern is thanked for editorial handling. This work was supported by PNRA 2018 grant number PNRA18 00247 – A to F. N.; A.B., M.C.D., M.M., and M.A. were funded by the IMPACt project (R164WEJAHH) to M. Alvaro.

329 **References**

- Barbaro, A., Domeneghetti, M. C., Goodrich, C. A., Meneghetti, M., Litti, L., Fioretti, A. M.,
 Shaddad, M. H., Alvaro, M., and Nestola, F. (2020a) Shock temperature recorded by graphite
 in ureilites from Almahata Sitta. 51st Lunar and Planetary Science Conference, abstract #1480.
- Barbaro, A., Domeneghetti, M. C., Goodrich, C., Meneghetti, M., Litti, L., Fioretti, A. M., Jenniskens,
 P., Shaddad, M. H., Alvaro, M., and others. (2020b) Graphite based geothermometry on
 Almahata Sitta ureilites meteorites. Minerals, submitted.
- Berkley, J.L., Brown, IV, H.G., Keil, K., Carter, N.L., Mercier, J.-C.C., and Huss, G. (1976) The
 Kenna ureilite: an ultramafic rock with evidence for igneous, metamorphic, and shock origin.
 Geochimica et Cosmochimica Acta, 40, 1429–1437.
- Berkley, J. L., Taylor, G. J., Keil, K., Harlow, G. E., and Prinz, M. (1980) The nature and origin of
 ureilites. Geochimica et Cosmochimica Acta, 44, 1579–1597.
- Bischoff, A., Goodrich, C.A., and Grund T. (1999) Shock-induced origin of diamond in ureilites. 30st
 Lunar and Planetary Science Conference, abstract #1100.
- Boynton, W. V, Starzyk, P. M., and Schmitt, R. A. (1976) Chemical evidence for the genesis of the ureilites, the achondrite Chassigny and the nakhlites. Geochimica et Cosmochimica Acta, 40, 1439–1447.
- Bundy, F. P., and Kasper J. S. (1967) Hexagonal diamond–A new form of carbon. Journal of
 Chemical Physics, 46, 3437–3446.
- Cloutis, E. A., Hudon, P., Romanek, C. S., Bishop, J. L., Reddy, V., Gaffey, M. J., and Hardersen, P.
 S. (2010) Spectral reflectance properties of ureilites. Meteoritics & Planetary Science 45, 10–11.
- Cody, G. D., Alexander, C. M. O'D., Yabuta, H., Kilcoyne, A. L. D., Araki, T., Ade, H., Dera, P.,
 Fogel, M., Militzer, B., and Mysen, B. O. (2008) Organic thermometry for chondritic parent
 bodies. Earth and Planetary Science Letters, 272, 446–455.
- 353 De Carli, P.S. (1995) Shock wave synthesis of diamond and other phases. Material Research and
 354 Society Symposium Proceedings, 383, 21–31.
- De Carli, P. S., Bowden, E., Jones, A. P., and Price, G. D. (2002) Laboratory impact experiments
 versus natural impact events. In Catastrophic Events and Mass Extinctions: Impacts and
 Beyond, Geological Society of America Special Paper 356, p. 595–605. Lunar and Planetary
 Institute, Houston, Texas.
- Frondel, C. and Marvin, U. B. (1967) Lonsdaleite, a hexagonal polymorph of diamond. Nature, 214,
 587–589.
- Fukunaga, K., Matsuda, J., Nagao, K., Miyamoto, M., and Ito, K. (1987) Noble-gas enrichment in vapour-growth diamonds and the origin of diamond in ureilites. Nature, 328, 141–143.
- Gillet, P. and El Goresy, A. (2013) Shock events in the Solar System: The message from minerals in
 terrestrial planets and asteroids. Annual Review of Earth and Planetary Sciences, 41, 247–285.

Goodrich, C. A., and Jones, J. H. (1987) Origin and evolution of the ureilite parent magmas: Multi stage igneous activity on a large parent body. Geochimica et Cosmochimica Acta, 51, 2255–
 2273.

- 368 Goodrich, C. A. (1992) Ureilites: A critical review. Meteoritics & Planetary Science, 27, 327–352.
- Goodrich, C. A., Hartmann, W. K., O'Brien, D.P., Weidenschilling, S. J., Wilson, L., Michel, P., and
 Jutzi, M. (2015) Origin and history of ureilitic material in the solar system: The view from
 asteroid 2008 TC₃ and the Almahata Sitta meteorite. Meteoritic & Planetary Science, 50, 782–
 809.
- Goodrich, C. A., Nestola, F., Jakubek, R., Erickson, T., Fries, M., Fioretti, A. M., Ross, D. K., and
 Brenker, F. E. (2020) The origin of diamond in ureilites. 51st Lunar and Planetary Science
 Conference, abstract #1411.
- Grady, M. M., Wright, I. P., Swart, P. K., and Rllinger, C. T. (1985) The carbon and nitrogen isotopic composition of ureilites: implications for their genesis. Geochimica et Cosmochimica Acta, 49, 903–915.
- Grund, T. and Bischoff, A. (1999) Cathodoluminescence properties of diamonds in ureilites: further
 evidences for a shock-induced origin. 62nd Annual Meteoritical Society Meeting, abstract
 #5074.
- Hanneman, R. E., Strong, H. M., and Bundy, F. P. (1967) Hexagonal diamonds in meteorites:
 Implications. Science, 155, 995–997.
- Hezel, D. C., Dubrovinsky, L., Nasdala, L., Cauzid, J., Simionovici, A., Gellissen, M., and
 Schonbeck, T. (2008) In situ micro-Raman and X-ray diffraction study of diamonds and
 petrology of the new ureilite UAE 001 from the United Arab Emirates. Meteoritics & Planaetary
 Sciences, 43, 1127–1136.
- Hintenberger, H., Jochum, K.P., Braun, O., Christ, P., and Martin, W. (1978) The Antarctic meteorite
 Yamato 74123 a new ureilite. Earth and Planetary Science Letters, 40, 187–193.
- Hough, R. M., Gilmour, I., Pillinger, C. T., Arden, J.W., Gilkess, K. W. R., Yuan, J., and Milledge, H.
 J. (1995) Diamond and silicon carbide in impact melt rock from the Ries impact crater. Nature 378,41–44.
- Koeberl, C., Masaitis, V. L., Shafranovsky, G. I., Gilmour, I., Langenhorst, F., and Schrauder, M.
 (1997) Diamonds from the Popigai impact structure, Russia. Geology, 25, 967–970.
- Le Guillou, C., Rouzaud, J. N., Remusat, L., and Bourot-Denise, A. (2010) Structures, origin and
 evolution of various carbon phases in the ureilite Northwest Africa 4742 compared with
 laboratory-shocked graphite. Geochimica et Cosmochimica Acta, 74, 4167–4185.
- Lipschutz, M. E. (1964) Origin of Diamonds in the Ureilites. Science, 143, 1431–1434.
- Lorentz, C.A., Shiryaev, A. A., Vlasov, I. I., and Borisovsky, S. E. (2019) Metamorphism of four
 desert ureilites and luminescence spectroscopy of defects in ureilitic diamonds. Meteoritics and
 Planetary Science, 54, 1197–1214.
- 402 Masaitis, V. L. (1998) Popigai crater: Origin and distribution of diamond-bearing impactites.
 403 Meteoritics and Planetary Science, 33, 349–359.
- 404 Meteoritical Bulletin Database (2020). Available: https://www.lpi.usra.edu/meteor/

Miyahara, M., Ohtani, E., El, A., Lin, Y., Feng, L., Zhang, J., Gillet, P., Nagase, T., and Muto, J.
(2015) Unique large diamonds in a ureilite from Almahata Sitta 2008 TC 3 asteroid. Geochimica
et Cosmochimica Acta, 163, 14–26.

- Murri, M., Smith, R. L., McColl, K., Hart, M., Alvaro, M., Jones, A. P., Németh, P., Salzmann, C. G.,
 Corà, F. and others. (2019) Quantifying hexagonal stacking in diamond. Scientific Reports 9,
 10334. https://doi.org/10.1038/s41598-019-46556-3
- Nabiei, F., Badro J., Dennenwaldt T., Oveisi E., Cantoni M., Hébert C., Goresy A. El, Barrat J., and
 Gillet P. (2018) A large planetary body inferred from diamond inclusions in a ureilite meteorite.
 Nature Communications, 9, 1–6.
- 414 Nagata, T. (1980) Magnetic classification of Antarctic meteorites. Proceedings of the 21st Lunar and
 415 Planetary Science Conference, p. 1789–1799. Lunar and Planetary Science Institute, Houston,
 416 Textas.
- Nakamuta, Y., and Aoiko, Y. (2000) Mineralogical evidence for the origin of diamond in ureilites.
 Meteoritics and Planetary Science, 35, 487–493.
- Nakamuta, Y., Kitajima, F., and Shimada, K. (2016) In situ observation, X–ray diffraction and Raman
 analyses of carbon minerals in ureilites: Origin and formation mechanisms of diamond in
 ureilites. Journal of Mineralogical and Petrological Sciences, 111, 252–269.
- Nèmeth, P., Garve, L. A. J., Aoki, T., Dubrovinskaia, N., Dubrovinsky, L., and Buseck, P. R. (2014)
 Lonsdaleite is faulted and twinned cubic diamond and does not exist as a discrete material.
 Nature Communications, 5, 5447, 1–5.
- 425 Németh, P., McColl, K., Smith, R. L., Murri, M., Garvie, L. A. J., Alvaro, M., Péc, B., Jones, A. P.,
 426 Corà, F., Salzmann and others. (2020a) Diamond-graphene composite nanostructures.
 427 Nanoletters, 20, 3611–3619.
- 428 Németh P., McColl, K., Garvie L. A. J., Salzmann C. G., Murri M., McMillan P. F. (2020b) Complex
 429 nanostructures in diamond. Nature Materials, 1–6. https://doi.org/10.1038/s41563-020-0759-8
- 430 Nestola, F., Goodrich, C. A., Morana, M., Barbaro, A., Jakubek, R. S., Chris, O., Brenker, F. E.,
 431 Domeneghetti, M. C., Dalconi, M. C. and others. (2020) Impact shock origin of diamond in
 432 ureilite meteorites. Proocedings of the National Academy of Sciences of the United States of
 433 America, 1-9. https://doi.org/10.1073/pnas.1919067117
- Ogilvie, P., Gibson, R. L., Reimold, W. U., Deutsch, A., and Hornemann, U. (2011) Experimental
 investigation of shock metamorphic effects in a metapelitic granulite: The importance of shock
 impedance contrast between components. Meteoritics & Planetary Science, 46, 1565–1586.
- Ohfuji, H., Itifune, T., Litasov, K. D., Yamashite, T., Isobe, F., Afanasiev V. P., and Pokhilenko N. P.
 (2015) Natural occurrence of pure nano-polycrystalline diamond from impact crater. Scientific
 Reports, 5, 14702, 1–8.
- Ross, A. J., Steele, A., Fries, M. D., Kater, L., Downes, H., Jones, A. P., Smith, C. L., Jenniskens, P.
 M., Zolensky, M. E., and Shaddad, M. H. (2011) MicroRaman spectroscopy of diamond and graphite in Almahata Sitta and comparison with other ureilites. Meteoritics & Planetary Science, 46, 364–378.
- Rubin, A. (2006) Shock, post-shock annealing, and post-annealing shock in ureilites. Meteoritics &
 Planetary Science, 41, 125–133
- Sabbah, H., Morrow, A. L., Jenniskens, P., Shaddad, M. H., and Zare, R. N. (2010) Polycyclic
 aromatic hydrocarbons in asteroid 2008 TC₃: Dispersion of organic compounds inside asteroids. Meteoritics & Planetary Science, 45, 1710–1717.

- Salzmann, C. G., Murray, B. J., and Shephard, J. J. (2015) Extent of stacking disorder in diamond.
 Diamond and Related Materials, 59, 69–72.
- Scherrer, P. (1918) Estimation of the size and internal structure of colloidal particles by means of
 röntgen. Journal of Mathematical Physics, 2, 98–100.
- Scott E. R. D., Keil K., and Taylor G. J. (1992) Origin of ureilites by partial melting and explosive
 volcanism on carbon-rich asteroids. Proceedings of the 23rd Lunar and Planetary Science
 Conference, pp. 1253–1254.
- Stöffler, D., Keil, K., and Edward, R. D. S. (1991) Shock metamorphism of ordinary chondrites.
 Geochimica et Cosmochimica Acta, 55, 3845–3867.
- Stöffler, D., Hamann, C., and Metzler, K. (2018) Invited Review Shock metamorphism of planetary
 silicate rocks and sediments: Proposal for an updated classification system. Meteoritics &
 Planetary Science, 49, 5–49.
- Takeda, H., Mori, H., Keizo, Y., and Shiraishi, K. (1980) Mineralogical examination of the Allan
 Hills achondrites and their bearing on the parent bodies. Memoirs of National Institute of Polar
 Reasearch. Special issue, 17, 119–144.
- 464 Urey, H. C. (1956) Diamond, meteorites, and the origin of the solar system. American Astronomical
 465 Society, 623–637.
- Varfolomeeva, T. D. (1971) Synthesis and investigation of polycrystalline diamond. PhD thesis,
 Institute for High Pressure Physics, USSR Academy of Sciences, 154.
- 468 Vdovykin, G. (1970) Ureilites. Space Science Reviews, 10, 483–510.