

Micro – Raman Spectroscopy of Diamonds from JaH 054 and Sahara 98505 Ureilites, Statistic Research

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Abstract. In this paper Raman spectra of diamonds from two different ureilites, JaH 054 and Sahara 98505, were measured. Obtained results for both ureilites showed the Raman shift ranged between 1321 cm^{-1} and 1336 cm^{-1} for JaH 054 and between 1329 cm^{-1} and 1336 cm^{-1} for Sahara 98505. FWHM parameter (full width at half maximum) varied also in wide range especially for Sahara 98505. Raman imaging was done for JaH 054 sample and diamonds of different Raman shifts (1321 cm^{-1} , 1328 cm^{-1} , 1330 cm^{-1}) were found in few tens μm sized area of carbon vein. Raman peaks of ureilitic diamonds were compared with literature data of laboratory diamonds produced under high pressure, under low pressure with MW PACVD method and with other ureilites. Presented research showed that even in highly shocked ureilites Raman shift versus FWHM parameter plots are similar with CVD diamonds for ureilites. However, the origin of diamonds in ureilites is not explained based on the obtained results, close coexistence of different diamonds in investigated ureilites suggests that the mechanism of diamond creation in meteorites was very complex and could be multi-step process.

Keywords: diamonds, ureilites, Raman Spectroscopy

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INTRODUCTION

Ureilites are ultramafic, coarse grained rocks which belong to primitive achondrites. They are second biggest achondrite group with 250 known classified specimens. First observed fall was in 1886 in village Novo – Urei in Russia. Ureilites are divided into two main subgroups, monomictic and polymictic. First one has typical mm in size olivine and pyroxene minerals. Spaces between minerals are filled by carbonaceous matrix and contain also iron and sulfides. Textures for this subgroup are described as “typical” (euhedral to anhedral olivine and pigeonite minerals with triple junctions) and much rarest “poikilitic” [1]. Second subgroup of ureilites are polymictic brecciated, they are mixture of typical ureilites and “extra ureilitic materials” (exotic clast). Matrix differs from monomictic ureilites, usually contains also suessite, chromite apatite and plagioclase [2].

Carbon in ureilites is represented by graphite (mostly), diamond, lonsdaleite, amorphous carbon and carbides [3]. As it was mentioned above carbon usually fills the spaces between olivine and pyroxene minerals, but sometimes it occurs also inside them. Diamonds are usually 1 – 10 μm in size, but quite often smaller grains – (100 nm - described in this paper or even few tenths of nm) occur [4]. The origin of diamonds in this enigmatic group has been still discussed by various authors, and it was proposed to be explained in various ways including the most accepted theory of metamorphic transformation of graphite during impact [5,6], as well as the theory suggesting the chemical vapor deposition (CVD) mechanism in the solar nebula [7-9].

Chosen for this research samples, JaH 054 and Sahara 98505, are typical monomictic ureilites. JaH 054 is classified as a medium to coarse grained rock with granular metamorphic texture. The main mineral phases are: olivine (Fo_{86} ; 0.2-0.7 wt. % Cr_2O_3 , 0.18 wt.% CaO) and pyroxene - pigeonite ($\text{En}_{83}\text{Wo}_5$ (0.9-1.2 wt.% Cr_2O_3). Vein like areas occur between olivine and pyroxene minerals, composed by graphite and diamond grains surrounded by thin metal inclusion). Total amount of carbon material was estimated to be equal 2.8 vol. %. Chromite, troilite (Fe-metal, Ni-Cr-rich) and Ni poor troilite occur as accessory minerals. Thin MgO-rich rims occur in silicates [10]. Sahara 98505 was classified as a highly shocked ureilite, with recrystallized olivines ($\text{Fa}_{18.8}$, $\text{Fs}_{12.9}$) [11].

EXPERIMENTS

The polished slices of two ureilites: JaH 054 and Sahara 98505 were examined. The choice of these ureilites was based on preliminary investigations showing that they possess relatively high diamond content [12]. Diamond grains were studied in situ on polished slices of the samples (Fig.1). The samples used were re-polished with non-diamond.



FIGURE 1. Polished slices of two ureilitic samples JaH 054 (left) and Sahara 98505 (right). Cube is 1 cm^3 in size.

Raman spectra were acquired with usage of confocal micro-Raman spectrometer T-64000 (Jobin-Yvon) equipped with the BX-40 microscope (Olympus). The 514.5 nm Ar line was used for sample excitation. Acquisition time and laser

power were adjusted to obtain spectra of sufficient quality. The laser beam diameter was c.a. 1.5 μm . All spectra were deconvoluted with Peakfit 4 software (Jandel) after the baseline correction.

Raman imaging was done on JaH 054 sample with use of WITec alpha RA instrument equipped with an one grating (600 g/mm, BLZ=500 nm) UHTS 300 spectrometer, Newton-CCD camera (1024 x 127 pixels) and Nikon 100x (NA=0.95) objective. Frequency doubled NdYAG laser (532 nm line) was used for sample excitation. A complete Raman spectrum was acquired at every image pixel, leading to a 2D array of Raman spectra. By evaluating intensities of different Raman bands, various Raman images can be evaluated.

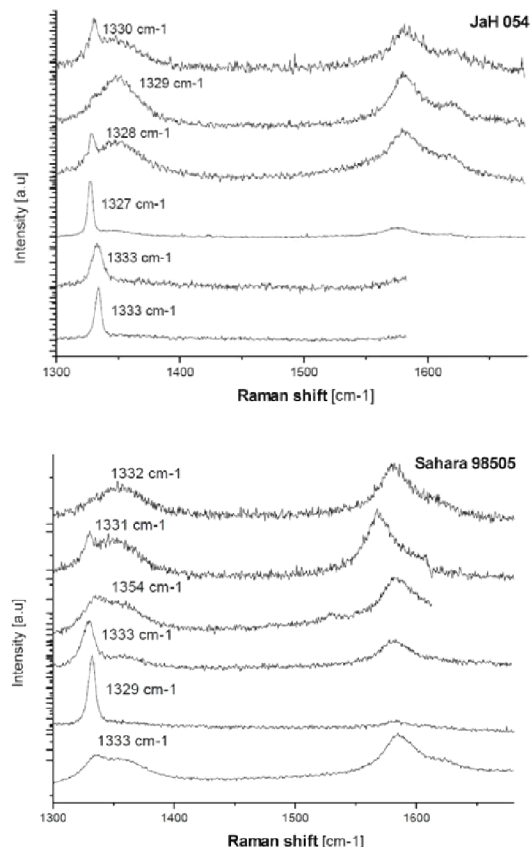


FIGURE 2. Exemplary Raman spectra for JaH 054 and Sahara 98505 ureilites illustrating the distribution of diamond peaks (band position attached to particular spectrum).

RESULTS

Presented statistic analysis is based on 43 different diamond peaks from JaH 054 and on 27 from Sahara 98505. Exemplary diamond and graphite peaks for both ureilites are shown in Figure 2. It is evident that the spectra correspond to areas containing pure diamond or graphite phases as well as to zones where both carbon allotropes coexist.

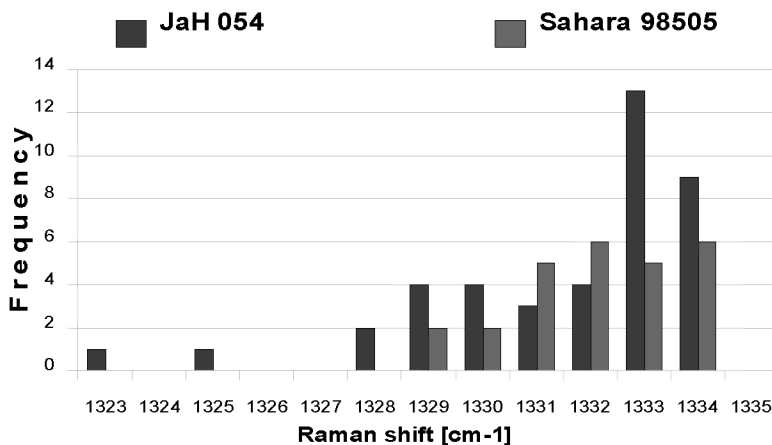


FIGURE 3. Distribution of the diamond Raman peak position in JaH 054 and in Sahara 98505 ureilites.

Obtained Raman shifts of diamond peaks for JaH 054 and Sahara 98505 varied from 1322 cm⁻¹ to 1334 cm⁻¹ and from 1329 cm⁻¹ to 1334 cm⁻¹ in Sahara 98505 respectively (Fig. 3). Also, a wide spread of FWHM (full width at half maximum) parameter was seen, from 3 cm⁻¹ to 13 cm⁻¹ for JaH 054, and from 5 cm⁻¹ to 38 cm⁻¹ in Sahara 98505 (Fig. 4).

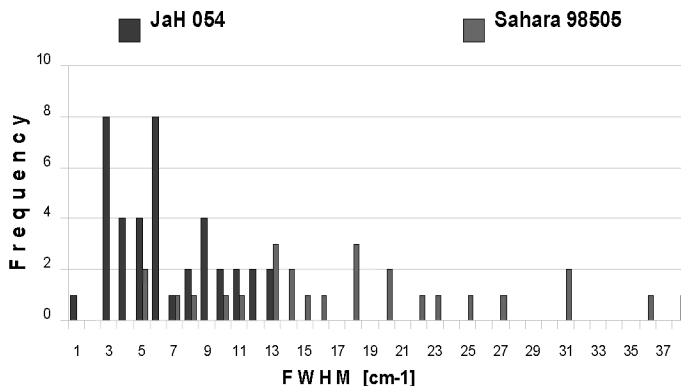


FIGURE 4. Distribution of the diamond Raman peak FWHM for JaH 054 and Sahara 98505 ureilites.

It is clear that distribution of FWHM of diamond peaks is relatively narrower for JaH 054 in comparison to Sahara 98505. Moreover the mean value of FWHM for JaH 054 is significantly smaller ($6,5 \text{ cm}^{-1}$), than for Sahara 98505 ($18,1 \text{ cm}^{-1}$). The FWHM of the diamond peak against the Raman shift of diamond band, however, does not show a great degree of correlation (Fig. 5, 6). It is worthy to notice that the results acquired in two points strongly differ in band position from the other ones. The measured value of the Raman shift 1323 and 1325 cm^{-1} suggests the presence of lonsdaleite [13] what will be discussed in details later. Similar Raman shift was found also in some different points by imaging method (compare to Figure 11). The mean values of diamond Raman shifts (if the mentioned above points were neglected) for both samples are practically identical and equal 1332 cm^{-1} , what is characteristic for terrestrial diamonds.

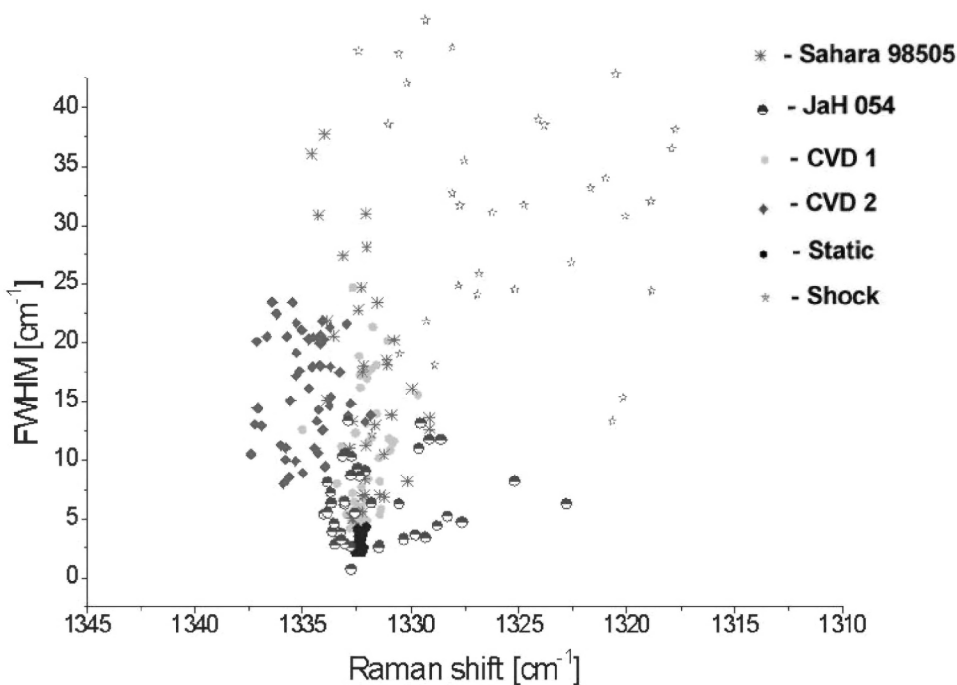


FIGURE 5. Comparison of FWHM vs. Raman band position for studied ureilites and terrestrial artificial diamonds synthesized by different method (more detailed description – see text) (after Miyamoto 1993).

To compare the diamonds occurring in investigated ureilites to artificial (laboratory manufactured) ones, which were prepared by different methods the FWHM vs. band position was plotted - see Figure 5. The points for artificial diamonds were redrawn after Miyamoto (Miyamoto 1993) [14], who studied different types of diamond. In this

work only some selected Miyamoto's results for laboratory diamonds were cited as follow diamonds produced under static high pressure (static HPHT), two types of CVD diamonds (1% of CH₄; Temp 705 °C; pressure 1330 Pa – CVD 1 and 1% of CH₄; Temp 1100 °C; pressure 6670 Pa – CVD 2) and diamonds obtained by shock method (also HPHT method, graphite is transformed under shock wave).

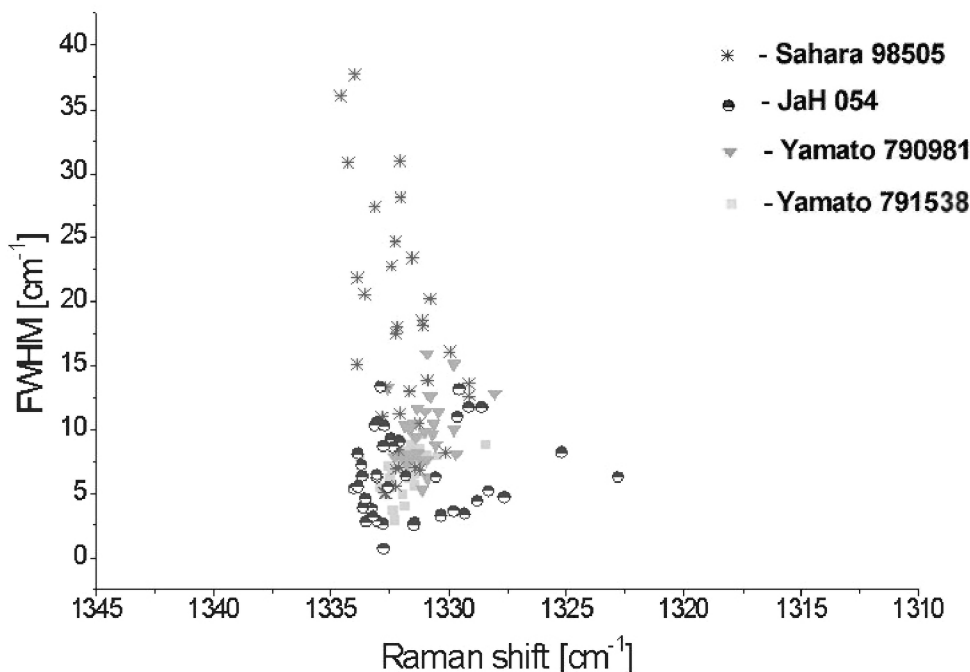


FIGURE 6. Comparison of FWHM vs. Raman band position for different ureilites Points for Yamato redrawn after Miyamoto 1993.

Figure 6 shows results for both studied ureilites and data for Yamato 791538 and Yamato 730981 cited after Miyamoto 1993. JaH 054 seems to be similar with both Yamato ureilites, however observed Raman shift (Fig. 6) varies in broader range of wavenumbers. In a case of Sahara 98505 sample the band positions of diamond peaks are located in the same range like it was found for Yamato, but it is necessary to notice that the FWHM are significantly more scattered for Sahara 985050 compared to other discussed ureilites. According to Figure 7, CVD diamonds are formed in low pressure and relatively low temperature [15]. Graphite and different polymorphs of carbon can be also formed in CVD-like processes.

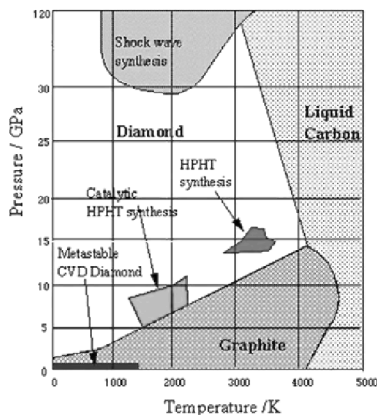


FIGURE 7. The P, T Phase and Reaction diagram for elemental Carbon (F. P. Bundy 1979).

Figures 8, 9 and 10 show Raman images of JaH 054 ureilite. In Fig. 8 the scan range of $9\ \mu\text{m} \times 9\ \mu\text{m}$ was divided to 100×100 pixels (=10000 spectra) with the integration time of 112 ms per spectrum. For analyzing the measurement three averaged spectra at three different regions of the sample were obtained. These three spectra were used in the basis analysis, a fit procedure, which leads to one image per corresponding spectrum.

The three images were color coded and combined into one image. The spectra on the right are the averaged spectra.

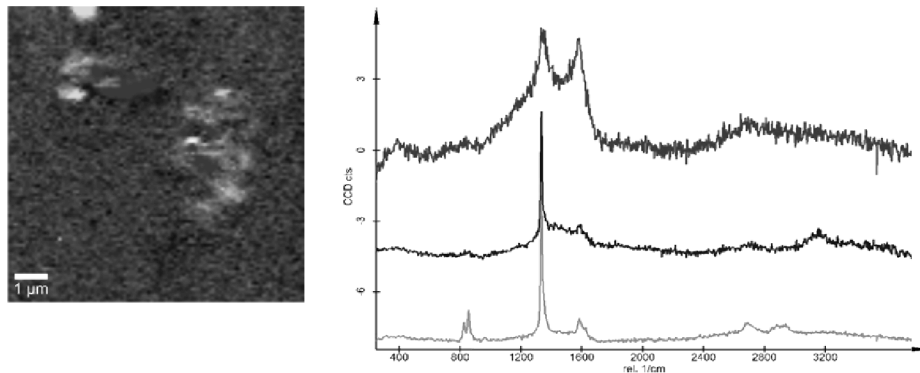


FIGURE 8. Raman mapping and spectra for JaH 054 showing different diamond peak.

The ureilite JaH 054 was measured in the Spectral Imaging Mode with the scan range $30\ \mu\text{m} \times 30\ \mu\text{m}$ and 120×120 pixels (=14400 spectra) with an integration time per spectrum of 102 ms. For analyzing the measurement, five averaged spectra were generated in the corresponding areas (compare Raman image on the left). With these spectra the basis analysis was calculated which led to five images. These five images were color coded and combined into one image (compare Raman image on the left).

The averaged spectra are pictured on the right. The colors of the spectra correspond to the colors of the image (Fig.9).

As a next step a zoom-in was performed with $10\text{ }\mu\text{m} \times 10\text{ }\mu\text{m}$ and 120×120 pixels (-14400 spectra) with an integration time per spectrum of 102 ms (Fig.10). Averaged spectra were obtained at the positions, marked with arrows. The corresponding spectra of the diamond line are shown in Figure 9. There is a shift of $8,3\text{ cm}^{-1}$ to the lower wavenumbers visible.

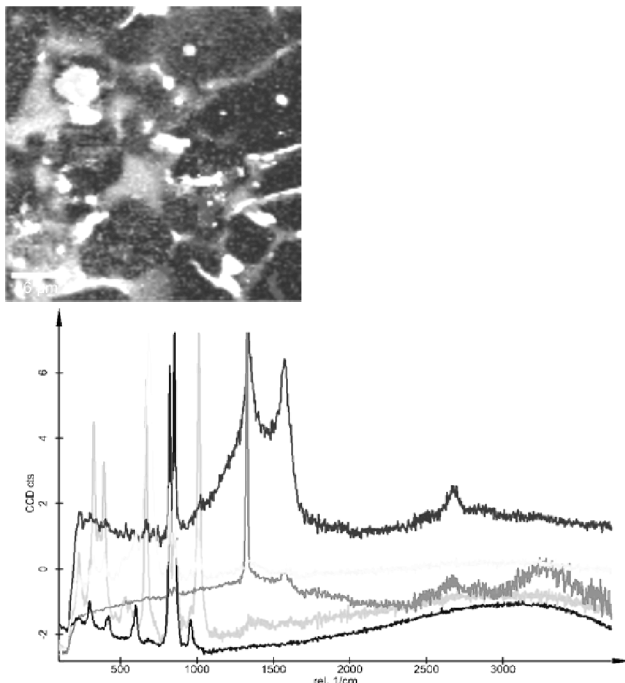


FIGURE 9. Presence of a variety of mineral phases in addition to the C-phases, likely representing olivines and pyroxenes in JaH 054 sample.

Figure 10 shows the existence of different diamond peaks, with different shifts, in the JaH 054 sample. This indicates the most probably the presence of different populations of diamonds, at the same place of the sample.

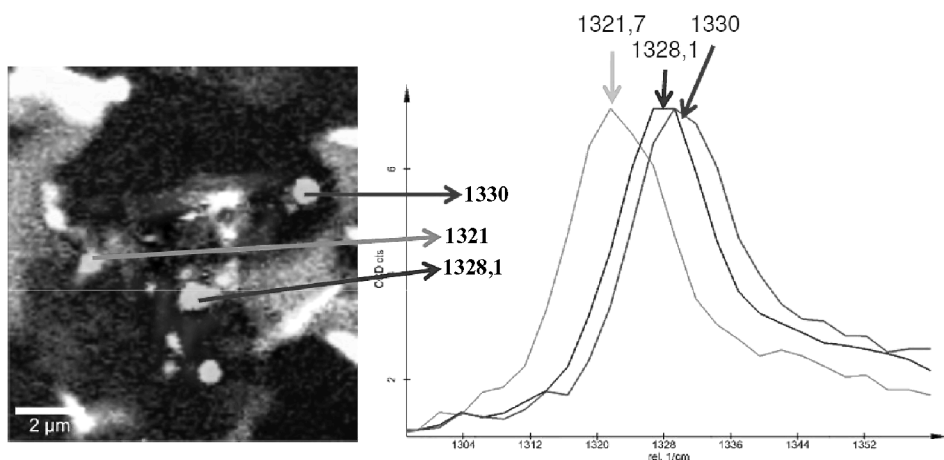


FIGURE 10. Possibly different generations of coexisting diamonds

Similar results (obtained with confocal micro-Raman spectrometer T-64000 Jobin-Yvon, during statistic research described above), showing different populations of diamonds, are shown in Figure 11, in both samples JaH 054 and Sahara 98 505. It is easy to see the similarities between a) and d) pictures in Figure 11. Wide “strange” bands consist of two diamond peaks, one around 1330 or 1331 cm^{-1} and the second at 1336 cm^{-1} .

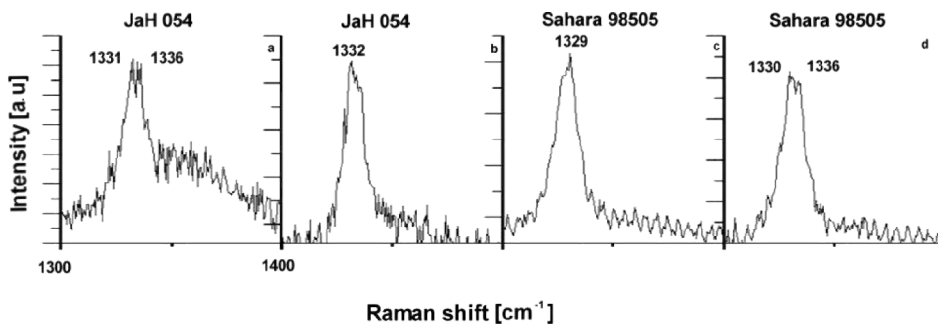


FIGURE 11. Chosen strange Raman peaks of diamond from urelites JaH 054(a, b) and Sahara 98505 (c, d).

DISCUSSION

Different types of carbon (diamond, probably lonsdaleite, graphite, with different degrees of order), show its presence in both ureilite samples: Sahara 98505 and JaH 054 (Fig.2.). Both samples show many similarities, but also differences. They were chosen because these highly shocked ureilites are both abundant with diamonds.

Diamonds in Sahara 98505 and JaH 054 are the most often found in the graphite veins, however, sometimes they were found inside silicates (olivines and pyroxenes). Various Raman shifts show the significant diamonds differences occurring inside the sample and among the samples (Figs 2-4,10, 11). FWHM parameter (full width at half maximum) is in wide range from $0,75\text{ cm}^{-1}$ to $13,37\text{ cm}^{-1}$ in JaH 054 (what is similar to literature ureilites), and $5,02\text{ cm}^{-1}$ to $37,65\text{ cm}^{-1}$ in Sahara 98505 (Figs. 4,6).

The Raman peak positions in some cases are shifted towards smaller wavenumbers (compared to monocrystalline natural diamond with Raman peak at 1332 cm^{-1}), this could indicate about the presence of hexagonal polytype of diamond - lonsdaleite.

One of the populations of diamond in JaH 054 sample correspond to Raman shifts in the range from 1322 cm^{-1} to 1325 cm^{-1} with FWHM parameters smaller than 10 cm^{-1} . These results can be interpreted as Lonsdaleite (hexagonal diamond). Lonsdaleite was found in Canyon Diablo, in ureilites and also in impactites (Ries, Popigai), but this carbon polymorph can be also manufactured in laboratory. For the first time in laboratory lonsdaleite was manufactured by direct static compression high-pressure conversion of graphite to hexagonal diamond made by Bundy in 1966 [24].

Lonsdaleite can be also obtained with the other methods, for instance in CVD process [16]. Raman spectra for lonsdaleite (proved with x-ray diffraction method) are described from 1320 cm^{-1} to 1327 cm^{-1} [17] for impactites, with characteristic wide FWHM $\sim 70\text{ cm}^{-1}$ so FWHM is different than in our results. Kagi et al. [13] described band position at 1323 cm^{-1} with FWHM of 10 cm^{-1} (so similar to our results) for ureilite Y 791538. One of the possible reasons of appearance of Raman shift, given by authors of the mentioned paper, is the presence of lonsdaleite. Smith et al don't agree that Kagi's 1323 cm^{-1} Raman shift [13] corresponds to lonsdaleite because of the difference in FWHM parameter. However, impactite diamonds can differ from ureilitic diamonds, different FWHM can indicate their different origin.

It is interesting that some of the peaks are shifted toward bigger wavenumbers: 1334 cm^{-1} , even 1335 cm^{-1} and 1336 cm^{-1} for both samples JaH 054 and Sahara 98505 (Figs. 3,5,8).

Diamond bands at 1334 cm^{-1} and 1336 cm^{-1} are probably related to internal stresses inside the diamond crystals, similarly to Lappajärvi impact diamonds in the paper of Moroz et al [18]. Similar stresses exist in laboratory made CVD diamonds grown on substrates with large mismatch in thermal expansion coefficients between diamond and the substrate. Ali et al. presented in their paper CVD diamond coatings onto cemented WC-Co dental burs. Raman spectroscopy investigations showed the diamond band at 1338 cm^{-1} . This shift was connected by authors with the stresses existing in the diamond film. The stress values present in the diamond film were calculated in the paper and obtained result was -3.4 GPa , in compression. This result was due to the difference of thermal coefficients for diamond and WC-Co (substrate of

dental burs). After the indentation, Raman peak shifted from 1338 cm^{-1} to 1334 cm^{-1} . This suggested that film became slightly less stressed (-1.13 GPa) and debonds slightly from the substrate. Stress free diamond film shows peak at 1332 cm^{-1} .

[19]

Fan et al. [20] indicate that stress in CVD diamond films can be caused by two reasons: thermal expansion mismatch between the film and substrate and intrinsic stress due to the film growth. Raman spectroscopy is used to determine the stresses in CVD diamonds. They obtained different diamond Raman shifts, from 1332 cm^{-1} (stress free diamond) to 1342 cm^{-1} . They also have results similar to our ureilite diamonds: 1333 cm^{-1} (biaxial stress according to Raman shift was calculated -0.57 GPa), 1334 cm^{-1} (-1.13 GPa), 1336 cm^{-1} (-2.27 GPa) [20].

Above research can be applied to understanding extraterrestrial diamonds. Stresses could appear during their growth or during cooling of hot matter of meteorite consisting diamonds. Intrinsic stresses can also appear because of the defects in crystal structure.

Figures 5 and 6 show the variations of diamonds Raman shifts positions versus FWHM parameter for JAH 054 and Sahara 98505 in comparison with literature data concerning ureilites diamonds and laboratory diamonds [14].

Figure 11 shows interesting coexistence of different generations of diamonds, first 1321 cm^{-1} , second 1328 cm^{-1} and 1330 cm^{-1} which occur in relatively small area in JaH 054 ureilite (few micrometers). Sizes of grains visible on image (Fig.10, on the left) are $1\mu\text{m}$ or less than $1\mu\text{m}$. According to peak features FWHM parameter seems to be relatively similar for these peaks, so only difference that occurs is Raman shift. Similar results are shown at Fig.11. Strange Raman peaks a) and d) are broadened and exhibit two similar maxima: 1331 cm^{-1} and 1336 cm^{-1} for JaH 054 and 1330 cm^{-1} and 1336 cm^{-1} for Sahara 98505. This can indicate about the presence of two different diamonds in one place (in the area where the measurement was taken). Diamond crystal corresponding to Raman shift at 1336 cm^{-1} probably exhibits internal stresses.

Basis on both theories of origin of diamond; HPHT (static or shock) and CVD, it is possible that different types of diamonds of different origin coexist in one sample. Cosmic radiation could also influence diamonds formation in space, they could be formed from CM (or also modified during their life) by irradiation of energetic particles.

Le Guillou [4] describes possibility of occurrence of two populations of diamonds in ureilite NWA 4742, one containing noble gases (typical, with unknown origin) and second formed by shock on graphite (noble gas free). Graphite doesn't contain the noble gases so diamond with graphite origin shouldn't contain noble gases as well. However, disordered carbon present in the sample, contains noble gases. It is possible that disordered carbon was formed by graphitization process from diamonds containing noble gases.

That's why the question about origin of diamonds in ureilites is connected with the question about origin of graphite in ureilites.

In Sahara 98505 and JaH 054 Raman peaks around 1350 cm^{-1} , 1580 cm^{-1} and 1620 cm^{-1} occur (not always all of them, Fig.2 shows the examples). In Raman spectra of perfect monocrystalline graphite there is only the G band in the first order region at 1580 cm^{-1} . The 1350 cm^{-1} band (D1) is commonly called "the defect band" and

appears in poorly-organized carbonaceous matter (CM) or microcrystalline graphite [21]. 1620 cm^{-1} (D2) [22] is another band appeared in the poorly organized CM. In JaH 054 and Sahara 98505 samples there is CM with different degree of order (disorder).

From this research we can't explain the origin of diamonds in ureilites. Probably they were formed in different processes, probably different families of diamonds of different origin coexist together in our samples of ureilites.

Basis on data taken from Miyamoto [14,25] Raman shifts and FWHM parameter can be helpful to answer a question about diamonds. Comparing studies of diamonds from laboratory (with well known condition) to diamonds from ureilites still don't give us clear answer. But according to Hezel 2008 Raman peak shape, shift and also width isn't a clear diagnostic information telling about origin of diamonds [23].

There are some questions which we can't answer at the moment. Why different diamonds coexist together, with small distances between them (few microns as in Fig.11 or in one place as "strange" diamond peaks indicate)? What is the origin of these different diamond populations at Fig.11? Do they have the same origin? How it happened that they coexist together?

CONCLUSIONS

Research of the two ureilites JaH 054 and Sahara 98505, based on micro-Raman spectroscopy, proves the occurrence of different kinds of diamonds in both samples. Various Raman shifts show the significant diamonds differences occurring both, inside the sample and among the samples. The Raman peak positions in some cases are shifted towards smaller wavenumbers, this could indicate about the presence of lonsdaleite. Interesting is that some peaks are shifted toward bigger wavenumbers: $1334 - 1336\text{ cm}^{-1}$ for both samples, this could indicate the presence of internal stresses inside diamonds crystals.

The diamond peaks most often coexist with graphite phases, but sometimes only diamond peaks are observed. This could be explained by the bigger size of diamonds in comparison to the area being sampled by the laser, or the graphite phase simply does not exist around these diamonds.

In few cases the diamond peak is broad and looks as though it has more than one maximum. It seems highly possible that different diamonds sometimes coexist together. Similar results have been obtained with Raman imaging method where distribution of different diamonds in the sample can be seen clearly.

FWHM of diamonds synthesized by CVD process usually range from 3 cm^{-1} to 25 cm^{-1} . The FWHM values of JaH 054 diamonds are similar to FWHM of CVD diamonds and differ significantly compared to shock-produced diamonds. However, different populations of diamonds probably could coexist in one ureilite sample. Diamonds of different origin (CVD, HPHT) or different conditions of their formation (pressure and temperature), or different internal stresses, or different history (impacts, change of temperature and pressure) probably can be found in one sample. Could different populations of diamonds reflect different events in the history of the ureilite parent body or the history of meteorite matter?

Future work with diamonds separated from ureilitic diamonds will hopefully shed more light on their origin and history.

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REFERENCES

1. C. A. Goodrich, *Meteoritics* **27**, 327-352 (1992).
2. R. Hutchison, *Meteorites: A Petrologic, Chemical and Isotopic Synthesis*, Cambridge University Press (2004).
3. A. Wright and J. Parnell, *Lun. Planet. Sci.*, **38**, #1228, (2007).
4. C. Le Guillou, J. N. Rouzaud, L. Remusat, M. Bourot-Denise A. Jambon, *Lun. Planet. Sci.*, **40**, #2108 (2009).
5. M. E. Lipschutz, *Science* **143**, 1431-1434 (1964).
6. A. Bischoff, C. A. Goodrich, T. Grund, *Lun. Planet. Sci.*, **30**, #1100 (1999).
7. K. Fukunaga, J. Matsuda, K. Nagao, M. Miyamoto, K. Ito, *Nature* **328**, 141-143 (1987).
8. J. Matsuda, K. Fukunaga, K. Ito, *Geochem. Cosmochim. Acta* **55**, 2011-2023 (1991).
9. S. Mitura, *J. Crystal Growth* **80**, 417-424 (1987).
10. S. S. Russell, M. Zolensky, K. Righter, L. Folco, R. Jones, H. C. Connolly, M. M Grady and J. N. Grossman, "The Meteoritical Bulletin, no. 89 September 2005", *Meteoritics Planet. Sci.* **40**, 208, (2005).
11. J. N. Grossman, "The Meteoritical Bulletin, no. 83, 1999 July", *Meteoritic and Planetary Science* **34**, 181, (1999).
12. T. Jakubowski, A. Karczewska, M. Kozanecki, A. Gucsik, A. Stanishevsky, S. Mitura, *Lun. Planet. Sci.*, **40**, #1382 (2009).
13. H. Kagi, K. Takahashi, A. Masuda, *Proc. Japan Acad.*, **66**, Ser. B (1990).
14. M. Miyamoto, T. Takase and Y. Mitsuda, *Mineral. J.*, **16**, 246-257 (1993).
15. F.P. Bundy, *J. Geophys. Res.* **85** (B12) 6930 (1980).
16. S. Bhargava and H. D. Bist, *Appl. Phys. Lett.* **67** (12), 1706-1708 (1995).
17. D. C. Smith and G. Godard, *Spectrochim. Acta Part A* **6903**, 1-8 (2008).
18. T. N. Moroz, S. A. Vishnevsky, N. A. Palchik, J. Raitala, 66th Annual Meteoritical Society Meeting (2003)
19. N. Ali, G. Cabral, H. Sein, W. Ahmed, V. F. Neto, J. Gracio, Euro PM 2002 Hard Materials Proceedings, Beaulieu Congress and Exhibition Centre, Lausanne, Switzerland, October 7-9th 2002, pages 154-159 (2002).
20. Q. H. Fan, A. Fernandes, E. Pereira, J. Grácio, *Diamond Rel. Material.* **8**, 645-650 (1999).
21. O. Beyssac, B. Goffe, J.-P. Petiet, E. Froigneux, M. Moreau, J.-N. Rouzaud, *Spectrochim. Acta Part A*, **59** 2267 (2003).
22. M. Perraki, A. Poyer, E. Mposkos, R. Kaindl, G. Hoinkes, *Earth Planet. Sci. Lett.* **241**, 672(2006).
23. D. C. Hezel, L. Dubrovinsky, L. Nasdala, J. Cauzid, A. Simionovici, M. Gellissen, T. Schonbeck, *Met. Planet. Sci.* **43**, 1127-1136 (2008).
24. F. P. Bundy, J. S. Kasper *J. Chem. Phys.* **46**, 3437 (1967).
25. M. Miyamoto, *Antarct. Meteorite Res.*, **11**, 171-177 (1998).