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Different diamonds in meteorites - DaG 868 and NWA 3140 ureilites

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Materials

ABSTRACT

Purpose: Ureilites are a rare type of meteorites containing tiny diamond grains. In our research we used two ureilites: NWA 3140 and DaG 868. The aim of this paper is to show the non-uniformity of carbon in ureilites, especially differences of ureilitic diamonds.
Design/methodology/approach: One of the best methods to examine different allotropic forms of carbon is Raman Spectroscopy. This method used to investigate diamonds provides a lot of information about diamond polytypes, crystals sizes, a level of defects and internal stresses, etc. 2D imaging was done with a Confocal Raman Imaging alpha 300 R WITec apparatus equipped with an Nd:YAG laser with 532 nm excitation. The spectra were collected with a high-sensitive confocal microscope connected to a high-throughput spectrometer equipped with a CCD camera. Mean and local elemental compositions of the samples were determined by an energy dispersive X-ray (EDX) method. A scanning electron microscope HITACHI S-3000 N was used to characterize microstructures (carbon veins) of the samples.
Findings: Different diamond generations were found in ureilites in the presented research with a wide range of Raman shifts from 1309 cm^{-1} to 1339 cm^{-1}. Also graphite and amorphous carbon were found.
Research limitations/implications: Presented research is another step to solve the problem about diamond origin in meteorites.
Practical implications: Understending diamonds and the other carbon phases in meteortites could help in manufacturing new carbon materials in laboratory.
Originality/value: Authors use Raman imaging to show distribution of diamonds in ureilites, this is pioneer research, results of DaG 868 and NWA 3140 are shown for the first time.
Keywords: Diamond; Meteorite; Ureilite; Raman Imaging

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1. Introduction

The presence of diamonds has been confirmed in different types of meteorites: carbonaceous chondrites, ureilites, and iron meteorites [1]. Meteoritic diamonds are of particular interest for research as they exist in different polytypes (3C, 2H, 6H, 8H, 10H, 21R) [2]. Their origin can be from impact processes (HPHT - high temperature and high pressure) on Parent Bodies in space or a CVD-like process (Chemical Vapor Deposition) or radiation induced [3-11]. Ureilite is the first meteorite where diamonds were found in 1888. Till now their origin is still unclear. Main minerals forming these enigmatic rocks are olivines and pyroxenes, whereas spaces between them are filled with carbonaceous matter, mostly graphite and diamonds [3]. Other carbon phases are: amorphous carbon, chaoite and fullerens. Comparing diamonds from meteorites and those manufactured in laboratory, we can understand better the processes and conditions of their formation. It is evident that further studies of both meteoritic and laboratory diamonds are closely related [1,3]. Before lonsdaleite was synthesized under laboratory conditions, it had been identified from the Canyon Diablo meteorite. There is still a lot to learn from nature.

Moreover, meteorites can give us clues about the beginnings of our Solar System by direct studies conducted within our laboratories rather than distant snapshots or telescope viewing. Since the material of meteorites is believed to have been created with the formation of the Solar System, further investigations will yield more knowledge of the origins of our Sun and planets. Such studies of the Earth are difficult as the geological activity has recycled the original composition of material. However, in the vastness of space, the original materials found in meteorites and their parent bodies, asteroids, have largely been preserved [1].

Ureilites are the second largest achondrite group classified as primitive achondrites. They are enigmatic due to their close relationship to chondritic matter - primitive oxygen isotopic ratios and achondritic igneous texture [12]. Currently there are 250 officially classified ureilites, in the great majority from hot and cold deserts. They are ultramafic coarse-grained rocks, composed mainly of olivine and pyroxene (pigeonite) [13,14]. Relatively high abundances of carbon (up to 6 vol. %) are characteristic of this group. Other accessory phases are iron and sulfide.

2. Experiments

In this research two polished slices of ureilites were examined: NWA 3140 (Morocco) and DaG 868 (Libya). The meteoritic samples were selected by preliminary studies of these ureilites. The first of them, NWA 3140, is a typical ureilite containing diamonds, whereas more interesting is DaG 868 classified as a slightly shocked ureilite, but also containing diamonds. Normally, a level of shock of ureilites is connected to the amount of diamonds they contain.

Mean and local elemental compositions of the samples were determined by an energy dispersive X-ray (EDX) method using an EDX Link 3000 ISIS X-ray microanalyzer (Oxford Instruments) and an X-ray microprobe analyzer EDX THERMO NORAN. A scanning electron microscope HITACHI S-3000 N was used to characterize microstructures (carbon veins) of the samples.

2D imaging was done with a Confocal Raman Imaging alpha 300 R WITec apparatus equipped with an Nd:YAG laser with 532 nm excitation. The spectra were collected with a high-sensitive confocal microscope connected to a high-throughput spectrometer equipped with a CCD camera.

The area of graphite vein in the studied ureilites was measured in the Spectral Imaging Mode, for instance 15μm x 15 μm and 100 x 100 pixels (=10000 spectra) with an integration time per spectrum of 112 ms. For analyzing the measurement, for instance two single spectra were taken. With those spectra, the basic analysis was conducted, which led to two images. In that data analysis method, each measured spectrum of the 2D spectral array is compared to basic spectra using a least square fit. Such basic spectra are either measured as single spectra from the pure sample components, or they can be created by averaging over various areas of the scanned surface. The obtained two images were color coded and combined into one image. The colors on the spectra correspond to the colors of the image.

3. Results and discussion

Carbon polymorphs in ureilites are represented by amorphous carbon, graphite, carbide, diamond and lonsdaleite [3]. Carbon is usually present in vein-like, long-shaped fills between mm-sized olivine and pyroxene crystals, sometimes inside these minerals, which is in good agreement with our SEM results (Figures 1-10).

Diamonds are present as micrometer-sized crystals (1 - 10 μm) set in fine granular graphite. The origin of diamonds in this enigmatic group is well-discussed by various authors, from the popular theory of metamorphic transformation of graphite during impact, to the process of chemical vapor deposition (CVD) in the solar nebula [3-11]. Ureilitic diamonds are related to their level of shock. Planetoids in space collide and different processes occur in ureilitic Parent Bodies. Some of authors suggest that diamonds are created from graphite during impact on ureilitic Parent Bodies, but also slightly shocked ureilite as DaG 868 possesses diamonds. The question is: why?

A possible explanation is that different generations of diamonds can be found in ureilites, coexistence of diamonds formed by impact diamonds can be found together with CVD-like diamonds. Recently the existence of nanodiamonds among other diamonds has been shown in ureilite [9].

Figures 1 and 6 show a SEM BSE view of DaG 868 and NWA 3140 ureilitic samples. The carbon veins are clearly seen. Figures 2, 3 and 7, 8 show a distribution of different elements in the same areas of the samples as in Figs.1 and 6. Figure 4 shows a composition of the carbon vein of DaG 868 (a yellow square in Fig. 1) and Fig.5 shows a composition of the whole area shown in Fig.1. Figure 9 shows a composition of the carbon vein of NWA 3140 (a yellow rectangular in Fig.6) and Fig.10 shows a composition of the whole area shown in Fig.6.

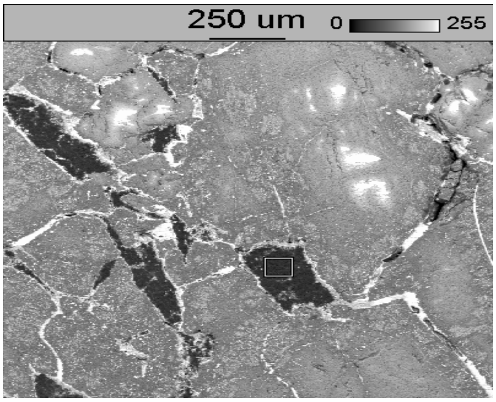

Fig. 1. SEM BSE view of the DaG 868 ureilite

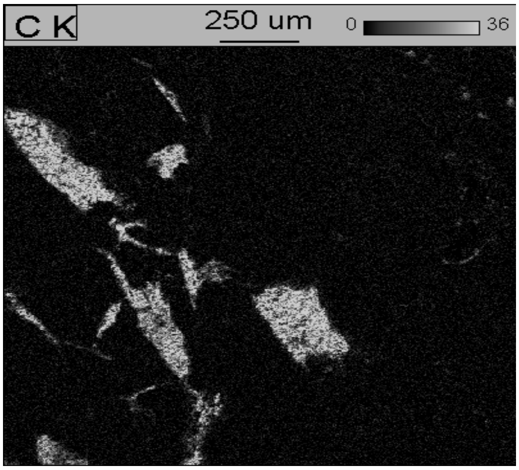

Fig. 2. SEM BSE view of the carbon distribution in DaG 868

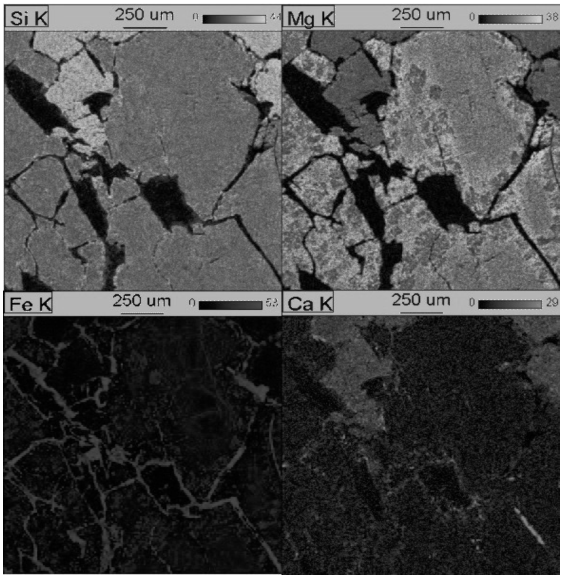

Fig. 3. Distribution of Si, Mg, Fe, and Ca in the DaG 868 sample

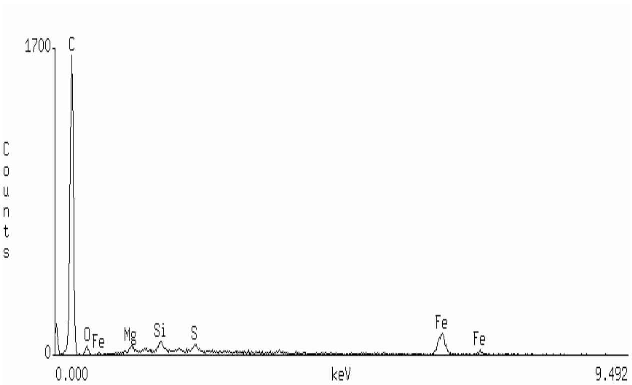

Fig. 4. Element composition of the yellow square in DaG 868

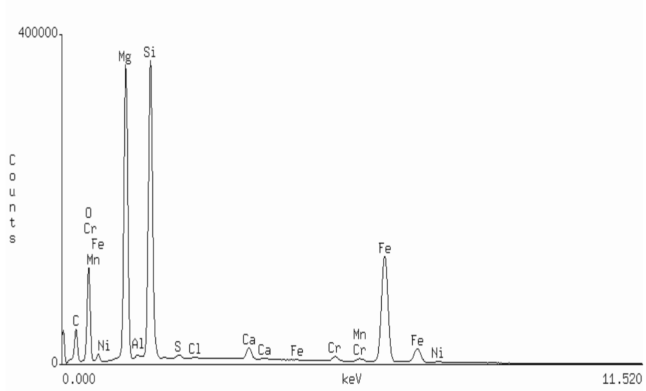

Fig. 5. Element composition of the whole area in DaG 868

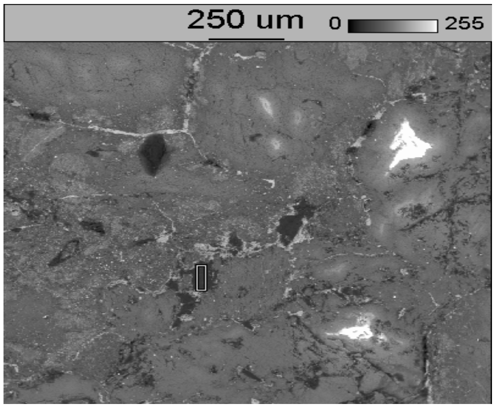

Fig. 6. SEM BSE view of the NWA 3140 ureilite

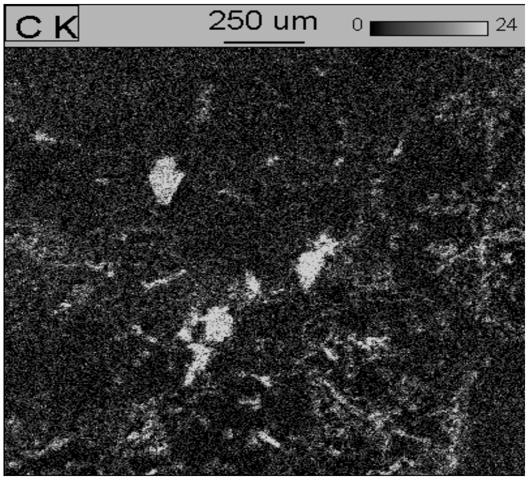

Fig. 7. SEM BES view of the carbon distribution in NWA 3140

Our previous results of two ureilites JaH 054 and Sahara 98505 show Raman shifts of diamond peaks and varied from 1322 cm $^{-1}$ to 1334 cm $^{-1}$ for JaH 054 and from 1329 cm $^{-1}$ to 1334 cm $^{-1}$ in Sahara 98505 [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. A distribution of FWHMs versus Raman shift of the above meteorites was compared with different laboratory-obtained diamonds and CVD diamonds have shown the most similarities in this statistical research.

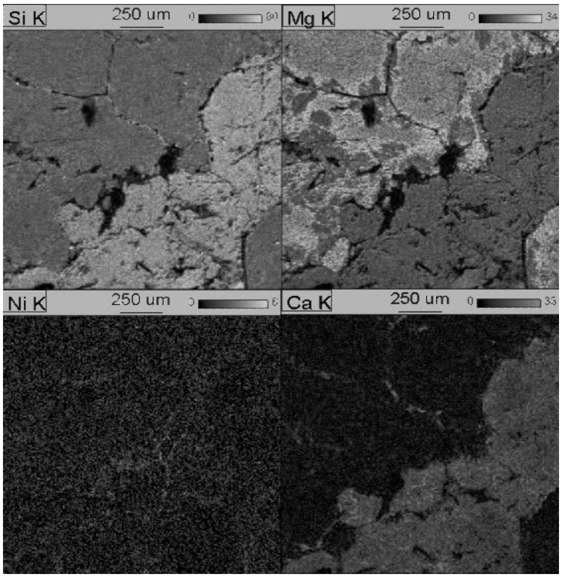

Fig. 8. Distribution of Si, Mg, Ni and Ca in the NWA 3140 sample

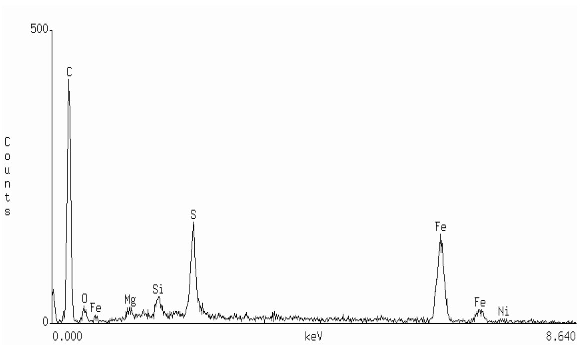

Fig. 9. Element composition of the yellow square in the NWA 3140 ureilite

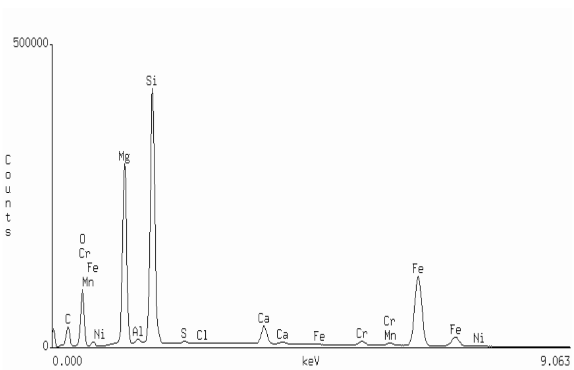

Fig. 10. Elements composition of the whole area in the NWA 3140 ureilite

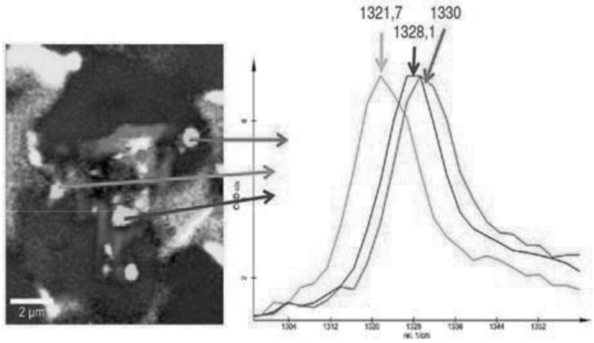

Fig. 11. Different generations of diamonds in JaH 054 occur in a small area of the sample [3]

Different diamonds coexist in a small area of one sample. The recent results of JaH 054 indicate that even more different diamond Raman peaks exist in the sample, for instance sharp peaks at 1309 cm^{-1} and 1315 cm^{-1}. The peaks shifted towards smaller wavenumbers indicate a possible presence of the polytypes with hexagonal symmetry [15,16]. Some of the shifts and broadening of the peaks could also show a presence of smaller diamond crystals (possibly nanodiamonds) [17].

The carbon phase differs strongly from sample to sample. Figure 13 shows characteristic diamond peaks for DaG 868: at 1332 cm^{-1} (Raman spectra 3, green color) and 1336 cm^{-1} (Raman spectra 1 and 2, red and blue color). A distribution of different carbon phases is presented in Fig.12. Colors in Fig.12 and Fig.13 correspond to each other. Peaks at 1350 cm^{-1}, 1580 cm^{-1} and 2700 cm^{-1} show a presence of graphite. Two additional peaks at around 1420 cm^{-1} and around 3100 cm^{-1} are characteristic of this sample. The authors have not found such peaks in other ureilites under examination until to now.

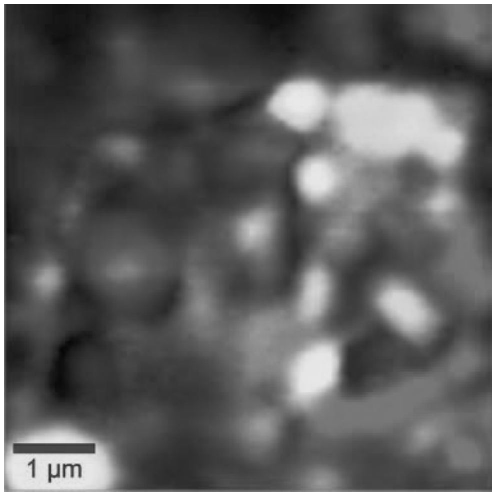

Fig. 12. Color coded Raman image of the DaG 868 ureilite carbon vein, the colors correspond to the Raman spectra in Fig. 13

NWA 3140 shows different diamond peaks, examples are presented in Figures 15-17. The diamond peaks at 1329 cm^{-1}, 1334 cm^{-1} and 1337 cm^{-1} are present. However, the most characteristic diamond peaks for this sample are: at 1330 cm^{-1} and 1332 cm^{-1} (the brightest areas at Fig.14). These peaks are sharp and the most often exist without other carbon phases or only with the graphite G band around 1580 cm^{-1} (graphite with high level of order). Raman spectra for each bright area show high level of uniformity, it means that the bright spots are diamond microcrystals (or sub-microcrystals).

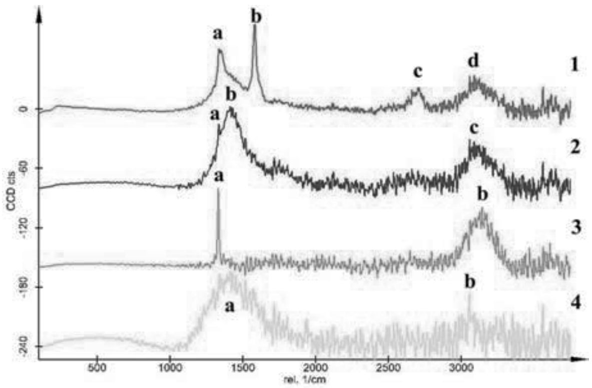

Fig. 13. Raman spectra of the DaG 868 ureilite carbon vein, 1 a) 1336 cm^{-1}, b) 1582 cm^{-1}, c) 2702 cm^{-1} d) 3059 cm^{-1} ; 2 a) 1336 cm^{-1}, b) 1414 cm^{-1}, c) 3058 cm^{-1} 3 a) 1332 cm^{-1}, b) 3143 cm^{-1} 4 a) 1414 cm^{-1}, b) 3059 cm^{-1}

The medium-dark areas show the existence of different diamond peaks shifted toward higher wavenumbers. These peaks are broader and the most often coexist with disorder carbon phase, D band around 1350 cm^{-1}. The shifts toward higher wavenumbers could indicate the presence of internal stresses in diamond crystals. Also graphite with different levels of order exists in the sample.

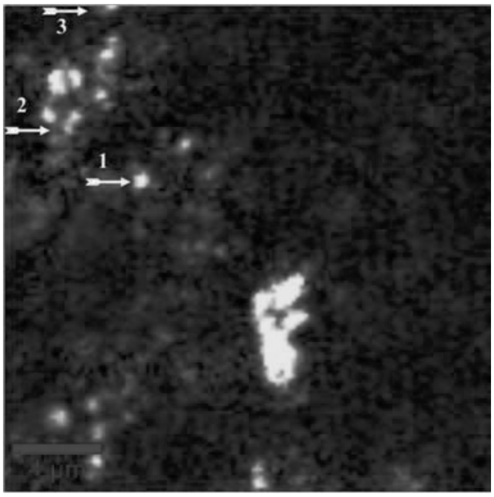

Fig. 14. Raman mapping of a chosen fragment of the NWA 3140 ureilite. Yellow areas show concentrations of diamonds (brighter color shows a higher intensity of the diamond Raman peak). White arrows show studied places

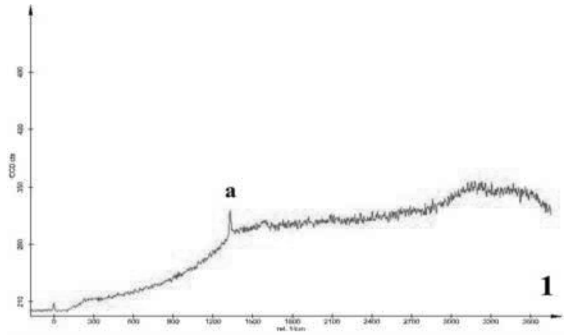

Fig. 15. Diamond Raman spectra of NWA 3140 a) 1329 cm^{-1}

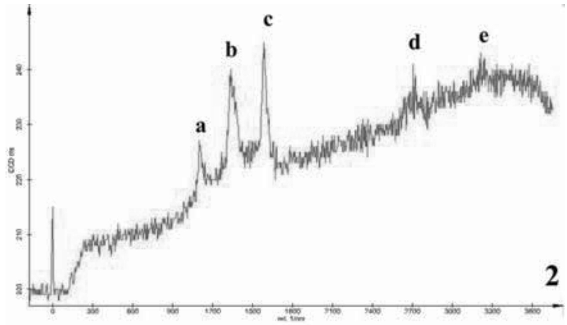

Fig. 16. Raman spectra of NWA 3140 a) 1098 cm^{-1} , b) 1337 cm^{-1} , c) 1586 cm^{-1} , d) 2705 cm^{-1} , e) 3214 cm^{-1}

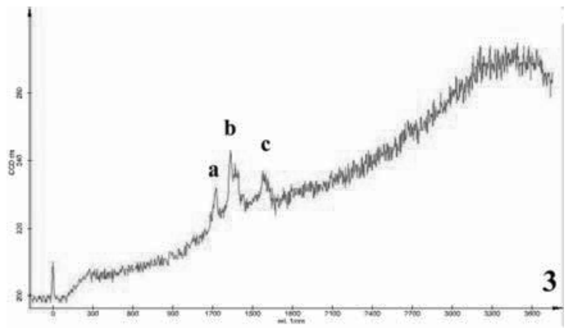

Fig. 17. Raman spectra of NWA 3140 a) 1226 cm^{-1} , b) 1334 cm^{-1} , c) 1576 cm^{-1}

The theories of diamond formation in space are based on the development of the artificial diamond synthesis. The high temperature, high pressure theory (HPHT) has been well-known for years and widely described. Another popular theory of the meteoritic diamond origin is a low-pressure process similar to the laboratory CVD (chemical vapor deposition) process which, depending on several parameters, can produce diamonds varying from nanometers to micrometers in sizes and also other allotropic forms of carbon (and different polytypes of diamond) [18,19,20]. Nanodiamonds can also be synthesized by the detonation method. Nanodiamonds of detonation origin are often compared to the presolar nanodiamonds found in primitive meteorites such as carbonaceous chondrites. As stated before, artificial diamonds and the process of their synthesis are our main source of knowledge on diamond formation in space. And, sometimes, quite to the contrary, a discovery of the material formed in space is the first step towards its synthesis in the laboratory (lonsdaleite is a good example).

4. Conclusions

The Raman imaging of ureilites shows many differences in their carbon phases. There are many different kinds of diamonds in meteorites. In two samples of ureilites examined in this paper, various diamond Raman peaks have been detected. It means that diverse diamond families, probably of different origin, coexist in ureilites. Some of diamonds are of micrometer sizes and exhibit a high level of the crystalline order. Some of them show many defects. The Raman imaging shows also the existence of submicron diamonds and probably the existence of conglomerates of nanodiamonds in ureilite samples. Diamond peaks are often shifted for lower wavenumbers, the peaks around 1324 cm^{-1}, 1315 cm^{-1}, 1309 cm^{-1} have been detected in the JaH 054 sample and described by the Authors in other papers. In DAG 868 and NWA 3140, there are Raman diamond peaks shifts from 1329 cm^{-1} to 1339 cm^{-1}. In some cases the shifts towards the lower wavenumbers could indicate smaller diamond crystal sizes (presence of nanodiamonds). But in many cases diamond Raman peaks are sharp and exhibit a high level of order. This shows the existence of different diamond polytypes in ureilites. The shifts towards higher wavenumbers can indicate a presence of internal stresses in meteoritic diamonds.

Such results show clearly how important is using the Raman imaging to show the whole area, and not to lose much interesting information. It is not straightforward to give a right interpretation of Raman spectra of ureilite carbon phases. Thus, both further research of this topic and an application of other techniques to examine the same samples are necessary.

Acknowledgements

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