Meteorites
Vol. 0, No. 0, 2011, 3–8
www.meteorites.pwr.wroc.pl

DIAMONDS IN UREILITES

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Abstract: The presence of diamonds in meteorites was confirmed for the first time in the Novo-Urei ureilite in 1888. Ureilites are a rare class of achondrites, often referred to as primitive achondrites. They are composed of olivine and pyroxene (pygeonite), as well as graphite inclusions often coexisting with diamonds.

The following three main hypotheses of diamond origin in ureilites have been proposed: the HPHT process, graphite-to-diamond conversion under shock compression due to impact on the parent body (the most popular theory, as of the time of publication), and the CVD process in the solar nebula.

The samples of all types of ureilites, from less shocked up to highly shocked, were examined using Raman Spectroscopy and Scanning Electron Microscopy.

The results show the presence of diamonds in all of our samples. Of particular significance is the comparison of Raman spectra of diamonds and graphite phases of different ureilites.

Keywords: Diamond properties and applications; diamond; meteorite; ureilite, Raman spectroscopy

INTRODUCTION

The presence of diamonds have been confirmed in different types of meteorites: carbonaceous chondrites, ureilites, and iron meteorites. Meteoritic diamonds are of particular interest for research as they exist in different polytypes (3C, 2H, 6H, 8H, 10H, 21R) (Phelps, 1999a), have different sizes (from nanometers up to millimeters), and are of different origin. As nanodiamonds contain isotopic anomalies, they are believed to have formed before our solar system and are thus called presolar. Phelps (1999b) underlines that the theories of meteoritic diamond genesis have been evolving in accordance with the development in diamond synthesis.

It is evident that further studies of both meteoritic and laboratory diamonds are very closely related. Before Lonsdaleite was synthesized under laboratory conditions, it had been identified from the Canyon Diablo meteorite. There is a lot to learn from nature.

Moreover, meteorites can give us clues about 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 investigation will yield more knowledge of the origins of our sun and planets. Such studies of Earth are difficult as 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.

One of the least understood groups of meteorites is the class of primitive achondrites called ureilites. The first of their kind were found in Central Russia in 1886 in the village of Novo-Urei and more have been found mainly within deserts such as the Sahara and Antarctica. They are the most unique of this meteorite group. Ureilites contain olivine and pyroxene (pigeonites) along with material rich in carbon and noble gases. Behind the origin of diamond in ureilites

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is a shock process and some authors claim that a low pressure process similar to CVD.

The aim of this work is to compare the similarities and differences of diamonds among five different samples of ureilites through Raman spectroscopy and scanning electron microscope-energy dispersive spectroscopy (SEM-EDS). Studies of the results along with comparison of the amount of shock of each meteorite may give further insight into the origin of these diamonds and ureilites. Presently, there has been little literature on the subject of the relationship between ureilites, diamonds, and how their connection may give more clues to origin of this enigmatic group. It is part of previous research concerning diamonds in meteorites (Szurgot et al., 2006; Karczemska et al., 2007; Gucsik et al., 2008).

EXPERIMENTAL

We examined five polished slices of ureilites from different locations: Sahara 98505 (Morocco), DAG 868 (Libya), Dhofar 836 (Oman), JAH 054 (Oman), NWA 2634 (Morocco). Selection of samples was based on their shock stages from less shocked (DAG 868) to highly shocked (Sahara 98505).

Mean and local elemental composition of the samples were determined by energy dispersive X-ray (EDX) method using EDX Link 3000 ISIS X-ray microanalyser (Oxford Instruments) and X-ray microprobe analyser EDX THERMO NORAN. Scanning electron microscopes Vega 5135 (Tescan) and HITACHI S-3000 N were used to characterize the microstructure of the samples.

Raman spectra were recorded using the confocal Raman micro-spectrometer T-64000 (Jobin-Yvon) equipped with the microscope BX-40 (Olympus). The 514.5 nm Ar line was used for sample excitation. Other parameters of spectrum acquisition (time, laser power) were adjusted to obtain spectra of sufficient quality. The laser beam diameter was 1.5 μm, the light intensity across the beam was of Gaussian distribution.

RESULTS

Scanning Electron Microscopy (SEM) pictures show characteristic black vein-like carbon phases which fill the spaces between mm-sized olivine and pyroxene (Fig. 1). Carbon can be seen enclosed in olivine and pyroxene (Fig. 1c). Carbon phases are usually rounded by iron phase (white color on SEM photographs).

Using microRaman spectroscopy we found diamonds in all five samples. The results of Raman spectroscopy (diamond peaks positions and full width at half maximum values – FWHM) from five ureilites are presented in table 1. A number of samples have several results from different locations in carbon veins. Figure 2 shows chosen Raman spectra of all five samples which have been studied.

DISSCUSSION

Ureilites are the second largest achondrite group classified as primitive achondrites. They are enigmatic due to their close relationship with chondritic matter - primitive oxygen isotopic ratios and achondritic igneous texture (Clayton & Mayeda, 1988). Currently there are 240 officially classified ureilites, in great majority from hot and cold deserts. They are ultramafic coarse-grained rocks, composed mainly of olivine and pyroxene (pigeonite) (Hutchinson, 2004). Relatively high abundances of carbon (up to 6 vol. %) are characteristic for this group. Other accessory phases are iron and sulfide. Carbon polymorphs in ureilites are represented by amorphous carbon, graphite, carbide, diamond and lonsdaleite (Wright & Parnell, 2007). Carbon is usually present in vein-like, long-shaped fills between mm-sized olivine and pyroxene crystals, sometimes even inside these minerals, what is in good agreement with our SEM results (Fig. 1).

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 vapour deposition (CVD) in the solar nebula (Miyamoto et al., 1988).

The theories of diamond formation in space are based on the development of diamond synthesis. The high temperature, high pressure theory (HPHT) has been well-known for years and widely described. Another popular theory of meteoritic diamonds' origin is a low-pressure process similar to the CVD process which, depending on several parameters, can produce diamonds varying in sizes from nanometers up to micrometers. Nanodiamonds can also be synthesized by 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 the contrary, a discovery of material formed in space is the first step towards its synthesis in the laboratory (lonsdaleite is a good example).

The presence of nitrogen signature in carbonaceous material of Novo-Urei-like meteorites (Fisenko et al., 2004) is an argument for the possible occurrence of nanodiamonds in ureilites.

Diamonds in ureilites were used as shock-level indicators from low to high shock levels (Goodrich, 1992). Some authors (Bischoff et al., 1999) describe occurrence of μm-sized diamonds and shock changes in olivine from ureilites as being related to their shock stages (from S1 to S6). They claim that diamonds cannot be found in weakly-shocked meteorites. Certain ureilites, however, like DAG 868, though classified as the least-shocked (studied in this paper), do contain diamonds. Takeda et al. (2001) describing DAG 868, suggests a non-CVD origin of diamonds in this ureilite due to low levels of pressure in catalytic transformation of graphite to diamond even in less-shocked rocks.

We obtained a few different Raman peaks of diamonds in our ureilite samples ranging from 1323 cm^{-1} in JAH 054, to 1334 cm^{-1} in Sahara 98505 (Tab. 1).

Table 1. Raman spectra peaks of diamonds from five ureilites

Ureilite Name	Diamond Peak Raman Spectra cm^{-1}	FWHM (full width at half maximum) cm^{-1}
DAG 868	a) 1332	9.7
Dhofar 836	b) 1328	11.2
	c) 1332	8.05
JAH 054	d) 1330	6.1
	e) 1321	8.3
	f) 1323	14.3
NWA 2634	g) 1332	4.3
	h) 1329	11.1
Sahara 98505	i) 1334	22.2
	j) 1333	15.2

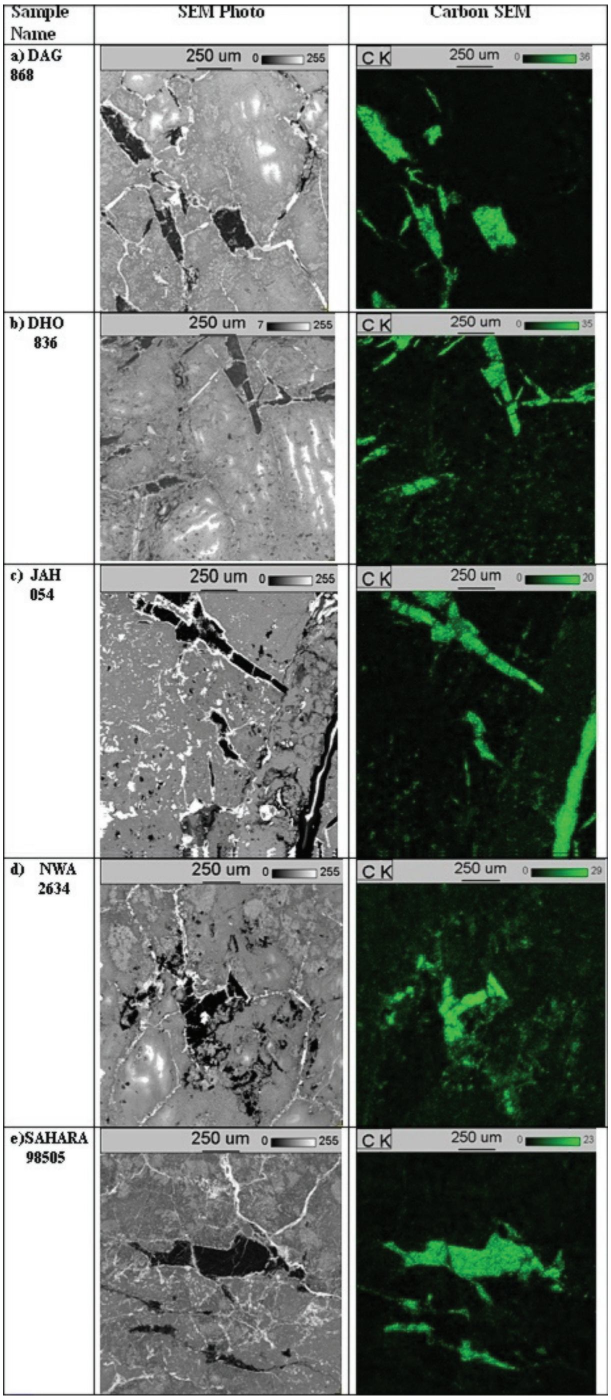

Fig. 1. Views from Scanning Electron Microscope (SEM), carbon SEM for five different ureilites, 1) DAG 869, 2) DHO 836, 3) JAH 054, 4) NWA 2634, 5) Sahara 98505

In JAH 054 we acquired a different Raman shifts from 1321 cm^{-1} to 1330 cm^{-1}. For the FWHM (full width at half maximum) parameter, we also have different results from narrow peaks like 4.3 cm^{-1} in NWA 2634, to broad peaks of 22.2 cm^{-1} in Sahara 98505 (Tab. 1 and Fig. 2). Figure 2 also shows the coexistence of diamond and graphite. In sample DHO 836 D band is 1332 cm^{-1} and G band is 1616 cm^{-1}, NWA 2634 diamond have 1329 cm^{-1} and graphite

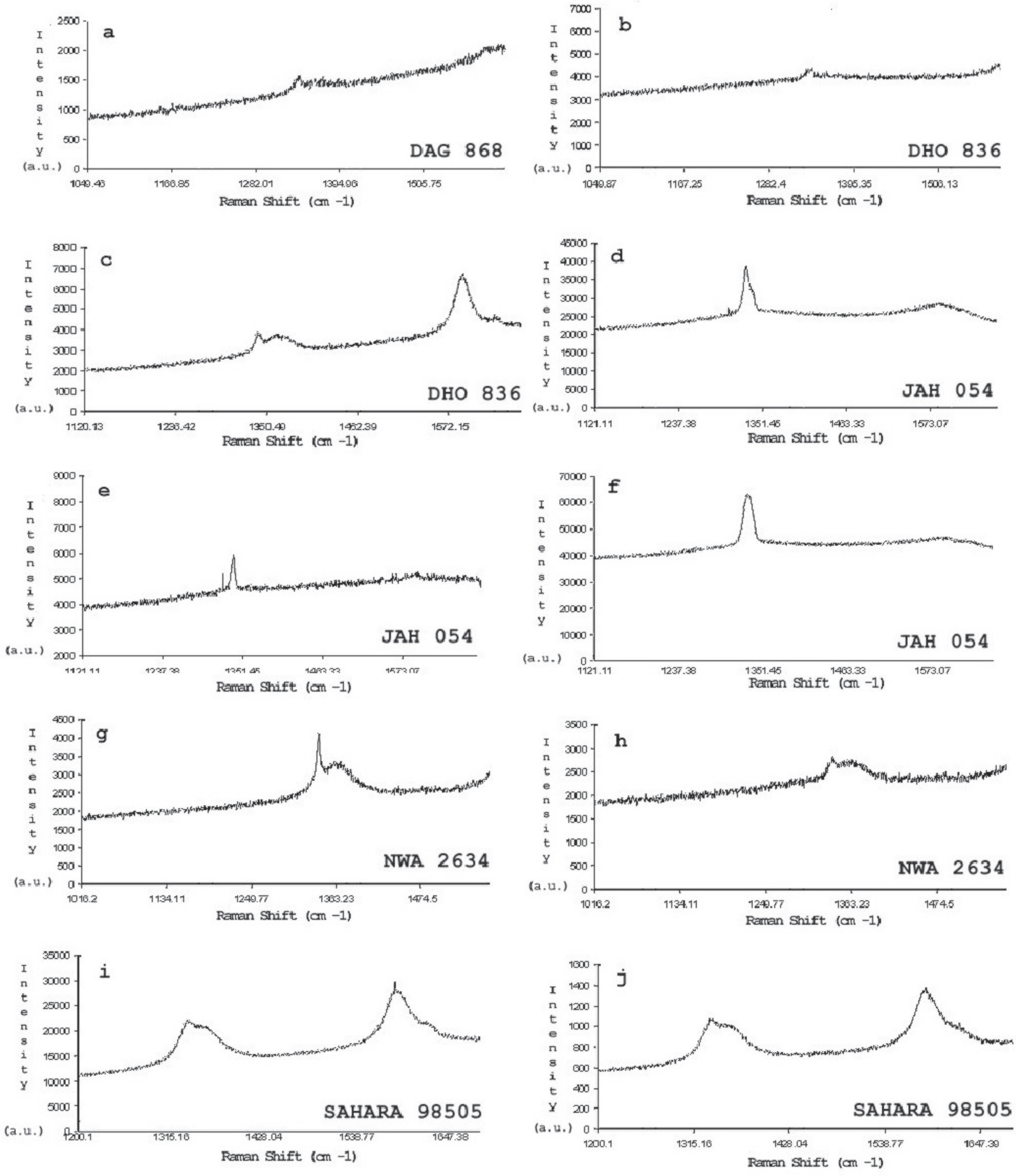

Fig. 2. Raman spectra of five examined ureilites

1354 cm^{-1}, in Sahara 98505 D band is 1333 cm^{-1} and G band is 1620 cm^{-1}. In 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 CM or microcrystalline graphite (Beyssac et al., 2003).The other bands in the second-order region, which appear in the poorly organized CM are: 1150 cm^{-1} (strongly debated), 1500 cm^{-1}, 1620 cm^{-1} (D2) (Perraki et al., 2006).

In a perfect monocrystalline diamond, the band of 1332±0.5 cm^{-1} appears, with a full width at half maximum (FWHM) of 1.65±0.02 cm^{-1}. The increased width and shift of this Raman peak indicates an increase in structural disorder or the very small crystal sizes and the compressive/tensile stresses in the lattice, respectively (Perraki et al., 2006; Yushin et al., 2005).

The other authors (Nemanich et al., 1988; Prawer & Nemanich, 2004; Morell et al., 1998) write that both monocrystalline and polycrystalline diamond of the grain size above ~20 μm exhibit the first strong and narrow (FWHM of about 1–3 cm^{-1}) order peak at ~1332 cm^{-1}. If the size of crystals decreases below a micrometer, the FWHM of diamond peak increases to values of about 10 cm^{-1} or more. It is caused by a decrease in crystal perfection and an increase of the non-diamond content in the sample.

Yushin et al. (2005) writes: "The diamond peak at ~1320 cm^{-1} is down-shifted and broadened (FWHM of 30 cm^{-1}) with respect to the single crystal diamond peak (1332 cm^{-1}). This downshift is thought to occur due to the phonon confinement or changes in the phonon DOS accompanying the decrease of particles size into the nanometer range."

In this research, the differences in Raman shift and FWHM in diamonds can be caused by shock changes, a decrease in crystal perfection (defects), different polytypes of diamonds, or different sizes of crystals.

Various Raman peaks and FWHM can be interpreted as diamonds of different sizes (of sub-micrometer size range), structural defects caused by shock changes during impact, or different diamond polytypes.

From our research (in the laboratory as well as in available literature), we believe that TPHT diamonds (micrometer-sized) and CVD diamonds (mostly nanometer-, but also micrometer-sized) can coexist together. The main difficulties in finding nanodiamonds (presolar diamonds) are the nano-sizes of grains and the fact that not every nanodiamond is of presolar origin.

Further research will be necessary to draw more precise conclusions.

CONCLUSION

Our research of five ureilites, based on micro-Raman spectroscopy, proved the occurrence of diamonds in Novo-Urei-like meteorites. Diamonds were found not only in highly-shocked ureilites, but also in the least-shocked specimens.

Various Raman shifts and FWHM do not lead to clear conclusions regarding examined diamonds formation.

ACKNOWLEDGEMENTS

We would like to express our most sincere appreciation to Jakub Radwan of Polish Meteorite Society who read, corrected, and commented on various parts of this text.

REFERENCES

Beyssac O., Goffe B., Petiet J.P., Froigneux E., Moreau M., Rouzaud J.N., 2003 – On the characterization of disordered and heterogeneous carbonaceous materials by Raman spectroscopy. *Spectrochimica Acta*, Part A, 59, 2267.

Bischoff A., Goodrich C.A., Grund T., 1999 – Shock-induced origin of diamonds in ureilites. *Lunar and Planetary Science XXX*, Abstract #1100.

Clayton R.N., Mayeda T.K., 1988 – Formation of Ureilites by Nebular Processes. *Geochim. Cosmochim. Acta* 52, 1313–1318.

Fisenko A.V., Verchovsky A.B., Seymanova L.F., Pillinger C.T., 2004 – Carbon, Nitrogen and Noble Gasses in diamond separates from the Novo-Urei ureilite. *67th Annual Meteoritical Society Meeting*. Abstract #5159.

Goodrich C.A., 1992 – Ureilites A critical review. *Meteoritics* 27, 327.

Gucsik A., Verchovsky A.B., Ott U., Marosits E., Karczemska A., Kozanecki M., Szurgot M., 2008 – Meteoritic nanodiamond: A Micro-Raman Spectroscopical Overview. *39th Lunar and Planetary Science Conference*, Abstract #1201.

Hutchison R., 2004 – Meteorites. A petrologic, chemical and isotopic synthesis. Cambridge University Press, New York.

Karczemska A., Kozanecki M., Szurgot M., Sokołowska A., Mitura S., 2007 – Raman spectroscopy studies of meteoritic diamonds. *Diamond Relat. Mater.* 16, 781, 1179–1185.

Karczemska A., Szurgot M., Kozanecki M., Szynkowska M.I., Ralchenko V., Danilenko V.V., Louda P., Mitura S., 2008 – Extraterrestrial, terrestrial and laboratory diamonds – Differences and Similarities. *Diamond Relat. Mater.* 17 (7–10), 1179–1185.

Miyamoto M., Matsuda J., Keisuke I., 1988 – On the vapour growth diamonds formation in the Solar Nebula. *Geophysical Research Letters* 15 (12), 1445.

Morell G., Quinones O., Diaz Y., Vargas I.M., Weiner B.R., Katiyar R.S., 1998 – Measurement and Analysis of Diamond Raman Bandwidths. *Diamond Relat. Mater.* 7, 1029.

Nemanich R.J., Glass J.T., Lucovsky, G. Shroder R.E., 1988 – Raman scattering characterization of carbon bonding in diamond and diamondlike thin films. *J. Vac. Sci. Technol., A, Vac. Surf. Films* 6 (3), 1783.

Perraki M., Proyer A., Mposkos E., Kaindl R., Hoinkes G., 2006 – Raman microspectroscopy on diamond, graphite and other carbon polymorphs from the ultrahigh-pressure metamorphic Kimi Complex of the Rhodope Metamorphic Province, NE Greece. *Earth and Planetary Science Letters* 241, 672.

Phelps A.W., 1999a – Interstellar diamond. II. Growth and identification. *Lunar and Planetary Science XXX*, Abstract #1753.

Phelps A.W., 1999b – Interstellar diamond. I Condensation and nucleation. *Lunar and Planetary Science XXX*, Abstract #1749.

Prawer S., Nemanich R.J., 2004 – Rama spectroskopy of diamond and doped diamond, *Philos. Trans. R. Soc. Lond. A* 362, 2477.

Szurgot M., Karczemska A., Kozanecki M., 2006 – Extraterrestrial diamond, [in:] Mitura S., Niedzielski P., Walkowiak B. (eds.), *Nanodiam*, PWN, Warsaw, 259–287.

Takeda H., Ishii T., Otsuki M., Nakamuta Y., Nakamura T., 2001 – Mineralogy of a New Weakly Shocked Ureilite, Dar Al Gani 868 with Diamonds. *64th Annual Meteoritical Society Meeting*, Abstract #5039.

Wright A., Parnell J., 2007 – Interpreting the Raman Signature of ureilite carbon. *Lunar and Planetary Science XXXVIII* Abstract #1228.

Yushin G.N., Osswald S., Padalko V.I., Bogatyreva G.P., Gogotsi Y., 2005 – Effect of Sintering on Structure of Nanodiamond. *Diamond Relat. Mater.* 14, 1721.

Publishers: Wrocław University of Technology, Faculty of Geoengineering, Mining and Geology
Polish Meteorite Society