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Investigation of inclusions trapped inside Libyan Desert Glass by Raman microscopy

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ABSTRACT

Several specimens of Libyan Desert Glass (LDG), an enigmatic natural glass from Egypt, were subjected to investigation by micro-Raman spectroscopy. The spectra of inclusions inside the LDG samples were successfully measured through the layers of glass and the mineral species were identified on this basis. The presence of cristobalite as typical for high-temperature melt products was confirmed, together with co-existing quartz. TiO_2 was determined in two polymorphic species, rutile and anatase. Micro-Raman spectroscopy proved also the presence of minerals unusual for high-temperature glasses such as anhydrite and aragonite.

KEYWORDS Libyan Desert Glass, Raman spectroscopy, inclusions, cristobalite, anatase, zircon, rutile

INTRODUCTION

Libyan Desert Glass (LDG) is one of the most mysterious geological materials found on Earth. It consists of about 98% of molten silica and 2% of admixtures which altogether make it equally beautiful and enigmatic. Its rare abundance is the reason of particular desire from both scientists and jewellers. Its beauty and value was already appreciated in the time of pharaohs or even earlier, by prehistoric humans [1,2].

Modern history of LDG begins by the end of the XIXth century. The first mention in literature was made in 1850 by Fulgence Fresnel, the French consul in Djeddah (Jedddah), who published his memoirs in *Bulletin de la Société de Géographie* (Paris) in 1849-1850 [3]. The treasure had to wait still more than 80 years till the expedition carried out in 1932 by P.A. Clayton from the Egypt Desert Survey, who collected the first pieces [4]. It wouldn't have turned so famous without the work of L.J. Spencer, whose enthusiasm to the mysterious silica glass pieces was reflected first in the article *Silica-glass from the Libyan Desert* in 1933 [5].

The quest for LDG was definitely challenging for everybody, who had a chance to experience it [5,6]. The precious pieces are scattered over an area of 6500 km^2 in the Western Desert of Egypt, south-east from the border with Libya (Fig.1). Herodot called everything to the west of the Nile as Libyan Desert and this is probably how the material got its name [6]. The pieces of LDG are located along the corridors between high dunes, in the area of the extreme desert extending between the Great Sand Sea and the Gilf Kebir Plateau (Fig 1) [1,5].

The mystery of the origin of Libyan Desert Glass

Chemically, LDG is pure silica, SiO_2. It is a natural glassy matter, transparent or yellowish, sometimes dark or milky. Quite often it contains air bubbles and inclusions appearing as streaks, ribbons, misty waves or simply solid spots. Although so enigmatic, it is not the only natural glass in nature. These materials can be divided into a few groups depending on their origin. Among these, there are volcanic glasses (obsidian, basalt glass) and tektites/impactites that were created due to a large amount of energy hitting the ground. Beside LDG, other materials belonging to this group are moldavite, Aouelloul impact glass, Muong Nong type, Darwin glass, and others. Fulgurites, however, present themselves as an exception. They are the result of a lightning glow discharge in the sand ("lightning in sand"), so they differ much from other members of the group (hollow tube shapes with rough texture, from 1 cm to 10 m long) [6].

The genesis of LDG is constantly under discussion. It has only one doubtless point - it is the age of LDG. It was estimated to be 28.5 million years old [1] and so far everybody seems to support this finding. The open question is how the LDG was created. Most scientists point to an impact process and most of the results are in favour of this hypothesis, with only one against – the lack of a crater. However, even if we consider the impact hypothesis, there is still a controversy if the meteorite actually hit the ground or exploded above its surface. Recently, Boslough and Crawford [7] presented a possible scenario, where the low altitude airburst explosion may be responsible for creating deposits of glass that appear to be a result of an impact but do not seem to be melted down by high pressure shock waves. The only clear example of this type phenomenon is the Tunguska event with an explosion magnitude within the range of 10-40 megatons (although according to Boslough and Crawford [7], it was in the order of 5 megatons). The next question is whether the conditions of formation are preserved inside the structure of LDG and how we are able to determine them.

There is still a discussion in the literature whether LDG is an impactite or a tektite, between which there is a substantial difference [8]. In fact, impactites (glasses and molten rocks) occur as large bodies inside a crater or on its edges, associated with shock metamorphosed minerals. Tektites are glasses ejected from their craters over large distances (so called strewn-fields), but their composition reflects the upper crustal layer, where they have been formed [9]. According to Giuli *et al.* [10], tektites were subjected to cooling under low pressure, while impactites were influenced by a gradient temperature and pressure. Pratesi *et al.* [8] are leaning towards the idea that high pressure quenching exerted also the formation of LDG which should then be classified as impactite.

As the investigation proceeds, there are more inconsistencies about classifying natural glasses. Gucsik *et al.* [11] investigated Aouelloul glass, Muong Nong-type and LDG; the results showed that Aouelloul glass experienced a relatively low temperature of formation; Muong Nong tektite was subjected to the highest temperature while LDG formation went on at medium temperatures. If Muong Nong belongs definitely to tektites and Aouelloul glass to impactites, it would leave LDG somewhere in the middle. However, if the material consisting of 98% silica was formed by melting, the temperature must have been 1800^{o}C or more [6,12].

Frischat *et al.* [13] confirmed a similarity between LDG and high temperature SiO_2 glasses which would support the theory of high temperature formation.

Some authors, however, are very definite in their conclusions. Giuli *et al.* [10] concluded, based on XANES analysis of the Fe oxidation state, that LDG is definitely an impactite, not a tektite. This idea was also supported by Faulques *et al.* [14] who analysed IR and Raman spectra of several natural glasses, proving a strong similarity in structure between LDG, Darwin glass and vitreous silica. On the other hand, Stebbins et al are in favor of the hypothesis that LDG does not retain a high pressure structure, despite its origin due to a hypervelocity impact [15].

The mystery of inclusions

The role of an extraterrestrial body participating in the formation of LDG seems to be eventually approved. According to the discussion presented above, it is not evident yet what happened after the explosion – the conditions of cooling and quenching are still not clear. The answer to this dilemma was searched for in the LDG inclusions. As far as the minerals inside LDG are concerned, the most abundant and most often presented in the literature is cristobalite [16]. Frischat *et al.* [13] mentioned mineral phases typical for high temperature and high pressure origin (wollastonite, baddeleyite, cristobalite, stishovite). It is well known that some silica polymorphs, e.g. coesite and stishovite, indicate a high pressure during formation, while others, e.g. cristobalite and tridymite, are evidence of a high temperature [8]. The presence of platinum group elements patterned as in chondrites was also detected, which would confirm the presence of extraterrestrial matter and, consistently, an impact as the way of formation [16].

Amorphous spherules inside the LDG structure, analysed by Pratesi *et al.* [1] would extend the temperature range up to 2100^{o}C because the spherules are far richer in Al, Fe and Mg and less in SiO_2, contrary to the glassy matrix. Cooling down liquid silica at atmospheric pressure would lead to separation of two immiscible solutions. Graphic ribbons discovered by the same research group [1] indicate the formation pressure to be in the range 5-7 GPa, otherwise, if higher, graphite would be replaced by diamond. Since all carbon allotropic forms (graphite, diamond, fullerenes and carbines) were found in terrestrial impact rocks, their presence in LDG cannot be excluded. However, it was hard to tell whether it would be a primary or secondary phase.

What can we say about the LDG origin so far? The nature of inclusions would speak in favour of high temperature and high pressure formation initiated by a meteoritic impact. However there are too many contradictions revealed through investigation of other physical and chemical properties of the glass; too many to announce its enigmatic origin finally revealed. Spencer stated that “It seemed easier to assume that it had simply fallen from the sky!” [17].

The aim of our work presented here was to contribute to the global attempt to solve the riddle of the LDG origin. We investigated several LDG specimens, focusing our attention on the molecular composition of inclusions. Micro-Raman Spectrometry (MRS) is the best technique that could be applied for this kind of material. Due to glass transparency, MRS gave us a chance to reach most of the inclusions without damaging the precious objects. Surprisingly, there are very few communications about MRS applications to analyse LDG [11,14,18].

EXPERIMENTAL

The specimens of LDG belong to the Academy for Mineralogy which premises, together with a geological museum, is located in Antwerp, Belgium. Several of them, with a size range up to a few cm, were investigated. Some of them were cut and polished to reveal the inclusions. The measurements were performed by MRS at the University of Antwerp, Department of Chemistry. We were able to reach most of the inclusions with the laser, however due to the very rough texture of the samples, it was simply impossible to place the sample properly under the objective. The instrument we applied was a Renishaw InVia Reflex (Renishaw, Wotton-under-Edge, UK) equipped with two lasers (514.5 and 785 nm), a CCD detector and a Leica microscope (20x, 50x, 100x objectives). Samples were scanned using a synchroscan mode from 100 to 2000 cm^{-1} at a spectral resolution of about 2 cm^{-1}; in an acquisition time from 10 to 30 s, the signal was accumulated. Data acquisition was carried out with the software package GRAMS (Galactic Industries, Salem, NH, USA). Spectral analyses were performed by comparison with spectra from an in-house spectral library as well as a commercially available one.

RESULTS and DISCUSSION

As it was mentioned before, MRS is very convenient to analyse inclusions in transparent samples without damaging them. First we measured Raman activity of glassy matrix. Fig. 2 shows a piece of LDG together with a Raman spectrum of its bulk material. Such a spectrum has been previously published [18]. The glassy matrix does not give a distinct Raman spectrum, just irregular background. However, a closer look at the spectrum in Fig. 2 allows us to distinguish some vibrational bands, also described elsewhere [11,14]. Two typical broad bands – one around 480 cm^{-1} and the other at 820 cm^{-1} – are typical for glassy silicate materials. The range 400-600 cm^{-1} is ascribed to bending in and between the SiO_4 tetrahedra associated with cationic motions; the range near 800 cm^{-1} is the symmetric motion of adjacent Si atoms with respect to a bridging oxygen (Si-O-Si) [14]. According to Faulques *et al* [14], the overall shape of the Raman spectrum is very much alike for both LDG and Darwin glass which – with no doubts – is an impactite, however far younger than LDG (only 730,000 years old).

The Raman band marked with a red arrow (Fig. 2) should be emphasised, hence this sharp (although not intense) peak would indicate the presence of fullerene. It was a small black spot deep under the surface; however we managed to record the spectrum. Although it seemed quite incredible for us that fullerenes could be found inside LDG, it has already been mentioned in the literature [1].

Figs. 3 to 8 present the other inclusions analysed by MRS. Cristobalite is the silica form most often reported as a component of LDG. It is widely assumed that its presence proves the temperature of glass quenching as above 1470^{o}C [18]. The shape of cristobalite inclusion presented in Fig. 3 is typical for LDG, with an almost ideally spherical form. However, we also found cristobalite as crushed, irregularly shaped inclusions (Fig. 3, lower photo). Moreover, its Raman spectrum is fairly disturbed by luminescence, probably due to a presence of transition metals or REE. As for other polymorphs of silica, tridymite is stable below 1470 and above 870^{o}C, while quartz – below 870^{o}. However, the presence of one form does not exclude the other one, which is clearly shown in Fig. 4. The Raman spectrum gives an undeniable confirmation of quartz being present in LDG; the question remains whether it is a primary or secondary mineral. In a cristobalite structure, each SiO_4 tetrahedron shares its oxygen atoms with adjacent tetrahedra; how likely it is then to convert cristobalite into quartz within 29 million years? A similar system of two TiO_2 polymorphs is presented in Figs. 5 and 6a. Rutile is a common accessory mineral formed in high-temperature and high-pressure metamorphic rocks. Anatase (and brookite) are less stable and revert to rutile at low temperatures (anatase at 915°C and brookite at 750°C). Considering that both rutile and anatase can be found as LDG inclusions, it leads to a doubt whether the temperature of cooling down was indeed so extremely high.

The spectrum shown in Fig. 6b belongs to zircon – a mineral also recognized as inclusion of LDG, however more often as a precursor of baddeleite (ZrO_2), which is a product of thermal decomposition of $ZrSiO_4$. In our investigation we didn't find any traces of baddeleite, but we definitely confirmed the presence of zircon, which would speak in favour of rather low or medium temperature of quenching.

The two inclusions pictured in Figs. 6c and 6d are even more mysterious than all described so far. Here we have two representatives of minerals which usually form sedimentary rocks. Its oceanic origin would be a good explanation of its occurrence in LDG, consistent with the hypothesis about water which filled in and finally eroded the missing crater. It would be very reasonable if these two soft minerals were found in the holes or cracks of our LDG specimens. However, these minerals were detected inside LDG objects, through a glass layer. In other words, these minerals must have appeared during the formation of LDG. There is an evidence of sedimentary minerals captured inside silica glass (Dakhleh Glass in Western Desert, Egypt), but the target rock in this case was completely different, which resulted in different glass chemistry (LDG is composed of 98% SiO_2, Dakhleh Glass only 50 to 60%) [19].

The inclusion in Fig. 7 was quite surprising as well. It is composed of at least two different phases – the white one, which MRS spectrum was only a big fluorescence hump, and the brownish one, which apparently contains amorphous carbon. MRS spectra in Fig. 7 represent different spots within the brown area. The two characteristic D and G band shape proves doubtlessly that carbon was there, but it doesn't give any explanation how organic matter could be preserved in hot molten silica.

There were also some inclusions which were difficult to determine by MRS; an example is given in Fig. 8. The white objects occurred a few times in the specimens; however, each time MRS spectrum was compromised by the fluorescence.

CONCLUSIONS

Several inclusions trapped inside the LDG specimens were successfully recognized by MRS. This technique was applied due to its non-destructive character because the examined objects are too precious to be damaged or altered in any way. Due to their transparent nature, it was possible to detect inclusions underneath the specimen surface. Moreover, if not compromised by fluorescence, MRS proves the presence of mineral species with no doubts. We confirmed that SiO_2 can be present as cristobalite and quartz; TiO_2 as rutile and anatase. Zircon was also detected, contrary to baddeleite which is usually reported as typical product of zircon decomposition in LDG. Unlike common hypotheses, our results confirmed the presence of low-temperature minerals inside LDG. The most unusual species were sedimentary minerals such as gypsum (anhydrite) and aragonite.

It would be useful to construct a hypothesis which could explain the origin of LDG together with all the inclusions. If the crater existed there would be no doubt to classify LDG as impactite similar to Darwin Glass – both species show flow-layered structures with elongated air bubbles; the structure of glassy matrix is also similar. LDG was proved to contain unusual patterns of Fe/Ir concentrations, representative for extraterrestrial matter. These facts are so far consistent with an impact way of formation, however this would implicate the high quenching temperature, which stays in contrast with low-temperature sediment minerals captured inside LDG and low-temperature polymorphs of silica. Let's assume that indeed there was an impact over the Earth surface, however not above the sandstone layer but over a sea. If the explosion had happened above or inside a shallow sea, it might have preserved the sediment minerals and also amorphous carbon from organic residues. The relatively big area of LDG abundance would suggest long distance transport of solidified pieces after their formation, although the shape of LDG specimens plus the lack of "honey-like swirls" do not support this theory. We believe that so far the best matching hypothesis might be very much alike to the one presented by Courty et al [20] referring to the impact-originated ejecta debris-jet dispersed along the Australian-Indian Ocean. Imagining a high tangential impact reaching first a shallow sea, where sediments are partially trapped by the large pieces and then flying again, propelled by vaporized sea water jet. Instead of one big crater, a series of shallow craters could have been produced and finally got eroded within 29 million years.

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List of Figures

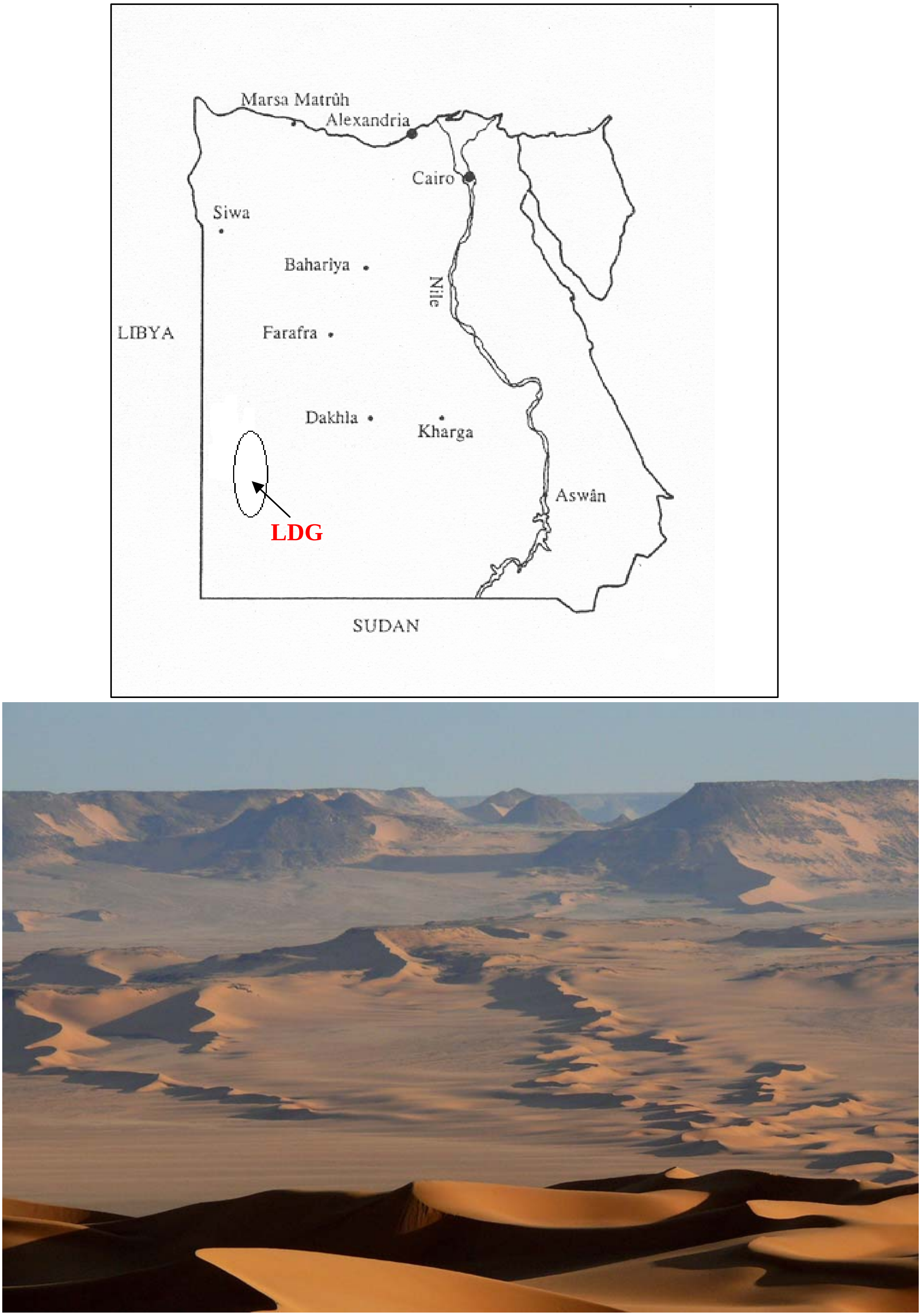


Fig.1: Map of Egypt with the outlined area rich with sand glass (LDG) and a view to Gilf Kebir Plateau (photo: Marcel Swaenen)

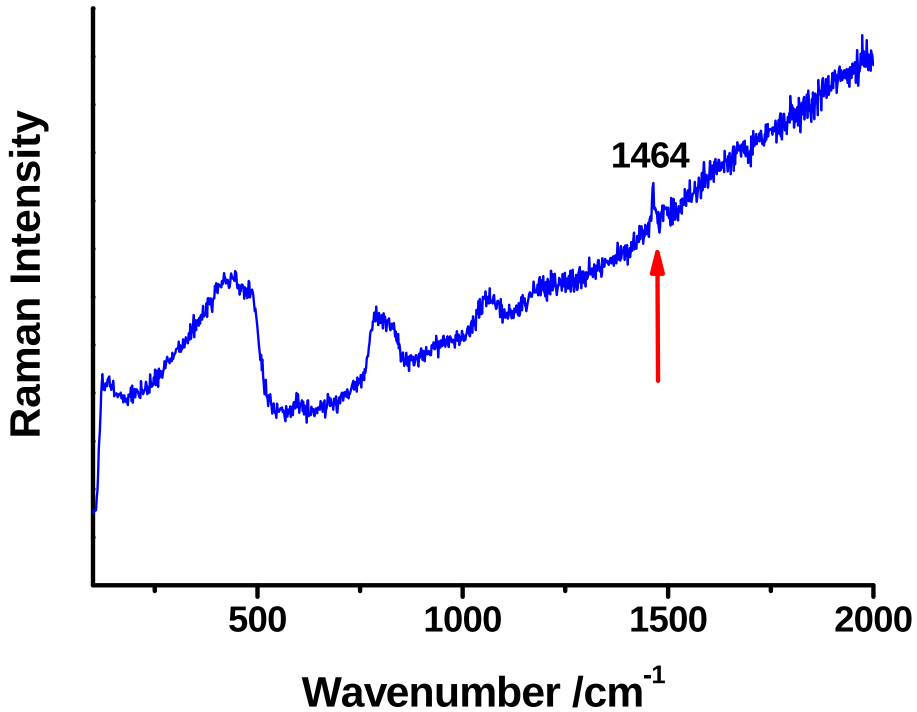
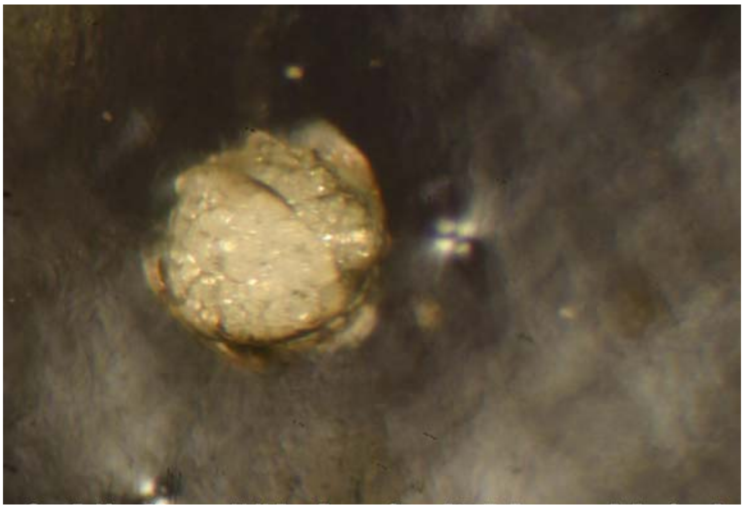
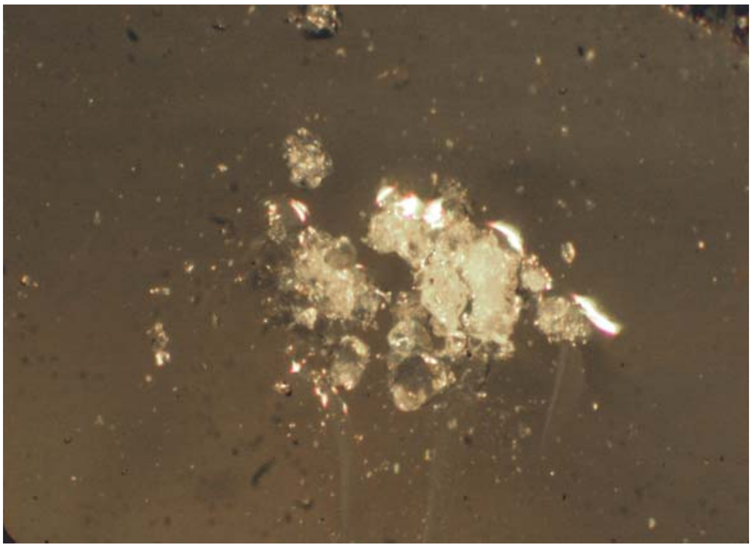


Fig.2: Above – a general view of a Libyan Desert Glass specimen (photo: Marcel Swaenen). Below - raw spectrum of glassy matrix and a black point inside, which is suggested to be fullerene.





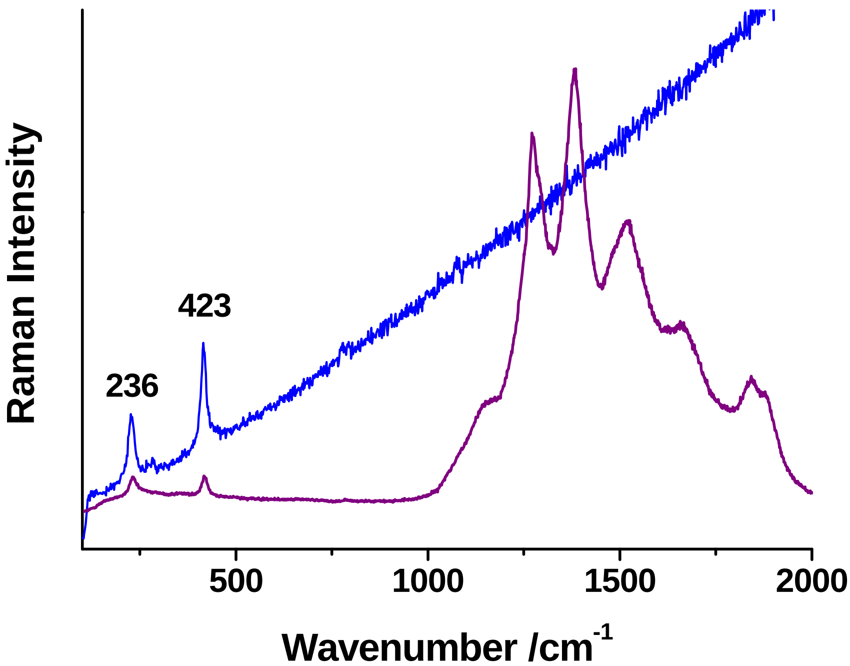
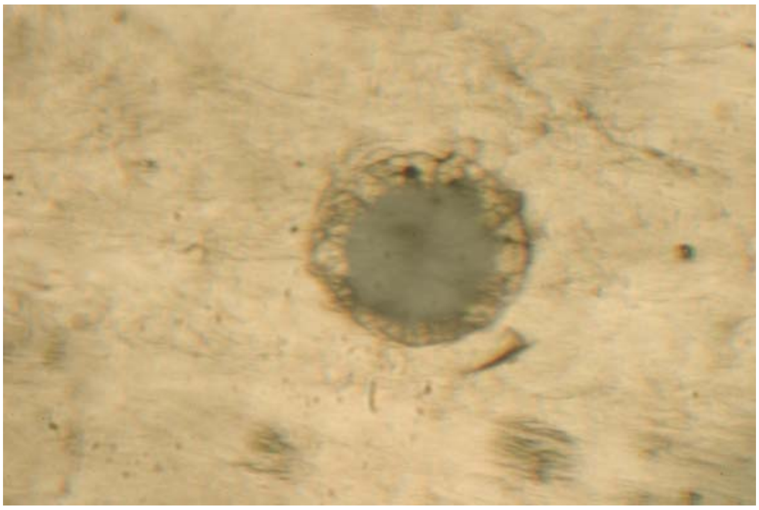
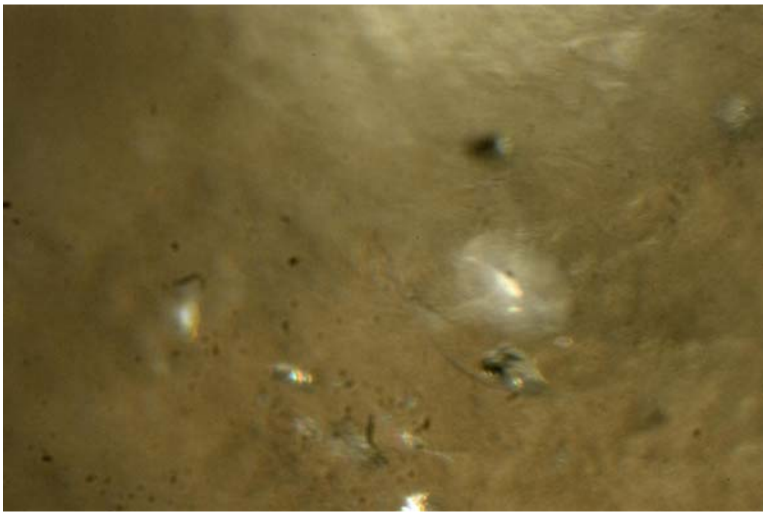

Raman Intensity
236
423
500
1000
1500
2000
Wavenumber /cm-1

Fig 3: Raman spectrum of cristobalite (upper line, upper photo) and Raman spectrum of cristobalite disturbed by luminescence (lower line, lower photo; the unusual shape of cristobalite inclusion is remarkable)





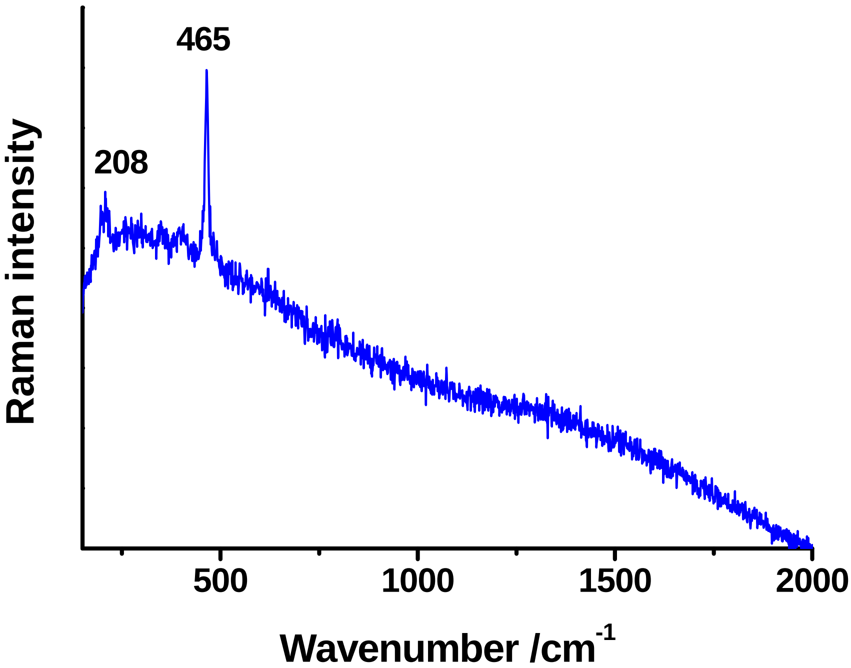

465
208
Raman intensity
500
1000
1500
2000
Wavenumber /cm-1

Fig. 4: Raman spectrum of quartz within two inclusions

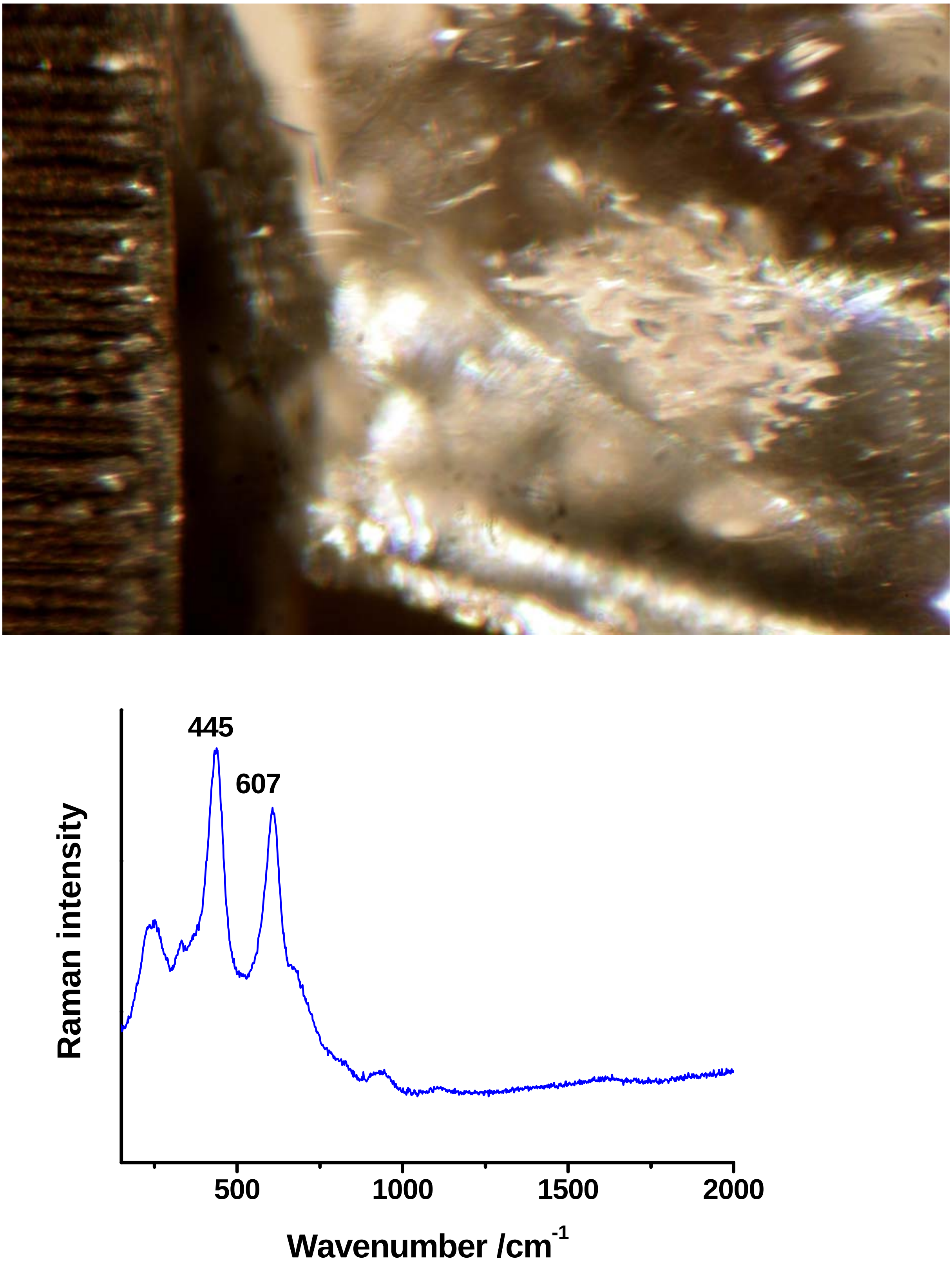


Fig.5: Raman spectrum of a rutile inclusion, most commonly, was present as white mist.

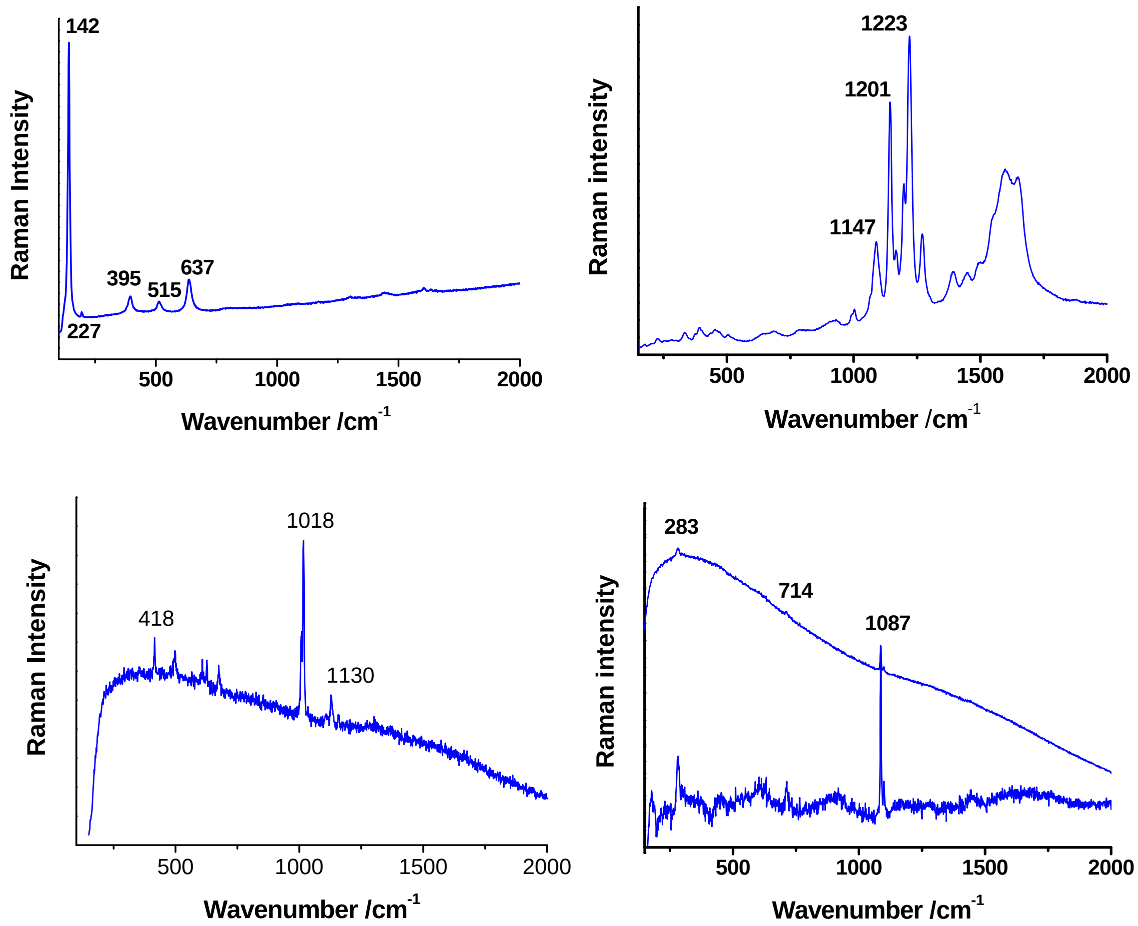
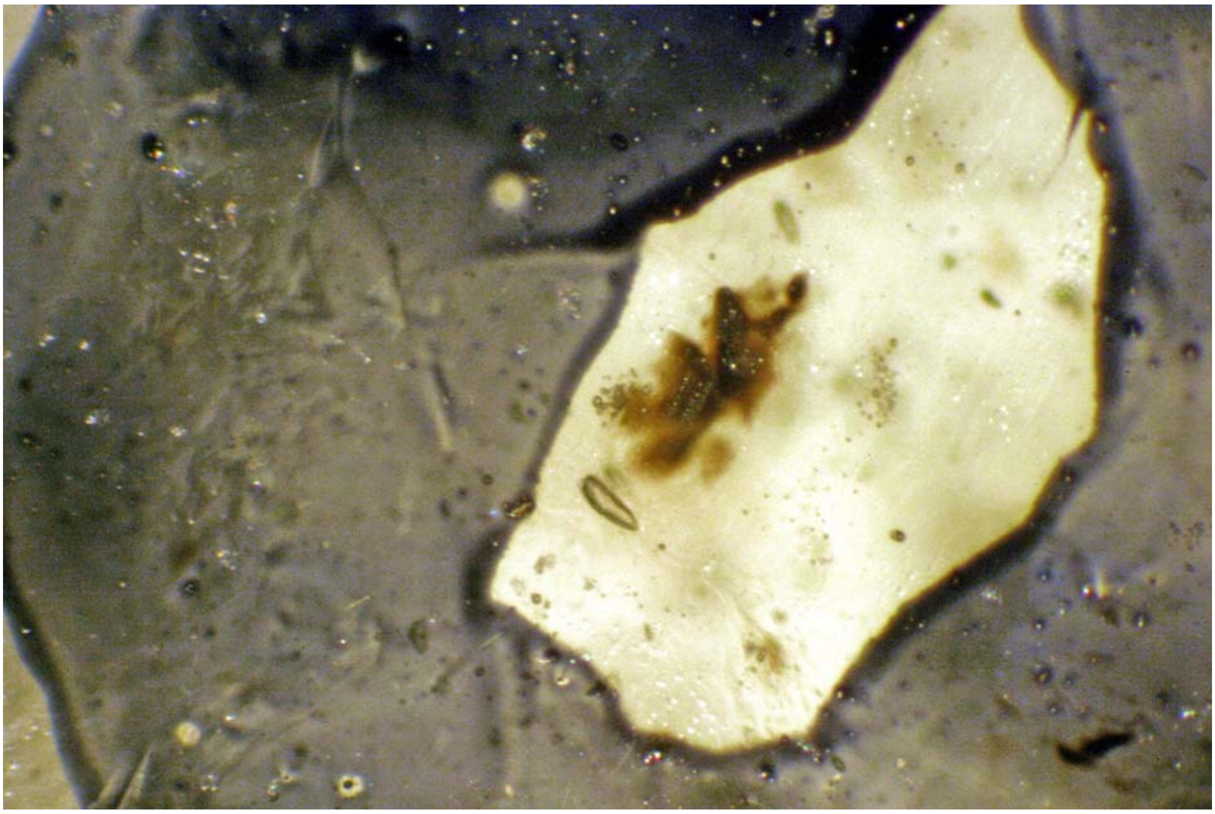


Fig.6: Raman spectrum showing an inclusion of: a) anatase; b) zircon; c) anhydrite; d) aragonite (the original spectrum - upper line, the spectrum with the background removed - lower line)



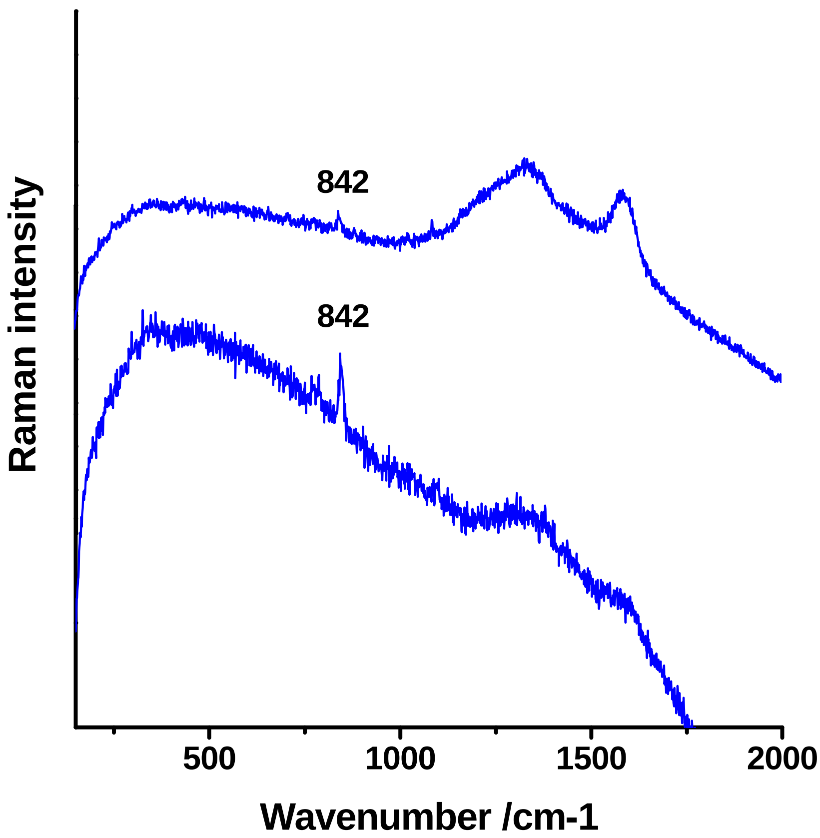
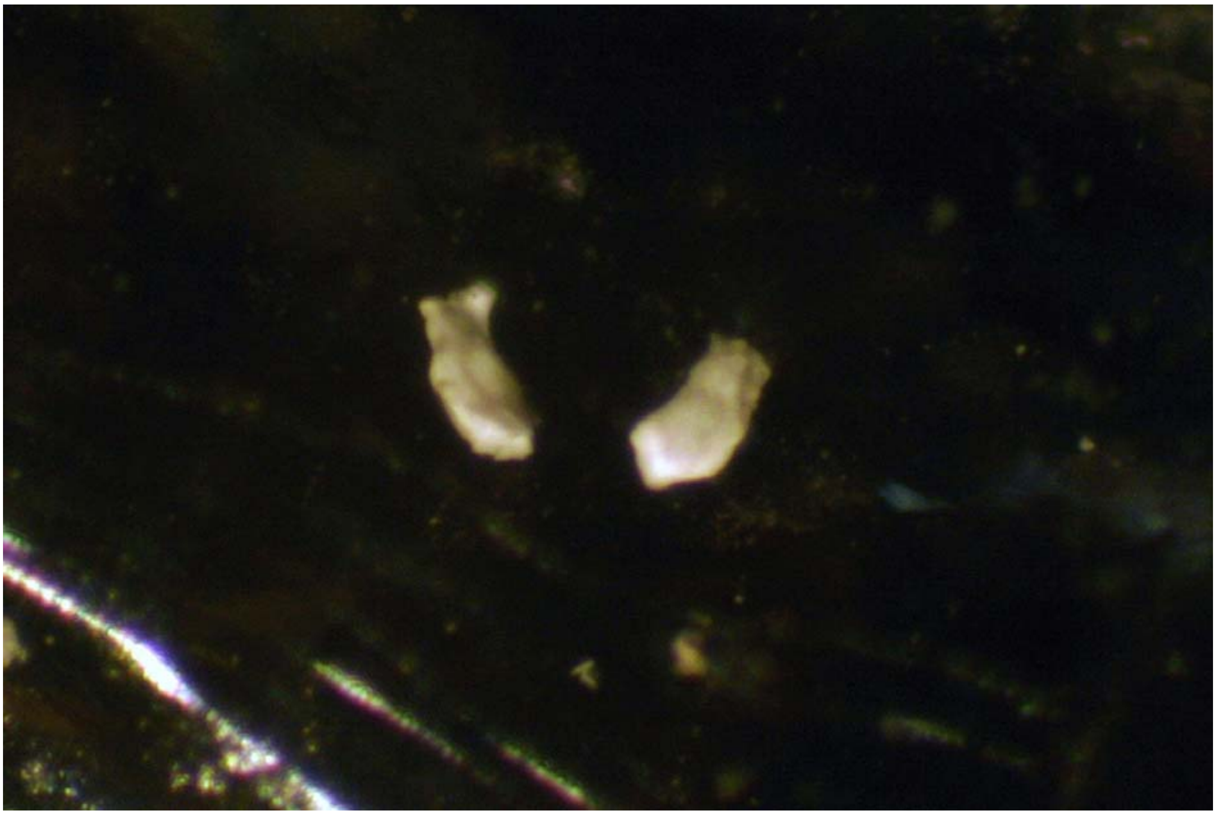


Fig 7: Raman spectrum showing a presence of amorphous carbon in one of the inclusions



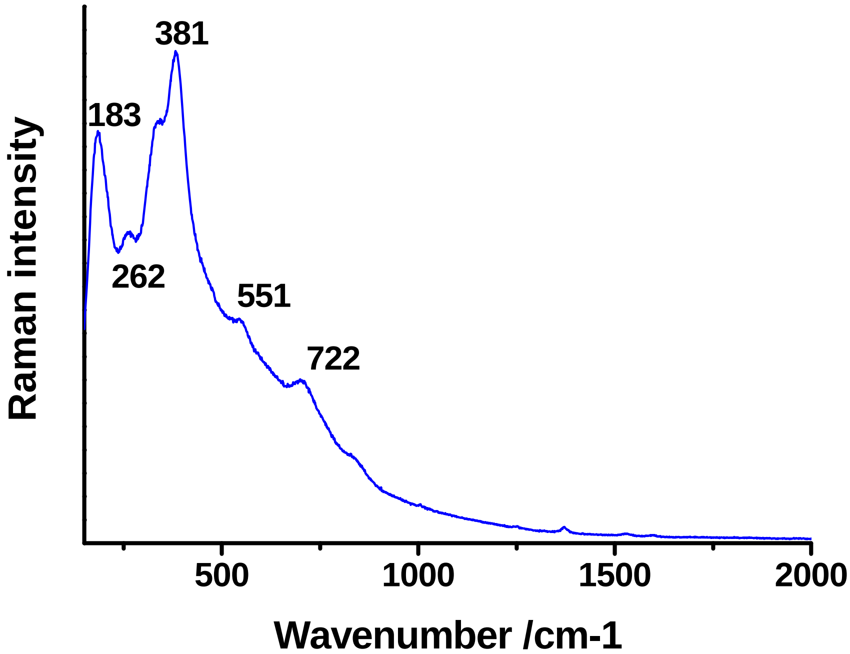


Fig.8: The Raman spectrum of an unidentified inclusion