

## **Spectroscopy of natural silica-rich glasses**

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Natural-silica-rich glasses (impactites, tektites and obsidians) have been investigated with infrared (IR), Raman and optical spectroscopy. Comparison with artificial glasses with silica-rich and alkali-rich compositions is made. The vibrational data of these compounds are discussed in relationship with their structures, particularly with respect to (i) Si–O–Si bonding differences, (ii) SiO<sub>4</sub>-ring arrangements, (iii) lattice disorder. IR spectra are strongly dependent on silica content: frequencies of the  $\nu_3$  and  $\nu_0$  bands increase with the silica content. A general finding in the Raman spectra of tektites, is the relationship between silica, alumina, sodium contents and the presence of vibrational bands peaked at very specific energies. Raman spectra of Libyan desert glass (LDG), Darwin glass (DG) and vitreous silica are almost identical with the typical doublet at 440–490 cm<sup>-1</sup> whereas in tektites the band at 440 cm<sup>-1</sup> has relatively less pronounced doublet structure. A common character of Raman spectra of tektites and obsidians is the appearance of broad bands centered around 1000 and 1600 cm<sup>-1</sup> due to substitutions of silicon by metals. Tektites have a strong absorption band at 1100 nm which originates from Fe<sup>2+</sup> ions. In the other glasses, this absorption is slightly shifted towards 1110–1130 nm. Additional sharp features of impactites and obsidians at 1380, 2210–2250 nm are completely absent in the absorption spectra of tektites. These bands are the signature of molecular water trapped inside the structure.

### **Introduction**

The aim of this paper is to present vibrational and optical spectroscopy experiments carried out on natural glasses (NG's): tektites, impactites and obsidians. In contrast to obsidians, NG's such as tektites and impactites are not igneous in origin and were most probably formed during meteoritic impacts. They are found in several strewn fields around the world (Dana's New Mineralogy, 1997). From the standpoint of physics, these materials are interesting because they were involved in explosive events at very high pressures during short periods of time and, in the case of tektites, were ejected at considerable distances (300 to 2000 km). Aerodynamic ablation, chemistry, inclusions, and water content of tektites act strongly in favor of this hypothesis.

Impactites like Darwin glass are materials which were not projected after impact but with properties close to tektites. The origin of one NG, Libyan desert glass (LDG) is not settled yet but it is also believed to be an impactite. In this work we provide further evidence of this origin.

Tektites in general are silica-rich glasses whose elemental composition is close to obsidians. Most of the NG's have the polymerized structure of the silicate skeleton in which Al atoms may replace Si atoms. Usual X-ray diffraction methods yield only the radial distribution functions and are not very sensitive to local range order. Therefore, vibrational and optical spectroscopies are necessary to gain further insights in these systems. Raman scattering is well adapted for the study of disordered materials, particularly in the case of NG's, magmatic materials, and synthetic glasses (McMillan and Piriou, 1983; White and Minser, 1984; McMillan, 1984). Although infrared and optical absorption spectroscopies are less sensitive to disorder than Raman spectroscopy, they have been used to determine for instance the water content of tektites which was found to

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**Table 1.** Origin, color and index of refraction of natural glasses

Glass	Name	Origin	Color	Index of refraction
TK1	Moldavite	Bohemia	bottle-green	1.490
TK2	Tektite Cau-Ca valley	Colombia	smoky grey	1.40
TK3	Australite	Charlotte Waters, Australia	black	1.505
TK4	Indochinite	China	black	-
TK5	Indochinite	Vietnam	black	1.512
LDG1	Lybian desert glass	Egypt	yellow	1.456
LDG2	Lybian desert glass	Egypt	transparent	1.458
LDG3	Lybian desert glass	Egypt	steel blue	-
DG	Mnt. Darwin glass	Tasmania, Australia	bottle-green	-
OB1	"Apache tear", obsidian	Arizona, USA	smoky brown	1.41.
OB2	"Rainbow" obsidian	Mexico	dark green	1.487

be very low (0.012% vs. 0.043%) in comparison to other natural glasses (Gilchrist et al., 1969). This low content indicates that tektites were quenched at pressures below 1 atmosphere during transit through the atmosphere immediately following impact. The samples studied in this work and their origin are listed in Table 1. Translucent light tektites (TK1 and TK2) are referred as L-tektites; for conciseness, black or dark tektites (TK3, TK4, TK5) are referred as D-tektites.

### Experimental details

Raman spectra were recorded using the  $\lambda_L = 514.5$  nm line of an Ar<sup>+</sup> laser with a Jobin-Yvon T64000 spectrometer equipped with a multichannel charge-coupled device (CCD) detector cooled at 77K. The glasses were analyzed under an Olympus microscope with a 100× times objective giving 2 micrometers spatial resolution in confocal setting. The polarized spectra are labelled either z(xx)z and z(xy)z, where z is the direction of incident and scattered light (backscattering geometry), (xx) and (xy) denote incident and scattered electric fields vectors parallel and perpendicular to each other, respectively. Fourier-transform Raman spectra were acquired out with a Bruker instrument using the 1064 nm excitation line of a Nd: YAG laser. Reflectance Fourier-transform infrared (FTIR) spectroscopic data were recorded with a 20 SXC Nicolet bench with 4 cm<sup>-1</sup> resolution. Optical spectra were taken with a Cary 5G

spectrophotometer. Experiments were conducted at room temperature.

Analyses were made with a Jeol 5800 LV scanning electron microscope (20 kV, 1.5 nA) coupled with an energy dispersive X-ray detector (Princeton Gamma Tech, IMIX-PTS). Trace elements were also detected with X-ray fluorescence spectroscopy (Tracor Spectrace 5000). Samples analyzed were 1.5 mm thick mirror-polished sections or faceted specimens. Some bulk, unfaceted samples were also analyzed. For each sample several analyses were made (Table 2). A synthetic glass S1 with a low silica content was used for comparison in IR and Raman experiments.

## Results and discussion

### Vibrations of silicates groups

The isolated (SiO<sub>4</sub>)<sup>4-</sup> tetrahedron has Td symmetry and therefore generates 4 vibrations: A<sub>1</sub>+E+2F<sub>2</sub>. E and F<sub>2</sub> are doubly and triply degenerate, respectively. The A<sub>1</sub> mode ( $\nu_1$ ) is a symmetrical stretch (tetrahedron breathing), the E mode ( $\nu_2$ ) is a bending involving silicon atoms. The first F<sub>2</sub> vibration ( $\nu_3$ ) is the stretching mode where the oxygen and silicon atoms move in opposite directions, whereas the other F<sub>2</sub> mode ( $\nu_4$ ) is a bending of Si atoms. It is worth noticing (Nakamoto, 1986) that only F<sub>2</sub> modes involve oxygen motions as it is also well established that for (SiO<sub>4</sub>)<sup>4-</sup> units the  $\nu_1$ ,  $\nu_2$ ,

**Table 2.** Composition of several natural glasses determined from EDX analysis Oxide percentages Chlorine in atomic percentage

Glass	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	MgO	K <sub>2</sub> O	Na <sub>2</sub> O	CaO	TiO <sub>2</sub>	Other
TK1, Moldavite	81.3	9.5	1.8	1.23	3.4	0.26	1.75	0.4	Zr, Rb Sr, Mn
TK2, Tektite Cau-Ca valley	74.9	12.5	0.8	0.1	4.6	3.6	0.6	0.1	0.13Cl
TK3, Australite	73.6	11.7	4.9	3.15	2.0	1.2	2.3	0.7	n.d.
TK4, Indochinite	72.7	13.5	4.6	1.9	2.5	1.3	1.8	0.7	n.d.
TK5, Indochinite	73.2	13.4	5.1	2.3	2.3	1.6	2.0	0.8	n.d.
LDG1, white	96.8	0.8	0.2	0	0	0.04	0.04	0.3	Zr, Sr
LDG2, Transparent	94.8	0.8	0.13	0	0	0	0.04	0	2 Rb, 1.2 Sr
LDG3, blue	95.4	1.04	0.31	0.18	0	0.01	0.03	0.08	2Rb, 0.9Sr
DG, Darwin glass	86.4	8.0	2.91	0.7	1.82	0	0	0.53	n.d.
OB1, Apache tear	69.5	13.7	0.6	0	5.4	5.5	0.5	0.3	0.07 Cl
OB2, "Rainbow" obsidian	74.4	11.3	1.7	0	4.4	4.5	0.2	0	n.d.
S 1, Synthetic glass	45.9	2.9	n.d.	n.d.	21.5	n.d.	28.9	n.d.	n.d.

$\nu_3$ , and  $\nu_4$  vibrational lines occur at respectively 819, 340, 956, 527  $\text{cm}^{-1}$ . All modes are Raman active, whereas only  $\nu_3$  and  $\nu_4$  are infrared active. In the solid state, however, the loss of symmetry due to the interconnections of tetrahedra relaxes the selection rules of isolated units, and all modes can be activated in IR.

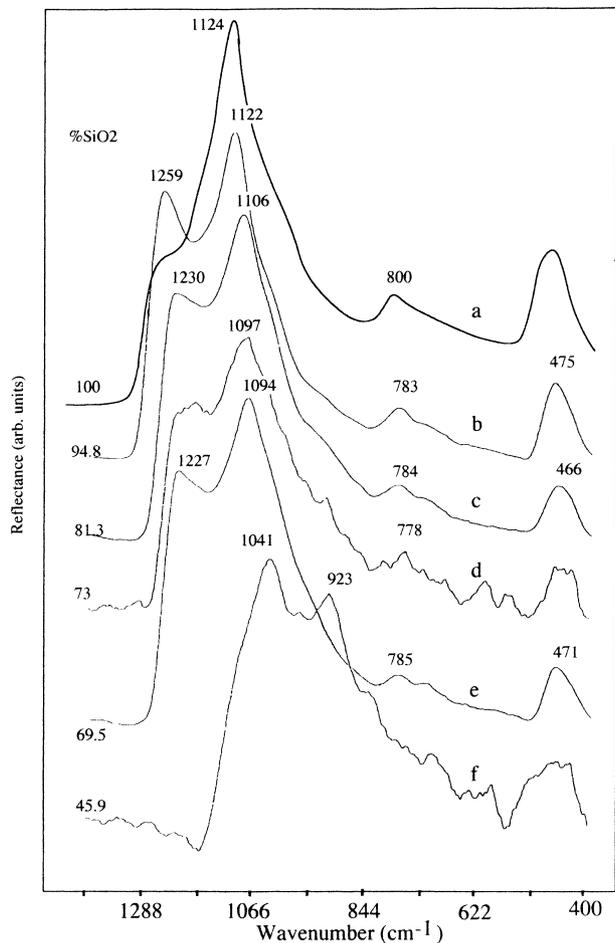
The vibrational frequencies of the silicate skeleton of oxide glasses occurs in three specific ranges (McMillan, 1984). From 400 to 600  $\text{cm}^{-1}$ , the vibrations involve bendings in and between the tetrahedra associated with cationic motions. These modes are strongly active in infrared and their scattering is intense. The vibration near 800  $\text{cm}^{-1}$  involve symmetric motions of adjacent Si atoms with respect to a bridging oxygen. The frequencies of these modes decrease with the Si-O-Si bridge angle. These modes are weakly infrared active and strongly Raman active. Finally, from 900 to 1200  $\text{cm}^{-1}$  Si-O vibrations prevail: the motion of oxygen atoms dominates the spectra and these frequencies increase with the degree of polymerization.

### Infrared spectra

The general shapes of the infrared spectra of tektites and silica glass exhibit obviously strong variations (Fig. 1). The common feature in the IR spectra is the occurrence

of two strong absorptions between 900 and 1300  $\text{cm}^{-1}$  whose energy depends the SiO<sub>2</sub> content of the glass. The first absorption component at low wavenumbers (923, 1094, 1106, 1124  $\text{cm}^{-1}$ ) is the  $\nu_3$  mode described above. The second absorption at higher wavenumbers (1041, 1230, 1259  $\text{cm}^{-1}$ ) is called by us  $\nu_b$ . Its wavenumber is likely connected with the structural disorder of the glasses. The most striking result is the frequency increase of the  $\nu_3$  and  $\nu_b$  bands with the Si content. In LDG (95% SiO<sub>2</sub>) the frequency of the ( $\nu_3$ ,  $\nu_b$ ) doublet is higher (1122, 1259  $\text{cm}^{-1}$ ) than in D-tektite (73% SiO<sub>2</sub>, 1097, 1220  $\text{cm}^{-1}$ ) and moldavites (81% SiO<sub>2</sub>, 1106, 1230  $\text{cm}^{-1}$ ). For the synthetic glass S1 (45.9% SiO<sub>2</sub>)  $\nu_3$  and  $\nu_b$  are located at 923 and 1045  $\text{cm}^{-1}$ , respectively. Our results agree with a previous report (Banerjee and Häger, 1993).

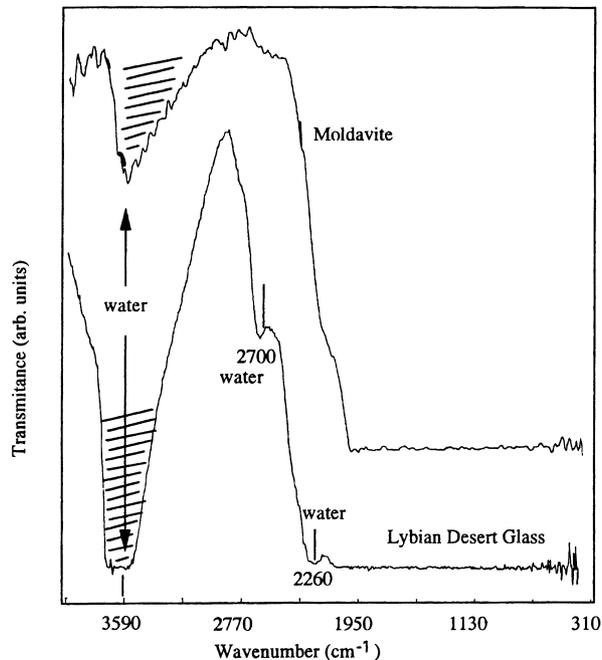
Two IR spectra taken in transmittance are presented in Figure 2 and show the bands at 2260, 2700 and 3590  $\text{cm}^{-1}$  in LDG1 and moldavite (TK1) samples with similar thickness. Two bands are due to combination modes of water molecules (2700  $\text{cm}^{-1}$ ) and OH-groups (2200  $\text{cm}^{-1}$ ). The band near 3600  $\text{cm}^{-1}$  is due to the OH stretches of both water and OH isolated groups (McMillan and Remmele, 1986). Qualitatively, it is obvious that LDG has a much higher water content than moldavite. The forthcoming results will confirm this point.



**Figure 1.** Infrared reflectance spectra of natural glasses and silica glass: a) vitreous silica glass—"Infrasil", b) Lybian desert glass LDG2, c) moldavite TK1, d) indochinite TK4, e) "Apache tear" obsidian OBI, f) alkali-rich synthetic glass S1 (46% SiO<sub>2</sub>)

### Raman spectra

The Raman spectrum of vitreous silica glass ("Infrasil") exhibits a broad feature between 100 and 550 cm<sup>-1</sup> (Fig. 3A, d). Note that it is relatively easy to reproduce theoretically this band with 4 Lorentzians of different intensities whose maxima are located at 315 and 389 cm<sup>-1</sup>, 445 and 488 cm<sup>-1</sup>. It is worth mentioning that these components coincide quite well with four intense superimposed Raman bands of fire opal which occur at 312, 410, 450 and 489 cm<sup>-1</sup>. In the spectrum of infrasil additional bands are found at 600, 610, 801, 840, 920, 945, 967, 984, 1043, 1068, 1160, 1183, 1220, 1605, 1655, and 1680 cm<sup>-1</sup> (Fig. 3B). For clarity they were not reported in this figure. As a help to identify the vibrational modes we use the assignments of previous publications (Bates, 1972; Etchepare et al., 1974, 1978; Sharma et al., 1981).

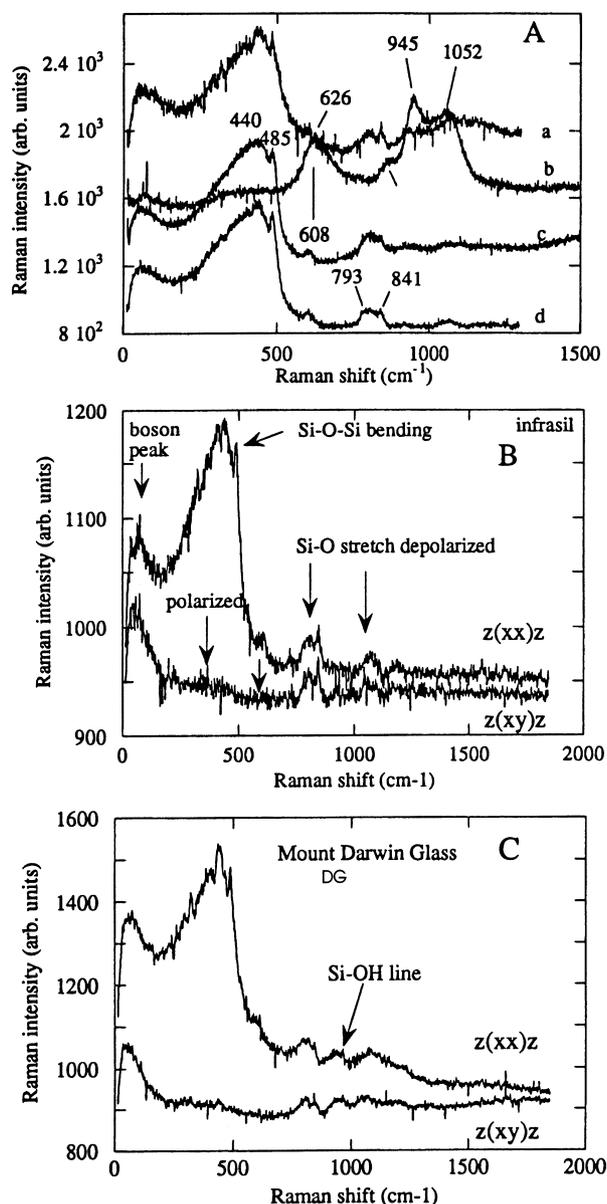


**Figure 2.** Infrared absorption spectra of water in moldavite (TK1) and Lybian desert glass (LDG1).

The spectra of Lybian desert glass (LDG1-3) and Darwin glass (DG) are almost identical to that of pure silica glass, with the typical doublet at 440-490 cm<sup>-1</sup> (Fig. 3A-a, c). For vitreous silica and these glasses, the bands below 650 cm<sup>-1</sup> (Si-O-Si bendings) are strongly polarized. The Boson peak at 50 cm<sup>-1</sup> and the other high wavenumber bands (Si-O stretching) are completely depolarized (Figure 3B, C). Duval et al. (1990) interpret it as the result of vibration localised in "blobs" that compose the glass and their size are in inverse proportion to the frequency.

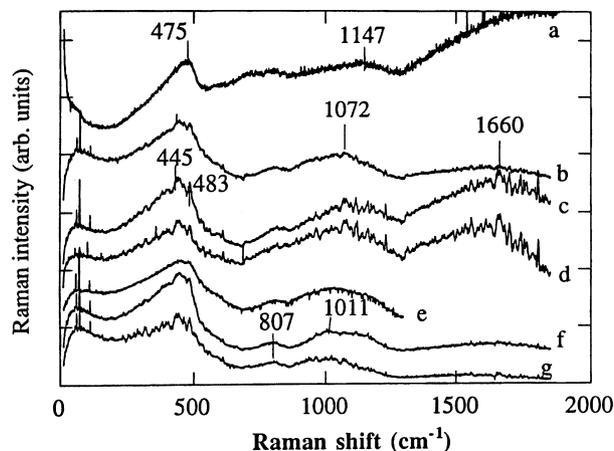
In the alkali-rich synthetic glass S1, the band at 430-490 cm<sup>-1</sup> is drastically reduced (Fig. 3A, b). The strongest bands are at 626, 867, and at 945-1052 cm<sup>-1</sup>. This is in sharp contrast with the silica-rich glass where the features around 600 and 1060 cm<sup>-1</sup> are very weak. We assume that the strong Raman doublet at 945-1052 cm<sup>-1</sup> is specific of the high alkali content (White and Minser, 1984; McMillan, 1984) and confirm that the broad band at 430-490 cm<sup>-1</sup> characterizes the silica framework which is in a much lesser proportion in S1.

Several Raman spectra of natural glasses and tektites are plotted in Figures 4 and 5. Spectra of moldavite (Fig. 5A), D-tektites (Fig. 5B) and obsidian (Fig. 5C) bear strong similarities. However, the Raman line-shapes do not resemble those obtained for vitreous silica and LDG glass. In particular, as displayed in Figure 4, the strong, broad and asymmetric band occurring with a maximum at 440 cm<sup>-1</sup> in the spectra of tektites has



**Figure 3.** Frame A: Raman spectra of a) Darwin glass DG (unpolarized), b) synthetic alkali-rich glass S1, c) yellow Lybian desert glass LDG1, d) vitreous silica glass-“Infrasil”. Frame B: Polarized Raman spectra of vitreous silica glass. Frame C: Polarized Raman spectra of Darwin glass.

relatively less pronounced doublet structure in comparison with vitreous silica glass and LDG. Clearly, the two components at 440 and 485  $\text{cm}^{-1}$  are much more intense, smooth, and pronounced in vitreous silica and LDG. The sharp peaks of medium intensity in the 600–1200  $\text{cm}^{-1}$  range are well expressed for vitreous silica, Darwin glass and LDG, whereas they are broadened, less resolved and smoothed in tektites. Raman spectroscopy thus confirms the structural difference between tektites and silica glass.



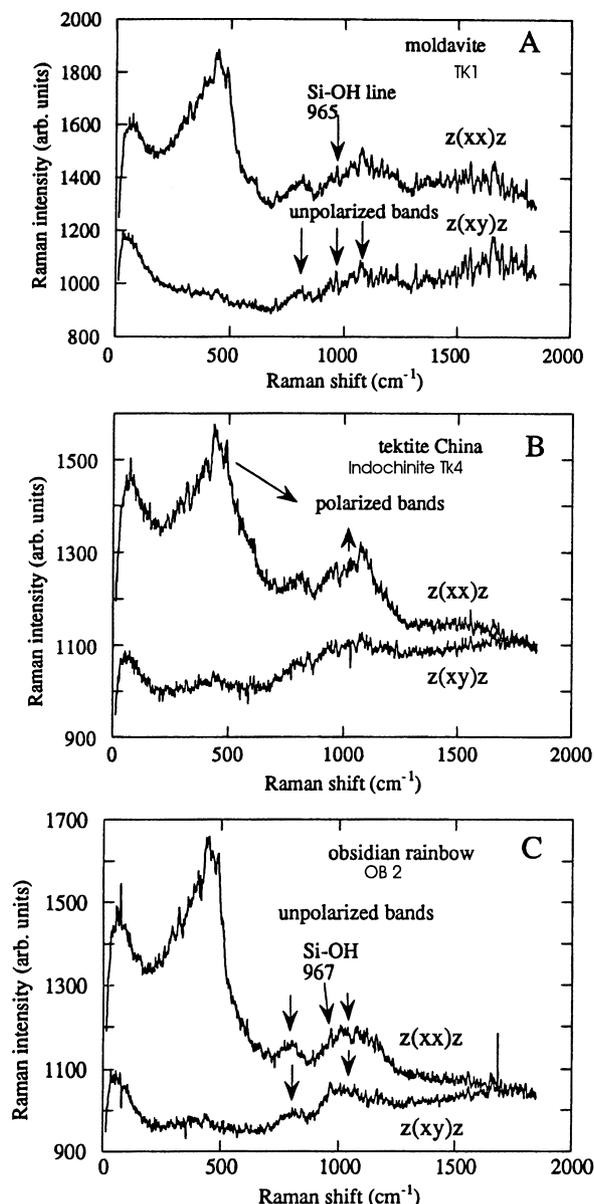
**Figure 4.** Raman spectra of natural glasses and tektites: a) “Apache tear” obsidian OB1, b) Indochinite TK4, c) moldavite TK1, d) tektite Cau-Ca TK2, e) australite TK3, f) “Rainbow” obsidian OB2, g) indochinite TK5.

Note the presence of the so-called D2 line at 608  $\text{cm}^{-1}$  in the Raman spectra of Darwin glass and LDG. The unpolarized spectra we recorded on both LDG and Darwin glasses (Fig. 3A, a, c) have a number of common features: a well expressed, intense doublet structure at 440–485  $\text{cm}^{-1}$ , the D2 line, and two medium bands at 793–841  $\text{cm}^{-1}$ . The overall lineshape of the spectra is almost the same. It is well-known that Darwin glass was produced 730000 years ago during an impact event with no transit into atmosphere, and therefore is an impactite (Gentner et al., 1973). Thus, vibrational spectroscopy provides support that LDG is also an impactite. In D-tektites, the Si-O bond gives two polarized strong bands at 1070 and 1200  $\text{cm}^{-1}$  (Fig. 5B). The 1130  $\text{cm}^{-1}$  band is ascribed to Al impurities and typical of Si-Al glasses (McMillan, 1984).

The spectrum of a dark obsidian (OB2) is closer to that of moldavite than to that of D-tektite since the bands above 650  $\text{cm}^{-1}$  are strongly depolarized (Figure 5C).

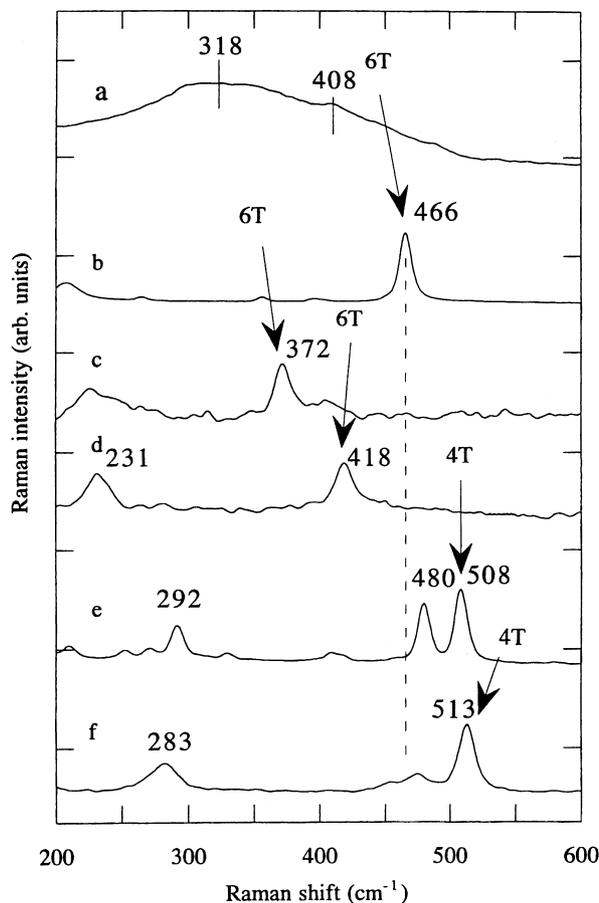
Spectra of infrasil glass (Fig. 3B) hardly show the weak line at 967 and 1630  $\text{cm}^{-1}$  characteristic of Si-OH and H-O-H bonds (McMillan and Remmele, 1986). The 967  $\text{cm}^{-1}$  line, although extremely weak, is seen in the spectra of moldavite, Darwin glass and obsidian (Figs. 4 and 5). This is a Raman signature of bonded water in the structure.

Spectra of  $\text{SiO}_2$  solids have common peculiarities correlated to motions of Si and O atoms in tetrahedral coordination. The bands above 600  $\text{cm}^{-1}$  are linked to the Si-O bond stretching whereas the twisting and bending modes of the Si-O-Si (in the tetrahedra) or T-O-T links (between tetrahedra) occur between 400–500



**Figure 5.** Polarized Raman spectra of natural glasses and tektites: A) moldavite, B) indochinite TK4, C) "Rainbow" obsidian OB2.

$\text{cm}^{-1}$ . In this latter region the Raman frequencies are correlated to the size of  $\text{SiO}_4$  rings in the silicate skeleton. Sharma et al. (1981) have shown that there should be a correlation between the strong modes at 465 and 521  $\text{cm}^{-1}$  in  $\alpha$ -quartz and coesite and the modes at 440 and 490  $\text{cm}^{-1}$  in silica glass. The frequency differences between the quartz polymorphs and silica glass (25 and 31  $\text{cm}^{-1}$ ) arise from differences in Si-O-Si bond angles. The cyclic structures with four  $\text{SiO}_4$  (in coesite or in feldspars) have a strong T-O-T mode above 500  $\text{cm}^{-1}$  (at 521  $\text{cm}^{-1}$  in coesite, 503 and 513  $\text{cm}^{-1}$  in anorthite and orthoclase) whereas six-ring cyclic structures



**Figure 6.** Fourier-transform Raman spectra of cyclosilicate compounds. The arrows show the  $\text{SiO}_4$ -ring-tracer band with the number of tetrahedra: a) fire opal for comparison, b) shocked quartz, c) elbaite tourmaline, d) cristobalite, e) albite  $\text{NaAlSi}_3\text{O}_8$ , f) orthoclase  $\text{KAlSi}_3\text{O}_8$ . Cristobalite is from inclusions in LDG.

(quartz, cristobalite and tridymite) have this mode below 500  $\text{cm}^{-1}$  (464, 416  $\text{cm}^{-1}$ : Fig. 6).

Such observations are particularly useful to ascribe spectral characteristics related to the distribution of cyclic units in silicate glasses. Raman spectroscopy can be used to discriminate three different structural configurations in silica glass. The bands at 440–490  $\text{cm}^{-1}$  and 500–520  $\text{cm}^{-1}$  are the signature of cyclic rings of six and four tetrahedra, respectively. The origin of the medium band often called D2 line at 608  $\text{cm}^{-1}$  is controversial. It has been first assigned to Si-O dangling bonds, i.e. to non-bridging oxygen atoms (NBO) occurring from structural defects generated by partial breaking of the Si-O-Si framework (Sharma et al., 1981). Another explanation of the D2 line is due to Galeener (1982) who ascribed it to the stretch of planar threefold  $\text{SiO}_4$  ring units (3T units). For the rest of our discussion we will keep both points of view.

Therefore, according to these data, the D-tektites contain mostly six-ring cyclic units. The LDG framework has both four- and six-membered rings, and 3T units if we take the view of Galeener. The relevant point to be underlined is that D-tektites and obsidians have lesser NBO's or lesser 3-membered  $\text{SiO}_4$  rings than impactites. The moldavite structure is not so clear-cut since a very weak D2 line is readily observed in  $z(xx)z$  geometry (Fig. 5A) although completely absent from the unpolarized spectra (Fig. 4). We conclude that the moldavite framework contains mostly six-membered rings with a small proportion of NBO's or 3T units.

Another point of discussion concerns the polarization of the bands. Since the Raman tensor reflects the symmetry of the system, and since the Raman intensity is proportional to the square of the polarizability, the Raman lines acquired in polarized light are of course linked to the local symmetry of the isolated vibrating group, for example in our case, to supramolecular  $\text{SiO}_4$  ring arrangements or to specific silicon bonding (Si-OH, Si-O, Si-Al). In glassy systems disorder affects the periodic arrangement of the atoms: the solid can present a random network or microcrystallite disorder in three dimensions. In perfect crystals periodicity of the lattice causes cancellation of dipole moments (IR activity) and polarizability (Raman activity) for all vibrational modes except those at phonon wavevector  $q=0$ . In amorphous solids, periodicity is absent and this rule no longer applies: intense, broad vibrational bands occur in the spectra and reflect the density of vibrational states  $g(\omega)$ , which is namely the histogram of the vibrational modes in the frequency range investigated. All vibrational modes, IR and Raman, are therefore allowed in the vibrational spectra (Barker and Sievers, 1975). The function  $g(\omega)$  is thus related to the vibrations in the solid as a whole and is in particular sensitive to structural long-range disorder. Thus, long-range order and crystallinity might in principle be probed by changes in  $g(\omega)$  and by the presence of sharp, intense features characterizing local oscillators. As a rule, an increase of polarization loss in a non-crystalline structure should be related to an increasing long-range disorder (or a decreasing long-range order) since the vibrational selection rules of the perfect crystalline solid do not apply. Application of this qualitative criterion to our glasses suggests that tektites have higher crystallinity than vitreous silica, Darwin glass, LDG and obsidian. The intense features of the glasses are completely polarized below  $500\text{ cm}^{-1}$ . This implies high degree of  $\text{SiO}_4$  ring organization and pronounced short-range order. Nevertheless, polarized spectra display systematic variations above  $500\text{ cm}^{-1}$  depending on the glass analyzed.

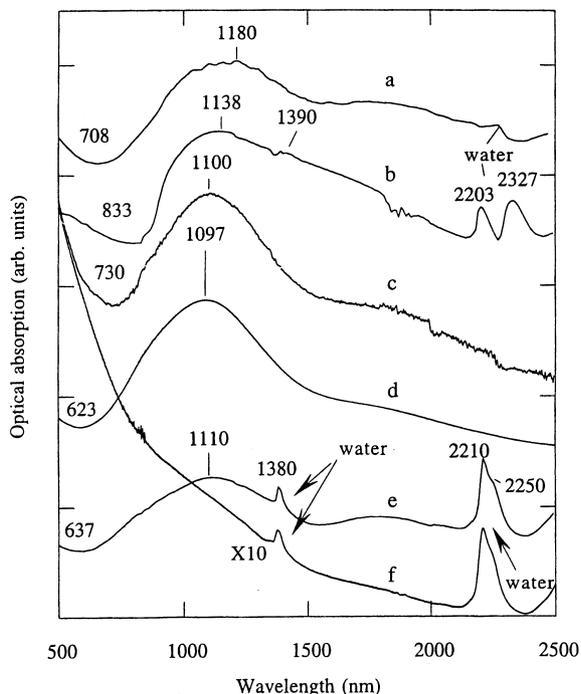
High polarization loss is observed for vitreous silica, impactites and obsidian, whereas for moldavite or for the TK4 tektite the  $z(xy)z$  spectra are strongly reduced in intensity. This may be explained by the chemical composition of D-tektites which have 10 to 14% of Al and a few % of other elements (Ca, Mg, Na, K). When Si atoms are substituted for these elements in the silicate skeleton the number of NBO's is reduced. Such defects modify the density of vibrational states of tektites and give rise to localized modes more or less polarized ( $1130\text{--}1140\text{ cm}^{-1}$ ) with high symmetry. In contrast, LDG and vitreous silica have little of these substitutional defects leaving a higher NBO figure. Also, the degree of order seems to be linked to the ratio between six- and four-membered rings, this ratio being higher for higher crystalline glasses.

Specific inclusions found in tektites like (gas bubbles and lechatelierite) were also probed with micro-Raman spectroscopy. Most of the bubbles are voids and confirm that the glasses were cooled in high atmosphere. In the case of LDG, micro-Raman spectroscopy shows that  $\alpha$ -cristobalite is the constituent of the small white inclusions (1-2 mm) in the bulk material (Fig. 6).

### Optical spectra

Figure 7 presents some absorption spectra taken in the visible-near IR region. Tektites have a strong absorption band at 1100 nm which originates from  $\text{Fe}^{2+}$  ions (Cohen, 1958; Bykov, 1996). In the other glasses, this absorption is slightly shifted towards 1110-1130 nm. Transparent LDG has a very weak absorption, in strong contrast to yellow (LDG1) and blue (LDG3 not shown here) samples which therefore contain a higher amount of ferrous iron. The set of results show that tektites are high in ferrous ion. In OBI we note a shoulder feature near 500 nm. In all the samples except OBI, LDG1, and LDG3 a weaker broad band appears with variable intensity between 1500 and 2100 nm, centered at 1800-1900 nm. These bands are from unknown origin.

Additional sharp features of impactites and obsidian at 1380, 2210-2250 nm (superimposed) are completely absent in the absorption spectra of tektites. These bands are the signature of molecular water trapped inside the structure (Adams, 1961). The fact they are relatively strong indicates that the proportion of water in obsidian is much higher than in tektites. The optical spectrum of the impactite Darwin glass does not exhibit strong bands at these positions whereas LDG does.



**Figure 7.** Optical spectra (VIS/NIR) of natural glasses: a) Darwin glass DG, b) Apache tear OB1, c) tektite TK5, d) moldavite TK1, e) Lybian desert glass yellow (LDG1), f) Lybian desert glass transparent (LDG2). The spectrum of the blue glass LDG3 is similar to that of LDG1.

### Conclusion

In summary, the vibrations which dominate the spectra of silica-rich glasses are those of basic units, i.e. the  $\text{SiO}_4$  tetrahedra, and of nanometric ring structures. In IR spectroscopy, the positions of the maximum absorptions are related to the  $\text{SiO}_2$  concentration of the glasses. The vibrational spectra are sensitive to the short-range order but yield also information about the overall long-range disorder. In the commonly accepted scheme a silica glass is composed of randomly connected  $\text{SiO}_4$  units "condensed" by Si-O-Si bonds. Both isolated and condensed group vibrations occur. The presence of ring structures, additionally, is now well established since the vibrational spectra appear well structured between 400 and 700  $\text{cm}^{-1}$ . From the studies of the intense band near 440  $\text{cm}^{-1}$  we conclude that natural glasses present an intrinsic short-range organization, to a lesser degree than in silica glass. Tektites appear to contain more 6-membered  $\text{SiO}_4$  ring units than impactites which have a structure close to vitreous silica with 6 to 3-membered  $\text{SiO}_4$  rings. The spectral detection of defect modes is also helpful for the structural determination of natural glasses. For instance, when Si-O-Si bridges are broken Si-O<sup>-</sup> bonds give strong

additional signatures from non-bridging oxygen atom (NBO) vibrations. In tektites the NBO's are nearly absent since these glasses contain Al, Fe, K, Mg, Ti atoms replacing Si atoms or entering the structure at defect sites which can be detected both with vibrational and visible absorption spectroscopies as is the case of  $\text{Fe}^{2+}$  ions. Raman spectra of LDG, Darwin glass and vitreous silica are almost identical and therefore their  $\text{SiO}_2$  frameworks are expected to be, in average, the same. However, tektites are characterized by Raman bands appearing around 1070  $\text{cm}^{-1}$  and 1600  $\text{cm}^{-1}$ . In obsidians, richer in alkali, the profile of the 1070  $\text{cm}^{-1}$  band is broadened towards higher wavenumbers (1120–1150  $\text{cm}^{-1}$ ) and this band is almost smeared out. It appears also that tektites possess the higher long-range order and higher polymerization than impactites, obsidians and vitreous silica which are less crystalline. This structure is likely connected with their low water content as probed with visible-near IR spectroscopy.

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