The Libyan Desert Silica Glass as a product of meteoritic impact: A new chemical-mechanical characterization

Marta Guzzafame
Francesco Marino[*]
Nicola Pugno[**]

Introduction

Silica Glass was discovered in 1932 by Patrick A. Clayton (Clayton, 1996) during the first direct crossing of the Great Sand Sea, in Egypt. Since its discovery, it resulted very interesting for the scientific community because of its mysterious origin (de Michele, 1997). It is about 29 million years old and its major compounds are: SiO_2 (about 98-99%), Al_2O_3 (about 1%), FeO (about 0.1%), and trace of Fe_2O_3 and TiO_2 (Diemer, 1996; Fudali, 1981). The chemical homogeneity of the Libyan Desert Silica Glass (LDSG) is clearly demonstrated by the results of trace-element analyses on many specimens.

The glass contains many types of inclusions (Diemer, 1996), such as bubbles, cristobalite spherulites, minerals and layered dark streaks, and two different types of glass can be distinguished on the basis of their colour: the yellow (richer of SiO_2) and the green glass (richer of Fe^{2+} and Fe^{3+} and other siderophile elements). In addition several specimens present a layered structure, showing yellow and green layers interchanged.

The mysterious and fascinating aspects of the LDSG are numerous: its origin and the triboluminescence (a particular type of luminescence that the glass shows when exposed to friction) are the main examples.

Several hypotheses about its origin were proposed by many scientists during these years, such as hydrothermal volcanic eruption (Cohen, 1961; Feller, 1996), the fall of a celestial body that produced melting of the bedrock (Rocchia *et al*., 1996), or a shower of solid materials originated elsewhere (O'Keefe, 1976). However, recent studies lead most researches to think that the LDSG is the result of the melting of a terrestrial material, and that the melting process could be the result of the impact or airburst of an extraterrestrial body (Rocchia *et al*., 1997).

The LDSG has been widely studied by several geologists and scientists, but this is the first time that it is investigated with nanoindentation techniques; new tests, typical of the Material Science have also been performed, with the aim to examine closely its physical properties.

Therefore, the aim of this paper is a chemical-mechanical characterization of some LDSG and outcropping rocks specimens, with particular attention on nanoindentations and wear tests. For the chemical-structural characterization, XRF Spectrophotometry and X-Ray analysis were performed.

Experimental

Glass and rock specimens were kindly provided by Vincenzo de Michele, Giancarlo Negro and Benito Piacenza, who collected them during the 1991-1996 field trips in the Western Desert carried out in agreement with the EGSMA (Egyptian Geological Service and Mining Authority), with the aid of the EGSMA Geologist Aly Barakat.

Two types of LDSG (yellow and green glasses) and three types of local rocks (Upper Cretaceous sandstones of different colours: red, pink and brown) were analyzed in the following tests.

XRF Spectrophotometry was performed with a Rigaku ZSX machine, using a Rh X-ray tube. Analysis was conducted on specimens of two yellow glasses, one green glass and a red sandstone, in order to distinguish between different types of glass on the basis of their composition, and to compare them with rocks collected in the desert near the place where the glass was found.

X-ray analysis was performed with a Philips PW 3830 diffractometer on a yellow glass powder, with 2θ between 10° and 65°.

Nanoindentations were performed in order to evaluate hardness and Young's modulus, and their dependence on the indentation depth, as well as to evaluate the glass homogeneity, especially in those pieces with a layered structure. These measurements were performed using a Nanoindenter XP with TextWorks 4 Software (MTS Nano Instruments,

[*] *Dept of Material Science and Chemical Engineering*
[**] *Dept of Structural Engineering and Geotechnics*
Politecnico di Torino
Corso Duca degli Abruzzi, 24
10129 Torino (Italy)
nicola.pugno @ polito.it

Fig. 1. The yellow LDSG and the related specimen prepared for the nanoindentation test.

Component	Yellow glass with bubbles	Yellow glass without bubbles	Green glass without bubbles	Red sandstone
SiO_2	97.1944	96.711	92.519	97.439
Al_2O_3	0.8581	1.191	1.880	1.116
Na_2O	0.8462	0.994	0.531	0.061
MgO	0.0776	0.112	0.132	0.178
TiO_2	0.0719	0.204	0.807	0.048
Fe_2O_3	0.0591	0.136	2.093	0.525
ZrO_2	0.0162	0.036	0.121	0.007
SrO	0.0018	0.023	0.018	-
CaO	0.0803	0.057	0.850	0.369
K_2O	0.2683	0.151	0.253	0.039
P_2O_5	0.0297	0.027	0.245	0.054
SO_3	0.1196	0.066	0.161	0.080
Cr_2O_3	-	-	0.031	-
MnO	-	-	0.030	-
Co_2O_3	-	-	0.012	-
NiO	0.0038	-	0.038	0.004
CuO	-	-	0.023	0.003
As_2O_3	-	-	0.005	-
Y_2O_3	-	-	0.005	-
BaO	-	-	0.128	0.037
Yb_2O_3	-	-	0.023	-

Table 1: XRF Spectrophotometry (values are in weight %).

Oak Ridge TN) and a Berkovich tip (XP Users Manual, 2002). Three different analyses were performed, with the aim to measure hardness (H) and Young's modulus (E) in different specimens, so the nanoindentation tests can be divided into three parts:

First part: Hardness and Young's modulus in a yellow glass specimen with a medium concentration of gas bubbles (Fig. 1). Indentation has been performed at different maximum depths: from 250 nm to 2 µm, with a step of 250 nm.

Second part: Hardness and Young's modulus in six different glass and rock specimens: G_y (yellow glass without bubbles), G_{yb} (yellow glass with bubbles), G_g (green glass without bubbles), G_{gb} (green glass with bubbles), R_r (red rock), R_p (pink rock). In every specimen 20 indentations were performed at two different depths (750 nm and 1500 nm).

Third part: Hardness and Young's modulus of a glass specimen. Indentations were performed in 4 different layers of a specimen, at two different depths (750 nm and 1.5 µm). Two yellow and two green layers have been chosen.

All specimens were cut using a Remet Micromet cutting-off machine with a 200 mm diameter diamond blade and then incorporated inside a resin support (a 30 mm diameter cylinder).

During every test the distance between the indentation points was increased by increasing the indentation depth in order to avoid their self-interactions (near the indentation point there are residual tensions and the following indentation would be affected by edge effects and tensions overlaps) (Pugno, 2007).

Lastly, wear resistance was evaluated with a non-standard test: two pieces of rocks (red sandstone R_r and brown sandstone R_b) and two pieces of yellow glass without bubbles (G_{y1} and G_{y2}) were mixed with corundum powder for 1500 minutes. Weight loss (wear rate) and superficial roughness variation were evaluated, using a Hommel Tester T1000 profilometer.

With regard to this test, some photographs of the surface were made with a SEM FEI Quanta Inspect 200 LV and an EDS EDAX Genesis probe, in order to observe the roughness variation on the surface of the glass.

This test is very interesting because it allows the evaluation of the effective wear resistance, in order to understand how the glass has survived for 29 millions of years without disappearing because of the erosion, and maybe why, instead, we can find no traces of the crater originated by the impacting body.

Results and Discussion

Results of the XRF Spectrophotometry, giving the glass chemical composition, are reported in Table 1.

The scattering pattern obtained with the X-Ray analysis is reported in Fig. 2. It shows that the glass is completely amorphous, as expected.

Nanoindentations results were analyzed with the Weibull's statistics, showing a good correlation (Weibull, 1939).

In the *first part* of the work an increasing behaviour of hardness and Young's modulus as a function of the indentation depth were observed, as shown in Table 2.

It can also be analyzed the value of the Weibull's modulus referred to Young's modulus and to the hardness (Table 2). The first one increases with the indentation depth, while the second one shows an irregular trend.

In the *second part*, instead, mean E and H in different glass and rocks specimens have been compared. The values are shown in Tables 3 and 4.

Rocks (R_r and R_p) present a lower value of H (with the smallest value of 5.8 GPa for R_r) and higher E than the LDSG (with a maximum value of 88.5 GPA for R_r) while, between the different types of glass, the green glass (G_g and G_{gb}) has greater H and E, with maximum values of 9.4 and 71.4 GPa respectively for G_g. In addition, E decreases with indentation depth in every specimen except for G_{yb} and H increases with indentation depth in every specimen except for G_g.

In regard to the *third part* of the nanoindentation work, the mean values of H and E measured in four different layers of a layered structured glass specimen are reported in Tables 5 and 6.

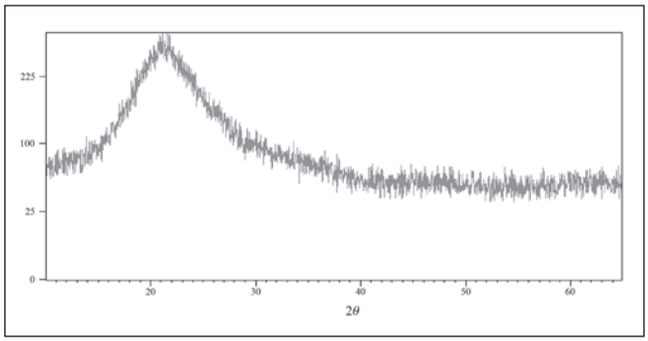

Fig. 2. X-Ray analysis on a powder of a yellow LDSG specimen; number of counts versus specimen-ray relative orientation.

N	Ind. depth (nm)	E (GPa)	H (GPa)	m(E)	m(H)
10	250	67.6	7.6	5.4	1.2
10	500	66.3	8.2	8.3	3.0
10	750	68.3	9.2	5.5	5.6
10	1000	67.5	9.4	48.2	22.9
9	1250	66.1	9.4	50.9	48.0
8	1500	65.3	9.4	48.1	25.5
10	1750	64.7	9.4	46.6	26.0
10	2000	64.0	9.4	61.0	41.0
	Mean Value	66.2	9.0	34.3	21.6

Table 2. Number of successful nanoindentations (N), mean values of E and H and Weibull's modulus referred to E and H at different indentation depths in a yellow glass specimen.

750 nm	N	E (GPa)	H (GPa)	m(E)	m(H)
G_y	17	68.3	8.4	11.0	8.6
G_{yb}	20	66.3	8.5	23.6	8.3
G_g	13	71.4	9.4	12.3	7.6
G_{gb}	18	71.3	9.3	51.2	24.4
R_r	20	84.5	5.8	4.3	2.0
R_p	17	86.9	8	5.8	2.5

Table 3. Number of successful nanoindentations (N), mean value of E and H and Weibull's modulus referred to E and H in different glasses and rocks at a depth of 750 nm.

1500 nm	N	E (GPa)	H (GPa)	m(E)	m(H)
G_y	17	67.9	8.7	10.2	6.3
G_{yb}	20	67.2	9.1	15.8	8.2
G_g	19	68.4	8.7	18.9	8.0
G_{gb}	20	70.7	9.3	31.6	17.0
R_r	17	88.5	7	4.7	2.3
R_p	-	-	-		

Table 4. Number of successful nanoindentations (N), mean values of E and H and Weibull's modulus referred to E and H in different glasses and rocks at a depth of 1500 nm.

From these data it can be observed that H and E at 1500 nm are irregular, while they increase at 750 nm, from the yellow layer L_{y1} (that is on the surface of the specimen) to the green layer L_{g4} (that is in the bulk).

In all these tests hardness increases surprisingly (Pugno, 2007) with the indentation depth, while a similar trend for the Young's modulus cannot be observed.

In the wear resistance test, the glass presents a lower wear rate, as shown in Table 7, this means that the glass has a greater erosion resistance than the rocks. The wear rate is calculated as $(W_i-W_f)/W_i$, where $W_{i,f}$ are the initial/final weights of the specimen.

In addition, also the mean superficial roughness (Ra) variation was measured, as reported in Table 8. From these values of Ra it can be concluded that all roughness values increase, except for the red sandstone, because R_r has been dressed.

It must be said that these are just preliminary tests; it should be considered that rocks are more irregular and porous than the glasses and their exposed surfaces are greater. These facts lead to a greater wear rate, but the wear rate per time and surface unit is quite the same for glasses and rocks, a little bit greater for glass. The tests are interesting but they would have to be conducted for a longer time to have a more readable wear rate, considering that 1500 minutes are a very limited time compared to the age of the glass. In addition, the glass shows a greater increase of Ra, but it was polished before the test while it was impossible to polish the rocks, because of their irregularity and porosity.

However these tests are a first, interesting estimate of the erosion resistance of the LDSG compared to the rocks of the desert.

Numerous photographs of the glass surface at 1000X and 3000X before and after the test (Fig. 3 and 4, showing G_{y1}) were taken. From these images it can be observed a greater superficial irregularity and roughness after the test, and from Fig. 4 it can be noted that the corundum particles remained embedded in the glass surface (this fact justifies the very low weight loss during the test).

Table 5. Number of successful nanoindentations (N), mean values of E and H and Weibull's modulus referred to E and H in different layers of a specimen at a depth of 750 nm.

750 nm	N	E (GPa)	H (GPa)	m(E)	m(H)
L_{y1}	8	35.3	3.4	5.3	3.0
L_{g2}	8	51.6	4.0	3.2	1.9
L_{y3}	17	64.0	8.0	7.6	2.7
L_{g4}	16	70.1	9.4	33.5	19.5

Table 6. Number of successful nanoindentations (N), mean values of E and H and Weibull's modulus referred to E and H in different layers of a specimen at a depth of 1500 nm.

1500 nm	N	E (GPa)	H (GPa)	m(E)	m(H)
L_{y1}	3	64.8	8.5	14.3	8.3
L_{g2}	10	40.3	4.2	3.1	2.1
L_{y3}	12	64.7	9.0	12.8	9.7
L_{g4}	18	66.6	9.2	57.4	34.1

	Initial weight (g)	Final weight (g)	Wear rate (%)	Wear rate per time and surface unit (%)
G_{y1}	3.2201	3.2174	0.08	0.001
G_{y2}	2.3415	2.3348	0.28	0.004
R_r	11.2214	11.2068	0.13	0.001
R_b	5.6594	5.6414	0.32	0.003

Table 7. Initial and final weights and wear rate of the different glass and rock specimens.

	Initial Ra (μm)	Final Ra (μm)
G_{y1}	0.186	0.412
G_{y2}	0.180	0.745
R_r	3.270	2.740
R_b	5.020	6.630

Table 8. Superficial Roughness before and after the erosion test.

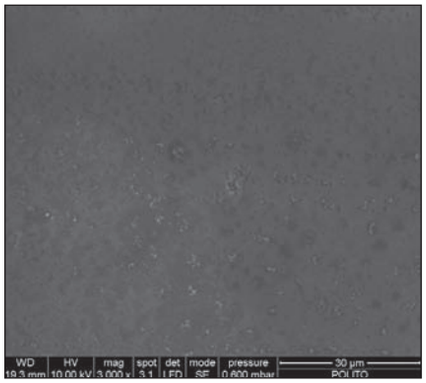

Fig. 3. Micrograph at 3000X of G_{y1} surface before the wear test.

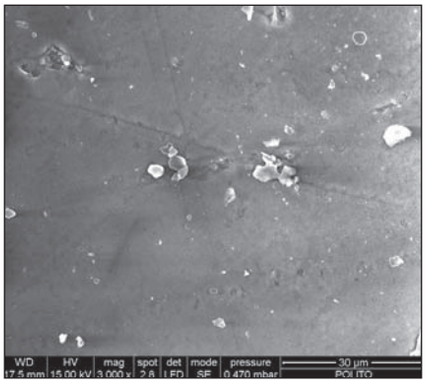

Fig. 4. Micrograph at 3000X of G_{y1} surface after the wear test (the white particles are the corundum particles embedded in the surface).

Conclusions

The mystery on the origin of the LDSG is still unsolved, but now new data are available. XRF Spectrophotometry confirms the expected chemical composition, similar for glass and rock, enhancing the impact origin hypothesis. In the glass there are siderophile elements such as Fe, Cr, Ni, Y, Cu and P: a trace of the meteorite impact body that produced the rocks melting and the formation of the glass (Diemer, 1996; Koeberl, 1997).

Nanoindentation technique showed its validity in the case of a hard and brittle material, permitting to evaluate the local Young's modulus and hardness of a material that could not be tested with traditional techniques because of its low toughness and high porosity. In addition, Young's modulus and hardness as function of the indentation depth were analized, and this is useful to evaluate the homogeneity of the glass and to understand its microstructure. In all tests it can be observed that hardness surprisingly increases (Pugno, 2007) with the indentation depth, while we cannot observe a unique trend for the Young's modulus, that sometimes increases and sometimes decreases with the penetration depth.

From the wear resistance test, it can be observed that the wear rate is similar for LDSG and rocks.

Acknowledgements

We wish to thank Vincenzo de Michele, Giancarlo Negro, Mario Di Martino and Benito Piacenza, who introduced us to the LDSG and gave us the specimens, Michele Petraroli, Daniele Ugues Silvia Ronchetti and Amadio Cortellazzi for the experimental help.
This paper is dedicated to the memory of Benito Piacenza.

References

Clayton P., 1997. Patrick Clayton's desert explorations 1920 to 1937. *Proceedings "Silica '96", Meeting on Silica Glass and related desert events*, University of Bologna, 1996.

Cohen A.J., 1961. The terrestrial origin of Libyan Desert Silicaglass. *Phys. and Chem. of glasses,* 2, 3: 83-86.

de Michele V. (ed.), 1997. *"Silica '96", Meeting on Silica Glass and related desert events*, University of Bologna, 1996.

Diemer E., 1997. Libyan Desert Glass: an impactite. State of the art in July 1996. *Proceedings "Silica '96", Meeting on Silica Glass and related desert events*, University of Bologna, 1996.

Feller M., 1997. Vitreus silica from the Sahara. *Proceedings "Silica '96", Meeting on Silica Glass and related desert events*, University of Bologna, 1996.

Fudali R.F., 1981. The major element chemistry of Libyan Desert Glass and the mineralogy of its precursor. *Meteoritics*, 16: 247-259.

Koeberl C., 1997. Libyan Desert Glass: Geochemical composition and origin. *Proceedings "Silica '96", Meeting on Silica Glass and related desert events*, University of Bologna, 1996

O'Keefe J.A., 1976. *Tektites and their origin*. New York-Amsterdam: Elsevier.

Pugno N.M., 2007. A general shape/size-effect law for nanoindenation. *Acta Materialia*, 55 1947-1953.

Rocchia R., E. Robin, F. Frolich, J. Amosse, J. Barrat, H. Meon, L. Froget L. and E. Diemer, 1997. The impact origin of Libyan Desert Glass. *Proc. "Silica '96", Meeting on Silica Glass and related desert events*, University of Bologna, 1996.

Weibull W., 1939. A statistical theory of the strength of materials. *Proc. Roy. Swedish Inst. Eng. Res.*, 151: 1.

XP Users Manual n° 16, 2002. MTS System Corporation.