A glass imitation of blue chalcedony

Henry A. Hänni[1], Shun Tien Wu[2], Yuan Xingqiang[3] and Tsai Wen-Po[4]

1. SSEF Swiss Gemmological Institute, Basel, Switzerland
2. Ten International Gem Institute, Kaohsiung, Taiwan
3. China University of Geoscience, Wuhan, P.R. China
4. Chang Chun Geological Institute, Chang Chun, P.R. China

ABSTRACT: A new artificial product on the Taiwan gem market, light blue translucent glass, is described and compared to natural blue chalcedony, blue opal and stained chalcedony. The gemmological characteristics of the materials are given and compared. Chemical ED-XFA tests indicate relatively high Na, Ca and low Al values in the glass compared with gemstones of the silica group, and also with such contents in natural glasses. IR spectra of the artificial glass and chalcedony are also quite different. Wollastonite was identified by Raman spectroscopy as a devitrification product forming fine felty fibres or small crystals up to 1 mm thick; they define the degree of translucency of this artificial calcium glass.

Keywords: Taiwan, blue chalcedony, glass imitation, wollastonite, ED-XFA

Introduction

Blue chalcedony is one of the most precious local gemstones in Taiwan. It occurs as irregular small veins in andesitic agglomerate north of Taitung, eastern Taiwan. After having been mined for decades, the deposits are now almost exhausted. Supplies therefore are scarce and many imitations of blue chalcedony are on the market, such as dyed blue chalcedony, dyed blue quartzite and blue opal. In 1998 we found another material resembling blue chalcedony on the market which was declared to originate from China. In the course of our study it turned out to be an artificial blue glass (*Figure 1*). Natural glasses have been encountered as obsidians, tektites and moldavite (see, for example, Tsai and Wu, 1997).

Figure 1: *A 12.50 ct cabochon-cut glass imitation of blue chalcedony from Taiwan. The 17 mm long sample shows horizontal banding and perpendicular fibrous pattern. Photo by H.A. Hänni, SSEF.*

ISSN: 1355-4565

The properties of blue chalcedony

Chalcedony is described as a fibrous aggregated form of silica which merges into agate when the banding becomes prominent (Webster, 1983). The microstructure of the sheaf-like fibre array (botryoidal structure) of silica allows some porosity in which natural or artificial pigments can impart colour. The whole structure of this cryptocrystalline material produces, depending on the direction of view, a more or less easily visible banded or polygonal pattern when inspected in transmitted light.

The properties of blue chalcedony from Taiwan have been widely studied by, for example, Huang (1965 and 1982), Chen (1969) and Chen and Zen (1982). So far we have not found any western reference for Taiwan blue chalcedony. The papers conclude that the colour of the Taiwanese blue chalcedony is usually homogeneous sky blue to greenish-blue, the material being semi-transparent to opaque, with a conchoidal fracture. The RI is 1.539, and SG is 2.58. A copper content of 0.01 to 0.02% has been reported, and a small uranium content of 0.002 to 0.0035 %wt gives rise to minor radiation (Huang, 1965).

Imitations

Imitations are substances that may substitute a given gemstone and may be natural gemstones or artificial products. Usually imitations are of lesser value than those that they imitate. The most popular imitations of natural blue chalcedony are dyed blue chalcedony, dyed blue quartzite and blue opal, but the new product described in this paper may also be convincing. Other substances to substitute for blue chalcedony are imaginable such as pectolite (Woodruff and Fritsch, 1989) or hemimorphite (Moses *et al.*, 1998), both of sky-blue colour with a definite structure. The properties of these imitations are listed in *Table I* and some examples in comparison are shown in *Figure 2*.

Figure 2: From left to right: (back) imitation blue chalcedony (glass), dyed blue quartzite, dyed blue chalcedony, (front) natural blue chalcedony (Taiwan), natural blue chalcedony (Taiwan), blue opal (Peru). Photo by H.A. Hänni, SSEF.

Most of the dyed blue chalcedony is free of inclusions and has a homogeneous colour distribution besides a faint 'agate' banding. Such a weak banding structure can be found in most chalcedony (*Figure 3*). Under a Chelsea filter the dyed material appears

Table I: *The properties of blue chalcedony and its imitations.*

Gemstone	RI (spot reading)	SG	Hardness
Blue chalcedony	1.53	2.58	6.5
Dyed blue chalcedony	1.53	2.60	6.5
Dyed blue quartzite	1.54	2.65	7
Blue opal	1.45	2.15	6
Sky-blue glass (chalcedony imitation)	1.54	2.57	5
Pectolite	1.60	2.81	5
Hemimorphite	1.62	3.45	5

reddish-brown. Since RI and SG are the same for the natural and treated blue chalcedony, we cannot distinguish them on the basis of these two properties.

Figure 3: Banding structure of dyed blue chalcedony. The banding of chalcedony is usually finer and more homogeneous, whereas bands in the imitation (Figure 1) appear more structured by parallel fibres. Photo by S.T. Wu.

Dyed blue quartzite possesses a slight porosity which allows the staining to penetrate along grain boundaries. Such material shows concentrations of dye between the quartz grains which are easy to detect when a penlight is used (*Figure 4*). The SG of quartzite is 2.65 which is distinctly higher than that of blue chalcedony (2.58).

Figure 4: In dyed blue quartzite the colour is always concentrated on grain boundaries and along fractures. Length of the stone is 8 mm. Photo by S.T. Wu.

Blue opal usually shows jelly-like inclusions (*Figure 5*) which may look similar to some inclusions in natural blue chalcedony (*Figure 6*), but with its RI of 1.45 and SG of 2.15 it can be distinguished from chalcedony. Blue opal appeared on the market some years ago and has been reported from Chile (Koivula and Kammerling, 1991) and Peru (Milisenda, 1995).

Figure 5: Jelly-like inclusions in blue opal from Peru. Length of the stone is 8.6 mm. Photo by S.T. Wu.

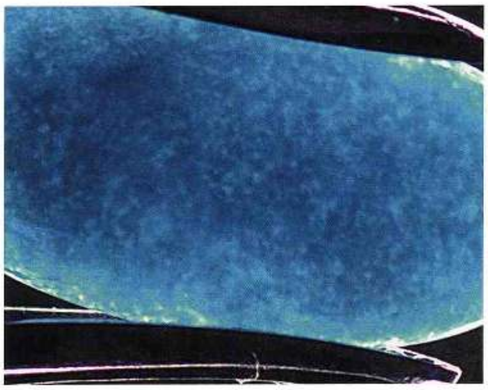

Figure 6: Jelly-like inclusions in natural blue chalcedony from Taiwan. Length of the stone is 14 mm. Photo by S.T. Wu.

Artificial blue glass

Artificial blue glass as an imitation for opaque or semi-transparent stones, such as lapis lazuli (Bosshart, 1983) or blue chalcedony could only be a convincing imitation when it is not transparent but has

Figure 7: Raw material of the sky-blue imitation stone, apparently glass slag. Length of piece is approximately 20 cm. Photo by S.T. Wu.

the same degree of translucency as the substance it is imitating. In order to make a glass translucent rather than transparent, its composition has to include some components that will oversaturate the melt and form crystals when the glass cools down. The process of devitrification may then allow the formation of, for example, devitrite, apatite, wollastonite, or fluorite and cristobalite, in the glassy groundmass (Hammer *et al.*, 1999). Such crystals can render a glass milky through to opaque (Bosshart, 1983; Harding *et al.*, 1989). The range of SG and RI values of artificial glass were shown by Webster (1983) in a diagram modified after Bannister.

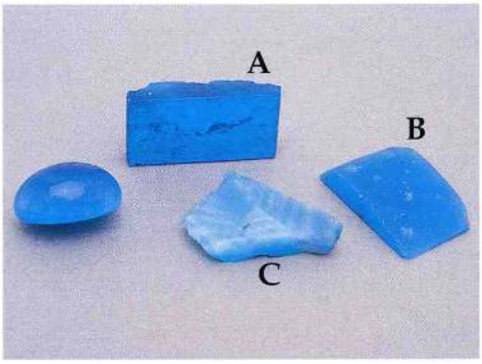

Figure 8: Three types of sanded samples of blue glass from Taiwan, with decreasing sizes of fibrous inclusions (coarse, medium, fine) correlating with decreasing transparency. A polished cabochon on the left is 17 mm long. Photo by H.A. Hänni, SSEF.

Macroscopic description

The pieces of rough glass are up to 20 cm across (*Figure 7*); they are inhomogeneous and consist of massive glass with what appears to be a slaggy top zone. Most of the glass is dark or sky blue, but next to the slaggy zone it is green. The degree of transparency is also not uniform. Most of the material is cut into cabochons or bangles. They vary in colour from light sky blue to dark sky blue and range from semi-transparent to semi-translucent (*Figure 8*).

The raw material available for investigation consisted of three different

Glass imitations of blue chalcedony

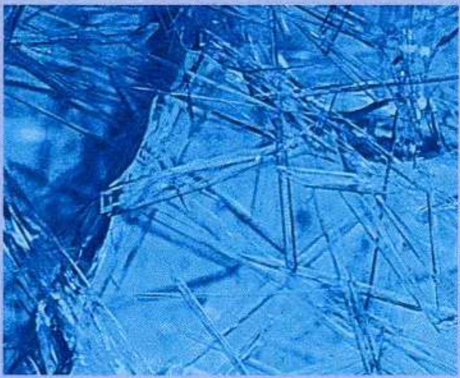

Figure 9: Sample A: Partially devitrified, and containing relatively coarse wollastonite crystals. Magnification approximately 15x. Photo by H.A. Hänni, SSEF.

Figure 10: Sample B: Partially devitrified, with medium sized wollastonite crystals. Magnification approximately 15x. Photo by H.A. Hänni, SSEF.

types, varying in their degree of transparency.

Sample A is semi-transparent and of darker blue colour than the other two types. It contains needle-shaped crystals in random orientation, which are clearly visible at 10x magnification (*Figure 9*).

Sample B is lighter in colour and more milky than sample A. Its inclusions cannot be resolved individually at 10x, but a few oddly shaped bubbles may be visible (*Figure 10*).

Sample C is light blue and almost opaque. Patterns of white banding are eye-visible and are confined to sectoral areas (*Figure 11*).

Figure 11: Sample C: Partially devitrified with very fine wollastonite crystals in a banding pattern. Magnification approximately 15x. Photo by H.A. Hänni, SSEF.

Microscopic description

With a magnification of 10x to 50x the imitation stones display features not expected from their macroscopic appearance. The darker blue and semi-transparent material A contains needle-shaped crystals and inclusions, randomly oriented. They have a four-sided cross-section and may be hollow or filled with glass (*Figure 9*). The medium blue variety of glass B shows similar but finer needles (*Figure 10*); gas bubbles are not common. The light blue variety C is almost opaque and contains dense aggregates of very fine needles. They are arranged as radiating bunches or form a kind of zebra banding (*Figure 11*). Gas bubbles or swirl marks may be hidden by the dense pattern of these inclusions.

Physical data

The RI of 1.54 and SG of 2.57 are values close to those of blue chalcedony. These data are shown in *Table I* with comparable data from other imitations.

The semi-transparent variety A of the glass showed a homogeneous aggregate structure under the polariscope. Under the Chelsea

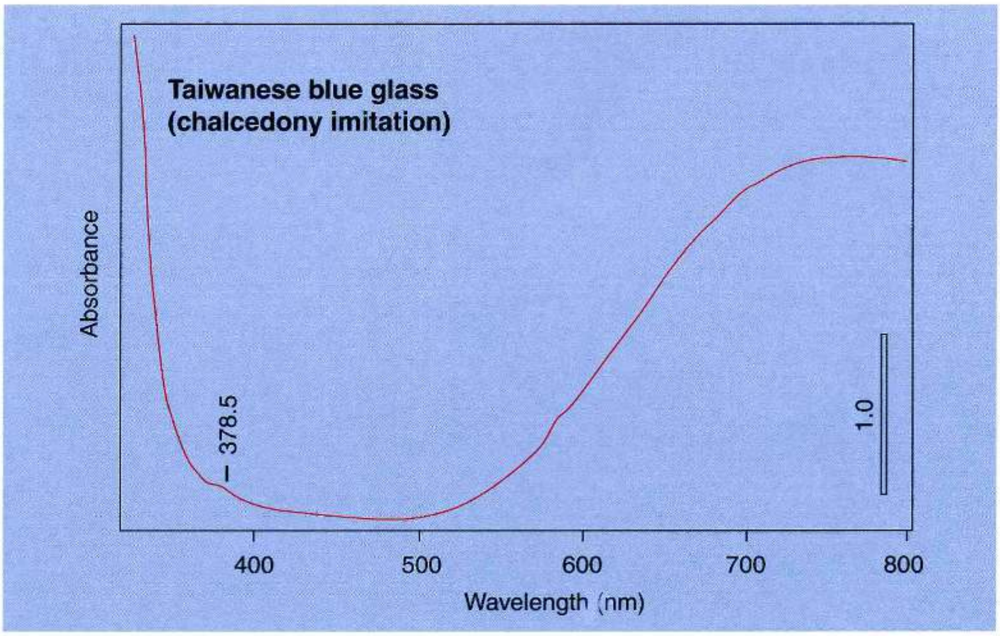

Figure 12: Blue glass chalcedony imitation absorption spectrum from 300-800 nm recorded on a Varian Cary 500 Scan spectrophotometer. The main transparent area is between approximately 400 and 500 nm (blue colours).

filter, the imitation stones appear green. With a hand-held spectroscope no spectral lines were observed. The UV-VIS spectrum recorded with a Varian Cary 500 Scan spectrophotometer is shown in *Figure 12.* It is characterized by general transmission between approximately 350 and 550 nm, and a weak absorption at 378 nm.

UV-reaction

In long-wave UV, the glass imitation stones showed weak bluish-white to

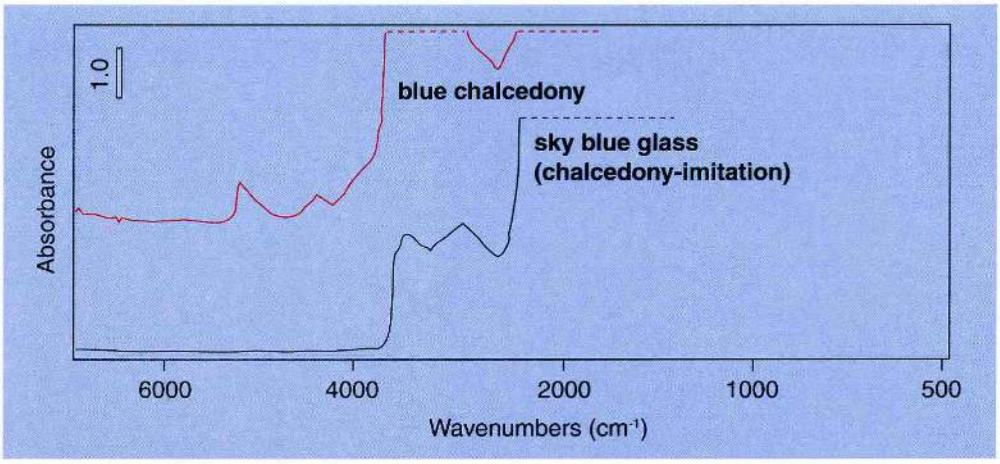

Figure 13: Infrared absorption spectra of blue chalcedony and its glass imitation recorded on solid samples. The spectra show characteristic differences.

yellowish-green luminescence, and moderate to strong yellowish-green luminescence in short-wave UV.

Infrared spectroscopic determinations

The infrared spectrum of natural blue chalcedony is shown in *Figure 13 upper*. The curve indicates complete absorption from 400 cm-1 to 2398 cm^{-1}, and strong absorption between 2689 cm^{-1} and 3758 cm^{-1} with two absorption bands at 4434 cm^{-1} and 5231 cm^{-1}.

The sky-blue glass imitation stones (B and C) have two absorption bands at 2927 cm^{-1} and 3464 cm^{-1} (*Figure 13 lower*) and lack peaks in the 4-5000 cm^{-1} region, a spectrum clearly different from that of blue chalcedony.

With a powder method where imitation glass is ground and mixed with KBr, we also found that the most important features of the infrared spectrum are the same as those of artificial glass (*Figure 14*): both have strong absorption in the 'fingerprint' area at 1053 cm^{-1} and pairs of small absorption bands at 651, 776 cm^{-1}, and 2932, 3450 cm^{-1}.

Chemical analyses

In order to obtain further information about the blue glass imitations, their chemical composition was investigated with a Tracor ED-XFA. The chemical analysis had first a qualitative character and helped to rule out the claim that the blue stones were chalcedony. A standardization for a semi-quantitative major element determination was done with artificial glass reference samples from the glass industry by conventional wavelength dispersive X-ray fluorescence spectrometry WDS-XFA

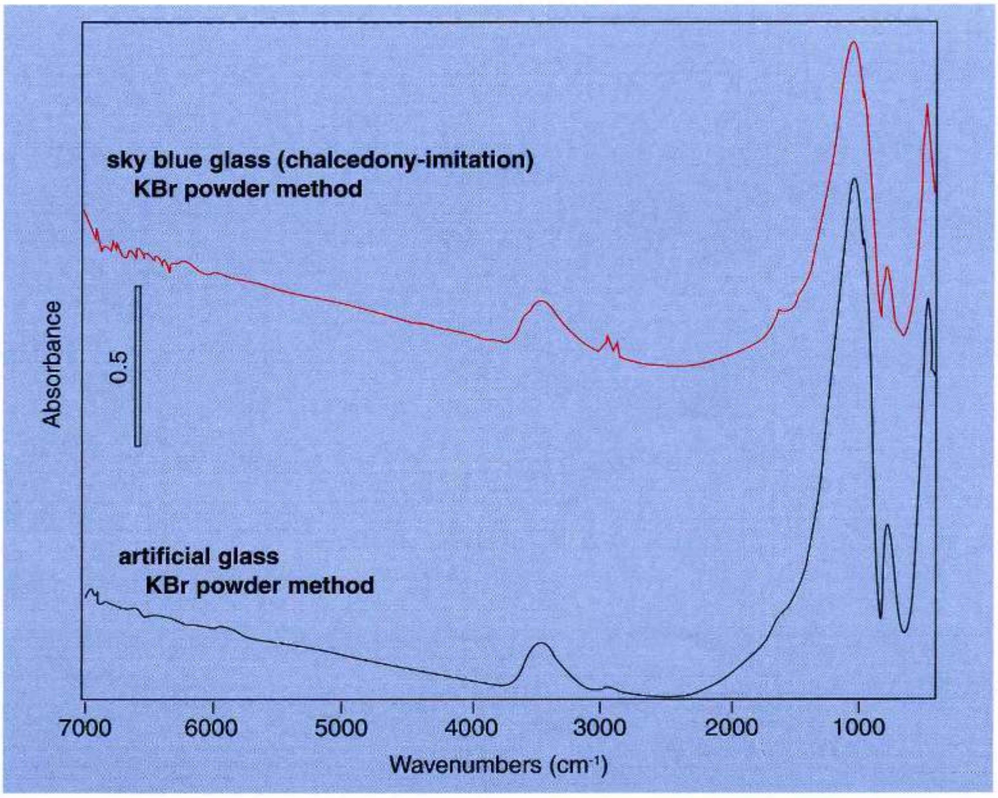

Figure 14: *Infrared absorption spectra of chalcedony imitation and window glass using a powder method with KBr tablets. The spectra show no significant differences.*

Table II: *Chemical composition of natural and artifical glass*

Oxide (%wt)	SiO_2	Al_2O_3	MgO	CaO	K_2O	Na_2O	TiO_2	Fe_2O_3	MnO	Cr_2O_3
Industrial glass references (WD-XRF analyses by J. Cerny)										
Olive standard	71.68	1.96	2.88	10.1	0.51	12.44	0.05	0.10	n.a	0.01
Brown standard	69.65	2.15	3.03	9.73	1.35	13.64	0.05	0.30	n.a	0.03
Green standard	71.57	1.65	2.12	10.29	0.67	12.71	0.06	0.33	n.a	0.22
Dark brown standard	78.02	2.27	2.45	10.43	1.09	12.38	0.06	0.29	n.a	0.03
Natural glass references (EMP analyses by H. Schwander)										
Obsidian Mexico	75.13	12.46	n.d.	0.25	4.75	5.24	0.08	2.01	0.08	n.d.
Obsidian USA	74.61	12.77	n.d.	1.12	5.74	4.50	0.15	1.04	0.08	n.d.
Tektite Thailand	75.13	12.93	0.96	2.32	2.51	0.29	0.61	5.09	0.15	n.d.
Moldavite CS	76.59	9.80	2.07	5.22	4.02	n.d.	0.27	1.75	0.29	n.d.
Taiwanese blue glass (ED-XRF analyses by P. Giese)										
Imitation rough (Sample A)	73.30	0.34	3.85	9.11	0.26	12.98	0.02	0.14	0.01	n.d.
Imitation rough TL (Sample B)	73.01	0.33	3.86	8.54	0.26	13.83	0.02	0.14	0.01	n.d.
Imitation rough TL (Sample C)	72.97	0.45	3.86	9.13	0.31	13.09	0.02	0.17	0.01	n.d.
Natural samples (ED-XRF analyses by P. Giese)										
Dyed quartzite	99.86	n.d.	n.d.	0.09	0.04	n.d.	n.d.	n.d.	n.d.	n.d.
Dyed chalcedony	99.98	n.d.	n.d.	0.02	0.03	n.d.	n.d.	0.01	n.d.	0.06
Blue opal	98.71	0.10	0.03	0.33	0.09	0.73	0.01	n.d.	0.01	n.d.
Taiwanese blue chalcedony	99.62	n.d.	n.d.	0.07	0.03	0.24	0.01	n.d.	0.04	n.d.
Taiwanese blue chalcedony	99.68	n.d.	0.11	0.11	0.05	n.d.	n.d.	0.01	0.04	n.d.

n.a. = not analysed n.d. = not detected Chemical data analysed by WD-XRF and ED-XRF are semi-quantitative; EMP data are quantitative.

Raman spectroscopic identifications

The Raman microspectrometer system (Renishaw 1000) is an excellent instrument for the mineralogical distinction of materials of similar appearance such as the blue chalcedony, stained quartzite, pectolite (larimar), blue hemimorphite, opal or glass (see also Hänni *et al.*, 1997). It is also excellent for identifying inclusions, so the method was used to identify the devitrification products in the blue glass (*Figure 15*). The Raman spectrum of a crystal inclusion (*Figure 16*) was matched with that of natural wollastonite in the SSEF Raman Data Search File, and confirmed its identity.

***Figure 15:** Surface of blue glass showing devitrification texture indicated by the wollastonite crystals. Some slender crystals are hollow. Magnification approximately 30x. Photo by H.A. Hänni, SSEF.*

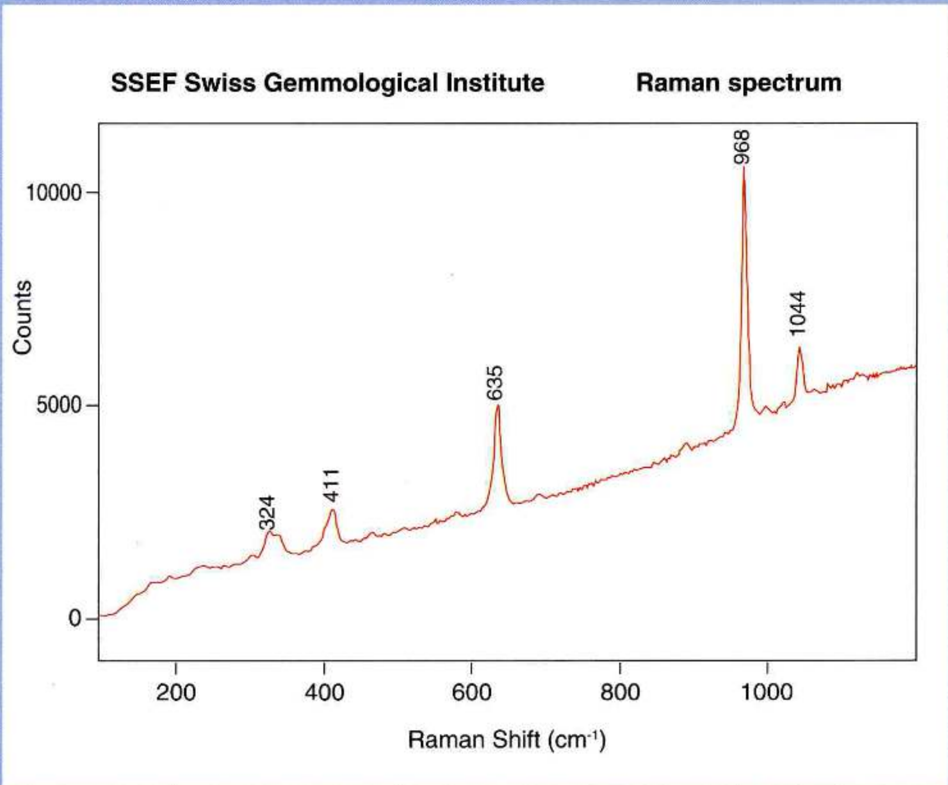

***Figure 16:** Raman spectrum of wollastonite crystal in blue glass.*

(Vetroconsult, Bülach, Switzerland). Natural glass samples of obsidian, tektite and moldavite had earlier been analysed by electron microprobe (Geochemical Laboratory, Basel University). The blue glass samples described in this paper were analysed by energy dispersive spectrometry, X-ray fluorescence analysis (EDS-XFA) at SSEF. The results are presented in *Table II*. Cu, Fe and As were found in trace quantities in the blue chalcedony imitation. The natural glasses are richer in Al, K and sometimes Fe, but poor in Ca. In contrast, the artificial glasses are richer in Ca, occasionally also in Na and relatively poor in Al (Weiner, 1983). This is because in the manufacturing of artificial glass Na, Ca, B or Li may be added in order to bring down the melting point.

The blue imitation glass is richer in Ca and Na and poorer in Al than natural glasses, proving its man-made origin and indicating that it belongs to the group of calcium glasses.

Discussion

The glass imitation of blue chalcedony is in many respects similar to natural chalcedony. A close microscopic inspection may however reveal the bundles of randomly oriented devitrification products, which in the lesser transparent material are in bunches or as radiating aggregates. Needles ordered in bands may give a zebra pattern to the sky blue material. The RI and SG of the glass are close to the values of chalcedony. Additional identification features lie in the infrared spectrum where the peak positions are typical for glass; chalcedony peak positions are quite different.

A chemical characterization of the material is most effective since it shows the compositional difference between chalcedony and natural glasses. The ED-XFA results obtained are typical for a calcium glass. The precipitation of wollastonite as a devitrification product is a result of the high calcium content of the material. Traces of Cu and Fe are responsible for the blue colour, traces of As are recommended in the manufacturing to reduce gas bubbles. It is possible that the blue glass is an industrial waste or slag, as proposed by Johnson *et al.* (1999). The relatively small amount of this product in the market is consistent with such an origin.

Conclusions

The described glass imitation of natural blue chalcedony is a convincing substitute which may intrigue gemmologists because of the similarity of their properties. When mounted, the identification of such stones could create difficulties. However, observation of microscopic features such as radiating fine or irregularly displaced coarser fibres of devitrification products, UV reaction and chemical differences, allow a safe identification. The sky blue stone is richer in Ca, Na and poorer in Al than natural glasses and indicates that it is artificial glass.

Acknowledgements

We thank Mr M.L. Lee for providing the blue chalcedony samples, and Ms S.F. Wang and Mr C.C. Huang for the samples of sky blue imitations. The standardization of ED-XFA glass analyses was carried out by Mrs J. Cerny of Vetroconsult (Bülach, Switzerland) and Professor W.B. Stern (Geochemical Laboratory, University of Basel) whom we thank also for fruitful discussions of the topic. We thank Mr P. Giese for analytical ED-XFA work and Dr M. Krzemnicki for graphic refinement, both of the SSEF Swiss Gemmological Institute in Basel.

References

Bosshart, G., 1983. Cobalt glass as a lapis lazuli imitation. *Gems & Gemology*, Winter, 228-31

Chen J.L., 1969. The test report of Taiwan blue chalcedony. *Taiwan Mining*, **21**(3/4), 17-20 (in Chinese)

Chen C.J., and Zen B.J., 1982. *The geological occurrence and mineralogical properties of Taiwan blue (purple) chalcedony*. Taiwan Mining Bureau (in Chinese)

Hammer, V., Stefan, J., and Brandstätter, F., 1999. Zur Verwendung künstlicher Gläser als Schmuckmaterial: Schwarzes und blaues Glas mit ungewöhnlichen Einschlüssen. *Z.Dt.Gemmol.Ges.*, **48**(3), 157-62

Harding, R.R., Hornytzkyj, S., and Date, A.R., 1989. The composition of an opaque red glass used by Fabergé. *Journal of Gemmology*, **21**(5), 275-87

Hänni, H.A., Kiefert, L., Chalain, J.-P., and Wilcock, I.C., 1997. A Raman microscope in the gemmological laboratory: first experiences of application. *Journal of Gemmology*, **25**(6), 394-406

Huang C.K., 1965. The two gemstones from Taiwan eastern area – blue chalcedony and nephrite. *Taiwan Mining*, 7(2-4), 58-65 (in Chinese)

Huang C.K., 1982. Gem minerals from Taiwan and their prospect. *Taiwan Mining*, **33**(2), 6-18 (in Chinese)

Johnson, M.L., and Koivula, J.I., 1999. Gem news: Blue slag glass from Sweden resembling opal. *Gems & Gemology*, **35**(1), 56-7

Koivula, J.I., and Kammerling, R.C., 1991. Gem news: Fine greenish blue opal. *Gems & Gemology*, **25**(2), 120-1

Milisenda, C., 1995. Gemmologische Kurzinformationen: Blaue Opale aus Peru. *Z.Dt.Gemmol.Ges.*, **44**(1), 5

Moses, T., Reinitz, I., and McClure, S.F., 1998. Lab notes: Hemimorphite, rough and fashioned. *Gems & Gemology*, **34**(1), 44-5

Tsai W.P., and Wu S.T., 1997. Natural glass gemstones. *Jewelry Circles*, **41**, 140-2 (in Chinese)

Webster, R., 1983. Gems. *Their sources, description and identification* (4th edn.). Butterworth, London

Weiner, K.L., 1983. Obsidians and gemmology. *Journal of Gemmology*, **18**(8), 745-60

Woodruff, R., and Fritsch, E., 1989. Blue pectolite from the Dominican Republic. *Gems & Gemology*, **25**(4), 216-25