

Iridescent natural glass from Mexico

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Abstract

Transparent brownish 'iris opal' from San Luis Potosí (Mexico) was found to be a natural glass exhibiting layered and botryoidal textures. SEM studies on these layers indicate that they give rise to the iridescent effect, which occurs by interference on layers each of approx. 2µm thickness. An X-ray diffraction pattern shows the material to be amorphous. Infra-red spectroscopy revealed the presence of SiOH groups, but no evidence of water. Microprobe analyses indicated a composition which includes the elements Si, Al, Cs, K and Na as main constituents, and Rb and Fe occur in trace amounts. DTA analysis up to 1200°C resulted in an ignition loss of 0.9% above 900°C.

Introduction

As far back as 1964, transparent light brown stones were mentioned in a gemmological publication (Barbour, 1964), and these are the subject of the present study (Figure 1). In a later report (Sinkankas, 1966) they were called *iris opal*. Leiper (1965) had already noted the presence of spherulitic inclusions. Electron microscopy (TEM) revealed the thin-layered texture, which was thought to be responsible for the iris effect. Viewed under strong illumination (Figure 2 and cover picture) and at the correct orientation, the stones exhibit specific colour effects due to optical interference.

Nowadays, it is known that the play of colours in gem opal represents a colour effect due to the diffraction of white light on a regular pattern of minute spheres (Sanders, 1964). This phenomenon, caused by a 3-dimensional diffraction lattice, needed to be compared with the apparently different mechanism in 'iris opal'. The terms hyalite, hyaline, opal, etc., used in the trade were also thought questionable, and initiated interest in the undertaking of this present study.

The *Iris Effect* as an interference phenomenon at thin layers has been known to gemmologists for a long time, but not however, in the case of opal! The iris agate mentioned by Webster (1983) exhibits iridescence colours because of interference at thin layers. We wish to differentiate between

interference at thin layers (2-dimensional) and diffraction in spatial (3-dimensional) lattices as the cause of colour in gemstones. The first (Iris Effect) can be considered to be a special case of the second (play of colour).

Both the iris effect and play of colour can occur in silica minerals, especially in iris quartz, the various opals and the variety hyalite, as well as in chalcedony and agate. The question arises as to which of these classes the studied material belongs.

Depending on origin and structure of coloured opals, they can be classified into distinguishable mineralogical types (Flörke *et al.*, 1985²). In general, it can be said that opal can be formed at low temperatures from aqueous gels. This type exhibits an amorphous character to X-ray diffraction, as shown in opal from some sedimentary rocks from Australia. Opal can also form at higher temperatures and contain crystalline components in the form of cristobalite and/or tridymite within the amorphous mass. It can occur in cavities in volcanic rocks. This opal is not amorphous to X-ray diffraction, but exhibits diffraction patterns representing the crystalline SiO₂ minerals present.

A recent publication (Gübelin 1987, see Figures 21 and 22), which describes black opal from Lightning Ridge, shows scanning electron micrographs. Figure 21 shows the familiar spatially ordered spherical packing, which can cause opalescence. Figure 22, on the other hand, shows a distinct layered structure. The accompanying text describes the material as 'glassy hyaline opal'. The 'sporadic and few cristobalite and tridymite spheres' mentioned cannot be seen in the figure, and as they do not represent dense, ordered patterns, they cannot produce the play of colours. For this reason, the narrow layers would therefore seem to play a more important role in explaining the opal-like behaviour of the 'hyaline opal'. Discussions with the author (Gübelin, 1988) clearly indicate that the latter material is most probably identical to the glass from Mexico examined in this study.

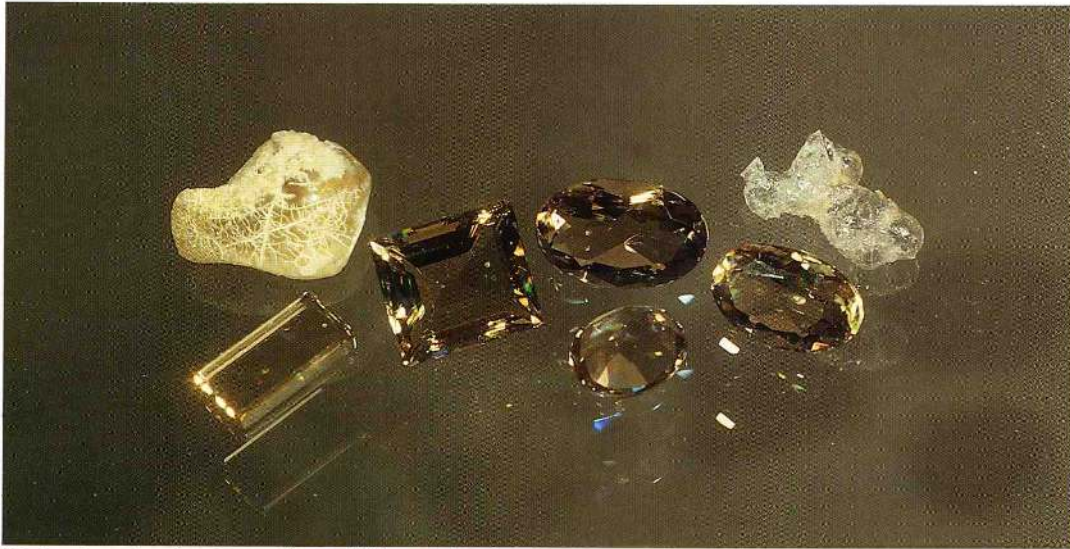


Fig. 1. A number of specimens of natural iridescent glass from Mexico. Rear left: natural untreated material; rear right: a frothy specimen of the glass after heating to 1200°C. The largest of the faceted stones weighs 3.2ct.

Origin and type of material

Our study material originates from the Tepetate and Lourdes area in the state of San Luis Potosí in Mexico (Koivula, 1988). Sinkankas (1966) also mentions a location near Durango. The host-rock is described as volcanic, probably a rhyolite, in whose cavities topaz and droplet-like to crusty forms of the studied glass occur. Reniform to grape-like masses are often called botryoidal forms. The iridescent glass occasionally forms caps on crystals of topaz, thus indicating a certain genetic relationship. Under the hand lens, the surfaces of the glass bodies (up to cm-large) and crusts can be seen to be composed of very fine step-like layers as sometimes seen on pearls, however in the case of the glass, some wedge-like features are often seen

(Figure 3). Older natural surfaces are often pitted, and may be either the result of corrosion or are larger open pores.

Gemmological and optical characteristics

The following studies were carried out on eight stones, some of which are faceted or polished, the remaining uncut. Their colour varies between light yellowish- and greenish-brown, and the form of all stones is botryoidal, identical to that of hyalite.

Note should be made here of the similarity of the surface to that of artificial glass. The fine botryoidal layers can be easily mistaken for 'swirl marks' in artificial glasses, and the stress-induced birefringence exhibited between polarizing filters and the low values for density and refractive



Fig. 2. Iridescent glass with botryoidal form, exhibiting spectral colours due to interference on thin layers.



Fig. 3. Natural surface of iridescent glass, showing concentric layered structure. Magnification 10x.

indices are also similar to those expected in glasses. Spherical inclusions also resemble the gas bubbles or vesicles seen in many glasses. However, closer optical study reveals the presence of conical segments of fine and bent layered stacks, slightly tilted one to another, which make up the single crusts and clumps. This is an unknown phenomenon in artificial glasses. The description of the hyalite structure (Flörke *et al.*, 1985) as a consequence of a 'layer-by-layer deposition from droplets, which have built up cone-like common contact surfaces' also fits iridescent glass accurately.

Small, spherical forms (spherulites) are found as inclusions, from which short cracks radiate, or which are surrounded by foliated fissures. The spherulites are amorphous (Figure 4).

The stones are isotropic under polarized light, although in thicker layers, stress-induced biref-

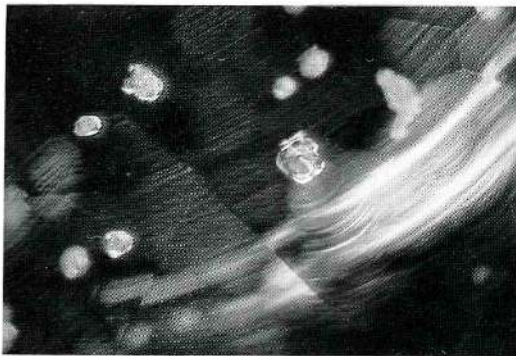


Fig. 4. Spherical inclusions (amorphous) with a 'wreath' of fine fissures, and finely layered botryoidal texture. Magnification ca. 20x.

ringence becomes evident (Figure 5). Using fibre optics, spectral colours are produced which follow the thin-layered texture when the stone is tilted (Figure 2). Density and refractive index data are presented in Table 1.

Table 1: Physical data for iridescent glass from San Luis Potosí (Mexico)

Density	2.241–2.270 g/cm ³ (Sinkankas 1966: 2.257)
Refractive index	1.462–1.467 (Sinkankas 1966: 1.4625)

The absorption spectrum contains no identifiable lines. It is characterized by a slight increase of the absorption from 900 to 450nm. From there, the curve becomes steeper and attains a maximum at

430nm. This confirms the findings of Liddicoat (1985), who noted additional bands at 495 and 460nm, and compared the spectrum with that of a uranium glass described in Webster (1983).

The iridescent glasses exhibit a weak to medium strong greenish fluorescence under long-wave ultra-violet radiation.

Comparison of the data with that for density and refractive indices of artificial glasses in the Bannister diagram (Webster, 1983) shows that the values fall in the region of the so-called opal glasses, without the iris glass specimens exhibiting the milkiness of these artificial products.

Scanning electron microscopy (SEM) study

Fracture surfaces of the iridescent glass were studied with a Philips 515 SEM with an attached energy-dispersive analyser (Tracor). Using this equipment images were formed and energy-

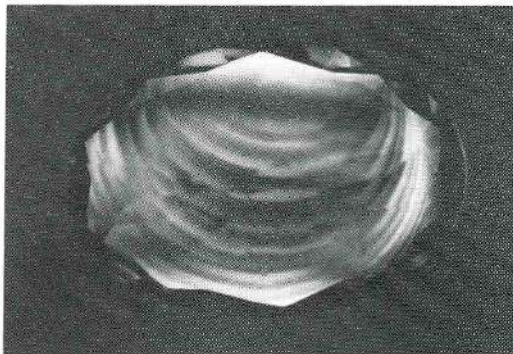


Fig. 5. Birefringence produced due to stress. Iridescent glass between crossed polarization filters.

dispersive X-ray spectra produced. As the technique requires a conducting surface, the specimen surfaces were coated with a thin layer of gold.

The SEM micrographs plainly show the finely-layered texture of the material, and the bent form of the individual layers is also clearly visible (Figure 6). The wedge-like features can be seen in detail where the individual sectors and cones touch each other. At higher magnification, layered structures, each only 2.5µm thick, are recognisable on a fracture surface (Figure 7). This observation agrees remarkably well with the figures and data in Sinkankas (1966), who reports an average width of the bands of 2.24µm. At these dimensions, the stacked layers exhibit interference in ultraviolet radiation (Jones, 1952), and the phenomenon of iridescence is adequately explained.

The numerous minute cracks seen in Figure 7 could possibly represent a partial structure, or could be interpreted as shrinkage cracks.



Fig. 6. SEM micrograph of the surface of a raw sample of iridescent glass revealing thin and bent layers as well as a few holes. White scale bar is 0.1mm long.

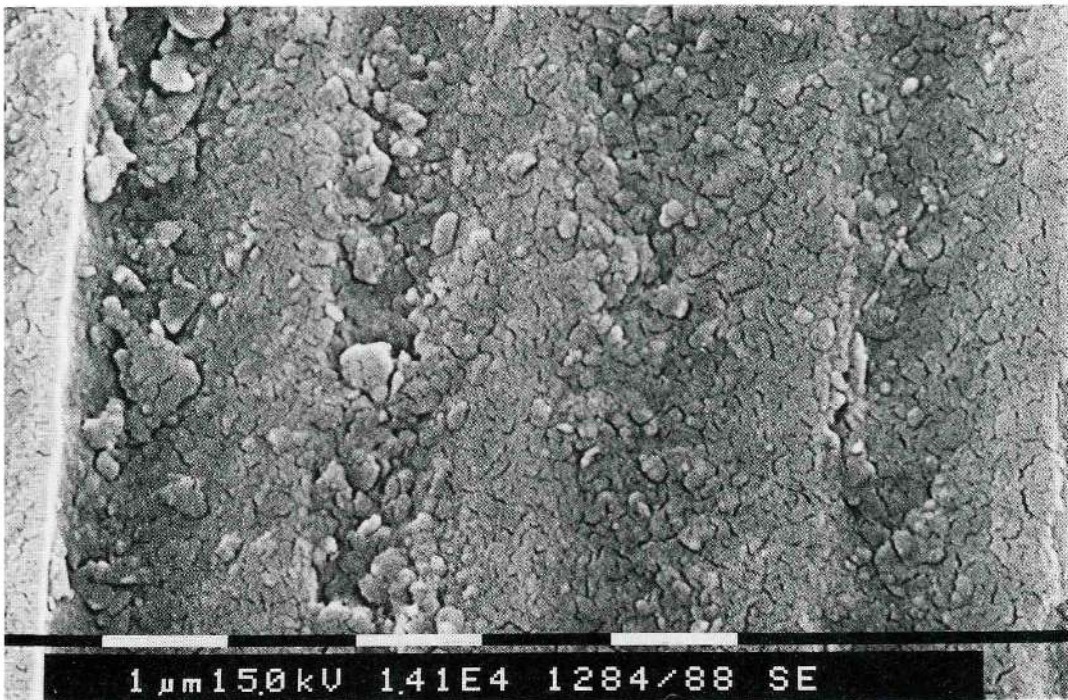


Fig. 7. SEM photograph of the surface showing the stepped nature caused by the emergence of the steeply inclined 2μm thick layers. The small crooked openings may be 'shrinkage cracks'. White scale bar is 1μm long.

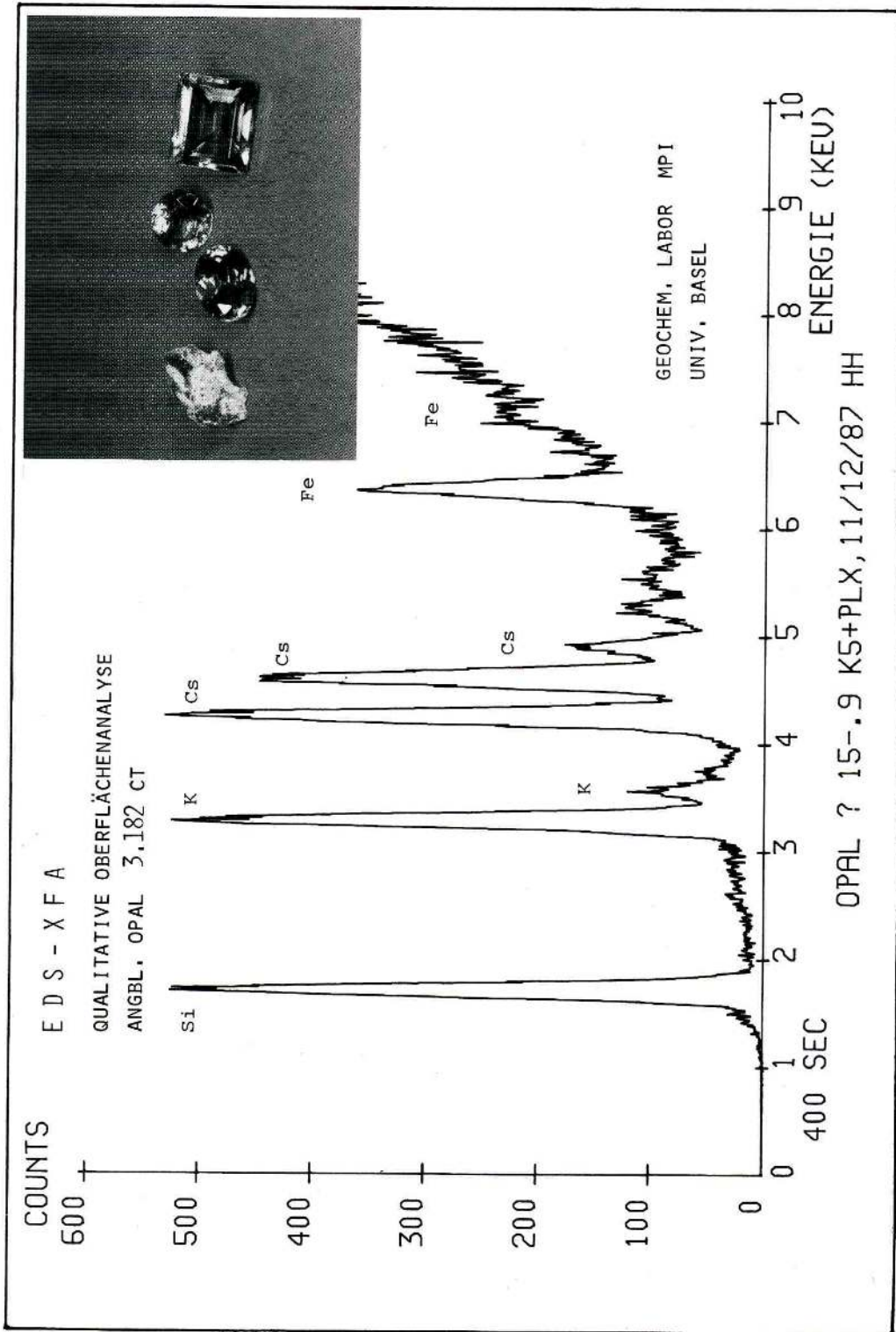


Fig. 8. General EDS-XRF spectrum of iridescent glass. The instrument conditions chosen only reveal the presence of the medium heavy elements.

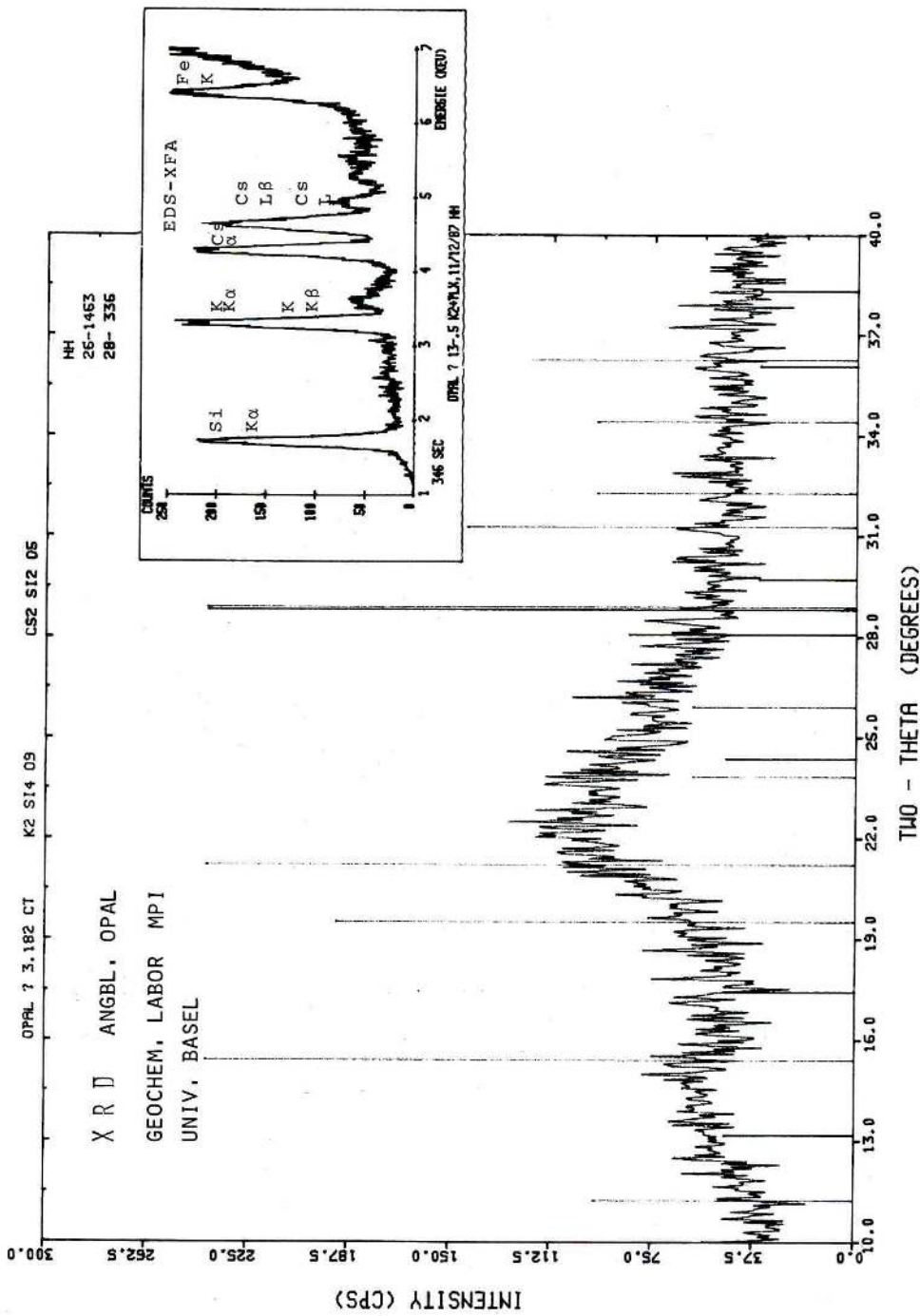


Fig. 9. X-ray diffractogram of iridescent glass from Mexico, showing the absence of crystallinity, thus indicating the amorphous character of the sample. The box (upper right) shows the EDXRF spectrum of Fig. 8.

Chemical study

No chemical data is presented in the publications cited. Our chemical study of iridescent glass was undertaken in a number of stages. Energy-dispersive X-ray fluorescence analysis (EDS-XFA) has been used in gemmology for some time now with success (Stern and Hänni, 1982). Qualitative analyses were undertaken using EDXRF (Figure 9). The spectra show the presence of elements which are for opal, to say the least, unusual. Apart from Si, K and Cs as major to minor elements, Fe, As and possibly U occur as trace elements.

The quantitative analysis of the major and minor components was undertaken with an electron probe microanalyser (Jeol JXA-8600), using a combination of EDS/WDS-analysis (Schwander and Gloor, 1980). The results of the quantitative analysis are presented in Table 2, supplemented by the semi-quantitative analysis for Cs, calculated from the SEM-EDS spectrum. Light elements and volatile components such as Li, B, Be, H₂O, CO₂, were omitted due to analysis problems encountered by such components. The fine-layered texture observed under the microscope appeared to be chemically homogeneous under the electron microprobe and no chemical zoning was indicated. However, chemical variations may exist, but lie below the resolution of the electron microprobe (EPMA).

Table 2: Chemical composition of iridescent glass from San Luis Potosí (Mexico)

SiO ₂	87.90 Wt.%
Al ₂ O ₃	3.64
Cs ₂ O	2.0
K ₂ O	1.93
Na ₂ O	0.55
Fe ₂ O ₃	0.02
	96.02%

Light elements with $Z < 11$ (e.g. Li, Be, B etc.) could not be analysed by EPMA.

A partial (EPMA) quantitative analysis in 1977 (pers. comm. Gübelin, 1988) was undertaken, most probably on the same material ('yellow hyaline', Mexico), and the contents of Si, Al, K, Na and Fe were similar to those given in Table 2. Values for Cs and Rb, however, are absent. From the analysis, the material thus cannot be regarded as opal nor as hyalite.

As opals (and hyalites) contain up to >99% SiO₂ (Flörke *et al.*, 1985¹), the Mexican material (which contains 12 Wt.% other elements) cannot by definition be considered to be opal.

X-ray diffraction studies

A powder diffraction film contained no lines and the material is thus amorphous. An X-ray diffraction study using a Siemens Kristalloflex diffractometer revealed a weak and broad intensity maximum at 22° 2θ [CuKα] and a second even weaker one at about 15° 2θ (Figure 8). Such weak 'bulges' of the background can be explained by the presence of an unordered network of SiO₄ tetrahedrons. The proven amorphous character of the material indicates the absence of C/T opal (with cristobalite and tridymite), which often occurs in some volcanic areas of Mexico. An X-ray study of one of the spherulitic inclusions (powder technique, Bradley camera) again resulted in the absence of any diffraction lines, indicating the amorphous nature of the inclusions.

Infra-red spectroscopy (IRS)

IRS is used when the presence of certain molecules, organic groups or water has to be determined. As all opals contain 1–12% water occurring mainly as molecular water, this specific study was of particular significance. The IR spectra did not show the presence of any molecular water. Spectral bands seen at 3600 and 4450 cm⁻¹ are assigned to Si-OH groups (Langer and Flörke, 1974). The content is <0.1 wt. %. A similar 'OH spectrum' is exhibited by certain silica glasses, which occur naturally as Libyan desert glass. A measurable hydrogen-content in the form of silanol groups (Si-OH) and the absence of molecular water (H₂O) are thus apparently characteristic of the Mexican iridescent glass and distinguish it from opal.

Thermal study

A thermo-gravimetric study using a Mettler thermobalance TA 3000 gave information on mass changes in the material when heated to 1200°C. Any water present will be expelled and the change in mass relative to temperature can be monitored. Heating the sample at 10°/minute initially revealed no change in mass until >900°C, at which stage a mass loss was registered attaining 0.92% at 1200°C. After heating, the appearance of the material had altered considerably and resembled a coarsely-blistered foam or froth. This behaviour is markedly different to that of opal, not only with the low ignition loss but also in this conversion to foam-like material. A subsequent study of the crystallinity showed that the material was still amorphous, and no cristobalite was formed as would have been the case with opal. Further studies are planned to determine the actual composition of the 0.92% material expelled during heating, using a heating arrangement in vacuum with a coupled mass spectrometer.

Discussion of results

The study has furnished much information which conflicts with the original idea that the Mexican material was hyalite or another variety of opal. A review by Flörke *et al.* (1985²) presents the non-crystalline and micro-crystalline SiO₂ minerals and their aggregates, known at that time, and hyalite is a specific sub-type and an amorphous variety of opal. The SiO₂ minerals and aggregates listed by Flörke *et al.* are chemically very pure in comparison with the iridescent glass studied in this publication and which contains about 12 % wt. of other elements. The 3% alkali metals are of particular interest. Some Li could well be present since the analytical total of 96% (EPMA) leaves 4% unaccounted for. Although hyalite contains 3-5% molecular water and about 1% silanol (Flörke *et al.*, 1985¹), less than 0.1% silanol was found in the Mexican glass. Thermal analysis of hyalite reveals a maximum weight loss around 275°C. This occurs only at >920°C with iridescent glass. On the basis of these substantial differences, iridescent glass cannot be considered to belong to the SiO₂ family, although some features similar to those of hyalite are observed: particularly the glassy appearance, the botryoidal form of the crusts, and possibly the large pore-like 'holes' (Figure 6), (Flörke *et al.*, 1985²). The occurrence and habit of the material is strongly reminiscent of hyalite.

The 'shrinkage cracks' seen in Figure 7 raise the question of whether these could have been formed by the migration or diffusion of molecular water originally present.

Finally, the question on the genesis of these unusual natural glasses is raised. We are used to linking the term 'glass' with a magmatic origin, but the extremely fine layers and the botryoidal texture would tend to discount this possibility. Thus we are left with the possible formation of this amorphous material from late-magmatic vapours, steams or aqueous solutions. The formation of iridescent glass is most plausibly explained by rhythmic deposition from steams, mainly indicated by the finely-layered texture. The latter may have been formed by successive deposits of chemically very different 2µm thick layers. In theory, therefore, a rhythmic deposition of (water-free?) opal with layers of alkali-rich substances is quite feasible. A steam phase could – in the rhyolitic area where the glass is found – quite easily have transported the alkalis. In future investigations, the precise composition of the steam must be determined and its function during formation of the glass and its subsequent disappearance explained.

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