COLORING OF TOPAZ BY COATING AND DIFFUSION PROCESSES: AN X-RAY PHOTOEMISSION STUDY OF WHAT HAPPENS BENEATH THE SURFACE

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Surface-treated topaz has become a viable alternative to topaz colored by irradiation. Unlike irradiation, which modifies the entire gemstone, coloration by chemical modification is limited to the near-surface region. The treatment techniques are well established, but less is known about how the processes involved create the desired appearance. In this study, X-ray photoemission spectroscopy in combination with sputter depth profiling proved successful in characterizing two fundamentally different coloration mechanisms of chemically treated topaz: colored coatings and diffusion-induced coloration.

Topaz [$Al_2SiO_4(F,OH)_2$] occurs as an accessory mineral in some granites and associated hydrothermally altered rocks, as well as in pegmatites, rhyolites, and other aluminous rocks. The crystallographic, optical, and chemical properties of topaz can vary with chemical composition, which reflects the petrogenesis of the rocks in which the individual crystal formed (Christiansen et al., 1983). However, most topaz is colorless as mined, so it is often color enhanced for use in jewelry.

One common method used to produce color centers in topaz consists of irradiating the gem with gamma rays, neutrons, or electrons, followed by low-temperature annealing (Nassau et al., 1978, 1985). Unfortunately, this procedure may induce radioactivity, thus requiring that the gems be stored safely until their activity has decayed below the legal limits. In some cases, depending on the procedure and the nature of the starting material, the decay process requires more than a year of storage, a costly delay for the owner of the topaz. In other cases, material has been released into the market prematurely (see, e.g., Ashbaugh and Shigley, 1993). Although no health impairments arising from treated gems with radioactivity below the legal limit have been reported, government, industry, and consumer groups alike are concerned about the potential risk should radioactive topaz inadvertently enter the gem market (see, e.g., Yonick, 2007; Kremkow, 2008).

In response to these concerns, two color enhancement processes that do not involve irradiation have been successfully developed. One is a coating, and the other is a diffusion-driven layer near the surface of the host gem. The main difference between these two treatments, as will be explained in more detail in the following sections, lies in the interaction of the added elements with the gemstone's surface.

While both of these techniques are well established and detailed descriptions of the procedures involved are available (Starcke et al., 1996; Pollack, 1997), less is known about the atomic-scale processes that occur during the color treatment. This article focuses on the principal mechanisms giving rise to

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See end of article for About the Authors and Acknowledgments.

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Figure 1. These three color-treated topazes were analyzed for this study: coated pink (left), diffusion-treated "Summer Blue" (middle), and diffusion-treated "Ice Blue" (right). All stones weigh 0.42 ct; photos by Tiroler Repro Druck.

coloration in topaz treated by these techniques. Not only is this information important from a scientific standpoint, but it may also help predict some relevant gemological properties.

For coated stones, the chemical and thermal durability of the color is determined by the composition of the coating and is independent of the substrate. Therefore, besides imparting color to a gem, the coating may also act as a protective layer. However, as with all coated gemstones, the differences in the physical properties between the stone and the color layer are also responsible for the main drawbacks of this technique. The difference in the thermal expansion coefficient may lead to severe stress at the interface when the gem is exposed to rapid temperature changes, so the coating could delaminate. Furthermore, the abrupt change in optical density (i.e., refractive index) between the coating and the gem causes angle-dependent interference effects in the wavelength of visible light (400–700 nm), which may give the gem an artificial appearance.

For diffusion-treated gems, the color treatment is more stable. Although the surface region is modified by the introduced ions, the relevant properties more closely resemble those of the topaz. Heat-induced stress or interference effects are no longer significant. The gem is unlikely to delaminate and has a more normal appearance to the unaided eye.

BACKGROUND

Coloration of some gemstones can be achieved without irradiation by introducing transition metal ions into the crystal lattice (see, e.g., Nassau, 1978). The resulting color (see, e.g., figure 1) is not only a function of the element(s) introduced, but it also depends very strongly on the valence state of that element and the symmetry of the neighboring host atoms, as well as on the chemical composition of the topaz (Nassau, 1978).

As noted above, two possibilities are available for coloring a gemstone with transition metals. In the coating process (figure 2, left), a thin film is deposited on the surface of the gem and has a well-defined interface of only a few nanometers thickness, which is much less than the wavelength of visible light. Chemical reactions as well as atomic exchange between the coating and the gem's surface, which are responsible for adhesion, are limited to this narrow interface. Therefore, the color effect produced by the coating arises solely from the coating itself; it is independent of the substrate's composition. The same coating would lead to the same color, whether the colorless substrate was topaz or any other material.

In the diffusion-driven process (figure 2, right), the coloring agent permeates the gem's surface. This may be accomplished either by depositing a precursor material on the surface or by embedding the stone in the desired matrix (Pollack, 1997), followed by heat treatment. As a result, various components migrate into deeper atomic layers and the elemental composition of the surface changes. This diffusion process results in substantial broadening of the interface. In fact, depending on the process parameters, it might be difficult to identify the interface. Instead, a complicated and sometimes oscillatory concentration gradient is established from the surface into the body of the gem. The material placed on the gem's surface (in the case of topaz, e.g., cobalt, chromium, or copper) does not in and of itself produce the resulting color; rather, it interacts with the chemical components of the host gem to produce the desired color.

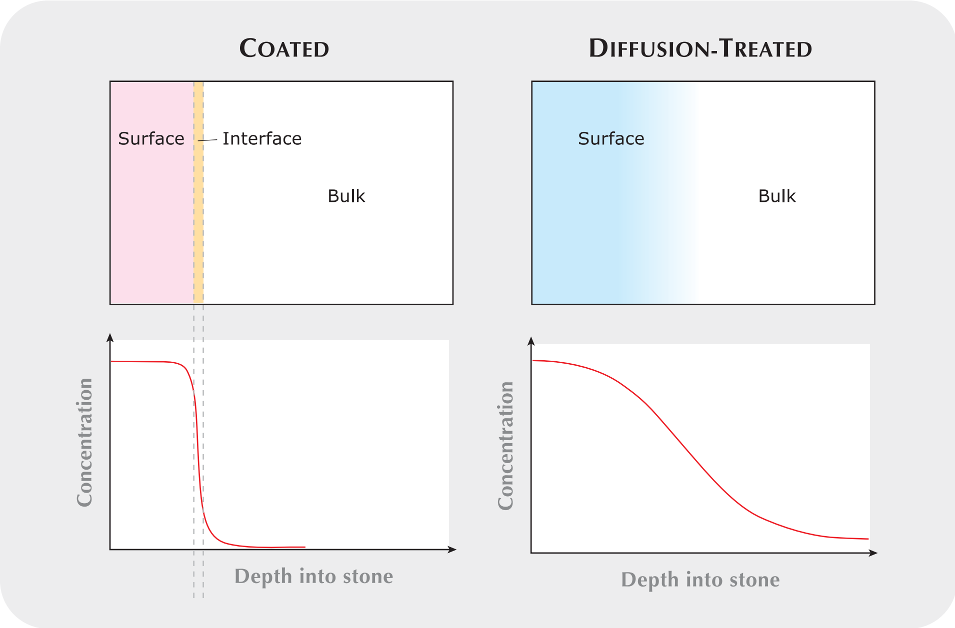

Figure 2. The diagram on the left represents a concentration profile typical of a coated stone, whereas the figure at right resembles that for a diffusion-treated gem. In both diagrams, the left side represents the gem's surface and the horizontal axis represents the depth into the stone.

MATERIALS AND METHODS

To investigate whether these two different procedures can be discriminated in commercially available gemstones, we analyzed three color-treated princess-cut examples, each weighing 0.42 ct, by X-ray photoelectron spectroscopy (XPS; see box A): a pink topaz, a "Summer Blue" topaz, and an "Ice Blue" topaz (again, see figure 1). All three gemstones were originally colorless and were selected as representative of each of these categories in the product line of D. Swarovski & Co.

The color of the pink treated topaz was achieved through the embedding of gold into SiO_2. The color of the Summer Blue topaz was achieved by exposing a colorless topaz to a cobalt-containing environment (cobalt oxide powder) accompanied by annealing under well-defined conditions at around 1000°C for more than three hours (Pollack, 1997). These same procedures were used to treat the Ice Blue topaz, with the addition of chromium.

XPS allows a detailed, quantitative analysis of elemental composition on and just below the surface of a gem. Compared to commonly used analytical techniques such as energy-dispersive X-ray (EDX) spectroscopy, XPS has the advantage of extreme surface sensitivity (providing information to a depth of up to 5 nm, compared to 1 μm for EDX) and the capability of reporting the concentration of elements down to 0.1 at.% (Hofland, 1998). When combined with argon ion etching, the surface sensitivity of XPS can create concentration profiles with high depth resolution.

XPS not only detects the concentration of elements, but it can also monitor changes in valence state (e.g., the oxidation state as a function of depth). In addition, it lacks undesirable matrix effects such as those encountered with SIMS (secondary ion mass spectrometry; Watts and Wolstenholme, 2003). Since the chemical state of the coloring elements (i.e., the exact oxidation state and the phases present after treatment) is not well known, quantification and therefore a subsequent analysis by SIMS or similar techniques is very difficult.

All XPS measurements were conducted at the Institute of Physical Chemistry at the University of Innsbruck with a Thermo Electron Corp. MultiLab 2000 XPS probe that features a double-focusing hemispherical electron energy analyzer with an electrostatic entrance lens. Depth profiling was conducted using a scanning argon ion sputter gun.

The analyses were done under ultra-high vacuum at a background pressure of 1×10^{-9} mbar. The specimens were first cleaned in an ultrasonic bath of acetone and water before they were introduced into the instrument. Survey spectra monitoring all elements present were taken initially and then after every sputter erosion cycle, to determine the actual surface composition and to avoid artifacts caused by impurities. The sputter spot size was 1×1 mm^2, whereas the focused spot size of the analyzing X-ray beam was kept below 0.4×0.4 mm^2. Ten scans per cycle were made to improve the signal-to-noise ratio.

Two additional samples of each color variety of treated topaz were analyzed with the same instru-

BOX A: XPS ANALYSIS

X-ray photoelectron spectroscopy is a very powerful surface science tool for investigating the composition of various solids. In gemology, it can be used in a variety of applications, such as investigating the origin of heat-induced color changes in rubies (Achiwawanich et al., 2006). A complete system costs approximately US$550,000.

In XPS, the sample is irradiated with X-rays of energy, hν, which are produced in an X-ray tube (Hofland, 1998). The X-rays are absorbed in an atom (e.g., atom A in figure A-1) and transfer their energy to a core electron. The core electron then has enough energy to overcome the binding energy, E_{bind}, and leaves the solid with a kinetic energy of $E_{kin} = h\nu - E_{bind}$. The kinetic energy, E_{kin}, is determined by an energy analyzer. Using the known X-ray energy, hν, and the determined kinetic energy, the binding energy can be calculated. The binding energy is specific to each element in the periodic table (compare magnitudes of the different binding energies between atoms A and B in figure A-1). Therefore, the observation of electrons at specific energies indicates the presence of the associated element in the sample. The number of such electrons detected is proportional to the concentration of the element within the probing depth.

The probing depth is limited by the mean free path of the ejected electrons in the sample (i.e., the average distance that electrons can travel before they get scattered and do not reach the analyzer). This distance is typically ~5 nm or less. Hence the technique is very surface sensitive. To obtain a concentration profile as a function of depth into the sample, one has to combine this technique with argon ion etching. Here the surface is eroded (sputtered) layer by layer using an ion beam with typical energies of 1–5 keV. The rate of erosion can be calibrated for topaz using films of known thickness, and spectra recorded after predetermined time intervals yield the element concentrations at the respective sputter depth.

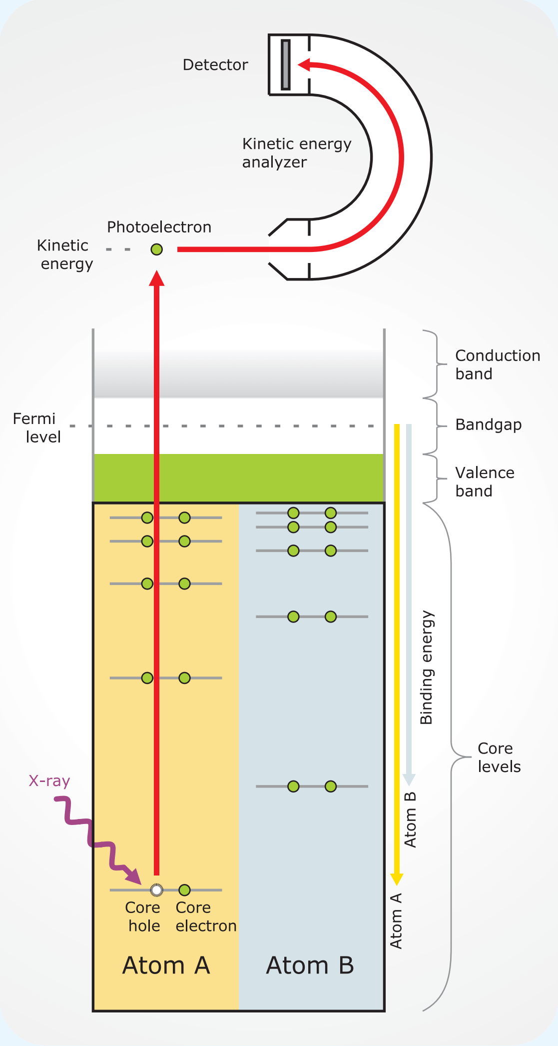

Figure A-1. In XPS, the X-ray photons are absorbed by an atom in a molecule or solid, leading to the emission of core (inner shell) electrons (green circles). The kinetic energy of the ejected electron (photoelectron) is characteristic for each element and detected by the energy analyzer.

ment using procedures that yield less accurate results (i.e., longer ablation time between analysis points) to evaluate the reproducibility of the measurements. To minimize edge effects and sputter-induced mixing, we scanned the ion beam over the analyzed area, thus eroding the sample almost layer by layer. After predetermined erosion periods (approximately one hour per cycle), we recorded the XPS spectra and monitored the change in chemical composition as a function of eroded depth. The sputter efficiency was calibrated using sputter targets of similar material (Al_2O_3 and SiO_2) and known thickness, so that the

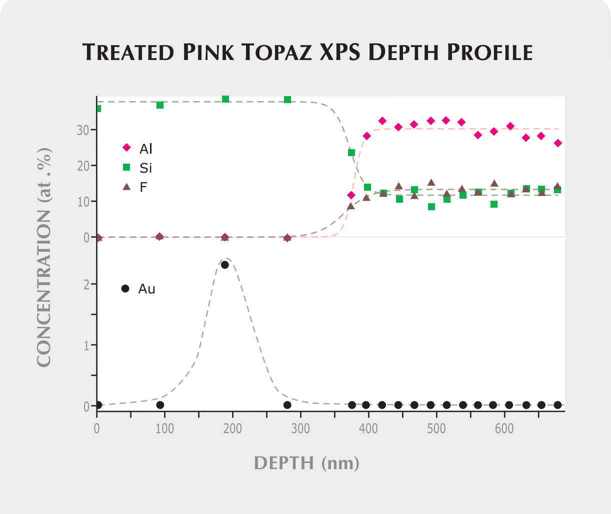

Figure 3. The distribution of elements in the pink treated topaz as a function of sputter depth is shown. The elements of the topaz lattice are plotted in the top graph, while the color-causing element, gold, is plotted in the lower diagram. The chemical patterns are consistent with a coated stone, and a comparatively sharp step in the individual components can be seen.

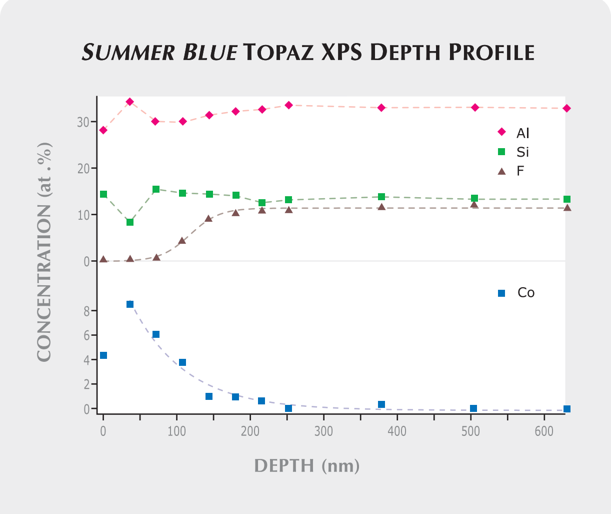

Figure 4. The lower graph in this elemental depth profile of the "Summer Blue" topaz shows the distribution of the color-causing component, Co. The trends in the graph follow the pattern expected for a diffusion-treated stone; no sharp step in the concentrations can be detected.

erosion time could be converted into a depth scale. Although the calibration has an estimated uncertainty of about 20%, the reproducibility of the experiments was excellent.

RESULTS AND DISCUSSION

Pink Coated Topaz. For the pink sample (figure 3), only SiO_2 was detected in the outermost surface region. At a depth of approximately 200 nm, a sharp gold component joined the Si signal in the spectrum, but it vanished after the next sputter cycle (280 nm). At approximately 350 nm, the composition changed dramatically: The Si signal decreased, Al became dominant, and fluorine rose from zero to 12 at.%.

From about 400 nm onwards, the composition remained constant—resembling that of pure colorless topaz. Within the limits of our experimental accuracy, we can state that no interdiffusion took place between the gold-bearing SiO_2 layer (present at a depth of ~200 nm) and the topaz (the component belonging to the topaz first appeared at 350 nm). The XPS signal of the gold did not overlap with any of the bulk components (Al, F), and we detected no significant diffusion of Al into the SiO_2 layer.

This treated stone showed no evidence of appreciable diffusion apart from the defined interface, which is limited to depths between 350 and 400 nm. This finding was supported by the angle-dependent reflection that was readily apparent when the stone was examined with the unaided eye; this results from the interference of the light with the coating.

"Summer Blue" Diffused Topaz. If there is no interdiffusion of the various elements, as we observed in the pink coated topaz, then one would expect a surface covered predominantly by "olive" green cobalt oxide or metallic cobalt in the Summer Blue topaz, depending on the oxidizing or reducing atmosphere in which it was annealed (Pollack, 1997). In addition, all the elements intrinsic to the topaz (Al, Si, F) should only be detectable once this surface layer has been eroded. However, the Summer Blue topaz revealed a completely different elemental distribution (see figure 4).

Unlike the coating on the pink treated topaz, the near-surface region (0–70 nm) of this blue treated topaz exhibited an alternating enrichment in Si and Al. Due to thermodynamic considerations, the surface tends to maximize its stability, so that a thin layer of the most stable components forms there. In the present case, this was a Si-rich layer. Therefore, the layer immediately beneath the surface was somewhat depleted of Si and exhibited a corresponding enrichment of Al and Co. In this sample, Co reached a concentration of about 8 at.%. This composition prevailed to a depth of about 80 nm.

From depths of ~80 to ~200 nm, the Co concentration decreased exponentially (which is characteristic of diffusion profiles according to Fick's law; Kittel, 2005), while the Al and Si concentrations approached those present in the bulk of the gemstone. F showed a steady, continuous rise in concentration throughout this depth region. As previously observed (Marques et al., 2002), fluorine is very sensitive to the destabilization of the crystal lattice, and can become volatile above 600°C if the crystal lattice is damaged; these temperatures were reached during the annealing step.

Therefore, F may be used as a tracer element indicative of the topaz bulk. Figure 4 shows a broad transition region where Co and F were detected simultaneously; measurable amounts of Co are visible in the spectra down to a depth of 380 nm. No sharp step in the concentration profile was observed in this treated topaz.

From these observations, we conclude that cobalt diffusion into the topaz is a prerequisite for the desired coloration. We did not detect any concentration threshold that would allow us to identify an interface between the surface coating and the gemstone. These findings are further supported by the optical properties of the stone. No interference effects were observed; the reflectance resembles that of natural topaz, indicating the lack of a well-defined phase boundary such as was observed in the pink treated topaz.

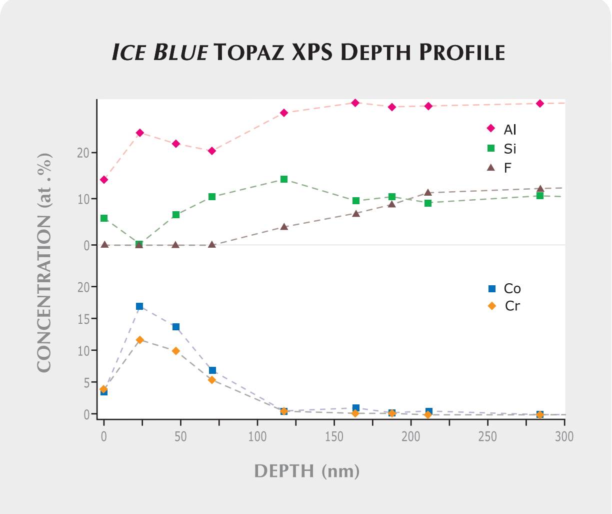

Figure 5. The elemental depth profile of the "Ice Blue" topaz reveals chemical trends that are consistent with coloration caused by diffusion of Co and Cr into the topaz.

"Ice Blue" Diffused Topaz. For the Ice Blue topaz, we observed a concentration profile (figure 5) that was slightly different from that of the Summer Blue sample, probably due to the addition of chromium. Although the outermost layer down to ~50 nm depth also exhibited an oscillatory concentration profile with Si enrichment at the surface, just below the surface the Si concentration decreased below the detection limit. Cobalt and chromium reached their maximum in this strongly Al-enriched region at 10–50 nm depth. However, unlike the chemical profile of the Summer Blue topaz, the concentration of F remained low until the Co and Cr levels had fallen to ~5 at.%, at about 80 nm depth. Only then did the fluorine concentration start to rise. After another ~40 nm, the Si and Al concentrations were close to those in the bulk of the topaz, but still varied slightly. The F signal attained its bulk value at 200 nm depth.

Because the Ice Blue topaz was treated in a procedure similar to that patented by Pollack (1997), we know that Al and Si were not components of the initial coloring agent. In a process similar to that observed with the Summer Blue topaz, Co and Cr likely diffuse into the gemstone and form a colored near-surface layer. We observed, however, a few significant differences. Co and Cr interdiffuse massively with the alumina component of the topaz, reaching a combined concentration maximum of almost 30 at.% at a depth of ~20 nm. Si and F were not present in this range. These findings suggest the formation of a new phase—one that may not be present in the Summer Blue topaz. The phase transformation could perhaps preclude F from incorporation into the newly formed phase or lead to a complete release of the fluorine into the atmosphere. The phase transformation leads to a Co-, Cr-, and Al-rich phase, perhaps a Co-Cr-aluminate spinel phase, which incorporates the transition metal into the lattice, thus preventing their further diffusion into the topaz.

In a sense, the new phase could be considered a coating on the topaz. However, the coating phase is produced by strong diffusion and is probably followed by a chemical reaction establishing a new phase in the near-surface region. Furthermore, although the decay of the Co and Cr concentrations creates a region that may be considered an interface, this interface is much broader than that observed in a typical coating process, as can be seen from comparison with the pink coated topaz. Additionally, traces of the transition metals are still present in deeper regions (200 nm). Thus we classify the color treatment of the Ice Blue topaz as a diffusion-induced process probably accompanied by phase transformation in the near-surface region.

This model is in good agreement with the empirical observations of the stone's appearance. Although the thickness of the color-bearing layer is in the range of the visible-light wavelength, no angle-dependent interference effects were observed, indicating the lack of a sharp change in refractive index.

SUMMARY AND CONCLUSION

Three color-treated (without irradiation) topazes from the product line of D. Swarovski & Co. were examined by XPS to determine the concentration profile of the colored surface. The resulting spectra revealed the mechanisms involved in the formation of the coating or layers responsible for the desired color. In the case of the pink treated topaz, a defined color layer with a sharp interface was detected. No evidence of any significant interaction between the gemstone and the gold-bearing SiO_2 surface layer was found. Color layers such as this can therefore be described as a coating.

The blue colors of treated topaz behaved differently. A considerable alteration of the outer surface of the topaz was detected. In the Summer Blue topaz, a diffusion profile of the cobalt into the topaz was clearly visible and no sharp interfaces were present. The situation becomes more complex when chromium is combined with cobalt in the surface treatment, as for the Ice Blue topaz. A stronger interdiffusion between the bulk elements (Si, Al) and the transition metals was observed.

The XPS results are in good agreement with some optical observations of the analyzed gemstones. As mentioned in the introduction, a sharp change in refractive index on a nanometer scale could cause interference effects. Indeed, the pink coated topaz showed such effects, in contrast to the blue diffusion-treated ones.

Additionally, we have shown that XPS analysis is an appropriate tool to investigate the mechanisms taking place near the surface during the coloration process. Simpler tests, such as etching the surface by hydrofluoric acid (Befi et al., 2006), may give a rough estimate of the thickness of the colored layer. However, such techniques (which are also destructive) cannot be used to establish whether diffusion of the various elements is occurring.

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