Geology and Mineralogy of Electric Opal TM : Green Daylight-Luminescing Hyalite Opal from Zacatecas, Mexico

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GEOLOGY AND MINERALOGY OF

Electric Opal™

Green Daylight-Luminescing Hyalite Opal from Zacatecas, Mexico

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In October 2013, five weathered specimens of botryoidal opal rough showing moderate green daylight luminescence were received from Ruben Avila (Gemimex), well-known El Paso-Juarez based importer of mineral specimens and lapidary rough from Mexico. Although weathered, the samples exhibited a distinctive color-change phenomenon, appearing near-colorless or pale-to-moderate yellow in incandescent light, changing to bright green in indirect sunlight. The reaction to this luminescence phenomenon by specimen collectors was immediate and very positive, so reconnaissance prospecting was undertaken to determine quality and quantity of material available. Initial prospecting showed that strongly colored specimen material was sparsely distributed but turned up a number of specimens composed of transparent lustrous drupelets* and blobs that showed a strong color change, some of which appeared facetable.

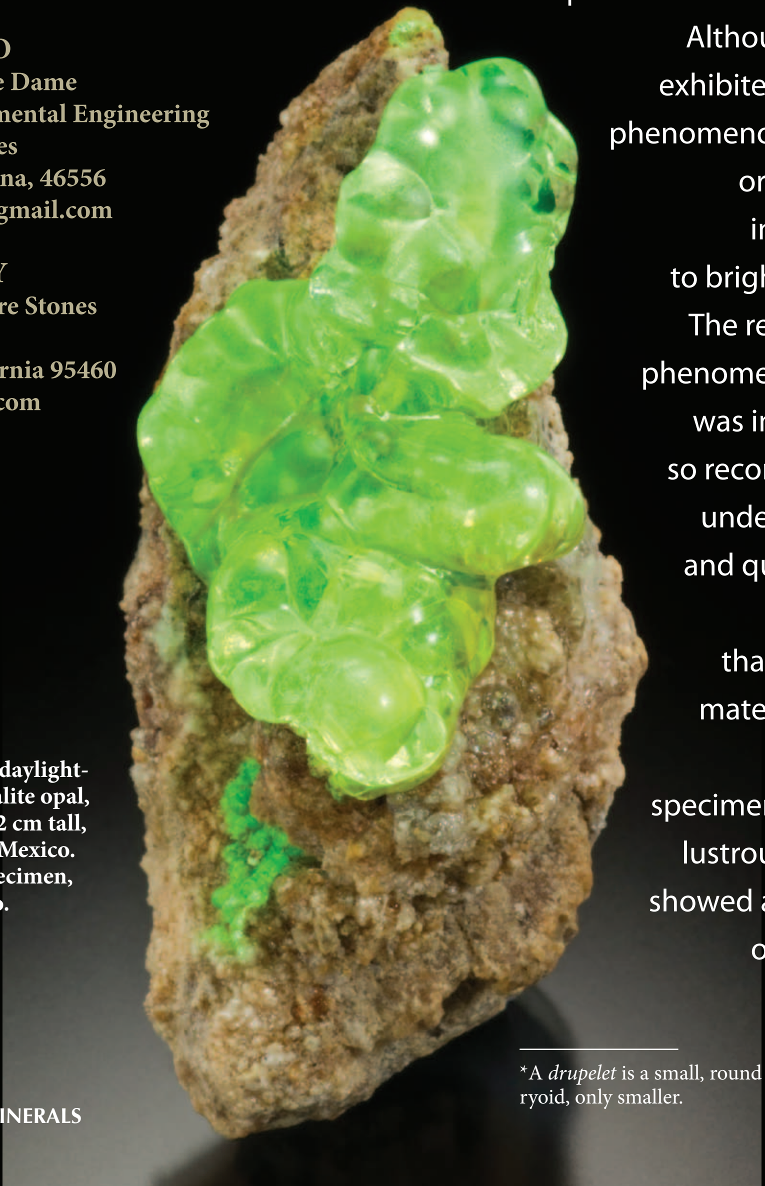

Figure 1. Green daylight-luminescing hyalite opal, Electric Opal 3.2 cm tall, from Zacatecas Mexico. Peter Megaw specimen, Jeff Scovil photo.

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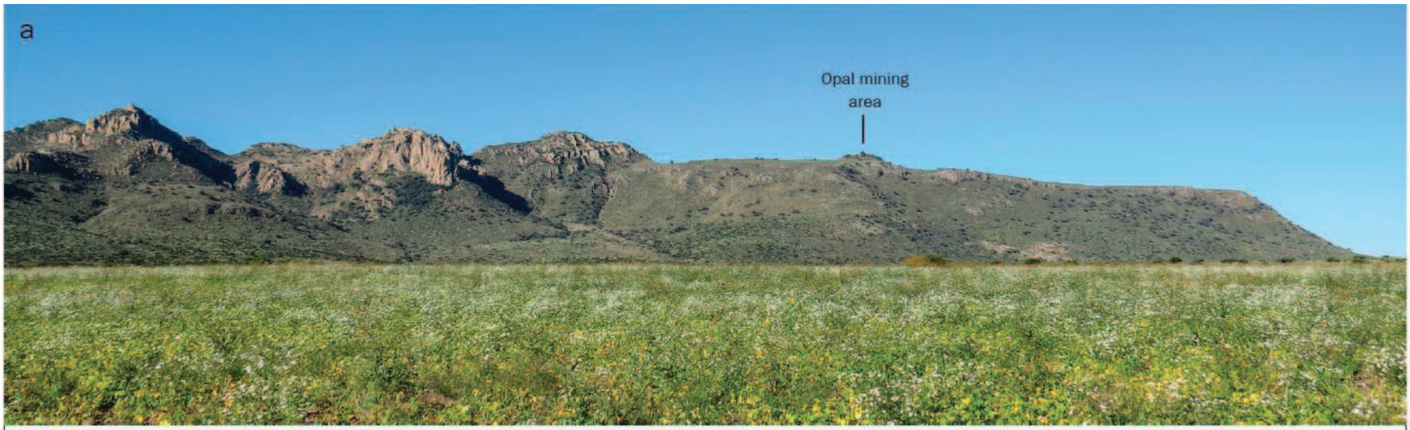
*A *drupelet* is a small, round individual mass of a mineral, much like a botryoid, only smaller.



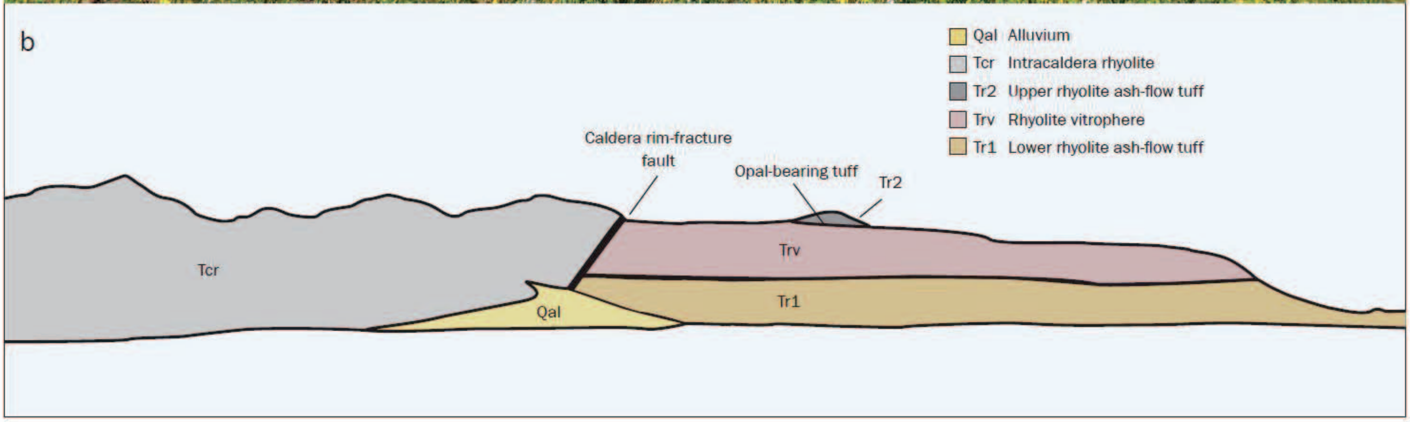


Figure 2a. **Panoramic view of Opal Mesa. The little knob in the middle of the view on top of the long flat mesa is the opal location (compare with fig. 4). The flat mesa is held up by a vitrophyric welded ash-flow tuff. Note the sharp break in ruggedness to the left; this is the margin of an eruption vent on the caldera ring fracture zone.**

Figure 2b. **Interpretive geologic section of figure 2a. Caldera ring fracture zone separates intracaldera unit Tcr from outflow units Tr1, Trv, and Tr2. Opal occurs in poorly welded Teo at the base of the knob held up by Tr2.**

The specimens attracted considerable attention at the February 2014 Tucson gem shows (Moore 2014), and consumer response to the first faceted gemstones was also very enthusiastic, so long-term exclusive access was secured by Ruben and his grandson (also named Ruben Avila), and a digging crew was engaged. The site lies at the top of a steep 250-meter-high mesa, so mining was exclusively manual. Work lasted about a year until production dropped off dramatically, and the project was abandoned.

Figure 3. **Location map showing Zacatecas State in Mexico; prepared by William Besse.**

Dr. Peter K. M. Megaw is an exploration geologist and mineral collector who focuses on the geology and mineralogy of Mexico.

Dr. Emmanuel Fritsch is a well-known French university professor and gemologist specializing in gem materials, among others, opals.

Dr. Tyler L. Spano is a uranium mineralogist and nuclear forensics scientist who focuses on the crystal chemistry and materials properties of U-rich minerals and inorganic phases.

Michael Gray, of Coast-to-Coast Rare Stones, brought nearly fifty years of faceting experience to cutting most of the larger Electric Opals that have been found.

Marketed as Electric Opal in allusion to the color change phenomenon, the faceted opals captured the immediate attention of the gemstone world, and research to characterize the material was swiftly undertaken, led by Emmanuel Fritsch (Fritsch, Spano-Franco, and Megaw 2014; Fritsch et al. 2015). This work showed them to be **Opal-AN**, the amorphous (A), glasslike opal variety consisting of hydrated silica molecules that are network-forming (N) (Flörke, Jones, and Segnit 1973; Rondeau et al. 2004). Also known as *hyalite,* Opal-AN does not have a regular array of spheres or any specific microstructure, so it is always "common" opal, and it does not exhibit play-of-color (Graetsch 1994). These studies also showed that although the daylight-induced green luminescence is related to the presence of trace amounts of the uranyl molecule $(UO_2)^{2+}$, the radioactivity of the opal is within background levels and does not pose any health concern. Freestanding lustrous botryoids make the most attractive specimens, with individual drupelets making standalone jewelry pieces. The specimen material is also facetable and can carry finished gemstone prices.

A series of acicular uranium-containing minerals are found with the opal, which locally covers them. The most prominent species were identified by Spano et al. (2015) with X-ray diffraction as meta-autunite, $Ca(UO_2)_2(PO_4)_2 \cdot 6–8H_2O$; haiweeite, $Ca(UO_2)_2[Si_5O_{12}(OH)_2] \cdot 6H_2O$; uranophane, $Ca(UO_2)_2(HSiO_4) \cdot 5H_2O$; and meta-uranospinite, $Ca(UO_2)_2(AsO_4)_2 \cdot 8H_2O$. Boltwoodite, $(K,Na)(UO_2)(SiO_3OH) \cdot 1.5H_2O$, was subsequently identified by Marcus Origlieri (pers. comm., 2016). Where encapsulated in opal, the uranium minerals are largely leached out leaving elongate tubes that frustrate faceters (Fritsch et al. 2015; Haag 2017). Some of these tubes are marked by linear arrays of minute purple fluorite cubes that presumably crystallized on the elongate uranium minerals before they were covered and leached out.

Location

The occurrence lies in the Sierra Madre Occidental Volcanic Province in the northwestern part of Zacatecas State, Mexico (fig. 3). (Detailed location information has been withheld at the surface owner's request.) The area is reached by approximately 25 kilometers of rough dirt roads that wind through bean and squash fields to the foot of a very steep, 250-meter-high mesa of welded rhyolite ash-flow tuff and vitrophyre (crystal-rich volcanic glass) where a rough trail about 1.5 kilometers long leads up a boulder-strewn and cactus-infested slope from the end of the road to the diggings. The digging area itself was in the middle of the broad top of the mesa and has spectacular panoramic views in all directions. The miners camped on-site, returning to their homes on weekends to clean up and assess each week's production.

Geology

The hyalite occurs in mid-Tertiary rhyolitic rocks typical of the Sierra Madre Occidental Volcanic Province (McDowell and Clabaugh 1979). During the mid-Tertiary (37–28 Ma ago) this region saw repeated, almost unimaginably explosive pyroclastic eruptions from hundreds of "super-volcanoes" similar to Yellowstone in the United States. These volcanoes begin as huge blisters of volatile-rich silicic magma tens to hundreds of kilometers in diameter. Instead of erupting though a central vent as familiar conical volcanoes do (compare Mount Fuji, Mount Rainier, or Vesuvius), these erupt around the circumference of the blister through an annular "ring-fracture zone" through which hundreds to thousands of cubic kilometers of foaming incandescent rhyolitic glass, ash, and rock fragments are ejected essentially instantaneously. The eruptive column can rise to more than 45 kilometers in altitude (Rosi et al. 1999) and on reaching maximum height, collapses back onto the earth's surface as a *pyroclastic flow* or *nue’e ardente* ("glowing cloud"). This incandescent flow spreads laterally on a cushion of superheated air, blanketing hundreds to thousands of square kilometers of the surrounding countryside and obliterating everything in its path (Rosi et al. 1999). During eruption, the center of the blister settles pistonlike into the underlying space left by the erupting magma, creating a circular depression called a *caldera* into which some of the hot ejecta pond. This creates a central overthickened *intracaldera* package surrounded by thinner *outflow* facies (Smith and Bailey 1968). Much of the erupting magma chills instantly into frothy siliceous volcanic glass that is promptly shattered into myriad tiny shards and pumice fragments that mix with fine volcanic ash to comprise *tuff.* As the eruptive pile cools, settles, and compacts, escaping heat and volatile vapors fuse the ejecta into a hard, compact rock known as *welded ash-flow tuff* or *ignimbrite.* In the most densely welded rocks, the tuff gets compacted into *vitrophyre,* a massive obsidian-like volcanic glass enclosing crystals and rock fragments. Thinner and cooler parts of the eruptive pile escape welding, leaving unconsolidated ash mixed with loosely bound crystals and rock fragments (*poorly welded crystal-lithic tuffs*). In all cases, the volcanic glass that makes up most of the tuff is unstable and decomposes over time through a process called *devitrification.* Devitrification affects poorly welded units more efficiently than densely welded units and liberates silica, uranium, iron, and other constituents from the decomposing volcanic glass, which initially go into volcanic vapors emanating from the cooling pile and circulating heated groundwaters that emerge as hot springs (Goodell and Waters 1981; Breit and Hall 2011). Devitrification continues more slowly after the volcanic pile has cooled off, releasing constituents into descending surface waters. Silica liberated at higher temperatures tends to precipitate as chalcedony or fine-grained quartz, whereas at lower temperatures opal is deposited (see following). Uranium and other liberated elements are also redeposited, in some cases as discrete species and in others within the framework structure of the chalcedony or opal.

The daylight luminescent hyalite occurs around the base of a 40 × 125-meter elongated knob that protrudes from the top of a 1.3-kilometer-long mesa composed of outflows from a 20- kilometer-diameter caldera whose ring-fracture zone lies 450 meters from the hyalite occurrence. The mesa is held up by a 90-meter-thick section of very densely welded rhyo-

Figure 4a. **View of Electric Opal Knob showing location of opal-hosting unit (Teo). Note resistant outcrops and large boulders of welded unit (Tr2) that protected the opal from erosion.**

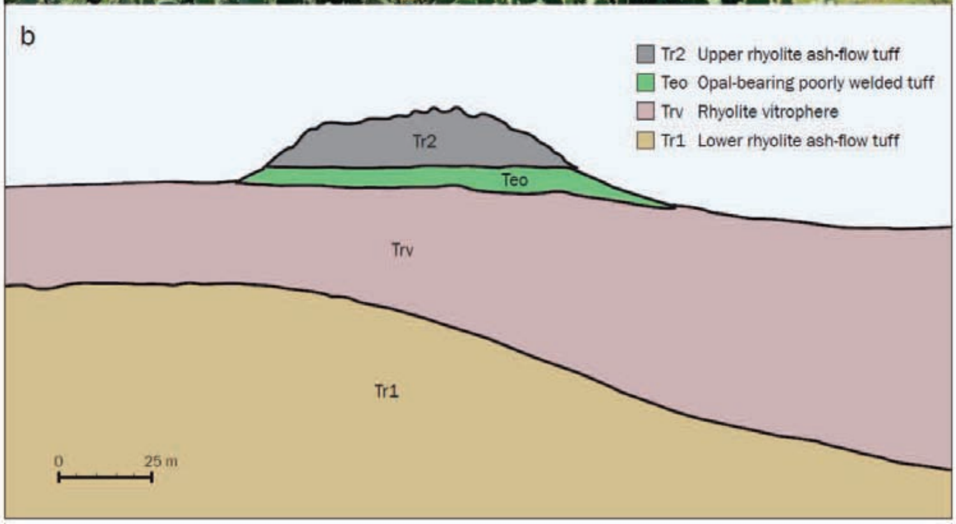


Figure 4b. **Interpretive geologic section of Electric Opal Knob.**

lite vitrophyre that overlies 160 meters of moderately welded ash-flow units (figs. 2 and 4).

The hyalite occurs at the top of a 10–15-meter-thick, poorly welded, crystal-rich rhyolite tuff that sits atop the vitrophyre and was protected from erosion by an overlying 30 × 100 meter remnant of a younger welded unit (fig. 4). The hyalite hosting unit probably once covered the entire mesa, but it, and any opal it contained, has long since eroded away.

The hyalite-bearing layer is composed of 3-mm to 5-cm rhyolite rock fragments mixed with 1–4-mm dipyramidal beta-quartz and limpid sanidine feldspar phenocrysts in a poorly welded porous tuffaceous matrix. The unit shows crude, broadly undulating layering with significant variations in size and number of rock fragments and phenocrysts (figs. 5 and 6). Some layers are composed almost entirely of phenocrysts and rock fragments, suggesting either winnowing in water or in the air blast accompanying its emplacement. The preponderance of features suggest that the unit was a "base-surge" deposit typical of the bottom of an ash-flow outflow eruption. This would have created a highly porous and permeable unit composed of glassy highly siliceous tuff through which groundwater

Figure 5 (left). **Outcrop of poorly welded crystal-rich Teo cut by iron oxide–stained fractures that the miners followed downward to find hyalite.**

Figure 6 (above). **Boulder of fragment-rich Teo showing corrosion pockets and hyalite fillings.**

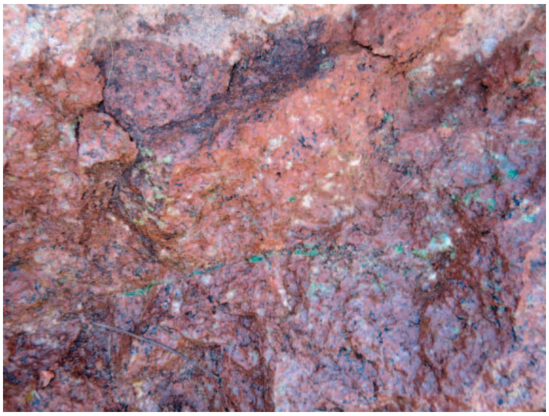


Figure 7 (left). **Excavation wall showing hyalite filling fractures and corrosion voids.**

Figure 8 (right). **Close-up view of a corrosion pocket with partial hyalite coating. This pocket produced several kilograms of good material.**

could readily percolate, leaching silica and uranium from the devitrifying glass, with precipitation of the opal and associated species in underlying voids and along fractures.

The hyalite occurs sparsely in voids and along the walls of open fractures cutting the host unit (figs. 6 and 7). Many of these fractures have local irregular embayments along their margins that appear to reflect corrosion of the host rock by fluids or vapors (fig. 8). The productive fractures are marked by iron oxide fillings flanked by Leisegang banding, and the voids are partially filled by iron oxide–rich clays. The hyalite locally fills the fractures completely, but more commonly it occurs as isolated blebs and botryoidal coatings to 30 mm in thickness, in most places covering less than 10 percent of the surface. The hyalite typically occurs alone, but locally it overgrows earlier uranium oxide minerals. Color and fluorescence vary widely within and between fractures and pockets, with less than 10 percent showing the strongest effects. Some of the best hyalite comes from the irregular corrosion pockets, again sparingly (fig. 8). The miners noted that the color is strongest within a meter or so of the surface and drops off rapidly below that, supporting the interpretation that the opal here formed through the groundwater-based weathering process already described (Gaillou et al. 2008). A few of the more productive fractures were followed 2–3 meters deeper but encountered no additional attractive material, suggesting that deeper excavation is probably unwarranted.

Mining

Mining of the hyalite was done exclusively with pry bars, picks and shovels, and a small gasoline-powered drill. The miners located and followed iron oxide–stained fractures, excavating until hyalite-bearing voids were encountered and continuing to depth until the color diminished. During the rainy season, water scooped from earlier excavations was used to sluice out the pockets and assist recognition of the better colored material. During the dry season, the clayey iron oxide fillings fell away readily to reveal the opal. The voids ranged from 2 to 20 cm across and produced a few kilograms each of rough, including matrix. Weekly production ranged from 100 to 200 kilograms total of opal-bearing rock, of which less than 5 percent was specimen or cutting quality.

Production

Approximately 30 kilograms of top-quality specimens, 10 kilograms of faceting rough, and 30 kilograms of chunks with areas suitable for cutting good cabochons were produced. Another 150 kilograms of moderate-quality and 250 kilograms of low-quality specimen materials were also mined. Production was abandoned when good material became too scarce to cover costs.

To date, perhaps fifty Electric Opal gemstones—ranging from about 1 carat to nearly 7 carats—have been faceted from the material by Michael Gray of Coast-to-Coast. The best of the stones have gone to the Smithsonian Institution, the Carnegie Museum of Natural History, and a few lucky

Figure 9. **Drupelets of hyalite on matrix (0.5–1.0 cm) under (a) incandescent light and (b) shaded sunlight. Peter Megaw specimens and photo.**

private collectors. Fritsch et al. (2015) and Haag (2017) detail the realities of faceting this opal. It has a low index of refraction, so the stones need to be cut deep to have decent brilliance, and the minute tubes (already mentioned) catch polishing compound, which is nearly impossible to remove. The low specific gravity means even a seemingly large stone has a low carat weight.

Mineralogy

Fluorite, CaF_2, occurs locally as linear groups of submillimeter dark purple cubes aligned along elongate tubular voids in massive hyalite. These voids mark where acicular uranium minerals that had become encrusted with fluorite were leached out.

Figure 10. Trilliant-cut 3.44-carat hyalite opal gemstone cut by Michael Gray, shown under two different lighting conditions: (a) incandescent light and (b) shaded daylight. Smithsonian Institution specimen, Ken Larsen photo (a), Tino Hamid photo (b).

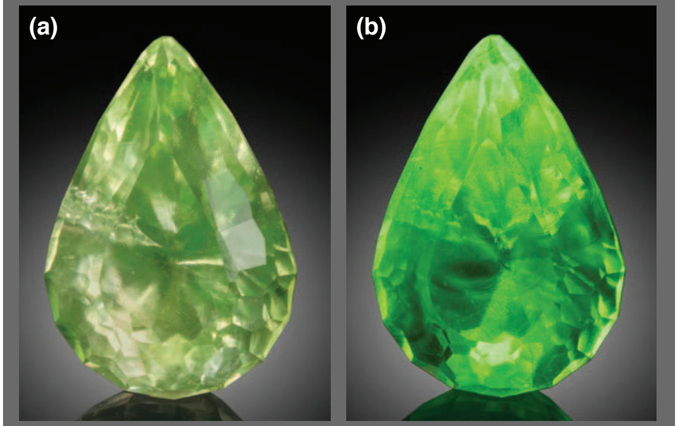


Figure 11. Pear-cut 5.25-carat hyalite opal gemstone cut by Michael Gray, shown under two different lighting conditions: (a) studio strobe light (daylight equivalent) and (b) shortwave ultraviolet. Carnegie Museum of Natural History specimen, Mark Mauthner photos.

Figure 12. Rough and cut (5.25-carat pear-shape cut by Mike Gray, see fig. 11) exhibit marking transition from minerals to gems in the Hillman Hall of Gems, Carnegie Museum of Natural History. Debra Wilson photo.

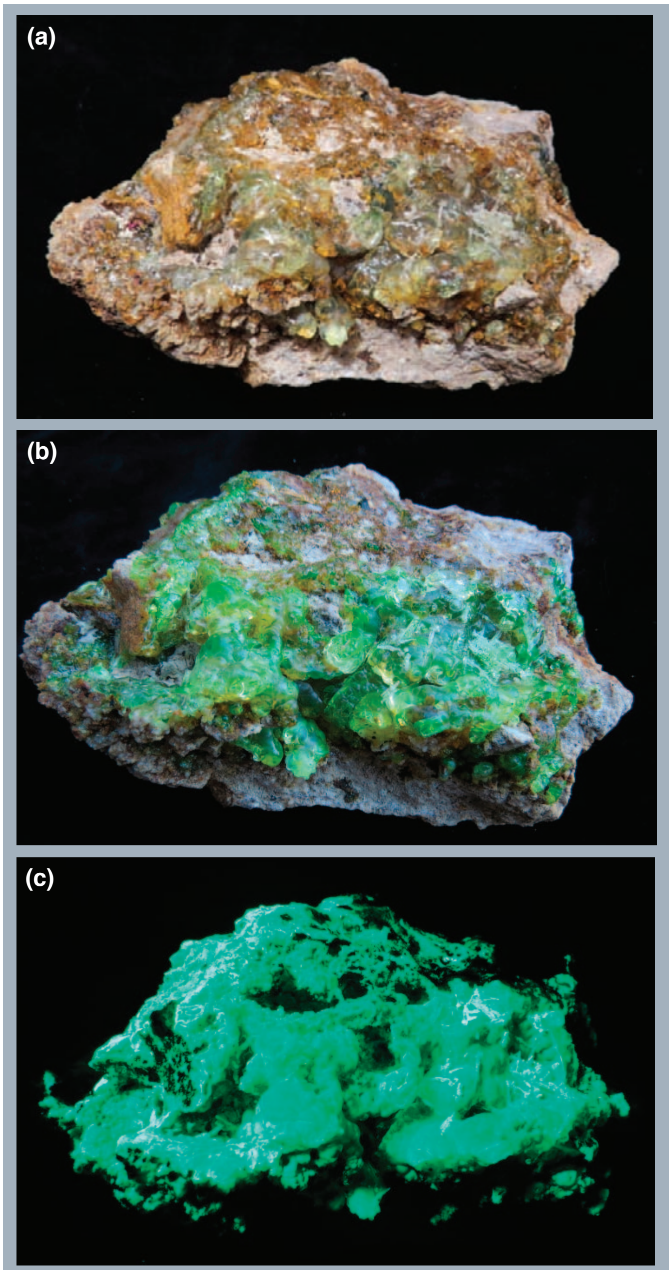


Figure 13. Hyalite opal specimen, 6 cm across, under three different lighting conditions: (a) incandescent light, (b) shaded daylight, and (c) shortwave ultraviolet. Peter Megaw specimen.

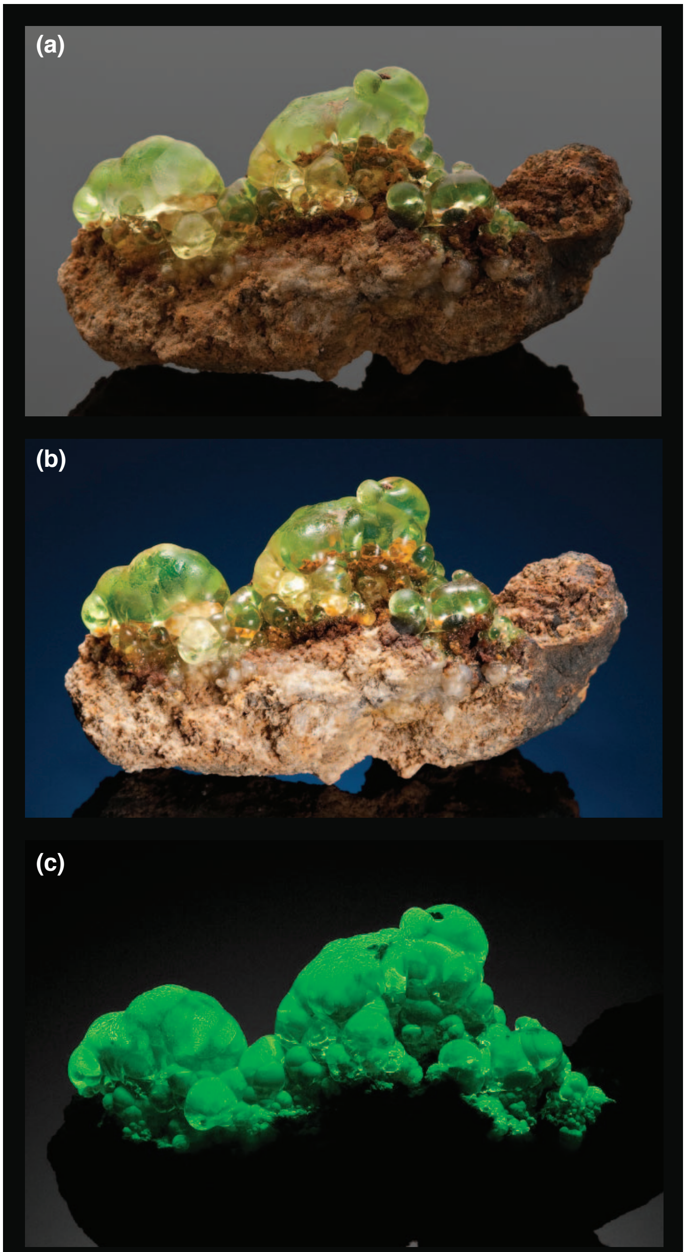


Figure 14. **Hyalite opal specimen, 5.6 cm across, under three different lighting conditions: (a) shaded daylight, (b) strobe light (daylight equivalent), and (c) shortwave ultraviolet. Peter Megaw specimen, Mark Mauthner photos.**

Hyalite, SiO_2. The green daylight-luminescing opal here has been identified as hyalite by a combination of its opal-AN Raman signal and its glassy texture in the scanning electron microscope (Fritsch et al. 2015). It occurs as botryoidal coatings and void fillings in a volcanic environment, as is usually the case for hyalite. Freestanding lustrous botryoids make the most attractive specimens, with individual drupelets making stand-alone jewelry pieces. The specimen material is also facetable and can carry finished gemstone prices. The opal's luminescence is due to dispersed uranyl ions, with a maximum emission at 524 nm and excitation in both the ultraviolet (UV) and the visible range (Fritsch et al. 2015). Although the opal may locally contain up to 0.3 weight percent UO_2, detailed radiation measurements recorded only very low levels of emitted radioactivity, so there is no danger in wearing this gem (Fritsch et al. 2015). Most "granite" kitchen countertops are more radioactive than this hyalite opal.

Origin of Daylight-Induced Luminescence

The main interest in this hyalite is its daylight-induced luminescence. Why is it observed in this opal and in almost no others? It is apparent from studies of this material (Fritsch et al. 2015) and the literature (in particular, Gaillou 2006; Gaillou, Fritsch, and Massayeau 2011) that most opals luminescing green under UV radiation show very similar excitation spectra to those of this hyalite (compare uranyl absorption in the violet and blue ranges). And indeed, most opals that fluoresce green under UV radiation also will show green luminescence under a 405-nm laser, which is visible light. However, our eyes do not perceive any green emission when these gems are observed in normal daylight. Why?

Several phenomena compete for the perception of a color: light transmitted (the body color), light scattered ("haze" in colorimetric terms), and light reflected (gloss) by an object. The most common result of light scattering is seen in milky gems (e.g., white diamond, jade, and opal) or the blue adularescence of moonstone, but luminescence is also a scattering phenomenon. The green color component of the hyalite described in this article belongs to scattered light encountering the eye. One of the matrix specimens examined by Fritsch et al. (2015) was covered by green-luminescing hyalite that abruptly graded into milky white hyalite that showed no daylight luminescence, although under UV radiation (or a 405-nm laser), the green luminescence was equally intense over the entire specimen. The emission spectra obtained from all of the opal on the specimen were the same, and, surprisingly, the excitation spectra also were identical. Therefore, the entire specimen also should have displayed the same green luminescence in daylight—if this phenomenon could be fully described by spectroscopy alone. Because the visual perception of

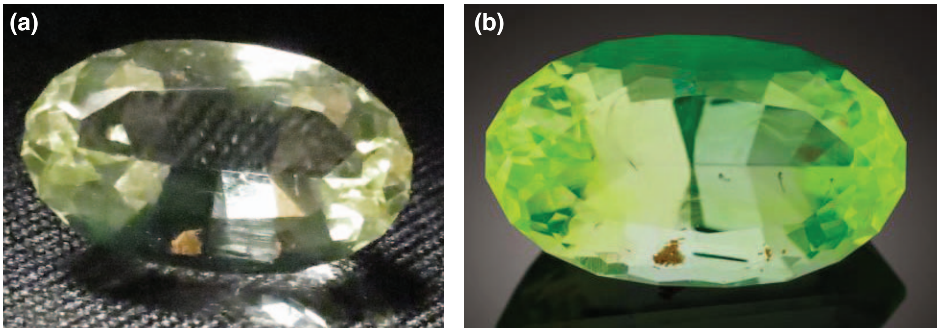


Figure 15. **Oval cut 2.81-carat hyalite opal gemstone cut by Michael Gray, shown under two different lighting conditions: (a) incandescent light, (b) shaded daylight. Peter Megaw specimen, Tino Hamid photo.**

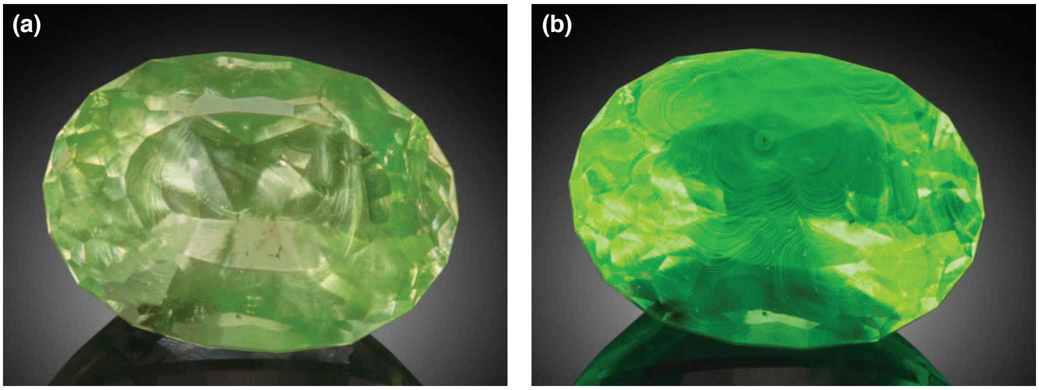


Figure 16. **Oval cut 3.93-carat hyalite opal gemstone cut by Michael Gray, shown under two different lighting conditions: (a) studio strobe light (daylight equivalent) and (b) shortwave ultraviolet. Peter Megaw specimen, Mark Mauthner photos, courtesy Heritage Auctions.**

the specimen was quite different, the daylight luminescence must be dependent upon the interplay of other factors. First, there must be an absence of any sort of luminescence quencher, such as Fe^{3+}. Second, an absence of other forms of scattering besides luminescence is important: for example, if the sample is milky, it is unlikely that daylight luminescence will be seen. This second condition implies that the gem has to be transparent. Third, the presence of uranyl ions is a prerequisite, probably in a certain range of concentration: if there is not enough, the luminescence will be too weak, and if there is too much, the molecules will absorb one another's emission through a process called *concentration quenching* or *self-quenching* (Fritsch and Waychunas 1993), reducing the overall luminescence. The excitation spectrum of the hyalite basically indicates that its luminescence may be excited by visible light, but other conditions, probably not limited to those cited above, are necessary for this rare phenomenon to occur.

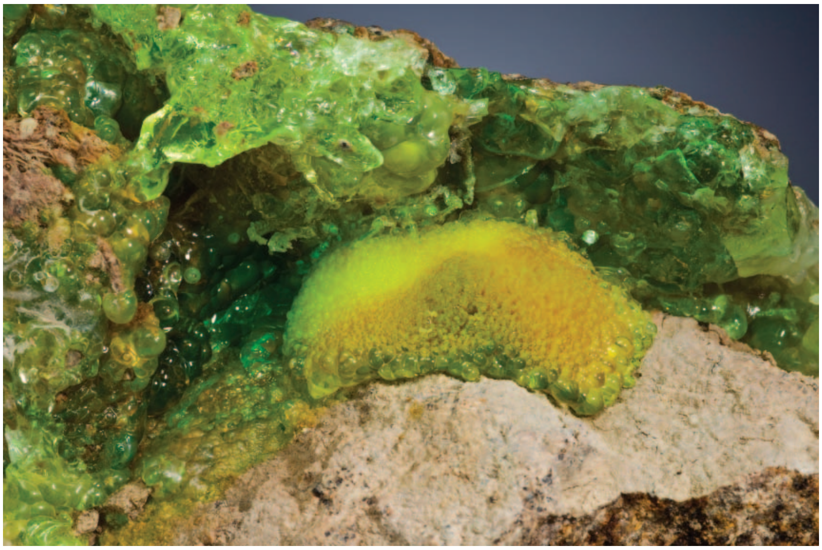


Figure 17. **Hyalite on boltwoodite, 3.5 cm. Peter Megaw specimen, Jeff Scovil photo.**

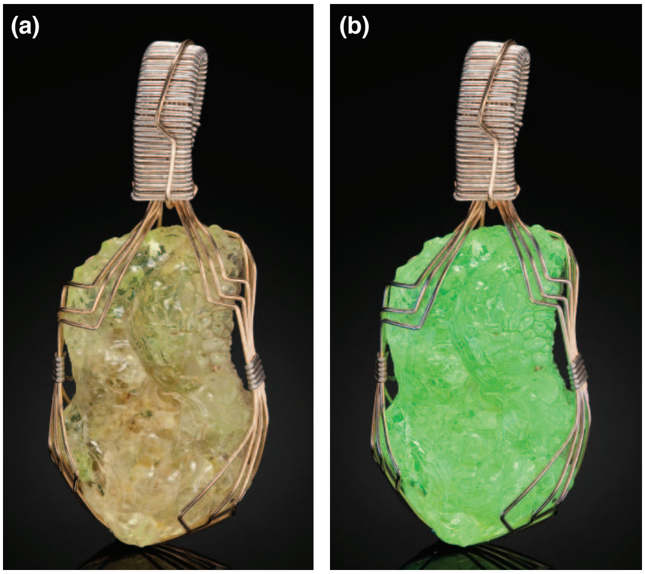


Figure 18. **Natural botryoidal hyalite opal mass, 6.6 cm, mounted in pendant: (a) studio strobe light (daylight equivalent), (b) shortwave ultraviolet. Allison Megaw specimen, Mark Mauthner photos.**

Uranium species. A number of hexavalent uranium species are found as microcrystals associated with, encapsulated by, and indeed flooded with the hyalite, which severely hampers their identification. The most prominent species were identified by Spano et al. (2015) with X-ray diffraction as meta-autunite, $Ca(UO_2)_2(PO_4)_2 \cdot 6\text{–}8H_2O$; haiweeite, $Ca(UO_2)_2[Si_5O_{12}(OH)_2] \cdot 6H_2O$; uranophane, $Ca(UO_2)_2(HSiO_4) \cdot 5H_2O$; and meta-uranospinite, $Ca(UO_2)_2(AsO_4)_2 \cdot 8H_2O$. Origlieri (pers. comm., 2016) subsequently identified boltwoodite, $(K,Na)(UO_2)(SiO_3OH) \cdot 1.5H_2O$.

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