The Anahí Ametrine Mine, Bolivia

By Paulo M. Vasconcelos, Hans-Rudolf Venk, and George R. Rossman

The Anahí mine, Bolivia, has produced large amounts of amethyst, citrine, and amethyst-citrine for the gem market. Field and experimental investigations conclusively show that the amethyst-citrine color combination in quartz crystals from Anahí is natural and does not result from laboratory treatment. The unusual color patterns probably result from the uncommon geologic conditions under which these quartz crystals formed, although the crystal chemical properties controlling the sector color zoning still elude explanation. From 1989 to the present, more than 100 tons of ametrine crystals, yielding 40–80 kg of cutting rough per ton, have been produced.

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One of the most interesting gem materials to appear on the market in recent years is the bicolored variety of quartz known as amethyst-citrine, bicolored amethyst, bolivianite, or ametrine* (figure 1). Although this material was well received when it first entered the international market in the 1970s, the natural or artificial origin of ametrine has been the subject of much controversy over the past decade. In 1981, Nassau showed that an amethyst-citrine color combination could be produced artificially in a naturally Brazilian amethyst sample by combined irradiation and heat treatment. Simultaneously, North American gem traders received conflicting reports about where the material was being mined (Vargas and Vargas, 1980; Nassau, 1981). As a result, speculation arose that ametrine was artificially produced.

Now, however, the open-door policy practiced by the current owners of the mine has made it possible to disseminate reliable information about the natural occurrence of ametrine (Verbin, 1993; Jones, 1993). The Anahí (pronounced a-na-e) ametrine mine is located in eastern Bolivia, near the border with Brazil (figure 2). The Anahí mine produces ametrine crystals, which are then selectively cut into amethyst, citrine, or amethyst-citrine. To gather information on the geology of the deposit and the formation of ametrine, as well as to collect material for further testing, the authors traveled to the mine in October 1992 (PMV) and August 1993 (PMV, HRW, and GRR). In this article, we present the results of these geologic and mineralogic studies, review mining and production at Anahí, and provide information on the properties of this material and on the possible cause of the unusual color combination found in this variety of quartz.

*Crystal chemical investigations indicate that this material is composed of intergrown amethyst and citrine. In this article, we will use the name ametrine to refer to this bicolored variety of quartz, since it has correct mineralogic implications and is already widely used in the gemstone trade.
The mining of ametrine is shrouded in legends, mystery, and international intrigue. According to Jean Marc Tressaître (1993), Europeans first learned of ametrine in the 17th century, when a Spanish conquistador presented samples to his monarch; the conquistador had received the ametrine mine as a dowry when he married a native princess—named Anahi—of the Ayoreos tribe. There is no further record of ametrine until the 20th century, although it is rumored to have reappeared in the 19th century in the hands of Uruguayan, Paraguayan, and Brazilian dealers. Note that Holden (1925) described bicolored amethyst-citrine quartz and Leinmüller (1951; as cited in Balitskaya and Balitskaya, 1986) described similar material purportedly from Brazil. There are also some accounts that the deposit was exploited sporadically by Indians from the local Ayoreos tribe, who sold their production in a missionary post in Rincón del Tigre to gemstone dealers from Puerto Suárez (figure 2). R. Colen and D. Reis, pers. comm., 1993).

We do know that gem production restarted sporadically in the 1960s (Litherland et al., 1986). Active exploitation did not occur until the late 1970s, when demand for gem-cutting material prop- pelled Brazilian gem dealers and Brazilian, Bolivian, and Paraguayan miners into the area. Because the deposit was located in a Bolivian state fiscal reserve, however, it was constitutionally closed to private mining. In fact, a military station was established nearby specifically to prevent such activities. Mining did continue, though, according to personal accounts by Brazilian miners/dealers who ventured into the region at the time, in exchange for “fees” negotiated with some of the local military authorities (R. Colen, pers. comm., 1993). The gem explorers traveled by boat along the Paraguay River to the village of Amolar (figure 2). From Amolar, they traveled west on jungle trails for 30 km, a two-day journey by foot. The miners hand-carried all the
Figure 2. The Anahi mine has remained virtually unknown because of difficult access to the often flooded Pantanal-Chaco region of South America. Although there is a small airstrip near the mine, the area is commonly reached by traveling via boat from Puerto Suarez to the Mandiod Lagoon, and then from the lagoon to the mine over 29 km of jungle trail. Because of legal restrictions (until 1989) on mining in the Anahi area and on importing the gem material into Brazil, early reports identified the source as being in Mato Grosso do Sul or Uruguay. Today, production from the Anahi mine is processed largely in the Brazilian gem centers of Belo Horizonte (BH), Governador Valadarees (GV), and Teiffilo Otoni (TO). Also abbreviated on the map is Santa Cruz de la Sierra (SCS).

tools and supplies necessary. They cobbled the rough material at the mine site, keeping only the gem-quality portions of the crystals. Often a new military commander or inspector would arrive unannounced in the area, forcing the illicit miners to flee through the jungle with their tools and whatever gem rough they had been able to recover.

Not only did the Bolivian government forbid mining in the Anahi area during this period, but the Brazilian government also had strict import restrictions that made it virtually impossible for gems mined in Bolivia to enter Brazil legally. To circumvent these restrictions, the miners smuggled the Bolivian ametrine into the state of Mato Grosso do Sul, Brazil (again, see figure 2). The gems were then registered with Brazilian fiscal authorities in Corumbá, as if they had been mined in Brazil. It was because of their need to protect their sources and trade ametrine within Brazil that gem dealers disseminated conflicting accounts about the mine location. Brazil near the Bolivian border (Aimes and Rossman, 1986), Brazil near the Uruguayan border (Vargas and Vargas, 1980), and the Brazilian state of Mato Grosso (Sauer, 1982) were claimed as production localities for ametrine. Other sources—including Bolivia (Nassau, 1981), Uruguay (Vargas and Vargas, 1980), and Brazil, Uruguay, and Bolivia (Balitsky and Balitskyaya, 1986)—were also cited in the international literature. Unfortunately, this ambiguity about the geographic source of ametrine contributed to the widespread belief that ametrine was manufactured in a laboratory in Brazil.

Although Nassau (1981) indeed showed that amethyst-citrine could be artificially generated from natural amethyst, there appear to be visual differences between the artificially generated sample illustrated in Nassau’s article and the ametrine available in the market. Our efforts to reproduce Nassau’s experiments (heat treating and irradiating Marabá amethyst) resulted in a bicolored stone that showed citrine and smoky amethyst, again very unlike the appearance of natural ametrine. In preliminary experiments, we have also observed differences in the optical spectra of Anahi citrine and those of citrine formed by heating Marabá amethyst. From a practical perspective, the quantities of ametrine commercially available and their low value at the time did not support the hypothesis that they had been produced by a complicated, expensive combination of irradiation and heat treatment. Furthermore, accounts by researchers and reputable gem dealers acquainted with the complex and politically sensitive situation in the ametrine mine explained the scarcity of published and official information (Koivula, 1987; Koivula and Kammerling, 1989). In addition, as early as 1986 some dealers displayed natural ametrine crystal
specimens during the Tucson gem and mineral shows that were morphologically unlike any commercially-produced synthetic quartz. Even so, rumors still persist that ametrine is only produced by treating amethyst or by synthesis.

In 1989, changes in the Bolivian constitution and mining code legalized mining in the fiscal reserves. A Bolivian company, Minerales y Metales del Oriente S.R.L. (M&M), acquired the concessions, officially named the mine Anahi in honor of the Ayoreo princess, and restructured the mining and trading of ametrine. Simultaneously, a change in Brazilian law legalized the importation of rough gem materials. Since then (up to July 1993), approximately 100 metric tons of mine-run ametrine has been traded at M&M’s offices in Puerto Suarez and Santa Cruz de la Sierra. Brazilian dealers buy most of the rough material and then have it processed at the gem-cutting centers of Belo Horizonte, Governador Valadares, and Te6filo Otoni for export. More recently, Brazilian dealers have been exporting large quantities of cobbled rough to Oriental cutting centers. Some of the rough has been used in carvings, and crystal specimens were again available at both the 1993 and 1994 Tucson shows (e.g., Koivula et al., 1993).

LOCATION AND ACCESS

The Anahi mine is located in Santa Cruz province, eastern Bolivia (figure 2), at 18°03’S, 57°48'42"W, approximately 30 km west of the border with Brazil. This region, known as Pantanal in Brazil and as Chaco in Bolivia and Paraguay, is characterized by lush tropical vegetation in the highlands and swamp vegetation in the flood plains of the Paraguay River. Access to the Anahi mine continues to be very difficult. To reach the Bolivian border town of Puerto Suarez, most visitors travel by air from La Paz via Santa Cruz, de la Sierra or by air from Rio de Janeiro. The quickest route from Puerto Suarez to the mining area is by chartered single-engine aircraft. A small dirt landing strip is operational during dry periods. A 3-km trail from the landing field to the mine can be traveled by foot or in the mining company truck. Access from Puerto Suarez is also possible by taking a six-hour speed boat trip up the Paraguay River to the MandiorC lagoon; from the lagoon to the mine, the traveler ventures along 29 km of jungle track. In recent months, the mining company has begun to use two boats to carry passengers and cargo to and from the mine.

GEOLOGY AND MINERALIZATION

The Anahi deposit (figures 3 and 4) occurs at the northern base of a dolomitic limestone hill, which is part of a north-south trending ridge that rises 200 m above the surrounding Pantanal plains. These north-south ridges are the surface expression of a 70-km-long regional fault system (figure 4). In the mineralized areas, these topographic features are probably formed by the hydrothermal alteration...
Granites, Granodiorites, Serpentinites, Quartzite, Limestones (Murcielago Group), Arkosic quartzite, Cherts and silcretes, Layered mafic intrusive, Consolidated alluvium, Quartz arenites, Recent alluvium, Faults, Amethyst occurrences.

Figure 4. The Anahi ametrine deposit occurs along a major regional fault system, along which other quartz deposits have been identified. In the immediate area of Anahi, the dominant host rock is a dolomitic limestone from the Murcielago Group, and silicification of the limestones, which renders them more resistant to weathering and erosion. Several quartz deposits occur along this regional fault system (Litherland et al., 1986), but significant amounts of gem-quality ametrine have been found only at Anahi. A nearby mine, appropriately named Mina Pobre (Poor Mine), also produces some low-quality (turbid) ametrine.

The carbonate rocks hosting the Anahi deposit belong to the Murcielago Group, a 500-m-thick flat-lying sequence of limestones. The carbonates are thought to have been deposited during a period of widening of a shallow continental sea, and they overlie a series of conglomerates, volcanic rocks, sandstones, shales, and banded iron and manganese formations, which rest unconformably on basement rocks. The deposition of the Murcielago carbonates and their subsequent folding are thought to have occurred during the Brasiliano Orogeny, between 500 and 900 million years (My) ago, when north-trending regional fault systems also developed (Litherland et al., 1986).

In the area of the Anahi mine, the Murcielago limestones occur as laminated grayish units with reddish, iron-stained horizons and as cream-colored massive carbonate rocks. X-ray diffraction analyses indicate that these rocks are dolomitic limestones. One petrographic study also indicates that the horizons are rich in iron oxides (mostly hematite), detrital quartz, and fine-grained white micas, probably muscovite.

The Murcielago carbonate units strike SS3°E and dip 35° to the southwest, but rotated and upright blocks are often found in the vicinity of the mine. The dolomite beds were strongly faulted and silicified in the mine area, with rotated limestone blocks cemented by massive milky quartz (figure 5).

The contact between the limestone and the quartz overgrowth is abrupt, and some limestone was dissolved before silica precipitation took place. In areas where the limestone blocks are large (up to 16 m) and open cavities between adjacent blocks are wide, the massive quartz overgrowth gradually becomes Figure 5. Quartz (Qlz) precipitates on the walls of vugs formed by dolomite (Dol) brecciation. Because these dolomite blocks are massive, they are routinely blasted to allow access to new pockets. At the contact with the dolomite, quartz is microcrystalline; it becomes coarse crystalline and milky away from the contact, and it etchingly forms euhedral crystals with tips that are purple and orange-yellow. The quartz-bearing cavities are often filled with clay minerals. Photo by P. Vasconcelos.
euhedral, forming crystals that are colored purple and orange-yellow toward the tip. These crystals grow toward the center of the open spaces. Some chambers are up to 5 m long, 3 m wide, and 5 m high—completely lined with prismatic quartz crystals (figures 5 and 6).

This style of mineralization, characterized by faulted and rotated blocks showing evidence of explosive fracturing followed by initially rapid mineral precipitation, is known as hydrothermal breccia (figure 7). The mineralizing solutions at Anahi were silica-rich, and quartz precipitated as a result of the decompression caused by limestone brecciation. The large sizes in which the crystals can occur suggest the migration of massive quantities of silica-rich solutions after initial brecciation. When hydrothermal fluids are suddenly depressurized they boil, in a manner similar to the loss of CO₂ when a soda bottle is opened. Boiling can be recognized by the presence of primary fluid inclusions with widely varying proportions of vapor and liquid phases within a single specimen (Roedder, 1984, p. 255). In quartz crystals from the Anahi mine, we—

Figure 6. Large euhedral ametrine crystals and clay minerals line the walls of one of the mineral cavities at Anahi. To recover the ametrine crystals, miners pry them from the milky base, often leaving gem-quality areas embedded in the matrix. The chamber shown here produced more than 10 metric tons of ametrine crystals. Photo by P. Vasconcelos.

Figure 7. This schematic cross-section depicts the geologic evolution of the deposit through time. When hot mineralized solutions form in the crust and migrate upward along porous and permeable rocks, they may reach a barrier presented by a less permeable horizon (A). The solutions get trapped by the obstacle, and the hydrostatic (water) pressure builds up. When the hydrostatic pressure becomes greater than the lithostatic (rock) pressure, the rocks burst open (B). The newly created fractures allow the solutions to migrate again. With the sudden release of pressure, the solutions are less able to hold dissolved constituents. This leads to rapid mineral precipitation. Overlying shales are subsequently weathered and eroded.
observed inclusions ranging from pure liquid to pure vapor, which further suggests that the deposit was formed by silica precipitation when the hydrothermal fluids boiled.

Ametrine-bearing vugs and chambers are often half-filled with white and red clay minerals (again, see figure 6). X-ray diffraction analyses indicate the presence of kaolinite, some smectites, quartz, hematite, goethite, and minor muscovite in the clay matrix.

**MINING METHODS**

The initial exploitation of the ametrine deposit was rudimentary; according to early miners, there was enough material buried in the soil profile and outcropping vugs that mining progressed by digging shallow pits and trenches. As the surface layers became depleted, small shafts and tunnels were lowered into bedrock, always following the trends of outcropping veins and cavities.

Currently, mining in Anahi proceeds solely by underground tunnels and shafts. Modernization and implementation of more efficient underground mining techniques was initially accomplished with the help of gem miners from Brazil, who worked on a contract basis. At present, the mine is solely operated by M&M personnel, under the direction of a Bolivian mining engineer. Approximately 60 miners work the deposit, a single nine-hour shift for six days a week.

The main breccia zone, where most of the ametrine-bearing vugs occur, is aligned approximately east-west on the hillside. Two main tunnels, roughly oriented north-south, reach this mineralized zone (figure 3). Within this zone, the irregular distribution of quartz veins and pods in the hydrothermal breccias requires mining along irregular tunnels to follow the mineralization. When the miners encounter large, massive dolomite blocks, they blast them. Blasting is commonly conducted twice a day, in the morning and late afternoon. The intricate network of interconnected tunnels makes air circulation difficult, and air quality is poor, particularly after blasting; a compressor is used to pump surface air into the tunnels. Barren host rock and the clay filling the cavities are removed in wheelbarrows (figure 8). Loose ametrine crystals are recovered from the mud—those attached to the milky quartz are pried from the walls. At the end of the shift, the daily ametrine production is removed.
from the tunnels, weighed, and stored in a fortified cabin. After washing and partial cobbing, the mine production is shipped to Puerto Suarez.

Until recently, the mine was actively exploited on only one level. Now, however, a vertical shaft has been lowered through mineralized host rock into a second level 15 m below the main tunnel. There is ample indication that this second level will be as productive as the first. The vertical continuity of the breccia system is still unknown, and the mine operators are planning a drilling program to determine the extent of future reserves. The mine is undergoing mechanization, and the gangue and mineralized products will soon be transported to the entrance by a small rail system.

ROUGH YIELD AND MARKETING
To assess the gem yield of typical Anahi mine run, one ametrine cluster weighing 37.5 kg (figure 9) was cobbled (figure 10), preformed, and cut (figure 11), yielding 1,763 ct of faceted stones from 1,942 grams of gem rough. These recoveries correspond closely to those obtained by cutting operations that process large quantities of ametrine, although tests run on 1,000-kg lots by M&M resulted in significantly lower yields.

Before cobbing, the crystals are bathed in boiling water to help shatter the milky areas. According to some cutters, this makes it easier to extract the best gem material, which is in the cores. In the laboratory, however, we subjected a series of ametrine slices cut perpendicular to the c-axis to thermal shock in hot water. We found that fractures will propagate from the milky crystal surfaces into the flawless cores, generally along a plane parallel to one of the prism faces. This result indicates that the thermal treatment potentially destroys perfectly viable and valuable gem material. The propagated fractures seem to correspond to the cleavage planes of quartz, as suggested by Frondel (1962, p. 106).

It is impossible to assess the total production of ametrine since the modern discovery of the Anahi deposit, because there are no records for the years of illicit mining activities. From 1989 to the present, however, M&M has recovered approximately 100 metric tons of rough crystals. Most of this material has been cut in Brazil, from where it has entered the gem market. M&M plans to establish a more vertically integrated operation, which will include—in addition to mining—cutting and marketing of loose gemstones, carvings, and collectible items. To achieve these goals, ametrine will be cobbled and sawed in a cutting operation in Santa Cruz de la Sierra before being released to the market.

MATERIALS AND METHODS
Field observations included precursory examination of several thousand crystals. On the order of 200 crystals were collected for more careful laboratory...
examination, and approximately 50 crystals were analyzed in detail by Fourier transform infrared (FTIR) spectroscopy, optical absorption spectroscopy, electron microprobe analysis, transmission electron microscope analysis, and optical microscopy. We commissioned the cutting of approximately 3,000 ct of stones (ametrines, citrines, and amethyst) from several crystals obtained at the Anahi mine. Specific-gravity measurement was performed on one representative citrine and one representative amethyst sample. The senior author measured the refractive indices of 8–10 samples of each variety at the GIA research laboratory.

The electron microprobe analyses were performed on the ARL-SEMQ electron microprobe at the University of California, Berkeley. Sample current was 60 nA, accelerating voltage was 20 kV, and the beam diameter was 2–3 μm. Standards used were Al₂O₃ for Al and FeSiO₃ for Fe; the results were checked by analyzing National Bureau of Standards trace-element standards 611, 612, and 614, and also analyzing Berkeley synthetic quartz standard 914 (1 ppm Al determined independently by atomic absorption spectroscopy) as unknowns. The calculated detection limits for the electron microprobe analyses were ~10 ppm for Al.

Figure 11. The crystal cluster shown in figure 9 yielded approximately 1,760 ct of faceted amethyst, ametrine, and citrine, as well as the “champagne”-colored material, in the range of hues and saturations shown here. Photo © Harold & Erica Van Pelt.
and 20 ppm for Fe. Two samples were also analyzed by micro X-ray fluorescence, a newly perfected technique (Gurvich, 1993), in the Fissons Instruments research laboratory in San Carlos, California.

Infrared spectra were obtained using a Nicolet 60SX FTIR spectrophotometer at the California Institute of Technology (Caltech). Specimens were examined in the form of basal slabs ranging from 1 mm to 1 cm thick. Individual regions were defined by 1-mm-diameter circular metal apertures. Our results were obtained at room temperature. On the order of 60 regions in eight samples were analyzed.

Optical absorption spectra were recorded at Caltech using a locally constructed diode array spectrometer designed to obtain spectra from small areas. It employs 1,024 cooled silicon diodes in an illuminated polychrometer which receives light from the area of interest in the sample directed through a per-optic cable. All areas analyzed by FTIR were also investigated for their optical absorption spectra.

Transmission electron microscopy of one amethyst and one citrine sector from an Anahi crystal was performed in a Jeol 100-kV transmission electron microscope (EM) at the University of California, Berkeley. The amethyst crystal was polished into a 30 µm section that was subsequently thinned by ion ablation for EM investigation. Specific gravity was calculated by the immersion method. Refractive indices were measured using a Duplex Duplex refractometer.

**MINERALOGY**

Ametrine crystals vary widely in crystal habit, size, and mode of occurrence. Some of the crystals are small (1-8 cm in length) and occur embedded in a clay and carbonate matrix. These specimens are well crystallized, showing euhedral habits and lustrous crystal faces (figure 12). The crystals are often gem quality, but the colors are not intense. An interesting feature of these small crystals is that the rhombohedral faces terminate in a c face, which is invariably etched. It is yet unclear whether the c faces are growth faces or the result of partial dissolution of the rhombohedral faces. Larger (10-40 cm long) crystals that lack c faces also occur loosely held in the clay matrix. The intensely colored, flawless areas commonly seen in these crystals yield the best gems from the deposit.

Most commonly seen at Anahi, however, are large, complex points and clusters (again, see figure 9), growing from a milky quartz base. These crystals line the walls of cavities, and they are attached to their neighbors near the base (again, see figures 5, 6, and 9). They display well-formed rhombohedral terminations devoid of c faces, but instead of hexagonal prisms there is a complex intergrowth of satellite crystals.

To date, two vugs in the Anahi mine revealed deeply etched crystals found floating in the red clay matrix (figure 13). They display a complex etching pattern: The prism faces are completely resorbed and the rhombohedral faces, where still preserved, display deep etching pits oriented at approximately 45° to the c-axis. The crystals invariably display frosty c faces or very low angle rhombohedral faces.

The etching process consumes most of the prisms, but often does not dissolve the rhombohedral faces, except at the tip of the crystal. The etched crystals occur in two main cavities located at the center of the mineralized area and associated with the major trend of mineralization. This suggests that they...
Deeply weathered clays show no signs of etching. Ametrine also occurs as rounded pebbles and cobbles that have been etched and abraded (again, see figure 13), which suggests significant mechanical weathering during transport in a sedimentary environment. Unfortunately, the area around the mine has been disturbed by previous mining activities, and it is not possible to identify if these cobbles came from ancient stream channels. One of the mine owners (Mario Urriolagoitia, pers. comm., 1993) indicated that some cobbles and pebbles were mined from the mud matrix within underground vugs. During geologic mapping, we noted that some underground cavities were filled with clay minerals, rock, and plant fragments which appeared to have fallen in from the surface, probably when the limestone "roof" weathered through. The cobbles and pebbles may have resulted from weathering and erosion of outcropping veins on the top of the mountain.

In addition to ametrine, the deposit also contains minor amounts of amethyst, milky white quartz, and smoky quartz crystals. The smoky crystals always occur in massive hematite/quartz veins sporadically associated with the breccia. The crystals are euhedral, very clean, and transparent, and up to 3 cm long.

Figure 13. Deeply etched crystals (here, 15 cm high) have been found in two main pockets within the mine; their appearance may reflect resorption of quartz during waning of the hydrothermal system. Rounded and etched cobbles and pebbles (here, about 5 cm in diameter) found around the mine are not significant economically, but they provide insight into the deposit's geologic and geomorphic history. They indicate that some ametrine may have been transported in a paleo river channel that once existed in the area. Note from the polished pebble the high-quality ametrine found in these unusual specimens. Crystal and pebbles courtesy of Minerales y Metales del Oriente S.R.L.; photo © Harold e1 Erica Van Pelt.

COLOR

The most striking characteristic of ametrines is their complex color distribution (figure 14). This color zoning is fairly consistent: The major rhombohedral r (101) sectors are purple, and the minor rhombohedral z (011) sectors are orange-yellow. The purple r sectors are invariably Brazil-twinned with both right- and left-handed quartz, while the orange-yellow z sectors show no Brazil-twinning. This can be established by viewing a slab with polarized light (as seen in figure 14D). Initial measurements suggest that the citrine sectors are either untwinned right-handed or untwinned left-handed quartz [K. Zito, pers. comm., 1994]. The boundaries between left- and right-handed quartz appear dark under crossed polarizers and are known as Brewster fringes (Brewster, 1823). The Brewster fringes appear dark under polarizers because when light travels through equal distances of right- and left-handed quartz, the state of polarization is unchanged (McLaren and Pitkethly, 1982). The distance between Brewster fringes varies from one crystal to another, but it generally ranges from 0.1 to 3 mm. Examination of Brewster fringes in the
Figure 14. A slice of an idealized ametrine crystal, cut perpendicular to the c-axis and through the rhombohedral faces, is illustrated in part A. The \( r \) \([10\bar{1}]\) sectors are Brazil twinned, and the \( z \) \([01\bar{1}]\) sectors are untwinned. Schematic illustration B shows a slice of the same crystal cut through the prism faces; it also displays Brazil-oriented \( r \) \([10\bar{1}]\) and untwinned \( z \) \([01\bar{1}]\) sectors. The diagram also illustrates the decrease in intensity—and even absence of color—in the interference zones near the crystal edges. When a crystal section is viewed in ordinary, unpolarized light (C), the untwinned orange-yellow sectors and the color banding in the twinned purple sectors are evident; when the slice is observed between crossed polars (D), one can see the details of the contacts between \( r \) and \( z \) sectors. Brewster fringes (dark) separate left-handed from right-handed quartz. The boundary between citrine and amethyst is a sharp crystallographic plane which the Brewster fringes roughly parallel. The citrine-amethyst boundary corresponds to the boundary of a significant change in trace-element composition. Photos by Robert Weldon.
icular to the c-axis, and the purple, orange-yellow, and colorless zones were analyzed by electron microprobe to determine differences in Fe and Al contents. The microprobe results (figure 16) indicate that the orange-yellow sectors invariably have a higher iron (Fe) content (68-125 ppm [parts per million] average) than the purple (19-40 ppm average) or the colorless (-17 ppm average) sectors. There is no noticeable variation in aluminum (Al) content between the sectors, but because the results obtained are near the calculated Al detection limits of the technique (10 ppm), it is impossible to rule out Al variability. We also analyzed 2-mm-diameter areas in the amethyst and citrine sectors by micro X-ray fluorescence. The results independently confirm the ranges and trends for Fe concentration identified by electron microprobe analysis.

Infrared spectroscopy also showed differences between the orange-yellow and purple sectors (figure 17). The room-temperature I.R. spectra of purple sect-

Figure 15. Cross-sections through large complex crystals beautifully illustrate the separation between the amethyst and citrine zones, as well as the intergrowth of many subsidiary crystals at the perimeter. The slab is 11 cm at its widest point and 1.3 cm thick. Photo © Harold vÖ Erica Van Pelt.

Figure 16. Electron microprobe analyses, taken across the three color sectors of the ametrine specimen shown here, indicate high iron concentrations in the untwinned citrine sectors, with lower total Fe contents for the Brazil-twinned amethyst (and colorless) sectors. Given the limitations of current analytical procedures, we could not resolve the Al content variation, if any. Start (S) and end (E) of traverse is shown in the photomicrograph.
Infrared spectra of near-colorless, amethyst, and citrine regions of an Anahi amethyst-citrine crystal [unpolarized spectra of (0001) slabs run at 25°C, presented normalized to 2.0-mm thickness and offset from zero for clarity] indicate a marked difference in peak shape between the amethyst and citrine sectors. The broad-band absorption in the citrine sector has been interpreted as indicating the presence of molecular water (Aines and Rossman, 1986).

The citrine sectors display similar spectra, except for the addition of a broad band superimposed on the sharp peaks that also occur in the amethyst sectors. This broad band has been attributed to small groups of water molecules trapped in the quartz structure during crystal growth, indicating that the orange-yellow bands are more hydrous than the purple bands (Aines and Rossman, 1984).

Optical absorption spectra of the ametrines display a strong absorption at 540 nm in the amethyst sectors and a slight absorption at the same wavelength for both the near-colorless regions and the citrine sectors (figure 18). The color of the citrine is controlled by the rising absorption in the violet end of the spectrum (400-500 nm), which favors the transmission of violet light. The color of the amethyst is controlled by the transmission windows centered near 440 nm and 730 nm, which favors the transmission of violet and red. Optical absorption spectroscopy of an oriented amethyst cube shows that the amethyst sectors are pleochroic, a feature commonly observed in amethyst in general. A similar cut citrine cube showed only a slight difference in absorption of light traveling perpendicular and parallel to the c-axis.

To test the color saturation in natural ametrine samples, we had a crystal slice submitted to 88 days of exposure to $^{137}$Cs gamma rays at Caltech (a total dose of 92 megarad). Comparison between the irradiated slice and a control sample indicates that radiation does not induce any significant color changes in ametrines. This result is significant, because some amethysts and citrines will turn smoky when irradiated.

GEMOLOGICAL PROPERTIES

Three distinct varieties of quartz are extracted from the ametrine crystals: citrine, amethyst, and ametrine (see figures 1, 11, and 19). The gemological properties of each variety are discussed separately below.

Citrine. The Anahi mine is one of the few commercial occurrences of natural citrine; most citrines available in the gem market today are produced by heat treating amethyst from Marahab (to a bright "golden" orange-yellow) or Rio Grande do Sul and Uruguay (to orange to orange-brown; Epstein, 1988). In thicknesses of a few millimeters to 1 cm, Anahi citrines typically range from orange-yellow to brownish/greenish yellow (figure 19) and are only weakly dichroic. The weak dichroism is consistent with small differences in the intensities of the optical absorption bands observed with light parallel and perpendicular to the c-axis.

To test the color saturation in natural ametrine samples, we had a crystal slice submitted to 88 days of exposure to $^{137}$Cs gamma rays at Caltech (a total dose of 92 megarad). Comparison between the irradiated slice and a control sample indicates that radiation does not induce any significant color changes in ametrines. This result is significant, because some amethysts and citrines will turn smoky when irradiated.
Figure 19. The ametrine crystals from Anahi produce citrine, amethyst, and ametrine gems in a broad range of hues. The largest stone in this photo, a round brilliant citrine, weighs 28.82 ct; the smallest, also a round brilliant, weighs 5.66 ct. Photo © GIA and Tino Hammid.

As compared to perpendicular to—the c-axis. At 400°C, heat treatment causes the color to become slightly paler and to lose some of the brownish or greenish hue. The color fades completely between 450° and 500°C. We did not observe any loss of color in the samples subjected to the sunlight fading tests described in the amethyst section below.

On the eight stones tested, we recorded typical refractive indices of $n = 1.541$ and $c = 1.550$. The specific gravity, measured hydrostatically, is 2.65.

The citrines we examined were generally inclusion free. When inclusions were present, they were usually two-phase fluid inclusions associated with secondary fractures in the crystals. We did not observe solid inclusions in any of the samples examined.

Amethyst. This is the principal gem produced in the Anahi mine, because of both its greater abundance and its economic value. Anahi amethysts range from near-colorless to intense violet-purple (figure 19). The amethyst sectors are strongly zoned, because of the irregular distribution of coloring agents controlled by the Brazil-twinning, and color zoning is visible in stones cut with the table nearly perpendicular to the c-axis. In general, fashioned amethysts from Anahi are a “purer” violet-purple, with none of the brown or yellow modification seen in amethyst from mines such as Mashib and Rio Grande do Sul, because the color zoning of the Anahi material forces gem cutters to totally eliminate the citrine bands from the amethyst rough during sawing. Amethysts from other mines are often cut incorporating both the “pure” purple-violet of the z sectors and the brownish purple-violet of the z sectors in the same stone. These mixed-sector stones often display the brownish undertone characteristic of z sectors.

Figure 20. The lower portion of this 12-cm-diameter ametrine slice was exposed to direct sunlight for 47 days on a rooftop in Oakland, California. The upper portion was retained in darkness, as a control. Spectroscopic measurement indicated that 33% of the amethyst color faded during this exposure. Photo by G. Rossman.
The refractive indices of typical Anahi amethyst, obtained from 10 stones, are $n = 1.541$ and $\varepsilon = 1.550$; again, S.G. was recorded to be 2.65. Because the amethyst is pleochroic, the color may vary from "pure" violet-purple to pinkish purple to blue, depending on the viewing angle relative to the optic axis.

Heat treatment will cause the amethyst color to fade progressively and finally disappear at 400°C. We found that the amethyst color also fades with long-term exposure to sunlight. We exposed half of an ametrine slice to direct sunlight on a rooftop in Oakland, California, from July 6 to August 21, 1993. Comparison between the control sample and the sample exposed to sunlight—both visually and with the optical spectrometer—indicates the loss of 33% of the color intensity during the experiment (figure 20). Along these same lines, it is interesting to note that crystals found on the surface of the hill above the mine often display only the citrine color. When one of these crystals was submitted to two days of $^{137}$Cs gamma rays at the California Institute of Technology (2.1 Mrad total dose), the amethyst color was restored to the $r$ sectors. Fading from prolonged exposure to sunlight appears to be a characteristic of amethyst in general. As is the case with all amethyst, amethyst or ametrine from the Anahi mine should not be worn for extended periods in bright light.

All of the Anahi amethysts we have examined so far are free from solid inclusions. However, we did note abundant fluid inclusions—both primary and secondary—which may cause a substantial decrease in yield. Primary fluid inclusions are oriented along the twin planes in the amethyst sectors. Partially healed fractures in the amethyst sectors are affected by the Brazil-twinning, which results in internal features referred to as a "rippled fracture inclusion" (Webster, 1983), "zebra striation" (Gübelin and Koivula, 1986), or "tiger stripes" (Webster, 1983). These internal features are characterized by liquid and two-phase inclusions (Schmetzer, 1987). Some inclusions appear to be 100% vapor, although a thin liquid film may actually wet the inclusion walls.

**Ametrine.** Until the late 1970s, according to Domingos Reis, one of the pioneers in ametrine cutting, most of the rough material from Anahi that reached the cutting centers in Brazil was selectively sawed, and only the amethyst sectors were used because the citrine color was considered undesirable. Two dealers in ametrine rough, Silvio Sbaraine and Emi Rolderbal, from Rio Grande do Sul, were among the first to suggest, in 1978 (D. Reis, pers. comm., 1993), that if tourmaline could be marketed in bicolored stones, then why not market bicolored quartz?

Ametrine encompasses the gemological properties described above for amethyst and citrine. Ametrine is unusual both for its sharp color zoning, which is due to the fact that the boundaries...
between the citrine and amethyst zones are crystallographically controlled, and the large size of the amethyst and citrine zones (see figure 14). Ametrines are typically cut to enhance the two colors, with the color boundary perpendicular to the table. Rectangular, parallelogram, square, or other shapes of angular geometry, together with step patterns of faceting, are commonly used (again, see figures 1, 11, and 19), rather than brilliant cuts, which mix colors through internal reflection. However, brilliant cuts have been used successfully in jewelry (figure 21). In addition, the color combination is ideal for carvings (figure 22), and new fashioning techniques that incorporate the amethyst and citrine sectors as part of an overall work of art have recently come into vogue (see cover to this issue, figure 1, and figure 23). Faceted pieces that contain mostly citrine intermixed with small sectors of amethyst attain a pleasant "champagne" or "peach" color (again, see figure 1).

In addition to the traditional cuts, some ametrine crystals can also be sliced perpendicular to the c-axis, yielding a zoned 'star-fruit' color combination, similar to that shown in figure 15.

**DISCUSSION**

All other significant amethyst deposits in production today (see, e.g., Epstein, 1988) occur as geodes in intermediate-to-acid flows in flood basalt provinces (Rio Grande do Sul), as veins in quartzites and quartz-arenites (Marabá, Jacobina, Vitoria da Conquista), or as late-stage crystallization around the quartz cores of pegmatites (Minas Gerais and Espirito Santo). The geologic conditions in which the Anahi ametrine deposit formed, hosted by carbonate rocks displaying evidence of hydrothermal brecciation, are fairly unusual. The silica-bearing fluids probably became alkali-rich by reacting with the limestone host rocks. These fluids were moderately enriched in Fe, as indicated by the precipitation of hematite bands within the breccia zones. The fine-grained muscovite found in the gem pockets, if precipitated by the hydrothermal solutions, indicates that these solutions were also K-rich. The style of mineralization indicates fast quartz precipitation immediately after brecciation, and slower quartz precipitation—conducive to the formation of large crystals—as the silica-bearing solutions migrated through the system.

It is likely that the temperature gradient within each gem pocket was small because of the substantial amount of hydrothermal solution that was probably trapped below the deposit before brecciation. Potassium in the system may have provided the natural radioactivity required for the formation of the color centers, although the present K contents in the cavities are too low to have provided the necessary background radioactivity (XRD analysis showed that muscovite, the K-bearing phase, was a minor phase in the gem pockets, although...
greater amounts may once have been present and subsequently destroyed during weathering.

Iron-rich potassium-carbonate alkaline solutions and a low temperature gradient in a hydrothermal cell are precisely the conditions necessary to produce the amethyst-citrine color combination in synthetic quartz, according to Balitskaya and Balitskaya (1986), who attribute the bicoloration to growth rates:

All this evidence suggests that the amethyst-citrine dichroism in synthetic quartz crystals grown on rhombohedral seeds must be related to certain threshold (critical) growth rates for the major and minor rhombohedral faces which govern the incorporation of either the amethyst-causing or the citrine-causing impurities by these faces. Below these critical values a face absorbs the amethyst-causing impurities, above them the citrine-causing ones. As the growth rates approach the critical values, both types of impurities are assimilated.

The amethyst color is traditionally attributed to the presence of Fe$^{4+}$ in quartz, in either interstitial (Cohen, 1985) or both interstitial and substitutional (Lehman and Bambauer, 1973) sites in the crystal structure. Citrine color in heat-treated amethyst has been attributed to submicroscopic particles of an iron oxide (Lehman and Bambauer, 1973), but the origin of color in natural citrine such as that from the Anahi mine has not been studied previously. The mechanisms believed to be involved in the formation of the color centers in amethyst are present in the Anahi deposit. They are: (1) a mode...
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z sectors, while the heating amethyst. Nassau (1981) has shown that corresponding to the z sectors. Thus, the high water content in the r sectors remains amethystine. The amethyst-citrine bicoloration in ametrines, we also analyzed amethyst crystals from Marabá by the techniques above. The Marabá amethysts revealed similar variations in trace Fe contents, slightly higher Al contents, Brazil-law twinning in the r sectors, and the same water-content variations displayed by the ametrine crystals. Yet, the Marabá crystals had a different color zoning pattern, with amethyst corresponding to the r sectors and smoky amethyst corresponding to the z sectors. Thus, the high water content in the z sectors could account for the unusual amethyst-citrine bicoloration. In ametrines, we also analyzed amethyst crystals from Marabá by the techniques above. The Marabá amethysts revealed similar variations in trace Fe contents, slightly higher Al contents, Brazil-law twinning in the r sectors, and the same water-content variations displayed by the ametrine crystals. Yet, the Marabá crystals had a different color zoning pattern, with amethyst corresponding to the r sectors and smoky amethyst corresponding to the z sectors. Thus, the high water content in the z sectors could account for the unusual amethyst-citrine bicoloration.

Heat can produce the citrine coloration, as evidenced by the commercial production of citrine by heating amethyst. Nassau (1981) has shown that amethyst-citrine bicoloration in Fe-bearing quartz can be produced by appropriate combinations of irradiation and heat treatment. Neuhann and Schmetzer (1984) have also shown that progressive heat treatment of amethyst from some localities may lead to the development of citrine color in the z sectors, while the r sectors remain amethystine. Our own observations show that Marabá amethyst, when heat treated to 475°C, will turn orange-yellow in the z sectors and colorless in the r sectors, and that irradiation and subsequent heat treatment as described by Nassau can restore a brownish amethystine color to the r sectors. Whether these observations are relevant to natural ametrine is uncertain.

After extensive geologic and experimental studies, we can only speculate that the amethyst-citrine bicoloration results from quartz precipitation at very specific geochmical conditions, temperatures, and growth rates. Unfortunately, no crystal-chemical mechanism to account for the bicoloration can be proposed, because the present understanding of the fundamental controls of color centers in amethyst and citrines is poor. Lack of reliable treatment data and infrared and optical spectra for amethyst bicoloration from other important localities also makes a comparison between the properties of ametrine and those of regular amethyst difficult.

CONCLUSIONS

The history of ametrine shows that gemologists must be careful when extrapolating experimental evidence to the marketplace. Experimental results are essential for testing the origin of gem materials and for protecting consumers from exposure to undisclosed treatments and synthetic gem materials. However, these experimental results must be weighed against other information in the community, i.e., political and economic factors that may hinder direct access to mining areas, cost to treat natural or produce synthetic materials, physical resemblance and similarity in properties between treated/synthetic materials and natural analogues, etc. Consideration of all these factors—combined with closer links and the exchange of reliable information between producers, researchers, and consumers—may help avoid misconceptions in the gem trade.

The information we have presented about the Anahi mine should finally settle the discussion of the natural versus artificial origin of ametrine. The ametrine available in the marketplace today is mined in Bolivia. It occurs in a hydrothermal breccia deposit hosted by carbonate rocks, and the amethyst-citrine color combination is ubiquitous in this deposit. Mineralogic investigations indicate that the amethyst sectors are Brazil-law twinned, and that they contain less iron and water trace impurities than the (untwinned) citrine sectors. The ametrine crystals were probably precipitated from an alkaline, Sr-, Fe-, and K-rich hydrothermal solution during pressure release by hydrothermal brecciation. However, more geologic, mineralogic, and crystallographic work is needed to determine the exact conditions necessary for the development of amethyst-citrine bicoloration in quartz.

In addition to its production of amethyst gems, the Anahi mine is a major source of high-quality faceting-grade amethyst. A substantial amount of
amethyst from this mine has already entered the world gem market. Carving-grade amethyst and ametrine are increasingly important products of this mine. The Anahi deposit also represents the first substantial source of natural, iron-containing reserves in the Anahi deposit will guarantee a world gem market. Carving-grade amethyst and crystals and slabs are yet another product of this mine. The Anahi deposit also represents the quantities. It is hoped that the inferred large amethyst from this mine has already entered the literature. Specimen-grade ametrine are increasingly important products of mine that are entering the market in significant quantities. It is hoped that the inferred large reserves in the Anahi deposit will guarantee a steady supply of good-quality amethyst, citrine, and ametrine for some time into the future.

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