RESEARCH ON GEM FELDSPAR FROM THE SHIGATSE REGION OF TIBET

Ahmadjan Abduriyim, Shane F. McClure, George R. Rossman, Thanong Leelawatanasuk,
Richard W. Hughes, Brendan M. Laurs, Ren Lu, Flavie Isatelle, Kenneth Scarratt, Emily V. Dubinsky,
Troy R. Douthit, and John L. Emmett

The existence of a natural red andesine deposit in China/Tibet has been the subject of controversy since 2006. In late September 2010, an international group traveled to the Shigatse region of Tibet and visited two reported andesine occurrences, at Zha Lin village and the Yu Lin Gu alluvial fan. These sites are located ~3 km from the previously investigated Bainang andesine mining area near Nai Sa village. The Zha Lin deposit appeared genuine, but the group could not confirm the authenticity of the Yu Lin Gu occurrence, and no primary andesine-bearing source rocks were found in either area. Some of the samples had glassy surface residues that are difficult to explain naturally, while initial argon isotopic measurements of a few Zha Lin and Yu Lin Gu andesines (without glassy residues) showed that they had not been heated. Laboratory studies of the Tibetan samples—and a comparison to known-treated red andesine from Inner Mongolia—showed that it may be possible to separate these feldspars using a combination of several advanced destructive techniques, but this methodology is not practical for gem testing laboratories. More detailed investigations will be needed to establish feasible identification criteria for natural-color andesine from Tibet.

Copper-bearing red to green plagioclase feldspar of gem quality has been known from Oregon for decades (e.g., Johnston et al., 1991). In 2002, a new gem plagioclase appeared on the market, allegedly from the Democratic Republic of the Congo (Fritsch, 2002; Krzemnicki, 2004; here referred to as the Congo), and similar material appeared in 2005 that was represented as being from Tibet (see, e.g., figure 1 and Laurs, 2005). Chemical analysis of red feldspars reportedly from Tibet (an autonomous region of China) and the Congo showed that they fall near the border of the andesine-labradorite compositional range (Abduriyim, 2009b; Rossman, 2011); for simplicity, this material will be referred to as andesine in this article.

Reports published in 2008 showed evidence that copper was being diffused into andesine in China and Thailand by a multi-step heating process (Furuya, 2008; Milisenda et al., 2008). While this was apparently being performed on an experimental basis in Thailand, commercial treatment was reportedly taking place in China by a professor in Xi'an (Lang, 2002). The starting material was alleged to be pale yellow andesine from Guyang County, Inner Mongolia, China. Suspicions about the authenticity of the "Chinese red feldspar" on the market circulated on the Internet and elsewhere (e.g., Furuya, 2008; James, 2008).

To address whether natural red andesine occurs in Tibet, in 2008 one of the authors (AA) and five gem dealers and a gemologist visited an alleged deposit called Bainang (or Bai Lang), located near Nai Sa village ~55 km southeast of Shigatse (or Xigazê; see figure 2; Abduriyim, 2008, 2009a,b). The visit was organized by Chinese miner Li Tong (Tibet Andesine, Shenzhen, China). Author AA also visited two deposits of pale yellow andesine in Inner

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See end of article for About the Authors and Acknowledgments.

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Figure 1. These andesines (6.71–15.51 ct) were represented as untreated (natural color) stones from Tibet. Courtesy of Do Win Development Co. Ltd.; photo by Robert Weldon.

Mongolia (Shui Quan and Hai Bou Zi, both in Guyang County), and samples were collected at each locality. In addition, he attempted to contact the Chinese treater in Xi'an, who was unwilling to meet with him.

The internal features and chemical composition of the Tibetan samples collected on the 2008 expedition were found to closely resemble the allegedly copper-diffused Inner Mongolian red andesine on the market, to the degree that doubt was cast on the natural origin of the Tibetan stones (Hughes, 2010; Rossman, 2011).

In an effort to resolve the controversy, other field trips to Tibet were carried out in 2009 by GemResearch Swisslab (GRS, Lucerne, Switzerland) and in 2010 by China's National Gemstone Testing Center (NGTC, Beijing). Dr. Adolf Peretti from GRS was taken by Li Tong to a Tibetan deposit located hundreds of kilometers away from the site of AA's 2008 Tibet trip (again, see figure 2), but Peretti concluded the occurrence was fake (Fontaine et al., 2010). On two expeditions in May and August 2010, teams from NGTC collected andesine samples from a reported deposit near Zha Lin village and at the Nai Sa–Bainang mine. They believed that these sites were probably "salted," but that the question could only be truly answered with a full geologic survey of the area (Wang et al., 2011).

Figure 2. The reported andesine mines visited by Abduriyim's 2010 expedition are located in south-central Tibet, ~55 km from Shigatse. Also shown is another reported andesine occurrence in Tibet (Gyaca) that Fontaine et al. (2010) determined was fake. The inset shows the locations of the reported Zha Lin, Yu Lin Gu, and Nai Sa–Bainang andesine localities in Tibet.

In late September 2010, another party visited Tibet that included authors AA, BML, RWH, TL, FI, and Young Sze Man of *Jewellery News Asia*. Accompanying them were Christina Iu (M. P. Gem Corp., Yamanashi, Japan), Li Tong and his wife, and He Qung (an employee of Mr. Tong's). They studied the reported andesine occurrence at Zha Lin village, as well as an additional locality called Yu Lin Gu (Abduriyim and Laurs, 2010; Abduriyim et al., 2010; Hughes, 2010; Leelawatanasuk, 2010). These areas are located ~3 km from the Nai Sa–Bainang mining area that AA visited in 2008. Due to the objection of a local monk who controls access to the land in this area, the party was unable to visit the Bainang mine. According to villagers interviewed by the expedition, the orange-red stones have been known in this region of Tibet for several decades or longer.

NEED TO KNOW

- At Zha Lin and Yu Lin Gu in southern Tibet, andesine pebbles are hosted by alluvial sediments, as at the nearby Nai Sa–Bainang occurence.
- Samples from all three localities showed overlapping gemological and chemical properties, except for traces of Ag in Yu Lin Gu andesine.
- Some of the samples had glassy surface residues, while initial argon isotopic measurements of pieces from Zha Lin and Yu Lin Gu (without glassy residues) showed no evidence of significant heating.
- No reliable and practical methodology was found for separating these feldspars from known-treated red andesine from Inner Mongolia.

This article reviews the geologic field information gathered by the expedition group and briefly summarizes results of laboratory work on the samples they collected, including their gemological properties, surface features, chemical and isotopic composition, and structural order as revealed by powder X-ray diffraction. In addition, this study gives observations of "matrix" specimens that were supplied through Li Tong, and also reports some initial experiments that investigated the diffusion of silver into andesine (since this element was detected in samples from the Yu Lin Gu occurrence). Due to space limitations, only brief excerpts of this research could be published here; full reports are available on the GIA website (www.gia.edu/research-resources/news-from-research/index.html). Although the andesine controversy is still not resolved, it is hoped that this article will provide a foundation for others who wish to pursue further studies of this material.

LOCATION AND ACCESS

With the exception of the occurrence visited by Dr. Peretti, the reported andesine deposits are located in Bainang County, ~55 km southeast of the region's second largest city, Shigatse (or Xigazê), in southern Tibet (figure 2 and table 1). All three localities (Nai Sa–Bainang, Zha Lin, and Yu Lin Gu) are situated within 2–3 km of one another. They are located ~8 km southeast of Bainang town, near the villages of Zha Lin (Zha Lin and Yu Lin Gu localities) and Nai Sa (Bainang mine).

From the capital city of Lhasa, it takes more than five hours to drive ~300 km to Shigatse on a paved road that crosses two passes at 4,900 and 5,088 m. From Shigatse, it takes another 1–2 hours to drive to the mining area on mostly paved roads. Foreigners are forbidden from visiting this area without authorization from both the Chinese government and local authorities.

GEOLOGIC SETTING

The andesine is hosted by alluvial sediments weathered from sedimentary formations consisting mainly of shale and clay-rich sandstone. These were described as Tertiary on a geologic map published by the Chinese government ("Qin Zang Gao Yuan . . . ," 2005), while Guilmette (2008) indicated that the sedimentary formations in this area are much older (Late Triassic). Mechanical weathering of these rocks created alluvial fans and stream-deposited gravels that locally contain pebbles of the andesine. No original host rocks for Tibetan andesine were found during any of the field studies mentioned

TABLE 1. Reported andesine deposits in Tibet.

Site	Coordinates
Bainang (South)	29°02.57'N, 89°22.17'E; 4,072 m (13,360 ft.)[a]
Bainang (North)	29°02.71'N, 89°22.18'E; 4,049 m (13,285 ft.)[a]
Zha Lin	29°03.95'N, 89°20.88'E; 3,929 m (12,891 ft.)
Yu Lin Gu	29°03.08'N, 89°20.76'E; 4,102 m (13,460 ft.)
Gyaca (Jia Cha) County, Shan Nan area[b]	29°08.07'N, 92°35.95'E; 3,400 m (11,155 ft.)

[a] *Coordinates for the Bainang localities are from Wang (2011).*

[b] *Visited by GemResearch SwissLab in 2009, but determined to be "salted."*

Figure 3. At Zha Lin, andesine was said to be mined from shallow pits such as those shown here. Excavations in this area by Abduriyim's 2010 Tibet expedition revealed andesine within silty sediments (inset). Photos by B. M. Laurs.

above, and the expected rock types (i.e., lavas of basaltic composition) are not shown on geologic maps of the area. Therefore, if such rocks previously existed in the area, they must have been tectonically displaced and/or have weathered away.

The following geologic descriptions are summarized from observations made during Abduriyim's 2010 expedition. At Zha Lin, andesine was found in gray silty sediments of an alluvial plain (figure 3). Miner Li Tong informed the team that local people recovered ~2 tonnes of andesine using simple hand-mining methods; shallow pits were visible over an area measuring approximately 200 × 100 m. The authors randomly selected several areas within and upstream from the former mining area and dug five pits up to 1.2 m deep. They found andesine in nearly all the pits, including those dug ~30 m upstream from the mining area under slow-growing thorn bushes at depths down to 30 cm (about 12 inches; figure 4). The discovery of andesine within pits dug in random, previously unexplored areas near the Zha Lin mining area is consistent with what we would expect for a genuine Tibetan andesine deposit.

The Yu Lin Gu occurrence (figure 5) is located on an alluvial fan 2 km upstream and to the southwest of Zha Lin. Andesine was locally concentrated in patches on the surface of the fan within gravel and rock fragments (figure 5, inset), and also in an intermittent creek on the fan. Local people reportedly picked up ~200 kg andesine from the surface; there was no evidence of any excavations. The team dug several pits, but recovered andesine only at the surface (or rarely within a few centimeters of the surface in a thin layer of loose silty sand). Because expedition members did not find samples at depth, they could not verify the authenticity of the deposit.

MATERIALS AND METHODS

Four matrix samples of andesine (as well as 12 pieces with small amounts of matrix attached) were examined by authors SFM and KS at GIA in Carlsbad and Bangkok, respectively, using a gemological microscope, Raman spectroscopy, and laser ablation–inductively coupled plasma–mass spectrometry (LA-ICP-MS). Additional matrix samples were studied at the California Institute of Technology using attenuated total reflection infrared spectroscopy. All the matrix samples were obtained indirectly through miner Li Tong, and stated to be from Tibet.

Figure 4. This 30-cm-deep pit was dug by Abduriyim's 2010 Tibet expedition under a thorn bush selected at a random location above the Zha Lin mining area. Several pieces of andesine were recovered from this pit. Photo by B. M. Laurs.

Unless otherwise indicated, all the additional samples described in this article were obtained on Abduriyim's 2010 expedition. These were personally collected by expedition members (for samples from Zha Lin and Yu Lin Gu, e.g., figure 6 [left and center]) or purchased by them in Nai Sa village (for samples from the Bainang mine area, which had reportedly been collected there by local people since 2007; see figure 6, right). In addition, in Guangzhou the group obtained a parcel of pale yellow andesine reportedly mined in Inner Mongolia, as well as two lots of red andesine that were reportedly copper-diffused in China using Inner Mongolian pale yellow andesine as starting material (figure 7)—either in Xi'an in 2004–2005 or in Shenzhen in 2007–2008. Hereafter, these Cu-diffused samples will be referred to as "known-treated" andesine. Operating conditions for the electron microprobe, LA-ICP-MS, and X-ray diffraction analyses described below are reported in the respective full articles on the GIA website.

The gemological properties (RI, SG, UV fluorescence, Chelsea filter reaction, spectroscope observations, and microscopic characteristics) of 198 pieces of reddish orange to orange-red andesine from Zha Lin and Yu Lin Gu were collected by author AA using standard instrumentation. From these, 95 were polished with two parallel windows, and were cleaned with acetone and aqua regia in an ultrasonic bath to remove surface contamination. In addition, 50 known-treated red andesine samples (from both Xi'an and Shenzhen) were characterized.

Author TL conducted a preliminary study of surface residues on four additional red Tibetan samples (one from Yu Lin Gu and three from Nai Sa–Bainang) and two red pieces of the known-treated andesine using a scanning electron microscope (SEM) at the Scientific and Technological Research Equipment Center, Chulalongkorn University, Bangkok, using a JEOL JSM-5800LV instrument equipped with an energy-dispersive spectrometer; it was capable of 200–10,000× magnification.


Figure 5. The Yu Lin Gu andesine occurrence consists of an alluvial fan where andesine has been found locally scattered on the surface and in an intermittent creek (photo by B. M. Laurs). The inset shows a red andesine pebble as it was found on the surface of the alluvium (photo by A. Abduriyim).

Quantitative chemical analysis using a JEOL JXA-8500 electron microprobe was carried out by author AA at NIMS (Tsukuba, Japan) on polished surfaces of eight orange-red and red samples (two each obtained at Zha Lin and Yu Lin Gu during the 2010 expedition, and two each of the known-treated stones from Xi'an and Shenzhen). Five spots were analyzed on each sample.

LA-ICP-MS trace-element data were obtained by author AA from 80 orange-red to red Tibetan samples (20 from Zha Lin and 40 from Yu Lin Gu obtained in 2010, and 20 from Abduriyim's 2008 expedition to Nai Sa–Bainang), 45 known-treated red samples (22 from Xi'an and 23 from Shenzhen), and 12 pale yel-

Figure 6. Some of the andesine samples obtained by Abduriyim's 2010 expedition are shown here. From left to right, the samples are from Zha Lin (0.10–1.14 g, personally collected), Yu Lin Gu (0.25–1.55 g, personally collected), and Nai Sa–Bainang (0.37–2.92 g, purchased in Nai Sa village). Photos by Robert Weldon.

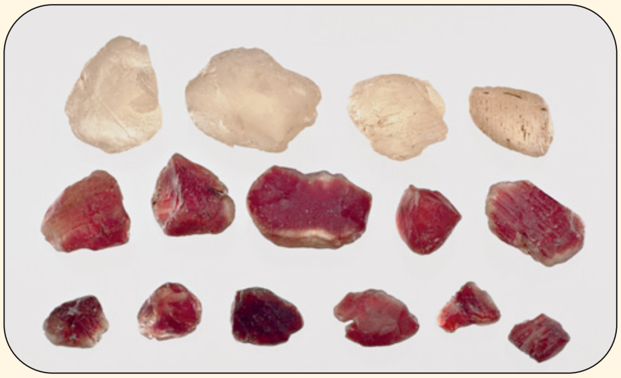


Figure 7. These samples, which were obtained in Guangzhou by Abduriyim's 2010 expedition, consist of pale yellow Inner Mongolian andesine (top row, 5.21–15.36 g) and red andesine that was reportedly treated in China using the Inner Mongolian starting material. The samples in the middle row were said to have been treated in Xi'an in 2004–2005, and those in the bottom row were reportedly treated in Shenzhen in 2007–2008. Photo by Robert Weldon.

low pieces from Inner Mongolia. The instrumentation consisted of a New Wave Research UP266 laser ablation system attached to an Agilent 7500a series ICP-MS at the GEMOC Key Centre, Macquarie University, Sydney, Australia.

Author AA also arranged for powder X-ray diffraction measurements at the Australian Museum on 42 samples to investigate whether the feldspar's lattice (unit cell) parameters were indicative of treatment. These consisted of 20 pieces of orange-red and red andesine from Tibet (5 from Zha Lin, 5 from Yu Lin Gu, and 10 from Nai Sa–Bainang), 10 red known-treated stones (five each from Xi'an and Shenzhen), and 12 pale yellow samples from Inner Mongolia. Data were collected with a Shimatsu LabX XRD-6000 X-ray diffractometer, and the lattice parameters were calculated by the least-squares method using CELLCalc software, with $\Delta 2\theta = 2\theta_{1\bar{3}1} - 2\theta_{131}$ to determine structural states based on measurement of the spacing between the $(1\bar{3}1)$ and (131) peaks of the powder X-ray diffraction pattern (Ribbe, 1972). To test whether the $\Delta 2\theta$ parameters were changed by heating, we selected two pale yellow Inner Mongolian samples for copper diffusion experiments. Each sample was cut into two pieces. Half of one sample (INMG-DF-001a) was buried in ZrO_2 powder mixed with 2–3% copper powder and diffused at 1160ºC for 50 hours, and half of the other stone (INMG-DF-002a) was packed into Al_2O_3 powder mixed with 2–3% copper powder and heated at 1000°C for 24 hours. The remaining halves were retained as control samples.

Argon isotope measurements were conducted in the Farley lab at Caltech on nine samples (one red piece from Abduriyim's 2008 expedition, six red pieces obtained during his 2010 Tibet trip, one red "Chinese" sample donated by Andegem, and one piece of yellow Inner Mongolian andesine). The samples were prepared and analyzed following the procedures described in Rossman (2011), except that each sample was wrapped in aluminum foil and placed under high vacuum overnight, and then was completely melted in a tantalum furnace (rather than being heated by a laser) for argon extraction.

Traces of silver have been detected in andesine collected from Yu Lin Gu (A. Abduriyim, unpublished data), so a set of diffusion experiments were conducted by authors RL, EVD, TRD, and JLE at Crystal Chemistry to better understand silver incorporation in plagioclase. Two sets (10 pieces each) of pale yellow andesine from Inner Mongolia were sliced into wafers ~3–3.5 mm thick. They contained various amounts of snowflake-like inclusions, fine particulate clouds, and some growth tubes. The samples were packed in ZrO_2 powder doped with 1% metallic silver. One set (cc1032-2) was diffusion treated at 1170ºC for 31 hours, and the other set (cc1032-3) was treated at the same temperature for 180 hours. The temperature was chosen to be near 90% of the solidus temperature of the material to facilitate efficient diffusion. One untreated sample and three samples from each treatment condition were sliced in half and the cut edges were polished for chemical analysis by LA-ICP-MS.

RESULTS AND DISCUSSION

Matrix Rock Observations. All the matrix material had a similar appearance, consisting of a light gray porous substance containing tube-shaped structures (figure 8, left). The matrix was found to be calcium carbonate (mostly calcite) that apparently formed by secondary precipitation (i.e., caliche). Such a matrix has not previously been reported for andesine.

Closer inspection of the specimens revealed additional features that were hard to explain. In many pieces, junctions between the andesine and matrix contained a transparent to translucent material that resembled liquid but was not. It "wetted" the surrounding matrix, filling in pores and making them shiny (figure 8, center), often forming a meniscus where the feldspar came in contact with the matrix. LA-ICP-MS chemical analysis of this contact material showed mostly aluminum with some silicon and calcium, as well as numerous trace elements. No

Figure 8. The matrix samples contained rounded pieces of andesine embedded in porous carbonate rock that had the appearance of caliche (e.g., left image). The junction of the andesine and the matrix, as well as the surrounding area, contained a material that made the porosity of the matrix look wet and shiny (center, field of view 4.0 mm). One specimen contained transparent blue fibers that were flexible (right, field of view 1.0 mm) and partially melted during Raman analysis, which produced spectra similar to nylon. Photos by K. Scarratt (left) and S. F. McClure.

spectral match—or polymers—were found using Raman spectroscopy.

Some of the specimens had fibers embedded in the matrix and in the contact material. In at least one specimen, the fibers were blue and flexible (figure 8, right). Raman analysis of the most accessible fiber proved difficult because it melted when exposed to the laser, even after the power level and laser frequency were changed. The best match for the (weak) Raman signal was nylon. We concluded that the fiber was man-made and could not have occurred naturally in the specimen. Further examination also revealed parts of insects stuck in the matrix.

One large matrix specimen was broken apart with a hammer, but no andesine was found inside. The two pieces of andesine originally visible on the surface of the specimen were both broken out of the matrix, and one of them had a flat cleavage surface that left a well-preserved imprint in the contact material where it was attached to the matrix. This area had a fine texture that was somewhat glassy, and it was completely unlike the surrounding matrix. It did not bear any resemblance to a natural material.

Analysis of small fragments (<250 μm) of the contact material by attenuated total reflection IR spectroscopy showed calcite plus some organic material, as indicated by C-H absorptions near 2900 cm^{-1}. In contrast, spectra of the matrix away from the andesine showed dominantly calcite. While not proof of an assemblage, this is consistent with the presence of an organic binder used to attach the andesine to the matrix.

Our observations suggest that the matrix specimens were manufactured. In addition, no specimens of this kind were seen by team members who visited the reported mine sites in Tibet.

Gemological Observations. The andesine samples collected from Zha Lin and Yu Lin Gu were generally visually indistinguishable from one another and from those obtained in Nai Sa village that were represented as being from the Bainang mining area (with exceptions indicated below). Most were transparent to translucent, but their overall gem quality was not high (again, see figure 6). In fact, very few of the samples would be expected to yield high commercial-quality cut gemstones. Most of the pieces were under a centimeter and the largest reached ~2 cm. Most were pale orangy red or red, with some rare pure red samples. Compared to andesine from the Nai Sa–Bainang area, the Zha Lin and Yu Lin Gu samples generally were a weaker red (again, see figure 6). Some stones showed blue-green or red zones or patches (e.g., figure 9), and any surface-reaching fractures were surrounded by a narrow colorless zone. In addition, a few of the Yu Lin Gu samples showed a distinct yellow color zone near their surface. Most samples also had a narrow colorless rim along their surface, and some stones showed concentric color zoning with green-blue and red bands (see, e.g., figure 14 in Rossman, 2011). All samples were rounded, with a smooth waterworn appearance and generally elongated shapes. A few andesines had broken cleavage surfaces, embayed areas that appeared to have been created by chemical etching, or areas with a melted glassy surface (see further description below). Etch features are common in known-natural feldspars from other sources such as Oregon, but to our knowledge melted glassy surfaces are not.

The gemological properties are summarized in table 2. RI and SG values for all samples fell in the range of andesine. The samples fluoresced weak chalky orange to long-wave UV radiation, and were dark red or inert under short-wave UV. They retained

Figure 9. These Tibetan andesine samples (0.20–1.01 g, from Yu Lin Gu) show various uneven blue-green or red zones. Surface-reaching fractures are surrounded by narrow colorless areas. Photo by A. Abduriyim.

TABLE 2. Gemological properties of rough andesine obtained in Tibet in 2010.

Color	Reddish orange, orange-red, and deep red, sometimes with a colorless rim and/or uneven green or bluish green zones, patches, or stripes.
Diaphaneity	Transparent to translucent
Appearance	Smooth rounded faces, some cleavage surfaces, surface etching, melted glassy surface
RI[a]	$\alpha = 1.550–1.552$, $\beta = 1.555–1.557$, $\gamma = 1.560–1.561$
Birefringence	0.009–0.010
Optic sign	Biaxial positive
SG	2.67–2.72
Pleochroism	Weak (red-green)
UV fluorescence	
Long-wave	Weak chalky orange
Short-wave	Dark red or inert
Chelsea filter	Red (for red samples)
Spectroscope	Broad absorption at 560 nm in red stones and a very weak band at 630 nm in green color zones.
Internal characteristics	Color zoning, twin lamellae, turbid milky clouds and particles, lath-like hollow channels, pipe-like growth tubes, irregular dislocations, fractures, uncommon tiny native copper grains or platelets

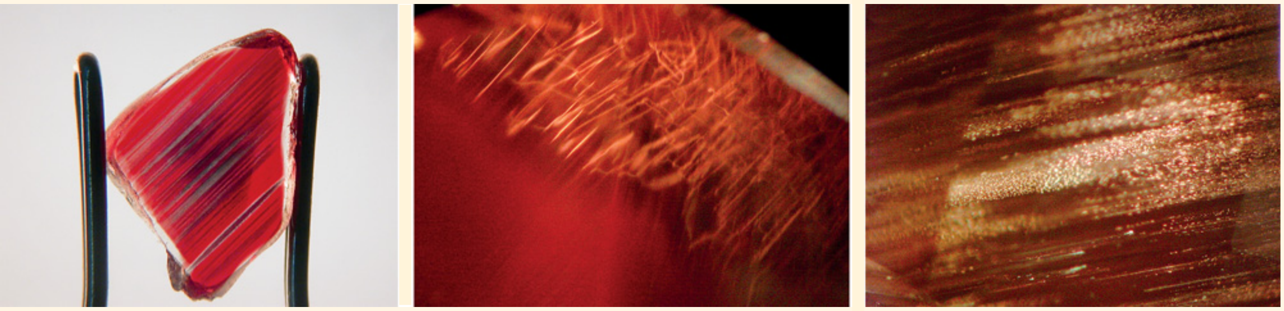
[a] *Measured on polished surface.*

their red appearance under a Chelsea filter. Some red stones appeared green in diffused transmitted light.

Microscopic examination revealed that most of the Zha Lin and Yu Lin Gu samples contained prominent twin lamellae parallel to {010}, turbid milky clouds and particles between the twin lamellae (figure 10, left), parallel lath-like hollow channels, pipe-like structures, irregular dislocations (figure 10, center), and fissures. A few stones also contained partially healed fractures that had no surface expression in reflected light. A very few samples contained native copper grains or platelets, which produced reddish orange schiller after polishing (figure 10, right). Similar copper platelets are known in Oregon labradorite, but those platelets tend to be much larger. No platelets were seen in any of the known-treated samples.

The known-treated samples contained pipe and tube-like structures, discoid fractures, a recrystallized white residue filling the lath-like hollow channels, and cloud-like inclusions. Overall these internal features resembled those seen in the Tibetan andesines. However, distinct concentric color fluctuations from the rim to the core were present in some of the known-treated stones (e.g., figure 11). These layer-by-layer color zones appeared more distinct than in the Tibetan samples examined.

Figure 10. Some internal features noted in the Tibetan andesine included turbid milky clouds and particles between twin lamellae (left), irregular dislocations (center), and rare schiller from the presence of native copper inclusions (right). Photomicrographs by F. Isatelle (left, magnified 10×) and A. Abduriyim (center and right, magnified 15–20×).



Surface Residue Features. Microscopic observation of the samples from all three reported Tibetan localities, as well as the known-treated andesines, revealed unusual glassy surface residues in the fractures, cavities, and depressions of some specimens, as reported previously in red andesine from Tibet or "China" (e.g., Abduriyim, 2009b; Lan et al., 2009; Rossman, 2011). However, many of the samples studied (~80–85%), whether Tibetan or known treated, did not show any residues, and residues were not present on any of the pale yellow andesine from Inner Mongolia. Of the six specimens examined by author SFM that were dug from two random holes above the main mining area in Zha Lin, three had these glassy residues in depressions or cavities.

The residues (e.g., figure 12) ranged from opaque to transparent and were colorless/white, yellow, orange, brown, or black. Microscopic examination of these residues typically showed characteristics of a viscous liquid that filled low areas and then solidified: a meniscus against the feldspar, columns of this material bridging gaps in the feldspar (e.g., figure 12, right), and gas bubbles. Dendritic formations of a metallic material were sometimes visible in the residues (for more on these, see the SEM study below).

On both the Tibetan and known-treated stones, the glassy residue material sometimes cemented small fragments of feldspar to the surface of the andesine, as documented previously (Rossman, 2011). Also seen were small fragments of quartz attached to the surface with a material identified by Raman analysis as amorphous silica.

Most of the Raman spectra we acquired on the residues did not match anything in our database. On a few samples, particularly in some dark areas, we obtained a good match with amorphous carbon. The chemistry of these residues was consistent between all of the Tibetan and known-treated samples that were analyzed. In agreement with the findings of Rossman (2011), compared to the host andesine, all the residues had relatively high levels of potassium and copper with trace amounts of numerous other elements.

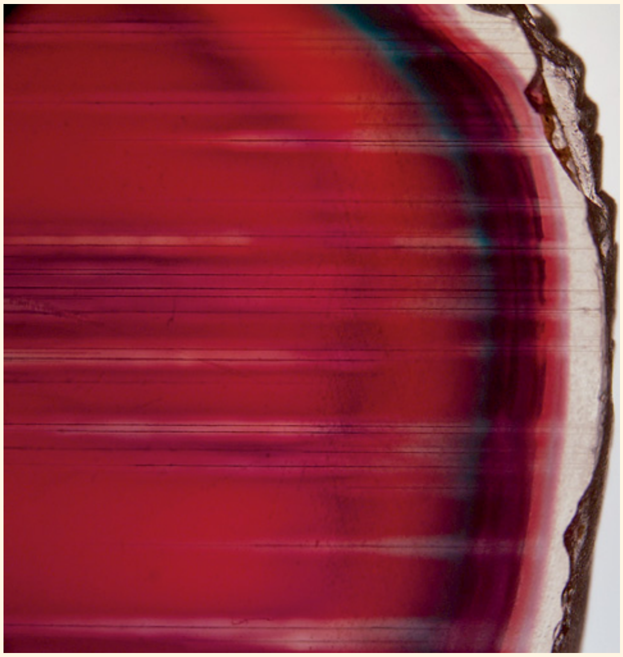


Figure 11. This known-treated andesine shows concentric color fluctuations. Photomicrograph by A. Abduriyim; magnified 22×.

At present, we do not know the origin of these residues or why there is quartz and feldspar fused to the surface of these stones.

SEM Study of Surface Features. SEM observations of red andesine samples from Yu Lin Gu and the Nai Sa–Bainang area showed percussion marks on their surfaces (figure 13, left) that appeared consistent with sedimentary transport. Whitish residues in some depressions and fractures proved to be crystalline materials containing silicon as their major constituent (probably microcrystalline silica or fine-grained quartz; figure 13, center). Some of these Si-rich patches on red andesine from Nai Sa–Bainang

Figure 12. Channels on these andesines are filled with a transparent yellow-brown glassy material (left, known-treated stone, image width 2.9 mm) or an opaque yellow substance partially bridging the gap in the specimen (right, from Zha Lin, image width 1.75 mm). Photomicrographs by S. F. McClure.

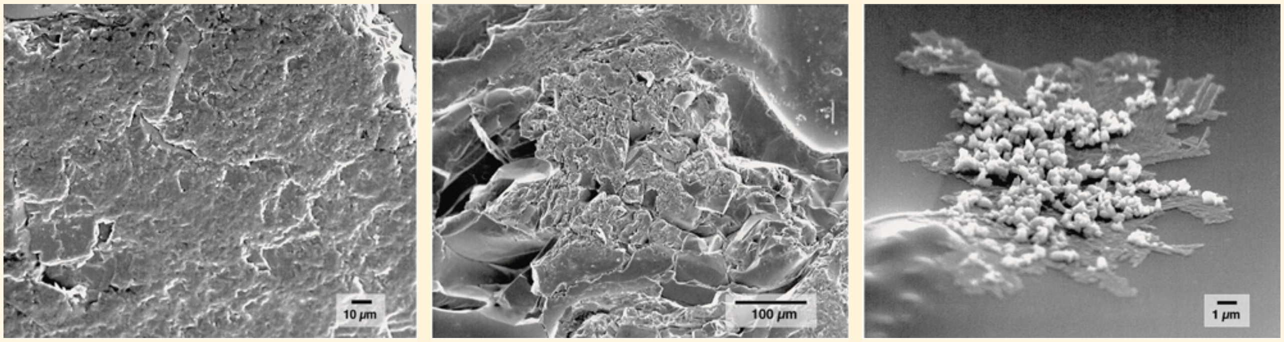


Figure 13. These SEM images of andesine surfaces show percussion marks (left) and a cluster of microcrystalline Si-rich material (center) on samples from Yu Lin Gu. The SEM image on the right of a sample from Nai Sa–Bainang shows dendritic copper growths with copper microclusters on top of a crystalline silica-rich material (right).

hosted tiny dendritic copper growths partially covered with copper-rich microclusters (figure 13, right).

SEM imaging of both of the known-treated andesines revealed mainly glassy surfaces and residues from prolonged treatment with a flux. An Al-rich compound was also observed (figure 14, left). No percussion marks were observed on these samples, but numerous copper-rich microclusters were seen on areas of silica-rich glassy residues (figure 14, right).

Chemical Composition. Microprobe analysis of two andesine samples from Zha Lin yielded a composition of $\mathrm{Ab}_{46–47}$:$\mathrm{An}_{49–50}$:$\mathrm{Or}_{3.5–3.8}$ (expressed as mol.% albite:anorthite:orthoclase). They plotted in the andesine field, near the border with labradorite. Two samples from Yu Lin Gu showed a similar range of major elements but with more varying anorthite contents ($\mathrm{An}_{51–58}$), which placed them in the labradorite field. With the exception of the An_{58} sample, these data overlap the compositions given by Rossman (2011) for samples from Tibet and "China." A similar composition was documented in the Nai Sa–Bainang andesine studied by Abduriyim (2009b). Microprobe analyses of four known-treated samples gave compositions of $\mathrm{Ab}_{46–49}$:$\mathrm{An}_{47–50}$:$\mathrm{Or}_{2.8–3.2}$, placing them in the andesine field at/near the border with labradorite, indistinguishable from the Tibetan samples. The Zha Lin and Yu Lin Gu andesine contained overlapping copper contents (0.04–0.15 wt.% CuO), similar to the range in the known-treated samples (0.04–0.11 wt.% CuO).

LA-ICP-MS analyses of samples from all three Tibetan localities showed a similar range of Li, B, Mg, P, K, Sc, Ti, V, Mn, Fe, Co, Ni, Cu, Zn, Ga, Ge, Rb, Sr, Y, Zr, Ba, and Pb, as well as the rare-earth elements La, Ce, Pr, Nd, and Eu. Copper ranged from 270 to 1200 ppmw, and tended to be higher in stones with a redder color. Li contents showed corresponding increases with Cu, while Ni concentrations were higher at the surface than the interior.

Traces of silver were recorded only in samples from Yu Lin Gu, ranging from 35 to 2900 ppmw. The concentration of Ag at the outer edge of the samples, where a colorless rim was visible, was much higher than the average inside the stones. Also, the amount of Ag appeared to diminish toward the center of the stones. In contrast, the distribution of Cu and other trace elements throughout the sam-

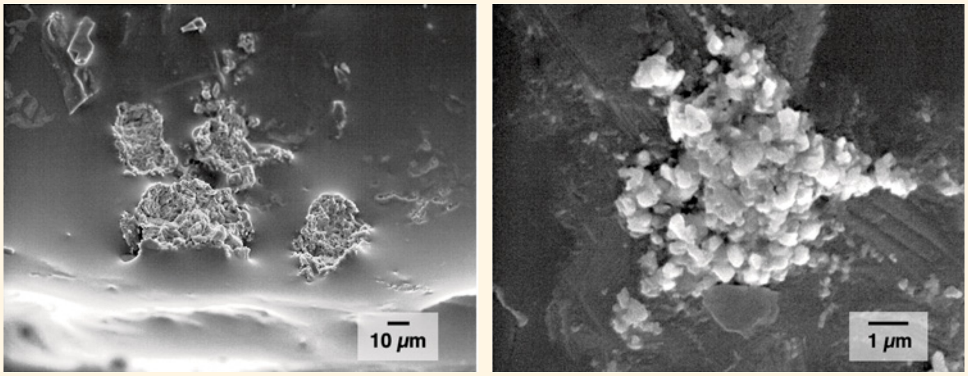


Figure 14. These SEM images of known-treated andesine samples show an Al-rich compound (left) and dendritic copper growths with copper microclusters on top of silica-rich glassy residue (right).

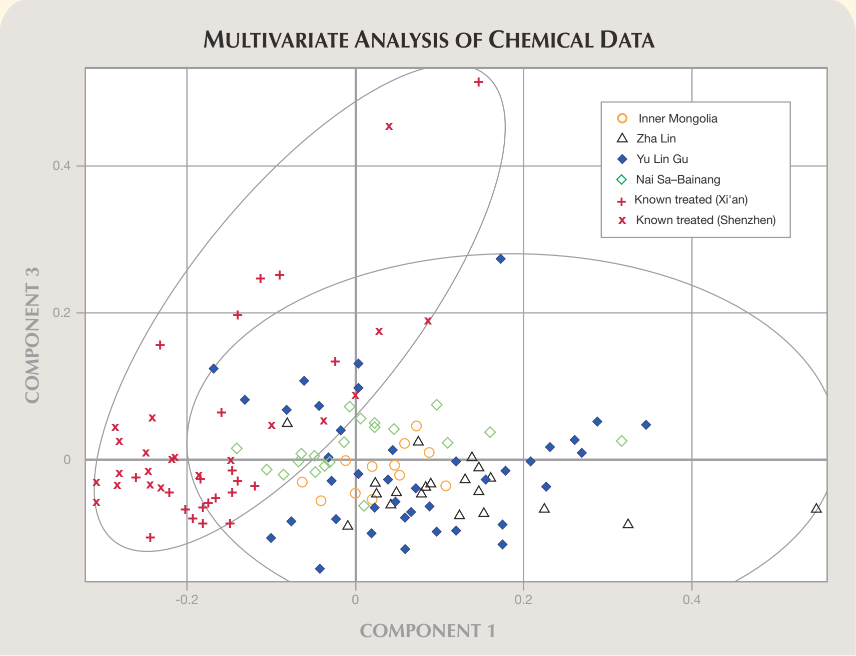


Figure 15. Trace-element data of the Tibetan/Inner Mongolian andesines and known-treated samples were processed by multivariate statistical analysis into this principal component diagram. Ten isotopes (^{39}K, ^{49}Ti, ^{57}Fe, ^{69}Ga, ^{88}Sr, ^{107}Ag, ^{137}Ba, ^{139}La, ^{140}Ce, and ^{208}Pb) were categorized into two parameters as component 1 and component 3. There is ~30% overlap between the two groups.

ples did not show any specific trends. Some stones from Zha Lin showed a very low amount of Ag at the surface (~0.12–0.26 ppm by weight) but none in their interior. Ag was not detected in any of the other stones.

The known-treated samples showed trace-element contents similar to those of the Tibetan stones, but the Cu content decreased from the rim toward the core in most of the samples. Barium contents were slightly lower (99–142 ppmw) than in the Tibetan andesine (123–166 ppmw).

Multivariate statistical analysis of the trace-element data yielded the principal component diagram in figure 15. Data are shown for the 80 samples from the three reported Tibetan localities and the 12 pale yellow samples from Inner Mongolia. The red symbols indicate the 45 known-treated samples. Although there was ~30% overlap between the two groups, the known-treated samples tended to have lower values for the component 1 parameter.

Powder X-ray Diffraction. Using the parameter of $\Delta 2\theta = 2\theta_{1\bar{3}1} - 2\theta_{131}$, combined with anorthite content, we can determine the Al/Si distribution among the four tetrahedral sites in the plagioclase structure (Ribbe, 1972). The diffraction data for five Zha Lin andesines gave values of Δ2θ = 1.9554°–1.9724°, while five samples from Yu Lin Gu yielded Δ2θ = 1.9572°–1.9700° and 10 from Nai Sa–Bainang were calculated as Δ2θ = 1.9539°–1.9668° (figure 16). Of the known-treated samples, five from Xi'an were in the range Δ2θ = 1.9574°–1.9886° and five from Shenzhen gave Δ2θ = 1.9720°–2.0047°. The tendency for the known copper-diffused samples to have a higher parameter is reflected by the degree of Al/Si disorder at the tetrahedral site. The temperature at which this disorder formed is probably higher than 800–900°C. The 12 pale yellow samples of Inner Mongolian andesine showed a significantly lower parameter of Δ2θ = 1.9161°–1.9506° compared to the Tibetan and known-treated samples.

Our copper diffusion experiments confirmed that the Δ2θ parameter can be changed significantly by high-temperature heating. Both diffused samples showed red and green colors, and the parameters changed from Δ2θ = 1.9264° to 1.9764°, and from Δ2θ = 1.9506° to 1.9811°. The high temperatures associated with laboratory diffusion of Cu into plagioclase are reflected in the increased disorder measured by powder X-ray diffraction.

Argon Isotopes. Rossman (2011) reported that argon isotopic analysis of red andesine samples collected by Abduriyim's 2008 expedition to the Nai Sa–Bainang mine gave a much lower ^{40}Ar/^{36}Ar ratio than untreated pale yellow andesine from Inner Mongolia. These observations led to the suspicion that those Tibetan samples had been treated by high-temperature copper diffusion, despite the conclusions of Abduriyim (2009a,b), who investigated the Bainang mine, that the deposit was authentic.

The results of argon isotopic measurements of andesines obtained on Abduriyim's 2010 expedition, and of other samples for comparison, are

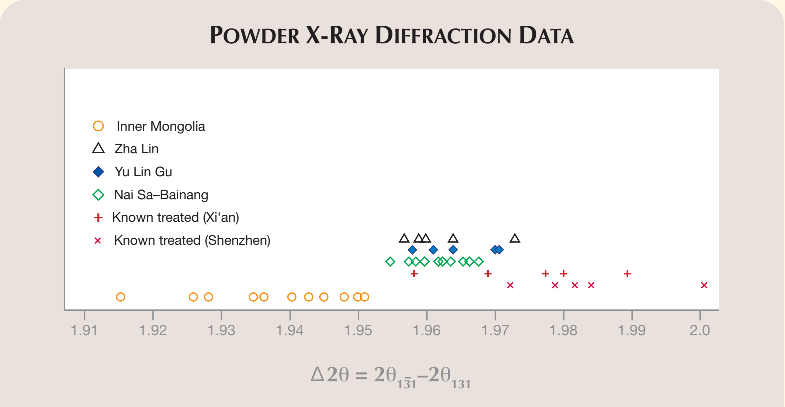


Figure 16. In this diagram, the $\Delta 2\theta$ values (calculated using the parameter of $\Delta 2\theta = 2\theta_{1\bar{3}1} - 2\theta_{131}$) obtained from powder X-ray diffraction data show some overlap between Tibetan andesine and known-treated samples. The untreated Inner Mongolian andesine samples have the lowest $\Delta 2\theta$ values.

shown in table 3 and figure 17. None of the samples tested for argon isotopes showed evidence of the glassy surface residues mentioned above. The pale yellow Inner Mongolian rough had a high ^{40}Ar/^{36}Ar ratio, comparable to the results obtained in 2008. In fact, it contained so much ^{40}Ar that it saturated the detection system. However, a rough red andesine from Andegem showed a low ratio, consistent with author GRR's previous isotopic measurements from the same sample and the conclusion that such material was diffusion treated at high temperatures. A rough red sample purchased in 2010 at Nai Sa village (said to be from the Bainang mine) showed an argon ratio somewhat comparable to the value obtained from an andesine collected at the mine by Abduriyim in 2008. The two samples from Yu Lin Gu showed very high argon ratios. The three stones from Zha Lin had elevated argon ratios comparable to those obtained from the pale yellow Inner Mongolian andesine examined in 2008.

Although the furnace heating procedure used in this study was different from the laser heating reported in Rossman (2011), a comparison of the data obtained by both techniques on sample GRR 2641 shows consistent ratios within expected variations. The present study indicates that the Yu Lin Gu and Zha Lin samples tested were not subjected to the heat treatment process usually applied to commercial red andesine. The nature of the Nai Sa–Bainang samples tested is more difficult to establish definitively. Their argon ratios were somewhat higher than those typically found in treated red andesine, but significantly below those observed in material from Yu Lin Gu and Zha Lin.

Diffusion of Ag in Feldspar. The untreated Inner Mongolian andesine contained no detectable silver. After diffusion treatment, the samples' coloration appeared unchanged but they contained surface-conformal concentrations of Ag. Those treated for 31 hours showed a maximum Ag content of ~900 ppmw, and silver was detectable to a depth of 0.7 mm. Samples treated for a much longer duration (180 hours) exhibited a lower maximum concentration of Ag at 200 ppmw, but silver was detectable to a greater depth of ~1.2 mm. For samples treated for both durations, a lower concentration of silver was detected near the surface as compared to several hundred micrometers below it.

The observed diffusion profiles through the sam-

TABLE 3. Argon isotope ratios of andesine reportedly from "China," Tibet, and Inner Mongolia.

Sample no.	Description	Source	Reported location	Test date	^{40}Ar/^{36}Ar
GRR 2641	Red rough	Andegem, 2008	"China"	July 20, 2009	650
GRR 2921	Red rough	Nai Sa–Bainang, 2008	Tibet	July 20, 2009	1631
72.49 TW	Red rough	Bainang, purchased in Nai Sa, 2010	Tibet	Dec. 23, 2010	1055
A382	Red rough	Yu Lin Gu, in creek, 2010	Tibet	Dec. 23, 2010	11525
29.17 TW	Red rough	Yu Lin Gu, on surface, 2010	Tibet	Dec. 23, 2010	11685
A330	Red rough	Zha Lin, 1.2 m deep pit at mine site, 2010	Tibet	Dec. 23, 2010	3884
A324	Red rough	Zha Lin, 30 cm deep pit under bush, 2010	Tibet	Dec. 23, 2010	6434
A347	Red rough	Zha Lin, on surface at mine site, 2010	Tibet	Dec. 23, 2010	4309
215.12 TW	Pale yellow rough	Litto Gems, 2010 donation	Inner Mongolia	Dec. 23, 2010	>6000

ples suggest that silver substitution in plagioclase is quite high. It is likely even higher than the diffusion profile suggested by the 31-hour experiment, because the drop in silver concentration at the surface of the sample indicates outward diffusion of silver during the experiment. This likely occurred because the vapor pressure of silver at 1170°C is ~0.12 torr, so it distills out of the zirconia carrier as the experiment proceeds. As it is depleted, some of the silver in the plagioclase diffuses back down the concentration gradient out toward the surface.

This experiment shows that silver—like copper—can diffuse into plagioclase under conditions that may exist in nature or may be created in the lab.

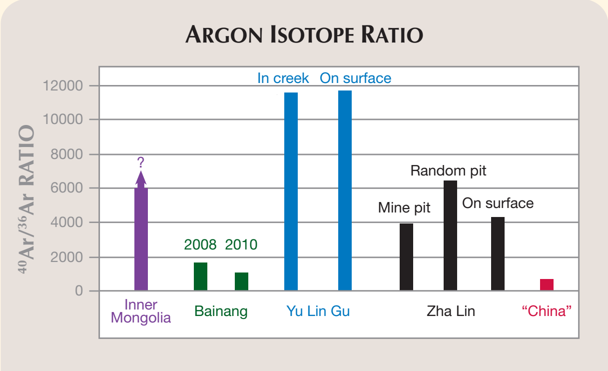


Figure 17. Elevated argon isotopic ratios were obtained for pale yellow andesine from Inner Mongolia, as well as red samples from Yu Lin Gu and Zha Lin that were collected during Abduriyim's 2010 expedition. Red andesines reportedly from the Bainang mine contain significantly less ^{40}Ar, while a "Chinese" red sample obtained from Andegem in 2008 shows a low ratio indicative of high-temperature heating.

CONCLUSIONS

Since 2005, gem-quality andesine represented as being from Tibet—mostly red to orange but also showing other colors and sometimes strong color zoning—has been available in the marketplace. This article mainly presents findings associated with Abduriyim's 2010 expedition, which visited two reported Tibetan andesine occurrences, Zha Lin and Yu Lin Gu, located near the previously investigated Nai Sa–Bainang mining area. The group found strong field evidence for a genuine andesine deposit at Zha Lin, but could not confirm the authenticity of the Yu Lin Gu occurrence. No primary andesine-bearing source rocks were found in either area. A more thorough geologic investigation of the region is still needed.

No matrix specimens were seen in the field; however, examination of matrix specimens represented as being from Tibet suggested they had been manufactured. The andesine samples obtained at Zha Lin and Yu Lin Gu by the 2010 expedition—for the most part, rounded pebbles—showed an overall low quality compared to the abundance of attractive gems represented as Tibetan in the marketplace. There was an overlap in gemological properties between the Tibetan and known-treated samples obtained by the expedition. The chemical properties also overlapped, except for the presence of significant amounts of Ag only in the Yu Lin Gu samples and a possible depletion of Ba in the known-treated stones. Multivariate statistical analysis of the chemical data gave a 30% overlap in the Tibetan and known-treated stones. A preliminary SEM investigation suggested that both the Tibetan and known-treated andesines may host surface residues consisting of copper-rich micro-clusters and patches of silica, but the crystallinity of the silica appeared different in the different sample types. Glassy surface residues were present on some of the Tibetan and known-treated stones. Powder X-ray diffraction data showed some overlap between Tibetan and known-treated stones. Argon isotopic studies indicated that the samples tested from Zha Lin and Yu Lin Gu (none of which had glassy surface residues) had not been exposed to the high temperatures associated with diffusion treatment.

Although some of the evidence obtained from field and laboratory studies is supportive of genuine natural-color andesine from Tibet, the inconclusive and sometimes contradictory results described above and in other studies (e.g., Rossman, 2011; Peretti et al., 2011) indicate that not all the stones represented as Chinese or Tibetan are authentic. Our research has shown that to date there is no reliable, realistic way to separate the natural Tibet material from the treated stones from Inner Mongolia. It is possible that this separation might be made using a combination of several advanced techniques, but most of them are expensive, destructive, and/or not widely available, so they are impractical for individual andesines. Therefore, at this time, GIA's laboratory reports on these stones state "Color origin cannot currently be determined." Additional research is needed to establish unambiguous identification criteria for stones of natural versus treated origin.

ABOUT THE AUTHORS

Dr. Abduriyim is a GIA consultant and was recently chief research scientist at the Gemmological Association of All Japan – Zenhokyo laboratory in Tokyo. Mr. McClure is director of Identification Services at GIA's laboratory in Carlsbad. Dr. Rossman is professor of mineralogy at the California Institute of Technology (Caltech), Pasadena. Mr. Leelawatanasuk is chief of the gem testing department at the Gem and Jewelry Institute of Thailand (Public Organization), Bangkok. Mr. Hughes is senior vice president of Sino Resources Mining Corp. Ltd., Hong Kong. Mr. Laurs is editor and technical specialist of Gems & Gemology *at GIA in Carlsbad. Dr. Lu is a research scientist, and Ms. Dubinsky is a research associate, at GIA's laboratory in New York. Ms. Isatelle is a geologist and Ph.D. candidate at the University of Nantes, France. Mr. Scarratt is managing director, Southeast Asia, for GIA and director of GIA's laboratory in Bangkok. Drs. Emmett and Douthit are principals of Crystal Chemistry, Brush Prairie, Washington.*

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