# THE CHINESE RED FELDSPAR CONTROVERSY: CHRONOLOGY OF RESEARCH THROUGH JULY 2009

George R. Rossman

Red copper-containing plagioclase feldspar from Oregon has been available for over a century. In the early 2000s, new localities for copper-bearing feldspar were reported from the Democratic Republic of the Congo and from Tibet or an unspecified locality in China. The new material has been the subject of widespread concerns about its geographic origin and natural color. In fact, extensive studies of its composition, spectroscopy, physical appearance, and isotopic properties suggest that much of the red andesine on the market is the product of laboratory diffusion of copper into pale yellow andesine from Inner Mongolia. All samples initially subjected to testing as part of this study gave strong evidence or suggestions of treatment. Traces of copper-containing fluxes found on rough stones, and measurements of argon isotopic composition in particular, demonstrate that the tested material was recently heated to high temperatures under conditions where copper diffusion could occur. These results apply to samples that were obtained through July 2009, but do not include samples from expeditions to Tibet in 2010.

This article presents the results of the author's studies at the California Institute of Technology that involve what has come to be known as Chinese red andesine (figure 1), and reviews the key events surrounding this controversy—much of which has transpired outside traditional forums for gemological research—since 2002. It follows a timeline up to mid-2009, after the initial rounds of testing of samples from an expedition to Tibet in 2008 (Abduriyim, 2008, 2009), but before more recent expeditions to purported mines in Tibet. A future article will present the results of testing of samples collected during the 2010 expedition described by Abduriyim and Laurs (2010) and Hughes (2010).

A chronology of the author's research to address the controversy is presented below. The results from studies of a variety of samples obtained from sources listed in the Acknowledgments are briefly summarized, including samples allegedly from the Congo, Tibet, and an unspecified Chinese locality, as well as those from mining districts in Oregon, and pale yellow plagioclase from Mexican localities and Inner Mongolia. Many individuals and organizations were especially generous with their materials and fully willing to cooperate with the investigations. Notably, these sources were not told beforehand about the type of testing that would be conducted on the samples provided. Furthermore, results of the testing were not released until recently, again to avoid the possibility that those tests could be manipulated by donors. Generally, the testing included observation with magnifications up to those of a scanning electron microscope (25,000×), chemical analyses, and spectroscopic and isotopic studies. A list of samples and an overview of the experimental methods is presented in box A, so as not to interrupt the chronology. A partial report of these results has

*Figure 1. Red andesine has been the subject of extended controversy regarding its source and the nature of its color. This specimen, represented as Tibetan, weighs 28.51 ct. Courtesy of Jacqueline Li; photo by Robert Weldon.*

previously appeared, based on a transcription of a talk presented by the author (Rossman, 2010).

Plagioclase is a feldspar solid-solution series with compositions ranging from albite (Na-rich) to anorthite (Ca-rich), which has been arbitrarily subdivided and named (e.g., *andesine*, *labradorite*, etc.) according to the anorthite component (see box B on page 28).

## PLAGIOCLASE LOCALITIES

**Copper-Bearing Plagioclase.** An early mention of copper-containing labradorite appears in a report by Anderson (1917), who studied specimens containing inclusions of copper in the Smithsonian's National Museum of Natural History. These showed a red aventurescence or less commonly were translucent with a pale green color. The labradorites were reported to be from Modoc County, California. This area still has not been confirmed as a source of such feldspar, but the author's examination of one of these crystals showed an appearance identical to sunstone from Lake County, Oregon, which is immediately north of Modoc County. (Although the feldspar variety *sunstone* was originally associated with hematite-bearing feldspars from India, Norway, and Tanzania, the copper-containing feldspar from Oregon is now widely known as *Oregon sunstone*.)

Natural copper-containing feldspar occurs in several additional deposits in south-central Oregon, as part of the Steens Mountain volcanic sequence. The composition ranges from labradorite to bytownite (~65–72 mol.% anorthite). It ranges from pale yellow to shades of red to green, and commonly contains thin flakes of native copper. A study of these feldspars by Hofmeister and Rossman (1985) was the first to discuss the origin of color in relationship to

the copper content and copper species. They showed that the pale yellow color is due to $Fe^{3+}$ and the red color is due to copper colloids, and proposed that the green color and strong green to colorless pleochroism is caused by an intervalence interaction between $Cu^+$ and $Cu^0$. They also showed that the material's schiller effect was produced by microscopic laths of native copper.

Subsequently (in 1980), another deposit in Oregon was discovered at what is now known as the Ponderosa mine in northwestern Harney County. This labradorite also contains copper platelets and occurs in the same color range (Johnston et al., 1991). Prior to 2002, Oregon was the only reported commercial source of red copper-containing feldspar.

Very rarely, copper impurities have been discovered in small plagioclase crystals from other localities, such as Miyake-Jima, Japan (Petrov, 2010; figure 2, left) and the Pinacate volcanic field in Sonora, Mexico (author's collection; figure 2, center).

**Commercial Deposits of Pale Yellow Plagioclase.** Gem-quality pale yellow labradorite occurs in large quantities in the Mexican state of Chihuahua, near Casas Grandes, but without copper platelets or the red and green colors (figure 2, right). This material has been available for many years, but has mostly been sold as mineral specimens until fairly recently (e.g., Laurs et al., 2006).

Pale yellow andesine from Inner Mongolia was first described in the Chinese literature in the early 1990s (Li, 1991 and 1992) and later documented in a master's thesis (Cao, 2006). Li (1991) noted that when the Inner Mongolia Geological Survey conducted a general investigation of the region's gem resources, local respondents reported a sedimentary

# BOX A: SAMPLES AND EXPERIMENTAL DETAILS

The samples studied by this author for the present article are listed in table A-1. Quantitative elemental microanalyses were conducted with a JEOL 8200 electron microprobe operated at 15 kV and 25 nA in a focused beam mode using Probe for Windows software. Analytical standards were anorthite ($CaK\alpha$, $AlK\alpha$, $SiK\alpha$), $TiO_2$ ($TiK\alpha$), fayalite ($FeK\alpha$), forsterite ($MgKa$), benitoite ($BaL\alpha$), and CuO ($CuK\alpha$). Analyses were processed with the CITZAF correction procedure (Armstrong, 1995).

Secondary electron and backscattered electron images were obtained with a LEO 1550VP field emission scanning electron microscope (FE-SEM). An Oxford INCA X-ray energy-dispersive spectrometer on the SEM was used for elemental analysis. Quantitative analyses were processed with the XPP correction procedure (Pouchou and Pichoir, 1991).

Vis-NIR absorption measurements were carried out using a custom-built diode array spectrometer system. A tungsten-halogen lamp was directed into a highly modified Thermo NicPlan infrared microscope with both silicon and InGaAs diode array detectors for extended wavelength coverage. Polarization was provided by a Glan-Thompson calcite polarizer. In some cases, spectra were also obtained in the UV range using an Ocean Optics HR2000 spectrometer with a deuterium lamp.

Argon isotopic measurements were conducted in the noble gas laboratory at Caltech following procedures similar to those reported by House et al. (2000) and Amidon and Farley (2010) for helium dating. For these measurements, samples were first examined with a binocular microscope for freedom from other phases. Then they were placed in an ultrasonic cleaner for 15 minutes and dried. Next, they were crushed with jaw pliers. The crushed fragments were separated under a microscope to select grains predominantly in the 1–3 mm range. Finely divided particles were excluded from the measurements to minimize surface area upon which atmospheric argon could absorb. Likewise, grains with extensive internal fractures were avoided. The selected grains were washed in purified ethanol to remove adhering particles and allowed to dry at about 50°C.

For the argon extraction, the washed grains were placed in 6 × 3 mm degassed platinum tubes crimped at one end. When filled, they were loosely crimped shut at the other end to retain the feldspar but to allow argon gas to escape. The tubes typically accommodated about 20 mg of sample. The capsules were weighed before and after filling to determine the exact amount of feldspar they contained.

The capsules were placed into wells in a copper planchette in the mass spectrometer line. After a thorough evacuation, the capsules were heated slightly above 1000°C by rastering a Nd-YAG laser across the surface for about 30 minutes. To ensure degassing, the sample was re-extracted by additional rounds of laser rastering. Once the gases were extracted, they were purified by passing them over SAES getters to remove nitrogen and other reactive gases. After expansion into a volume of about 1.5 liters, the argon was cryogenically focused into a magnetic sector mass spectrometer (MAP 215-50), where the argon isotopes were counted. The data were then processed with software to provide the necessary instrumental corrections.

These measurements were intended not to provide a high-accuracy age date, but to clearly indicate if the isotopic ratios of the argon in the samples showed geologic time buildup of radiogenic $^{40}Ar$ from the decay of naturally occurring $^{40}K$. Ratios near those of atmospheric argon would indicate that they had been recently heated to temperatures sufficient to drive out the radiogenic argon.

**TABLE A-1.** Feldspar samples used in detailed analytical investigations.

| Sample number | Claimed locality[a] | Source | Sample type[b] | Methods used[c] |
|---|---|---|---|---|
| GIA-a | Tibet | GIA | Red rough | Argon |
| GRR 289 | Mexico | Caltech Collection | Pale yellow rough | EMP |
| GRR 1613 | Rogers mine, Oregon | Author's collection | Near-colorless rough | EMP |
| GRR 1615 | Ponderosa mine, Oregon | Chris Johnston | Colored rough | EMP, SEM |
| GRR 2058 | Ponderosa mine, Oregon | Chris Johnston | Near-colorless rough | EMP |
| GRR 2390 | Tibet | Palagems.com | Red rough | Argon |
| GRR 2428 | Tibet | Palagems.com | Red rough | EMP, argon |
| GRR 2520 | Tibet | Ion International | Red faceted | Optical absorption |
| GRR 2560 | Chihuahua, Mexico | B. Barker | Pale yellow rough | SEM |
| GRR 2570 | Chihuahua, Mexico | D. Wallace | Pale yellow rough | EMP, SEM |
| GRR 2607 | "China" | JTV | Pale yellow rough, red rough | EMP |
| GRR 2611 | Dust Devil mine, Oregon | Ion International | Pale red rough | SEM |
| GRR 2616 | Tibet | Ion International | Red faceted | SEM |
| GRR 2629 | Chihuahua, Mexico | B. Barker | Pale yellow rough | EMP, SEM |
| GRR 2630 | "China" | DSN | Red faceted | SEM, argon |
| GRR 2632 | Oregon | Chris Rose | Pale colored rough | SEM |
| GRR 2633 | Oregon | Chris Rose | Red rough | EMP |
| GRR 2635 | "China" | Bangkok dealer | Red rough | SEM, argon |
| GRR 2639 | Chihuahua, Mexico | Andegem | Pale yellow rough | EMP |
| GRR 2641 | "China" | Andegem | Red and green rough | EMP, SEM, argon |
| GRR 2642 | "China" | Andegem | Red and red/green faceted | Argon |
| GRR 2645 | "China" | JTV | Red faceted | SEM |
| GRR 2646 | Inner Mongolia | JTV | Pale yellow rough | SEM, argon |
| GRR 2649 | "China" | DSN | Pale yellow rough | SEM, argon |
| GRR 2650 | "China" | DSN | Red faceted Olympic gems | EMP, SEM |
| GRR 2651 | "China" | Andegem | Pale yellow rough | EMP, argon |
| GRR 2652 | "China" | Andegem | Multicolored rough | Visual examination |
| GRR 2654 | Dust Devil mine, Oregon | Karla Proud | Red rough | EMP |
| GRR 2655 | "China" | Andegem | Pale yellow faceted | Argon |
| GRR 2659 | "China" | Andegem | Green faceted | Argon |
| GRR 2679 | Tibet | JTV | Red rough | EMP, argon |
| GRR 2886 | Tibet | Jacqueline Li | Red rough | EMP, argon |
| GRR 2887 | Tibet | Jacqueline Li | Red faceted | EMP, argon |
| GRR 2902 | Congo | GemFrance | Red faceted | EMP, argon |
| GRR 2921 | Tibet | GAAJ | Red rough | EMP, argon |
| GRR 2923 | Inner Mongolia | GAAJ | Pale yellow rough | EMP, argon |
| JTV-1 | "China" | JTV | Red faceted | Argon |
| GS 0.44 | Tibet | Ion International | Red faceted | EMP |
| GS 0.45 | Tibet | Ion International | Red faceted | EMP |
| GS 0.46 | Tibet | Ion International | Red faceted | EMP |
| GS 0.47 | Tibet | Ion International | Red faceted | EMP |
| GS 0.50 | Tibet | Ion International | Red faceted | EMP |
| GS 0.55 | Tibet | Ion International | Red faceted | EMP |
| GS oval | Tibet | Ion International | Red faceted | EMP |
| GS 0.98 | Tibet | Ion International | Green faceted | Optical absorption |

[a] Only the samples from the Rogers mine were collected by the author. The localities for all others were stated by the donors.
[b] Several of the sample numbers represent batches of multiple crystals or gemstones.
[c] EMP = electron microprobe analysis; argon = argon isotope study; SEM = scanning electron microscopy, including energy-dispersive spectroscopy; many samples were also subjected to optical absorption spectroscopy.

*Figure 2. In addition to Oregon, copper-containing feldspar has been reported from Miyake-Jima, Japan (left, 15 mm wide), and the Pinacate volcanic field, Mexico (center, 15 mm wide, with copper platelets). Pale yellow labradorite from Casas Grandes, Mexico (right, 0.55 ct each), is available in large quantities; this material does not contain copper. Photos by Mark Garcia (left) and G. R. Rossman (center and right).*

occurrence extending about 20 × 4 km that contained transparent feldspar. Abduriyim (2008) reported that up to 100 tonnes of this andesine have been mined annually. The properties given in this report agree with many subsequent analyses (e.g., Abduriyim and Kobayashi, 2008, and data below).

Several other localities have produced colorless to pale yellow gem-quality plagioclase, but not in commercial quantities.

*Figure 3. These 9 × 12 mm (2.78–3.44 ct) andesines supplied by Andegem were reportedly fashioned from material mined "in China." These samples were selected to show the maximum range of color variation, and are therefore photographed table-down. Photo by G. R. Rossman.*



## CHRONOLOGY OF ANALYSES AND RESULTS: 2002 TO MID-2009

**Initial Analytical Work.** In 2002, a new locality for red plagioclase feldspar was announced. Gem dealer Dr. Laurent Sikirdji (GemFrance) reported that one of

### NEED TO KNOW

- Studies from 2002 to mid-2009 show that red (and green) Cu-bearing andesine-labradorite reportedly from Tibet, "China," and the Democratic Republic of the Congo have overlapping chemical and physical properties.

- Traces of copper-containing fluxes on the surface of rough stones and argon isotopic measurements indicate these feldspars have been heated to high temperatures in the presence of Cu.

- Evidence up to mid-2009 suggests that laboratory diffusion of Cu into pale yellow feldspar from Inner Mongolia (but not Mexico) could account for some or all of the "Asian/Congolese" feldspar in the market.

- This does not eliminate the possibility that andesine deposits in Tibet that were documented in 2010 are genuine.

his suppliers in Bangkok first showed him red andesine in January 2002, and told him it came from an unspecified locality in the Democratic Republic of the Congo (O'Meny, 2002). He sent samples to Dr. Emmanuel Fritsch at the University of Nantes, France, who published the first report about this red andesine (Fritsch, 2002). Krzemnicki (2004) further characterized this material and showed that it had a greater saturation of color and contained more copper
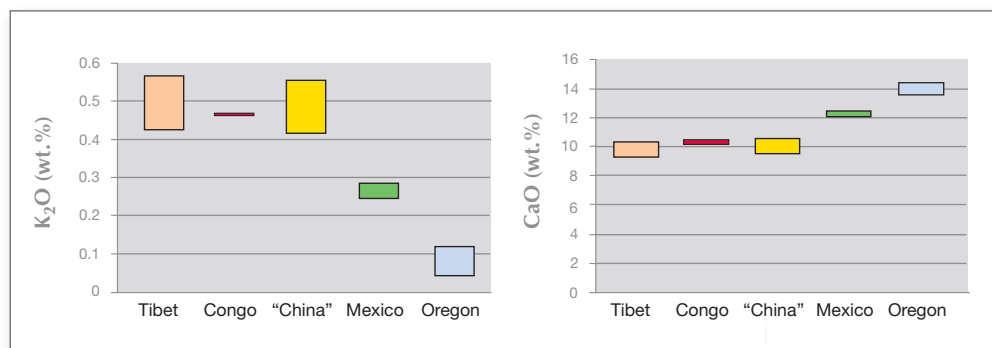
*Figure 4. Electron microprobe analyses show no distinction between feldspars allegedly from Tibet and "China," but there are clear differences from those of Mexico and Oregon.*

than the Oregon stones, but that its optical absorption spectrum was otherwise similar to the Oregon material. The initial analyses reported by these authors indicated that Dr. Sikirdji's samples had a lower Ca content than feldspar from Oregon, and that their composition fell slightly below and above the nomenclature boundary between andesine and labradorite. (Hereafter, plagioclase of such composition will be referred to as "andesine" for simplicity.)

The exact geographic origin remained undisclosed at the time, and stories soon began to circulate that gem dealers could not confirm the Congo source (Laurs, 2005). Because rough stones and matrix specimens were unavailable, questions arose about the authenticity of the material, or at least the accuracy of its reported locality.

In April and August 2005, this author (and GIA) received a few rounded red pebbles from William Larson of Palagems.com. Their origin was represented to Mr. Larson as Chinese (Tibetan and otherwise). The optical spectra of these samples closely resembled those of Oregon sunstone, indicating that copper was the cause of color. Later that year, Laurs (2005) published a brief report on material represented as Chinese that was obtained at the 2005 JCK show in Las Vegas. This report also contained information from Chinese dealer Jacqueline Li (Do Win Development Co., Ltd.), who offered a modest quantity of red feldspar (including rough material) at the 2006 Tucson show. She claimed it originated from an unspecified Tibetan mine worked by her husband's relatives. As this material entered the market, samples made their way to gem testing laboratories, and some of them were sent to Caltech in May and June 2006 for electron microprobe analysis. Around this time, the author heard concerns that the material might be treated by someone in China who had invented a method to produce red feldspar. Others in the industry had also heard about an unspecified treatment process (Hughes, 2010). The situation was further confused as early as 2006 because vendors were representing the origin of the red (and green)

andesine both as Tibet and China (figure 3), with no clear indication if these represented the same or different localities (Federman, 2006).

The author's detailed electron microprobe analyses of the red and green feldspars received in May–June 2006 indicated that they were members of the plagioclase series and their compositions ranged between $An_{47}$ and $An_{50}$, which placed them in the andesine compositional range (again, see box B)

Additional electron microprobe analyses of feldspars purportedly from the Congo, Tibet, "China," Mexico, and the two main Oregon districts, conducted from 2006 through 2009 (table 1), showed that the compositions of the Congolese, Tibetan, and "Chinese" samples overlapped and were easily distinguishable from those found in Mexico and Oregon (figure 4). Most of the former group fell in the andesine nomenclature range, though some contained slightly more than 50 mol.% anorthite ($An_{50}$),

**TABLE 1.** Electron microprobe analyses of selected feldspars from various claimed localities.

| Sample no. | Claimed locality | Composition[a] |
|---|---|---|
| GRR 2902 | Congo | $An_{50-52}$ |
| GRR 2616 | Tibet | $An_{44}$ |
| GRR 2630 | "China" | $An_{43-49}$ |
| GRR 2635 | "China" | $An_{44-46}$ |
| GRR 2641 | "China" | $An_{43-48}$ |
| GRR 2645 | "China" | $An_{45-47}$ |
| GRR 2649 | "China" | $An_{44-49}$ |
| GRR 2650 | "China" | $An_{42-51}$ |
| GRR 2646 | Inner Mongolia | $An_{40-49}$ |
| GRR 2560 | Mexico | $An_{52-54}$ |
| GRR 2570 | Mexico | $An_{53}$ |
| GRR 2629 | Mexico | $An_{52-57}$ |
| GRR 1615 | Oregon | $An_{67-69}$ |
| GRR 2611 | Oregon | $An_{61-65}$ |
| GRR 2632 | Oregon | $An_{60-73}$ |

[a] Determined with multiple analyses on samples from each batch. A single number is used when the range of analytical values, expressed as two significant digits, does not exceed the value given.
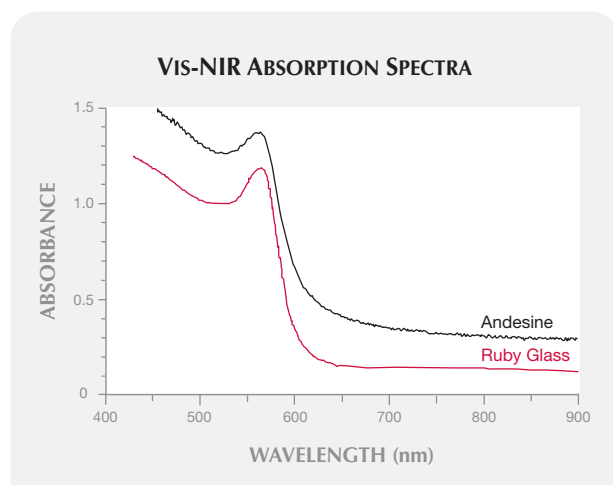
Figure 5. This representative Vis-NIR spectrum of a red andesine reportedly from Tibet (~6 mm thick) is similar to that of a 1-mm-thick copper ruby glass (the latter adapted from figure 2 of Capatina, 2005, p. 284).
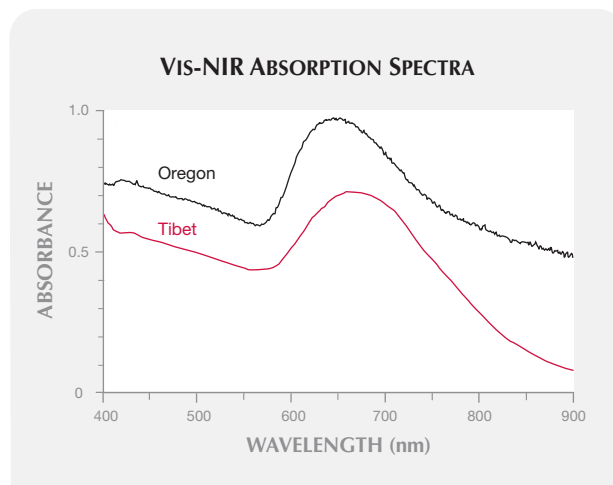


Figure 6. The Vis-NIR spectrum of a faceted green andesine allegedly from Tibet (6 mm thick) shows the greatest absorption in the red portion of the spectrum, similar to a green labradorite from Oregon (2 mm thick).

placing them in the labradorite range. The full microprobe analyses appear in the *G&G* Data Depository (see gia.edu/gandg) and are summarized in figure B-1.

In 2008, we conducted 87 additional chemical analyses with a scanning electron microscope (SEM) using energy-dispersive spectroscopy (EDS). Although SEM-EDS analyses are slightly less accurate than electron microprobe data, they are generally quicker to obtain and less costly, and could still readily distinguish among feldspars alleged to be from the Congo, Tibet/"China," Oregon, and Mexico. These SEM-EDS analyses confirmed the results obtained with the electron microprobe (again, see table 1). Specifically, they showed that the Congolese, Tibetan, and "Chinese" samples fell within the same range of major elements and that they were distinct from the Mexican and Oregon feldspars.

Spectroscopic studies beginning in 2006 and con-

tinuing through 2008 demonstrated that the origin of color in the Tibetan/"Chinese" material was the same as in the Oregon sunstone. Dozens of optical spectra were obtained on both red and green andesine samples. The red stones had a dominant absorption band at about 565 nm and rising absorption in the blue region (figure 5). This spectrum bore a strong similarity to that of Oregon sunstone and to decorative red glass known as "copper ruby glass." This glass owes its color to colloids of copper metal (Nakai et al., 1999; Capatina, 2005) and, by analogy, it is reasonable to conclude that red andesine does as well.

The green andesine tested in this study showed strong green to colorless pleochroism, similar to the green Oregon labradorite. The absorption of the green material reached a maximum in the 650 nm region and showed much greater absorption in the red portion of the spectrum (figure 6) than did the



Figure 7. This "burned" red andesine (25 mm across) was said to have been heated to change it from pale yellow to red. Photos by G. R. Rossman (left, interior view) and Mark Garcia (right, surface of sample).
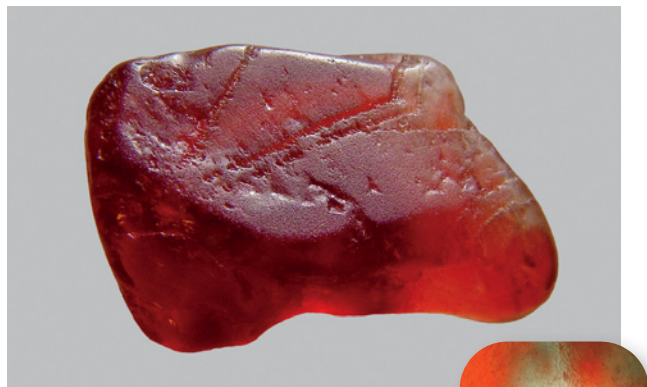
Figure 8. Some rough samples of andesine purportedly from Tibet/"China" showed features that appeared to be etch pits, as in this 17 mm andesine sold to a Bangkok dealer in mid-2003 from a supplier who stated it was mined in China. The pit in the inset is 32 µm wide. Photos by Mark Garcia and G. R. Rossman (inset).

red andesine. There was some variability in the position of the absorption maximum of the green andesine samples, due to the superposition of absorption features from the red regions, and from the $Fe^{2+}$ in the feldspar. The spectrum was generally comparable to that of the green Oregon feldspar reported by Hofmeister and Rossman (1985).

In mid-2006, the author was told by a red andesine customer about a rumor that the Tibetan/"Chinese" material was being treated by a laboratory process in Asia. Although this andesine did have features reminiscent of diffusion, that alone did not prove laboratory treatment, since the Oregon sunstone is also most likely a product of diffusion—*natural* diffusion in the earth.

Red andesine soon became popular with consumers, and in the mid-2000s television networks such as Jewelry Television (JTV) and the Direct Shopping Network (DSN) sold "Chinese" andesine as natural material based on reports issued by various gemological laboratories. In 2007 JTV sent an on-air personality known as "Jewel Hunter Jack" to find the origin of the red feldspar. He ultimately traced the material to an area of Inner Mongolia where significant quantities of pale yellow andesine were being mined, but he saw no red material. He was told that the pale yellow feldspar had to be heated to bring out its "inherent" color, but he was not given the opportunity to actually witness the treatment process. He returned with samples of yellow
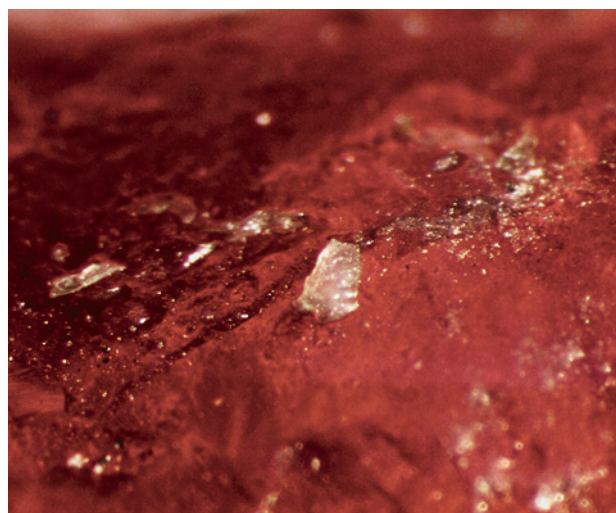
and "burned" red andesine (e.g., figure 7).

The pale yellow rough obtained by JTV in Inner Mongolia and rough examples of "burned" feldspar made their way to the author's laboratory by late January 2008 for additional testing. Our analyses of the pale yellow andesine found no copper that could have given rise to the red color with heat treatment alone. Consistent with these analyses, heating experiments of the pale yellow andesine conducted under controlled oxygen fugacity conditions failed to achieve any red color, as did treatment with gamma radiation. By early February 2008, JTV announced that the material originated in Inner Mongolia. Shortly thereafter, concerns about diffusion treatment of andesine became widespread and public (see, e.g., James, 2008a,b; Kratochvil, 2008).

Several of this author's observations on rough stones reportedly from Tibet/"China" also raised questions about their natural origin. Surfaces appeared etched and some showed pits of approximately square pyramidal shape (figure 8). Fragments of feldspar were found attached to the surface but in a different crystallographic orientation from the underlying material, which suggested that separate pieces of feldspar had become fused together (figure 9).

Even more interesting was the presence of a glassy material in cracks and recesses on the surface of some of the rough samples. SEM-EDS analysis of a thin layer of this glass-like material near a fused particle showed a higher concentration of potassium than the feldspar, and a much higher concentration

Figure 9. This 0.3-mm-wide fragment of feldspar was fused to the surface of an andesine sample by a glassy substance. Photo by G. R. Rossman.

of copper (figure 10). These observations strongly suggested, but did not prove, that the feldspar had been heated in a copper-containing flux to allow the
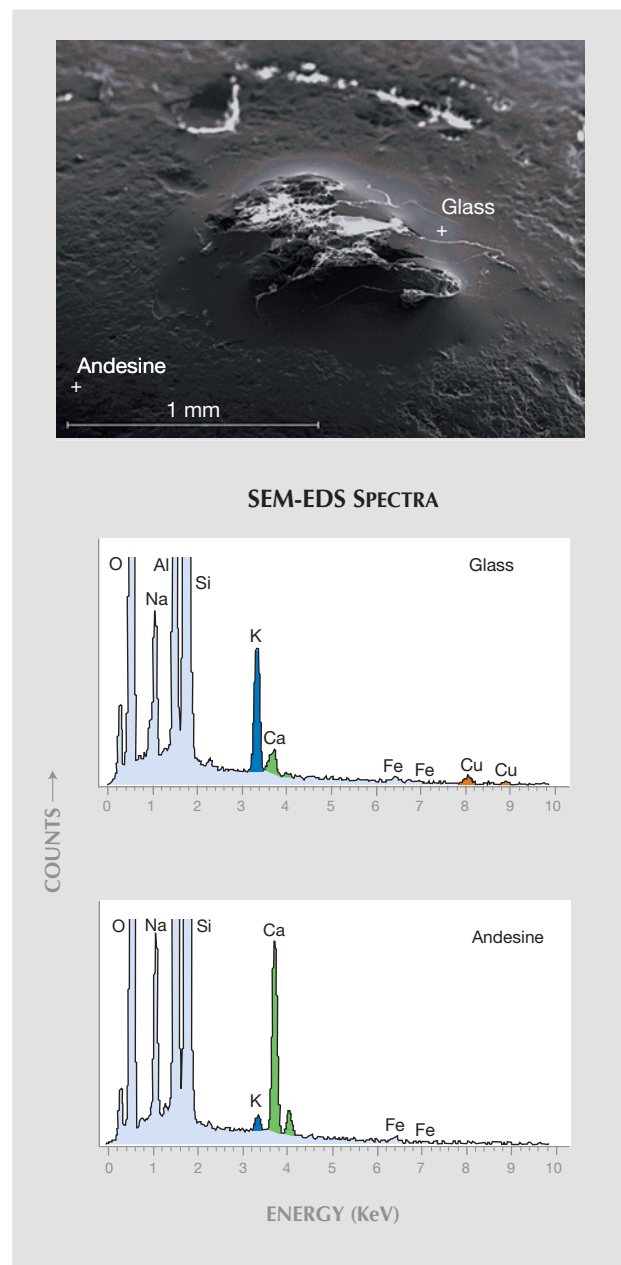


Figure 10. Scanning electron microscopy shows the smooth, glassy region surrounding a fragment fused to the surface of a rough andesine reportedly from Tibet/"China." The SEM-EDS spectra show much greater potassium (K) and copper (Cu) contents in the glassy material than in the andesine, consistent with the possibility that this sample has been in contact with a copper-containing flux. Image by Chi Ma.

diffusion of copper. In ceramics, copper compounds are well-known ingredients in red-colored glazes. And, as noted above, copper is also known to produce a red color when dispersed as colloidal particles.

**Diffusion of Copper into Plagioclase.** Diffusion experiments conducted in our laboratory in September and October of 2008 found that copper easily enters plagioclase at temperatures above 1200°C, a result independently observed by others (Furuya, 2008; Emmett and Douthit, 2009). Our results also showed that copper diffuses into plagioclase much more readily than cobalt or nickel. These experiments were consistent with the possibility that red andesine was a product of laboratory diffusion, but were not absolute proof that diffusion actually was being used as a treatment process. The fact that something *can* be done is not proof that it *is* being done.

**The 2008 GAAJ Expedition.** Even so, by 2008 there was substantial evidence that much of the red andesine on the market was treated by a method involving high-temperature diffusion of copper into pale yellow andesine from Inner Mongolia. Yet questions remained about the existence of a natural red andesine mine in Tibet. To address this possibility, an expedition that included representatives of the Gemmological Association of All Japan–Zenhokyo (GAAJ), the Japan Germany Gemmological Laboratory (JGGL), and JTV visited an area near Shigatse, Tibet, that was identified as the Bainang mine. There they were told that gem-quality feldspar had been mined from an alluvial deposit since 2006 (Abduriyim, 2008, 2009). Eighteen samples of rough from this expedition were provided to the author by the GAAJ and JTV representatives.

**Further Analytical Work.** *Argon Isotopic Analyses.* More stringent proof of high-temperature treatment was offered by argon isotopes. Potassium-40 ($^{40}K$) is a naturally occurring radioactive isotope in many minerals, including feldspar. Over geologic time, $^{40}K$ decays to argon-40 ($^{40}Ar$), a gas with a 1.3 billion year half-life. $^{40}Ar$ is called *radiogenic* argon because it forms by radioactive decay. It remains within the crystal structure but can escape if heated sufficiently. For example, while mineral crystals are held in a magma chamber, the heat of the magma quickly drives out the Ar gas. Once the volcano erupts, the crystal will ultimately reach a much cooler environment, such as when it sits near the surface of the

| Sample no. | Claimed locality[a] | $^{40}Ar/^{36}Ar$ ratio |
|---|---|---|
| 2902 | Congo | 527 |
| 2390 | Tibet | 356 |
| 2428 | Tibet | 346 |
| 2679 | Tibet | 366 |
| 2886 | Tibet | 338 |
| 2679-a | Tibet | 296 |
| 2679-b | Tibet | 296 |
| 2679-c | Tibet | 366 |
| 2887-b | Tibet | 491 |
| 2921-a | Tibet | 360 |
| 2921-b | Tibet | 486 |
| GIA-a | Tibet | 802 |
| GIA-a | Tibet | 728 |
| 2630-a | "China" | 306 |
| 2630-b | "China" | 320 |
| 2635-a | "China" | 557 |
| 2635-b | "China" | 900 |
| 2641 | "China" | 340 |
| 2642 | "China" | 796 |
| 2659 | "China" | 619 |
| JTV-1 | "China" | 475 |
| JTV-1 | "China" | 549 |
| 2649 | Inner Mongolia | 4816 |
| 2651-a | Inner Mongolia | 5875 |
| 2651-b | Inner Mongolia | 1769 |
| 2651-w | Inner Mongolia | 2490 |
| 2655 | Inner Mongolia | 8204 |
| 2646 | Inner Mongolia | 2923 |
| 2923 | Inner Mongolia | 2282 |

[a] Sample masses ranged from 8.4 to 24.8 mg. Different samples from multiple-sample batches are designated by different letters. Two portions of a single sample of JTV-1 and GIA-a were run at different times.

earth after eruption. The $^{40}Ar$ returns over geologic time via decay from $^{40}K$, but it is trapped within the crystal because near-surface temperatures are not high enough to remove it. In the case of andesine, traces of potassium were detected in all of the Tibetan/"Chinese," Inner Mongolian, and Congolese feldspars tested. All had a chemical composition of approximately $(Na_{0.51}Ca_{0.47}K_{0.02})[Al_{1.44}Si_{2.55}Fe_{0.01}]O_8$. Radiogenic argon would have built up over time in the ground, but when heated in the laboratory, it would escape.

The argon released from natural, untreated feldspar will have a high ratio of $^{40}Ar$ to $^{36}Ar$ (the latter isotope exists naturally in air and can enter feldspars along cracks and cleavages). But if the feldspar was previously heated in a moderate- to high-temperature laboratory process, such as required for copper diffusion, then most of the radiogenic argon would have been released, and the experimental measurement would yield an $^{40}Ar$-to-$^{36}Ar$ ratio close to that of air

(about 300). Thus, this measurement would offer a clear indication of whether a specific sample had ever been subjected to heat treatment.

Argon-release experiments were conducted from August 2008 through July 2009 on pale yellow andesine rough from Inner Mongolia that was obtained by Jewel Hunter Jack and from GAAJ (2008 expedition), DSN television, and Andegem. Also tested were a variety of rough and faceted red stones labeled as Tibetan or Chinese that were obtained from the same sources, as well as a Bangkok dealer, GIA, Palagems.com, and Jacqueline Li. An additional green faceted stone from China was obtained from DSN. Again, none of the donors knew beforehand what types of testing would be conducted. To be certain that the heat generated during faceting did not invalidate our argon experiments, a sample of yellow rough was faceted by Andegem and then tested with the other samples.

Our experiments involved laser heating the sample to a temperature of about 1000°C under high vacuum, followed by analysis of the argon in a mass spectrometer (see box A and table 2). Experiments on portions of rough yellow andesine that had been heated for two hours to various temperatures (table 3) showed that the temperature of the laser extraction would not cause all of the sample's argon to be released, but it would clearly indicate if the sample had been heated to a temperature high enough to release *most* of the radiogenic argon. One experiment heated a red andesine to a temperature that completely melted the sample (>1450°C). Under these conditions, the release of argon was more complete, but the step heating and melting experiments showed that it was difficult to release all of the radiogenic argon on a laboratory time scale, even after the sample was melted.

Despite these caveats, the results (figure 11) show a striking difference between the yellow

TABLE 3. Argon-release experiments on sample 2651.[a]

| Sample treatment | $^{40}Ar/^{36}Ar$ ratio |
|---|---|
| None | 1769 |
| 200°C | 1272 |
| 400°C | 1096 |
| 600°C | 1005 |
| 800°C | 760 |
| 1000°C | 595 |

[a] Heated for two hours at the stated temperatures in a laboratory furnace under air. Sample masses ranged from 18.3 to 21.6 mg.
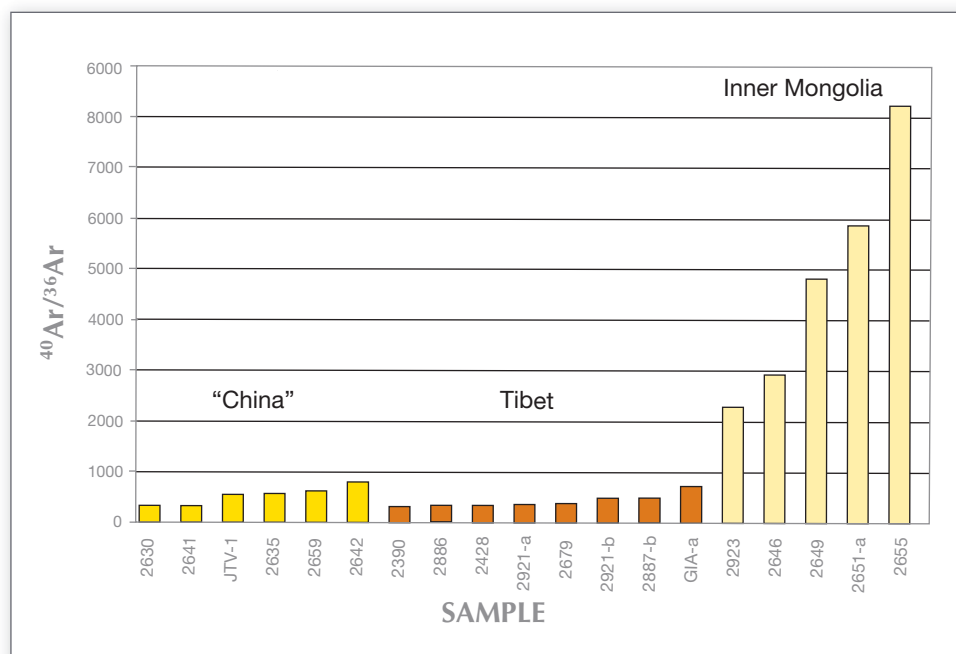
Figure 11. Argon-release experiments conducted on red and green andesine reportedly from Tibet and "China," and on pale yellow andesine from Inner Mongolia, showed significant differences in the ratio of radiogenic $^{40}Ar$ to $^{36}Ar$, which indicate that the Tibetan and "Chinese" samples were depleted of their radiogenic argon by recent exposure to high temperatures. Samples of yellow rough originally stated to be from "China" are placed in the Inner Mongolia results.

rough from Inner Mongolia, which had high ratios of $^{40}Ar$ to $^{36}Ar$, and the red Tibetan/"Chinese" rough and faceted stones, which all had values near atmospheric or slightly above. It was clear the red samples recently had been heated to high temperature.

*Scanning Electron Microscopy.* SEM study of a red andesine from the 2008 GAAJ expedition revealed smooth areas on the sample that resembled the fused glass on the treated Inner Mongolian andesine. Chemical analyses of one such area showed that it was high in potassium and contained copper, much like the glass observed on the treated andesine. Furthermore, small particles of copper sulfide and a copper-iron-zinc alloy were attached to the surface of the stone (figure 12). The argon isotopic ratio (sample 2921-b) indicated that the sample recently had been heated to high temperature.

*Additional Isotopic Analyses.* A pale yellow Inner Mongolian rough from Andegem and two Tibetan stones from JTV (obtained on the 2008 expedition to the Bainang mine) were dissolved under clean-laboratory conditions and examined with solution ICP–mass spectrometry. The analyses mainly targeted lead isotopes that form from the decay of naturally radioactive thorium and uranium. Thorium-232 has a half-life of about 14 billion years and decays to lead-208. Uranium-238 has a half-life of about 4.5 billion

**TABLE 4.** Isotope ratios for andesine samples.

| Isotope ratio | Inner Mongolia (yellow) | Tibet (red) |
|---|---|---|
| $^{207}Pb/^{208}Pb$ | 4.0 ± 0.1 | 4.1 ± 0.1 |
| $^{208}Pb/^{206}Pb$ | 2.0 ± 0.1 | 2.1 ± 0.1 |
| $^{88}Sr/^{43}Ca$ | 13.7 ± 0.1 | 13.6 ± 0.1 |
| $^{137}Ba/^{43}Ca$ | 0.13 ± 0.01 | 0.14 ± 0.01 |
| $^{66}Zn/^{88}Sr$ | 0.0003 ± 0.00005 | 0.0004 ± 0.00005 |



Figure 12. These SEM images show microscopic particles of copper sulfide (left) and a copper-iron-zinc alloy (right) attached to the surface of an andesine sample from the 2008 GAAJ expedition to Tibet. Images by Chi Ma.
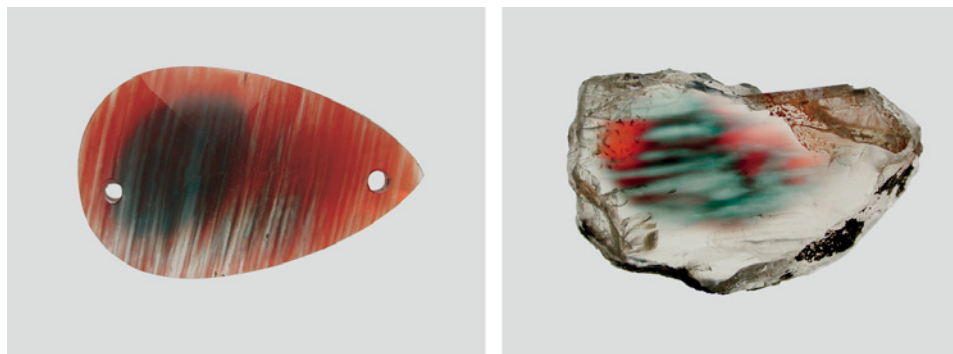
*Figure 13. Color bands were seen in much of the andesine reportedly from Tibet and "China" (left, 23 mm wide), but also in some samples from Oregon (right, 19 mm wide, from the Ponderosa mine). Photos by G. R. Rossman.*

years and decays to lead-206, whereas uranium-235 has a half-life of about 700 million years and decays to lead-207. It is extraordinarily unlikely that two deposits of feldspar separated by 2,300 km would have formed with the same geologic age, the same trace concentrations of uranium and thorium, and the same proportions of uranium and lead isotopes.

The results showed the isotopic ratios were essentially identical within measurement error (table 4), suggesting that the samples were from the same source. Some additional isotopic ratios of divalent minor and trace elements measured in the analyses also were strikingly similar in the feldspars from the two localities. The combination of the argon contents, SEM studies, and various isotopic ratios made it very difficult to accept that these samples came from different deposits.

**Differences in Appearance.** Differences between the Oregon sunstones and the Tibetan/"Chinese" red andesine examined by this author ranged from subtle to obvious. The latter material generally had far fewer copper flakes than the Oregon sunstones. A much larger proportion of the Tibetan/"Chinese" samples contained linear bands of color (again, see figure 3 and figure 13, left), though some banding was also seen in a fraction of the Oregon sunstones (figure 13, right). The pattern of core-to-rim color zoning favors green cores in the Tibetan/"Chinese"

material and red cores in the Oregon sunstones, but exceptions do exist (e.g., figure 14). However, none of these differences offers proof of laboratory treatment. The coloration of both materials appears to be the result of diffusion: natural diffusion in the case of Oregon sunstone, probably occurring during the eruptive event, and laboratory diffusion in the case of the Tibetan/"Chinese" andesine we tested.

**The Olympic Games Andesine.** In August 2008, the author examined stones that had been internally laser-engraved (Garabedian and Garabedian, 2009) with an image of the Olympic rings and sold as a souvenir of the 2008 Summer Games held in Beijing (figure 15, left). Claims surfaced on the Internet that these were actually Mexican labradorite, diffused and sold as Tibetan/"Chinese" feldspar (James, 2008b). Chemical testing easily distinguished these souvenirs from Mexican material and showed that they were identical in composition to the heated Asian andesine (figure 15, right).

**A Mine in the Democratic Republic of the Congo?** A single faceted red andesine represented as coming from the Democratic Republic of the Congo was obtained from GemFrance in April 2009. It was subjected to argon-isotopic studies in July 2009, and fell within the same range as samples stated to be from Tibet and China (table 2). Furthermore, its chemical
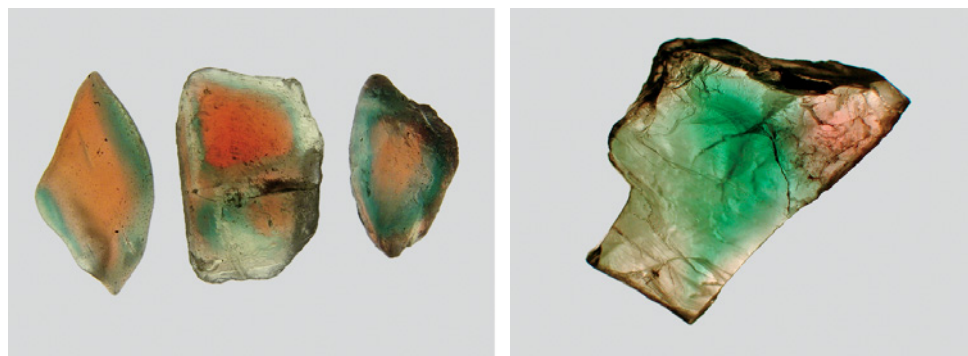


*Figure 14. Although green cores are typical of concentrically zoned Tibetan/"Chinese" andesine, some samples contain red cores (left, 1.5–2.3 cm). Likewise, most zoned Oregon labradorites have red cores, but some have green cores (right, 1.8 cm). Photos by G. R. Rossman.*

# Box B: Feldspar Nomenclature

The common feldspars are a group of minerals that span a range of compositions with varying proportions of sodium, potassium, and calcium in addition to aluminum and silicate. They are classified into *alkali feldspars* and *plagioclase feldspars*.

The alkali feldspars form a continuous solid solution between the sodium feldspar albite and the potassium feldspars—sanidine, orthoclase, and microcline—where the three names reflect the degree of silicon and aluminum ordering on the tetrahedral sites, which in turn determine if the feldspar is monoclinic or triclinic. They tend to have comparatively little calcium in their compositions. Collectively, they are called K-feldspars after the chemical symbol for potassium (K).

The plagioclase feldspars form a continuous solid solution between the sodium feldspar albite and the calcium feldspar anorthite (see table B-1). There can also be minor amounts of potassium replacing some of the sodium and of iron replacing some of the aluminum. Historically, the plagioclase feldspars have been subdivided into six different names depending on the proportions of sodium and calcium in their composition.

Feldspar compositions are commonly plotted on a ternary diagram that indicates the proportions of potassium, sodium, and calcium (figure B-1). On this diagram, the range of analyzed compositions (by electron microprobe analysis) are indicated for feldspars from Tibet/"China," Inner Mongolia, Mexico, and Oregon (from Lake County, and also the Ponderosa mine in Harney County). Because the Asian feldspars occur on both sides of the 50% calcium proportion boundary, some are classified by the nomenclature as *andesine* (less than 50%), and some are *labradorite* (more than 50%).

Feldspar nomenclature can be even more complicated. During growth from a melt in a magma chamber, plagioclase feldspar often changes composition such that the inner portion of the crystal can have a somewhat different composition than the rim. Consequently, a single crystal may have different names depending

on the portion analyzed. In this case, the plagioclase nomenclature distinction does not indicate a fundamental difference in the feldspar other than a minor difference in composition.

The Asian feldspars are also displaced vertically from the horizontal axis due to their slightly higher potassium content. It is this potassium that makes the argon isotope analysis possible.
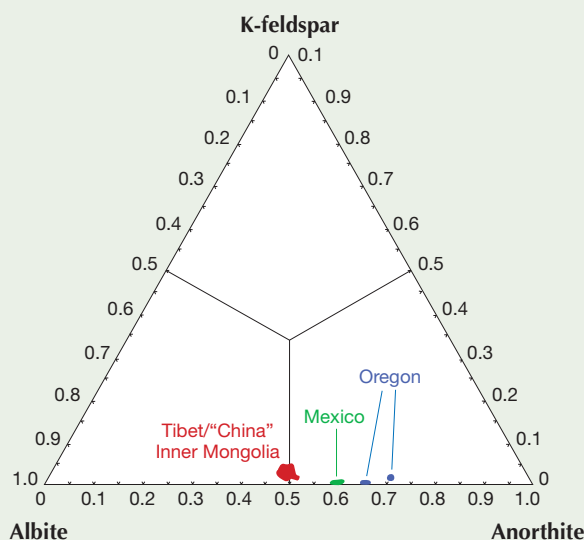


*Figure B-1. The chemical composition of plagioclase samples from Tibet/"China," Inner Mongolia, Mexico, and Oregon analyzed by the author are depicted in this ternary diagram.*

**TABLE B-1.** Plagioclase feldspars.

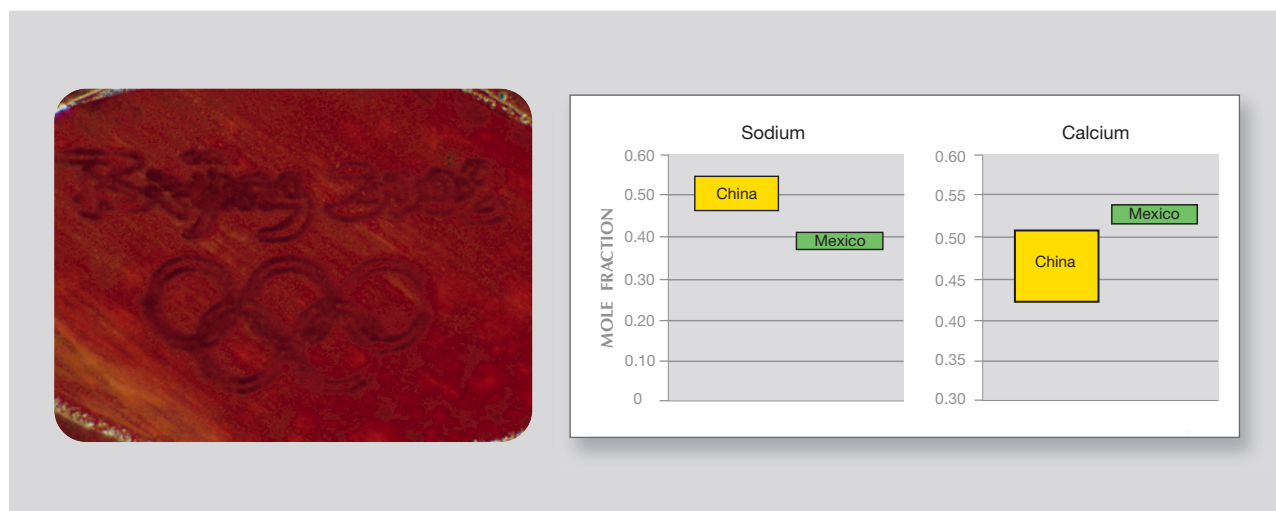|  | Na | Ca |
|---|---|---|
| Albite | 100–90% | 0–10% |
| Oligoclase | 90–70% | 10–30% |
| Andesine | 70–50% | 30–50% |
| Labradorite | 50–30% | 50–70% |
| Bytownite | 30–10% | 70–90% |
| Anorthite | 10–0% | 90–100% |

Figure 15. Red laser-engraved andesine in faceted 5 × 7 mm ovals was sold by DSN as souvenirs of the 2008 Beijing Olympics. Comparison of the proportions of sodium and calcium between these samples and Mexican feldspar clearly reveals their differences. The composition of the emblem-engraved stones falls within the range of the heated Asian andesine. Photo by G. R. Rossman.

composition matched the treated Tibetan/"Chinese" feldspar (see *G&G* Data Depository). These results clearly raise doubts that there is a Congolese source of natural red andesine.

## SUMMARY THROUGH MID-2009

Andesine from Tibet/"China" (e.g., figure 16) has been surrounded by controversy. Many of the results presented above have already appeared to some extent on the Internet (e.g., "Special issue on red feldspar," 2009) and have been observed independently by various individuals and laboratories worldwide. Rumors of possible treatment were known early in this author's work on the material, but definitive proof was lacking.

The argon-isotope results offer the most compelling evidence of widespread high-temperature treatment of Tibetan/"Chinese" andesine. Coupled with the observation of what appear to be copper-containing fluxes on the surface, and the occasional microscopic bits of copper compounds attached to the stones, the case for copper-diffused andesine from Inner Mongolia is strong. In fact, according to Christina Iu (pers. comm., 2011), it is now freely admitted by some Asian dealers. Nevertheless, this does not eliminate the possibility that there is also a source of natural-color andesine in Tibet, and samples obtained from a subsequent expedition in September 2010 (e.g., Abduriyim and Laurs, 2010) have been the focus of further research that will be reported in a future article.

Figure 16. The source and natural versus treated color origin of "Chinese" andesine continues to be controversial. These stones (5.90–21.45 ct) were cut from material reportedly mined in Tibet. Courtesy of Litto Gems; photo by Robert Weldon.

# REFERENCES

Abduriyim A. (2008) Gem News International: Visit to andesine mines in Tibet and Inner Mongolia. *G&G*, Vol. 44, No. 4, pp. 369–371.

Abduriyim A. (2009) A mine trip to Tibet and Inner Mongolia: Gemological study of andesine feldspar. News from Research, www.gia.edu/research-resources/news-from-research/andesine-mines-Tibet-Inner-Mongolia.pdf, Sept. 10.

Abduriyim A., Kobayashi T. (2008) Gem News International: Gemological properties of andesine collected in Tibet and Inner Mongolia. *G&G*, Vol. 44, No. 4, pp. 371–373.

Abduriyim A., Laurs B.M. (2010) Additional field research on Tibetan andesine. *G&G*, Vol. 46, No. 4, pp. 310–311.

Amidon W.H., Farley K.A. (2010) Mass spectrometric $^3$He measurements in $^4$He-rich phases: Techniques and limitations for cosmogenic $^3$He dating of zircon, apatite, and titanite. *Geochemistry Geophysics Geosystems*, Vol. 11, No. 10, Art. Q10004 [9 pp.].

Anderson O. (1917) Aventurine labradorite from California. *American Mineralogist*, Vol. 2, p. 91.

Armstrong J.T. (1995) CITZAF: A package of correction programs for the quantitative electron microbeam X-ray analysis of thick polished materials, thin films, and particles. *Microbeam Analysis*, Vol. 4, pp. 177–200.

Cao Y. (2006) Study on the feldspar from Guyang County, Inner Mongolia, and their color enhancement. Master's thesis, China University of Geosciences, Beijing [in Chinese].

Capatina C. (2005) The study of copper ruby glass. *Ceramics-Silikáty*, Vol. 49, No. 4, pp. 283–286.

Emmett J., Douthit T. (2009) Copper diffusion of plagioclase. News from Research, www.gia.edu/research-resources/news-from-research/Cu-diffusion-Emmett.pdf, Aug. 21.

Federman D. (2006) Gem Profile: Andesine feldspar. *Modern Jeweler*, www.modernjeweler.com/print/Modern-Jeweler/Andesine-Feldspar/1$52, March.

Fritsch E. (2002) Gem News International: Red andesine feldspar from Congo. *G&G*, Vol. 38, No. 1, pp. 94–95.

Furuya M. (2008) Copper diffusion treatment of andesine and a new mine in Tibet. *JGGL Gem Information*, Vol. 37–38, pp. 1–11 [in Japanese].

Garabedian A.C., Garabedian M. (2009) *Method for Introducing Inclusion Image into Gemstone*. United States Patent Application US 2009/0269702 A1.

Hofmeister A.M., Rossman G.R. (1985) Exsolution of metallic copper from Lake County labradorite. *Geology*, Vol. 13, pp. 644–647.

House M.A., Farley K.A., Stockli D. (2000) Helium chronometry of apatite and titanite using Nd-YAG laser heating. *Earth and Planetary Science Letters*, Vol. 183, No. 3-4, pp. 365–368.

Hughes R.W. (2010) Hunting Barack Osama in Tibet: In search of the lost andesine mines. www.ruby-sapphire.com/tibet-andesine.htm, Nov. 3.

James R. (2008a) Sunrise over Oregon. www.yourgemologist.com/ISGForumsBoard/showthread.php?t=5566, Apr. 17.

James R. (2008b) ISG report on the diffusion treatment of andesine! www.yourgemologist.com/ISGForumsBoard/showthread.php?t=5569, Jul. 23.

Johnston C.L., Gunther M.E., Knowles C.R. (1991) Sunstone labradorite from the Ponderosa mine, Oregon. *G&G*, Vol. 27, No. 4, pp. 220–233.

Kratochvil G. (2008) The Great andesine scam. www.jewelcutter.com/articles/andesine_scam.htm, May 17.

Krzemnicki M.S. (2004) Red and green labradorite feldspar from the Congo. *Journal of Gemology*, Vol. 29, No. 1, pp. 15–23.

Laurs B.M. (2005) Gem News International: Gem plagioclase reportedly from Tibet. *G&G*, Vol. 41, No. 4, pp. 356–357.

Laurs B.M., Rockwell K., Breeding C.M. (2006) Gem News International: Labradorite from Chihuahua, Mexico. *G&G*, Vol. 42, No. 4, pp. 274–275.

Li H. (1991) Discovery of feldspar type moonstone gem in Inner Mongolia. *Bulletin of Geological Science and Technology*, Vol. 11, pp. 136–137 [in Chinese].

Li H. (1992) Preliminary study of labradorite-moonstone from Inner Mongolia. *Jewellery*, Vol. 1, No. 6, pp. 45–47 [in Chinese].

Nakai I., Numako C., Hosono H., Yamasaki K. (1999) Origin of the red color of Satsuma copper-ruby glass as determined by EXAFS and optical absorption spectroscopy. *Journal of the American Ceramic Society*, Vol. 82, No. 3, pp. 689–695.

O'Meny C. (2002) Interview de Laurent Sikirdji. www.abc-luxe.com, Sept. 13.

Petrov A. (2010) Anorthite and native brass from Miyake-Jima, Tokyo. www.mindat.org/article.php/976/Anorthite+and+Native+Brass, July.

Pouchou J.-L., Pichoir F. (1991) Quantitative analysis of homogeneous or stratified microvolumes applying the model "PAP." In K.F.J. Heinrich and D.E. Newbury, Eds., *Electron Probe Quantitation*, Plenum Press, New York.

Rossman G.R. (2010) Pierre de soleil de l'Oregon et feldspath rouge de Chine, la controverse. *Revue de Gemmologie a.f.g.*, No. 172, pp. 5–10.

Special issue on red feldspar (2009). News from Research, www.gia.edu/research-resources/news-from-research/special-issue-homepage.html, Aug. 21.