Fluid Inclusions Confirm Authenticity of Tibetan Andesine

Can Tibetan andesine now be certified?

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Introduction

Untreated copper-bearing feldspar of a rich red color is found in nature, but gem-quality pieces are scarce. For decades the major occurrence has been in Oregon (USA), but gem-quality red feldspar also occurs in Japan (Furuya & Milisenda, 2009) and elsewhere.

Beginning in 2002, gem-quality red plagioclase feldspar entered world gem markets. The source was originally stated as the Congo and later morphed into Tibet. By 2007, suspicions that such stones were the result of a treatment were widespread. These suspicions were confirmed in early 2008 (Furuya, 2008), when the treatment was revealed as one of copper diffusion into otherwise lightly-colored plagioclase. This was confirmed by laboratory experiments which replicated the treatment (Emmett & Douthit, 2009).

Still, the question remained. Was there a genuine red feldspar mine in Tibet? If so, how would one separate such stones from the treated material? This question challenged the gemological community, resulting in several expeditions to the alleged Tibetan localities for sample collection and subsequent testing.

Figure 1. R.W. Hughes collecting red andesine at Zha Lin (Tibet), 29 September 2010. (Photo: Brendan Laurs)

Figure 2. Copper-bearing red collected by Abduriyim from Yu Lin Gu and view into the valley. (Photos: Ahmadjan Abduriyim)

The first of these forays was in 2008 to Bainang, southeast of Shigatse. A group led by Ahmadjan Abduriyim collected numerous samples and found the deposit to be credible. However, two subsequent visits (to two widely separated deposits, one of which was adjacent to Bainang) suggested copper-bearing andesine occurrences in Tibet were being "salted" (Fontaine et al., 2010; Wang et al., 2010).

Finally, in September 2010, yet another expedition visited Tibet, this time collecting specimens at Zha Lin and Yu Lin Gu (a valley adjacent to Bainang; see Figures 1–2) and confirmed the natural occurrence of copper-bearing andesine (Abduriyim, 2009; Abduriyim et al., 2011a–b; Hughes, 2010).

What follows is a result of the testing to date.

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Figure 3. Map of Tibet showing the location of the Bainang/Zha Lin/Yu Lin Gu andesine mines southeast of Shigatse, along with the Gyaca locality visited by Adolf Peretti in 2009. (Map: R.W. Hughes)

Figure 4. Author Detlef Günther analyzing fluid inclusions with a 193 nm ArF excimer ablation system coupled to an ICP-MS for the elemental analyses.

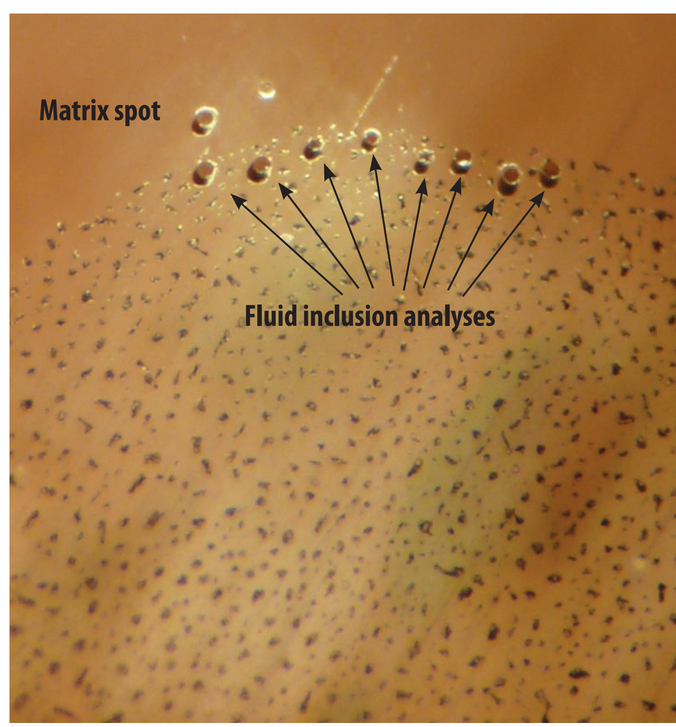
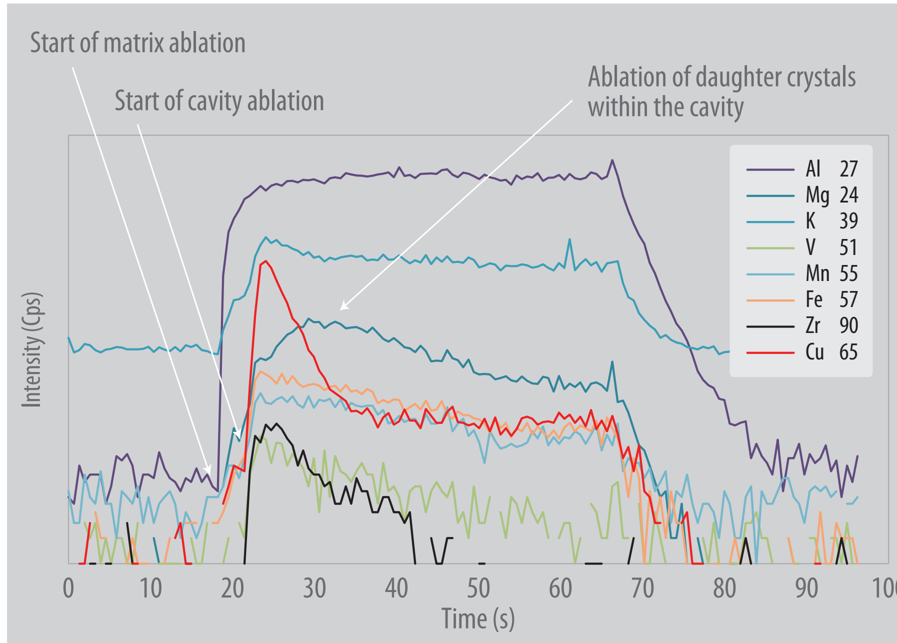


Figure 5. The fluid inclusion trail that was measured in a sample of Tibetan andesine purchased by Adolf Peretti in Gyaca and analysed by Detlef Günther.

Figure 7. A summary of transient signals for the ablation into a multiphase fluid inclusion. The Al signal intensity represents the matrix of the andesine. The dashed elements Cu, Zr and K are indicators for the fluid or vapor phase of the fluid inclusion. The transient signals of Fe, Mn, and Co represent the ablation of the solid crystals contained in the inclusion. It can be seen that the signals of these elements increase more slowly as the liquid or vapor phase containing elements, which is due to the different ablation process. The different elements (e.g. Fe, Mn) indicate that the fluid contained different elements at high concentration, which are preserved as crystals in the inclusion.



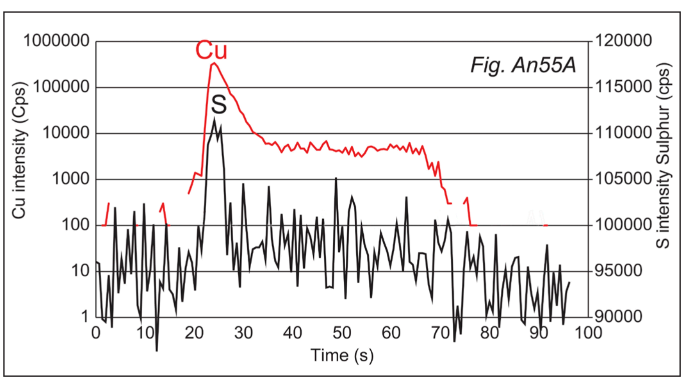


Figure 6. The transient signal of copper and sulfur from the fluid inclusions in Figure 5 indicates that these two elements are well correlated. The detection of sulfur is most interesting and its concentration must be very high, since the overall sensitivity of sulfur in ICP-MS is low in comparison to other elements *(Guillong et al., 2008).*

A Whiff of Smoke

Following this last field visit, specimens were subjected to a battery of sophisticated tests. The breakthrough occurred with the discovery of a new trace element, silver (Ag), combined with copper isotope measurements using a state of the art femtosecond laser ablation-MC-ICP-MS instrument on samples from AP, RWH and AA (see also Abduriyim et al., 2011).

These analyses were further cross-checked by radiogenic argon measurements, crystal structure analyses, and by an extensive suite of further tests including fluid inclusion analyses and a detailed SEM study on surface particles (Peretti et al., 2011). Silver concentrations were exclusively found in natural andesine from Tibet and not in diffusion-treated samples.

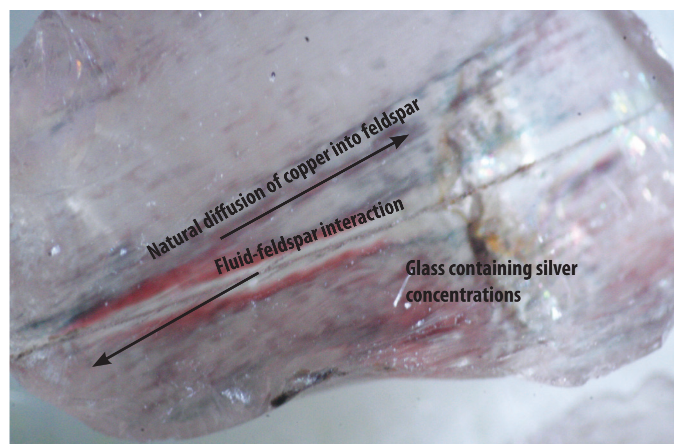


Figure 8. This copper-bearing andesine from Yu Lin Gu (Tibet) shows an isolated color zone, with red and green bands associated with a fluid inclusion trail. Red stripes are found at a 30° angle from the fluid inclusion trail. Copper naturally diffused into these zones, directly emerging from the fluid inclusion trail. The fluid inclusion trails emerged from a glass-like substance at the surface of the sample. Fluid inclusions and the color-zoning in the stone formed after the formation of the feldspar itself and is clearly linked to an entry point containing glass-like materials and a hydrothermal alteration event. Sample hand-collected by RWH.

Smoke Turns to Fire

The final proof came with the analysis of fluid inclusions. In 2009, AP visited an alleged andesine deposit in Gyaca County, east of Lhasa. While there, he purchased 2 kg of rough andesine, as well as hand collecting some specimens. Later, after analyzing a specimen from RWH, he realized that fluid inclusions might hold the key. Out of the 2 kg, he found 50 stones likely to have fluid inclusions. These were polished and just three pieces were found with fluid inclusions. Two were analyzed, both

Figure 9. Copper-bearing andesine such as this 25.86-ct stone is sold around the world as Tibetan. It is likely that most of this material is diffusion treated.

The Question of Dichroism

It has been suggested that Oregon sunstone can be separated from Chinese stones by dichroism, with only Oregon stones showing pronounced red/green dichroism. Our investigations have shown that extreme red/green pleochroism is not an exclusive property of Oregon sunstone, but is also found in some types of Tibetan andesine (see Figures 10–11). Although dichroism is generally weak in the Tibetan material, some Tibetan stones have exhibited strong dichroism.

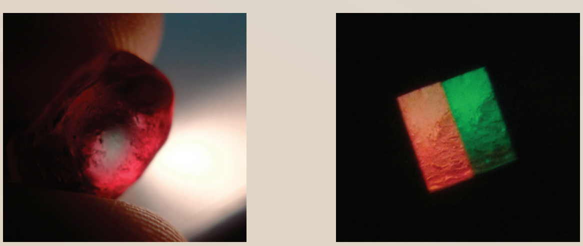


Figure 10. This rough red andesine (left) was collected in Tibet by RWH during the 2010 expedition and loaned to GRS. A green core was visible in one direction and when viewed with a dichroscope, a strong dichroism was detected (right). GRS- Ref-9ct.

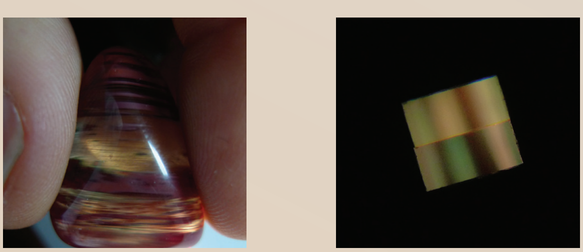
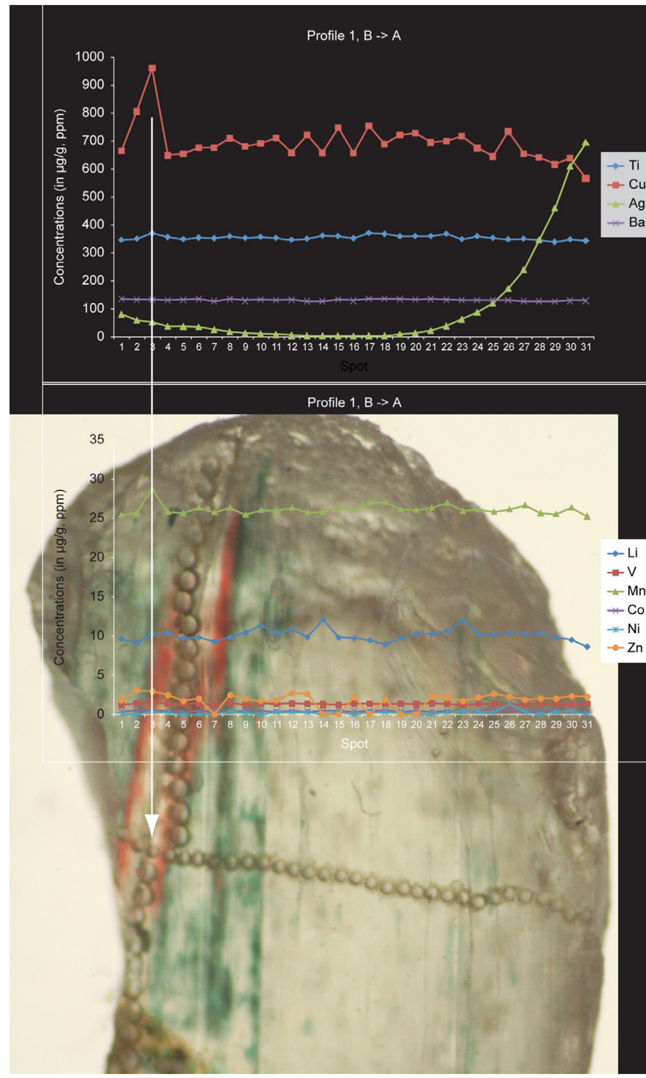


Figure 11. Tibetan copper-bearing andesine with stripes of alternating green, red and light yellow body color from the GRS collection. Dichroscope inspection in one direction revealed that every color band had a different dichroic effect, ranging from almost none, weak to medium (from orange to green). GRS-REF9620-41ct.

Figure 12. Concentration profile across an upper Yu Lin Gu copper-bearing andesine perpendicular to a fluid inclusion trail. Part of the lower left corner was taken off and used for further argon and copper-isotope testing. The two chemical profiles show a pronounced increase of Cu in the area of the fluid inclusions, but an increase in the Ag concentration towards the rim of the natural surface of the crystal. Sample hand-collected by RWH.



hand collected. These tiny pockets trapped in the andesine during formation were analyzed for "chemical fingerprints." The fingerprints revealed the presence of sulfur (S) and copper (Cu) in the vapor/liquid phases and the presence of daughter minerals composed of iron (Fe), manganese (Mn) and cobalt (Co) (Figures 5–6) (Peretti et al., 2011). At the same time, the other features were remarkably similar to stones collected in 2010 by the expedition to Zha Lin and Yu Lin Gu.

Traces of uranium (U) and Light Rare Earth Elements (LREE), including La, Ce, Pr, Nd, Sm and Eu were also found in the fluid inclusion compositions (the presence of U was actually predicted by the GIA's John Koivula after observing green fluorescence from surface residues; pers. com. January 2011).

Opening the Chinese Box – A Geologic Model for Tibetan Andesine

For the past several years, gemologists have struggled with the question of Tibetan andesine. No less than four separate expeditions have brought seeming answers but—like a Chinese box—as one is opened, yet another appears.

Much speculation is related to the lack of time on site. Outsiders face not just political restrictions, but an immense land of low population density and elevations of 4000–5000 m or greater. *The moon is more hospitable*. That said, some have braved the extreme conditions and detailed the geology.

Studying the geologic evidence and specimens collected by the expeditions, there appear to be areas that could host andesine deposits:

Tibet andesine is likely at least 35 (±3.7) million years old (Peretti et al., 2011). Andesine of Zha Lin must have seen a metasomatic-hydrothermal event after its first formation. Argon data shows a large andesine age range (approx. 3–35 million years or more). If this age spread is natural and unrelated to artificial diffusion treatment, it needs to be explained by geologic events. Furthermore, the evidence indicates that copper diffused into the andesine through a sulphur-rich fluid, while silver diffusion occurred only locally (mostly in samples from Yu Lin Gu); we believe the latter was associated with a potassium-rich glass. It does not necessarily follow the copper-diffusion pattern in the andesine samples.

Hypothetically Speaking

While this account includes a number of assumptions, it is backed up by fieldwork and lab data. We speculate that andesine formed as phenocrysts in andesite rocks by a first and older volcanic event. These rocks were intruded by potassic volcanic rocks some 30–40 million years later.

During the latter intrusion, the older andesine phenocrysts were assimilated and subjected to metasomatism. It was probably in this phase that diffusion of silver from a potassic-rich melt into the andesine occurred (approx. 3–4 million years ago). Copper-diffusion appears to have been controlled by sulphur-rich fluids that were decoupled from the glass. The potassic volcanic melts may have picked up copper and silver as well as other elements such as uranium from ore deposits on their path through the Indian crust. This provided the ingredients for a natural diffusion process involving copper through a hydrothermal overprint of andesine phenocrysts. During its complex life span, the Tibetan andesine lost argon, resetting some of these geologic clocks to younger ages (Peretti, 2011).

Thinking Inside the Box

But what of that Chinese box? During discussions of the scenarios for Ag-bearing andesines at Yu Lin Gu, one of the authors (AP) revisited a paper on Tibetan geology (Ding et al., 2003). In doing so, he remembered a conversation with a Tibetan miner years before. The man said he was unsure of the locality name, but it was something like "Jedu," and pointed to a place on a map.

Recently, Peretti pulled out the map the man had marked so many years before and compared it to the geological map in the geological paper. At that location was a place called Wenbu, and the rock types matched exactly the formation scenario sketched above. Excitedly, he called RH to give him the news. Hughes googled "Wenbu" and told Adi: "You're not going to believe this. Wenbu is in Nyima County." *Huh?* Hughes continued: "Nyima was the name first mentioned years ago as the source of the Tibetan andesine."

Thus as we opened one box, yet another appeared.

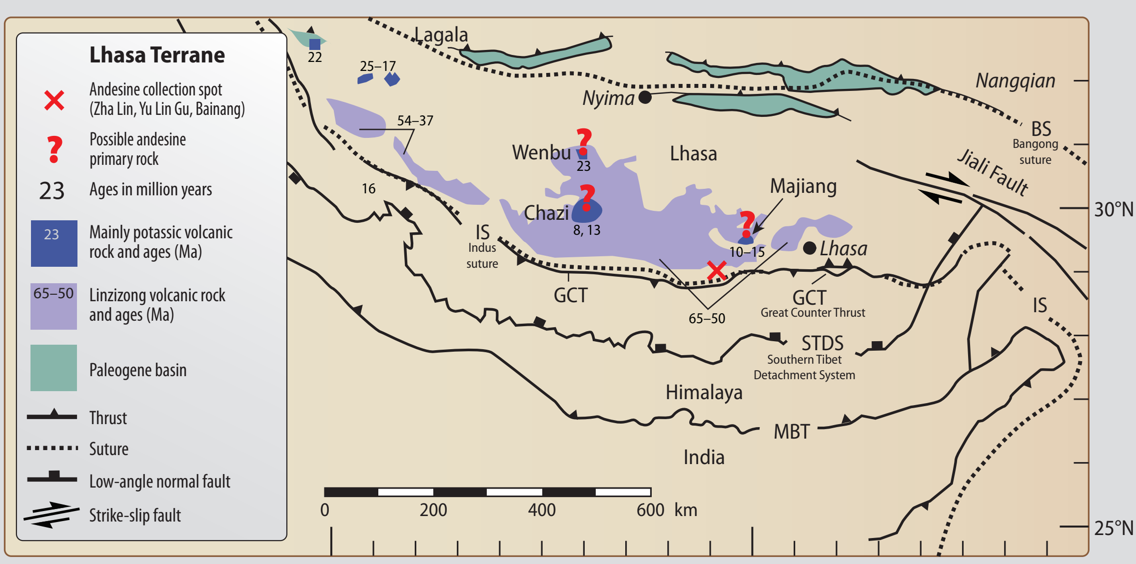


Figure 13. Geological map of Tibet showing possible andesine source rocks. (Map: Billie Hughes after Ding, 2003 and Peretti, 2011)

A Geological Model of Red Andesine Formation

Based on element distributions inside the andesine (Cu and Ag separation) and the results of the fluid inclusion analyses, it was possible to come one step closer to geological models that can explain the formation of andesine from Tibet. Previous and similar research (Audetat et al., 1998; Peretti, 2011) allows an interpretation of the geological process that led to the formation of red andesine in Tibet (e.g. sulfur and copper-rich vapor separation from silver-rich fluids due to specific geological events). Red Tibetan andesine is formed by a hydrothermal overprint of a volcanic andesine. The S- and Cu-rich fluids reacted with the feldspar and natural diffusion of copper occurred within certain crystallographic directions (Figures 5–7).

This hypothesis is based on the first and preliminary fluid inclusion study, which is currently not quantitative and needs further investigation. However, based on the published research (Audetat et al., 1998), it is now possible to isolate a group of natural copper-bearing Tibetan andesines from the new material (locality of Yu Lin Gu); these can be confirmed as authentic and not diffusion-treated.

Can Tibetan Andesine Now Be Certified?

Hand collection of samples in Tibet and subsequent testing strongly suggest there is a natural occurrence of red andesine in the vicinity of Yu Lin Gu/Zha Lin/Bainang. Silver has been found in traces from every collection spot to date. However, nothing seen by observers in Tibet would account for the large quantity of fine faceted red andesines that have appeared in world markets since 2002. Logic would thus dictate that any faceted red andesine of Chinese origin would be assumed to be treated unless proven otherwise.

This begs the question. Is it possible to separate natural Tibetan andesines from treated stones? While much work remains to be done, studies to date show that such separations are possible, albeit only using extremely sophisticated and sometimes destructive methods.

Certainly the presence of silver as a trace element in andesine is an indication of natural origin. The silver distribution patterns shown by Peretti et al (2011, Figs. An42A and An43A) in Tibetan andesine were experimentally reproduced by Lu et al. (2011). They concluded that it is theoretically possible that such diffusion patterns could be formed during a diffusion process under natural geological conditions.

To date silver has not been found in any known treated andesines. But this does not preclude treaters adding silver to fool gemologists and recent experiments have shown that this is possible (Abduriyim et al., 2011b; Lu et al., 2011). Stones obtained before the release of information about silver in andesine can still be certified, but future tests must take into consideration the possibility of the addition of silver during treatment.

Unless more destructive testing methods can be used, the origins of the red, gem-quality andesines widely available on the market will remain unknown. Thus, for the time being, it is prudent to consider any faceted red Chinese andesine to be treated or undeterminable unless documented as natural by a laboratory report based on sophisticated tests such as those detailed above.

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