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Argon Isotope Studies of Andesine Collected During the 2010 Expedition to Tibet

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Abstract

Argon isotope studies of samples returned from the 2010 expedition to Tibet showed that the tested andesines from Yu Lin Gu and Zha Lin contained high concentrations of radiogenic argon and indicated that they had not been subjected to a copper diffusion process.

INTRODUCTION

Previously, Rossman (2011) reported the results of an examination of the argon isotopic composition of red andesine obtained by various sources. The underlying principle for these studies is that the minor potassium content of these feldspars consists, in part, of the isotope ^{40}K, which slowly decays to ^{40}Ar over geologic time. As long as the feldspar remains in a magmatic system, the temperatures are so high that the radiogenic argon will quickly diffuse out of the feldspar. Once the crystal cools to near-ambient temperatures, however, this radiogenic argon will be retained within the crystal and its concentration will build over geologic time.

Previous studies showed that the samples of commercial red andesine from various sources were greatly depleted in radiogenic argon compared to the pale-yellow andesine from Inner Mongolia that is now acknowledged to be the starting material of the copper diffusion process. Likewise, green andesine and andesine of mixed green and red colors also were depleted in radiogenic argon. A sample collected during Abduriyim's 2008 expedition to the Nai Sa–Bainang mine was also tested. It gave a much lower $^{40}Ar/^{36}Ar$ ratio than untreated pale yellow andesine from Inner Mongolia, but was somewhat elevated above the values found in most other red andesines from sources identified as Democratic Republic of the Congo, China, and Tibet. This observation, coupled with the presence of glassy, copper-enriched silicate material at the sample's surface and small pieces of copper compounds attached to the surface of the sample, led to the suspicion that those Tibetan samples had been treated by high-temperature copper diffusion, in spite of the observations of Abduriyim (2009a,b), who investigated the Bainang mine, and concluded that the deposit was authentic.

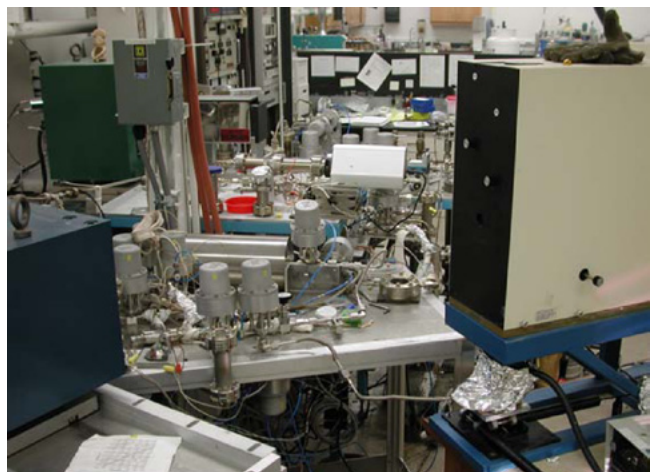

Figure 1. Laser heating system (box on the right) and gas purification system (on table) for argon analysis. Photo by George R. Rossman.

Figure 2. Platinum capsule containing about 20 mg of crushed andesine for argon isotope analysis. Photo by George R. Rossman.

The previous studies were mostly conducted by laser heating (Fig. 1) crushed samples contained in platinum capsules (Fig. 2) and monitoring the $^{40}Ar/^{36}Ar$ ratio evolved from the sample. The released gases were first purified and then sent to a mass spectrometer (Fig. 3).

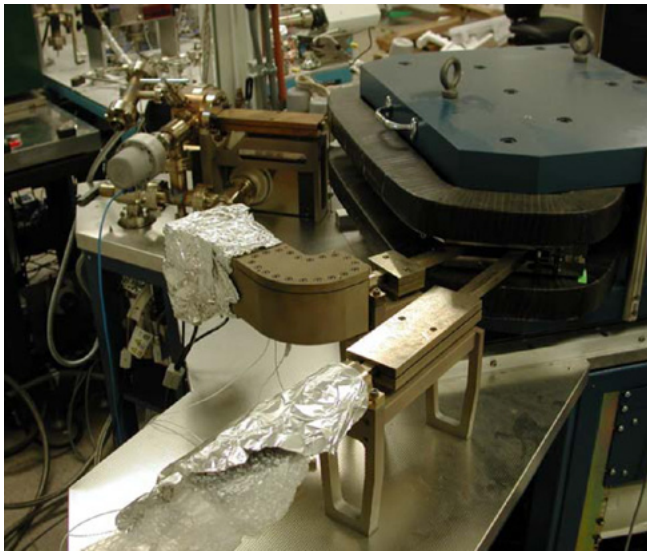

Figure 3. Mass spectrometer for Ar isotope analysis. Photo by George R. Rossman.

These measurements were not designed to age-date the sample, but rather to see if there was a lack of radiogenic argon released at temperatures somewhat less than or equal to the temperatures that may have been used to diffuse copper into the andesine.

Studies of the samples returned from the 2010 expedition to Tibet

A new round of argon isotopic measurements was conducted on samples obtained during Abduriyim's 2010 expedition. These studies were conducted by a slightly different method. In these experiments, larger quantities (~200 mg) of crushed samples were wrapped in aluminum foil (Fig. 4) and thoroughly out-gassed under high-vacuum before they were dropped into a tantalum furnace (Fig 5) that could heat the samples to temperatures above the melting point of andesine. The released gases were then purified and analyzed in a fashion comparable to that used in the previous analyses.

Figure 4. Sample wrapped in aluminum foil for argon extraction in the furnace. Photo by George R. Rossman.

The results from the samples collected in 2010 and of other samples for comparison, are shown in Table 1 and Figure 6. It is important to mention that none of the samples tested for argon isotopes showed evidence of the glassy surface residues and fused bits of feldspar commonly found in treated rough and on the original sample from the 2008 Bainang expedition.

Samples were prepared by first subjecting them to ultrasonic cleaning in dimineralized water for 15 minutes, followed by examination under a microscope for surface residues of soil and additional ultrasonification if such residues were found. After drying, the samples were coarsely crushed in a jaw

pliers. Pieces free of any natural surface were separated by tweezers under a low-power microscope until about 250 mg of pieces were obtained. These pieces were then cleaned under 95% ethanol in an ultrasonic cleaner to remove adhering fine-grained material. After drying and weighing, they were wrapped in an approximately 4 cm square of aluminum foil. After loading into the instrument, they were evacuated overnight to remove air from the system at a pressure of about 10^{-6} torr. During the analysis run, each sample was individually dropped into the heated region of the furnace and brought up to temperature in steps as the isotopic composition of the evolved gases was measured.

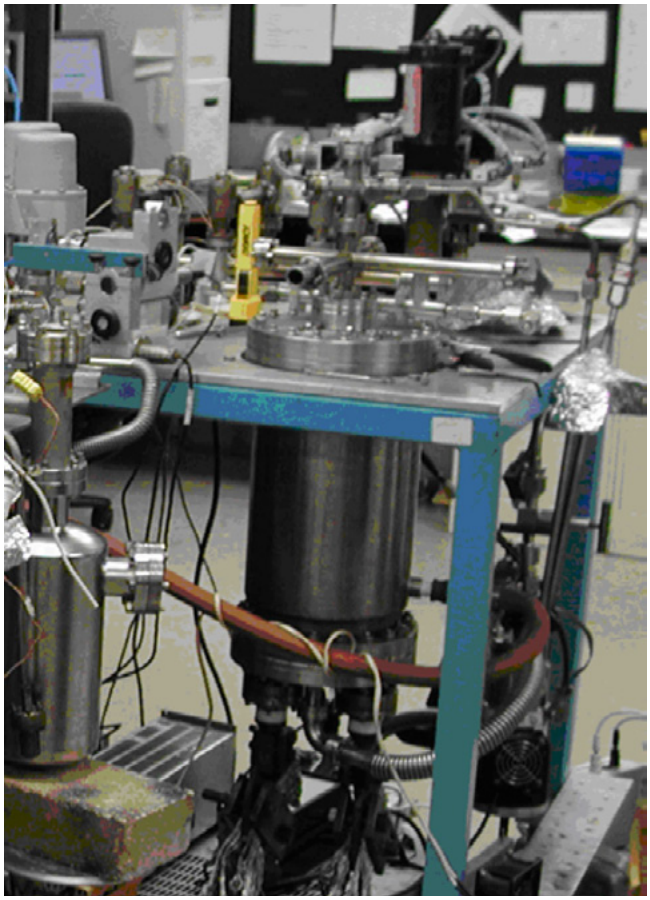

Figure 5. Furnace used to extract argon isotopes. Photo by George R. Rossman.

The first sample examined was a piece of pale yellow Inner Mongolian rough donated by Litto Gems in 2010. It had a high $^{40}Ar/^{36}Ar$ ratio, comparable to the results obtained in 2008 from a piece of yellow rough obtained from Andegem. In fact, it contained so much ^{40}Ar that it saturated the detection system, which was initially set to an overly high sensitivity for these measurements. However, a rough red andesine from Andegem extracted in the tantalum furnace showed a low ratio, consistent with the author's previous isotopic measurements from the same sample using the laser-heating method. The conclusion remains that the faceted red stone was diffusion treated at high temperatures.

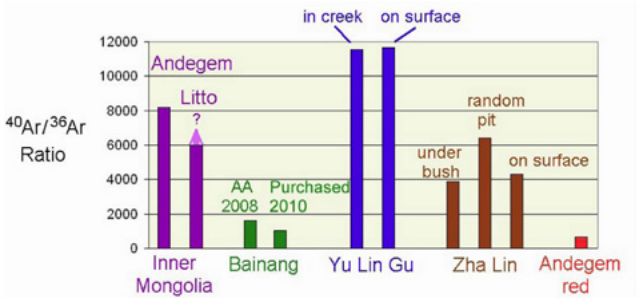

Figure 6. Results of argon extraction experiments on samples collected during the 2010 expedition, pale-yellow andesine from Inner Mongolia, a sample from the 2008 expedition to Bainang, and a faceted red gemstone.

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. These samples had radiogenic ratios far below the Inner Mongolian rough, but slightly elevated above the values from the faceted red andesine gemstones of the current and previous measurements. They also gave argon ratios much lower than those from the other two localities sampled in the 2010 expedition.

The two samples from Yu Lin Gu showed very high argon ratios. They are the highest two ratios obtained to date. The three stones from Zha Lin also had elevated argon ratios comparable to those obtained from several of the pale yellow Inner Mongolian andesines examined in 2008. The samples measured included a sample obtained on the surface and samples obtained from pits excavated during the 2010 expedition.

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 nearby Yu Lin Gu and Zha Lin.

Additional Studies on Argon Retention in Andesine

Because we noticed that several of the andesines studied in the first round of argon extraction experiments had $^{40}Ar/^{36}Ar$ ratios somewhat above the value of argon in air (a value that would be expected in these experiments if all the radiogenic argon had been removed), a few experiments were conducted to gain information about the retention of argon in andesine. In the first experiment, two samples of pale yellow rough from Inner Mongolia obtained from Andegem (GRR 2651) were heated for different lengths of time at different temperatures and then subjected to argon extraction in the tantalum furnace. The first, heated at 1200°C for 30 days, gave a low value of 302 and the second, heated at 1300°C for 48 hours, gave a value of 356, possibly indicating less than complete extraction of radiogenic argon. The unheated sample gave a ratio of 2751.

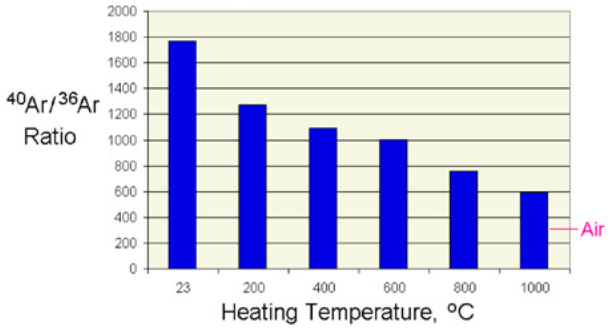

Figure 7. Argon ratios obtained from aliquots of andesine heated for 2 hours at the indicated temperature and extracted by the laser-heating method showing that some radiogenic argon remains even after heating at 1000°C.

An additional experiment to examine argon retention had been conducted by the laser-heating method. It involved heating aliquots of pale yellow andesine rough (GRR 2651) for two hours at 200, 400, 600, 800, and 1000°C. The results in Figure 7 show that even the 1000°C heating did not extract all the radiogenic argon. Likewise, an experiment showed that if a sample (GRR 2635) previously heated by the laser used in the laser-extraction method was reheated, the amount of argon released was much smaller than the argon released during the original heating, but the $^{40}Ar/^{36}Ar$ ratio was much higher (Fig. 8). Besides illustrating that radiogenic argon is quite retentive in andesine, these results all raise the possibility that that actual process used to diffuse copper into andesine may occur at lower temperatures than those used in the experiments by Emmett and Douthit (2009).

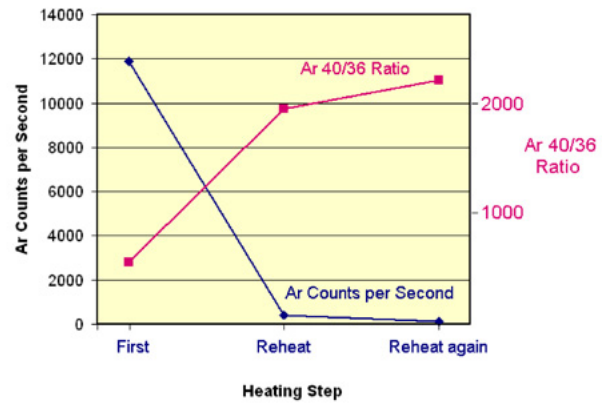

Figure 8. Reheating experiment of a red andesine rough, GRR 2635, obtained from a Bangkok gem dealer in 2008.

Residual Questions

The feldspars used in this study were devoid of the glass and fused material seen on the surface of many rough red andesines in the previous study, but most did not appear suitable for gem use. Figures 9-11 show cleavage fragments of some of the andesines used for the second round of argon studies reported herein. The particular studies reported in this article do not address some fundamental issues: Do naturally occurring, gem-quality copper-containing feldspars occur at these localities? Are the feldspar samples analyzed from this region representative of common feldspars at these localities? Are andesines from these localities subjected to copper diffusion? Are copper-diffused feldspars from Inner Mongolia mixed in with naturally occurring copper-containing feldspars at these localities?

ACKNOWLEDGMENTS

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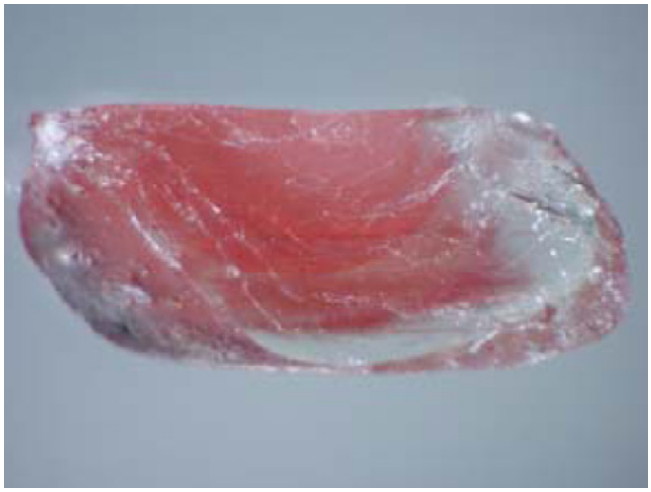

Figure 9. Andesine purchased from a villager, said to be from Bainang, Tibet. Field of view: 1.0 cm. Photo by George R. Rossman.

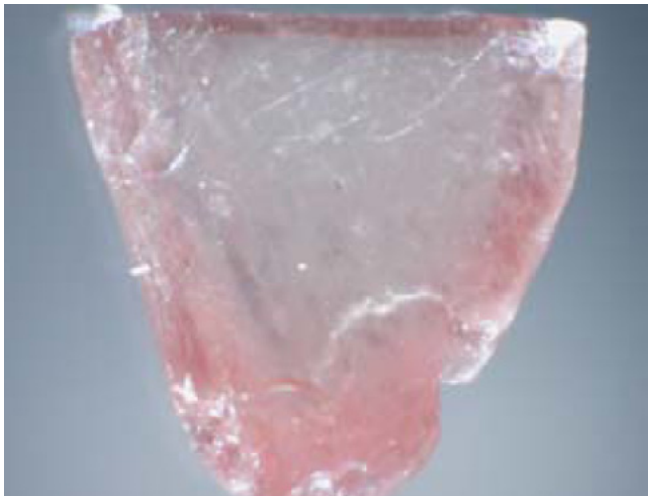

Figure 10. Andesine from the creek at Yu Lin Gu, Tibet. Field of view: 7.0 mm. Photo by George R. Rossman.

Figure 11. Andesine from a 1.2 m deep pit at Zha Lin, Tibet. Field of view: 1.0 cm. Photo by George R. Rossman.

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Note: This report accompanies the following article: Abduriyim A., McClure S.F., Rossman G.R., Leelawatanasuk T., Hughes R.W., Laurs B.M., Lu R., Isatelle F., Scarratt K., Dubinsky E.V., Douthit T.R., Emmett J.L. (2011) Research on gem feldspar from the Shigatse region of Tibet, *Gems & Gemology*, Vol. 47, No. 2, pp. 167–180.