GIA NEWS FROM RESEARCH

Silver Incorporation in Inner Mongolian and Tibetan Andesine

Ren Lu, Emily V. Dubinsky, Troy R. Douthit, and John L. Emmett

Abstract

Silver incorporation in plagioclase feldspars have been studied on a set of Inner Mongolian and Tibetan samples. Silver distribution profiles in laboratory diffused Inner Mongolian samples and a set of silver-bearing Tibetan samples were analyzed by laser ablation–inductively coupled plasma mass spectrometry (LA-ICP-MS). Diffusion properties and their implication to incorporation temperature and time scale in these materials were discussed.

INTRODUCTION

Recently, silver has been detected from the plagioclase specimens collected in the alluvial deposit near the Yu Lin Gu area in Tibet (Ahmadjan Abduriyim, personal communication). In light of the proof that copper may be incorporated in plagioclase in nature (Hofmeister and Rossman, 1985) or in the laboratory (Emmett and Douthit, 2009)—and that sorting this question out can be quite difficult after multiple reports have circulated through the trade—it is worthwhile to consider the natural and treatment-induced presence of other ions in plagioclase. Consequently, a set of diffusion experiments has been designed and conducted to facilitate better understanding of silver incorporation in these materials.

EXPERIMENTAL

Sample characterization and preparation.

Two sets of feldspar materials were studied. One set consisted of Inner Mongolian materials used for the silver diffusion study, and the other set contained Ag-bearing Tibetan materials from the Yu Ling Gu deposit. Both sets were provided by Dr. Abduriyim, who obtained them during his field trips to Tibet in 2008 and 2010. Detailed geological and gemological information are fully discussed by Abduriyim (2009) and McClure (2009).

The Tibetan silver-bearing plagioclase materials showed orange-red, bluish gray coloration with extensive dislocation networks and red patches (figure 1). The rough stones were cut from the center portion and doubly polished and cleaned for chemical analysis. A colorless rim about 200–300 microns thick was present in these samples.

The natural plagioclase material from the Inner Mongolian deposit showed a pale yellow color with various amount of snowflake-like inclusions, fine particulate clouds, and some growth tubes (figure 2). These materials were sliced into about 3–3.5 mm thick wafers. Two sets of samples of 10 pieces in each group were diffusion treated. Samples were packed in ZrO_2 powder doped with 1% metallic silver and treated at 1170°C for 31 hours and 180 hours, respectively. To facilitate efficient diffusion, a treatment temperature near 90% of solidus temperature of the material was chosen.

The methodology for our silver diffusion experiment was

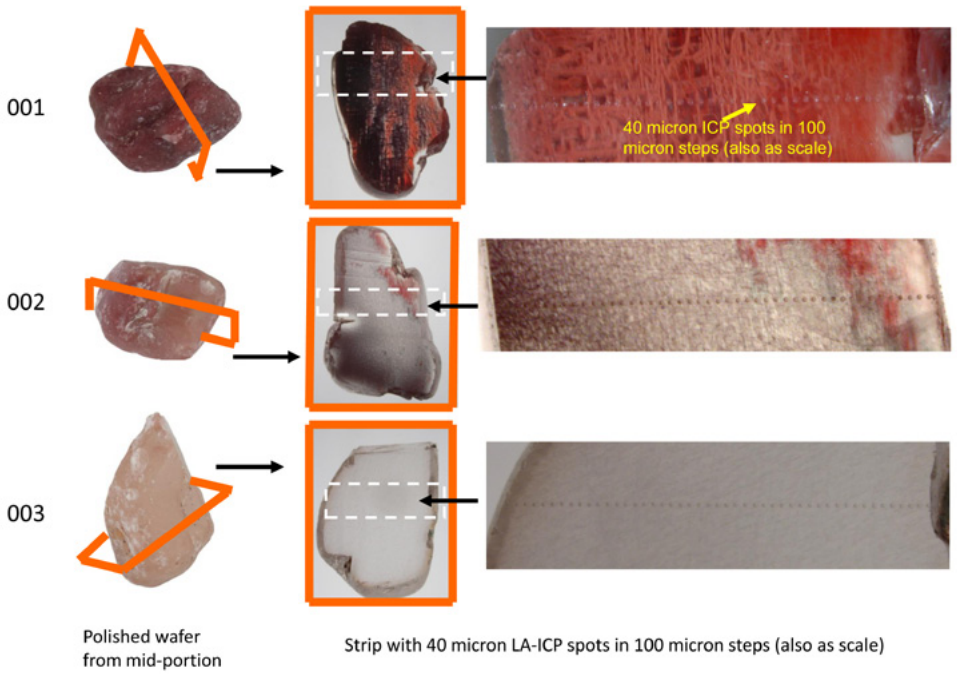


Figure 1. Silver-bearing plagioclase samples from Yu Lin Gu, Tibet, showed orange-red and bluish gray coloration and series of dislocation networks. A polished wafer was prepared from the middle area of each sample as indicated and LA-ICP-MS spot analyses were performed at 100-micron steps across the wafer surface. Photos by Jian Xin (Jae) Liao and Ren Lu.

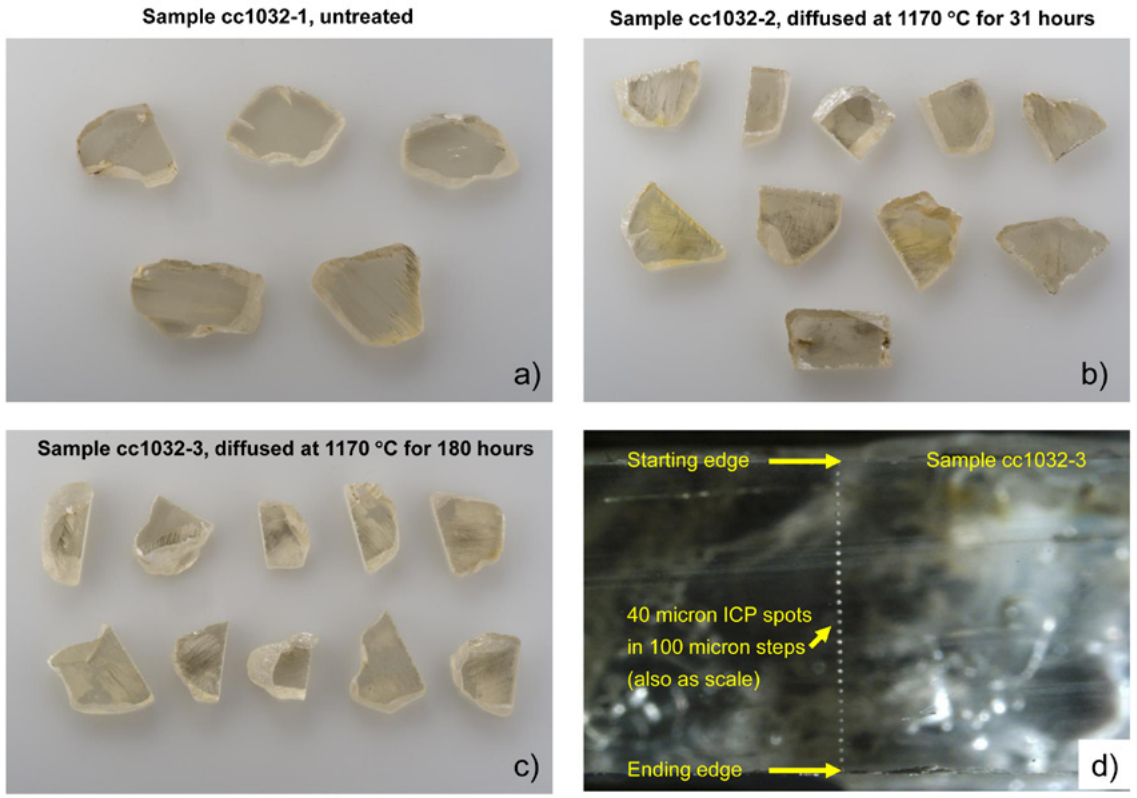


Figure 2. Natural plagioclase samples from Inner Mongolia were pale yellow prior to diffusion treatment (a). The color did not change noticeably after silver diffusion experiments conducted at 1170°C for 31 hours (b) and 180 hours (c). Diffused samples were cut in half and polished, and LA-ICP-MS spot analyses were performed at 100-micron steps across the wafer surface (d). Photos by Jian Xin (Jae) Liao and Ren Lu.

similar to that applied in a set of copper diffusion experiments using materials from various localities, including similar Inner Mongolian samples (Emmett and Douthit, 2009). A detailed discussion was given on methodologies including diffusion temperature and duration, and chemical environment in which diffusion experiments were conducted (Emmett and Douthit, 2009).

Three diffused Inner Mongolian samples from each treatment condition were further cut in halves and the cut edges were polished and cleaned for chemical analysis. One untreated natural sample was similarly cut and polished for comparison.

LA-ICP-MS ANALYSIS

Element concentration profiles were analyzed for both the Inner Mongolian and Tibetan materials across the polished surfaces by LA-ICP-MS. Analyses were collected using a Thermo Fisher X-Series II ICP mass spectrometer equipped with a UP213, a fifth harmonic laser at 213 nm, from Electro Scientific Industries. Concentration profiles across the sample were established with 40-micron laser spots in 100-micron intervals. The ablation conditions were: 7 Hz repeat rate, 40 second dwell time, and ~9 J/cm2 laser fluence. The NIST 610 and 612 glass standards were applied as internal reference for element concentration.

RESULTS

Chemical analysis indicated compositions near the midpoint in the plagioclase series between albite ($NaAlSi_3O_8$) and anorthite ($CaAl_2Si_2O_8$), with only a minor orthoclase ($KAlSi_3O_8$) component: $(Na_{0.54\text{-}0.42}Ca_{0.43\text{-}0.55}K_{0.03})(Al_{1.65\text{-}1.87}Si_{2.34\text{-}2.12}Fe_{0.01})O_8$ for Inner Mongolian and $(Na_{0.51\text{-}0.47}Ca_{0.46\text{-}0.50}K_{0.03})(Al_{1.91\text{-}2.03}Si_{2.08\text{-}1.96}Fe_{0.01})O_8$ for Tibetan materials.

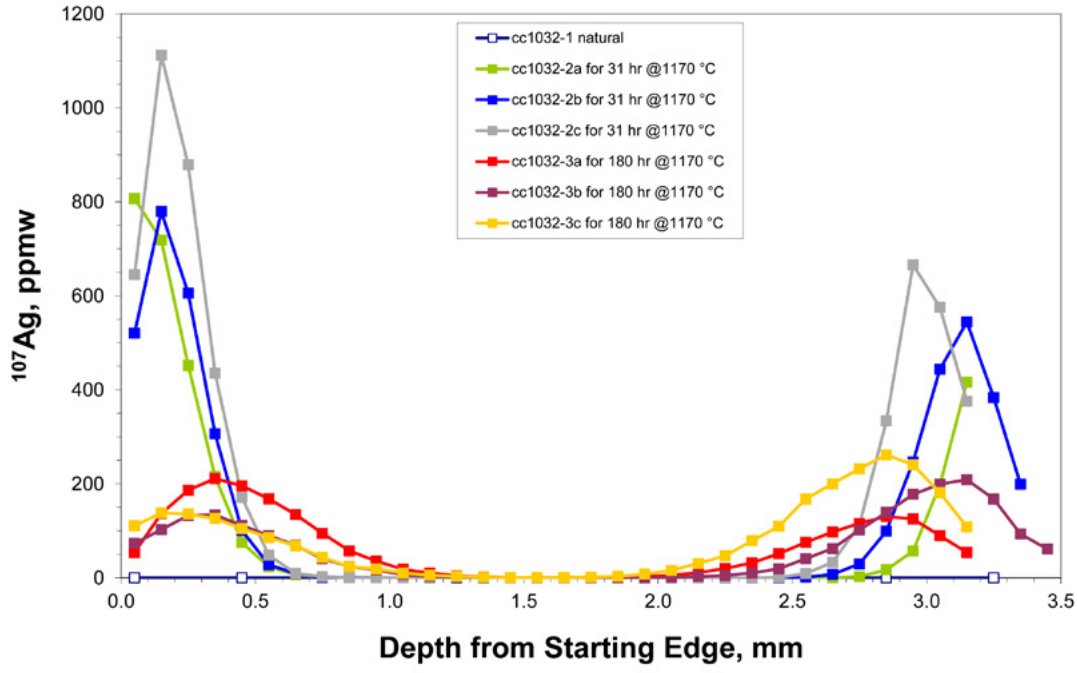


Figure 3. Shown are silver concentration profiles for diffusion-treated Inner Mongolian plagioclase samples. Samples treated for 31 hours showed higher overall silver concentrations than those treated for 180 hours. A lower silver concentration immediately adjacent to the sample surface, as compared with several hundred microns below it, suggests that silver diffused outward during the experimental runs, likely because the zirconia carrier was depleted of silver due to vaporization.

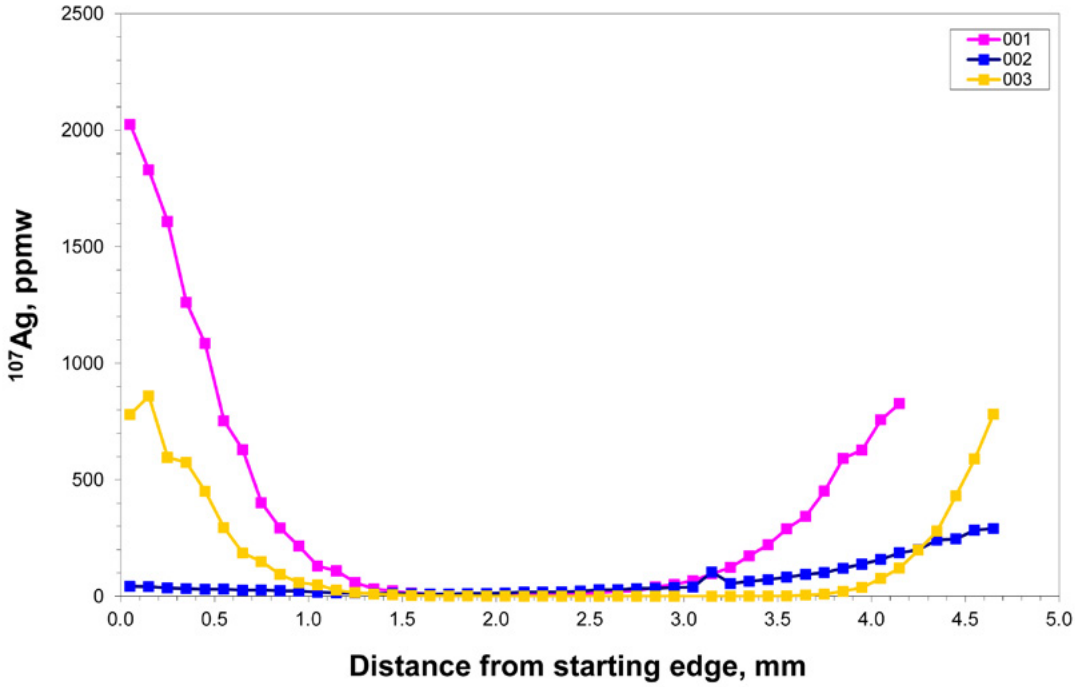


Figure 4. The silver concentration profiles for samples from Yu Lin Gu, Tibet, showed smooth decreases inward from the rim.

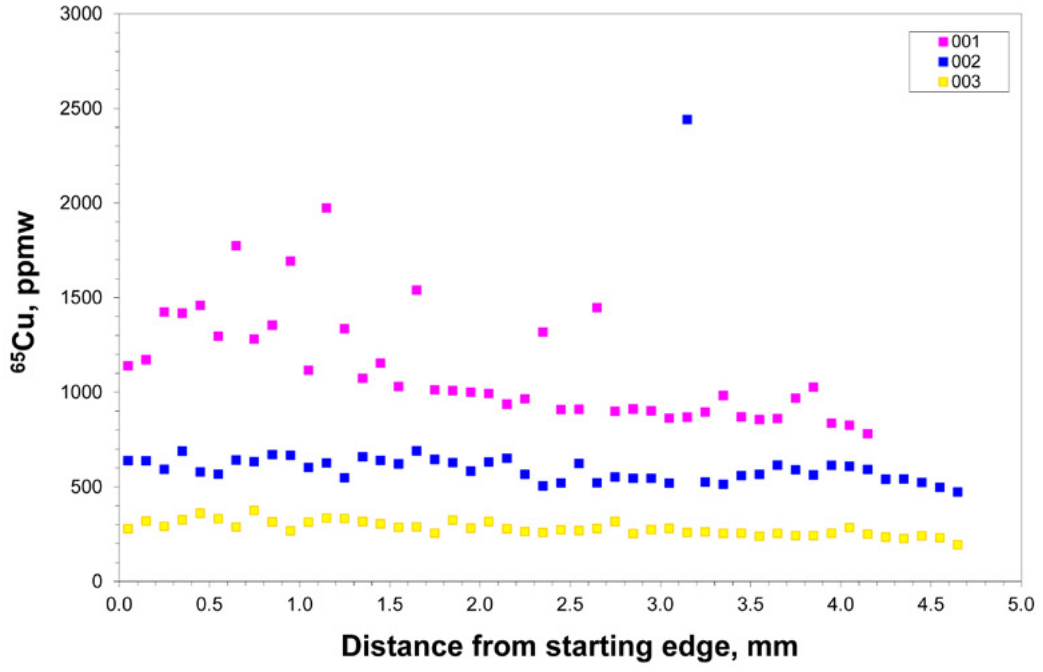


Figure 5. The copper concentration profiles for samples from Yu Lin Gu showed even distribution for slightly red materials and scattered distribution for strongly colored red materials.

Natural, untreated Inner Mongolian samples showed no detectable amount (<1 ppmw) of silver (figure 1, sample cc1032-1). Treated samples (cc1032-2, cc1032-3) showed pale yellow colors similar to those of untreated natural samples. Samples treated for 31 hours showed a maximum concentration of silver at ~800–1100 ppmw, detectable through a depth to 0.7 mm. Samples treated for a much longer duration of 180 hours exhibited a lower level of maximum concentration of silver at ~130–260 ppmw, detectable through a greater depth, to about 1.2 mm. A lower concentration was detected near the surface on samples treated for both durations, which reflects outward diffusion of silver during extended experimental duration as the supply of silver in the ZrO2 carrier is depleted by vaporization. These samples showed copper near the detection limit (<1 ppmw) or in trace amounts (<15 ppmw, see figure 3).

Silver was previously detected in materials obtained from the Yu Ling Gu area in Tibet by Dr. Abduriyim (personal communication). Silver concentration ranged from the detection limit (<1 ppmw) up to 2889 ppmw. However, the concentration determination is based on limited sampling with few data points, and therefore a spatial distribution of silver in these samples was not firmly established.

The current study attempted to provide a detailed concentration profile of silver so that its incorporation mechanism and efficiency can be assessed. Silver concentration ranged from ~300–2000 ppmw in the tested samples (figure 4). In comparison to silver-diffused samples from Inner Mongolia, an outward diffusion with lower concentration near sample boundaries was not clearly indicated.

Tibetan materials bear an appreciable amount of copper, ranging from ~250 to 600 ppmw in even distribution for slightly red materials to between ~800 and 1500 ppmw with large scatter in concentration for strongly red colored materials (figure 5). The variability observed for strongly colored material is possibly due to variation in internal microstructures. A Cu concentration between ~200 and 300 ppmw was previously observed by Fontaine et al. (2010) (sample group C and figure 6 therein) and between 268 and 1168 ppmw by Abduriyim (personal communication) in similar materials from Yu Ling Gu, Tibet.

Concentration profiles similar to that of silver were not observed for other elements in the Tibetan materials tested or in silver-diffused Inner Mongolian materials.

DISCUSSION

The origin of the pale yellow color in plagioclase has been attributed to trace amounts of Fe^{3+} in these materials (Hofmeister and Rossman, 1983). The red and green colors have been associated with the presence of copper as possibly Cu^{1+} or Cu^{0}, or both (Hofmeister and Rossman, 1985).

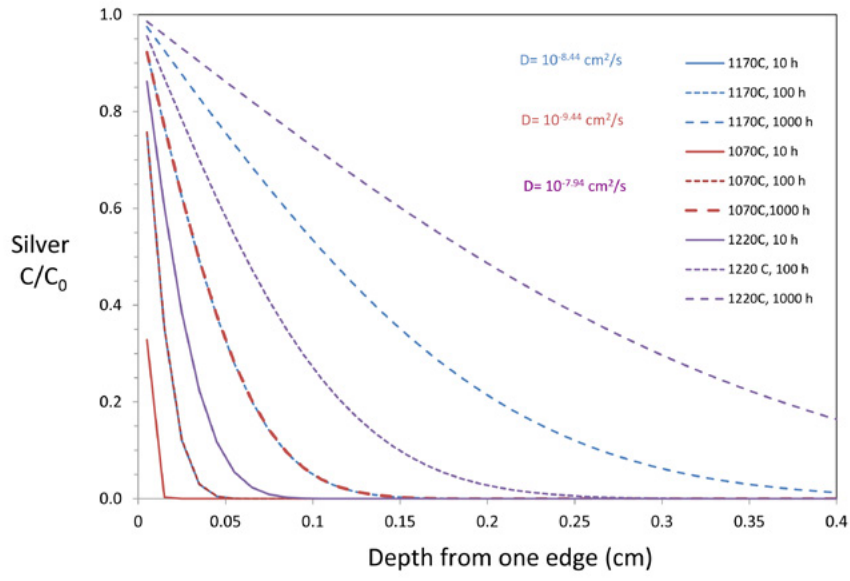
We would expect silver nanoparticles in plagioclase to produce a yellow coloration, as they do in glass (Weyl, 1951; Bamford, 1977). Yet silver-diffused Inner Mongolian samples showed virtually no change in color from the original pale yellow hues, which suggests that silver remains as an ion. Silver should diffuse in plagioclase as a silver ion—rather than an atom—because the host material is quite ionic. The same behavior is expected of copper. However, copper gets reduced to metal under similar conditions (probably by Fe^{2+}). The silver diffusion experiments were conducted in air, and it is likely that Ag remains as ions in the run products. The reduction of Ag to metal atoms—and thus the yellow coloration—will probably develop only during treatment at low oxygen partial pressures. Note that we have not run our silver diffusion experiments over a wide range of pO_2, as Emmett and Douthit (2009) did for their copper diffusion studies.

The observed diffusion profiles in the treated Inner Mongolian samples suggest that silver solubility in plagioclase is quite high. It is likely even higher than the diffusion profile of the 31-hour experiment suggests, 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 crucible was open to the air, and the vapor pressure of silver at 1170°C is approximately 0.12 torr (Paule and Mandel, 1991), so it distills out of the zirconia carrier as the experiment proceeds. As it is depleted, some the silver in the plagioclase

diffuses back down the concentration gradient out toward the surface. Thus, we do not see saturation solubility in our data.

It is interesting to note that the diffusion profiles observed in the 31- and 180-hour experiments are not characteristic of one-dimensional diffusion into a semi-infinite slab. The precise solution to the model requires a boundary condition of constant diffusant concentration (silver in this study) at the surface. Using an approximation of the diffusion coefficient (D) for the 1-D case ($x/(Dt)^{1/2}=2$) to model our data along the portion of the diffusion profile for the 31-hour experiment where silver concentration decreases with increasing depth, we calculate a silver diffusion coefficient (D_{Ag}) of 3.6 x 10^{-9} cm^2/s. For comparison, if we assume a silver solubility limit of approximately 1000–6000 ppmw and use the solution to the 1-D model to determine D_{Ag}, we calculate values in the range of 1–7 x 10^{-9} cm^2/s.

We compared our estimated D_{Ag} of 3.6 x 10^{-9} cm^2/s to previously reported values of D at the same homologous temperature (the temperature of a material expressed as a fraction of its solidus temperature using the Kelvin scale; 0.91–0.95 for this study) for other monovalent cations (namely, K^+ and Na^+) in plagioclase feldspar of similar compositions, which were approximately 1 x 10^{-11} and 1 x 10^{-9} cm^2/s, respectively, at 1170°C (Behrens et al. 1990; Giletti and Shanahan 1997). Even given the rather large error in our D_{Ag} calculations, it appears we can conclude that D_{Ag} is larger than D_K at the same homologous temperature. This behavior is expected, as Ag^+ (1.15 Å; or 0.95 Å as Ag^{2+}; Shannon 1976) is appreciably smaller than K^+ (1.38 Å) and should diffuse faster. But our estimate for D_{Ag} is roughly the same as that reported for D_{Na}. Given that silver and sodium have similar ionic radii in six-fold coordination (1.15 and 1.02 Å, respectively; Shannon 1976) and also considering that our approximation of D_{Ag} is likely accurate within no better than an order of magnitude, the similarity in approximations is not surprising.



Solution to one-dimensional diffusion into a semi-infinite slab for all x>0 and t>0 assuming constant surface doping:

$$C = C_0\left[1 - erf\left(\frac{x}{2\sqrt{Dt}}\right)\right]$$

t=time
x= distance from edge of slab
D= diffusion coefficient
C= concentration at all x>0
C_0= concentration at surface

Figure 6. Shown are solutions to the equation describing one-dimension diffusion into a semi-infinite slab for a series of temperatures and times. Note the overlap between certain time and temperature combinations, such as 100 hours at 1170°C and 1000 hours at 1070°C.

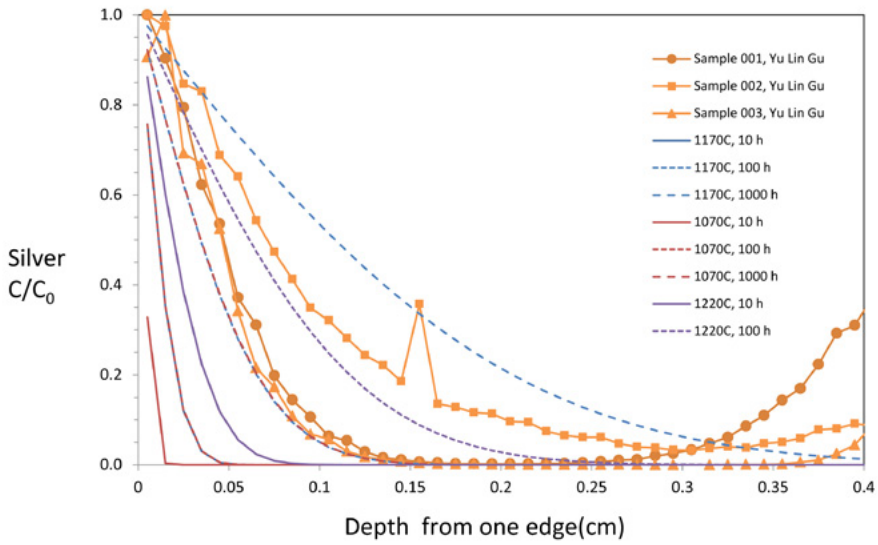


Figure 7. Plotted as normalized concentrations, assuming maximum silver concentration in a sample represents the solubility limit of the sample, the silver concentration profiles measured for the Yu Lin Gu andesine samples show curves similar to those calculated for one-dimensional diffusion.

The results of our experiments can be used to approximate the diffusion behavior of silver under a range of experimental conditions. We chose to model it as 1-D diffusion in a semi-infinite slab assuming constant surface doping for several different temperatures and durations. Data in the literature for other 1+ and 2+ cations in plagioclase report temperature dependences of logD of about one logarithmic unit per 100 degree temperature interval (Cherniak, 2010). Assuming similar temperature dependence for D_{Ag}, for example, we can estimate from our experimentally determined D_{Ag} (1170°C) that D_{Ag} (1220°C) is ~$10^{-7.94}$ cm^2/s and that D_{Ag} (1070°C) is ~$10^{-9.44}$ cm^2/s.

The assumption of constant surface doping is likely quite reasonable in many production-scale diffusion treatment processes. In the experiment we conducted (several samples packed in ~20 grams of ZrO_2) the surface-to-volume ratio is very high and thus the carrier was depleted rapidly; for a production batch (e.g., 10–20 kg of labradorite in a large amount of molten flux), the surface-to-volume ratio would be much lower, and thus the surface concentration of Ag would probably remain nearly constant. Furthermore, the vapor pressure of silver is strongly temperature dependent, and it is likely that a reduction of 100–200°C would nearly eliminate the vaporization loss from even from fairly small experiments.

The calculated diffusion profiles for three time intervals (10, 100, and 1000 hours) at three different experimental temperatures (1070, 1170, and 1220°C) are shown in figure 6. These curves show that for a given temperature, short diffusion times produce steep concentration gradients, whereas longer experimental runs result in shallower gradients. They also illustrate how the time required to produce a particular concentration gradient is impacted by temperature dependence of the diffusion coefficient. For example, note that the concentration profiles for 1000 hours at 1070°C and 100 hours at 1170°C overlap exactly with one another, as do the concentration profiles for 100 hours at 1070°C and 10 hours at 1170°C. If we were to extrapolate our calculations to lower temperatures and plot additional concentration profiles, we would also see that the curves for 100 hours at 1170°C, 1000 hours at 1070°C, 10,000 hours at 970°C, and 100,000 hours at 870°C would all overlap.

For comparison, we plotted the silver concentration profiles measured for the Tibetan andesine in terms of normalized concentration, assuming that the maximum

concentration measured for a sample represented the solubility limit of that sample (figure 7). Interestingly, the silver concentration profiles measured for these materials resemble the profiles characteristic of 1-D diffusion with constant surface doping. In particular, samples 001 and 003 closely resemble the curves for 100 hours at 1170°C and 1000 hours at 1070°C. Following the point made above, these samples would also resemble concentration profiles produced by 1,000,000 hours (i.e., 114 years) at 770°C or 10,000,000 hours (i.e., 1,140 years) at 670°C. A laboratory diffusion process with constant surface doping would reasonably be described by conditions of 100 hours at 1170°C or 1000 hours at 1070°C; longer duration at lower temperature likely describes natural diffusion under geologic conditions.

It is curious that silver shows a diffusion profile in the Tibetan material, while copper does not. We would expect the diffusion coefficients of the two elements to be roughly similar, so their dissimilar profiles suggests that the processes did not occur at the same time or in the same environment, whether in nature or in the lab.

CONCLUSIONS

The results of our diffusion studies with Inner Mongolian material show that silver diffuses readily into plagioclase under the proper experimental conditions. After treatment, the samples appeared visually similar to the untreated samples. Interestingly, the high vapor pressure of silver could limit its ultimate incorporation into plagioclase during diffusion treatment if the experiment is run long enough. If all the undiffused silver in the carrier vaporizes during treatment, the silver that has diffused into the plagioclase will diffuse back down its concentration gradient and exit the stone. Our diffusion results illustrate that we did not see saturation solubility, even during a short-duration experiment. Furthermore, our results indicate that the diffusion coefficient of silver in plagioclase is quite high—even higher than our estimate of 3.6×10^{-9} cm^2/s, which is accurate within no better than an order of magnitude. There is clearly much to learn about this system, and about the diffusion behavior of other metal ions in plagioclase.

The distribution of silver in Tibetan material bears some resemblance to the concentration profiles observed in the diffused Inner Mongolian samples. The concentration of copper, in comparison, was evenly to irregularly distributed. Simple mathematical modeling of one-dimensional diffusion into a semi-infinite slab produces concentration curves for silver that reasonably describe the measured silver concentration profiles in the Tibetan material. The calculated concentration curves represent a range of time and temperature conditions that could reasonably be produced in the laboratory or in nature.

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