Copper Diffusion in Plagioclase

John L. Emmett & Troy R. Douthit

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There has been public conjecture that the red andesine and labradorite gems in the marketplace are not natural, but are instead relatively colorless material that has been diffused with copper in the laboratory to produce the red coloration. The first step in elucidating this situation is to determine whether or not copper can be easily diffused into these plagioclases. To make this determination we conducted a set of experiments from June through October of 2008, using a variety of andesine/labradorite plagioclases. In what follows, the methodology for these experiments and their results are presented.

Our general approach for exploratory diffusion experiments is to embed the test samples in a refractory oxide powder that has been doped with the element which we wish to diffuse. The embedded samples are then heated to the maximum temperature consistent with the materials involved and held at that temperature for sufficient time to be able to observe a significant diffusion layer, if one forms.

The first decision to make in planning such experiments is the temperature at which the diffusion experiments will be run. In the gemological world, diffusion coloration was first encountered with the diffusion of titanium into pale blue or colorless corundum to produce a deep blue coloration (Kane, Kammerling et al. 1990). This was followed by beryllium diffusion into corundum to produce many different coloration effects (Emmett and Douthit 2002). It is well known that these processes are conducted at very high temperatures (1750-1900°C) and thus it is thought by many that all diffusion processes require such temperatures. This is not the case. The diffusion coefficient for any pair of materials (substrate and diffusant) increases exponentially with temperature up to the melting point of the substrate when mixing or compound formation usually dominates the interaction. A rule of thumb is that diffusion rates scale by the fraction of the substrate melting temperature, measured from absolute zero, at which the experiment is conducted. Thus diffusion into corundum with a melting point of ~2050C (2323K), at 1850°C (2123K) is at ~90% of the melting point. If one then conducts a diffusion experiment on a material with a 1250°C melting point, one would expect roughly similar diffusion coefficients at ~1110°C.

To evaluate what temperature we can conduct diffusion into plagioclases we need to examine their phase diagram, shown in figure 1.

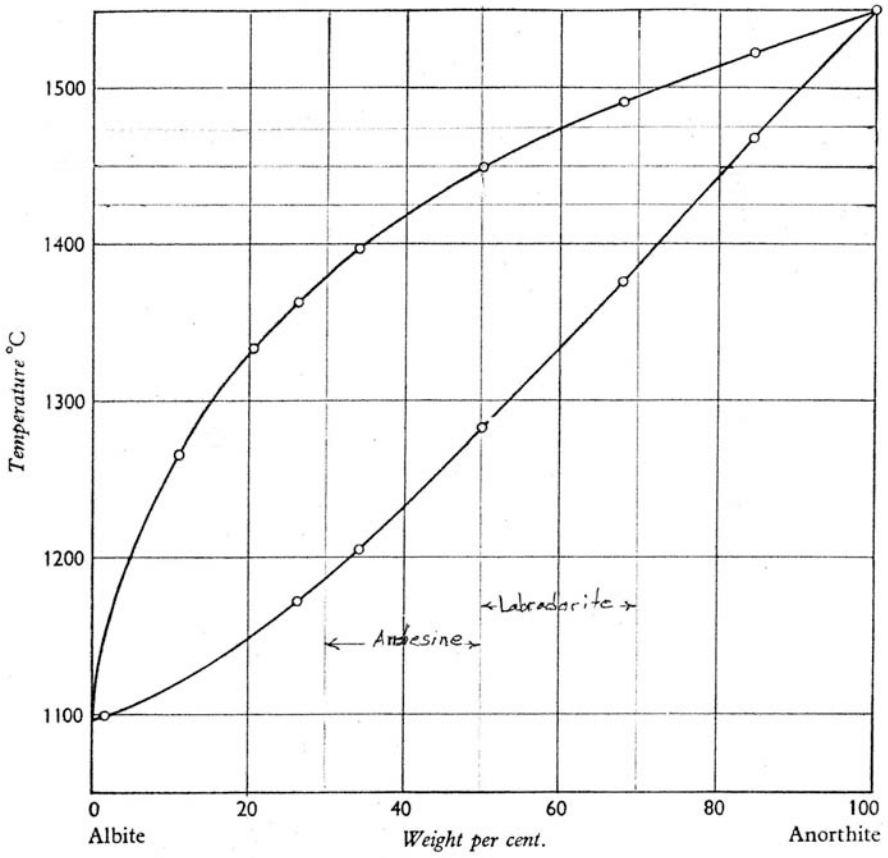

Figure 1. Phase diagram of the plagioclase feldspars (Bowen 1913).

Figure 1 shows that the plagioclases are comprised of a solid solution of albite and anorthite and thus the melting characteristics are a function of composition. The lower of the two curves in Figure 1 is termed the solidus, and below this curve the material is fully solid. The upper curve is termed the liquidus, and above this curve the material is fully liquid. Between these two curves is a region in which both liquid and solid material coexist. What is interesting is that the solid phase and the liquid phase in this region are of different composition. If one heats a plagioclase of 50% anorthite to 1350°C, and then waits for equilibrium to be established, the solid phase will have the composition given by the solidus curve at 1350°C, which is about 67% anorthite, while the liquid phase will have the composition given by the liquidus curve at 1350°C, or about 25% anorthite. If the cool down from this state is rapid, hours instead of months, the resulting solid will be a mixture of crystals with different compositions. Since the two compositions have different indices of refraction, the mixture will scatter light leading to translucency instead of transparency. Thus in planning a diffusion experiment it is important to stay below the solidus. Since the composition of our samples covers a range around 50% anorthite, we must stay safely below 1250°C.

There is a second consideration in choosing the temperature and that is the reaction between copper oxide and plagioclase. If a copper diffusion experiment is conducted in air the primary copper specie will be CuO. In principle CuO can react with plagioclases to produce a liquid phase below the melting point of CuO (~1235°C) and below the solidus of the plagioclase.

It is necessary to avoid the formation of liquid phases for the reason outlined above, but more importantly because with the formation of a liquid phase there is no longer any control of the solubility of Cu ions in the crystal, and new compounds might form as well. There are no phase diagrams for plagioclase and CuO, but we can gain some insight by looking at the phase diagrams for CuO and the constituent oxides of plagioclase, Al_2O_3, SiO_2, and CaO. Liquid phases are present in these phase diagrams at temperatures as low as 1020°C. These low temperatures indicate that we may not be able to avoid the appearance of a liquid phase and thus will have to control copper solubility by employing a very low copper concentration. From the foregoing considerations, we chose a copper dopant concentration of 1% and a temperature range of 1000 – 1200°C for the diffusion experiments.

Choosing the refractory oxide carrier for the copper is the next issue. Again we are concerned about chemical reactions between the plagioclase and the oxide carrier. For the oxide carrier we considered Al_2O_3, ZnO, MgO, and ZrO_2. Tests were run by embedding polished plagioclase plates into each of these oxides and heating at 1200°C for 100 hours in air. In all cases there was damage to the polished surfaces indicating chemical reaction. However, there was only very minimal damage with ZrO_2, so it was chosen for the diffusion runs.

Choosing a duration for a diffusion run is always a compromise between doing experiments rapidly and diffusing for long enough that the diffusion layer is easily visible. Estimating that an economic commercial process would probably not exceed about 2000 hours (~3 months), and noting that rough stones have been examined that are in the range of ~2 cm thick, we can guess at a diffusion coefficient of the order of 10-7 cm^2/sec or larger. Since diffusion depth only increases with the square root of time, one week long diffusion runs should give us a 2-3 mm colored diffusion layer, perhaps more.

For these experiments, material from four different sources was made available to us. Plagioclase from the Casa Grande Mine in Mexico was provided by Bill Barker of Barker and Company. Material from the Ponderosa Mine in Oregon was provided by John Woodmark of the Desert Sun Mining Company. Material from Mongolia was provided by Jerry Sisk of JTV. Material from the mines near Plush, Oregon was provided by Bart Curran of Columbia Gem House. Eric Braunwart and Bart Curran of Columbia Gem House arranged for the rough to be sawed into plates 3-4 mm thick and polished on both surfaces.

Each diffusion run tested five pieces from each of the four locations cited above. We consider five pieces to be the minimum for a meaningful experiment, and 20 would have been better if available. The stones were embedded in ZrO_2 containing 1% copper metal (-300 mesh), and placed in alumina crucibles. All samples were heated for 160 hours. Three temperatures were used – 1170°C, 1100°C and 1000°C, with all runs in air. Polished surface damage occurred for all runs as expected, but was minimal at 1000°C. All samples were repolished following diffusion. The results are shown in the photographs of figures 2-12.

Two conclusions are immediately clear – copper can diffuse very rapidly in some plagioclase samples, and a wide variety of phenomenology is produced. In some cases it appears the copper diffuses by bulk or lattice diffusion, while in others clearly pipe or short circuit diffusion is predominant. The latter is shown by the fact that the copper travels rapidly along dislocation bundles or other structural imperfections. This is particularly clear in figures

3 and 5. In some cases the green coloration often seen within natural material is also observed within red regions producing dark colored areas.

The diffusion rate appears to fall rapidly with temperature as shown by the minimal coloration of the samples diffused at 1000°C. However, even here there is considerable variation sample to sample. This is shown dramatically by the single sample in figure11 that is such a deep red color that it appears black in the photo.

These experiments were run solely to answer the question "does copper diffuse rapidly in plagioclase?" The answer is clearly yes. Understanding the phenomenology would require much more extensive experimentation and analysis. Clearly the diffusion is rapid enough that an economic commercial process could have been easily developed.

Bowen, N. L. (1913). "The melting phenomena of plagioclase feldspars." American Journal of Science, 4th series **35**: 577.

Emmett, J. L. and T. R. Douthit. (2002, September 4). "Beryllium diffusion coloration of sapphire: A summary of ongoing experiments." Retrieved March 20, 2003, 2003, from http://agta.org/cnsumer/gtclab/treatedsapps04.htm.

Kane, R. E., R. C. Kammerling, et al. (1990). "The identification of blue diffusion-treated sapphires." Gems & Gemology **26**(2): 115-133.

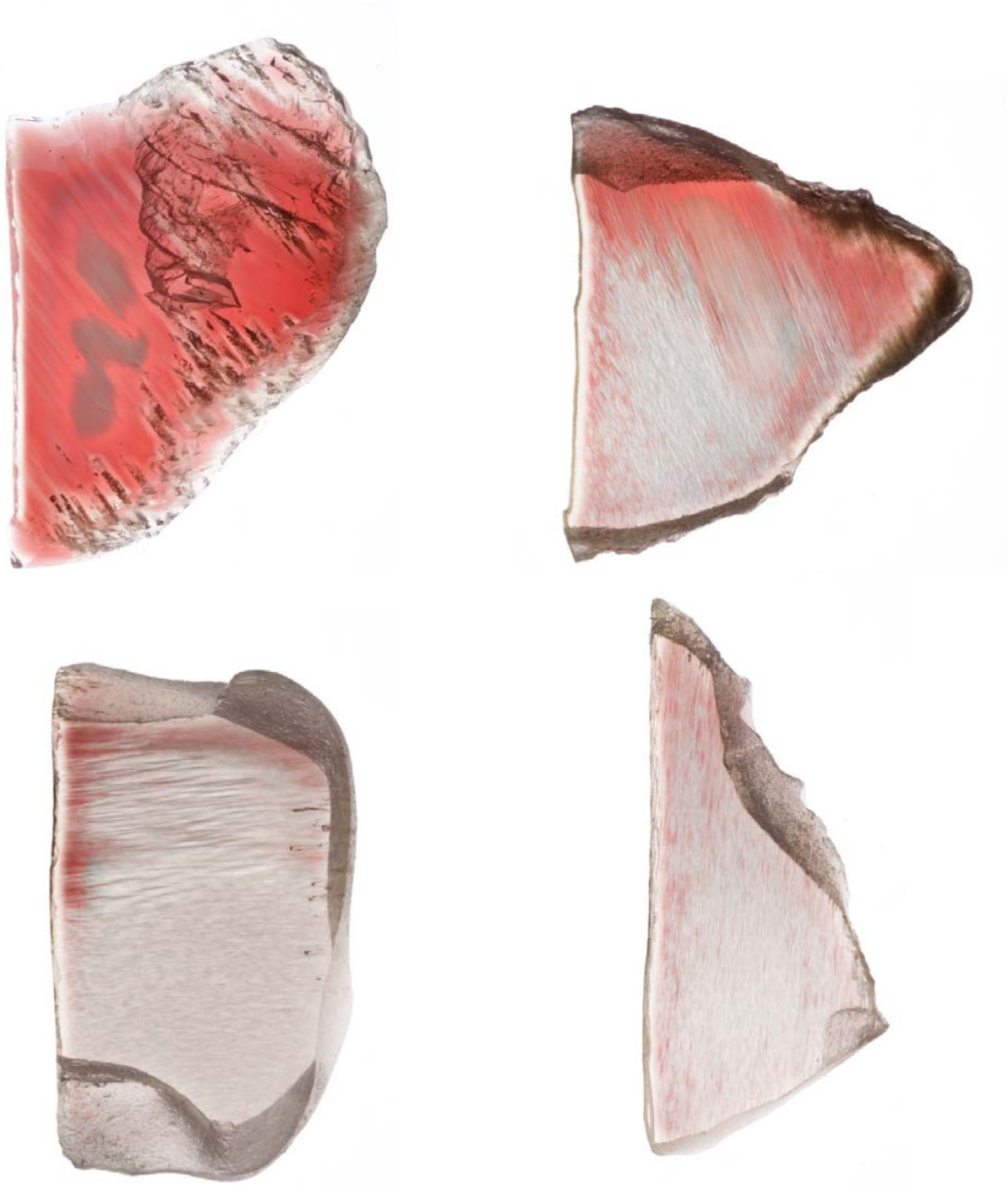

Figure 2. Mongolia Samples, 1170°C.

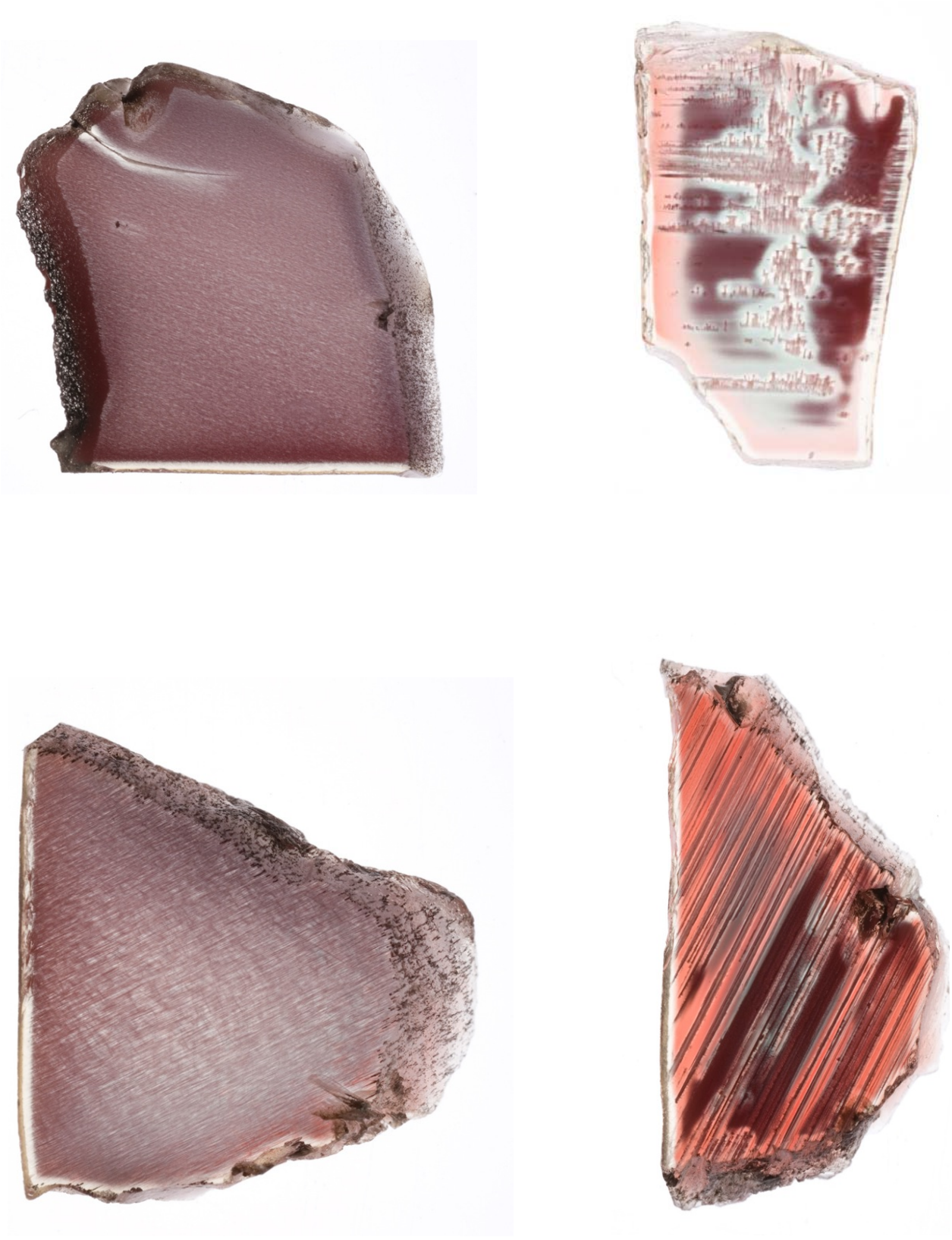

Figure 3. Mexico Samples, 1170°C.

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Figure 4. Plush, Oregon Samples, 1170°C.

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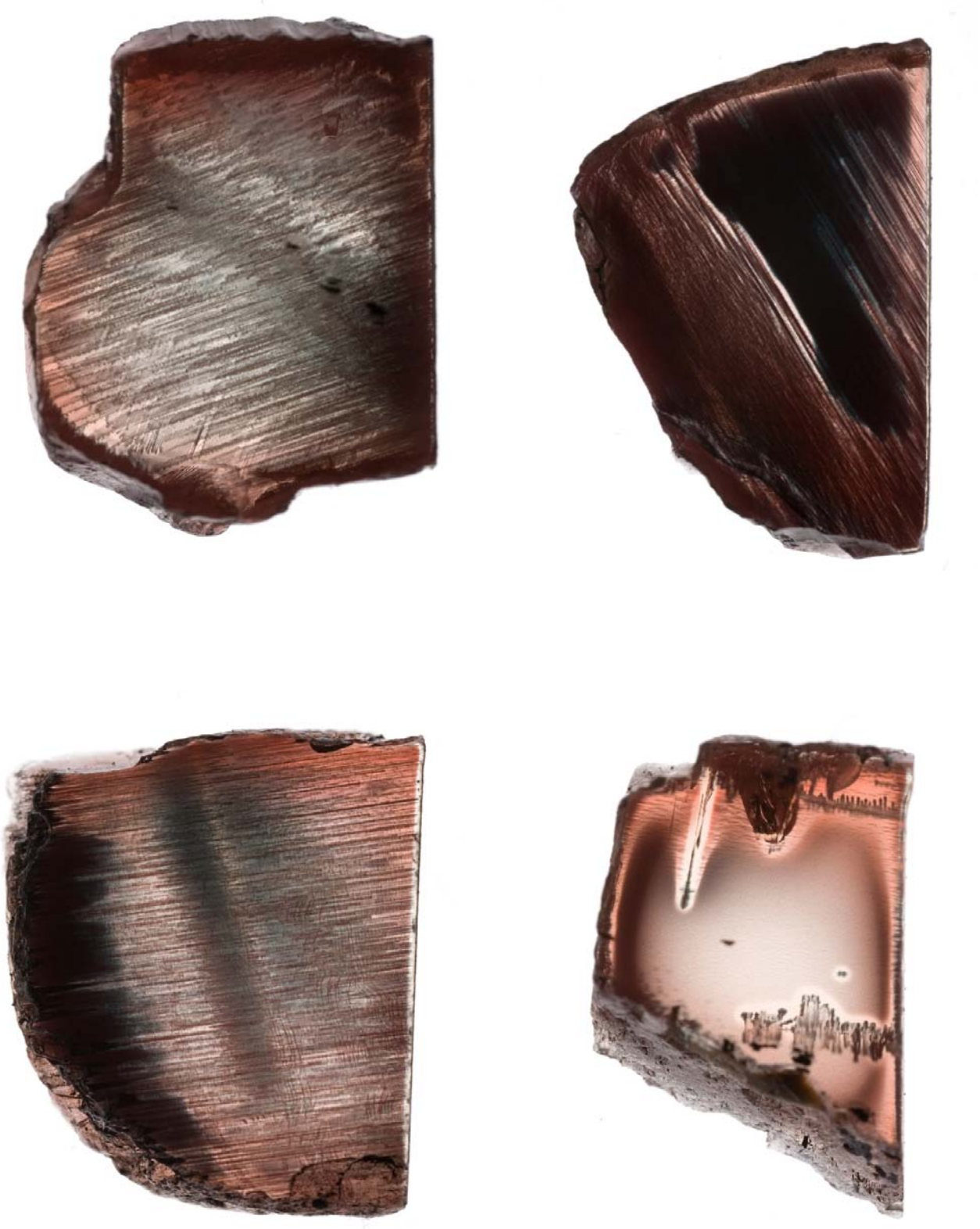

Figure 5. Mexico Samples, 1100°C

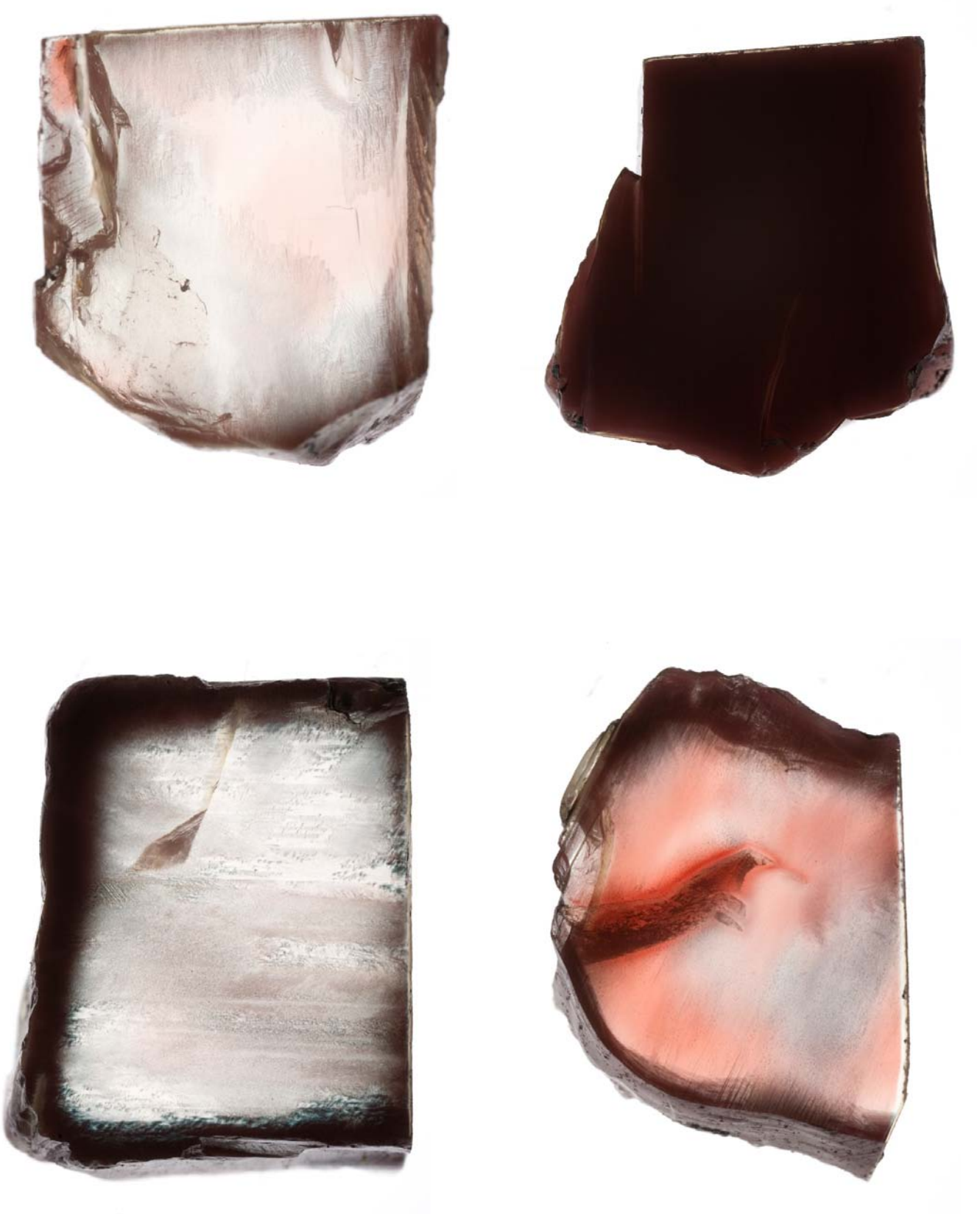

Figure 6. Ponderosa Mine, Oregon, 1100°C.

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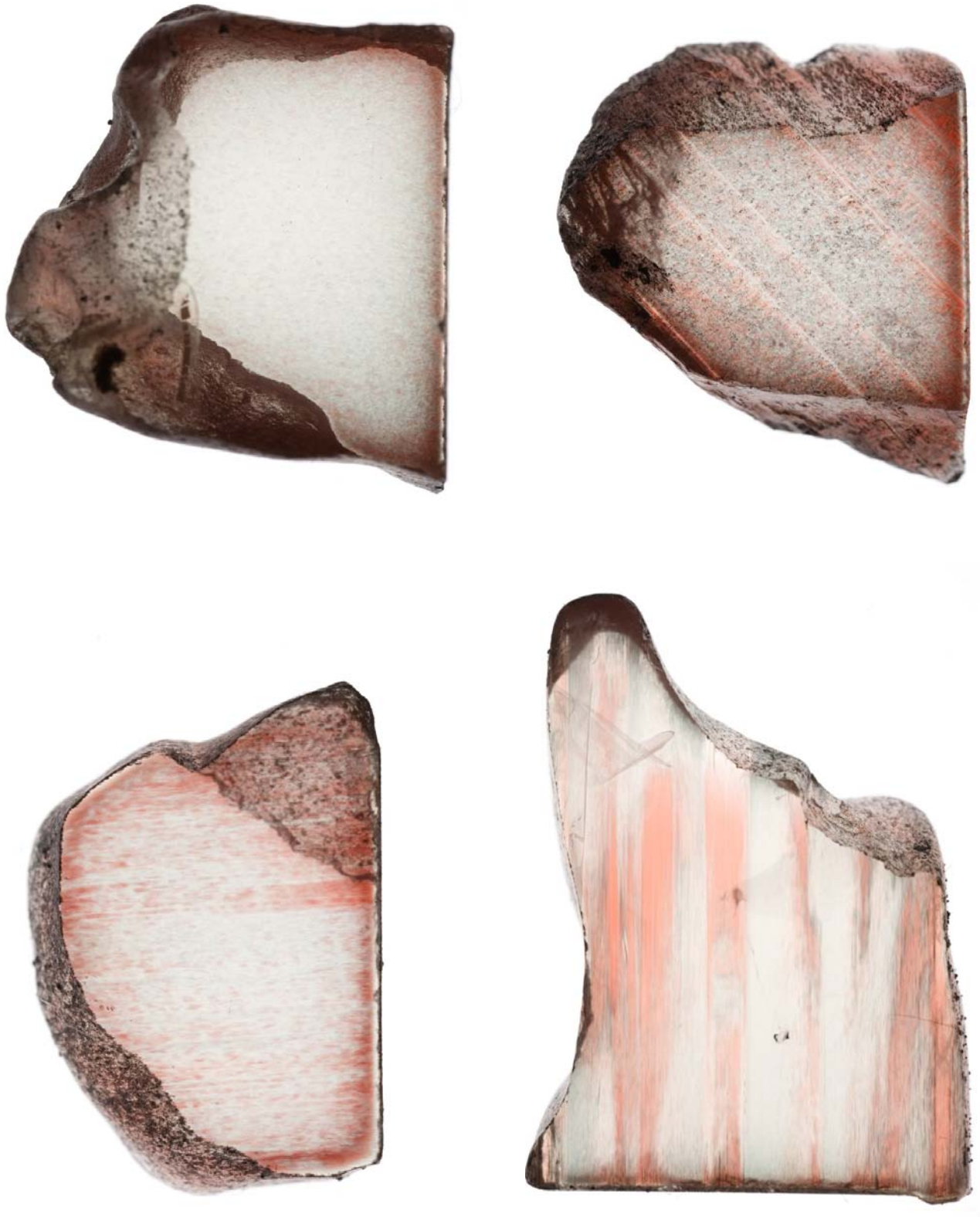

Figure 7. Mongolia Samples, 1100°C.

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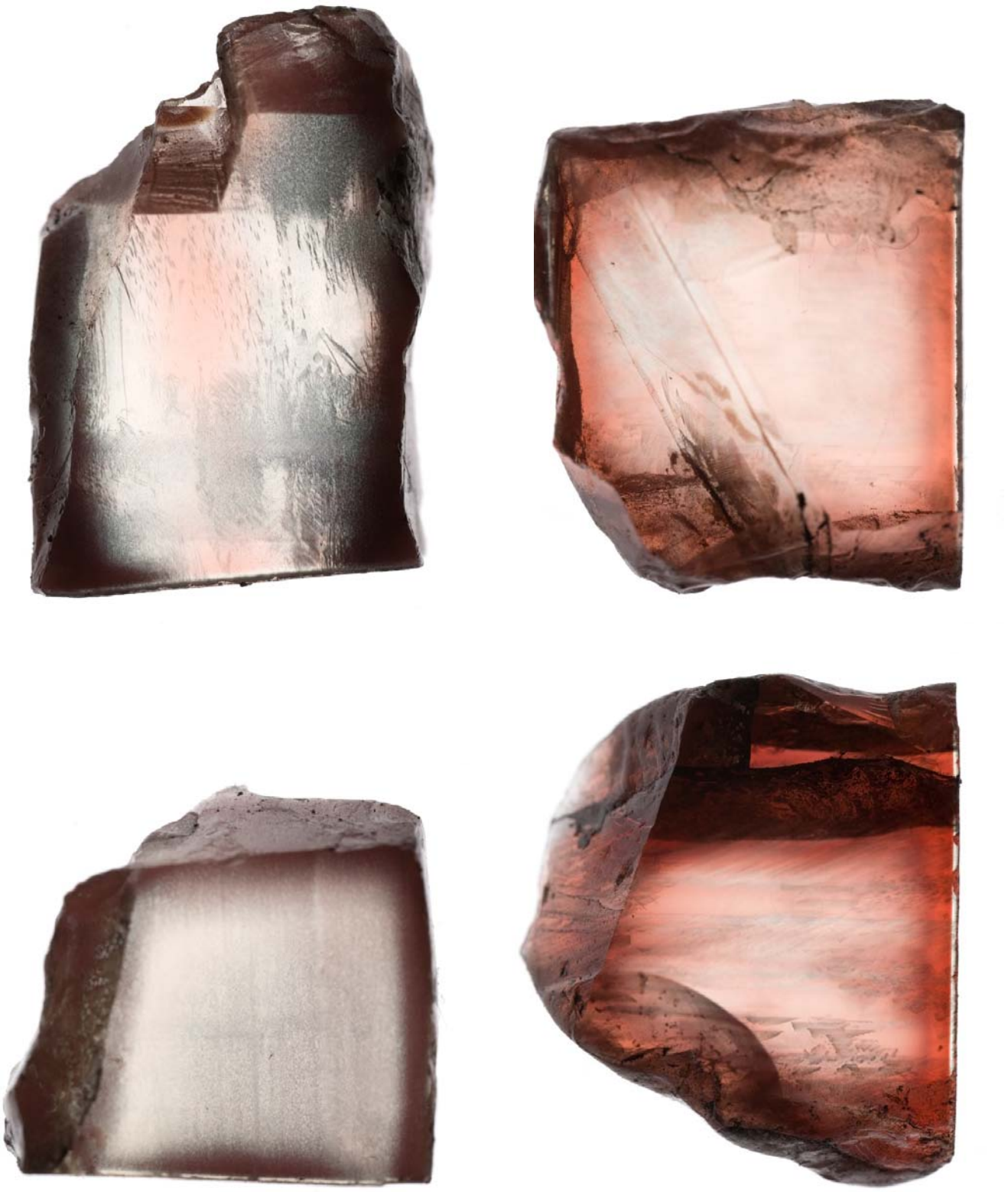

Figure 8. Plush, Oregon Samples, 1100°C.

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Figure 9. Mongolia Samples, 1000°C.

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Figure 10. Mexico Samples, 1000°C.

J.L. Emmett and T.R. Douthit. Copper Diffusion in Plagioclase. News from Research, September 10, 2009. www.gia.edu/research-resources/news-from-research

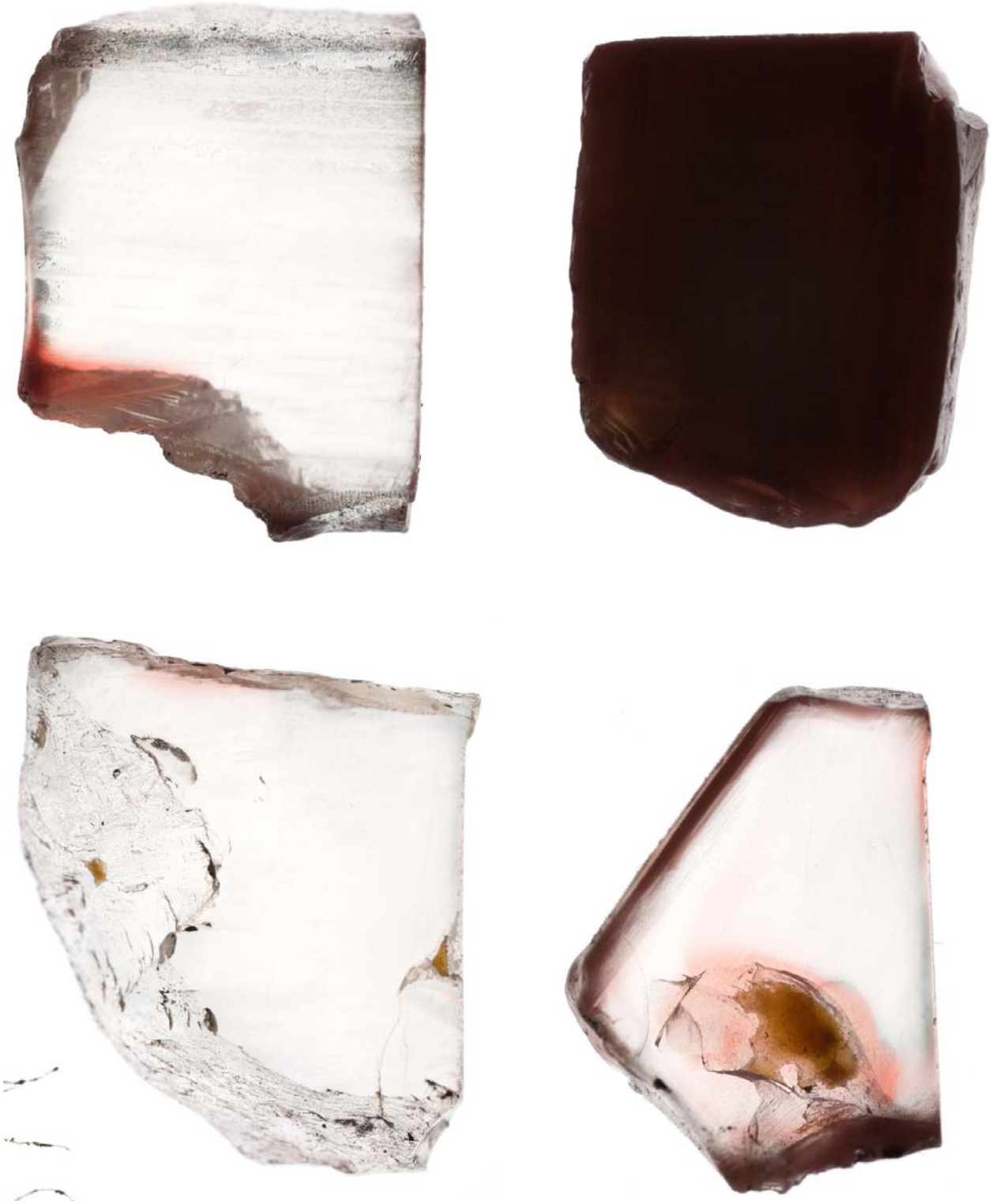

Figure 11. Ponderosa Mine, Oregon, 1000°C.

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Figure 12. Plush, Oregon Samples, 1000°C.

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