

# Identification of Natural and Treated Red Feldspar

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## ABSTRACT

The main objective of this research is to identify natural red feldspar and treated feldspar. The results of twelve red feldspar samples in this study can be concluded the red color occurs from copper. The mechanism of copper diffusion takes place along a dislocation line as pipe diffusion. The red color layers from rim toward core were not found in untreated feldspar samples. Also, the mottled color (red and green) were not found distinct in treated feldspars and glistering cloud along red zone were found only in natural red feldspar samples. It is difficult to identify the untreated and treated feldspar from only internal feature. The absorption spectra help to know about pleochroism of the red feldspar, which has mottled color (red and green). All treated feldspars in the study were not shown different polarized spectra in 0p and 90p. LA-ICP-MS result of both natural red and treated red feldspars, the copper content along twinning is higher than perpendicular twinning direction. However, their contents are different in each their red color areas, as in the inner area of natural red feldspars have high copper content while the treated red feldspars have this high content in the outer area or rim of the stones.

**Keywords:** Red feldspar, Treated red feldspar, Copper diffusion

## 1. Introduction

The gem-quality of red plagioclase feldspars entered to the gem market since 2002 from Congo (Fritsch, 2002) and later these gems were found in Tibet. Andesine and labradorite are species of these red and green gem feldspars. After that until nowadays in the trade has news about treated process as copper diffusion in feldspar (Hughes, 2011). Therefore, the merchants and customers interest in the untreated red color of these gemstones and want to know if theirs red colors are natural come from treatment.

Therefore, it is interesting to study to know how to identify natural and treated red feldspar in the gem market (figure 1).

## 2. Materials and Method

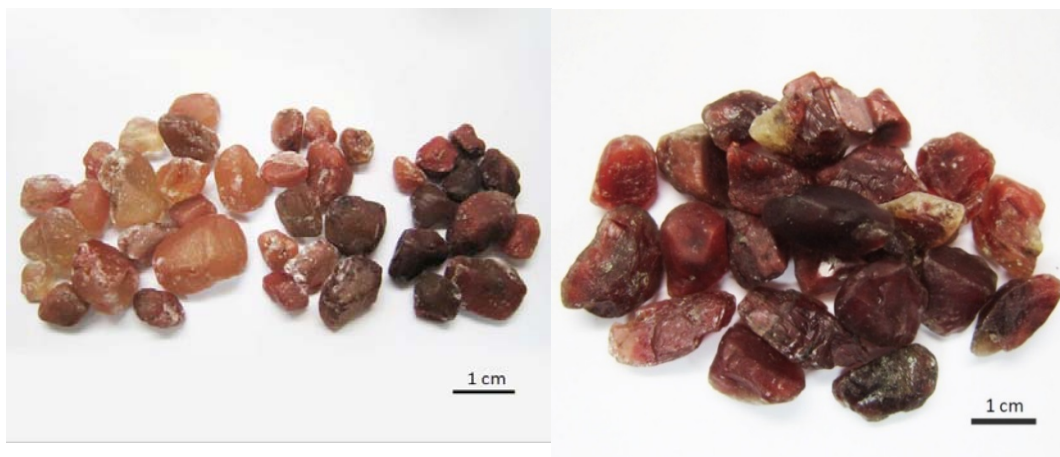
Eighteen samples of untreated and treated red feldspars were selected for this study. All of these samples were provided by Mr.Thanong Leelawatanasuk, Head of Gem Testing Laboratory, The Gem and Jewelry Institute of Thailand (Public Organization) (GIT). He was accompanied by the international research team and visited Tibetan andesine

occurrences for sample collection field observation. Thirteen natural plagioclases (including twelve red stones and one very light yellow sample) were separated from five copper-diffused plagioclases which the dealer declared them that treated red plagioclase

from Mongolia. Only the represented samples in figure 2 were polished one side for analyses. General properties and specific features were determined using basic gem equipment and advanced instruments, respectively.



**Figure 1.** Natural red feldspar; 0.71 ct (left) and treated red feldspar; 1.12 ct (right) in the gem market.



**Figure 2.** Represented sample collection under this study including untreated and treated samples ranging in size, from 1.44 to 19.10 ct.

All analyses were performed at GIT in which research facilities including standard gemological testing, *i.e.*, refractometer

measurement of refractive indices, hydrostatic balance for determination of specific gravity, London dichroscope for observation of

pleochroic colors, long- and short-wave UV lamps observation of fluorescence. Internal features were observed under a gemological microscope. UV-Vis-NIR spectrophotometer (Model Lambda 950 series, Perkin Elmer) was used for observation of UV-Vis-NIR absorption spectra within the range of 300 – 800 nm.

Quantitative chemical analyses using a JEOL Electron Probe Micro-Analyzer (EPMA), Model JXA-8100 super probe, based at Department of Geology, Faculty of Science, Chulalongkorn University. Standards used for calibration were pure oxide and mineral standards including wollastonite for Si and Ca, corundum for Al, jadeite for Na, potassium titanium phosphate for K and Ti, fayalite for Fe, pure copper for Cu and Strontium Barium Niobate for Sr. Analyses were performed at 15kV (accelerating voltage), with a beam current of about 24 nA and focused beam (probe diameter) smaller than 1  $\mu\text{m}$ . Measuring times were set at 30 seconds and 10 seconds for peak counts and background counts, respectively. These EPMA analyses were focused on major and minor compositions.

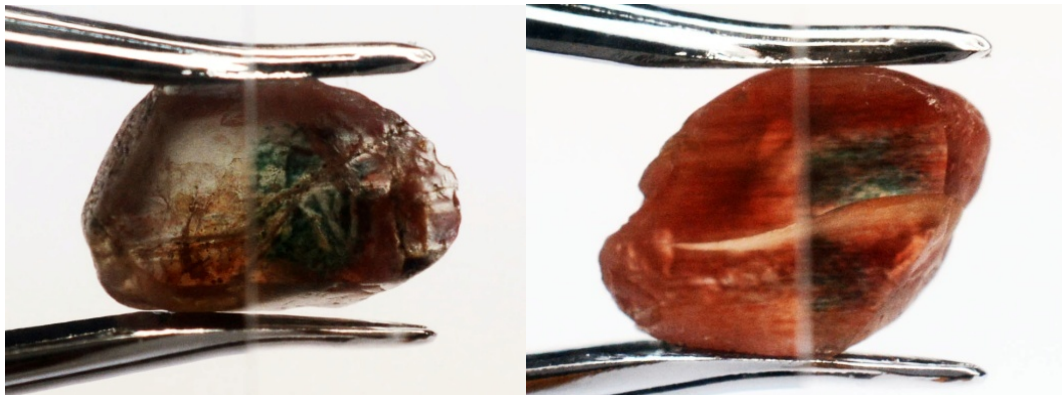
Quantitative analysis of trace elements were also carried out using a Laser Ablation - Inductivity Coupled Plasma - Mass Spectrometry (LA-ICP-MS), Agilent Technologies (Model 7500 series) based at the GIT. The NIST glass standards (*i.e.*, NIST 612 and NIST 610) and basalt glass standards

(*i.e.*, BBMT1 and BNV-1G) were used as external standards whereas  $^{26}\text{Al}$  was the internal standard. Data refining was carried out using GLITTER 4.0 software.

### 3. Gemological Property

Colors of plagioclase feldspar samples (both treated and untreated stones) are mostly light red to red and only a natural sample is light yellow. The refractive indices (RI) range between 1.560 to 1.562 for  $n_\gamma$  and 1.550 to 1.555 for  $n_\alpha$  with birefringences of about 0.007 to 0.010 and specific gravity (SG) between 2.63 to 2.68. These property ranges fall within the common range of feldspar.

In addition, ultraviolet (UV) lamps both short wave (SW) and long wave (LW), were engaged for observation of fluorescence. Both untreated and treated red feldspars are inert to very weak red under SWUV and inert to weak pinkish orange under LWUV. On the other hand, fluorescence of very light yellow sample is weak pinkish orange under SWUV and inert under LWUV. Pleochroism of all red feldspar samples can be observed under a London dichroscope in day light. Untreated red feldspars show weak to strong dichroic colorless or light green to green (figure 3). There is no pleochroic red color observed in all of these samples; therefore, dichroic color could not be observed in the treated red feldspars (mostly red to dark red).

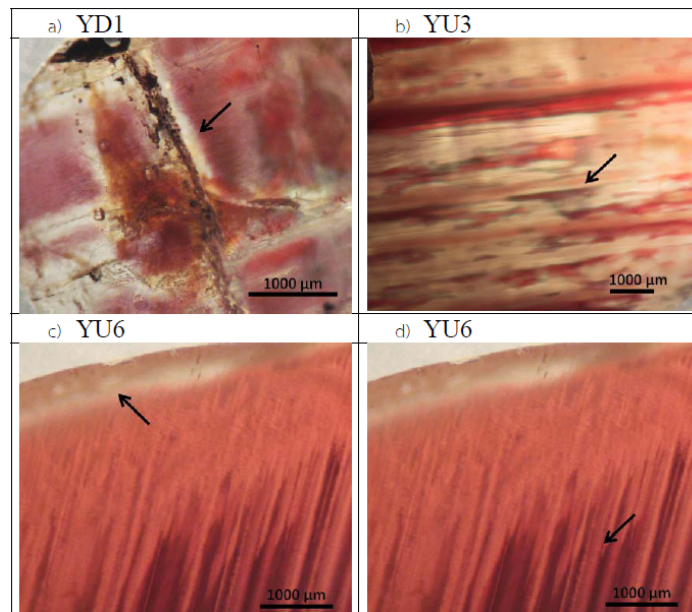


**Figure 3.** Distinct dichroism of the natural red feldspar is clearly observed under London dichroscope (sample no. YD1 (left) and YLA3 (right)).

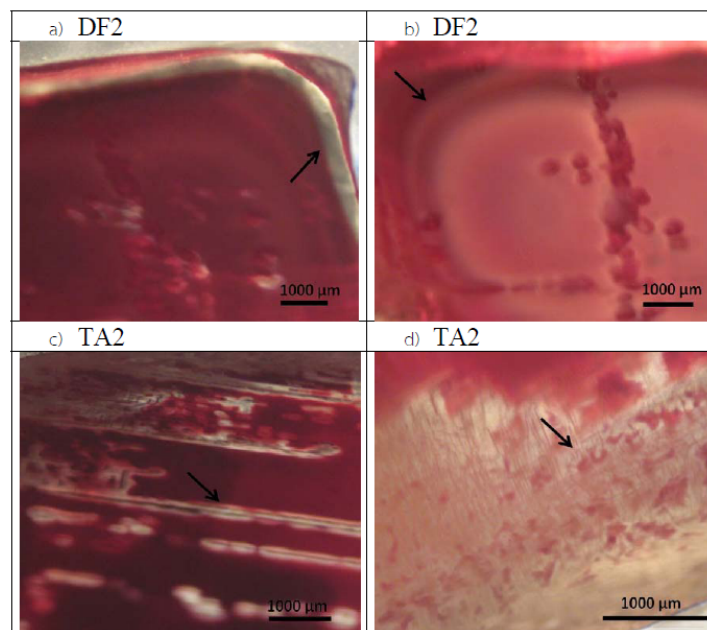
Microscopic investigation revealed some crucial internal features as shown in figures 4 and 5. They include oriented tubes, fingerprint, irregular tubes, colorless rim, colorless zone around fingerprint or fracture, mottled color (red and green), milky cloud along red zone, glistering cloud along red zone and red color layer from rim towards

core. Although, internal features in natural and treated stones are quite similar, the red color layers from rim towards core were not found in the natural feldspar samples whereas mottled color (red and green) and glistering cloud along red zone were not found in the treated feldspar samples. Summary of internal characteristics found in untreated and treated red feldspar samples present in Table 1.

Internal characteristic of plagioclase feldspar	Untreated	Treated
1. Oriented tubes	✓	✓
2. Irregular tubes	✓	✓
3. Colorless zone from surface (rim)	✓	✓
4. Colorless zone around red tubes	✓	✓
5. Colorless zone around fingerprint or fracture	✓	✓
6. Mottled color (red and green)	✓	✓
7. Milky cloud along red zone	✓	✓
8. Glistering cloud along red zone	✓	-
9. Red color layer from rim towards inner core	-	✓



**Figure 4.** Representative internal features of untreated feldspar including (a) colorless zone around fingerprint (YD1), (b) mottled color (red and green) along tubes and twinning (YU3), (c) colorless rim and (d) oriented coarse red tubes with glistering (YU6).

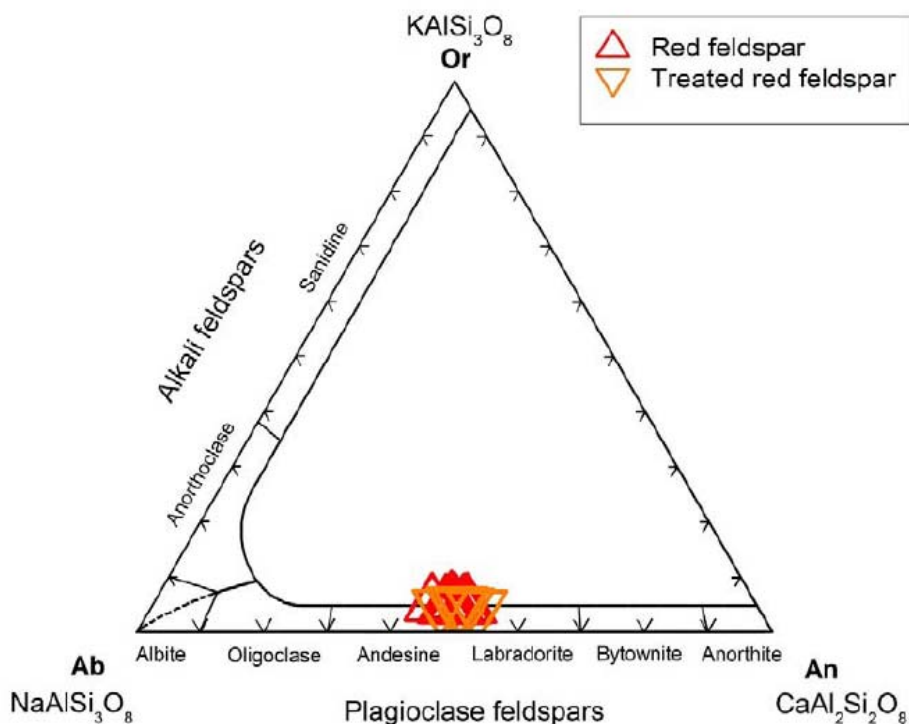


**Figure 5.** Representative of internal features of treated feldspar show (a) colorless rim, (b) circular of milky red cloud from core to rim (DF2), (c) colorless zone around irregular and (d) straight red tubes (TA2).

#### 4. Mineral Chemistry

EPMA analyses yielded similarly chemical compositions of these feldspar samples. They vary in narrow ranges of 56-58% SiO<sub>2</sub>, 26-28 % Al<sub>2</sub>O<sub>3</sub>, 9-10% CaO and about 5% NaO<sub>2</sub> with trace amounts of K<sub>2</sub>O, TiO<sub>2</sub>, FeO and CuO. Copper was also analyzed because it appears to be crucial cause of red coloring in these feldspars. However, all results indicate that copper contents are lower than the EPMA

detection limit. Therefore, LA-ICP-MS was engaged to analyze copper and other trace elements, which will be reported later. Recalculation based on 8 oxygen (O) atoms shows atomic proportions of K<sub>2-5</sub>, Na<sub>44-50</sub> and Ca<sub>48-51</sub> (see Tables 2 and 3). Ternary atomic plots of Ca-Na-K (figure 6) show composition of intermediate calcium plagioclase (An<sub>48-51</sub>) which fall between andesine and labradorite ranges.



**Figure 6.** Ternary atomic plots of feldspar indicating the similar composition of all samples including natural red feldspars and treated red feldspars.

Table 2. Chemical analyses of feldspar samples from EPMA

Sample	Red feldspar				Treated red feldspar			
	YD1	YU3	YU5	YLA3	TA0	TA1	TA2	DF1
SiO <sub>2</sub>	55.84	58.39	55.82	55.97	58.00	55.97	55.14	55.58
TiO <sub>2</sub>	0.05	0.07	0.09	0.08	0.13	0.04	0.06	0.00
Al <sub>2</sub> O <sub>3</sub>	27.52	26.33	27.40	27.34	26.61	27.25	27.28	27.51
FeO*	0.42	0.33	0.41	0.39	0.37	0.34	0.33	0.32
CaO	9.81	9.02	9.98	9.89	9.14	9.85	9.73	9.30
Na <sub>2</sub> O	5.28	5.40	5.23	5.31	5.28	5.15	5.35	5.37
K <sub>2</sub> O	0.50	0.49	0.45	0.42	0.46	0.46	0.51	0.00
CuO	0.08	0.05	0.09	0.07	0.05	0.10	0.05	0.00
Total	99.54	100.10	99.51	99.49	100.06	99.21	98.45	98.09
Formula 8(O)								
Si	2.530	2.612	2.530	2.535	2.598	2.540	2.525	2.529
Ti	0.002	0.002	0.003	0.003	0.004	0.001	0.002	0.002
Al	1.470	1.389	1.465	1.460	1.405	1.458	1.473	1.482
Fe <sup>3+</sup>	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Fe <sup>2+</sup>	0.071	0.203	0.079	0.079	0.2007	0.106	0.041	0.111
Na	0.464	0.468	0.460	0.466	0.459	0.453	0.475	0.452
Ca	0.476	0.432	0.485	0.480	0.439	0.479	0.477	0.464
K	0.029	0.028	0.026	0.024	0.026	0.026	0.030	0.028
Cu	0.003	0.002	0.003	0.002	0.002	0.003	0.002	0.003
Total	4.980	4.939	4.977	4.977	4.938	4.969	4.989	4.968
%Ab	47.88	50.42	47.38	48.04	49.66	47.30	48.36	47.85
%An	49.12	46.58	49.96	49.49	47.50	49.95	48.63	49.19
%Or	3.00	2.99	2.66	2.48	2.84	2.75	3.01	2.96

Trace element analyses obtained from LA-ICP-MS were focuses on copper (Cu) silver (Ag) and iron (Fe) which Cu may be the main cause of red coloring in both natural and treated red feldspar. In addition, Ag and Fe usually occur as associated element of Cu in the natural deposit.

Copper (Cu): varies from about 311 to 1417 ppm (av.  $797.57 \pm 185.37$  ppm) in untreated red feldspar and about 379 to 833 ppm (av.  $491.38 \pm 36.41$  ppm) in treated red feldspar. The average Cu content of untreated samples is almost two times higher than that of treated samples (see figure 7).

For untreated samples, the Cu contents in colorless area vary from about 311 to 1020 ppm (av.  $760.70 \pm 154.76$  ppm) whereas those in red area vary from about 436 to 1417 ppm (av.  $815.72 \pm 202.10$  ppm). The average Cu content of inner red area is higher than average content of colorless rim.

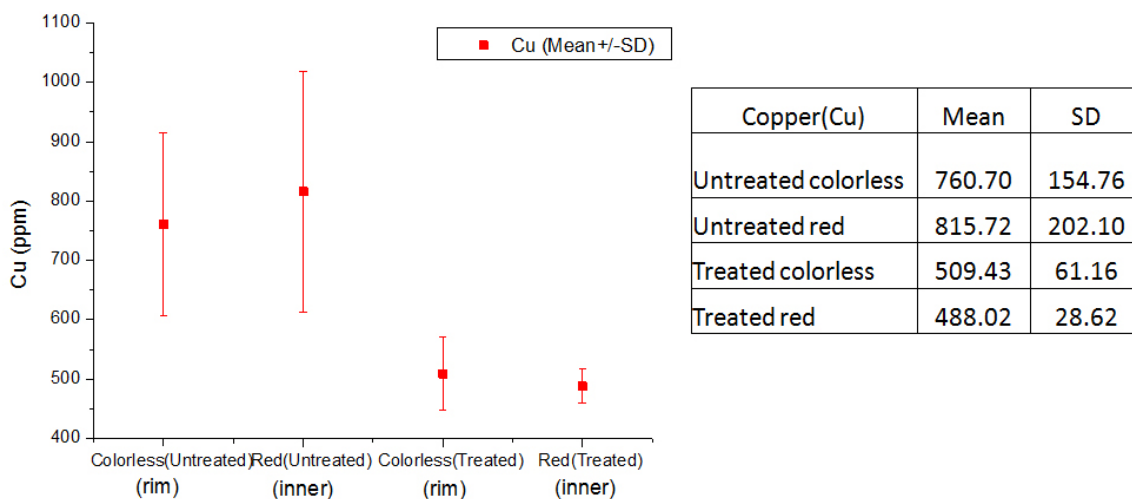
For treated samples, the Cu contents in colorless area vary from 444 to 833 ppm (av.  $509.43 \pm 61.16$ ) whereas those in red area vary from 379 to 613 ppm (av.  $488.02 \pm 28.62$  ppm). The average copper content from colorless area (rim) is higher than content from red area (inner).

Silver (Ag): vary from 0 to 790 ppm (av.  $91.01 \pm 196.96$ ) in untreated red feldspar and about 0.00 to 1.01 ppm (av.  $0.01 \pm 0.07$  ppm) in treated red feldspar. The average Ag content

of untreated samples is very higher than treated samples (see figure 8).

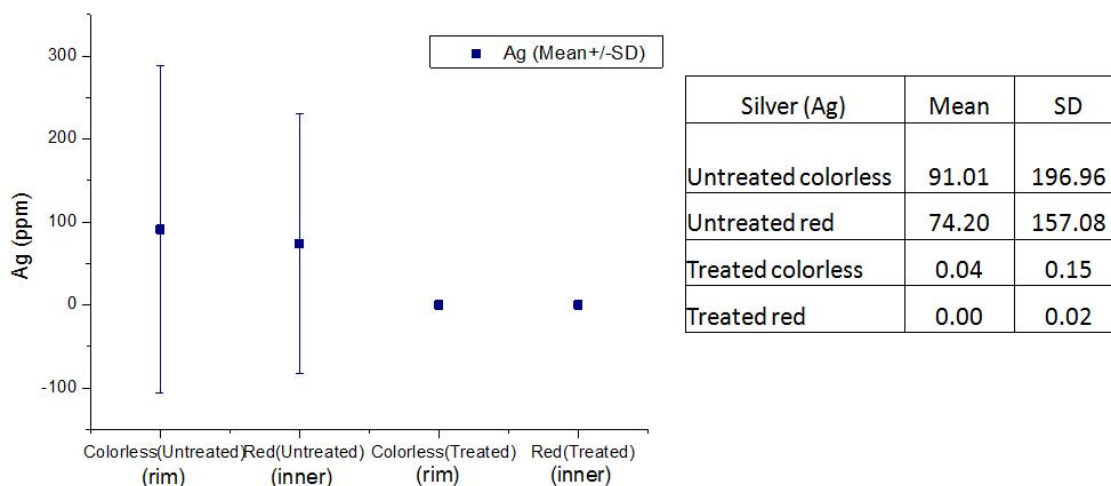
For untreated samples, the Ag contents in colorless area vary from about 0 to 790 ppm (av.  $91.01 \pm 196.96$  ppm) whereas those in red area vary from about 0 to 710 ppm (av.  $74.20 \pm 157.08$  ppm). The average Ag contents from colorless area (rim) is slightly higher than content from red area (inner).

For treated samples, the Ag contents in colorless area vary from 0.00 to 1.01 ppm (av.  $0.04 \pm 0.15$  ppm) whereas those in red area vary from about 0.00 to 0.30 ppm (av.  $0.00 \pm 0.02$  ppm) The average Ag contents from colorless rim is very slightly higher than content from inner red area. Almost datas of this content are belower than the detection limit.



**Figure 7.** Comparative graph of copper (Cu) content from untreated and treated plagioclase; colorless (rim) and red (inner) area.





**Figure 8.** Comparative graph of Silver (Ag) content from untreated and treated plagioclase; colorless (rim) and red (inner) area.

**Iron (Fe):** vary from about 1858 to 3164 ppm (av.  $2570.55 \pm 331.54$  ppm) in untreated plagioclases and vary from about 1536 to 2810 ppm (av.  $2075.68 \pm 302.73$  ppm) in treated plagioclases. The average of Fe content in untreated samples is higher than treated samples. And Fe content is much higher than others trace elements such as manganese, copper, silver and barium (figures 10 and 11).

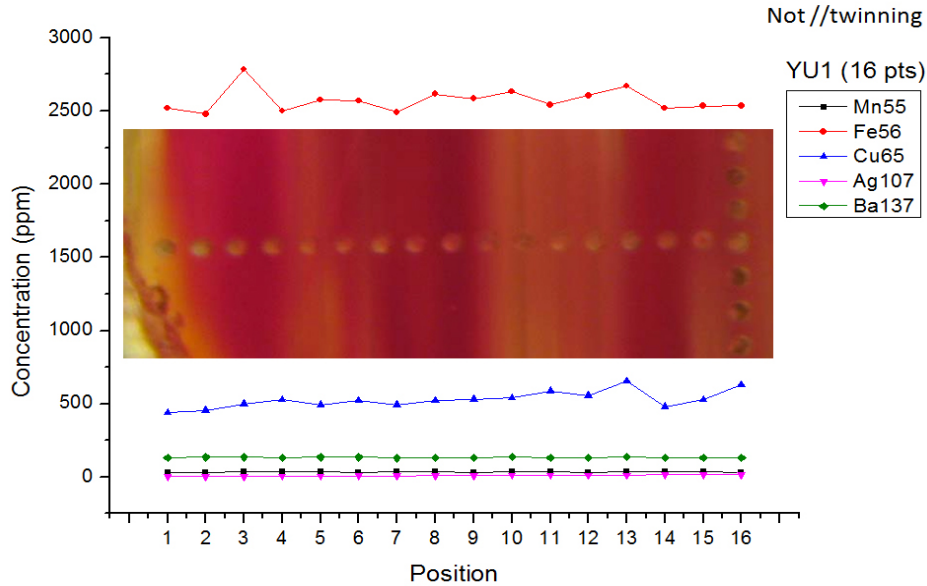
For untreated samples, the iron contents in colorless area vary from 1858 to 3164 ppm (av.  $2401.50 \pm 391.62$  ppm) whereas those in red area vary from 1888 to 3062 ppm (av.  $2656.26 \pm 275.05$  ppm) The average iron content from inner red area is higher than content from colorless rim.

For treated samples, the iron contents in colorless area vary from 1535.86 to 2809.88 ppm (av. 2203.56 ppm, SD  $\pm 308.66$ ) and in

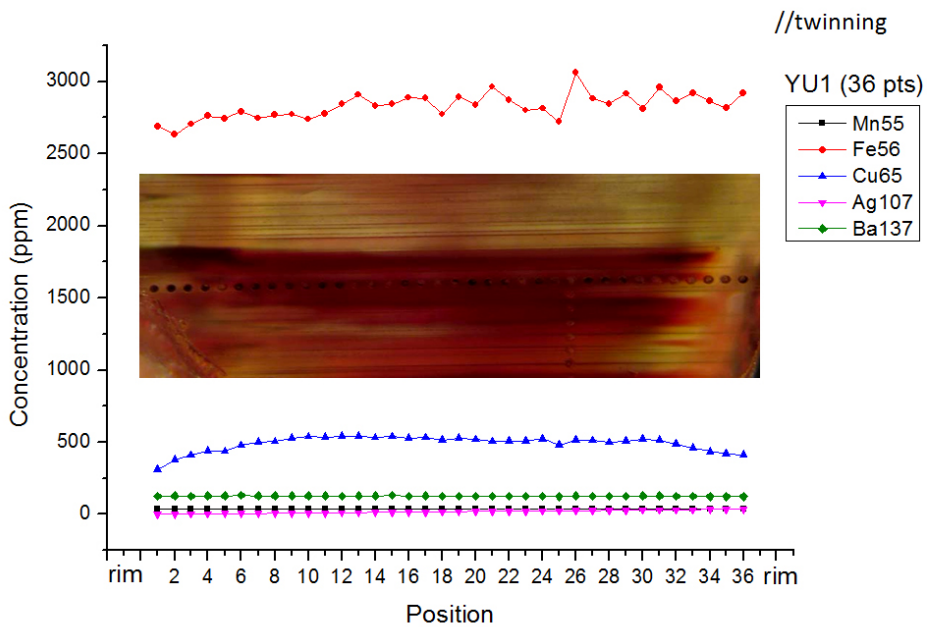
red area vary from 1578.99 to 2737.57 ppm (av. 2051.94 ppm, SD  $\pm 296.25$ ). The average iron content of colorless area (rim) is slightly higher than content of red area (inner).

The LA-ICP-MS analyses of untreated samples show high copper content along red tubes or twinning (figures 11 and 12). Comparative the copper content in treated red feldspar, sample no.TA0 is represented. This sample can be separated to be three color area such as colorless, light red and red, respectively, from rim to inner.

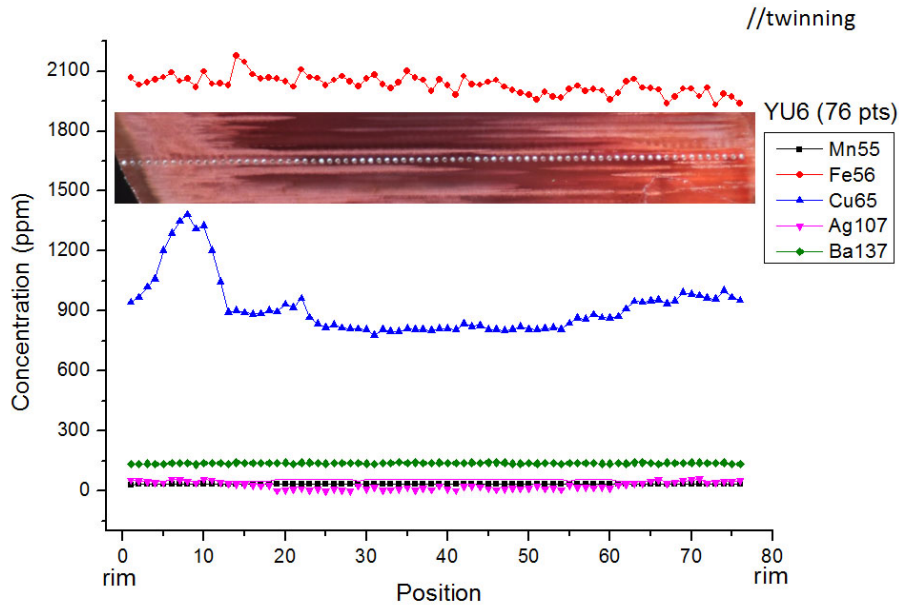
The result of this treated feldspar, the copper content along twinning is higher than perpendicular twinning direction. The copper content in light red area is higher than the red area that is in the inner (figures 12 and 13).



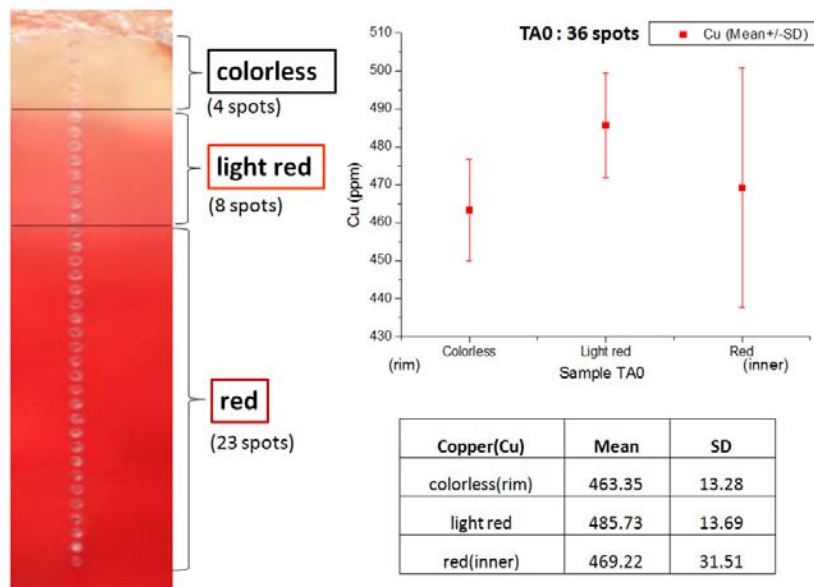
**Figure 9.** Profiles of 5 elements (Mn, Fe, Cu, Ag and Ba) in untreated feldspar 16 spots cross the twinning from rim (colorless) to inner (red).



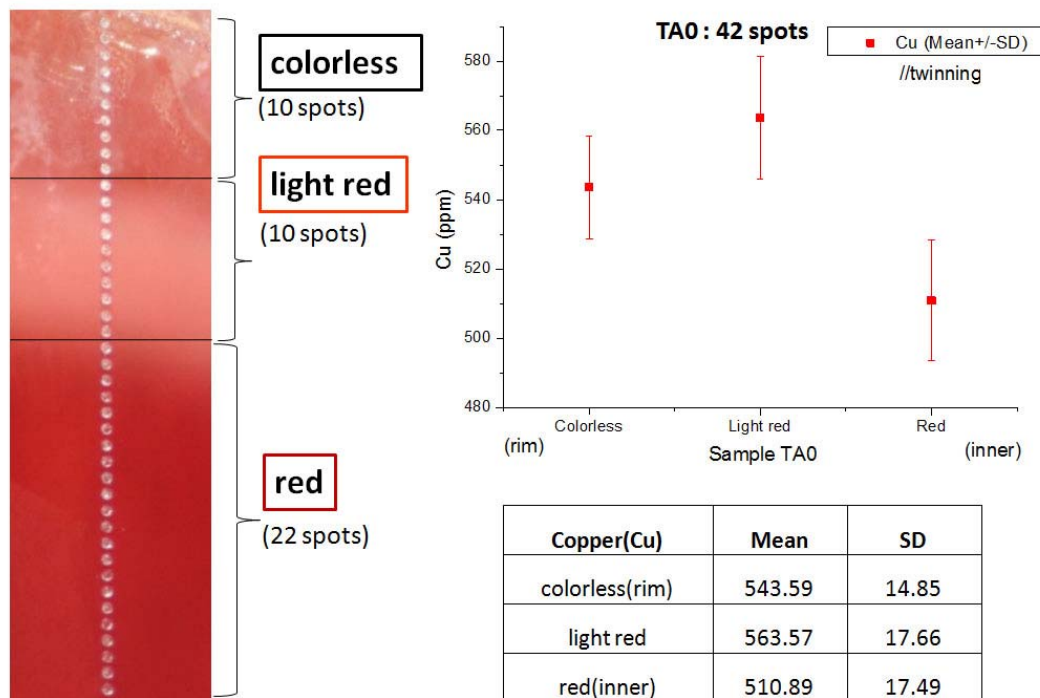
**Figure 10.** Profiles of 5 elements (Mn, Fe, Cu, Ag and Ba) in untreated feldspar 16 spots along the twinning from rim to rim.



**Figure 11.** Profiles of 5 elements (Mn, Fe, Cu, Ag and Ba) in untreated feldspar 16 spots along the twinning from rim to rim. Along red tube has high copper content.



**Figure 12.** Comparative graph of copper (Cu) content in treated feldspar (sample no. TA0) 36 spots analyses along perpendicular twinning. Mean and SD were calculated from each area such as colorless (4 spots) light red (8 spots) and red (23 spots).



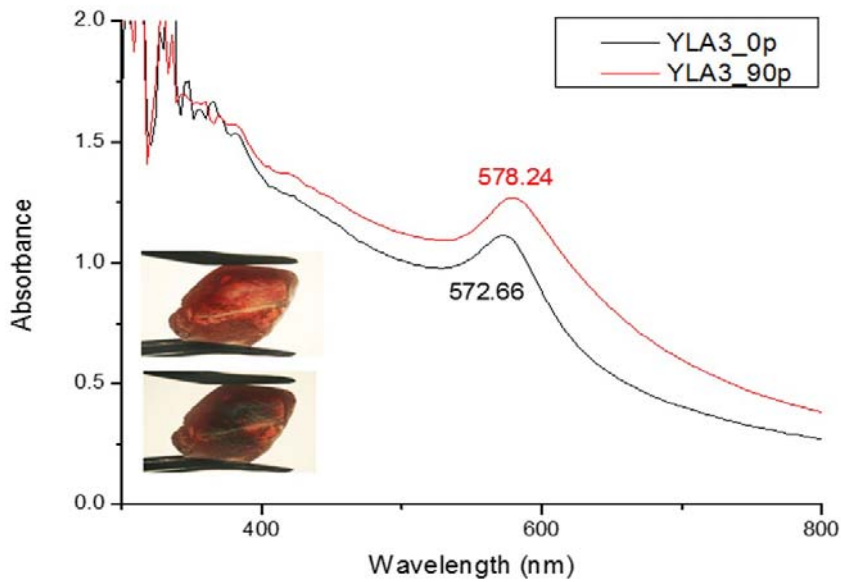
**Figure 13.** Comparative graph of copper (Cu) content in treated feldspar (sample no. TA0) 42 spots analyses along twinning. Mean and SD were calculated from each area such as colorless (10 spots) light red (10 spots) and red (22 spots).

## 5. Spectroscopy

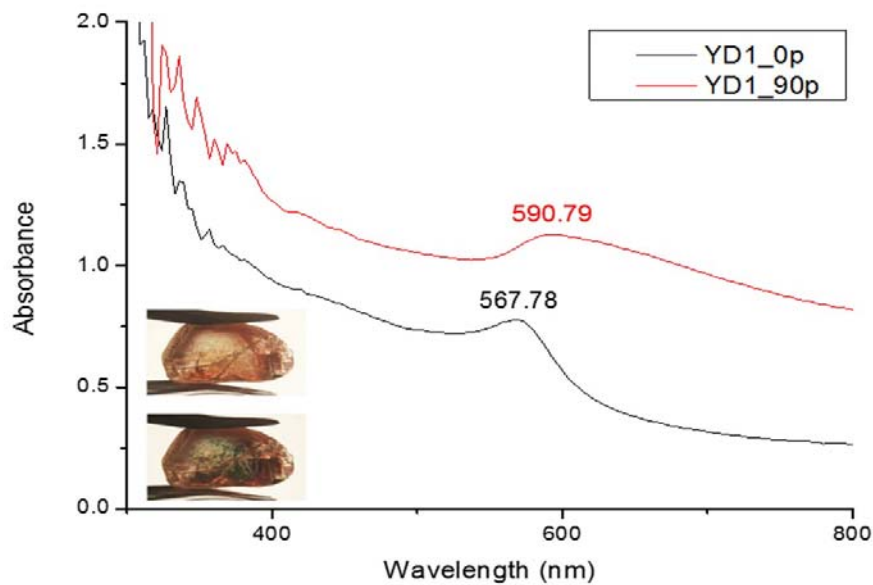
To set sample for using UV-VIS-NIR spectrophotometer, the polarized spectra of each sample oriented in the position, which show maximum pleochroism under dichroscope observation. These results cannot be defined to exact spectra are gamma, alpha or beta. Therefore, in this study, two directions of polarized spectra when the filter was perpendicular at 0 and 90 degree called '0p' and '90p', respectively.

The UV-Vis spectra of untreated red feldspar show range of distinct absorption band at about 568 to 599 nm (0p) and at 573 to 595

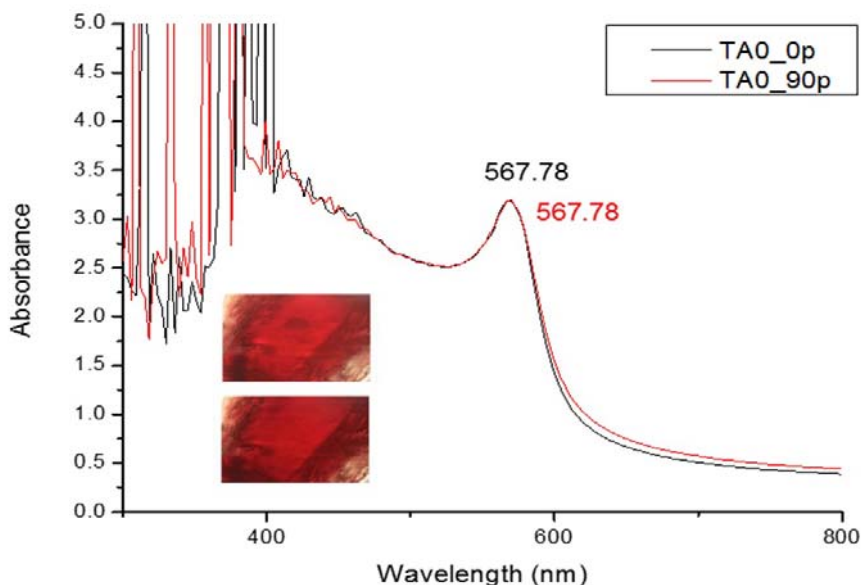
nm (90p). In two samples (YD1 and YLA3) that have strong color of pleochroism (colorless to green) show more different absorption (figure 14 and 15) than the samples that have weak to moderate pleochroism color. The UV-Vis spectra of treated red plagioclases (copper-diffused feldspar) show distinct range of absorption band at 568 to 597 nm (0p) and at 568 to 579 nm (90p). The absorption patterns of samples in both 0p and 90p are quite similar as the treated red feldspar sample (figure 16).



**Figure 14.** UV-Vis spectra of untreated red plagioclase (sample no. YLA3) show the polarized absorption bands at about 573 nm (0p) and at 578 nm (90p).



**Figure 15.** UV-Vis spectra of untreated red plagioclase (sample no. YD1) show the distinct polarized absorption bands at about 568 nm (0p) and 591 nm (90p).



**Figure 16.** UV-Vis spectra of treated red feldspar (sample no. TA0) show the polarized distinct absorption peaks at about 568 nm (both in 0p and 90p).

## 6. Discussion and Conclusion

### 6.1 Discussion

The internal characteristic of untreated and treated red feldspars are such as oriented tubes, fingerprint, irregular tubes, colorless zone from surface (rim), colorless zone around fingerprint or fracture, mottled color (red and green), milky cloud along red zone, glistening cloud along red zone and red color layer from rim towards the core. In this study, the red color layers from rim towards the core were found only in treated red feldspars. The mottled color (red and green) and glistening cloud along red zone were found in natural red feldspars.

According to Hofmeister and Rossman (1985), the color in labradorite from Oregon (USA) is correlated with the concentration of copper. Red labradorite shows highest copper

content (150-200 ppm CuO). The color is further dependent on Cu exsolution temperature, rate of Cu diffusion and aggregation ( $\text{Cu}^0$  colloids) and state of copper ( $\text{Cu}^0$  or  $\text{Cu}^+$ ) while in this study, the copper content of all twelve red feldspar samples varies from about 311 to 1417 ppm (av.  $797.57 \pm 185.37$  ppm). According to Hofmeister and Rossman (1985) and Krzemnicki (2004), red labradorite, the band at 560 to 580 nm combined with a general increase of absorption towards ultraviolet is attributed to intrinsic absorption by tiny  $\text{Cu}^0$  particles which are too small to scatter light ( $<22$  nm), and produces a red colour. The band-shift from 560 nm towards shorter wavelengths, coupled with a broadening size of the  $\text{Cu}^0$  colloids. The copper colloids are most probably of a very similar size and measure only a few nanometers. In this study, the spectra of the natural and treated red feldspars are very similar to treated feldspars

in the range about 568 to 599 nm spectral region.

Chemical analyses of all plagioclase feldspar samples from EPMA, the chemical composition, contents of these plagioclase feldspars are approximately 55-58%wt SiO<sub>2</sub>, 26-28 %wt Al<sub>2</sub>O<sub>3</sub>, 9-10%wt CaO and 4.8-5.4%wt NaO<sub>2</sub> with the trace amount of TiO<sub>2</sub>, FeO, K<sub>2</sub>O, CuO and SrO. A composition of Ab<sub>44.34-50.42</sub>:An<sub>47.00-51.00</sub>:Or<sub>2.48-4.52</sub> expressed as mol.% albite : anorthite : orthoclase. These plotted in the andesine – labradorite field. This result is a similar field with Abduriyim (2009).

LA-ICP-MS analyses of untreated and treated feldspars show range of major and traces elements. The untreated feldspars show a similar range of many trace elements with treated feldspar samples. Only copper content can be shown the different profiles along tubes or twinning as the result in this study, copper content along twinning is higher than perpendicular twinning direction. The concentration profiles of copper of natural red feldspars in this study are similar with the andesines collected from Yu Lin Gu in Tibet (Peretti, 2011).

## 6.2 Conclusion

The main objective of this research is to identify natural red feldspar and treated feldspar. In this study, all results can be

concluded the red color occurs from copper. The mechanism of copper diffusion takes place along a dislocation line as pipe diffusion. The red color layers from rim toward core were not found in untreated red feldspar samples. Also, the mottled color (red and green) were not found distinct in treated feldspars and glistening cloud along red zone were found only in natural red feldspar samples. It is difficult to identify the untreated and treated feldspar from only internal feature. The absorption spectra help to know about pleochroism of the red feldspar which has mottled color (red and green). All treated feldspars in the study were not shown different spectra in PPL and XPL. LA-ICP-MS result of both natural red and treated red feldspars, the copper content along twinning is higher than perpendicular twinning direction. However, their contents are different in each their red color areas, as in the inner area of natural red feldspars have high copper content while the treated red feldspars have this high content in the outer area or rim of the stones.

## 7. Acknowledgements

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