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The Potential for diffusing Copper into Tourmaline

Preparation for initial experimentation

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Introduction

There has been some discussion within the gemological community concerning the possibility that some tourmaline on the market particularly those from Mozambique, may have been diffused with Cu (James, 2009a, James, 2009b, James, 2009c)¹. While the author and her colleagues have not observed any characteristics that might lead them to believe that such a situation exists in the market today (e.g., see (Koivula J. I., 2009, Koivula, 2009, Wise, 2009), Wise, 2009), as Paraíba tourmaline (LMHC, 2007)² is a commercially important gem material it was felt that some experimental gemology to investigate the feasibility of such a treatment was required.

Over the last few months an assortment of tourmaline has been acquired. The stones have been analyzed, sorted and selected (Figure 1) for the copper diffusion experiments. These experiments are presently underway (March 2009) and are being carried out by John L. Emmett of Crystal Chemistry located in Brush Prairie, WA. Details of these experiments and their results will be available and published once complete.

Pre-treatment Examination

For this study a total of 30 faceted blue, green, blue-green, and violet samples have been examined; all are tourmaline and stated to be from Mozambique (Figure 1).

¹ For a detailed description of diffusion processes see Emmett, J. L., Scarratt, K., F. McClure, S., Moses, T., Douthit, T.R., Hughes, R., Novak, S., Shigley, J.E., Wang, W., Bordelon, O., Kane, R.E. (2003) Berillium Diffusion of Ruby and Sapphire. *Gems & Gemology*. 39. 2. available at http://www.giathai.net/pdf/Beryllium_G&G_2003-02.pdf.

² A blue (electric blue, neon blue, violet blue), bluish green to greenish blue or green elbaite tourmaline, of medium to high saturation and tone, mainly due to the presence of copper (Cu) and manganese (Mn).

Standard gemological properties including refractive index (RI), specific gravity (SG), and UV fluorescence have been determined for each stone and in addition UV-Vis-



Figure 1: Thirty tourmalines selected for diffusion experiments seen here before treatment. NIR, IR, Raman and LA-ICP-MS analyses have been recorded (Abduriyim, 2006).

Standard gemological properties

Refractive indices for the group were determined to be in the ranges $n_o = 1.639-1.642$, and $n_e = 1.619-1.620$, with birefringence being $= 0.019-0.021$. The SGs were determined to be between $3.04 - 3.08$. Under UV radiation the stones were inert to faint blue in LWUV and inert in SWUV.

Microscopic characteristic

All samples exhibited typical tourmaline inclusions. These included trichites (Laur, 2008), irregular and partially healed fissures (Figure 2, Figure 3 and Figure 5) and parallel growth tubes (Figure 4 and Figure 5). Some were cracked and some of these cracks were frosty in appearance.



Figure 2: Partially healed fissures in one of the tourmaline selected for diffusion experiments.



Figure 3: Partially healed fissures in one of the tourmaline selected for diffusion experiments.

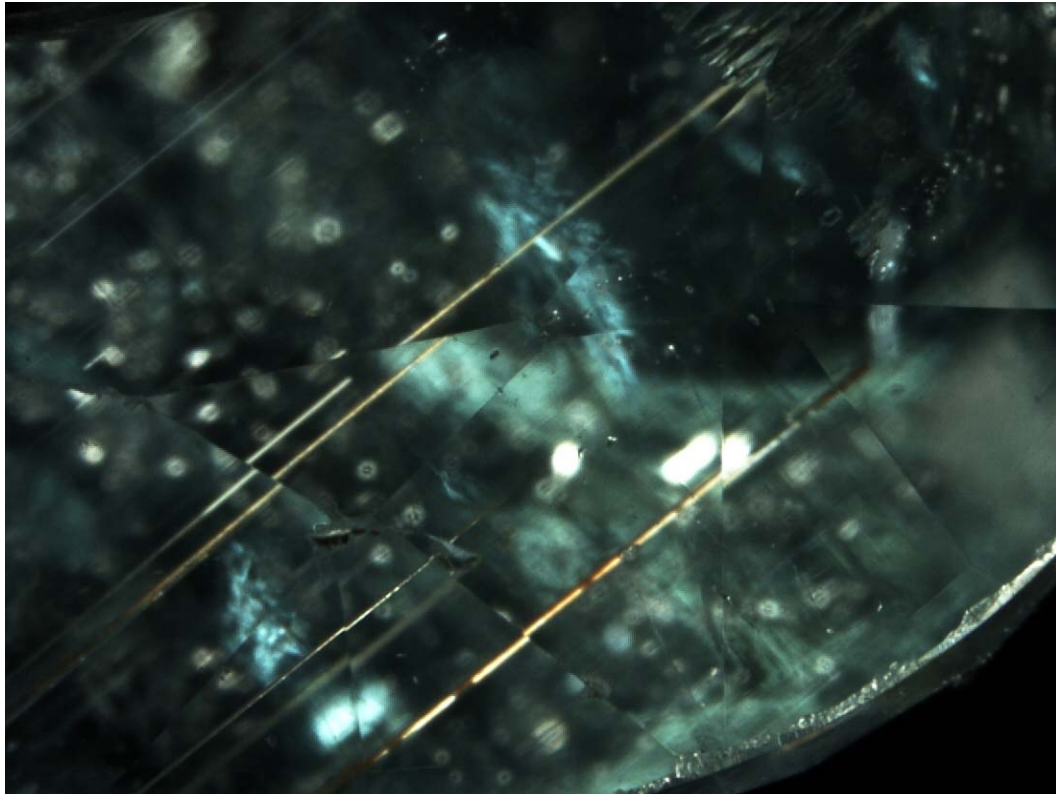


Figure 4: Yellow and red-brown hollow tubes in one of the tourmaline selected for diffusion experiments

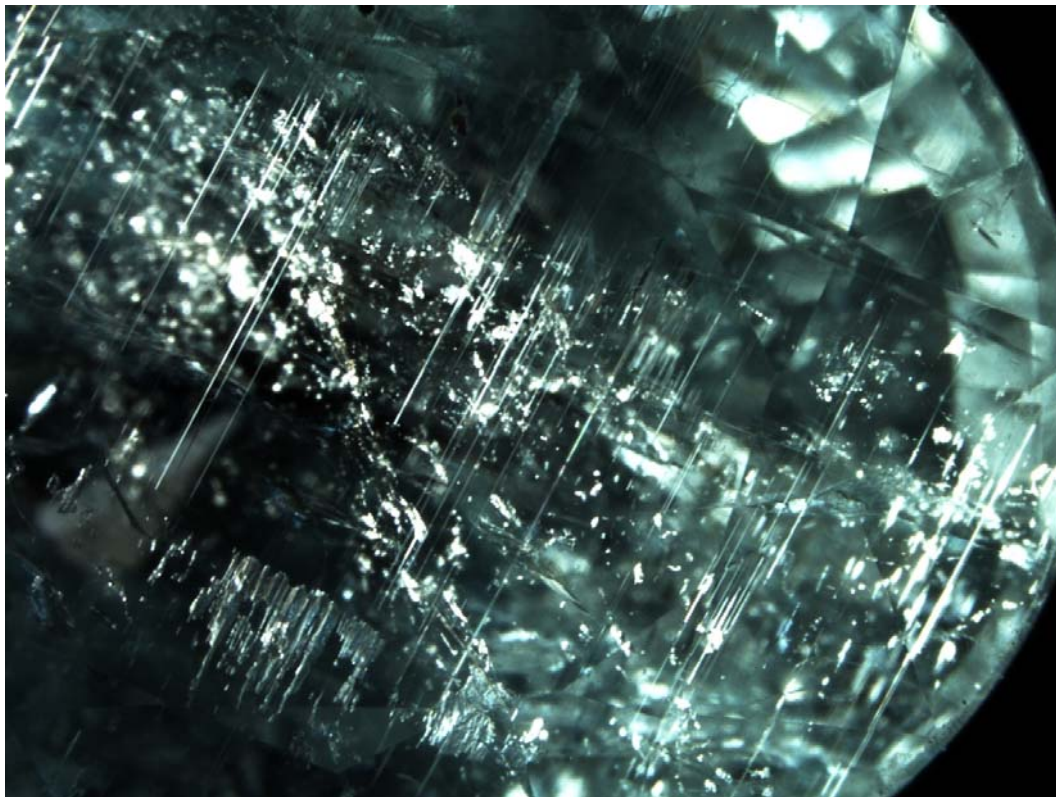


Figure 5: Partially healed fissures and parallel growth tubes arrange in same direction in one of the tourmaline selected for diffusion experiments

UV-Vis-NIR spectroscopy

UV-Vis-NIR absorption spectra displayed a very weak but sharp peak at about 415nm and broad band at about 515 nm, which are attributed to Mn^{2+} and Mn^{3+} , respectively (Fritsch, *et al.*, 1990). Two different spectra types were found in the group. The first (Figure 6) recorded broad bands at approximately 695 and 920nm that are attributed to Cu (Fritsch, *et al.*, 1990). The maxima are located at about 690 and 900nm in the $E \perp C$ direction and about 740 and 940nm in the $E // C$ direction. The second (Figure 7) recorded a broad band with a maximum at about 720nm, assigned to intervalence charge transfer $Fe^{2+} \leftrightarrow Fe^{3+}$ (Fritsch, *et al.*, 1990). Both types of tourmaline spectra showed sharp bands in the near infrared between 1400 and 1500nm that are assigned to O-H stretching vibrations (Fritsch, *et al.*, 1990).

IR spectroscopy

Infrared spectra recorded for all samples were the same (Figure 8). The spectra are characterized by broad bands at about 7593, 7120, 6993, 6775 cm^{-1} which are attributed to hydroxyl (O-H) stretching and 4599, 4538, 4439, 4345, 4212, 3909 cm^{-1} which are attributed to M-OH bonding where M maybe Al, Fe, Mn, etc (Reddy, 2007).

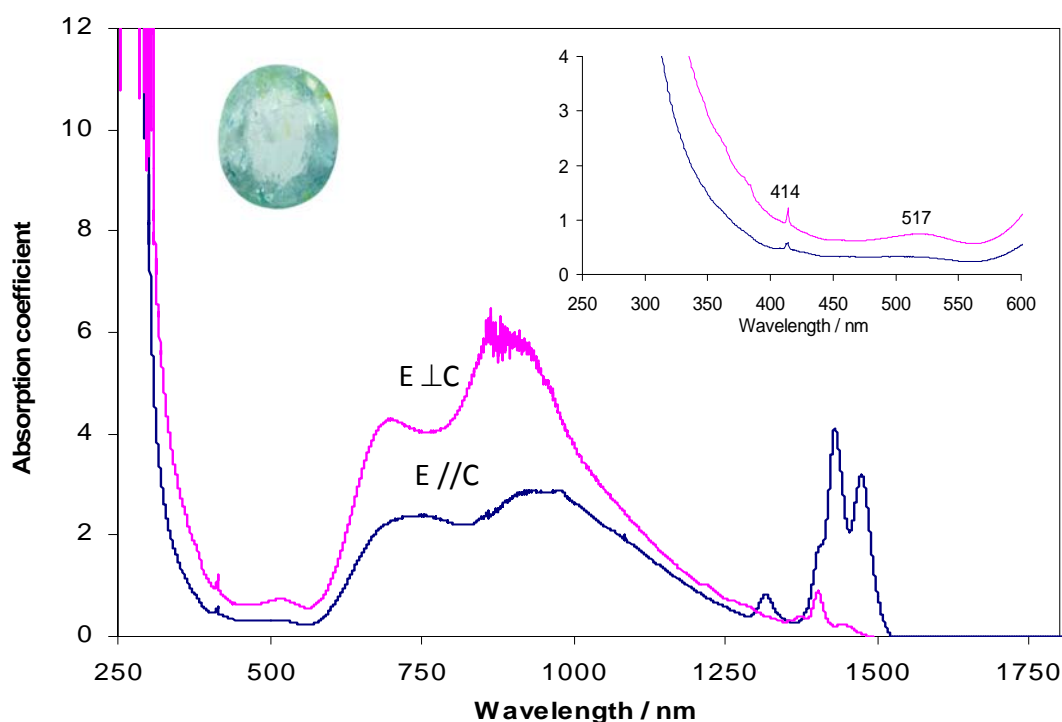


Figure 6: An example of the first of two types of UV-Vis-NIR spectra noted for this group of 30 tourmaline. The FeO concentration of this sample is 105.6 ppmw.

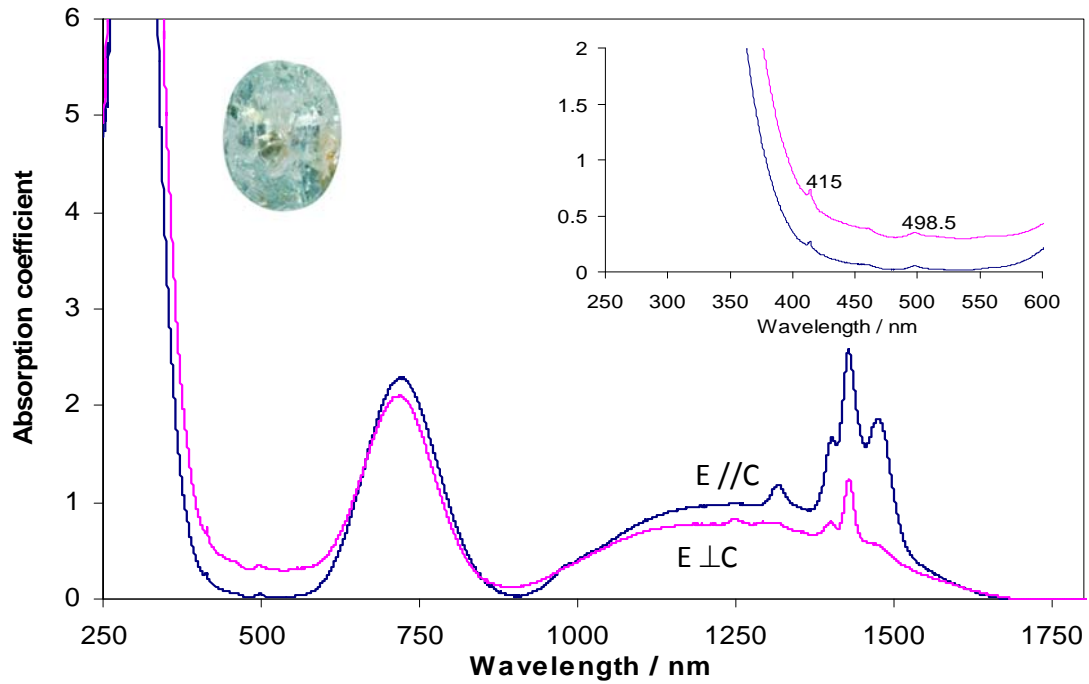


Figure 7: An example of the second of two types of UV-Vis-NIR spectra noted for this group of 30 tourmaline. FeO concentration of this sample is 7222.9 ppmw.

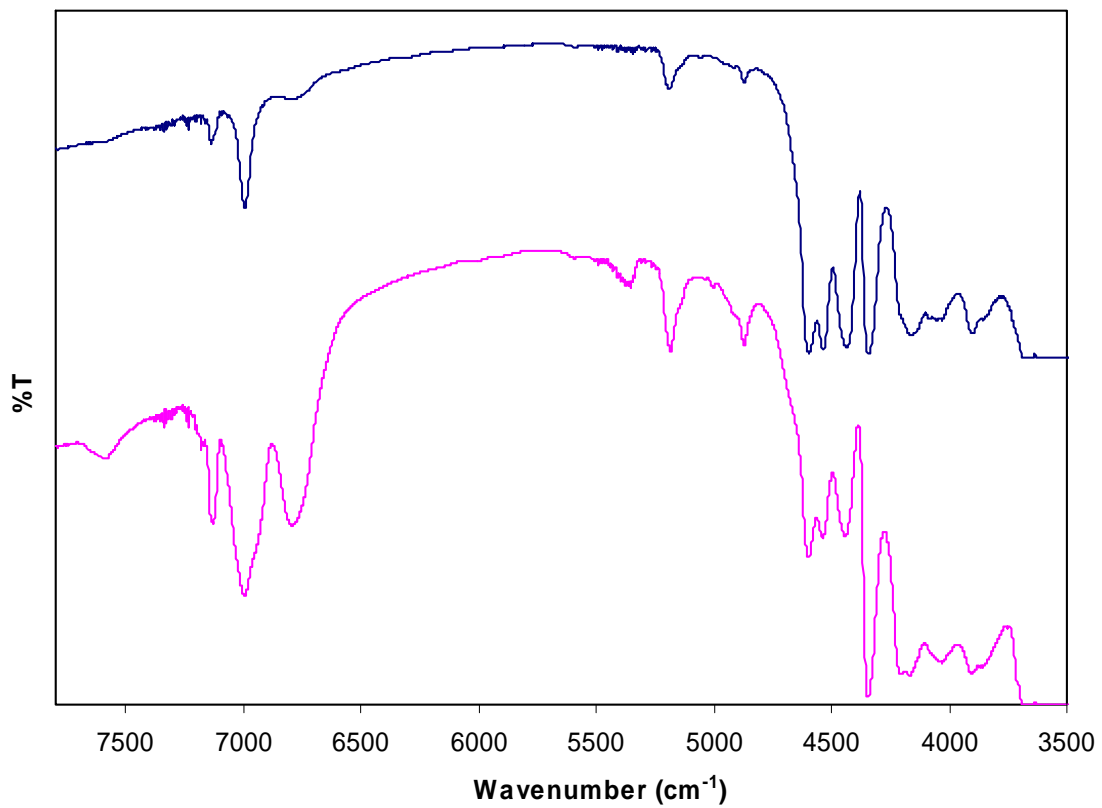


Figure 8: Examples of the infra-red spectra common to all 30 tourmaline samples.

Laser-ablation inductively coupled plasma mass spectrometry (LA-ICP-MS)

A New Wave UP-213 laser-ablation coupled with a Thermo X series II ICP-MS was used to obtain the full chemistry of all 30 samples (Figure 1). The laser-ablation parameters were; 40um spot diameter, ~10 J/cm² laser fluence, 7 Hz repetition rate, and 25 second dwell time. NIST 610 and 612 glass reference material were used to calibrate and boron was used as internal standard. Boron was assumed as 3.26% for all tourmaline in this study. All tourmaline were elbrite with 0.13-0.46 wt% CuO (1076.8 to 3636 ppmw of Cu) and 0.21-2.62 wt% MnO (1631.2 to 20260 ppmw of Mn) with the exception of two samples that did not contain Cu. In this study, most of violetish blue tourmalines have no Fe concentration while some (but not all) green tourmalines do have Fe content.

The process:

An attempt is now being made to diffuse the stones described here with Cu. Once this process is complete all stones will be examined and their data collected once more. The before and after data will be compared and presented.

To do diffusion type experiments with a new gemstone, there are usually three steps, see Table 1.

Table 1: The four steps of a diffusion experiment

Step 1
Take some pieces and heat them to various temperatures to see how high a temperature one can heat the stone without damage such as shattering, decomposition, etc.
Step 2
Imbed the stones in various oxide powders (Al ₂ O ₃ , ZnO, ZrO ₂ , MgO, etc.) and heat to the maximum safe temperature determined in step 1, for about 50 hours. Then determine which powder can be used by seeing which powder does not chemically react with the gemstone.
Step 3
Mix -300 mesh copper metal powder or copper oxide powder into the oxide chosen in step 2, and heat at the temperature determined in step 1 for 150 to 200 hours.
Step 4
Cut and polish the stones in cross section and look for evidence of diffusion.

Initial experiments involving step 1 and step 2 have been carried out on the first 15 stones (which usually damages the stones). With these stones John Emmett has included some light pink, some yellow and some Paraiba colored tourmaline. The step 1 results so far are as follows.

- The pink tourmaline becomes colorless at both 700 and 800°C and shows no damage.
- The yellow tourmaline becomes a dark gold brown color at 700 and 800°C without damage.

- The Paraiba colored tourmaline develops a very large number of internal curved fractures at both 800 and 700°C. What is interesting is that some of the fractures show a copper colored 'residue', even though no copper was involved except that naturally in the stone.

John Emmett is currently running experiments at lower temperatures to find some point at which the material does not fracture. The Paraiba type tourmalines are usually heated to about 545°C to develop good color, so that temperature should be safe except for fracturing by fluid inclusions.

Annex A:



Figure 9 Blue-green copper-bearing tourmaline (polished surface at center revealing the fracture related pinkish purple coloration), weighing 59.979 cts. Photo by Adirote Sripradi.

It has been suggested that the pinkish purple coloration surrounding surface reaching growth tubes and fractures in known natural untreated tourmaline is caused by natural radioactive fluids penetrating the stone (Koivula J. I., 2009, Koivula, 2009). Further, in the latest GRS journal (Peretti A. 2009), the authors supported this assumption and deduced that the purple “halos” are indeed most likely induced by irradiation after detecting the presence of trace concentrations of the elements uranium and thorium within in the related cracks and tubes.

Following the lead of Koivula and Peretti et.al, GIA Laboratory, Bangkok, set about a process to confirm their results with further similar specimens. In particular a blue-green copper-bearing tourmaline with pinkish purple zones associated with growth tubes and fractures was obtained (Figure 9) from Richard Hughes (Senior Vice-President, Gemstone Marketing and Testing for NCS Group Co. Ltd.) In this study, the chemistry of the tourmaline sample was examined in detail to see if any radioactive elements such as uranium or thorium could be detected in the pinkish purple zones.

Raman spectroscopy was used (prior to any fabrication) to confirm that this stone was tourmaline. The inclusions present are the classic (tourmaline) trichites, partially healed fissures and growth tubes of which some are filled with a yellow material. Pinkish purple color zones are clearly evident and appear associated with some fractures and growth tubes. (See Figure 10 to Figure 13)



Figure 10: Partially healed fissures and growth tubes in the tourmaline examined for this study

Analysis of the rough surface

Prior to any fabrication, Laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) was used to obtain a general chemical analysis of the stone and with this information establish that it was a Cu containing tourmaline as well as the most likely country of origin. The stone was found to contain 0.11 wt% CuO (847 ppmw of Cu; %RSD=12.24) and 2.25 wt% MnO (17434 ppmw of Mn; %RSD=6.66) establishing the type of tourmaline and following the use of a proprietary program, which compares several other trace elements, the country of origin was established as Mozambique (Abduriyim A., 2006).

Further, using LA- ICP-MS to map the chemistry of the rough surface a series of 24 samplings were taken of the stone from the green area right up to a fracture that contained a pinkish purple coloration (Figure 14). Neither thorium (^{232}Th) nor uranium (^{238}U) were detected in the green area however, both were detected in some pinkish purple colored areas (Figure 15 and Figure 16).



Figure 11: Yellow and red-brown hollow tubes breaking the surface of this tourmaline.



Figure 12: Unusual pinkish purple coloration in growth tubes and cracks in the sample stone.



Figure 13: An unusual pinkish purple cloud surrounding a growth tube in the tourmaline.

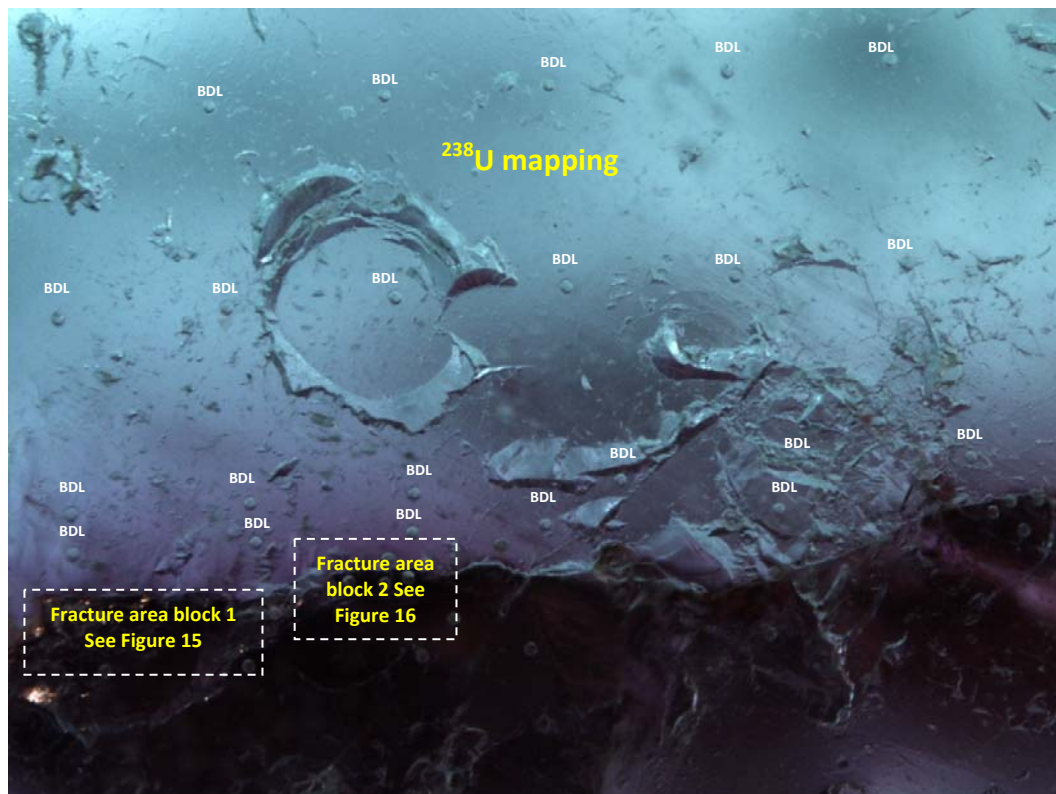


Figure 14: Photomicrograph of the ^{238}U mapping of the Mozambique tourmaline analyzed with by LA-ICP-MS (at the rough (un-ground) surface for this study. Each spot in the green area was below the detection limit (BDL) of the instrument for ^{238}U . The detection limit for ^{238}U was 0.01 ppmw).

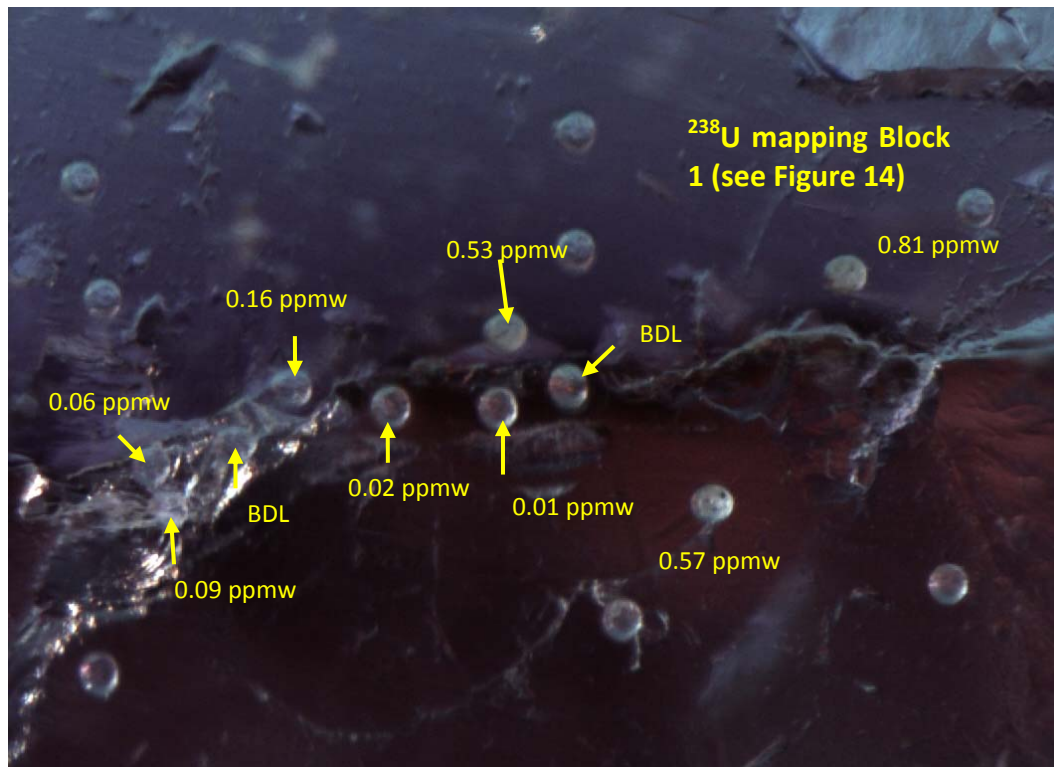


Figure 15 Enlarge photomicrograph of the ^{238}U mapping from figure 14.

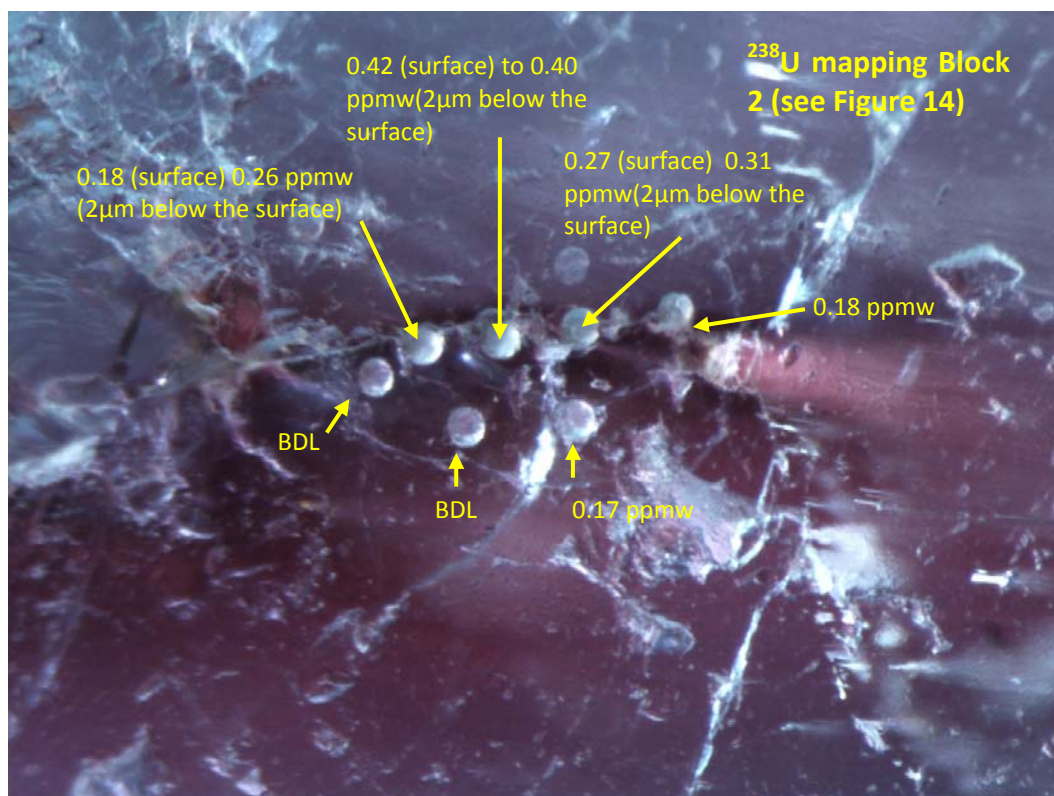


Figure 16 Enlarge photomicrograph of the ^{238}U mapping from figure 14.

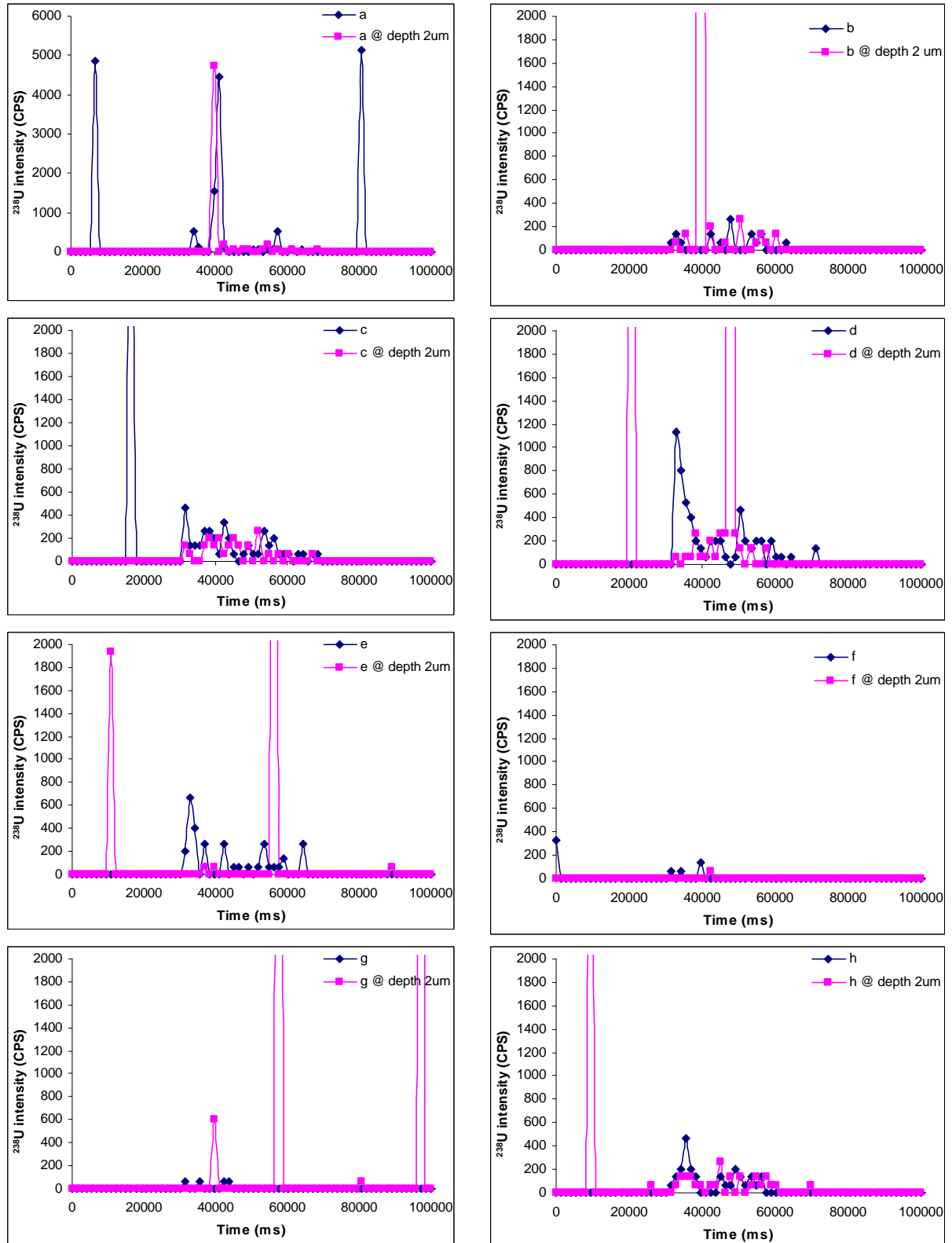


Figure 17 Photomicrograph of the spots analyzed by using LA-ICP-MS after the stone had been ground down 0.5 cm. Each spot was analyzed at the ground down surface (first number in the following pairs for each spot) and 2 μ m below the surface (second number in the following pairs for each spot).

Analysis of the fabricated surface

To reach within the unusual pinkish purple color zone and to determine that the results were not confined to the surface only, the stone was ground down in the area of a pinkish purple zone that was associated with a fracture (Figure 17), by approximately 0.5 cm and cleaned with acetone. The pinkish purple color zone was then analyzed along the fracture at the new ground down surface as well as 2 μ m below this; the analysis points are marked in Figure 17 as 'a' through to 'o'. The results show that only the analysis points within the pinkish purple zones contain ^{238}U , while areas away from the fracture and outside the color zone showed no ^{238}U concentrations. The ^{238}U concentrations for each analysis point in Figure 17 are recorded at the surface (first number in the following pairs for each spot) and 2 μ m below the surface (second number in the following pairs for each spot); BDL and 0.04 ppmw at spot a; BDL and 1.38 ppmw at spot b; BDL and 0.07 ppmw at spot c; 0.06 and 0.40 ppmw at spot d; 0.03 ppmw and BDL at spot e; BDL at spot f and g; 0.03 and BDL at spot h; 0.22 and 0.10 ppmw at spot i; 0.02, 0.02 and 0.01 ppmw at spot j; BDL at spot k; 0.32 and 0.43 at spot l; 0.02 and 0.01 ppmw at spot m; 0.04 and 0.08 ppmw at spot n; BDL and 0.04 ppmw at spot o.

The ^{238}U intensities for each analyzed point are set out in Figure 18 and the concentrations are shown in Table 2. It was also observed that the variation in ^{238}U partially correlated with the variation in ^{232}Th Figure 19.



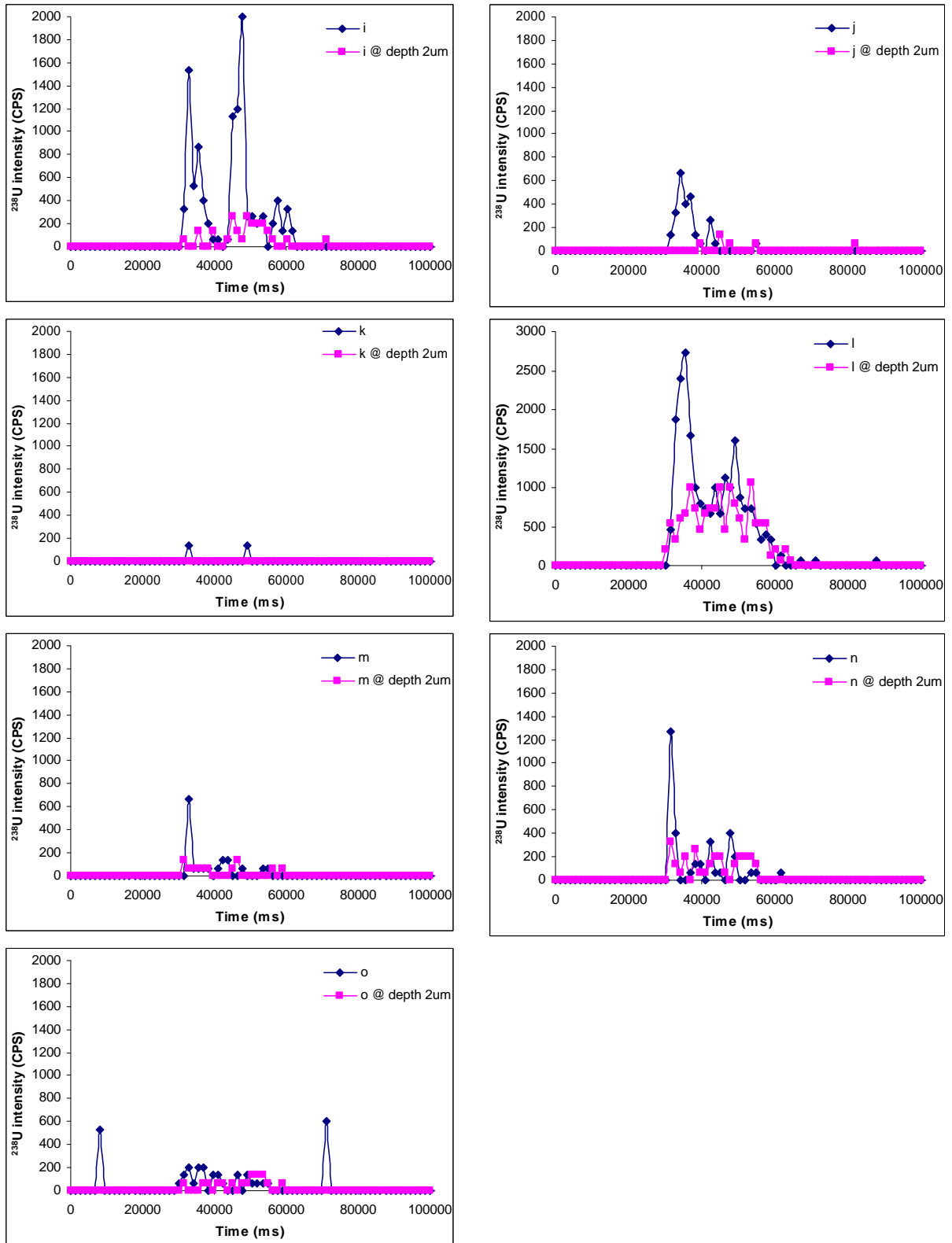


Figure 18: ^{238}U Intensity versus time on each spot in the pinkish purple colored fracture in the tourmaline in Figure 17 where blue and pink indicate laser spots on the ground down surface and $2\mu\text{m}$ below the surface, respectively.

Table 2: ^{238}U and ^{232}Th concentrations in ppmw on the pinkish purple color fracture Figure 17.

Spot (s)	^{238}U (ppmw)		^{232}Th (ppmw)	
	Ground down surface	2 μm below the ground surface	Ground down surface	2 μm below the ground surface
a	BDL	0.04	0.05	0.06
b	0.06	1.38	0.03	0.05
c	BDL	0.07	0.07	0.09
d	0.06	0.40	0.04	0.05
e	0.03	BDL	BDL	BDL
f	BDL	BDL	0.01	BDL
g	BDL	BDL	0.01	0.01
h	0.03	BDL	0.04	0.03
i	0.22	0.10	0.03	0.04
j	0.02	0.02	0.01	0.04
k	BDL	BDL	0.01	0.01
l	0.32	0.43	0.49	0.58
m	0.02	0.01	0.02	0.01
n	0.04	0.08	0.04	0.05
o	BDL	0.04	0.04	0.04

Note: The laser-ablation parameters for this experiment were; 40 μm spot diameter, ~ 10 J/cm 2 laser fluence, 7 Hz repetition rate, and 25 second dwell time. NIST 610 and 612 glass reference material were used to calibrate and boron was used as internal standard. Boron was assumed as 3.26% for this tourmaline. Detection limit (BDL) was 0.01 ppmw for both ^{238}U and ^{232}Th .

Discussion

This simple one specimen study confirms that uranium and thorium were present within a pinkish purple colored fracture in a tourmaline and that these elements are confined to the areas close to the fracture and within the pinkish purple colored zone. These results tend to support the assumptions and conclusions of Koivula and Peretti et.al that these pinkish purple areas appear to be induced by radioactive materials (fluids) entering fractures and growth tubes in tourmaline.

Clearly more specimens need to be analyzed before a better understanding of the mechanisms involved is achieved, however it would appear that an alternative and more likely cause for these color concentrations in tourmaline has now been firmly established. Certainly the assumption that these color concentrations are produced

artificially by one of the diffusion processes has been put to question and been found to be lacking in substance.

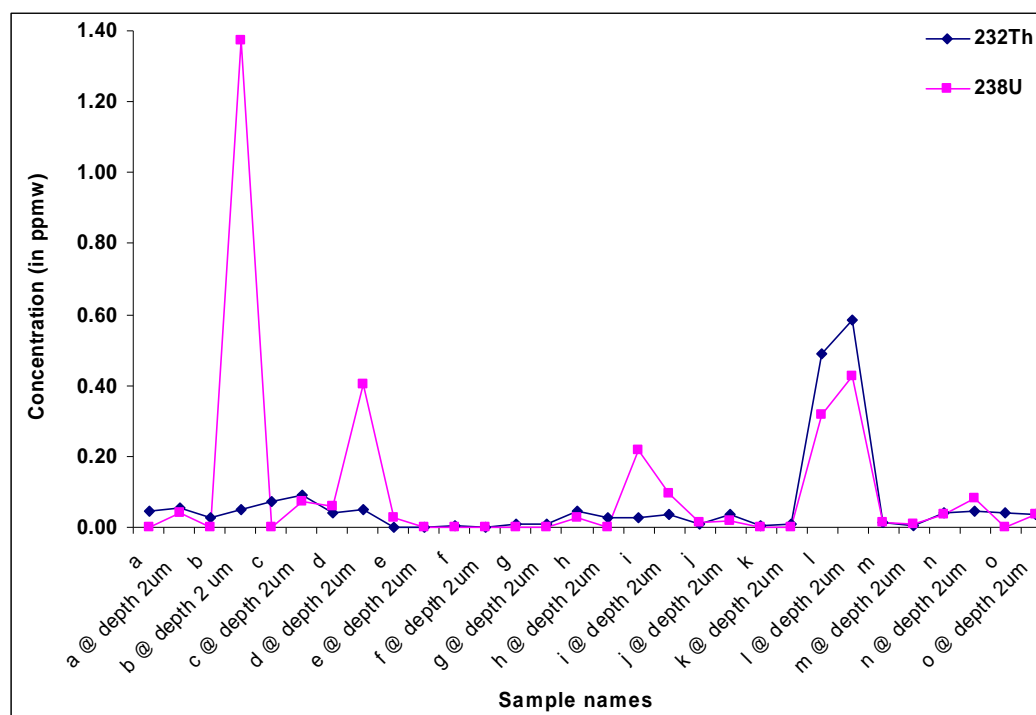


Figure 19: Variation in ^{232}Th and ^{238}U in pinkish purple colored fractures in this tourmaline.

Acknowledgements

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