Université Claude Bernard Lyon 1

Diplôme Universitaire de Gemmologie 2017/2018

New trapiche-like sapphires from Hamadan (Iran)

Niloofar Mousavipak

Nasim Mousavipak

1. INTRODUCTION TO HAMADAN SAPPHIRE

A new sapphire deposit has been discovered in Iran. This is the first deposit for this gem in the country. Resulting from a fortuitous discovery, the discoverer kept the secret until now. The exploitation of the deposit could begin in the coming years. The operating area, accessible only by 4x4, is located away from the city of Hamadan (or Hamedan) (Fig.). It is one of the main cities of Iran in the western and mountainous region of the country on the border of Iranian Kurdistan (Fig.).

We have gathered the samples from the mine .some of the samples have gem quality and their appearance is trapiche like. These sapphires are associated with the Alvand pegmatitic formation which is closely related to regional magmatic rocks saturated with aluminum, thus explaining the crystallization of corundum.

1.1. LOCATION

A new deposit of sapphires has been discovered in Iran in Hamadan. Hamadan is one of the western provinces of Persia, situated at 282 km to the southwest of Tehran between latitudes 33°59’ and 35°48’ north and longitudes 47°34’ and 49°36’ east.

Figure 1. Map of Iran with the location of Hamadan city

Figure. Satellite map (Google Earth) of the Hamedan locality

The aim of this thesis is to recognize the elements in this kind of sapphire and analyses the major elements in this sapphire and how to treat the samples (heat treatments) to improve their quality.

1.2. GEOLOGICAL CONTEXT

Metamorphic and igneous rock complexes of Hamadan area is part of a metamorphic belt called Sanandaj-Sirjan.

Pegmatitic formation of Alvand, related to regional magmatic rocks associated with low pressure metamorphism and partial melting.

Local saturation in aluminum explains the crystallization of corundum.

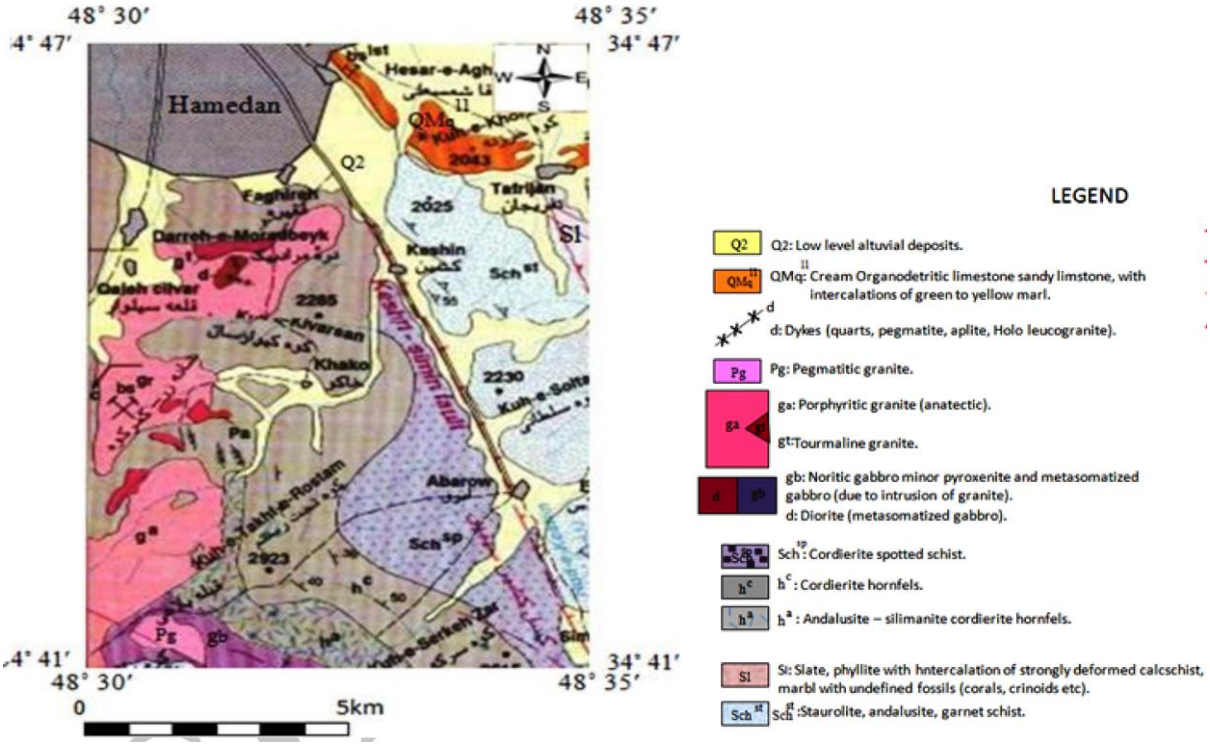

Figure. Geological map of the Hamedan area (Sheikhi & Hadi, 2015)

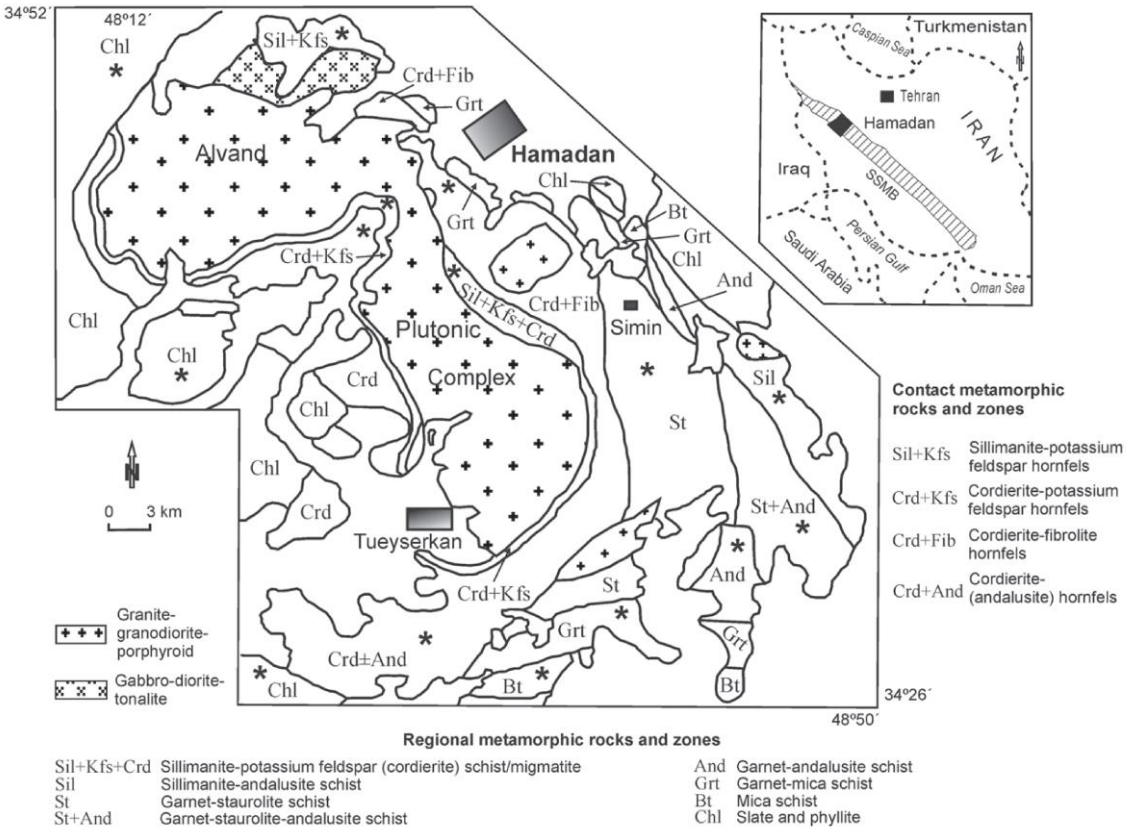

Figure. Simplified geological map of the Hamedan region in the Sanandaj-Sirjan Metamorphic Belt showing the Alvand Plutonic Complex and major metamorphic zones of the region (Sepahi et al. 2009).

1.3. SAMPLING OF HAMADAN SAPPHIRES

We have gathered large number of sapphire samples from mine and at first we have started with gemological study and finally we have treated the samples with different temperature and different time to have a best result. [When ?]

In this case we have used the infra-red and Raman spectroscopy, Renishaw and the gemological instruments for analyzing the samples with Standard Gemological Techniques and heat treatment method to improve the color of sapphire in an electric Furnace in physics department of Claude Bernard Lyon 1 university.

Figure 2. Trench with sapphire outcrops (Hamadan)

Figure 3. Sapphire from mine

Figure 4. Sapphire from mine

2. GEMOLOGICAL CHARACTERISTICS OF SAPPHIRE

Sapphire is a variety of corundum. When a corundum variety is termed "sapphire" it indicates the blue variety. It can be a pure blue but ranges from greenish blue to violetish blue. Any other color (except red, which is named ruby) will have a prefix before "sapphire", such as "yellow sapphire».

Sapphires has various color such as pink, yellow, orange, purple, green.

The name is derived from the Greek word "sappheiros" which means "blue" corundum, α-Al2O3, has a trigonal crystal symmetry. The crystal structure of corundum is hexagonal close packing of O2– anions, in which two-thirds of the octahedral sites are occupied with the aluminum ions Al3+. The coloration of corundum is mainly caused by 3d-transition metal ions, such as Cr, Ti, Fe and V, which replace the Al3+ ions in the structure during the crystallization (Bgasheva et al., 2012)

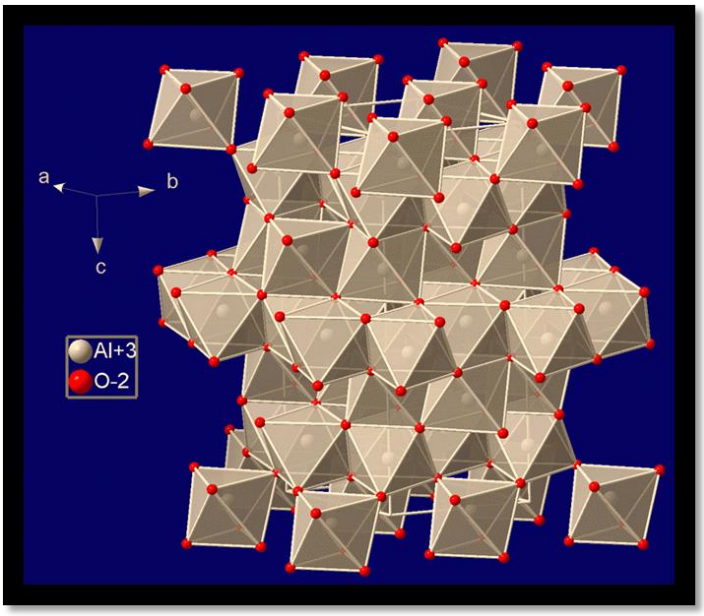

Figure 5. Crystal structure of corundum (sapphire)

Coordination?

Fe2+, Ti4+, Ti3+, Cr3+

2.1. SAPPHIRE STRUCTURE

- Family: Corundum
- Chemical composition: Al_2O_3
- Crystal system: Hexagonal
- Hardness (Mohs scale): 9
- Specific gravity: 4 ±0,05
- Refractive index: 1,762 - 1,770 +0,008 - 0,004
- Birefringence: 0,008
- Optical character: Uniaxial

Most common phenomena in sapphire are asterism, color change and trapiche.

2.2. TRAPICHE STRUCTURE

Trapiche is a spanish word which means a mill made of wooden rollers used to extract juice from cane. It was first used to describe a similar feature observed in some Colombian emeralds by McKague (1964) and studied in detail by McKague (1964) and Nassua and Jackson (1970). Trapiche textures in sapphire is usually purple-pink and whitish gray.

Trapiche sapphires occurences:

- Sutara, Russian Far East (Buravleva et al., 2016)
- Southern Vietnam (Kwansirikul et al., 2016)
- Tasmania (Vertriest et al., 2016)
- Pailin, Cambodgia (Saeseaw et al., 2017)

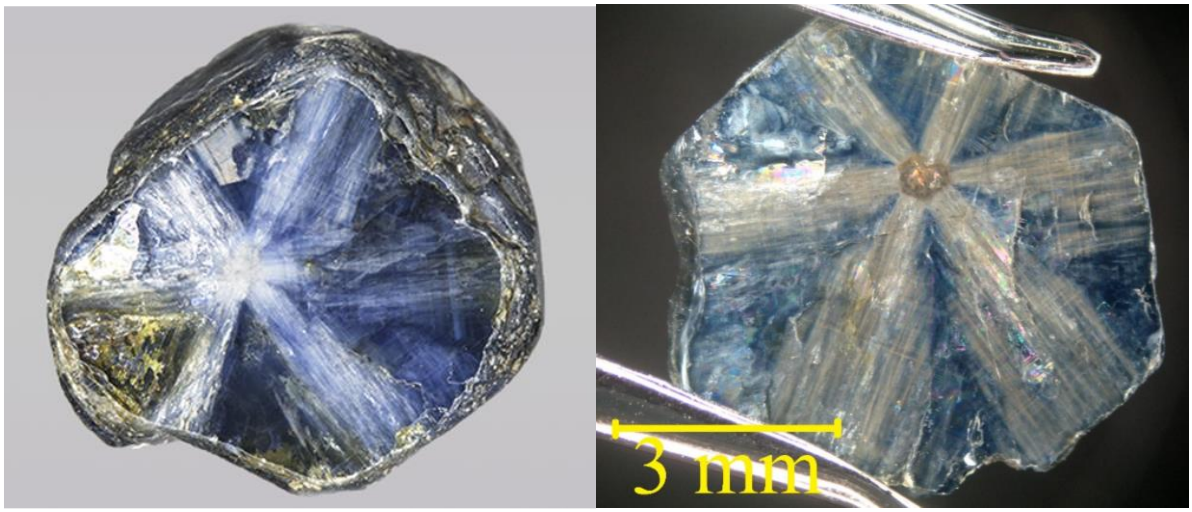

Figure. Trapiche sapphire from Tasmania (Vertriest et al., 2016) and from South Vietnam (Kwansirikul et al., 2016)

Figure . Trapiche sapphire bearing-rock from Sutara (2.8 × 2.0 cm) with mica (Buravleva et al., 2016)

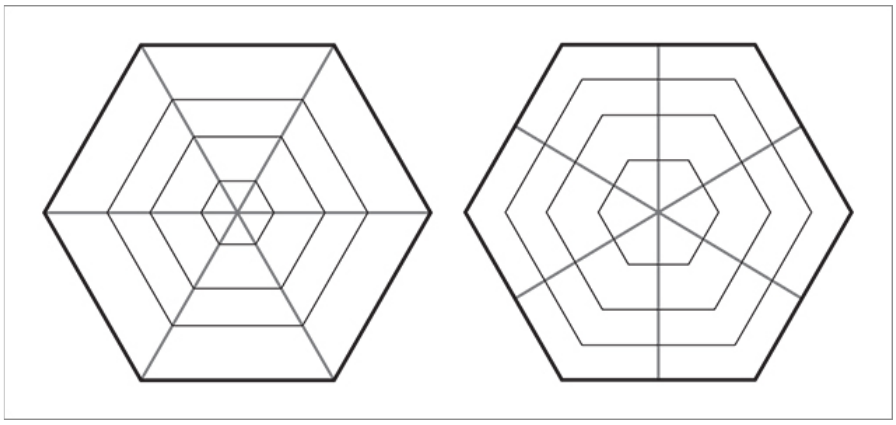

Figure. Trapiche (left) vs. trapiche-type (right) patterns in corundum (Vertriest et al., 2016)

Bergman J. (2016) Trapiche: the rising star. InColor, 32-40.

Giuliani G. & Pignatelli I. (2016) “Trapiche” vs “trapiche-like” textures in minerals, InColor, 1, 45-46.

Pal or black sapphire has no gem quality value. Color and clarity are very important for determining the gem quality of sapphire. Heat treatment could improve the color quality but in this case there is a risk: the sapphire could be broken or lose their color completely.

2.3. COLOR-ENHANCEMENT BY THERMAL TREATMENTS

Kwansirikul et al. (2016) heated trapiche-like sapphire from South Vietnam under an oxidizing condition to lighten the dark blue color of the samples, and heated under a reducing condition to intensify the blue color. Their results show that heating at 1200 °C can lighten the dark blue color and heating at 1400 °C can change brown to blue colors. Heating the samples at a temperature higher than 1400 °C can intensify the blue color in the samples.

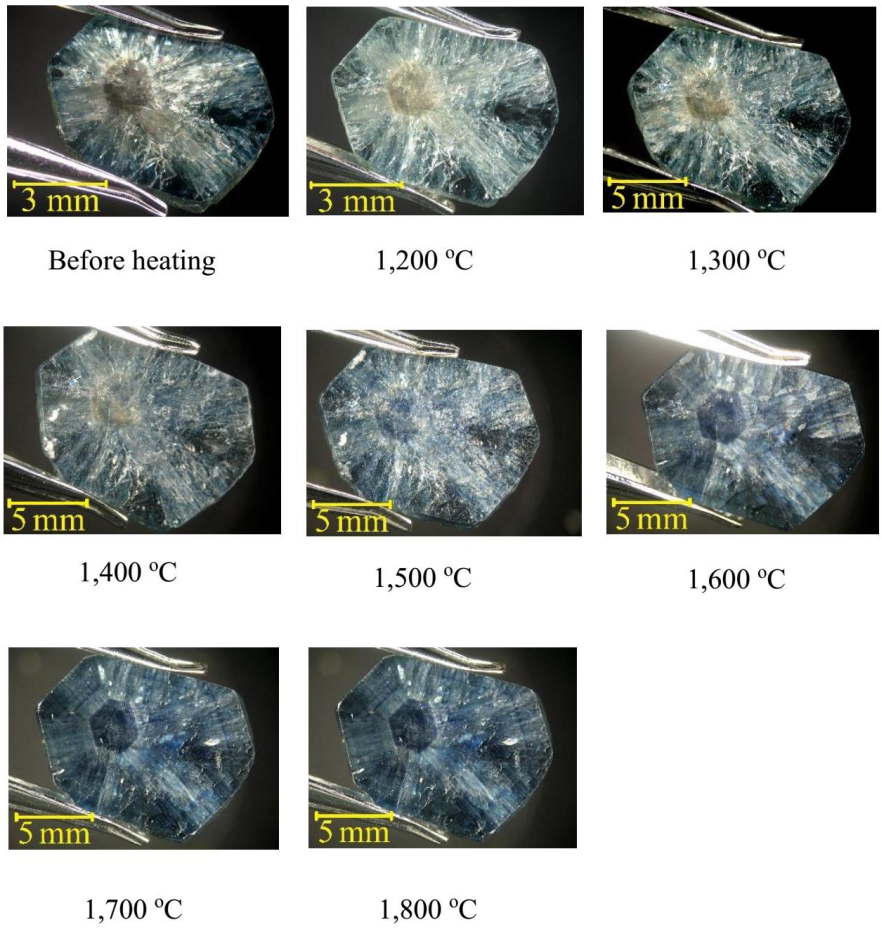

Figure. Progressive changes in trapiche-like blue sapphire sample before and after heat treatment at different maximum temperatures under oxidizing condition (Kwansirikul et al., 2016)

3. SAMPLES AND ANALYTICAL METHODS

3.1. STUDIED SAMPLES

Description of the samples, number, size….

3.2. ANALYTICAL METHODS

The spectroscopy is a branch of physics that deals with the study of the radiations absorbed, reflected, emitted or scatted by a substance. Radiation deals with photons (electromagnetic radiation) but spectroscopy deals with interaction of neutrons, electrons and protons. There is variety of spectroscopies as many as the number of possible classification according to the radiation used the state of the matter (solid, liquid, or gas) interacting with the radiation.

3.2.1. OPTICAL ABSORPTION

We used OceanOptics USB2000 portable spectrometer to record the absorption's signal of samples.

Optical absorption spectra were conducted using a compact integration sphere and an Ocean Optics USB2000 spectrometer allowing to record absorption spectra without getting through the samples. The sphere is non-absorbent.

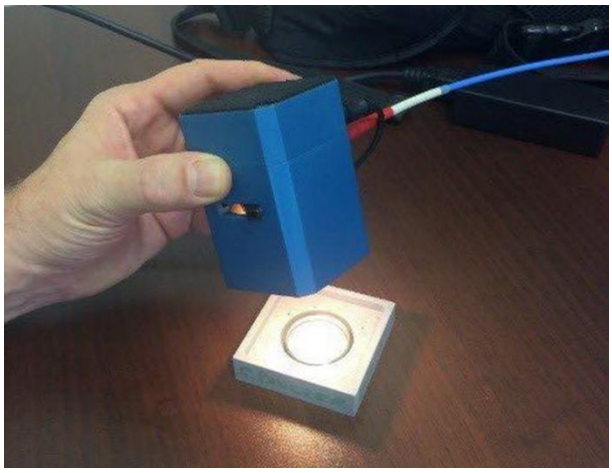

Figure 7. Portable optical absorption spectroscopy

3.2.2. RAMAN SPECTROSCOPY

Sir Chandrasekhara Venkata (physics -1930) discovered the Raman in 1928 accidently. When a beam of colored light entered a liquid, a fraction of the light scattered was of a different color, dependent on material property. This radiation effect of molecular scattering of light bears his name as 'Raman Effect', from which many applications in photonic communications and spectroscopy evolved. Nowadays Raman spectroscopy is very important in gemological study and it perform non-destructive identification and characterization of gemstones.

We have used Raman Renishaw for taking the Raman shift of our samples. In that case we have tested the Raman in different parts of our samples. For examples in trapiche part of our samples and another part of theme. After taking the Raman shift we have used the CrystalSleuth software for determining their minerals

Figure 9 .Raman Renishaw spectrometer

Equipments ?

Laser excitations?

3.2.3. PHOTOLUMINESCENCE

Excitation 473 nm using the Aramis spectrometer

3.2.4. X-RAY DIFFRACTION

Powder diffraction of the sapphire samples conducted at the Henri Longchambon laboratory (ISA, Lyon)

Photo

3.2.5. XRF ANALYSES

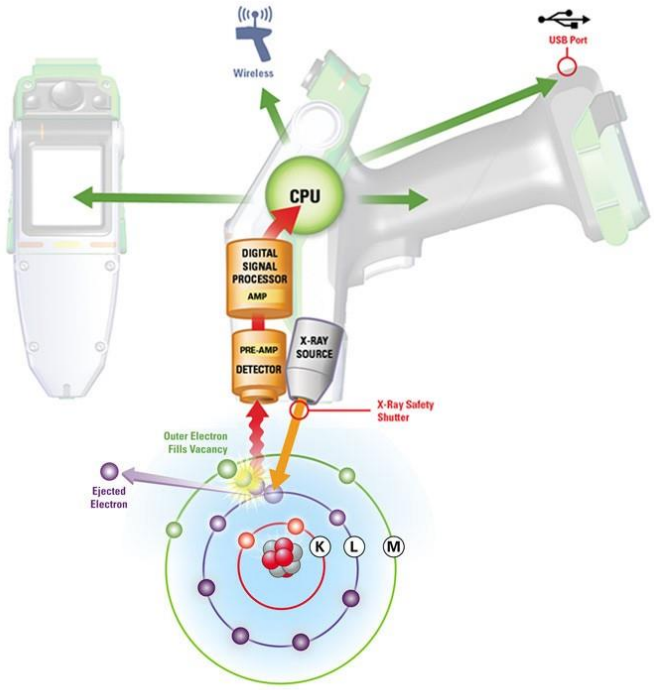

Figure. Set-up principle of the Niton handheld x-ray fluorescence spectrometer

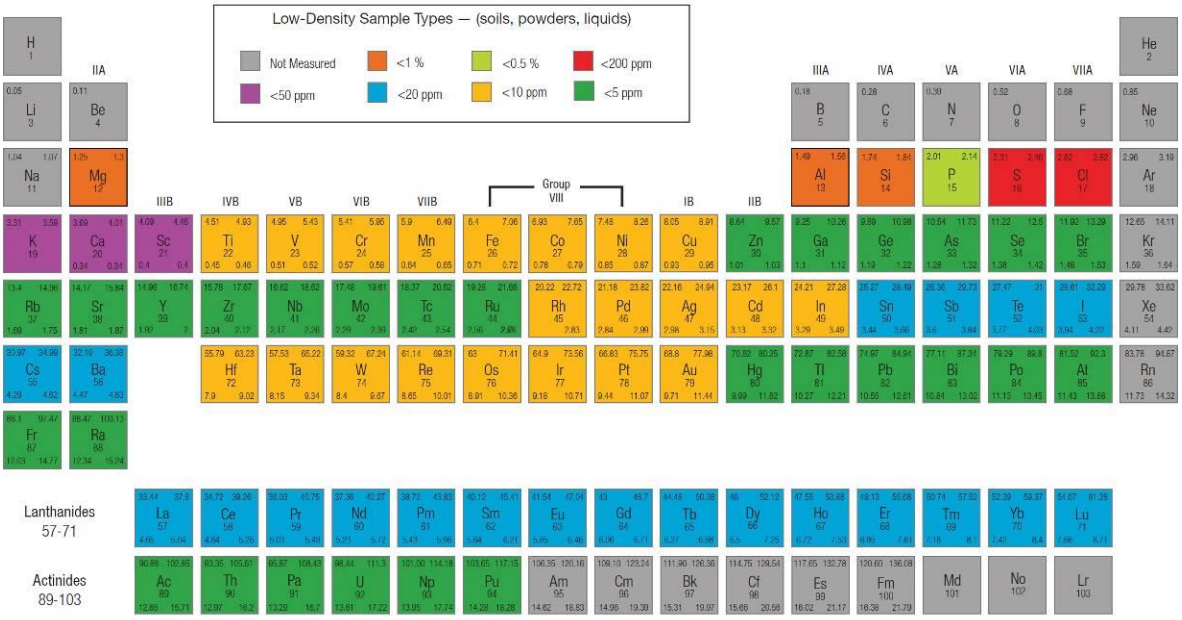

Figure. Periodic table of the element analyzed by XRF with their limit of detection.

4. RESULTS

4.1. OPTICAL ABSORPTION

The atom, ion or molecule has quantified energy levels, on which are distributed its electrons. When they absorb a photon of energy, the energy level increase

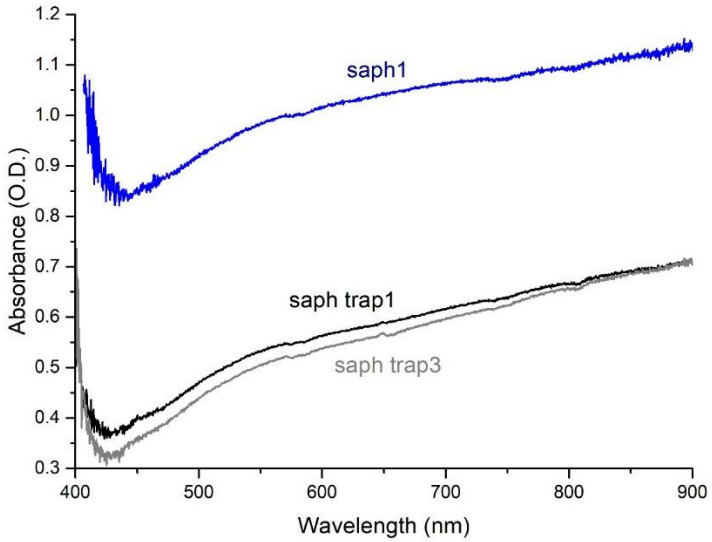

Figure 8. Optical absorption spectra of Hamadan sapphire samples

(The absorption data will be added)

4.2. RAMAN SPECTROMETRY

What excitation ?

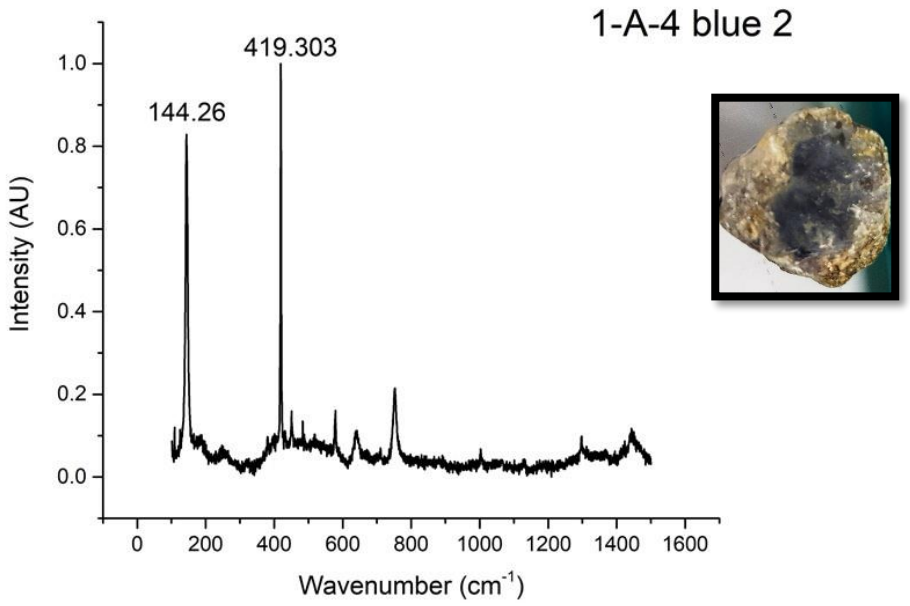

Figure 9. Raman spectrum of the blue part of the trapiche sapphire

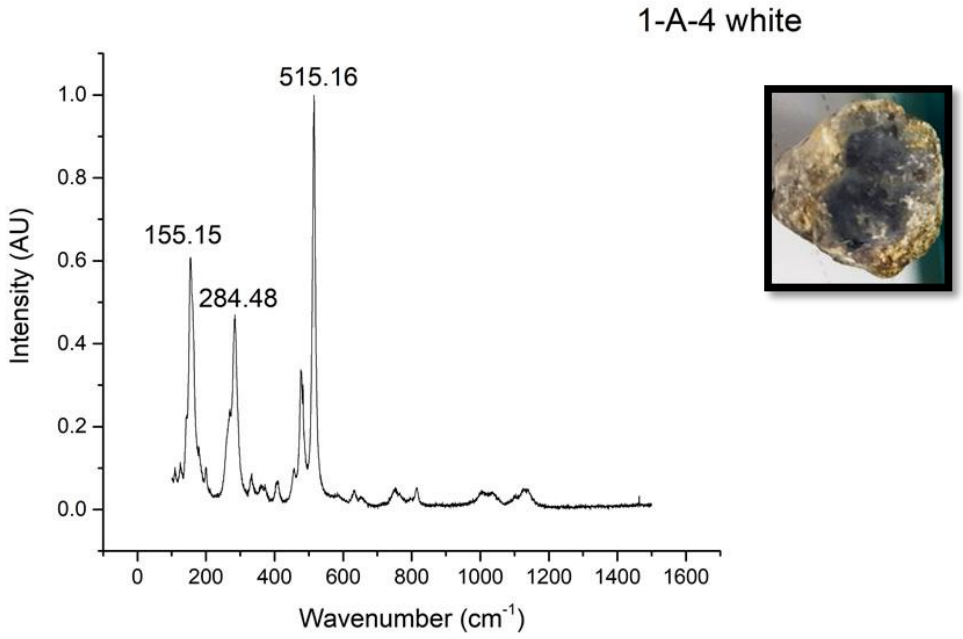

FIGURE 11- RAMAN SPECTRUM OF THE WHITE PART OF SAMPLE 1

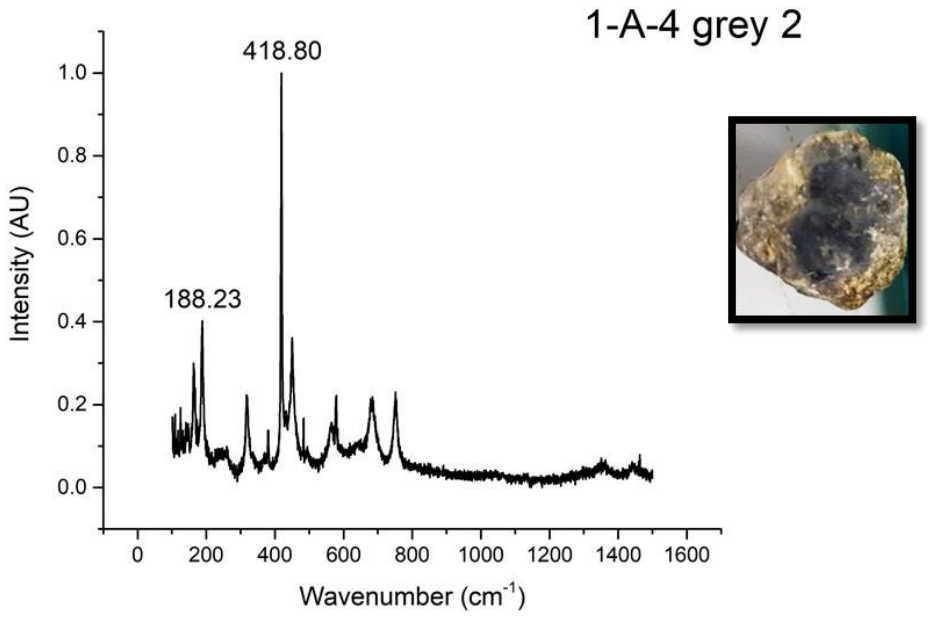

FIGURE 12- RAMAN SPECTRUM OF THE GREY PART OF SAMPLE 1

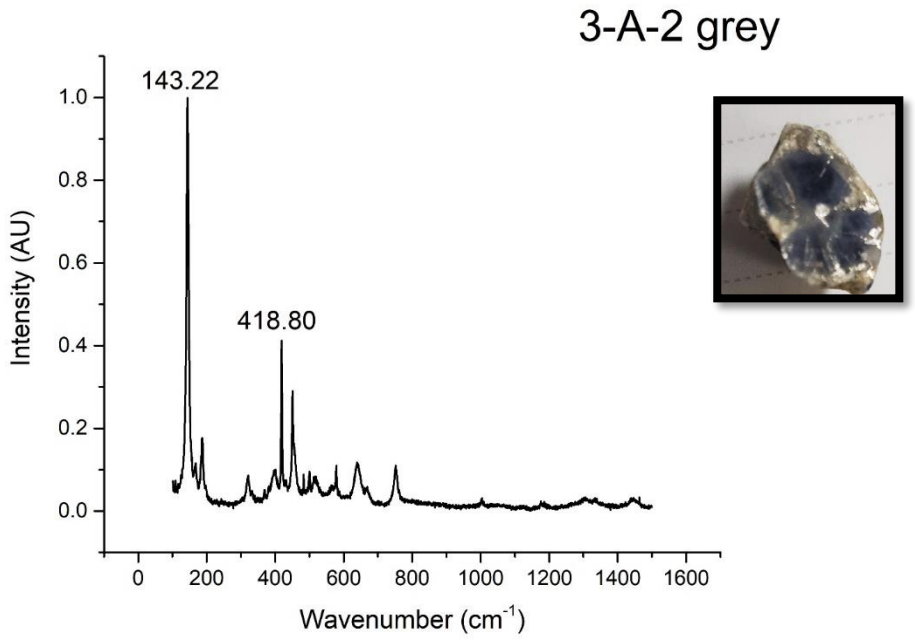

FIGURE 13- RAMAN SPECTRUM OF THE GREY PART OF SAMPLE 1

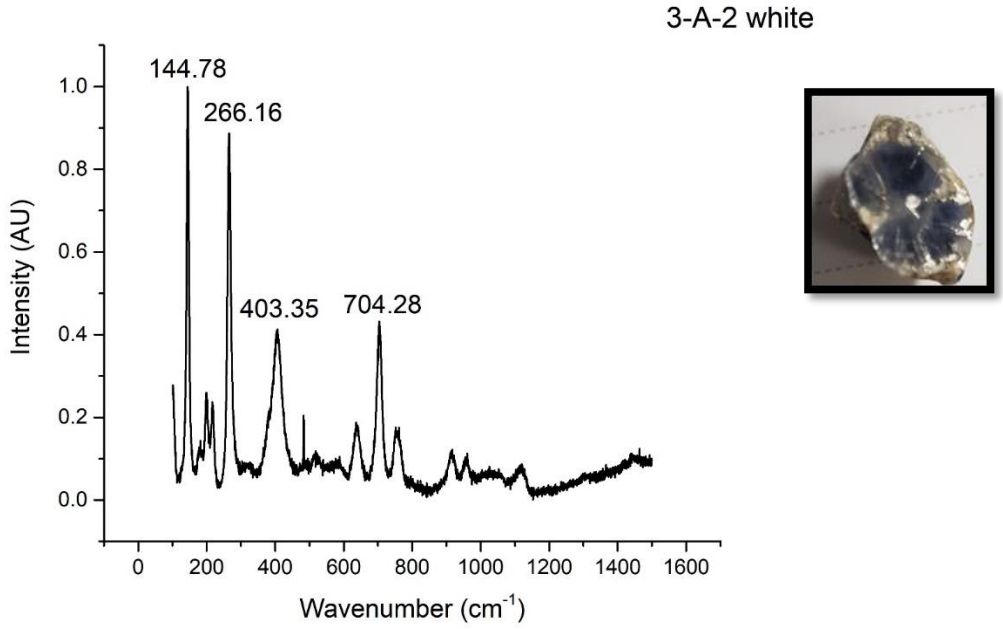

FIGURE 14- RAMAN SPECTRUM OF THE GREY PART OF SAMPLE 1

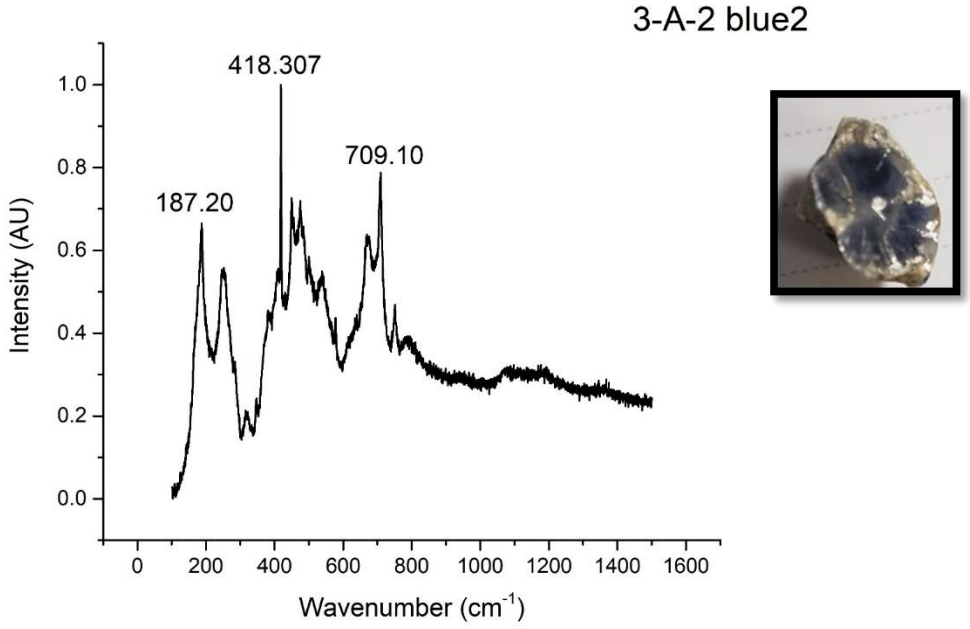

FIGURE 15- RAMAN SPECTRUM OF THE BLUE PART OF SAMPLE 1

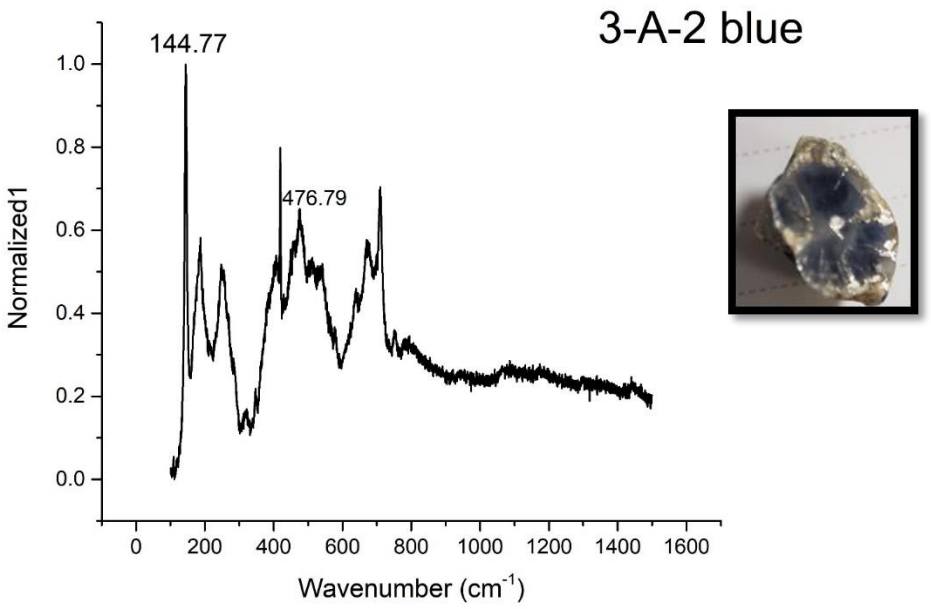

FIGURE 16- RAMAN SPECTRUM OF THE BLUE PART OF SAMPLE 1

IDENTIFYING THE RAMAN SIGNATURE WITH CRYSTALSLEUTH SOFTWARE

After the taking the Raman shift With the Renishaw Raman spectroscopy. We have used the Crystal Sleuth software in order to determine the minerals of each samples.

HOW TO USE CRYSTALSLEUTH [TO BE IN ANNEXES]

Select the open or spectrum file

Remove spectrum background with the Remove Background' button in the toolbar

Raman search

SAPPHIRE DATA ANALYZING WITH CRYSTALSLEUTH

We have analyzed our Raman shift that we have taken with Renishaw, in crystal sleuth we have find out that the different mineral exist in our trapiche sapphire.the result is:

Sapphire 1-

4.3. PHOTOLUMINESCENCE

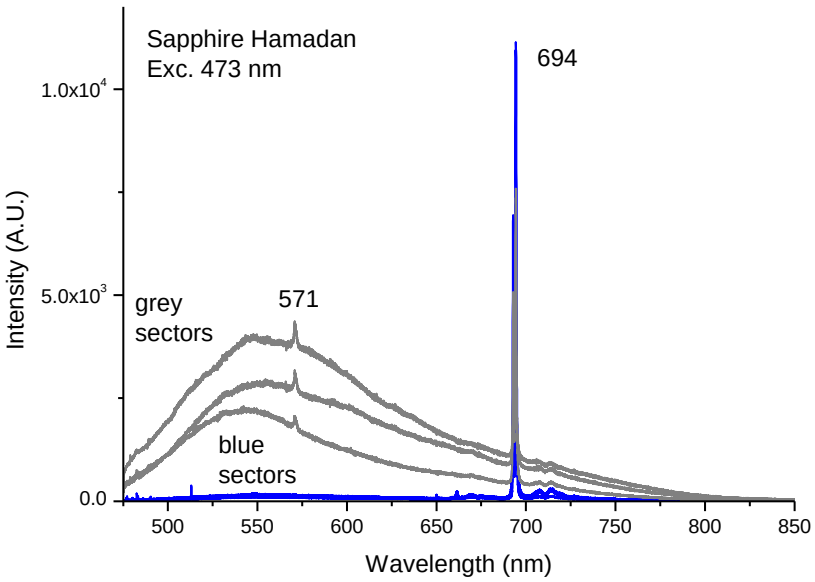

Figure. Photoluminescence spectra of Hamadan trapiche-like sapphire (Exc. 473 nm). Blue and grey sectors.

4.4. X-RAY DIFFRACTION (XRD)

4.5. X-RAY FLUORESCENCE (XRF)

	Mean Blue sector	*SD*	Mean Grey sector	*SD*
nb	8		2	
Fe	2321	*507*	7063	*4805*
Ti	1094	*140*	775	*151*
Cr	bld	bld	0	
V	bld	bld	0	

Figure. XRF mean concentration of sapphire blue and grey sectors

5. THERMAL TREATMENTS AND COLOR ENHANCEMENT

Samples cut in slices

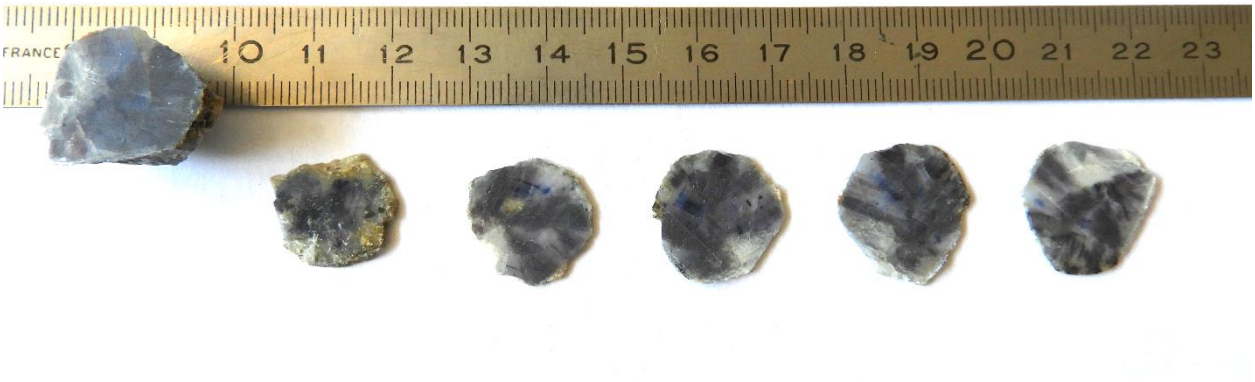

Figure. Sapphire crystal cut in slices

5.1. THERMAL TREATMENTS

List here the conditions of treatment

5.2. COLOR MODIFICATIONS

Comparison of photos before and after heating

Figure.

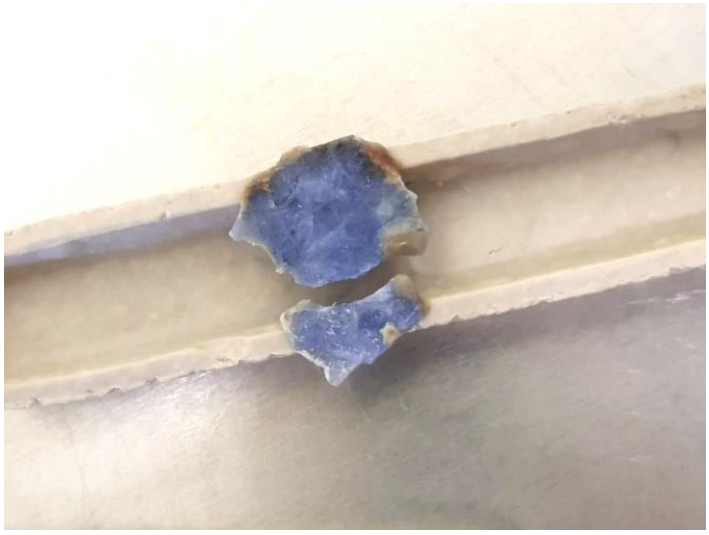

Figure.

5.3. CHARACTERIZATION OF HEATED SAPPHIRES

RAMAN

XRD

CONCLUSION

To be modified

The sapphires of the Hamadan area are characterized by their dark color, a high percentage of trapiche-like structure and a high concentration of iron (>2000 ppm) and titanium (>1000 ppm). The blue corundum sectors present a high amount of diaspore (and lazulite ?) while the greyish ones have numerous muscovite inclusions. Those associated phases could have syn-crystallized with corundum and/or generated during alteration.

Thermal treatments will be conducted to improve the sapphire transparency and color.

If this treatment will be efficient, it may be a chance for the gem trade in Iran.

BIBLIOGRAPHY

Bergman J. (2016) Trapiche: the rising star. InColor, 32-40.

Buravleva S.Y. et al. (2016) Sapphires from the Sutara placer in the Russian Far East. Gems & Gemology, 52, 3, 252-264.

Giuliani G. & Pignatelli I. (2016) “Trapiche” vs “trapiche-like” textures in minerals, InColor, 1, 45-46.

Kwansirikul K. et al. (2016) – Experimental heat treating of trapiche-like blue sapphire of Southern Vietnam. Suranaree J. Sci. Technol. 23(4):409-419.

Saeseaw S. et al. (2017) An in-depth study of blue sapphires from Pailin, Cambodgia. GIA News from research, December 22.

Sepahi A. A., Jafari S. R. and Mani-Kashani S. (2009) Low pressure migmatites from the Sanandaj-Sirjan metamorphic belt in the Hamedan region (Iran). Geologica Carpathica, 2009, 60, 2, 107-119.

Sheikhi G.R. & Hadi A.M. (2015) Pegmatites characteristics of south Hamadan: sapphire gemological study approach. Geochemistry, 4, 3, 269-282.

Kwansirikul K., Thanasuthipitak P. and Thanasuthipitak T. (2016) Experimental heat treating trapiche-like blue sapphire of South Vietnam. Suranaree J. Sci. Technol., 23, 4, 409-419.

Vertriest W. et al. (2016) Trapiche-type sapphire from Tasmania. Gems & Gemology, 52, 4, 430-431.