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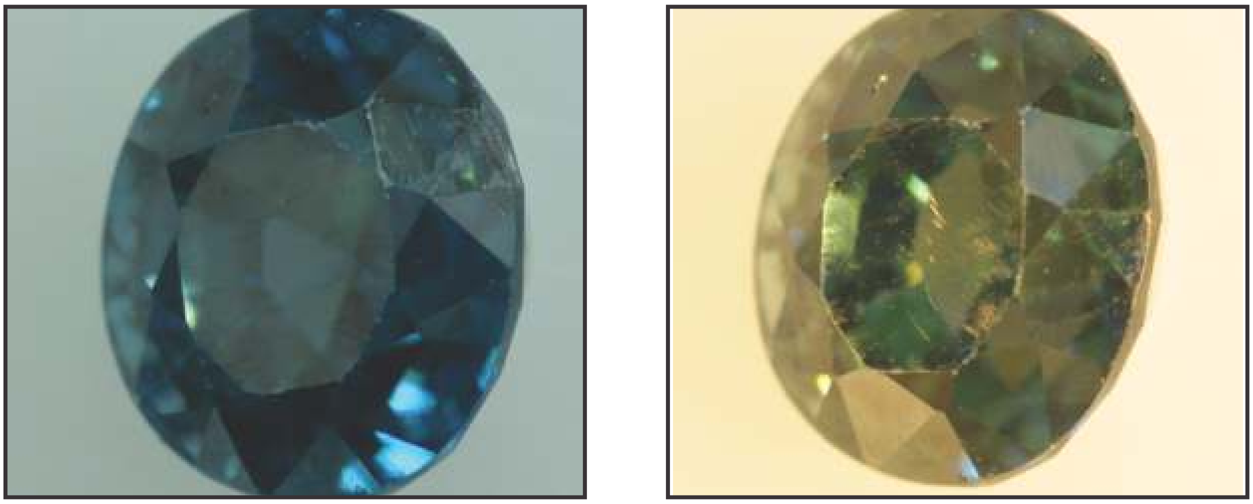
Gemstones showing unusual colour changes

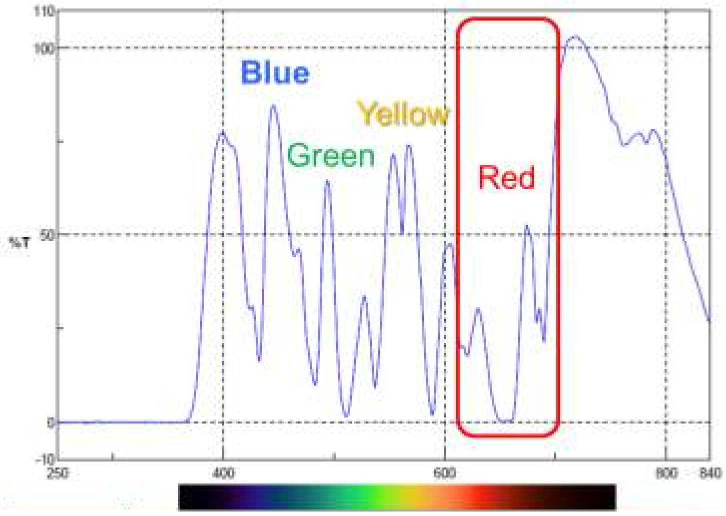
Masaki Furuya
Japan Germany Gemmological Laboratory, Kofu, Japan

The regular color change in gemstone is identified as showing green in the daylight and changing to red in the incandescent light like alexandrite. But the color change in gemstones is not so simple. There are some gemstones showing unusual color changes.

The Burmese blue zircon shows the so-called "reverse color change" which is an opposite direction color change from regular ones as it changes from blue to green under the incandescent light. (Regular color change stones show green under daylight) This is because of its complex absorption like below chart. And this complex absorption is due to the rare earth elements such as Y, Er, Ho, Dy and also U4+(Bosshart, 2006). In this spectrum, there are many valleys of transmission. And the transmission in red is relativelyweak but also it has strong yellow transmission. It does not give a red color under incandescent light and but gives yellow tint to blue body of zircon to cause green color.

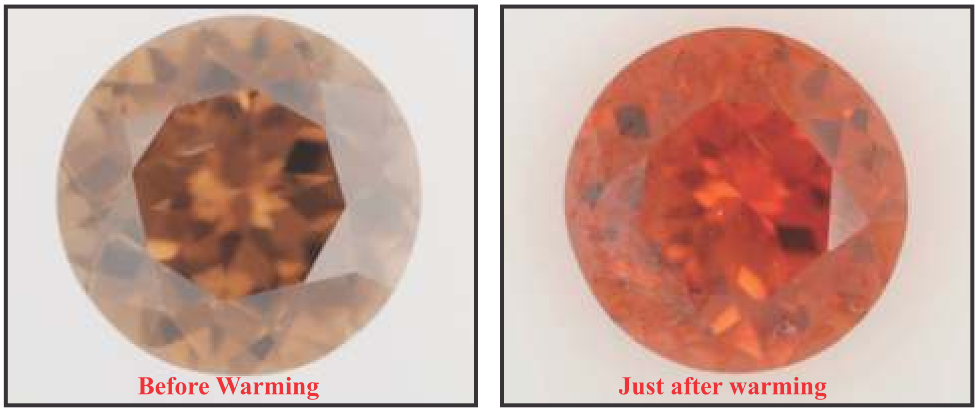


"Reverse color change" zircon from Myanmar

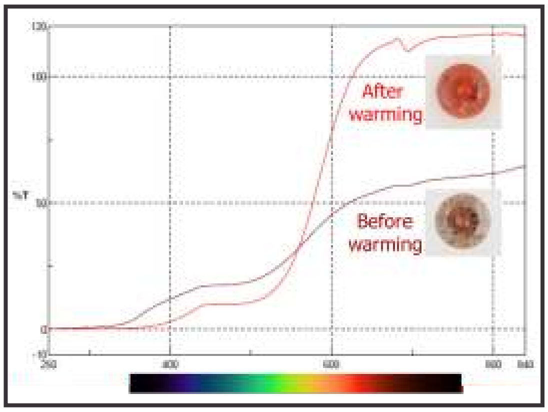


Transmission spectrum of reverse color change zircon

The other unusual color change in zircon is teneblescence (thermo chromism). This type of zircon does not change its color by different lighting, but it changes its color by quick warming. It changes the color from brown to bright orange red just by warming it with a lighter on the spoon in 20-30 seconds (200-300C). And it turns back in 3 to 10 minutes by leaving it or in just a few second by strong lighting.


Before Warming
Just after warming

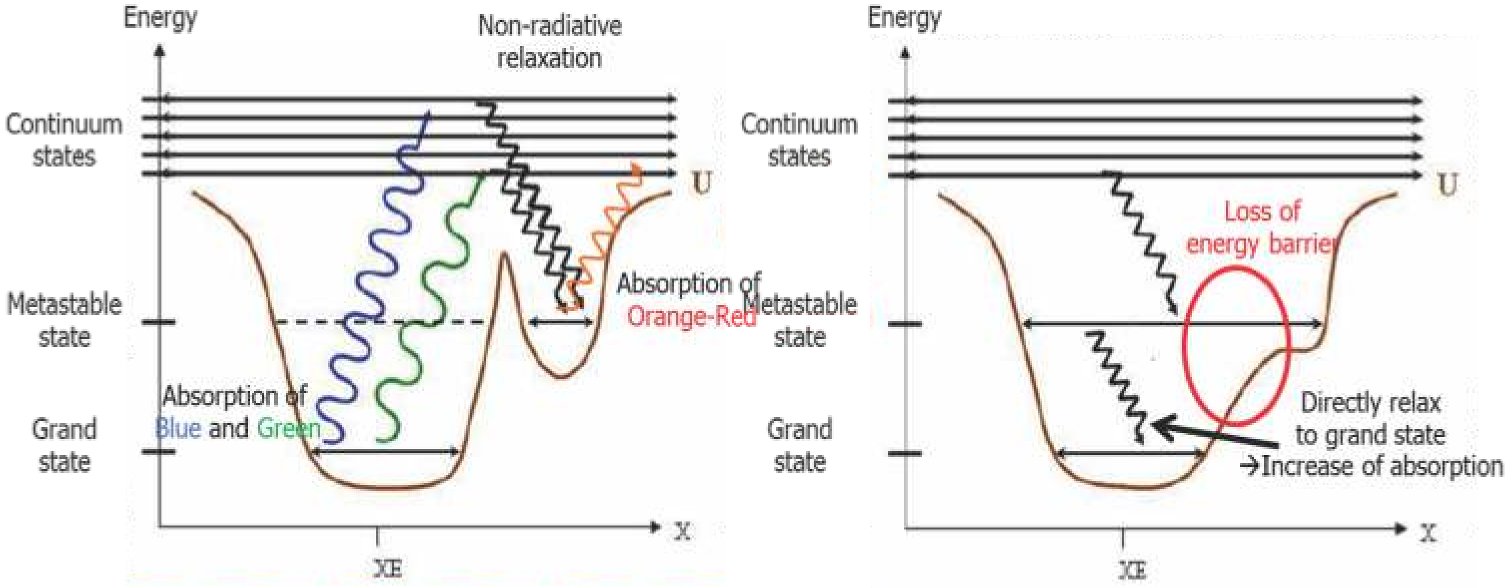
Tenebrescent zircon from Africa



The change of spectra of tenebrescent zircon by warming

In its spectra of before warming, there were halfway transmissions of violet to green (380-550nm) and a little higher transmission of orange to red, these gave the dull brown color. And after the heating, the former transmission decreased and latter increased. This clear spectrum gives the vivid orange color to the stone.

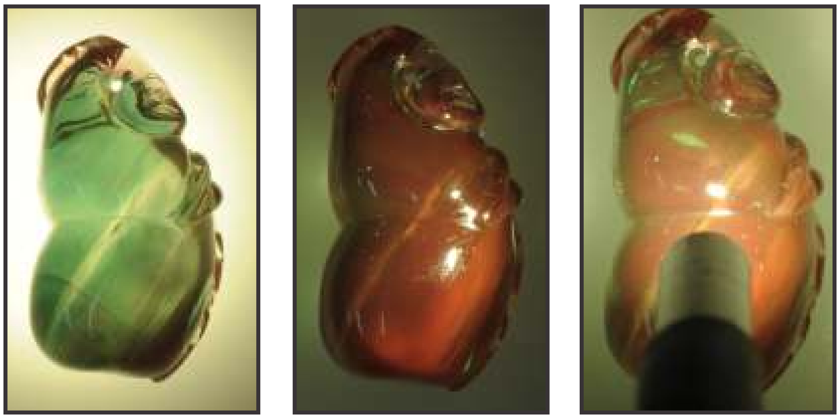
This mechanism is complex. Generally the some elections at grand state absorb the some specific energy of the light (blue and green) to get excited to change to continuum states. These some "specific" absorptions of energy cause the color of orange-red (which is not absorbed). And after the electron get excited, it relaxes (get back) to the grand state to absorb the light again. But in this type of zircon there is an energy barrier, which stops the relaxing electron at the metastable state and it again causes a little absorption of orange-red. Thus, before warming, there were hallwayabsorptions of blue, green and orange-red. However this energy barrier disappears under the high temperature.Thus when it is warmed enough, the excited election which absorbs blue and green light can directly return to grand state and it also loses orange-red absorption and increase blue and green absorption and loses the orange-red absorption. This mechanism causes the color change in zircon. Also, this energy barrier can be created again by absorbing blue and green light. It also causes the returning of the color after warming.



Before warming
After warming

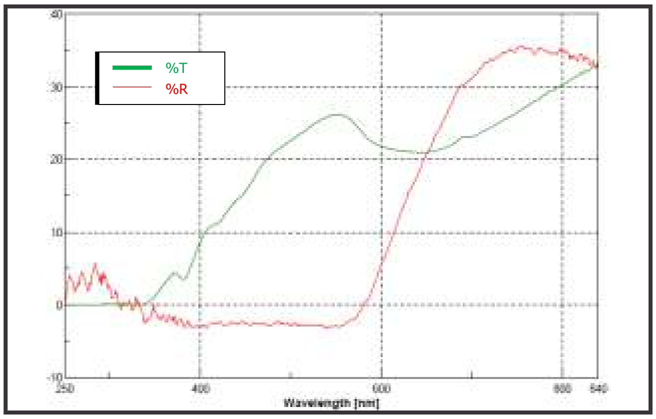
The mechanism of tenebrescnec in zircon (Cited from BrianQ's post in GemologyOnline)

And the last gemstone showing the unusual color change is andesine from Tibet. Some andesine shows green color when it is lighted with transmitted light from specific direction but it shows orange color by reflected light from side or above. This color change is obvious with the comparison of transmission and reflection spectra. In a transmission spectrum, there is wide strong transmission at green. But in a reflection, there is only orange to red reflection.



Lighted from below **Lighted from side** **Lighted from above**

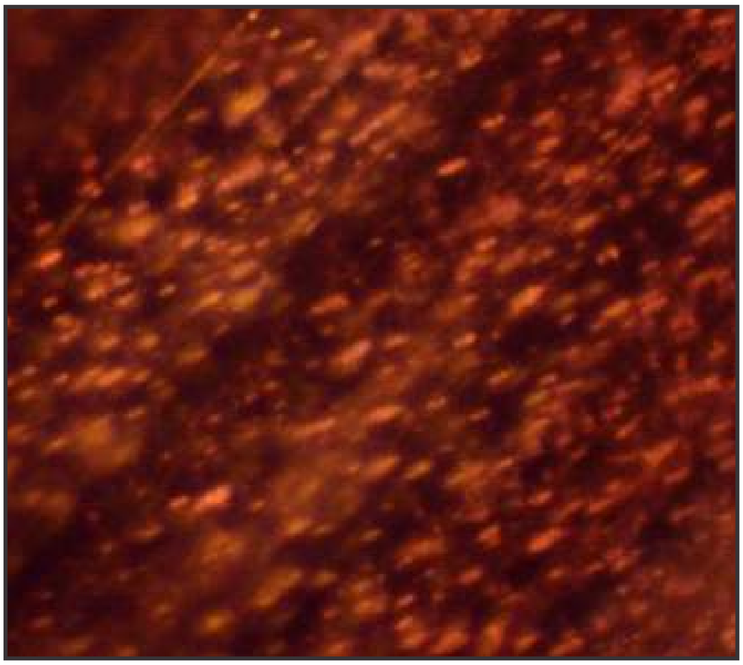
Carving of andesine from Tibet (Lighted with same light from different directions)



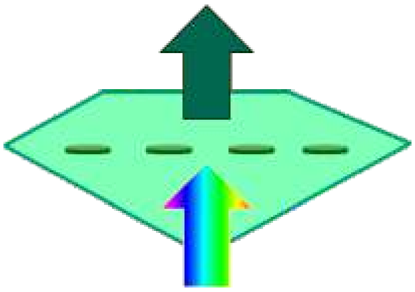
UV-Vis spectra of andesine with transmission and reflection measurements

This effect is due to andesine's copper platelet inclusion allocated parallel to each other. In andesine, if the copper platelet lighted from below to transmit, it shows green color. But when it is lighted from other direction and the light is reflected at the copper platelet, it shows orange-red color.

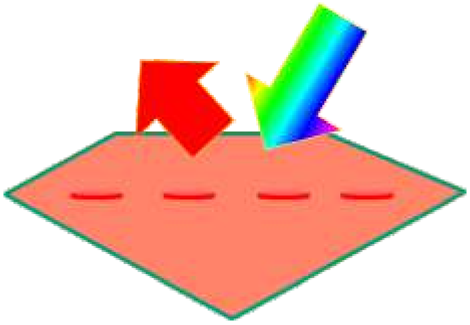
But this type of effect is seen only when the copper platelet inclusion is enough thin and tiny. Thus the feature of the platelet inclusion may be like a Usambara effect of tourmaline.



Copper platelet inclusion in andesine



Transmitted from perpendicular to platelet



Lighted from above

The different appearance of green andesine with different lighting

As mentioned above, the mechanism of color change in gemstone is not simple and there are many types of color changes. Such features are also one of the attractive aspects of the gemstones.

References:

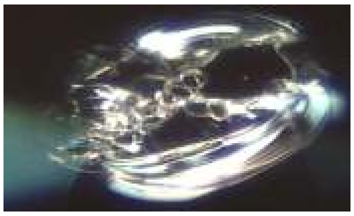
Bosshart G.et al., Gems &Gemology 2006 Summer "Rare reverse color change in blue zircon from Myanmar"
BrainQ, Gemology online Gemology chat 2009 "Thread of zircon"

Two rare gems with a similar appearance: serendibite and sapphirine

Miran Heo and Kook-Whee Kwak
Wooshin Gemological Institute of Korea

Figure 1. 1.81ct serendibite (left) and 0.42ct sapphirine (right)

Recently, two rare gems with a similar appearance, a serendibite and a sapphirine, were examined in Wooshin (Figure 1). These stones were of a round and an oval cut respectively, with dark colors which reminiscent of the ink blue sapphires from Australia, and transmitted light weakly. Serendibite and sapphirine are alumino- silicate minerals belonging to the Sapphirine supergroup. Within the supergroup, Ca-dominant serendibite with the chemical formula $Ca_4(Mg_6Al_6)O4[Si_6B_3Al_3O_{36}]$ belongs to the Rhönite group, while Mg-dominant sapphirine with the chemical formula $Mg4(Mg3Al9)O4[Si3Al9O36]$ belongs to the Sapphirine group. The name serendibite comes from the old Arab name Serendib for Sri Lanka, where the stone was first found, and sapphirine was named for its resemblance to sapphire. Here we present the gemological and analytical test results of the serendibite and sapphirine samples.

Sample	**Serendibite**	**Sapphirine**
Weight	1.81ct	0.42ct
Color	Dark greenish blue	Dark greenish blue
R.I.	1.704-1.709	1.701-1.726
Birefringence	0.005	0.025
S.G.	3.45	3.49
Pleochroism	Strong Dark blue/greenish yellow/green	Strong Dark blue/greenish blue/yellow
LW & SW UV	Inert	Inert
Internal features	 Rectangular crystal inclusion	 Crystalline inclusions surrounded by a liquid film

Spectroscopic Properties

Infrared spectroscopy

In the range of 4000 ~ 2000cm^{-1}, sapphirine exhibited broad absorption band centered at 3548 and 3435cm^{-1}, while serendibte exhibited broad absorption band centered at 3495 and 3330cm^{-1}, weak absorption at 2635cm^{-1}, and a strong absorption peak at 2560 cm^{-1} (Figure 2). Sapphirine absorbed at 962, 809, 713 cm^{-1} and serendibite absorbed at 970 and 807 cm^{-1} in the range of 2000 ~ 500 cm^{-1}.

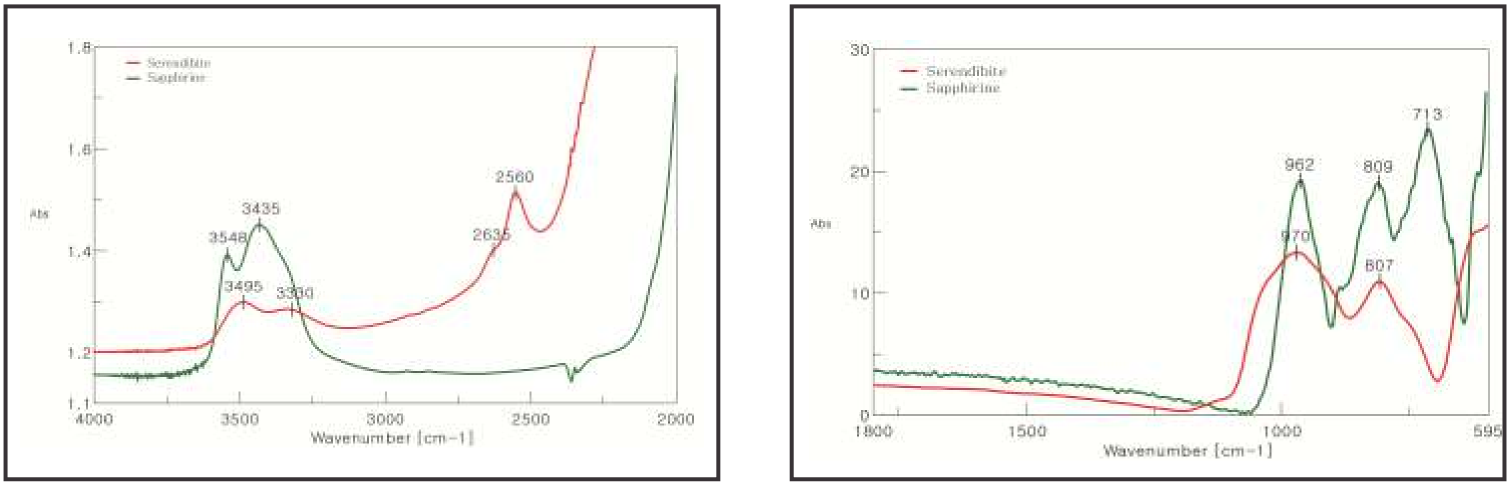


Figure 2. Infrared spectra of serendibite (red) and sapphirine (green)

UV-Vis spectroscopy

Serendibite had weak absorptions at 412, 438, 463nm, and deep absorption centered at around 670nm. The absorption band around 670nm is known to be related to the strong pleochroism. Sapphirine showed weak absorptions at 436 and 461nm.

PL(Photoluminescence) spectroscopy

Serendibite measured with 514-nm laser excitation showed a strong PL peak at 690 nm and a weak peak at 713 nm (Figure 3). Sapphirine showed PL peaks at 680 and 685nm, a strong peak at 688 nm, and weak peaks at 700 and 710 nm. The results of the spectroscopic analyses including the infrared and PL spectra of the two samples are consistent with the serendibite and sapphirine measurement data in Gems & Gemology [2] and the RRUFF [3].

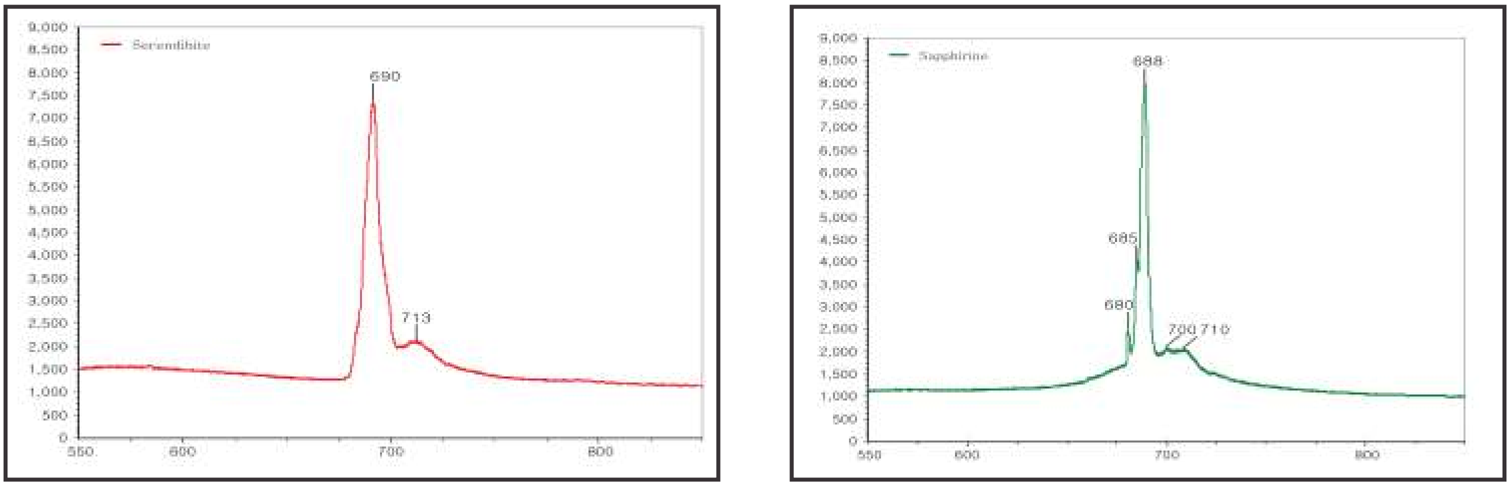


Figure 3. PL spectra of serendibite (left) and sapphirine (right)

In the EDXRF analysis, serendibite was found to contain trace elements such as Fe, Ti, V, Cr, and Mn in addition to the main components Al, Si, Ca, and Mg. Sapphirine contained main components Al, Mg. Si and trace elements such as Fe, Ga, Cr, Mn, and K.

References

[1] E. S. Grew, U. Hålenius, M. Pasero, J. Barbier, Recommended nomenclature for the sapphirine and surinamite groups (sapphirine supergroup), Mineralogical Magazine, 72(4), pp. 839-878, 2008

[2] Karl Schmetzer, George Bosshart, Heinz-Jürgen Bernhardt, Edward J. Gübelin, and Christopher P. Smith, Serendibite from Sri Lanka, Gems & Gemology, 38(1), pp. 73-79, 2002

[3] RRUFF project (http://rruff.info)

A Report on the new ornamental gemstone from Pakistan: Sannan–Skarn

At the recently concluded GIT2016 Henry A. Hänni, Leander Franz & Zhou Wei, Basel, Switzerland presented an interesting paper on a new deposit of complex fine-grained rocks found in Western Pakistan. The material is characterised by its more or less green colour, due to chrome. The mineral components vary strongly in short distances and the minerals (hydrogrossular, diopside, aegirine, winchite, pectolite, chlorite, natrolite, sodalite etc.) are not well known by gemmologists. A common term to name the material is skarn, as it describes a rock formed by metasomatic replacement of a parent rock, commonly a calc-silicate rock, transformed in a metamorphic process. Sannan is a specific modifier that describes the skarn from the new occurrence.

Earlier in the Hong Kong Jewellery and Gem Fair September 2015 a significant volume of this green material was sold to gemstone dealers under the name Maw Sit Sit. The most interesting question was if a second prominent source of Maw Sit Sit outside of Myanmar was found in Pakistan. After a preliminary test it became clear that this material has nothing in common with Maw Sit Sit although specific gravity and refractive index may show overlaying data.

Fig 1 Sannan Skarn from Pakistan

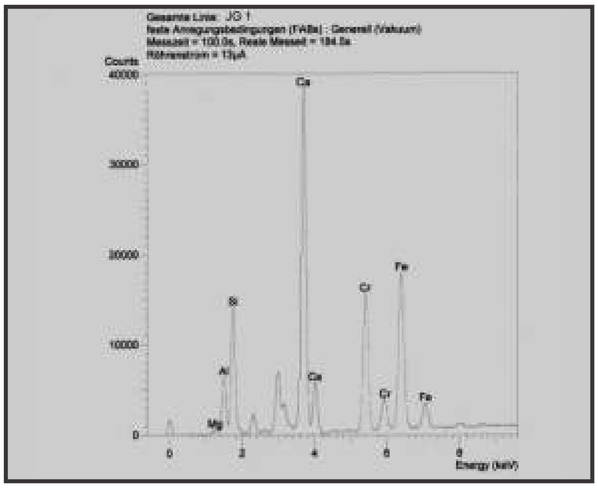


Fig 2 EDXRF spectrum of Sannan Skarn

Sannaan Skarn is greenish-grey to dark green coloured rock and has a fine grained, randomly oriented texture. Specific gravity is determined to be 3.26. When this rock was analysed winchite, aegirine, grossular, diopside, chlorite, pectolite, natrolite, and some accessory minerals were identified. Specifically, the results from this thin section analyses are as follows: Under the microscope, euhedral crystals of zoned hydrogrossular, up to 0.6 mm wide are found in the dark green areas. They are surrounded by large green prismatic diopside of grey-brownish colour and often encased by streaks and bands of chlorite. In the brighter areas, chlorite is missing and calcite occurs in fissures. Tiny accessory opaque minerals are octahedra of magnetite. The rock is a calcite-chlorite-hydrogrossular-diopside skarn. Thin sections show radiating clusters of short prismatic aegirine (Na-Fe-pyroxene, $NaFe^{3+}Si_2O_6$) dominate with single aegirine crystals of up to 0.3 mm showing a strong pleochroism from luminous green to yellow-green. In interspaces, subordinate fillings of agglomerated pectolite ($NaCa_2Si_3O_8(OH)$) form yellow-brown prismatic crystals. The lighter green margin shows a mylonitic texture with lenticular and linear concentrations of pectolite and chlorite as well as heavily fractured aegirine. The rock is a chlorite-pectolite-aegirine skarn. Winchite crystals (sodic-calcic amphibole $(CaNa)Mg_4(Al,Fe^{3+})Si_8O_{22}(OH)_2$) of up to 1 mm size are inter grown with smaller, dark green aegirine crystals. The white zones consist purely of sodalite ($Na_8(Al_6Si_6O_{24})Cl_2$). The rock is thus an aegirine-natrolite-winchite skarn with sodalitic parts. The results of the crystal-optical analysis were confirmed by micro-Raman spectroscopy.

Qualitative chemical results were performed with ED-XRF. The analyses vary from sample to sample, due to their inhomogeneous composition. In all samples, the presence of Cr was identified. As a representative ED-XRF analysis of Sannan-Skarn spectrum is shown Fig2. Calcium is a main constituent in all samples. This represents a main difference to Maw Sit Sit. The umbrella under which the varying green rocks from the new source in Belochistan (W-Pakistan) can be named is skarn. Sannan-Skarn is the recommended trade name for this new ornamental gemstone. The green colour is due to chromium that is present in most of the constituent minerals. The opaque material is suitable for cabochons, spheres, and carvings and other jewellery items. It is not to be confused with Maw Sit Sit from which it is clearly different. Sannan-Skarn can either be differentiated from Maw Sit Sit by EDXRF by checking for Ca, or by micro-Raman spectroscopy through the identification of aegirine, winchite, hydrogrossular and the other minerals listed above. Similar results are expected by using micro FTIR.

(With the kind permission of Dr. Henry Hänni)

Sphene from India

Jayshree Panjikar and Aatish Panjikar
PANGEMTECH- Panjikar Gem research & Tech Institute, Pune India

In the recent years Mettur Taluk of Salem district of Tamil Nadu has been producing sphene or titanite found in some hydrothermal veins of very high grade metamorphosed rocks of this area.

Fig1. Reddish brown colour sphene from Mettur

Gemmological and spectroscopic features of these faceted samples were investigated. Laser Raman, FTIR, UV-Vis spectroscopy and EDXRF were used. The characteristic microscopic inclusions were a variety of fluid inclusions, two phase, liquid films, liquid filled capillaries, feathers, healed feathers, large cavities filled with mother liquor very similar to inclusions in aquamarine only difference being the very high birefringence giving rise to double outlined inclusions and very high grade dispersion. These fluid inclusions were observed to be of different generations with specific orientation with respect to the c-axis. Nature of inclusions, spectroscopic analyses have helped to throw light on the crystallization of the sphene in the pegmatite.

Fig2. Green colour sphene from Mettur

Materials and Methods: Samples of sphene were examined using standard gemmological methods to determine their optical properties, hydrostatic specific gravity, UV fluorescence and microscopic features.

Non-polarized UV-Vis spectra for all samples were collected using JASCO F660 spectrophotometer over the 350nm - 800nm range. Mid Infrared spectra of 5 samples were collected in transmission mode by a JASCO FT/IR-6600 with a resolution of 4cm-1.

Qualitative analyses were carried out using EDXRF. Raman spectra were used to determine the nature of the inclusions.

Results

The colour of the faceted sphene ranged from strong yellowish green to reddish brown to greenish yellow, with diaphaneity transparent with sub adamantine lustre. Strong pleochroism was noted in all the stones with prominent colours as green, orange and yellow. All stones displayed strong dispersion with red and green flashes. Refractive indices were over the limit. Specific gravity was determined using hydrostatic method and was in the range, SG= 3.52-3.56. All samples were totally inert under long wave and short wave ultraviolet radiations. In both incandescent light and natural daylight 2 of the sphene appeared brownish yellow and when observed under 6500K the colour changed to brownish green.

Microscopic inclusions: Microscopic examination of specimen revealed strong doubling, straight and angular transparent growth lines, and partially-healed fractures, with two phase inclusions, negative crystals containing a liquid and a doubly refractive crystal and few small crystals. Crystal of apatite was observed just below the surface of one of the specimen (Fig 3). Two phase inclusions were noticed in all specimens (Fig 4). Fluid inclusions were prominent with liquid feathers crisscrossing rarely individual liquid feather was observed (Fig 5). High birefringence of sphene causes strong doubling (Fig 6) and also the dispersion makes inclusions spectacular. Excessive temperature gives rise to stretched feathers of liquid (Fig 7) and cooling of the volatiles trapped in the crystal gives rise to the formation of droplets of liquid (Fig 8). Liquid filled capillaries, feathers, healed feathers, stretched feathers, large cavities filled with mother liquor very similar to inclusions in aquamarine only difference being the very high birefringence giving rise to double outlined inclusions and very high grade dispersion were the characteristic features.

Fig 3 Crystal of Apatite

Fig 4 Two phase inclusions

Fig 5 Liquid feathers

Fig6 Strong doubling

Fig 7 Stretched feathers of liquid

Fig 8 Droplets of liquid

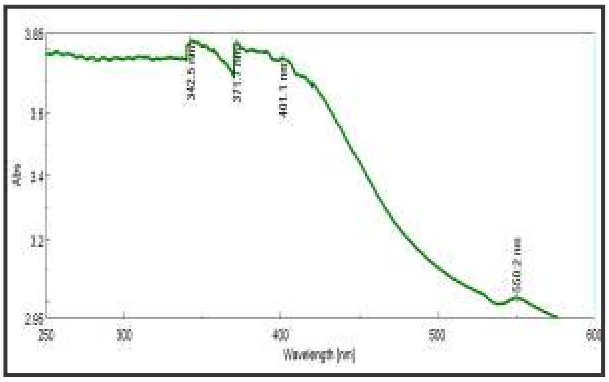


Fig 9 The UV-Vis spectrum of sphene from Mettur

UV-Vis Spectra: The UV-Vis spectra were typical for sphene with two peaks at 371nm and 342nm related to Fe3+. Absorption peak at 550nm is attributed to rare earth elements typical for sphene (Fig 9)

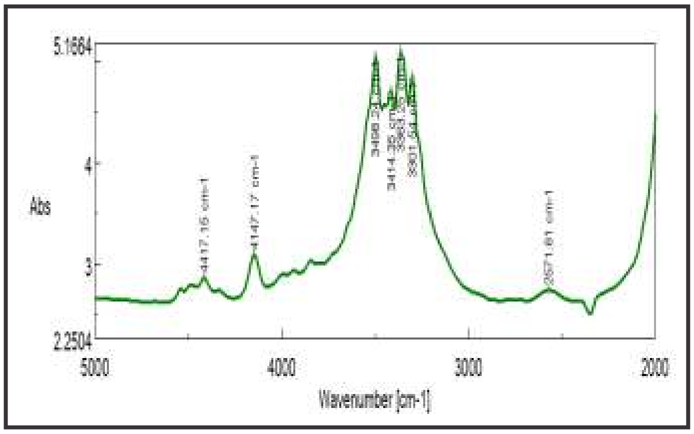


Fig 10 The FTIR spectrum of sphene from Mettur

FTIR Spectra

The infrared spectra (Fig 10) collected in the mid IR range of 2000 to 5000cm-1 using Jasco FTIR contained the absorption bands typical for sphene. Absorption bands for water molecules were seen in the region of 3300 to 3400cm-1 .

Chemical composition:

The EDXRF spectroscopy indicated Si, Ca, and Ti as expected along with varying amounts of Al, Fe, Nb, Zr, and Nd with some Y.

Discussion:

Mettur sphene has crystalline inclusions of apatite, mica and a long elongated crystal which may be an amphibole. Most of the investigated sphene had a large variety of fluid inclusions which are characteristic for pegmatites with significant hydrothermal activity. This would mean that the sphene have crystallized from a hot aqueous solution. The evidence for which can be further had from the fluid inclusions which show network of fluids. Besides, these fluid inclusions are distinctly categorised into first and second generation inclusions. The first generation fluid inclusions are larger and oriented with respect to the "c" axis whereas the other inclusions do not show any particular orientation. Gogoi et al have interpreted from petrographic and mineral chemical studies of this area that when basaltic magma intruded the crystallizing granite magma chamber, initially the two compositionally different magmas may have existed as separate entities. The first interaction that took place between the two phases is diffusion of heat from the relatively hotter mafic magma to the colder felsic one followed by diffusion of elemental components like K and incompatible elements from the felsic to the mafic domain. Once thermal equilibrium was attained between the mafic and felsic melts, it allowed the felsic magma to back-vein into the mafic magma. The influx of back-veined felsic melt into the mafic system disrupted the equilibrium conditions in the mafic domain wherein minerals like amphibole, plagioclase and biotite were crystallizing. This led to the incongruent melting of amphibole and biotite to form liquids of sphene composition. Meanwhile, plagioclase continued to grow in the mafic-turned-hybrid system with a different composition after the advent of felsic melt as indicated by compositional zoning in plagioclase crystals. The newly produced sphene-liquid, owing to its higher affinity for felsic phase than mafic, got incorporated into the back-veining felsic melt forming a distinct liquid of its own. The felsic melt also incorporated crystallizing plagioclase grains in it from the mafic matrix. The mixture of felsic melt, sphene-liquid and plagioclase crystals flowed through the biotite, amphibole and plagioclase dominated matrix towards the low pressure zones to occupy the spherical void spaces left behind by escaping of gases/volatiles forming the sphene. This inclusion study to some extent reiterates the interpretation of Gogoi et al.

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