1.   Introduction

Sapphires are among the oldest and most sought after gemstone variety in the world. They come in arguably the most diverse mix of colors of any gemstone and from many sources the world over. Sapphires from different deposits around the world are all created in earth processes that are unique to that location. And in turn they show distinct characteristic features that can sometimes be used to identify their place of origin and provide clues to the unique geological process responsible for their genesis. These features commonly include habit, color, trace element chemistry, and most notably inclusions of various solids, liquids, or gasses that were trapped at some point during crystal growth.

Sapphires bought and sold in the marketplace often have huge premiums placed on stones if a certification of origin can be secured. Rubies certified as being from Burma and sapphires from Kashmir will nearly always sell for more than comparable material from Thailand, Sri Lanka, or any other location. Therefore it can be extremely valuable to conclusively determine the origin of gemstones. For more purely academic reasons there has been much work done recently on trying to better define the classification of corundum into specific genetic models. The evolution of these models has been debated and revised many times in the last several decades. With the discovery and subsequent study of sapphires from new locations valuable knowledge may be gained to further the theories on corundum genesis.

This paper is an attempt to uncover the distinguishing features of sapphires from the Tunduru region of southern Tanzania. There is a striking lack of published information on the gem deposits of Tunduru. Often information about the formation and location of gems is fraught with secrecy. It seems likely that research similar in nature to this has been carried out but lies hidden in the files of the few world gem laboratories that will issue origin reports on gems purported to hail from this part of East Africa. This is one of the primary reasons for the undertaking of this study.

The gem deposits of East Africa are quite young in terms of discovery when compared to their eastern cousins in Sri Lanka and India. Sapphires from the Tunduru area are an especially recent find. Unlike deposits in Asia that have been documented for centuries and even millennia these deposits were only fully recognized in the mid 1990's. Little published gemmological work has been done on these sapphires. All of the sapphires from the Tunduru region are from alluvial and elluvial deposits and their in situ origin can only be speculated. Tunduru is known to produce 16 different gem mineral species (Clannin, 2007). Many of the sapphires being produced are of top color and quality. In the future Tunduru may come to hold a distinguished place among world sapphire localities.

1.1   Aims and Objectives

The first aim of this study is to become familiar with several advanced gemological techniques. These include the microphotography of gems and inclusions within gems and the use of Laser Raman techniques to analyze and identify inclusions within gems. These skills along with basic gemmological observations will make possible the identification of as many characteristic features from the Tunduru sapphire as possible with the objective of using these characteristics to discuss possible in situ deposit locations, to consider genetic models of formation and to aid in the future identification of Tunduru

sapphire for scientific and commercial purposes. This study will focus on external observation of the appearance of the sapphires as well as detailed study of the internal characteristics of the sapphires. It is hypothesized that the sapphires are metamorphic in origin.

2.   Location and History

Tunduru is one of the 5 districts of the Ruvuma Region in southeast Tanzania. It is bordered to the North by the Lindi Region, to the East by the Mtwara Region, to the South by Mozambique and to the West by the Namtumbo District. Tunduru lies in the southernmost of nine major river drainage basins in Tanzania (Government of Tanzania Ministry of Water and Irrigations, 2007). The Southern Coast Basin is comprised of five major independent river systems draining into the Indian Ocean. The largest of these is the Ruvuma River and its tributaries which cover some 52,200 km^2.

Figure 1. Tanzania and location of Tunduru District.

All rivers in the Tunduru area are tributaries of the Ruvuma. Mining in Tunduru takes place in a wide area from the Selous game reserve in the north to the southern Mozambique border formed by the Ruvuma River. Mining takes place along the Muhuwesi, Mtetesi, Lumesule, Nampunga, Ngapa, and

the Ruvuma rivers, also to the north near the Liwale region in the Nanbalapi, Ngurumahinga, and Mbwemburu rivers. (Hughes and Pardieu, 2008)(Clannin, 2007).

Tunduru is known to produce gemstones of nearly every type and color imaginable. In a study of the 1996 mining season compiled by Clannin (2007), there were 17 different gem mineral species, with 46 different varieties found. Clannin lists the relative occurrence of the different gem species using a ranking as follows: very common, common, occasional, rare and very rare. For corundum, only the ruby red and padparadscha colors are rarely found. The most commonly occurring gem species are quartz, chalcedony quartz, spinel, tourmaline and garnets.

According to Clannin (2007) sapphires were first discovered east of Tunduru near the town of Songea in 1993/1994 and were soon followed by finds on the Muhuwesi River. By early 1995 Thai mining organizations had moved in and were setting up large scale operations. Foreign gem buyers came in droves and soon Tunduru had become one of the largest mining areas in Tanzania. However in 1996 in response to what they feared as a loss of revenue due to the uncontrolled flow of gemstones out of the country the Tanzanian government shut down all mining by foreign nationals and revoked their claims (Clannin 2007). After this decree most all of the Thai and Sri Lankan dealers left Tanzania for
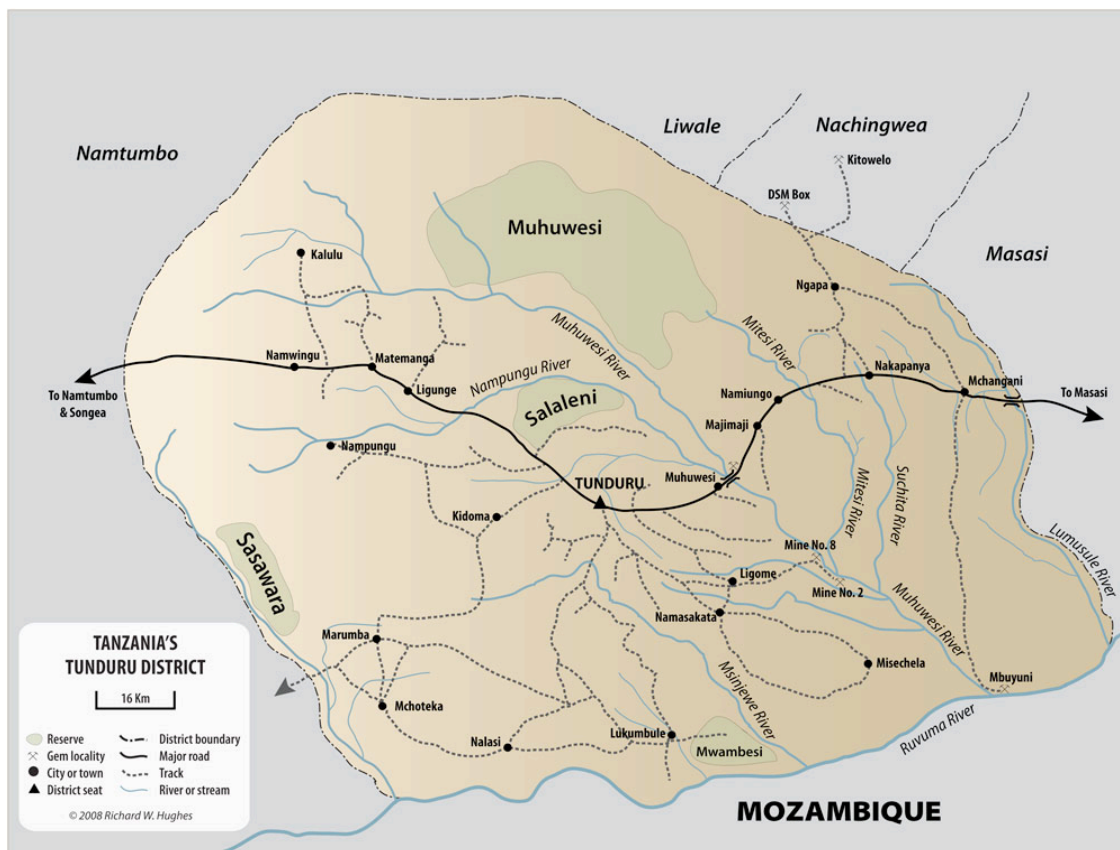

Figure 2. Tunduru area mining map from Hughes (2008)

Madagascar and the prodigious new sapphire deposits at Andranondambo and later at Ilakaka (Hughes and Pardieu, 2008). During the time from 1994 to 1998 little mining took place at Tunduru and it wasn't until 2002 and the realization of the profits to be made with the advent of beryllium diffusion treatment

3

that foreign buyers returned in bulk and serious mining was resumed. Since then the output of Tunduru sapphire has been largely steady with fluctuations due to miners moving in and out of the region commonly to pursue other mining strikes.

3.   Geology of Tunduru and the East African Gem Belt

East Africa contains many primary gemstone deposits. These deposits can essentially be split into three categories based on their geology (Keller, 1992). The first of these is deposits related to the 2.5 billion year old Tanzanian Shield that makes up a large portion of central Tanzania. This large stable granitic block is known to contain over two hundred kimberlite pipes. Diamonds found within these kimberlite pipes are the only significant gem species to be hosted by this geological formation (Keller, 1992). The second category of gem deposits are those associated with Upper Cenozoic to Pleistocene volcanics, specifically alkaline basalts related to the East African Rift. The gems found within this formation particularly the sapphires are likely similar in nature to similar volcanic deposits in Australia, China, and Thailand-Cambodia (Keller, 1992).

The third type of deposit within East Africa are those associated with the Mozambique Metamorphic Belt (Keller, 1992). According to Kroner (1984), the Mozambique belt is a 4,000-km/2,400-mi long belt of high-grade metamorphic rocks, formed by the collision of the east and west Gondwana continental plates, representing a mobile belt which underwent several phases of folding and metamorphism before its final phase of regional metamorphism some 600 million years ago at the end of the Precambrian. The belt can be found from Saudia Arabia south all the way to Antarctica and can also be found in Sri Lanka and Madagascar (Clannin, 2007). According to Clannin (2007), these are predominately high-grade metamorphic rocks including gneisses, marbles, metaphelites and quartzite. In Tanzania these are known collectively as the Ubendian-Usagaran system of rocks (Clannin, 2007). These rocks themselves produce gemstones of nearly every species most notably ruby, sapphire, tanzanite, tsavorite, emerald, alexandrite, uvite-dravite tourmalines, and pyrope-almandine-spessartine garnets (Keller, 1992). They also contain numerous pegmatite intrusions that are thought to contribute to the production of many gem species including some of the more interesting rare element containing gems (Keller, 1992).

Lying on top of the Ubendian-Usgaran system are the Karroo and Kalahari formations. Both the Karroo and Kalahari formations are gemmiferous, the most productive parts being the tillites of the Karroo and the fluvial conglomerates of the Kalahari (Clannin, 2007). The use of the terms Karroo and Kalahari formations is based on the age of deposition and whether the sediments are pre-Cretaceous Peneplain or post-Cretaceous Peneplain respectively. According to Clannin (2007), the Karroo began its depositional phase at the beginning of the Hercynian Orogeny during the Carboniferous and continued until the breakup of the Gondwanaland Paleocontinent. During this glacial period the Dwyka tillite, found in many places in Africa south of the equator, was deposited in bottoms of valleys and depressions cut into the pre Karroo basement and rests non-conformably on top of these basement rocks (Furon, 1963). These depressions are especially well developed in East Africa and were subsequently filled with Karroo sediments (Clannin, 2007). Similarly aged Karroo sediments can be found in many countries including Kenya, Madagascar, India, Malawi and Mozambique. In Mozambique the

Karroo formation is found in the northwest around Lake Malawi in the Tete and Nyasa Districts. All the rivers that drain from this region are tributaries to the Ruvuma and are gemmiferous (Clannin, 2007). Material from the Kalahari formation conglomerates is derived directly from the underlying basement rocks and the Karroo formation. It is in the Karroo and Kalahari formations that most of the alluvial gem deposits near Tunduru lie (Clannin, 2007).

4. Literature Review

4.1 *Inclusion and photographic references*

Inclusions in gemstones are commonly studied as a means of discovering information about their formation and sometimes their origin. Koivula, (2008) states that "inclusions are most useful in determining the type of geologic environment their host came from". His most recent book Photoatlas of Inclusions in Gemstones Vol. 3 is the major reference source upon which comparisons of inclusions in gemstones of differing localities will be based. The Photoatlas Vol. 3 has excellent photographs and descriptions of many inclusions from Tunduru and many other deposits from the greater Mozambique Metamorphic Belt specifically those in East Africa, Sri Lanka, and Madagascar.

4.2. *Classification of corundum deposits*

Recently much work has been done to further the classification of corundum according to the genetic processes responsible for their creation. Corundum, as a mineral is encountered in wide variety of rock types. It is relatively common in many metamorphic rocks of varying lithologies and its pressure-temperature stability domain is vast; for example the mineral appears during forest fires on bauxite soils at atmospheric pressure (Simonet C. F., 2008), and as a high pressure phase in diamonds (Watt, 1994). There are numerous different gem corundum locations around the world and many have been described in detail in various geological and gemological literature. For the purposes of this study the classification scheme to be used will be that proposed by Simonet, Fritsch, and Lasnier (2008). Any genetic processes and potential in situ deposit locations will be considered using this system (Fig 3).
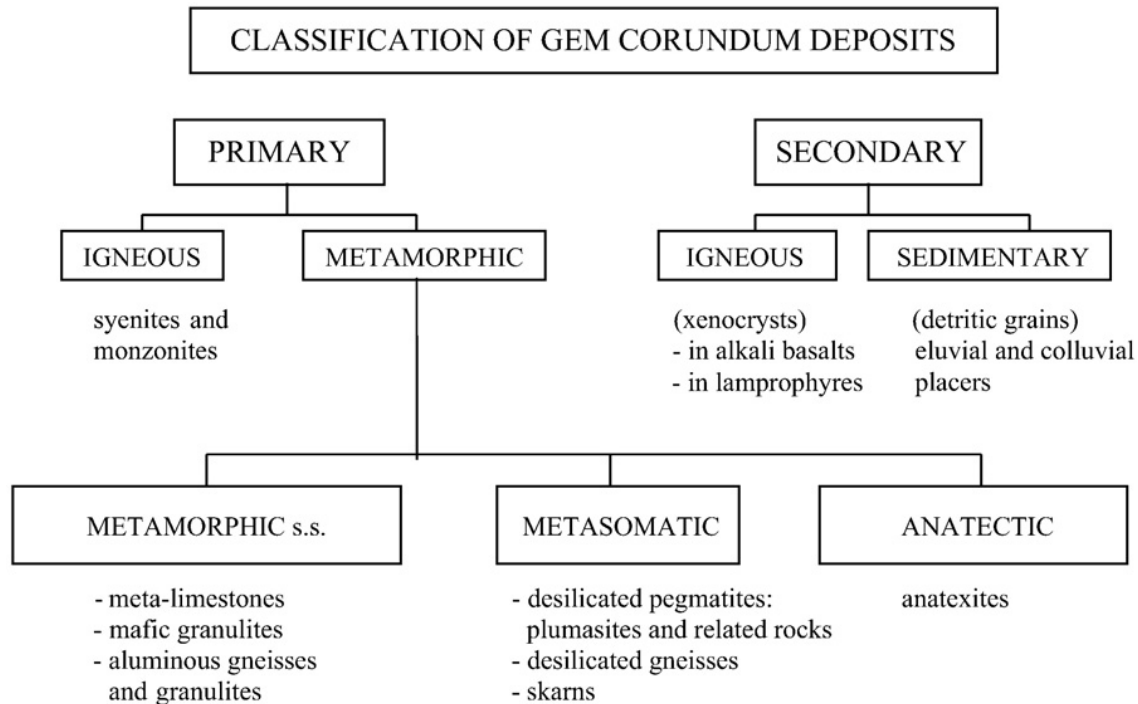
CLASSIFICATION OF GEM CORUNDUM DEPOSITS

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                    PRIMARY                          SECONDARY

          IGNEOUS        METAMORPHIC         IGNEOUS      SEDIMENTARY

       syenites and                       (xenocrysts)   (detritic grains)
       monzonites                         - in alkali basalts   eluvial and colluvial
                                          - in lamprophyres     placers


       METAMORPHIC s.s.        METASOMATIC           ANATECTIC

    - meta-limestones      - desilicated pegmatites:      anatexites
    - mafic granulites        plumasites and related rocks
    - aluminous gneisses   - desilicated gneisses
      and granulites       - skarns
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Figure 3. Classification scheme for gem corundum deposits from Simonet, Fritsch, and Lasnier (2008).

4.3.   Primary gemstone deposits with possible links to Tunduru

According to Simonet et al. (2008) corundum deposits in Tanzania are known to exist associated with many different types of geological processes. The gems in Tunduru may come from a source that has been completely eroded over millions of years, from deposits that have not yet been discovered, from known deposits in other locations as a product of erosion and transportation by water or from some combination of these. Because of the lack of published work on the origins of Tunduru corundum a major focus of this study is to review work published on the various corundum deposits that are thought to have formed during the Pan-African orogeny under similar conditions to those that may be responsible for the Tunduru sapphire. The corundum deposits of East Africa have numerous geologic similarities to those in southern Madagascar, south India, and Sri Lanka (Giuliani, 2007).

<mark>PAGE 28 CAN MIN MOZ BELT FIGURE</mark>

4.3.1   Magmatic deposits

The most prominent sapphire deposit near to Tunduru is the deposit at Garba Tula in Central Kenya. Sapphires here are found in situ in alkaline igneous rock. The rock, a syenite is a vertical dyke emplaced in a series of biotite and hornblende bearing gneisses of the Mozambique Belt (Simonet et. al., 2004). Sapphires from this deposit range in color from a dark inky blue to a golden yellow with many shades of blue and green in between. The crystals typically display either a barrel or truncated bipyramid shape and commonly can reach rather large sizes up to 10 cm.

4.3.2. Metamorphic deposits

4.3.2.1. Gem Corundum bearing aluminous gneisses and granulites

Though intact primary deposits of this type in Tanzania are not well documented they are one of the major corundum deposits associated with the Mozambique Belt (Simonet et. al., 2008). The best example of this type of deposit is in southern Sri Lanka. In Sri Lanka the rich alluvial gem deposits are located in the Precambrian Highland-Southwestern Complex formed of granulitic rocks. These rocks are now considered to be an eastern extinction of the Mozambique Belt. Proposed sources for the sapphires include gneisses, skarns, and charnockites. The general consensus of many of the world's corundum experts on the genesis of the Sri Lankan corundum deposits is based on a study published by Rupasinghe and Dissanayake (1985). The following is a description of how these deposits are thought to have formed taken from Hughes (1997). "Charnockites (orthopyroxene-bearing granites), which make up an integral part of the gem-bearing Highland Group, are thought to have played a key role. It is hypothesized that aluminous sediments derived from weathering and transportation of material from an Al-rich continental crust were deposited in the Highland Basin. Such pelitic sediments were subsequently deformed and metamorphosed under granulite-facies conditions caused by continental collision. Contemporaneous intrusions of basic charnockites of basaltic chemistry into the Al-rich sediments caused their desilication, resulting in the formation of corundum, spinel, cordierite and sapphirine. The pegmatites, with which gem minerals like beryl, chrysoberyl and tourmalines are associated, are thought to be derived from a charnickite parent." Interestingly this original source rock has been completely weathered away and the gemstones are all that is left.

A corundum occurrence similar in nature to Tunduru and many in Sri Lanka is the one at Ilakaka, Madagascar. These giant paleoplacer deposits are the result of the erosion of the Isalo Mountains (Koivula and Gubelin, 2008). The exact primary deposits of these gemstones are unknown but are generally accepted to have been associated with granulites formed during the Pan-African orogenesis situated in the Isalo Mountains that have been completely destroyed by weathering (Koivula and Gubelin, 2008) (Rakotondrazafy et al., 2008). The deposits produce very fine blue, pink, violet, orange, yellow and colorless sapphires along with zircon, alexandrite, topaz, garnet, spinel, andalusite and tourmaline (Rakotondrazafy et al., 2008). This assemblage of many various colors of corundum and the other associated gem minerals is very similar to those reported at Tunduru (Clannin 2007).

4.3.2.2 Corundum bearing mafic granulites

Many corundum deposits in Tanzania are closely related to basic and ultrabasic rocks specifically corundum bearing mafic granulites. Most of these rocks are ornamental rather than gem quality such as the "anyolite" from Longido; however some have been known to produce facetable material such as those at Losongonoi (Simonet et al., 2000) which have produced significant quantities of gem quality ruby. The Chimwadzulu Hill area of Malawi described by Rankin,(2002) and Hughes (1997) is known to produce ruby and many different colors of fancy sapphire. These are related Ultramafics intruded within gneisses, they are recovered in situ from an epidotized amphibolite.

4.3.2.3 Corundum bearing meta-limestones

Several primary corundum deposits of interest lie to the north and northwest of Tunduru. The majority of these deposits are ruby deposits and can be classified according to Simonet et. al., (2008) as metamorphic s.s. associated with meta-limestones, specifically those near the town of Mahenge (personal observation, 2007). Mahenge is some 170 miles north west of Tunduru. It sits atop a limestone plateau that forms part of the ancient Eastern Arc Chain of mountains. Two of the important mining areas are at Ipanko and Lukande. In both of these areas gems are mined in secondary placer deposits and occasionally in primary deposits that are sometimes very close; only some 100 meters at Ipanko (Pardieu, 2005). The primary deposits here are marble deposits PICTURE. They are known to produce various colors of spinel, ruby and pink sapphire. Other deposits nearby are located at Morogoro. These occur mostly in secondary deposits but are noted to occur in primary deposits associated with marbles (Hänni and Schmetzer, 1991), agglomerates of mica and kyanite (Hughes R. 1997) and as a product of anatexis (Altherr et al. 1982). Ruby and sapphire of very high quality were found near the village of Winza in November of 2007 (Pardieu, 2009).Here the corundum is related to "dikes" of amphibolitic rocks that belong to the Paleoproterozoic Usagaran Belt (Schwarz, 2008). The geology of Tanzania is such that there is a gradual slope from the Tanzanian Craton leading gradually down to the Indian Ocean. All of these deposits lie generally to the north and northwest of Tunduru and it is possible that they are located in what could have been paleo river systems that were responsible for the deposition of rubies into the Tunduru area.

4.3.3.   Metasomatic deposits

East Africa also has numerous sapphire deposits associated with metasomatized pegmatites closely related to plumasites. The best known of these is the deposit at Umba Tanzania. In the Umba Valley deposit desilicified pegmatitic veins intruded a serpentinite plug that itself is embedded in country rock composed of gneisses, granulites and limestones (Gubelin and Koivula, 2008). The pegmatite is thought to have come from anorthositic rock that became drained of magnesia and silica when it made contact with the serpentinite during emplacement (Gubelin and Koivula, 2008). The plumasites, those rocks chiefly containing corundum, then appeared as a result of hydrothermal processes. Umba is famous for producing an amazing variety of fancy sapphire colors. African gemstone pioneer John Saul is said to have made a reference collection of over 100 distinct sapphire colors from Umba, excluding greys and parti-colored stones (Hughes, 1997).

5.   Samples, Methodology and instrumentation.

5.1   Thick Wafers

The majority of this study is based on the photography and Raman spectroscopic analysis of inclusions within fifty gem corundum samples. The samples were acquired from prominent gemmologist and author Richard Hughes. The samples were all purchased in October of 2007 during a field expedition to document new sources of gem corundum in east Africa. They were purchased in the town of Maji Maji, a regional centre for gemstone trade conveniently located in the heart of the Tunduru mining area. As this town is located in such a remote area it is highly unlikely that the gems could have come from

anywhere other than the surrounding mining area which is the area considered in this study. The samples used in the study have been cut and polished using diamond saws and laps into approximately 1mm thick wafers. The larger size of these wafers compared to the usually much thinner wafers used for many petrological and geological studies provides a greater space for the hosting of inclusions. It is these inclusions around which the study is based. The samples all range from 0.08 cts to 0.92 cts.

5.1.1   Basic gemological examination. The first step was to test all 50 wafers to be sure that they are in fact corundum. This was carried out using a Duplex II gemological refractometer and methylene iodide. The refractometer is a basic gemological tool that allows for the measurement of the refractive index of a gemstone. While corundum from different world localities may have differing refractive indices their birefringence is extremely consistent at 0.008. This simple test with the refractometer should be enough to weed out any other gem species of similar appearance.

5.1.2   Photomicroscopy. All of the thick wafers were examined using a Nikon SMZ 1500 stereoscopic microscope with an attached Nikon DS-Fi1 digital camera. Magnifications beginning at 20X and up to 600X was performed as needed to record inclusions of interest. Considered by many to be the best definition of inclusion is that given by Kiovula (1991): "Broadly defined, an inclusion is any irregularity observable in a gem- by the unaided eye or some tool such as a hand lens or microscope. The 'irregularity may be a substance, such as a solid mineral crystal, a fracture, or a growth pattern that produces some optical effect." Inclusions will be characterized according to the system provided by Gubelin and Koivula (1986), which is based upon their age in relation to that of the host crystal. These are termed protogenetic, or pre-existing for those inclusions that formed before the host and are strictly of a solid nature. Syngenetic, is used for inclusions that have formed at the same time as the host. These can include solids and semi solids such as crystals and glasses and primary cavities such as negative crystals. Lastly secondary or epigenetic is used for inclusions that formed after the host finished growth. Examples of secondary inclusions are exsolved crystals such as rutile and ilmenite and secondary cavities in the form of healed fractures.

5.1.3.   Laser Raman Analysis. All inclusions of interest were examined using the Renishaw Laser Raman Microspectrometer (LRM). Laser Raman is a fast, non destructive analysis method that can easily identify inclusions within corundum. Raman spectra were obtained in confocal mode using an Ar-ion laser at 514.5 nm. Count times of 30 seconds were generally adequate to produce reasonable spectra. A pure silicon standard with a single strong peak at 521 cm^{-1}, was used to calibrate the system before all sessions .Raman shifts are reproducible to within +/- cm^{-1}. Identification of the mineral and fluid inclusions was based on their characteristic Raman peaks utilizing the searchable Renishaw mineral database, the Kingston University mineral database, the RRUFF™ Project (Downs, 2006) online searchable database and the University of Siena Department of Science (2003) searchable Raman database. Some difficulties were experienced in obtaining Raman spectra from inclusions in the corundum samples. This was largely due to strong laser induced fluorescence above 800cm^{-1}. Often this led to the Raman spectra being produced only showing the very top of many characteristic Raman peaks. Absorption of the laser light by the host corundum when attempting to retrieve spectra from inclusions deep within the polished sections also caused some difficulty. This was often overcome by limiting Raman analysis to inclusions near the surface of the samples.

5.2   Rough Parcel

The second group of samples studied for this paper consists of a parcel of rough gemstones purchased by myself in the town of Maji Maji in October of 2007. The parcel offered for sale appeared to be mostly corundum but upon quick examination with a hand lens and spectroscope it was quickly evident that there were also several other gem species notably spinel and garnet. All pieces of rough were first separated into groups according to color. They were then examined by eye with a hand lens and with a hand held spectrometer. One of the primary tasks was to judge the level of weathering in hopes of providing information for discussion on the possible distance they had traveled from their original in situ deposit location. Due to the degree of weathering of the samples identification by common gemological methods such as the refractometer or microscope analysis was very difficult and sometimes impossible. Thirdly they were examined using the Renishaw Laser Raman Microspectrometer to conclusively determine their gem species.

6.   Data and Analysis

6.1   Rough parcel. Of the rough parcel purchased in Maji Maji 126 of 164 samples were corundum. Other gem species identified were spinel, garnet, zircon, quartz, and chrysoberyl.

Gem Species	Color	# of samples	Percentage of parcel	Percentage of Species
Corundum	All	124	75.6%	
	Red/Pink	25		20%
	Blue	33		27%
	Yellow	17		14%
	Violet	21		17%
	Colorless	28		22%
Spinel	All	13	8%	
	Blue	7		
	Violet	3		
	Pink	3		
			8%	
Garnet All	All	13		
Pyrope/Almandine	Pink	5		
Hessonite	Orange/Brown	2		
Spessartine	Orange/Brown	4		
Grossular	Yellow/Green	2		
Zircon	Green/Brown	5	3%	
Chrysoberyl	Green/Yellow	2	1%	
Quartz	Colorless	7	4%	

These findings go nicely with a list by Clannin (2007) that describes the 16 different gem species found in the Tunduru area and the frequency with which they are found. All gem species found in the

parcel aside from corundum and chrysoberyl are noted by Clannin (2007), as common in Tunduru alluvials. Nearly all the samples were heavily weathered and had a rounded to sub-rounded shape, very few euhedral samples seem to have survived the mechanical and chemical processes responsible for the formation of these secondary deposits. Of the few crystals that showed habit the most common were spindle shaped hexagonal bipyramids. One sapphire had a very interesting shape consisting of well developed prism and bipyramid forms.
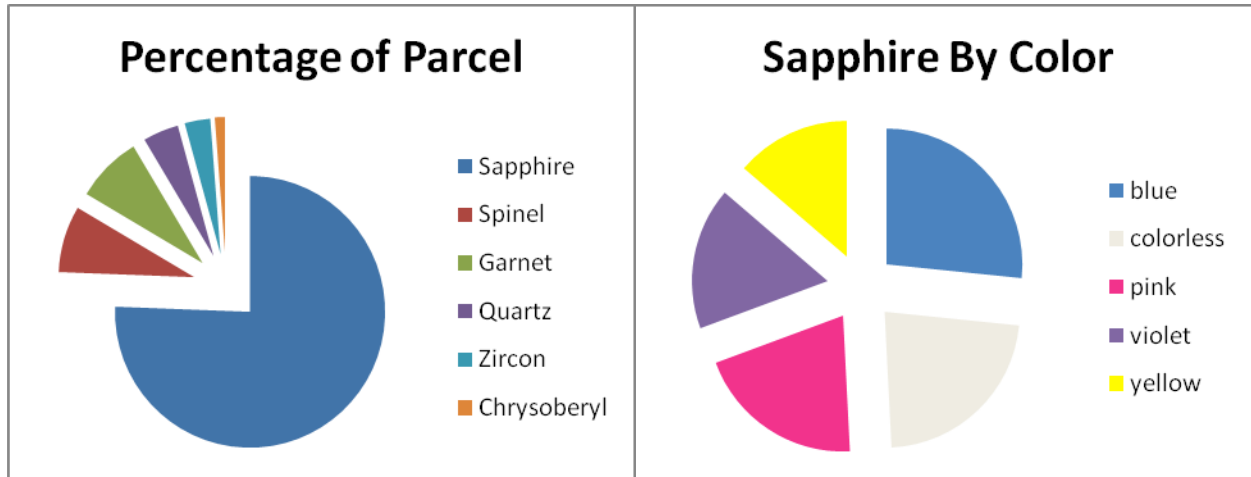
Figure 4. Chart with percentage of parcel by gem species   **Figure 5. Chart showing corundum percentage by color.**

Figure 6. Some of the many colors of sapphire found at Tunduru.

Figure 7. when not water worn pebbles Tunduru sapphires occasionally show bipyramid and prism forms.

6.2.   Thick Sections

6.2.1   Refractometer. Upon examination with the refractometer all fifty samples were determined to have consistent refractive indices between 1.768 and 1.780. All samples also had a birefringence of between .008 and .010. From these initial observations all fifty samples are presumed to be corundum.

6.2.2.   Solid Inclusions

Rutile, TiO_2, was the most common solid mineral inclusion in the fifty samples (nearly 80%). Rutile is a common mineral inclusion in sapphires from both metamorphic and magmatic sources all over the world. It was usually present as long thin epigenetic needles, but also as clouds of microscopic particles that commonly followed planes of trigonal symmetry. Both these forms of rutile are created by exsolution of titanium oxide that occurs as gem crystals cool and lose some of their ability to contain impurities within their crystal structures. Rutile may exsolve into several forms. The most common of these is as thin needle like crystals that may either be long and slender or knife or arrow shaped. They are so thin that when illuminated by a strong light source iridescent colors can be seen due to the interaction of these thin films with light. Bundles of these needles are commonly referred to as "silk". Rutile silk is easy to recognize as it always exsolves in corundum in three directions intersecting at 60 and 120 degrees in the basal plane. Changes in temperature are responsible for the different morphologies of rutile.
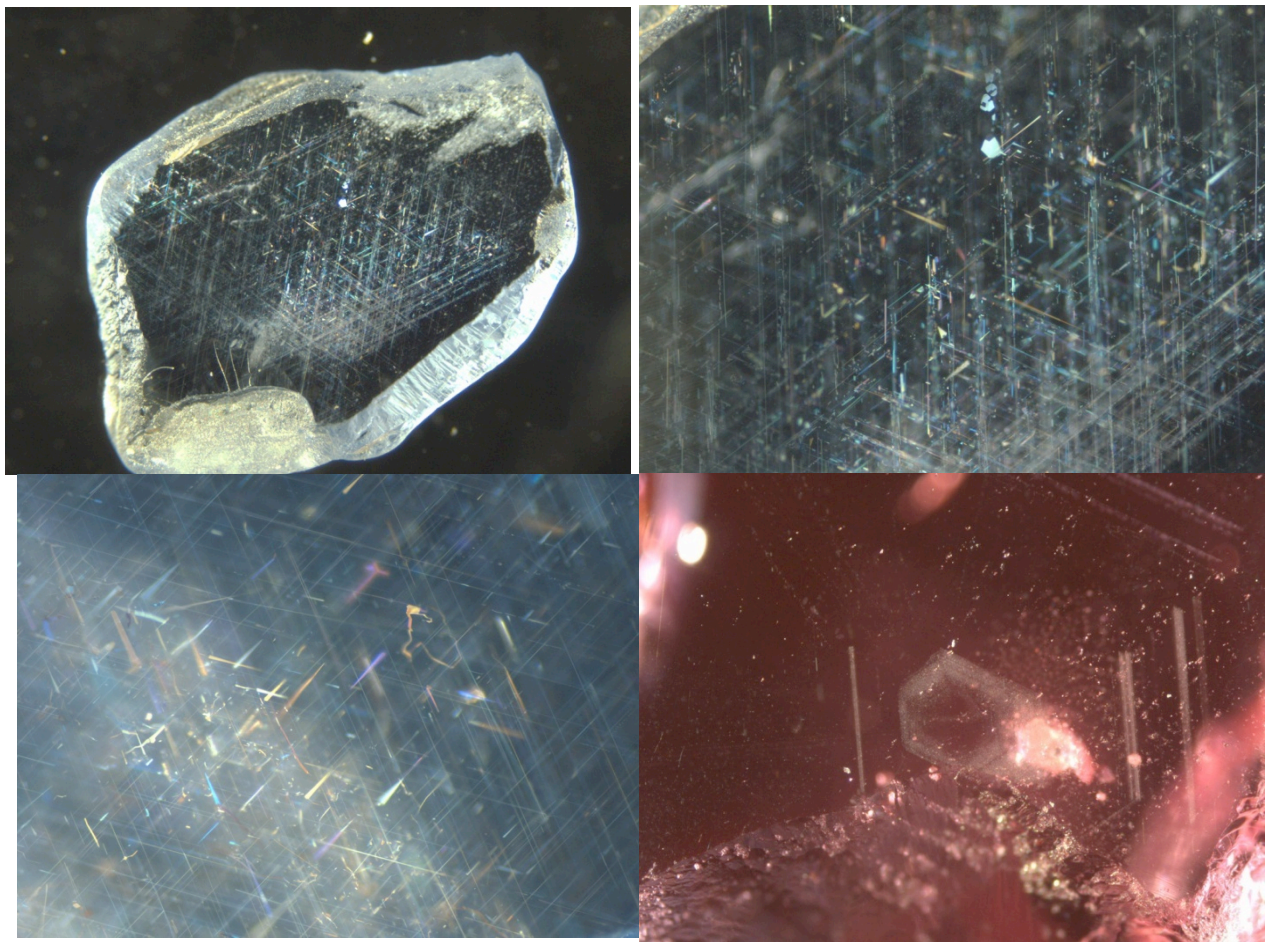
Figure 8. Exsolved rutile needles at 20X and again at 50X using oblique and darkfield illumination and microscopic rutile particles following hexagonal symmetry.
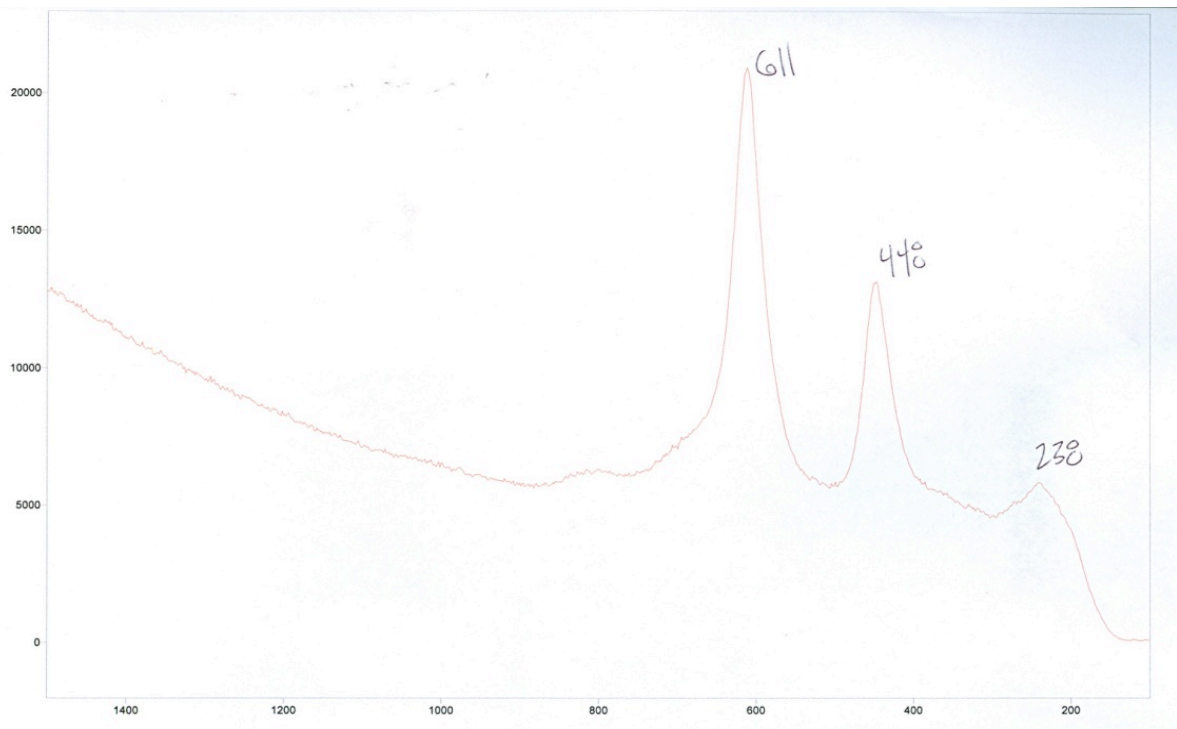
Figure 9. Raman spectra of rutile showing characteristic raman peaks.
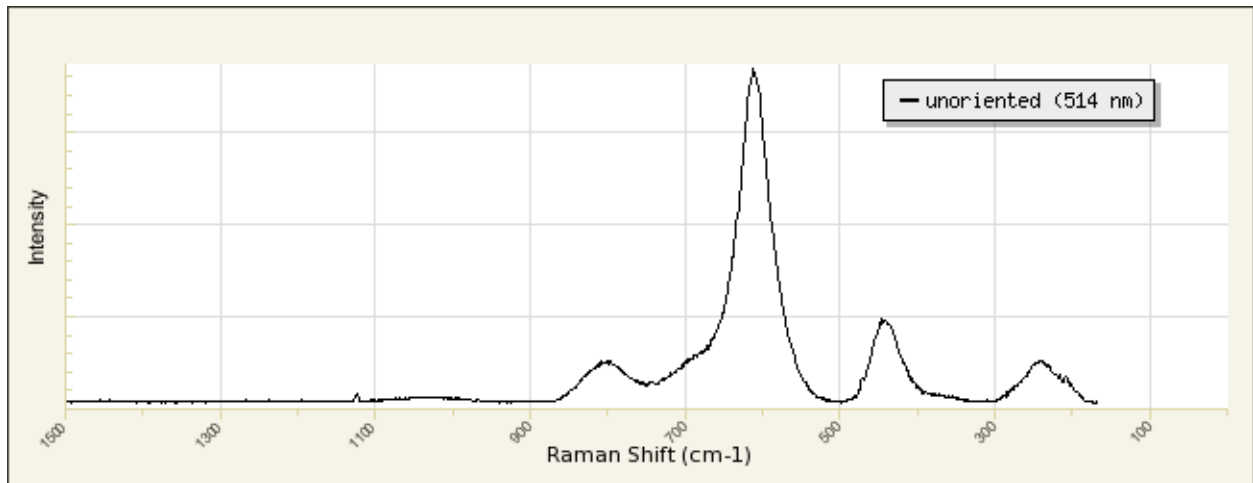
Figure 10. Rutile raman spectrum from specimen ID: R040049 RRUFF Database.

Zircon, ZrSiO$_4$, was the second most common mineral inclusion found in the fifty samples. It was found both as single isolated crystals often with other smaller inclusions inside and randomly oriented in both small and large clusters. Most of the zircons are somewhat stubby, sub-rounded prismatic crystals. Often the zircons had sickle shaped or halo-like stress fractures around them due either to thermal expansion or radioactivity. Known as one of the "transitory minerals" because they are not typical of any single geochemical condition, zircons are among the most common mineral inclusions found in corundum from both magmatic and metamorphic sources (Gubelin and Koivula, 1986). Zircon inclusions offer a wealth of information about the host corundum to the gemologist. They are a sure sign of natural origin and they can also be highly diagnostic in determining heat treatment. None of the zircon inclusions in the samples showed any evidence of decrepitation haloes, this can guarantee that all samples are natural and unheated.
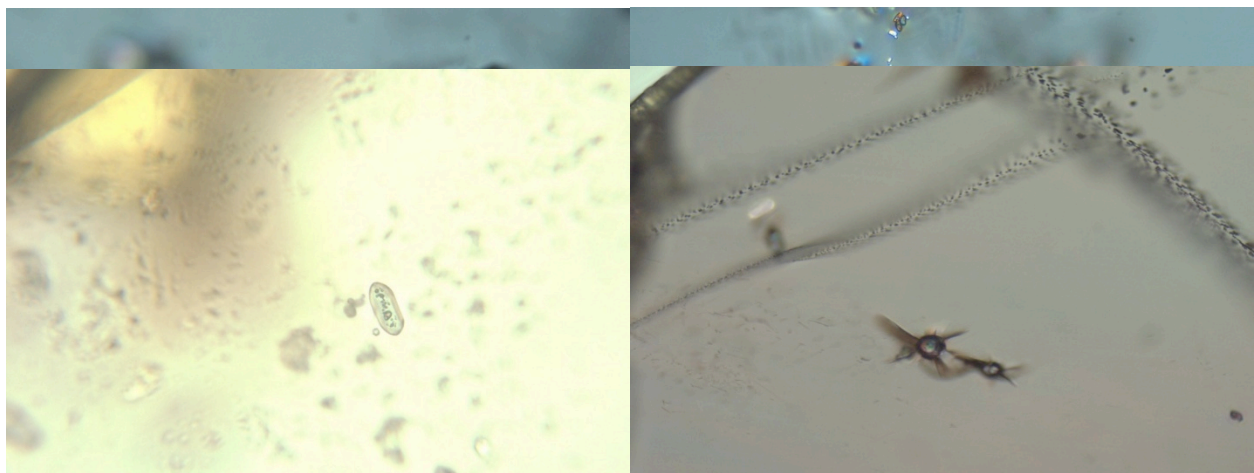
**Figure 11. Zircon inclusions in clusters, alone, and with stress fractures.**
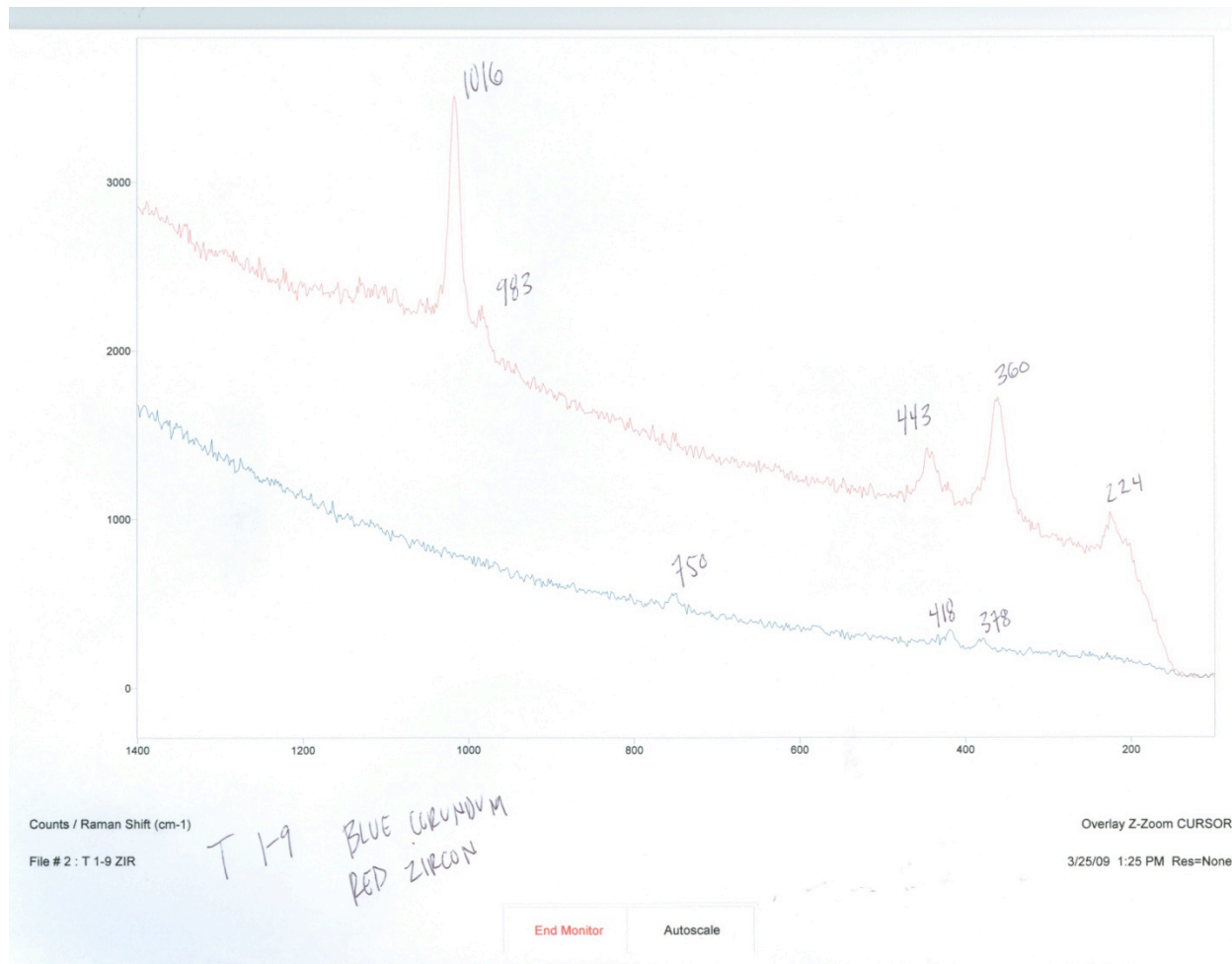
Figure 13. Zircon Raman spectra with host corundum spectra below.
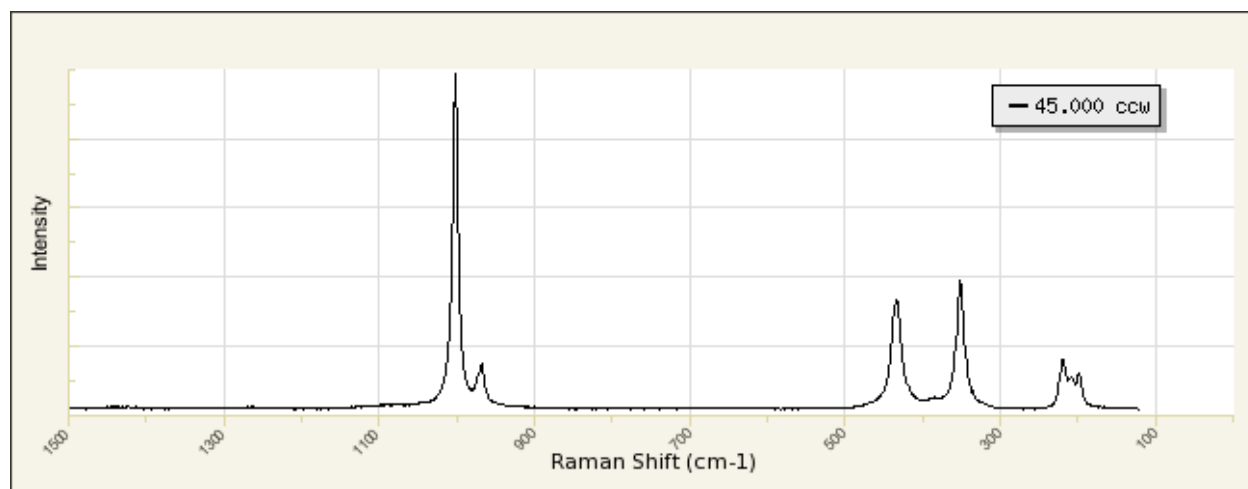
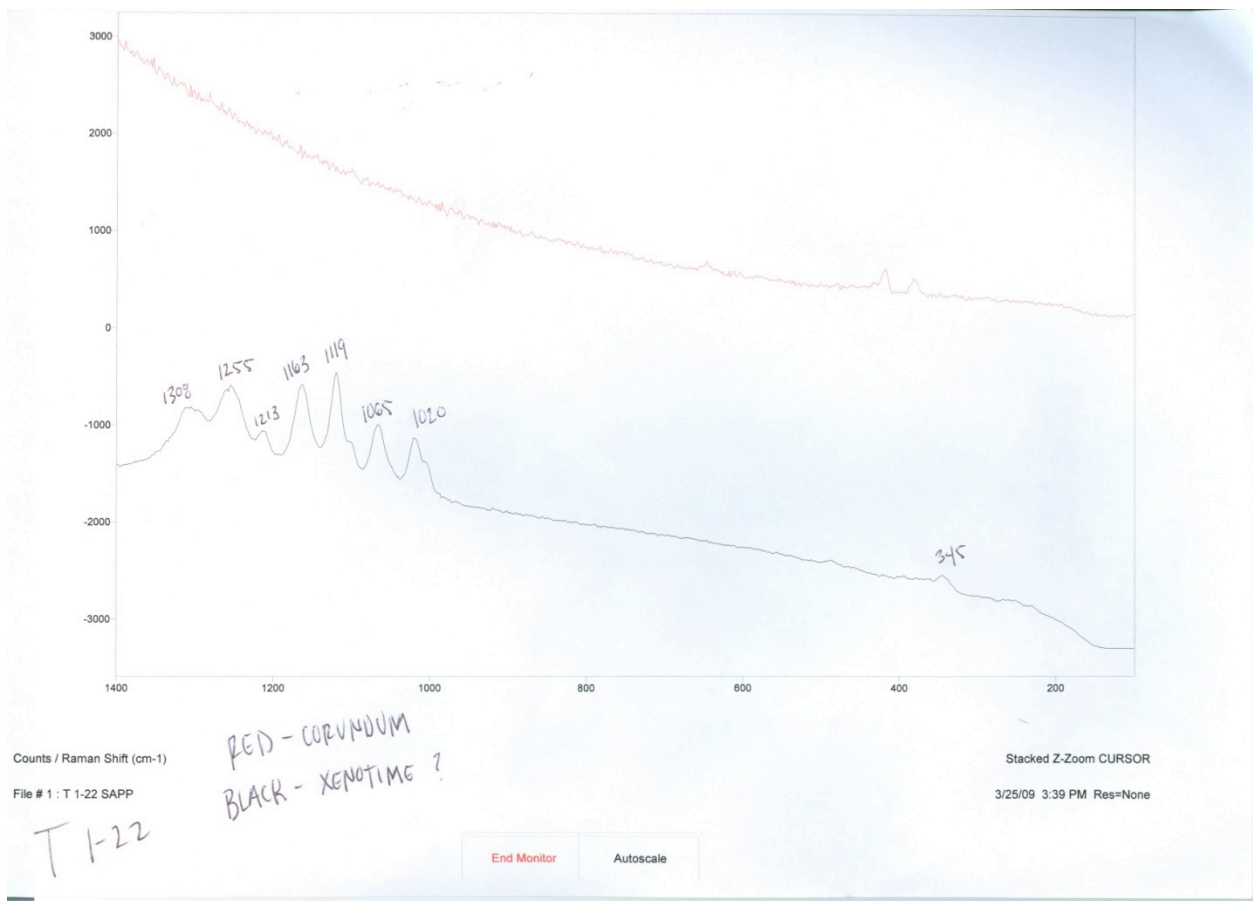**Figure 12. Zircon raman spectrum from RRUFF Database specimen ID: R050034.**

15

Phlogopite mica - KMg3(Si3Al)O10(F,OH)2 was found in many samples. It is red-brown and usually takes a somewhat tabular form, occasionally it is semi prismatic. Thin uneven flat fractures are common. According to the Web Mineral Database phlogopite is typically found associated with contact and regional metamorphism of limestones and dolomites and with ultramafic igneous rocks. According to Gubelin and Koivula (2008) it is a common inclusion in metamorphic sapphires from East Africa, Madagascar, and Sri Lanka. About it they state, "a typically metamorphic mineral, it emphasizes the origin of its host sapphire from metamorphic actions".

Monazite - (Ce,La,Nd,Th)PO4, and Xenotime, YPO4 were both found in numerous specimens. Both rare earth element containing minerals that testify to the presence of lanthanides when the sapphires formed. Monazite generally appears as golden-brown to red-brown rounded crystals. Xenotime either occurred as small rounded crystals or as groups of very small crystals forming cloudy masses. According to Gubelin and Koivula (2008), these inclusions are often found in metamorphic sapphire from East Africa, Madagascar, and Sri Lanka. Both of these minerals especially xenotime are regularly present in the company of zircons.
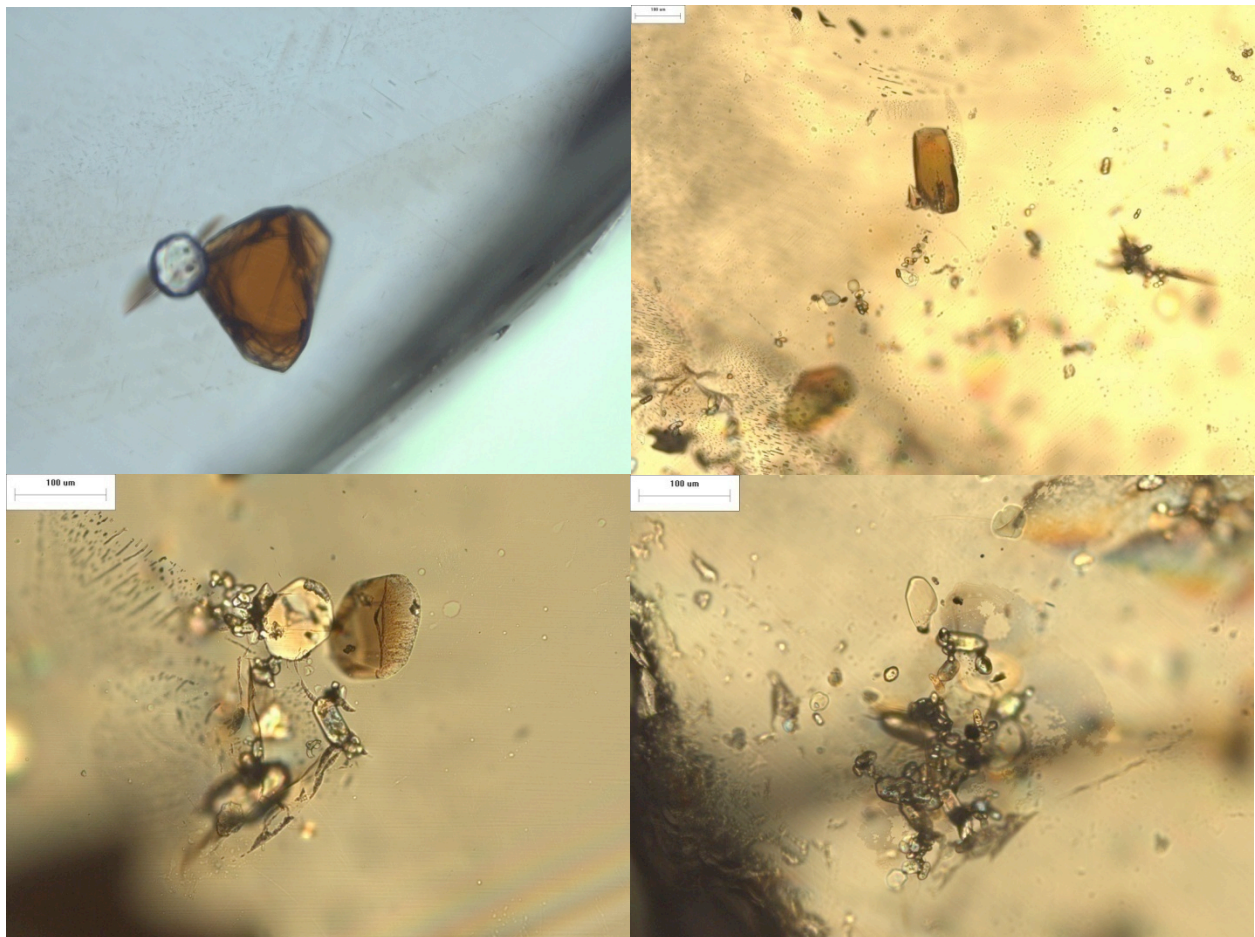
Figure 14. Top, Brown phlogopite crystals. Bottom, golden-brown tabular monazite crysatals surrounded by clusters of ircons, phlogopite and xenotime 200X.
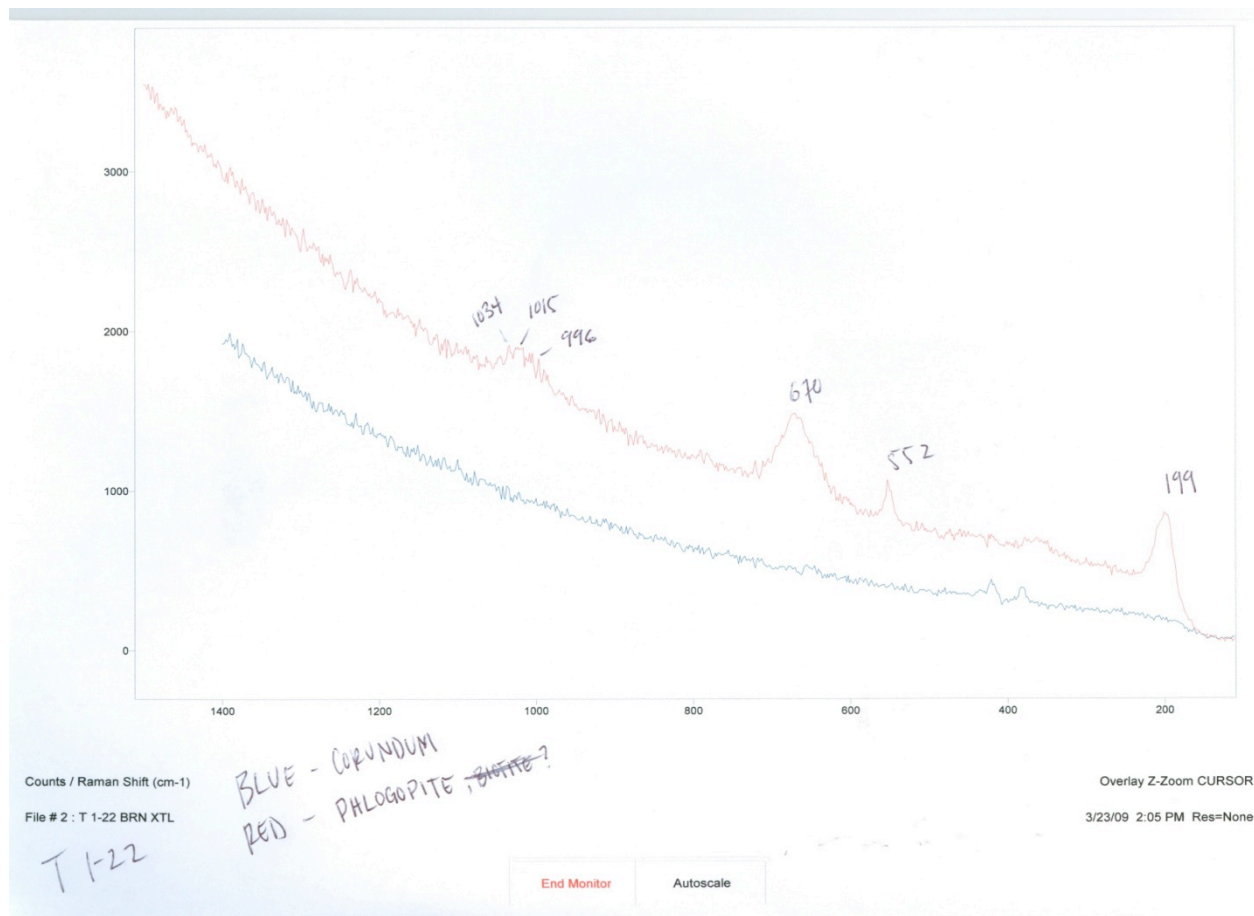
Figure 16. Phlogopite Raman spectra with host corundum spectra below.
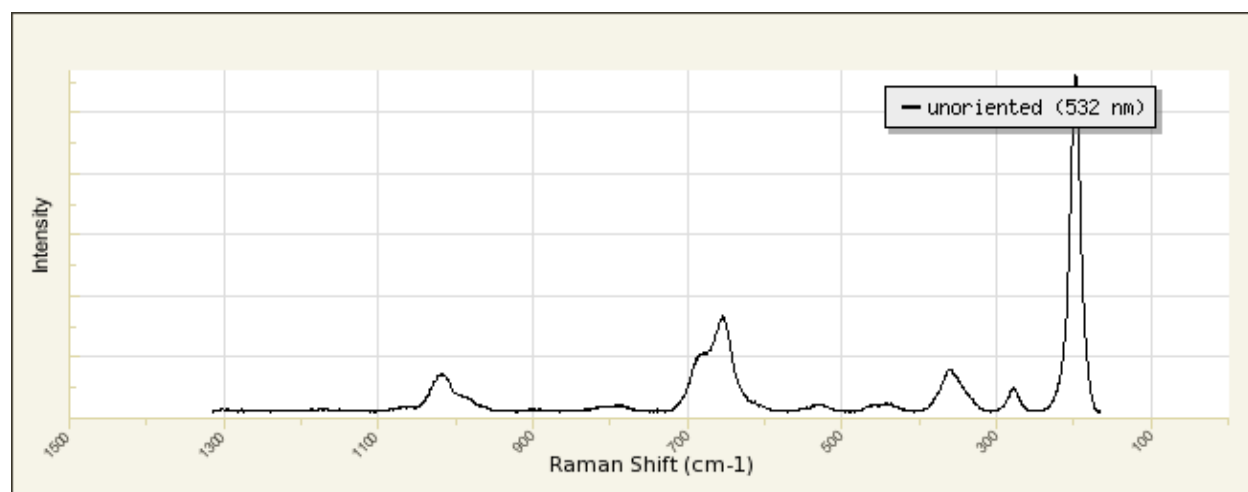
Figure 15. Phlogopite Raman spectrum from RRUFF Database specimen ID: R040144.

Figure 17. Xenotime Raman spectrum with host corundum spectrum above.
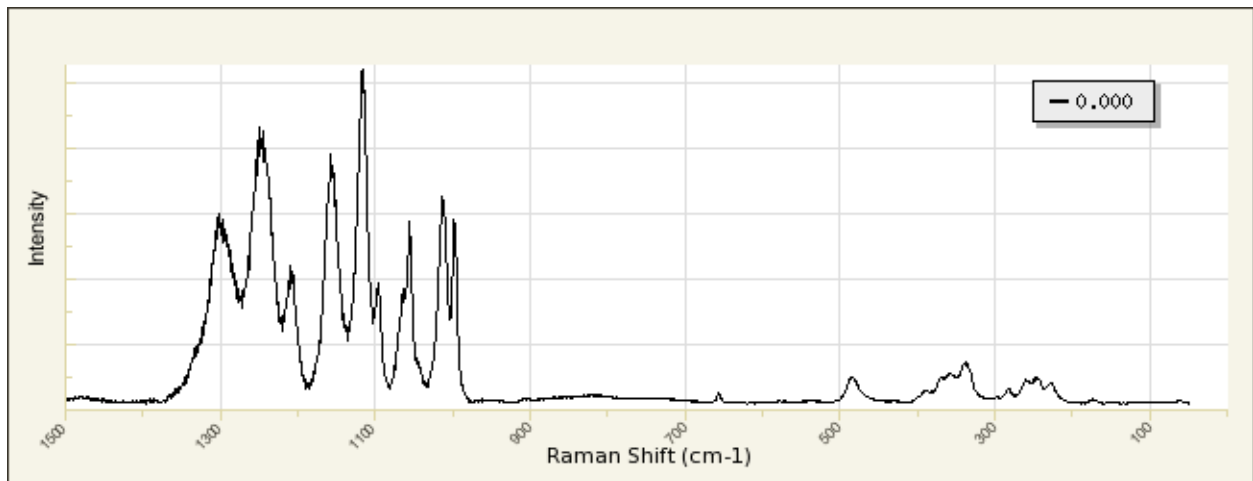
Figure 18. Xenotime Raman spectrum from RRUFF Database specimen ID: R050178.

18
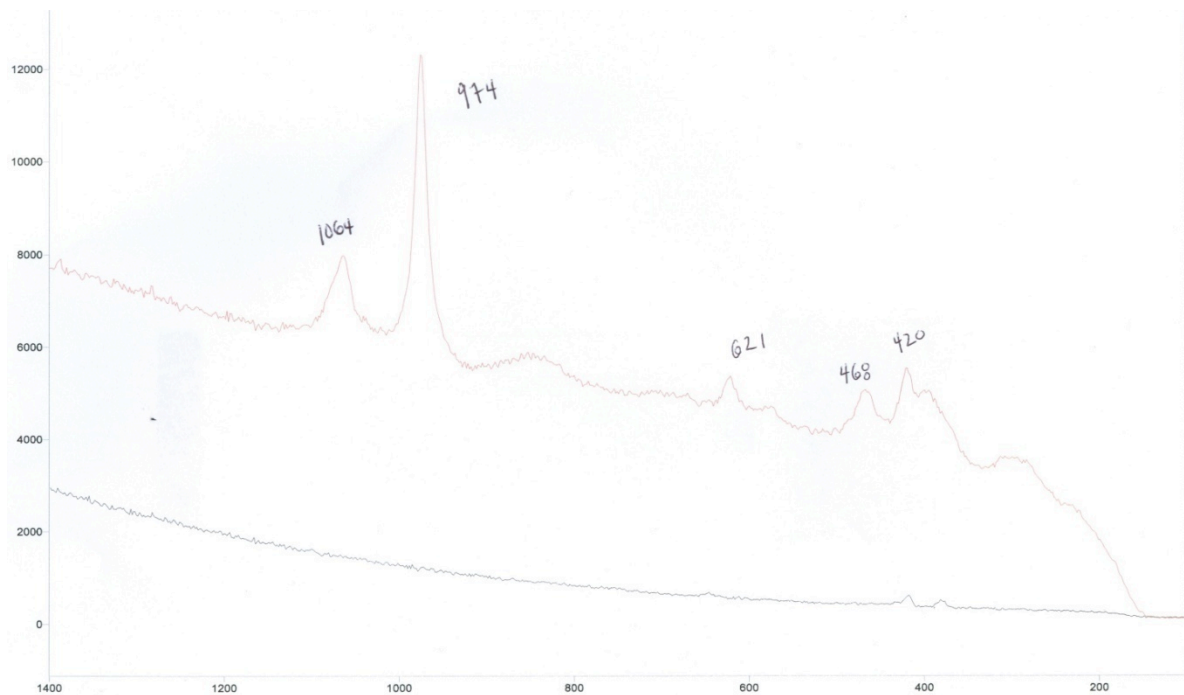
man Shift (cm-1)   RED - MONAZITE

-22MONZ   BLACK - CORUNDUM

Overlay Z-Zoom CURSOR

5/14/09 12:22 PM Res=None

Figure 20. Raman spectrum of monazite over spectrum of host corundum.
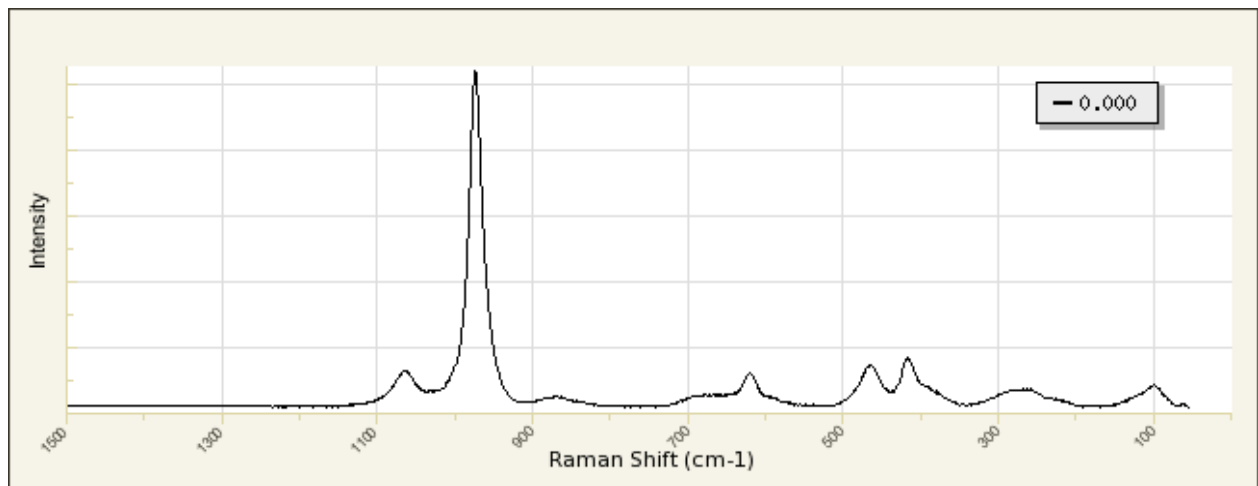
Figure 19. Monazite raman spectrum from RRUFF Database specimen ID: R040106.

Calcite - CaCO3 was found in numerous specimens. In some it showed classic rhombohedral habit. In others is showed a dogstooth habit or a more rounded shape. Calcite inclusions can be found in corundum from both magmatic and metamorphic sources. According to Gubelin and Koivula (2008) and Hughes (1997), it can be found in metamorphic sapphire from East Africa, Madagascar and Sri Lanka.
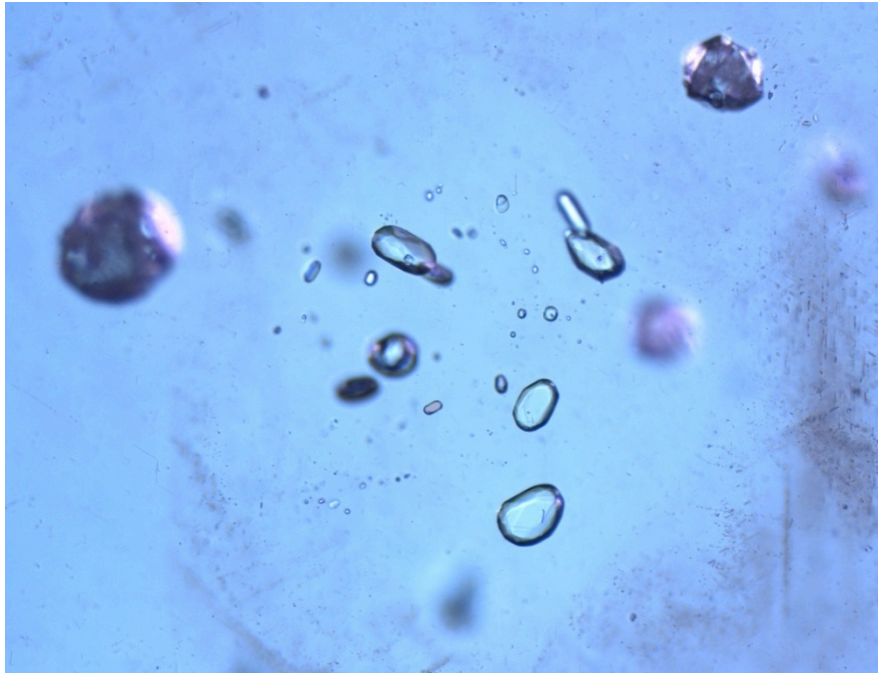

Figure 21. Group of semi rounded calcote crystals 100X oblique and darkfield illumination.
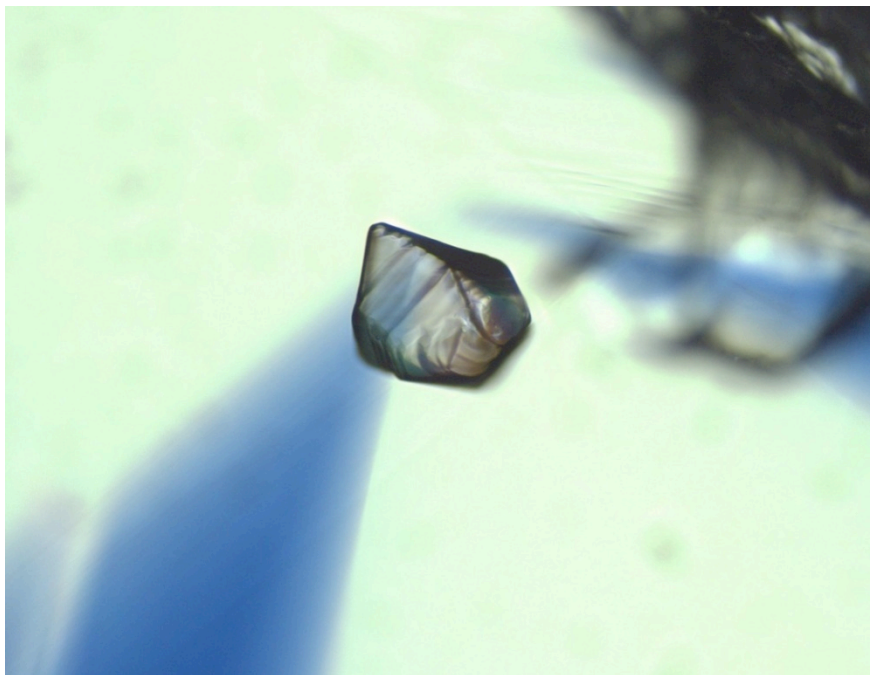
Figure 22. Single calcite crystal showing dogstooth habit brightfield illumination 100X.
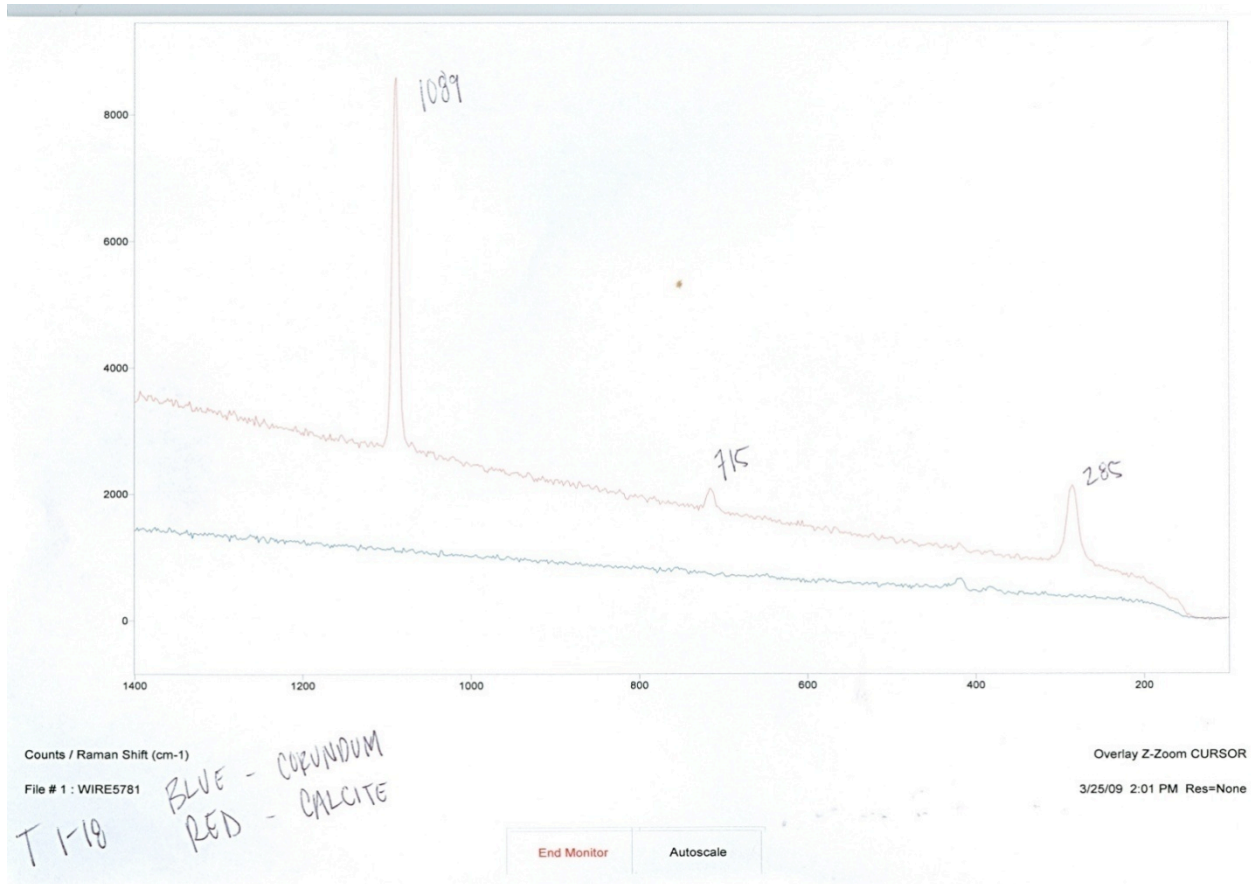
Figure 23. Calcite raman spectra with host corundum spectra below.
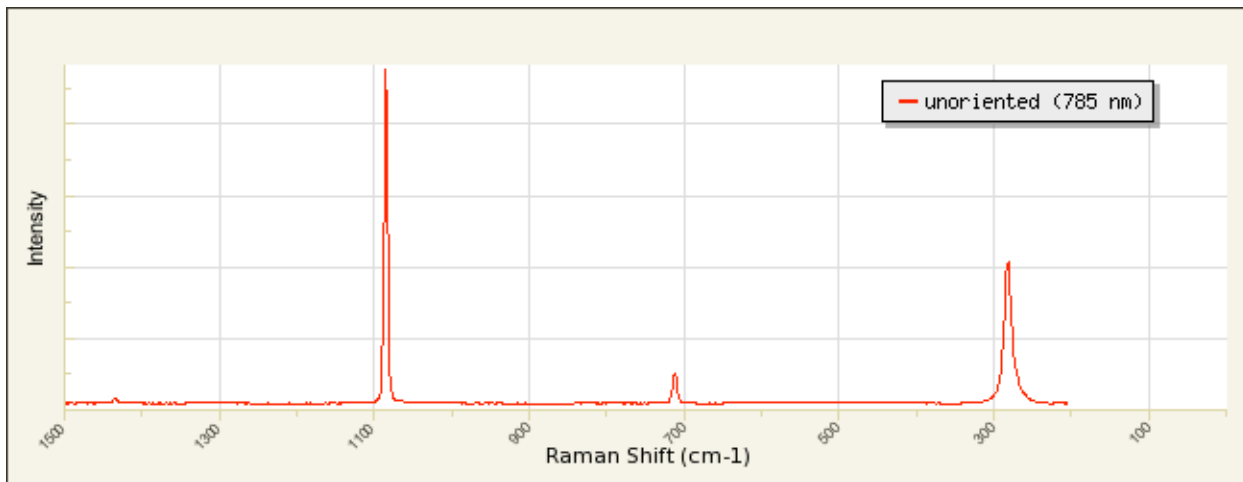
Figure 22. Calcite raman spectrum from RRUFF Database specimen ID: X050034.

Apatite - Ca5(PO4)3(OH,F,Cl) was identified in numerous samples. In mostly appeared as well formed hexagonal crystals that were easy to recognize. In several it appeared as a very corroded. Apatite is found as an inclusion in both magmatic and metamorphic sapphires. According to Gubelin and Koivula (2008), and Hughes (1997), it can be found in metamorphic sapphire from East Africa, Madagascar and Sri Lanka.
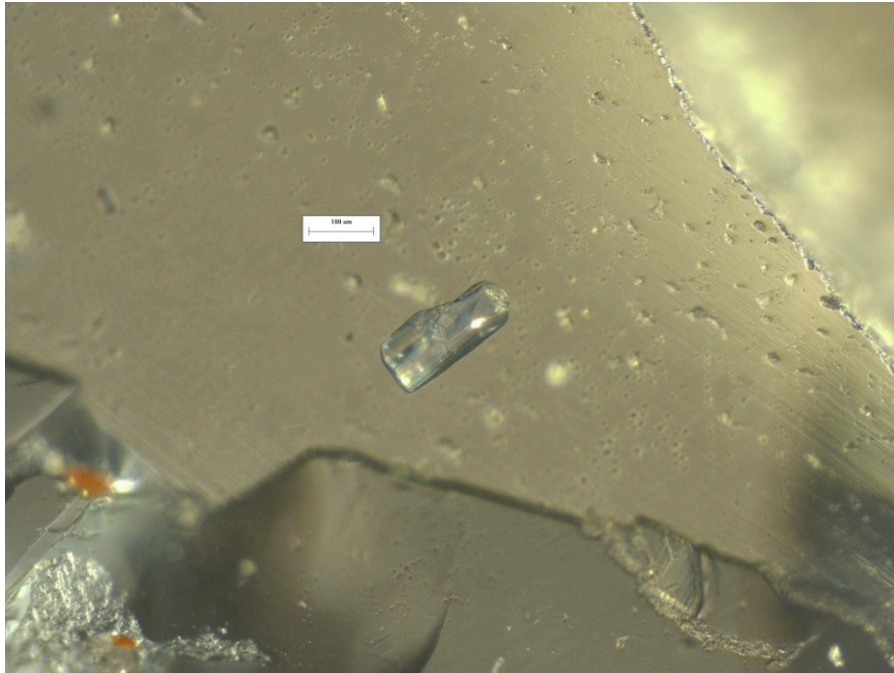
Figure 25. Hexagonal apatite crystal 200X dark field and oblique illumination.
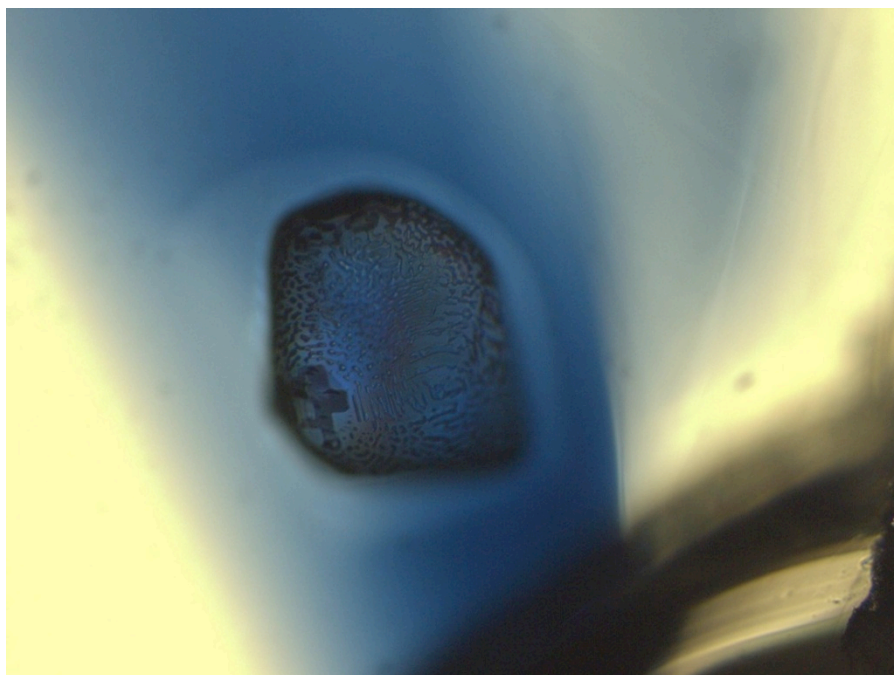
Figure 24. Heavily corroded apatite crystal, possibly a protogenetic inclusion 200X light field illumination.

23
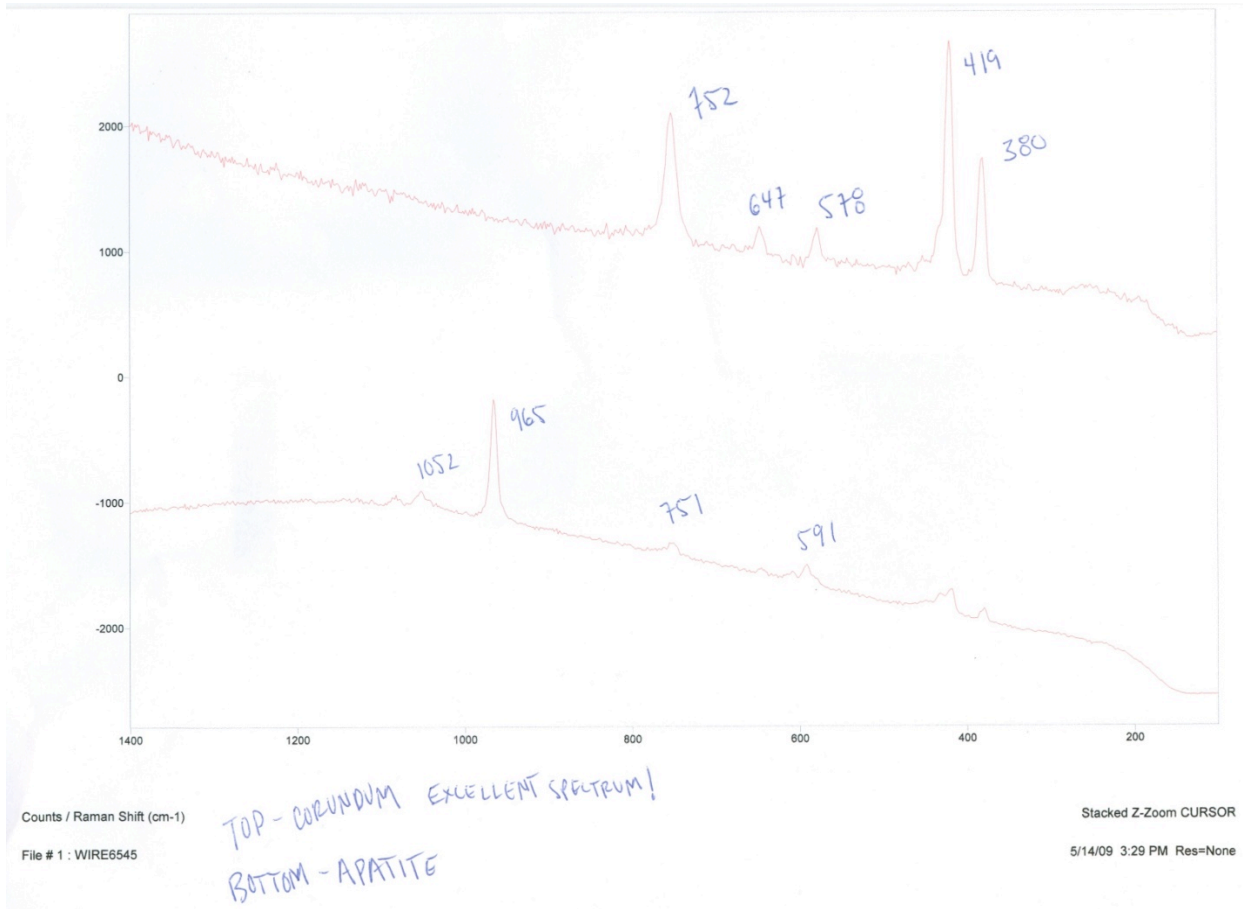
Figure 27. Apatite Raman spectra with host corundum spectra above.
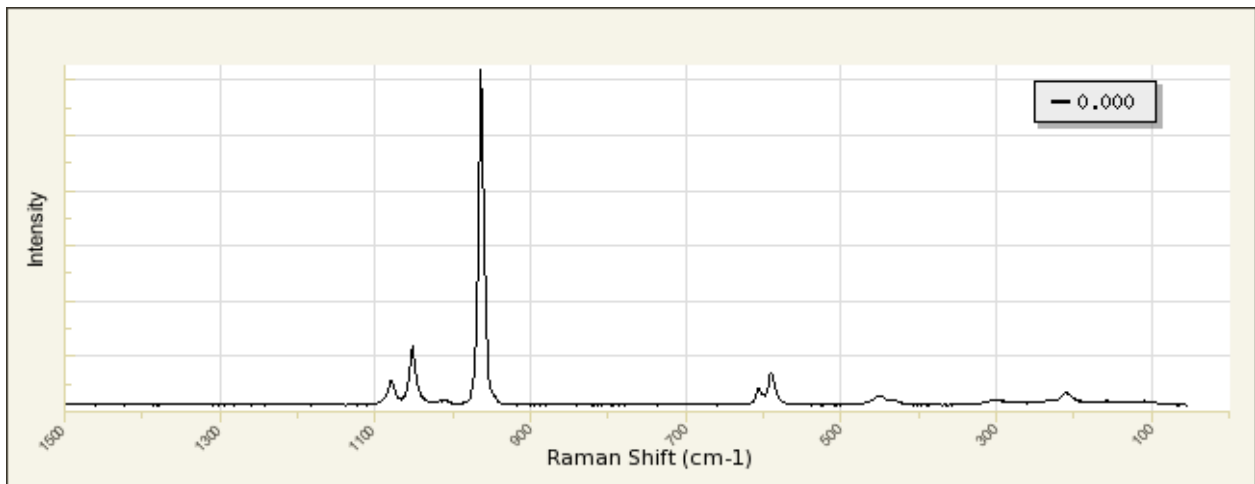
Figure 26. Apatite Raman spectrum from specimen ID: R050369 RRUFF Database.

Feldspar, the exact type of the feldspar is unknown, as the Raman spectra analysis is very similar to several varieties. Feldspar inclusions can be found in both magmatic and metamorphic sapphire.
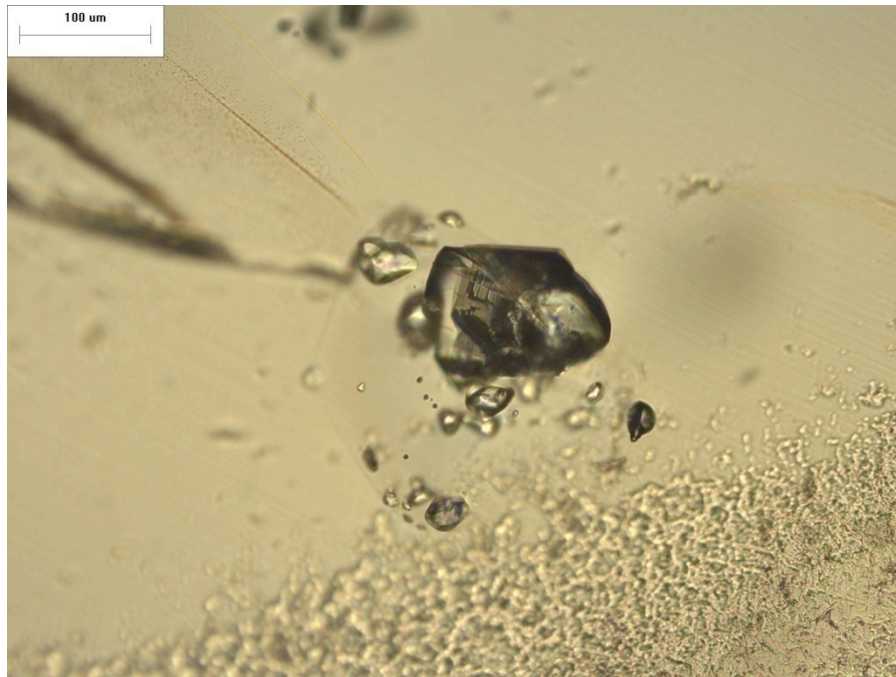

Figure 28. Feldspar crystal with several other smaller crystals surrounding it 100X.

Muscovite mica - $KAl_2(Si_3Al)O_{10}(OH)_2$ was found in one sample. Muscovite is commonly associated with granitic pegmatites. In the Photoatlas Vol. 3 by Gubelin and Koivula (2008), it is identified as an inclusion in pegmatitic influenced sapphire from Burma and in metamorphic sapphire from Sri Lanka where granitic pegmatites are known to intrude sporadically into the country rocks.
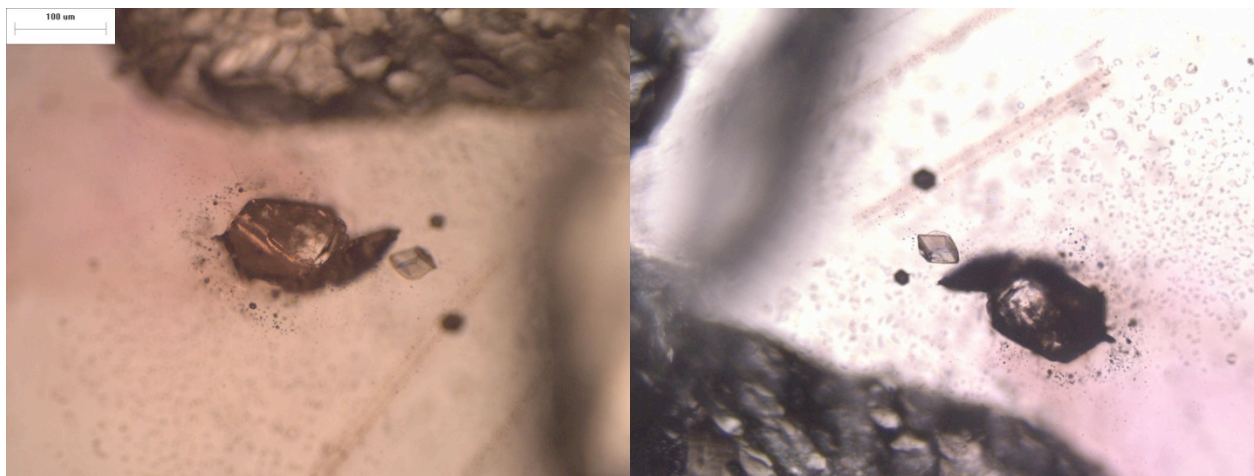

Figure 29. Corroded muscovite crystal with two well formed hexagonal muscovite platelets and unknown rhombohedral crystal 100X bright-field illumination.
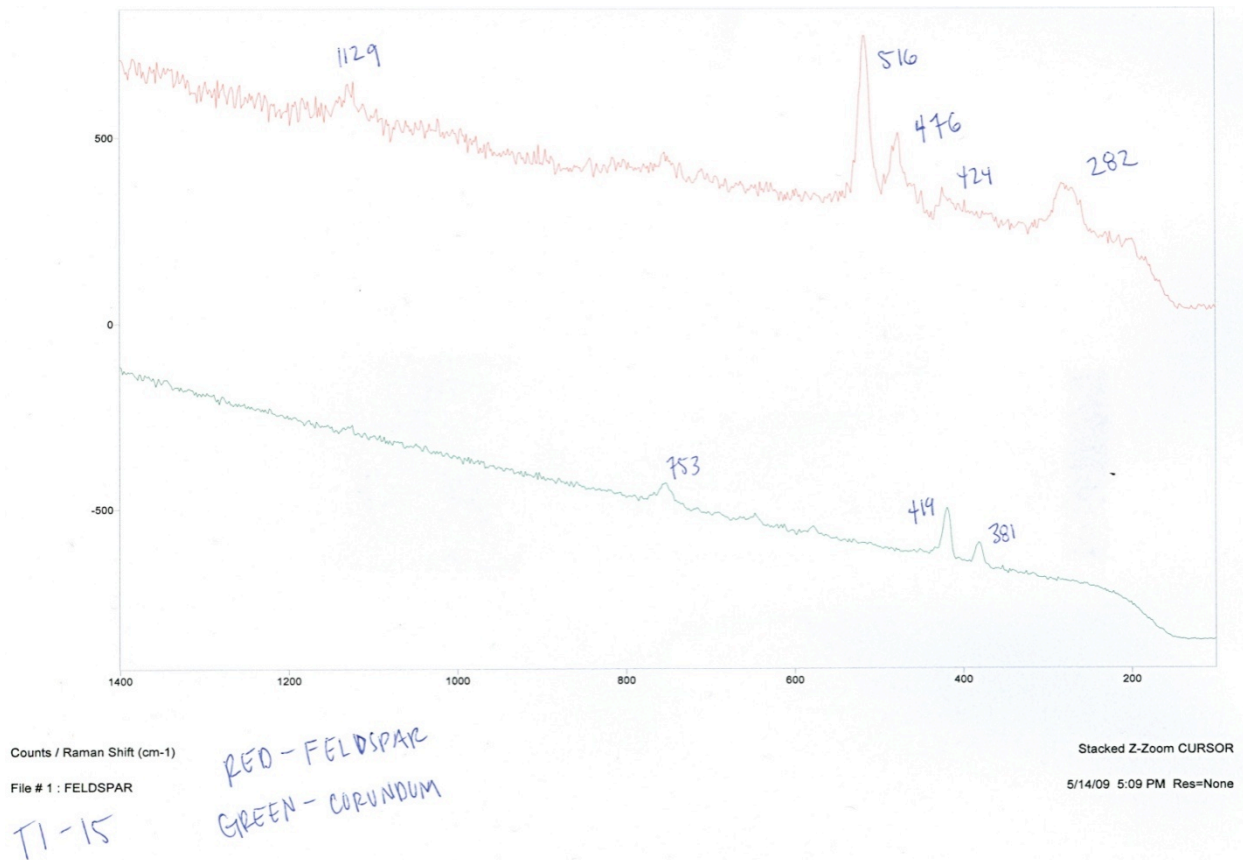
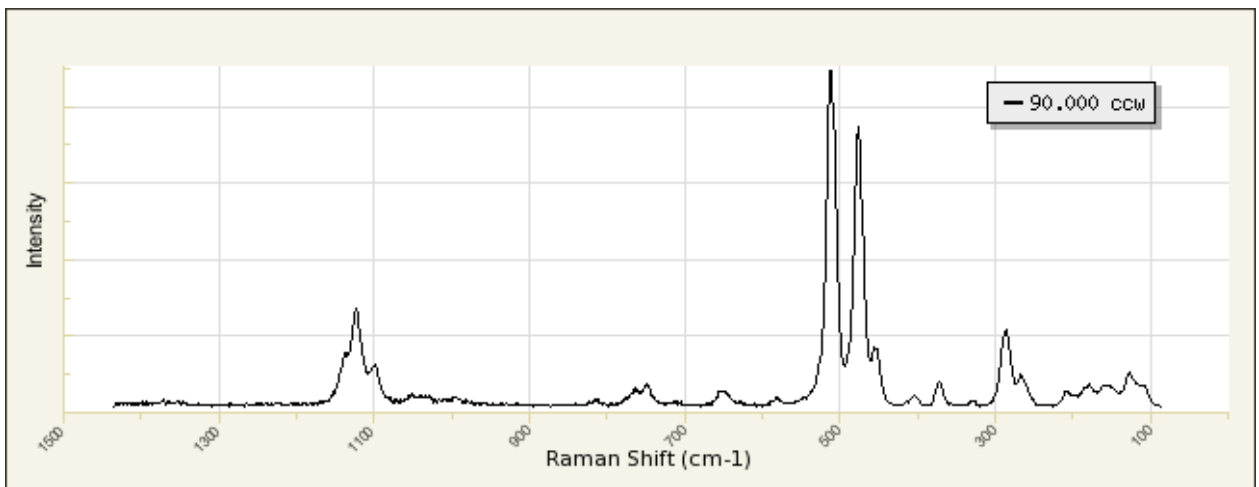**Figure 31. Feldspar raman spectra with host corundum spectra below.**

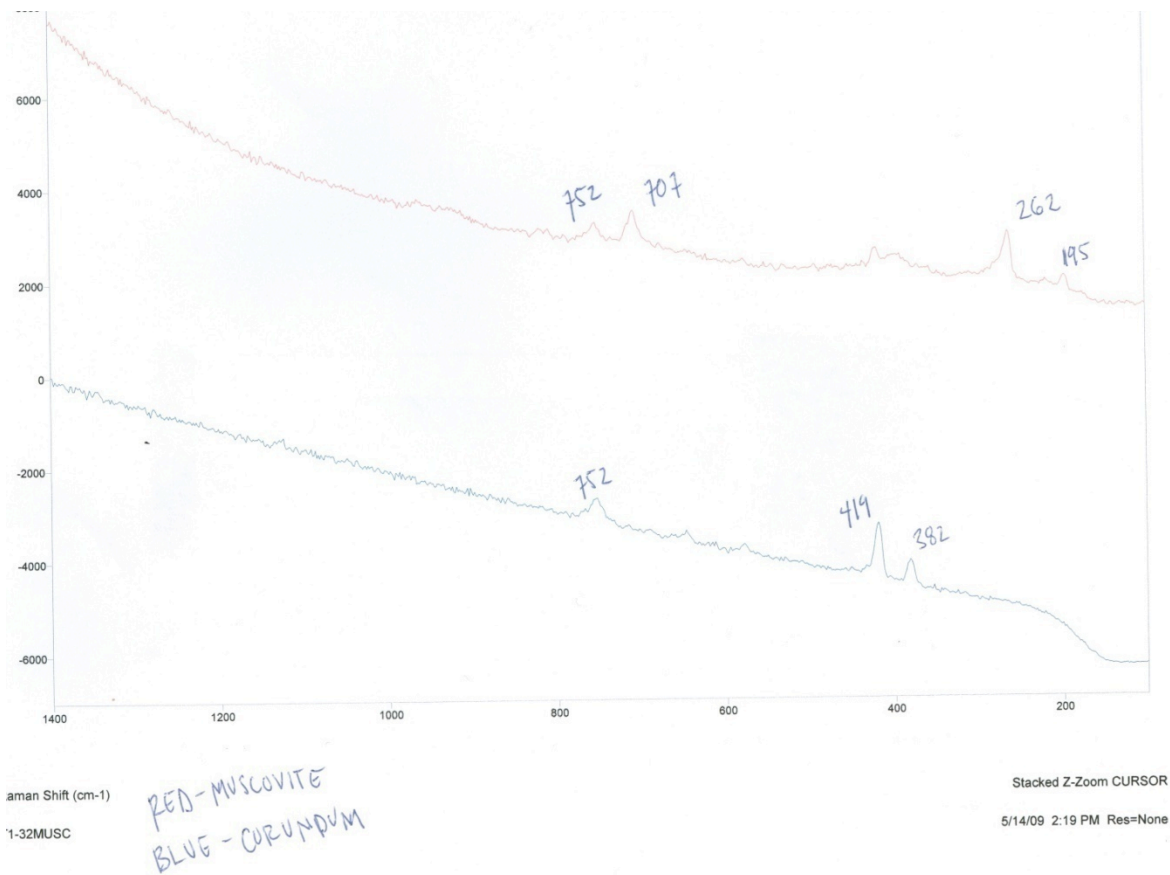**Figure 30. Feldspar raman spectrum from RRUFF Database specimen ID: R040154.**

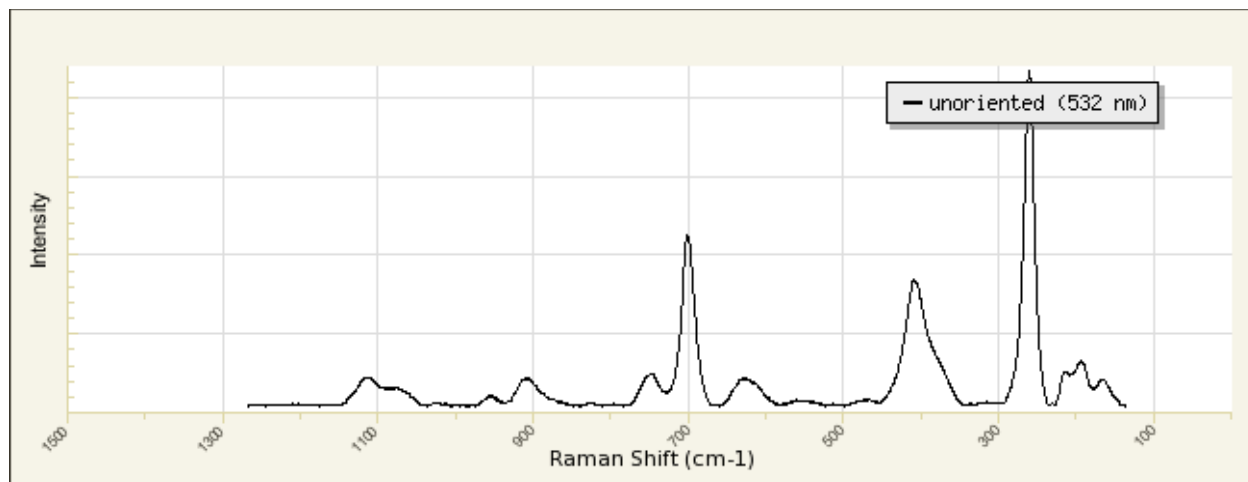**Figure 33. Muscovite raman spectra with host corundum spectra below**

Figure 32. Muscovite raman spectrum from RRUFF Database specimen ID: R040104.

Fluorite, CaF_2, was found in only one specimen. Many of the fluorite inclusions appeared to be one solid mass but upon further analysis with the microscope and the Laser Raman they turned out to be calcite and fluorite crystals growing together. Fluorite seems to be an uncommon inclusion in both ruby and sapphire. The only reference found to fluorite as an inclusion comes from the Gubelin and Koivula (2008). It states that fluorite is sometimes found as an inclusion in sapphires from the Andranondambo metamorphic skarn-type deposit in southern Madagascar.
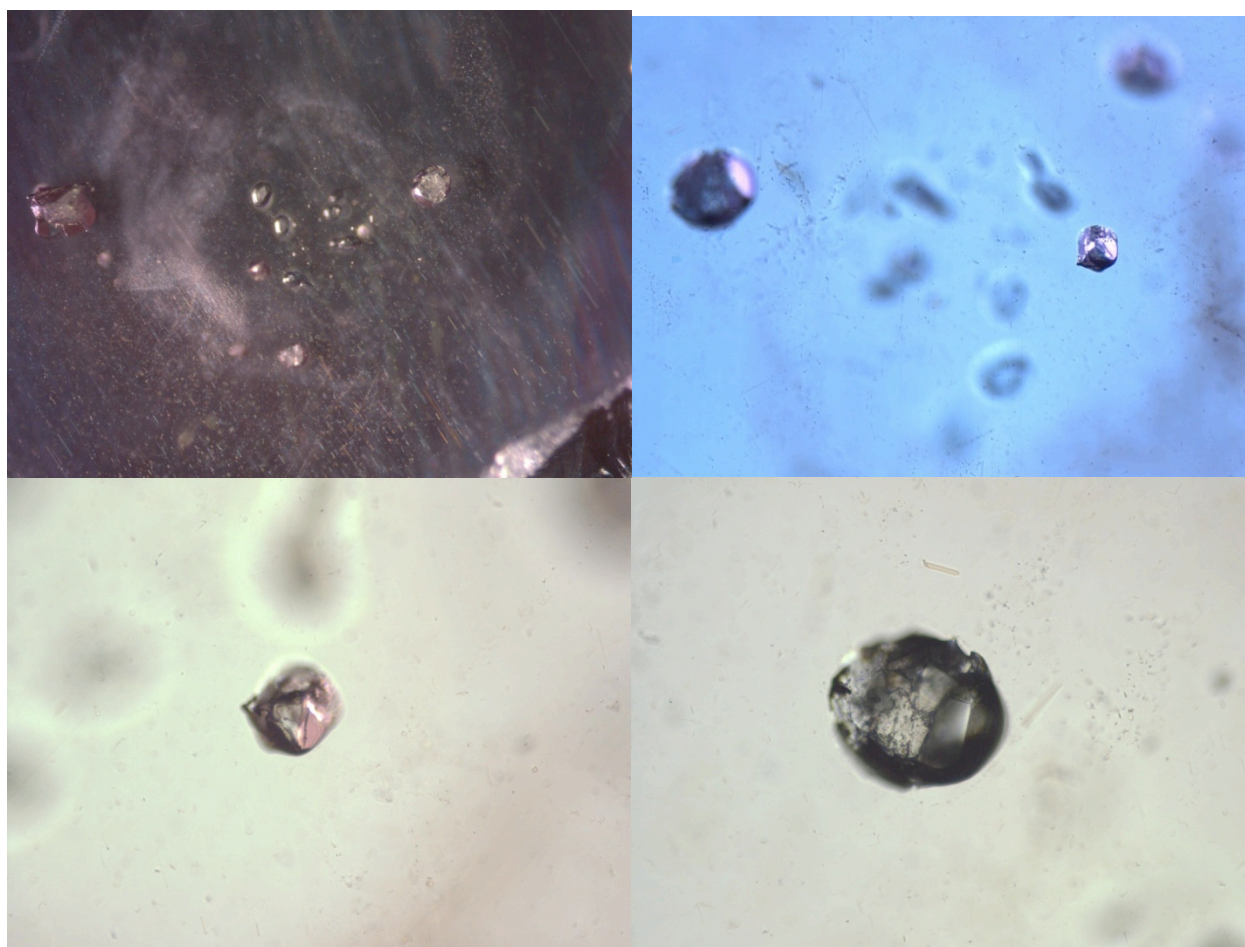

Figure 34. Top fluorite and calcite crystals 50X and 100X. Bottom left, fluorite octahedral in front with rounded, semi corroded calcite crystal attached at back. Bottom right, corroded calcite crystal with fluorite crystal attached on right 200x.
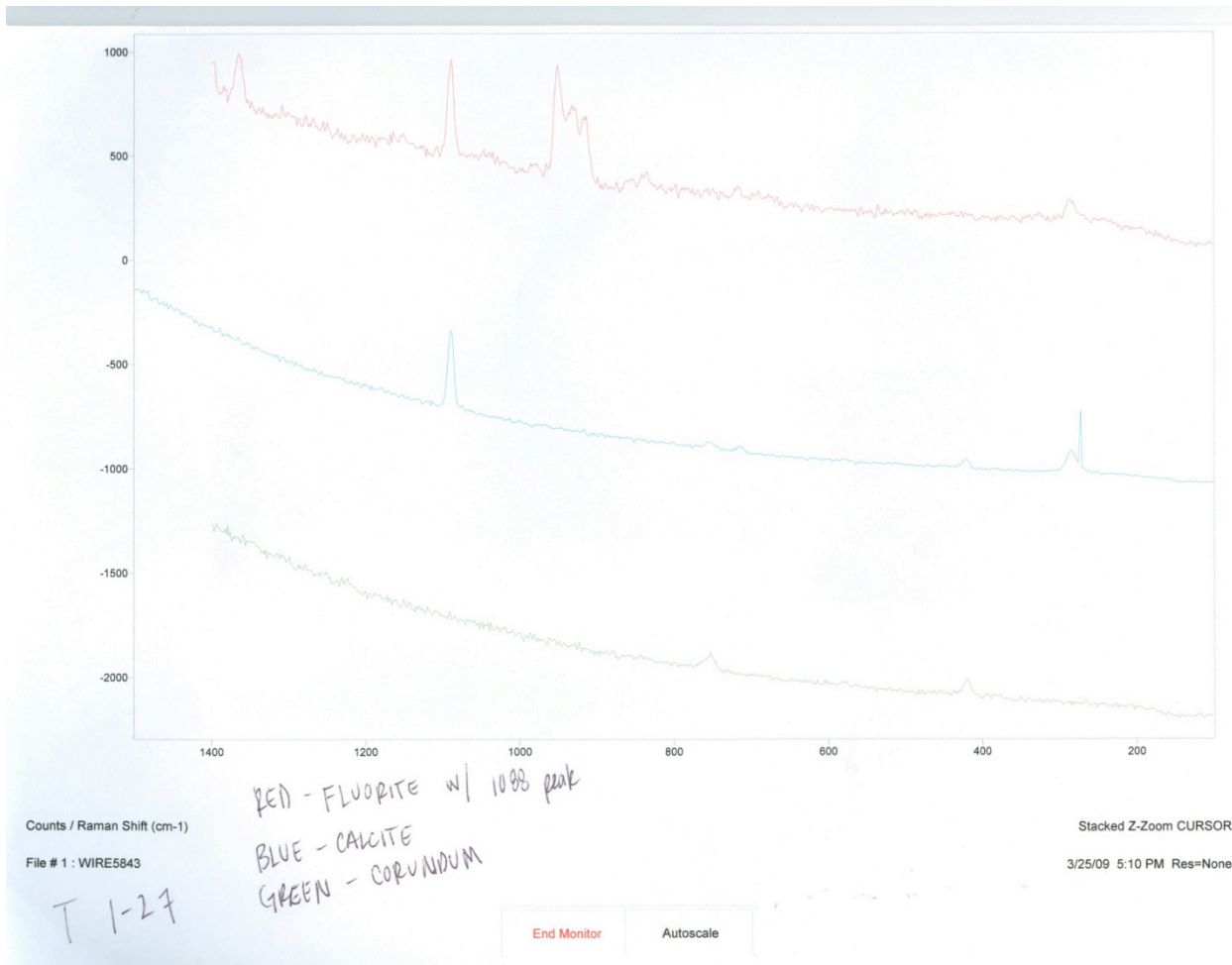
Figure 36. Raman spectra from fluorite octahedron attached to calcite crystal.
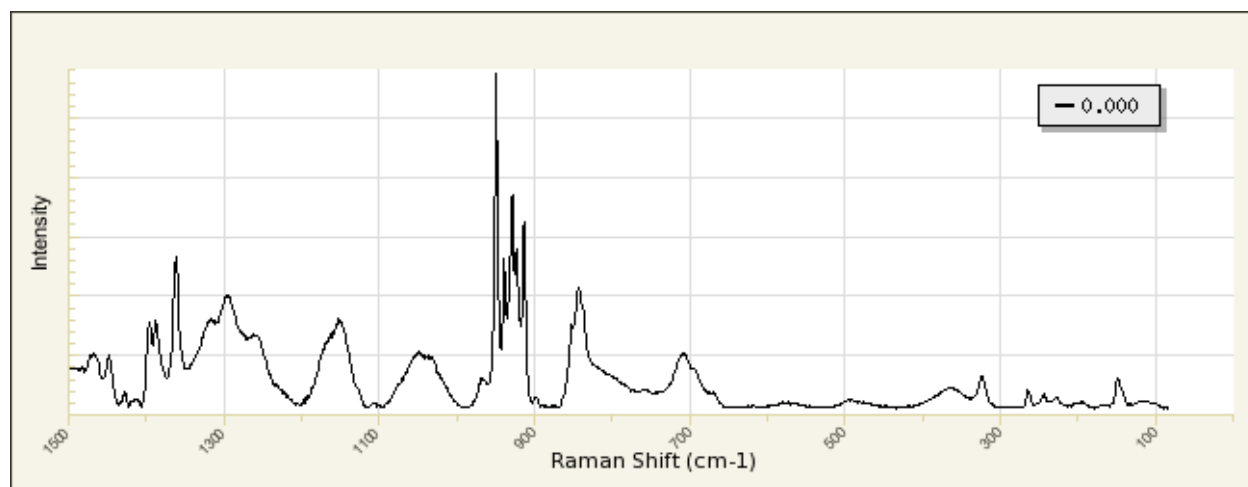

Figure 35. Fluorite raman spectrum from RRUFF Database specimen ID: R040099.

29

6.2.3 Fluid Inclusions

For the most part the samples were sparsely populated with primary fluid inclusions. Those primary fluid inclusions identified were often relatively large, showed good semblance of crystal shape and tend to form in patterns analogous to crystal growth planes or as isolated inclusions. According to Roedder (1984), the trapping of primary fluid inclusions can occur in a number of ways, the most common being rapid uneven growth. They may also form by subparallel growth trapping fluids, covering of previous etch pits caused by partial dissolution, disturbed growth near a fracture that occurred while the crystal is growing, or by the enclosure of a protogenetic solid object. Primary fluid inclusions identified were commonly either two phase containing liquid CO_2 and diaspore, or three phase, containing CO_2 liquid and vapor and diaspore crystals. There were also three phase inclusions that appear to contain CO_2 gas and liquid plus another liquid phase. This other substance is hypothesized to be H_2O based on the premise that CO_2 and diaspore, $AlO(OH)$, have been conclusively identified therefore the solution that formed these sapphires was likely composed largely of H_2O, CO_2, and Al. But as the characteristic H_2O Raman peaks are beyond $3000cm^{-1}$ it was impossible to prove this due to the high fluorescence produced by the sapphires in response to laser excitation. Similarly in some samples negative crystals are hypothesized to contain H_2O as characteristic CO_2 Laser Raman peaks were not found and the spectra were dominated by fluorescence. Several negative crystals also contained a dark flaky substance that is thought to be graphite but could not be conclusively identified with the Laser Raman. Inclusions similar to those identified are found in metamorphic sapphires from Tanzania (Gubelin and Koivula, 2008), Malawi (Rankin, 2002), and Sri Lanka (Hughes, 1997).

Secondary fluid inclusions were still relatively sparse but somewhat more common than primary fluid inclusions. Secondary fluid inclusions are epigenetic inclusions, meaning that they formed after the host crystal stopped growing. They form when a crystal cracks due to some form of stress and the crack is subsequently filled with the fluid that is present at the time. This fluid can act as a solvent if heated enough and can cause the interior walls of the fracture to dissolve starting a process of healing. The secondary fluid inclusions present in the Tunduru sapphire take a great variety of forms. They were also commonly filled with combinations of CO_2 liquid and vapor.
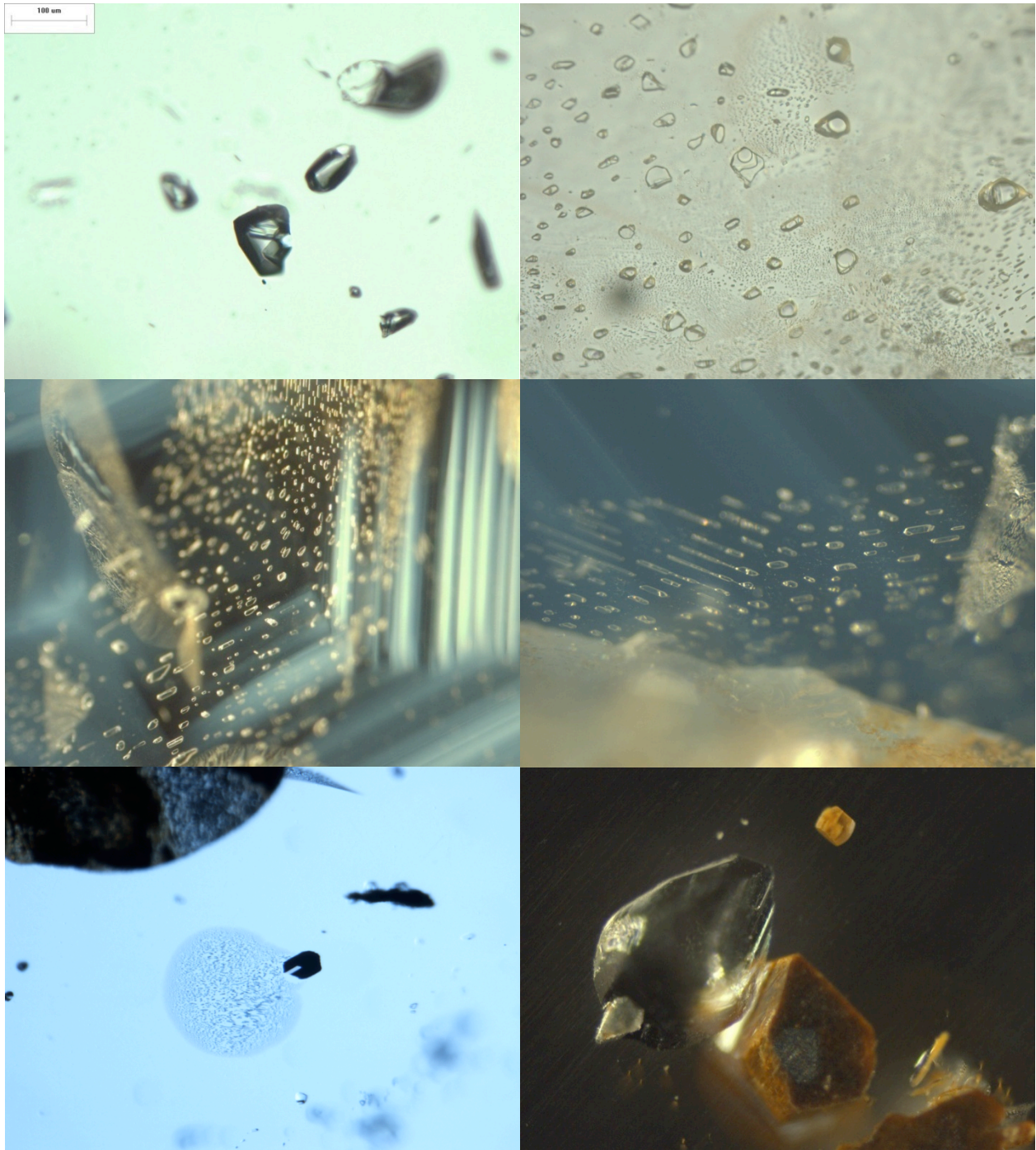
Figure 37. Top left: cavity filled with CO2 liquid, vapor, diaspore crystal and unknown crystal 400X. Top right: multi phase primary inclusions containing mixture of CO2 liquid and vapor, another liquid, and diaspore crystals. Middle: multi phase primary inclusions in the foreground following the trigonal symmetry of the sapphire, in the background a secondary fluid inclusion "fingerprint" 400x. Bottom: a single primary negative cavity containing diaspore crystal with partially healed "fingerprint". Primary inclusions with iron staining showing bipyramidal habit.
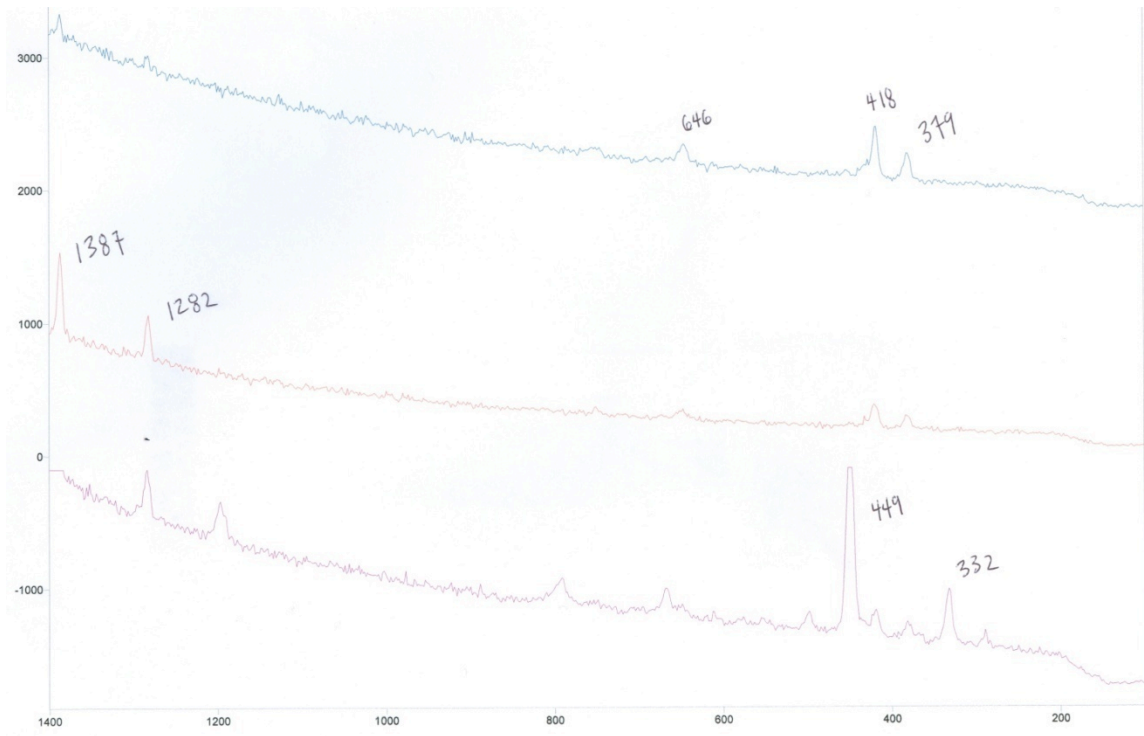
Figure 39. Top, host corundum Raman spectra, middle CO2 Raman spectra, bottom diaspore Raman spectra.
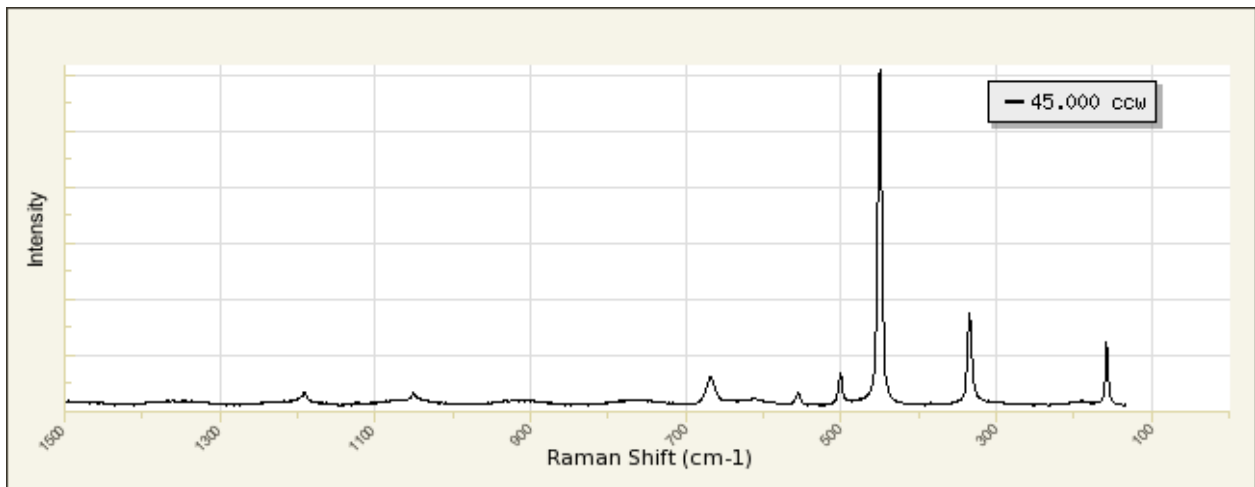

Figure 38. Diasopre raman spectrum from RRUFF Database specimen ID: R060287

6.2.4   Growth Zoning

Many of the thick sections showed prominent color zoning. The first group is composed of mostly colorless sapphire that shows blue color zoning usually appearing in the center of the samples. Often the internal zoning mirrors the external crystal shape. Also the zoning always forms parallel to one or more crystal planes showing the internal representation of pinacoid, bipyramid and rhombohedron forms. Crystals grow by successive layers that grow one at a time over previous layers. When a corundum crystal grows the solution that it is growing out of may or may not have the necessary transition elements to impart color. If there is enough of the coloring agent or agents (for the color blue in corundum Fe and Ti) they will be used up in growth along the outside layer of the crystal that is forming. When the coloring agent has been completely exhausted the corundum will continue to grow but with successive layers devoid of color until growth stops or a new source of color is found.

Color zoning is common in all types of corundum but zoning of this type is extremely similar to that found in sapphires from Andranondambo, Madagascar. In these sapphires the zoning is commonly referred to as a blue phantom and it mirrors internal distribution of external crystal faces. The sapphires at Andranondambo are formed from skarn deposits where the skarn process was initiated by the invasion of a granitic magma into limestone and thus forcing the silica to abandon the limestone which in the course of extensive regional metamorphism, was altered to marble (Gubelin and Koivula, 2008). According to Gubelin and Koivula (2008) these sapphires" grew from CO_2 rich fluids of complex chemical composition and with minor concentrations of fluorine, water and metals such as aluminium, chromium, iron, titanium and zinc as well as other elements (Mg, SI, CA, NA, K, P, Zr, U, and TH)." Mineral inclusions that mark these sapphires are baddeleyite, calcite, feldspar, fluoroapatite, fluorite, phlogopite, thorianite, wollastonite, zirkelite and zircon (Gubelin and Koivula, 2008).

The second type of zoning seen in many of the samples was also a blue zoning, but was always in stones with a pink or pink-violet body color. This combination of pink and blue gave many of the stones a violet color that is very pleasing. This zoning also often follows internal crystal planes most commonly rhombohedral, but just as often was random creating stones that are partly blue and partly pink with a gentle transition between the two colors. One fifth of the samples showed this mixing of blue and pink very well and several others showed it to a lesser extent.

There were also numerous geuda sapphires among the fifty samples. According to Hughes (1997), geuda is a Singhalese word used to describe certain low quality sapphires that respond well to heat treatment first found in Sri Lanka but now also in Madagascar and Tanzania. Geuda sapphire comes in numerous different categories including blue geuda, diesel geuda, milky geuda, silky geuda, and waxy geuda. Geuda stones can be pink, blue, yellow or white but all characteristically contain an abundance of titanium in the form of exsolved rutile. The exsolved rutile gives the rough stones a cloudy or milky appearance sometimes referred to as "diesel" because of its resemblance to diesel oil (Hughes, 1997). This excess of titanium in the form is rutile can be absorbed by the crystal lattice of geuda sapphire when properly heat treated to create beautiful blue sapphire out of material that previously had little or no aesthetic value. The majority of geuda sapphires in the samples fall into the milky or silky categories.
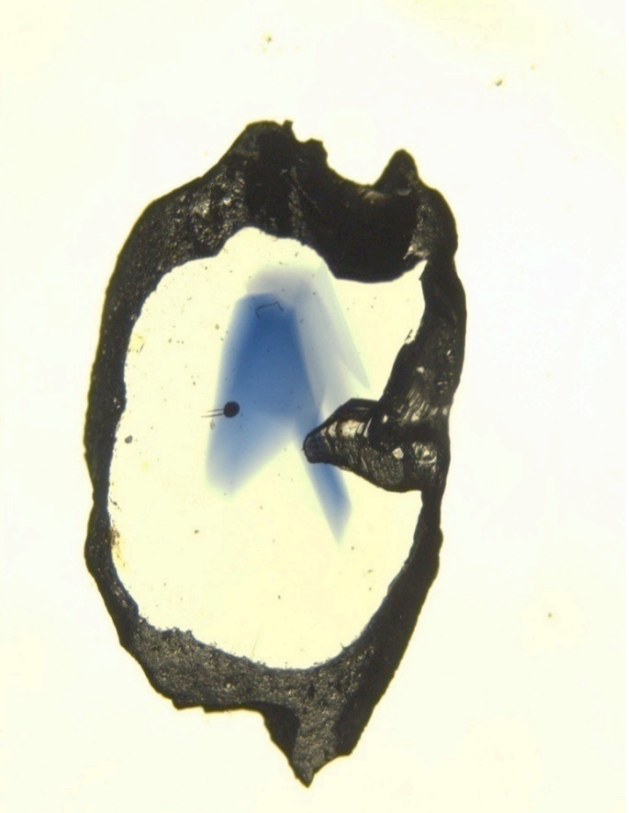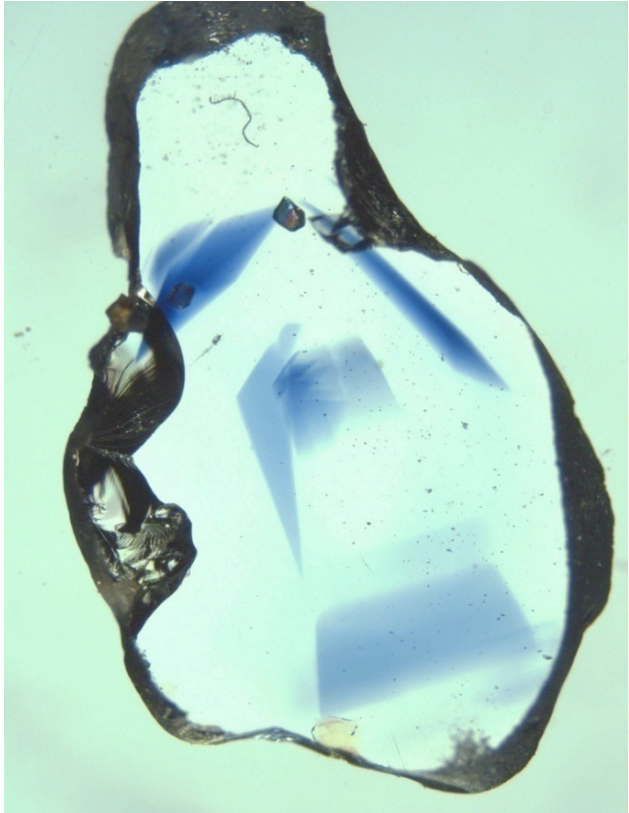
Figure 40 and 42. Blue growth zoning mirrors internal distribution of external crystal faces, basal pinacoid, rhombohedra, and various bipyramid forms can be recognized 20X light field illumination. Blue and pink zoning following internal crystal faces 20X.

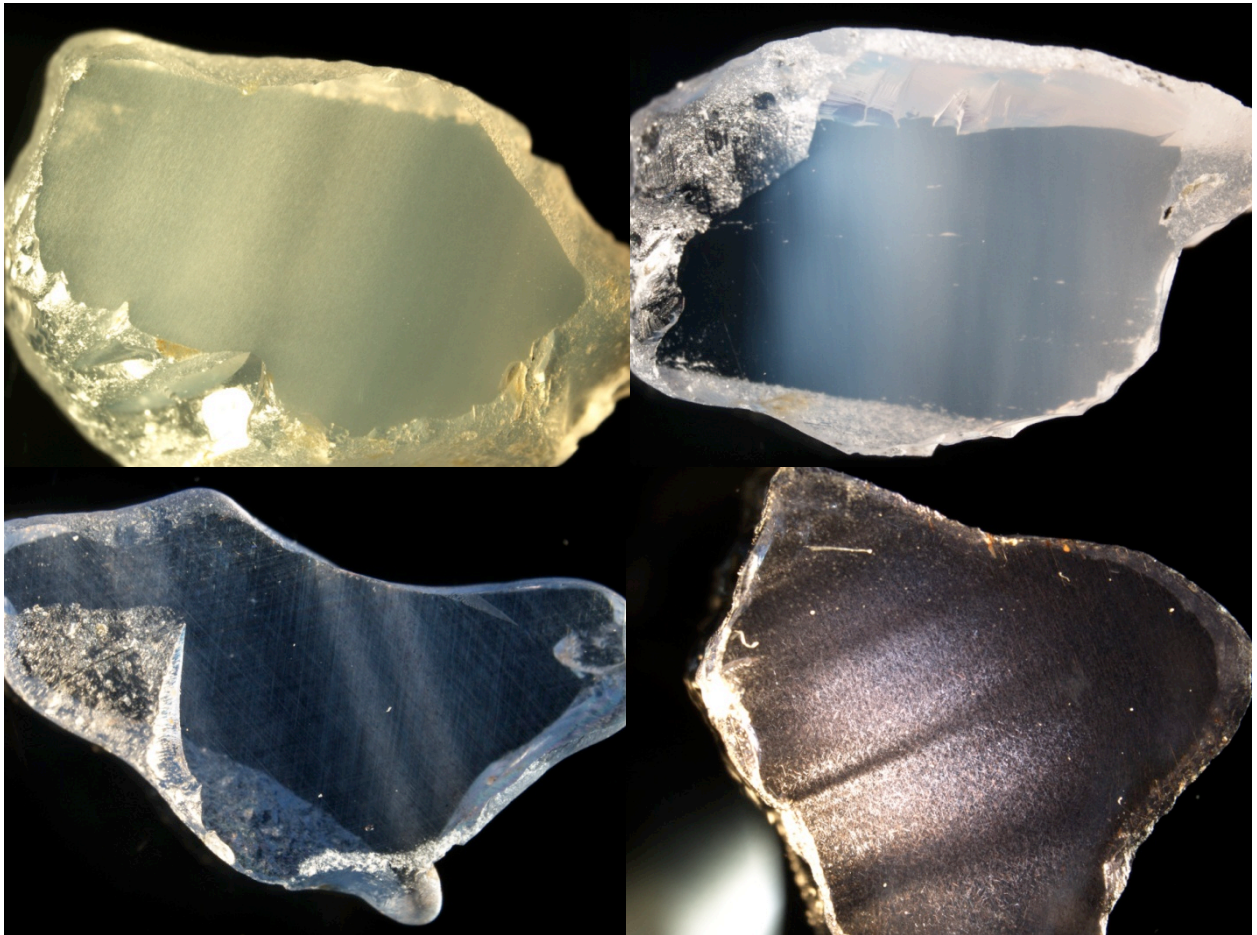Figure 42. Ten samples showing pronounced blue and pink color zoning.

Figure 41. Gueda sapphire from Tunduru Tanzania.

6.   Discussion

The vast majority of observations made about Tunduru sapphire would suggest that they are metamorphic in nature, specifically metamorphic s.s. and possibly metasomatic. Firstly, the wide range of color and the presence of geuda sapphire are indicative of a metamorphic source. The only sapphire deposits in the world known to produce such a variety of colors are the metamorphic deposits of Sri Lanka and Madagascar and the metasomatic pegmatite influenced deposits of the Umba Valley. Magmatic sapphires from alkali basalts tend to be dominantly zoned with the colors blue, green and yellow (BGY suite). These sapphires are among the best studied in the world. Sutherland et al. (1996) in a systematic study of sapphires from basalt fields in Australia and Southeast Asia compiled a list of primary solid inclusions that characterize these BYG magmatic sapphires. One of the most common of these is the Fe and Si rich glassy melt inclusions. These inclusions are completely absent from the Tunduru sapphire. Similarly some of the most common inclusions in the Tunduru sapphire such as phlogopite and monazite have not been reported from the BGY suite.

Individually, the inclusions in the Tunduru samples commonly include minerals that are strongly associated with metamorphic and sometimes pegmatitic sources such as phlogopite and muscovite. The inclusions when taken as an entire suite show a striking similarity to sapphires from known alluvial and primary metamorphic deposits. Specifically, in Madagascar, these include those from Ilakaka, which are characterized by an inclusion suite consisting of apatite, monazite, rutile, xenotime and zircon, and those from Andranondambo marked by calcite, feldspar, phlogopite, fluorite, rutile, zircon and "blue phantom" zoning (Gubelin and Koivula, 2008). The samples also show a serious resemblance to metamorphic sapphires from Sri Lanka. The most striking being the abundance of rutile silk and the long thin appearance of the needles. The lack of primary fluid inclusions present in the samples also supports the proposed metamorphic source. According to Roedder (1984), crystals grown from metamorphic sources are relatively deficient in primary fluid inclusions simply because they were largely supplied with nutrients through solid solution from other crystals or along microscopic grain boundaries. Those fluid inclusions that were found however were very similar to those documented from Sri Lanka (Gubelin and Koivula, 2008) and Chimwadzulu, Malawi (Rankin, 2002) which are known to posses negative crystals containing a solution of water or carbon dioxide or both, accompanied by their vapor bubbles with enclosed daughter crystals of diaspore, graphite and calcite.

Considering these sapphires are millions upon millions of years old it is not entirely surprising that they show very little in the way of crystal forms, however sapphires from all over the world are known to have a fondness for developing into one or two specific habits. Of the few samples recovered showing any crystal forms the most common were suggestive of a spindle shaped hexagonal bipyramid habit similar to those found in Sri Lanka and Kashmir (metasomatic + pegmatite) (Hughes, 1997). The extremely water worn appearance and the little or any crystal form or habit suggests that these sapphires either have traveled a very long distance from their source, came from a source that was very heavily eroded or both. It is interesting to note that two of the locations they most resemble in terms of inclusions, the alluvial deposits Ilakaka and Sri Lanka, both come from parent rock sources that have been almost entirely eroded. As the Tunduru deposits have been known for close to two decades and a source has not been identified it seems highly likely that the sapphires may come from a similarly

eroded source. However it must be noted that aside from gems and cashew nuts the area around Tunduru is most well known for man eating lions and tsetse flies. These natural hazards plus the abundance and wealth of the alluvial gem deposits have led to little known exploration for in situ deposits. The fact that the alluvial deposits in Tunduru seem to be randomly distributed and that the gemstones found comprise such an amazing variety of species and of colors it seems highly likely that the gems came from numerous primary deposits.

7.   Considerations for Further Research

7.1   Trace element ratio analysis. Recently much work has been done comparing the trace element content of sapphires from many different world locations. Specifically when they are plotted as an Fe_2O_3/TiO_2 vs. Cr_2O_3/Ga_2O_3 diagram.

7.2   Oxygen isotope analysis. Recently the use of isotopic composition of framework oxygen in corundum has been used to help determine geologic origin of corundum. This is done by extracting oxygen from the corundum and measuring the ratio of ^{18}O and ^{16}O with a mass spectrometer. The most suitable instrumentation for these analyses is LA-ICP-MS.

References

Altherr, R. O., (1982): Corundum and kyanite bearing anatexites from the Precambrian of Tanzania. *Lithos* , 15, 191-197.

Clannin, J., (2007): Alluvial Gem Deposits of Southern Tanzania.

Downs, R. T., (2006): The RRUFF Project: an integrated study of the chemistry, crystallography, Raman and infrared spectroscopy of minerals. *Program and Abstracts of the 19th General Meeting of the International Mineralogical Association*. Kobe, Japan.

Giuliani, G., Ohnenstetter, D., Garnier, V., Fallick, A. E., Rakotondrazafy, M., Schwartz, D., (2007): The geology and genesis of gem corundum deposits. *Mineralogical Society of Canada Short Course Series.* Vol 37, 23-78. Canada.

Government of Tanzania Ministry of Water and Irrigations. (2007): Water Basins. Retrieved May 1, 2009, from Ruvuma River and Southern Coast Basin: http://www.maji.go.tz/basins/ruvintro.php

Hänni, H., and Schmetzer, K. (1991): New rubies from the Morogoro area, Tanzania. *Gems and Gemology* 27, 156–167

Hughes, R.W., and Pardieu, V. (2008): Gem Resources of Tanzania Pt 1. Retrieved April 10, 2009, from Ruby Sapphire.com: http://ruby-sapphire.com/tanzania-ruby-sapphire-spinel.htm

Hughes, R.W., (1997): Ruby and Sapphire. Boulder, Co: RWH Publishing.

Hughes, R.W., (2006): Sorcerers & Sapphires: A Visit to Madagascar. Retrieved April 5, 2009, from Ruby-Sapphire: http://www.ruby-sapphire.com/madagascar_ruby_sapphire.htm

Keller, P., (1992): Gemstones of East Africa. Phoenix, AZ.: Geoscience Press.

Gubelin, E., and Koivula, J., (1986): Photoatlas of Inclusions in Gemstones (4th edn.). Basel: Opinio Verlag.

Gubelin, E., and Koivula, J., (2008): Photoatlas of Inclusions in Gemstones Volume 3. Basel: Opinio.

Koivula, J., (1991): Inclusion of the Month: Native element Inclusions. *Lapidary Journal*, Vol. 44. No. 11, p. 48.

Kroner, A. (1991): African Linkage of Precambrian Sri Lanka. *Geologie Rundschau*. 80, 429-440.

Pardieu, V., (2005): An update on Ruby and Sapphire mining in South East Asia and East Africa. Retrieved May 1, 2009, from FieldGemology.org: http://fieldgemology.org/gemology%20tanzania%202005.php

Pardieu, V., (2009): The Winza ruby and Sapphire mining area, Mpwapwa district, Dodoma province, Tanzania. Retrieved may 1, 2009, from FieldGemology:

http://fieldgemology.org/Gemology%20tanzania%20ruby%20sapphire%20dodoma%20mpwapwa%20winza.php

Rakotondrazafy, A., Giuliani, G., Ohnenstetter, D., Fallick, A.E., Rakotosamizanany, S., Andriamamonjy, A., Ralantoarison, T., Razanatseheno, M., Offant,Y., Garnier, V., Maluski, H., Dunaigre, C., Schwarz D., Ratrimo, V. (2008): Gem corundum deposits of Madagascar: A review. *Ore Geology Reviews*. 34, 134–154.

Rankin, A. (2002). Natural and heat-treated corundum from Chimwadzulu Hil, Malawi. *Journal of Gemmology*. 28.2. 257-264.

Rupasinghe, M. and Disssanayake C. (1985). Charnickites and the genesis of gem minerals. *Chemical Geology.* 53. 1-16.

Schwarz, D., (2008): Rubies and Sapphires from Winza, Central Tanzania. *Gems & Gemology*. 44.No. 4, 322-347.

Sunderland, F.L., Hoskin, P.W., Fanning, C.M., Coenraads, R.R., (1998): Models of corundum origin from alkali basaltic terrains: a reappraisal. *Contrib Mineral Petrol.* 133. 356-372.

Simonet, C., Okundi, S., Masai, P., (2000): General setting of colored gemstone deposits in the Mozambique belt of Kenya. Proceedings of the 9th Conference of the Geological Society of Kenya. 123-138. Nairobi.

Simonet, C. Fritch, E., Lasnier, B. (2008). A Classification of Gem Corundum Deposits Aimed Towards Gem Exploration. *Ore Geology Reviews*. 33. 127-133.

University of Siena. (2003): Geofluids Laboratory. Raman Spectroscopy Database.

Watt, G. (1994): A high-chromium corundum (ruby) inclusion in diamond from the Sao Luis alluvial mine, Brazil. *Mineralogical Magazine*. 58. 490-493.