

THE EFFECTS OF F-OH⁻ SUBSTITUTION ON THE CRYSTAL STRUCTURE OF PEGMATITIC TOPAZ

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ABSTRACT

Pegmatites are intrusive igneous rocks that are characterized by unusually large grain sizes ($> 20\text{mm}$). There are two main geochemical types of granitic pegmatites, LCT and NYF. LCT pegmatites are rich in the elements lithium (Li), cesium (Cs), and tantalum (Ta) and are usually associated with orogenic granites. NYF pegmatites are related to anorogenic granites and are enriched in niobium (Nb), yttrium (Y), and fluorine (F). Topaz is a fluorine-rich mineral that commonly occurs in pegmatites; however, topaz is more common in NYF pegmatites than in LCT pegmatites. The focus of this study is to examine the changes in topaz crystal structure caused by F-OH^- substitution and to investigate the structural changes due to temperature in order to determine if there are structural differences between topaz from LCT pegmatites and topaz from NYF pegmatites.

In this study, 30 topaz samples from 25 localities were analyzed for unit-cell parameters, fluorine content, trace element content, and heating effects. Cell parameters were calculated from X-ray diffraction data, and fluorine content was obtained by electron microprobe analysis. As consistent with other topaz studies (Alberico et al. 2003), the b unit-cell dimension decreases with increasing F content. Also consistent was a less defined decreasing trend in the a unit-cell dimension as F content increases. No correlation was found between the c cell

dimension and any other cell-dimension or compositional variation. Plots of the pegmatitic topaz from this study show distinct and separate linear trends between NYF and LCT pegmatites when comparing the b unit-cell dimension to the F content. Trace element analysis by X-ray fluorescence shows the presence of Ge, Cr, Pb, Ga, W, and Rb but yields no correlation between trace elements and unit-cell variations. Selected samples were chosen for a heat study. Samples were heated at 700°C for 1 hour. After heating, the unit-cell volume of the topaz generally decreased but no trends separating NYF pegmatites from LCT pegmatites were found.

CHAPTER 1

INTRODUCTION

During the summer of 2006, I participated in the Smithsonian Research Training Program. My advisor was Dr. Michael Wise in the Department of Mineral Sciences at the National Museum of Natural History in Washington D.C. Dr. Wise taught me the basics of pegmatology and the importance of studying these rocks.

Pegmatites are intrusive igneous rocks that form in the late stages of granite formation and are characterized by extremely large grain sizes. Because pegmatites contain the last minerals to crystallize, they must accommodate all the elements that were in the last bit of melt. For this reason, pegmatites contain unusual compositions. Granitic pegmatites commonly concentrate economic quantities of industrial and gemological materials. Industrial materials include beryllium, lithium, and fluorine. The element beryllium, found in the common pegmatite mineral beryl, is used in computers, ceramics, electrodes, musical instruments, and as moderators in nuclear reactors. Lithium is found in the minerals spodumene and lepidolite and is used in batteries, high temperature lubricants, and even drugs for treatment of manic depressive disorders. Fluorine is used in fluoro-chemicals, hydrofluoric acid, and the fluorochloro hydrocarbons that are used in air conditioning and refrigeration systems. Minerals such as, feldspar, quartz, mica, beryl, and fluorite are sources of these important elements.

Pegmatites are also renowned for their large gem quality minerals. Spodumene (kunzite, hiddenite), beryl (aquamarine, emerald, heliodore, morganite, and red beryl), tourmaline, apatite, topaz, fluorite, and corundum (sapphire, ruby) are all found in pegmatites. Pegmatites are critical to the economy and to technological development so it is important to understand their genesis.

Unraveling the origin and history of pegmatites requires study of the crystal chemistry of pegmatite minerals as well as the petrology of pegmatite systems. Trace elements, modifications in crystal shape, and even the color of some minerals can provide information about melt chemistry and pressure-temperature conditions of pegmatite formation. Regional tectonic settings affect both the chemistry of the pegmatite and the physics of intrusion.

Pegmatite nomenclature is an integral part of pegmatology. Pegmatite types are usually divided by chemistry. However it is rare to get a sample that represents the entire chemistry of the pegmatite. We rely on the mineralogy of the pegmatite to help us determine the type of pegmatite. However, many minerals can occur in more than one type of pegmatite making identification difficult. For example, the mineral topaz is rich in the element fluorine. Because of this, we might assume that the pegmatite that produced the topaz is an NYF- type pegmatite (characterized by high fluorine content), but topaz also occurs in LCT-type pegmatites. In these cases, other markers must be used to determine the nature of the pegmatite. This study focuses on the crystal chemistry of the pegmatite mineral topaz. We explore the differences in crystal structure of topaz

from NYF-type pegmatites and topaz from LCT-type pegmatites to determine if pegmatite identification can be made based on crystal structure variations in pegmatite minerals.

CHAPTER 2

BACKGROUND

X-Ray Diffraction (XRD)

X-Ray beams are high energy photons produced by electronic transitions in atoms. As an electron drops from an outer shell to a lower energy shell, energy is lost in the form of a photon. The energy of this photon depends on the atom and the shells involved in the transition. High energy photons are X-rays. X-ray beams are usually generated by heating cathodes. X-rays created in vacuum conditions are accelerated towards the sample by collimators. Some x-ray machines use monochromators to eliminate x-rays of undesirable wavelengths (Griffen 1992).

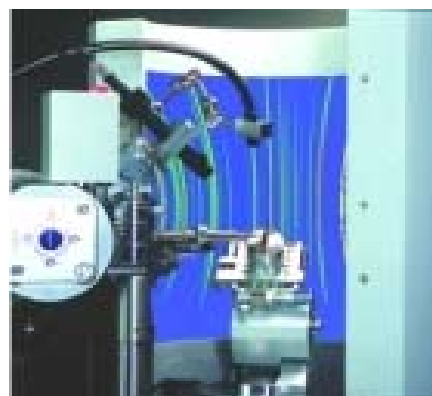


Figure 2-1 D/MAX RAPID II X-ray Diffractometer:
X-rays from the column diffract after hitting the sample. The diffracted beam makes the diffraction pattern on the

X-ray diffraction is used in mineralogy to identify minerals phases, to determine unit cell parameters, and to determine attributes of crystal structures. Both single crystals and powder samples can be used in x-ray diffraction. Single crystals are more commonly used in the determination of crystal structures while powders are used in the determination of unit cell parameters. The essence of x-ray diffraction is Bragg's law. Diffraction can take place only when the lattice planes in a crystal are oriented relative to the incident beam so that Bragg's law is

satisfied. Powder diffraction utilizes samples ground with a mortar and pestle. The large amount of crystals in random orientations raises the probability that Bragg's law will be satisfied for each of the planes capable of diffracting (Griffen 1992).

After acquiring data from X-ray diffraction, peaks in the diffraction

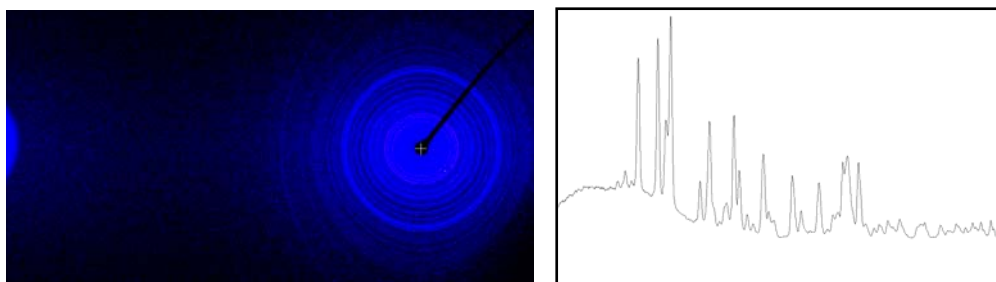


Figure 2-2 X-Ray Diffraction Pattern of topaz from Mursinka, Russia: Each bright ring, moving out from the center on the image above corresponds to the peaks moving from left to right on the graph below.

patterns are converted into d space values and then into unit cell parameters. A common method for refining data is the Rietveld method. The Rietveld method is based on numerical processes to recover three-dimensional crystal structure data from a one dimensional diffraction pattern. This method only works for digitized data and requires the knowledge of approximate lattice parameters, space group symmetry, and atomic coordinates. The method also takes into account instrumental and sample conditions such as scale factors, peak broadening, background, and preferred orientation.

X-ray Fluorescence (XRF)

X-rays are also used in X-ray fluorescence spectroscopy. Wavelength Dispersive Spectroscopy (WDS) uses primary incident X-rays to excite (fluoresce) X-rays in the specimen. Characteristic x-rays are produced in the

sample in the same way that the incident beam is produced. Energy is produced when outer electrons drop to fill vacancies in lower shells. XRF is used to determine major element concentrations or trace element abundances in a specimen. XRF is most effective for elements heavier than sodium.



Figure 2-3 X-ray Fluorescence Spectrometer: X-rays excite the sample causing fluorescence. Image from NMNH

Electron Probe Microanalysis (EPMA)

Commonly referred to as a "microprobe", the electron probe microanalyser utilizes an electron beam instead of an x-ray beam. EPMA uses Wavelength Dispersive Spectrometry (WDS) as well as Energy Dispersive



Figure 2-4 Electron Probe Microanalyzer Facilities: The "microprobe" uses an electron beam to determine composition information over small areas. Image from NMNH.

Spectrometry (EDS) (Griffen 1992). In WDS, elements are quantified based on the wavelength of x-rays emitted from the sample. Using wavelength and the Bragg equations, the x-rays can be produced for individual elements. Each WDS detector measures one element at a

time. EDS determines elemental components by measuring the energies for the x-rays being emitted from the sample. Each EDS detector measures the entire energy spectrum at once (Griffen 1992).

Topaz

Topaz is an aluminum silicate commonly used as a precious gemstone. Topaz is sometimes a constituent of refractory porcelain (King 2000). The name

topaz comes from the Greek word “Topazos” meaning “to seek”. This refers to

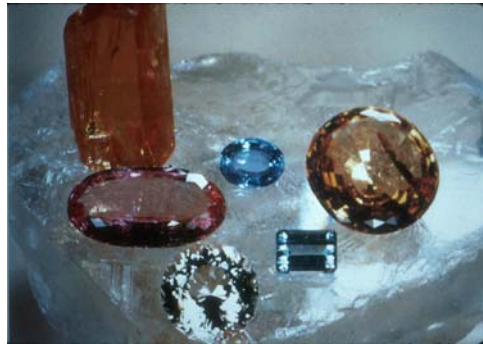


Figure 2-5 Colors of topaz: Topaz colors include colorless, white, yellow, pink, red, orange, brown, green, blue, and violet. Picture from Darby Dyar.

the island of Geziret Zabarget in the Red Sea (Gaines et al. 1997). The island was a hidden source of precious gemstones in ancient times. The island’s most important export was the mineral that we know today as peridot (King 2000). In ancient times, peridot was actually called

topaz. Later, topaz became the general term for yellow gemstones. Other gemstones, referred to as topaz, include yellow sapphire (oriental topaz), yellow andradite (topazolite), citrine (Madeira topaz), and even smoky quartz (smoky topaz). The species we know today as topaz was first recognized as such in 1737 by Henckel (Gaines et al. 1997).

Physical and Optical Properties

Topaz crystals typically have a granular, massive, or columnar habit (Bernard and Hyršl 2004). The crystals are vitreous and transparent to opaque and inclusions are common. Topaz has sub-conchoidal to uneven fracture with perfect cleavage in the {001} plane.

The cleavage plane in topaz breaks the weak Al-F and Al-O bonds (Hoover



Figure 2-6 Topaz from the National Gem Collection: These are two of the world’s largest gem quality topaz (70lbs and 111lbs). In the center, the “American Golden” topaz is 22,892.5 carats. Picture from NMNH.

1992). Topaz is brittle but has a hardness of 8. Topaz can be colorless, white, yellow, pink, red, orange, brown, green, blue, or violet. The vibrant blue color in gem topaz is the result of artificial irradiation. Most colors in topaz are caused by color centers, while others have been linked to trace amounts of transition metals. Topaz colors caused by color centers may fade when exposed to sunlight (Bernard and Hyršl 2004). In thin section, topaz appears colorless, yellow, red, or blue in transmitted light. Optically topaz is biaxial (+) with a $2V$ of $48^\circ - 68^\circ$.

Crystal Structure

The crystal structure of topaz was determined independently by Alston and West (1928) and Pauling (1928). The topaz structure is made up of silica tetrahedra and aluminum octahedra. Topaz is a nesosilicate (orthosilicate). In

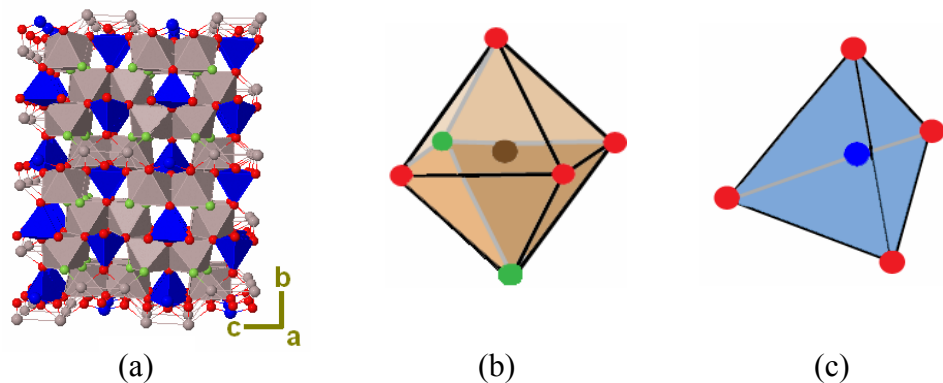


Figure 2-7 The Crystal Structure of Topaz: (a) Topaz has an orthorhombic crystal structure. The chains of aluminum octahedra are normal to the c axis. (b) Aluminum octahedra have 1 aluminum atom, 4 oxygen atoms, and 2 fluorine/hydroxyl atoms (c) Silica tetrahedra have 1 silica atom and 4 oxygen atoms.

nesosilicate structures, the tetrahedra do not share oxygen with other tetrahedra.

In the case of topaz, the silica tetrahedra share each of their oxygen with aluminum octahedra (Hoover 1992). The aluminum octahedra are joined by shared edges (edges with 2 oxygen) creating kinked chains normal to the c axis (z

crystallographic axis). This arrangement creates alternating close-packed layers of O, F and O normal to the b axis. Topaz belongs to the orthorhombic crystal system. It is in the space group Pbnm and the point group $2/m\ 2/m\ 2/m$ (Anthony et al. 1995). The space group Pbnm is true of topaz when the fluorine-hydroxyl sites are equivalent and the structure is disordered. Ordering in relation to hydroxyl content was suggested by Akizuki et al. (1979) to explain anomalous optical properties in some topaz. As more hydroxyl substitutes for fluorine, the symmetry of the crystal is reduced to monoclinic and eventually triclinic symmetry (Bernard and Hyršl 2004).

Trace Elements

Generally, topaz has few trace elements. Germanium, which substitutes for Si has concentrations in the range of 200-400ppm. Cr, which substitutes for Al, can range in concentration from 20ppm to 500ppm (Hoover 1992). Mn usually has concentrations less than 30ppm (Gaines et al. 1997). For the elements B, Li, and Na concentrations of >100ppm have been reported but normal ranges for these elements are 40-60ppm. Other elements found in topaz include Nickel (80ppm), V (<20ppm), and Cobalt (<8ppm) (Hoover 1992). Radiogenic helium was reported in topaz from the Volyn region of Ukraine (Hoover 1992).

F-OH substitution

There is a solid solution between fluoro-topaz (F end member) and hydroxyl topaz (OH^- end member). Hydroxyl is a diatomic molecule of hydrogen and oxygen connected by a covalent bond. Hydroxyl topaz is not found in nature

but it has been synthesized at high pressure (Wunder et. al 1993, 1999 and Rosenberg 1972, 1978). Natural topaz ranges from nearly end member fluoro-topaz to $\text{Al}_2\text{SiO}_4(\text{F}_{1.4}\text{OH}_{0.6})$. The highest reported OH^- content is 0.55 reported by Zhang et. al (2002) in topaz from ultra high pressure rocks in the Sulu Terrane in Eastern China. Orthorhombic topaz has 8 symmetrically-equivalent locations for F and OH^- . OH^- can substitute into as many as three of these sites. The maximum value for OH^- substitution (naturally) is about 30% (Gaines et al. 1997). When two OH^- molecules occupy neighboring sites a significant H-H repulsion causes a deflection of the protons (Ainse and Rossman 1985). This is the basis of the proton avoidance model mentioned by Churakov and Wunder (2004).

Occurrence and Distribution

Topaz is most commonly found in igneous rocks. Topaz is found in late magmatic to post magmatic peraluminous granites and pegmatites (Bernard and Hyršl 2004). Fluorine rich vapors in rhyolites contribute to the formation of topaz in volcanic settings (Gaines et al. 1997). About 80% of worldwide topaz deposits are pegmatites. Rhyolites make up 10% of the deposits. The remaining 10% is made up of greisens (hydrothermal deposits), metamorphism, and alluvial sediments (Menzies 1995). Topaz is commonly associated with tourmaline, beryl, microcline, albite, fluorite, cassiterite, zinnwaldite, and quartz.

Pegmatites

Pegmatites are intrusive igneous rocks that form in the late stages of granite crystallization. Pegmatites form in a variety of sizes, shapes, and

orientations (Brisbin 1986). Pegmatites generally have sharp and irregular contacts. The large crystals of pegmatites are the result of rapid (days to months) cooling in water and volatile rich melts. Volatiles, also known as fluxes, like water, fluorine, boron and phosphorous lower the viscosity as well as the solidus temperature of the melt facilitating the large crystals and internal zoning within the pegmatite bodies. Rare Earth Elements (REE) and incompatible elements are often concentrated in pegmatite melts leading to unusual mineralogy in many pegmatite bodies.

Pegmatites are classified on a variety of criteria including structure, chemistry, mineralogy and depth of emplacement (Černý and Ercit 2005). Černý (1990, 1991) proposed a classification system for pegmatites that groups the rocks into three petrogenic categories: NYF, LCT, and mixed.

NYF

NYF pegmatites are enriched in the elements Nb, Y, F, I, Zr, U, REE's, Mo, Sb, Bi. Common minerals include potassium feldspar, quartz, plagioclase, and biotite. NYF pegmatites are peralkaline. The parent granites of NYF pegmatites are homogenous to somewhat differentiates, subaluminous to



Figure 2-8 Pegmatitic Texture: Pegmatites generally contain crystals 20cm or larger. These large crystals can be attributed to rapid cooling in a volatile rich melt. Image from Dr. M. A. Wise (NMNH)

metaluminous¹ A to I type granites. Some parent granites may have peraluminous and peralkaline parts (Černý and Ercit 2005). Černý and Ercit (2005) suggests several origins for these granites: 1) Differentiation of mantle-derived magmas 2) Melting of middle or lower crust protoliths 3) Melting of undepleted igneous lithologies in an orogenic setting 4) Melting of crust pre-enriched in NYF elements by mantle derived fluids.

LCT

LCT pegmatites are enriched in Li, Rb, Cs, Be, Sn, Ta, Nb, B, P, F. The concentrations of RRE are relatively low (Černý and Ercit 2005). Common LCT minerals include beryl, columbite, lepidolite, and tantalite. The parent granites of LCT pegmatites are peraluminous S and I type granites. These granites are strongly fractionated with varied textures. Černý and Ercit (2005) suggests that LCT pegmatites and their parent granites are derived from melting of meta-igneous rocks or melting of undepleted upper to middle crust protoliths.

Mixed

Mixed pegmatites display both LCT and NYF mineralogies and chemistries. Origins include the formation of LCT phases in highly evolved NYF pegmatites (Černý and Ercit 2005). Mixed pegmatites are rare.

Sample Localities

All samples used in this study are part of the mineral collections of the Mineral Sciences Department at the Smithsonian National Museum of Natural

¹ Molar proportions $Al/(Na+Ca+K)$: >1 Peraluminous, =1 Metaluminous, <1 Peralkaline

History. There are a total of 32 samples representing 26 geographic localities. Two samples were later excluded due to undesirable sample condition. Of the 32 samples 30 were analyzed representing 25 geographic localities. There are two samples each from Viitaniemi, Erajarvi, Finland, Devil's Head, Colorado, USA, Erongo, Namibia, Volodarsk, Volyn, Ukraine, and Powatan, Virginia, USA. The Herbb-2 pegmatite samples from Powatan, Virginia are samples from the research collection of Dr. Michael Wise. There are 19 topaz samples from NYF pegmatites and 11 topaz samples from LCT pegmatites. Topaz is more common in NYF pegmatites than in LCT pegmatites due to the elevated concentrations of F in NYF pegmatites.

The Little Three & Palomar, California, USA localities (Figure 2-9, #1&2) are associated with the Peninsula Ranges Batholith. The granite intruded about 100Ma ago as older island arcs were accreted to the western continental margin (Menzies 1995). The Platte Mountain, Devils Head, Tarryall, & Mt. Antero Colorado, USA localities (Figure 2-9, #4-7) are associated with the 1000Ma Pikes Peak batholith. Topaz at Mt. Antero occurs in mairolitic cavities (Bernard and Hyršl 2004). The Morefield & Amelia, Virginia, USA pegmatites (Figure 2-9, #8&9) have an estimated age of 250Ma. Neither age or physical proximity links these pegmatites to a parent granite (Smerekanicz and Dudas 1999). The Herbb #2 Pegmatite in Powatan, Virginia, USA (Figure 2-9, #10) is part of a NE-trending belt of pegmatites. The pegmatite is located in the Piedmont province in central Virginia. Stoneham (Lord Hill) & Fisher Quarry, Maine, USA (Figure 2-9,

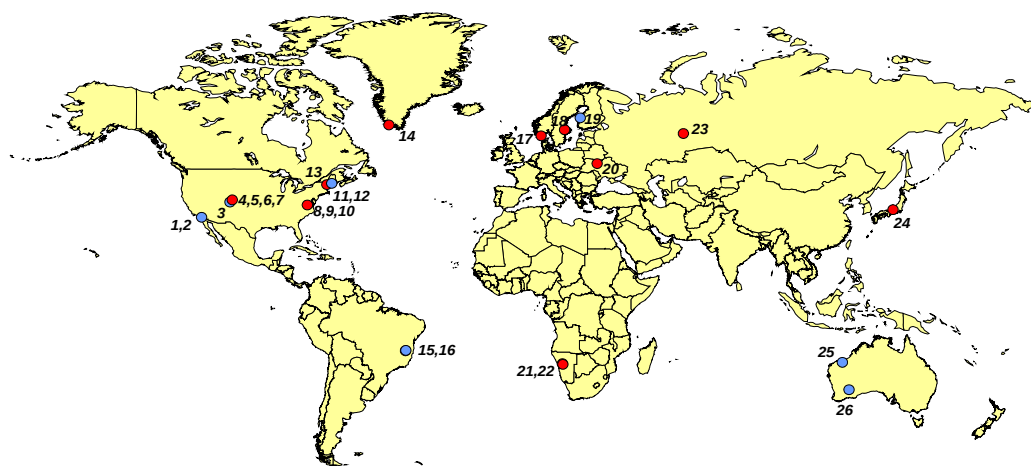


Figure 2-9: Map of Topaz Sample Localities: A total of 32 samples representing 26 worldwide localities were prepared for examination in the current study. Red points correspond to NYF sample localities and blue points correspond to LCT sample localities.

#11&12) are late Paleozoic pegmatites surrounded by high grade metamorphic rock. The Baldface Mountain, New Hampshire, USA locality (Figure 2-9, #13) is associated with the Mesozoic White Mountain batholith. Two samples from Ivigtut, Greenland (Figure 2-9, #14) were excluded from analysis. The two samples contained significant amounts of cryolite. Virgim de Iapa, Minas Gerais, & Minas Gerais, Brazil (Figure 2-9, #15&16) are late or post-orogenic granites 520 to 510 Ma in age (Menzies 1995). Iveland, Norway (Figure 2-9, #17) is known for its Be, Th, Zr, and REE- rich pegmatites. Volodarsk, Ukraine (Figure 2-9, #20) is an anorogenic cavity bearing pegmatite with an estimated age of 1770Ma (Menzies 1995). The pegmatites in Spitzkopje & Erongo, Namibia (Figure 2-9, #21&22) are associated with the Neoproterozoic Damara orogenic belt. The magmatism of the belt is related to the continental rifting that separates South America and Africa (Frindt and Haapala 2005). The Mursinka, Russia

(Figure 2-9, #23) pegmatite formed as a result of the Carboniferous to Permian age collision between the Russian and Siberian platform. This is the same collision that formed the Ural Mountains (Menzies 1995). Age and parent granite information could not be found for the following localities: Ohio City, Colorado, USA (Figure 2-9, #3), Broddbo Sweden (Figure 2-9, #18), Viitaniemi, Finland (Figure 2-9, #19) Takayama, Japan (Figure 2-9, #24), Wodgina, Australia (Figure 2-9, #25), Grossmont, Australia (Figure 2-9, #26).

CHAPTER 3

METHODS

Sample Selection

Each sample had at least 2g of material free of inclusions. This is the least amount needed to perform both the X-ray diffraction analysis and the Electron microprobe analysis. Samples that contained at least 4g of material were analyzed for trace elements by X-ray fluorescence spectroscopy. After XRF analysis, samples with remaining material were used for a heat study. All analyses were carried out at the facilities of the National Museum of Natural History, Smithsonian Institution in Washington D.C.

X-ray Diffraction (XRD)

Small chips (<4mm) of each sample were ground to a fine powder with a mortar and pestle. A small amount of acetone was used to aid in the grinding. The powdered samples were mounted on glass fibers 1cm to 1.5cm in length. The tip of the fiber was dipped into epoxy and then into the powder. Ideally, a sphere of the sample formed on the tip of the fiber. The glass fibers were mounted on a diffractometer holder. Clay was used to stabilize the fiber on the holder.

Seven samples were selected for a heat study. Un-powdered samples were placed in crucibles and heated in a box furnace at 700°C for 1 hour. Samples were

allowed to cool in the crucibles for 2 hours. Samples were then powdered and mounted on glass fibers using the same methods as the unheated samples.

The samples were analyzed in a Rigaku D/MAX RAPID II Microdiffractometer. This diffractometer has a curved imaging plate. The imaging plate data were analyzed using Rigaku's [AreaMax](#) software. Samples were analyzed with Mo radiation and 0.3mm collimator at atmospheric pressure for 10 minutes each. Data were taken from 3° to 60° (2 θ). Phase identification was performed with Jade 7 software developed by Materials Data, Inc. Unit cell parameters were refined using the Rietveld method by means of General Structure Analysis System (GSAS). GSAS was written by Allen C. Larson and Robert B. Von Dreele from the Los Alamos National Laboratory. The EXPGUI (Graphical user interface for GSAS experiment [.EXP] files) was written by Brian H. Toby of the National Institute of Standards and Technology Center for Neutron Research.

X-Ray Florescence (XRF)

Samples were milled and sieved to 200 mesh; 1.6 g of the sample was combined with 0.4 grams of cellulose and shaken for 5 minutes in a glass jar to homogenize the mixture. The mixture was then pressed into a pellet for analysis. Samples were analyzed on a Phillips PW 1480 machine with an accelerating voltage of 80kV and a beam current of 30 μ A

Electron Probe Microanalyzer (EPMA)

Chips of the samples were placed in epoxy mounts and polished. The polished sections were sputter coated with carbon. The samples were analyzed in a JEOL 9800R/5 Electron Probe Microanalyzer with an accelerating voltage of 15kV, a beam current of 20 μ A and a beam diameter of 10 μ m.

CHAPTER 4

RESULTS

Thirty topaz samples were analyzed. Each sample has been identified by both the Smithsonian National Museum of Natural History catalogue number and a sample name used for identifying samples on graphs in this study.

Table 4-1: Sample Identification Information

NMNH Catalogue Number	Sample Name	Locality	Type
R7789	N1	Tarryall, Colorado	NYF
102995	N2	Platte Mountain, Colorado	NYF
97413	N3	Devil's Head, Colorado	NYF
C5672	N4	Mt. Antero, Colorado	NYF
C5333	N5	Devil's Head Colorado	NYF
B15037	N6	Takayama, Japan	NYF
173756	N7	Erongo, Namibia	NYF
173783	N8	Erongo, Namibia	NYF
B15060	N9	Spitzkopje, Namibia	NYF
R9029	N10	Baldface Mountain, New Hampshire	NYF
114926	N11	Iveland, Norway	NYF
49006	N12	Broddbo, Sweden	NYF
C3006	N13	Mursinka, Russia	NYF
122055	N14	Volodarsk, Volyn, Ukraine	NYF
122053	N15	Volodarsk, Volyn, Ukraine	NYF
Herbb-2-11	N16	Powatan, Virginia	NYF
Herbb-2-15	N17	Powatan, Virginia	NYF
96540	N18	Amelia, Virginia	NYF
135287	N19	Morefield, Virginia	NYF
128246	L1	Grossmont Pegmatite, Australia	LCT
128217	L2	Wodgina, Australia	LCT
143082	L3	Minas Gerais, Brazil	LCT
R18199	L4	Virgem da Lapa, Minas Gerais, Brazil	LCT
87592	L5	Little Three, San Diego Co., California	LCT
124320	L6	Palomar, California	LCT
98106-1	L7	Ohio City, Colorado	LCT
R11839	L8	Viitaniemi, Erajarvi, Finland	LCT
R19246	L9	Viitaniemi, Erajarvi, Finland	LCT
45801-1	L10	Stoneham, Maine	LCT
14930	L11	Fisher Pocket, Topsham, Maine	LCT

Sample L11, was originally considered an NYF sample. Subsequent data (Figure 4-2b) shows that the topaz sample most likely comes from a section of the pegmatite that has LCT characteristics. For this reason, the sample will be considered LCT for the duration of this study.

EMPA data show the range of major element abundances in pegmatitic topaz. Fluorine content ranges from 18.1588 (L9-Finland) to 20.2146 (N8-Erongo).

Table 4-2: Major Element Concentrations

NMNH Catalogue Number	Sample Name	wt% Si	wt% Al	wt% F	Total
128246	L1	32.3868	55.2698	19.178	98.7598
128217	L2	32.4604	55.426	18.5686	98.6368
143082	L3	32.3234	55.4634	19.4414	99.0424
R18199	L4	32.247	55.2884	18.2306	98.09
87592	L5	32.3722	55.418	19.0934	98.8442
124320	L6	32.2862	55.399	18.5722	98.4374
98106-1	L7	32.659	55.6442	18.2068	98.844
R11839	L8	32.0976	55.034	18.392	97.7798
R19246	L9	32.313	55.2982	18.1588	98.1242
45801-1	L10	32.2794	55.576	18.9148	98.8058
R7789	N1	32.3172	55.8922	19.4322	99.4596
102995	N2	32.50	55.93	20.01	100.01
97413	N3	32.495	55.4016	19.7576	99.335
C5672	N4	32.5884	55.9424	20.1304	100.1852
C5333	N5	32.242	55.9112	19.9926	99.728
B15037	N6	32.3244	55.1182	18.693	98.2648
14930	L11	32.3814	55.6308	18.925	98.9688
173756	N7	32.4912	55.998	20.0896	100.12
173783	N8	32.083	55.6578	20.2146	99.4438
B15060	N9	32.137	55.4862	20.071	99.2432
R9029	N10	32.239	55.4116	20.086	99.2794
114926	N11	32.3326	55.1006	18.5882	98.1948
49006	N12	32.0694	55.0112	18.6866	97.8994
C3006	N13	32.1824	55.1156	18.5672	98.0474
122055	N14	32.3008	55.4622	20.0274	99.3578
122053	N15	32.0552	55.1336	19.764	98.6312
Herbb-2-11	N16	32.1764	55.2044	18.725	98.2218
Herbb-2-15	N17	32.1102	54.925	18.847	97.9466
96540	N18	32.5728	55.7716	19.6768	99.7362
135287	N19	32.2706	55.095	18.9046	98.3104

Table 4-3 shows the unit cell parameters of the topaz samples. Error in the last decimal place is given in parentheses.

Table 4-3: Unit Cell Dimensions

NMNH Catalogue Number	Sample Name	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	Volume(Å ³)
128246	L1	4.6520(1)	8.8061(3)	8.3929(3)	343.82(3)
128217	L2	4.6546(2)	8.8093(6)	8.3940(4)	344.19(4)
143082	L3	4.6530(2)	8.8037(4)	8.3891(3)	343.65(3)
R18199	L4	4.6547(2)	8.8109(3)	8.3946(3)	344.28(3)
87592	L5	4.6519(2)	8.8052(4)	8.3899(3)	343.66(3)
124320	L6	4.6526(2)	8.8087(5)	8.3884(4)	343.78(4)
98106-1	L7	4.6547(2)	8.8112(3)	8.3916(3)	344.17(3)
R11839	L8	4.6555(2)	8.8082(4)	8.3896(3)	344.03(3)
R19246	L9	4.6546(1)	8.8097(3)	8.3914(2)	344.10(2)
45801-1	L10	4.6541(1)	8.8069(2)	8.3922(2)	343.98(2)
R7789	N1	4.6509(3)	8.8018(6)	8.3971(5)	343.75(5)
102995	N2	4.6496(1)	8.7976(3)	8.3930(2)	343.32(2)
97413	N3	4.6503(1)	8.8002(3)	8.3925(3)	343.45(3)
C5672	N4	4.6503(3)	8.7974(6)	8.3885(5)	343.18(5)
C5333	N5	4.6502(2)	8.7983(4)	8.3938(3)	343.42(3)
B15037	N6	4.6523(1)	8.8048(3)	8.3923(3)	343.77(2)
14930	L11	4.6541(1)	8.8076(2)	8.3908(2)	343.95(2)
173756	N7	4.6494(2)	8.7984(5)	8.3902(4)	343.22(4)
173783	N8	4.6511(2)	8.7972(4)	8.3938(3)	343.45(3)
B15060	N9	4.6509(3)	8.7978(6)	8.3987(5)	343.66(5)
R9029	N10	4.6499(1)	8.7982(3)	8.3924(3)	343.34(3)
114926	N11	4.6537(3)	8.8041(6)	8.3956(5)	343.99(5)
49006	N12	4.6524(1)	8.8039(3)	8.3907(2)	343.20(2)
C3006	N13	4.6535(2)	8.8058(3)	8.3909(3)	343.84(3)
122055	N14	4.6492(1)	8.7971(3)	8.3913(3)	343.20(2)
122053	N15	4.6498(2)	8.7980(3)	8.3925(3)	343.33(3)
Herbb-2-11	N16	4.6530(2)	8.8060(3)	8.3883(3)	343.70(3)
Herbb-2-15	N17	4.6525(2)	8.8028(4)	8.3915(3)	343.67(3)
96540	N18	4.6513(2)	8.8002(4)	8.3888(3)	343.38(3)
135287	N19	4.6528(2)	8.8036(3)	8.3923(3)	343.76(3)

The *a* unit cell dimension ranges from 4.6492Å (N14-Volodarsk) to 4.6555Å (L8-Finland). The *b* unit cell dimension ranges from 8.7971Å (N14-Volodarsk) to 8.8112Å (L7-Ohio City). The *c* unit cell dimension ranges from 8.3883Å (N16-Powatan) to 8.3971 Å (N1-Tarryall). The highest unit cell volume

is $344.28\text{\AA}^3$ (L4-Virgin de Lapa) and the smallest value is $343.18\text{\AA}^3$ (N4-Mt. Antero).

Figure 4-1: a Unit Cell Dimension Plots

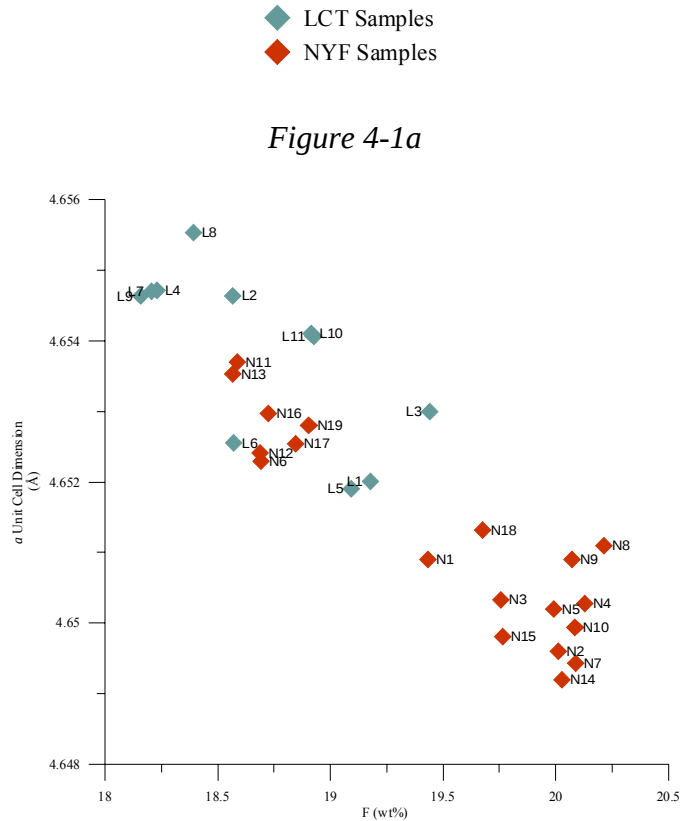


Figure 4-1 shows the a unit cell dimension compared to weight percent fluorine (a), weight percent fluorine with fluorine content error bars (b), and unit cell volume. There is a general decreasing trend when comparing the a unit cell dimension to weight percent fluorine. When a trend line is plotted (not shown) the correlation coefficient is 0.82. There is an increasing linear correlation between the a unit cell dimension and the unit cell volume (Figure 4-1c). LCT samples have higher a cell dimensions and lower F contents than NYF pegmatite samples.

Figure 4-1b

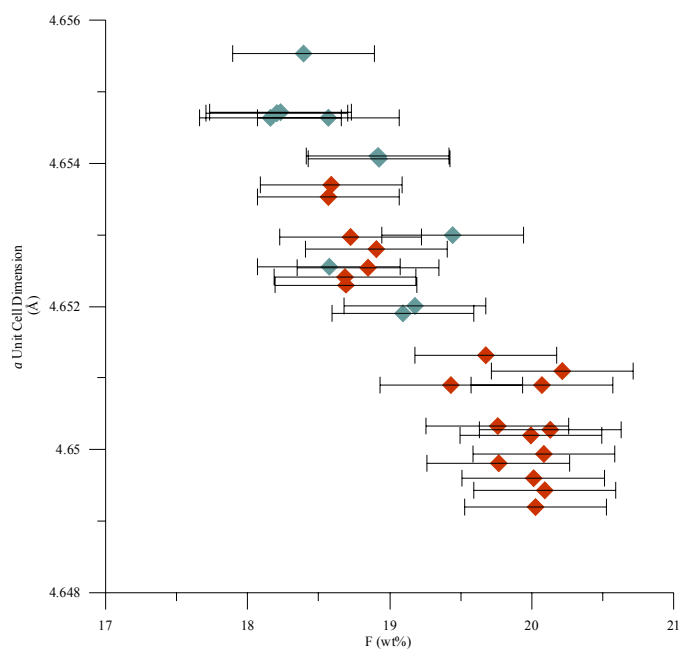


Figure 4-1c

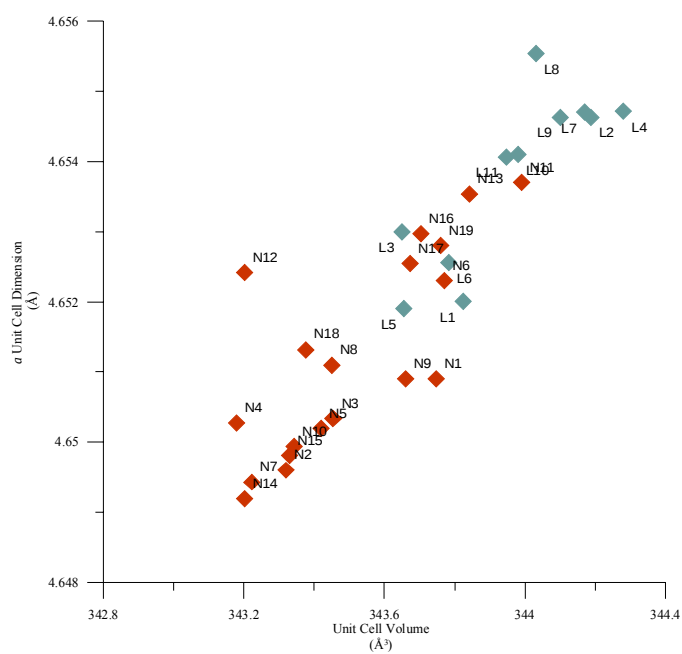


Figure 4-2: *b* Unit Cell Dimension vs. Weight Percent Fluorine

Figure 4-2a

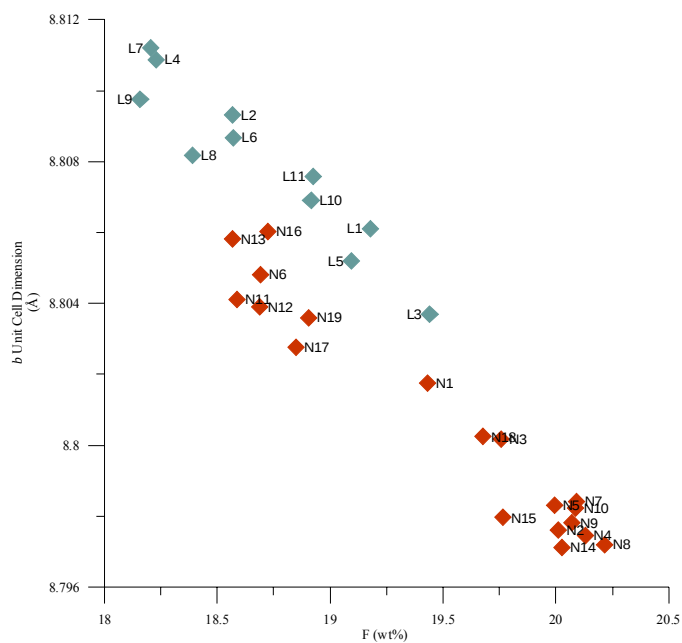


Figure 4-2b

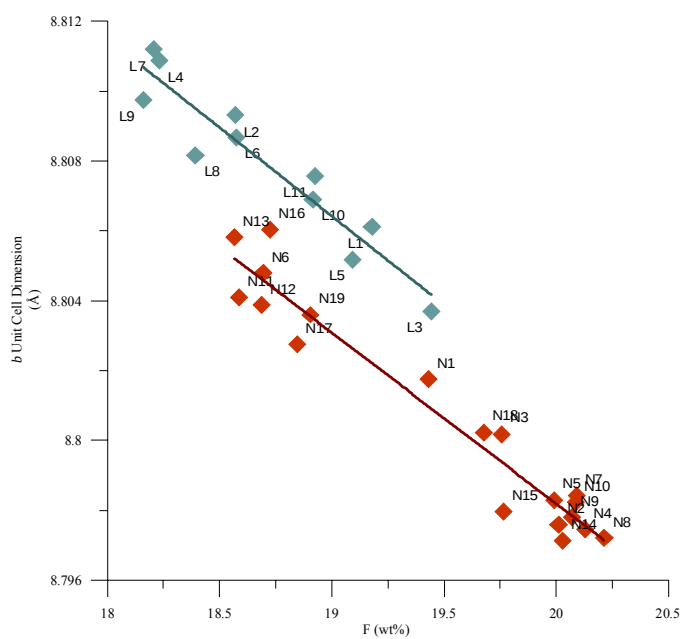


Figure 4-2c

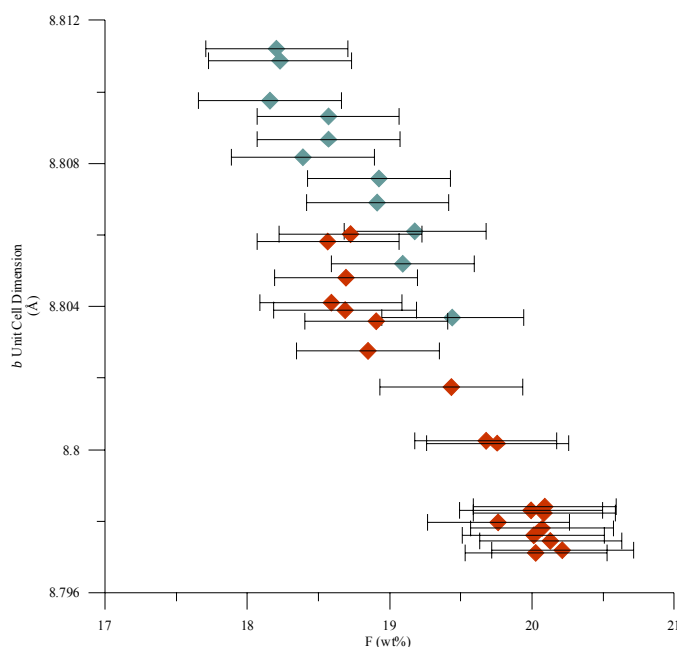


Figure 4-2 shows the *b* unit cell dimension vs. weight percent fluorine. From an initial literature research, we knew that the *b* unit cell dimension would have the best correlation with fluorine content. What we did not expect was the distinction between the two types of pegmatites (Figure 4-2b). There are two distinct linear trends in the graph. The R^2 value for the LCT trend line is 0.89. The R^2 value for the NYF trend line is 0.94. The error bars for weight percent fluorine are shown in Figure 4-2c. The error in the fluorine content does not negate the validity of the separate trends.

Similar to the *a* unit cell dimension, there is an increasing trend in the *b* Unit Cell Dimension vs. Unit Cell Volume plot (Figure 4-3).

Figure 4-3: *b* Unit Cell Dimension vs. Unit cell volume

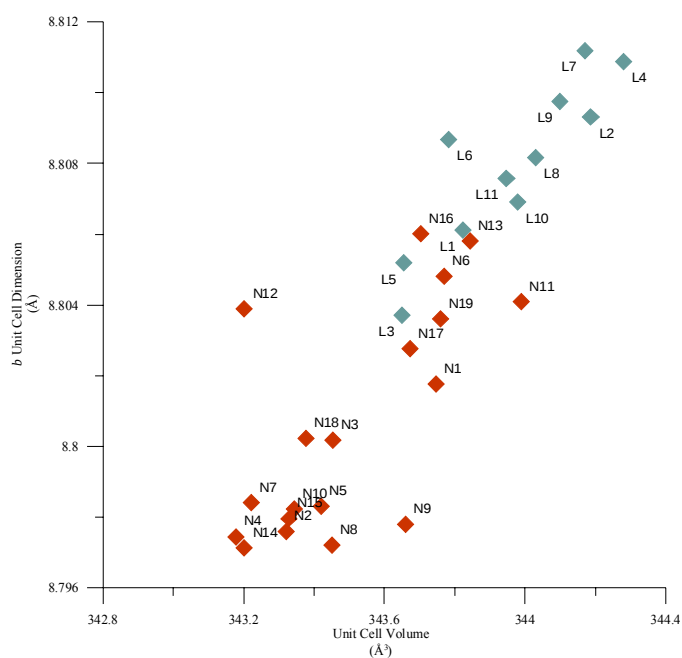
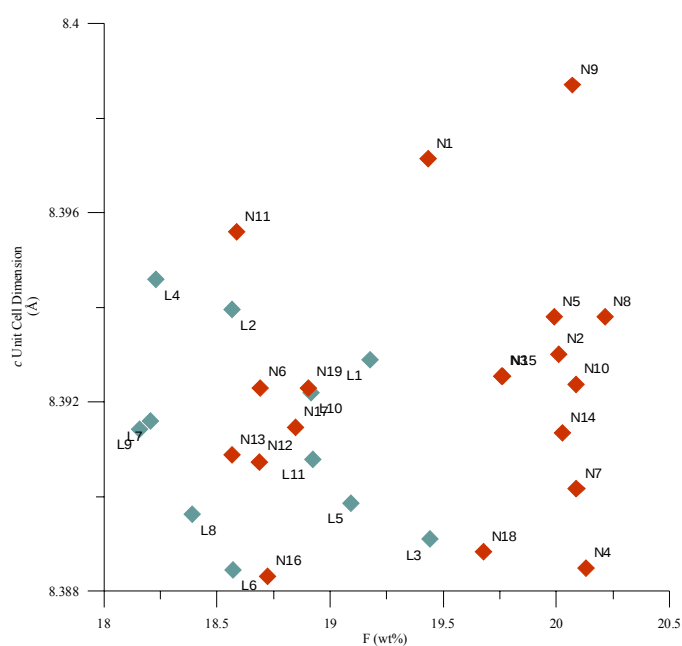


Figure 4-4: *c* Unit Cell Dimension Plots

Figure 4-4a



In Figure 4-4a the c unit cell dimension is plotted against weight percent fluorine. Subsequent graphs (Figure 4-4b-e) show that there is a consistent lack of trends between the c unit cell dimension and other compositional data and unit cell data.

Figure 4-4b

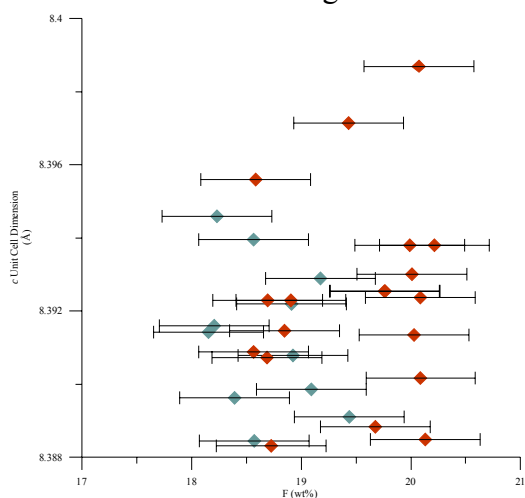


Figure 4-4c

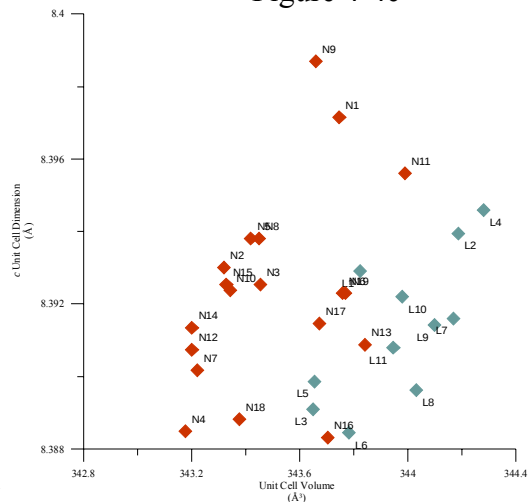


Figure 4-4d

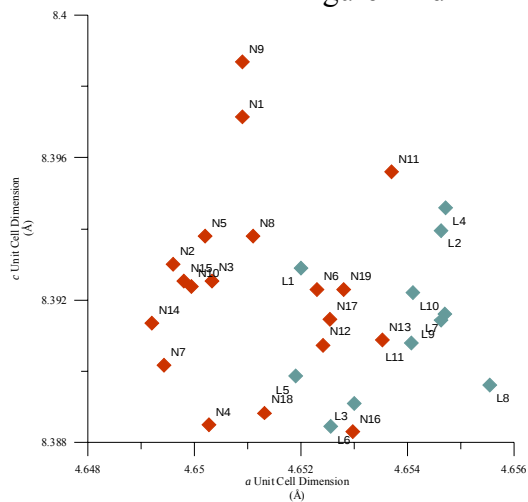


Figure 4-4e

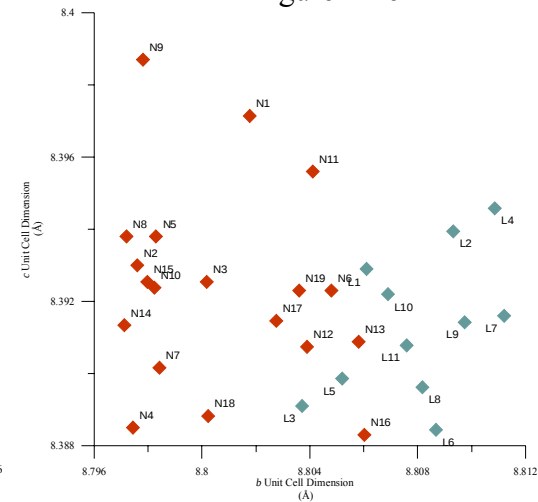
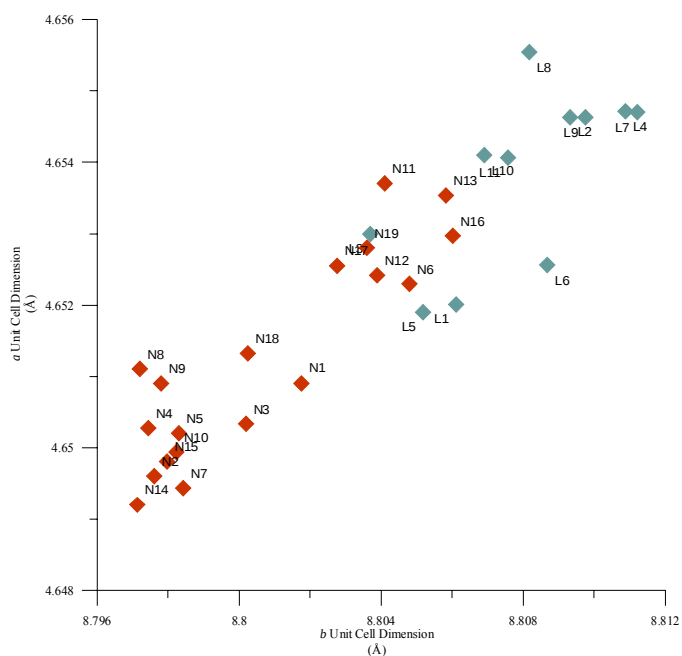


Figure 4-5: *a* Unit Cell Dimension vs. *b* Unit Cell Dimension



When comparing the *a* unit cell dimension to the *b* unit cell dimension there is an increasing trend. It appears that there is a variable affecting the *c* unit cell dimension that is not affecting the *a* or *b* unit cell dimension.

Overall, the unit cell volume of topaz decreases with increasing fluorine content (Figure 4-6a). This is expected because both the *a* and *b* unit cell dimension decrease with increasing fluorine content. The error bars for fluorine content is shown in Figure 4-6b. LCT topaz samples have higher unit cell volumes and lower fluorine contents than NYF topaz samples.

Figure 4-6: Unit cell volume vs. Weight percent Fluorine

Figure 4-6a

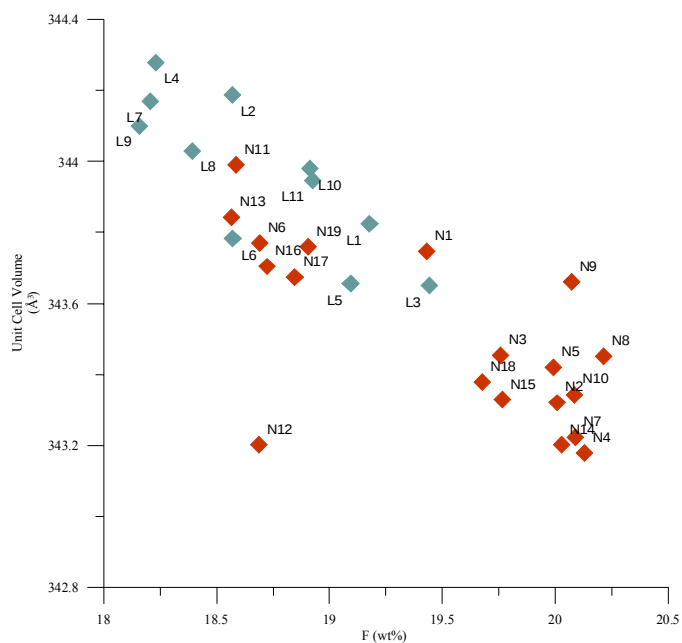


Figure 4-6b

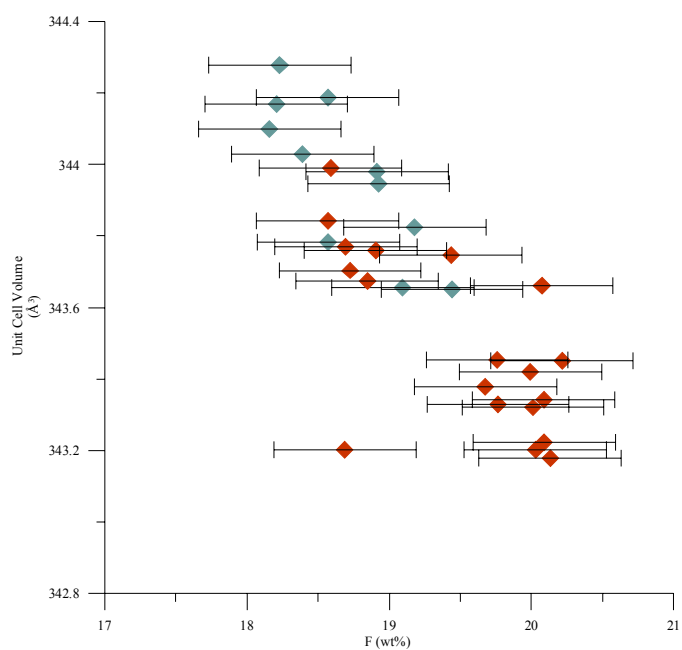


Figure 4-7: Comparison of Previous Studies (*b* Unit Cell Dimension vs. Weight Percent Fluorine)

Figure 4-7a

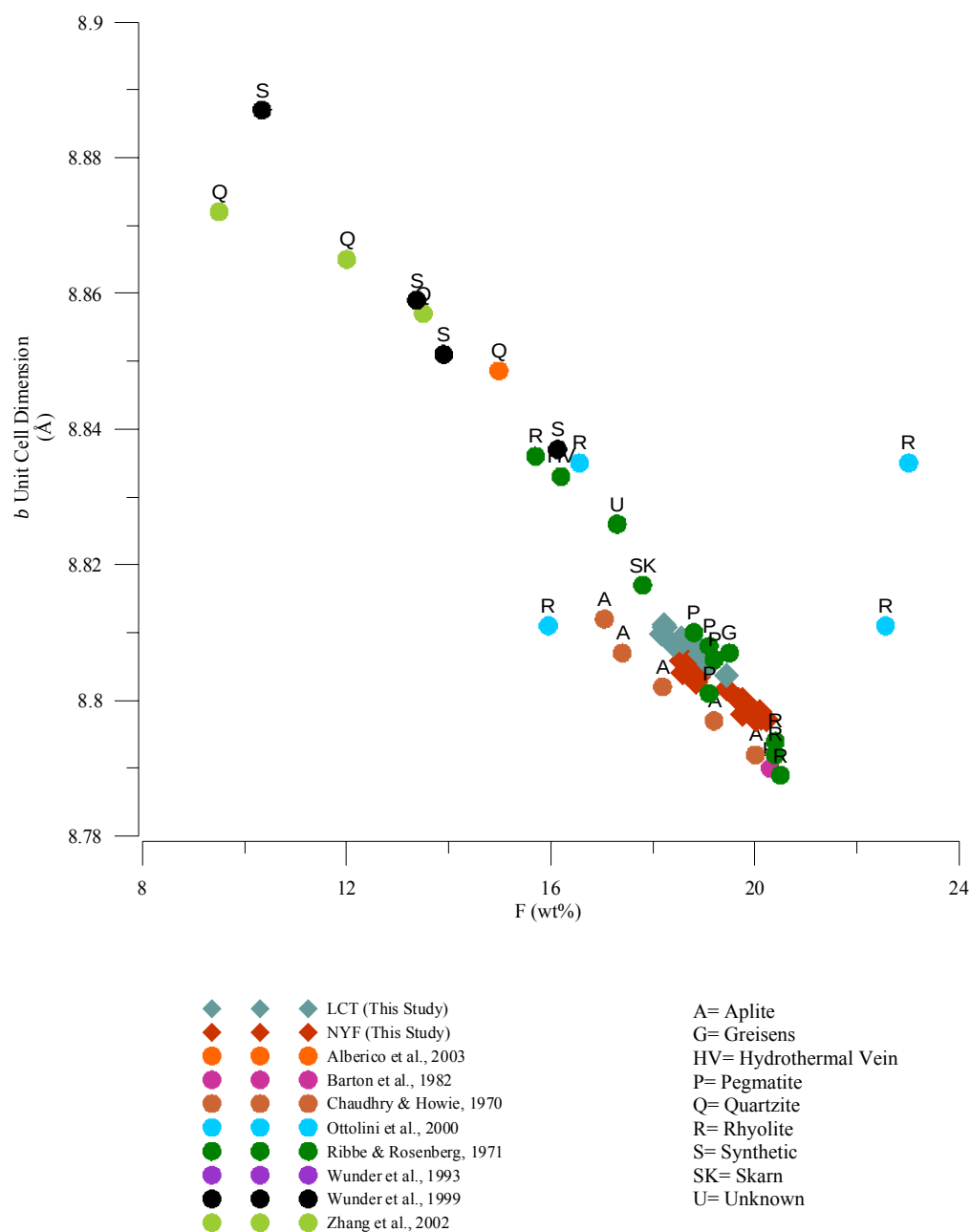
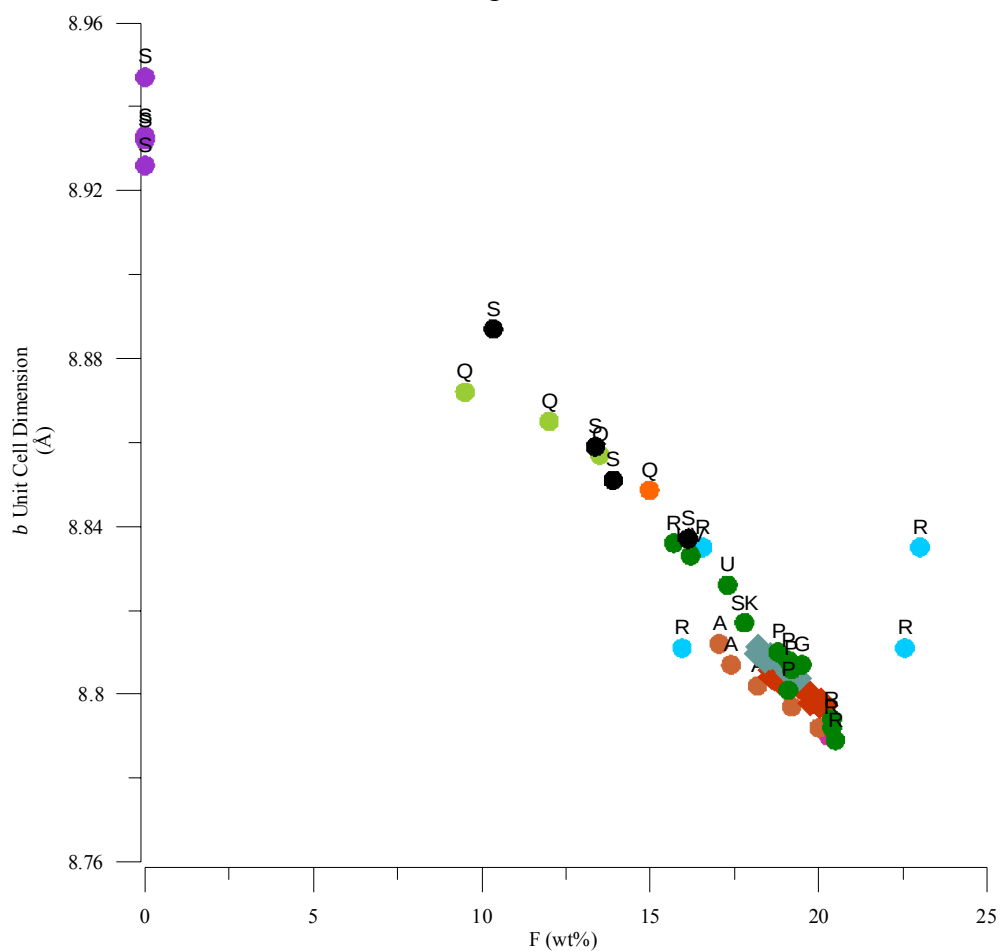


Figure 4-7 shows the *b* unit cell dimension vs. weight percent fluorine for data from 9 studies (including the current study). Figure 4-7a excludes Wunder et

al. (1993) which is end member hydroxyl-topaz. This plot was adapted from a similar plot in Alberico et al. (2003). Of the studies plotted, the only other study that examined pegmatite samples was Ribbe and Rosenberg in 1971. There were 4 topaz samples used in that study. In Figure 4-7a it is interesting to note that the

Figure 4-7b



synthetic sample plot with the quartzite samples (Zhang et al. and Wunder et al.) and the igneous samples plot together (Barkley, Ribbe and Rosenberg, Barton et al., Chaudhry and Howie, and Ottolini et al.). Two rhyolite samples from Ottolini et al. (2000) do not fit the decreasing trend of the other samples. Ottolini et al.

analyzed two topaz samples from Thomas Range, Utah. Two fluorine contents were reported for each sample (both are plotted on the graph); one with an APF correction and one without. The corrected fluorine values put the F content well over the calculated maximum value of 20.7. Ottolini et al. (2000) suggested that the corrections were necessary, however comparisons with the other data in Figure 4-7 show that the APF correction used by Ottolini et al. was not only unnecessary but incorrect. The uncorrected values lie within the decreasing trend of the other samples.

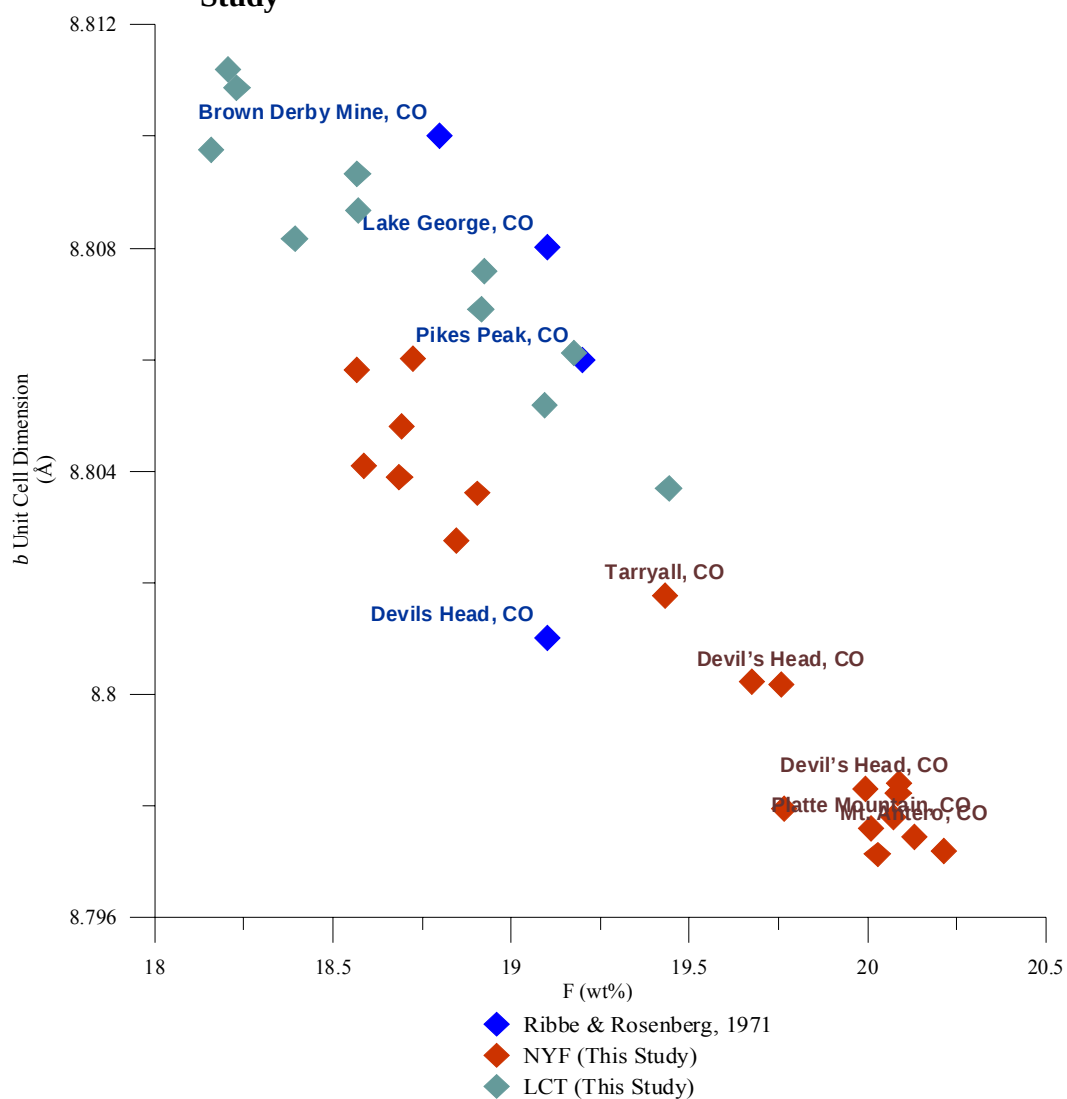
In 1967 and 1971, P.H. Ribbe and P.E. Rosenberg made great strides in the understanding of the crystal chemistry and structure of topaz. In the 1967 study, Rosenberg analyzed 14 topaz samples from various locations for unit cell dimensions. No chemical analysis was done in this study but Rosenberg alluded to the influence of F-OH⁻ substitution on the crystal structure of topaz. In 1971 Ribbe and Rosenberg did a study reusing the samples from Rosenberg's 1967 study.

Figure 4-8 shows Ribbe and Rosenberg's (1971) pegmatite data plotted with the data from this study. All of the samples that have names shown are from the same pegmatite area in Colorado and are associated with the Pikes Peak batholith. This means they should plot in similar regions of the graph. Ribbe and Rosenberg's data is consistently lower in fluorine and have higher *b* cell dimensions than the data from this study. Differing microprobe conditions or differences in unit cell refinement could account for these inconsistencies. Ribbe

and Rosenberg did not report the microprobe conditions for their analysis.

Microprobe conditions are particularly important to know because it is fairly easy to drive off fluorine and hydroxyl if the electron beam is too large.

Figure 4-8: Pegmatite Data from Ribbe and Rosenberg (1971) and This Study



Ribbe and Rosenberg (1971) derived determinative curves for fluorine in topaz based on unit cell and optical measurements. Many studies following this

paper used the equations to calculate the fluorine content of their samples. In 2003, Alberico et al. used topaz data from 8 studies (including their own analysis and Ribbe & Rosenberg's data) to create improved linear regression curves for the determination of fluorine content based on unit cell parameters of topaz:

Ribbe & Rosenberg (1971):

$$\begin{aligned}\text{wt \% F} &= 465.5 - 1.3(\text{volume}) \\ \text{Correlation Coefficient} &: 0.881 \\ \text{wt \% F} &= 892.5 - 99.2(b) \\ \text{Correlation Coefficient} &: 0.967\end{aligned}$$

Alberico et al. (2003)

$$\begin{aligned}\text{wt \% F} &= 1215.87 - 257.27(a) \\ \text{Correlation Coefficient} &: 0.982 \\ \text{wt \% F} &= 1236.35 - 138.23(b) \\ \text{Correlation Coefficient} &: 0.982\end{aligned}$$

Table 4-4 details the fluorine content from this study compared with values calculated from the correlation equations of Ribbe & Rosenberg (1971) and Alberico et al. (2003). The average differences are shown below the corresponding columns. The average difference was calculated by finding the difference between the EPMA data from this study and the calculated data and averaging the absolute values. The errors in the EPMA data for this study for wt% F are 0.5. This is consistent with other studies. The average difference from the correlation equations (with the exception of Ribbe & Rosenberg's volume equation) fall well within the error for all studies.

Table 4-4: Comparison of Calculated Fluorine Content and EMPA Data

NMNH Catalogue Number	Sample Name	This Study	R&R (b)	R&R (Vol)	A et al. (a)	A et al. (b)
R19246	L9	18.1588	18.5729	18.17	18.37283	18.5784
98106-1	L7	18.2068	18.42896	18.079	18.35533	18.37782
R18199	L4	18.2306	18.46199	17.936	18.35121	18.42385
R11839	L8	18.392	18.72993	18.2597	18.13922	18.79721
C3006	N13	18.5672	18.96315	18.5041	18.65505	19.12219
128217	L2	18.5686	18.61595	18.0569	18.37231	18.63839
124320	L6	18.5722	18.67914	18.5821	18.9064	18.72644
144926	N11	18.5882	19.13328	18.313	18.6126	19.35926
49006	N12	18.6866	19.15431	19.3374	18.94268	19.38856
B15037	N6	18.693	19.06384	18.599	18.97278	19.2625
Herbb-2-11	N16	18.725	18.94262	18.6848	18.80041	19.09358
Herbb-2-1	N17	18.847	19.26651	18.7238	18.91001	19.5449
135287	N19	18.9046	19.18288	18.612	18.84414	19.42837
45801-1	L10	18.9148	18.85552	18.326	18.50969	18.97221
14930	L11	18.925	18.78826	18.3689	18.51767	18.87849
87592	L5	19.0934	19.02565	18.7472	19.07543	19.20928
128246	L1	19.178	18.93409	18.5288	19.0479	19.08169
R7789	N1	19.4322	19.36551	18.6289	19.33193	19.68285
143082	L3	19.4414	19.17296	18.755	18.79269	19.41455
96540	N18	19.6768	19.51669	19.1099	19.2249	19.89352
97413	N3	19.7576	19.52195	19.0098	19.47909	19.90084
122053	N15	19.764	19.74237	19.1723	19.61415	20.20799
C5333	N5	19.9926	19.70864	19.054	19.51305	20.16099
102995	N2	20.01	19.77808	19.184	19.66741	20.25775
122055	N14	20.0274	19.825	19.3374	19.77109	20.32313
B15060	N9	20.071	19.75824	18.742	19.33296	20.23011
R9029	N10	20.086	19.71499	19.1541	19.57994	20.16984
173756	N7	20.0896	19.69743	19.3114	19.71037	20.14537
C5672	N4	20.1304	19.79326	19.3686	19.49375	20.2789
173783	N8	20.2146	19.81776	19.015	19.2815	20.31304
Average Difference:			0.2562	0.5298	0.2966	0.2765

Table 4-5: Unit Cell Dimensions of Selected Samples After Heating

NMNH Catalogue Number	Sample Name	a(Å)	b(Å)	c(Å)	v(Å ³)
135287	N19	4.6521(1)	8.8030(3)	8.3916(2)	343.66(2)
173756	N7	4.6494(1)	8.7966(3)	8.3917(2)	343.21(2)
114926	N11	4.6532(1)	8.8068(3)	8.3898(2)	343.82(2)
98106-1	L7	4.6553(1)	8.8112(3)	8.3896(2)	344.13(2)
114926	N11*	4.6533(2)	8.8057(4)	8.3917(3)	343.85(3)
102995	N2	4.6491(1)	8.7966(2)	8.3911(2)	343.16(2)
R18199	L4	4.6547(2)	8.811(2)	8.3892(2)	-

Samples were heated for 1 hour at 700°C. This temperature was chosen because topaz begins to break down into mullite at 950°C. Two samples representing N11 were analyzed. Figure 4-9 shows the unit cell parameters vs. weight percent fluorine for the heated samples.

Figure 4-9: Heated Unit Cell Data

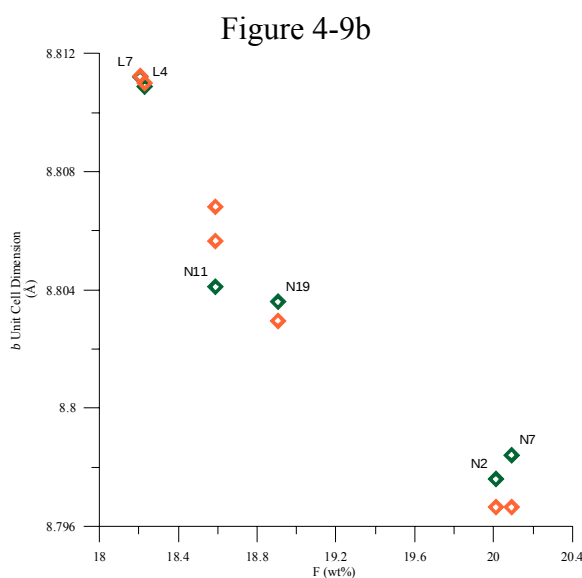
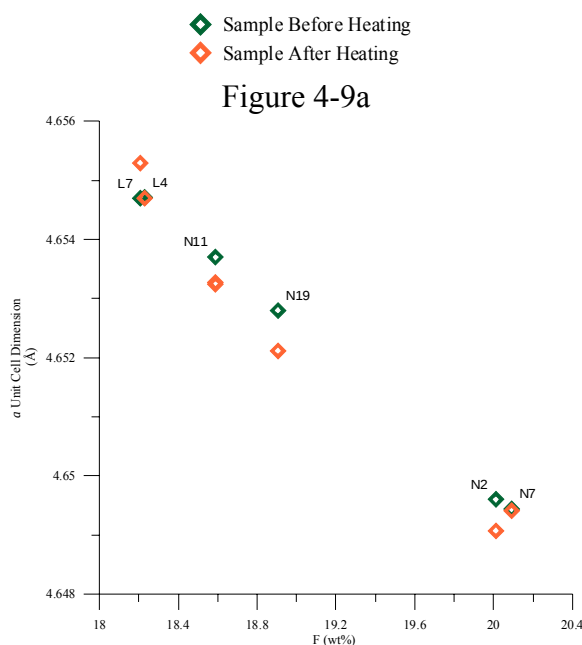


Figure 4-9c

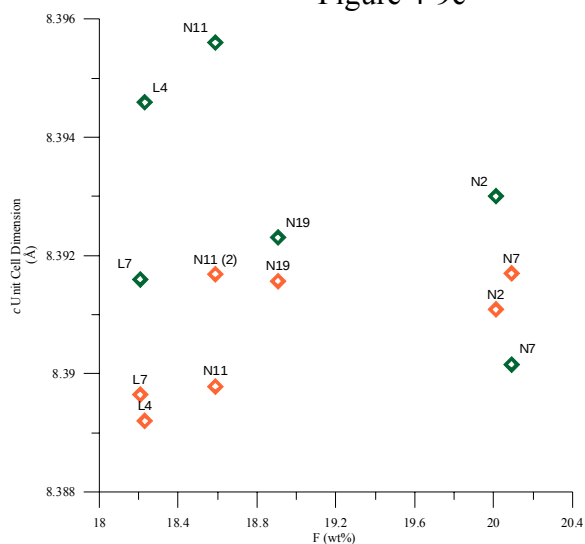
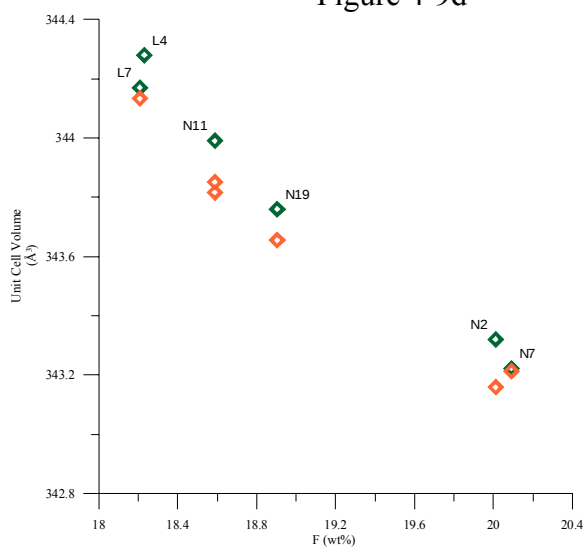


Figure 4-9d



Heating data was inconsistent both within each graph and from graph to graph. While all of the samples showed a decrease in volume, there was no trend in the amount of decrease (Figure 4-9d). In Figure 4-9a and b, 3 samples decrease, one sample increased and 2 samples stayed the same. In figure 4-9c, 5 samples

decrease and 1 sample increased. It is important to note that the “maverick” samples are different in each graph.

Samples were analyzed for trace elements using x-ray florescence. The data supports previous research that found topaz has very few trace elements.

Table 4-6: Trace Element Concentrations in ppm

NMNH Catalogue Number	Sample Name	Pb	Ga	W	Rb	Cr
R11839	L8	13	9	7	17	20
45801-1	L10	12	10	9	15	23
R18199	L4	12	11	8	32	22
143082	L3	11	11	7	13	26
98106-1	L7	11	12	7	20	21
R19246	L	12	11	4	14	21
128217	L2	12	11	5	27	23
R7789	N1	12	11	6	14	22
122055	N14	11	12	7	14	27
49006	N12	12	11	7	19	27
C3006	N13	12	12	7	14	21
135287	N19	14	18	5	14	22
102995	N2	12	11	7	14	26
114926	N11	13	12	5	19	22

Concentrations of the elements Sn, Pb, As, Tl, Ga, W, Ta, Cs, Rb, Nb, Zr, Sr, Zn, Nb, Zr, Y, Sr, Rb, Zn, Cu, Ni, Co, Cr, V, and Ba were recorded for this study. Of the elements tested, only Pb, Ga, W, Rb, and Cr occurred in abundances higher than the detection limit of the spectrometer (Table 4-6). The trace elements that were present were consistent in all samples. There was no standard for germanium so that analysis was qualitative rather than quantitative (Figure 4-10 and Figure 4-11).

Figure 4-10: Qualitative Analysis of Ge In NYF Samples

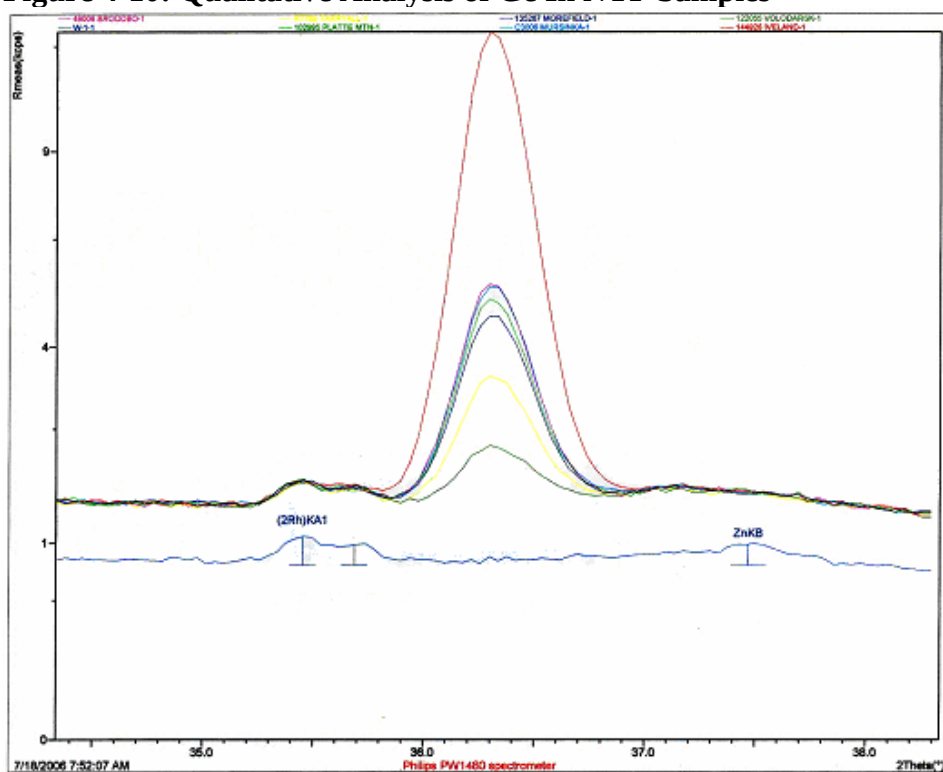
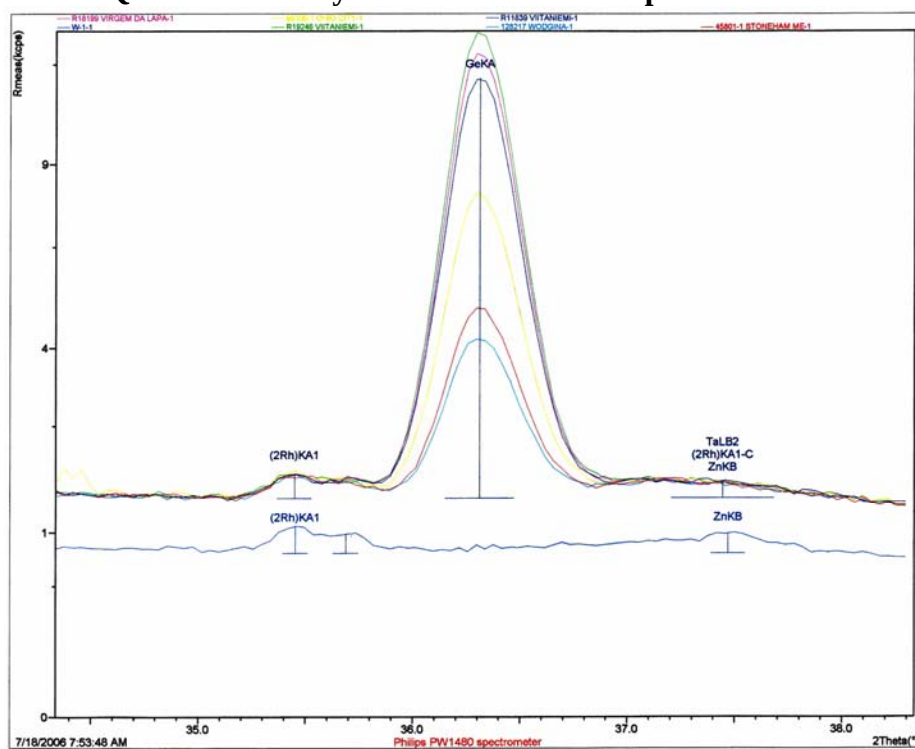


Figure4-11: Qualitative Analysis of Ge In LCT Samples



CHAPTER 5

DISCUSSION & CONCLUSION

For all topaz, the *b* unit cell dimension decreases with increasing fluorine content. From initial literature research, we knew that the *b* unit cell dimension would have the best correlation with fluorine content. The distinction between the two types of pegmatites was not expected. In pegmatitic topaz, the *b* unit cell dimension is higher for a given wt% fluorine in LCT pegmatites than in NYF pegmatites and can be used to distinguish between the two types of pegmatites. The distinction could be related to the relative differences in aluminum concentrations in the pegmatite melt.

There is a coupled substitution, Al^{+3} for Si^{4+} and F^{1-} for O^{2-} , which occurs in topaz. Hoover (1992) suggests that as Al substitutes for Si, the crystal lattice will expand in a similar manor to the expansion due to F-OH^- substitution. In high Al environments, topaz should have more F and larger unit cell volumes. LCT pegmatites have a higher molar ratio of Al (peraluminous) compared to the peralkaline NYF pegmatites. Although NYF pegmatites are peralkaline, they are enriched in fluorine. The data support the hypothesis that LCT pegmatites have larger unit cell volumes than NYF pegmatites, but the NYF samples in this study have the higher fluorine contents.

The F/OH^- content of topaz can be reasonably estimated using determinative curves from Ribbe & Rosenberg (1971) and Alberico et al. (2003).

With the exception of Ribbe & Rosenberg's equation for volume, the average difference between calculated wt% F and EMPA wt% F falls within the error of microprobe analysis. Determinative curves utilizing the *b* unit cell dimension had the least average difference.

Selected samples were analyzed for trace element content. As expected, the samples had very few trace elements and the concentrations of elements that were present were consistent in all the samples. Quantitative analysis of Ge relation to unit cell parameters and bulk chemistry was not possible but qualitative graphs show no distinction between levels of Ge in NYF pegmatites and levels in LCT pegmatites.

The *c* unit cell dimension, which corresponds to both the *z* crystallographic axis and the plane of cleavage, showed relationship to bulk chemistries, trace elements, or other unit cell parameters. Heating should lead to an expansion in the crystal lattice normal to its plane of weakest bonds. This would be normal to *c* (Hoover 1992). After heating, unit cell volumes decreased and the *c* unit cell dimension decreased. The implication is that the lattice of the cooled crystal did not represent the changes that occurred while the topaz was at temperature. No bubbles were apparent in the topaz after heating suggesting that no gasses or elements were being driven off. Subsequent research determined that ordering is a possible reason for the *c* cell dimension data. Not only can F-OH⁻ be ordered, but H can be ordered within the H1 and H2 sites. The H in the hydroxyl molecule can order in the two sites in a variety of ways and at a variety of lattice

energies. The ordering of H between these two positions can lead to both orthorhombic and monoclinic symmetries in the crystal (Northrup et al 1994). Dana (1997) reports the occurrence of triclinic topaz in hydrothermal veins near Ouro Preto, Brazil. In the triclinic topaz, H is ordered in one site (Dana 1997). Heating data from the current study were inconclusive on the role of ordering in topaz on the *c* unit cell dimension. Further investigation of ordering and disordering of topaz through pressure and temperature studies is necessary.

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