

The phosphoferrite group:
Variation in chemical composition of minerals found in Rapid Creek,
Yukon Territory, Canada.

by

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1. Abstract

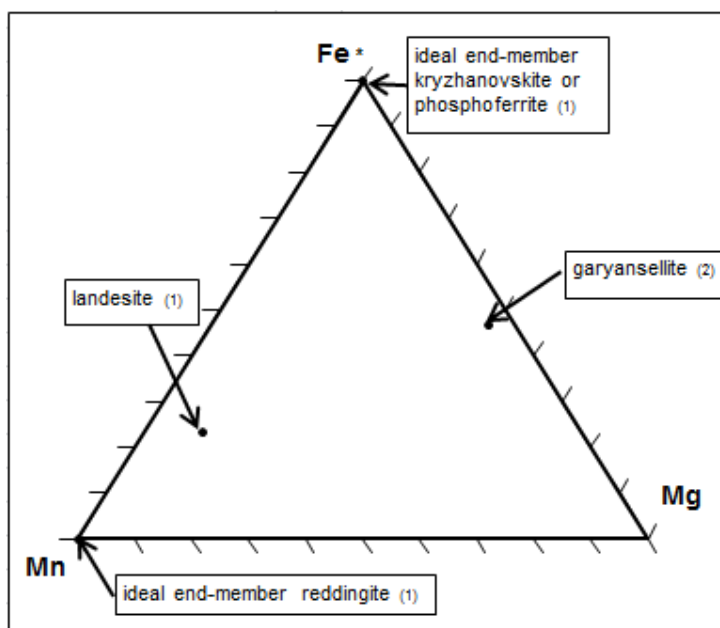
In Rapid Creek, Yukon Territory, Canada significant mineral discoveries occurred in the 1970s to 1980s, including garyansellite (Mg, Fe^{3+})₃(PO_4)₂(OH,O) • 1.5H₂O and kryzhanovskite Fe^{3+} ₃(OH)₃(PO_4) in the phosphoferrite group. Since then, the phosphoferrite group minerals at this locality have not been re-examined. A combination of mineralogical analytical techniques was applied to identify and determine a nomenclature scheme for this mineral group. Analytical techniques such as Raman spectroscopy, scanning electron microscopy, single crystal X-ray diffraction, electron microprobe analysis and X-ray powder diffraction were used. The specimens analyzed for this research were identified as garyansellite, Mg-rich intermediate kryzhanovskite, and zoned minerals of garyansellite and Mg-rich intermediate kryzhanovskite. The presence of these minerals has verified the findings of Sturman & Dunn (1984) and Robinson *et al.* (1992). The data obtained also indicated that variation exists between the specimens and the garyansellite and kryzhanovskite described in the literature and databases. Hence, further in-depth study should be conducted on these specimens to determine whether a new mineral could exist in the phosphoferrite group.

2. Introduction

2.1. General description of the phosphoferrite group

The phosphoferrite group is a group of hydrated phosphates with the general formula $A_3(\text{PO}_4)_2 \cdot n\text{H}_2\text{O}$, where $A = \text{Fe}^{2+}, \text{Fe}^{3+}, \text{Mg}, \text{Mn}^{2+}$ and n is dependent on the oxidation state of the cations (Gaines *et al.* 1997). There are three natural ideal end-members in this group which form a complex triple series—reddingite $\text{Mn}^{2+}_3(\text{H}_2\text{O})_3(\text{PO}_4)_2$, phosphoferrite $\text{Fe}^{2+}_3(\text{H}_2\text{O})_3(\text{PO}_4)_2$ and kryzhanovskite $\text{Fe}^{3+}_3(\text{OH})_3(\text{PO}_4)_2$ (Moore *et al.* 1980). In addition, this group contains two natural intermediate members —landesite $(\text{Mn}^{2+}\text{Mg})_9\text{Fe}^{3+}_3(\text{PO}_4)_8(\text{OH})_3 \cdot 9\text{H}_2\text{O}$ (Moore, 1964) and garyansellite $(\text{Mg}, \text{Fe}^{3+})_3(\text{PO}_4)_2(\text{OH},\text{O}) \cdot 1.5\text{H}_2\text{O}$ (Sturman & Dunn, 1984)(Figure 1).

Figure 1: Mineralogical relationship of the phosphoferrite group minerals based on Fe, Mn and Mg molecular proportion. * Fe expressed as Fe total which takes into account of both Fe^{2+} and Fe^{3+} .
(1) (Moore *et al.* 1980) and (2) (Sturman & Dunn, 1984)



According to Moore *et al.* (1980), the cations and elements in A occupy two non-equivalent octahedral crystallographic sites, $M(1)$ and $M(2)$ thus giving the formula, $M(1)M(2)_2[\text{H}_2\text{O},(\text{OH})]_3(\text{PO}_4)_2$. Furthermore, Moore *et al.* (1980) suggested that the smaller cations prefer the $M(1)$ site on the inversion centre and the larger cations are distributed over the $M(2)$ sites with no symmetry. Another notable structural characteristic of the phosphoferrite group is the PO_4^{3-} tetrahedra joining to sheets and chains of octahedral coordinated cations and water (Gaines *et al.* 1997) (Figure 2a and 2b). Minerals in the phosphoferrite group crystallize in the orthorhombic space group $Pbna$, with point group $2/m \ 2/m \ 2/m$ (Ginzburg, 1950, Palache *et al.* 1951, Sturman & Dunn, 1984).

Figure 2a: Ball-and-stick model of phosphoferrite mineral
(Downs & Hall-Wallace, 2003)

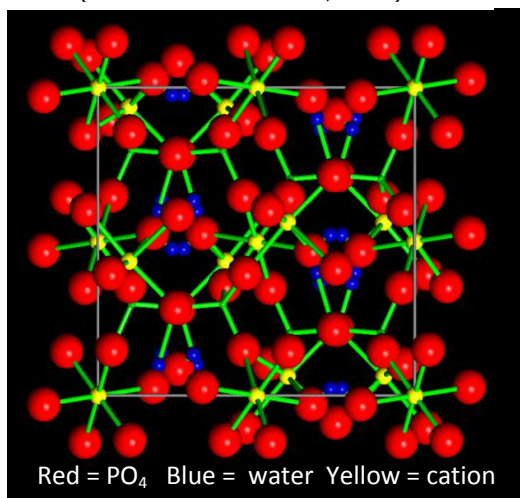
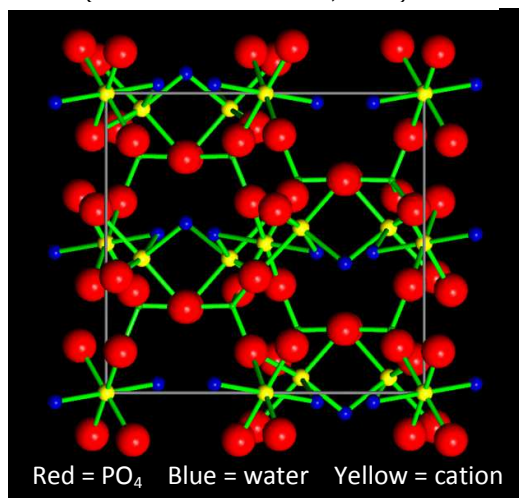


Figure 2b: Ball-and-stick model of kryzhanovskite mineral
(Downs & Hall-Wallace, 2003)



2.2. Description of the minerals within the phosphoferrite group

Reddingite is a manganese-dominated member of the phosphoferrite group. Both $M(1)$ and $M(2)$ sites are occupied with Mn^{2+} ions (Moore *et al.* 1980). It has unit cell $a = 9.49 \text{ \AA}$, $b = 10.08 \text{ \AA}$ and $c = 8.70 \text{ \AA}$ (Moore *et al.*, 1980). Uncertainty values for unit cell data of reddingite were not provided in the literature.

Landesite is a rare hydrated manganous-ferric phosphate derived from reddingite (Moore, 1964). Crystal unit cell are $a = 9.458(3) \text{ \AA}$, $b = 10.185(2) \text{ \AA}$ and $c = 8.543(2) \text{ \AA}$ (Moore, 1964).

Phosphoferrite is a ferrous-dominated member of the phosphoferrite group. It has unit cell $a = 9.406(2) \text{ \AA}$, $b = 10.024(3) \text{ \AA}$ and $c = 8.670(2) \text{ \AA}$ (Moore *et al.* 1980). Phosphoferrite is known to undergo rapid oxidation in the presence of air and light at low temperature (Moore, 1971). The most likely mechanism that accounts for this process is by the auto-oxidation-reduction by cleavage of protons from water ligands (Moore, 1971). Moore (1971) conducted an experiment and found that at 240°C phosphoferrite oxidizes to kryzhanovskite.

Kryzhanovskite is the structurally stable ferric equivalent of phosphoferrite with its charge balanced being maintained by the substitution of OH for H_2O (Moore, 1971, Robinson *et al.* 1992). It has unit cell $a = 9.450(2) \text{ \AA}$, $b = 10.013(2) \text{ \AA}$ and $c = 8.179(2) \text{ \AA}$ (Moore *et al.* 1980). Kryzhanovskite is often present in an intermediate form with the formula $MnFe^{3+}_2(PO_4)_2(OH)_2 \cdot H_2O$ (Robinson *et al.* 1992) and may have minor amount of magnesium (Anthony *et al.* 2000). Moore (1971) stated that the temperature for intermediate kryzhanovskite formation is too low for manganese oxidation. As a result, the manganese cation remains as Mn^{2+} , a reduced state.

Garyansellite is the magnesium analogue of kryzhanovskite, yet there is no structural data to definitively support that garyansellite adheres to the general formula of the phosphoferrite group (Sturman & Dunn, 1984). It has unit cell $a = 9.452(4) \text{ \AA}$, $b = 9.890(5) \text{ \AA}$ and $c = 8.198(4) \text{ \AA}$

(Sturman & Dunn, 1984) and minor amounts of manganese may be present (Anthony *et al.* 2000). Garyansellite is the most recently discovered mineral in the group. It was first discovered at an outcrop on the east side of Rapid Creek, Yukon Territory, Canada (Robinson *et al.* 1992) and was named in 1984 (Sturman & Dunn, 1984).

A common problem that arises during the identification of hydrated iron and manganese phosphates, such as phosphoferrite-kryzhanovskite and reddingite-landesite, is when the Fe^{2+} and Mn^{2+} oxidize without significant change in crystal structure (Moore, 1964). As a result, it is extremely difficult to identify whether the mineral is in the reduced or oxidized form. A method to overcome this problem is to apply Mössbauer spectroscopy. It is a technique that measures the shift in nuclear energy level of atoms (Royal Society of Chemistry, 2012). The shift conveys chemical, structural and magnetic properties of the material (Royal Society of Chemistry, 2012). Hence, it is often used to examine the oxidation states of iron and manganese in minerals.

2.3. Location of study

Minerals in the phosphoferrite group can be found in various part of the world. For example, the Royal Ontario Museum collection contains phosphoferrite from South Dakota, USA; kryzhanovskite and landesite from West Germany; reddingite from Brazil; and garyansellite from Yukon Territory, Canada. However, for the purpose of this study, only the phosphoferrite group minerals found in Rapid Creek, Yukon Territory, Canada will be examined. The Rapid Creek region is located in the Richardson Mountains, north of the Arctic Circle at approximately Latitude $68^{\circ} 39' \text{N}$, Longitude $134^{\circ} 48' \text{W}$ (Robinson *et al.* 1992) (Figure 3).

Figure 3: Satellite image showing the location of Rapid Creek, Yukon Territory (Google Earth, 2013). Image is not to scale.



2.4. Geology of the Rapid Creek region

The Rapid Creek region lies in the Beaufort Mackenzie Basin, a 155,000 km² extensional and faulting sedimentary basin (Robinson *et al.* 1992). The basin is composed of a thick flysch sequence of turbidite sandstone, mudstones and shale (Robinson *et al.* 1992). The flysch sequence is overlaid by the Rapid Creek Formation which comprises of interbedded ironstone and shale units. The phosphate minerals are found in microcrystalline inclusions, sparry replacement cements, veinlets and fracture surfaces at Rapid Creek (Robinson *et al.* 1992).

2.5. Mineralogy of the Rapid Creek region

The two minerals within the phosphoferrite group that are described to-date in the Rapid Creek region are kryzhanovskite and garyansellite (Robinson *et al.* 1992). The kryzhanovskite at this locality typically exist in its intermediate form, with the chemical formula $\text{MnFe}^{3+}_2(\text{PO}_4)_2(\text{OH})_2 \cdot \text{H}_2\text{O}$. The mineral is also relatively enriched with magnesium (Robinson *et al.* 1992). Furthermore, most of the samples collected by Robinson *et al.* (1992) displayed evidence of zoning within individual crystals. Robinson *et al.* (1992) also suspected some samples may contain zones of garyansellite. Crystals of kryzhanovskite and garyansellite from this locality are very similar in colour and form. They range from chocolate to clove to reddish brown (Robinson *et al.* 1992) and typically exist as subhedral to euhedral crystals.

2.6. Purpose and objective of study

In the 1970s and 1980s, major phosphate mineral discoveries occurred at Rapid Creek, Yukon Territory. Since then, the phosphate minerals from this locality have not been further analysed until recently. Tait *et al.* (2011) discovered bobdownsite at Big Fish River, an area in close proximity to Rapid Creek, by applying new mineralogical analytical techniques. Due to the availability of new analytical techniques, a re-investigation on the phosphoferrite group mineral found in Rapid Creek will be conducted. The main objective of this study is to use various analytical techniques, such as Raman spectroscopy, scanning electron microscopy (SEM), single crystal X-ray diffraction (XRD), electron microprobe analysis (EMPA) and X-ray powder diffraction, to identify and determine a nomenclature scheme for the phosphoferrite group minerals found in Rapid Creek. Furthermore, the chemical variation of these minerals will be studied to verify the findings of zoned minerals stated by Robinson *et al.* (1992).

3. Methodology

Prior to the main data analysis process, several steps were taken to obtain the grains of interest. First, possible phosphoferrite group minerals on specimens were identified under a microscope. Second, these possible grains of interest were analysed using Raman spectroscopy to confirm their identity. Grains with greater than 75% match with either kryzhanovskite or garyansellite in the RRUFF spectra database and are well developed crystals were extracted from the specimens. Third, the grains were submerged into a beaker of ethanol solution and placed in the ultrasonic bath for 15 minutes for cleansing. The grains were then air dry and analysed.

For this research, a combination of analytical techniques was used to accurately identify the specimens of interest. This includes non-destructive data collection techniques such as Raman

spectroscopy, SEM, XRD and EMPA, and destructive data collection techniques such as X-ray powder diffraction.

3.1. Raman Spectroscopy

Raman spectroscopy is an analytical technique that uses the theory of inelastic scattering caused by a laser source. When the laser interacts with the sample, absorption of the electromagnetic (EM) wave takes place, which transforms the molecules into oscillating dipoles (Princeton Instrument, 2012). The dipoles emit EM energy with a different photon frequency with respect to the original laser frequency, which is known as the Raman Effect (Princeton Instrument, 2012). According to Princeton Instrument (2012), there are three different types of frequencies — Stokes frequency, Anti-Stokes frequency and Rayleigh scattering. Stokes frequency is when the emitted frequency is lower than the original laser frequency. This occurs when the molecules in the sample absorb EM energy in their basic vibrational state. Anti-Stokes frequency is when the emitted frequency is higher than the original laser frequency. This occurs when the molecules in the sample are already in their excited vibrational state. The excess energy is released and the molecules return to their basic vibrational state. Rayleigh scattering is when there is no change in emitted frequency with respect to the laser frequency. This occurs when the sample contains no Raman-active mode molecules. The molecules would still be excited by the EM energy, yet it would return back to its original vibrational state by emitting the same amount of EM energy absorbed.

Different structural groups in minerals will produce different scattering patterns. Hence, Raman spectroscopy is highly accurate at identifying the mineral groups in the specimens. However, one of the shortcomings of Raman spectroscopy is the lack of accuracy at differentiating minerals within the same structural group. For example, it can accurately identify phosphate minerals from silicate minerals but not minerals within the phosphate group. This is because PO_4^{3-} tetrahedra are present in all phosphate minerals; hence the phosphate peak at 950 to 975 cm^{-1} is present in all phosphate mineral spectra (Tait *et al.* 2011). Nonetheless, the mineral contains other structural groups and elements, which will produce more scattering patterns. These scattering patterns are used in combination to increase the accuracy of mineral identification. However, kryzhanovskite and garyansellite, the two minerals of interest in this study, have similar chemical and structural formula, which results in nearly identical Raman spectra (Figure 4).

For both the initial identification and main data analysis of the grains of interest, the single spot testing function was used on the Raman spectrometer. Due to the varying appearance and morphology of the grains under the Raman microscope, multiple areas of interests were tested on the same grain with the same acquisition parameters. The parameters used in Table 1 produced spectra which contain minimal amount of fluorescence and maximum amount of Raman scattering. More than 100 spectra were acquired and compared to a database with 5129 pre-determined RRUFF spectra using a program called, CrystalSleuth. These comparisons allowed the identification of minerals present and most importantly whether or not the samples were phosphoferrite group minerals.

Figure 4: Similarities in kryzhanovskite and garyansellite Raman spectra obtained from RRUFF database (University of Arizona, 2009)

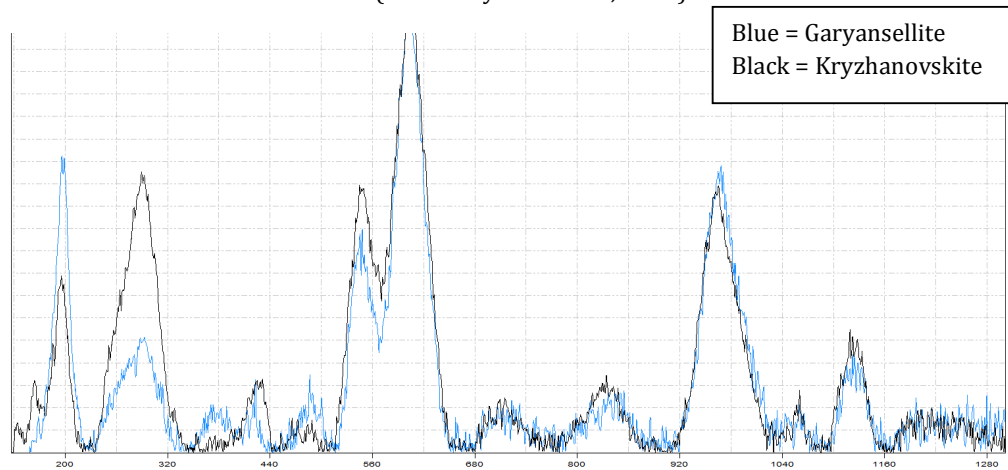


Table 1: Raman spectroscopy acquisition parameters

Laser	532 nm
Filter	D1
Hole	400 nm
Silt	100 nm
Acquisition	Multiple window acquisition for 30 seconds. Range 100 to 3600 cm^{-1}

3.2. Scanning Electron Microscopy (SEM)

Due to the similarities of the phosphoferrite group minerals in Raman spectroscopy, other analytical techniques were used to differentiate the minerals. SEM detects and analyses X-rays emitted from a sample that is under electron bombardment. The X-ray spectrum is displayed according to energy dispersive X-ray spectroscopy (EDS) (Barker & Fournelle, 1996). EDS is used for qualitative elemental analysis which determines the presence of elements and their relatively abundance in the tested sample. Hence, if the sample occurs as an ideal member of the phosphoferrite group, the SEM analysis would facilitate the differentiation between reddingite, kryzhanovskite/phosphoferrite, landsite and garyansellite. However, most natural minerals, including the phosphoferrite group minerals, do not occur as ideal members. According to Anthony *et al.* (2000), the garyansellite sample at Rapid Creek contains minor amounts of aluminium and manganese at 0.1 wt% and 2.7 wt%, respectively. Also, Robinson *et al.* (1992) stated that the kryzhanovskite at this locality typically has non-end member composition, is relatively enriched in magnesium and often exhibits zoning. As a result, there is some degree of uncertainty when using SEM analysis for the identification of phosphoferrite group minerals found in Rapid Creek.

Another shortcoming of the EDS, especially with grained samples, is the incorrect sample geometry during data collection (Barker and Fournelle, 1996). X-rays emitted from a sample may be blocked and do not reach the detector if the sample is tilted incorrectly. This is often shown by very low amount of X-rays detection, which is expressed as low output counts. Furthermore, spectra peaks of different elements may overlap during data analysis. As a result,

auto-elemental identification by the software may not be completely reliable and manual interpretation of results is required.

Despite the shortcomings mentioned above, the EDS is still a very useful tool for determining the chemical variation and compositional zoning of the samples. EDS produces individual elemental images with an electron beam rastering over the area of interest (Goodge, 2012^a). The elements detected and displayed are chosen by the scientist. Also, the elemental maps are displayed more distinctly when the dwell time of the electron beam is set for a longer time period. For this research, the dwell time was set at 30 seconds and the following elements were measured: Al, C, Ca, Fe, K, Mg, Mn, Na, Ni, O, P, S and Si. The images were edited and combined using an image editing program to allow the identification of elemental rich and poor areas. Areas of interest that were mapped were also recorded as backscatter electron (BSE) images, where elements are displayed in different shades of grey due to differing atomic numbers (Goodge, 2012^b).

3.3. Single Crystal X-ray Diffraction (XRD)

XRD is a method which determines the structure of atoms in a crystal. Since each mineral has a different atomic arrangement, the unit cell data obtained from XRD can help identify the nomenclature of the tested sample.

Ideally, a single euhedral symmetrical homogenous crystal is mounted on a glass fibre with epoxy glue. The glass fibre is then mounted on a small cylindrical brass mount, which in turn is placed into the instrumental sample holder. The position of the crystal is adjusted so that the XRD analysis conducted with the instrument, Bruker Single Crystal X-ray D8 Venture, would result in accurate preliminary unit cell data. If further unit cell data is collected, a crystal lattice structure model using the program APEX 2 could be produced. The crystal structure would aid the determination of a refined unit cell. However, it is extremely rare to encounter and extract a single crystal of a phosphoferrite group mineral found in Rapid Creek that is not zoned or twinned. Nonetheless, preliminary unit cell determination was carried out on grains of interest that are euhedral, relatively small and have little zoning or twinning. XRD was conducted because unit cell data for phosphoferrite group minerals are different (Table 2), which allows the identification of the mineral.

Table 2: Summary of phosphoferrite group mineral unit cell data
Uncertainty values for reddingite were not stated in the literature

Phosphoferrite Group Mineral	Unit Cell		
	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)
Reddingite (Palache <i>et al</i> , 1951)	9.49	10.08	8.70
Phosphoferrite (Palache <i>et al</i> , 1951)	9.460(2)	10.024(3)	8.670(2)
Kryzhanovskite (Ginzburg, 1950)	9.450(2)	10.013(2)	8.179(2)
Landesite (Palache <i>et al</i> , 1951)	9.458(3)	10.185(2)	8.543(2)
Garyansellite (Sturman & Dunn, 1984)	9.452(4)	9.890(5)	8.198(4)

3.4. Electron Microprobe Analyzer (EMPA)

EMPA quantitatively determines elemental concentration on surfaces of polished specimens, most commonly on thin sections (Jansen & Slaughter, 1982). The beam of high energy electron scans the surface of the specimen as a spot, line or rectangular area. Similar to the SEM, the electrons interact and release energy in the sample which is then re-emitted as X-rays with specific wavelengths. The specific wavelength determines the presence of an element whilst the intensity of the X-rays determines the elemental concentration (Jansen & Slaughter, 1982). Contrary to the SEM, EMPA uses wave dispersive X-ray spectroscopy (WDS) for detecting and counting X-rays (Donovan, 2006). WDS is more sensitive to low elemental concentrations than EDS (Donovan, 2006) and is therefore considered to be more accurate and precise when determining chemical composition of the sample. Furthermore, EMPA requires the use of standards to calibrate the characteristic X-ray wavelengths of the elements. For this research, a polished carbon coated thin section was analysed using a combination of spot and line scans.

3.5. X-ray Powder Diffraction

X-ray powder diffraction requires a small amount of sample to be powdered. For this research, data was collected by the Bruker D8 Advance X-ray diffractometer using acquisition parameters stated in Table 3. The acquired patterns were compared with 39,410 existing diffraction patterns from the International Centre for Diffraction PDF-4/ Minerals database (ICDD, 2012) using the program, DIFFRAC EVA. Due to the higher amount of patterns in the X-ray diffraction database, it allows for a more accurate match of tested material to minerals than the RRUFF database for Raman spectroscopy. Furthermore, the database contains multiple X-ray diffraction patterns of different specimens of the same mineral. This further enhances the accuracy of a match as minerals typically vary in chemical composition.

Table 3: X-ray powder acquisition parameters

Twin primary	Göbel Mirror
Twin secondary	5.5 mm secondary motorized silt
Physical silt	0.6 mm
Air scatter screen	Present
Lynx eye	Angular opening 2.9° Upper Discriminator 0.250 V Lower Discriminator 0.19 V
2 Theta	Start = 10° Increment = 0.01° Finish = 70°
Time	0.6 seconds per step
Voltage	40 kV
Current	40 mA

4. Results

Mineralogical data is collected on two series of the phosphoferrite group minerals found in Rapid Creek, Yukon Territory, Canada. The first series is called *RC* and was collected by Professor Kimberly Tait and Ian Nicklin during the summer of 2012. The second series is called the *M* series which was collected by curators of the Royal Ontario Museum in the 1970s and 1980s. The *M* series is catalogued in the Royal Ontario Museum collection.

4.1. *RC* series

In the *RC series*, a total of 17 specimens were examined using Raman spectroscopy, SEM, and XRD. The specimens were labeled RC1 to RC17 and grains of interest from these specimens were labeled with sequential alphabetical letters (Appendix 1).

4.1.1. Raman spectroscopy

Raman spectra of three representative specimens (RC1_B, RC5_A and RC17_A) are compared with kryzhanovskite R060927 and garyansellite R070392 spectra from the RRUFF database (Figures 5 & 6). Kryzhanovskite R060927 was collected in Yukon Territory, Canada and is currently held at the Royal Ontario Museum under the catalogue number M52411 (University of Arizona, 2009). Garyansellite R070392 was collected in Rapid Creek, Yukon Territory, Canada and is currently held at Westaus Mineral Museum under the catalogue number 1004504 (University of Arizona, 2009). Spectra 2 and 3 represent the typical Raman signature shown by the *RC* series phosphoferrite group minerals. In terms of spectral bands shifts and intensity, these two spectra are very similar to the spectra of kryzhanovskite and garyansellite in the RRUFF database. The very strong doublet at 520 to 650 cm^{-1} represent Fe(Mn)OH deformation (Frost, 2002). The sharp peak at 950 to 975 cm^{-1} represents the symmetric stretching of PO_4^{3-} (Tait *et al.* 2011). The similarities in Raman spectra represent similar structural formula of the specimens. However, spectra 2 and 3 have two dissimilarities with the kryzhanovskite and garyansellite found in the RRUFF database - the indistinctive peaks between 660 to 900 cm^{-1} and less pronounced peaks between 975 to 1100 cm^{-1} . The peaks between 975 to 1100 cm^{-1} in spectra 2 and 3 correspond to the moderate intensity peak at 1080 to 1100 cm^{-1} in spectra 4 and 5 (Figure 5), which represent asymmetric stretching of PO_4^{3-} (Tait *et al.* 2011). Hence, RC5_A and RC17_A have weaker asymmetric stretching of PO_4^{3-} than the phosphoferrite group minerals found in the RRUFF database. When compared to spectra 2 to 5, spectrum 1 displays higher spectral fluctuations and the presence of fluorescence. The fluctuations are a result of high background noise. An example of fluorescence in spectrum 1 is displayed between 900 and 1150 cm^{-1} . Only one broad peak is displayed when compared to the presence of several peaks in spectra 2 to 5 (Figure 5).

Figure 5: Raman spectra of **1)** RC1_B **2)** RC5_A **3)** RC17_A **4)** Kryzhanovskite obtained from RRUFF database (University of Arizona, 2009) **5)** Garyansellite obtained from RRUFF database (University of Arizona, 2009).

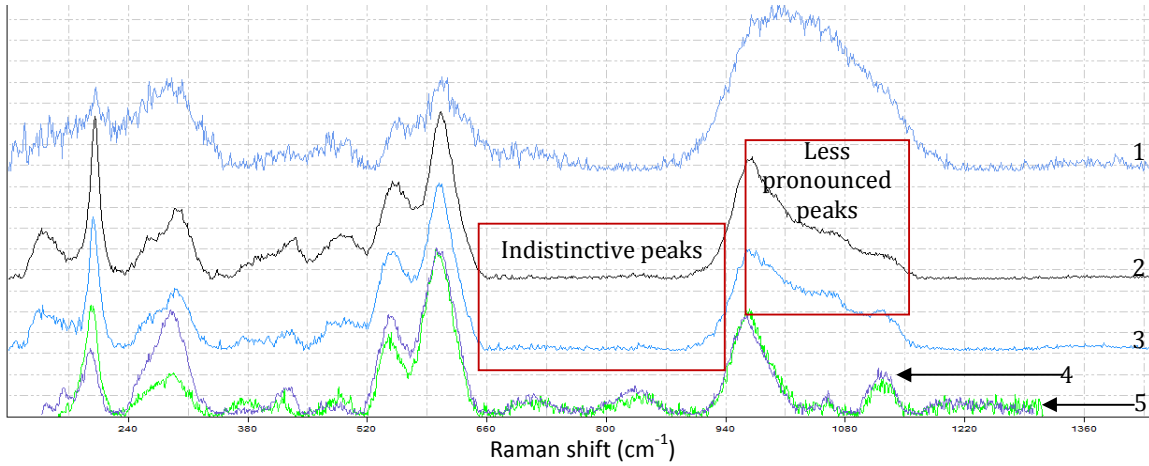
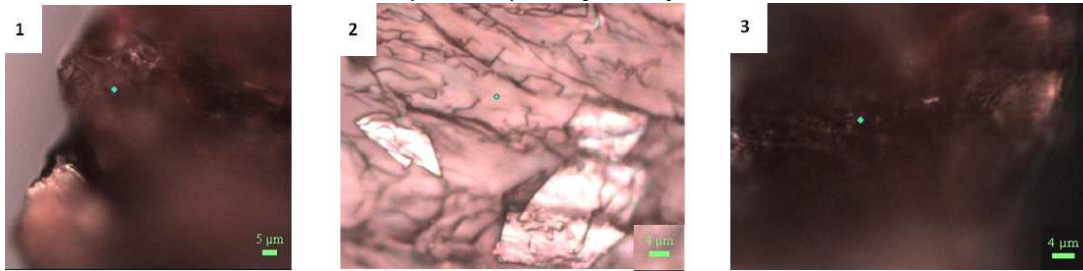


Figure 6: Microscopic view of areas tested to obtain spectra **1)** RC1_B **2)** RC5_A **3)** RC17_A. Green dot marks the exact point where the data was collected. Scale bar in 1), 2) and 3) represent 5 μm , 4 μm and 4 μm respectively.

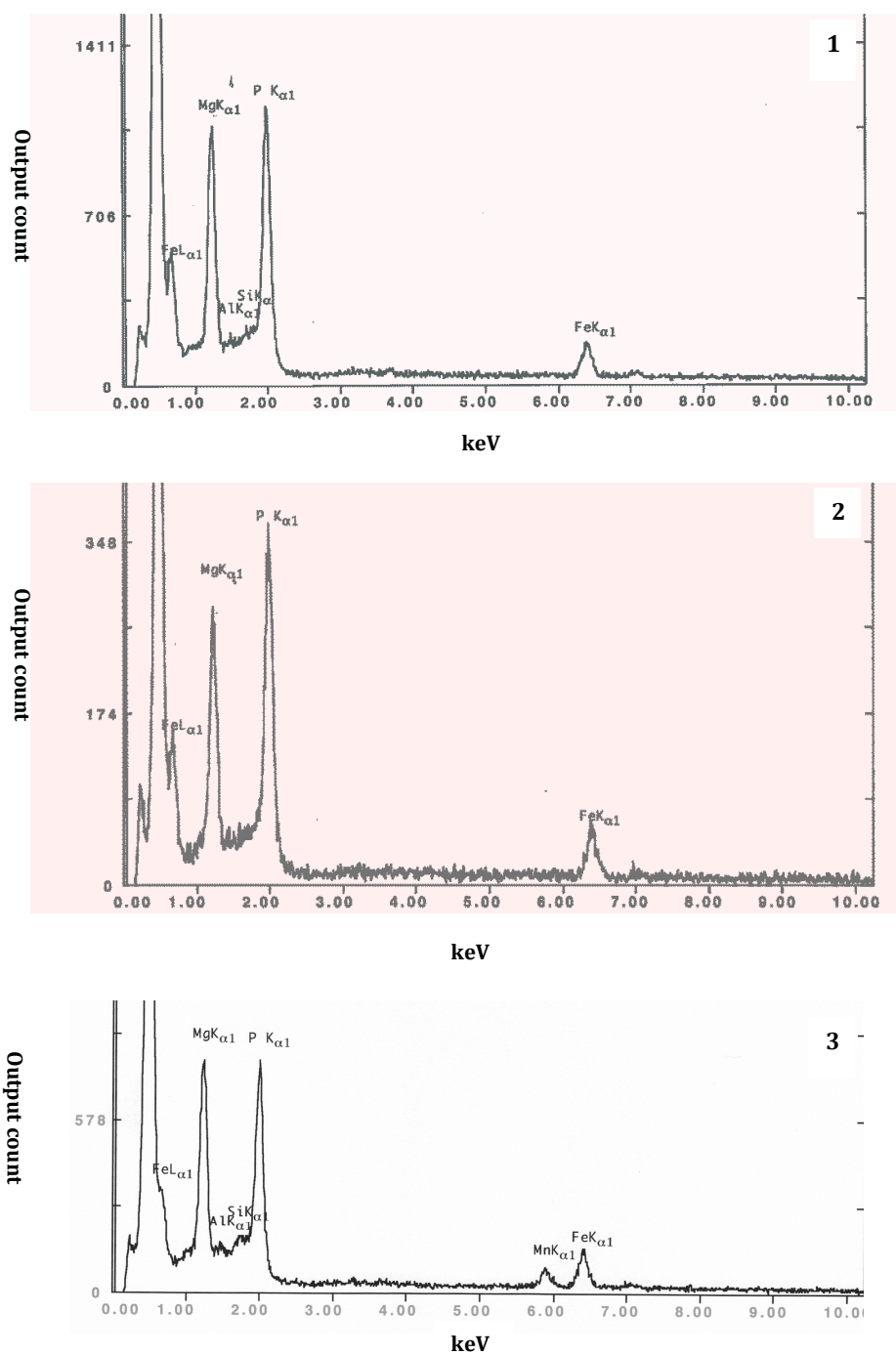


4.1.2. Scanning Electron Microscope (SEM)

Energy Dispersive Spectroscopy (EDS)

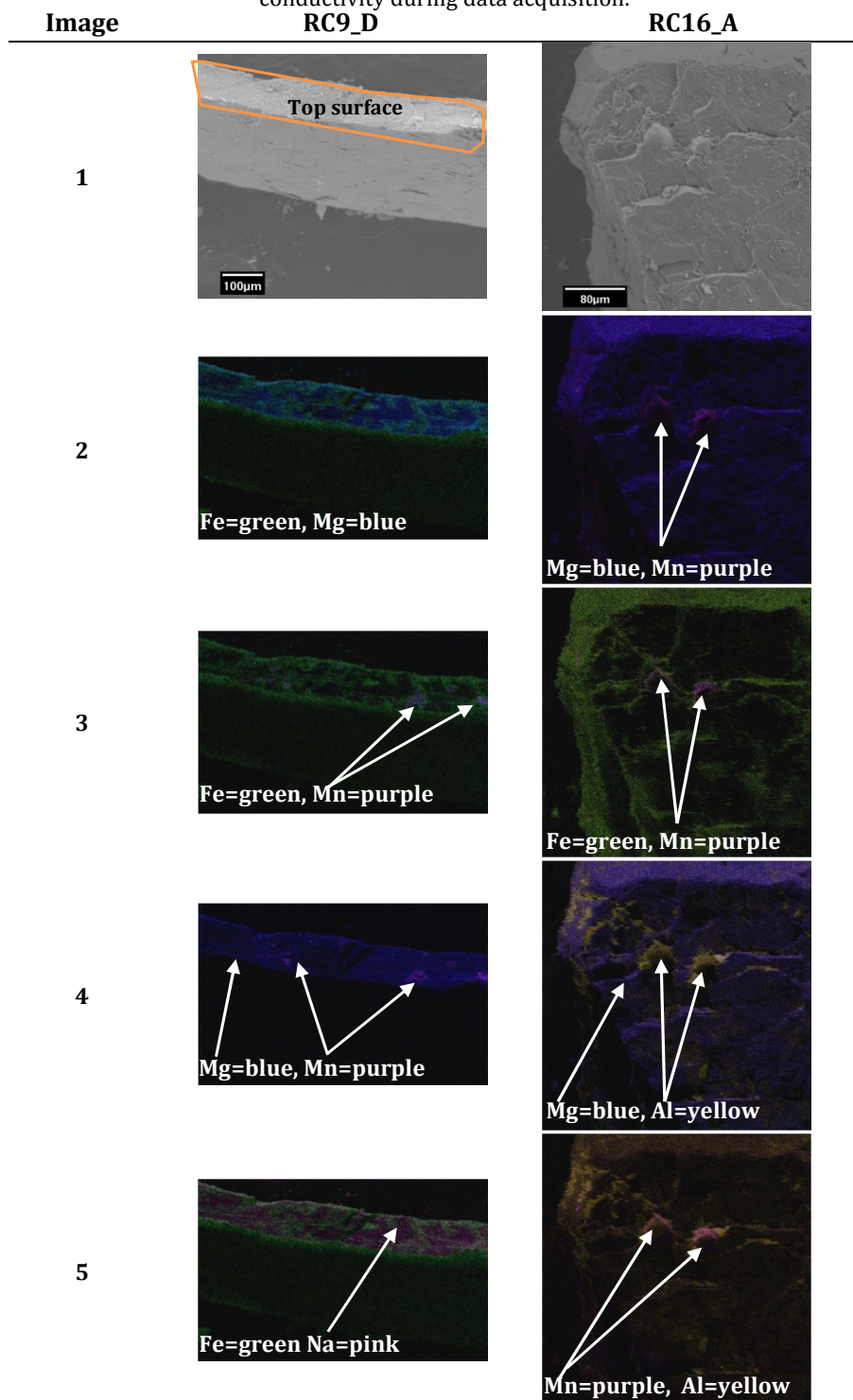
Despite the structural similarities in RC5_A and RC17_B, the two specimens have chemical variation (Figure 7.2 and Figure 7.3). RC5_A has an ideal chemical composition of garyansellite with iron, magnesium, and phosphorous (Sturman & Dunn, 1984). RC17_A contains major amounts of iron, magnesium, manganese, and phosphorus, which are elements found in kryzhanovskite (Ginzburg, 1950) and intermediate kryzhanovskite (Robinson *et al.* 1992). The sample also contains minor amounts of aluminum and silicon, which are likely to be products of weathering such as kaolinite $\text{Al}_2\text{SiO}_5(\text{OH})_4$. RC1_B (Figure 7.1) has a similar chemical composition to both RC17_A and RC5_A, with an absence of manganese when compared to RC17_A and presence of aluminum and silicon when compared to RC5_A.

Figure 7: Energy Dispersive X-ray spectra of **1)** RC1_B **2)** RC5_A **3)** RC17_A



Elemental Map

Figure 8a: RC9_D: **1)** BSE image; RC9_D Elemental Map: **2)** Fe-Mg **3)** Fe-Mn **4)** Mg-Mn **5)** Fe-Na
 Figure 8b: RC16_A: **1)** BSE image; RC16_A Elemental Map: **2)** Mg-Mn **3)** Fe-Mn **4)** Mg-Al **5)** Mn-Al
 The colours in these images may look different to the colour stated on the image due to the effects of pixel overlapping in combined layers. Some maps have lines across them due to poor electron conductivity during data acquisition.



In order to facilitate easy visualization and interpretation, only two elements are shown for each elemental map (Figure 8a and Figure 8b). RC9_D has a high concentration of magnesium at the center top surface of the grain and is surrounded by a high concentration of iron at the outer edge (Figure 8a.2). Manganese is only present in minor amounts on the top surface (Figure 8a.4). An interesting feature in RC9_D is the two black lines on the top surface of the grain. It is distinctly visible in Figure 8a.2 and Figure 8a.4 when magnesium is displayed, but faintly visible when magnesium is not displayed (Figure 8a.3). Furthermore, RC9_D has a high sodium concentration on the top surface (Figure 8a.5), yet sodium does not commonly occur in phosphoferrite group minerals (Ginzburg, 1950, Palache *et al.* 1951, Sturman & Dunn, 1984). Hence, RC9_D may not be a phosphoferrite group mineral and may be alluaudite $\text{Mn}^{2+}\text{Fe}^{3+}_2(\text{PO}_4)_2(\text{OH})_2 \cdot \text{H}_2\text{O}$, a mineral that can also be found in Rapid Creek, Yukon Territory (Fisher, 1955, Robinson *et al.* 1992).

For RC16_A, iron and magnesium are the dominant elements shown in the area of interest. Manganese and aluminum occur in high concentration at the tip of the two lobe-shaped features (Figure 8b.2 to Figure 8b. 5). In Figure 8b.5, the two lobes are shown in pink despite the fact that the colours used for elemental mapping is purple and yellow for manganese and aluminum, respectively. This is a result of pixels overlaps in combined image layers.

4.1.3. Single Crystal X-ray Diffraction (XRD)

Table 4: Preliminary unit cell data of RC series samples with published data.
[1] (Palache *et al.* 1951), [2] (Ginzburg, 1950), [3] (Sturman & Dunn, 1984), [4] (Downs, 2006)

Sample	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)
RC1_B	9.46	9.88	8.18
RC5_A	9.48	9.85	8.16
RC6_E	9.45	9.88	8.14
RC9_D	9.53	9.94	8.17
RC12_B	9.41	9.87	8.15
RC15_A	9.48	9.90	8.20
Phosphoferrite [1]	9.460(2)	10.024(3)	8.670(2)
Reddingite [1]	9.49	10.08	8.70
Kryzhanovskite [2]	9.450(2)	10.013(2)	8.179(2)
Landesite [1]	9.458(3)	10.185(2)	8.543(2)
Garyansellite [3]	9.452(4)	9.890(5)	8.198(4)
RRUFF M37306_C [4]	9.4507(6)	9.8597(8)	8.1512(7)

Most of the RC series unit cell data displayed in Table 4 do not closely match with the unit cell data of the phosphoferrite group minerals published in the literature. However, unit cell data of RC1_B is very similar to garyansellite, with only 0.01Å difference in each crystallographic axis. Also, data for crystallographic axes *a* and *c* of RC6_E and RRUFF M37306_C are very similar. RRUFF M37306_C is the garyansellite type specimen found in Rapid Creek, Yukon Territory, Canada and is catalogued in the Royal Ontario Museum collection. It is also the same specimen as M37306_BP and M37309_C of which preliminary XRD data analysis was conducted (Section 4.2.4)

4.2. M Series

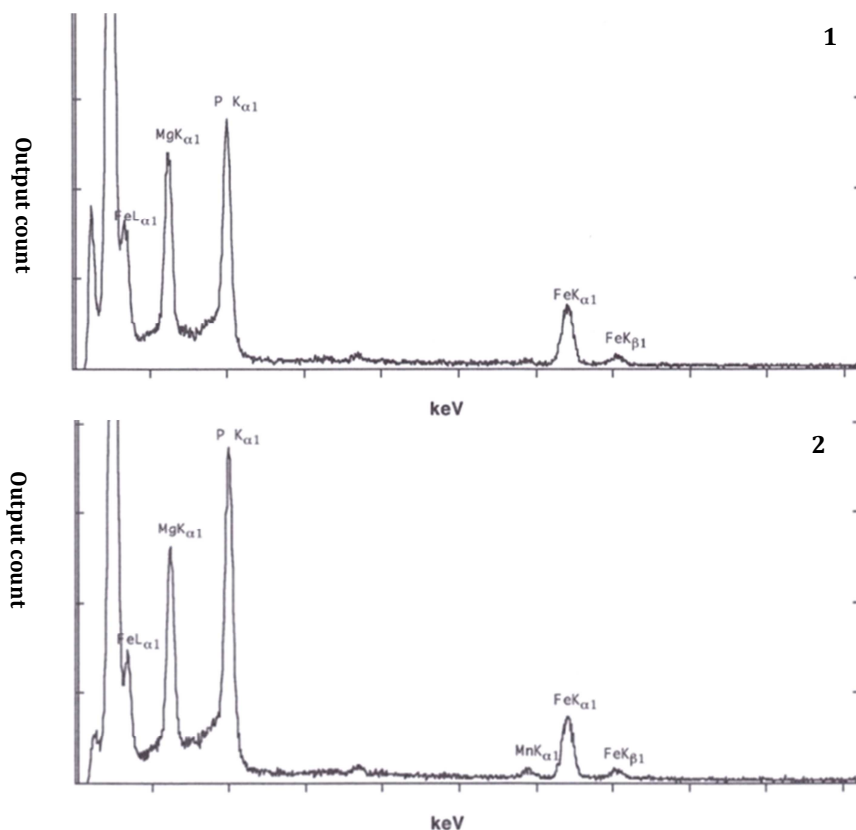
The *M* series are specimens that are catalogued in the Royal Ontario Museum collection. For this research, seven specimens were examined (Appendix 2). The grains of interests were named after the specimen number provided by the Royal Ontario Museum followed by sequential alphabetical letters. The letter “P” in the specimen name indicates the sample was powdered and the sequential number indicates different analytical trials. Extensive data collection has been conducted on M55955, including: SEM, EMPA and X-ray powder diffraction. XRD was also conducted on two crystals of garyansellite type specimen, M37306. The grains of interest were labeled as M37306_BP and M37306_C. “BP” is an abbreviation for broken pieces where the crystal was obtained from the fragmented pieces in the collection box. Sample M37306_C is obtained from methylene iodide separation method, <400 μ m heavy fraction (2/3). This separation method was also used for the sample RRUFF Garyansellite R1000209 (University of Arizona, 2009).

4.2.1. M55955 - SEM

Energy Dispersive Spectroscopy (EDS)

The energy dispersive X-ray spectra of different areas of interest on the powdered sample of M55955 (Figure 9) display the presence of typical phosphoferrite group elements (Ginzburg, 1950; Palache *et al.* 1951, Sturman & Dunn, 1984). In Figure 9.1, only magnesium is present whilst in Figure 9.2 both magnesium and manganese are present.

Figure 9: Energy Dispersive X-ray spectra of **1)** M55955_P1 **2)** M55955_P2



The chemical variation of different areas of interest on the M55995 thin section in terms of manganese, iron and magnesium molecular proportion is illustrated in a ternary plot (Figure 10). The ternary plot indicates that most areas of interest have an Mg-rich intermediate composition between ideal end-member kryzhanovskite or phosphoferrite and garyansellite, which would be referred to as Mg-rich intermediate kryzhanovskite for this study. There is one outlier point with high manganese and iron proportion which corresponds to intermediate kryzhanovskite.

A comparison on the Fe-Mg ratio of collected EDS data from M55955 thin section and Robinson *et al.*'s (1992) data is made (Figure 11). Both set of data show an inverse relationship between magnesium and iron total. However, data collected by Robinson *et al.* (1992) are more scattered and have a higher Fe-Mg ratio than the data collected from M55955.

Figure 10: Mineralogical relationship between M55995 with phosphoferrite group mineral based on Fe, Mn and Mg molecular proportion. * Fe expressed as Fe total which takes into account of both Fe^{2+} and Fe^{3+} . (1) (Moore *et al.* 1980), (2) (Sturman & Dunn, 1984), (3) (Robinson *et al.* 1992)

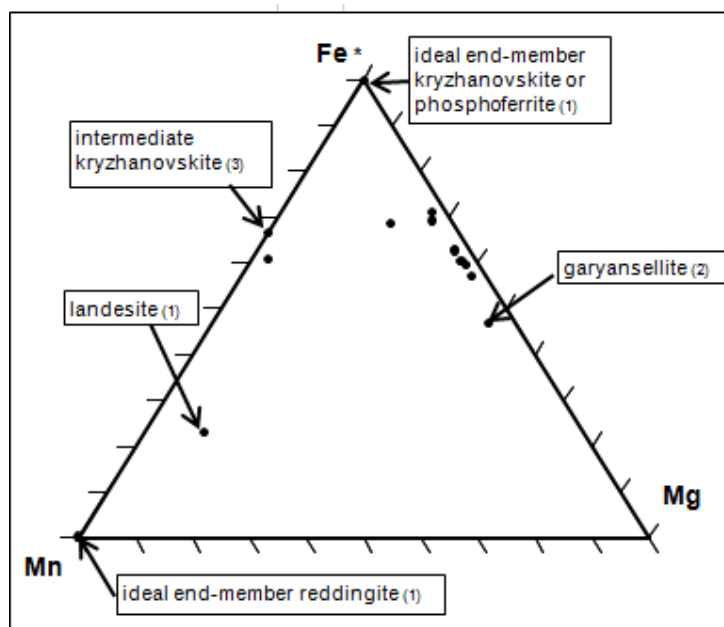
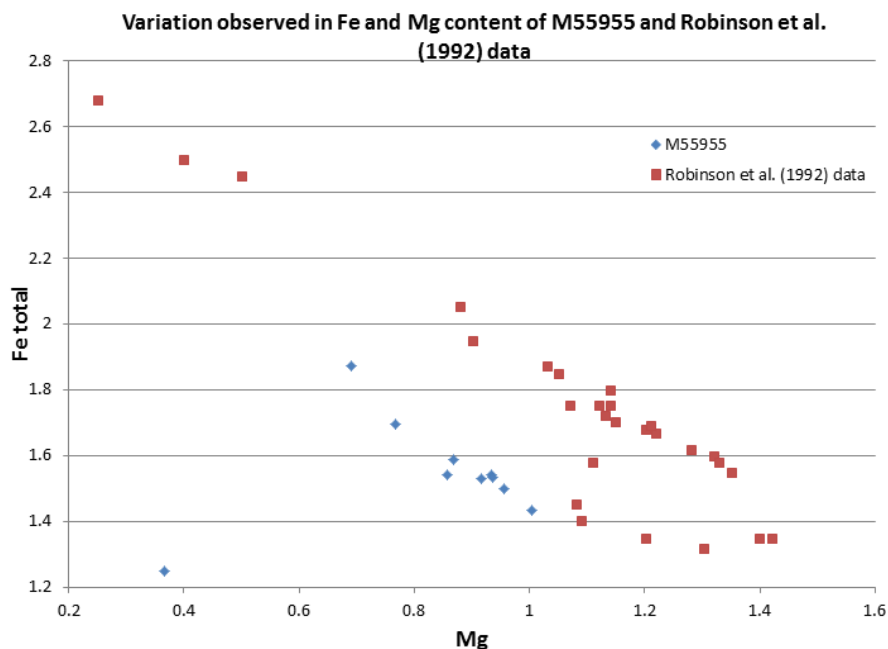


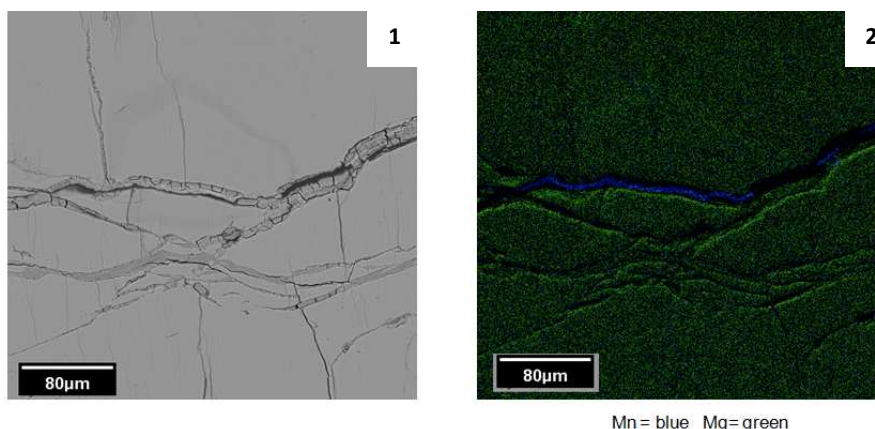
Figure 11: Fe–Mg ratio of M55955 thin section areas of interest and Robinson *et al.* (1992) data



Elemental map

Elemental mapping was conducted on the thin section of M55995. The lighter or brighter the feature is in a BSE image (Figure 12.1), the higher the atomic number of the element (Goodge, 2012^b). This is because higher atomic number atoms have greater cross-sectional area, which would increase the probability of elastic scattering when the electron beam interacts with the sample (Goodge, 2012^b). As a result, there will be a higher proportion of backscattered electrons reaching the detector and would produce a brighter image. Despite the high variation in atomic number as shown in various shade of grey (Figure 12.1), there is little variation in magnesium and manganese concentration (Figure 12.2). The main area of interest has high concentration of magnesium with minor amounts of manganese. Most of the lines seen in Figure 12.2 are artefacts of cracks with an exception to one line which contains high concentrations of manganese in some regions.

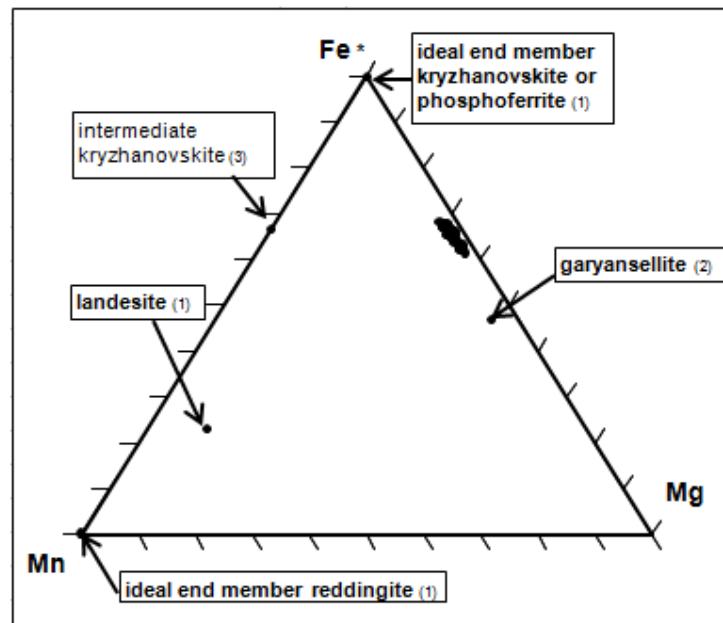
Figure 12: M55955: **1)** BSE image **2)** Elemental Map Fe-Mg



4.2.2. M55955 - Electron Microprobe Analyser (EMPA)

Similar to Figure 10, chemical variation data obtained from the EMPA on the M55955 thin section is plotted on a ternary diagram (Figure 13). The areas of interest examined are different from the areas in Figure 10. However, the areas examined under EMPA also have a Mg-rich intermediate kryzhanovskite composition, which correlates to Figure 10. Nonetheless, the points plotted using EMPA data is more precise than the points plotted using EDS data.

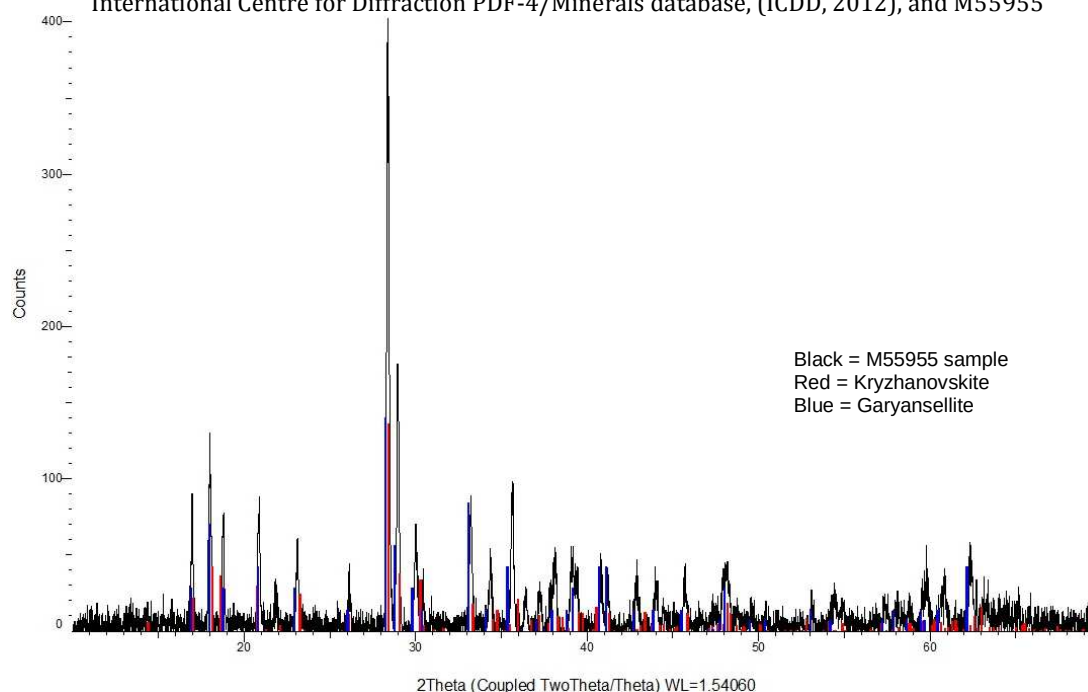
Figure 13: Mineralogical relationship between M55955 with phosphoferrite group mineral based on Fe, Mn and Mg molecular proportion * Fe expressed as Fe total which takes into account of both Fe²⁺ and Fe³⁺. (1) (Moore *et al.* 1980), (2) (Sturman & Dunn, 1984), (3) (Robinson *et al.* 1992)



4.2.3. M55955 - X-ray Powder Diffraction

The X-ray powder diffraction pattern obtained from M55955 does not match with the kryzhanovskite or garyansellite patterns obtained from the International Centre for Diffraction database (Figure 14). The sample appears to be an intermediate mineral between kryzhanovskite and garyansellite.

Figure 14: X-ray powder diffraction pattern of kryzhanovskite and garyansellite obtained from International Centre for Diffraction PDF-4/Minerals database, (ICDD, 2012), and M55955



4.2.4. M37306- Single Crystal X-ray Diffraction (XRD)

Preliminary unit cell data for samples M37306_BP and M37306_C do not closely match with the unit cells of published data (Table 5). However, data for individual crystallographic axis of these samples closely matches with crystallographic axis of different minerals. For example: crystallographic axis a of M37306_C matches with kryzhanovskite, garyansellite and RRUFF M37306_C. Crystallographic axis b of M37306_C matches with garyansellite. However, there is approximately 0.04Å difference in crystallographic axis c of M37306_C and garyansellite.

Table 5: Preliminary unit cell data of M37306 with published data. M37306_C and RRUFF M37306_C are different grains but are both garyansellite type specimen separated by heavy fraction. [1] (Palache *et al.* 1951), [2] (Ginzburg, 1950) [3] (Sturman & Dunn, 1984), [4] (Downs, 2006).

Sample	a (Å)	b (Å)	c (Å)
M37306_BP	9.46	9.86	8.16
M37306_C	9.45	9.89	8.16
Phosphoferrite [1]	9.460(2)	10.024(3)	8.670(2)
Reddingite [1]	9.49	10.08	8.70
Kryzhanovskite [2]	9.450(2)	10.013(2)	8.179(2)
Landesite [1]	9.458(3)	10.185(2)	8.543(2)
Garyansellite [3]	9.452(4)	9.890(5)	8.198(4)
RRUFF M37306_C [4]	9.4507(6)	9.8597(8)	8.1512(7)

5. Discussion

5.1 RC Series

5.1.1. Raman Spectroscopy and Energy Dispersive Spectroscopy (EDS)

The combination of data obtained from Raman spectroscopy and EDS is useful in mineralogical identification of specimens. In Figure 5, RC5_A is a phosphoferrite group mineral and has a very similar spectrum to both kryzhanvoskite and garyansellite. This is because Raman spectroscopy cannot adequately differentiate minerals in the same group due to their structural similarities. The shortcomings of Raman spectroscopy can be resolved with the use of EDS. RC5_A shows the ideal chemical composition of garyansellite with iron, magnesium and phosphorus (Figure 7.2). Furthermore, after acquiring Raman spectroscopy data for RC5_A, the laser beam created a hole in the tested area of interest (Figure 6.2). This phenomenon has rarely occurred as the acquisition parameters have been tested many times to obtain optimal data collection without damaging the samples. Although the sample has been damaged, this incident has provided further evidence to support that RC5_A can be classified as garyansellite. This is because minerals with higher water content are more sensitive to the energy emitted by the laser. Garyansellite $(\text{Mg, Fe}^{3+})_3(\text{PO}_4)_2(\text{OH},\text{O}) \cdot 1.5\text{H}_2\text{O}$ (Sturman & Dunn, 1984) is a more hydrated phosphoferrite group mineral than the intermediate kryzhanovskite $\text{MnFe}^{3+}_2(\text{PO}_4)_2(\text{OH})_2 \cdot \text{H}_2\text{O}$ commonly found in Rapid Creek (Robinson *et al.* 1992). Hence, RC5_A can be classified as garyansellite.

RC17_A has a very similar Raman spectrum to RC5_A (Figure 5.3 & Figure 5.2 respectively), yet the chemical compositions of the samples are different. RC17_A (Figure 7.3) contains iron, magnesium, manganese and phosphorus as major elements with minor amounts of aluminum and silicon, whilst RC5_A (Figure 7.2) contains iron, magnesium and phosphorus only. This is another example which indicates the shortcomings of Raman spectroscopy in attempts to differentiate minerals within the same structural group. The presence of both Mg and Mn, and their relative abundance suggest RC17_A is Mg-rich intermediate kryzhanovskite. The minor amounts of Al and Si are likely to be weathered minerals such as kaolinite, $\text{Al}_2\text{SiO}_5(\text{OH})_4$.

The chemical composition of RC1_B is very similar to RC5_A except for the presence of minor amounts of Al and Si. However, the Raman spectrum is significantly different from RC5_A at approximately 900 to 1150 cm^{-1} . At this Raman shift, RC1_B (Figure 5.1) displays only one broad peak whilst RC5_A (Figure 5.2) displays one pronounced peak and two minor (weak) peaks. The difference in peaks cannot be due to the presence of minor amounts of aluminum and silicon because RC17_A (Figure 5.3) also have these two minor elements yet the Raman spectrum is very similar to RC5_A. Therefore, the possible reason for the difference in peaks is the high background noise and fluorescence displayed as high fluctuations in the RC1_B spectrum.

5.1.2. Elemental Map

In RC9_D (Figure 8a), there is a high concentration of iron and magnesium with minor amounts of manganese. Hence, the sample can be classified as garyansellite. The blue and green colours are saturated (purely blue and purely green, not a cyan colour), which indicate the magnesium and iron concentrations have remained relatively distinct (Figure 8a.2). High magnesium concentration is located on the center top surface of the grain, whilst high iron

concentration is located at the outer edge of the top surface and on the side of the grain. This suggests that the magnesium and iron in this grain cannot readily substitute each other, a uncommon phenomenon that exists in ferro-magnesium minerals. The inability for iron and magnesium to readily substitute each other is due to three reasons. First, the ionic radius of iron and magnesium are different. Fe^{2+} , Fe^{3+} and Mg^{2+} have ionic radius of 75pm, 69pm and 86pm respectively (Shannon, 1976). The differences in ionic radii of these ions are quite large, especially between Fe^{3+} and Mg^{2+} . Hence, sites that are specific to either Fe^{3+} or Mg^{2+} will not readily accept the other ion. Second, there are two non-equivalent octahedral crystallographic sites, $M(1)$ and $M(2)$ (Moore *et al.* 1980). According to Moore *et al.* (1980), the smaller cations in phosphoferrite group minerals prefer the $M(1)$ site on the inversion centre and the larger cations are distributed over the $M(2)$ sites with no symmetry. Hence, Fe^{2+} and Fe^{3+} is likely found at the $M(1)$ site whilst Mg^{2+} is likely found at the $M(2)$ sites. Due to this site preference, iron and magnesium can not readily substitute each other. Third, the valences of elements are different. Mossbauer spectroscopy was conducted on type specimen garyansellite (M37306) and found that the iron mainly exists as Fe^{3+} in garyansellite (Appendix 3.1 and 3.2). Furthermore, this corresponds to the mineral formula of garyansellite, $(\text{Mg}, \text{Fe}^{3+})_3(\text{PO}_4)_2(\text{OH}, \text{O}) \cdot 1.5\text{H}_2\text{O}$, where iron exist as $3+$ state (Sturman & Dunn, 1984). Since iron exists as $3+$ state and magnesium exists as $2+$ state, the cations cannot readily substitute each other.

RC9_D also contains a high concentration of sodium on the top surface of the grain (Figure 8a.5). According to Ginzburg (1950), Palache *et al.* (1951) and Sturman & Dunn (1984), sodium does not exist or exist in trace amounts in phosphoferrite group minerals. Therefore, there is a possibility that RC9_D is not garyansellite. Nonetheless, there is a possible explanation for the 'presence' of sodium yet the sample can still be classified as an phosphoferrite group mineral. Sodium and magnesium have similar k-alpha energy values, at 1.04keV and 1.25keV respectively (Bearden, 1967). Hence, the presence of sodium may actually be the presence of magnesium. This is further supported by the fact that multiple energy dispersive spectra were taken on the sample, and the presence of sodium was not indicated.

Similar to RC9_D, RC16_A has a high concentration of iron and magnesium with minor amount of manganese in the area of interest. High concentrations of manganese and aluminum are also present at the tip of the two lobe-shaped features (Figure 8b.2 to Figure 8b.5). These two features are visually and morphologically different to the surrounding area of interest when viewed under the microscope. According to the EMPA data published in the handbook of mineralogy (Anthony *et al.* 2000), garyansellite has minor amounts of MnO and Al_2O_3 at 2.7% and 0.1%, respectively. Hence, the presence of minor amount of manganese and aluminium does not affect the classification of the sample as garyansellite.

5.1.3. Single Crystal X-ray Diffraction (XRD)

When taking into account that most phosphoferrite group crystals found in Rapid Creek are either twinned, zoned or a combination of both, the 0.01Å difference in unit cell data between RC1_B and garyansellite is a promising find. The small difference in unit cell is within error (see numbers in brackets in Table 4), which may be due to systematic error or minor chemical variation in the grain. The high similarity in unit cell values further supports the classification of the sample as garyansellite using Raman spectroscopy (Figure 5.1) and EDS (Figure 7.1).

An attempt is made to further refine the unit cell data of RC1_B. After integrating multiple sets of RC1_B unit cell data, statistical values of spot shape correlation, the average difference between observed and predicted X, Y, Z, and spot shape profiles by detector region indicate it is possible to further refine the unit cell data (Appendix 4.1, 4.2 and 4.3). However, statistical values of R_{sym} are approximately 30% (Appendix 4.4). These R_{sym} values deviated greatly from the ideal R_{sym} of less than or equal to 8% (Bruker AXS Inc., 2004). Low R_{sym} values increase the likelihood of solving the crystal structure, which aids further refinement of unit cell data. Hence, due to the high R_{sym} , further refinement of unit cell data for RC1_B cannot be conducted.

5.2. M Series

5.2.1. M55955

Contrary to the RC series where mineralogical analytical data generally suggest that the sample is either garyansellite, kryzhanovskite or Mg-rich intermediate kryzhanovskite, data collected from M55955 suggest that the sample could be one of the three minerals mentioned above. EDS data on one area of interest of the powdered sample suggests the sample is garyansellite due to the presence of iron, magnesium and phosphorus (Figure 9.1). However, data on another area of interest on the powdered sample suggests that the sample is kryzhanovskite due to the presence of iron, magnesium, manganese and phosphorus (Figure 9.2). X-ray powder diffraction (Figure 14) of M55955 also illustrates the same controversy, where the sample pattern is an intermediate between the garyansellite and kryzhanovskite patterns found in the International Centre for Diffraction database. Furthermore, EDS (Figure 10) and EMPA (Figure 13) data indicate that the specimen is a Mg-rich intermediate kryzhanovskite. In the elemental map (Figure 12.2), the majority area of interest has a high concentration of magnesium with minor amounts of manganese which suggests the sample is garyansellite. However, one of the cracks has a very high concentration of manganese which suggests the sample is kryzhanovskite. The data mentioned above all seem to support Robinson *et al.*'s (1992) findings regarding the presence of intermediate kryzhanovskite $\text{MnFe}^{3+}_2(\text{PO}_4)_2(\text{OH})_2 \cdot \text{H}_2\text{O}$ and the presence of zoned garyansellite and kryzhanovskite at the Rapid Creek locality. Since all the data above supports Robinson *et al.*'s (1992) findings, the Fe:Mg ratio (Figure 11) for Robinson *et al.*'s (1992) data should be similar and not higher than the data collected from M55955. Nonetheless, the differences in ratio can be accounted for by chemical variations in natural minerals.

5.2.2. M37306

Preliminary unit cell data for both samples tested do not closely match with any unit cell data values published for the phosphoferrite group minerals (Table 5). Only certain crystallographic axis data matches with certain phosphoferrite group minerals. Attempts are made to further refine the preliminary unit cell data so that the unit cell data for this sample matches more closely with the phosphoferrite group minerals. However, due to the lack of ideal single crystal characteristics on the two samples, data were considered as non-ideal (Appendix 5.1 to 5.4 for M37306_BP; Appendix 6.1 to 6.4 for M37306_C) (Bruker AXS Inc., 2004) for further refinement which prevented refined unit cell data collection.

6. Conclusion

The re-examination of the phosphoferrite group minerals using combined application of mineralogical analytical techniques – Raman spectroscopy, scanning electron microscopy, single crystal X-ray diffraction, electron microprobe analysis and X-ray powder diffraction – enable the identification and nomenclature scheme determination of the specimens examined in this research. The specimens are garyansellite, Mg-rich intermediate kryzhanovskite or zoned mineral of garyansellite and Mg-rich intermediate kryzhanovskite (Table 6). This corresponds to and verifies Robinson *et al.*'s (1992) findings regarding chemical variation of the phosphoferrite group minerals present in Rapid Creek.

Table 6: Nomenclature summary of specimens mentioned in this thesis

Mineral	Specimen
Garyansellite	RC1B, RC5_A, RC9_D, RC16_A, M37306
Mg-rich intermediate kryzhanovskite	RC17_A
Zoned mineral with both garyansellite and Mg-rich intermediate kryzhanovskite	M55955

The major limitation in this research was the ability to obtain quality single crystal samples from the specimens. The samples contain twinning, zoning or the combination of both which prevented further crystallographic unit cell refinement, an important technique for mineral classification.

However, the presence of Mg-rich intermediate kryzhanovskite in the Rapid Creek specimens necessitates future studies to be conducted. This is because the mineral is neither an ideal end-member kryzhanovskite ($\sim 100\%$ Fe^{3+} in the M sites), an intermediate kryzhanovskite ($\sim 66.6\%$ Fe^{3+} and $\sim 33.4\%$ Mn^{2+} in the M sites) nor garyansellite ($\geq 50\%$ Mg^{2+} and $< 50\%$ Fe^{3+}). Hence, there is a possibility that a new mineral may be defined. Future studies may include data collection on refined unit cell data of Mg-rich intermediate kryzhanovskite.

7. Acknowledgement

I will like to sincerely thank my NSERC USRA and undergraduate thesis supervisor, Professor Kimberly Tait for this research opportunity, her continual support and guidance. In addition, I would like to thank the following staff in the mineralogy department at the Royal Ontario Museum: Brendt Hyde, for his valuable guidance; Ian Nicklin for the *RC* series samples; and Katherine Dunnell.

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9. Appendix

Appendix 1: Specimens in the RC series and the analytical techniques used on each specimen

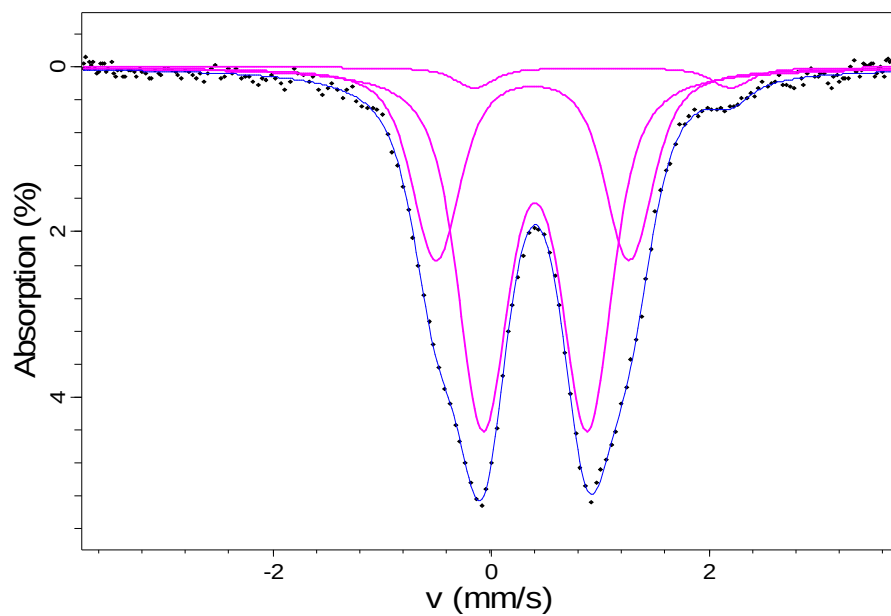
Sample	Analytical Techniques			
	Raman Spectroscopy	EDS	Elemental Mapping	XRD
RC1_A	x	x		
RC1_B	x	x		x
RC1_C	x	x		
RC1_D	x	x		
RC2_A	x	x		
RC2_B	x	x		
RC2_C	x	x		
RC3_A	x	x		
RC3_B	x	x		
RC4_A	x	x		
RC5_A	x	x		x
RC5_B	x	x		
RC5_C	x	x		
RC5_D	x	x		
RC6_A	x	x		
RC6_B	x	x		
RC6_C	x	x		
RC6_D	x	x		
RC6_E	x	x		x
RC6_F	x	x		
RC7_A	x	x		
RC7_B	x	x		
RC7_C	x	x		
RC8_A	x	x		
RC8_B	x	x		
RC9_A	x	x		
RC9_B	x	x		
RC9_C	x	x		
RC9_D	x	x	x	x
RC10_A	x	x		
RC10_B	x	x		
RC11_A	x	x		
RC11_B	x	x		
RC12_A	x	x	x	
RC12_B	x	x		x
RC13_A	x	x		
RC13_B	x	x		
RC14_A	x	x		
RC14_B	x	x		

RC15_A	x	x		x
RC15_B	x	x		
RC16_A	x	x	x	
RC16_B	x	x		
RC17_A	x	x		
RC17_B	x	x		

Appendix 2: Specimens in the *M* series and the analytical techniques used on each specimen

Sample	Analytical Techniques					
	Raman Spectroscopy	EDS	Elemental Mapping	XRD	EMPA	X-ray Powder Diffraction
M55955	x	x	x		x	x
M37306	x	x		x		
M23156	x	x				x
M54932	x	x	x			
M52772	x	x				x
M34639	x	x				x
M34312	x	x				x

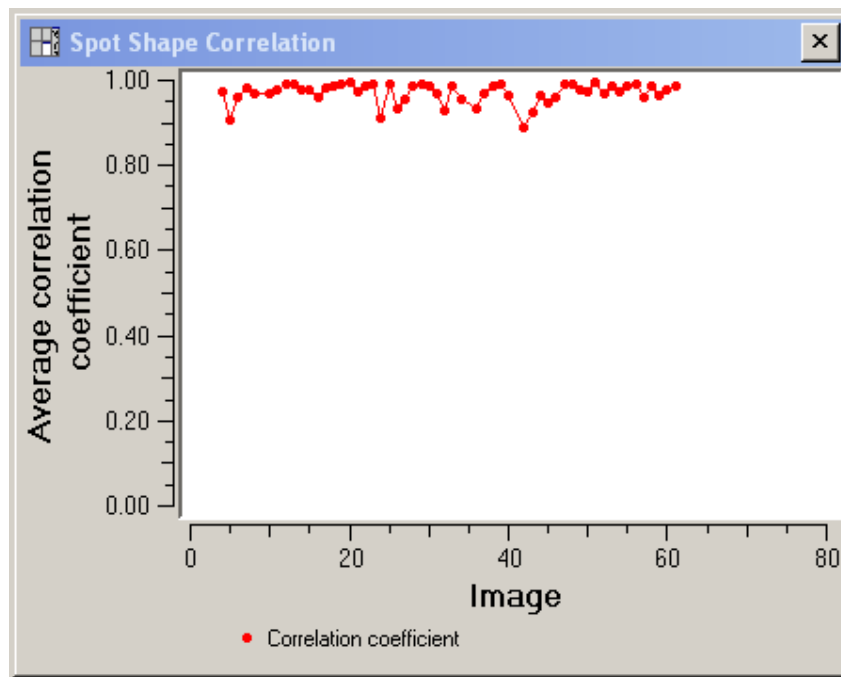
Appendix 3.1: Room-temperature Mössbauer spectrum of garyansellite, fitted using a Voigt-based quadrupole-splitting-distribution method to a model having two Fe^{3+} sites and one Fe^{2+} site (each with a single Gaussian component).



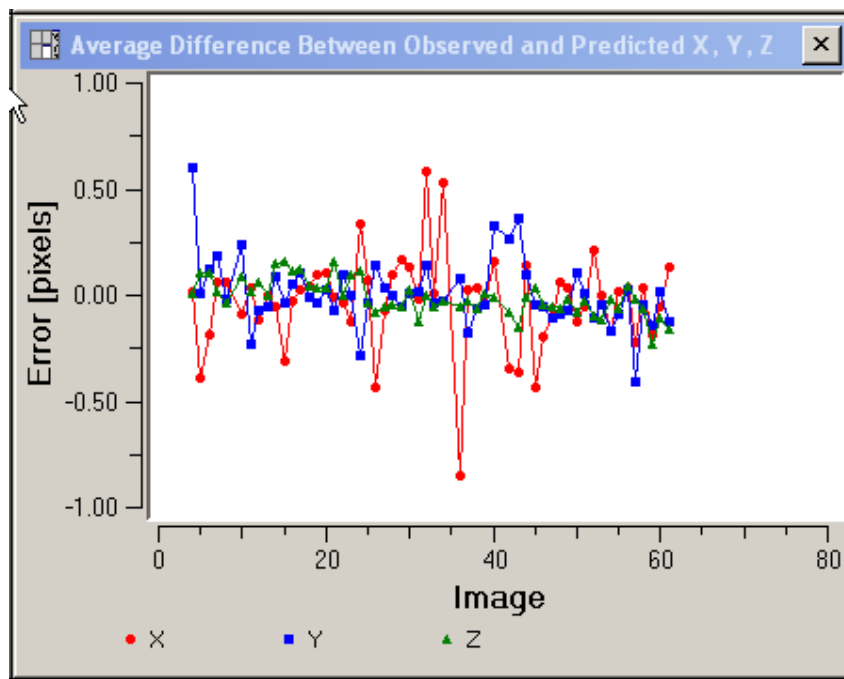
Appendix 3.2: Mössbauer parameters for garyansellite.

Fe site	CS (mm/s)	QS (mm/s)	Rel. area (%)
Fe^{3+} (a)	0.41	0.96	63(3)
Fe^{3+} (b)	0.39	1.77	34(3)
Fe^{2+}	1.03	2.35	3(1)

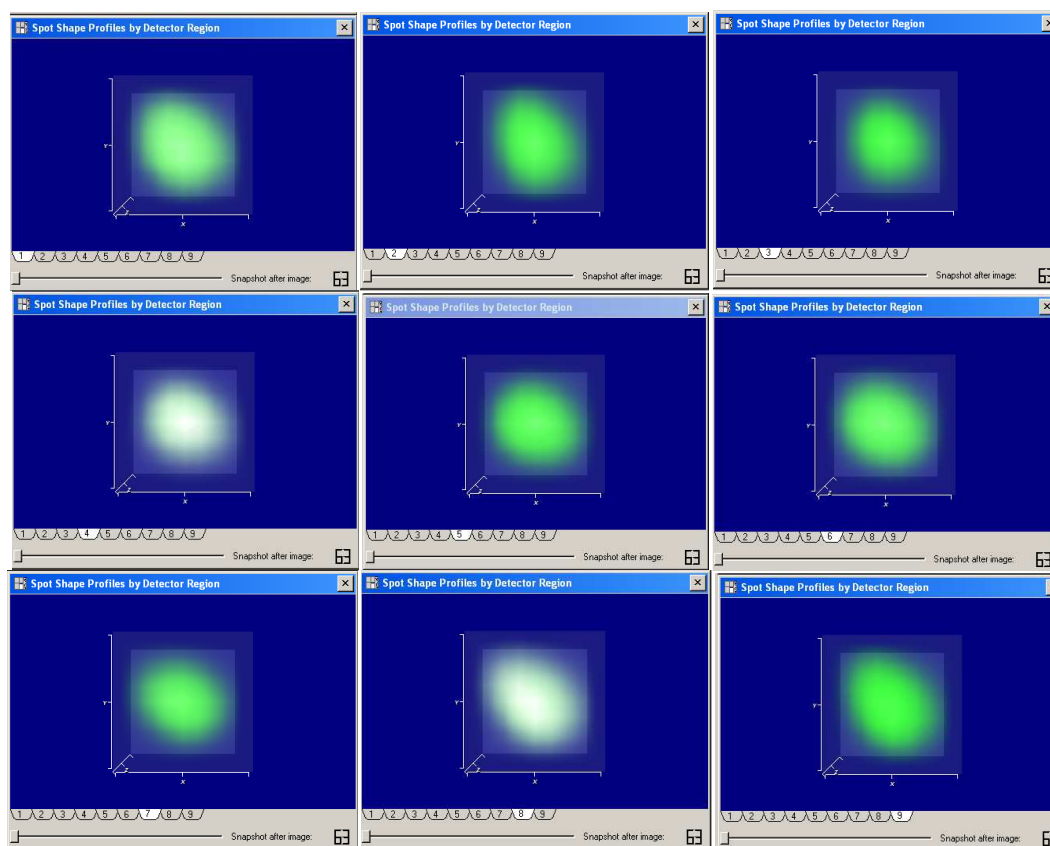
Appendix 4.1: Spot shape correlation statistical values of RC1_B. According to the XRD user manual provided by Bruker AXS Inc (2004), the closer the correlation coefficient is to 1.00, the more ideal the data is for further unit cell refinement



Appendix 4.2: Average difference between observed and predicted X,Y,Z statistical values of RC1_B. According to the XRD user manual provided by Bruker AXS Inc (2004), the error for the data should be within +/- 1.00 pixels for possible further unit cell refinement



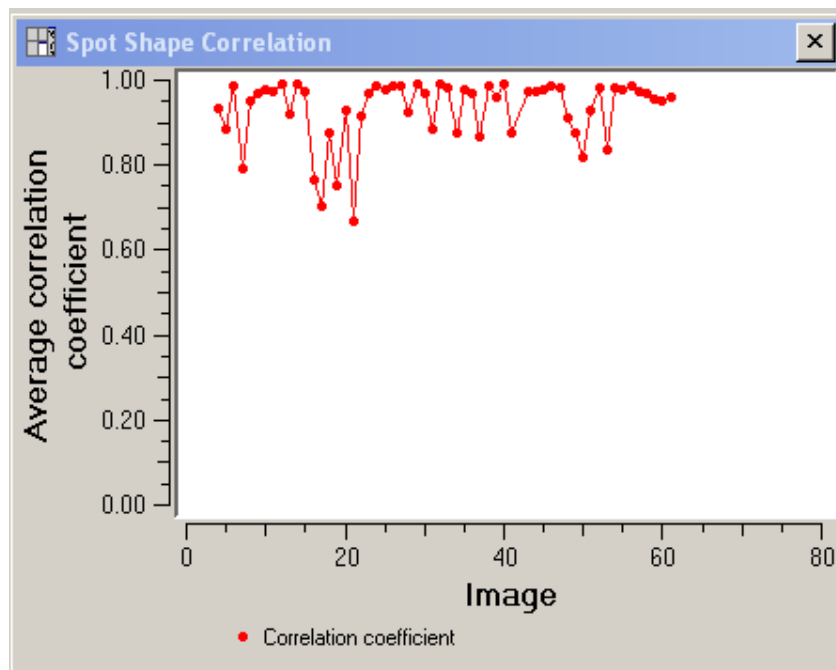
Appendix 4.3: Nine spot shape profiles by detector region of RC1_B. According to the XRD user manual provided by Bruker AXS Inc (2004), the spot shape profile for the data should be circular for possible further unit cell refinement. Furthermore, a green spot represent high intensity of data points collected and a white spot present low intensity of data points collected.



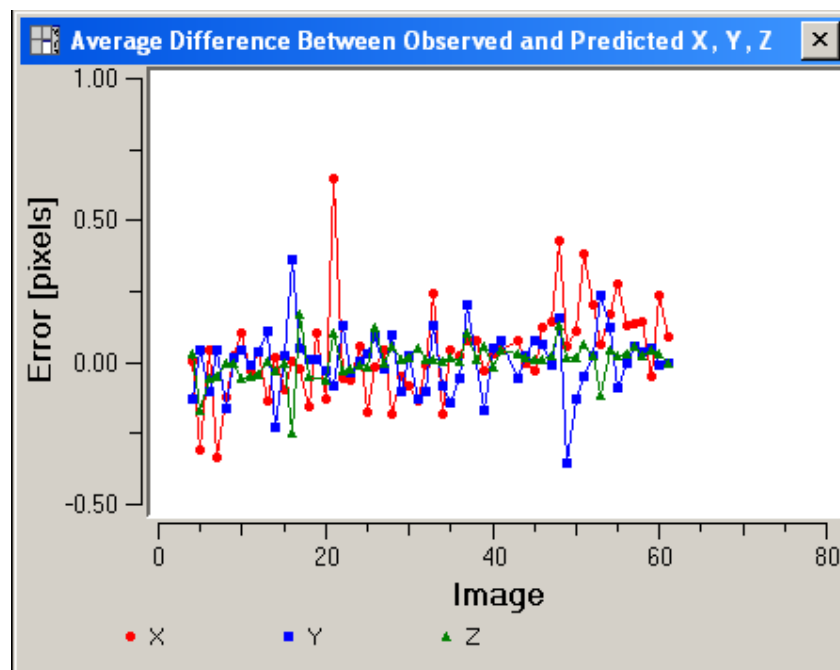
Appendix 4.4: R_{sym} statistical values of RC1_B. According to the XRD user manual provided by Bruker AXS Inc (2004), R_{sym} value of 8% and below is ideal for further unit cell refinement.

Angstrms	#Obs	Theory	%Compl	Redund	Rsym	Pairs	%Pairs	Rshell	#Sigma	%<2s
to 1.216	866	875	98.97	3.79	0.302	827	94.51	0.302	348.03	0.3
to 0.965	1744	1753	99.49	3.69	0.289	1684	96.06	0.266	259.24	0.7
to 0.843	2624	2633	99.66	3.49	0.282	2548	96.77	0.241	177.38	1.3
to 0.766	3519	3528	99.74	3.29	0.278	3401	96.40	0.238	145.91	2.6
to 0.711	4381	4390	99.79	3.12	0.275	4213	95.97	0.217	102.01	3.1
to 0.669	5259	5270	99.79	2.97	0.272	5038	95.60	0.205	86.85	6.0
to 0.636	6141	6152	99.82	2.85	0.270	5858	95.22	0.205	86.50	7.4
to 0.608	6988	7006	99.74	2.70	0.269	6365	90.85	0.206	67.77	7.1
to 0.585	7708	7881	97.80	2.56	0.269	6452	81.87	0.185	61.61	7.3
to 0.565	8115	8801	92.21	2.49	0.269	6496	73.81	0.170	38.17	9.6

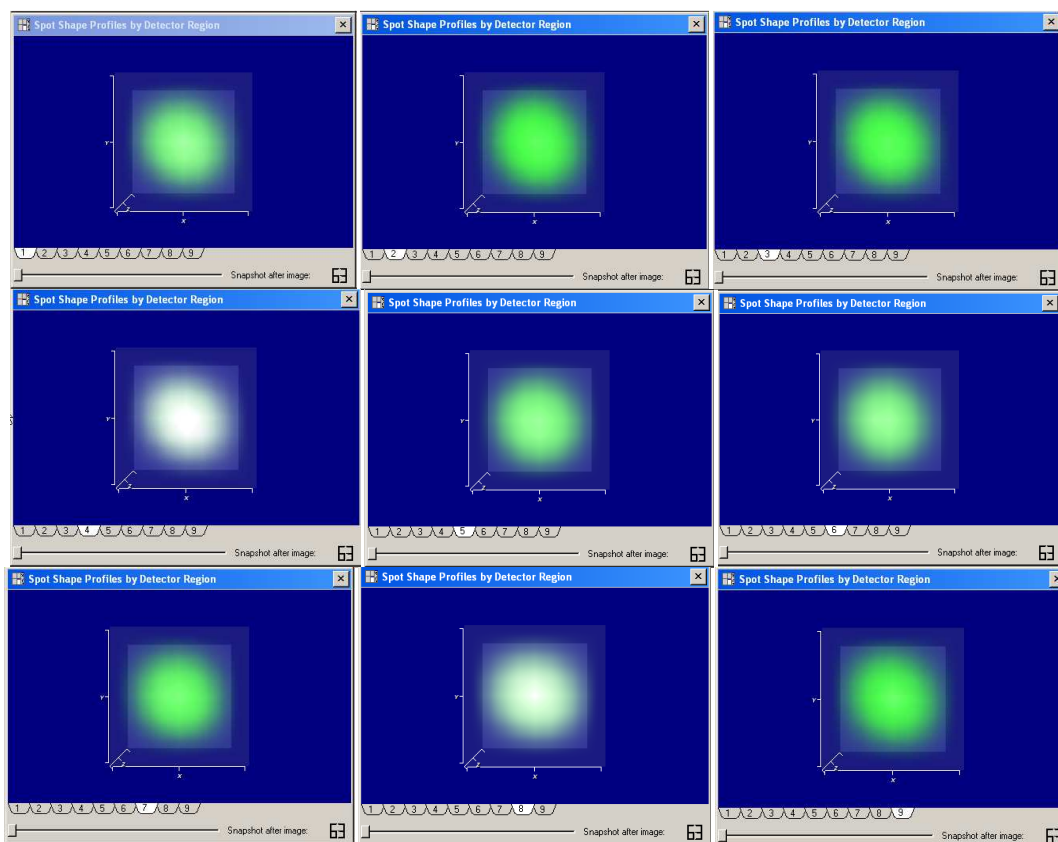
Appendix 5.1: Spot shape correlation statistical values of M37306_BP. According to the XRD user manual provided by Bruker AXS Inc (2004), the closer the correlation coefficient is to 1.00, the more ideal the data is for further unit cell refinement



Appendix 5.2: Average difference between observed and predicted X,Y,Z statistical values of M37306_BP. According to the XRD user manual provided by Bruker AXS Inc (2004) , the error for the data should be within +/- 1.00 pixels for possible further unit cell refinement



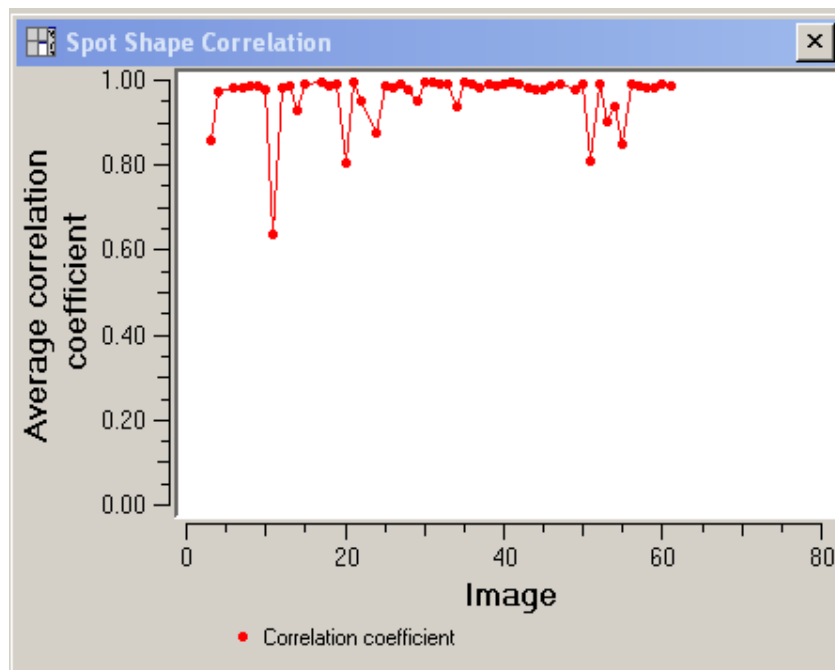
Appendix 5.3: Nine spot shape profiles by detector region of M37306_BP. According to the XRD user manual provided by Bruker AXS Inc (2004), the spot shape profile for the data should be circular for possible further unit cell refinement. Furthermore, a green spot represent high intensity of data points collected and a white spot present low intensity of data points collected.



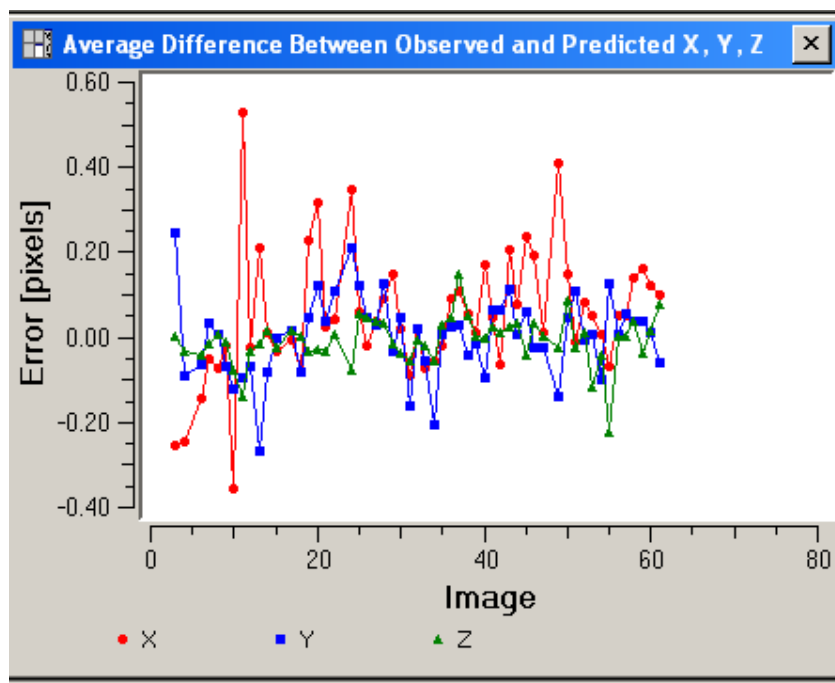
Appendix 5.4: R_{sym} statistical values of M37306_BP. According to the XRD user manual provided by Bruker AXS Inc (2004), R_{sym} value of 8% and below is ideal for further unit cell refinement.

Angstrms	#Obs	Theory	%Compl	Redund	Rsym	Pairs	%Pairs	Rshell	#Sigma	%<2s
to 1.255	202	267	75.66	3.93	0.035	180	67.42	0.035	117.21	9.7
to 1.025	398	470	84.68	3.96	0.037	358	76.17	0.041	60.18	11.9
to 0.905	582	664	87.65	3.90	0.037	527	79.37	0.037	52.89	12.6
to 0.827	761	858	88.69	3.81	0.038	693	80.77	0.053	30.58	16.7
to 0.770	938	1055	88.91	3.72	0.039	857	81.23	0.048	31.21	16.4
to 0.726	1094	1237	88.44	3.65	0.039	1001	80.92	0.052	22.08	17.6
to 0.691	1255	1424	88.13	3.58	0.040	1151	80.83	0.060	18.26	22.1
to 0.661	1413	1616	87.44	3.52	0.041	1293	80.01	0.058	16.16	22.4
to 0.636	1559	1798	86.71	3.46	0.041	1428	79.42	0.052	17.95	21.1
to 0.615	1670	1986	84.09	3.40	0.041	1525	76.79	0.069	14.97	26.4

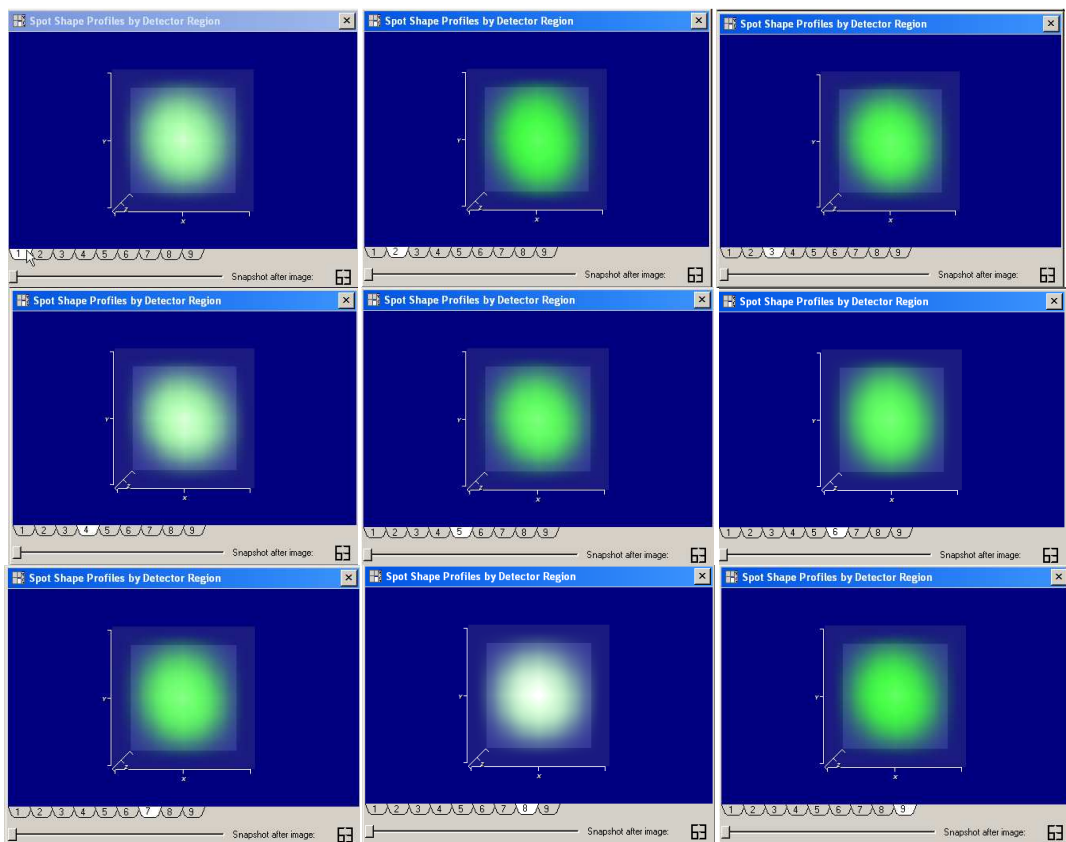
Appendix 6.1: Spot shape correlation statistical values of M37306_C. According to the XRD user manual provided by Bruker AXS Inc (2004), the closer the correlation coefficient is to 1.00, the more ideal the data is for further unit cell refinement



Appendix 6.2: Average difference between observed and predicted X,Y,Z statistical values of M37306_C. According to the XRD user manual provided by Bruker AXS Inc (2004) , the error for the data should be within +/- 1.00 pixels for possible further unit cell refinement



Appendix 6.3: Nine spot shape profiles by detector region of M37306_C. According to the XRD user manual provided by Bruker AXS Inc (2004), the spot shape profile for the data should be circular for possible further unit cell refinement. Furthermore, a green spot represent high intensity of data points collected and a white spot present low intensity of data points collected.



Appendix 6.4: R_{sym} statistical values of M37306_C. According to the XRD user manual provided by Bruker AXS Inc (2004), R_{sym} value of 8% and below is ideal for further unit cell refinement.

Angstrms	#Obs	Theory	%Compl	Redund	Rsym	Pairs	%Pairs	Rshell	#Sigma	%<2s
to 1.252	210	268	78.36	3.72	0.074	171	63.81	0.074	171.98	4.7
to 1.023	418	476	87.82	3.81	0.073	363	76.26	0.069	100.36	6.5
to 0.903	612	670	91.34	3.71	0.072	524	78.21	0.070	87.11	8.6
to 0.824	803	861	93.26	3.60	0.073	665	77.24	0.075	50.19	11.7
to 0.768	1001	1059	94.52	3.48	0.072	791	74.69	0.067	52.61	10.7
to 0.724	1192	1251	95.28	3.37	0.072	900	71.94	0.067	36.31	12.7
to 0.689	1372	1434	95.68	3.28	0.072	989	68.97	0.066	31.26	15.1
to 0.660	1564	1630	95.95	3.18	0.072	1075	65.95	0.066	29.68	14.9
to 0.635	1741	1815	95.92	3.11	0.071	1152	63.47	0.062	26.54	20.4
to 0.613	1870	2007	93.17	3.02	0.071	1185	59.04	0.069	21.85	21.5