Rapid detection and quantification of coffinite – USiO$_4$

A thesis submitted in fulfilment of the requirements for the degree of

Doctor of Philosophy

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November 2017
DECLARATION OF AUTHENTICITY

I certify that except where due acknowledgement has been made, the work is that of the author alone; the work has not been submitted previously, in whole or in part, to qualify for any other academic award; the content of the thesis is a result of work which has been carried out since the official commencement date of the approved research program; and, any editorial work, paid or unpaid, carried out by a third party is acknowledged.

I acknowledge the support I have received for my research through the provision of an Australian Postgraduate Award (APA) Scholarship.

________________________________________

For and on behalf of William L. Andrews

November 2017

ABSTRACT

Coffinite (USiO₄) is an ore mineral ubiquitous in U mineralised systems was recently characterised via near infrared (NIR) which encompasses the short wavelength infrared (SWIR) spectrum, which yielded active absorbance bands (Baron et al, 2014). These absorbance bands are associated to U⁴⁺ electron transfer between <U-O> bonds in the octahedral position (Fig. i) (Zhang et al, 2002; Zhang et al, 2009). This study aims to test the assertions made by Baron et al (2014), where coffinite was detected in natural samples by developing a method for detection and estimating the relative abundance of coffinite in ores. This was achieved by manufacturing 18 well constrained synthetic mineral mixtures containing hydrothermally synthesised coffinite and utilising these mixtures as a standard for the determination of coffinite abundance of a uranium ore.

Figure i | Coffinite atomic coordination showing U in the octahedral position relative to O.
ACKNOWLEDGMENTS

I wish to thank my supervisors Prof. Suresh Bhargava, Dr. James Tardio, and Dr. Mark Pownceby for their support and guidance throughout my doctoral studies. I would also like to thank Dr. Andy Wilde for his assistance in providing access to Valhalla drill and associated data. Mr. Stafford McKnight of Federation University (Ballarat, VIC) has also been integral to this project’s success in way of providing access to a field spectrometer enabling the validation of methods defined herein. Mr Stewart Parker for provision of a pXRF during field studies.

A Students in Mining grant was graciously received from PanAlytical who provided access to an ASD TerraSpec4 and TSG software for one month and financial assistance to present at Goldschmidt 2016. Without the assistance of Dr. Scott McMaster, Dr. Hailey Reynolds, Dr. Rahul Ram, and Nebeal Farris my success in chemistry laboratory practices would not have been achievable. This study would not be possible without the support of my wife Sayaka, extended family, and friends. There is no doubt that difficult periods throughout my PhD studies have been made tolerable through the help of kendo and the tutelage provided by my sensei Dr. Khay-Lin Teoh.

To all I am forever grateful.

PUBLICATIONS


CONFERENCES


# TABLE OF CONTENTS

1. INTRODUCTION ............................................................................................................... 12
   1.1 INTRODUCTION ........................................................................................................ 12
   1.2 AIMS ................................................................................................................................ 13
   1.3 OUTCOMES ................................................................................................................ 14

2. SPECTRAL STUDIES AND COFFINITE REVIEW ......................................................... 15
   2.1 THE EVOLUTION OF MINERAL SPECTROSCOPY .................................................. 15
   2.1.0 MINERAL SPECTROSCOPY APPLICATIONS ......................................................... 16
      2.1.1 Mineral identification ......................................................................................... 16
      2.1.2 Exploration ......................................................................................................... 16
      2.1.3 Remote sensing .................................................................................................. 17
      2.1.4 Geometallurgy ................................................................................................... 18
   2.3 SUMMARY .................................................................................................................. 19
   2.4 URANIUM AS A RESOURCE ..................................................................................... 19
   2.5 COMMODITY AND ECONOMIC DEMANDS ......................................................... 21
      2.5.1 Exploration and resources .............................................................................. 21
      2.5.2 Production and demand ................................................................................... 23
   2.6 URANIUM GEOCHEMISTRY .................................................................................... 24
   2.7 SOURCE: ROCKS AND FLUIDS ............................................................................ 27
      2.7.1 Rocks .................................................................................................................. 27
      2.7.2 Fluids ................................................................................................................ 29
   2.8 URANIUM DEPOSIT CLASSIFICATION ................................................................. 29
   2.9 COFFINITE ............................................................................................................... 31
      2.9.2 COFFINITE AND MINERAL SPECTROSCOPY .................................................. 34
         2.9.2.1 Spectral similarities between Zircon ZrSiO$_4$ and uranothorite-coffinite ... 35
         2.9.2.2 Spectral characteristics of the coffinite-uranothorite solid solution .......... 35
         2.9.2.3 Spectral identification of 3 or more minerals in complex mixtures .......... 37
         2.9.2.4 Coffinite behaviour in the natural environment and mineralised uranium systems .......................................................... 37
         2.9.2.5 Factors that may influence spectral characteristics ................................. 39
   2.9.3 SUMMARY ............................................................................................................ 41

3. MATERIALS AND METHODS ......................................................................................... 42
   3.1 COFFINITE SYNTHESIS .......................................................................................... 42
      3.1.1 PRECURSORS (U$_3$O$_8$, UO$_2$, and UCl$_4$) .................................................... 42
         Preparation of UO$_2$ ............................................................................................... 42
3.1.2 HYDROTHERMAL SYNTHESIS ................................................................. 44
3.2 X-RAY DIFFRACTION ............................................................................. 44
3.3 INFRA-RED SPECTROSCOPY ................................................................. 44
  3.3.1 PERKIN ELMER FRONTIER FT-IR/NIR (NIRA II attachment) ......... 44
  3.3.2 ASD TerraSpec 4 HI-RES ................................................................. 47
3.4 X-RAY FLUORESCENCE (XRF) ............................................................. 48
  3.4.1 PORTABLE XRF .............................................................................. 48
  3.4.2 LABORATORY XRF .......................................................................... 49
3.5 SCANNING ELECTRON MICROSCOPY ............................................... 49
  3.6 CLAY EXTRACTION ............................................................................. 50
3.7 HEAVY MINERAL SEPARATION ......................................................... 50

4. COFFINITE CHARACTERISATION ......................................................... 52
  4.1 INTRODUCTION .................................................................................... 52
  4.2 X-RAY DIFFRACTION (XRD) ............................................................... 52
  4.3 NEAR INFRARED ................................................................................. 53
  4.4 SCANNING ELECTRON MICROSCOPY (SEM) .................................... 55
  4.5 SUMMARY ............................................................................................ 57

5. QUANTIFYING COFFINITE IN SYNTHETIC MINERAL MIXTURES .......... 58
  5.1 INTRODUCTION .................................................................................... 58
  5.2 MINERAL CO-ADDITIVES ................................................................. 58
    5.2.1 XRD and NIR characterisation ...................................................... 59
  5.3 MINERAL MIXTURES .......................................................................... 60
    5.3.1 Major element chemistry ............................................................. 62
    5.3.2 Mineral mixture XRD analysis ....................................................... 64
  5.4 MINERAL MIXTURE NIR SPECTRA ................................................... 65
  5.5 PEAK INTENSITY METRICS ............................................................... 68
    5.5.1 Feature ratios in relation to coffinite concentration ..................... 69
    5.5.2 Feature ratios in relation to uranium grade .................................... 71
  5.6 SUMMARY ............................................................................................ 72

6. DEPOSIT GEOLOGY .................................................................................. 73
  6.1 GEOLOGICAL SETTING ....................................................................... 73
  6.2 DEPOSIT RESOURCES AND GEOLOGY ............................................. 75
    6.2.1 Metasomatite/Albitite uranium deposits ........................................ 75
    6.2.2 Resources ..................................................................................... 75
    6.2.3 Mineralisation ................................................................................. 76
6.2.4 Ore assemblages .................................................................................................................. 77
6.3 ORE GENESIS ......................................................................................................................... 79

7. DETECTION AND ABUNDANCE DETERMINATION OF COFFINITE IN URANIUM ORE ......................................................................................................................... 81

7.1 INTRODUCTION ..................................................................................................................... 81
7.1.1 Experimental (Material and Methods) ................................................................................ 82

7.2 INFRA-RED SPECTROSCOPY ............................................................................................... 84
7.2.1 NIR results from drill core .................................................................................................. 86
7.2.2 Intra-spectral relationships ................................................................................................. 87
7.2.3 Quantification of coffinite using intra-spectral metrics ....................................................... 89

7.3 COFFINITE CONCENTRATION RELATIONSHIPS ............................................................. 91

7.4 X-RAY FLUORESCENCE ....................................................................................................... 92
7.4.1 Chemical compositional analysis ......................................................................................... 93

7.5 SUMMARY ............................................................................................................................. 97

8. VALIDATION OF COFFINITE IN DRILL CORE ................................................................. 99

8.1 INTRODUCTION ..................................................................................................................... 99

8.2 HEAVY MINERAL SEPARATION ......................................................................................... 104
8.2.1 NIR spectroscopy of separate fractions .............................................................................. 104
8.2.2 XRD of separate fractions ................................................................................................ 106

8.3 ELECTRON MICROSCOPY OF DRILL CORE .................................................................... 107
8.3.1 Examination of coffinite grains ......................................................................................... 110
8.3.2 U and Si molar relationships ............................................................................................ 111

8.4 DISCUSSION .......................................................................................................................... 112

8.5 SUMMARY ............................................................................................................................. 113

9. CONCLUSION AND RECOMMENDATIONS ........................................................................ 115

9.1 CONCLUSION ....................................................................................................................... 115
9.1.1 Unaddressed variables ..................................................................................................... 115

9.2 RECOMMENDATIONS FOR FUTURE STUDY .................................................................... 117
LIST OF FIGURES

Figure 1-1 | Project sequence and scheme of hierarchy .................................................. 14
Figure 2-1 | Spectral signature diagram of minerals from Hunt .............................................. 15
Figure 2-2 | IR bands for remote sensors with respect to atmospheric transmittance plotted on the Y-Axis .............................................................................................................. 18
Figure 2-3 | Scatter plot showing the relationship between energy density and specific energy of various resources .............................................................................................................. 21
Figure 2-4 | Approximate correlation of terms used in major resources classification .............. 23
Figure 2-5 | Uranium exploration expenditure in Australia from 2011-2014 ................................ 24
Figure 2-6 | Tripartite framework showing both three end-member uranium mineralising systems .................................................................................................................................. 31
Figure 2-7 | Aqueous equilibrium diagram of the UO$_2$-H$_2$O-CO$_2$ system at 25$^\circ$ C and 1 atm ........................................................................................................................................ 33
Figure 2-8 | MIR spectra of synthetic coffinite, thorite, and natural zircon .................................. 35
Figure 2-9 | Spectral reflectance bandwidths of peaks and shoulders for common clay minerals and their associated bonds found in natural samples for the NIR-SWIR spectrum ........................................................................................................ 39
Figure 2-10 | Ternary plot of the U-Th-Si system minerals .......................................................... 40
Figure 3-1 | Laboratory equipment configuration for the synthesis of UCl$_4$ .......................... 46
Figure 3-2 | Hydrothermal procedure for coffinite synthesis .................................................. 48
Figure 3-3 | Coverage of the NIRA II and TerraSpec4 in relation to the electromagnetic spectrum ................................................................................................................................. 49
Figure 3-4 | Perkin and Elmer Frontier FT-IR with NIRA II attached ........................................ 50
Figure 3-5 | ASD TerraSpec$^4$ HI-RES fitted with contact probe collecting analysis on drill core ........................................................................................................................................... 50
Figure 3-6 | Olympus Innov-X Delta portable XRF with soil foot collecting analysis on drill core ........................................................................................................................................... 51
Figure 4-1 | XRD patterns of synthetic coffinites showing the relationship between bragg peaks for PDF 11-0420 (coffinite) ........................................................................................................ 56
Figure 4-2 | NIR spectra of synthetic coffinite separates .......................................................... 57
Figure 4-3 | BSE image of coffinite aggregate C3.2 showing EDX semi quantitative wt. % spot element analysis and major element maps .................................................................................. 59
Figure 4-4 | EDX point analysis of mixed coffinite showing U/Si mol. ratio ................................ 60
Figure 5-1 | XRD patterns with corresponding NIR spectra obtain from the NIRA II (a & b) coffinite; (c & d) zircon, whole crystal left hand side (LHS), crushed sample right hand side (RHS); (e & f) chlorite; (g & h) glaucophane; and (i & j) quartz

Figure 5-2 | Chemical and mineral concentration scatter plots based on XRF analysis and mineral concentrations shown in Tables 5.1 and 5.2. (a) U₃O₈ vs coffinite, (b) Fe₂O₃ vs MgO, (c) MgO vs Na₂O, (d) CaO vs Na₂O

Figure 5-3 | XRD patterns for minerals and batches in relation to coffinite bragg peaks. Note the low magnitude of zircon (zr) peaks in batch two mixtures

Figure 5-4 | NIR spectra from lab and portable spectrometers; (a) NIRA II batch one; (b) TerraSpec®4 batch one; (c) NIRA II batch two; (d) TerraSpec®4 batch two; (e) NIRA II batch three; (f) TerraSpec®4 batch three

Figure 5-5 | Scatter plots showing Coffinite features in relation to concentration; (a) 1135 nm; (b) 1500 nm; (c) 1550 nm; (d) 1675 nm; (e) 2130 nm; and (f) 1550-1500 nm. NIRA II left hand side (LHS); TerraSpec4 (TS4) right hand side (RHS)

Figure 5-6 | Scatter plots showing the differing reflectance ratios derived from coffinite features relative to coffinite concentration; (a) 1500/1135 nm; (b) 1550/1135 nm; (c) 1675/1135 nm; (d) 2130/1135 nm; and (e) 1550/1500 nm

Figure 5-7 | Scatter plots showing select ratios for coffinite features in relation to uranium grade: (a) 1500/1135; (b) 1550/1135; (c) 1550/1500

Figure 6-1 | Overview map showing the location of substantiative uranium deposits within the Mount Isa Inlier and respective subprovinces

Figure 6-2 | District stratigraphy for the Western Fold Belt Subprovince of the Mount Isa Inlier. Note U-Pb ages of units which bound the Eastern Creek Volcanics

Figure 6-3 | Grade and tonnage of metasomatic style uranium deposits; green dots are deposits listed in table 6.1, blue dots are various analogous deposits globally. Values for grade and tonnage for Mount Isa ore bodies obtained from Wilde et al, (2013)

Figure 6-4 | Valhalla 7744850 mN cross-section, adapted from Wilde et al, (2013). Uranium mineralisation occurs mainly in the albite lithology

Figure 6-5 | QEMSCAN modal mineral analysis of Valhalla uranium ore

Figure 6-6 | (a) Moderately altered fine-grained sediment; (b) Laminated intensely altered rock; (c) Brecciated intensely altered rock; (d) lower left dashed line exemplifies sigmoidal feature of a quartz mineral fish & (e) Uraninite, hematite, dolomite, chlorite rock. Polished thin section slides taken for the purposes of coffinite NIR spectral validation in this study

Figure 7-1 | Satellite photograph of the Valhalla deposit area showing collar positions of drill holes surveyed. Albite host rock shown in green is projected to the surface for reference (ore body does not outcrop at the surface)
Figure 7-2 | a) comparison between NIR spectra from the TerraSpec4 and the NIRA II instruments. Solid red lines are TerraSpec4; dashed blue lines are NIRA II spectra. b) inset of a showing the extent of the spectra depicted in c-j. Figures c-j show 1500 +/- 1550 nm features used to identify U-Zr silicates during the spectral survey of this study, note the magnitude of peak features in relation to overall NIR spectra (Fig 7-2 a)………………………88

Figure 7-3 | Scatter plots showing the relationship between the 1500 nm feature and know coffinite quantities in batches 1-3 with coffinite quantities calculated from linear regression based on batches 1-3. a) NIRA II measurements; b) TerraSpec®4 measurements...........................................90

Figure 7-4 | Scatter plots demonstrating the strong relationship of the 1550 and 1500 nm features between drill core and synthetic mineral mixtures (batches 1-3). a) NIRA II measurements, b) TerraSpec®4 measurements..........................91

Figure 7-5 | Frequency distribution plots for the 1500 nm features in drill core for; a) NIRA II measurements, b) TerraSpec®4 measurements.........................................................92

Figure 7-6 | Frequency distribution plots for the 1550 nm features in drill core for; a) NIRA II measurements, b) TerraSpec®4 measurements.................................................................93

Figure 7-7 | Scatter plot show coffinite concentration based on linear regression defined by synthetic mineral mixtures (batches 1-3) using the 1550/1500 coffinite feature ratio. a) NIRA II measurements, b) TerraSpec®4 measurements...........................94

Figure 7-8 | Frequency distribution plots for the 1550/1500 metric in drill core for; a) NIRA II measurements, b) TerraSpec®4 measurements.................................................................95

Figure 7-9 | Strip logs for drill holes showing relationships between lithology, coffinite concentration (NIRA II results) U company assay + pXRF, Zr company assay + pXRF results. Scales remain unchanged for all plots, lithology plotted to depth of assay sampling.................................................................96

Figure 7-10 | a) Uranium company assay data and pXRF plotted against coffinite concentration derived from NIRA II spectral results. b) Zircon company assay data and pXRF plotted against coffinite concentration derived from NIRA II spectral results, Batch three not shown due to batch one plotting over the top at 2.5 wt. % coffinite. Batches 1 and 2 are synthetic mixtures (Chapter 5).................................................................................................................................98

Figure 7-11 | Dendogram showing the chemical relationships from pXRF analysis......................100

Figure 7-12 | a) Scree plot showing the degree of variance between principle components (PC) 1-10. b) Biplot for PCs 1 and 2 showing the relationship for chemical compositions and the 1500, 1550 position and intensity relationships.................................................................101

Figure 8-1 | NIRA II results of the 1550/1500 nm metric plotted against coffinite concentrations derived from the linear regression of synthetic mineral mixtures (not plotted). Blue labels are diffraction patterns examined in this section, yellow labels are samples which were processed for heavy mineral separation (section 8.2).................................104

Figure 8-2 | XRD patterns for samples; (a) VDDH083 132, (b) VDDH049 254. Mineral phases identified; albite (ab), calcite (cal), dolomite (dol), quartz (qtz), and riebeckite (rbk). Accentuated bragg peaks for coffinite (PDF 11-0420) are shown for reference......................106
Figure 8-3 | XRD patterns for samples; (a) VDDH049 223, (b) VDDH082 140. Mineral phases identified; albite (ab), calcite (cal), dolomite (dol), quartz (qtz), and riebeckite (rbk). Accentuated bragg peaks for coffinite (PDF 11-0420) are shown for reference...

Figure 8-4 | XRD patterns for samples; (a) VDDH083 113, (b) VDDH063 86. Mineral phases identified; albite (ab), dolomite (dol), quartz (qtz), and riebeckite (rbk). Accentuated bragg peaks for coffinite (PDF 11-0420) are shown for reference...

Figure 8-5 | Scatter plot showing the strong relationship between the 1500nm and 1550 nm features observed in heavy mineral separate fractions taken from four different samples of Valhalla drill core. Original NIRA II drill core measurements are plotted for each respective sample included in the heavy mineral separation process...

Figure 8-6 | Heavy mineral separates measures of 1550/1500 ratios plotted against results from linear regression derived synthetic mixture studies; (a) VDDH037 320-321, (b) VDDH039 241-242, (c) VDDH064 52-53, and (d) VDDH081 60-61...

Figure 8-7 | BSE image of coffinite and EDX mapping from ore presenting with 1500 nm and 1550 nm peak features. Chemistry expressed as elemental wt. %...

Figure 8-8 | BSE images of coffinites found at Valhalla...

Figure 8-9 | a) Scatter plot showing the relationship between U and Si mol. % for coffinite grains found at Valhalla and hydrothermally synthesised coffinites described in chapter four. b) Relative frequency distribution for U/Si mol. ratios of Valhalla coffinites. c) Relative frequency distribution for U/Si mol. ratios of synthetic coffinites from this study...

LIST OF TABLES

Table 1-1 | Uranium minerals characterised using IR techniques, references listed in order of characterisation method listed in the methods column...

Table 2-1 | Concentrations of U and Th in the Earth’s crust; mantle; N-MORB: Normal Mid-Ocean Ridge Basalt (ppm)...

Table 2-2 | Average uranium concentration for various reservoirs in the Earth’s crust; note the increase in concentration relative to fractionation in respective reservoirs...

Table 2-3 | Orthosilicate crystal structures...

Table 2-4 | Properties and variables for coffinite stability...

Table 3-1 | Specifications for the Perkin Elmer Frontier FT-IR/NIR...

Table 3-2 | Specifications for the ASD TerraSpec®4 HI-RES spectrometer...

Table 4-1 | Temperature, Time, and pH constraints used for synthesising coffinite in this study and consequent precipitate yields...

Table 4-2 | Mol. % composition of point analysis defined in Fig. 4-3, note U/Si mol. ratio being close to 1:1...
Table 5-1 | Proportion of each mineral co-additive per mixture and corresponding mineral weight percentages (wt.%). Abbreviations Cof (coffinite), Zrn (zircon), Chl (chlorite), Qtz (quartz), and Gln (glaucophane). Batch mixtures are listed in order of decreasing coffinite concentration........................................................................................................................................65

Table 5-2 | Select major elements of synthetic mineral mixtures from XRF analysis. Batch mixtures are listed in order of decreasing coffinite concentration.................................................................66

Table 5-3 | Correlation coefficients and linear regression equations for select coffinite absorption feature ratios between the NIRA II, TerraSpec4, and both instruments combined..................................................................................................................................................73

Table 5-4 | Correlation coefficients and linear regression equations for coffinite feature ratios in relation to $U_3O_8$ wt.% between the NIRA II, TerraSpec4, and instruments combined........................................................................................................................................74

Table 6-1 | JORC compliant mineral resource for the albitite stye uranium deposits in the Western Fold Belt Subprovince..................................................................................................................................................79

Table 7-1 | Summary of XRF data for intervals where spectral features associated with coffinite were observed, values in ppm unless otherwise stated.................................................................100

Table 8-1 | SEM, EDX chemical analysis of individual coffinite grains, values expressed at wt. % oxides. Values do not add to 100 % due to averaging of several analyses in each grain........................................................................................................................................114
INTRODUCTION

1.1 INTRODUCTION

Many uranium minerals have been successfully characterised via infrared (IR) techniques (Table 1-1). Secondary U minerals are over represented in these studies with primary or ubiquitous U ore minerals receiving significantly less examination. Recently Baron et al, (2014) characterised coffinite (USiO₄) using near infrared (NIR) and demonstrated the capability to identify it in natural samples. Resultant of these findings it may be possible to apply this method to rapid ore characterisation with the intent on determining coffinite abundance in natural samples.

Table 1-1 | Uranium minerals characterised using IR techniques, references listed in order of characterisation method listed in the methods column. Ore minerals of uranium highlighted in grey.

<table>
<thead>
<tr>
<th>Mineral name</th>
<th>Formula</th>
<th>Method</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>andersonite</td>
<td>Na₂CaUO₂(CO₃)₃·6H₂O</td>
<td>raman; NIR</td>
<td>Stefaniak et al, 2009; Weier et al, 2005</td>
</tr>
<tr>
<td>arsenouranylite</td>
<td>Ca(UO₂)(AsO₄)(OH)₂·6H₂O</td>
<td>raman</td>
<td>Frost et al, 2009¹</td>
</tr>
<tr>
<td>autunite</td>
<td>Ca(UO₂)(PO₄)·8H₂O</td>
<td>raman</td>
<td>Weier et al, 2009</td>
</tr>
<tr>
<td>boltwoodite</td>
<td>(K,Na)[(UO₂)(SiO₃)OH]·1.5H₂O</td>
<td>NIR; TRLFS</td>
<td>Arnold &amp; Bauman, 2009</td>
</tr>
<tr>
<td>coffinite</td>
<td>USiO₄</td>
<td>raman; MIR; NIR</td>
<td>Clavier et al, 2014; Steif et al, 1955; Baron et al, 2014</td>
</tr>
<tr>
<td>compreignacite</td>
<td>K₃[(UO₂)₃(OH)]·7H₂O</td>
<td>TRLFS</td>
<td>Arnold &amp; Bauman, 2009</td>
</tr>
<tr>
<td>demesmaekerite</td>
<td>Pb₃Cu₃(UO₂)₃(SeO₃)₆(OH)₆·2H₂O</td>
<td>NIR; MIR</td>
<td>Frost et al, 2008</td>
</tr>
<tr>
<td>derriksite</td>
<td>Cu₃(UO₂)(SeO₃)₆(OH)₆</td>
<td>NIR; MIR</td>
<td>Frost et al, 2008</td>
</tr>
<tr>
<td>guilleminite</td>
<td>Ba₃(UO₂)(SeO₃)₆·3H₂O</td>
<td>NIR; MIR</td>
<td>Frost et al, 2008</td>
</tr>
<tr>
<td>haweeite</td>
<td>Ca₁[(UO₂)₃(SiO₁₂)(OH)]·(H₂O)₃</td>
<td>raman</td>
<td>Frost et al, 2006¹</td>
</tr>
<tr>
<td>haynesite</td>
<td>(UO₂)₃(SeO₃)₂(OH)·5H₂O</td>
<td>NIR; MIR</td>
<td>Weier et al, 2008; Frost et al, 2009²</td>
</tr>
<tr>
<td>liebigite</td>
<td>Ca₃UO₂(CO₃)₃·11H₂O</td>
<td>NIR</td>
<td>Weier et al, 2005</td>
</tr>
<tr>
<td>rutherfordine</td>
<td>UO₂·CO₃</td>
<td>NIR</td>
<td>Weier et al, 2005</td>
</tr>
<tr>
<td>sklodowskite</td>
<td>Mg₂(UO₂)₃(SeO₃)₉·5H₂O</td>
<td>NIR</td>
<td>Weier et al, 2005</td>
</tr>
<tr>
<td>sklodowskite</td>
<td>Cu₃(UO₂)₃(SeO₃)₉·6H₂O</td>
<td>NIR</td>
<td>Weier et al, 2005</td>
</tr>
<tr>
<td>soddyte</td>
<td>(UO₂)₃SiO₂·2H₂O</td>
<td>raman; NIR</td>
<td>Frost et al, 2006¹; Weier et al, 2005</td>
</tr>
<tr>
<td>uraninite</td>
<td>UO₂</td>
<td>raman; NIR</td>
<td>Schoenes, 1987; Griffiths &amp; Hubbard, 1991</td>
</tr>
<tr>
<td>uranophane</td>
<td>Ca(UO₂)₃(SiO₂OH)₂·5H₂O</td>
<td>raman; NIR</td>
<td>Frost et al, 2006²; Weier et al, 2005</td>
</tr>
<tr>
<td>uranopilite</td>
<td>(UO₂)₃SO₄(OH)·12H₂O</td>
<td>NIR</td>
<td>Weier et al, 2005</td>
</tr>
<tr>
<td>vanmeersscheite</td>
<td>U(OH)₄[(UO₂)₃(PO₄)₂(OH)₂]·4H₂O</td>
<td>raman</td>
<td>Frost et al, 2009¹</td>
</tr>
</tbody>
</table>
This study tests the assertions of Baron et al (2014) and attempts to develop a method of coffinite abundance determination while assessing the effectiveness of NIR as a method for rapid ore characterisation for coffinite specific ores in an albitite style U deposit.

1.2 AIMS

This study is designed using two separate approaches (Fig 1-1):

*Synthetic mineral mixtures*

1. Demonstrating a method of utilising synthetically prepared samples and mineral mixtures by developing standards to establish a limit of detection (LOD) and the ability to quantify coffinite. Coffinite is mixed with well-defined mineral co-additives of varying spectral bands commensurate with uranium ores and natural samples. In doing so a rough limit of detection and quantification of coffinite concentration based on NIR band intensities is applied to natural samples to determine abundance.

*Uranium ores*

2. Applying the above methods developed in the synthetic mixtures as standards for the study of Valhalla uranium deposit, Mount Isa, Queensland. Where linear regression based on intra spectral features demonstrated in uranium ore are understood to be associated to electron vibrations of U⁴⁺.
1.3 OUTCOMES

Throughout the course of this study the following outcomes have been achieved:

- Application and identification of coffinite spectral features to determine the limits of detection in synthetic matrixes containing both spectrally active and inactive gangue minerals.
- Thorough spectral and pXRF surveys of drill core in a uranium deposit were conducted and used to determine mineral-chemical whole rock relationships.
- Validated the presence of coffinite by examining thin sections via electron microscopy.

**Figure 1-1** | Project sequence and scheme of hierarchy.
Chapter 2

SPECTRAL STUDIES AND COFFINITE REVIEW

2.1 THE EVOLUTION OF MINERAL SPECTROSCOPY

Abney and Festing (1881) were the first to record NIR spectral responses of organic fluids present in a test tube with the use of photographic plates. A method for defining up to six components of hydrocarbon fluid mixtures was later developed (Brattain et al., 1943). Following the advent of the Kubelka Munk Theory (Kubelka and Munk, 1931; Kubelka, 1948; Yang, and Kruse, 2004), Hunt et al (1950) defined principle NIR absorption bands for different minerals and inorganic compounds. Later investigations demonstrated the ability to use NIR for both qualitative and quantitative analysis of multiphase mixtures, where it was noted there were linear relationships between peak intensities and concentrations of minerals (Hunt and Turner, 1953). Hunt (1977) was later able to attribute which peak features were responsible for a large series of minerals in relation to electronic and vibrational processes (Fig. 2-1). The value of identifying some of these vibrational features in alteration minerals with the use of remote sensing was later recognised (Hunt, 1979).

Figure 2-1 | Spectral signature diagram of minerals from Hunt (1977).
2.1.0 MINERAL SPECTROSCOPY APPLICATIONS

Following the investigations and methods pioneered by Hunt and co-workers, a vast array of mineral spectroscopy applications in the field of earth sciences were developed including: mineral identification (Clark et al. 1990), exploration (Zhang et al, 2001; Wilde et al, 2004; Chang et al, 2011; Mathieu et al, 2017), remote sensing (Cudahy, 2016; Salles et al, 2016; De Boissieu et al, 2017), and geometallurgy (Prado et al, 2016).

2.1.1 Mineral identification

Although the field of mineral identification is relatively dated as evidenced in this review it continues to expand as both spectrometers and minerals become readily available to more researchers. An example of this is the application of IR spectroscopy to identify rare earth element (REE) minerals where IR features considered to be the effect of REE\(^{3+}\) electron vibrations, are now assigned to REE phosphate minerals xenotime (YPO\(_4\)) and monazite ((Ce,La)PO\(_4\)) (Turner et al, 2016) an REE fluorocarbonates (Turner et al, 2014).

2.1.2 Exploration

Metrics for mineral chemistry of micas and consequently thermal genetic relationships have been demonstrated with the use of IR. Chang et al (2011) were able to correlate short wavelength infrared (SWIR) features to an indirect measure of illite crystallinity (IC) to what was considered to be a temperature dominant control of IC (Frey, 1987) in porphyry and epithermal deposits. This proxy was demonstrated on the Pebble Porphyry Cu-Au-Mo deposit where the highest gold and copper grades were observed in association with reduced AlOH absorbance features due to pyrophyllite and sericite alteration (Harraden et al, 2013). Another observation made at these deposits was the relationship between the alunite (KAl\(_3\)(SO\(_4\))\(_2\)(OH)\(_6\)) \(\lambda\) 480 nm spectral feature which shifts in relation to mineral composition (Thompson et al, 1999) and the Na/(Na+K) ratio where a higher wavelength position correlated with greater Na concentration. This higher concentration of Na in alunite is positively correlated to higher formation temperatures (Stoffregen and Cygan, 1990). Where these IR features are found to be a proxy for temperature they can be applied as a
tool for minerals exploration as a vector towards thermal sources e.g. intrusions and epithermal occurrences.

### 2.1.3 Remote sensing
Remote sensing methods have the advantage of being able to obtain vast amounts of data enabling the comparison between temporal and spatial variables at regional to mineral deposit scales. Various remote sensing data products are available for geoscience applications (Fig. 2-2) which vary in both spatial and spectral resolution with surveys obtained from space and airborne sensors (van der Meer et al, 2014). The use of lithology classification for mapping purposes using Landsat data was demonstrated by Cracknell and Reading (2013) where remote sensed data was coupled with geophysical datasets to generate thematic maps using machine learning algorithms (MLAs). The space borne monitoring of mine waste has also been demonstrated using a series of complimentary techniques e.g. spectral ground truthing, X-Ray Diffraction, geochemistry, and remotely sensed data (Mielke et al, 2014).

![Image of IR bands for remote sensors with respect to atmospheric transmittance plotted on the Y-Axis; from van der Meer (2014).](image-url)
2.1.4 Geometallurgy

Geometallurgy is a relatively new field which focusses on improved efficacy of ore process recoveries using multiple complimentary techniques to characterise ores by in situ or online measuring techniques and laboratory analysis. Obtaining an enhanced understanding of the geometallurgy of ore bodies, including uranium deposits, (Bowell et al, 2011; Boisvert et al, 2013; Pownceby and Johnson, 2014) improves mitigation of economic and environmental risks. Depending on assemblages IR techniques can be a valuable tool in rapidly characterising ores for this purpose. The iron ore, copper, gold, uranium (IOCG-U) Olympic Dam deposit in South Australia has been the subject of such IR characterisation studies. Mineral spectroscopy investigations at Olympic Dam using thermal infrared (TIR) and NIR include: the mineral chemistry of phengite (K(AlMg)2(OH)4(SiAl)4O10) (Tappert et al, 2013); hematite abundance (Tappert et al, 2011); and plagioclase (NaAlSi3O8)-(CaAl2Si2O8), k-feldspar (KAlSi3O8), and chlorite ((Mg,Fe)3Al(AlSi3)O10(OH)8) characteristics (Mauger et al, 2016).

These studies provided valuable information about mineral speciation abundance and composition of the ore which allowed for a better understanding of the process requirements for resource optimisation in relation to reconciliation between the grade of mill feed and the processed result. Geoenvironmental characterisation is a subset of geometallurgy where the goal is to characterise ore with the intent of mitigating against acid rock drainage (ARD) by separating non-acid forming (NAF) from potential acid forming (PAF) waste or heavy metals eg. arsenic, sulfur and lead. Fox et al (2017) demonstrated the ability to determine carbonate mineral speciation between Ca-Mg-Fe-Mn solid solution mineral systems using thermal infrared (TIR), where it was noted that rapid acid neutralising minerals such as calcite (CaCO3) and ankerite (Ca(Fe,Mg,Mn)(CO3)2) are easily identified.
2.3 SUMMARY

The field of mineral spectroscopy continues to evolve, new discoveries in IR mineral behavior and improvements to photo spectrometers will ensure the development of new applications using these techniques. Further improvements on reliability and models specific to particular applications will make IR spectroscopy a viable solution to many online monitoring systems, which will drive efficiencies for many processes.

2.4 URANIUM AS A RESOURCE

Uranium has three differing utilities of application being:

1. nuclear medicine and research to produce \(^{99m}\)Tc (Ruth, 2009) \(^{51}\)Cr, \(^{131}\)I, \(^{192}\)Ir, \(^{32}\)P, \(^{153}\)Sm, \(^{90}\)Yt (Medical radioisotopes, 2017);
2. munitions including depleted uranium (DU) (Bleise et al, 2003) and warheads (Fetter et al, 1990); and
3. nuclear energy (Abram and Ion, 2008).

Due to the use of uranium in weaponry it is often considered malicious with questions of moral hazard often posed surrounding the efforts of resource exploitation. Proliferation concerns now exist surrounding simple technological advances of enrichment using the separation of isotopes by a laser excitation (SILEX) method which have provided a more efficient means in the production of \(^{238}\)U from UF\(_6\). These efficiencies are considered a global security risk due to the size of such production plants and their required energy use (Snyder, 2016). Despite negative sentiment it is still harnessed as a source of energy for diversified domestic power supply with continued research and development toward small modular reactors (SMRs) (Vujić et al, 2012).

One of the virtues often associated with nuclear power is the energy density (Fig. 2-3) of U being over ten billion times more energy-dense than petroleum (Layton, 2008). Nuclear energy is considered to have lower greenhouse gas emissions than fossil fuel technologies (Lenzen, 2008) however an excess of 100 studies (Sovacool, 2008;
references contained within) consider the total emissions attributed throughout the entire supply chain e.g. greenhouse emissions through mining, milling, enrichment, plant construction, and rehabilitation. These investigations are often highly variable relying on unpublished or secondary data sources. Sovacool (2008) concludes that although nuclear energy is by no means emission free it is much better (from a purely carbon-equivalent emissions standpoint) than coal, oil, or natural gas electricity generators.

Regardless of the sentiment surrounding U it will remains in use for applications which benefit many (such as medical applications). The intention of the remaining sections of this chapter is to provide a summarised review of the literature available surrounding uranium’s economic value and geochemical behaviours, while emphasising some of the lesser-known properties of the element in geological systems.

![Scatter plot showing the relationship between energy density and specific energy of various resources](image)

**Figure 2-3** | Scatter plot showing the relationship between energy density and specific energy of various resources note axis are logarithmic data from Layton (2008).
2.5 COMMODITY AND ECONOMIC DEMANDS

Mudd (2014) defines several critical issues surrounding global energy sectors being:

- greenhouse gas emissions from fossil fuels;
- peak oil and the end of an error of cheap conventional oil;
- social and environmental impacts from fracking;
- energy security concerns; and
- economic competitiveness of energy resources.

Mudd (2014) notes some workers (Switkowski, 2006; Suppes & Storvick, 2006) consider nuclear power capable of addressing such issues. The commodity market for uranium has demonstrated extreme volatility over the last century. In 1973 the U price increased to US$13.2/kg U\textsubscript{3}O\textsubscript{8} later surging to a record US$88.2/kg in 1978 (Mudd, 2014). By the early 2000s the U price had dropped to US$16.42/kg U\textsubscript{3}O\textsubscript{8} later experiencing gradual increases by 2003. In 2007 U reached US$300/kg U\textsubscript{3}O\textsubscript{8} later plummeting to US$97/kg U\textsubscript{3}O\textsubscript{8} by 2009 (Mudd, 2014).

Some variables which have affected U price over time are:

- nuclear catastrophes e.g. Three Mile Island (1979), Chernobyl (1986), Fukushima (2011);
- cartel activity (Venturini, 1982);
- environmental remediation of abandoned U mines;
- geotechnical failure/rock fall e.g. the flooding of the Cigar Lake U mine (World Nuclear News, 2010).

2.5.1 Exploration and resources

Exploration for uranium and development activities in 2007 and 2008 accelerated at a rate not observed in the 20 years previous, which was attributed to the increased spot price up until mid 2007 (OECD/IAEA, 2009). International expenditure for these activities equated to USD 1.64 billion in 2008 representative of a 133% increase from 2006 figures, of which 80% was devoted to domestic activities. At 2008 rates of consumption, identified resources (Fig.
2-4) are sufficient for a period exceeding 100 years to supply the global demand for nuclear power. From 2015 internationally some 437 nuclear reactors were connected to the grid with 70 reactors under construction. Australia the world’s third largest uranium producer behind Kazakhstan and Canada produced 4,976 t U in 2014 (OECD, 2016). Although OECD acknowledges resource figures are dynamic as they are related to commodity prices and demand.

This is exemplified by the total increase in identified resources from 2007 to 2009, equivalent to > 13 years of supply based on 2009 consumption figures. Demonstrating the stimulating effect of uranium price impact on resource totals and exploration discoveries by market based incentives. OECD (2009) cite increased Australian efforts associated to these market incentives which led to the following new deposit and significant occurrence discoveries: Double 8 (Western Australia), Beverley North and Blackbush (South Australia), Ranger 3 Deeps, Thunderball, N147, and Crystal Creek (Northern Territory). More recently however Australia has experienced declining levels of uranium exploration expenditure where it has significantly reduced by 79 % from 2011 levels to AUD 39.5 million in 2014 (Fig. 2-5). The OECD (2016) attributes the reduction in exploration expenditures to weak uranium prices and a global trend of lower exploration budgets.
2.5.2 Production and demand

In 2008 uranium production totalled 43 800 t eU, which is an 11% production increase from 2006. From late 2008, 438 commercial nuclear reactors (globally) supplied power to the grid requiring ~ 59 065 t eU to generate a net capacity of 373 GWe. By 2035 it is projected that an increased capacity of between 150-210% will be required for world consumption. Consequently, annual international uranium reactor related requirements are projected to rise to between 87 370 t eU and 138 165t eU for the same period (OECD, 2009).

Future debate regarding the contribution of nuclear power in a diversified energy sector requires an understanding of U market behaviour and consideration of positive and negative effects on commodity prices. Historical market evidence and previous price movements due to varying reasons offers an ideal understanding of U market volatility. This historical data should be taken under consideration and provide perspective to future planning around U resources and mining.
2.6 URANIUM GEOCHEMISTRY

Uranium is a markedly lithophile element whose redox state is easily varied. The hexavalent (U\textsuperscript{6+}) and the tetravalent (U\textsuperscript{4+}) uranium species are considered to be the most geochemically and mineralogically significant (Dahlkamp, 1993). U\textsuperscript{6+} has a uniform radius of 0.80 Å and U\textsuperscript{4+} a varying radius of 0.97Å with a co-ordination number of 6 (octahedral) and 1.01 Å with a co-ordination number 8 (cubic). Generally, U\textsuperscript{4+} is stable in subsurface environments. Cuney (2009) acknowledges that uranium geochemistry is chiefly governed by oxidation state with U\textsuperscript{6+} dominant under oxidising conditions and associated to proximal surface settings where U\textsuperscript{4+} is converted by UV photo-oxidation, auto-oxidation, and near surface oxidative weathering mechanisms (Hazen et al., 2009). Dahlkamp (1993) states that uranium occurs in three mineral groups: uranium ore minerals, accessory minerals, and complex ore minerals. Uranium ore minerals comprised predominantly of U\textsuperscript{4+} include uraninite (UO\textsubscript{2}), coffinite (USiO\textsubscript{4}) and brannerite (UTi\textsubscript{2}O\textsubscript{6}). Whilst minerals containing predominantly U\textsuperscript{6+} include the associated triuranium octaoxide (U\textsubscript{3}O\textsubscript{8}) and accommodating, oxyhydroxides, phosphates, arsenates, vanadates, and silicates (Skirrow et al. 2009). Oxidising fluid environments form uranyl ions (UO\textsubscript{2}\textsuperscript{2+}) developing more than 40 complexes with carbonate, chloride, fluoride, hydroxyl, phosphate, silicate, and sulphate anions (Langmuir, 1978). These complexes are associated to varying fO\textsubscript{2} and pH. Uranyl-carbonates are common at high pH and low temperature, with an intermediate fO\textsubscript{2}. Phosphates are dominant at a neutral pH. Sulphates and chlorides are important at acidic pHs where reducing environments cause the solubility of U\textsuperscript{4+} to be very low.
Higher $U^{4+}$ solubility is restricted to high temperature conditions and is controlled by the presence of fluoride complexes (Cuney, 2009). Uranium mineralisation in most deposits is a mechanism of decreased $f_O_2$ due to the contrast of oxidised U-bearing fluids with ‘reductants’ such as carbon in the form of organic matter, hydrocarbons including $CH_4$ and graphite, ferrous iron bearing minerals, and reduced sulphur in sulfide minerals, $H_2S$ gas and aqueous $H_2S$ (Skirrow et al, 2009).

Burns and Finch (1999) established the existence of $U^{5+}$ in the mineral wyartite and electrochemical studies of pentavalent uranium yielded dissolution (Goldik et al. 2004; Santos et al. 2006; Broczkowski et al. 2007) while demonstrating possible circumstances of such oxidations. $U^{5+}$ has also been identified at the surface associated with altered uraninite, strengthening the importance of pentavalent uranium. In fluid melt based experiments, Peiffert et al. (1996) reports that under relative reducing conditions dissolved U in melt is primarily composed of $U^{4+}$ and possibly $U^{5+}$ attested by colourless glasses. Hazen et al. (2009) considers that while $U^{5+}$ has little volumetric impact on the formation of most uranium minerals, the transformations of $U^{4+} \rightarrow U^{5+}$ and $U^{5+} \rightarrow U^{6+}$ could be essential for enabling uranium’s ubiquitous mobility in current atmospheric conditions. Peiffert et al., (1994, 1996) in their fluid-melt studies showed that uranium dissolves in silicate melts relative to the degree of depolymerisation, which is reliant on temperature, excess alkalis, and Ca/Al ratios. The increase of any one of these variables allows for greater melt depolymerisation.

The strongest parameter affecting U solubility in haplogranitic melt with concomitant aqueous fluid complexes is melt agpaicity (Na+K/Al in cations). Increasing agpaicity from 0.7 (peralkaline) to 1.6 (peraluminous) escalates solubility from ppb to percent levels (Peiffert et al. 1996). Skirrow et al. (2009) cautions that extrapolations of thermodynamic data beyond
300°C are problematic, as the speciation of uranium complexes at these conditions becomes less clear and may involve U⁴⁺, U⁵⁺, and U⁶⁺ dependant on fO₂ of any given system. Effects of this in igneous melts are demonstrated by Burnham and Berry (2012), where under controlled zircon synthesis partition coefficient errors for U are asymmetric and the change in partitioning is represented over a wider range than expected. This indicates that U⁴⁺ and U⁵⁺ (and/or U⁶⁺) must be in the system.

Minimal effects on U solubility are experienced in the presence of CO₂ and/or Cl, as these types of complexes are considered to have low solubilities in felsic melts (Cuney, 2009). However, it should be noted that chloride-bearing experimental systems have exhibited partition coefficients 1.5-2.5 magnitudes higher than in fluoride and CO₃-bearing systems with equivalent Na+K/Al ratios. Surprisingly, the increase in U solubility by fO₂ merely increases by a factor of 3. Silicate melts are capable of partitioning fluorine (Christiansen and Lee, 1986), which depolymerises them and increases U solubility. So much that the U⁴⁺ component of uraninite (UO₂(aq)) in controlled experiments dissolves easily at pH < ~4 and at temperatures as low as 25°C consequently forming U⁴⁺-F complexes (Langmuir 1978).

In elevated temperature, chloride and fluoride-bearing environments, U⁶⁺ and U⁴⁺ complexes can be significant as increases in pH and/or cooling can result in uranium deposition regardless of fluid redox state (Skirrow et al., 2009). Some of these processes are attributed to changes in ligand activity, for instance where F⁻ and acid rich magmatic-hydrothermal fluids meet with carbonate wall rocks producing fluorite. As a result U⁶⁺ and U⁴⁺ fluoride complexes become unstable precipitating out uraniferous minerals, with or without the involvement of redox changes.
Oxidised aqueous solutions generally host uranium in uranyl complexes, whilst tetravalent U being hosted in ore minerals relies on reduction as a catalyst for precipitation. Uranium-bearing oxidised fluids encountering suitable ‘reductants’ achieve this. The general understanding of uranium mineralisation is underpinned by mobilisation of U$^{6+}$ in oxidised aqueous solutions as the transport method with accumulation occurring as a result of reduction, although it has been shown that there are other variables (pH and salinity) that possess catalytic effects to achieve the effect of accumulation or trapping ore.

2.7 SOURCE: ROCKS AND FLUIDS

2.7.1 Rocks
Michard and Albarede, (1985) acknowledge that U and Th undergo a complex series of fractionation events, beginning with preferential incorporation of U into hydrothermally altered oceanic crust. Asymmetric distribution of these elements can result in differing sources (Table 2-1). Uranium along with K and Th continue to be fractionated at subduction zones, where they are extracted from the slab by hydrous fluids/melts. Subsequent melting in the mantle wedge produces island arc magmas that are generally in Large Ion Lithophile Elements (LILE) (McCulloch and Gamble 1991). Bailey and Ragnarsdottir (1994) consider uranium to be present in these magmas in higher proportions relative to other LILE based on the contrast between U/Th ratios in arc magmas of 0.4-0.7, compared to Mid-Oceanic Ridge Basalt (MORB) and Oceanic Island Basalt (OIB) (0.2-0.3). The dominant mechanism for initial U accumulation from ppb to ppm levels is likely to be chemical fractionation (Hofmann, 1988) because fertile reservoirs for U are generally considered to be crustal residual fluids derived from felsic igneous rocks (Table 2-2).

<table>
<thead>
<tr>
<th></th>
<th>Undepleted mantle</th>
<th>Ocean Crust (N-MORB)*</th>
<th>Continental crust</th>
<th>Continental enrichment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Th</td>
<td>0.08</td>
<td>0.15</td>
<td>3.5</td>
<td>x 44</td>
</tr>
<tr>
<td>U</td>
<td>0.02</td>
<td>0.05</td>
<td>0.91</td>
<td>x 46</td>
</tr>
</tbody>
</table>

Table 2-2 | Average uranium concentration for various reservoirs in the Earth’s crust; note the increase in concentration relative to fractionation in respective reservoirs.

<table>
<thead>
<tr>
<th>Reservoir</th>
<th>U (ppm)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bulk Silicate Earth</td>
<td>0.02</td>
<td>Palme and O’Neill (2007)</td>
</tr>
<tr>
<td>Crust</td>
<td>1 – 2.7</td>
<td>Plant et al. (1999)</td>
</tr>
<tr>
<td>MORB</td>
<td>0.05 – 0.15</td>
<td>Workman and Hart (2005)</td>
</tr>
<tr>
<td>OIB</td>
<td>1</td>
<td>Plant et al. (1999)</td>
</tr>
<tr>
<td>Granite</td>
<td>10</td>
<td>Plant et al. (1999)</td>
</tr>
<tr>
<td>High-grade ore deposits</td>
<td>10⁴ - 10⁵</td>
<td>Plant et al. (1999)</td>
</tr>
</tbody>
</table>

Suitable source rocks for uranium mineralisation are generally alkaline and peraluminous granites resultant of partial melts from arkosic sedimentary rocks and low degree melting of supracrustal sources. Cuney (2009) notes four types of felsic igneous rocks that are fertile sources for U being:

1. peralkaline;
2. metaluminous high-K calcalkaline rocks;
3. peraluminous rocks generated by partial melting of supracrustal rocks and;
4. alaskites analogous to granitoid dykes within migmatites.

Alaskites are formed by relatively low levels of partial melting of upper crustal rocks and are weakly peraluminous in composition. These modal rocks typically contain ~ 10 ppm U, which is significantly greater than average crustal values of 3-4 ppm. Peraluminous leucogranites are associated with large uranium deposits having an increase in peraluminosity proportionate to fractionation. Uraninite saturation is achieved in low-temperature melts if the U concentration of the source is above crustal tenor, post
monazite and zircon fractionation (Cuney et al. 1990). Intrusive rocks of this composition are always enriched in U and other high field strength elements (HFSE) (Eby 1992). Uranoan thorite (Th, U)SiO$_4$ commonly crystallises in high-K metaluminous granites during fractionation and can contain up to 30 wt.% UO$_2$, representative of an easily transported source able to accumulate elsewhere post granite emplacement.

2.7.2 Fluids
Deposition of nearly all major uranium deposits have involved aqueous fluids (Skirrow et al., 2009), which can be divided into three markedly differing origins. Skirrow et al., (2009) notes them to be:

1. magmatic-hydrothermal;
2. ‘metamorphic’ (including reacted fluids with metamorphic rocks), and
3. hydrosphere-derived (meteoric water, lake water, seawater, groundwater).

The two key processes to uranium ore formation are fluid-rock reactions and fluid mixing; these processes are generally preserved in the form of zoned alteration mineral assemblages. These alteration zones are centred on the gradient between oxidised and reduced domains of U mineralising systems (Skirrow et al., 2009).

2.8 URANIUM DEPOSIT CLASSIFICATION

In the case of many U deposits questions remain regarding (1) the composition of mineralising fluids, (2) uranium mobilisation, transport, and redepositon conditions, and (3) repetitive redistribution (Dahlkamp 2009). This loosely correlates to some U mineral systems source-transport-accumulation-preservation (STAP) model (Hill and Hore, 2011). Dahlkamp (2009) bases deposit typology chiefly on descriptive data, providing principle criteria of deposit types in order to benefit economic geologists. Skirrow et al., (2009) gives the descriptive criteria for deposit typology merit, but also considers limitations when assessing undiscovered or unrecognised styles of mineralisation. These authors also propose a differing classification scheme centred on physio-chemical behaviour in three end-member uranium systems (Figure 2-6).
Partitioning behaviour of uranium between melt and coexisting magmatic fluid is an underpinning control on the genesis of magmatic-related uranium mineralisation.

Experimental uranium partition coefficients between fluid and melt (D(U)\textsubscript{fluid-melt}) increases with decreasing Na+K/Al ratio in the melt.

In oxidising settings e.g. hematite-magnetite solubilities of up to 970 ppm, uranium has been recorded in fluid, carried by chloride and hydroxyl-chloride complexes (Peifferet et al., 1994, 1996; Skirrow et al., 2009). The controlling effects on uranium behaviour are not confined to the redox domain, as pH and Eh (fO\textsubscript{2}) have been demonstrated to have an effect on U behaviours (Figure 2-7). Although Hostetler and Garrels, (1962) demonstrate the effects on U in aqueous systems at a low temperature (25°C) these effects can easily take place in hydrothermal-magmatic deposits where more basic fluids may come into contact with CO\textsubscript{3} hosted wall rocks creating a buffer and increasing the stability of uraninite and coffinite.
2.9 COFFINITE

The uranium bearing mineral, coffinite, an orthosilicate named after geologist Reuben Clare Coffin (Steiff et al, 1955) was first characterised from natural samples using x-ray powder pattern indexing, optical microscopy, and detailed leaching studies. Hoekstra and Fuchs (1956) were able to synthesise coffinite utilising a hydrothermal method and noted the tetragonal structure from x-ray powder patterns and an isomorphous relationship to thorite (ThSiO₄) and zircon (ZrSiO₄) among other orthosilicates (Table 2-3) which included similarities in mid-infrared (MIR).

Figure 2-7 | Hostetler and Garrels, (1962) aqueous equilibrium diagram of the UO₂-H₂O-CO₂ system at 25°C and 1 atm. Boundaries between solid phases and dissolved species are drawn for total ionic activity of 10⁻⁶. Diagram shows the complexity of uranium in an aqueous system without redox reactions.
Table 2-3 | Orthosilicate crystal structures.

<table>
<thead>
<tr>
<th>Name</th>
<th>Formula</th>
<th>Space group</th>
<th>$a$ (Å)</th>
<th>$c$ (Å)</th>
<th>$Z$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coffinite</td>
<td>USiO$_4$</td>
<td>I 4$_1$/amd</td>
<td>6.93</td>
<td>6.25</td>
<td>3</td>
</tr>
<tr>
<td>Thorite</td>
<td>ThSiO$_4$</td>
<td>I 4$_1$/amd</td>
<td>7.13</td>
<td>6.32</td>
<td>4</td>
</tr>
<tr>
<td>Zircon</td>
<td>ZrSiO$_4$</td>
<td>I 4$_1$/amd</td>
<td>6.604</td>
<td>5.979</td>
<td>4</td>
</tr>
<tr>
<td>Hafnon</td>
<td>HfSiO$_4$</td>
<td>I 4$_1$/amd</td>
<td>6.5725</td>
<td>5.9632</td>
<td>4</td>
</tr>
</tbody>
</table>

The impetus for identifying and understanding coffinite behaviour is due to it being often found in economic proportions in many uranium ore deposits and for environmental measures where formation can occur due to long-term release of UO$_2$ fuel sources from spent nuclear fuel (SNF) facilities (Ewing, 2015).

2.91 SYNTHESIS

As stated earlier the synthesis of coffinite (USiO$_4$ $n$H$_2$O) was first reported by Hoekstra and Fuchs (1956). The mineral properties were then later discussed by Fuchs and Hoekstra (1959) where coffinite was examined using infrared spectroscopy (Fig 2-8). It was 50 years until another documented study of coffinite synthesis was undertaken (Pointeau et al, 2009). From that time there has been a substantial number of studies (Table 2-4) into the synthesis and behaviour of coffinite in relation to (U,Th)SiO$_4$ solid solution series (Costin et al, 2011; Costin et al, 2012; Szenknect et al, 2013; Clavier et al, 2014; Labs et al, 2014); postulation on natural formation (Janeczek et al, 2011; Mesbah et al, 2015); thermodynamic investigations (Guo et al, 2015); solubility studies (Szenknect et al, 2016); and radioactive induced amorphization (Lian et al, 2009).
Table 2-4 | Properties and variables for coffinite stability.

<table>
<thead>
<tr>
<th>Variable</th>
<th>Conditions</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thermal</td>
<td>25 ºC-500 ºC (in air)</td>
<td>Fuchs and Hoekstra (1959)</td>
</tr>
<tr>
<td></td>
<td>25 ºC-1 000 ºC (in vacuum)</td>
<td></td>
</tr>
<tr>
<td>Pressure</td>
<td>0-17 GPA* (room temperature)</td>
<td>Zhang et al (2009)</td>
</tr>
<tr>
<td></td>
<td>*phase change complete at 23 GPA</td>
<td></td>
</tr>
<tr>
<td>Solubility</td>
<td>log(^{+}) K(_{s\text{USiO}}\text{, cr}) = -5.25 ± 0.05</td>
<td>Szenknect et al (2016)</td>
</tr>
<tr>
<td>Constant</td>
<td>(at 25 ºC and 1 bar)</td>
<td></td>
</tr>
<tr>
<td>Radioactivity</td>
<td>0.28 displacements per atom (dpa)*</td>
<td>Lian et al (2009)</td>
</tr>
<tr>
<td></td>
<td>(room temperature)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(phase decomposition temperature 334.85°C)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(irradiation source 1 MeV Kr(^{2+}))</td>
<td></td>
</tr>
</tbody>
</table>

Figure 2-8 | Mid infrared spectra of synthetic coffinite, thorite, and natural zircon, adapted from Fuchs and Hoekstra (1959)
In the natural environment coffinite mineralisation is considered to occur as a replacement to uraninite (Langmuir, 1978) and is expressed as (Eqn. i). Natural uraninite is often non-stoichiometric and coffinite may incorporate a significant hydrous component - the reaction was defined in more detail (Janeczek and Ewing, 1992) (Eqn. ii), then later refined (Guo et al., 2015) (Eqn. iii).

\[
\begin{align*}
UO_{2(s)} + H_4SiO_4(aq) & \rightarrow USiO_4(s) + 2H_2O(l) \quad \text{(i)} \\
UO_{2+x(s)} + H_4SiO_4(aq) & \rightarrow USiO_4(s) \cdot 2H_2O(l) + 0.5xO_2(g) \quad \text{(ii)} \\
USiO_4(s) + 2H_2O(l) & \rightleftharpoons UO_{2(s)} + Si(OH)_4(aq) \quad \text{(iii)}
\end{align*}
\]

### 2.92 COFFINITE AND MINERAL SPECTROSCOPY

Many secondary uranium minerals have been examined in different domains throughout the infra-red (IR) spectrum (Bell and Biggers, 1965; Frost and Cejka, 2009; Arnold et al. 2011) yet no IR based method has been successfully employed in applications that can enhance deposit grade determination or vectoring for mineral exploration. This is considered due to the spectral peaks for $\text{U}^{4+}$ in minerals being either non-existent or being poorly resolved in conjunction with complex mineral assemblages. Recent studies have alluded to the potential for coffinite ($\text{USiO}_4$) and uranoan thorite ($\text{Th}_1\gamma\text{U}_\gamma\text{SiO}_4$) to thorite ($\text{ThSiO}_4$) solid solutions to provide a proxy for determination in complex matrixes (Baron et al. 2014). These findings offer the foundations for the development of new techniques in the near-infrared (NIR) spectrum to innovate online monitoring and in field detection of uranium ores dependent upon the style of mineralisation, assemblage, and host rock characteristics.
2.921 Spectral similarities between Zircon \((ZrSiO_4)\) and uranothorite-coffinite
Zircon is isomorphic with coffinite and often incorporates uranium into its crystal structure, as such it is an ideal analogue to understand uranium behaviour in silicate minerals. Zhang et al., (2002) was able to simulate zircon metamictization and spectrally characterise changes at varying degrees of radiation damage. Results showed that radiation damage lead to the disappearance of \(U^{5+}\) bands near 6668 and 9030 cm\(^{-1}\) (1499.70 and 1107.42 nm) and the occurrence of additional peaks near 6650 and 8969 cm\(^{-1}\) (1503.76 and 1114.95 nm) - these are similar to the peaks defined by Baron et al., (2014) in coffinite and uranothorite being 1500 and 1509 nm. Note the zircon spectra shown in figure 2-9 reveals two distinct peaks at 1113.5 and 1478 nm, the latter peak was shown to be resultant of \(U^{4+}\) ion replacing \(Zr^{4+}\) (Nasalda et al. 2001).

2.922 Spectral characteristics of the coffinite-uranoan thorite solid solution
A continuous series between the end members thorite and coffinite has been long established (Fuchs and Gebert, 1958) - natural analogues were also revealed to exist by Smits (1989) in U ore bearing reefs of Witwatersrand, South Africa. Until recently there had been little work done on characterising the minerals via infra-red in this binary system until Clavier et al., (2014) synthesised anhydrous coffinite, uranoan thorite, and thorite under reducing conditions (Costin et al. 2012) and characterised U-Th silicate minerals using Raman and FTIR spectroscopy. No band associated to OH groups was detected due to their anhydrous nature and therefore the interpretation of the spectral data could be determined on the chemical compositions between the end members. Synthetic uranothorite (uranium concentration of \(x=0.2\) and \(x=0.32\)) revealed NIR spectral peaks at 1134, 11347, 1442, 1500, 1554, 1678 and 2165 nm. For samples with greater uranium concentrations (\(x=0.8\) and coffinite \(x=1\) USiO\(_4\)) peaks were 1134, 1422, 1509, 1678 and 2140 nm (Fig. 2-9) (Baron et al. 2014). The absorptions between 1000 nm to 1800 nm are attributed to \(U^{4+}\) electron transitions (Zhang et al. 2009). \(U^{4+}\) electron energy levels and spectra were well characterised by Zhang et al., (2003) for uranium doped synthetic zircon. However well
characterised these peaks are, between this spectrum Zhang et al., (2009) acknowledges the two peaks at 1417 nm and 1681 nm to potentially be associated to differing energy levels of U⁴⁺ in coffinite and identifies a new peak at 1503 nm and considers this to be a contribution of U⁵⁺. This peak is located between those found by Baron et al., (2014) 1500 nm for uranothorite and 1509 for coffinite.

For this reason the peak shifts noted between the uranothorite-coffinite solid solution should be viewed with a degree of caution due to the relative stability of Th₁₋xUₓSiO₄ in relation to ZrSiO₄ however it should be noted that the samples synthesised by Clavier et al., (2014) were not pressure tested and reveal no evidence of oxidation post purification (they were also shown to be anhydrous). In any case there is a requirement to treat spectral results involving peaks association with natural samples with a judicious understanding of the geological terrane and mineralogical assemblage from which they originate.

---

**Figure 2-9** | Shows the spectral reflectance bandwidths of peaks and shoulders for common clay minerals and their associated bonds (Bishop et al., 2008; Doublier et al. 2010) found in natural samples for the NIR-SWIR spectrum. Spectra for illite, chlorite, smectite, zircon, and quartz (Clark et al. 2007) are plotted for comparison. Spectral peaks for uranothorite and coffinite are labelled (Baron et al. 2014) and their stoichiometric ratios for uranium are shown in red and blue.
2.923 Spectral identification of three or more minerals in complex mixtures
Natural ore or rock chip samples often host complex mineral assemblages with multiple mineral phases in existence, whilst some of these phases are not spectrally active (dependant on the limitations of instrument used) however they may prove detrimental to the collection of reliable data. Those minerals which are active and coexist with each other may have overlapping absorption bands. Yang and Huntington, (1997) modelled varying mixes of muscovite, kaolinite, alunite, and montmorillonite (active components) in conjunction with quartz and potassium feldspar (inactive NIR components). This was done using a PIMA-II (Portable Instrument Mineral Analyser-II). All spectrally active mineral fractions were doped to a concentration of <10wt %. From these mixes it was possible to identify the presence of spectrally active minerals down to a fraction of 2.06 wt.% This shows that it is possible to identify particular accessory minerals in complex matrixes and that similar methods may be successfully applied to others.

2.924 Coffinite behaviour in the natural environment and mineralised uranium systems
It should be acknowledged that experiments conducted with binary end members and being synthesised with anhydrous compositions are vastly different to those same products found in natural systems. These are often extremely hydrous and host a varying composition of elements (Förster, 2006). Indeed it is further noted that thorite forms intermediate solid solutions between coffinite (Fig. 2-10).
Fürster, (2006) notes the absence of this dilemma being acknowledged throughout the literature with few exceptions (e.g. Pointer et al., 1988; Hansley and Fitzpatrick, 1989) and identifies that many of these species share a common feature where they do not total 100 wt.%. This inconsistency in electron microscopy provides no direct checks against theoretical stoichiometry and is apportioned to numerous influences, being: 1) absorbed molecular H₂O or OH where substituted for SiO₂; 2) elements not included in the analysis which are present in the crystal structure; 3) small grains and narrow zones of homogeneity, which may cause small concentrated beam sizes to require additional time for analysis and consequently destroy samples being interrogated; 4) voids and micro-fractures (via regional metamorphism or alpha decay); 5) hexavalent U; 6) nano-inclusions unrecognisable via BSE, and 7) analytical artifacts from adjacent phases.

**Figure 2-10 |** Ternary plot of the U-Th-Si system. N= 92 (Deditius et al. 2008; Förster, 2006; Min et al. 2005; Bros et al. 2003; Janeczek et al. 1999; Smits, 1989) Shaded field defines the coffinite-thorite solid solutions as defined by Smits (1989) and Förster (2006).
**Natural Environment**
Preferential coffinite crystalisation has been observed over uraninite where sulfides are present (Janeczek and Ewing, 1992; Fayek et al., 1997). Based on this Deditus et al., (2008) suggests coffinite is more stable under reducing, Si-rich conditions than uraninite.

**Mineralised Uranium Systems**
In natural systems Coffinite is often fine grained in nature (Pointer et al, 1988; Min et al, 2005; Deditus et al, 2010), however coarse-grained coffinite has been observed at the Mt. Taylor Mine, New Mexico, where it is most abundantly hosted in the sandstones of the Upper Jurassic Morrison Formation (Hansley and Spirakis, 1992). Coffinite is also known to occur in large proportions with a “bulls eye” type of texture in the Liuerquiqi granite in SE China (Min et al, 2005).

### 2.925 Factors that may influence spectral characteristics
Variables that may impact the spectral behaviour of a material being examined may include one or more of the following:

1. Mineralogy;
2. Cation composition;
3. Crystallinity (disorder);
4. Water (free, adsorbed, absorbed, structural);
5. Particle/grain size;
6. Orientation;
7. Mixtures;
8. Organic matter (OM).

Analysis can be hampered by dark coloured rocks yielding aspectral measurements (Chang and Yang, 2012) with no discernible peaks, this may also occur due to the abundance of dark coloured minerals e.g. uraninite (UO$_2$) the primary uranium ore mineral often found in association with coffinite. An example could be the difference between chlorite which is a dark ferromagnesium clay and potassic white mica (KWM – illite, muscovite, and other diagenetic clays), where the spectra may differ. Another example may be the complication in obtaining the 2130 nm feature in the presence of KWM where the Al-OH feature could create difficulty in determining the influence of coffinite at these proximal wavelengths.
Although Baron et al, (2014) investigated the spectral relationships between U-Th in a silicate system there are limited studies surrounding U-Zr silicate systems in respect to NIR. This presents challenges for complex ores where spectral peaks from several minerals may be observed eg. intermediate solid solutions between coffinite-thorite-zircon.

Additional spectral complexities may eventuate if coffinite is found with rare earth element (REE) phosphate minerals such as xenotime (Y,Yb(PO₄)). Turner et al (2016) noted REE³⁺ absorptions occurred in similar ranges for U absorption bands identified by Zhang et al (2004); Zhang et al (2009) which were considered related to U. This suggests that diagnostic peaks associated with U in coffinite are not restricted to silicate minerals and further investigations are required to determine the effect of uranium in other mineral species.

**Grain size and crystallinity**
Non-linear relationships can exist in pure and multiphase mixtures where the fine grained nature of a material is considered responsible (Johnson et al, 1983; Mustard and Hays 1997; Milliken and Mustard 2007). Synthetic coffinites used in previous spectral studies (Costin et al, 2012; Baron et al, 2014) were crystalline as evidenced by well-defined XRD patterns however natural coffinites may be amorphous depending on conditions at the time of crystal growth or an effect of α-decay of U (Weber, 1993), therefore a direct correlation between natural and synthetic coffinite crystals is difficult to obtain and may be another variable which requires addressing to understand NIR coffinite feature intensities. For these reasons, it may be the case that coffinite concentrations observed in natural ores are slightly non-linear in relation to spectral intensities.

**Water**
Depending on mineral assemblages and environmental exposure to water e.g. surficial or phreatic interferences, which may be problematic to identifying diagnostic spectral features of mineral species. Specifically, where bound water features are known to occur at 1410 and
1910 nm and adsorbed features at 1460 and 1970 nm (Bishop et al, 1994). Furthermore, the combined roles of grain size and water content on NIR spectra are poorly understood, with the capability to determine simultaneous spectral effects between grain size and water content confined to unconsolidated sediments (Verpoorter et al, 2014). Studies investigating these combined effects in other materials are highly desirable to improve mineral NIR spectroscopy methods applied to multi-phase materials.

2.93 SUMMARY

Content defined in this review demonstrates the continuous evolution and improvements in the field of mineral spectroscopy. These advances coupled with firm geochemical knowledge of mineral systems offers new pathways in the application of NIR. Where known analytical advantages e.g. limited sample preparation, rapidity, reproducibility, and reduced cost of analysis; offer incentives to develop methods for efficient detection and quantification. Suitable applications for such a technique would include; natural resource exploitation in the form of rapid ore characterisation techniques and environmental monitoring/remediation e.g. where coffinite may form as a secondary alteration product from the release of spent nuclear fuel (Ewing, 2015). This study makes attempts to develop such techniques through the synthesis of coffinite and characterization of NIR spectral features in well constrained mineral mixtures as an analogue for a metasomatic U ore. Comparisons between synthetic mixtures and natural U ores are investigated to determine the effectiveness of NIR techniques for the identification and quantification of coffinite in an ore body.
Chapter 3

MATERIALS AND METHODS

3.1 COFFINITE SYNTHESIS

The method for hydrothermal synthesis of coffinite used in this study (Reynolds, 2013) was adapted from Fuchs and Hoekstra (1959). Chemical reagents used for this method were of laboratory grade with the exception of ammonium diuranate:

- Ammonium diuranate: \((\text{NH}_4)_2\text{U}_2\text{O}_7\)
- Carbon tetrachloride: \(\text{CCl}_4\)
- Sodium metasilicate: \(\text{Na}_2\text{SiO}_3\)
- Sodium hydroxide: \(\text{NaOH}\)
- Sodium bicarbonate: \(\text{NaHCO}_3\)

3.1.1 PRECURSORS (\(\text{U}_3\text{O}_8\), UO\(_2\), and UCl\(_4\))

**Preparation of UO\(_2\)**

Ammonium diuranate \(((\text{NH}_4)_2\text{U}_2\text{O}_7)\) was the initial raw material which was required to be synthesised to pitchblende \((\text{U}_3\text{O}_8)\), this was achieved by heating in a tube furnace at 600 °C for 5 hours in air. It was then required to obtain uraninite \((\text{UO}_2)\) similarly at parameters of 1000 °C for 5 hours under reducing conditions using a flow of Ar/H\(_2\) at a mixture of 95 % and 5 % respectively.

**Uranium tetrachloride (UCl\(_4\))**

**Setup**

Coffinite synthesis requires uranium to be soluble in water thus enabling the hydrothermal reaction, for this reason UCl\(_4\) was prepared. This approach was derived from Wilson’s (1973) original method and adapted from Reynolds (2013). Due to the hydroscopic nature and susceptibility of oxidation the preparation of UCl\(_4\) and subsequent coffinite \((\text{USiO}_4)\) were undertaken in *dry inert (reduced)* conditions, therefore a positive flow of nitrogen gas (N\(_2\)) was maintained throughout.
A quartz boat containing UO$_2$ was placed in a quartz reaction tube, which was housed in a tube furnace. A dropping funnel containing carbon tetrachloride (CCl$_4$) was placed at the required receptacle (Fig. 3-1) and a thermo couple attached to the reaction tube with the heating element directly below the dropping funnel position. At this point the system was shut by the addition of a flask in an ice bath and a sulphuric acid bubbler, the atmosphere and was then purged using a dry flow of N$_2$.

![Diagram](image)

**Figure 3-1** | Laboratory equipment configuration for the synthesis of UCl$_4$.

**Process**

Once the system was purged the tube furnace was heated to 400 °C and the thermo couple set to 100 °C. Upon temperature equilibrium, a surplus of CCl$_4$ was added drop-wise at ~ 20 mL/hr, this ensured the UO$_2$ reacted completely to form uranium tetrachloride (UCl$_4$) (Eqn. 1).

**Equation 1**  
$$\text{UO}_2(\text{s}) + \text{CCl}_4(\text{aq}) \rightarrow \text{UCl}_4(\text{s}) + \text{CO}_2(\text{g})$$
When the reaction had completed, \( \text{N}_2 \) flow was increased and the quartz boat now containing \( \text{UCI}_4 \) was quickly moved into a transfer tube located on the relief end of the reaction tube. Once the \( \text{UCI}_4 \) was in position caps were sealed on the transfer tube effectively sealing the \( \text{UCI}_4 \) in an inert environment. The resulting \( \text{UCI}_4 \) manifested as a mossy dark green powder.

### 3.1.2 HYDROTHERMAL SYNTHESIS

Due to the requirement of coffinite being prepared under inert conditions in a glove bag all precursors and chemical reagents were weighed separately prior to the final preparation phase. Doing so reduced the risk of contamination, error, and provided more room inside the glove bag during the final process.

**Process**

Prior to beginning the synthesis of coffinite (USiO₄) the encapsulating glove bag was purged three times using dry \( \text{N}_2 \). Once purged 5 mmol of sodium metasilicate (\( \text{Na}_2\text{SiO}_3 \)) and a separate 5 mmol of \( \text{UCI}_4 \) were both dissolved in 50 mL of degassed water. A round bottom flask was used as the receptacle and physically swishing the solution in a circular motion until it was observed to completely dissolve facilitated the dissolution of the \( \text{Na}_2\text{SiO}_3 \).

At this point 20 mL \( \text{UCI}_4\text{[aq]} \) was added drop-wise to the \( \text{Na}_2\text{SiO}_3\text{[aq]} \), this was done via a glass pipette where care was taken for the tip to be submerged in the \( \text{Na}_2\text{SiO}_3\text{[aq]} \) and was gently moved through the fluid while adding the \( \text{UCI}_4\text{[aq]} \). It was considered that these measures ensured the limited interface with the internal atmosphere and provided maximum distribution for inter-fluid reaction as a green gel forms almost instantly upon addition of the \( \text{UCI}_4\text{[aq]} \).
The consequent solution had a pH \( \approx 2.4 \) an additional 2 M sodium hydroxide solution was then added drop-wise to accelerate gel formation with a resultant pH \( \approx 10 \). The solution was then buffered to pH \( \approx 8.5 \) using the required amount of NaHCO\(_3\) for the solution to contain \( \sim 0.5 \) M carbonate ions. The final solution was then poured into a teflon lined steel autoclave and heated to 250 °C in a muffle furnace for 24 hours (Fig 3-2) where it is considered the process outlined in equation two took place.

**Equation 2**  
\[
UCl_4(\text{aq}) + Na_2SiO_3(\text{s}) + 2H_2O(\text{aq}) \rightarrow 4HCl(\text{aq}) + USiO_4(\text{s}) + Na_2O(\text{aq})
\]

On completion of the heating phase the autoclave was removed and allowed to cool before opening. The process resulted in a black-dark blue precipitate of coffinite which was washed repeatedly in degassed water and dried in a binder oven at 30 °C.
3.2 X-RAY DIFFRACTION

For verification and final analysis of precursors, final synthetic coffinite, whole rock, natural mineral separates, and synthetic mineral mixes; standard X-ray diffraction analysis (XRD) was obtained on a Bruker D4 X-Ray Diffractometer using a CuKα source. A 1° divergence slit was used to analyse a 2θ range between 5 and 90° with a step size of 0.02° and 2 s/step. Database matches were obtained from the PDF-2 database using Bruker Diffrac.EVA version 4.2.0.31 software.

3.3 INFRA-RED SPECTROSCOPY

Two instruments were used throughout this project with their spectral coverage defined in figure 3-3.

![Figure 3-3](image)

**Figure 3-3** | Coverage of the NIRA II and TerraSpec4 in relation to the electromagnetic spectrum.

3.3.1 PERKIN ELMER FRONTIER FT-IR/NIR (NIRA II attachment)

For laboratory-based analysis the bench top NIRA II (Fig: 3-4). Analysis were conducted at a resolution of 8 cm\(^{-1}\), a data interval of 1 cm\(^{-1}\), scan type background, and 200 scan acquisitions. The instrument has the following specifications listed in table 3-1.

<table>
<thead>
<tr>
<th>Table 3-1</th>
<th>Specifications for the Perkin Elmer Frontier FT-IR/NIR.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wavelength range</td>
<td>1000-2500 nm</td>
</tr>
<tr>
<td>Resolution</td>
<td>8 cm(^{-1}); interval 0.25 cm(^{-1})</td>
</tr>
<tr>
<td>Number of scans</td>
<td>200</td>
</tr>
<tr>
<td>SWIR detector</td>
<td>InGaAs</td>
</tr>
<tr>
<td>Beam splitter</td>
<td>CaF(_2)</td>
</tr>
</tbody>
</table>
3.3.2 ASD TerraSpec 4 HI-RES

For field studies of drill core and synthetic mineral mixture validations the ASD Inc. TerraSpec®4 HI-RES mineral spectrometer was awarded from the manufacturer for one month of use. The instrument has the following specifications listed in table 3-2:

Table 3-2 | Specifications for the ASD TerraSpec®4 HI-RES spectrometer.

| Wavelength range          | 350-2 500 nm  |
|                          | 2 8571-4 000 cm⁻¹ |
| Resolution               | 3 nm @ 700-1 400 nm |
|                          | 6 nm @ 1 400-2 100 nm |
| Scanning time            | 100 ms |
| VNIR detector            | (350-1 000 nm) 512 element silicon array |
| NIR detector             | (1 001-2 500 nm) graded index InGaAs photodiode, TE cooled |

The unit was used with the contact probe adapter fitted for rapid analysis and mobility (Fig 3-5). Pilot studies were conducted in accordance with those recommended by Chang and Yang (2012) where it was considered that 120 scans at 12 seconds were performed three times at each sample interval would be sufficient for this study.
3.4 X-RAY FLUORESCENCE (XRF)

Due to this study being conducted under the guise of two differing components (field and laboratory) the former required the utilisation of a portable XRF analyser and the later used a CSIRO provided instrument. Due to equipment availability, it was not possible to compare laboratory derived samples with the portable analyser.

3.4.1 PORTABLE XRF

An Olympus Innov-X DP4000 model (Ta tube) was used for XRF analysis on drill core samples of interest. Analyses were taken by irradiating the sample for 40 seconds on each of the three beams. The instrument was used with a soil foot attachment to negate movement during collection (Fig 3-6). Certified standards were measured at every 20th analysis these were checked regularly and reflected a rough proportion difference between inter-standard concentrations observed in the certified wet chemistry.

Figure 3-6 | Olympus Innov-X Delta portable XRF with soil foot collecting analysis on drill core.
3.4.2 LABORATORY XRF
Laboratory analysis for mineral separates and synthetic mixtures was conducted on a Bruker S8 Tiger WD-XRF. Sample preparation involved accurately weighing approximately 0.5 g of each sample into 95% Pt/Au crucibles with approximately 5 g of 12-22 lithium tetraborate:metaborate flux previously dried at 550°C. The sample was pre-oxidised over an oxy-propane flame burner to bring the contents of the crucible to between 650°C to 700°C while oxygen was bled into the top of the crucible. The sample was held at this temperature for approximately five minutes before the mixture was fused into a homogeneous melt over an oxy-propane flame at a temperature of approximately 1 050°C for approximately ten minutes. A commercially available ammonium iodide doped cellulose tablet was added approximately 100 seconds before the molten glass was poured into a 32 mm Ø 95% Pt/Au mold and heated to a similar temperature. Air jets then cooled the mold and melt for approximately five minutes. The resulting glass discs were analysed on a Philips PW2404 XRF system using a control program developed by Philips and algorithms developed in-house by CSIRO.

3.5 SCANNING ELECTRON MICROSCOPY
An FEI Quanta 200 ESEM, fitted with an Oxford X-MaxN 20 EDXS Detector and Gatan Alto Cyro stage were used for the interrogation of synthetic samples.

Working distance 10 mm
Voltage 15 kV

3.6 CLAY EXTRACTION
A garnet bearing chlorite schist was used to obtain chlorite for this study. The rock was disaggregated in a clean zip lock bag contained in an exterior calico bag then crushed using a hammer. Clay samples were not milled to ensure the preservation of the crystal lattice. Fines were then placed in a container with distilled water where it underwent ultrasonic irradiation for one minute, promoting detachment of clays from other minerals.
The water-rock powder mixture was then transferred to a cylinder. To disperse the sample further a pinch of sodium hexametaphosphate was added while gently stirring the water column with a spatula. Particle size separation was achieved by gravity settling based on Stokes law in a distilled water column. The settling time for particle sizes can be estimated according to the gravity constant, particle diameter, water temperature and viscosity, mineral density and mineral shape. Fractions of < 15 μm, < 10 μm, and < 5 μm were separated. As the settling of small sized fractions would take too long, a centrifuge was used. To coagulate suspended particles each fraction was centrifuged and consequently concentrated at the bottom of each centrifuge vial. Condensed clays were then rinsed from each vial and placed in an oven at 30 °C to evaporate remaining water.

\[ v_s = \frac{2}{9} \frac{(P_p-P_f)}{\mu} g R^2 \]

Stokes Law where:
- \( v_s \) = particle settling velocity
- \( g \) = gravitation acceleration
- \( P_p \) = particle mass density
- \( P_f \) = fluid mass density
- \( R \) = radius of particle
- \( \mu \) = dynamic viscosity

### 3.7 HEAVY MINERAL SEPARATION

This separation involves: (a) removal of altered and weathered surfaces with a rock hammer and/or core saw, (b) removal of remaining internally altered or weathered zones post hydraulic pressing, crushing samples to a gravel ~ 1 cm in diameter, (c) milling of crushed sample in a tungsten-carbide ring grinder, (d) repeatedly milling and sieving sample to < 500 μm, (e) grains were then processed through an oscillating flotation separation table ‘wifley table’ that split the sample into three different proportions based on density. The heaviest fraction is retained for further processing.

Crystal variety and abundance reduction was attempted by further separation using a magnetic field, dividing the magnetic from the non-magnetic material. The non-magnetic
sample was then decanted into a heavy liquid for density separation. The solution was lithium heteropolytungstates (LST) in the form of highly soluble hydrated crystals. Grains with a greater density than the liquid sank and those less remained suspended or neutrally buoyant. The heavy crystals (including zircons) come to rest at the bottom of the vesicle from where they are drained. The heavy crystals are then washed in water and placed in an oven to dry.
Chapter 4

COFFINITE CHARACTERISATION

4.1 INTRODUCTION

This chapter deals with the characterisation of 17 samples of synthetic coffinite generated in this study (Table 4-1) encompassing XRD, NIR, and SEM (EDX). Analytical methods and synthesis details are discussed in chapter three. Suitable concurrence between synthetic coffinite separates and elementary chemical and crystallographic data was observed.

Table 4-1 | Temperature, Time, and pH constraints used for synthesising coffinite in this study and consequent precipitate yields.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Time &amp; Temp.</th>
<th>UCl₄ (g)</th>
<th>NaSiO₃ (g)</th>
<th>NaSiO₃ + UCl₄</th>
<th>NaOH</th>
<th>Buffer</th>
<th>Yield (g)</th>
<th>Total yield (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1.2</td>
<td>24 hrs @ 250 °C</td>
<td>1.8972</td>
<td>1.6113</td>
<td>2.52</td>
<td>11.5</td>
<td>9.22</td>
<td>0.604</td>
<td>1.1458</td>
</tr>
<tr>
<td>C2.2</td>
<td>24 hrs @ 250 °C</td>
<td>1.8978</td>
<td>0.6119</td>
<td>2.02</td>
<td>9.96</td>
<td>8.4</td>
<td>0.6148</td>
<td>1.2329</td>
</tr>
<tr>
<td>C3.2</td>
<td>24 hrs @ 250 °C</td>
<td>1.8969</td>
<td>0.6135</td>
<td>2.29</td>
<td>10.9</td>
<td>8.56</td>
<td>0.5762</td>
<td>1.0756</td>
</tr>
<tr>
<td>C4.1</td>
<td>24 hrs @ 250 °C</td>
<td>1.8976</td>
<td>0.6115</td>
<td>2.39</td>
<td>10.5</td>
<td>8.7</td>
<td>0.5865</td>
<td>1.1537</td>
</tr>
<tr>
<td>C4.2</td>
<td>24 hrs @ 250 °C</td>
<td>0.6124</td>
<td>2.64</td>
<td>10.15</td>
<td>8.48</td>
<td>0.5672</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C5.1</td>
<td>24 hrs @ 250 °C</td>
<td>1.8975</td>
<td>0.6115</td>
<td>2.44</td>
<td>10.17</td>
<td>8.56</td>
<td>0.5295</td>
<td>1.1106</td>
</tr>
<tr>
<td>C5.2</td>
<td>24 hrs @ 250 °C</td>
<td>0.6131</td>
<td>2.46</td>
<td>9.82</td>
<td>8.45</td>
<td>0.5811</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C6.1</td>
<td>24 hrs @ 250 °C</td>
<td>1.8973</td>
<td>0.6124</td>
<td>2.44</td>
<td>10.9</td>
<td>8.7</td>
<td>0.4774</td>
<td>0.9482</td>
</tr>
<tr>
<td>C6.2</td>
<td>24 hrs @ 250 °C</td>
<td>0.6172</td>
<td>2.46</td>
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<td>8.55</td>
<td>0.4708</td>
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</tr>
<tr>
<td>C7.1</td>
<td>48 hrs @ 250 °C</td>
<td>3.7978</td>
<td>1.2207</td>
<td>2.4</td>
<td>8.9</td>
<td>8.7</td>
<td>1.3018</td>
<td>2.8506</td>
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<td>C7.2</td>
<td>48 hrs @ 250 °C</td>
<td>1.2215</td>
<td>2.23</td>
<td>8.88</td>
<td>8.4</td>
<td>1.5488</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C8.1</td>
<td>144 hrs @ 250 °C</td>
<td>3.7986</td>
<td>1.2214</td>
<td>2.41</td>
<td>8.87</td>
<td>8.76</td>
<td>1.4224</td>
<td>2.8588</td>
</tr>
<tr>
<td>C8.2</td>
<td>144 hrs @ 250 °C</td>
<td>1.2214</td>
<td>2.4</td>
<td>10.71</td>
<td>8.95</td>
<td>1.4364</td>
<td></td>
<td></td>
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<tr>
<td>C9.1</td>
<td>144 hrs @ 250 °C</td>
<td>3.7967</td>
<td>1.2209</td>
<td>2.41</td>
<td>8</td>
<td>8.19</td>
<td>1.3437</td>
<td>2.6072</td>
</tr>
<tr>
<td>C9.2</td>
<td>144 hrs @ 250 °C</td>
<td>1.2209</td>
<td>2.62</td>
<td>8.29</td>
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<td>1.2635</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C10.1</td>
<td>24 hrs @ 250 °C</td>
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<td>1.2214</td>
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<td>8.72</td>
<td>1.5075</td>
<td>3.062</td>
</tr>
<tr>
<td>C10.2</td>
<td>24 hrs @ 250 °C</td>
<td>1.2227</td>
<td>2.69</td>
<td>9.05</td>
<td>8.77</td>
<td>1.5545</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
4.2 X-RAY DIFFRACTION (XRD)

On completion of coffinite synthesis each separate batch was ground to a fine powder for powder XRD analysis. All diffraction patterns for synthetic coffinite separates were matched with Bragg peaks defined from powder diffraction file (PDF 11-0420) for the same mineral (Fig 4-1). No trends were evident from the comparison of characteristic peaks and mineral synthesis conditions e.g. heating duration or pH of solutions. There were however some peaks characteristic of amorphous SiO$_2$ and nanometric UO$_2$ however no specific conditions could be identified causative of such by-products. These peak artefacts found in synthetic coffinites were also identified in other studies (Labs et al, 2013) where in some cases further processing was undertaken at the expense of coffinite preservation (Clavier et al, 2013). This approach was deliberately avoided due to concerns surrounding potential degradation of the final product and the nature of a later investigation relating to synthetic ore analogues, where it was considered that the existing material would be more applicable to the study.

![Figure 4-1](image)  | XRD patterns of synthetic coffinites showing the relationship between Bragg peaks for PDF 11-0420 (coffinite). Note minor phases of SiO$_2$ and UO$_2$ present in several batches of coffinite.
Figure 4-2 | NIR spectra of synthetic coffinite separates (a-e) NIRA II analysis, (f-j) TerraSpec®4 analysis.
4.3 NEAR INFRARED

Following crystallographic confirmation of coffinite, samples were examined using laboratory (NIRA II) and portable (TerraSpec®4) NIR instruments (Fig 4-2). Absorption features evidenced by Baron et al (2014) were replicated using both instruments for all separates. Despite the evidence of low intensity peaks for mostly amorphous silica and nanometric-UO₂, NIR spectral interference was not observed for these features (Bergmann et al, 2012; Griffiths and Hubbard, 1991).

4.4 SCANNING ELECTRON MICROSCOPY (SEM)

Prior to crushing coffinite for powder XRD, aggregates were prepared for examination under SEM using backscattered electron (BSE) imaging and energy dispersive x-ray (EDX) analysis (Fig 4-3). Semi quantitative analysis provided an ideal proxy for comparison to stoichiometric coffinite with a 1:1 ratio between U and Si (Table 4-2), results of synthetic coffinite were comparable to stoichiometric coffinite. In some cases, e.g. data point five (Fig 4-3; Table 4-2) elevated levels of uranium were detected. This result could be due to defects in the surface being measured due to topographic irregularities or a more likely influence due to the presence of nanometric UO₂. The precipitation of UO₂ is considered to occur when longer heating times are used during the hydrothermal synthesis. Ponteau et al (2009) suggests an instability of coffinite over time and noted longer heating times (84 h vs. 24 h) favouring the precipitation of greater proportions of UO₂, suggesting that coffinite decomposes over time to UO₂ and a Si-rich amorphous phase at 250°C.
In preparation for the synthetic mineral mixture part of the study (see chapter five) coffinite batches were dry mixed together for 20 minutes using a mechanical shaker. This combined coffinite mixture was then washed an additional 10 times using degassed water in an attempt to remove any uranyl sulphate that may have been present. On completion of oven drying, a pressed disk was then mounted for further SEM and EDX analysis. A similar approach was used to Szenknect et al, (2016) where the distribution of U/Si mole ratios for the entire coffinite mixture was examined as a proxy for overall mineral composition. Results show that the overall coffinite mixture was a relatively purified sample (Fig. 4-4).

Table 4-2 | Mol. % composition of point analysis defined in fig. 4.3, note U/Si mol. ratio being close to 1:1.

<table>
<thead>
<tr>
<th>Data point</th>
<th>U mol. %</th>
<th>Si mol. %</th>
<th>O mol. %</th>
<th>U/Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>18.67</td>
<td>18.05</td>
<td>63.29</td>
<td>1.03</td>
</tr>
<tr>
<td>2</td>
<td>19.42</td>
<td>20.14</td>
<td>60.44</td>
<td>0.96</td>
</tr>
<tr>
<td>3</td>
<td>18.65</td>
<td>19.72</td>
<td>61.63</td>
<td>0.95</td>
</tr>
<tr>
<td>4</td>
<td>19.33</td>
<td>19.96</td>
<td>60.72</td>
<td>0.97</td>
</tr>
<tr>
<td>5</td>
<td>38.56</td>
<td>22.20</td>
<td>39.24</td>
<td>1.74</td>
</tr>
<tr>
<td>6</td>
<td>18.58</td>
<td>21.66</td>
<td>59.76</td>
<td>0.86</td>
</tr>
</tbody>
</table>

Figure 4-3 | BSE image of coffinite aggregate C3.2 showing EDX semi quantitative wt. % spot element analysis and major element maps. Molar % are shown below in table 4.2.
This suggests that most of the U was either incorporated into coffinite during the hydrothermal phase of the synthesis or that the thorough purification method of washing the coffinite precipitate was effective in removing any soluble residues.

![Graph showing U/Si (mol. ratio) frequency distribution](image)

**Figure 4-4** | EDX point analysis of mixed coffinite showing U/Si mol. ratio (black), results from Szenknect et al, (2016) relating similar analysis to composition of synthetic coffinite separate. This distribution obtained in this study shows strong similarities between the purified and pure samples (in red).

### 4.5 SUMMARY

Hydrothermally synthesised coffinites used in this study were validated via XRD and SEM techniques. Spectra derived from laboratory and portable instruments yield appropriate features in concurrence with other research examining coffinite in the NIR spectrum. Frequency distribution of molar % U/Si ratios reveal a relationship between the mineralogical purity and speciation of the coffinite mixture. Comparison between XRD and EDX reveal a relatively purified sample with remnant UO₂ and SiO₂. No trends are identified in relation to XRD peaks and NIR features, this suggests limited to no effect on coffinite spectra in relation to minor impurities present. These results provided the required confidence to proceed with additional investigation of coffinite NIR spectral behaviours in synthetic polymineralic systems.
Chapter 5

QUANTIFYING COFFINITE IN SYNTHETIC MINERAL MIXTURES

5.1 INTRODUCTION

This chapter discusses the approach and methods used to quantify coffinite in synthetic and natural mineral co-additives which were combined in varying mixture concentrations in order to represent natural ore analogues. Infrared spectroscopy studies have demonstrated the ability to characterize and in some cases quantify mineral abundance of ores using chemometric analysis (Basile et al, 2010; Wells and Chia, 2011) or specific peak feature characteristics (Haest et al, 2012). Synthetic mineral mixture studies have demonstrated success in determining mixture composition and mineral species abundances (Sunshine and Pieters, 1993; Russell and Fraser, 1994). This chapter examines 18 mineral mixtures containing synthetic coffinite in varying concentrations and the spectral intensities of related features across the mixture dataset.

5.2 MINERAL CO-ADDITIVES

Mineral co-additives were chosen to generate synthetic mixtures similar to a uranium ore analogue. The mineralogy/composition of the synthetic mixtures used were determined based on the mineralogy of samples from the Valhalla uranium deposit located in Mount Isa, Queensland, Australia. Synthetic mixture compositions were defined from QEMSCAN™ studies on Valhalla ore (Wilde et al, 2013) (further defined in Chapter 6).

Mineral separates used in this study consisted of:
- Coffinite \( \text{USiO}_4 \)
- Chlorite \((\text{Mg,Fe})_{12}[(\text{Si,Al})_8\text{O}_{20}]\text{OH}_{16}\)
- Quartz \(\text{SiO}_2\)
- Zircon \(\text{ZrSiO}_4\)
- Glaucophane \(\text{Na}_2\text{Mg}_2\text{Al}_2[\text{Si}_8\text{O}_{22}]\text{OH}_2\)

Chlorite crystals were obtained from a garnet-bearing schist, where an in-water gravity separation method (Poppe et al, 2001) was used to separate required grain sizes from the
aggregate rock (see chapter 3). To remove surficial impurities large crystals of gem grade quartz and zircon were bathed in an aqua regia solution for 48 hours then rinsed thoroughly. Any crystals that contained visible inclusions or discolouration were excluded from the study.

Before mixing mineral co-additives together all separates with the exception of chlorite were ground in a ring mill to approximately \( \leq 5 \mu m \) in size. Chlorite was excluded from the grinding process as grains of the required size were able to be sorted using the initial water separation method and to reduce the risk of lattice damage to softer minerals in the ring mill. All separates were dried in a binder oven set at 30 °C for 48 hours prior to characterization analysis.

5.2.1 XRD and NIR characterisation
Separates were examined using a combination of XRD and NIR analysis (Fig 5-1). Each mineral co-additive was successfully validated against a powder diffraction file (PDF). Results provided confidence of mineral purity and NIR spectral behaviour prior to their inclusion in mixtures. All coffinite batches were mixed together and showed no differences to the sole batch measurements for XRD and NIR analysis (see Chapter 4).

Zircon was included in the study to investigate the ability to deconvolute spectra containing it and coffinite, as zircon is found in association with the U minerals at Valhalla. Zircon showed similarities with coffinite in NIR where they were observed to share an absorbance feature at 1500 nm and a proximal feature between 1105 and 1135 nm (Fig 5-1 b & d). The chlorite clay mineral displayed distinct absorption combination bands for Fe-OH at 2250 nm and Mg-OH at 2330 nm and a lesser OH overtone band at 1400 nm (Fig 5-1 f). A similar combination band for Mg-OH at 2300 nm was observed in glaucophane (Fig 5-1 h). Although all minerals were dried before analysis of NIR reflectance broad H₂O and/or OH absorbance bands were observed among the mineral separates. This was particularly the case for quartz.
(Fig 5-1 j) which is not reported to be particularly spectrally active in the NIR region. It is considered that these features are a product of fluid inclusions within the quartz crystal which may also result in more complicated OH bonding when the mineral is crushed to fine grains.

5.3 MINERAL MIXTURES

Mixture concentrations
In total 18 mineral mixtures were made with concentrations of varying proportions to the sum of 10 grams (Table 5-1). Three batches were created; batch one contained decreasing concentrations of coffinite with zircon being absent; batch two was composed of similar decreasing concentrations of coffinite with zircon present at a steady concentration (10 wt.%), coffinite concentrations in these batches ranged between 0.15 and 5 wt.% Batch three contained a steady concentration of coffinite (2.5 wt.%) and increasing concentrations of zircon (0.3-10 wt.%). Quartz was used as the incrementally increasing bulk mineral throughout the batches, this allowed for the modification of coffinite concentrations and more spectrally active minerals to remain at relatively constant proportions. To encourage homogeneity co-additives were physically mixed dry, using a mechanical shaker for a period of 15 minutes.
Figure 5-1 | XRD patterns with corresponding NIR spectra obtain from the NIRA II (a & b) coffinite; (c & d) zircon, whole crystal left hand side (LHS), crushed sample right hand side (RHS); (e & f) chlorite; (g & h) glaucophane; and (i & j) quartz.
Table 5-1 | Proportion of each mineral co-additive per mixture and corresponding mineral weight percentages (wt.%). Abbreviations Cof (coffinite), Zrn (zircon), Chl (chlorite), Qtz (quartz), and Gln (glaucophane). Batch mixtures are listed in order of decreasing coffinite concentration.

<table>
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<tr>
<th>Mix</th>
<th>Cof (g)</th>
<th>Cof wt.%</th>
<th>Zrn (g)</th>
<th>Zrn wt.%</th>
<th>Chl (g)</th>
<th>Chl wt.%</th>
<th>Qtz (g)</th>
<th>Qtz wt.%</th>
<th>Gln (g)</th>
<th>Gln wt.%</th>
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<td>70</td>
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<td>7.2188</td>
<td>72.188</td>
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<td>20</td>
</tr>
</tbody>
</table>

5.3.1 Major element chemistry
To obtain a proxy for uranium grade and as a measure of mineral concentration validation of mixture major element compositions were obtained by laboratory XRF (Table 5-2). As expected uranium values displayed a strong correlation to coffinite concentration ($R^2 0.9$) (Fig 5-2 a). Where zircon exceeded 1.25 wt.% in the mixtures (batches two and three) however uranium was observed to decrease slightly in relation to batch one. Although the concentrations for coffinite were similar between batches one and two it is considered that there was a small amount of dilution that may have occurred when adding additional zircon to the later batches which may account for the divergence in uranium concentrations evident between batch one and two.
Iron and magnesium concentrations show good agreement to chlorite values between batch one and two however the separation between batch two and three cannot be accounted for when considering the chlorite as the concentration (5 wt.%) is constant in both batches (Fig 5-2 b). It is considered that a combination of glaucophane and quartz may have contributed to this particularly where iron may have substituted for magnesium in glaucophane and iron possibly being contained within inclusions in the case of quartz. Sodium and magnesium values behave in accordance with the concentrations for glaucophane (Fig 5-2 c), where batches one and three share the same constant concentration (20 wt.%) and batch two differed proportionally due to lower concentrations of glaucophane (10 wt.%), a small degree of separation is observed between the Mg values of batches one and three. This separation is considered to occur due to lesser concentrations of chlorite (10 and 5 % respectively). A similar relationship is observed for sodium and calcium (Fig 5-2 d), which is considered a more direct measure of glaucophane concentrations.

<table>
<thead>
<tr>
<th>Mix</th>
<th>U$_2$O$_3$ (%)</th>
<th>ZrO$_2$ (%)</th>
<th>TiO$_2$ (%)</th>
<th>Fe$_2$O$_3$ (%)</th>
<th>SiO$_2$ (%)</th>
<th>Al$_2$O$_3$ (%)</th>
<th>CaO (%)</th>
<th>K$_2$O (%)</th>
<th>MgO (%)</th>
<th>Mn$_3$O$_4$ (%)</th>
<th>Na$_2$O (%)</th>
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</thead>
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<td>0.099</td>
<td>4.39</td>
<td>80.3</td>
<td>3.94</td>
<td>0.285</td>
<td>0.051</td>
<td>3.83</td>
<td>0.017</td>
<td>1.38</td>
</tr>
<tr>
<td>Mx6</td>
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<td>0.021</td>
<td>0.103</td>
<td>4.65</td>
<td>81.8</td>
<td>4.08</td>
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<td>0.047</td>
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<td>0.020</td>
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<td>79.1</td>
<td>3.98</td>
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<td>0.042</td>
<td>3.94</td>
<td>0.018</td>
<td>1.39</td>
</tr>
<tr>
<td>Mx3</td>
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<td>4.46</td>
<td>78.6</td>
<td>3.91</td>
<td>0.277</td>
<td>0.04</td>
<td>3.87</td>
<td>0.019</td>
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</tr>
<tr>
<td>Mx4</td>
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<td>0.010</td>
<td>0.112</td>
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<td>0.277</td>
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<td>3.96</td>
<td>0.019</td>
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<td>0.017</td>
<td>1.90</td>
<td>0.009</td>
<td>0.69</td>
</tr>
<tr>
<td>Mx10</td>
<td>0.395</td>
<td>3.63</td>
<td>0.038</td>
<td>2.35</td>
<td>83.5</td>
<td>2.05</td>
<td>0.148</td>
<td>0.016</td>
<td>2.01</td>
<td>0.014</td>
<td>0.71</td>
</tr>
<tr>
<td>Mx11</td>
<td>0.213</td>
<td>3.62</td>
<td>0.035</td>
<td>2.32</td>
<td>83.9</td>
<td>2.03</td>
<td>0.145</td>
<td>0.015</td>
<td>2.01</td>
<td>0.011</td>
<td>0.71</td>
</tr>
<tr>
<td>Mx12</td>
<td>0.096</td>
<td>3.59</td>
<td>0.042</td>
<td>2.39</td>
<td>83.7</td>
<td>2.06</td>
<td>0.149</td>
<td>0.014</td>
<td>2.04</td>
<td>0.013</td>
<td>0.71</td>
</tr>
<tr>
<td>Mx13</td>
<td>1.55</td>
<td>3.80</td>
<td>0.041</td>
<td>3.22</td>
<td>78.1</td>
<td>3.03</td>
<td>0.258</td>
<td>0.024</td>
<td>3.19</td>
<td>0.015</td>
<td>1.38</td>
</tr>
<tr>
<td>Mx14</td>
<td>1.62</td>
<td>3.50</td>
<td>0.041</td>
<td>3.36</td>
<td>82.1</td>
<td>3.13</td>
<td>0.281</td>
<td>0.025</td>
<td>3.31</td>
<td>0.016</td>
<td>1.45</td>
</tr>
<tr>
<td>Mx15</td>
<td>1.67</td>
<td>1.72</td>
<td>0.044</td>
<td>3.37</td>
<td>83.6</td>
<td>3.09</td>
<td>0.273</td>
<td>0.027</td>
<td>3.26</td>
<td>0.014</td>
<td>1.41</td>
</tr>
<tr>
<td>Mx16</td>
<td>1.64</td>
<td>0.856</td>
<td>0.044</td>
<td>3.30</td>
<td>84.8</td>
<td>3.05</td>
<td>0.274</td>
<td>0.024</td>
<td>3.21</td>
<td>0.013</td>
<td>1.41</td>
</tr>
<tr>
<td>Mx17</td>
<td>1.71</td>
<td>0.450</td>
<td>0.043</td>
<td>3.36</td>
<td>84.8</td>
<td>3.12</td>
<td>0.278</td>
<td>0.024</td>
<td>3.30</td>
<td>0.013</td>
<td>1.44</td>
</tr>
<tr>
<td>Mx18</td>
<td>1.66</td>
<td>0.221</td>
<td>0.047</td>
<td>3.28</td>
<td>85.6</td>
<td>3.04</td>
<td>0.266</td>
<td>0.024</td>
<td>3.18</td>
<td>0.016</td>
<td>1.39</td>
</tr>
</tbody>
</table>
5.3.2 Mineral mixture XRD analysis

Coffinite concentrations was not discernible from XRD patterns observed between mixtures or separate batches. Major mixture components of chlorite have distinguishing peaks which overlap coffinite features at ~ 19, 25, and 31 degrees from 2 theta. Quartz also has overlaps for coffinite at ~ 36 and 50 degrees from two theta (Fig. 5-3).

Two significant peaks for zircon are observed (~ 20 and 27 degrees from two theta) in all diffraction patterns in batch two where zircon was doped into the mixture at a steady concentration of 10 wt. %. Even at this relatively high concentration the diagnostic peaks for zircon are observed to be minor in magnitude in contrast to the other co-additives.

In batch three where the zircon composition was modified by halving the concentration starting from 10 wt. % in Mx13, diagnostic features for zircon are no longer evident at Mx15 which had a zircon concentration of 2.5 wt. %.
This suggests that coffinite being isomorphic with zircon would only be detectable at concentrations $\geq 10$ wt. % using XRD analysis.

Figure 5-3 | XRD patterns for minerals and batches in relation to coffinite bragg peaks. Note the low magnitude of zircon (zr) peaks in batch two mixtures.
5.4 MINERAL MIXTURE NIR SPECTRA

Mineral mixtures were examined with the Perking Elmer Frontier FT-IR/NIR fitted with a NIRA II attachment and compared with an ASD TerraSpec®4 IR spectrometers. In general, the characteristic spectral features unique to coffinite were observed in the mixtures using both NIR spectrometers (Fig 5-4) however the 1422 nm feature identified in the pure coffinite separate (Fig. 5-1 b) was not observable in any of the mixtures due to interference by the presence of strong O-H absorption features from glaucophane and to a lesser degree from chlorite. This feature also presented differently between the different spectrometers with the NIRA II showing multiple sharp absorptions whereas the TerraSpec®4 displayed a single broad feature at the same wavelength. Major mineral co-additives appeared to be concordant with their concentrations and peak intensities with the coffinite 1135 nm peak relatively strong throughout the mixture series and contrasting well against the broad peak between 1000 nm and 1200 nm considered to be the effect of the presence of both the chlorite and quartz.

The asymmetric shoulder of the 1135 nm feature seen in NIRA II spectra with high concentrations of coffinite was not as pronounced in measurements taken with the TerraSpec®4 for samples at the same concentration. Another feature which did not show good cross spectrum detection was the 1550 nm peak which was not readily observable in mixtures containing < 2.5 wt.% coffinite (< 1.6 wt.% U₃O₈) using the TerraSpec®4 (Fig. 5-4 b & d) this may be attributed to lesser capabilities associated to portable instruments and the magnitude of the discrete feature being measured. The NIRA II results for batch three (Fig 5-4 e) show a well-distributed set of spectra caused by a combination of variation in overall reflectance and diagnostic coffinite spectral features. This runs counter to some of the previous results observed in batches one and two, when considering that batch three was dosed with a continuous concentration of coffinite (2.5 wt.%).
It is likely that the increasing amount of zircon added to the mixture increased the sample’s overall albedo while also decreasing the absorption intensity for the coffinite peaks. The measurements taken from the TerraSpec®4 for the same batch (Fig 5-4 f) show a more repeatable relationship between the spectra however this may relate more to the TSG™ software processing which removes the overall observed albedo from the sample. Diagnostic peak intensities for coffinite were observed to behave in a linear nature relative to concentration throughout the mixtures. Strong correlations were observed across all the features with the NIRA II able to measure all the features throughout the sample set. The characteristic ~ 2:1 relationship between the 1550 and 1500 nm was evident throughout the mixtures offering a suitable intra-spectral metric for coffinite quantification. Minor variation in peak intensities was evident between batches one and two (Fig 5-4 a-d), where batch two showed stronger absorbance values for coffinite peaks. It is thought this may be due to the lesser amounts of spectrally active minerals in the second batch where there was 50% less chlorite and glaucophane than what was originally contained in batch one.
Figure 5-4 | NIR spectra from lab and portable spectrometers; (a) NIRA II batch one; (b) TerraSpec® 4 batch one; (c) NIRA II batch two; (d) TerraSpec® 4 batch two; (e) NIRA II batch three; (f) TerraSpec® 4 batch three.

5.5 PEAK INTENSITY METRICS

The sole peak intensity of absorbance features attributed to coffinite revealed strong correlations in relation to respective mineral concentrations using both laboratory and portable instruments (Fig 5-5). Due to differing results generated between the instruments and the *intra-spectral* behavior of the diagnostic peaks assigned to coffinite e.g 1550-1500 nm (Fig 5-5 f), feature ratios were investigated as a proxy for comparison between the instruments (Fig 5-6).
5.5.1 Feature ratios in relation to coffinite concentration

In most cases, there remained a loose spread between batch and instrument results however some ratios revealed strong correlations. This was evident for the 1550/1135 and 1550/1500 ratios (Fig 5-6 b & e) where $R^2$ values of 0.87 and 0.89 were obtained for the overall dataset respectively. The 1550/1500 results demonstrated strong linear correlations when examining the NIRA II and TerraSpec4 results in isolation (Table 5-3). Ratios for 1500/1135 did not reveal weaker cross correlations with the TerraSpec4 yielding an $R^2$ value of 0.3143, this demonstrates the limitations associated with portable instruments when dealing with such NIR absorption features.
These results offer a good foundation for linear regressions in the pursuit of quantifying coffinite in lesser constrained mineral assemblages.

Table 5-3 | Correlation coefficients and linear regression equations for select coffinite absorption feature ratios between the NIRA II, TerraSpec4, and both instruments combined. See plots (Fig 5-6)

<table>
<thead>
<tr>
<th>1500/1135</th>
<th>1550/1135</th>
<th>1675/1135</th>
<th>2130/1135</th>
<th>1550/1500</th>
</tr>
</thead>
<tbody>
<tr>
<td>NIRA II</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>R²</td>
<td>0.8833</td>
<td>0.8973</td>
<td>0.9089</td>
<td>0.7417</td>
</tr>
<tr>
<td>y</td>
<td>0.0185x + 1.0415</td>
<td>0.0226x + 1.0407</td>
<td>0.0275x + 1.0387</td>
<td>0.0125x + 1.0569</td>
</tr>
<tr>
<td>TerraSpec4</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>R²</td>
<td>0.3143</td>
<td>0.9026</td>
<td>0.4845</td>
<td>0.0968</td>
</tr>
<tr>
<td>y</td>
<td>0.0139x + 1.0816</td>
<td>0.0363x + 1.0134</td>
<td>0.0239x + 1.0859</td>
<td>0.0085x + 1.0943</td>
</tr>
<tr>
<td>Instruments combined</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>R²</td>
<td>0.4458</td>
<td>0.8742</td>
<td>0.5671</td>
<td>0.1463</td>
</tr>
<tr>
<td>y</td>
<td>0.0167x + 1.06</td>
<td>0.0268x + 1.0358</td>
<td>0.0263x + 1.0605</td>
<td>0.0093x + 1.0792</td>
</tr>
</tbody>
</table>

Figure 5-6 | Scatter plots showing the differing reflectance ratios derived from coffinite features relative to coffinite concentration; (a) 1500/1135 nm; (b) 1550/1135 nm; (c) 1675/1135 nm; (d) 2130/1135 nm; and (e) 1550/1500 nm.
5.5.2 Feature ratios in relation to uranium grade

Zhang et al (2001) utilised various IR feature ratios to investigate their effectiveness for quantitative analysis in binary and ternary mineral mixtures with varying degrees of success. In this study ratios 1500/1135, 1550/1135, and 1550/1500 displayed strong correlations to the uranium grade (Table 5-4, Fig 5-7). The 1550/1500 results in the NIRA II performed marginally better than the TerraSpec®4 and is probably due to the instrument sensitivity differential between laboratory and portable units. Results between the two instruments for the 1550/1135 metric differ yielding a stronger $R^2$ value for the TerraSpec4 however this is due to the limited results being recorded for this instrument due to the weak absorption feature only being recorded at coffinite concentrations > 2.5 wt.%. The ratio combining the two most prominent features (1500/1135) performed best using the NIRA II however there was a significant difference between all batches of the TerraSpec4 as well as comparing results of the same batches between both instruments. For this reason, it is considered this metric to be the least desired when determining uranium grade for coffinite in ores.

Table 5-4 | Correlation coefficients and linear regression equations for coffinite feature ratios in relation to $U_3O_8$ wt.% between the NIRA II, TerraSpec4, and instruments combined. See plots (Fig 5-7)

<table>
<thead>
<tr>
<th>Feature Ratio</th>
<th>NIRA II</th>
<th>TerraSpec4</th>
<th>Combined</th>
</tr>
</thead>
<tbody>
<tr>
<td>1500/1135</td>
<td>$R^2 = 0.8495$</td>
<td>$R^2 = 0.3011$</td>
<td>$R^2 = 0.4287$</td>
</tr>
<tr>
<td></td>
<td>$y = 0.0293x + 1.0411$</td>
<td>$y = 0.022x + 1.0813$</td>
<td>$y = 0.0264x + 1.0596$</td>
</tr>
<tr>
<td>1550/1135</td>
<td>$R^2 = 0.8608$</td>
<td>$R^2 = 0.896$</td>
<td>$R^2 = 0.8434$</td>
</tr>
<tr>
<td></td>
<td>$y = 0.0357x + 1.0403$</td>
<td>$y = 0.0636x + 1.0004$</td>
<td>$y = 0.0429x + 1.0344$</td>
</tr>
<tr>
<td>1550/1500</td>
<td>$R^2 = 0.9929$</td>
<td>$R^2 = 0.823$</td>
<td>$R^2 = 0.844$</td>
</tr>
<tr>
<td></td>
<td>$y = 0.0048x + 0.9989$</td>
<td>$y = 0.0081x + 0.995$</td>
<td>$y = 0.0061x + 0.9989$</td>
</tr>
</tbody>
</table>
5.6 SUMMARY

Through well constrained mineral mixtures containing known concentrations of coffinite, NIR feature intensities observed in coffinite are proportional to the concentration of coffinite in mineral mixtures. With the exception of the 1422 nm feature absorption peaks were identifiable throughout mineral mixtures using the NIRA II laboratory spectrometer. Major element analysis yields results show concurrence to mineral composition between the mixtures, especially between uranium grade and coffinite concentrations. The two best feature ratios identified for the measure of coffinite concentration are the 1550/1500 band ratio and the 1550/1135 band ratio respectively. These same ratios also provide a measure of uranium grade where coffinite is the only major uranium bearing mineral present.
Chapter 6

DEPOSIT GEOLOGY

6.1 GEOLOGICAL SETTING

The Valhalla uranium deposit is located 40 km north of the town of Mount Isa, north-west Queensland (Fig. 6-1). The deposit is situated within the multiply deformed and highly altered Western Fold Belt Subprovince of the Mount Isa Inlier. The Proterozoic (541-2500 Ma) terrane is largely undercover however it demonstrates distinctive geophysical characteristics which exhibit a north-south trend extending from the Gulf of Carpentaria to the Cork Fault (Betts et al. 2006) which separates the Mount Isa Terrane from the Thompson Orogen (Spampinato et al., 2015), just south of Mount Isa.

Valhalla is one of 107 known uranium occurrences identified within the Palaeoproterozoic (1600-2500 Ma) metasediments and mafic volcanic rocks that belong to the Leichhardt River Fault Trough (McKay and Miezitis 2001). These occurrences are often lenticular to tabular, uraniferous zones hosted within packages of metabasalts and pelitic to psammitic metasediments of the Eastern Creek Volcanics (Fig. 6-2).
Most of these occurrences are subeconomic however Valhalla, Skal, Anderson’s Lode and Warwei-Watta represent significant U resources (Hutton et al, 2012).

Figure 6-2 | District stratigraphy for the Western Fold Belt Subprovince of the Mount Isa Inlier. Note U-Pb ages of units which bound the Eastern Creek Volcanics constrain the age of U mineralisation. Stratigraphic sequence adapted from (Page et al, 2000; Neumann et al, 2006) U-Pb ages contained within.
6.2 DEPOSIT RESOURCES AND GEOLOGY

Valhalla a metasomatite/albitite U deposit was discovered in 1954 from which time it has been mapped and drilled by four different companies who sought a minable uranium reserve within the Mount Isa district (Polito et al 2009).

6.2.1 Metasomatite/Albitite uranium deposits

These deposits are typified by the contemporaneous association between uranium mineralisation and metasomatism of the host rock by differing fluids (Pownceby & Johnson, 2014). Metasomatic fluid alterations result in sodic +/- carbonate assemblages (Cuney, 2009; Dahlkamp, 2009). Due to these strong sodic fluids parent host lithologies are often altered to an albitite a lithology primarily composed of albite (NaAlSi₃O₈). As such the terms metasomatite and albitite are often used interchangeably. These deposits form in strongly deformed rocks where mineralisation is structurally controlled by faults/shears which provide fluid pathways and suitable voids for uranium mineral precipitation e.g. veins selvages, brecciated stockwork.

6.2.2 Resources

The Western Fold Belt uranium deposits collectively have a JORC compliant resource (Table 6-1) of 104.6 Mlb (measured and indicated) and 37.5 Mlb (inferred) (“Resource Status Mount Isa,” 2017). Valhalla and Skal make up a large proportion of the uranium credit with the other satellite ore bodies being less voluminous in resources. When comparing the uranium endowment of these deposits to analogues globally (Fig. 6-3) they are of moderate grade and size. The Valhalla deposit being the primary focus of this study contains a uranium resource defined by 446 drill holes exceeding 93 km in length. The measured resource of 16 Mt averages 819 ppm with a 230 ppm U cut-off and contains ~ 13 100 t of U₃O₈.
Table 6-1 | JORC compliant mineral resource for the albitite stye uranium deposits in the Western Fold Belt Subprovince.

<table>
<thead>
<tr>
<th>Deposit</th>
<th>Cut-off ppm U_3O_8</th>
<th>Grade (ppm)</th>
<th>t U_3O_8 Mt</th>
<th>Grade (ppm)</th>
<th>t U_3O_8 Mt</th>
<th>Grade (ppm)</th>
<th>t U_3O_8 Mt</th>
</tr>
</thead>
<tbody>
<tr>
<td>Valhalla</td>
<td>230</td>
<td>16.0</td>
<td>819</td>
<td>13 116</td>
<td>18.6</td>
<td>840</td>
<td>15 662</td>
</tr>
<tr>
<td>Skal</td>
<td>250</td>
<td>14.3</td>
<td>640</td>
<td>9 177</td>
<td>1.4</td>
<td>519</td>
<td>3 430</td>
</tr>
<tr>
<td>Odin</td>
<td>250</td>
<td>8.2</td>
<td>555</td>
<td>4 534</td>
<td>5.8</td>
<td>590</td>
<td>3 324</td>
</tr>
<tr>
<td>Bikini</td>
<td>250</td>
<td>5.8</td>
<td>497</td>
<td>2 868</td>
<td>6.7</td>
<td>493</td>
<td>3 324</td>
</tr>
<tr>
<td>Anderson's Lode</td>
<td>250</td>
<td>1.4</td>
<td>1 499</td>
<td>2 079</td>
<td>0.1</td>
<td>1 639</td>
<td>204</td>
</tr>
<tr>
<td>Watta</td>
<td>250</td>
<td>5.6</td>
<td>404</td>
<td>2 260</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Warwai</td>
<td>250</td>
<td>0.4</td>
<td>365</td>
<td>134</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mirrioola</td>
<td>250</td>
<td>2.0</td>
<td>555</td>
<td>1 132</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Total and average grade: 16.0 819 13 116 48.3 711 34 320 31.1 547 17 016

Figure 6-3 | Grade and tonnage of metasomatic style uranium deposits; green dots are deposits listed in table 6.1, blue dots are various analogous deposits globally. Values for grade and tonnage for Mount Isa ore bodies obtained from Wilde et al, (2013).

6.2.3 Mineralisation

Uranium mineralisation is observed in various settings in the Mount Isa Inlier. Valhalla is recognised to be a form of epigenetic (Wilde et al, 2013) and shear hosted mineralisation (Hutton et al, 2012). The ore body is hosted in a thick package of metasediments that are bound by the metamorphosed basic Eastern Creek Volcanics (Fig. 6-4) in the Western Fold Belt.
Belt (Polito et al, 2009). Uranium is hosted in the north-south striking albitite with lesser amounts being found in the chlorite-rich schist located at the periphery; an increase in grade is associated with the plunge of the intersection lineation of bedding and the albitite host rock. (Wilde et al, 2013).

6.2.4 Ore assemblages
Mineral modal analysis via QEMSCAN (Fig. 6-5) revealed the ore to be largely composed of albite (NaAlSi₃O₈), the sodium rich plagioclase end member, with lesser amounts of the sodium rich amphibole riebeckite (Na₂(Fe²⁺₃Fe³⁺₂)Si₆O₂₂(OH)₂) (Wilde et al 2013). Other accessory phases include fluorapatite, anatase, chlorite, and lesser sulphides. Fabrics akin to rocks found in shear zones are apparent with strongly mylonitised and brecciated features throughout with varying degrees of albitisation. Samples observed in this study reflect the descriptions and classifications assigned by Polito et al (2009) and include:
**Moderately altered fine-grained sediment**

Moderately altered fine-grained sediment (MAFS) found at the extremities of the ore zone is observed to host relict sedimentary structures indicative of clastic sediments (Fig. 6-6 a). The clastic grains exhibit replacement by albite and lesser amounts of calcite and amphibole. Deformation of grains and mineral re-growths in the form of strain shadows and may present as multi or single phase sigmoidal type structures known as mineral fish (Passchier & Coelho, 2006). These mineral fish defined (Fig. 6.6 d lower left) are mostly composed of quartz throughout the Valhalla host rock.

**Laminated and intensely altered rock**

Laminated and intensely altered rock (LIAR) shown in (Fig. 6-6 b) demonstrate mineral partitioning between each lamination with mineral grains observed to grow in an elongated direction favouring the orientation of the lamination. This texture is similar to mylonites (Wilde et al, 2013).

**Figure 6-5** | QEMSCAN modal mineral analysis of Valhalla uranium ore data obtained from Wilde et al (2013).

**Figure 6-6** | (a) Moderately altered fine-grained sediment; (b) Laminated intensely altered rock; (c) Brecciated intensely altered rock; (d) lower left dashed line exemplifies sigmoidal feature of a quartz mineral fish & (e) Uraninite, hematite, dolomite, chlorite rock. Polished thin section slides taken for the purposes of coffinite NIR spectral validation in this study.
**Brecciated and intensely altered rock**  
Brecciated and intensely altered rock (BIAR) shown in (Fig. 6-6 c) displays cemented sub-angular to angular clasts ranging from millimetres to centimetres in size. This ore type is considered to host the best uranium grades (uraninite and coffinite) at Valhalla (Wilde et al 2013).

**Uraninite, hematite, dolomite, chlorite rock**  
Uraninite, hematite, dolomite, chlorite rock (UHDC) (Fig. 6-6 d & e) is considered to be rare within the deposit (Polito et al 2009; Wilde et al, 2013). Anastomising veins of uraninite, hematite, carbonate and chlorite are present which envelope sigmoidal grains of quartz.

### 6.3 ORE GENESIS

The source of uranium in the Mount Isa Inlier and the mechanisms responsible for concentrating it in economic proportions is much debated. Most recently McGloin et al (2016) proposed a mechanism where orogenic fluids mobilised elements including uranium hosted in highly metamict zircons. These fluids were considered to originate from granites rich in U-Th-K similar to the Kitty Plains Microgranite (KPM) a north- eastern component of the radiometrically anomalous Sybella batholith (Connors & Page, 1995; McLaren et al, 1999) which intruded the Eastern Creek Volcanics (Gregory et al, 2005). The fluids are thought to have accumulated along shear zones where they concentrated uranium. Cuney (2016) posits a different mineral source considering that the average concentration of U in zircon to be 764 ppm (Belousova et al 2013) instead favouring minerals like uranoan thorite and allanite where such phases can host up to 30 wt% and several wt% UO₂ respectively (Cuney and Friedrich, 1987) however these phases are not evidently abundant within the Mount Isa inlier.
McGloin and Tomkins (2016) do not contest the U tenor of uranoan thorite and allanite but cite Förster’s (2006) work on intermediate solid solutions in relation to U-Th-Zr in silicate systems, where minerals like uranoan thorite are akin to uranoan zircon and can host substantial concentrations of uranium. The high U-Th zircons examined in the KPM are interpreted to become metamict within ~100 Ma, thus allowing U, Zr, and REE mobility (McGloin and Tomkins 2016).

Polito et al (2009) conducted exhaustive work on Valhalla including hydrogen and oxygen isotope studies in an attempt to match signatures of spatially associated sedimentary sources including the underlying Bottle Tree Formation and nearby Mount Guide Quartzite (Fig. 6-2). It was noted that the $\delta D_{\text{fluid}}$ values in hosted in illite from the lower Mount Guide Quartzite (Polito et al 2006) are similar to those found in syn-ore forming amphibole at Valhalla however $\delta^{18}O_{\text{fluid}}$ values from the same source exceed the values observed in the same assemblage at Valhalla. This suggest that there are at least two or more fluids responsible for the mineralisation, thus supporting the claims by McGloin et al (2016) regarding an intrusive derived fluid source is most likely responsible for the ore at Valhalla.
DETECTION AND ABUNDANCE DETERMINATION OF COFFINITE IN URANIUM ORE

7.1 INTRODUCTION

Following the successful proof of concept to identify and quantify coffinite in mixtures analogous to uranium ore (Chapter 5), the Valhalla uranium deposit was examined to test the effectiveness of this new application on natural ore. This survey would involve studies on a series of diamond drill holes which intersected the ore body at various depths hosting a range of uranium concentrations. Successful IR spectral studies using mineral mixtures and applying them to natural samples have been demonstrated for bauxite (Basile et al, 2010), nickel laterite (Wells and Chia, 2011), iron (Haest et al, 2012) ores, and clay mineralogy (Zhang et al, 2001).

Despite the application of metrics outlined in Chapter 6 additional complexities are unavoidable when examining natural ore material. In the case of this investigation analysis is taken from consolidated rock (drill core) which differs to the powders engineered in the preceding chapter. Natural ore is often variable in grain size which in some cases can generate non-linear IR results for respective minerals (Milliken and Mustard, 2007). Variation in mineral species composition can also be problematic particularly where darker coloured minerals exist reducing IR reflectance precision (Chang and Yang, 2012). Peak overlaps with co-existing minerals may also generate difficulties in detecting the presence of specific mineral species.
7.1.1 Experimental (Material and Methods)
The initial survey employed the use of a portable UVVisNIR spectrometer (TerraSpec®4) and a portable XRF (Innov-X DP4000) (collection methods and instrument specifications are given in Chapter 3). Some 21 000 NIR and 1 900 pXRF measurements were taken from 51 drill holes (Fig 7-1). The NIR spectral survey was conducted with the intent on identifying coffinite utilising the 1500 nm feature defined by Baron et al (2015). Based on the findings regarding coffinite concentration in synthetic mixtures. This feature was considered to be intense enough in natural ore samples while having limited interference from other gangue mineralogy in the measured material. Some 200 intervals displayed the 1500 nm feature and were consequently sectioned from the drill core for further analysis. Selected drill core samples were also analysed using a laboratory NIR spectrometer (NIRA II), optical and electron microscopy, and powder Xray Diffraction (XRD).
Figure 7-1 | Satellite photograph of the Valhalla deposit area showing collar positions of drill holes surveyed. Albitite host rock shown in green is projected to the surface for reference (ore body does not outcrop at the surface)
7.2 INFRA-RED SPECTROSCOPY

A total of 155 samples displayed absorption bands at 1500 nm and 1550 nm – two bands which are found in the NIR spectra of coffinite. These bands were exclusively detected within the albitite host rock, chiefly within the confines of the uranium rich ore zone defined by company resource assays. These bands were found with varying intensities (Fig. 7-2).

Figure 7-2 | a) comparison between NIR spectra from the TerraSpec4 and the NIRA II instruments. Solid red lines are TerraSpec4; dashed blue lines are NIRAII spectra. b) inset of a showing the extent of the spectra depicted in c-j. Figures c-j show 1500 +/- 1550 nm features used to identify U-Zr silicates during the spectral survey of this study, note the magnitude of peak features in relation to overall NIR spectra (Fig 7-2 a).
In some cases, only the 1500 nm peak was discernible from analysis eg Figures 7-2 c) & j).

Due to the requirement of relating intra-spectral features to ascertain coffinite concentrations these occurrences were excluded from the quantification study. Some likely reasons for only seeing one band is 1) a high abundance of zircon and lower concentrations of coffinite; 2) in the sole Zr-U silicate mineral being measured abundance favoured the Zr end member; 3) interferences from other gangue minerals. Peak features for other minerals were also identified throughout the spectral survey, multiple sharp narrow bands at the 1400 nm and 2300 nm position are indicative of the sodic amphibole riebeckite \((\text{Na}_2\text{Fe}^{2+}_3\text{Fe}^{3+}_2\text{Si}_{8}\text{O}_{22})(\text{OH})_2)\), the multiple narrow peaks observed at ~1400 nm are similar to those observed in glaucophane the calcic amphibole endmember used as a mineral co additive in synthetic mineral mixtures discussed in Chapter five of this study. The chlorite features of the Fe-OH 2250 nm and Mg-OH 2330 nm were present throughout. The detection of these assemblages corresponds with those detailed by Wilde et al (2013) for the Valhalla deposit (see Chapter 6).

Some coffinite peaks defined by Baron et al (2015) and this study (Chapter 5, Fig. 5-1 b) eg. 1135, 1422, 1675, and 2130 nm are absent from the measurements taken on Valhalla ore. It is considered the absence of discernible peaks at these wavelengths is most likely due to the diversity of mineral speciation of the ore where many minerals have features that may overlap with these bands, in some cases these overlaps have intensities which exceed those expected for coffinite.
7.2.1 NIR results from drill core

Although the survey of drill core revealed 1500 nm +/- 1550 peak all samples that displayed the 1500 nm peak were checked (N=191) in relation to the synthetic mixtures discussed in chapter five. Results for linear regression based on the sole 1500 nm peak yielded poor results (Fig. 7-3), with values for coffinite in poor agreement with the actual concentrations of coffinite in synthetic mixtures. The TerraSpec®4 (Fig. 7-3 b) displayed more distribution in 1500 nm peak intensity and therefore a higher distribution in calculated coffinite concentration whereas the NIRA II (Fig. 7-3 a) presented with a tighter dataset in terms of 1500 nm intensity and coffinite concentration.

Calculated values for coffinite obtained from the TerraSpec®4 were almost three times greater than the NIRA II. The vast difference between the values may be due to the differing software used in processing the data from the TerraSpec®4 instrument. The values for reflectance between drill core and batches is a function of the differing albedo (shade/brightness) between the material being sampled. This variation in albedo is also seen throughout the drill core dataset for both instruments and exemplifies the requirement to utilise intra-spectral metrics for specific mineral features for the purposes of quantification.

Figure 7-3 | Scatter plots showing the relationship between the 1500 nm feature and know coffinite quantities in batches 1-3 with coffinite quantities calculated from linear regression based on batches 1-3. a) NIRA II measurements; b) TerraSpec®4 measurements.
7.2.2 Intra-spectral relationships
Due to the strong intra-spectral relationship observed for the 1550 and 1500 nm peaks in pure coffinite samples and the synthetic mixtures containing coffinite (Chapters 4 & 5), measurements of these features were compared to the synthetic mixtures and drill core (Fig. 7-4). Due to the subtle nature of the lesser 1550 peak fewer intercepts of drill core were detected for this feature. The NIRA II detected 96 and the TerraSpec®4, 86 intervals for this feature.

Both instruments yield strong correlations for the 1550 and 1500 nm features ($R^2 = 0.9$). The slope between drill core and batches 1-3 for NIRA II measurements (Fig. 7-4 a) demonstrates strong precision and accuracy for measured coffinite features as separate slope measurements between the two datasets are almost alike. Results seen for the TerraSpec®4 (Fig. 7-4 b) are constrained to a lesser extent however a strong similarity in slope is also evident. TerraSpec®4 results from the synthetic study (Chapter 5) only provided nine usable results demonstrating a 1550 nm peak with the feature undetectable at coffinite concentrations < 2.5 wt. % versus the NIRA II yielding a full set of 18 results at the 1550 nm feature detecting coffinite down to 0.15 wt. %.
The lesser reproducibility of data associated to portable instruments coupled with the difficulty detecting the subtle 1550 nm peak attributed to the difference in slopes between the synthetic mineral mixtures and drill core measurements from the TerraSpec®4. The lower precision and accuracy is also exemplified in the spread of the drill core dataset which can be readily seen when comparing both instruments.

These issues are easily observed when examining the frequency distribution between both instruments and comparison between both the 1500 nm and 1550 nm peak positions from measurements of the same instrument (Figs. 7-5 & 7-6). Distribution of the detected 1500 nm feature from measurements from the NIRA II (Fig. 7-5 a) are positively skewed favouring lower values of reflectance (absorption peaks of high intensity), values are more tightly distributed when comparing those from the TerraSpec®4 (Fig. 7-5 b). Detected values for the 1500 nm feature from the TerraSpec®4 favour a more negatively skewed distribution with favourable detection of less intense results, this suggests that the instrument has a lower degree of sensitivity than that of the NIRA II.

![Figure 7-5 | Frequency distribution plots for the 1500 nm features in drill core for; a) NIRA II measurements, b) TerraSpec®4 measurements.](image)

The subtler 1550 nm peak was less evident throughout the drill core data only being displayed 96 times versus 179 instances for the 1500 nm peak in from the NIRA II measurements and 86 times versus 191 from measurements by the TerraSpec®4.
Distributions shared the same trend in skewing for both instruments as those observed for the 1500 nm feature (Fig. 7-6). The general spread in distribution of the 1550 nm feature also reflected similarly with those seen for the 1500 nm from results of the same instrument.

7.2.3 Quantification of coffinite using intra-spectral metrics
Noting the strong correlative relationships between the 1550 and 1500 nm features demonstrated in drill core and synthetic mineral mixture data, ratio metrics from the mineral mixture study (Chapter 5) and linear regression results were applied to the drill core data to quantify coffinite (Fig. 7-7). Results from the laboratory based NIRA II spectrometer revealed a tight distribution in coffinite concentrations between 0.33 and 2.34 wt. % with no measurements detected below the approximate limit of detection of < 0.15 wt. % coffinite.

Results obtained from the portable TerraSpec®4 displayed a more distributed pattern regarding coffinite concentration from -3.91 to 45.97 wt. % coffinite, these calculated concentrations breach the confines of the synthetic mixture study for lower levels of detection and results at higher concentrations are unrealistic when considering the ore composition and overall uranium grades found throughout the Valhalla deposit (Wilde et al, 2013).
Again, the lesser capabilities surrounding precision and accuracy for portable instruments is demonstrated from these results. The synthetic mineral mixtures used as standards established the lower limit of detection to be approximately 2.5 wt. % when using the 1550/1500 ratio where the limiting factor was the detection of the 1550 nm peak feature.

Frequency distributions between instruments for the 1550/1500 ratio share a positive skew with the TerraSpec®4 being slightly more pronounced (Fig. 7-8). Distributions are more tightly confined for both instruments when comparing the ratio to separate 1500 and 1550 nm features this is due to the ability of each instrument to detect the subtle 1550 nm peak thus constraining the data distribution.
7.3 COFFINITE CONCENTRATION RELATIONSHIPS

Results of coffinite concentration obtained from the more realistic NIRA II findings were checked against deposit relationships, specifically depth and lithology while compared with associated U and Zr concentrations at corresponding intervals downhole (Fig. 7-9). All instances of quantifiable NIR features were observed to occur within the ore zone confined to the albitite and riebeckite (albitite subset) lithologies. Contact features eg. faults or boundaries between differing rock types did not demonstrate any strong associations for NIR coffinite values. Coffinite quantities did not demonstrate correlations between grades of U or Zr throughout assay or XRF datasets (Fig. 7-10).

Figure 7-9 | Strip logs for drill holes showing relationships between lithology, coffinite concentration (NIRA II results) U company assay + pXRF, Zr company assay + pXRF results. Scales remain unchanged for all plots, lithology plotted to depth of assay sampling.
7.4 X-RAY FLUORESCENCE

A portable XRF was used to obtain chemical analysis of the same points measured on the drill core for NIR analysis. This was conducted with the intention to investigate associations between detected coffinite mineralogy and geochemistry.

Details of data collection are set out in the methods section (Chapter 3). A total of 1902 XRF analysis were obtained throughout the deposit. The approach of analysing the same point with pXRF as the NIR study proved to be moderately valuable due to the fact that stronger correlations were observed between the pXRF analysis compared to company laboratory assay data.

This was demonstrated more so in the U chemical data (Fig. 7-10 a) where $R^2$ values for pXRF were 0.139 and assay data results with 0.007 values. Zircon $R^2$ values (Fig. 7-10 b) displayed a closer relationship between pXRF and assay $R^2$ values being 0.147 and 0.015 respectively.

Due to the presence of other uranium minerals in the ore (Wilde et al, 2013) it is not expected that there would be a strong correlation between coffinite abundance and U concentration. The disparity between the chemical values can also be explained by the difference and analytical and sampling methods used throughout the company dataset; for example some intervals were measured using laboratory XRF, inductively coupled mass spectrometry, and down hole gamma logging. In comparison to the point analysis approach used for the pXRF collection in this study which was considered more fit for purpose when comparing NIR results taken from the exact same material. It is considered for this reason that the chemical correlations are stronger for pXRF than assay chemical results. It should be noted that the coffinite concentrations exceed those expected to be seen for uranium concentrations in assemblages where coffinite is the sole or dominant uranium mineral.
This is obvious when observing the difference between the coffinite values for batches one and two (Fig. 7-10 a), this disparity suggests another mineral may also be responsible for the spectral results and may help to explain why there is a slightly stronger correlation observed in the pXRF zircon results. The concentration of Zr is much greater than that of U at many data points which also suggests that the mineral zircon is not entirely responsible for the spectral results observed in the Valhalla drill core NIR results.

7.4.1 Chemical compositional analysis
Analysis from NIR and pXRF were processed using the R software environment (R Development Core Team, 2008). A summary of the results (Table 7-1) provides an overview of the data. The geochemical data was investigated to examine elemental interrelationships. Due to particular elements having a significant proportion of analysis with values below the limit of detection (<LOD), eg. Th (85%); As, Bi, Mo, Rb, Cr, S (20-50%) it was considered prudent to examine this compositional analysis in the form of log-ratio transformed data (Boogaart, et al., 2014).
This approach allows the grouping of elements in the form of a dendogram (Fig. 7-11) according to their variance of the pair-wise log-ratios (Aitchison, 2003; van den Boogaart and Tolosana-Delgado, 2013). Uranium was observed to have a strong relationship with potassium while also being closely related to phosphorus, lead, bismuth, and zirconium. Potassium is probably related to a residual signature from potassium feldspar which was altered to albite while phosphorus is associated to apatite. Lead and bismuth’s association to uranium and zirconium is likely to be a function of radioactive decay as both elements are daughter products of uranium which are included into the crystal structure of the mineral zircon.

Rubidium also closely related is a high field strength element and is often found in association with uranium in many natural systems. This dendogram approach was also used with coffinite spectral features however they were not observed to show any relationship with uranium, as such further investigation was conducted using principal component analysis (PCA).
Table 7-1 | Summary of XRF data for intervals where spectral features associated with coffinite were observed, values in ppm unless otherwise stated.

|       | U  | Sr | Th | P  | S % | K % | Ca % | Ti % | V   | Cr  | Mn  | Fe % | Ni  | Cu  | Zn  | As  | Zr  | Mo  | Pb  | Bi  | Rb  |
|-------|----|----|----|----|-----|-----|------|------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| % of data < LOD | 0  | 0  | 85 | 0  | 22  | 0   | 0    | 0    | 0   | 28  | 0   | 0   | 1.9 | 2.5 | 0.6 | 36  | 0   | 42  | 0   | 46  | 49  |
| Max   | 5306 | 997 | 159 | 6959 | 5.2 | 4.09 | 38.3 | 2.78 | 1488 | 236 | 3680 | 23.3 | 133 | 8446 | 3199 | 83  | 49599 | 114 | 2657 | 1750 | 315 |
| Min   | 26  | 20  | 0  | 221 | 0   | 0.05 | 0.6  | 0.08 | 38  | 0   | 82  | 1.4  | 0   | 0   | 0   | 0   | 0   | 320 | 0   | 10  | 0   | 0   |
| Mean  | 1107 | 285 | 0  | 1260 | 0.7 | 0.37 | 9.8  | 0.98 | 383 | 37  | 996 | 9.4  | 52  | 324 | 169 | 10  | 6256 | 19  | 310 | 73  | 18  |

Figure 7-11 | Dendogram showing the chemical relationships from pXRF analysis.
**Principal Component Analysis (PCA)**

Principal components were checked to observe their degree of variance where principal components one and two demonstrated the most significant variances (Fig. 7-12 a). These components (PCs 1 and 2) were then plotted against each other (Fig. 7-12 b) to further identify inter-relationships of spectral and chemical features. The biplot demonstrates the relationship of chemical and spectral variables as a function of ‘closeness’ in relation to each vector. Again, uranium demonstrates strong relationships with K, Pb, P, Rb, Zr, and Bi and validates the results shown in the dendogram. The NIR 1500 and 1550 nm features plot a vector approximately 45 degrees from the uranium vector and much further from the Zr vector. The only element in this vector that is mineralogically associated to the 1500 and 1550 nm peaks is Th which can be included in thorite (ThSiO₄) which is isomorphic with coffinite. Although it is observed to have a relationship here it should be noted that 85% of the data points recorded Th at levels less than the instrument’s limits of detection. The paucity of Th data throughout the analysis means the relationship between the NIR features and Th is most likely unreliable.

![Figure 7-12](image)

**Figure 7-12** | a) Scree plot showing the degree of variance between principle components (PC) 1-10. b) Biplot for PCs 1 and 2 showing the relationship for chemical compositions and the 1500, 1550 position and intensity relationships.
The 1500 and 1550 nm feature intensities vector close to each other also demonstrating a
strong relationship this is also reflected in the spectral data from observations in both
synthetic mixtures and natural samples (Fig. 7-4).

7.5 SUMMARY

NIR spectral features of 1500 and 1550 nm indicative of coffinite +/- zircon are detectable
using both laboratory and portable spectrometers. The strong correlation between the
intensities of the 1500 and 1500 nm peak are repeated in natural ore material as observed
in the synthetic mineral mixtures study of this thesis. Utilising synthetic mixtures (Chapter 5)
as standards to quantify coffinite in ore, reasonable results were derived using the
laboratory spectrometer with results ranging from 0.33 – 2.4 wt. % coffinite. These values
plot within the confines of the concentrations used for the synthetic mineral study. Although
the portable spectrometer was able to identify the presence of the same spectral features in
drill core the results were much less reliable showing a much stronger variation, yielding
coffinite concentrations from 3.91 – 45 wt. %. These results are certainly unrealistic and
perhaps relate to the limitations associated to portable instruments eg. precision and
accuracy. These limitations would have a strong effect on recording reliable data on subtle
spectral features like the 1550 nm peak used to quantify coffinite in this study.

When comparing the concentrations of U and Zr with the spectrally derived mineral
concentrations there is a strong disparity between the two. Coffinite concentrations plot
well beyond those expected to be observed for uranium concentrations in a mono-mineralic
pure coffinite assemblage.

This is also the case when taking Zr values into and the mineral zircon into consideration and
suggests that the mixtures may not be entirely fit for purpose when applied to uranium ores
of this nature. The relationship between associated chemistry of coffinite +/- zircon
assemblages and NIR spectral features is tenuous and demonstrates the complexity and variation observed in natural less constrained material. To determine the effectiveness of these techniques further detailed validation is required.
Chapter 8

VALIDATION OF COFFINITE IN DRILL CORE

8.1 INTRODUCTION
Following the detection of coffinite using the 1500 nm coffinite peak from NIR spectroscopy and the quantification application developed in chapter five, validation of coffinite was pursued. Investigative techniques included; heavy mineral separation, XRD, NIR, and microscopy (optical and electron).

8.2 XRD OF OFF CUTS
Off cuts from all drill core intervals which yielded coffinite quantification based on linear regression using the standards were investigated using XRD in order to validate the presence of coffinite. For brevity six intervals (Fig. 8-1, blue labels) will be discussed in relation to their mineral content and XRD detection of coffinite, these samples are representative of the entire sample set.

Figure 8-1 | NIRA II results of the 1550/1500 nm metric plotted against coffinite concentrations derived from the linear regression of synthetic mineral mixtures (not plotted). Blue labels are diffraction patterns examined in this section, yellow labels are samples which were processed for heavy mineral separation (section 8.2).
The diffraction patterns (Figs. 8-2; 8-3; 8-4) are shown in decreasing order of coffinite quantities reported by the NIR method developed in this study. Strong peaks were observed for the sodic amphibole riebeckite (rbk), albite (ab) and lesser amounts of quartz (qtz) were observed in all XRD patterns of samples analysed. Less pronounced phases included carbonate minerals dolomite (dol) and calcite (cal). Some phases known to occur at Valhalla (Chapter 6) were absent from XRD patterns throughout the sample set including apatite, zircon, chlorite, sulphides, and Fe/Ti oxides (sphenes).

The absence of these minerals is most likely due to: 1) minerals being present in the form of an accessory phase (< 1 % of the ore by volume); 2) The XRD instrument being unable to detect particular phases even when present at concentrations > 5 %. This is evidenced in chapter five (Fig. 5-3) where known diffraction peaks for coffinite in well constrained mixtures ranging from 0.15 – 5 wt. % coffinite. Results from the synthetic mineral study also suggest that the limit of detection for coffinite via XRD analysis would be ~10 wt. %. This assertion is reasonable when considering the XRD patterns from batch three, mixtures 13 and 14 (Fig. 5-3) where isomorphic zircon is barely determinable at a concentration of five wt. % but far more distinctive at 10 wt. % in mixture 13.
Figure 8-2 | XRD patterns for samples; (a) VDDH083 132, (b) VDDH049 254. Mineral phases identified: albite (ab), calcite (cal), dolomite (dol), quartz (qtz), and riebeckite (rbk). Accentuated Bragg peaks for coffinite (PDF 11-0420) are shown for reference.
Figure 8-3 | XRD patterns for samples; (a) VDDH049 223, (b) VDDH082 140. Mineral phases identified; albite (ab), calcite (cal), dolomite (dol), quartz (qtz), and riebeckite (rbk). Accentuated bragg peaks for coffinite (PDF 11-0420) are shown for reference.
Figure 8-4 | XRD patterns for samples; (a) VDDH083 113, (b) VDDH063 86. Mineral phases identified: albite (ab), dolomite (dol), quartz (qtz), and riebeckite (rbk). Accentuated Bragg peaks for coffinite (PDF 11-0420) are shown for reference.
8.2 HEAVY MINERAL SEPARATION

With the intent of concentrating coffinite from samples at Valhalla to increase spectral feature signatures. Four, one meter sections of quartered drill core which displayed NIR coffinite features were processed using heavy mineral separation methods (Chapter 3). Samples were examined using laboratory based NIR spectroscopy. Due to equipment availability, the separate fractions were not examined using the TerraSpec®4. This section compares the results of the synthetic mineral mixture (Chapter 5) and drill core quantification studies (Chapter 7) with NIR peak features from the heavy mineral separates discussed herein.

8.2.1 NIR spectroscopy of separate fractions

Four samples which demonstrated NIR coffinite features and a wide distribution between the 1500 nm and 1550 nm bands were chosen for heavy mineral separation process. (Fig. 8-5):

1. VDDH037 320-321;
2. VDDH039 241-242;
3. VDDH064 52-53; and
4. VDDH081 60-61

This process separated out differing phases based on grain size, weight, and magnetism. The process is generally designed with the intent of separating zircons for U-Pb dating however on this occasion it was considered that the approach may suit for the extraction of coffinite which has similar physical properties.
Depending on the composition of the original sample, the heavy mineral separation process generates up to six sample splits. The final process being gravity separated in a solution of highly soluble-hydrated crystals known as lithium heteropolytungstates (LST) is where perceived crystals of zircon would be able to settle to the bottom of this solution and was the perceived settling point for the extraction of coffinite in the case of this study. This final fraction is known as the heavys split, results for the four samples which underwent this process vary widely and coffinite concentrations based on NIR methods developed in this study did not behave as first predicted (Fig. 8-6). Sample splits which only displayed NIR coffinite features are reported for each interval.

Figure 8-5 | Scatter plot showing the strong relationship between the 1500 nm and 1550 nm features observed in heavy mineral separate fractions taken from four different samples of Valhalla drill core. Original NIRA II drill core measurements are plotted for each respective sample included in the heavy mineral separation process.
This drill core interval contained the highest initial value of NIR coffinite abundance at 1.95 wt. % (Fig. 8-6 a). When processed the heavy fraction did undergo an upgrade in abundance with respect to NIR coffinite features however three parental splits displayed higher abundances in coffinite being; wifely split, mag frantz, and the highest being the non-magnetic frantz. This fraction demonstrated a NIR coffinite upgrade of 143 % to 4.75 wt. % coffinite.

**VDDH037 320-321**

On this occasion, the heavys component behaved as predicted with an upgrade to 1.8 wt. % coffinite (Fig. 8-6 b) or an improvement of 28 %. A 2.3 % reduction in NIR coffinite abundance was observed for the ultra-fine grained wifely component.
Discernible spectral features obtained from these splits demonstrated minimal upgrading in NIR coffinite abundance for most of the splits except for the non-magnetic frantz component (Fig. 8-6 c). This split demonstrated a 13 % upgrade from the initial drill core interval.

This interval displayed the most counter intuitive results with the heavys and magnetic frantz splits yielding downgrades of 3 % and 60 % respectively. The largest upgrade of 16 % is displayed in the ultra-fine grained wifely split with a NIR abundance of 0.9 wt. %.

8.3 ELECTRON MICROSCOPY OF DRILL CORE

Polished thin sections were examined using scanning electron microscope (SEM) fitted with complementary backscattered electron (BSE) imaging and energy dispersive x-ray (EDX) analytical capabilities. Polished thin sections examined using a raster search pattern for coffinite grains. Chemical values (Table 8-1) for coffinite displayed UO$_2$ as the dominant oxide species followed by SiO$_2$. Due to the nature of the sample and adjacent mineral phases additional species are present including, Fe$_2$O$_3$, Al$_2$O$_3$, MgO, CaO, NaO and TiO$_2$. The relationship to these phases is shown in figure 8-7. Lead was only detected in two of the grains and represents a daughter product of uranium decay. Oxides of Zr and P were detected in several grains, the presence of Zr is indicative of potential intermediate solid solution system between coffinite and zircon. Phosphorous is present in coffinites simply due to availability and inclusion into the mineral structure.

The results of additional chemical species are explained by Förster, (2006) where complicating factors experienced examining similar silicates were (1) voids and microcracks, (2) hexavalent U, (3) submicrometer-sized inclusions not recognised in BSE imaging, and (4) analytical artefacts from neighbouring phases. Another issue to be considered is whether
the instrument has enough power (Kv) to resolve distinctive peaks for respective elemental species, in the case of this study the detection of vanadium provides a good example of this. Both U and V share x-ray peaks close to each other and the results for V in this study are artefacts of U peaks within the EDX spectra. This is further demonstrated by the absence of V from whole rock geochemical data and absence of mineral phases which host the element (Chapter 7)
Table 8-1 | SEM, EDX chemical analysis of individual coffinite grains, values expressed at wt. % oxides. Values do not add to 100 % due to averaging of several analyses in each grain.

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8.3.1 Examination of coffinite grains

Coffinites were observed to occur as interstitial growths favouring cracks and to a lesser degree mineral grain boundaries. Grain sizes ranged from between three to twenty microns in diameter. Of the coffinites observed none were seen to host separate mineral inclusions or appeared crystalline in nature, lacking any discernible crystal faces.

Figure 8-7 | BSE image of coffinite and EDX mapping from ore presenting with 1500 nm and 1550 nm peak features. Chemistry expressed as elemental wt. %.

Two differing styles of coffinite mineralisation were observed being the crack filling type which was observed to favour the metamorphic fabric of the rock and be fractured in multiple places resembling a crackled texture (Fig. 8-8 a). The second being the interstitial growths (Fig. 8-7, 8-8 b & c). This second variety exhibited a more malleable texture sometimes presenting with a coliform like banding (Fig. 8-8 b) or blebs (Fig. 8-8 c). The crackled variety of coffinite is considered to have formed pre-syn deformation due to it’s fractured nature and the interstitial style is interpreted to have grown during late-post deformation.
8.3.2 U and Si molar relationships
Stoichiometrically the uranium and silicon molar relationships for coffinite are 1:1 this molar ratio offers a simple proxy to observe the chemistry of natural and synthetic coffinites and as demonstrated in chapter four is an ideal measure of mineral purity (Szenknecht et al, 2016). As such coffinite, uranium and silicon relationships were investigated and compared with synthetic coffinites from this study. The coffinites from the Valhalla deposit displayed lower molar values for U than Si (Fig. 8-9 a). This is obviously due to the genetic relationship of mineral growth in natural systems dependent on element availability as demonstrated in the data (Table 8-1) and varying conditions eg. pressure, temperature, redox, pH, and salinity. Ratios of U:Si in natural coffinites (Fig. 8-9 b) display a more narrow distribution in frequency withstanding minor outliers when compared with synthetic coffinite used in the mineral mixture study (Fig. 8-9 c).
It is difficult to validate the methods of NIR coffinite detection and abundance determination from results obtained in this study. Analysis of powder XRD throughout the dataset provides no indication of coffinite +/- zircon throughout the ore. Whole rock geochemistry (see Chapter 7) provides a tenuous indication of the potential of such minerals to exist with the ability to at least provide a loose spatial domain e.g. (Fig. 7-9). Difficulties in determining coffinite via XRD are most likely due to the mineral concentration of measured samples containing concentrations of coffinite below the limits of detection of the instrument. This issue is exemplified by the inclusion of zircon (isomorphic to coffinite) being difficult to detect in moderately complex mineral mixtures below 10 wt. %.

**Figure 8-9** | a) Scatter plot showing the relationship between U and Si mol. % for coffinite grains found at Valhalla and hydrothermally synthesised coffinites described in chapter four. b) Relative frequency distribution for U/Si mol. ratios of Valhalla coffinites. c) Relative frequency distribution for U/Si mol. ratios of synthetic coffinites from this study.

### 8.4 DISCUSSION

It is difficult to validate the methods of NIR coffinite detection and abundance determination from results obtained in this study. Analysis of powder XRD throughout the dataset provides no indication of coffinite +/- zircon throughout the ore. Whole rock geochemistry (see Chapter 7) provides a tenuous indication of the potential of such minerals to exist with the ability to at least provide a loose spatial domain e.g. (Fig. 7-9). Difficulties in determining coffinite via XRD are most likely due to the mineral concentration of measured samples containing concentrations of coffinite below the limits of detection of the instrument. This issue is exemplified by the inclusion of zircon (isomorphic to coffinite) being difficult to detect in moderately complex mineral mixtures below 10 wt. %.
The ore at Valhalla is more complex in nature e.g. mineral composition and grain size variation and therefore it is realistic for not coffinite peaks to be present in XRD patterns obtained in this study where the maximum NIR coffinite abundance was determined to be \(~2.34\) wt. \% (via NIR A II), which would make it very challenging to detect using XRD. Another challenge which should be considered is whether the coffinite grains remain crystalline or if they are an amorphous phase which may have eventuated due to radioactive decay (Lian et al, 2009), if so it would also not be possible to determine the presence of coffinite in the ore.

The variability displayed in the heavy mineral separate results is most likely accounted for due to the differing types and sizes of coffinite grains observed in the SEM component of this study. The non-uniformity in grain size often being very small, fractured, and often existing as interstitial growths could cause variability in where coffinite may be distributed throughout the separation process. Small grains of the crackled variety of coffinite may have easily been washed off into the ultra-fine grained portion of the heavy mineral split. Interstitial growths could have easily been retained in the non-magnetic frantz fraction if they were not disaggregated from other minerals in the ore e.g. albite or riebeckite.

8.5 SUMMARY

Due to the low concentrations of coffinite observed in Valhalla U ore and perhaps the crystallographic amorphous properties of coffinite it is difficult to cross correlate NIR coffinite abundance with XRD methods attempted in this study. Additional complementary methods may yield better results.

One such approach may be the employment of micro NIR in conjunction with raster mapping of the samples surface which may be in the form of a thin section slide of polished puck. Raster mapping based on the coffinite NIR features defined by Baron et al (2014) and those discussed in this study (Chapters 4 & 5) may provide a more rapid approach than
electron microscopy techniques. Coupling micro NIR spectral properties with other micro
chemical analysis such as electron probe micro analyser (EPMA) or laser ablation inductively-
coupled plasma mass spectrometry (LA-ICP-MS), would provide a stronger understanding of
coffinite NIR behaviour in relation to chemical properties. These approaches will remain
challenging due to the crystal size coffinite is found and can be synthesised to. This may also
mean these approaches are not yet possible with present day instruments as such advances
in this field may not occur until the development of next generation spectrometers.
Chapter 9

CONCLUSION AND RECOMMENDATIONS

9.1 CONCLUSION

Coffinite is demonstrated to be detectable via NIR in uranium ores and synthetic mineral analogues. Quantification is possible in well constrained mineral mixtures of known compositions however the effectiveness of this method to determine coffinite concentrations in natural samples is still questionable due to several unaddressed variables. Therefore, coffinite quantification determined from drill core should only be considered a rough proximation of mineral abundance based on the methods used in this study.

9.1.1 Unaddressed variables

The following are variables that require consideration when using the application of this NIR technique developed in this study and should be viewed as a caveat emptor for mineral spectroscopy of complex materials.

Mineral interferences

As Chang and Yang (2012) demonstrated the mineral composition of a rock which contributes to it’s overall shade can cause complications depending on the instrument and the particular spectral feature being measured. Uranium ores are no exception as dark minerals e.g. uraninite, chlorite, and organic materials can often be found on large proportions. Zircon which was demonstrated to have an overlap at 1500 nm (Zhang et al, 2002; Zhang et al, 2003) is also problematic and this NIR band was not able to be deconvolved through the synthetic mineral mixture approach (Chapter 5) of this study. The NIR properties of REE phosphate minerals characterised by Turner et al (2016) demonstrate additional similarities with coffinite where band are proximal to REE$^{3+}$ absorptions.
**Grain size variation**
In a complex ore material, it can be difficult to replicate all variables conceived including grain sizes. Which may vary by distribution spatially and by mineral species. The synthetic mineral mixtures developed in this study could not possibly reflect the grain size variation which exists in the Valhalla deposit or any other mineralised system for that matter. Synthetic mixtures demonstrated a linear relationship to coffinite concentrations however non-linear relationships are demonstrated to occur in pure and multiphase mixtures (e.g. Johnson et al, 1983; Mustard and Hays 1997; Milliken and Mustard 2007).

**Crystallinity**
The degree of structural order in a crystal in relation to the NIR spectral behaviour of coffinite is partially understood with in-situ pressure experiments conducted by Bauer et al (2014) however the last investigation to examine these effect in relation to NIR was conducted by Zhang et al (2009). Despite these empirical studies offering an understanding what pressure minerals in the U-Zr silicate system undertake phase changes towards scheelite-type structures (space group 4/mmm) at ≈15 GPa more useful investigations of the effects on metamictization (crystal destruction through α-decay) to amorphous crystal states under NIR are not yet reported.

**Water**
Except for investigations made by Verpoorter et al (2014) the combined effects of grain size and water on natural samples remain weakly defined. This may be problematic if applying this technique to online monitoring used in resource extractive environments where moisture from various inputs may cause interferences.

Measurements of relatively undisturbed material may also contain moisture from environmental inputs e.g. meteoric and phreatic sources which may interfere with diagnostic spectral identification. Interferences can occur at: 1410 nm and 1910 nm for bound water; 1460 and 1970 nm for adsorbed features (Bishop et al, 1994).
9.2 RECOMMENDATIONS FOR FUTURE STUDY

Due to the limitations of present day NIR spectrometers complimentary techniques should be investigated with the intent of proving the effectiveness of the present technique or improving upon it. Such complimentary techniques and approaches could include micro-spectral studies using both NIR and raman. Raster mapping using such techniques may quickly quantify U-Zr-Th silicate phases enabling quantification and validation of initial survey results derived from drill core in this study. The rapid identification of such features using these techniques may identify larger phases that can be investigated using LA-ICP-MS analysis.

Future investigations into NIR mineral spectroscopy in this field may include:

- Measuring the effects of radiation damage and how they affect both XRD and NIR properties of coffinite may also provide new insights in U physical interactions within silicate crystals.
- Investigate the spectral behaviour of coffinite in relation to grain size and temperature stability.
- Additional NIR multiphase studies containing zircon type minerals, REE$^{3+}$ minerals, uraninite and U$_3$O$_8$.

As with all research there are many avenues of investigation yet to be explored and tangible outcomes are the subject of time and continuous improvement of the technology used in such investigations. There is little doubt that the present understanding of NIR behaviour of such phases examined in this study will continue to expand over time as such technological advances occur.


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