# REMOTE SENSING APPLICATIONS FOR CARBONATITE ASSESSMENT AND MAPPING USING VNIR AND SWIR BANDS AT AL-UYAYNAH, UA E

By

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## A DISSERTATION

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#### ABSTRACT

## REMOTE SENSING APPLICATIONS FOR CARBONATITE ASSESSMENT AND MAPPING USING VNIR AND SWIR BANDS

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This dissertation undertakes the experimental analysis of multispectral reflectance data to remotely differentiate and lithologically map the extrusive carbonatites from the adjoining rock units in the Al-Uyaynah region located within the northeastern terrain of UAE. The study employs visible/near-infrared (VNIR), shortwave-infrared (SWIR) spectral measurements developed in the laboratory using ASD, Landsat OLI, and the Advanced Spaceborne Thermal Emission and Reflection Radiometer (ASTER) images of extrusive carbonatites in Al-Uyaynah metamorphic sole units. Chapter 1 of the study is a succinct overview of the entire effort. It also encompasses the context of remote sensing and the use of the reflected spectrum from visible to shortwaveinfrared in mineral exploration. In particular I focus on carbonatite identification and analysis for the purpose of geological mapping. In Chapter 2 of this study, I perform tests and analyses on new Landsat 8 image data over Al-Uyaynah- UAE so as to examine the validitity of this system for medium resolution distantly sensed reflectance measurements. Specifically, I examine the utility of Landsat 8 imagery to define carbonatite outcrops and relevant lithological components. Chapter 3 of the study examines the Thermal Emission and Reflection Radiometer (ASTER) VNIR and SWIR data over the Al-Uyaynah region. In this Chapter I leveraged an existing low resolution geologic map, ASD laboratory measurements, and field data to examine the spatial distrubtion of carbonatites, alkali volcanics, metavolcanics, and an ophiolite complex using ASTER imagery. I further tested the efficiency of four different mapping algorithms for their utility in effectively

discriminating between the units and their locations. Chapter 4 of my dissertation examines the relationship between the composition and spectral charachteristics of carbonatite rocks. In this Chapter, carbonatite samples were examined spectrally within the visible near infrared (VNIR) and short wave infrared (SWIR) bands using a lab-based spectroradiometer device (ASD). The carbonatite rocks samples, were analyzed geochemically to determine the major oxides components in the weight percentage (wt%) using X-ray fluorescence (XRF). Inductively Coupled Plasma-Mass Spectrometer (ICP-MS) techniques were then applied in order to determine the rare earth elements (REEs) concentrations in the carbonatites. The ASD spectra and the chemical analysis results offered us a deep understading of the connection between the rock composition and spectral behavior of Al-Uyaynah carbonatite rocks. In Chapter 5 of this study, the entire research effort is combined in a synthesis that links the outcomes from each chapter into a comprehensive study of the spectral characteristics of carbonatites from the Al-Uyaynah region. Pathways for further of research are also recommended. This investigation is significant as it presents: (1) New ways of employing multispectral systems, Landsat 8 and ASTER, for use in the geological mapping of carbonatites; (2) Methods to recognize the mineralogical indicators for ferro/calcio-carbonatites; (3) evalutions of mapping algorithms and creates rankings based on their precision and accuracy for utilization in complex metamorphosed geologic terraines.

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# TABLE OF CONTENTS

LIST OF TABLES	ix
LIST OF FIGURES	X
CHAPTER 1	1
DISSERTATION PHASES AND BACKGROUND	1
1.Introduction	1
2.Carbonatite	5
2.1.Carbonatite definition and subtypes	5
2.2 Carbonatite petrogenesis	8
2.3 Rocks spatially connected with carbonatites	9
2.4 Carbonatite tectonic settings	11
2.5 Economic significance of carbonatite	13
3.Detecting, assessing, and analyzing carbonatites and surrounding rock units at Al-	
Uyaynah, UAE using remote sensing techniques	17
4. Understanding carbonatite chemistry using spectral analysis devices (ASD) and	
geochemical approaches	22
5.Dissertation phases	22
REFERENCES	24
CHAPTER 2	30
CARBONATITE IDENTIFICATION USING LANDSAT 8 VNIR-SWIR BANDS AT A	L-
UYAYNAH, UAE	30
Abstract	30
1.Introduction	31
2.AI-Uyaynah	33
3. Methods	34
3.1.Landsat 8 data calibration	34
3.2.Landsat data analysis	37
3.3. Field work and ASD spectral measurements	37
3.4. The spectral angle mapper (SAM)	38
4.Results	38
4.1.The image processing results	38
4.2.Carbonatite endmember spectral characteristics	42
4.2.1.The ferro-carbonatite	42
4.2.2. The calcio-carbonatite	44
4.2.3. The difference between ferro/calcio-carbonatite endmembers	46
4.2.4.Other endmembers	46
4.3. The SAM classification results	49
5.Discussion	49
5.1.Distribution of calcio/ferro-carbonatites units	53
5.2. Distribution of other non-carbonatite units	54
6.Conclusion	55

APPENDIX	57
REFERENCES	59
HAPTER 3	63
COMPARISON OF MAPPING METHODS AND SPECTRAL ANALYSIS TO	
STER DATA AT AL-UVAVNAH AREA UAE	63
Abstract	63
1 Introduction	65
2 Geologic background of study	68
2.1 Carbonatite location and outcrops	60 68
2.1 Carbonaute rocation and outerops	00
3 Methods	71
3.1 ASTER data calibration	71
3.2 ASTER data analysis	71
3.2.1 Dimensionality reduction	72
3.2.7 Endmember extraction	72
$3.2.2$ Endmember extraction $\frac{1}{1000}$	75
3.3 Classification methods	75 77
3.3.1 The Binary Encoding Classification (BEC)	77
3.3.2 The Spectral Information Divergence (SID)	79
3.3.3 Spectral Angle Mapper (SAM)	77 80
3.3.4 Support Vector Machines (SVM)	80
3.4 Post classification assessments	02 8/
4 Field surveys and ASD measurements	0 <del>4</del> 86
4. Field surveys and ASD measurements	80
5.1 Noise reduction and andmembers extraction	07
5.1 Noise reduction and endmembers extraction	07
5.2 Englishe	91
5.2.1 Calche	91
5.2.2 Aikan ampinoole minerals	92
5.2.5 HOII IIIIIIetais	92
5.2.4 REE IIIIIelais	93
5.3 1 Dinery Encoding Classification (DEC)	94
5.3.2 Spectral Information Divergence (SID)	90
5.3.2 Spectral Angle Mapper (SAM)	90
5.3.5 Spectral Angle Mapper (SAM)	90
5.5.4 Support vector Machine (SVM)	97
U. Discussion and a combonation datasticn tool nonformance at an alternate locality	····· 9/
7. Testing 5 vivi as a carbonatile detection toor - performance at an alternate locality	110
O. UUIUUUUUUI	110
	113
KEFEKENUED	121
TAPTER 4	127
	141

DERIVING THE GEOCHEMICAL CHARACTERISTIC OF CARBONATITES USING VISIBLE NEAR INFRARED AND SHORT WAVE INFRARED	5
SPECTROSCOPY	
Abstract	
1.Introduction	
2.Background	
3.Study area location and geology	
4.Methods	137
4.1.Sample preparation	
4.2.Spectral Analysis using ASD	137
4.3.Geochemical analysis	
5.Results	141
5.1.Carbonatite Spectra	141
5.1.1.Calcite related absorption	141
5.1.2. Iron related absorption	
5.1.3.Rare earth element (REE) related absorption	145
5.1.4.Major element analysis by XRF	
5.2.Geochemical impact of weathering on major element composition	151
5.3.CIPW normative mineral composition	153
5.4. Trace element analysis by LA-ICPMS	154
6.Discussion	
6.1. The relationship between bulk composition and carbonatite spectra	
6.2. The spectra of a carbonatite weathered surface	169
6.3.Nd spectra absorption features in carbonatite rocks	170
7.Conclusion	
REFERENCES	175
CHAPTER 5	
CONCLUSION AND RECOMMENDATIONS	
1.Dissertation Synthesis	
2.Dissertation conclusion	
3. Recommendations and outlooks for carbonatite prospectors	

# LIST OF TABLES

Table 1.1. Occurrence of rocks accompanying carbonatites [Count is number of deposits; % is percentage of deposits with related rock type, data were acquired from USGS Open-File Report [1]
Table 1.2. Shows the rare earth element (REE)- Major bearing minerals [9]
Table 2.1. The values of threshold that used for dividing the results of statistical kappa coefficient degrees of agreement. From [3-5]. The values close or equal to 1.0 specify perfect agreement; while any values between 0.85-0.99 show excellent agreement, and any kappa coefficient values of between 0.75-0.85 would be a very good agreement. The lesser degree of agreement were classified as: good if the kappa coefficient values were between 0.4-0.55; fair agreement between 0.40-0.55 values; and kappa coefficient values between 0.4-0.05 or fewer show poor to no agreement. The SAM map accuracy assessment displays overall accuracy with 66.92%. Kappa Coefficient is 0.58, which falls into the 'good' category
Table 3.1. The values of threshold that used for dividing the results of statistical kappacoefficient degrees of agreement. From [52, 57].103
Table 4.1. Illustrates the major oxides distribution of selected Al-Uyaynah carbonatite samples evaluated using XRF. All carbonatite samples contain calcium concentrations 26-45 Wt. %. The lower concentrations of carbonate were recorded in ferro-carbonatites fresh and weathered samples and those ferro-carbonatites exhibit a higher abundance of iron and silica in comparison to calcio-carbonatites
Table 4.2. Shows the distributions of REEs of selected carbonatite field samples from Al-Uyaynah field. The REE (ppm) were analyzed by (LA-ICP-MS)
Table 4.3. Shows the CIPW normative mineral compositions were calculated for Al-Uyaynahcarbonatite samples from the whole rock XRF geochemical data

# LIST OF FIGURES

Figure 1.1. Illustration of the ranges of the electromagnetic spectrum showing the most crucial ranges for mineral sensing spectroscopy applications - the visible/near infrared (VNIR), and short-wave infrared (SWIR) [10]
Figure 1.2. Global distribution of Nb– and REE–bearing carbonatite deposits [6]7
Figure 1.3. Classification diagram of carbonatite based on its chemistry; modified from [12] 7
Figure 1.4. Displays the tectonic setting of Al-Uyaynah area within Arabian plat. (modified from [7])
Figure 1.5. Map of the northern eastern of UAE indicating the location of the Al-Uyaynah area and general geological units left, modified from [1, 2]. (b) ASTER 3,2,1 natural color image right
Figure 1.6. Rare elements (REEs) and selected high field strength element distribution in the mantle and earth's crust, which is normalized to CI chondrite [9]
Figure 1.7. Geological map of Al-Uyaynah area showing the extrusive carbonatites (modified from [8])
Figure 1.8. A comparison between the occurrence of rocks accompanying carbonatites [Count is number of deposits; % is percentage of deposits with related rock type, data used in this diagram were obtained from table3 of USGS Open-File Report [6]
Figure 2.1. A map of the northern eastern of UAE indicating the location of the Al-Uyaynah area and general geological units, modified from [1, 2], and Landsat 8 natural colored image of Al-Uyaynah area shows the location of study area (right)
Figure 2.2. A field view of Al-Uyaynah carbonatites (fig. 1), (a) shows the ferro-carbonatites outcrops of the northern end of the study area, (b, and c) show a close view of ferro-carbonatites. (d) Shows the extruded calcio-carbonatite, and (e, f) illustrates a close view of calcio-carbonatite. 36
Figure 2.3. MNF eigenvalue plot for study area (Al-Uyaynah). All MNF bands have eigenvalues values greater than 1. The lowest band (7) has eigenvalue equal to 1.23, which means it contains coherent data. However, the first three bands contain more spatially coherent information than the others

Figure 2.4. MNF images of Landsat 8 VNIR-SWIR bands for study area. Images 1-7, display a single gray band, while image 8 shows a combination of first three MNF bands (1, 2 and 3 as RGB). Image 9 shows natural color image (Landsat Bands 3, 2, 1 (RGB)) for comparison (Not MNF image)
Figure 2.5 Show a 3-D Scatter plot of the end-members data cloud (image bands 1-3 were used as plot axes). The identical rock units were characterized by the same color
Figure 2.6. ASD Resampled spectra to Landsat 8 of (a) ferro-carbonatite and (b) calcio- carbonatite
Figure 2.7. A laboratory reflectance spectra (ASD) of samples, (a) ferro-carbonatite and (b) calcio-carbonatite (left). (a) A zoom of spectral region 0.5-0.6 $\mu$ m of laboratory reflectance spectra (ASD) of REE absorption are near 0.589, 0.567, and 0.56 $\mu$ m, and (b) A zoom of spectral region 2000-2400 nm of laboratory reflectance spectra (ASD) calcite (CO <sub>3</sub> , MgO) REE absorption are near 2.32-2.35 $\mu$ m and calcite has weak absorption at 1.6 $\mu$ m
Figure 2.8. Landsat 8 image endmembers spectra of (a) calcio-carbonatite in red color and (b) ferro-carbonatite in green color; within VNIR-SWIR bands
Figure 2.9. The image n-D spectra were extracted from Landsat OLI image used in SAM classification
Figure 2.10. SAM n-D classification map of Al-Uyaynah area shows the extrusive carbonatites and the lithology unites
Figure 2.11. Geological map of Al-Uyaynah area shows the extrusive carbonatites (modified from British geological survey, 2006)
Figure 2.12. A Comparison between the rock units' distribution that classified correctly, in percent, of SAM map based on the results of the confusion matrix accuracy assessment. SAM method gave, overall, a good result after comparing SAM map to the field ground truth regions.
Figure 3.1. ASTER spectral transmittance of band pass filters were used in this research, modified from[13]
Figure 3.2. (a) Map of the northern eastern of UAE indicating the location of the Al-Uyaynah area and general geological units, modified from [23, 24]. (b) ASTER 3, 2, and 1 natural color image

Figure 3.3. A field view of Al-Uyaynah carbonatites (fig. 1), (a) shows the ferro-carbonatites outcrops of the northern end of the study area, (b, and c) show a close view of ferro-carbonatites.

(d) Shows the extruded calcio-carbonatite, and (e, f) illustrates a close view of calcio-carbonatite.

Figure 3.4. A MNF eigenvalue plot for study area (Al-Uyaynah). All MNF bands have eigenvalues values greater than 1. The lowest band (9) has eigenvalue equal to 2.53, which means it contains coherent data. However, the first 5 bands contain more spatially coherent information than the other bands
Figure 3.5 MNF images of ASTER VNIR-SWIR bands for study area. Images 1-9, display a single gray band, while image 10 shows a combination of first three MNF bands (1, 2 and 3 as RGB) for comparison
Figure 3.6. Show a 3-D Scatter plot of the end-members data cloud (image bands 1-3 were used as plot axes). The identical rock units were characterized by the same color
Figure 3.7. Shows a random sampling of pixels that were generated from the defined ROIs. These random pixels were used as a reference to assess the mapping outcomes of the BEC, SID, SAM, and SVM methods
Figure 3.8. Shows how the SAM method classifies the image. The smaller the angles between the endmember and pixel, the more of a match there exists with the endmember spectrum. Where pixels surpass the defined angle threshold, they are not categorized. The figure was modified from [37].
Figure 3.9. Linear Support Vector Machine illustration. The SVM training algorithm is used to find a hyperplane that divides the image pixels to a separate number of classes. Modified from [41, 42]
Figure 3.10. Laboratory reflectance spectra (ASD), showing REE absorption near 0.589, 0.567, and 0.56 $\mu$ m and (CO <sub>3</sub> , MgO) absorption near 2.32-2.35 $\mu$ m, and near 1.6 $\mu$ m for calcite absorption
Figure 3.11. The resampled laboratory reflectance spectra (ASD) of ferro-carbonatite and calcio- carbonatite
Figure 3.12. A zoom-in of the spectral region 0.5-0.6 $\mu$ m of laboratory reflectance spectra (ASD), showing REE absorption near 0.589, 0.567, and 0.56 $\mu$ m (left), and a zoom-in of the spectral region 0.2-2.4 $\mu$ m of laboratory reflectance spectra (ASD) showing (CO <sub>3</sub> , MgO) absorption near 2.32-2.35 $\mu$ m, and near 1.6 $\mu$ m for calcite absorption
Figure 3.13. ASTER image endmembers spectra of calcio-carbonatite and ferro-carbonatite; in VNIR-SWIR bands

Figure 3.19.	Geological map of Al-Uyaynah area showing the mapped area of extrusive	
carbonatites	(modified from [1]	102

Figure 3.20. A comparing of confusion matrix over all accuracy, and kappa coefficient results. The binary encoding classification (BEC) overall accuracy is 43.59%; the calculated Kappa Coefficient is 0.32. This recognized as No agreement 'not even poor results' in the classification standard category. The Spectral Information Divergence (SID) map shows a good discrimination among ferro/calcio-carbonatite and other the rock units. The accuracy assessment of the overall accuracy is 68.3%; the Kappa Coefficient is 0.58, which is known as "good results" in the category. SAM performs the second best result with an Overall accuracy of 81.54%. The calculated Kappa Coefficient is a mere 0.75 placing into the very good agreement category of the Kappa Coefficient statistic. The Support Vector Machine (SVM) digital-mapping results with an overall accuracy of 97.58%. The calculated Kappa Coefficient is 0.97. This recognized as excellent in the classification standard category. 103

Figure 3.21. A Comparison between the rocks unit's distribution that classified correctly, in percent, of BEC map based on the results of the confusion matrix accuracy assessment. BEC method gave, overall, the poorest result after comparing BEC to the field ground truth regions.

Figure 3.22. A Comparison between the rocks unit's distribution that classified correctly, in percent, of SID map based on the results of the confusion matrix accuracy assessment. SID method gave, overall, a fair result after comparing SID to the field ground truth regions....... 115

Figure 3.23. A Comparison between the rocks units' distribution that classified correctly, in percent, of SAM map based on the results of the confusion matrix accuracy assessment. SAM method performs the second best result, overall good agreement, after comparing SAM to the field ground truth regions
Figure 3.24. A Comparison between the rocks unit's distribution that classified correctly, in percent, of SVM map based on the results of the confusion matrix accuracy assessment. SVM method performs the second best result, overall an excellent agreement, after comparing SVM to the field ground truth regions
Figure 3.25. Shows the ferro-carbonatite layers that intruded into metasediments unit of the Hatta Zone. Modified from [3]
Figure 3.26. shows the location and the geological map of the Hatta zone Modified from [2, 3] 
Figure 3.27. The Support Vector Machine (SVM) digital-mapping of the Hatta carbonatite, shows the best result with an overall accuracy of 99.85%. The calculated Kappa Coefficient is 0.99
Figure 4.1. The range of the electromagnetic spectrum, showing most crucial ranges for minerals sensing spectroscopy applications. The visible/ near infrared (VNIR), and short-wave infrared (SWIR), modified from [17]
Figure 4.2. A field view of Al-Uyaynah ferro-carbonatites, (a) shows the ferro-carbonatites outcrops of the northern end of the study area, (b, and c) show a close view of ferro-carbonatites. (d) hand sample from ferro-carbonatite area
Figure 4.3. A field pictures of Al-Uyaynah calcio-carbonatites (a) shows the calcio-carbonatites outcrops of the northern part of the study area, (b, and c) show a close view of clacio-carbonatites. (d) a hand sample calcio-carbonatite
Figure 4.4. Example of the field spectra of ferro-carbonatite. The original reflectance graph in red, and the reflectance after applying the continuum removal method in green. Absorption depth, area, and center are labelled
Figure 4.5. Shows calcite absorption bands in USGS spectra library (left) [36], and calcite absorption area which recorded in calcio-carbonatite (right). The absorption was observed in the area between $2.312-2.345 \mu m$ , and the deepest absorption point was recorded at $2.34 \mu m$ of fresh calcio-carbonatite.
Figure 4.6. Illustrates calcite absorption bands in ferro-carbonatites. The absorption was between $2.312-2.345 \mu m$ of the spectra wavelength, and the deepest absorption point was at $2.34 \mu m$ of much of ferro-carbonatites

Figure 4.16. Relationship between neodymium concentrations (ppm) and the spectra absorption depth of carbonatites spectra. The neodymium absorption depths were calculated based on

Figure 4.19. Shows the absorption center ranges of Nd measured from the carbonatite spectra.

# **CHAPTER 1**

#### DISSERTATION PHASES AND BACKGROUND

## **1.Introduction**

Remote sensing science is characterized by the evaluation and examination of data obtained from indirect physical interaction with the materials or objects [13]. In this study, remote sensing denotes the procedures used to measure electromagnetic energy as photons reflected by earth surface materials. Remote sensing acquires electromagnetic energy in distinct ranges of wavelength bands [14]. Remote sensing sensors usually analyze the electromagnetic energy at distinct wavelengths that are reflected, scattered, and emitted from Earth's materials all through the electromagnetic energy spectrum, from nearly 0.3 to 15  $\mu$ m[15]. The reflective spectrum covers the ranges of about 0.38 to 3.0 µm; it characterizes that portition of the solar reflected energy, or spectrum, that is utilized specifically in remote sensing [15], and especially useful in identifying geological materials and mapping. According to many scholars e.g., [14, 16], differences in the electromagnetic spectrum are likely the consequence of the interaction between the electromagnetic waves and components of the rocks/materials (e.g., elements and minerals). This process thus allows for the remote recognition of Earth materials by detecting the reflected energy, and also possibility of mapping of the distribution of these minerals based on their spectral characteristics. The electromagnetic energy emitted or radiated from the sun has been modeled by

a 6000° K blackbody curve [14]. Solar radiation or energy passes through the atmosphere in particular transmission windows. These windows allow the shorter visible (VIS) from 0.38 - 0.72 µm, near-infrared (NIR) from 0.72 - 1.3 µm, and shortwave-infrared (SWIR) from 1.4 - 2.5 µm, to reach the earth surface, which are then partially absorbed and re-emitted or reflected. It is theese reflected waves that are recorded by remote sensing sensors [14, 15].

Since the early 1960s, the scope of remote sensing has broadened extraordinarily in terms of its application to geological mapping and mineral exploration. At its inception, remote sensing was employed as a quick and cost-effective way to analyze to spatial variations in lithology [17, 18]. During the 1970s, geologists employed remote sensing techniques using airborne systems [19]. Further advances came in the early 1980s with the development of hyper-spectral methods for Earth analysis [20]. The spectral resolution used in the modern-day remote sensing has greatly improved and is now particularly useful for distinguishing mineral types and rock groups [16, 18, 20]. Specifically, it has been shown that a broad range of minerals such as carbonates, clays, and hydroxides can be sensed through this method (e.g. [21]). The empirical literature showed the capability of the remote sensing approaches to identify and map minerals and rocks based on its particular spectra which are significant for exploring the mineral deposits [22-24]. The multispectral platforms employed in the past, i.e., TM and Landsat MSS, have been employed for analyzing structures and common geomorphic surveys on a large scale [24, 25]. The Landsat TM system has been employed for the surveying of minerals by using the absorption features in two SWIR bands sensitive to alteration minerals in particular [25, 26]. The Advanced Spaceborn Thermal Emission and Reflection Radiometer (ASTER) expanded remote sensing capabalities to include the visible/near infrared (VNIR), short-wave infrared (SWIR), and thermal infrared (TIR)

spectra, which have great significance in mineral surveying [27]. The ASTER sensor is capable of detecting more bands than previous sensors, which allows geologists to chart rocks and minerals on the surface of the earth with more precision and accuracy [26, 28].

The ranges between 0.45 to 2.5  $\mu$ m of the reflectance spectra wavelengths are considered an essential part of the spectrum for geo-remote sensing applications (Figure 1.1). These ranges can be utilized in defining the composition of minerals on the basis of absorption characteristics [29-31]. Carbonatites that are enriched with about fifty percent or more of calcite minerals display a strong absorption feature of the CO<sub>3</sub><sup>2-</sup> ion, which is recognized easily within the range of 2.2-2.33  $\mu$ m [32]. The iron minerals and REE elements, which may found in ferro-carbonatite in abundance, also impact reflectance spectra. The iron absorption characteristics exhibit a distinctive absorption and are pronounced within the window of 0.9-1.3  $\mu$ m [21]. REE absorption features are principally linked to electronic transitions in Nd<sup>3+</sup>, which generates absorption characteristics in the wavelength ranges between 0.5 and 0.8 um [30, 33]. A blend of these absorption features could yield a basis for the creation of carbonatite maps using remote-sensing data.

The reflection spectra properties of carbonatites have previously been applied to prior investigations to produce maps of carbonatite complexes using aircraft sensors. AVIRIS (Airborne Visible / Infra-Red Imaging Spectrometer) data were employed to identify the Ice River carbonatite complex and showed slight absorption properties



**Figure 1.1.** Illustration of the ranges of the electromagnetic spectrum showing the most crucial ranges for mineral sensing spectroscopy applications - the visible/near infrared (VNIR), and short-wave infrared (SWIR) [10].

located at 0.58, 0.74, 0.80, and 0.87 um, which suggest a neodymium absorption feature [34]. Likewise, novel investigation of the Sarfartoq carbonatite in Greenland was carried out by adopting a mix of spectral techniques to separate between carbonatite, fenite, and hematised rocks, with a special focus on the Nd<sup>3+</sup> reflectance feature [35]. Generally, little attention has been paid to detecting carbonatite occurrences using satellite-based sensors.

In this research, we have focused on examining in what way remote sensing approaches can be employed to observe carbonatite distribution. These rocks, which contain minerals rich in rareearth elements (REE), have substantial economic significance. This study analyzed the spectral characteristics of carbonatites by employing Landsat 8 and ASTER datasets to map the spatial distribution of Al-Uyaynah carbonatites in UAE. This research offers new ways to more efficiently understand carbonatite spectra and map carbonatite distribution. We anticipate that our work will result in the development of techniques for REE ore deposit exploration and investigation.

### 2. Carbonatite

### 2.1. Carbonatite definition and subtypes

Carbonatite is defined based on its major minerals, and in the IUGS system of categorization as igneous rock that comprised of carbonate minerals with modal percent exceeding 50 % [36]. The sub-types of carbonatite are defined as below:

(i) A rock is referred to as a calcite carbonatite, or calcio-carbonatite, when the dominant carbonate mineral is calcite. The term sövite is applied if the calcio-carbonatite is coarse-grained, and alvikite if it is fine-grained. Although both sövite and alvikite are calcio-carbonatites, they can exhibit distinctly different chemical compositions with regards to trace elements [37].

(ii) The "ferro-carbonatite" name was used for around thirty years, however, is not defined adequately [38]. The IUGS system determines it as a carbonatite mineralogically where the major carbonate minerals are rich in iron, but chemically was defined as a carbonatite [36, 38]. Gittins and Harmer recognized these difficulties and recommended the use of the term "ferro-carbonatite" for Fe-rich carbonatites only for cases in which the modal mineralogy of the rocks is unknown i.e. that the ferro-carbonatite expression should be utilized, and use of terms such as "siderite carbonatite, magnetite-calcite carbonatite, etc. for cases in which the modal mineralogy is known [38].

(iii) Magnesium-rich carbonatites are dolomite-bearing and occasionally are referred to as "beforsite," although this term is becoming obsolete; the terms dolomite carbonatite or magnesiocarbonatite are currently preferred [39].

(iv) Natro-carbonatite is a fine-grained carbonatite lava composed primarily of nyerereite and gregoryite [(Na, K)<sub>2</sub>CO<sub>3</sub>]. This is an exceptionally rare carbonatite form, and its occurrence is at present restricted to Oldoinyo Lengai, Tanzania [40].



Figure 1.2. Global distribution of Nb- and REE-bearing carbonatite deposits [6].



Figure 1.3. Classification diagram of carbonatite based on its chemistry; modified from [12].

Carbonatites have been found at many locations worldwide. These locations were plotted on a global map [6] by the U.S. Geological Survey (USGS) Mineral Resources Program (Figure 1.2). In this research our study area, Al-Uyaynah, is one of these areas where carbonatite is known to exist. It was discovered by Woolley and others in 1991. They found two particular magma types (calcio and ferro-carbonatites), that comprise the Al-Uyaynah carbonatite [41]. These two varieties of carbonatite, represent the majority of carbonatites found globally (Figure 1.5, and 1.7), and therefore they are useful analogs for studies of carbonatites more broadly. We utilize existing geological studies of our region to provide structural, mineralogical, and chemical data that are the basis for the current research effort [41].

### 2.2 Carbonatite petrogenesis

The concept of carbonatite magma was initially proposed by Eckermann in 1948 [42, 43]. It was not, however, fully accepted by the scientific community at that time [42, 43]. In 1960-61, sodium-carbonate lava erupted from the Oldoinyo Lengai volcano in Tanzania[44]. The observation and successful experimental studies performed on carbonatite-melts (e.g. [45-47]), which seemed to confirm their existence, settled many of these initial arguments. Globally in 1987 about 56 carbonatite occurrences had been identified [48, 49], but this number has grown and there are currently more than 500 carbonatites known [50]. Since carbonatite was initially discovered, many arguments have centered on the existence and definition of carbonatite magmagenesis [51-53], and these issues persist to this day [54]. Despite the continued ambiguity in terms of carbonatite origin, studies on these unusual rocks have progressed dramatically in terms of our

undertanding of their phase stability, major and trace element characteristics and isotopic fingerprints [55].

In the period before 1960, there was little recognition of the role of the mantle in the genesis of carbonatites and indeed the role of the mantle for the genesis of very alkalic rocks in general [54]. In the early 1960s, the earth's mantle was documented as the source of the majority of carbonatite magmas, as the newly collected <sup>87</sup>Sr/<sup>86</sup>Sr data on carbonatites showed that it was actually of mantle origin [54]. While the utimate origin of carbonatites is considered to be mantle-derived, the precise mechansims by which carbonatite magmas are generated is still uncertain. Most modern scholars favor three primary carbonatite generation mechanisms: 1) primary melt product of mantle; or 2) derivation by liquid-immiscibility (immiscible separation of carbonate liquid from an alkalic magmas); 3) the final-products of low-pressure silicate-melt fractional crystallization [52]. In our study area, Al-Uyaynah carbonatite petrochemical data shows a mantle origin for the Al-Uyaynah carbonatites, which has been previously interpreted to have been formed in a volcanic island environment set within a transitional region of continental to oceanic crust [11, 41, 56].

2.3 Rocks spatially connected with carbonatites

Previous authors have defined the common rock types that are usually found in and around a carbonatite deposit. The majority of rocks that are spatially associated with carbonatites are generally metasomatic and magmatic rocks. From the over 350 reported localities, carbonatites are usually associated with the silicate rocks of quite variable composition [57, 58]. The common rock



Figure 1.4. Displays the tectonic setting of Al-Uyaynah area within Arabian plat. (modified from [7]).

types are divided into five groups: 1) alkaline rocks, 2) alkaline ultramafic and mafic rocks, 3) alkaline nepheline-feldspathoid syenitic rocks, 4) metasomatic rocks, and 5) carbonatitic rock sedimentary deposits that are associated with the carbonatite itself (Figure 1.8 and Table. 1) [58].

#### 2.4 Carbonatite tectonic settings

Carbonatite deposits are ordinarily restricted to a stable continental portion of a tectonic plate, i.e. among the well-developed old crust of the Earth such as cratons, shields, and crystalline blocks within cratons [59]. Carbonatites are commonly restricted to alkaline magmatic provinces controlled by intracontinental rift and fault systems within these broad regional structures [6, 58, 59]. Some carbonatite deposits are exceptions and can occur in a Foreland Belt through the western edge of the North American continent [6, 60]. Also there are two identified other carbonate occurrences (particularly relevant to this study) that are related to the oceanic basins (Canary Island and Cape Verde Islands) [59].

Generally, the structural framework of our focus site - the Al-Uyaynah zone - results from a sequence of thrust sheets, dipping to the east and southeast [56]. These Mesozoic thrust sheets were formed at some point during the closing of the southern Tethys Sea. The latest formed oceanic-crust, which is characterized now as the Semail Ophiolite, was obducted over the north-eastern portion of the margin of the Arabian plate (Figure 1.4) [41, 61, 62]. The sediments and volcanic rocks between the Arabian continent and the oceanic crust slab were amalgamated as narrow thrust layers within the accumulated allochthonous unit [41, 61, 62]. These young layers were gradually thrust and folded toward the south-west direction [41]. As a result, the Al-Uyaynah



**Figure 1.5.** Map of the northern eastern of UAE indicating the location of the Al-Uyaynah area and general geological units left, modified from [1, 2]. (b) ASTER 3,2,1 natural color image right.

zone carbonatite and the associated metamorphic rocks were structurally covered by the Semail Nappe, and were then later thrust over the continental margin sediments [11, 41, 56, 61].

#### 2.5 Economic significance of carbonatite

Major mineral deposits associated with carbonatite rocks are counted as one of the ultimate rare earth elements sources. Rare earth elements (REEs) are composed of the lanthanide elements plus scandium and yttrium, which have comparable physical characteristics and are often observed in the same deposits [59]. REEs comprise the light REE (LREE) elements from lanthanum to gadolinium, and heavy REEs (HREEs) terbium to lutetium [58, 59]. The most abundant source of the Light REE from Lanthanum (La) to Europium (Eu), are in difficult to find REEs bearing minerals like monazite-Cerium (Ce) and bastnasite/bastna<sup>--</sup>site (Ce) (Table. 2), which produce about 70- to 80% of the global LREE supply [9]. The heavy REEs from Gadolinium (Gd) to Lutetium (Lu), are frequently found in accessory minerals in alkaline and acidic rocks [9, 63].

REEs are not uncommon; however, economically extractable deposits are rare [58]. During past few decades, the needs for REEs have expanded significantly because of their extensive and varied uses in leading technology products, such as green energy products. The importance of these deposits has resulted in a growing economic rivalry between suppliers and consumers of REE, and also raised environmental concerns due to the increase in mining activities. For much of the 20th century, the Mountain Pass deposit, in the United States, was the world's predominant source of REEs [64]. However, with declining activities there, the U.S. has turned to be imports of REEs from another countries (Brazil 37%, China 25% of global REEs deposits) [65].

Global REE production comes from just a few locations (Figure 1.2). As a consequence, exploring and locating new sources of REE deposits has become a critical priority [58].

Igneous rocks, like carbonatites, are recognized as important hosts of REEs, which manifest in an array of unusual minerals [12, 66]. The REEs are found in carbonatite accessory minerals, which include biotite, ankerite, amphiboles, hematite, pyroxenes, ilmenite, pyrite, etc. [58]. The REEs are typically concentrated in calcio, mangiesio and ferro-carbonatites, however, the highest REEs abundances are commonly found in ferro-carbonatite [12]. REEs are typically concentrated in calcio. The highest percentage of REEs are typically concentrated in carbonatite spectrates are founded in bastnäsite 53–79 wt%, parasite 58–63 wt%, and synchysite 48–52 wt% [9].

In our study area, calcite is the major mineral phase in the calcio-carbonatites, which also include a significant amount of apatite, as well as opaque minerals such as magnetite. The typical composition of the calcio-carbonatites lapilli is 40% calcite, 20-30% apatite, and 20-40% opaque minerals [41]. The Al-Uyaynah ferro-carbonatites are richer in silicate, iron minerals, and (REEs) compared to calcio-carbonatites. The ferro-carbonatite comprises of calcite, amphibole, biotite, opaque minerals, and abundant allanite. The allanite in ferro-carbonatites usually occurs as crystal accumulations, and the REEs are concentrated in these accumulations as allanite-Ce [41].



**Figure 1.6.** Rare elements (REEs) and selected high field strength element distribution in the mantle and earth's crust, which is normalized to CI chondrite [9].



Figure 1.7. Geological map of Al-Uyaynah area showing the extrusive carbonatites (modified from [8]).

**3.** Detecting, assessing, and analyzing carbonatites and surrounding rock units at Al-Uyaynah, UAE using remote sensing techniques.

The initial aim of this investigation was to examine the remote sensing techniques for detecting and mapping carbonatites distribution in the in Al-Uyaynah region at UAE. The research surveys carbonatites, by employing the Visible/Near Infra-Red (VNIR) and Short Wave Infra-Red (SWIR), with two datasets: (1) the latest multispectral sensor (Landsat 8 OLI), and (2) ASTER imaging.

The first study carries out an examination of Landsat 8 OLI data to map the distribution of carbonatites. This approach is novel given that the Al-Uyaynah area had not been explored prior to this study with Landsat 8 imagery through mapping algorithms. The SAM algorithm was employed to locate and to identify carbonatite occurrences and map carbonatite distribution. Our results were compared with available geological maps and field ground truth data to evaluate the utility of Landsat 8 imagery ability in carbonatite mapping.

The second study examines ASTER imaging to also map carbonatites in Al-Uyaynah area. In this experiment, four different data processing techniques were used to identify carbonatites: Spectral Information Divergence (SID), Support Vector Machine (SVM), Spectral Angle Mapper (SAM), and the Binary Encoding Classification (BEC). These algorithms were used, to classify the study area using ASTER image, digitally map carbonatites and adjust rock components. The results are illustrated in digitally-produced maps which highlight the pixels that correspond to specific endmember-spectra among other classes of a different kind. Out of the methods tested,



Figure 1.8. A comparison between the occurrence of rocks accompanying carbonatites [Count is number of deposits; % is percentage of deposits with related rock type, data used in this diagram were obtained from table3 of USGS Open-File Report [6]

Rock group	Rocks	Count	%
Carbonatitic	Carbonatitic breccia	18	30
	Carbonatitic agglomerate	7	12
Alkaline	Syenite	20	33
	Trachyte	9	15
	Nordmarkite	4	7
	Alkaline granite, pegmatite	3	5
Alkaline nepheline-feldspathoid	Nepheline-syenite	21	35
syenitic	Ijolite	16	27
	Melteigite	7	12
	Phonolite	5	8
	Foyaite	4	7
	Nephelinite	3	5
	Urtite	3	5
	Malignite	2	3
	Shonkinite	2	3
	Okaite	2	3
	Tephrite		2
	Melilitolite	1	2
Alkaline ultramafic and mafic	Pyroxenite (incl. bebedourite)	17	28
	Lamprophyre, monchiquite, alnoite	9	15
	Phoscorite	7	12
	Jacupirangite	6	10
	Gabbro, diabase	6	10
	Peridotite	5	9
	Tuff	5	9
	Dunite	4	7
	Basalt	1	2
Metasomatic	Fenite	7	12
	Glimmerite	5	8
	Albitite	3	5
	Silexite	1	2

**Table 1.1.** Occurrence of rocks accompanying carbonatites [Count is number of deposits; % is percentage of deposits with related rock type, data were acquired from USGS Open-File Report [1].

Mineral <sup>b</sup>	Formula <sup>c</sup>	Rare element (wt% range or	Major deposit type(s) <sup>d</sup>	Localities: key examples (past, present, and potential producers)	
Bastna <sup>~</sup> site	LREECO <sub>3</sub> (F,OH)	53–79 SREE <sub>2</sub> O <sub>3</sub>	Carbonatites and associate metasomatic rocks, altered peralkaline feldspathoid rocks	Mountain Pass <sup>U</sup> , Bayan Obo <sup>Ch</sup> , Weishan <sup>Ch</sup> , Maoniuping <sup>Ch</sup> , Nechalacho <sup>Ca</sup>	
Parisite	CaLREE <sub>2</sub> (CO <sub>3</sub> ) <sub>3</sub> (F,OH) <sub>2</sub>	58–63 SREE <sub>2</sub> O <sub>3</sub>	Carbonatites and associate metasomatic rocks, hydrothermal deposits	Mountain Pass <sup>U</sup> , Bayan Obo <sup>Ch</sup> , Weishan <sup>Ch</sup> , Snowbird <sup>U</sup>	
Synchysite	CaREE(CO <sub>3</sub> ) <sub>2</sub> (F,OH)	48–52 SREE <sub>2</sub> O <sub>3</sub>	Carbonatites and associate metasomatic rocks, altered peralkaline feldspathoid and granites	Barra do Itapirapua <sup>~B</sup> , Lugiin Gol <sup>M</sup> , Ak-Tyuz <sup>K</sup> , Nechalacho <sup>Ca</sup>	
Monazite	(LREE,Th,Ca)(P,Si)O <sub>4</sub>	38–71 wt% SREE <sub>2</sub> O <sub>3</sub>	Carbonatites and associate metasomatic rocks	Mountain Pass <sup>U</sup> , Bayan Obo <sup>Ch</sup> , Eneabba <sup>A</sup> , Mt	
			P-rich nelsonite, weathering crusts; placers	Mount Weld and WIM 150 <sup>A</sup> , Kangankunde <sup>Ma</sup> , Tomtor <sup>R</sup> , Steenkampskraal <sup>SA</sup> , Manavalakurichi <sup>I</sup>	
Xenotime	(HREE,Zr,U)(P,Si)O <sub>4</sub>	43–65 SREE <sub>2</sub> O <sub>3</sub>	Carbonatites and associate metasomatic rocks, weathering crusts, placers	Lofdal <sup>N</sup> , Ak-Tyuz <sup>K</sup> , Pitinga <sup>B</sup> , Tomtor <sup>R</sup> , Mt Weld and WIM 150 <sup>A</sup> , Kinta and Selangor <sup>Ms</sup>	
Churchite Gadolinite	HREEPO <sub>4</sub> 2H <sub>2</sub> O REE <sub>2</sub> FeBe <sub>2</sub> Si <sub>2</sub> O <sub>10</sub>	43–56 SREE <sub>2</sub> O <sub>3</sub> 45–54 SREE <sub>2</sub> O <sub>3</sub>	Weathering crusts Granitic pegmatites	Chuktukon <sup>R</sup> , Mt Weld <sup>A</sup> Ytterby <sup>S</sup> , Strange Lake <sup>Ca</sup> , Barringer Hill <sup>U</sup>	
Rutile Loparite	(Ti,Nb,Ta,Fe,Sn)O <sub>2</sub> (Na,REE,Ca,Sr,Th) (Ti,Nb,Ta)O <sub>2</sub>	56 Ta <sub>2</sub> O <sub>5</sub> , 34 Nb <sub>2</sub> O <sub>5</sub> , 7 SnO <sub>2</sub>	Carbonate metasomatic rocks, granitic pegmatites, placers, weathering crusts Peralkaline feldspathoidal rocks	Bayan Obo <sup>Ch</sup> , Greenbushes <sup>A</sup> , Kinta Valley <sup>Ms</sup> , Morro dos Seis Lagos, and Borborema <sup>B</sup> Karnasurt and Umbozero <sup>R</sup>	
Fergusonite	REENbO <sub>4</sub>	28–38 SREE <sub>2</sub> O <sub>3</sub> , 20	Metasomatic carbonate and peralkaline feldspathoid rocks, granitic pegmatites	Bayan Obo <sup>Ch</sup> , Barringer Hill <sup>U</sup> , Nechalacho <sup>C</sup>	
tantalite	(Fe,Mn,Mg)(Nb,Ta,Ti) <sub>2</sub> O <sub>6</sub>	Nb <sub>2</sub> O <sub>5</sub> , 1 Ta <sub>2</sub> O <sub>5</sub> 43–57 SREE <sub>2</sub> O <sub>3</sub> , 40–55 Nb <sub>2</sub> O <sub>5</sub> , 0.8 Ta <sub>2</sub> O <sub>5</sub>	Carbonatites and associate metasomatic rocks, granites, and granitic pegmatites, placers	1 Ta <sub>2</sub> O <sub>5</sub> Carbonatites and associate metasomatic rocks, granites, and granitic pegmatites, placers         0.8 Ta <sub>2</sub> O <sub>5</sub> Carbonatites and associate metasomatic rocks, granites, and granitic pegmatites, placers	Blue River <sup>Ca</sup> , Bayan Obo <sup>Ch</sup> , Greenbushes and Wodgina <sup>A</sup> , Koktokay and Yichun <sup>Ch</sup> , Pitinga and Mibra <sup>B</sup> , Kenticha <sup>E</sup> , Marropino <sup>Mz</sup> , Nord-Kivu and Sud-Kivu <sup>DRC</sup>
Mineral <sup>b</sup>	Formula <sup>c</sup>	Rare element (wt% range or max. content)	Major deposit type(s) <sup>d</sup>	Localities: key examples (past, present, and potential producers)	
Tapiolite Wodginite	(Fe,Mn)(Ta,Nb) <sub>2</sub> O <sub>6</sub> (Mn,Fe)(Sn,Ti)(Ta,Nb) <sub>2</sub> O <sub>8</sub>	72-86 Ta <sub>2</sub> O <sub>5</sub> , 9 Nb <sub>2</sub> O <sub>5</sub> 56-85 Ta <sub>2</sub> O <sub>5</sub> , 15	Granitic pegmatites Granitic pegmatites	Tanco <sup>Ca</sup> , Greenbushes <sup>A</sup> Tanco <sup>Ca</sup> , Greenbushes, and Wodgina <sup>A</sup>	

 Table 1.2. Shows the rare earth element (REE)- Major bearing minerals [9]
		Nb <sub>2</sub> O <sub>5</sub> , 3–18 SnO <sub>2</sub>			
Ixiolite	(Ta,Nb,Mn,Fe,Sn,Ti) <sub>4</sub> O <sub>8</sub>	70 Ta <sub>2</sub> O <sub>5</sub> , 72 Nb <sub>2</sub> O <sub>5</sub> , 20 SnO <sub>2</sub>	Granitic pegmatites	Tanco <sup>Ca</sup> , Borborema <sup>B</sup>	
Pyrochlore	(Ca,Na,Sr,Ba,Pb,K,U) <sub>2</sub> x (Nb,Ti,Ta,Zr,Fe) <sub>2</sub> O <sub>6</sub> (F,OH) <sub>1</sub> y nH <sub>2</sub> O	29–77 Nb <sub>2</sub> O <sub>5</sub> , 16 Ta <sub>2</sub> O <sub>5</sub> , 22 wt% REE <sub>2</sub> O <sub>3</sub>	Carbonatites and associated phoscorites Peralkaline granites and associated Pegmatites, fenites, weathering crusts	Barreiro and Catala <sup>°</sup> o I and II <sup>B</sup> , Oka, Niobec and Strange Lake <sup>Ca</sup> , Tomtor, Chuktukon, Tatarskoye, Bol'shetagninskoye and Belaya Zima <sup>R</sup> , Lueshe and Nord-Kivu <sup>DRC</sup> , Pitinga <sup>B</sup>	
Microlite Baddeleyite	(Ca,Na,Pb,U,Sb,Bi) <sub>2</sub> x (Nb,Ta,Ti) <sub>2</sub> O <sub>6</sub> (OH,F) <sub>1</sub> y (Zr,Hf,Nb,Fe)O <sub>2</sub>	46–81 Ta <sub>2</sub> O <sub>5</sub> , 20 Nb <sub>2</sub> O <sub>5</sub> , 9 SnO <sub>2</sub> 88–99 ZrO <sub>2</sub> , 4.8 HfO <sub>2</sub> , 6.5 Nb <sub>2</sub> O <sub>5</sub>	Granites and granitic pegmatites Phoscorites, altered peralkaline feldspathoid syenites, carbonate metasomatic rocks, placers	Tanco <sup>Ca</sup> , Greenbushes <sup>A</sup> , Koktokay and Yichun <sup>Ch</sup> Kovdor and Algama <sup>R</sup> , Palabora <sup>SA</sup> , Poc <sub>s</sub> os de Caldas <sup>B</sup>	
Zircon	(Zr,Hf,HREE,Th,U) (Si,P)O <sub>4</sub>	64–67 ZrO <sub>2</sub> , 1.5 HfO <sub>2</sub> , 19 SREE <sub>2</sub> O <sub>3</sub>	Placers; peralkaline, feldspathoid syenites (including altered varieties)	Jacinth-Ambrosia and Eneabba <sup>A</sup> , Richards Bay <sup>SA</sup> , Manavalakurichi and Chavara <sup>I</sup> , Poc,os de Caldas <sup>B</sup> , Nechalacho <sup>Ca</sup>	

Table 1.2. (cont'd)

the high accuracy rates (successful algorithms) were defined as the ones to offer the best ways for carbonatite mapping.

# 4. Understanding carbonatite chemistry using spectral analysis devices (ASD) and geochemical approaches.

The second goal of the investigation was to increase our understanding of VNIR and SWIR spectral frameworks of carbonatite rocks through petrochemical analysis, to build a more comprehensive understanding of chemical environments of the Al-Uyaynah carbonatite, UAE. Spectroscopy is a quick and affordable way of analyzing the carbonatite mineralogy. In this research, the carbonatite samples were evaluated and examined by utilizing the Analytical Spectral Device (ASD) device. Inductively Coupled Plasma Mass Spectrometry (ICP-MS) procedures were used to determine rare-earth elements (REE) and other trace elements of the whole rock samples. X-ray Fluorescence (XRF) was utilized to investigate the whole-rock composition major oxides. These geochemical analyses permit us to test linearly the relationship between the major oxides/elements absorption features of carbonatite spectra and its concentration in carbonatites.

# **5.**Dissertation phases

The research is written within a manuscript format with a view to enable the current researcher to compile and submit individual research papers derived from its chapters to peerreviewed journals. The current effort focuses initially on the utilization of SWIR and VNIR of the multispectral image data to map carbonatites and neighboring lithologies in Al-Uyaynah area, UAE (Chapter 2, 3).

In the final phase of this study, ASD reflectance spectra data were obtained through handsample from the carbonatites in of Al-Uyaynah, UAE. These samples were analyzed and compared to find out the ideal wavelength ranges that can assist us in detecting, identifying, and mapping the ferro/calcio-carbonatites. The research was aided by a geochemical analysis by employing XRF, ICP-MS to offer a comparative perspective to ASD petrogenetic properties and to assess the carbonatites spectra (Chapter 4). The final chapter, Chapter 5, provides a synthesis of the entire research results as a whole and suggestions for future research area suggested in these two fields.

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# **CHAPTER 2**

# CARBONATITE IDENTIFICATION USING LANDSAT 8 VNIR-SWIR BANDS AT AL-UYAYNAH, UAE

# Abstract

Carbonatites, which are significant hosts of economically important rare-earth elements (REE), are challenging to locate as they may crop out as small bodies with indistinct field characteristics. Here we examine the spectral reflectance characteristics of a previously well-exposed carbonatite that is located in the northeastern part of the United Arab Emirates (UAE). We focus on the VNIR-SWIR bands between 0.45 to 2.2  $\mu$ m, given this range is sensitive to the influence of carbonatite minerals in the reflectance spectra. The Spectral Angle Mapper (SAM) algorithm was utilized to identify carbonatites using the endmembers that were extracted from a Landsat-8 OLI image. The SAM digital map displays a "good" result, with a calculated kappa coefficient of 0.58, and an overall accuracy of about 67%. Our results therefore suggest that it is possible to map and assess carbonatite distribution from medium spatial resolution (Landsat 8 OLI) images for exploration purposes, but the technique suffers from accuracy issues that may negatively impact its usage for quantitative assessment of resource potential.

# **1.Introduction**

Carbonatites are one of the most significant hosts for economically important Rare Earth Elements (REE) such as neodymium (Nd), cerium (Ce), europium (Eu), and lanthanum (La) [6]. Identification of these carbonatites is often a challenge, as they commonly appear as smaller bodies within larger-scale features [6, 7]. Remote sensing provides an opportunity to identify carbonatite deposits, but the techniques applied require appropriate spectral resolution and the capability to identify the spectrally significant features associated with carbonatites. Here we examine the feasibility of using Landsat 8 OLI images for carbonatite detection by examining a well-exposed carbonatite occurrence in the United Arab Emirates (UAE).

Remote sensing techniques have been a standard tool in mineral exploration over the past four decades. Initially, these techniques were applied as a rapid and cost effective way to study the chemical variability of surface rock types in order to map the lithological variation [8, 9]. Modern remote sensing sensors have an improved spectral resolution that is useful in distinguishing between different rock groups and mineral types [10, 11]. Specifically, it has been demonstrated that a broad range of minerals, such as clays, carbonates, and hydroxides can be indicated by the use of remote sensing spectral analysis (e.g. [12]).

Multispectral satellite sensors can cover the VNIR (visible/ near infrared), SWIR (short wave infrared), and TIR (thermal infrared) bands, which are important in mineral exploration [13]. The VNIR and SWIR bands are typically a valuable source of information about transition metal absorption, specifically iron minerals, and also are sensitive to some of the rare-earth elements

(REE) [11, 12]. In particular, the wavelength region (0.45 to 2.5  $\mu$ m) of the reflectance spectrum is specifically used to indicate the composition of minerals based on absorption features [12, 14].

Carbonatites, which contain more than 50% carbonate minerals, exhibit a particularly strong  $\text{CO}_3^{2-}$  absorption feature between 1.65 and 2.2-2.33 µm [15]. For carbonatites enriched in iron (ferro-carbonatites) there is an additional absorption feature between 1.0 and 1.3 µm [16]. While these absorption features are distinctive, they are not uniquely diagnostic of carbonatites; other carbonate rocks such as limestone and marble also exhibit similar absorbance peaks. In addition, REEs, which can be a significant component in carbonatite magmas, exhibit absorption in the wavelength range between 0.5 and 0.9 µm that is dominantly attributed to electronic transitions in Nd<sup>3+</sup> [17, 18] By combining these absorption features we may resolve lithological ambiguities and allow for distinction between igneous (i.e. carbonatites) and sedimentary (e.g. limestone) carbonate rocks.

The absorption spectral features of carbonatites have been used in previous research to create maps of carbonatite complexes that are detectable from aircraft sensors. AVIRIS (Airborne Visible / Infrared Imaging Spectrometer) images were used to distinguish the Ice River Carbonatite complex, and showed minor absorption features located at 0.58, 0.74, 0.80, and 0.87 µm, which is characteristic of Nd<sup>3+</sup> [19]. Recent studies of the Sarfartoq carbonatite in Greenland by Bedini and Tukiainene were conducted using spectral mixing methods to distinguish between carbonatite, fenite, and hematised surface rock, with particular attention to the Nd<sup>3+</sup> reflectance characteristics [20].

In this study, we use Landsat 8 spectral data [21] obtained within the Visible/Near Infra-Red (VNIR) and Short Wave Infra-Red (SWIR) bands to map extrusive carbonatite occurrences at Al-Uyaynah in the northwestern Oman Mountains. We evaluate the utility of Landsat 8 OLI data and the SAM classification method for mapping carbonatite distribution. We find that this method has utility for exploration purposes but suffers from accuracy issues that may negatively impact its usage for quantitative assessment of resource potential.

#### 2.Al-Uyaynah

The study area for this project is the Al-Uyaynah carbonatite field of the United Arab Emirates, which is located approximately 18 km to the southwest of Dibba city (Figure. 2.1). The Al-Uyaynah carbonatite is mapped as part of metamorphic sole of Samail ophiolite, which contains exposures of sub-aerially erupted carbonatites within oceanic metasediments [7]. The Al-Uyaynah carbonatite has previously been interpreted as an accreted volcanic island predating the Samail ophiolite [7]. The exposures (about 10-50 m) are an ideal location to undertake a remote sensing study (Figure 2.1).

The Al-Uyaynah carbonatite is composed of two typical magma types (calcio- and ferrocarbonatite) (Figure 2.2), which are also broadly representative of most global carbonatite occurrences. The carbonatite complex is comprised of ~10-50 m thick layers with lapilli, which require a sub-aerial origin [7]. The main mineral phase in the calcio-carbonatites is calcite. However, these carbonatites also contain abundant apatite, and opaque minerals such as magnetite. The typical composition of these lapilli is 40% calcite, 20-30% apatite and 20-40% opaque minerals [7]. The existing whole rock geochemical data show that ferro-carbonatites have higher modal abundances of silicates in comparison calcio-carbonatites. Representative minerals of ferrocarbonatites are allanite (Ce), amphibole (alkali) and occasionally strontian barite. Allanite in ferro-carbonatites usually occurs as crystal accumulations. These accumulations concentrate REEs and result in trace elements heterogeneously distributed within the rock [7].

# 3. Methods

# 3.1. Landsat 8 data calibration

The Landsat 8 OLI multispectral images were obtained from the USGS as a Level1 T-Terrain Corrected (orthorectified) image [21]. This image was acquired on May 27<sup>th</sup>, 2014 with 2.87 % cloud cover, which is centered away from the area of interest for this study. Overall image quality is 9 out of 9 on a NASA scale. The Landsat OLI sensor acquires images in the spectral range of 0.43 - 2.29  $\mu$ m (VNIR-SWIR) with a 30-meter pixel resolution, and within the panchromatic band at a 15-meter resolution. The standard data product of Landsat 8 is georeferenced in Universal Transverse Mercator (UTM) map projection using a World Geodetic System datum (WGS-84) [21]. The pre-processing steps applied to the Landsat 8 VNIR-SWIR 30 meter resolution datasets were: (1) conversion of the raw digital image to sensor radiance using Landsat Calibration data and (2) application of the QUick Atmospheric Correction (QUAC) model, that is accessible in the Environment for Visualizing Images (ENVI) software [22], in order to eliminate the atmospheric contributions.



**Figure 2.1.** A map of the northern eastern of UAE indicating the location of the Al-Uyaynah area and general geological units, modified from [1, 2], and Landsat 8 natural colored image of Al-Uyaynah area shows the location of study area (right).



**Figure 2.2.** A field view of Al-Uyaynah carbonatites (fig. 1), (a) shows the ferro-carbonatites outcrops of the northern end of the study area, (b, and c) show a close view of ferro-carbonatites. (d) Shows the extruded calcio-carbonatite, and (e, f) illustrates a close view of calcio-carbonatite.

#### 3.2. Landsat data analysis

The Minimum Noise Fraction (MNF) method is a linear transformation function utilized to differentiate noise from data and to diagnose dimensionally coherent spectral data [22, 23]. A forward MNF transform was applied to the image by inspecting eigenvalues and the seven MNF gray bands (Figures 2.3, 2.4.1), in order to identify which bands had coherent data. We utilized the Pixel Purity Index (PPI) to find the spectrally extreme pixels, or pure, pixels within the image [22, 23]. The PPI is calculated by frequently projecting a n-D (n-dimensional) scattergraph on an indiscriminate unit vector [22, 23]. The PPI functions were applied on an MNF image with 20,000 iterations, and then the results were visualized using n-D visualizer (n-D scatter plots). We selected pixels of the unit vector to be the spectral reflectance end-members.

#### 3.3. Field work and ASD spectral measurements

Rock samples were collected during a field expedition in December 2010. These samples were analyzed using an Analytical Spectral Device (ASD) spectroradiometer at the University of Toledo, Ohio, U.S.A. Spectral measurements were performed in a laboratory using an ASD FieldSpec-3 Hi-Res Spectroradiometer. Illumination was provided by a 1000W 3200K Quartz Halogen lamp. A 10 degree foreoptic was employed. Spectra were acquired for each sample. All samples were normalized to a Spectrol lab standard with well-characterized spectral properties. Lab spectra were resampled to OLI bands for comparison using the spectral resampling function in ENVI [22].

#### 3.4. The spectral angle mapper (SAM)

We selected the Spectral Angle Mapper (SAM) algorithm as our mechanism for image classification as it has previously been successfully applied to problems involving mineral identification and geological mapping [e.g.[4, 24]]. SAM is a physical method used to classify an image by comparing and matching the angle between the pixel vector and an end-member spectral vector in n-D space [22, 23, 25]. A smaller angle shows a better match to spectral endmembers; pixels exceeding the maximum angle of the end member's threshold are not counted in the classification [26]. The technique is effective given that it does not require any assumptions for numerical/statistical distribution of input- information in carrying out a classification [27]. Furthermore, the technique suppresses the impact of effects caused by topographic shading [25]. In this study, our image was classified based on the SAM algorithm using the extracted endmembers' reflectance spectra. In the output each image represents one end member (see more details in results section).

# 4. Results

# 4.1. The image processing results

Landsat 8 OLI bands, which cover the VNIR and SWIR spectral range  $(0.433-2.95 \ \mu m)$ , were chosen to perform the MNF transformation. The results of this transformation included eigenvalues and eigenimages (MNF images), which were used to assess the dimensionality of the data by comparing MNF images with MNF eigenvalues (Figure 2.3). The larger eigenvalues



**Figure 2.3**. MNF eigenvalue plot for study area (Al-Uyaynah). All MNF bands have eigenvalues values greater than 1. The lowest band (7) has eigenvalue equal to 1.23, which means it contains coherent data. However, the first three bands contain more spatially coherent information than the others.



**Figure 2.4.** MNF images of Landsat 8 VNIR-SWIR bands for study area. Images 1-7, display a single gray band, while image 8 shows a combination of first three MNF bands (1, 2 and 3 as RGB). Image 9 shows natural color image (Landsat Bands 3, 2, 1 (RGB)) for comparison (Not MNF image).



**Figure 2.5** Show a 3-D Scatter plot of the end-members data cloud (image bands 1-3 were used as plot axes). The identical rock units were characterized by the same color.

(greater than 1) contain the greater portion of inherent information, and bands with eigenvalues close to 1 contain noise [22]. All MNF bands used have eigenvalues values greater than 1.23; however, the first three bands (1-3) contain more spatially coherent information than the other four bands (4-7) as shown in Figures. 2.3 & 2.4.

4.2. Carbonatite endmember spectral characteristics

#### 4.2.1. The ferro-carbonatite

The ferro-carbonatite image endmember spectra extracted from the OLI image showed absorption features of calcite ( $CO_3^{2^-}$  ion) at 1.6 µm as a weak absorption, which then descended gradually to reach the Landsat OLI sensor limit at 2.2 µm (Figure 2.8). The laboratory (ASD) spectra of ferro-carbonatite showed that calcite has a stronger absorption in the window between 2.2 to 2.33 µm (Figure 2.5, and 2.7b). Ferro-carbonatites have a higher modal abundance of silicates, which manifest as dark inosilicate minerals (alkali amphibole) [7]. The hydroxyl ion in Al-OH and Mg-OH of amphibole minerals displays absorption characteristics at 1.4 µm and 2.2-2.3 µm [13]. The presence of alkali amphibole minerals in the ferro-carbonatite image endmember spectra results in an increase in values of the absorption near 2.1 µm and reaches the strongest absorption at 2.2 µm; this is more obvious in the ASD spectra of the ferro-carbonatite showed that alkali amphibole minerals have 1.4, 2.15, 2.16, and 2-2.2 µm absorptions. The high concentration of ferric iron (Fe<sup>3+</sup>) and REE in minerals within the



Figure 2.6. ASD Resampled spectra to Landsat 8 of (a) ferro-carbonatite and (b) calcio-carbonatite.



**Figure 2.7.** A laboratory reflectance spectra (ASD) of samples, (a) ferro-carbonatite and (b) calcio-carbonatite (left). (a) A zoom of spectral region 0.5-0.6  $\mu$ m of laboratory reflectance spectra (ASD) of REE absorption are near 0.589, 0.567, and 0.56  $\mu$ m, and (b) A zoom of spectral region 2000-2400 nm of laboratory reflectance spectra (ASD) calcite (CO<sub>3</sub>, MgO) REE absorption are near 2.32-2.35 $\mu$ m and calcite has weak absorption at 1.6  $\mu$ m.

rocks lowers the reflectivity or increases the absorption over the visible/very near infrared (VNIR) [28]. The absorption in the VNIR bands of the ferro-carbonatite image spectrum from 0.865-0.9  $\mu$ m could be because of the existence of ferrous-ions in the ferro-carbonatite, and ferric-ions (Fe<sup>3+</sup>) in its weathered surface. Apatite (Nd<sup>3+</sup>) absorption behavior is present as a weak absorption near 0.589, 0.567, and 0.560  $\mu$ m in the ferro-carbonatite ASD spectra (Figure 2.7a). This absorption is not clear in the image endmember spectrum but we have noted a lower reflectivity at 0.589, and 0.567  $\mu$ m. Ferro-carbonatites are rich in allanite (Ce), resulting in low absorption at 0.45 - 0.5  $\mu$ m in both the ASD and image endmember spectra.

#### 4.2.2. The calcio-carbonatite

The calcio-carbonatite image endmember has absorption features of calcite that fall gradually from 2.1-2.2  $\mu$ m (sensor limit). Calcio-carbonatites contain fewer silicate minerals but more calcite than ferro-carbonatites, reflecting stronger absorption characteristics between 2.0 and 2.2  $\mu$ m. The ASD spectra of calcio-carbonatites show a strong absorption between 2.2-2.33  $\mu$ m (Figures 2.5, and 2.7b). Alkali amphibole is present as a secondary mineral in calcio-carbonatite and has a weak vibrational absorption near 1.4 and 2.2  $\mu$ m in the ASD spectra, but is not detected at 1.4  $\mu$ m in the calcio-carbonatite image endmember due to the atmospheric H<sub>2</sub>O vapor absorption bands (0.9-1.5  $\mu$ m).



**Figure 2.8.** Landsat 8 image endmembers spectra of (a) calcio-carbonatite in red color and (b) ferro-carbonatite in green color; within VNIR-SWIR bands.

4.2.3. The difference between ferro/calcio-carbonatite endmembers

Ferro-carbonatite and calcio-carbonatite have similar behaviors or absorption within the visible band, between 0.865-0.9  $\mu$ m, due to the presence of iron oxides on the surfaces of weathered outcrops. Furthermore, the presence of calcite in both calcio- and ferro-carbonatites results in an increase in absorption at 2.1 and 2.2  $\mu$ m. Some distinction between the two rock types is evident due to the greater percentage of calcite within the calcio-carbonatites, which manifests as more absorption at 2.2  $\mu$ m. REE absorption features make ferro-carbonatite distinguishable from calcio-carbonatite in ASD spectra. The weak absorptions near 0.605, 0.589, 0.567, and 0.45 -0.5  $\mu$ m of the ferro-carbonatite ASD is due to the high abundance of REE-bearing minerals (allanite (Ce), and apatite).

#### 4.2.4. Other endmembers

Within the study area there are a number of other (non-carbonatite lithologies (Fig. 9) which must be assessed in order to fully classify our Landsat image:

(i) The alkaline volcanic unit. This unit is dominated by deformed basaltic alkali volcanic rocks (sub/green schist facies). Alkali basalts typically have high concentrations of Na<sub>2</sub>O [28], which causes a weak absorption close to 0.65  $\mu$ m [28]. The endmember of alkaline rocks shows this same weak absorption close to 0.65-0.68  $\mu$ m. Furthermore, the alkali basalt endmember exhibits aluminum hydroxide (Al-OH) absorption characteristics from 2.1 to 2.2  $\mu$ m.

(ii) The metavolcanic unit. This unit's n-D spectrum displays absorption features of phlogopite, in which it shows absorption from 1.6 to 2.2  $\mu$ m, and within the visible band (0.45  $\mu$ m) (Figure 2. 9). These spectral features are due to absorption by the transition pair of Fe<sup>2+</sup> and Fe<sup>3+</sup> ions in phlogopite [28]. The OH lattice in magnesium hydroxide (Mg-OH) and aluminum hydroxide (Al-OH) of metavolcanic 'phlogopite' causes electronic and vibrational transition features responsible for the reflected energy consumption and absorption in the metavolcanic unit n-D spectra at 1.6, which decreases gradually to 2.2  $\mu$ m.

(iii) The ophiolite complex. The average image spectra from the ophiolite complex has several absorption bands between  $1.6-2.2 \mu m$ . It is, however, absorbed strongly in the area of 2.2  $\mu m$  due to the high abundances of silicates (e.g., olivine).

(iv) The red chert unit. This unit is rich in silicate minerals (quartz) and contains iron oxides. The red chert endmember spectrum has silicate absorption near 2.2  $\mu$ m, and iron oxide absorption characteristics from 0.865  $\mu$ m to 0.443  $\mu$ m (Figure 2.9).

(v) Schist formation. Chlorite (Mg-Fe-O) and muscovite (Al-OH) are the major minerals in these rocks, which has created an absorption feature in the VNIR band (0.4-0.09  $\mu$ m). In addition, a weak Al-OH absorption at 2.1-2.2  $\mu$ m, caused by muscovite, is evident in the schist image endmember.



Figure 2.9. The image n-D spectra were extracted from Landsat OLI image used in SAM classification.

#### 4.3. The SAM classification results

The Spectral Angle Mapper algorithm (SAM) algorithm was utilized in the calculation of the spectral likeness between endmembers and image spectra [23, 25, 26]. SAM was applied to the Landsat 8 image, using ENVI 5.1 software, in order to indicate and map both types of carbonatites and other rock units around it based on extracted reflectance endmembers. Afterward, the results of SAM method were compared to the field ground truth data and the geological map in order to generate the accuracy assessment, which was calculated using a confusion-matrix method [22, 29]. The performance of the SAM filtering method displays overall a "good" differentiation between ferro/calcio-carbonatite and other units (Figure 2.10, 2.11, and 2.12). The accuracy assessment of the SAM shows overall accuracy with 66.92%. Kappa Coefficient is 0.58, which falls into the 'good' category [3, 4] (Table 1). We must emphasize that this assessment is for the image as a whole– accuracy in terms of carbonatite differentiation was significantly more robust as discussed below.

#### **5.**Discussion

Comparing the distribution of spectrally defined lithological units to geologically mapped terrains is central to the assessment of any exploration remote sensing technique. Our area contains seven spectrally-defined endmembers which outcrop in a complex pattern as defined in the existing geological map. Our overall accuracy assessment of 66.92% is a composite of the mismatch between spectrally predicted and observed lithologies at any point for all these units. However,

Lower Bound	Degree of Agreement	Upper Bound	Lower Bound
<0.05	No	0.05	< 0.05
0.05	Very Poor	0.20	0.05
0.20	Poor	0.40	0.20
0.40	Fair	0.55	0.40
0.55	Good	0.70	0.55
0.70	Very Good	0.85	0.70
0.85	Excellent	0.99	0.85
0.99	Perfect	1.00	0.99

**Table 2.1.** The values of threshold that used for dividing the results of statistical kappa coefficient degrees of agreement. From [3-5]. The values close or equal to 1.0 specify perfect agreement; while any values between 0.85-0.99 show excellent agreement, and any kappa coefficient values of between 0.75-0.85 would be a very good agreement. The lesser degree of agreement were classified as: good if the kappa coefficient values were between 0.4-0.55; fair agreement between 0.40-0.55 values; and kappa coefficient values between 0.4-0.05 or fewer show poor to no agreement. The SAM map accuracy assessment displays overall accuracy with 66.92%. Kappa Coefficient is 0.58, which falls into the 'good' category.



**Figure 2.10.** SAM n-D classification map of Al-Uyaynah area shows the extrusive carbonatites and the lithology unites.



Figure 2.11. Geological map of Al-Uyaynah area shows the extrusive carbonatites (modified from British geological survey, 2006).

accuracy values vary significantly from unit to unit. To fully assess the class distribution accuracy and the potential reasons for error, below we discuss each mapped class.

### 5.1. Distribution of calcio/ferro-carbonatites units

Utilizing the SAM method, we were able to distinguish both calcio and ferro-carbonatites from other major rock units. The discrimination of calcio-carbonatites (82.50 % of class accuracy) was better than ferro-carbonatites with 70.72 % accuracy (Table 2), and Figure 2.12. The spatial distribution of calcio/ferro-carbonatites closely matched the reference geological map. Despite these good correlations, the 17.5 % mismatch for calcio-carbonatites and 29.28% for ferrocarbonatites requires examination. We found that this inaccuracy resulted from: (1) The nondetection of some calcio-carbonatites due to the variable size range of carbonatite bodies (approximately 10-50 meters). (2) Sub pixel contamination, caused by the presence of multiple rock types within 30 square meter pixel size of the Landsat 8 OLI image, may confound the SAM algorithm. (3) Spectral similarity between carbonatite units, the alkaline volcanic formation, and metavolcanic rocks in close geographic proximity can further complicate pixel discrimination. Carbonatites and alkaline volcanic rocks both contain alkaline amphibole, while surrounding metamorphic rocks contain micas (chlorite and phlogopite) that may also be found in carbonatites. These compositional and spectral similarities between carbonatites and surrounding rock types led the SAM algorithm to map these quite distinct lithological units as one contiguous spectrallydefined unit (Figure. 2.10, 12).

#### 5.2. Distribution of other non-carbonatite units

The Ophiolite complex, as illustrated using the SAM method, matched the available geological maps with approximately 94.5% (Figure. 10, 11, and Table 2). The SAM map of metavolcanic unit is about 50% accurate in comparison to the metavolcanic formation in the western part of the geologic map. Due the spectral likeness, the SAM algorithm mapped some of metavolcanic units as alkaline volcanic rocks (Figure 2.10, and 2.12).

The alkaline volcanic unit, which is dominated by deformed basaltic alkali volcanic rocks (sub/green schist facies), was mapped using the SAM algorithm. A comparison of the geological maps with the alkaline distribution shows about 20% of it were accurately classified.

The SAM map shows red chert in the areas between the ophilite and alkaline volcanic units, which matches the geological map with 32%. However, in the south portion of our study area, the red chert formation was classified by the SAM algorithm as Metavolcanic (Figure 2.10, and 2.12). This was due to the high proportion of silicate minerals in both units in this region.

The schist formation, was clearly mapped using the SAM method, and shows a strong correlation (94.5%) between the spectrally identified schist endmember and the mapped schist unit in the north-western part of the geologic map.

# 6. Conclusion

This paper offers a review of Landsat 8 OLI data and SAM algorithm validation for use in mapping of carbonatite outcrops. Landsat imagery remains among the most popular remote sensing datasets for geological mapping and mineral exploration. Our results, which provide an assessment of the new Landsat 8 capabilities in a well-studied carbonatite setting, are therefore of particularly broad utility to the geologic remote sensing community.

The primary rocks of the study area (extrusive carbonatites) were well-represented by the calculated endmembers. Ferro-carbonatite rocks were mapped with an accuracy of 70.72%, with better results from the calcio-carbonatite endmember, which has an accuracy of 82.5%. Challenges in the discrimination of ferro-carbonatite with the SAM algorithm arose because these highly deformed bodies are relatively narrow (generally only a few meters in width) and are located close to the alkali mélange unit. Mixtures of the units can prove problematic for the SAM algorithm, which does not take the sub-pixel mixing into account, and Landsat 8, which has medium spatial resolution and limited spectral range in the SWIR bands (1.57 - 1.65 and 2.11 - 2.29  $\mu$ m). These limitations produce ambiguity in the observations and make it difficult to clearly distinguish carbonatite from other rocks. Further complicating factors were the iron oxide minerals that were found in weathered outcrops – these coatings resulted in some similarities between calcio-carbonatite and ferro-carbonatite weathered surface spectra.

In conclusion, our comparison of the medium resolution geological map of the Al-Uyaynah extrusive carbonatite with the results of the SAM algorithm showed "good" results. The

inaccuracies noted between mapped and spectrally-inferred lithological units, result from the spatial resolution limitations of Landsat 8, and the fact that endmember selection was complicated by sub-pixel mixing between variable rock cover types. Despite these issues, we have demonstrated that this method proves effective for geologic mapping and mineral general exploration purposes.
APPENDIX



Figure 2.12. A Comparison between the rock units' distribution that classified correctly, in percent, of SAM map based on the results of the confusion matrix accuracy assessment. SAM method gave, overall, a good result after comparing SAM map to the field ground truth regions.

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# **CHAPTER 3**

# A COMPARISON OF MAPPING METHODS AND SPECTRAL ANALYSIS TO IMPROVE CARBONATITE MAPPING USING VNIR AND SWIR BANDS OF ASTER DATA AT AL-UYAYNAH AREA, UAE

# Abstract

This study demonstrates an evaluation of ASTER multispectral data analysis and interpretation in the range of visible/near-infrared (VNIR) and Short Wave Infrared (SWIR) and mapping methods for lithological mapping of carbonatites. Carbonatites, which are usually rich in economically significant minerals/elements such as rare-earth elements (REE), are part of the metamorphic sole of Samail ophiolite that is located in the northeastern terrane of United Arab Emirates (Al-Uyaynah area). In this study, we have examined four different algorithms to identify carbonatites: Binary Encoding Classification (BEC), Support Vector Machine (SVM), Spectral Information Divergence (SID), and Spectral Angle Mapper (SAM). These algorithms were applied to identify the integral correlation between carbonatite and neighboring rock units. The results are shown as digital-based maps that highlight pixels that correspond to particular endmember-spectra among different kinds of class. Out of the methods we tested, the SVM distribution map displays the most robust results; the agreement with field ground truth ROIs data is excellent with overall accuracy at 97.58%, and with a calculated kappa coefficient of 0.97. The SAM, SID, and BEC yield overall accuracy between 81%-43% respectively and kappa coefficient between 0.75 for SAM to 0.32 for BEC. To confirm our finding, the SVM mapping method was tested on another carbonatite, the Hatta carbonatite, located in a region 60km south our main study area (about 60 Km). Hatta shares the same petrogenetic history and major geochemical characteristics as the Al-Uyaynah area. The result shows that SVM mapped the Hatta carbonatites with an excellent overall result of 99% accuracy and a kappa coefficient of 0.99. Our results, which over both carbonatite localities exhibit excellent results, highlight the potential utility of the SVM technique applied to ASTER data for further carbonatite exploration and mapping.

#### **1.Introduction**

This research is focused on examination of ASTER (Advanced Spaceborne Thermal Emission and Reflection Radiometer) image information (Table. 1, and Figure 3.1) to map the Al-Uyaynah carbonatite, a small area within the metamorphic sole of Samail ophiolite, located within northeastern Oman's mountains. Carbonatites are typically important hosts for economically useful minerals/elements; such as rare earth elements (REE), which include cerium (Ce), lanthanum (La), neodymium (Nd), and europium (Eu) [4]. Carbonatite detection is often a challenge, as it commonly appears as narrow bodies within larger-scale features [5]. To address this challenge, a more widespread use of spectral base sensors, with worldwide coverage and proper wavelength resolution is required.



Figure 3.1. ASTER spectral transmittance of band pass filters were used in this research, modified from[13].

The application of remote sensing for mineral/element exploration and mapping has expanded remarkably since the early 1960s. Initially, remote-sensing was used as an affordable and quick method to analyze the chemical deviation of surface rocks types in order to map the lithological variance within a region [6, 7]. Multi-spectral satellite sensors include the visible/near-infrared (VNIR), shortwave infrared (SWIR), and thermal infra-red (TIR) spectra that are crucial to mineral exploration [8, 9]. The Advanced Spaceborne Thermal Emission and Reflection Radiometer (ASTER) acquires images in the (VNIR, SWIR, and TIR) ranges-spectra, which are important in mineral exploration [10]. The ASTER sensor can reveal more bands than the old sensors within the spectral range sensitive to minerals and rocks at the earth's surface [11]. Previous researchers pointed out that ASTER compares favorably with the precision of other sensors and has an advantage for geological mapping [12] by having better reflectance spectra, allowing for the identification of assemblages of specific minerals or groups of minerals [7].

Contemporary remote-sensing detectors like ASTER have a greater spectral bandwidth that is beneficial for the differentiation of rock bands and minerals [14, 15]. Mainly it has been shown that a wide array of minerals such as clays, carbonates, and hydroxides could be recognized through the usage of remote-sensing spectral analysis methods (e.g.[9]). The VNIR and SWIR bands' data typically are an invaluable source of information regarding transition elements' absorption, particularly iron species like Fe<sup>2+</sup> and Fe<sup>3+</sup> [8, 15, 16]. The area of the reflectance spectrum from 0.45 to 2.5  $\mu$ m is important in determining the composition of minerals on the basis of absorption characteristics [9, 15, 17].

Carbonatites, which are enriched with about 50% or more of calcite minerals, exhibit a particularly strong absorption characteristic of the  $CO_3^{2-}$  ion, which observed within the range between 2.31-2.33 µm of the SWIR band [18].

The absorption features of iron-rich carbonatites are pronounced in the range of wavelengths between 1.0-1.3 µm [19]. Iron and REEs, which may occur in carbonatites in abundance, but are not typically found in most other carbonates, may be an important factor in distinguishing carbonatites from other economically less valuable carbonate rocks. The REE spectrum is largely related to electronic transitions in  $Nd^{3+}$ , which is clearly shown by absorption features in the wavelength ranges between 0.5 and 0.9 um [9, 20]. A mixture of these absorption characteristics can serve as a foundation for the creation of carbonatite maps through remote sensing. The absorption spectra attribute of carbonatites has already been employed in previous investigations to generate maps of carbonatite complexes that are detectable by aircraft sensors. AVIRIS (Airborne Visible / Infra-Red Imaging Spectrometer) scenes were utilized to recognize the Ice River carbonatite complex, and revealed slight absorption characteristics situated at 0.58, 0.74, 0.80, and 0.87 um, which suggests a neodymium absorption feature [21]. Similarly, recent studies of the Sarfartoq carbonatite in Greenland were conducted using a mix of spectral techniques to differentiate between carbonatite, fenite, and hematised areas of exposed rock, with special focus on the Nd<sup>3+</sup> reflectance feature [22]. Comparatively little work on carbonatite identification has been attempted using satellite-based sensors.

The aims of this research are: (1) to investigate and assess the extent of the Al-Uyaynah carbonatite by analyzing the spectral response utilizing ASTER visible near infrared (VNIR) and short wave infrared (SWIR) bands, (2) to produce a more accurate classification of the ASTER dataset of carbonatite distribution by utilizing both spectral and spatial information, and (3) to assess ASTER system performance for carbonatite mapping.

# 2. Geologic background of study

## 2.1 Carbonatite location and outcrops

The area of interest for this research project is the Al-Uyaynah carbonatite of the United Arab Emirates. This region is approximately 18 kilometers to the southwest of Dibba city (Figure. 3.2). The Al Uyaynah carbonatite is mapped as a member of the metamorphic sole of Samail ophiolite, which is comprised of exposures of sub-aerially erupted carbonatites within oceanic metasediments [5]. The Al Uyaynah carbonatite has formerly been construed as a volcanic accretionary island pre-dating the Samail ophiolite [5]. The outcrops are well-exposed and are roughly 10-15 meters thick of many of adjacent layers in plan view, making this region a useful locale to study remote sensing techniques applied to carbonatites (Fig.

2).



**Figure 3.2**. (a) Map of the northern eastern of UAE indicating the location of the Al-Uyaynah area and general geological units, modified from [23, 24]. (b) ASTER 3, 2, and 1 natural color image.



**Figure 3.3**. A field view of Al-Uyaynah carbonatites (fig. 1), (a) shows the ferro-carbonatites outcrops of the northern end of the study area, (b, and c) show a close view of ferro-carbonatites. (d) Shows the extruded calcio-carbonatite, and (e, f) illustrates a close view of calcio-carbonatite.

#### 2.2 Geochemistry of Al-Uyaynah Carbonatite

The Al Uyaynah carbonatites are divided on the basis of the chemical compositions and grain size into two common magma types: calcio-carbonatite and ferro-carbonatite (Figure 3.3). These magma types are found in a majority of carbonatites worldwide [5]. The carbonatite complex is comprised of many contiguous layers; and each layer thick is roughly between 10 to 15 meters. These layers contain lapilli, which requires eruption within a subaerial environment [5]. Calcite is the major mineral phase in the calcio-carbonatites, but the calcio-carbonatites also include a significant amount of apatite, as well as opaque minerals such as magnetite. The typical composition of the lapilli is 40% calcite, 20-30% apatite, and 20-40% opaque minerals [5]. Based on the current whole-rock geochemical data, ferrocarbonatites exhibit larger abundances of silicate minerals compared to calcio-carbonatites. Representative ferro-carbonatite minerals are allanite (Ce), amphibole (alkali), and occasionally strontian barite. Allanite typically occurs as crystal accumulation in ferrocarbonatites [2]. These accumulations concentrate REEs, resulting in a heterogeneous dispersion of trace elements within the rock [5].

#### 3. Methods

# 3.1 ASTER data calibration

ASTER multispectral bands (VNIR-SWIR) that were utilized in this research were acquired from the Land Processes Distributed Active Archive Center (LP DAAC) which is based at the USGS Earth Resources Observation and Science (EROS) Center in Sioux Falls, South Dakota. ASTER data was acquired of the Al-Uyaynah area on 02-05-2002. The data was obtained as AST\_07 Surface Reflectance and Crosstalk Corrected SWIR as Hierarchical Data Format (HDF) product [25].

The ASTER AST\_07 product is geo-referenced in Universal Transverse Mercator (UTM) map projection arrangement and World Geodetic System datum (WGS-84) [25]. It already includes atmospherically corrected data of Level-1B. The surface reflectance of VNIR was produced by utilizing the 3 VNIR bands (0.52 - 0.86  $\mu$ m). The SWIR surface brightness is created by applying a crosstalk correction algorithm, then utilizing 6 SWIR bands between 1.60 - 2.43  $\mu$ m of a Level-1B of ASTER scene.

#### 3.2 ASTER data analysis

## 3.2.1 Dimensionality reduction

The Minimum Noise Fraction (MNF) method is a linear transformation utilized to differentiate noise from data and identify inherent spectral information dimensionally [13]. Each of the 9 measured ASTER bands ( $0.52 - 0.86 \mu m$ ) were incorporated for processing in the MNF transformation. MNF was applied to the scene in order to recognize and evaluate which bands contained data that was coherent, and which had noise. This was achieved by examining the MNF gray bands along with eigenvalues diagram (Figure 3.4 and 5). (see the result section).



**Figure 3.4.** A MNF eigenvalue plot for study area (Al-Uyaynah). All MNF bands have eigenvalues values greater than 1. The lowest band (9) has eigenvalue equal to 2.53, which means it contains coherent data. However, the first 5 bands contain more spatially coherent information than the other bands.



**Figure 3.5** MNF images of ASTER VNIR-SWIR bands for study area. Images 1-9, display a single gray band, while image 10 shows a combination of first three MNF bands (1, 2 and 3 as RGB) for comparison

#### 3.2.2 Endmember extraction

The study image has present within it many different rock units. Each unit exhibits different spectral values, which must be de-convoluted. Finding and extracting the representative endmembers is an important step that must occur prior to the image segmentation processing of our study area. In this research, the endmembers were determined and extracted from ASTER data by utilizing the Pixel Purity Index (PPI) tool of ENVI software. The Pixel Purity Index (PPI) represents the intensity of pure pixels within an image

[13, 26]. The PPI is often determined by projecting the n-D (n-dimensional) scattergraph on an indiscriminate unit vector [13, 26]. The PPI functions were applied on the MNF images with 5,000 iterations, and then the results were visualized using n-D visualizer (n-D scatter plots). Pixels located on the corners of the unit vector were assigned to be the spectral reflectance end-members (Figure 3.6). After that, the extracted end-members were utilized to classify the ASTER image and map the carbonatites (see the result section).

# 3.2.3 Defining the regions of interest (ROIs)

Regions of Interest (ROIs) are defined as potential targets of a raster that were identified based on a geological map of the area and field information. For this project, we focus on areas of carbonatite, and examine the correlation between previously identified exposure and predicted occurrences in our post classification accuracy assessment [13]. ROIs were identified in this study based on the 1:50 000 lithological map [1], and ground-truth



**Figure 3.6.** Show a 3-D Scatter plot of the end-members data cloud (image bands 1-3 were used as plot axes). The identical rock units were characterized by the same color.

locations or rock units that were collected during our field trip. The ROIs were defined using ENVI 5.1 software ROI tool and were based on ASTER image coordinates. The defined ROIs were utilized to produce a random sampling of pixels (Figure 3.7). These random sampling of pixels were utilized to evaluate the mapping outcomes of the BEC, SID, SAM, and SVM algorithms (See section 5.3. Classification results and accuracy assessment).

# 3.3 Classification methods

The image categorization method can be employed on the basis of spectral analysis approach and statistical classification techniques that summarize relevant pixels in meaningful categories [27, 28]. For image examination and analysis, the spectral match base methods are more feasible given that the rocks and minerals usually tend to have distinct spectral absorption characteristics[27, 29]. Quite a few image categorization techniques rely on the spectral method of analysis and have been developed for charting out geological maps [30]. They include the Spectral Information Divergence (SID) algorithm, the Binary Encoding Classification (BEC), the Spectral Angle Mapper (SAM), and Support Vector Machines (SVM). In this study, these approaches were examined to determine the most robust method to discover and map carbonatite and other relevant compositions within the area concerned. Classification results were compared, so as to assess these algorithms, with the data from the field and geological maps.



**Figure 3.7.** Shows a random sampling of pixels that were generated from the defined ROIs. These random pixels were used as a reference to assess the mapping outcomes of the BEC, SID, SAM, and SVM methods.

#### 3.3.1 The Binary Encoding Classification (BEC)

The Binary Encoding Classification (BEC) is a method that encodes the endmember spectra information and image data into binary numbers and is dependent on whether the band values fall below or above the mean of spectrum [31]. This algorithm analyzes and

compares or matches every encoded endmember through the encoded image spectra and then creates a category image [13, 31].

In order to make a lithological map in the present study, the binary encoding match algorithm was employed due to the many advantages it offers including: 1) it is a relatively simple algorithm [31]; 2) it is quite efficient for classifying minerals/elements with differentiated absorption characteristics [31, 32]; 3) it is also useful to measure the process of extraction since it has the sensitivity to band positions and is unaffected by albedo (brightness) difference [32]. Consequently, this method might be useful for mapping of the complex nature of our study area using medium special resolution (ASTER data), (See the section 5.2.7 for results of applying this method).

# 3.3.2 The Spectral Information Divergence (SID)

The Spectral Information Divergence (SID) technique, which is derived from the idea of the theory of divergence in information, is applied to explain the spectrum statistics [33]. This method employs a divergence measure to assign pixels into endmember spectra [13, 34]. The likeness between the spectra among pair pixels is measured by examining the amount of difference of probabilistic behaviors amongst their spectra [35]. The smaller the divergence is between pixel and endmember, the greater the probability that the pixels of endmember and image spectra are comparable [13, 34]. The pixels with measurements that are larger in relation to the maximum divergence threshold are not categorized [13].

For the study of carbonatite, the SID algorithm has potential utility as it is able to measure the spectral variance of an individually mixed pixel from a probabilistic viewpoint [35]. This feature is useful given that each pixel of our research area image encompasses mixed rock units due to the medium resolution nature of the dataset and the size of the outcrops. The SID algorithm also has the benefit of finding the spectral similarity between pixels and endmembers and exhibits effective separability among of the mineral endmembers [36]. Therefore, this method is particularly useful for mapping of the complex geology of our study area using ASTER datasets.

# 3.3.3 Spectral Angle Mapper (SAM)

The SAM algorithm is a physical technique used to identify an image focused on fitting and comparing the angle in the space between the pixel vector to an end-member image spectral vector in the n-dimensional space [13, 26, 37]. The smaller the angles between the endmember and pixel, the more of a match there is with the endmember spectrum; where



**Figure 3.8.** Shows how the SAM method classifies the image. The smaller the angles between the endmember and pixel, the more of a match there exists with the endmember spectrum. Where pixels surpass the defined angle threshold, they are not categorized. The figure was modified from [37].

pixels exceed the defined rock unit endmember maximum angle threshold are not categorized (Figure 3.8) [13].

In our region, the complicated topography and geology make distinct endmembers less pronounced. The SAM algorithm has potential to resolve the distinct endmembers over other more typically used spectral-based methods because: 1) the SAM technique is an efficient technique for finding and outlining the likeness between the image spectra and reference spectra [13, 37]; 2) SAM is

not impacted by shading which can enhance or isolate the rock units reflectance features [38], and 3) SAM does not require any presumptions with regard to the statistical- distributions of the input information in carrying out segmentation as is common in parametric procedures [39].

# 3.3.4 Support Vector Machines (SVM)

Support Vector Machines (SVM) is a supervised classification approach produced from the statistical learning theory that frequently produces efficient classification outcomes from noisy and complicated data [34]. SVM dissociates the images units using a decision surface (optimal hyperplane) that increase or maximize the border among the groups of classes (support vectors) (Figure. 3.9) [13, 34].



**Figure 3.9.** Linear Support Vector Machine illustration. The SVM training algorithm is used to find a hyperplane that divides the image pixels to a separate number of classes. Modified from [41, 42].

In this research, we have utilized the SVM method as it has the following strengths: 1) The method has the capacity to utilize a limited number of training data sets to regularly

deliver higher characterization precision than the conventional methods [40]; 2) The learning-procedure central to the method (structural risk minimization), offers a good classification without needing prior knowledge, even with very high dimension of the input space [41]; 3) SVM is a non-parametric

classification and commonly used in studies where noisy and complex data are present [42]; 4) The SVM learning method discovers the decision boundary or hyperplane between the image data with iterative process to separate the likely groups, based on the defined endmembers, and then maximizes the distance between each group from the hyperplane (Figure. 3.9) [43, 44]. The hyperplane option that is available in the SVM method was employed to help to decrease the chances of misclassification in our study area; 5) SVMs have been shown to be generally robust since as they have control parameters options [42].

3.4 Post classification assessments

A comparison and accuracy calculation was made to allow a better understating of the different products' relative performance in the identification of lithologies for our ASTER scenes. The evaluation of the performance of BEC, SID, SAM, and SVM is used in this study. The computing of kappa coefficients and overall accuracies were calculated using a

confusion-matrix [13, 45]. The confusion-matrix (error matrix) approach is most extensively used to characterize the classification accuracy of digital mapping of remote sensing data; the error matrix is appropriate for many accuracy assessments [45]. Many scholars have suggested utilizing the "error matrix" method in reviewing the accuracy of the mapping product, and it is currently counted as a standard method for accuracy measurement (e.g. [46-48]). In order to enhance measurements of accuracy, the kappa coefficient statistical tool is also frequently applied[49]. However, there remains some disagreement as to the utility of standard accuracy estimation measurements like the kappa coefficient for the calculation of the accuracy of remote sensing classified images [50, 51]. Specifically, much of the remote sensing information is influenced by diversified pixels, which may confound simple statistical tools (e.g.[50]). Nevertheless, it remains valuable as an indicator of classification result accuracy. Specifically, the kappa coefficient is still considered to be the most appropriate method for rank-ordering of the mapping results accuracy's agreement [52].

One of the most useful ways to utilize Kappa for mapping results assessment and comparison was provided by Landis and others [52, 53]. They have categorized the different ranges of kappa coefficient values based on based on the agreement degree [52]. They suggested that the values greater than roughly 0.75-0.85 indicate a very good agreement; values greater than 0.85-0.99 indicate excellent agreement, and values of close or equal to 1.0 would be perfect agreement. In contrast, lesser levels of agreement were classified as: good if the kappa coefficient values were between 0.4-0.55; fair agreement between 0.40-0.55 values; and values of 0.4-0.05 or less indicate poor to no agreement as illustrated in

Table.2 [52, 53]. It is worth mentioning that the accuracy, meaning, and measurement of classification may depend ultimately on the demands of an individual project [47, 54]. In this research, we used the accuracy calculation for evaluating and ranking the segmentation results from BEC, SID, SAM, and SVM algorithms (See section 6. Classification results and accuracy assessment).

#### 4. Field surveys and ASD measurements

Rock samples and location information were gathered during field surveys in December 2010. The weathered and fresh surfaces of the returned samples were examined and analyzed utilizing an Analytical Spectral Device (ASD) spectroradiometer (Fig. 3.9). All reflectance spectral measurements were made in the laboratory utilizing an ASD FieldSpec-3 Hi-Res Spectroradiometer, which is located within the Department of Environmental Sciences at the main campus of the Univesity of Toledo. A 1000W 3200K Quartz Halogen lamp provided illumination. A 10-degree foreoptic was employed. Reflectance spectra were obtained for both unweathered and weathered surfaces for every sample. All spectra were normalized to a Spectrion lab standard with well characterized spectral properties. All ASD-Laboratory spectra were resampled to the ASTER system (VNIR-SWIR) using spectral resampling tool available in ENVI software [13].

# 5. Results

5.1 Noise reduction and endmembers extraction

ASTER bands covering the VNIR and SWIR spectral range (0.433–2.95  $\mu$ m) were selected for the MNF transformation procedure. The outcomes of this transformation contained eigenvalues and eigenimages (MNF images), which were used to evaluate the data dimensionality by comparing MNF pictures with MNF eigenvalues (Figure 3.4). Bands with higher eigenvalues (greater than 1) comprise the main share of inherent information, and bands with lower eigenvalues ( $\leq 1$ ) contain noise [13]. The eigenvalues for all MNF bands are above 11.23. However, more spatially coherent data were present in the first three bands (2 to 3) as compared the rest of the bands (4-7), as illustrated in Figures 3.5.

In order to determine endmembers, the MNF images containing coherent data (1-9 bands) were analyzed utilizing the PPI technique with 20,000 iterations. These end-members were then visually examined using an n-D visualizer (n-D scatter plots). Pixels at the corners of each dataset were then selected as class types using the region-of-interest (ROI) tool. After the purist pixels had been defined by using n-D scatter-graphs, the distinct pixels were marked and recognized as regions of interest (ROI) with the ASTER Image. The calculations for mean-spectra for ROI classes were extracted and were utilized as endmembers for further image classification. Additionally, a supported field based ground-truth (ROI's) mean-spectra were used along with image endmember spectra in classification and rock units mapping.



**Figure 3.10.** Laboratory reflectance spectra (ASD), showing REE absorption near 0.589, 0.567, and 0.56  $\mu$ m and (CO<sub>3</sub>, MgO) absorption near 2.32-2.35  $\mu$ m, and near 1.6  $\mu$ m for calcite absorption.



Figure 3.11. The resampled laboratory reflectance spectra (ASD) of ferro-carbonatite and calciocarbonatite.



**Figure 3.12.** A zoom-in of the spectral region 0.5-0.6  $\mu$ m of laboratory reflectance spectra (ASD), showing REE absorption near 0.589, 0.567, and 0.56  $\mu$ m (left), and a zoom-in of the spectral region 0.2-2.4  $\mu$ m of laboratory reflectance spectra (ASD) showing (CO<sub>3</sub>, MgO) absorption near 2.32-2.35  $\mu$ m, and near 1.6  $\mu$ m for calcite absorption.



Figure 3.13. ASTER image endmembers spectra of calcio-carbonatite and ferro-carbonatite; in VNIR-SWIR bands.

#### 5.2 Endmembers' spectral characteristics

To unravel the endmember spectra, we have evaluated the possible causes for the distinct absorbencies in the ferro- and calcio carbonatite. Broadly we have found that calcite, iron, REE, and silica-based minerals dominate the spectra.

# 5.2.1 Calcite

Calcite is the major mineral phase in calcio-carbonatite, constituting about 40% of its lapilli composition. While less abundant, significant volumes of calcite are also present in ferro-carbonatites. The calcio-carbonatite and ferro-carbonatite image endmembers show a clear calcite ( $CO_3^{2-}$  ion) absorption feature at 2.336 µm (Fig. 3.12). This is consistent with the ASD spectra of both carbonatite types, which also show a strong absorption of calcite at 2.336 µm (Fig. 3.10- 3.12).

Some distinction between the two rock types is evident due to the greater percentage of calcite within the calcio-carbonatites, which manifests as more distinct absorption peak at 2.336  $\mu$ m in both ASD and image end-members in comparison to ferro-carbonatites (Fig. 3.10, and 3.12).

#### 5.2.2 Alkali amphibole minerals

The alkali amphibole group of minerals are a major constituent of the ferrocarbonatites, but only a secondary mineral in calcio-carbonatite [5]. The hydroxyl ion associated with the hydrosilicates, Mg-OH and Fe-OH, of alkali amphibole [55, 56] generate distinct absorption features at 1.4  $\mu$ m and 2.2-2.3  $\mu$ m [8]. The ferro-carbonatites image endmember displays hydroxyl ion (OH) absorption at 2.26  $\mu$ m, caused by the Mg-OH and Fe-OH components of alkali amphibole minerals. The ferro-carbonatites ASD laboratory spectra is consistent with the image endmember absorptions. However, it also displays a greater number of OH absorption features at the ranges 1.4, and from 2 to 2.226  $\mu$ m of the spectrum (Fig. 3.10).

In contrast, the alkali amphibole forms as only a secondary mineral within the calciocarbonatite. Some minor absorption near 1.4  $\mu$ m of ASD spectrum was observed (Figure. 3.10). However, this absorption is not detected in the ASTER image calcio-carbonatite endmember (Figure 3.13), because the atmospheric (H<sub>2</sub>O vapor) absorption prevents the use of these band ranges (0.9-1.6  $\mu$ m) for reliable mineral identification.

### 5.2.3 Iron minerals

Ferrous and ferric ions ( $Fe^{2+}$ ,  $Fe^{3+}$ ), are present in iron oxide minerals in both of ferrocarbonatite and calcio-carbonatites outcrops. This is quite evident in the field as a rustweathered surface, as rough outcrop with a crust of iron oxides. Iron minerals, magnetite and
hematite, are among the major minerals forming the ferro-carbonatite matrix, however, iron minerals are secondary minerals in the calcio-carbonatite [5]. Iron minerals diagnostic absorption features were recorded by many scholars, (e.g., [17]), within the very-near infrared (VNIR) ranges. In our study area, the ferro-carbonatite and calcio-carbonatite spectra show that the iron oxides were recorded by ASD and ASTER instruments for the weathered outcrops in both of ferro/calcio-carbonatites near 0.804  $\mu$ m, for both image end members and ASD spectra (Figure 3.10, and 3.12).

Ferro-carbonatites have more iron minerals (magnetite and hematite) than calciocarbonatite. These iron minerals caused additional absorption in the area between 0.661-0.804  $\mu$ m of the ferro-carbonatite image end member and ASD spectra, and weak Fe<sup>3+</sup> absorptions at 2.26  $\mu$ m, and this may facilitate a differentiation between the two carbonatite spectra.

## 5.2.4 REE minerals

Rare earth elements (REE) are found in great abundance in carbonatite lavas, frequently forming distinctive mineralogies. Within our study area, ferro-carbonatite has a significant abundance of rare earth element bearing minerals, while calcio-carbonatite contains significantly lower concentrations [5]. REE spectral absorption features have previously been reported in the USGS digital spectral library within the visible region [17]. Our ferro-carbonatite ASD spectra show REEs absorption features in the area between 0.45 - 0.56  $\mu$ m (Fig. 3.12). However, the ASTER image endmembers did not show REEs absorption features due to the ability detection limits of medium spectral and special resolution sensor (ASTER).

In contrast to ferro-carbonatites, neither calcio-carbonatite the image endmember nor ASD spectra of calcio-carbonatites exhibited REEs absorption characteristics. This is the result of likely low REE abundances in calcio-carbonatite lavas.

5.3 Classification and accuracy assessment

Evaluation and accuracy calculations permit us to develop a better understating of the various mapping products performances in the classification of

lithologies from ASTER scenes. The determination of kappa coefficients and overall accuracies were calculated using a confusion-matrix method [13, 45]. The comparison of the confusion matrix overall accuracy information and the kappa coefficient results for the analysis of four different mapping methods are illustrated in table 3.1 and figure 3.20. The evaluation of the performance of each method (BEC, SID, SAM, and SVM) is addressed in the sub-sections below.



Figure 3.14. The image endmember spectra were extracted from Landsat OLI image and are utilized as endmembers for further image classification.

### 5.3.1 Binary Encoding Classification (BEC)

The first method we tested was the Binary Encoding Classification (BEC). The BEC algorithm encodes endmember spectra and image data into zeros and ones and then compares each encoded data point to create a map [13, 31]. The overall accuracy of the BEC map is 39 %. The calculated kappa coefficient, which measures classification performance relative to chance, is 0.31, (Fig. 3.15). These results are indicative of 'No agreement' in the classification standard category (Table 3.1, and Fig. 3.20) [52, 57].

# 5.3.2 Spectral Information Divergence (SID)

The second method utilized was the Spectral Information Divergence (SID) approach. The SID map shows a fair discrimination among ferro/calcio-carbonatite and other the rock units (Fig. 3.16 and 3.20). The accuracy assessment of the SID shows overall accuracy 52%. The kappa coefficient is 0.47, which falls into the 'fair category [52, 57].

## 5.3.3 Spectral Angle Mapper (SAM)

The Spectral Angle Mapper (SAM) classification was employed in the calculation of the spectral matches between endmembers and image spectra [21-23]. SAM achieves the second best results (Figure 3.17 and 3.20) with an overall accuracy of 61 %. The calculated Kappa Coefficient is 0.56, placing this method into the 'good' agreement category of the kappa coefficient statistic.

#### 5.3.4 Support Vector Machine (SVM)

The Support Vector Machine (SVM) digital-mapping results shown in Figure 18 achieved the best results, with an overall accuracy of 86.4% (Figure 3.18). The calculated kappa coefficient is 0.85. This is recognized as 'excellent' in the classification standard category (Table 3.1, and Fig. 3.20) [52, 57].

#### 6. Discussion

Our experimental approach of using four different methods (BEC, SID, SAM, and SVM) to map and differentiate carbonatites from other rocks unit highlighted significant performance differences among the algorithms (see the table's 3.2-3.5 in appendix). The observed variable results likely reflect the following issues when interpreting data from this region: 1) the variable topography of the study area leads to the data being complicated by shadows or different illumination factors in the same unit or between rock units; 2) the minerals' similarity in composition within rock formations, e.g., the existence of silicate minerals in many units, contributes to the complexity of some algorithms' performance during the analysis process; 3) The image 30 m<sup>2</sup> pixel (medium resolution) results in quite mixed pixels with multiple rock units in each pixel; Despite these practical difficulties, some algorithms performed well, while others did not. Below we outline the particular characteristics of each algorithm which may have impacted its performance in this instance.



**Figure 3.15.** The binary encoding classification (BEC) map shows very poor discrimination among ferro/calcio-carbonatite and other the rock units. The accuracy assessment of the overall accuracy is 39%, the Kappa Coefficient is 0.31, this recognized as "No agreement" in the classification standard category.



**Figure 3.16.** The Spectral Information Divergence (SID) map shows fair differentiation between rock units. The accuracy assessment of the SID shows an overall accuracy with 52%; the Kappa Coefficient is 0.47, which is known as "fair results" in the category.



**Figure 3.17.** The Spectral Angle Mapper (SAM) classification performs the second best result with an Overall accuracy of 61%. The calculated Kappa Coefficient is 0.56 placing into the good agreement category of the Kappa Coefficient statistic.



**Figure 3.18.** The Support Vector Machine (SVM) digital-mapping shows the best result with an overall accuracy of 86.4%. The calculated Kappa Coefficient is 0.85 placing into the excellent agreement category of the Kappa Coefficient statistic.



**Figure 3.19.** Geological map of Al-Uyaynah area showing the mapped area of extrusive carbonatites (modified from [1].

Lower Bound	Degree of Agreement	Upper Bound
<0.05	No	0.05
0.05	Very Poor	0.20
0.20	Poor	0.40
0.40	Fair	0.55
0.55	Good	0.70
0.70	Very Good	0.85
0.85	Excellent	0.99
0.99	Perfect	1.00

**Table 3.1.** The values of threshold that used for dividing the results of statistical kappa coefficient degrees of agreement. From [52, 57].



**Figure 3.20.** A comparing of confusion matrix over all accuracy, and kappa coefficient results. The binary encoding classification (BEC) overall accuracy is 43.59%; the calculated Kappa Coefficient is 0.32. This recognized as No agreement 'not even poor results' in the classification standard category. The Spectral Information Divergence (SID) map shows a good discrimination among ferro/calcio-carbonatite and other the rock units. The accuracy assessment of the overall accuracy is 68.3%; the Kappa Coefficient is 0.58, which is known as "good results" in the category. SAM performs the second best result with an Overall accuracy of 81.54%. The calculated Kappa Coefficient is a mere 0.75 placing into the very good agreement category of the Kappa Coefficient statistic. The Support Vector Machine (SVM) digital-mapping results with an overall accuracy of 97.58%. The calculated Kappa Coefficient is 0.97. This recognized as excellent in the classification standard category.

The BEC algorithm achieved poor results since it was designed to encode the information of image pixels and end-member's spectra into binary numbers. Encoding spectrum, to 0 or 1, has a drawback in lithological mapping since: 1) the study area has a complicated geology. Encoding causes a loss of some of the valuable details for both the endmembers spectral characteristics and image information; 2) The BEC has classified the image based on the winning class based on whether the band values fall beneath or over the class mean [31]. In our study, many rock units exhibit an abundance of silicate minerals, and the similarity in these minerals make the rock units hard to distinguish using this method.

The SID algorithm shows a fair result, but it did not generate a better map than SAM and SVM methods for many reasons: 1) SID analyzes the spectra as random or irregularly variable and then measures the divergence between spectra [35]. Our research area has: 1) complicated lithological features, consequently this stochastic approach did not consider the spatial arrangement of some rock units and thus produced an abnormal map; 2) SID is less sensitive to the shadow factors in the spectrum as compared with the SAM method [58]. This decreases the spectral values of outcrops in the shadowy areas, and produces a less accurate mapping result; 3) In our multispectral image, a pixel is commonly a mixture of many of rocks with similar spectral features, SID is unable to resolve these complex pixels effectively.

The SAM algorithm achieved a 'good' mapping result for the following reasons: 1) This method is effective at grouping image pixels, because the angle is independent between the endmember image pixels [37]; 2) it also resistant to the impact of shading and enhances the rock's spectra by isolating its reflectance spectra from the shadow effects [38], and 3) SAM does not require any statistical distribution assumptions of the data in order to create a classification - as is common in other parametric procedures [39]; 4) the only drawback of this technique is the problem of spectral mixtures in pixels as described above. SVM method was judged the best technique and achieved the 'excellent' result since: 1) the SVM is a linear method that discovers hyperplane, allowing the method to separate the likely rock groupings. By increasing the distance of units from the hyperplane, the hyperplane agent reduces the chance of misclassification [43]; 2) SVM was designed based on a statistical learning machine (theory) that frequently yields efficient classification outcomes from noisy and complicated data [41]; 3) because of its capacity to operate with a small number of training classes, it is capable of performing at a higher characterization precision than the other methods [40].

The calcio/ferro-carbonatites n-D spectra show that the calcio/ferro-carbonatites distribution in the central region of the study area, measured from north to south, closely matched both field ground truth ROIs reference geological maps. SVM and SAM classification maps show calcio/ferro-carbonatites distribution in the central region of the study area, measured from north to south. SVM was the most successful in distinguishing between major rock units, particularly in the discrimination of calcio-carbonatites (98.96% of class accuracy), and ferro-carbonatites with 91.01% accuracy (Figure 3.24, and Table 3.5). SAM was able to discriminate calcio- carbonatites with 57.29% accuracy, and correctly identified 87.64% of ferro-carbonatites (Figure 3.23, and Table 3.4). Calcio/ferro-

carbonatites were distinguishable by both SAM and SVM algorithms, but the SVM method gave the best result after comparing SVM to field ground truth regions of interest. However, the classification error in calcio-carbonatites and in ferro- carbonatites SVM map were found to be a result of three factors. Firstly, it is possible for some carbonatites to remain undetected due to the fluctuation in the sizes of carbonatite bodies. Secondly, it is possible for sub-pixel contamination to take place because of the varying types of rock present in the ASTER image within a 30 square meter pixel size. Lastly, there is possible imprecision caused by the spectral similarity between metavolcanic rocks, carbonatite units, and the alkaline volcanic formation in the neighboring geographic area. The calcio and ferro-carbonatite accuracy results may also be impacted by the low numbers of pixels (<100 pixels) that were selected at random by the ENVI software when evaluating the mapping outcomes.

The alkali volcanic unit was mapped by employing SVM and SAM algorithms, in the eastern and western regions of carbonatite units, which is dominated by deformed basaltic alkali volcanic rocks (sub/green schist facies). The SVM algorithm mapped this unit with 72.48% accuracy, while the SAM method yielded 36.70% accuracy. The 27.52% error in the SVM map was due to the likeness of the absorption feature of silicate in alkali basalts and ferro-carbonatites. These resemblances generated some confusion for the SVM method during the analysis and created an overlap between ferro-carbonatites and the alkali volcanic unit in the southern area of our study.

The SVM and SAM maps of the metavolcanic unit correspond closely with the previously mapped metavolcanic unit in the western part of the geologic map. The SVM class accuracy for the metavolcanic unit is 78.26%, though it much poorer with SAM at 40.22%. The error likely relates to the composition of the metavolcanic units, which are rich in silicates, as are the alkali volcanic rocks and red-chert. Therefore, these spectral similarities caused overlap between rock units in contact areas; especially, in the eastern portion of the study area where accuracy is less robust.

The ophiolite complex, is well characterized using the SVM and SAM methods. The image results matched the ROI's and available geological maps, classify ophiolite with 99.43% accuracy (SVM), and 94.29% with the SAM method. The ophiolite mapped with high accuracy using both SVM and SAM because there is a large non-distributed mass of the ophiolite unit in study area image (about 11.7 Km<sup>2</sup>), which resulted in enhanced classification performance (Figure 3.24, and Table 3.5), and (Figure 3.23, and Table 3.4).

Red chert as indicated in geological maps is in the regions between alkaline metavolcanic units to the west and the ophiolite unit to the eastern side of the map, and extends in north to south orientation. The red chert unit was mapped with SVM at 78.74% accuracy but only 47.24% accuracy with the SAM classification scheme. However, we noticed that the red-chert unit in the south region of the study area was categorized as metavolcanic by the SVM algorithm, despite the overall low error in terms of absolute percentage. The red chert was badly categorized using the SAM method, as it relies on the

matching of the spectral features; both the red-chert and metavolcanic units have a high percentage of silicate minerals, leading to errors in this technique.

## 7. Testing SVM as a carbonatite detection tool - performance at an alternate locality

In the above mapping experiments, we have found that the SVM algorithm achieved the best results among all tested methods. To verify the utility of the SVM technique for carbonatite identification and mapping, we examined an alternate area which exhibits carbonatites. This area has similar tectonic and petrogenetic environment. The Hatta carbonatite area is located approximately 60 km to the south of the main study area (Figure 3.26). This area is located on the west side of Semail Ophiolite Complex, within the Hatta transform fault zone, UAE. The extrusive carbonatite in Hatta zone was discovered within the deep sea metasedimentary unit and is comprised of lenses and layers [2]. The layers average thickness range between 2-50m (Figure 3.25), and the weathered outcrop of these layers are colored with dark brown from the iron oxides [2]. These layers' exhibit calcite and silicate (quartz) veins. In our primary study area (Al-Uyaynah) there are two types of carbonatite (ferro/calcio-carbonatite) present. Despite the Hatta zone sharing the same petrogenetic history and major geochemical background as Al-Uyaynah carbonatite, in the Hatta zone, there is only one kind of carbonatite, which was found to be similar to ferrocarbonatite [2]. The Hatta ferro-carbonatite lapilli in this area consist of carbonate, apatite, monazite, allanite, and titanite as major minerals. The minor minerals are alkali amphibole, chlorite, and quartz [2].

We used ASTER (VNIR-SWIR) bands to analyze and map Hatta carbonatites. The data was obtained from Land Processes Distributed Active Archive Center (LP DAAC) as AST\_07 as surface reflectance and crosstalk corrected SWIR bands as Hierarchical Data Format (HDF) product [25]. The data were already geo-referenced in UTM projection system and World Geodetic System datum (WGS-84) [25].

We followed the same post classification procedures that were done over Al-Uyaynah area as described above. The Minimum Noise Fraction (MNF) method was used to the image nine bands in order to understand our data, calculate, and separate the coherent information from the bands that had noise. The MNF bands along with eigenvalues plot diagram were inspected, and it showed that we can use all nine band in the analysis and classification because it contains inherent information. The Endmembers were extracted by using the Pixel Purity Index (PPI) tool in order extract of the represented endmembers of rock units. The iron oxides in the carbonatites, and carbonate minerals, were key characteristics used in discovering the carbonatite spectra during pre-classification passes. Based on these endmembers we performed the SVM classification. The Support Vector Machine (SVM) method was applied to the Hatta image and achieved 'excellent' mapping result, illustrated in Figure 3.27, with an overall accuracy of 99.85%. The calculated Kappa Coefficient is 0.99. The carbonatite was mapped with this method with about 86% accuracy. The SVM miss-mapped carbonatite with 14% error due to the similarity in minerals between the meta-sediments and ferro-carbonatite.

# 8. Conclusion

This research presents a review of ASTER multispectral information analysis and interpretation in visible/near-infrared (VNIR), and Short Wave Infrared (SWIR) ranges for lithological mapping of carbonatites and surrounding rock units. ASTER is one of the best multispectral-remote sensing sensors for mineral mapping. A medium spatial resolution (15-30m) of ASTER images provides enough spectral ranges to detect carbonatite complexes, which can be relatively narrow.

In this study, we have successfully distinguished and mapped eight rock units using ASTER data, and generated acceptable separability between rock formations. The best differentiation between end-members was obtained through use of the SVM method, yielding 86.3% (excellent) overall agreement with the field ground truth ROIs and the existing published geological map. While useful, the SAM algorithm provided a map with 61.03% overall agreement (Good) with the field's ROI data and the geological map.

Our primary targets are the extrusive ferro- and calcio-carbonatites rocks - these units were well classified using these techniques. Ferro-carbonatite rocks were mapped with 91.01% accuracy by SVM, but are much poorer resolved using SAM (87.64%). The calcio-carbonatite endmember is similarly well resolved, 98.96% accuracy using SVM, and 57.29% of class accuracy with the SAM. While excellent classifications, some degree of error is noted:

(1) Mapping of ferro-carbonatite was more difficult at the southern region using both methods (SVM and SAM), as in this region deformed structures are present resulting in comparatively thin/ narrow rock units (a few meters in width). This problem is particularly acute near to the mélange (alkali volcanic) unit. The mixed appearance of the rock units' spectral likeness can contribute to the problematic calculations within the SVM and SAM algorithms and results in a non-recognition of sub-pixel spectral contamination.

(2) Complexity in distinguishing between ferro- and calcio-carbonatite endmembers results from the similar richness in iron oxide minerals in weathered surface layers of these rocks, causing a marked similarity in spectra. This similarity in the appearance of altered surfaces created some mis-classification in the SVM and SAM classifications in certain areas of the upper northern portion of the carbonatite complex. Accordingly, weathered/altered calcio-carbonatite might be mapped as ferro-carbonatite because of the shared iron oxide and hydroxide spectral characteristics.

(3) Our techniques identified carbonatite pixels in regions where the geologic map does not indicate the presence of this unit. However, given the difficulties in mapping carbonaite in the field, it may have escaped detection in prior maps. Indeed, smaller occurrences of carbonatite are geologically feasible in any of the units below the Samail ophiolite. Thus this error may in fact result from a more accurate determination of carbonaite occurrence in the mixed and complex units of this area. Other geologic units in the region that are rich in silicates and hydroxyl minerals (alkali volcanic mélange, metavolcanic and chert formations) share similar vibration energy features, making them difficult to robustly classify. However, despite the similar characteristics, the SVM separated these units with 'excellent' degrees of accuracy while SAM separated these units with 'good' levels of precision. Given such units may commonly be found in the vicinity of carbonanites in other environments (in particular the alkali volcanic units), this separation is important for the broader application of the technique presented herein.

Through comparison of field data and the geological map of the Al-Uyaynah extrusive carbonatite, the moderate spatial resolution results derived using SVM, SAM, SID, and BEC algorithms, the following findings have been reached: 'excellent' results were acquired with SVM method and a 'good' results have been obtained using SAM algorithm regardless of the spatial resolution restrictions of ASTER data, along with the reality endmembers with complicated sub-pixel mixing between irregular rock types. The categorization map created using SVM from ASTER image; illustrates that this process SVM) provides an efficient method for carbonatite rocks/mineral exploration and geologic mapping of these type of rock units in general.

APPENDIX



BEC Overall Accuracy = 38.6735% Kappa Coefficient = 0.3062

Figure 3.21. A Comparison between the rocks unit's distribution that classified correctly, in percent, of BEC map based on the results of the confusion matrix accuracy assessment. BEC method gave, overall, the poorest result after comparing BEC to the field ground truth regions.

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U	Unclassified	Chert formation	Metavolcanic formation 1	Schist formation	Alkaline volcanic rocks	Calcio- carbonatite	Ferro- carbonatite	Metavolcanic formation 2	Ophiolite complex	
Ophiolite complex	0.57	0	7.43	1.14	0	0	0	1.14	77.14	
Metavolcanic formation 2	0	0	23.53	0	8.82	2.94	20.59	36.76	2.94	
Ferro-carbonatite	0	0	0	0	4.49	4.49	89.89	1.12	0	
Calcio-carbonatite	2.08	11.46	0	0	10.42	57.29	18.75	0	0	
Alkaline volcanic rocks	0.92	14.68	3.67	0	45.87	6.42	23.85	0.92	0	
■ Schist formation	6.49	7.79	7.79	55.84	1.3	0	0	2.6	0	
Metavolcanic formation 1	0	15.22	20.65	3.26	21.74	6.52	9.78	6.52	6.52	
Chert formation	3.15	33.07	7.87	21.26	6.3	7.09	3.94	7.09	0.79	

SID Overall Accuracy = 51.7347% Kappa Coefficient = 0.4605

**Figure 3.22.** A Comparison between the rocks unit's distribution that classified correctly, in percent, of SID map based on the results of the confusion matrix accuracy assessment. SID method gave, overall, a fair result after comparing SID to the field ground truth regions.

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Ŭ	Chert form	ation	Metavolcanic formation 1		Schist formation		Alkaline volcanic rocks		Calcio- carbonatite		e	Ferro- carbonatite		Metavolcanic formation 2		nic 2	Ophiolite complex			
Ophiolite complex	0		0		0			0			0			0		0			94.29	
Metavolcanic formation 2	8.82		20.59			0		0			0		16.18		54.41			0		
Ferro-carbonatite	0		0			0			8.99		3	3.37		87.64			0		0	
Calcio-carbonatite	19.79		1.04		0			10.42			5	7.29		11.46		0			0	
Alkaline volcanic rocks	22.94		2.75		0.92			36.7			8	8.26		24.77		0.92			0	
■ Schist formation	10.39		10.39		62.34			0			0			0		0			1.3	
Metavolcanic formation 1	17.39		40.22			5.43			10.87			0		7.61		15.22			0	
Chert formation	47.24		12.6		22.83			2.36			6.3			3.94		1.57			C	)

SAM Overall Accuracy = 61.0204% Kappa Coefficient = 0.5619

**Figure 3.23.** A Comparison between the rocks units' distribution that classified correctly, in percent, of SAM map based on the results of the confusion matrix accuracy assessment. SAM method performs the second best result, overall good agreement, after comparing SAM to the field ground truth regions.

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	Chert formation		n Me for	Metavolcanic formation 1		Schist formation		Alkaline volcanic rocks			Calcio- carbonatite		Ferro-carbonatite		atite	formation 2		nic 2	Opl cor	hiolite nplex		
Ophiolite complex		0		0		0		0				0			0			0			99.43	
Metavolcanic formation 2		0		4.41		0		0				0		1.47			92.65			0		
Ferro-carbonatite		2.25		0		0		2.25				3.37		91.01			1.12				0	
Calcio-carbonatite		1.04		0		0			0			98.96		0				0			0	
Alkaline volcanic rocks		4.59		0.92		0			72.48			4.59		15.6			1.83				0	
Schist formation		3.9		14.29		76.62		0				0		0			0			0		
Metavolcanic formation 1		11.96		78.26		1.09		2.17				0		2.17			3.26			0		
Chert formation	,	78.74		8.66		1.57		5.51			2.36			0.79			0.79				0	

SVM Overall Accuracy = 86.3265% Kappa Coefficient = 0.8464

**Figure 3.24.** A Comparison between the rocks unit's distribution that classified correctly, in percent, of SVM map based on the results of the confusion matrix accuracy assessment. SVM method performs the second best result, overall an excellent agreement, after comparing SVM to the field ground truth regions.



Figure 3.25. Shows the ferro-carbonatite layers that intruded into metasediments unit of the Hatta Zone. Modified from [3]



Figure 3.26. shows the location and the geological map of the Hatta zone Modified from [2, 3]



**Figure 3.27.** The Support Vector Machine (SVM) digital-mapping of the Hatta carbonatite, shows the best result with an overall accuracy of 99.85%. The calculated Kappa Coefficient is 0.99.

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# **CHAPTER 4**

# DERIVING THE GEOCHEMICAL CHARACTERISTIC OF CARBONATITES USING VISIBLE NEAR INFRARED AND SHORT WAVE INFRARED SPECTROSCOPY

## Abstract

Rare Earth Elements (REE) have become an increasingly important natural resource considering their central role in the development of new green technologies. Locating REE deposits that are economically feasible for exploitation is a challenge. In this investigation, spectroscopic methods are utilized for the identification of carbonatite, an important host of REEs. The visible and near infrared (VNIR) and short wave infrared (SWIR) wavelength band of two common varieties of carbonatite (ferro- and calcio-carbonatite) were examined to correlate the spectral absorbances with the carbonatite's geochemical properties. Through our investigation, we found that carbonatites have three key geochemical components which yield distinctive and correlatable spectral signatures (calcite, iron, and, neodymium). Calcite is a major mineral within carbonatite, and displays vibrational absorption between 2.312–2.345 µm for both fresh and weathered surfaces of all carbonatite samples we tested. The absorption depth is variable and generally depends on the calcite concentration within a sample. The most pronounced calcite absorption was recorded from a fresh surface of a calcio-carbonatite sample at 2.33 µm. REE (Nd) absorption, is evident in both ferro- and calcio-carbonatites between 0.7 to 0.774 µm. However,

the most pronounced absorption  $(0.742 \ \mu m)$  is observed for fresh surface samples of ferrocarbonatite; calcio-carbonatites exhibit less absorption on both weathered and fresh surfaces. Feoxides exhibit absorption within the VNIR region between 0.866-1.69  $\mu$ m, with the most pronounced iron oxide absorption recorded from the fresh surface of a ferro-carbonatite at 1.167 µm. In this research, geochemical analysis was utilized to enhance the interpretations of spectral data by examinaing the correlation between spectral absorption and elemental abunadance. Spectral absorption depths for calcium, neodymium, and iron of fresh and weathered carbonatite surfaces were plotted against geochemically determined concentrations of these elements derived by XRF and LA-ICPMS analysis of the same sample billets. The results show a positive relation  $(\mathbb{R}^2 \ 0.8 \ \text{to} \ge 0.9)$  between absorption depths and the carbonatite's geochemical composition. We examine the relationship of carbonatite Nd absorption spectra with the available published data about Nd absorbtion in world carbonatites and find significantly more scatter, with values of R<sup>2</sup> of ~0.6. While there is some degree of positive correlation between absorption depths and Nd concentration within carbonatites, the scatter reflects complexities in making such spectralgeochemical correlations. In particular, the difference between a carbonatite fresh interior and weathered exterior spectra may result in a less robust correlation. Overall, our results suggest that it is possible to derive the geochemistry of carbonatite key indicators (calcite, neodymium, and iron abundances) using a spectroradiometer instrument and methods if care is taken to consider both fresh and weathered carbonatite surfaces, as well as the heterogeniety of the sample.
## **1.Introduction**

The growth of new green technologies has been accompanied by an increasing industrial demand for rare earth elements (REEs) – critical components in high-efficiency engines. Global REE production comes from just a few locations, as a consequence, locating new exploitable sources of REEs has become a critical economic and security priority [1]. Most exploitable deposits of REEs are hard to find and usually concentrate within REE-bearing minerals in carbonatites [2]. Remote sensing provides a mechanism by which new deposits of carbonatite may be identified, though challenges remain in constraining the spectral characteristics of these rocks. Mapping carbonatite without reference spectra is often complicated by the different minerals/elements present, and the limited outcrop footprint of carbonatites, which are often embedded within large-scale geological units [3]. Examination of previous studies that sought to identify carbonatite by spectroscopic approaches reveals key outstanding questions that remain unresolved: i) What are the suitable key minerals/elements that can be used to unambigiously indicate carbobnatite? ii) What is the difference between a carbonatite fresh interior and weathered exterior spectra? iii) Does the grain size and carbonatite homogeneity affect the spectral behavior? iv) How do the spectral features correlate with carbonatite REE concentrations? The establishment of carbonatite reference spectra, and an examination of its detailed characteristics can improve on the existing difficulties in mapping of carbonatite. To address these issues, we carefully examined selected samples (for both fresh interiors and weathered exteriors) of REE-enriched carbonatite from the Al-Uyaynah fields (UAE), using both spectroscopy to assess the spectral characteristics of the rocks and inductively coupled plasma mass spectrometry and X-ray fluorescence (XRF) spectrometer to determine the geochemical composition of the rocks.

The main objectives of research are: (i) to develop an understanding of the spectral charachterisitcs of the carbonatites spectroscopy by examining their spectral reflectance within visible, near infrared (VNIR) and short wave infrared (SWIR) bands utilizing an analytical spectral device (ASD), (ii) acquiring a more comprehensive understanding of the geochemical properties of the Al-Uyaynah carbonatites by using geochemical analysis methods (XRF and LA-ICP-MS) on the same samples, and (iii) testing the linearity of the relationship between the absorption features of carbonatite spectra and their concentration in carbonatites by chemically analyzing the same material as was charachterized spectrally. This approach miminizes the potential for mismatches caused by inhomogenity within a carbonatite surface (e.g. presence of absence of large REE-bearing crystals). This experiment presents the laboratory reflectance spectra of ferro- and calcio-carbonatites that were collected from the well-exposed Al-Uyaynah area-fields located in the UAE. The new carbonatite spectra may contribute novel Nd-rich spectra increasing our understanding of carbonatite spectroscopy, and also expanding the spectral data to the spectroscopy community. These data provide the first comprehensive analysis of carbonatite spectra from both fresh and weathered surfaces of carbonatities and has broad application to the identification of carbonatites by remote sensing methods.

## 2.Background

Spectroscopy is the discipline of studying the interaction between matter and light [4]. Usually, the interaction with matter generates a range of observable optical/physical phenomena such as absorption, transmission, and reflection giving information about minerals/elements of the parent rocks [5]. A number of authors [6-8] have carried out research on rock-forming minerals by

employing absorption properties of reflectance spectra in the visible and near infrared (VNIR) and shortwave infrared (SWIR) bands (Figure 4.1). The absorption in the spectral wavelength is caused by two general processes: 1) electronic processes and 2) vibrational processes [9]. The mineral/element absorption features in visible and near infrared (VNIR) bands are mostly specified by the electronic transitions or processes like charge transfer effect, and crystal field effect [10-12]. The spectra absorption features result from the change in state of energy that follows the absorption of a photon. Meanwhile the atoms and ions have distinct states of energy within the crystal lattice that vibrate in response to incident radiation creating absorption in SWIR bands[5, 13]. Furthermore, the spectral absorption features of minerals are caused by the partially filled electron shells (crystal field effect) of transition elements like Fe, Co, and Cr, which is the main electronic process that controls the absorption properties in minerals [5, 8, 13]. Vibrational processes cause the absorption characteristics of mineral spectra at specific locations within the SWIR and TIR bands [5, 13, 14]. Electronic transitions appears to govern mineral spectral properties at VNIR wavelength areas more than vibrational processes [15]. The vibrational processes happen mainly because of vibrational movement in the mineral crystal lattices, like, minor displacements of the atoms regarding their resting states [16]. Three modes are present with vibrational processes and include overtone, combination, and fundamental vibrations [5, 13]. Generally, vibrational processes are a result of the occurrence of hydroxyl ion (OH<sup>-</sup>), carbonate  $(CO_3^{2-})$ , water (H<sub>2</sub>O), and other relevant minerals [18].

In analyzing the composition of minerals/elements on the basis of absorption characteristics, the VNIR and SWIR bands of the reflectance spectrum are quite important [19-21]. Carbonatites, which are enriched with about 50% or more of carbonate minerals, exhibit a



**Figure 4.1.** The range of the electromagnetic spectrum, showing most crucial ranges for minerals sensing spectroscopy applications. The visible/ near infrared (VNIR), and short-wave infrared (SWIR), modified from [17].

particularly strong absorption characteristic of the  $CO_3^{2^-}$  ion detected readily within the range of 2.3-2.35 µm of SWIR bands [5, 22]. The VNIR bands' data typically are an invaluable source of information regarding iron (Fe<sup>2+</sup> and Fe<sup>3+</sup>) [5, 16, 19]. Inside the VNIR bands of wavelengths between 0.8-0.9 µm the absorption features of iron-rich carbonatites are pronounced [23-25]. Some carbonatites contain significant amounts of rare earth elements (REE), like cerium (Ce), europium (Eu), neodymium (Nd), and lanthanum (La) [2]. The REE spectrum is largely related to electronic transitions, which are clearly shown by the spectra absorption properties in the VNIR wavelength in the area between 0.5-0.8 um [20, 26].

The spectral absorption properties of carbonatites have been used in previous studies to create maps of carbonatites, which are measurable from aircraft reflectance spectroscopy. For example, AVIRIS (Airborne Visible / Infrared Imaging Spectrometer) images were used to identify the Ice River Carbonatite complex and showed minor absorption features located at 0.58, 0.74, 0.80, and 0.87 µm, which is characteristic of Nd<sup>3+</sup> [27]. Bedini and Tukiainene employed spectroscopic spectra to distinguish between carbonatite, fenite, and hematised surface rock, with particular attention to the Nd<sup>3+</sup> reflectance characteristics of Sarfartoq carbonatite in Greenland [28]. Recent contributions [29] discussed the possibility of spectroscopic approaches (hyperspectral remote sensing), within VNIR-SWIR wavelengths to distinguish neodymium in carbonatite and alkaline igneous rocks that accommodated REEs. These authors analyzed collections of carbonatite which were obtained from previous research and museum collections of carbonatites with a wide geographic distribution. This study reported that Nd absorption features in carbonatite is the most pronounced among the REE absorption characteristics in the VNIR-SWIR spectrum.

### **3.Study area location and geology**

The Al-Uyaynah fields are located approximately 18 km to the southwest of Dibba city, in Fujairah state of the UAE. The Al-Uyaynah fields contain extrusive carbonatites, which lie within the metamorphic mélange unit to the west side of the Semail ophiolite complex. These carbonatites have been previously studied and interpreted as sub-aerially erupted volcanics within oceanic metasediments as an accreted volcanic island predating obduction of the Semail Ophiolite Complex [3]. The Al-Uyaynah carbonatites are comprised of ~10-50 m thick layers with abundant lapilli. The presence of the lapilli requires a sub-aerial origin. The carbonatites are described as being composed of two typical magmas [3]. The Type 1 carbonatite contains calcite as the main mineral phase and is generally comparable to calcio-carbonatites. These carbonatites also contain abundant apatite and opaque minerals such as magnetite. The typical composition

of these lapilli is 40% calcite, 20-30% apatite and opaque minerals [3]. The Type 2 carbonatite contains higher modal abundances of silicates in comparison Type 1 (calcio-carbonatites). The representative minerals are calcic, amphibole, biotite, and abundant of opaque minerals such as magnetite and is geochemically equivalent to ferro-carbonatites. Allanite in ferro-carbonatites usually occurs as crystal accumulations. These accumulations concentrate REEs and result in trace elements heterogeneously distributed within the rock [3].



**Figure 4.2.** A field view of Al-Uyaynah ferro-carbonatites, (a) shows the ferro-carbonatites outcrops of the northern end of the study area, (b, and c) show a close view of ferro-carbonatites. (d) hand sample from ferro-carbonatite area.



**Figure 4.3.** A field pictures of Al-Uyaynah calcio-carbonatites (a) shows the calcio-carbonatites outcrops of the northern part of the study area, (b, and c) show a close view of clacio-carbonatites. (d) a hand sample calcio-carbonatite.

## 4. Methods

### 4.1. Sample preparation

Samples of carbonatites were collected from the Al-Uyaynah field during a field expedition in December 2010 (Fig. 4.2 and 4.3). The samples were prepared in the research facilities of the Department of Geological Sciences at Michigan State University. Each carbonatite sample was cut into rectangular cubes using a diamond slab saw, with care taken to preserve the weathered surfaces, and to exposure fresh interior surfaces. The interior surfaces of billets were polished using a rotary sanding plate. Billets were washed using an ultrasonic cleaner filled with deionized water to eliminate unwanted materials like clay, dust, and polishing grit. The cleaned samples were then placed on a hot plate at about 60°C to dry them off.

### 4.2. Spectral Analysis using ASD

The prepared sample billets were analyzed using an ASD FieldSpec-3 Hi-Res Spectroradiometer located at the Department of Environmental Sciences at the main campus of the Univesity of Toledo. The Illumination source was provided by a 1000W 3200K Quartz Halogen lamp with a 10-degree foreoptic. For each sample, reflectance spectra were obtained for both unweathered and weathered surfaces over the wavelength range from 0.35 to 2.5  $\mu$ m. The spectral resolution of ASD is 3 nm for VNIR band, and 8 nm for SWIR band. All spectra were normalized to a Spectrion<sup>®</sup> lab standard.

To normalize the carbonatite laboratory spectra, we utilized the continuum removal method [30]. Continuum removal is a method of reflectance spectra normalization that reduces the spectral albedo background or continuum, and is computed by dividing every spectrum by the corresponding continuum line [30]. This technique improves differences in the absorption shape of individual mineral properties [31], and permits a comparison of individual absorption features from other spectral mineral databases. We utilized the continuum removal tool, (PRISM version 1.0) [32], from USGS and which is embedded in the ENVI software system [33]. The tool was utilized to normalize carbonatite spectra and to distinguish the accurate positions of the absorption center, and to measure the absorption depth of formed by each mineral/element. The wavelength of the laboratory reflectance spectra is shown in Figure 4.4.

### 4.3. Geochemical analysis

The same samples that were used in spectroscopy analysis were then re-polished gently and cleaned again after the spectra measurement was completed. The billets were crushed in a steel jaw crusher and hand powdered using agate mortar and placed in glass container. Samples were placed in a vacuum oven at 110°C for a minimum of 24 hours. These powdered samples were blended with dehydrated lithium tetraborate (Li<sub>2</sub>B<sub>4</sub>O<sub>7</sub>) using methods described in [34] to make a glass disk. The mixture ratio (3:9 or 1:9) was based on the powdered samples' volume. To ensure full oxidation during sample fusion, an oxidizing agent, ammonium nitrate (NH<sub>4</sub>NO<sub>3</sub>; 0.5g) was added. The final mixtures were subsequently heated and melted in platinum crucibles and gently agitated in an orbital mixer at 1000°C until homogeneous melts were achieved. The melts were then poured into platinum moulds and transferred to a hot plate to anneal, then to a ceramic plate



**Figure 4.4.** Example of the field spectra of ferro-carbonatite. The original reflectance graph in red, and the reflectance after applying the continuum removal method in green. Absorption depth, area, and center are labelled.

to cool to room temperature and form glass disks. These glass disks made from carbonatite powders were subsequently analyzed for major oxide concentrations in weight percent of whole rock. This was accomplished by utilizing a Bruker S4 Pioneer wavelength dispersive X-ray fluorescence (XRF) spectrometer at Michigan State University, and analyzed using the silicate LDF method, following the protocol of [34].

The trace elements, including rare-earth element concentrations in parts per million (or ppm), were derived using a laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) at Michigan State University's geochemistry lab on the same samples. The laser ablation analysis was performed based on the methods described in [35]. The laser ablation was conducted for 180 seconds as surface scans at 10  $\mu$ m /s with a diameter about 110  $\mu$ m, operating a Photon-Machines Analyte (G2 193 nm) excimer laser set at 4.1 mJ/cm-2 fluence and 10 Hz repetition rate. The carbonatite glass samples were placed within a 15×15 cm HelEx sample chamber, which is capable of operating about 30 mounted samples and standards in one processing. The chamber containing glass samples was evacuated and a helium (0.75 L/min high-purity at 1 atm) carrier gas flux was used to carry the ablated material to the ICPMS. Shortly before analysis, samples were pre-ablated at 100  $\mu$ m/s with a 150  $\mu$ m beam to avoid or eliminate possible contamination of sample surfaces. To decrease molecular interferences on light masses and enhance the detection limits, the ICPMS (Thermo Scientific ICAP Q quadrupole) was set to kinetic energy dispersion (KED). The LA-ICP-MS data were analysed using Qtegra software supplied by Thermo to extract the REE concentrations. The results of XRF and LA-ICP-MS analysis results are illustrating in tables 4.1 and 4.2.

## 5. Results

#### 5.1. Carbonatite Spectra

#### 5.1.1. Calcite related absorption

Results show, broadly, that the spectra are dominated by calcite, iron, and REEs. Carbonate minerals have systematic vibrational absorption peculiarities in the SWIR band, that can be utilized for distinguishing the influence of carbonate minerals on bulk rock spectra bands [5, 22]. These vibrational absorption bands are evident in carbonate spectra because internal vibrations of the C-O bond within the SWIR band occurs in the area between 2.30–2.35 µm [22, 23].

Within our study, calcite is the dominant phase in both calcio- and ferro-carbonatites, however within calcio-carbonatite, it is more prevalent comprising around 40% of its lapilli compositions [3]. The wavelength area that correlates to calcite absorption, was measured based on the normalized laboratory spectra (continuum removal) results of both ferro- and calcio-carbonatite samples. The absorption center was observed between  $2.312-2.345 \mu m$  for fresh interior and weathered exterior of all carbonatite samples (Figure 4.5 and 4.6). The most pronounced or deepest absorptions were recorded at 2.33 µm of the calcio-carbonatite fresh interior surface. In contrast, a less significant absorption was found in this area for the interior surfaces of



**Figure 4.5.** Shows calcite absorption bands in USGS spectra library (left) [36], and calcite absorption area which recorded in calcio-carbonatite (right). The absorption was observed in the area between  $2.312-2.345 \mu m$ , and the deepest absorption point was recorded at  $2.34 \mu m$  of fresh calcio-carbonatite.



**Figure 4.6.** Illustrates calcite absorption bands in ferro-carbonatites. The absorption was between  $2.312-2.345 \mu m$  of the spectra wavelength, and the deepest absorption point was at  $2.34 \mu m$  of much of ferro-carbonatites.

ferro-carbonatite samples due to the relatively lower calcite abundance (Figure 4.6). The weathered exteriors of calcio- and ferro-carbonatite display a somewhat less pronounced absorption in comparison to the inner surfaces. This observation is consistent with our observations of less carbonate on these weathered exterior surfaces. The correlation between the calcite concentration and wavelength absorption depths were plotted (absorption depth vs %) and show a positive linear correlation with an  $R^2$  value of 0.8 (Figure 4.14).

### 5.1.2. Iron related absorption

Iron oxides have diagnostic electric processes or charge transfer absorption features in the VNIR band [5, 16, 19]. Many scholars have recorded the absorption features of iron oxides, (e.g. [21]), within the visible near infrared ranges (VNIR). They report the pure iron oxide absorption feature in the area between 0.9-1.0  $\mu$ m. Fe<sup>2+</sup> displays absorption near 1.0  $\mu$ m, while minerals that exhibit Fe<sup>3+</sup> absorption characteristics (e.g., hematite), have a diagnostic absorption around 0.9  $\mu$ m [5].

In our sample suite, ferrous and ferric ions ( $Fe^{2+}$ ,  $Fe^{3+}$ ) occur within iron oxide minerals in ferro-carbonatites and also in the weathered exterior of calcio-carbonatites. This charachteristic is quite noticeable in the field, and manifests as a coating of iron oxdies showing a rusted appearance on the weathered exterior of the carbonatites. In the ferro-carbonatites iron-oxide minerals (magnetite and hematite) are important phases, whereas iron-oxide minerals are just a subordinate phase in calcio-carbonatites [3]. The normalized spectra (continuum removal normalized) of the ferro and calciocarbonatite samples both exhibit absorption in the VNIR region, but values for the absorption center vary due to spectral impurity recorded between  $0.885-1.037\mu$ m. Iron-rich minerals (magnetite and hematite) are abundant in the ferro-carbonatite fresh interior more so than the clacio-carbonatite (though weathered surfaces of both rock types exhibited such minerals). The deepest absorptions were observed at  $0.885 \mu$ m and around  $0.907 \mu$ m for ferro-carbonatite (Figure 4.7, and 4.17). Iron oxide concentrations are greater in the weathered/fresh surface of ferrocarbonatites as compared to calcio-carbonatites, and these absorption features can be applied in differentiating between the spectra of the two carbonatites. However, carbonatite spectra are unusual and spectral impurity is evident. This causes slight shifting of the absorption center in comparison to that reported for pure iron oxides in the literature. Overall the Fe absorption depth in carbonatites was well correlated with concentration (R<sup>2</sup> > 0.8) (Figure 4.18).

### 5.1.3. Rare earth element (REE) related absorption

The rare earth element (REE) absorption bands are defined via electronic field transition absorption features [26]. The REEs spectral absorption is commonly measurable within the visible region [21], which is clearly shown by absorption features in the VNIR wavelength ranges between 0.5- 0.87 um [20, 26]. Neodymium (Nd) absorption features are most notable among the REE, therefore, Nd is one of the key elements for the entire REE group [29].

In the Al-Uyaynah carbonatites, ferro-carbonatites have higher concentrations of REEbearing minerals in their lapilli, while calcio-carbonatite have considerably lower concentrations.



**Figure 4.7.** Shows iron oxides from USGS spectra library (left) [36], and the iron oxide absorption area that is observed in ferro-carbonatite (middle). The iron absorption was recorded in the area between  $0.8-1.26\mu$ m. The deepest absorption point was recorded around  $0.885 \mu$ m of fresh ferro-carbonatite and  $1.037 \mu$ m for the weathered part. The calcio-carbonatite shows shallow absorption in both fresh and weathered surfaces, however, the iron oxide absorption was more pronounced in weathered outcrop.



**Figure 4.8.** Shows neodymium (Nd) from USGS spectra library (left) [36], and the Nd absorption area that was observed in ferro-carbonatite (right). The Nd absorption spanned the area from  $0.7-0.78\mu$ m. The deepest absorption was recorded around  $0.74 \mu$ m.



**Figure 4.9.** Neodymium (Nd) absorption area that was observed in ferro-silico-carbonatite weathered surface (left) and fresh interior (right). The Nd absorption depth is higher (at 0.705  $\mu$ m) in fresh surfaces in comparison to weathered surfaces.



**Figure 4.10.** Nd absorption in calcio-carbonatite was verified. The deepest absorption point was recorded around  $0.752\mu m$  of the weathered surface of the calcio-carbonatite spectrum. The un-weathered part shows a shallower absorption at  $0.751 \mu m$ .

The normalized spectra of ferro- and calcio-carbonatite samples indicate REE-related absorption features in the VNIR wavelength range between 0.7 to 0.774  $\mu$ m (Illustrated in Figure 4.8 and 4.10). The Nd absorption depth is variable, as the impact of iron interference is known to decrease the Nd absorption features [37] in some specimens. The deepest point of absorption is for fresh interior surfaces of ferro-carbonatite, and is observed at 0.705  $\mu$ m (Figure 4.9). The weathered exterior surface of ferro-carbonatite exhibits a spectrum with a similar Nd absorption center between 0.705 - 0.742  $\mu$ m (Figure 4.15). However, in calcio-carbonatites, the normalized ASD spectra shows a Nd absorption center at 0.751  $\mu$ m for the fresh interior surface, and at 0.752 for the exterior weathered surface. The calcio-carbonatites' Nd absorptions are less pronounced than those recorded in the ferro-carbonatite spectra due to of the lower Nd concentration in the calcio-carbonatite. The coefficient of determination of the Nd concentration vs its absorption depth exhibits a positive correlation (R<sup>2</sup>> 0.9 for Nd), (Figure .16).

### 5.1.4. Major element analysis by XRF

For the purpose of linking the spectral data to the viability of discriminating carbonatites through spectral analyses, the same representative set of samples that were collected from the Al-Uyaynah carbonatite were chemically analyzed. The major oxides were determined by using the XRF Silicates LDF method noted above.

Woolley and others conducted geochemical research on the carbonatites of the Al-Uyaynah area during 1991. They divided the Al-Uyaynah carbonatites based on petrologic features into two distinct groups: i) Type 1, which is similar in composition to average calcio-carbonatite; ii) Type

2 is a silico-carbonatite which is chemically similar to average ferro-carbonatites (here we use the term ferro-carbonatite). The geochemical data determined from this study are shown in Table 4.1. Included in this table are data of average Type 1 and average Type 2 carbonatites from Woolley (1991) and worldwide average calcio- and ferro-carbonatite compositions.

The results obtained from XRF analysis of our samples as major oxides distribution in wt. % were compared with the compositions of published samples presented by Wooley, which show a very analogous composition to the average of carbonatite. The average chemical data of our samples also show clearly two groups of carbonatites, calcio and ferro-carbonatite, that falls within the ranges that are stated in literature.

### 5.2. Geochemical impact of weathering on major element composition

The variation between the fresh and weathered surface of both varieties of carbonatite were examined. The CaO concentrations are about 42 wt. % for weathered to 45 wt. % for fresh part of calcio-carbonatite, suggesting some CaO loss. The CaO concentrations in ferro-carbonatite samples are universally lower than calcio-carbonatite, however these too exhibit CaO less in weathered surfaces (26-29 wt.%) in comparison to fresh interiors (29-29.9 wt.%) (Figure 4.11). The weathered rind of all samples are dominated by Fe-oxides. The Fe<sub>2</sub>O<sub>3</sub> concentration is about 21wt.% in the ferro-carbonatite weathered surface, while only 17 wt.% in the fresh interior. Similarly, the calcio-carbonatite weathered exterior also exhibits higher concentrations of Fe<sub>2</sub>O<sub>3</sub> (13%) in comparison to its fresh interior (10%). SiO<sub>2</sub> concentrations do not show as clear a variation, in weathered ferro-carbonatite SiO<sub>2</sub> ranges from 13-21wt.%, while its between 15-24



**Figure 4.11.** Illustrates The CaO, Fe2O3 and SiO2 concentration in the weathered exterior and fresh interior from selected field samples of Al-Uyaynah carbonatite. The CaO is higher in calcio-carbonatite, while the iron oxides are greater in ferro-carbonatites. The weathered part of carbonatites contains more iron oxides than the fresh part of the rock. SiO2 has higher concentrations in ferro-carbonatite samples versus calcio-carbonatites.

wt.% in fresh ferro-carbonatite samples. The  $SiO_2$  concentration in the calcio-carbonatite weathered surface is 3.6 wt.%, and is 3 wt.% in the un-weathered fresh interior of the calcio-carbonatite. MgO, Na<sub>2</sub>O, and K<sub>2</sub>O concentrations are higher in weathered ferro- and calcio-carbonatites versus the fresh interior.

# 5.3. CIPW normative mineral composition

CIPW normative mineral compositions were calculated for Al-Uyaynah carbonatite samples from the whole rock geochemical data. Calculations were performed using a spreadsheet macro prepared by Kurt Hollocher after Johannsen, 1931. The mineral assemblages are shown in Table 4.3. All samples possess the same basic calculated mineral assemblage but have variation of weight percentage of the different phases within the assemblage. Calcio-carbonatite (samples 5 and 5-1) have the highest calcite at 66% and 55%, respectively. The amount of apatite is 15.39% for fresh and 18.52% for weathered portion. Fe-oxides are second lowest. Ferro-carbonatite samples (samples 1, 2,4,27 and 28) have lowest calcite content. Correspondingly they have higher content of silicate minerals and also have the highest amount of apatite (21-27%). These samples also have the highest amount of Fe-oxides. In all samples, calcite is slightly lower in concentration for the weathered portion of the rock. The Fe-oxides exhibit the same trend of being slightly increased in the weathered portion over the fresh rock.

#### 5.4. Trace element analysis by LA-ICPMS

In 1984, Cullers and others undertook a detailed study of REE concentrations in carbonatites, and pointed out that carbonatites have the highest concentration of REEs of any igneous rocks [38, 39]. Furthermore, there was predictable variability between carbonatite varieties, whereby the concentration of REEs increase progressively from calcio-carbonatite, to magnesio-carbonatite, to ferro-carbonatite [39]. Our results are broadly consistent with these global observations - ferro-carbonatites from the Al-Uyaynah carbonatite are significantly more enriched in REE in comparison to calcio-carbonatites. Ferro-carbonatite samples (1, 1-1, 4, 4-1, 27, 27-1) show overall greater enrichment in REEs to calcio-carbonatite samples (5, 5-1) and also possesses a greater LREE to HREE enrichment.

The REE results from this study are compared with existing REE data from the Al-Uyaynah carbonatites [39] and the world average values of calcio- and ferro-carbonatites (Fig 4.12). Our data show good agreement with the two types of carbonatites noted in prior studies [39]. Furthermore, our ferro-carbonatite samples (greater LREE to HREE enrichment and overall enrichment) correspond well with the global average value for ferro-carbonatite. Similarly, calciocarbonatites from our study agree with global average values for calcio-carbonatite. The ICP-MS analyses of Al-Uyaynah carbonatite interior and weathered surfaces generally display enrichment in LREEs concentrations in the weathered portion over fresh interior (Table 4.2).

Sample	Name	SiO2	TiO2	Al2O3	Fe2O3	MnO	MgO	CaO	Na2O	K2O	P2O5	LOI	Total (%)
1	Ferro- carbona tite	24.34	0.25	1.67	8.91	0.23	5.09	26.15	1.81	0.09	1.41	28.42	98.37
1_1	Rich in silicates	21.89	0.31	1.77	9.23	0.48	4.46	29.65	1.28	0.2	4.17	25.31	98.75
2		23.52	0.19	1.6	9.05	0.54	4.89	27.79	1.67	0.07	1.31	27.96	98.59
2-1		35.5	0.31	2.46	12.98	0.3	7.37	14.48	2.5	0.12	2.16	20.16	98.34
4	Ferro- carbona tite	15.07	1.29	2.21	17	0.43	8.12	29.5	0.02	0.01	9.65	16.1	99.4
4-1		16.24	1.26	2.29	16.18	0.46	8.5	29.33	0.03	0.03	9.36	15.79	99.47
5	Calcio- carbona tite	3.02	0.77	1.1	10.26	0.6	1.76	45.27	0	0	6.73	29.89	99.4
5-1		3.6	0.96	1.34	13.53	0.53	2.08	42.19	0	0.01	8.19	26.83	99.26
27	Ferro- carbona tite	14.91	1.31	2.18	17.18	0.43	8.05	29.87	0.02	0.01	9.44	15.99	99.39
27-1		13.53	1.65	3.09	21.83	0.52	7.87	26.66	0.04	0.02	12.26	11.88	99.35
28		11.45	1.4	2.39	18.2	0.41	6.71	31.38	0.02	0.01	10.32	17.06	99.35
28-1		15.77	1.42	2.65	18.59	0.46	8.62	27.04	0.03	0.02	10.56	14.23	99.39

**Table 4.1.** Illustrates the major oxides distribution of selected Al-Uyaynah carbonatite samples evaluated using XRF. All carbonatite samples contain calcium concentrations 26-45 Wt. %. The lower concentrations of carbonate were recorded in ferro-carbonatites fresh and weathered samples and those ferro-carbonatites exhibit a higher abundance of iron and silica in comparison to calcio-carbonatites.

Samples	Name	Ba	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Но	Er	Tm
1	Ferro-carbonatite	126	11257	17630	1702	5467	590	154	380	39	162	22	45	5
1_1	Rich in silicates	659	7522	11921	1143	3601	400	106	262	29	125	18	39	4
2		301	9384	15048	1410	4441	471	123	303	34	155	24	55	7
2_1		143	14552	22857	2143	6822	708	181	438	46	194	28	61	7
4	Ferro-carbonatite	245	553	1432	148	592	99	28	77	9	39	6	13	1
4_1		223	537	1394	146	590	100	28	77	9	39	6	13	1
5	Calcio-carbonatite	592	403	1023	105	421	71	20	55	6	29	5	10	1
5_1		672	505	1275	131	524	89	26	70	8	36	6	12	1
27		217	567	1414	148	592	101	28	77	9	39	6	13	1
27_1	Ferro-carbonatite	267	755	1731	184	743	127	35	98	11	50	8	17	2
28		145	604	1532	159	643	110	31	85	10	43	7	14	2
28_1		278	614	1519	161	654	112	31	87	10	44	7	15	2
W.clcio	Woolley average of ferro-carbonatite	426	516	1045	0	470	74	21.8	57	6.7				2.2
W.ferro	Woolley average of ferro-carbonatite	1949	5878	8668	0	2501	287	82	215	20.9				6.4
Avg. calcio	world average of ferro-carbonatite		608	1687	219	883	130	39	105	9	34	6	4	1
Avg. ferro	world average of ferro-carbonatite		2666	5125	550	1618	128	34	130	16	52	6	17	1.8

Table 4.2. Shows the distributions of REEs of selected carbonatite field samples from Al-Uyaynah field. The REE (ppm) were analyzed by (LA-ICP-MS).

Input analysis	Units	28	28_1	27	27_1	5	5_1	4	4_2	2	2_1	1	1_1
SiO2	%	11.45	15.77	14.91	13.53	3.02	3.6	15.07	16.14	23.52	35.5	24.34	21.89
TiO2	%	1.4	1.42	1.31	1.65	0.77	0.96	1.29	1.46	0.19	0.31	0.25	0.31
A12O3	%	2.39	2.65	2.18	3.09	1.1	1.34	2.21	2.57	1.6	2.46	1.67	1.77
Fe2O3	%	18.2	18.59	17.18	21.83	10.26	13.53	17	18.92	9.05	12.98	8.91	9.23
FeO	%												
MnO	%	0.41	0.46	0.43	0.52	0.6	0.53	0.43	0.48	0.54	0.3	0.23	0.48
MgO	%	6.71	8.62	8.05	7.87	1.76	2.08	8.12	8.7	4.89	7.37	5.09	4.46
CaO	%	31.38	27.04	29.87	26.66	45.27	42.19	29.5	27.12	27.79	14.48	26.15	29.65
Na2O	%	0.02	0.03	0.02	0.04	0	0	0.02	0.04	1.67	2.5	1.81	1.28
K2O	%	0.01	0.02	0.01	0.02	0	0.01	0.01	0.02	0.07	0.12	0.09	0.2
P2O5	%	10.32	10.56	9.44	12.26	6.73	8.19	9.65	10.73	1.31	2.16	1.41	4.17
CO2	%	17.06	14.23	15.99	11.88	29.89	26.83	16.1	13.23	27.96	20.16	28.42	25.31
SO3	%												
S	%												
F	%												
Cl Sr	%	2042	2262	2802	2204	2700	2070	2566	2177	2810	1501	2050	2012
Ba	ppm	136	2285	2805	2304	5200 598	5970 671	2300	321	2019	122	96 96	636
Ni	ppm	33	39	33	42	13	16	33	38	381	459	330	241
Cr	ppm	11	21	12	26	37	16	20	0	277	285	196	152
Zr	ppm	1904	1886	1771	2194	1248	1604	1758	1953	445	513	418	595
Norms													
Quartz		1.0807	2.3995	2.5131	1.3012	0.0739	0.0717	2.5398	2.6508	14.579	21.203	14.715	13.263
Plagioclase		0	0	0	0	0	0	0	0	0	0	5 0	0
Orthoclase		0.11	0.2201	0.1407	0.2172	0.2392	0.3231	0.1501	0.2391	0.4847	0.6714	0.5144	1.3418
											8	3	9

Table 4.3. Shows the CIPW normative mineral compositions were calculated for Al-Uyaynah carbonatite samples from the whole rock XRF geochemical data.

					]	Table 4.3.	(cont'd)						
Input analysis	Units	28	28_1	27	27_1	5	5_1	4	4_2	2	2_1	1	1_1
Nepheline		0	0	0	0	0	0	0	0	0	0	0	0
Leucite		0	0	0	0	0	0	0	0	0	0	0	0
Kalsilite		0	0	0	0	0	0	0	0	0	0	0	0
Corundum		2.2815	2.4815	2.0958	2.9134	1.0416	1.2487	2.1046	2.4314	1.3847	2.0544	1.4109	1.4039
											7	1	5
Diopside		0	0	0	0	0	0	0	0	0	0	0	0
Hypersthene		16.095	20.432	19.513	18.734	4.3256	5.0568	19.512	20.871	11.217	16.248	11.426	10.354
											6	4	
Wollastonite		0	0	0	0	0	0	0	0	0	0	0	0
Olivine		0	0	0	0	0	0	0	0	0	0	0	0
Larnite		0	0	0	0	0	0	0	0	0	0	0	0
Acmite		0	0	0	0	0	0	0	0	0	0	0	0
K2SiO3		0	0	0	0	0	0	0	0	0	0	0	0
Na2SiO3		0	0	0	0	0	0	0	0	0	0	0	0
Rutile		0.9	0.8548	0.8001	1.0136	0.094	0.3534	0.7744	0.8805	0	0	0	0
Ilmenite		0.8513	0.9431	0.9018	1.0698	1.2644	1.1084	0.8928	0.9984	0.3323	0.5211	0.4279	0.5487
											4	3	6
Magnetite		0	0	0	0	0	0	0	0	1.1977	0.1756	0.1016	0.6800
											5	4	1
Hematite		17.527	17.691	16.719	20.863	10.124	13.206	16.401	18.222	7.5082	11.368	7.9603	8.1338
											1	1	8
Apatite		23.027	23.284	21.285	27.148	15.386	18.522	21.57	23.944	2.7951	4.4297	2.9443	9.0051
											9	7	7
Zircon		0.3685	0.3607	0.3463	0.4214	0.2475	0.3146	0.3408	0.378	0.0824	0.0912	0.0757	0.1114
											5		4
Perovskite		0	0	0	0	0	0	0	0	0	0	0	0
Chromite		0.0023	0.0043	0.0025	0.0053	0.0079	0.0034	0.0042	0	0.0549	0.0543	0.0380	0.0304
				_	_		_	_	_		_	2	9
Titanite		0	0	0	0	0	0	0	0	0	0	0	0
Pyrite		0	0	0	0	0	0	0	0	0	0	0	0
Halite		0	0	0	0	0	0	0	0	0	0	0	0
Fluorite		0	0	0	0	0	0	0	0	0	0	0	0
Anhydrite		0	0	0	0	0	0	0	0	0	0	0	0
Na2SO4		0	0	0	0	0	0	0	0	0	0	0	0
Calcite		30.913	22.557	30.602	18.189	64.488	55.153	29.197	22.57	43.138	18.533	39.484	40.498
											8	5	9
Na2CO3		6.8315	8.7264	5.0699	8.0823	2.7393	4.6646	6.488	6.7865	16.33	23.348	19.875	13.926
											9	3	7

	<b>Table 4.3.</b> (cont'd)												
Input analysis	Units	28	28_1	27	27_1	5	5_1	4	4_2	2	2_1	1	1_1
Total		99.988	99.954	99.99	99.958	100.03	100.03	99.975	99.972	99.103	98.700	98.974	99.298
											5	9	8
Fe3+/(Total		100	100	100	100	100	100	100	100	100	100	100	100
Fe) in rock													
Mg/(Mg+Total		42.209	47.879	48.14	41.664	25.364	23.346	48.619	47.67	51.701	52.937	53.089	48.908
Fe) in rock											8	7	4
Mg/(Mg+Fe2+		100	100	100	100	100	100	100	100	100	100	100	100
) in rock													
Mg/(Mg+Fe2+		100	100	100	100	100	100	100	100	100	100	100	100
) in silicates													
Ca/(Ca+Na) in		99.885	99.8	99.879	99.729	100	100	99.877	99.734	90.192	76.194	88.868	92.753
rock											2	7	9
Plagioclase An		0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
content		1 1007	0 (10)	0 (500	1 5104	0.0101	0.00.10	<b>a</b> (000	<b>a</b> 0000	15060	01.074	15.000	14 605
Differentiation		1.1907	2.6196	2.6539	1.5184	0.3131	0.3949	2.6899	2.8899	15.063	21.874	15.229	14.605
Index		2 200	2 2252	2 20 47	2 222	2 0701	2 0 2 0 4	2 1059	2 2502	2 9 4 2 6	3	9	5
		3.209	3.2353	3.2047	3.323	2.9701	3.0384	3.1958	3.2383	2.8436	2.8964	2.8260	2.8834
Coloulated		2 0000	2 9021	2 0052	2 0146	2 2001	2 8270	1 0020	2 20/1	2 7 4 0 2	ð 2 6901	1	2 7600
Liquid density		2.8922	2.8921	2.8833	2.9140	2.8091	2.8579	2.0030	2.8941	2.7492	2.0891	2.1551	2.7600
ilquid defisity,											3	0	/
Galculated		0 101	0.158	0 165	0 177	0.253	0.240	0 163	0 157	0.068	0.0480		0.084
viscosity dry		-0.191	-0.156	-0.105	-0.177	-0.235	-0.249	-0.105	-0.157	-0.008	1	0.0574	-0.084
Pas											1	0.0374	
Calculated		-0 194	-0 168	-0 172	-0 184	-0 248	-0 244	-0 171	-0 166	-0.073	0.0371	_	_
viscosity wet		0.171	0.100	0.172	0.101	0.210	0.211	0.171	0.100	0.075	3	0.0625	0.0951
Pas											5	0.0020	0.0701
Estimated		1920.1	1840.8	1856.7	1881.9	2074.7	2064	1853.7	1834.1	1695	1470.7	1679.2	1725.9
liquidus temp.,											2	3	2
°C													
Estimated		-3.454	-1.678	-1.875	-2.756	-11	-10.27	-1.808	-1.616	0.0985	0.1685	0.1089	0.0089
H2O content,											8	9	
wt. %													
Normalized													
analysis													
SiO2		11.45	15.77	14.91	13.53	3.02	3.6	15.07	16.14	23.52	35.5	24.34	21.89
TiO2		1.4	1.42	1.31	1.65	0.77	0.96	1.29	1.46	0.19	0.31	0.25	0.31
A12O3		2.39	2.65	2.18	3.09	1.1	1.34	2.21	2.57	1.6	2.46	1.67	1.77
Fe2O3		18.2	18.59	17.18	21.83	10.26	13.53	17	18.92	9.05	12.98	8.91	9.23

Input analysis	Units	28	28 1	27	27 1	5	5 1	4	4 2	2	2 1	1	11
FeO		0	0	0	0	0	0	0	0	0		0	0
MnO		0.41	0.46	0.43	0.52	0.6	0.53	0.43	0.48	0.54	0.3	0.23	0.48
MgO		6.71	8.62	8.05	7.87	1.76	2.08	8.12	8.7	4.89	7.37	5.09	4.46
CaO		31.38	27.04	29.87	26.66	45.27	42.19	29.5	27.12	27.79	14.48	26.15	29.65
Na2O		0.02	0.03	0.02	0.04	0	0	0.02	0.04	1.67	2.5	1.81	1.28
K2O		0.01	0.02	0.01	0.02	0	0.01	0.01	0.02	0.07	0.12	0.09	0.2
P2O5		10.32	10.56	9.44	12.26	6.73	8.19	9.65	10.73	1.31	2.16	1.41	4.17
CO2		17.06	14.23	15.99	11.88	29.89	26.83	16.1	13.23	27.96	20.16	28.42	25.31
SO3		0	0	0	0	0	0	0	0	0	0	0	0
S		0	0	0	0	0	0	0	0	0	0	0	0
F		0	0	0	0	0	0	0	0	0	0	0	0
Cl		0	0	0	0	0	0	0	0	0	0	0	0
Sr		0.3597	0.27	0.3315	0.2725	0.3888	0.4695	0.3035	0.2575	0.3334	0.1775	0.4671	0.3444
_											1	2	9
Ba		0.0152	0.0311	0.0236	0.03	0.0668	0.0749	0.0266	0.0358	0.031	0.0136	0.0107	0.0710
NT.		0.0042	0.005	0.0042	0.0052	0.0017	0.002	0.0042	0.0040	0.0495	2	2	
IN1		0.0042	0.005	0.0042	0.0053	0.0017	0.002	0.0042	0.0048	0.0485	0.0584	0.042	0.0306
Cr		0.0016	0.0031	0.0018	0.0038	0.0054	0.0023	0.0020	0	0.0405	0.0416	0.0286	0 0222
CI		0.0010	0.0051	0.0010	0.0050	0.0054	0.0025	0.0027	0	0.0+05	5	5	2
Zr		0.2572	0.2548	0.2392	0.2964	0.1686	0.2167	0.2375	0.2638	0.0601	0.0693	0.0564	0.0803
		0.2072	0.20.10	0.2072	0.220.	011000	0.2107	0.2070	0.2000	010001	010070	6	7
Total		99.988	99.954	99.99	99.958	100.03	100.03	99.975	99.972	99.103	98.700	98.974	99.298
											5	9	8
Ferric iron													
selection													
Normalized		n	n	n	n	n	n	n	n	n	n	n	n
analysis													
total=100%?					1	1	1			1		1	
User Fe3+/FeT		1	1	1	1	1	1	1	1	1	1	1	1
Norm						NT.		OV					
calculation						No	orm seems	UK					
CHECK													

Table 4.3. (cont'd)



**Figure 4.12.** REE distribution patterns of carbonatite from Al-Uyaynah (this study) compared with those previously published (Woolly. 1991)., and the global average of carbonatite. The values are normalized to C1-chondrite [40]. The diagram (a) illustrates the REE distribution of ferro-carbonatite that were collected from fields vs the Al-Uyaynah carbonatites of Woolley 1991 [39], and world average of ferro-carbonatite. (b) shows the REE distribution of calcio-carbonatite and average global and Woolley average of calcio-carbonatites.

## 6.Discussion

The results of the combined geochemical and spectroscopy study on carbonatite shows that carbonatite spectral behavior is governed by: 1) The bulk composition as reflected in mineral/element concentrations; and 2) The presence or absence of a weathered surface. It is noted that potential carbonatite heterogeneity may impact attempts to correlate spectral behaviors and geochemically determined concentrations.

## 6.1. The relationship between bulk composition and carbonatite spectra

Overall results show that elemental concentrations of major and minor elements are strongly correlated with the depth of the absorption features of carbonatite spectra. This correlation holds for absorption features that are directly related to elemental vibrations (i.e.  $Nd^{3+}$ , Fe), and those where the geochemical composition is a proxy for a bond related absorption - CaO as a proxy for CaCO<sub>3</sub> and the C-O bond. On the basis of these spectral responses for carbonatites, the characteristic mineralogy of the carbonatite may be simplified to calcite, iron-bearing phases (oxides, chlorite, micas, amphibole, titanite, stilpnomelane), and REE-bearing phases (i.e. apatite, Ce-allanite and Ce-monazite). The subsequent discussion focuses on elemental concentrations rather than these minerals individually.

This geochemical analysis (XRF and ICP-MS) of the Al-Uyaynah carbonatite clearly distinguish two groups (calcio-carbonatite and ferro-carbonatite), each with its own characteristic spectra. Both carbonatite types contain differing proportions of calcite, iron-bearing phases, and

REE-bearing phases. Ferro-carbonatites contain a lesser amount of calcite and are more enriched in iron-bearing and REE-bearing phases. In contrast, calcite is the most abundant mineral in calciocarbonatite, with a correspondingly lower concentration of iron-bearing phases and REE-bearing phases. Results showed that the carbonatites' laboratory spectra were controlled by three key minerals/elements:

1) Calcite concentration within carbonatites has a strong influence on the absorption depth of the carbonatite spectra in SWIR area between 2.312–2.345  $\mu$ m of the wavelength. This calcite absorption was detectable in samples with calcite concentrations as low as 18% (calcite-poor ferro-carbonatite). The calcio-carbonatite contains about ~55-64 % CaCO<sub>3</sub> (per normalization) and exhibit a greater absorption depth than the ferro-carbonatites. The correlation between the concentration and wavelength absorption depth of our results show a positive linear correlation with an R<sup>2</sup> value about 0.8 (Figure 4.14).

2) Elemental iron (Fe<sup>2+</sup>, Fe<sup>3+</sup>), present in the form of an array of iron-bearing minerals within the carbonatites, generated absorptions in the spectrum between  $0.885-1.037\mu$ m. Our work shows that the ASD instrument detected iron absorption over the full range of Fe<sub>2</sub>O<sub>3</sub> concentrations present within our suite (~9-21 wt. %). The concentration of iron-bearing minerals is greater within the ferro-carbonatites compared to calcio-carbonatites, generating a more pronounced absorption within the ferro-carbonatite samples. The iron absorption depth in carbonatites is well-correlated with concentration (R<sup>2</sup> > 0.8) (Figure 4.18). Complexities in the relationship between the iron-absorption spectrum and the elemental concentration of Fe as reported by XRF analysis are possible due to the variable oxidation state of iron. Carbonatites contain minerals where iron is



Figure 4.13. Calcite absorption center ranges measured from the carbonatite spectra.



**Figure 4.14.** Statistical comparison between calcite concentrations of carbonatites and the equivalent laboratory spectra absorption depth records. The change in absorption depth due to the increase the calcite concentrations of carbonatite samples spectra measured with the ASD in the laboratory. The  $R^2 \sim 0.8$  (slope close to 1) was found among measured depth and chemically measured calcite concentrations in weight percentage.


Figure 4.15. Displays the absorption center ranges of neodymium measured from the carbonatite spectra.





**Figure 4.16.** Relationship between neodymium concentrations (ppm) and the spectra absorption depth of carbonatites spectra. The neodymium absorption depths were calculated based on continuum removal method of carbonatite spectra, and Nd concentrations were measured using, LA-ICP-MS. The coefficient of determination of the Nd concentration vs its absorption depth displays a confident correlation (R2 > 0.9).



Figure 4.17. Shows the absorption center ranges of iron oxides measured from the carbonatite spectra.



**Figure 4.18.** The iron oxides absorption feature depths of the carbonatite spectra were evaluated. The regression relationships were used to understand the connection between iron oxides absorption depths and its concentrations in carbonatites. The change in absorption depth with the increase of the iron concentrations in carbonatites has good correlation (R2 > 0.8).



Figure 4.19. Shows the absorption center ranges of Nd measured from the carbonatite spectra.



**Figure 4.20.** Nd concentration (in ppm) plotted against the spectra absorption depth of carbonatites from this study and others [29]. The neodymium absorption depths were calculated based on continuum removal method of carbonatite spectra. The coefficient of determination of Nd concentration vs its absorption depth shows a positive correlation ( $R^2 > 0.6$ ).



**Figure 4.21.** Shows Nd and iron concentration (in ppm) plotted against spectra absorption depth. In the samples with high REE-Nd concentration and low iron, the absorption is greater in depth.

present in both  $Fe^{2+}$  (amphibole, mica, chlorite) and  $Fe^{3+}$  (iron-oxides). Given that XRF analysis calculates all iron as  $Fe^{3+}$ , the distribution of iron between the oxidation states from this geochemical analysis is unknown. On the basis that  $Fe^{2+}$  (1 µm) and  $Fe^{3+}$  (0.9µm) have different absorption peaks, interference between the peaks may result in imprecision in the combined iron absorption depth.

3) The spectrum of REEs, which is dominated by Nd<sup>3+</sup>, is evident as an absorption feature in the VNIR spectrum between 0.7 to 0.774  $\mu$ m. Unsurprisingly the Nd<sup>3+</sup> absorption depths for carbonatites are more pronounced in samples with higher REE concentrations. An important outcome from these results is, however, that Nd concentrations within a carbonatite must exceed 1000 ppm before it is detectable using ASD spectroscopic methods. The coefficient of determination of the Nd concentration vs. its absorption depth exhibits a positive correlation (R<sup>2</sup>> 0.9 for Nd), (Figure 4.16).

### 6.2. The spectra of a carbonatite weathered surface

Remote sensing sensors (hyperspectral and multispectral) scan only the surface layer of rock outcrops. Such weathered surface layers may exhibit significantly different spectral signatures to the rock beneath. Carbonatite, in particular, is prone to surface degradation and alteration of its surface. Despite the broad acknowledgement of the significant impact of this issue, sample spectra collected in the lab frequently rely upon fresh cut surfaces. Utilizing these unrepresentative spectra to interpret remote sensing images during carbonatite exploration or mapping, could introduce an unconstrained source of ambiguity.

This study examined the spectroscopic and geochemical differences between the fresh interior and weathered exterior of both ferro- and calico-carbonatites. There was a consistent increase in the abundance of iron and REEs on the weathered exterior in comparison to the fresh interior in both ferro- and calcio-carbonatites (Table 4.2). Accordingly, the iron and Nd<sup>3+</sup> absorption depths were typically greater in the weathered exterior spectra in comparison to the fresh interiors. In contrast, the abundance of calcite in the fresh interior was higher than the weathered exteriors in all carbonatites tested. Therefore, the calcite absorption depths were greater in the fresh interior spectra in comparison to the weathered exteriors. More importantly, the particular features of the weathered exterior of carbonatites (high in iron, and REEs) may actually result in making carbonatite more detectable using field spectroscopy instruments like ASD, and hyperspectral remote sensing. While there was a lower calcite content in the weathered exterior, it was still present within the spectra. These results suggest that the weathered exterior of carbonatite might serve as a better remote sensing target because of the higher concentration of REEs and iron, combined with evidence of a C-O bond from the remaining calcite. Thus, while the weathered surface may enhance carbonatite detection, ambiguity may remain as to the actual content of REE because of elemental redistribution.

### 6.3. Nd spectra absorption features in carbonatite rocks

The application of spectroscopic techniques to characterize carbonatite rocks is uncommon. To our knowledge, such work has been undertaken in only few other studies. That study examined a wider array of global carbonatites[29], and did not consider highly constrained samples such as those presented herein. The results of this prior study are broadly similar to our results and thus the datasets are examined in tandem. There are, however, differences among the datasets: 1) the previously published spectra were collected on a different aliquot of rock to that used for geochemical analysis. Indeed, the geochemical data is from work published from multiple studies and labs. Carbonatite is known to have potentially extreme heterogeneity in terms of REE distribution due to the concentration of REEs in particular phases. Accumulations of coarse allanite, monazite, or apatite, for example, in one part of the rock that may have been analyzed geochemically may lead to difficulties when correlated with a spectral signal taken on a surface from another part of the sample lacking such accumulations. 2) Prior studies examined only fresh interior surfaces of the carbonatite, limiting the application of such spectra in real world conditions where field outcrops are dominated by weathered surfaces. Furthermore, it was not possible to apply the full range of parallel transformations to these spectral results, as the published data were not in a digital format.

Our results are comparable with earlier examinations, showing that the Nd<sup>3+</sup> absorption center was found at ~0.744  $\mu$ m. When comparing the combined Nd concentrations (data from this study and the previously published data) with the spectral absorption depths, it resulted in the R<sup>2</sup> values that are > 0.6 (Figure 4.20). Despite the poorness of the linear fit of the data, the results do show a rough positive relationship between the Nd concentrations and the spectra absorption depth (Figure 4.18, 4.20, and 4.21).

Difficulties in measuring the relationship between Nd concentration and  $Nd^{3+}$  absorption depths are further complicated by the impact of iron in terms of spectral interference. Studies which examined artificial sample mixtures (iron + Nd) showed that when iron oxide reaches more than 10%, it significantly hinders REE-related absorption depth [37]. The impact of this interference has been noted and indeed some of the scatter evident in our combined dataset may arise from the high concentration of iron in some samples. The impact of iron interference for samples from our study is potentially significant give  $Fe_2O_3(T)$  concentrations in our samples are ~9-21 wt.%, which may cause REEs absorption depth reduction (figure 4.21).

### 7. Conclusion

Our interpretation of the normalized carbonatite sample spectra, prepared using the continuum removal method, is that carbonatite minerals and elemental concentrations are generally characterized by multiple diagnostic absorption features within the VNIR and SWIR wavelengths. However, these characteristic absorption bands are variable between different types of carbonatites. The spectroscopic outcomes of this investigation show that three key minerals'/elements' (calcite, iron oxides, and REE-Nd) absorptions were very distinctive in their reflectance spectra, demonstrating a direct connection between carbonatite spectra and the geochemical results. The concentration of calcite in carbonatites has a substantial effect on the absorption depth between 2.312–2.345 µm of carbonatite spectra. The deepest absorption was recorded in calcio-carbonatite. The correlation between the calcite concentration and wavelength absorption depth shows a positive linear correlation with an  $R^2$  value about 0.8. The absorption features between 0.885-1.037 $\mu$ m of the wavelength are caused by iron (Fe<sup>2+</sup>, Fe<sup>3+</sup>), which occurs within iron-bearing minerals of carbonatites. The iron absorption was detected in all our samples and the absorption depths were greater in ferro-carbonatite samples than in calcio-carbonatite samples. The absorption depth of iron in our samples is well-correlated with concentration ( $R^2 >$ 

0.8). The REE absorption features that are governed by Nd<sup>3+</sup> are recorded in VNIR area between 0.7 to 0.774  $\mu$ m. In the samples with high REE-Nd concentration, the absorption depth is greater. The Nd concentration vs. its absorption depth scatterplots diagram shows a positive correlation with R<sup>2</sup>> 0.9.

Presented here is the first comparison of the impact of the development of a weathered surface on carbonatite spectra. The weathered exterior consistently exhibits increased concentrations of iron and REE, with a corresponding drop in carbonate concentrations. These geochemical variations were evident within the rock spectra, with more pronounced absorptions on weathered surfaces. These results suggest that weathered carbonatite surfaces may be easier to detect using local spectroscopic methods or in remote hyperspectral sensing images of carbonatites. It is also note that care must be taken when predicting potential REE resources from the magnitude of these spectra given that the weathered surface is thus not representative of the whole rock concentration of REEs.

The Nd spectral absorption depth from this study was compared with available published dataset. The results were compatible with earlier analyses. Most Nd absorption centers were measured around 0.744  $\mu$ m. The scatterplot diagram shows that the samples with Nd concentrations more than 1000 ppm are more distinguishable in laboratory spectra than samples with less Nd abundance. The high concentration of iron in some samples reduced the Nd absorption depth, in particular for samples with Fe<sub>2</sub>O<sub>3</sub> more than 13 wt.%. All Nd concentrations were plotted against the spectral absorption depths and the R<sup>2</sup> values are > 0.6. However, despite the potential for carbonatite heterogeneity, the results show positive correlation.

While this study has helped to constrain carbonatite spectroscopy, more investigation is needed to enhanced interpretations of REE spectra. In particular, focused research on the relationship between iron concentration and Nd spectra are needed to fully interpret spectral results.

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# **CHAPTER 5**

# **CONCLUSION AND RECOMMENDATIONS**

### 1. Dissertation Synthesis

The main objectives of this dissertation are to explore remote sensing data, mapping algorithm techniques, and spectroscopic applications to identify and map carbonatite distribution at Al-Uyaynah area-UAE. The research surveys carbonatites by employing the Visible/Near Infra-Red (VNIR) and Short Wave Infra-Red (SWIR) with three datasets: (1) the latest multispectral sensor (Landsat 8 OLI), (2) ASTER imaging and (3) Analytical Spectral Device (FieldSpec-3 Hi-Res ASD) Spectroradiometer. Whole rock geochemical analysis of major element oxide and REE concentrations in carbonatites were determined using Standardized X-ray fluorescence (XRF) and Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS). Geographic distribution of carbonatites was outlined (chapter 2) by an examination of Landsat 8 OLI data validation, as it is considered to be one of the most widely accessed open-data sources used for geological mapping. This presents a novel approach of exploring the Al-Uyaynah area, utilizing new Landsat 8 imagery through mapping algorithms. Following this investigation, carbonatite distribution in Al-Uyaynah area was examined utilizing ASTER data processed with four various mapping processing algorithms: the Binary Encoding Classification (BEC), Spectral Information Divergence (SID), Spectral Angle Mapper (SAM), and Support Vector Machine (SVM) (Chapter 3). These mapping algorithms were employed to analyze and digitally classify carbonatites and spatially adjunct geological units with the tested outcomes ranked based on their accuracies. The third investigation explores carbonatite chemistry using spectral analysis devices (ASD) and geochemical approaches to develop a comprehensive understanding of chemical environments of the Al-Uyaynah carbonatites. These geochemical data allow for testing of the relationship between the major oxides and REEs spectral absorption features of carbonatite spectra and their concentrations in carbonatites linearly (chapter 4). The overall findings of all dissertation chapters are summarized in this section, employing this information to assess the effectiveness of Landsat 8, ASTER, Analytical Spectral Device (ASD) data for carbonatites mapping in Al-Uyaynah area. Moreover, the broader impacts concerning the utility of these datasets and the tested mapping algorithms in future exploration will also be addressed.

## 2. Dissertation conclusion

Remote sensing imagery has been a standard tool for exploration and mineral mapping over the past four decades, initially utilized as a rapid and cost-effective approach to analyzing the chemical variability of surface rock and mapping of lithological units [8, 9]. In this research, I have analyzed two multispectral satellite systems in terms of their utility for carbonatite indication and mapping; the newest generation of Landsat satellites (Landsat 8 OLI) and ASTER visible/nearinfrared (VNIR); and Short Wave Infrared (SWIR) data. Both Landsat and ASTER imagery remains the most popular open-source remote sensing data and are widely used by the geologic and remote sensing communities. The performances of both systems were compared for use in carbonatite mapping, and an assessment of these systems validates their efficacy in the mapping of carbonatite units. ASTER outperformed the other systems, suggesting that spectral resolution is more crucial when it comes to carbonatite mapping, as it provides more spectral bands in SWIR to detect carbonatite key minerals.

Of the many image categorization techniques that rely on the spectral method, we examined four mapping methods (BEC, SID, SAM, and SVM) to determine the best method to detect and map carbonatite and other associated rock units within the study area. The classification method maps were compared with the field ground truth data, resulting in variability among their results. The best discrimination between the image's end-members was achieved using the SVM algorithm, producing 86% (excellent) overall agreement with the field ground's truth and the current published geological map. The SAM algorithm provided a good map with 61% accuracy whereas the other two classifiers (BEC, SID) performed poorly. Despite the excellent classification that was obtained using the SVM learning algorithm, some degree of classification error was observed: i) Carbonatite complexes generally appear in fields as small units within larger-scale features, complicating the mapping process. ii) The similar richness in iron oxide minerals in the weathered outcrop of ferro- and calcio-carbonatite layers resulted in difficulty in separating the units. iii) The mapping of ferro-carbonatites using the SVM algorithm was more challenging in the southern region because they are narrow and structurally deformed units that occur near the alkali volcanic rocks. The blended appearance of the rock units makes it difficult to separate the units using the SVM algorithm. Regardless of this difficulty, our overall experiment results suggest the SVM algorithm is useful for mapping carbonatites using remote sensing data.

One of the objectives of this research was to analyze the spectral features carbonatites utilizing field spectraradiometer of chemically analyzed rocks. In this regard, we investigated whether the reflectance spectroscopy, in the area between to the 0.45 to 2.5 µm, can be utilized to identify and detect carbonatite minerals/elements. Spectra derived using the continuum removal method show multiple diagnostic absorption features within VNIR and SWIR bands. Specifically, the investigation shows three key minerals/elements leading to very distinctive absorptions in the reflectance spectra (calcite, iron, and REE-Nd). Comparing the spectra of the carbonatites to the geochemical analyses demonstrates positive correlation between the observed absorption depth and the carbonatite key minerals/elements abundances leading to a promising novel approach to more quickly and at lower cost distinguish between types of carbonatite. The presence of VNIR spectral features resulting from REE-Nd<sup>3+</sup> make it possible to identify potential REE ore deposits for the purpose of prospecting. This research outcome adds to data on carbonatite system data can be overcome by laboratory or field reflectance spectroscopy.

### 3. Recommendations and outlooks for carbonatite prospectors

Digital mapping based on remote sensing dataset and algorithm techniques, like those previously reported within this dissertation, will not eliminate the necessity for the traditional field based geological mapping. Rather, digital mapping offers the most cost-effective and time-saving technique for generating maps that can be used as a guide for field investigation. This is particularly valid when it comes to large scale area mapping. Given the spatial association of carbonatites with silicate rocks that share some spectral features with carbonatites, such field investigations remain a critical component in prospecting. Mapping algorithms are many and produce different results depending on how the algorithms manage image data. Depending on the algorithms efficiency and the quality of remote sensing dataset, a resulting carbonatite map can be poor, or highly accurate. High accuracy maps will allow researchers to focus their field investigation. In this research, we tested four algorithms to map carbonatite units. The highest mapping accuracy was accomplished utilizing the SVM algorithm. This algorithm illustrates the advantage of artificial intelligence or support vector machine learning algorithm (SVM) over strictly static algorithms used in this research (BEC, SID, SAM). Additional examination is required using high-resolution sensors to determine whether the overall carbonatite mapping accuracy could be increased by using the SVM learning algorithm to produce object-based carbonatite mapping.

Geospatial researchers are currently enjoying one of the most fertile periods for Earth observing data. The remote sensing sensors are scanning the earth's surface at ever finer spatial resolutions. The continuing decline of the expense of these data will help researchers pose new questions and challenges that will result in the advancement of carbonatite identification and geological mapping in general.