



**GEOLOGY, MINERALOGY AND THE OCCURRENCE OF RARE EARTH ELEMENTS
IN THE COAL DEPOSIT AT THE UITKOMST COLLIERY (UTRECHT COALFIELD),
KWAZULU-NATAL, SOUTH AFRICA**

By

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MINERAL SCIENCES, FACULTY OF SCIENCE AND AGRICULTURE, UNIVERSITY
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2025

DECLARATION

I, Sibusiso Maseko, with student number [REDACTED], declare that the dissertation titled "Geology, mineralogy and the occurrence of rare earth elements in the coal deposit at the Uitkomst Colliery (Utrecht Coalfield), KwaZulu-Natal, South Africa", hereby submitted to the University of Limpopo has not been previously submitted by me for a degree at this or any other university; that it is my work in design and in execution, and that all material contained herein has been duly acknowledged.



05/11/2024

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Date

DEDICATIONS

This Master of Science dissertation is dedicated to my mother, Ms Sphiwe Maseko.

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ABSTRACT

The Utrecht Coalfield is one of the coalfields of the Main Karoo Basin, which is currently underexplored and there is no information regarding the REEs concentration. Before extracting the REEs, it is significant to examine the distribution and concentration of REEs within the host rock, in this case, coal. The purpose of the study is to explore the mineralogical and geochemical characteristics and occurrence of REEs in the coal deposits at the Utrecht Coalfield (Uitkomst Colliery). Seventeen samples from three different seams (Gus, Alfred, and Fritz) were analysed using petrography, ultimate analysis, proximate analysis, and X-ray diffraction (XRD) analysis. The REEs concentration in the samples was determined by inductively coupled plasma (ICP-MS) techniques, whereas scanning electron microscopy with energy dispersive spectroscopy (SEM-EDS) as a direct method and Pearson's correlation as an indirect method was used to determine the mode of occurrence of the REEs in the samples from the Utrecht Coalfield. The Vryheid Formation in the Utrecht Coalfield consists of sandstones, siltstones, shale, and mudstone, with minor coal seams. The average thickness of the Eland, Fritz, Alfred, and Gus seams is 0.30 m, 0.21 m, 1.21 m, 1.12 m, and 1.26 m, respectively. The samples were dominantly inertinite rich with lesser liptinite and vitrinite macerals and were categorised as medium-rank- C. The Gus, Alfred and Fritz seams had an average ash content of 14.9%, 29.9% and 18.4%, respectively. Few of the samples were low sulphur coals whereas others were medium sulphur coals. The dominant minerals detected by the XRD are quartz and kaolinite with lesser pyrite. The sum concentration of REEs ranged from 23.15 to 173.50 ppm, with an average of 101.43 ppm. The average REEs concentration for the Gus Seam was 79.47 ppm, 120.79 ppm for the Alfred seam, and 137.63 ppm for the Fritz seam. The samples had REEs concentrations higher than that of Worlds and USA Coals except for samples CMB-L1, CB2-L1, CB1-L2, CB2-L2, and CB2-S1. Furthermore, samples CB1-L1, CMB-D, JCBH08B, and JCBH20 had REEs concentrations higher than that of Chinese Coals. The Pearsons' correlation indicated a mixed inorganic-organic affinity of REEs as shown by the positive correlation. The SEM-EDS analysis in the samples revealed that the REEs have inorganic and organic affinities. The coal-forming environment was weakly reducing to oxidizing, favouring REEs enrichment. The provenance is predominantly a felsic source region,

likely a mixture of Archean and post-Archean rocks, including sedimentary sources with granitic, tholeiitic, and alkalic basalt. The Utrecht Coalfield is not promising for REEs extraction.

Keywords: *Utrecht Coalfield, Coal, Critical elements, Rare earth elements, Mineralogy.*

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LIST OF ACRONYMS

BSE	Back-scattered electrons
EDS	Energy Dispersive Spectrometry
HREEs	Heavy Rare Earth Elements
ICP-MS	Inductively Coupled Plasma Mass Spectrometry
LREEs	Light Rare Earth Elements
MREEs	Medium Rare Earth Elements
PPM	Parts Per Million
REEs	Rare Earth Elements
RoVmr	Mean Random Vitrinite Reflectance
SEM	Scanning Electron Microscope
st. dev	Standard Deviation
TREEs	Total Rare Earth Elements
UCC	Upper Continental Crust
Vol. %	Volume Percentage
w. %	Weight Percentage
XRD	X-ray diffraction
REO	Rare earth oxide

CHAPTER 1

INTRODUCTION

1.1 Background of the study

The Utrecht Coalfield, in the KwaZulu-Natal Province, is a major coal-producing area that has been mined for over a century (Spurr et al., 1986). The coalfield forms part of the larger Karoo Supergroup within the Main Karoo Basin. The coals of the Utrecht Coalfield are hosted within the Permian Vryheid Formation of the Ecca Group (Spurr et al., 1986). The coalfield contains various coal seams with variable thicknesses and qualities, which include the Targas, Coking, Dundas, Gus, Rider, Alfred, Fritz and Elands coal seams. Previously, the Dundas, Gus and Alfred coal seams were known as the Yard, Main and Moss seams, respectively (Spurr et al., 1986). Coal mining at the Welgheich Colliery commenced in 1889, with production starting in 1896 (Hancox and Gotz, 2014; Barker, 1999; Spurr et al., 1986). The coals in the Utrecht Coalfields are less marketable when compared to other coals from the KwaZulu-Natal area, except for some coking coal from the Balgray Colliery. Spurr et al. (1986) documented that the coals have been intruded by dolerites and that the coal has elevated phosphorus and sulphur levels, which affected the coal development.

Following the study of Goldschmidt and Peters (1933), coal deposits have received significant attention as an alternative source for rare earth elements (REEs) globally. This was further fuelled by the economic crisis of demand and supply in 2009, known as the rare earth crisis (Dushyantha et al., 2020). China dominates the global market of REEs, contributing about 90% of the total world's supply (Watkins et al., 1995). The fifteen lanthanides, including lanthanum (La), cerium (Ce), praseodymium (Pr), neodymium (Nd), promethium (Pm), samarium (Sm), europium (Eu), gadolinium (Gd), terbium (Tb), dysprosium (Dy), holmium (Ho), erbium (Er), thulium (Tm), ytterbium (Yb) and lutetium (Lu), along with yttrium (Y) and scandium (Sc), are termed rare-earth elements (REEs) by the International Union of Pure and Applied Chemistry (IUPAC) (Watkins et al., 1995).

Due to their chemical similarities and shared mineral deposits with lanthanides, yttrium and scandium are also categorized as REEs. Catalytic converters, flat-screen televisions, mobile phones, wind turbines, energy-efficient lighting, rechargeable batteries, medical equipment, electrical vehicles, and disc drives are all examples of emerging and niche technologies that use REEs. These elements contribute to several manufacturing capabilities, including reduced energy usage, downsizing, speed, higher efficiency, thermal stability, and durability because of their unique magnetic, chemical, luminous, and physical properties. Wagner and Matiane (2018) reported that the REEs of the Witbank and Highveld coalfields have an average total rare earth elements (TREEs) concentration of approximately 111 ppm. Chitlango (2023) documented a TREEs concentration of about 225.45 ppm for density-fractionated coals from the Waterberg Coalfield, while Hazza et al. (2022) reported a concentration of 219.53 ppm for high-ash coals from the same coalfield. Furthermore, Chitlango (2023), Hazza et al. (2022) and Wagner and Matiane (2018) highlighted the importance of exploring other coalfields for their REEs potential. As a result, this study intends to provide insight into the mineralogical and geochemical characteristics of the Utrecht Coalfield, as well as investigate the occurrence of REEs in the coal-bearing units of the Utrecht Coalfield at the Uitkomst Colliery.

1.2 Problem statement

Coal is being considered as a potential raw material for rare earth elements (REEs), which has recently garnered substantial interest (Seredin and Dai., 2012; Seredin, 1996). REEs consumption is rapidly increasing as new energy and energy storage technologies are developed (Cornelius et al., 2021; Wagner and Matiane, 2018), and conventional REEs deposits cannot meet the world's high demand for REEs (Eterigho-Ikelegbe et al., 2021). Prospecting for REEs from alternative sources, such as coal, is therefore critical. Although South Africa has 6% of the world's coal resources and produces approximately 254 million tons (Mt) of coal per annum, coal research as a possible alternative source for these REEs receives little attention (Eterigho-Ikelegbe et al., 2021). Only a few coalfields in South Africa (i.e., the Witbank and Waterberg) have been studied for major elements in

coal, coal-forming environments, and coal quality (Eterigho-Ikelegbe et al., 2021; Cornelius et al., 2021; Ripfumelo, 2017; Blissett et al., 2014; Seredin, 1996; Watkins et al., 1995). These studies were primarily on sedimentary geology and environmental elements, with little emphasis on mineralogy and critical elements that are associated with coal. The mineral and organic maceral constituents of coal vary greatly even in coal seams within the same locality or coalfields (Cornelius et al., 2021; Ripfumelo, 2017; Seredin, 1996; Watkins et al., 1995). Consequently, the concentration and modes of REEs occurrence in coal vary significantly across regions and even within the same coalfield. The Utrecht Coalfield is one of the coalfields in the KwaZulu-Natal Province that provides basic fuel to the country (Mokoena et al., 2022). However, the geochemical and mineralogical characteristics of these coals in relation to REEs are unknown. Furthermore, the occurrence and distribution of REEs within the coal are also unclear. To fill this research gap, this study characterises the coal and investigates the occurrence of REEs in the coal of the Utrecht Coalfield at the Uitkomst colliery.

1.3 Location of study area

The Uitkomst colliery holds a mining right located on various portions of the farms Klipspruit 178 HT, Vaalbank 103 HT, Waterval 157 HT, Margin 420 HT, Rusterwacht 151 HT, Uitkomst 95 HT, Jericho C 413 HT, Jericho 400 HT, Jericho A 414 HT, Jackalsdraai 299 HT and Kweekspruit 22 HT, in the magisterial district of Utrecht in the KwaZulu-Natal Province of South Africa. Geographically, the area is situated at longitudes 29°40' E and 30°30' E and latitude of 27°20' S and 27°50' S. The mining area covers approximately 11,169.48 hectares (Ha), located about 20 km northwest of the town of Utrecht and 23 km northeast of the town of Newcastle (Figure 1.1).

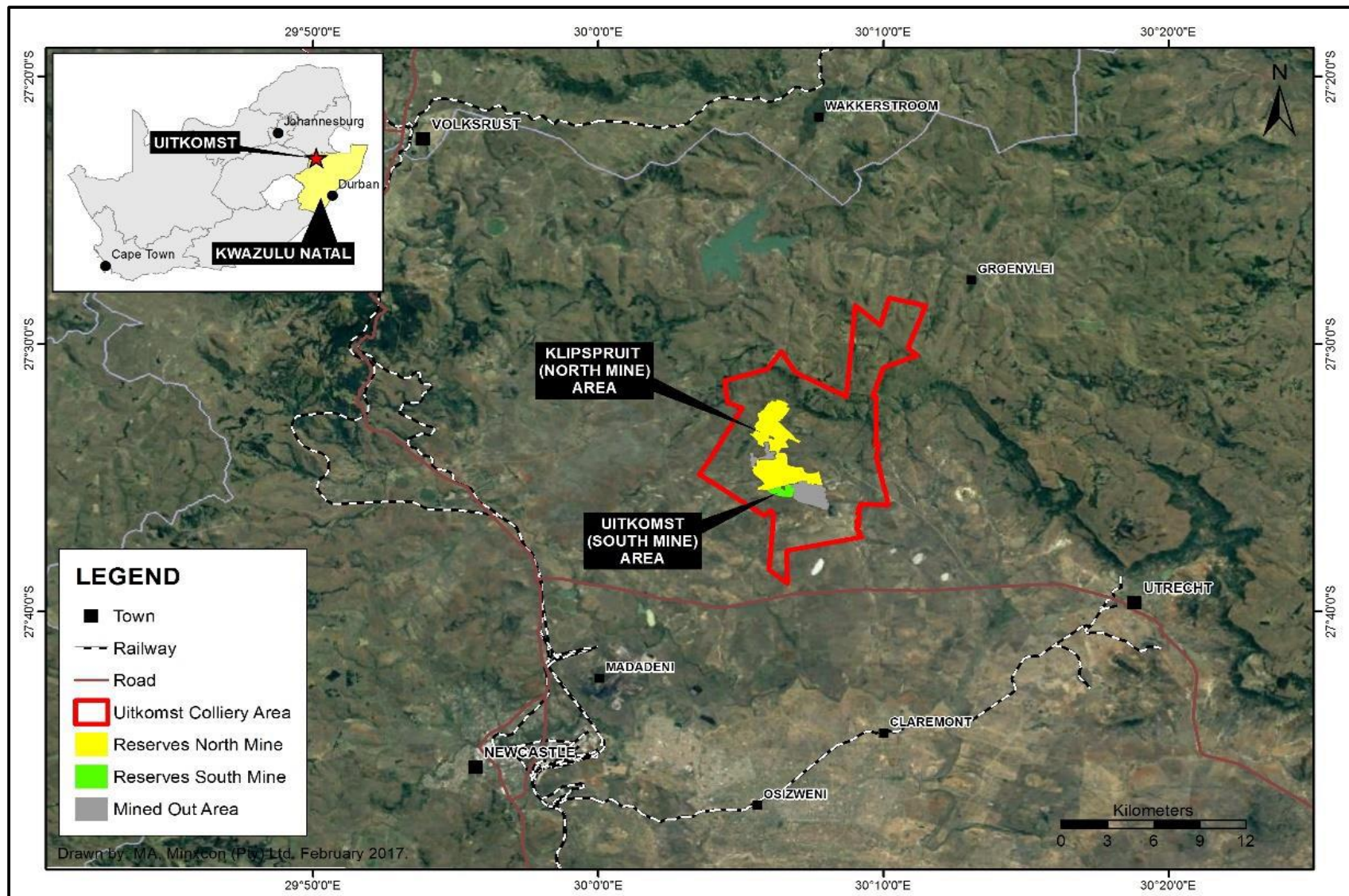


Figure 1.1: Location of the study area (MC Mining, 2017).

1.4 Rationale of the study

The lack of sufficient REEs is a global concern, and recent research has focused on the economic potential of REEs in coal (Harrar et al., 2022; Huang, 2019; Wagner et al., 2018). Global demand for these REEs for use in electronic and related components is increasing, and recent mining schemes and electronic recycling programs have revealed that coal is a potentially large untapped resource for REEs (Eterigho-Ikelegbe et al., 2021; Huang, 2019; Wagner et al., 2018; Blissett et al., 2014; Seredin, 1996). The coal deposits in South Africa have been identified in the following basins: the Main Karoo, Springbok Flat, Waterberg, Tuli and Tshipise basins (Wagner et al., 2018). The Utrecht Coalfield is one of the nineteen known coalfields in South Africa, which forms part of the Eccar Group in the Main Karoo Basin under the subdivision known as the Vryheid Formation (Bell et al., 2001). South Africa has the world's sixth largest coal resource, with exploitable reserves amounting to 31 billion tonnes, or 11% of the entire global coal reserves (Eterigho-Ikelegbe et al., 2021; Blissett et al., 2014). In the chain of resources used to produce REEs, coal has the potential to play a substantial role, with an estimated 50 Mt or more of REEs in coal sources worldwide. This is more than 50% of the accessible ore minerals with REEs in the globe (Akdogan et al., 2022; Taggart et al., 2022; Cornelius et al., 2021; Ripfumelo, 2017). Due to the need to diversify the source of REEs, South Africa has significant opportunities to join in the world's supply. In fact, South Africa can take advantage of this opportunity to considerably contribute to the long-term supply of these high-tech metals as one of the regions with abundant REEs deposits. As a result, this research is critical for accurately estimating the economic potential of REEs in the Utrecht Coalfield.

The search for alternative resources becomes increasingly important as the gap between the international REEs supply and demand widens, particularly for countries that rely heavily on imports (i.e., South Africa). In 1988, two deposits in South Africa were estimated to contain 2.187 million metric tonnes of known and proven exploitable REE reserves (Nyale et al., 2013). These deposits are the Richards Bay's placer monazite and the Phalaborwa Complex's rare earth-bearing apatite (An, 2014; Connelly et al., 2005).

South Africa was number three in the world at the time, behind China and the United States, but the nation never established a REEs mining and refining sector. In addition, other potential REEs sources (i.e., coal and carbonaceous shale) in South Africa have not been investigated to ascertain their economic potential. Research in mineralogy and geochemistry is crucial to unravel the origin, distribution, occurrence modes and evaluation of REEs in coal (Seredin and Dai., 2012; Watkins et al., 1995). Characterising the Utrecht Coalfield and investigating the occurrence of REEs in the coal may contribute to the understanding of coal as an alternate source of REEs. In fact, the findings of this study can assist in classifying the coal as a probable economic source of REEs. As a result, this study is critical to exploit coal deposits for their economic benefit.

1.5 Aim and objectives

The aim of this study is to investigate the mineralogical and geochemical characteristics, and occurrence of REEs in the coal deposits at the Uitkomst Colliery. The objectives of the study will be to:

- (i) identify the lithology and measure the stratigraphic successions of the Vryheid Formation at the Uitkomst Colliery.
- (ii) determine the mineralogical composition of the coal at the Uitkomst Colliery.
- (iii) identify and quantify the dominant maceral groups in the coal.
- (iv) determine the quality and rank of the coal at the Uitkomst Colliery.
- (v) investigate the occurrence and concentration of REEs in the coal of Uitkomst Colliery.
- (vi) determine whether the coal in the Utrecht Coalfield contain economically exploitable resource for REEs.

1.6 Research questions

The underlying research questions are:

- (i) what is the mineralogical composition of the coal at the Uitkomst Colliery?
- (ii) do the coal have the minerals that host REEs?

- (iii) what is the rank of the coal, and does the rank have any correlation or relationship with the occurrence of REEs?
- (iv) what are the concentration and patterns of REEs distribution in coal?
- (v) if the REEs are present in the coal, can the enrichment of these REEs be considered economically feasible or regarded as another source for REEs?

1.7 Limitations of the study

At the Uitkomst Colliery, four boreholes (AD3BH2, AD3BH3, JCBH08 and JCBH20) that targeted the Gus Seam, Alfred Seam, and the Fritz Seam were made available by the mine. However, since the Gus Seam had already been sampled by the mine from these boreholes, no further samples could be obtained. As a result, additional sampling of the Gus Seam had to be conducted on the underground mining operation. Given that the Gus Seam is the sole focus of current mining operations, the Alfred and Fritz seams could not be sampled in the underground mining operation. Consequently, samples from these seams were collected only from the boreholes. The Fritz Seam, however, was present in only two of the boreholes and was relatively thin, resulting in only two samples being available for analysis. In contrast, the Alfred Seam, which was of sufficient thickness in the boreholes, allowed for more sampling. While this study provides insight into the Fritz Seam, the limited number of samples collected means that the findings for this seam are based on a smaller dataset, and this should be considered when drawing conclusions from the results. The number of boreholes and samples reflects the practical constraints of material availability and accessibility, as well as the variability in seam thickness and distribution. The approach prioritised the use of available resources to ensure representation across the seams, while logistical and geological factors, such as the thinness of the Fritz Seam and mining focus on the Gus Seam, inevitably limited sample diversity. These considerations underline the practical challenges of sampling in the Utrecht Coalfield and their influence on the dataset.

CHAPTER 2

LITERATURE REVIEW

2.1 Geology of the Main Karoo Basin

The Main Karoo Basin in South Africa stands out from other Karoo Basins in southern Africa due to the presence of the thickest and most complete mega-sequence of Permo-Carboniferous to Jurassic age sediments within the south-western Gondwana continent (Catuneanu et al., 1998). It serves as a benchmark for categorising Karoo Basins across central and southern Africa (Figure 2.1). Except for the Drakensberg Group, which comprises volcanic rocks, all formations within the Karoo Supergroup are sedimentary (Catuneanu et al., 2005). The Main Karoo Basin lies between the Kaapvaal Craton (Cargonian Highlands) to the north and the Cape Fold Belt to the south (Tankard et al., 2009). After a 30 Ma hiatus known as the Permian-Triassic boundary, which denotes the shift from the Cape Basin to the stable Karoo Basin, there was a period of widespread elevation that occurred due to the amalgamation of Pangea (Tankard et al., 2009).

The Late Carboniferous to Early Jurassic Karoo Basin then emerged as a tabular cratonic cover, reaching up to 125 Ma (Tankard et al., 2009). Based on the interpretation of Johnson et al. (2006) and Catuneanu et al. (1998), the Karoo formed behind an inferred magmatic arc and fold-thrust belt. According to McCarthy and Rubidge (2005), the deposition of the vast sequence of sedimentary of the Karoo Supergroup occurred from about 310 Ma to 182 Ma. The rocks of the Karoo Supergroup exhibit a complicated history of shifting temperatures, sea levels and tectonic processes (Baiyegunhi, 2017; Catuneanu et al., 2005).

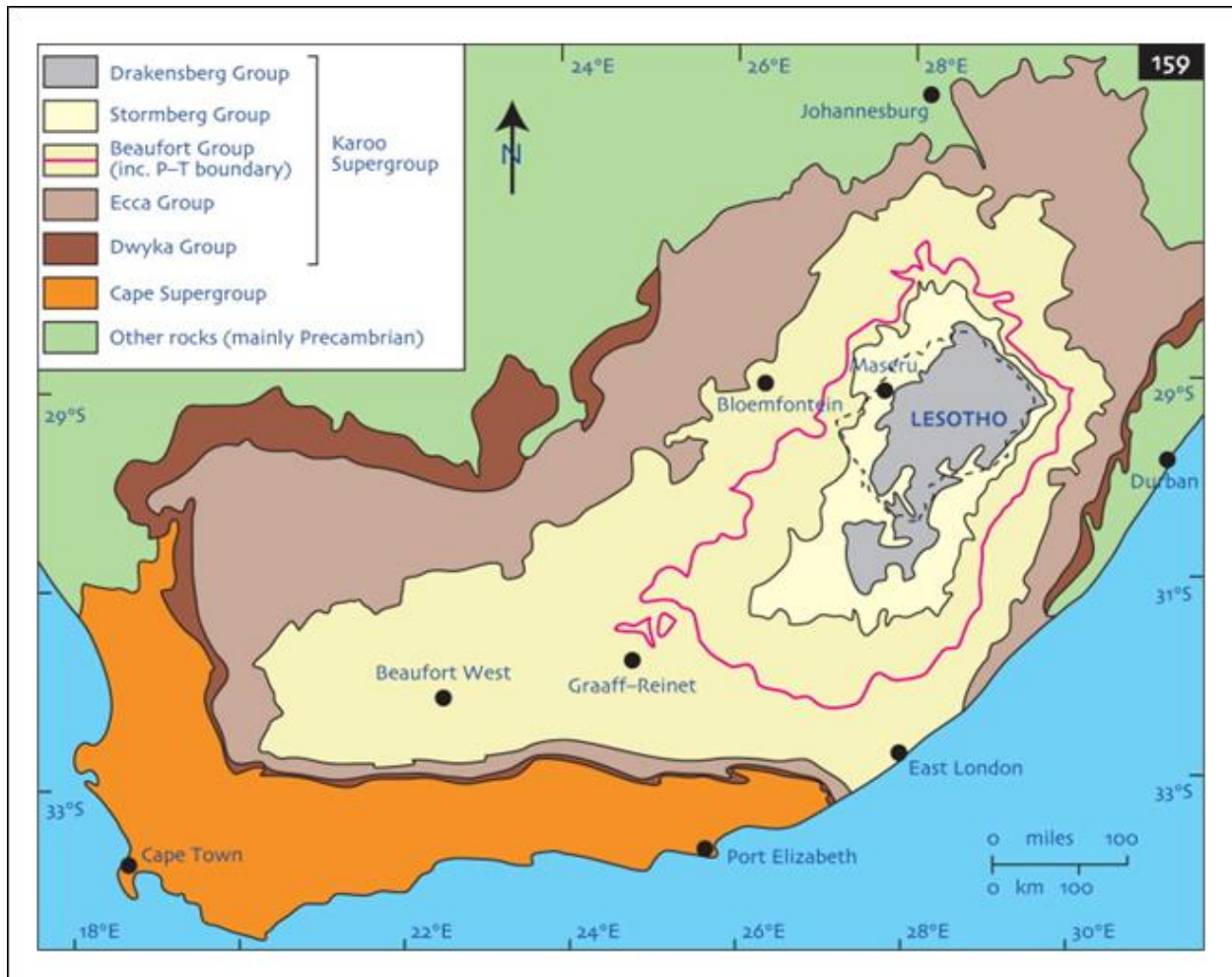


Figure 2.1: Geological map of the Main Karoo Basin (Rubidge, 2005).

2.2 Tectonic Setting

The development of the Main Karoo Supergroup occurred within the broader context of the fragmentation of the Gondwana supercontinent during the late Paleozoic to early Mesozoic Era (Catuneanu et al., 1998; Figure 2.2). This period was marked by significant tectonic events, including the rifting and separation of the Gondwanan landmasses, which ultimately gave rise to the modern continents of Australia, Antarctica, India, South America and Africa.

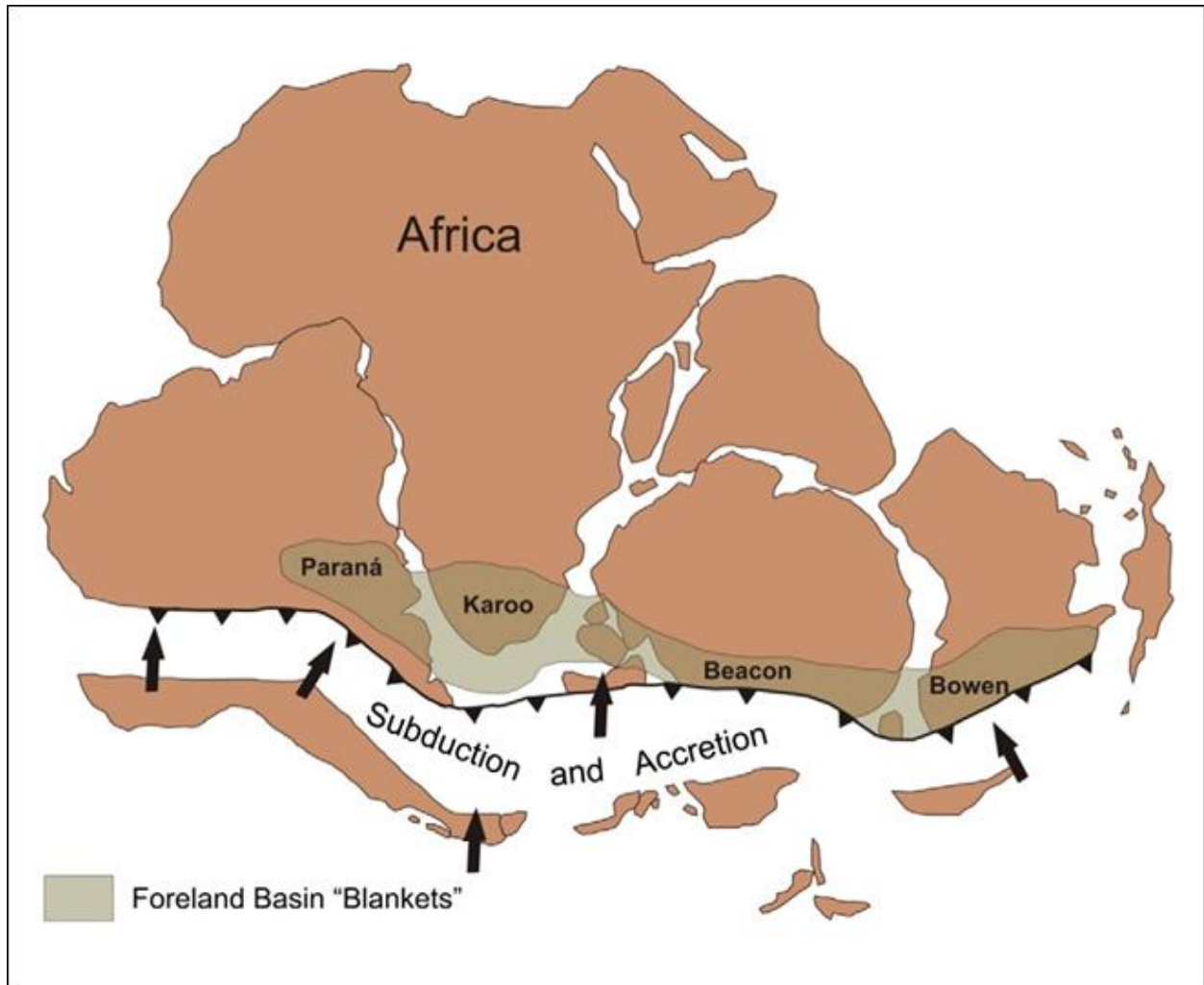


Figure 2.2: The Karoo Basin's location (After de Wit and Ransome, 1992; Hancox and Goetz, 2014).

The tectonic processes that shaped the Main Karoo Supergroup can be attributed to the interaction between regional tectonic forces and the underlying geodynamic processes within the mantle (Tankard et al., 2009). One key factor was the extensional stresses acting on the lithosphere, leading to the thinning and stretching of the crust. Extensional tectonics created a series of rift basins in the interior of Gondwana, where the Main Karoo Basin developed (Catuneanu et al., 2005). The sedimentary successions of the Main Karoo Basin were deposited in various environments, including fluvial systems, lakes, swamps, and shallow marine settings (Fildani et al., 2009; Catuneanu et al., 2005; Rubidge et al., 2000). These depositional environments were influenced by changes in

climate, temperature, sea level and subsidence associated with the tectonic processes occurring during the fragmentation of Gondwana (Johnson et al., 2006; Catuneanu et al., 2005; Rubidge et al., 1995; Tankard et al., 1982).

The Karoo Supergroup is recognized as a retro-arc foreland basin, suggesting that the basin developed in relation to a subduction zone and the presence of a fold belt (Johnson et al., 2006; Catuneanu et al., 2005). According to this model proposed by Catuneanu et al. (2005), there is a volcanic active source area located to the north of the ancient Pacific subduction zone. The subduction zone is represented in the model as a foredeep, forebulge, and back-bulge flexural province. The formation of the Karoo Basin resulted from a trans-extensional foreland system experiencing subsidence and tilting processes within a strike-slip tectonic setting (Lindeque et al., 2011; Tankard et al., 2009; Johnson et al., 2006), which means that the basin formed as a result of both compression and extension forces acting simultaneously. Furthermore, the tectonic development of the basin can be linked to the collisional tectonics occurring in the region, as well as distant southward subduction. Collisional tectonics refers to the convergence and subsequent collision of tectonic plates, leading to the formation of mountain ranges and fold belts. In the case of the Karoo Supergroup, the thin fold-belt within the basin indicates the effects of such collisional tectonics (Lindeque et al., 2011).

Tankard et al. (2012) challenged the aforementioned model by highlighting the absence of a nearby magmatic arc and the lack of on-lapping characteristics typically observed in flexural foreland basins. Instead, an alternative interpretation was proposed for the development of the Karoo Basin based on the interaction of rigid crustal blocks and the weak boundary fault zones in the southern African lithosphere. The model that was proposed by Tankard et al. (2012), suggests that the Karoo Basin should be seen as a sinistral strike-slip orogen, resulting from the oblique reactivation of the southern Namaqua suture. The late Karoo foreland basin was thought to have formed as a result of boundary forces linked to the Cape Fold Belt (Tankard et al., 2012; De Wit and Ransome, 1992). Pysklywec and Mitrovica (1999) reported that the blocks sink due to the mantle flow which drives the subsidence through dynamic topography. Mantle movement caused the subsidence and was complicated by foundation block changes or varying

degrees of foundering. This may have functioned as the boundary of a buried basin, affecting the position of the shelf edge similarly to a passive margin (Tankard et al., 2009).

2.3 Stratigraphy

The deposition of the Karoo Supergroup occurred from the late Carboniferous to the early Jurassic, and it is mostly comprised of mudstone, shale, siltstone and sandstones (Catuneanu et al., 2005). Deposited between the late Carboniferous and early Permian periods, the Dwyka Group forms the lowest unit of the Karoo Supergroup and consists of glacial sequences (Johnson et al., 2006; Catuneanu et al., 2005; Figure 2.1). The sedimentation that resulted in the formation of the Dwyka Group is estimated to have occurred approximately 300 million years ago (Catuneanu and Elango, 2001). The lithofacies of the Dwyka Group consist of mudstone, sandstone, conglomerate and diamictites (Visser, 1986). Sediments that were deposited during the early to middle Permian period make up the Eccca Group, which overlies the Dwyka Group (McCarthy and Rubidge, 2005; Figure 2.1). Minor conglomerate, siltstone, mudstone, sandstone and coal are the lithologies that make up the Eccca Group (McCarthy and Rubidge, 2005). The sedimentation of the Eccca Group is reported to have occurred in a clastic wedge (Tankard et al., 2009; Catuneanu et al., 2005).

The Eccca Group contains important coal deposits that formed from the accumulation of organic material in the swamps and wetlands that existed during this time. In the north of the basin, the Eccca Group is subdivided into three formations, from base to the top, the Pietermaritzburg, Vryheid and Volksrust formations. These formations cannot be completely correlated to the southern part of the basin. The Vryheid Formation is believed to have been deposited contemporaneously with the upper Prince Albert Formation and Whitehill Formation, whereas the Volksrust is considered to grade into the Tieberg Formation (Catuneanu et al., 2005). The clastic wedge Vryheid Formation is considered to be thinning out in the southern and southwest parts of the basin, whereas it is much thicker in the east and northeastern sides of the basin (Catuneanu et al., 2005; Johnson et al., 1996). Additionally, the Volksrust Formation indicates the final transgressive phase,

where initial deltaic progradation in northern areas led to the formation of the upper part of the Vryheid Formation.

The terrestrial sediments of the late Permian to middle Triassic Beaufort Group show a finning-up sequence and generally contain fine-grained siltstone, mudstones and sandstones that were deposited in different fluvial environments (Visser, 1995). The Beaufort Group is known for the abundant fossil record, particularly of early mammal-like reptiles and other vertebrates that provide important insights into the advancement of life on Earth (McCarthy and Rubidge, 2005). The Upper Karoo Supergroup previously referred to as the Stormberg Group, lies above the Beaufort Group, following a basal unconformity (Catuneanu et al., 2005; McCarthy and Rubidge, 2005). It is composed of continental sediments, which were deposited between 230 and 200 Ma, during the late Triassic to Early Jurassic periods (Johnson et al., 2006; Catuneanu et al., 2005; Figure 2.3). Moreover, the Molteno, Elliot and Clarens formations are the three subdivisions of the Upper Karoo (Stormberg Group).

The Molteno Formation is composed of medium- to coarse-grained sandstones, the Elliot Formation consists of a sequence of sandstone and mudstone, whereas the Clarens Formation represents the final stage of Karoo sedimentation and comprises of fine-grained sandstone and sandy siltstone (Johnson et al., 2006; Catuneanu et al., 1998). Furthermore, the Clarens Formation was deposited in a desert environment with several cross-bedding structures. There is also the occurrence of the Drakensberg Group, which intruded the sequence of the Karoo Supergroup, made up of volcanic rocks (i.e., mafic, felsic and rhyolitic) that erupted during the Late Triassic about 182 Ma (Baiyegunhi, 2017; McCarthy and Rubidge, 2005). Additionally, the eruption of the Drakensberg Group terminated the Karoo Supergroup sedimentation. The Upper Karoo Group is renowned for its extensive fossil record, which includes early mammals, amphibians, and reptiles, including dinosaurs (McCarthy and Rubidge, 2005).

		FORMATION		165	
PERIOD	GROUP	WEST OF 24°E	EAST OF 24°E	ASSEMBLAGE ZONES	
JURASSIC	←	DRAKENSBERG	DRAKENSBERG		
			CLARENS		
TRIASSIC	STORMBERG		ELLIOT		
			MOLTENO		
		BURGERSDORP	Cynognathus		
PERMIAN	BEAUFORT		KATBERG	Lystrosaurus	
			Palingkloof Mbr	Dicynodon	
			Elandsberg Mbr		
			Barberskrans Mbr		
			Daggaboersnek Mbr		
			Oudeberg Mbr	Cistecephalus	
			MIDDLETON	Tropidostoma	
				Pristerognathus	
				ABRAHAMSKRAAL	Tapinocephalus
				Eodicynodon	
			CARB.	DWYKA	ELANDSVLEI
TIERBERG/ FORT BROWN	FORT BROWN				
LAINSBURG/ RIPON	RIPON				
COLLINGHAM	COLLINGHAM				
WHITEHILL	WHITEHILL				
PRINCE ALBERT	PRINCE ALBERT				

Figure 2.3: Stratigraphy of the Karoo Supergroup (Hancox and Rubidge, 2001).

2.4 Coalfields in South Africa

The number of coalfields in South Africa is debated in the literature, however, 19 are usually agreed upon (Figure 2.4), encompassing around 9.7 million hectares (ha) (Hancox and Gotz, 2014). Bredel (1987) estimated the country's coal reserves to be around 55 gt, which was later reported to be around 32.15 gt (Prevost, 2015). The majority of these resources are in the provinces of Mpumalanga and Limpopo. The coal reserves are spread across several coalfields, each of which has a distinct lithology, geology and coal seam rank. The coalfields are distinguished based on origin, rank, mode of sedimentation and distribution of the coal (Hancox, 2016; Hancox and Gotz, 2014). However, the focus of this study is on the Utrecht Coalfield.

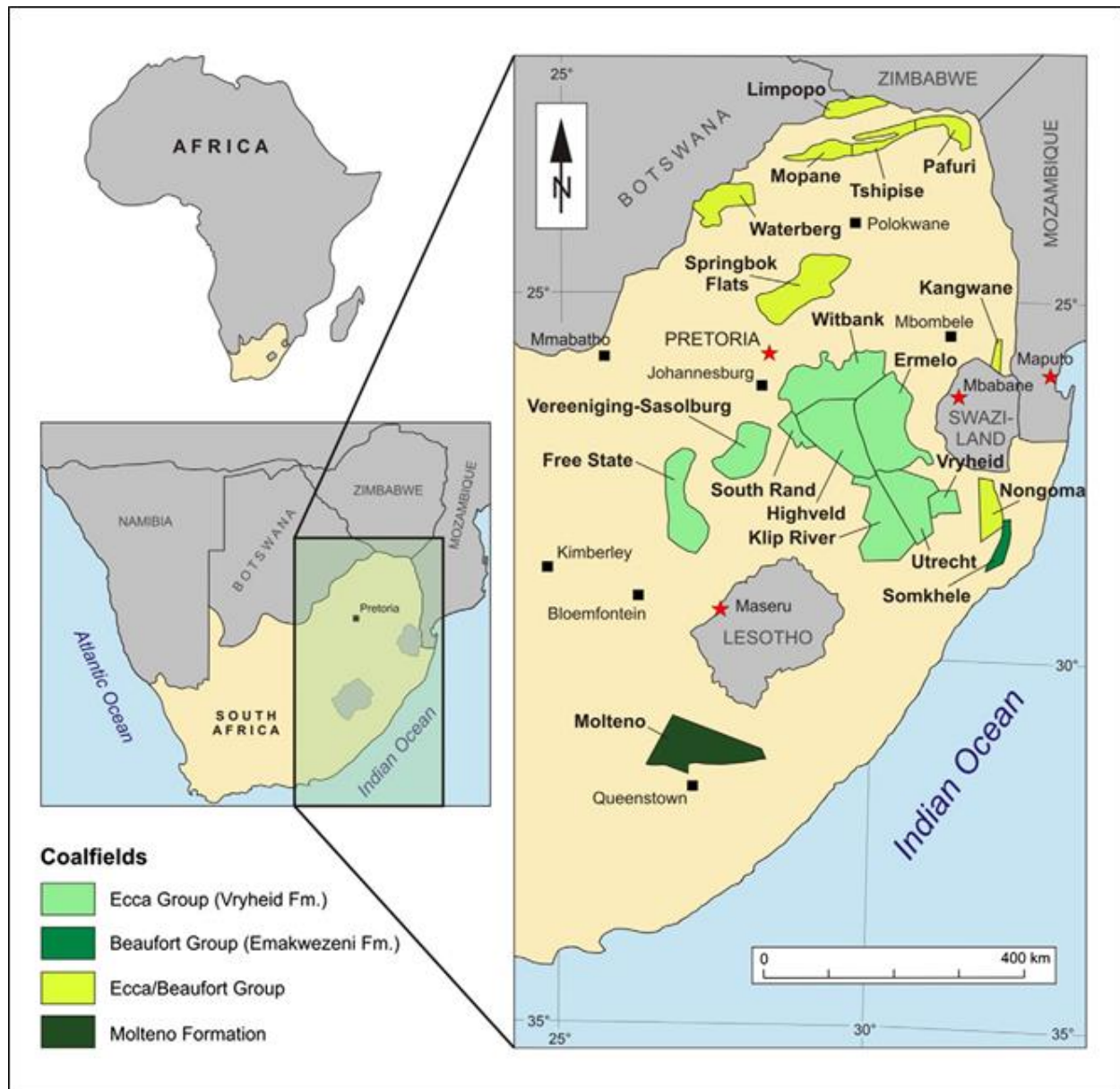


Figure 2.4: Coalfields in South Africa (Hancox and Gotz, 2014).

2.4.1 Utrecht Coalfield

The Utrecht Coalfield is in the northernmost region of the KwaZulu-Natal province in South Africa, covering a surface area of approximately 500 000 hectares in the magistral district of Paulpietersburg and Utrecht (Spur et al., 1986; Figure 2.4). The coalfield stretches out from the township of Pualpietersburg in the northeast, in a south-westerly route across the Schurweberg and Elandsberg mountain ranges. The Utrecht and the

Klip River coalfields are separated by an area intruded by dolerites and the coalfield lies adjacent to the Ermelo Coalfield in the north (Figure 2.4). The Utrecht Coalfield is separated from the Vryheid Coalfield by a coal barren area whereby the seams were removed as a result of erosion (Spurr et al., 1986). The area containing coal is confined to a highly dissected, mostly dolerite-capped plateau that rises to a maximum elevation of about 2275 m above sea level (Spurr et al., 1986).

In the early and mid-1960s, extensive exploration activities took place in the Utrecht Coalfield, resulting in the establishment of collieries such as Umgala, as well as the Balgray and Zimbutu parts of the Welgedacht Exploration Company (Spurr et al., 1986). Subsequently, in the 1980s, the Alfred Seam, located on the Zoetmelksrivier 86 farms, was commercially mined through both open-pit and underground operations. This mining activity yielded an approximate annual production of 200,000 metric tons of anthracite coal (Spurr et al., 1986). Furthermore, eight collieries were operational by the end of 1981, with three producing steam coal, one producing coking coal, and four producing anthracitic coal. Additionally, during that period, the quantity of coal sold that came from the Utrecht Coalfield exceeded 3.5 million tons, representing a significant production peak since the start of mining operations in the 1890s.

2.4.2 Stratigraphy of the Utrecht Coalfield

The stratigraphy of the Utrecht Coalfield in South Africa includes a series of sedimentary rocks deposited during the Permian and Triassic periods. The coal-containing formations of the Utrecht Coalfield are part of the larger Eccra Group, which is a major subdivision of the Karoo Supergroup (Hancox and Gotz, 2014). The stratigraphic sequence of the Utrecht Coalfield is subdivided into several distinct units, each representing a different depositional environment and period (Spurr et al., 1986; Figure 2.5). The lowermost unit in the stratigraphy of the Utrecht Coalfield is the Dwyka Group, although it is not extensively developed in this coalfield (Hancox and Gotz, 2014; Spurr et al., 1986). The Dwyka Group represents glacial deposits and consists of a mixture of tillites (glacially derived sediments) and associated diamictites (unsorted glacial deposits). The Eccra

Group overlies the Dwyka Group, and it is the main coal-bearing unit within the Utrecht Coalfield.

The Eccca Group is subdivided into several formations, from oldest to youngest, the Volksrust Formation and contains predominantly red and purple mudstones and siltstones. The Vryheid Formation overlies the Volksrust Formation, and it is the principal coal-containing formation, making it the primary target for mining operations in the Utrecht Coalfield. The Vryheid Formation consists of alternating layers of coal, carbonaceous siltstones, sandstones, and mudstones. The Umsimbithi Formation overlies the Vryheid Formation, and it comprises interbedded sandstones, mudstones and siltstones. The Klip River Formation that makes up the uppermost unit of the Eccca Group in the Utrecht Coalfield consists of mudstones, siltstones and sandstones. The Beaufort Group unconformably is overlying the Eccca Group in the Utrecht Coalfield. However, it is not extensively developed in this region (Figure 2.5).

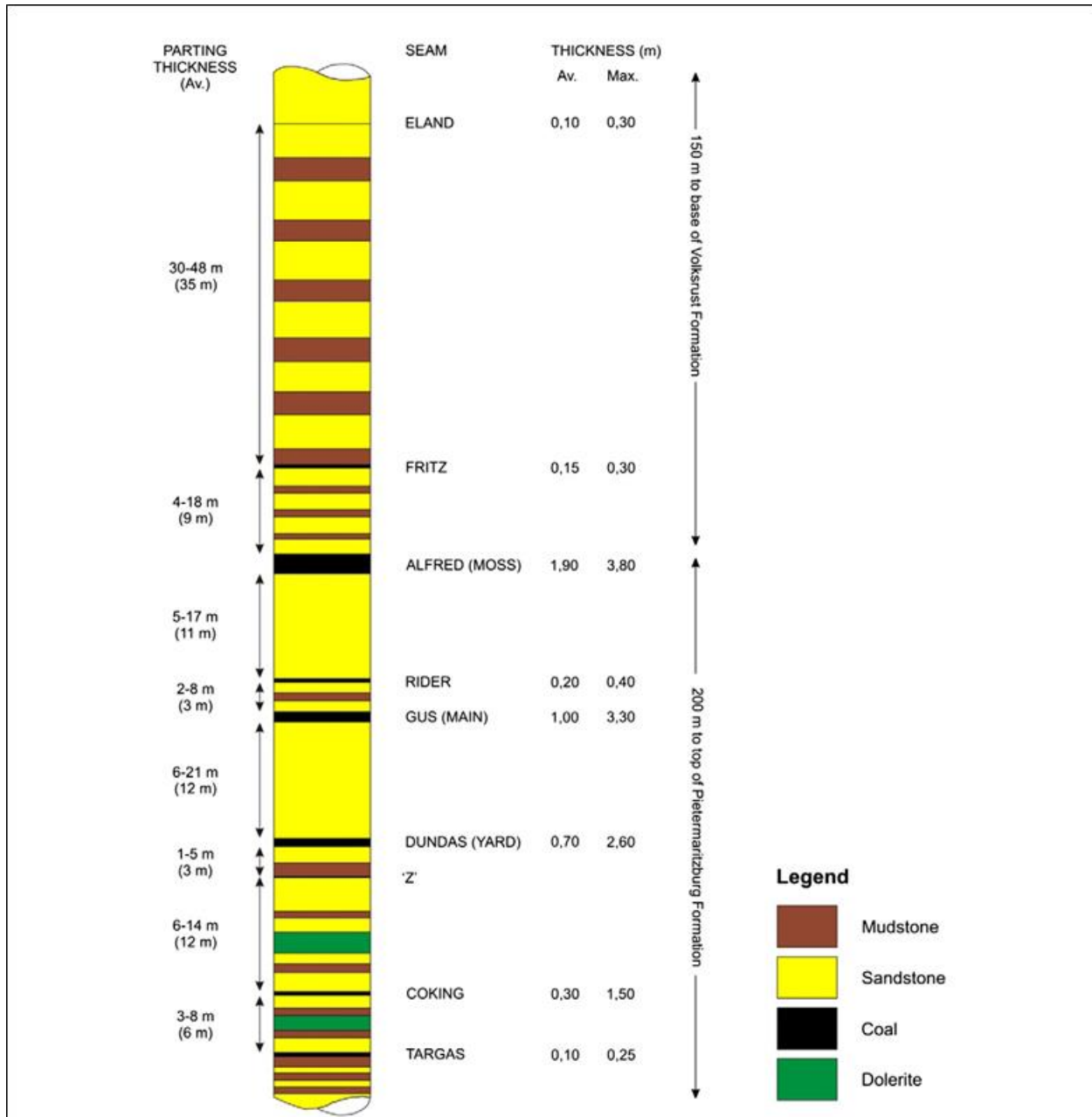


Figure 2.5: Stratigraphy of the Utrecht Coalfield (After Hancox and Gotz, 2014; Spurr et al., 1986).

2.4.3 Coal seams of the Utrecht Coalfield

The Utrecht Coalfield in South Africa contains several economically significant coal seams, including the Alfred, Gus, Coking and Dundas coal seams. Additionally, seams

such as the Eland, Fritz, Rider and Targas coal seams are present but are very thin and cannot be extracted using the technology available today (Hancox and Gotz, 2014). As documented by Spurr et al. (1986), the Coking seam has a maximum thickness of about 1.5 m at Makateeskop, and it is typically thin with an average thickness of approximately 0.9 m. The seam is made up of high-quality coal that is mostly bright and thinly banded, with sporadic sandstone or siltstone partings within the seam where it thickens. The floor and roof rocks of the Coking seam are typically competent, composed of medium- to fine-grained or medium- to coarse-grained sandstones.

According to Spurr et al. (1986), the Dundas seam is situated roughly 15 m above the Coking seam and can reach a maximum thickness of 2.6 m. In the western part of the Utrecht Coalfield, the thickness of the Dundas seam varies considerably. However, in areas where it has been mined, it has reached around 2 m in thickness. The Dundas seam consists of an upper section with a mix of dull and bright coal layers, a fraction of bright coal, and a lower zone with mixed coal and fines (Hancox and Gotz, 2014). It yields bituminous coal and has been exploited by Kangra Holdings at Longridge for export-quality anthracite. Hancox and Gotz (2014) documented that the Gus seam (Figure 2.5) is the most heavily exploited in the Utrecht Coalfield, and it is situated about 17 m above the Dundas seam. In the southern part of the coalfield, the seam averages over 1 m in thickness, reaching a maximum of approximately 3.3 m. In the northern part of the coalfield, the seam splits into upper and lower sub-seams, separated by a sandstone layer, ranging from 3 m to 12 m in thickness. Near the town of Utrecht, the Gus seam can be divided into three distinct quality zones or plies. The lower half is typically of poor quality, consisting of dull coal with a continuous siltstone or mudstone layer, while the middle and upper parts are primarily composed of bright coal. The competence of the roof and floor of the seam varies significantly, being very poor at the Kempslust Colliery, where thinly laminated fine-grained sandstone forms an exceedingly weak roof, but it is relatively high near the town of Utrecht (Spurr et al., 1986).

The Alfred seam is located around 14 m on top of the Gus seam (Figure 2.5). On average, the thickness of the Alfred seam ranges between 1.9 m and 3.8 m (Spurr et al., 1986). This seam is a compound seam that is made up of three distinct layers in some places

(i.e., Zoetmelksrivier) with thickness varying from 1.5 m to 3 m. The upper portion of the coal seam is made up of high-ash and low-quality coal and carbonaceous mudstone (Hancox and Gotz, 2014). Additionally, except for the areas that are in proximity to the dolerite intrusions, the roof of the Alfred seam has been widely thought to be of average competence. Likewise, medium- to coarse sandstone that is sturdy enough to sustain mechanical equipment typically makes up the floor.

2.4.4 Geology of the Utrecht Coalfield

According to Hancox and Gotz (2014), the Klip River Formation, which represents the basement rocks, does not significantly influence the development, quality, or distribution of the seams in the Utrecht Coalfield. The rocks of the Dwyka Group, typically associated with coal-bearing formations, are either not present or developed thinly across most parts of the coalfield. Instead, the Pietermaritzburg Formation, which is composed of mudstones and siltstones, directly overlies the basal rocks in most areas. In the Klip River Coalfield, the Pietermaritzburg Formation exhibits a coarsening-upward sequence, advancing into bioturbated delta plain and delta front sandstones and siltstones in the lowest portion of the Vryheid Formation (Cadle and Hobday, 1977). The Vryheid Formation with a total thickness of about 300 m in the west and 380 m in the east, encompasses the coal region of interest. This coal zone includes multiple fluvially dominated, fining-upward cycles of conglomeratic sandstones, typically topped by carbonaceous shales or coal seams. Above the coal zone, there are sequences of regressive deltaic deposits that are predominantly composed of sandstones. In the northern of the coalfield, the Volksrust Formation is present at the surface. Spurr et al. (1986) noted a thickness of approximately 70 m for this formation in a borehole near Schurvekopje, intersecting the Beaufort Group. Similar to other areas in KwaZulu-Natal, the Volksrust Formation predominantly consists of dark grey siltstones and mudstones.

2.5 Coal origin and formation

Coal is a sedimentary complex heterogeneous rock formation composed of various plant matter called macerals and varying proportions of inorganic materials (Jovanovski et al.,

2023; Falcon, 2013). Furthermore, owing to its combustion characteristics, coal is categorized as a fossil fuel and serves as an energy source in a variety of industries. Coal is formed through a complex process of organic matter accumulation, preservation, and compaction. According to the World Coal Institute (2008), coal formation in the northern Hemisphere during the Carboniferous period has been dated to be from 299 Ma to 360 Ma. Swaine (1990) described the formation of coal in three stages: biochemical, microbial and geochemical. The microbial stage involves the initial formation of peat under wet and acidic conditions, typically near areas affected by rising seas or subsiding land, facilitating rapid decay of plant matter. The biochemical stage commences when sediments abruptly overlie the peat. Lastly, the geochemical stage begins as the organic material undergoes compaction and alteration (Swaine, 1990).

The organic matter is primarily derived from the remains of plants that lived in wetland environments, such as swamps, bogs, and marshes (McCarthy and Rubidge, 2005). As these plants died and accumulated, the organic materials were buried by sediment, such as sand, clay, or mud, forming a layer of peat (Figure 2.6). The sediment layers prevented the organic material from decaying by limiting the amount of oxygen and microbial activity available. The weight of the overlying sediment then compacted the plant material, driving off water and other volatile components and increasing the concentration of carbon. Over millions of years, the pressure and temperature in the sedimentary basin are increased, causing further chemical changes to the organic matter (Hatch and Affolter, 2004). This process, known as coalification, resulted in the formation of coal, which is a sedimentary rock composed mainly of carbon-rich organic matter. Coal, often referred to as rock, and primarily consists of decomposed organic matter (plants) rich in carbon. The composition of coal includes a variety of organic components known as macerals, along with a smaller proportion of inorganic minerals (Chen et al., 2018; Flores, 2014). When combusted, coal releases heat energy, which is utilized in power machinery like steam engines or to generate electricity using turbines.

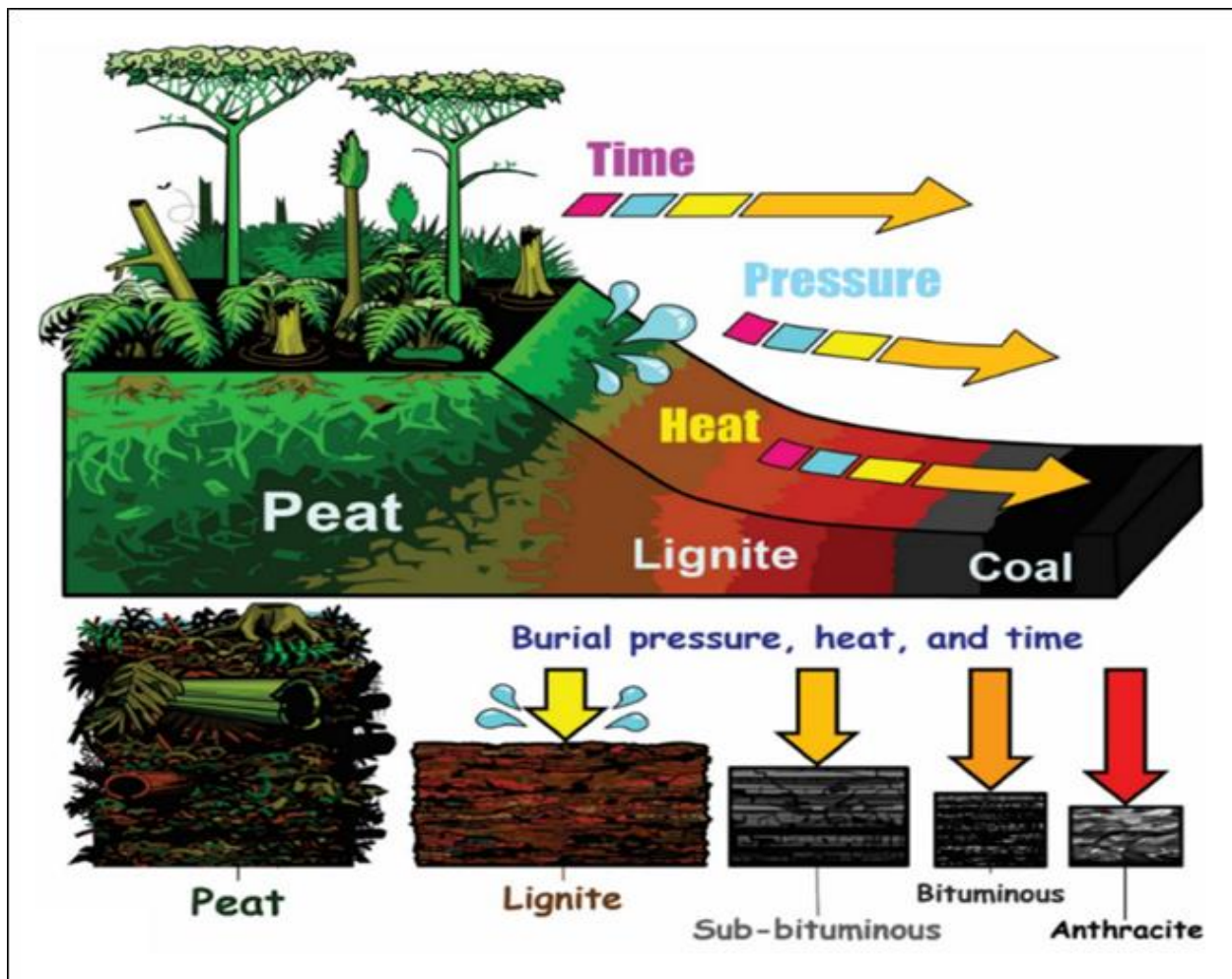


Figure 2. 6: Coal formation (Jovanovski et al., 2023).

2.6 Coal Composition

2.6.1 Macerals

The nomenclature "maceral" was initially coined by Stopes (1935) to describe the complex of biological units resulting from a forest tree that fell into a waterlogged swamp. In this process of coal formation, the tree partially decomposed and underwent maceration. However, the resulting maceral did not become uniform throughout; instead, it retained distinct regions with varying optical properties under a microscope. These regions may have different chemical compositions and properties (Pickel et al., 2017). Later shortened to "macerals," which refers to optically homogeneous aggregates of organic materials. Macerals possess unique chemical and physical characteristics and

naturally occur in igneous, metamorphic and sedimentary materials found on Earth. Macerals are formed by the coalification of plant tissues and have different physical and chemical properties from other minerals, which have a stable internal composition and structure (Pickel et al., 2017). The properties of macerals are closely associated with the degree of coalification (Wang et al., 2019).

Through petrographic analysis, macerals can be classified into three main categories: vitrinite, liptinite, and inertinite. The most prevalent form of maceral is vitrinite and it is composed mainly of carbonized cell walls from woody tissue, liptinite is formed from remains of plant material that is highly resistant to degradation, and inertinite is derived from hydrogen-rich plant and decomposition products (Wang et al., 2019). Coal macerals provide valuable information about the depositional environment, thermal maturity, and coal quality (Wang et al., 2019). Macerals are defined as recognizable, visually distinct entities within coal that are derived from organic matter. Macerals can be distinguished from one another according to their chemical and physical properties, such as reflectance, fluorescence, and morphology.

2.6.1.1 Formation of macerals

The governing factors on which the accumulation of macerals relies in the early stages of peatification involve pH, Eh, climatical conditions, tectonic controls, and the type of plants (Wagner et al., 2018). In oxygenated conditions, the plant matter will undergo disintegration, which will result in very little remains of the plant residue, but in deoxygenated conditions, the process of mouldering is favoured (Wagner 2018; Falcon, 2013). Furthermore, this results in the aerobic bacteria and fungi producing hydrogen-deficient humiric substances, and the cellular and sap contents in the plant tissue dissipate, leading to drying and darkening of the cell walls, reducing the vegetable matter to charcoal-like bands of wood and detrital grains. This process is the formation of fustrinite and it is called fustrinization. If the peat is partially covered, peat formation progresses to form humiric acids or gelification of the wood (Wagner et al., 2018; Falcon, 2013; Falcon and Snyman, 1986; Stach et al., 1982). According to Stach et al. (1982), the processes that follow are humirification, followed by gelification, and then vitrification

occurs later. It is responsible for the alteration of the plant tissue into first huminite and later vitrinite (Figure 2.7).

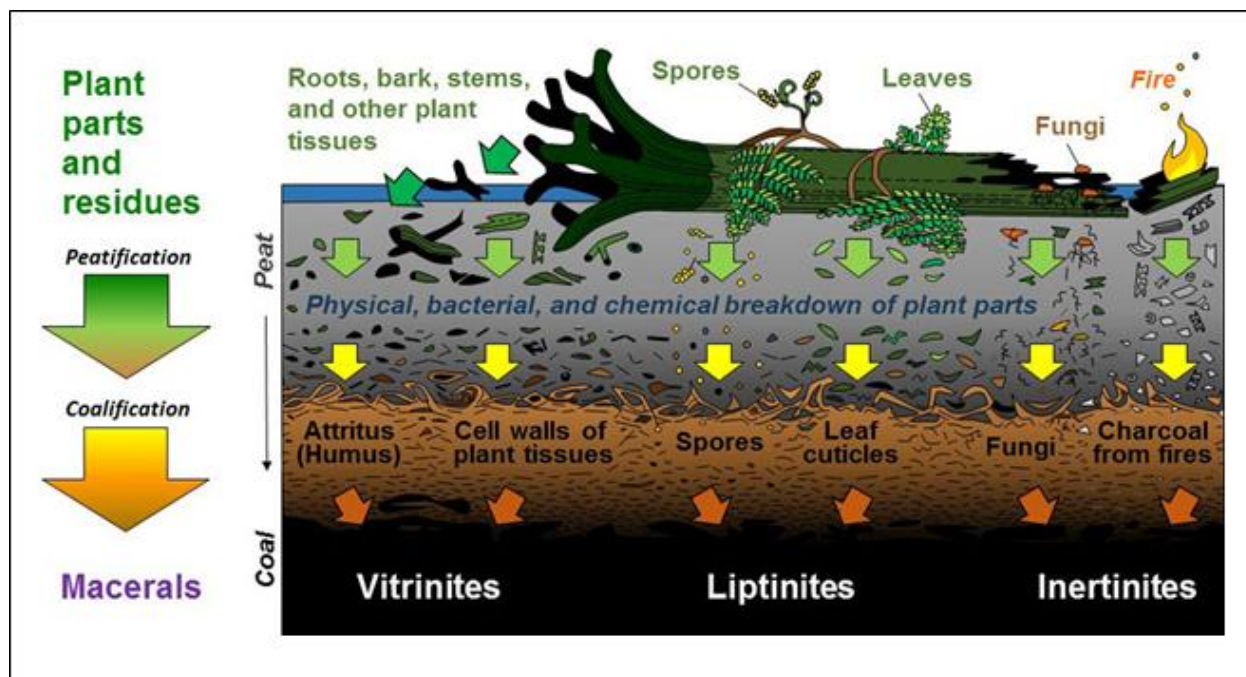


Figure 2.7: Maceral formation (After Falcon and Snyman, 1986; Stach et al., 1986).

2.6.1.2 Liptinite

The macerals that are known as liptinite originate from plant components that are not humifiable (Taylor et al., 1998; Table 2.1). These macerals primarily consist of relatively hydrogen-rich remnants, such as fats, waxes, resins, and sporopollenin. In terms of reflectance, liptinite macerals typically exhibit the lowest values compared to other macerals at a given rank. Their composition and reflectance characteristics differentiate them from other macerals found in coal. Additionally, fluorescence properties have emerged as significant secondary distinguishing features for liptinite (Pickel et al., 2017). These fluorescence properties, such as autofluorescence and changes in fluorescence intensity and spectral shift with increasing rank, provide additional information for identifying and studying liptinite macerals. In reflected white light, liptinite appears as a dark grey to black and the fluorescence colours exhibited by liptinite macerals encompass a spectrum ranging from green-yellow (Pickel et al., 2017). According to the ICCP System

(1994), the macerals belonging to the liptinite group can be further differentiated into liptodetrinite, bituminite, alginite, chlorophyllinite, resinite, exudatinite, suberinite, sporinite and cutinite. These different macerals within the liptinite group represent various organic components with distinct characteristics and compositions (Pickel et al., 2017).

Table 2.1: Showing liptinite macerals (After ICCP, 1994).

Maceral Subgroup	Form
Sporinite	Exines of micro to megaspores; typically compressed at higher rank but also aligned with sediments; well-preserved; varying structure and wall thickness; unique botanical forms. Liptinite's widely prevalent form.
Cutinite	Derived from stem and leaf cuticles. Long, typically jagged, unique plant shapes that are parallel to layering. Serrations solely on a single edge are possible.
Exudinite	Intense fluorescence is produced from hydrogen-rich sources, and it is found as a secondary maceral occupying cavities, and vacant cells (e.g., liptinite).
Resinite	Pod-shaped, globular, or irregular substances that appear in distinct forms and can fill cellular cavities or take the form of amorphous shapes in vitrinitic lenses. It is made up of cell excretions and can exhibit red internal reflections. The word corpogelinite, or secretinite, is used when the reflectance is higher or is comparable to vitrinite.
Alganite	Planktonic or benthic, solitary or in colonies, spherical, elongated, semi-compressed, unique and well-preserved in botanical form. Subcategories include telalginite, which is more structurally different than lamalginite and is uncommon in humic coals.

Suberinite	An uncommon lignite form with a well-defined cell structure, derived from subaerous tissues, with strong fluorescence. Due to rank, not found in southern Africa.
Bituminite	Amorphous breakdown by-product that is more fluorescently intense and has a lower reflectance than vitrinite. Occurs as a groundmass made up of tiny granules, or as bands, threads, wisps, or streaks. Very rare.

In coking processes, liptinite is essential because it produces the most desirable by-products, such as volatile matter, in high quantities. It is known that liptinite is rich in hydrogen and serves as the main source of liquid petroleum in rocks that are petroleum source rocks. It is interesting to note that the onset of hydrocarbon formation from liptinite macerals differs between various varieties of liptinite and takes place at various thermal maturities. This variation onset further emphasizes the significance of liptinite in petroleum generation processes (Pickel et al., 2017).

2.6.1.3 Vitrinite

The vitrinite macerals exhibit a greyish colour and typically have a reflectance value that falls between those of the lighter inertinites and the darker liptinites. This range allows for the distinct recognition of the three maceral groups. Vitrinites originate from humic material, as defined by the ICCP (1998). In coal, vitrinites can be observed in various forms: as comparatively pure layers or lenses with thicknesses that range from micrometres to centimetres, as a continuous phase binding other coal components in the groundmass, or as amorphous fills in pores, fissures, and cells (Table 2.2). As isolated layers, lenticular bodies, or angular or rounded grains of vitrinite can be found in sedimentary rocks.

The term "huminite" was first introduced by Sza'decky-Kardoss (1949), to describe a structural component present in brown coals, which are now commonly known as lignites and it is a precursor of vitrinite. However, since 1970, the International Committee for

Coal and Organic Petrology (ICCP) has redefined the term "vitrinite" and now uses it to classify a specific maceral group within lignites (brown coals). In later years, an alternate term "vitrinite" was used to categorize coals of low, medium, and high rank, as outlined by the ICCP in 1998 (Sýkorová et al., 2005). Furthermore, it is highlighted that the term "huminite" is used for lignites or soft brown coals and it is specifically identified by its related macerals. In the case of sub-bituminous coal, which represents the highest quality within the low-rank coal category, vitrinite is used instead. According to ICCP (2001), the fluorescence colour and intensity of vitrinite macerals vary within the group and are influenced by the coal rank and the degree of bituminization. The fluorescence colours are reddish-orange to reddish-brown, with the most pronounced fluorescence observed in the attrital component of vitrinite (Ottenjann et al., 1982). Vitrinite is a soft maceral and does not exhibit relief compared to the liptinite and inertinite macerals that are present. When compared to the macerals of other groups, it is distinguished by having comparatively higher oxygen concentrations, as documented by ICCP (2001) and van Krevelen (1993).

Table 2.2: Vitrinite macerals (after ICCP, 1994; ICCP, 2001).

Maceral Subgroup	Maceral	Form
Telovitrinite (Preserved botanical cell structures may or may not be visible)	Telinite	Cell walls of recognized plant tissues that have undergone coalification and are largely intact
	Collotelinite	Generally employed as a rank indicator, more or less uniform strata with no discernible structure that may display mottling in low-rank coals.
Detrovitrinite (finely fragmented vitrinitized plant remains)	Vitrodetrinite	A secondary maceral composed of discrete, tiny, varying-shaped vitrinitic fragments
	Collodetrinite	Compact, mottled vitrinitic groundmass binding other coal constituents.

Galovitrinite	Gelinite	The secondary maceral is a pure colloidal gel that fills cavities and other fissures uniformly.
	Corpogelinite	Unstructured, uniform, and discrete humic cell infillings

Huminite is formed from the organic components present in the cellular makeup of roots, stems, barks, and leaves, as well as parenchymatous and woody tissues. These tissues consist of lignin, cellulose, and tannin. The preservation and visibility of cell structures within huminite vary depending on the decomposition process, coal rank, humification and gelification levels (Taylor et al., 1998; Sykes et al., 1994). Vitrinite is found in coal seams that originate from the anaerobic preservation of lignocellulosic material in swamp environments (Sýkorová et al., 2005). It is also present in shales interbedded with coal, where rapid deposition of mineral and organic matter has occurred. As a prominent component of most coals, vitrinite significantly impacts numerous industrial processes involving coal utilization. The properties of vitrinite play a crucial role in a wide range of applications, where coal is utilized. Studies by Diessel (1992) and Mackowsky (1977) have highlighted the importance of vitrinite in various industrial processes. In medium-rank coals, vitrinite demonstrates a propensity to fuse during the carbonization process. This fusion behaviour of vitrinite has notable implications for the course and outcomes of hydrogenation and combustion processes. The work by Bengtsson (1984) further underscores how vitrinite fusibility influences the products and progression of hydrogenation and combustion reactions.

2.6.1.4 Inertinite

The word "inertinite" suggests that the minerals of this group are relatively more inert compared to the macerals belonging to the liptinite and vitrinite groups (Table 2.3). In carbonization processes, inertinite macerals tend to act as diluents, meaning it has a lower reactivity and plays a role in reducing the overall reactivity of the coal. This characteristic of inertinite macerals was first described by Stach (1952). As stated by the International Committee for Coal and Organic Petrology (ICCP) in 2001, the maceral

group known as inertinite consists of macerals that exhibit higher reflectance in low- and medium-rank coals and in sedimentary rocks of similar rank when compared to the macerals belonging to the liptinite and vitrinite groups. The inertinite macerals are further separated from vitrinite by having no or even lesser fluorescence. The origin and post-depositional history of the inertinite macerals affect the shape and degree of preservation of the cell structures within them.

According to ICCP (2001), the most highly reflecting components of inertinite macerals exhibit colours ranging from grey, greyish white to yellowish white. It is important to note that the grey levels displayed by inertinite macerals are more indicative of the depositional conditions rather than the degree of coalification. Initially, the inertinite group included fusinite, semifusinite, sclerotinite, and micrinite. However, sclerotinite was subsequently replaced by micrinite and inertodetrinite, and additional macerals such as funginite and secretinite were included based on similarities in their technological and optical properties (ICCP, 2001). Additionally, in thermally immature sediments and low-rank coal, vitrinite exhibits a dark grey colour. However, in sedimentary rocks of equal rank or medium and high-rank coal, the colour ranges from light grey to white.

Table 2. 3: Organic macerals of the inertinite group (After ICCP, 2001; ICCP, 1994).

Maceral Subgroup	Maceral	Form
Telovitrinite Detrovitrinite	Fusinite	Hard, highly reflective, typically entire or broken cellular structure (Bogen structure), no fluorescence, and a cause that is contested between incomplete combustion in peat fires and/or advanced oxidation.
	Semifusinite inert	Formed from wood (more commonly found in Northern Hemisphere coals) or leaves (particularly in Gondwana coals); exhibits uneven anisotropy, a common component of southern African coals; intermediate

		structure and reflectance between vitrinite and tusinite in the same coal.
	Semifusinite (reactive)	At the same rank, reflectance values are similar to vitrinite, but the maceral displays structure and potentially partial anisotropy. Fungal remnants are highly reflective of single or multicelled fungal spores, sclerotia, hyphae, and mycelia, which are more prevalent in low-rank coals in Asia and Nigeria and nearly nonexistent in coals in the southern African region.
Galovitrinite	Funginite	Sclerotia, hyphae, mycelia, single or multi-celled fungal spores, and other fungi are highly reflective in coal from the Northern Hemisphere and low-rank coals from Asia and Nigeria but virtually completely missing in coal from southern Africa.
	Seecinite	Morphologies that are round to oblong, non-cellular, vesicled to non-vesicled, and typically have high reflectivity; may display a spectrum of reflectance; was formerly known as sclerotinite; Unknown origin, maybe oxidized resins; widely used worldwide.
	Micrinite	Round to rectangular, noncellular, vesicled to nonvesicled forms, usually with high reflectivity; may display variety of reflectances; used to be known as sclerotinite; Unknown origin, maybe oxidized resins; widely spread throughout the world.
	Macrinite	Amorphous, compact, structureless, large inertinite of varying shape; variable origin, including metabolic products of fungi/ bacteria, invertebrate faeces, or flocculated humic matrix compounds partially oxidized; occurs widely, but normally rarely.

	Inertodetrinite	Fusinite fragments are not included in this category of discrete inertinitic pieces, which range in size from 2 to 10 microns and have a variety of shapes. An organic precursor that has been oxidized or fusinized and subjected to mechanical crushing, desiccation, and attrition before or during decomposition yields secondary maceral.
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2.6.2 Minerals

Xuiyi (2011) has documented that over 150 minerals have been identified in coal, the number was later re-updated to over 200 by Finkelman et al. (2020), as shown in Table 2.4. There are two established groups in which minerals in coal occur, which are intrinsic organic matter and extrinsic mineral matter (Falcon and Synman, 1986). Furthermore, the intrinsic organic matter comes from the original plant tissue from the living plant (inclusive of the trace elements). According to Wagner et al. (2018), the minerals matter in coal occurs as sub-microscopic grains and organic metal complexes (i.e., siderite and pyrite), while the extrinsic mineral matter is formed after peatification by water which percolates through pores, fractures and cavities. The extrinsic minerals are observed to be occurring as nodes. The mineral matter has been further subdivided by Xuiyi (2011) into:

- i. Inorganic elements associated with macerals.
- ii. Crystalline mineral particles.
- iii. Non-crystalline mineral detritus.
- iv. Inorganic components contained in coal's surface and pore water.
- v. Dissolved salts.

According to Xiuyi (2011) and Ward (2002), inorganic matter in coal can be characterised as syngenetic, epigenetic and detrital. Furthermore, this can be indicative of the origin of the minerals and their formation stages.

The syngenetic minerals refer to the minerals, which formed concurrently with the accumulation of plant debris (Xiuyi, 2011). Furthermore, these can be classified into two groups (i.e., early and late syngenetic formation) as stated by Ward (2002). The early syngenetic minerals form in the early stages of peat formation, while the late syngenetic minerals form during gelification. Additionally, it is generally linked to the deeper buried peatification stage of coal formation (Xiuyi, 2011; Ward, 2002). Epigenetic minerals form after coalification and during the process whereby the coal has achieved its current rank or grade (Xiuyi, 2011). These minerals, also known as adventitious or excluded mineral matter, can be found within the fissures of coal. According to Ward (2002), clay, illite, silica, siderite, ankerite, marcasite, pyrite, chlorite and dawsonite are examples of minerals which formed as a result of epigenetic mineralization. Furthermore, detrital minerals are deposited into the peat by pyroclastic and epiclastic processes, wind and moving water.

Table 2.4: Minerals in coal (after Xiuyi, 2011).

Mineral groups	Minerals
Selenides	Penroseite, clausthalite, hakite
Sulphides	Sphalerite, galena, siegenite, melnikovite, cooperite, marcasite, pyrite, argentite, tetrahedrite, chalcocopyrite, bornite, pyrrhotite, chalcocopyrite, ullmannite, platarsite, ferroselite, chalcocite, arsenopyrite, realgar, millerite, cinnabar, orpiment, stibnite, bismuthinite, glaucodot, herzenbergite, covellite
Hydroxides	Chalcophanite, lepidocrocite, brucite, bauxite, goethite, diasporite, boehmite, gibbsite, portlandite, and limonite
Sulphates	Alunite, jarosite, polyhalite, celestite, epsomite, alunogen, mirabilite, kieserite, natrojarosite, linarite, barite, gypsum, szomolnokite, anhydrite, and melanterite.
Arsenide	Lollingite

Hydroxides	chalcophanite, gibbsite, lepidocrocite, brucite, bauxite, goethite, boehmite, portlandite, gibbsite, and diaspora
Silicates	hydromuscovite, staurolite, montmorillonite, biotite, chloritoid, allanite, zeolite, kyanite, topaz, tourmaline, feldspar, serpentine, garnet, pyroxene, illite, epidote, sphene, sericite, olivine, canasite, chlorite, dickite, glauconite, kaolinite, actinolite, leucite, talc, andalusite, ferrihalloysite, pyrophyllite, coffinite, zircon, muscovite, fenaksite, halloysite, mixed-layer clay minerals, barytolamprophyllite, and gadolinite.
Nitrates	Nitronatrite
Oxides	Rutile, brookite, cassiterite, anatase, hetaerolite, magnetite, spinel, and chromite, hematite, cristobalite, ilmenite, corundum, quartz
Intermetallic compound	Ferroplatinum
Carbonates	Azurite, dawsonite, strontianite, aragonite, magnesite, barytocalcite, siderite, ankerite (ferroan dolomite), and dolomite
Vanadate	Tyuyamunite, carnotite
Amorphous mineral	Opal, volcanic glass
Tungstate	Scheelite
Halides	Halite, sylvine, bischofite, fluorite
Phosphates	Xenotime, berlinite, svanbergite, florencite, gorceixite, autunite, torbernite, vivianite, and goyazite, phosphorite, monazite, apatite.
Vanadate	Carnotite, tyuyamunite
Native element	Gold, platinum, mercury, sulphur, selenium, graphite

2.7 Coal rank/quality

The rank of coal is indicative of the degree of coalification, coal metamorphism, or maturation brought about by changes in the process, including changes in temperature, time, or pressure due to peat burial or proximity to heat after peat deposition. Coal is classified into different ranks, such as lignite, sub-bituminous, bituminous, and anthracite, depending on its properties, such as heating value, sulphur content and carbon content (O'Keefe et al., 2013). According to Falcon (2013), the reduction of moisture and volatile matter was thought to be the primary cause of the general changes in coal rank, which led to an increase in carbon content, but this has been disapproved as a fundamental way of determining the rank of all coals. Furthermore, it has been noted that only the rank of vitrinite-rich coal can be determined using carbon content or volatile matter, as the relationship between loss of volatile matter and consequent increment in carbon is linear, but for both liptinite and inertinite-rich coals the relationship is not. Inertinite-rich coals are considered to have limited volatiles to release, while liptinite coals release volatiles very fast as the rank of the coal increases (Falcon, 2013). Therefore, the vitrinite reflectance as described by the standard SANS 7404-5 proved that with an increase in coal rank, the optical reflectance of vitrinite rises, thus being the preferred method for the determination of the rank of coal (Ward and Suárez-Ruiz, 2008; Figure 2.8).

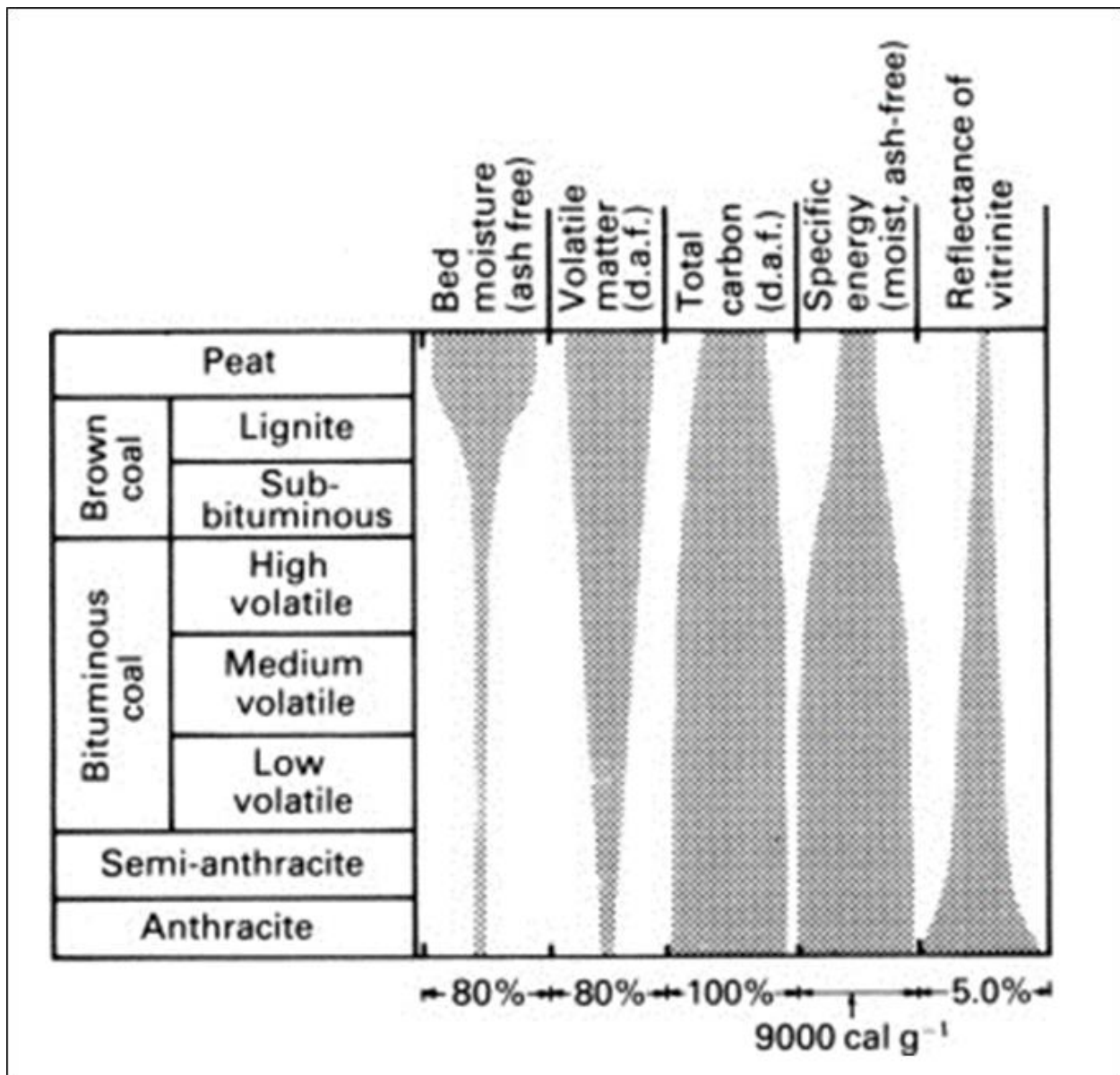


Figure 2.8: Changes in certain important coal qualities as rank advances (Ward and Suárez-Ruiz, 2008).

2.8 Coal uses

Coal serves primarily as a source of energy for the production of electric power. Within coal-fired power facilities, bituminous coal, sub-bituminous coal, or lignite is combusted. The resulting heat from this coal combustion is harnessed to transform water into high-pressure steam, which in turn propels a turbine, generating electricity (EIA, 2023).

Some specific varieties of bituminous coal can be employed in the production of steel. Coal utilized for steel production must possess high carbon content while maintaining low levels of moisture, ash, sulphur, and phosphorous. Coal meeting these criteria is referred to as metallurgical coal (Trippi et al., 2020; EIA, 2018, 2023). Additionally, coal finds diverse applications in various industries such as cement manufacturing, the creation of carbon fibres and foams, pharmaceuticals, the production of tars, the development of synthetic petroleum-based fuels, and as a source of heating for residential and commercial purposes.

2.8.1 Coking coal

Coal varieties suitable for coke production are referred to as coking coals or metallurgical coals. Coking coal is used in the production of coke for the steel industry and has various other applications, including use in foundries, blacksmithing, building, heating and brewing (Trippi et al., 2020). In 2016, South Africa ranked as the fifth-largest exporter of coking coal globally, following Australia, Indonesia, Russia, and Colombia, as reported by the IEA in 2018. Thomas (2013) stated that in order to be suitable for coke production, coals need to exhibit specific key attributes. These include low levels of mineral matter, phosphorus and sulphur. The coal should also fall into the bituminous rank category and possess a greater proportion of vitrinite.

Coke is a dense, and permeable solid characterised by high carbon content and minimal impurities and finds application in blast furnaces within the steel manufacturing sector (Trippi et al., 2020). In addition, coke is generated through the process of heating metallurgical coal to temperatures ranging from 1000 °C to 1100 °C within a reducing environment. A procedure that typically spans from 12 to 36 hours, whereby in the course of carbonization, the coal undergoes a transformation where it becomes liquefied and sheds most of its volatile components. Ultimately, solidifying into a dense, porous substance characterised by a high carbon content and mixed with water or nitrogen after cooling (Figure 2.9).

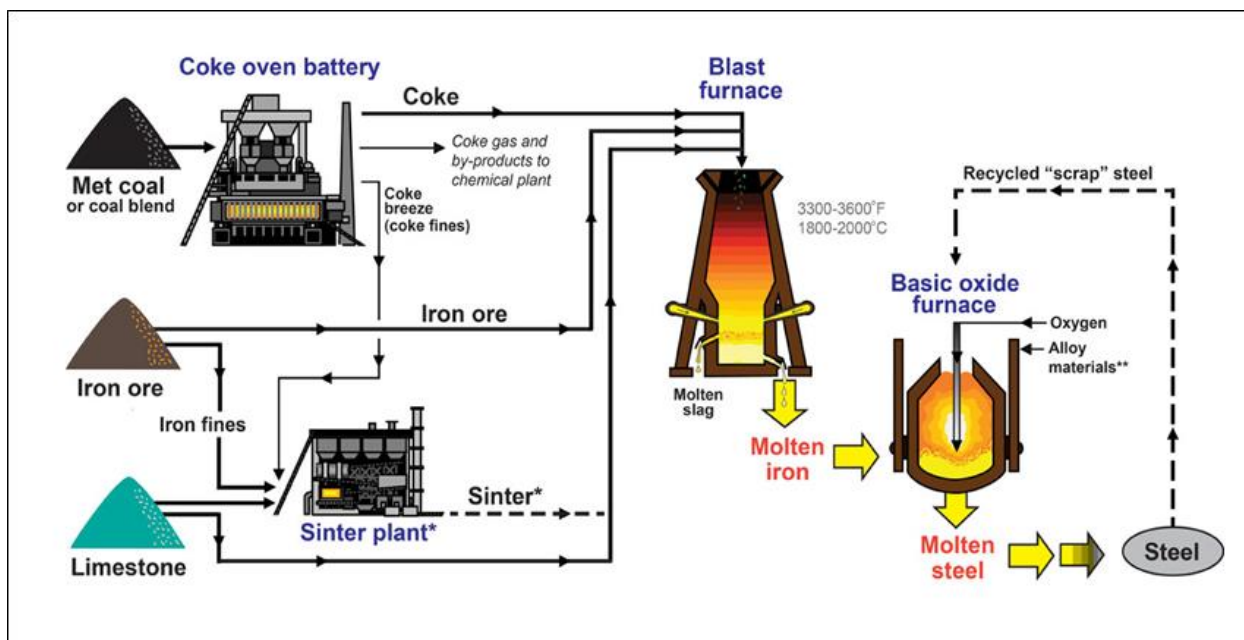


Figure 2.9: Process of coking (Kentucky Geological Survey, 2018).

2.9 Rare earth elements

Scandium, yttrium and the fifteen elements on the periodic table with atomic numbers ranging from 57 (La) to 71 (Lu) make up the group of seventeen rare earth elements (REEs). This grouping of elements is due to their shared chemical and physical characteristics (Dushyantha et al., 2020; Figure 2.10). As documented by Dushyantha et al. (2020) and Voncken (2016), REEs were first discovered in the 18th century. Promethium (Pm), the sole rare earth element among them, is synthetic (De Lima and Leal Filho, 2015). Scandium and yttrium are also regarded as REEs because of their geochemical behaviour, which is comparable to that of lanthanides (Sc only occurs in aquatic media) (Voncken, 2016; McLennan and Taylor, 2012). REEs possess special characteristics known as the lanthanide contraction, seen by a decrease in the ionic radii as the atomic number increases, unlike other elements whereby ionic radii increase as the atomic number increases (Dushyantha et al., 2020; Gupta and Krishnamurthy, 2005).

For the past two decades, China has dominated REEs mining and production; as a result, other nations like Japan and the USA are nearly entirely reliant on imports from China

(Du and Graedel, 2013). As of 2018, REEs production in the United States was primarily limited to a single mine in California, which produced just 9% of the world's output. Meanwhile, China held a dominant position in the global REEs market, contributing approximately 70% of the global production (Gambogi, 2019).

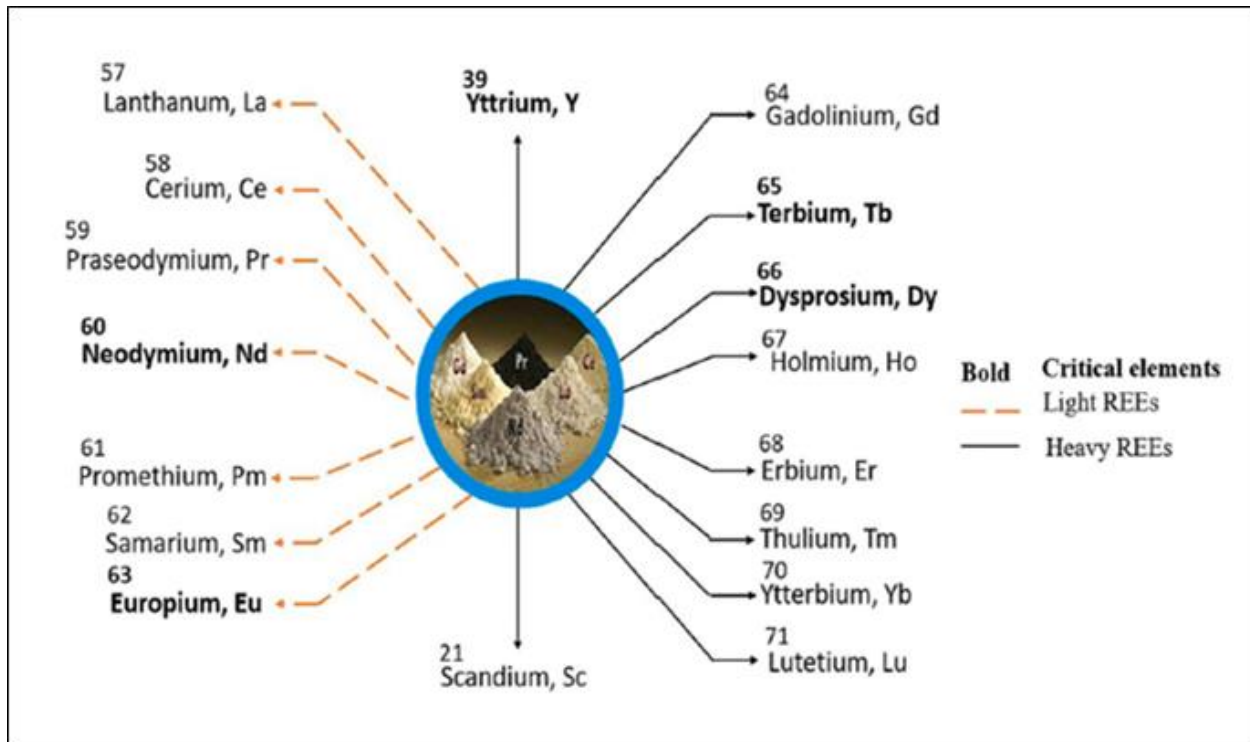


Figure 2.10: Photograph showing rare earth elements and their atomic number (Eterigho-Ikelegbe et al., 2021).

2.9.1 Types or groups of rare earth elements

There are three types of geochemical division of rare earth elements. Firstly, REEs are divided into the light REEs (LREEs) and heavy REEs (HREEs). The LREEs comprise lanthanum (La), cerium (Ce), praseodymium (Pr), neodymium (Nd), promethium (Pm), and samarium (Sm), while the HREEs comprise europium (Eu), gadolinium (Gd), terbium (Tb), dysprosium (Dy), erbium (Er), thulium (Tm), ytterbium, lutetium (Lu) and yttrium (Y). Despite having an atomic number of 39 and being relatively light, yttrium (Y) is categorized with the heavy rare earth elements (HREEs) because of its physical and chemical similarities to them (Van Gosen et al., 2017). A threefold classification was by

Seredin and Dai (2012), which grouped the REEs into light REEs (Eu, Gd, Tb, Dy and Y), heavy REEs (Ho, Er, Lu, Tm and Yb), and medium REEs (Sc, La, Ce, Pr, Nd, Pm and Sm). Additionally, the heavy REEs are less common than the light REEs. In terms of their economic viability, Serdin and Dai (2010) classified REEs into the critical (CREEs), uncritical (UCREEs) and excessive. The critical consists of Nd, Eu, Tb, Dy, Y and Er, the uncritical being the La, Pr, Sm and Gd, and the excessive REEs being Ce, Ho, Tm, Yb and Lu (Figure 2.11).

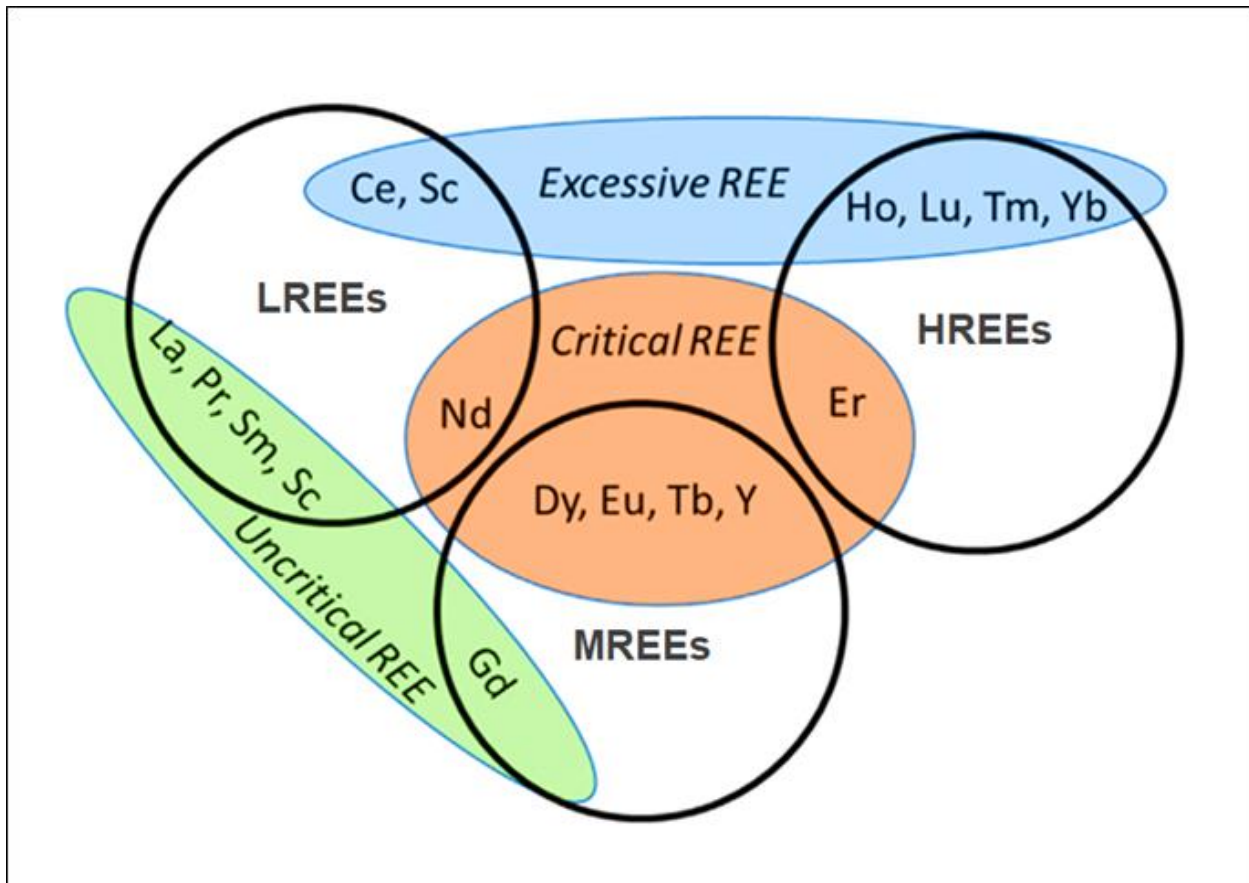


Figure 2.11: Classification of REEs into light (LREEs), medium (MREEs) and heavy (HREEs) (Franus et al., 2015).

2.9.2 Occurrence of rare earth elements

In contrast to what their name implies, REEs are typically more plentiful than precious metals (i.e., platinum, silver and gold), with average crustal abundances ranging from 150 ppm to 220 ppm; however, REEs rarely produce economically feasible ore deposits due

to their distinct geochemical characteristics (Van Gosen et al., 2014; Long et al., 2010). In the phosphate, silicate, carbonate, oxide, and halide forms, about 250 REE-bearing mineral forms have so far been identified and REEs have never been found occurring as pure metals (Dushyantha et al., 2020; Al-Ani et al., 2018; Van Gosen et al., 2017; Jordens et al., 2013; Gupta and Krishnamurthy, 2005). Furthermore, the factors affecting the supply of REEs are that the mineral deposits are scarce and that the elements are not found occurring in equal proportions, which makes the distributions unpredictable. Due to their considerable economic content and recovery, only a select number of minerals (i.e., bastnaesites and xenotime, monazite) have been developed for commercial production of REEs (Jordens et al., 2013).

2.9.2.1 Monazite

Similar to bastnäsite [(Ce,La,Nd,Th)PO₄], monazite is a phosphate mineral that contains around 70 percent rare earth oxide (REO), predominantly Ce, La, Pr, and Nd (varies between 83.55 and 94.55% of the total REO based on the deposit), making it a cerium-type mineral that is selective (Dutta et al., 2016; Jordens et al., 2013). China, Australia, the USA, South Africa, Brazil, Sri Lanka, and Thailand often have the highest concentrations of monazite (Kumari et al., 2015; Pandey, 2011). Beach sands have been noted as the most important ore deposits for monazite, and it is proposed that the concentration is a result of gravitational separation (Jordens et al., 2013; Zhang and Edward, 2012).

2.9.2.2 Bastnaesite

According to Jordens et al. (2013), the rare earth oxide, predominantly Ce, La, and Nd, makes up over 70% of the fluorocarbonate mineral bastnäsite [(Ce,La)CO₃(F,OH)]. Bastnaesite is considered one of the most abundant sources for REEs extraction, especially the light REEs (Dutta et al., 2016; Jordens et al., 2013). As documented by Dushyantha et al. (2020) and Gupta and Krishnamurthy (2005), bastnaesite deposits are primarily discovered in Mianning in the Sichuan Province of China and the Mountain Pass region of California in the United States.

2.9.2.3 Xenotime

The rare earth oxide content of xenotime, a yttrium phosphate mineral is about 67 percent, and it contains substantially less Ce, La, Pr, and Nd than bastnäsite or monazite (Gupta and Krishnamurthy, 2005). Xenotime has a formula $[(Y,HREE)PO_4]$, despite its scarcity, xenotime is significant because, combined with the Chinese ion-adsorbed rare earth containing clays, it is a significant source of HREEs (Jordens et., 2013). China, the USA, Australia, Mongolia, South Africa, Scandinavia, and Indonesia are just a few of the countries that have Xenotime placer deposits (Mudd and Jowitt, 2016; Lolon and Rahman, 2014; Gupta and Krishnamurthy, 2005).

2.9.2.4 Alternative minerals containing rare earth elements

Long et al. (2010) documented that tengerite, ancylite, florencite, britholite, kainosite, euxenite, allanite, samarskite, aeschynite, fergusonite, parisite and synchisite are REE-bearing minerals (Table 2.5). Furthermore, the forms of these minerals include oxides, carbonates, phosphates, silicates, hydroxides and halides.

Table 2.5: Potential or viable REE-bearing minerals (Long et al., 2012).

Mineral	Chemical formula	REO %	ThO ₂ %	UO ₂ %	Mineral	Chemical formula	REO %	ThO ₂ %	UO ₂ %
Oxides and hydroxides					Carbonates				
Aeschynite	[(Ce,Th,Ca...)(Ti,Nb,Ta) ₂ O ₆]	-	-	-	Ancylite	Sr(Ce,La)(CO ₃) ₂ (OH)(H ₂ O)	46 - 53	0-0.4	0.1
Brannerite	(U,Ca,Y,Ce)(Ti,Fe) ₂ O ₆	4	4	63	Bastnäsite	(Ce, La,Y)CO ₃ F	70-74	0-0.7	–
Cerianite	(Ce ⁴⁺ ,Th)O ₂	82	5	–	Parisite	Ca(Ce,La) ₂ (CO ₃) ₃ F ₂	59	0-0.5	0-0.3
Euxenite	(Y,Er,Ce,U,Pb,Ca)(Nb,Ta,Ti) ₂ (O,OH) ₆	–	–	–	Synchysite	Ca(Ce,Nd,Y,La)(CO ₃) ₂ F	51	–	–
Fergusonite	YNbO ₄	42-52	0-0.9	1-2.5	Tengerite	Y ₂ (CO ₃) ₃ .n(H ₂ O)	–	–	–
Loparite	(Ce,Na,Ca)(Ti,Nb)O ₃	32-34	0.8	–	Phosphates and fluorides				
Perovskite	(Ca,REE)TiO ₃	<37	0-2	≤0.05	Britholite	(Na,Ce,Ca) ₅ (OH)[(P,Si)O ₄] ₃	33-61	0.5-21	0.2-1.5
Pyrochlore	(Ca,Na,REE) ₂ Nb ₂ O ₆ (OH,F)	2.6	0.2	0-10	Brockite	(Ca,Th,Ce)(PO ₄).H ₂ O	7-24	24-45	3
Samarskite	(Y,Er,Fe,Mn,Ca,U,Th,Zr)(Nb,Ta) ₂ (O,OH) ₆	–	–	–	Cheralite	(Ca,Ce,Th)(P,Si)O ₄	27-43	28-32	4
Uraninite	(U,Th,Ce)O ₂	0.9-5	0.2-14	70-91	Churchite	YPO ₄ .H ₂ O	50-53	–	–
Phosphates and fluorides					Silicates				
Britholite	(Na,Ce,Ca) ₅ (OH)[(P,Si)O ₄] ₃	33-61	0.5-21	0.2-1.5	Allanite	Ca(Ce,La,Y,Ca)Al ₂ (Fe ²⁺ ,Fe ³⁺)(SiO ₄)(Si ₂ O ₇)O(OH)	3-51	0-5	0-3

Brockite	$(\text{Ca,Th,Ce})(\text{PO}_4)\cdot\text{H}_2\text{O}$	7-24	24-45	3	Chevkinite	$(\text{Ca,Ce,Th})_4(\text{Fe}^{2+},\text{Mg})_2(\text{Ti,Fe}^{3+})_3\text{Si}_4\text{O}_{22}$	40-45	0.7-0.8	–
Cheralite	$(\text{Ca,Ce,Th})(\text{P,Si})\text{O}_4$	27-43	28-32	4	Eudialyte	$(\text{Na,Ca,REE})_5(\text{Fe}^{2+}\text{Mn})(\text{Zr,Ti})[(\text{Si}_3\text{O}_9)_2](\text{OH,Cl})$	0.4 7	–	≤ 0.09
Churchite	$\text{YPO}_4\cdot\text{H}_2\text{O}$	50-53	–	–	Gadolinite	$\text{Y}_2\text{Fe}_2+\text{Be}_2\text{Si}_2\text{O}_{10}$	51-55	0 0.9	–
Crandallite	$\text{CaAl}_3(\text{PO}_4)_2(\text{OH})_5\cdot\text{H}_2\text{O}$		–	–	Gerenite	$(\text{Ca,Na})_2(\text{Y,REE})_3\text{Si}_6\text{O}_{18}\cdot 2\text{H}_2\text{O}$		–	
Florencite	$(\text{La,Ce})\text{Al}_3(\text{PO}_4)_2(\text{OH})_6$	18-32	1.4	–	limorite	$\text{Y}_2(\text{SiO}_4)(\text{CO}_3)$	69	–	–
Fluocerite	$(\text{La,Ce})\text{F}$	83	1.6	–	Kainosite	$\text{Ca}_2(\text{Ce,Y})_2(\text{SiO}_4)_3\text{CO}_3\cdot\text{H}_2\text{O}$	38	0.03	–
Gagarinite	$\text{NaCaY}(\text{F,Cl})_6$	55-57	–	–	Sphene	$(\text{Ca,REE})\text{TiSiO}_5$	0-4.5	–	0.06
Gorceixite	$(\text{Ba,REE})\text{Al}_3[(\text{PO}_4)_2(\text{OH})_5]\cdot\text{H}_2\text{O}$		–	–	Steenstrupine	$\text{Na}_{14}\text{Ce}_6\text{Mn}_2\text{Fe}_2(\text{Zr,Th})(\text{Si}_6\text{O}_{18})_2(\text{PO}_4)_7\cdot 3\text{H}_2\text{O}$	30-31	2	–
Goyazite	$\text{SrAl}_3(\text{PO}_4)_2(\text{OH})_5\cdot\text{H}_2\text{O}$		–	–	Thalenite	$\text{Y}_2[\text{Si}_2\text{O}_7]$	63-64	–	–
Monazite	$(\text{Ce,L,Th,Nd,Y})\text{PO}_4$	35-71	0-20	0-16	Thorite	$(\text{Th,U})\text{SiO}_4$	≤ 3	72-82	8-16
Rhabdophane	$(\text{Ce,L})\text{PO}_4\cdot\text{H}_2\text{O}$	58-69	0.7	0.4	Zircon	$(\text{Zr,REE})\text{SiO}_4$	0-10.5	0-2	0-5
Xenotime	YPO_4	52-57	0.4	0-5					

2.9.3 Uses of rare earth elements

The earliest known usage of REEs was lanthanum oxide in a commercialized gas mantle in Vienna during the 1890s (Szabadváry, 1988; Neary and Highley, 1984). Since then, the use of REEs in several industrial sectors—particularly in the fields of green energy and defence—has become essential (Dushyantha et al., 2020). The primary uses of the REEs (i.e., Pr, Nd, Gd, Dy, and Tb) are thought to be permanent magnets. The second-highest REEs consumption is in catalytic compounds, Ce and La are utilized as stabilizers (Dushyantha et al., 2020; Mancheri et al., 2019; Koerth-Baker, 2012). The detailed uses of REEs are summarized in Figure 2.12 and Table 2.6.

Table 2.6: Industrial applications and uses of REEs (Balaram, 2019; Naumov, 2008).

Chemical symbol	Name	Applications
Sc	Scandium	E-beam tubes, very strong Al-Sc alloys
Y	Yttrium	Glasses, microwave filters, phosphors, capacitors
La	Lanthanum	Vehicle catalysts, phosphors, pigments, glasses, ceramics, and glasses
Ce	Cerium	ceramics, phosphors, glasses, polishing powders, and catalysts
Pr	Praseodymium	Glasses, ceramics, and pigments
Nd	Neodymium	Catalysts, IR filters, constant magnets, and glass pigments
Pm	Promethium	suppliers of measurement instruments and tiny nuclear batteries
Sm	Samarium	nuclear industry, microwave filters, and permanent magnets
Eu	Europium	Phosphors
Tb	Terbium	Phosphors
Dy	Dysprosium	ceramics, nuclear industry, and phosphors
Ho	Holmium	lasers, the nuclear business, and ceramics
Er	Erbium	glass dyes, optical fibers, nuclear industries, and ceramics
Tm	Thulium	image visualization in medicine with electron beam tubes
Yb	Ytterbium	Chemistry and metallurgy

Lu	Lutetium	catalysts and single-crystal scintillators
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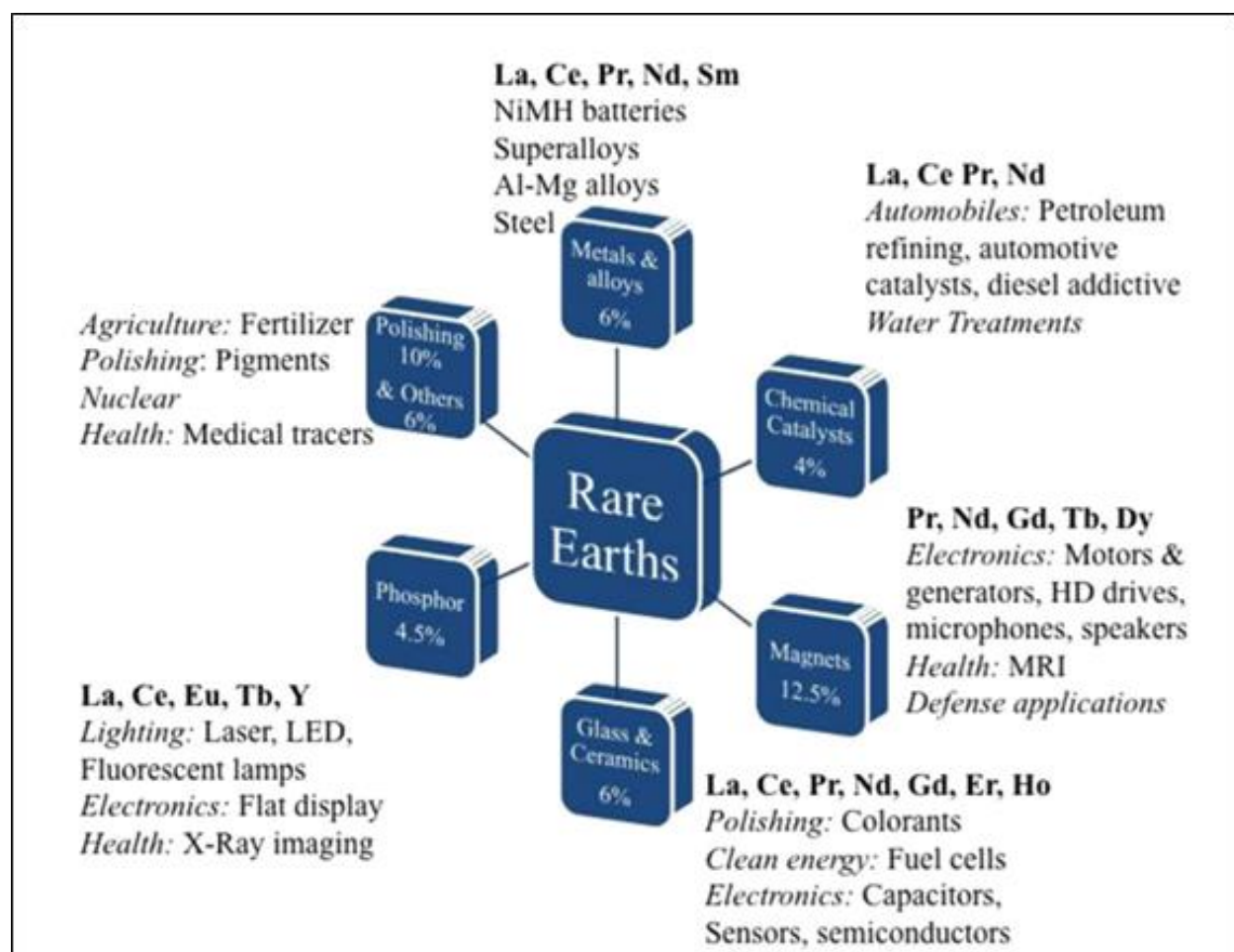


Figure 2.12: Uses and applications of REEs (After Dutta et al., 2016; Alonso et al., 2012; Kingsworth, 2010).

2.10 Rare earth elements in coal

The study of Goldschmidt and Peters (1933) was one of the earliest works conducted on REEs from coal, and that is approximately about 91 years ago (Dai et al., 2016). This has stimulated further interest in the investigation of coal as a resource for REEs all over the world by many researchers (Gambogi, 2019; Voncken, 2016; Long et al., 2012; Seredin and Dai, 2012; Seredin, 1991). According to Seredin and Dai (2012), although coal basins having significant concentrations of REEs were discovered, the conventional deposit of

REEs seemed to meet the demand until 2009, when there was an economic crisis regarding the supply of these rare metals.

Based on globally recoverable coal reserves and the average rare earth concentration, the amount of REEs associated with coal deposits was calculated to be more than 61 million metric tonnes, more than half of the traditional rare earth ore reserves and enough to satisfy the world's REEs demand for several centuries (Zhan et al., 2015; Rutledge, 2011). While the average estimated concentration of REEs of World Coals is 68.5 ppm, which is nearly 2.5 times less than the 168.4 ppm found in the upper continental crustal rocks (Seredin and Dai, 2012; Taylor and McLennan, 1985). According to Seredin and Dai (2012), some coals or coal ashes contain REEs concentrations that are on par with or greater than those present in common REEs ores, such as carbonatites, alkaline granites, and weathering crusts. The Fire Clay coal bed in the east of the United States (500-4000 ppm REEs), the Sydney Basin in Nova Scotia, Canada (72-483 ppm REEs) and the Far East coalfields in Russia (300-1000 ppm REEs) are just a few well-known coal beds with extraordinarily high REEs contents. The cut-off grade for REEs in coal, typically ranging from 115 to 130 parts per million (ppm), determines the suitability of the ore for recovering rare earth elements (Zhang et al., 2015).

2.11 Abundance of coal and rare earth elements

Saredin and Dai (2012) listed several potential processes that could lead to high or low REEs levels in coal, including acidic volcanic eruptions with ash leakage, hydrothermal activity, surface water enrichment and groundwater penetration. Rare earth elements in coal are found concentrated in minerals like zircon, xenotime, allanite, monazite and clay minerals like illite and kaolinite (Zhang et al., 2015). According to Zhang et al. (2015), fifty million metric tons of REEs, or around half of the REEs resource of traditional sources of rare earth materials are thought to exist in coal. Furthermore, it is evident that REEs are either included or linked with either macerals or the mineral matter in coal. In addition to coal as a potential alternate source of REEs, other sources include coal discard, coal acid mine drainage, and coal fly and bottom ash.

China has been recognised as the leading producer of coal for the past 30 years (Harrar et al., 2022). According to Zhang et al. (2017) and Xie et al. (2014), China has total coal resources of 5569.75 billion tons at 2000 m of vertical depth and 1017.65 billion in proven current resources tons and reduced 141.595 billion tons at the end of 2019 (Mao and Tong, 2023; BP, 2020). South Africa is home to the 6th largest exploitable coal deposits in the world, with 53 gigatons with reserves of about 33.8 billion tonnes (Prevost, 2004, 2005), 5% of global coal reserves and 97% of Africa's hard coal (DMR, 2009). According to Wood (2019), the annual production of coal in 2019 amounted to 254 megatons, ranking it seventh internationally. As reported by the Energy Council (WEC, 2016), South Africa is the sixth-largest coal producer in the world due to the energy generation being heavily dependent on coal. Moreover, 95% of the electricity in the country is produced by coal power plants.

CHAPTER 3

METHODOLOGIES

3.1 Fieldwork

The fieldwork for the research study consisted of core logging and sampling at the Uitkomst Colliery in KwaZulu-Natal.

3.1.1 Core logging

Core logging is the process of measuring and documenting lithology, mineralogy, texture, and geological structures using cylindrical rock samples, or cores. Over five days, drill cores from boreholes JCBH08, JCBH20, AD3BH2, and AD3BH3 were logged at the core yard of the Uitkomst Colliery. This involved observing and recording variations in colour, grain size, lithology, and sedimentary structures. Tools such as spraying buckets, log sheets, pencils, permanent markers, hand lenses, masking tape, cameras, grain size charts, and measuring tapes were used. Wetting the cores with a water-filled spraying bucket enhanced the visibility of lithological, textural, and colour changes. Thicknesses of stratigraphic units were measured using tapes, with readings taken at each change in lithology, colour, and texture. Photos of the core samples, especially notable features, were taken. All stratigraphic data, including thicknesses and detailed descriptions of lithology, textures (grain sizes and sorting), rock contacts, and sedimentary structures, were recorded on log sheets.

3.1.2 Sample collection

A total of seventeen coal samples were collected from the Vryheid Formation at the Uitkomst Colliery. Of these, ten samples were from the Gus seam, five from the Alfred seam, and two from the Fritz seam. Seven samples were obtained from boreholes, while the remaining ten were collected from the underground mining operation. Among the borehole samples, two were from borehole JCBH08 and three from borehole JCBH20, all of which were from the Alfred Seam. Boreholes AD3BH3 and AD3BH2 each provided one sample for the Fritz seam. Although the Gus Seam was encountered in these

boreholes, it had already been sampled by the mine, prompting further sampling in the underground mining area. In this area, a total of ten samples were collected from three different sections:

- Section 1: Four samples were collected, two were taken from the middle and lower Gus (CMB-S1 and CB2-S1), while the other two samples (CMB-D and CB2-D) were collected near a dolerite intrusion.
- Section 2: Three samples were obtained from the upper, middle and lower parts of the Gus Seam, labelled CB1-L2, CMB-L2 and CB2-L2, respectively.
- Section 3: Three samples were taken from the upper, middle and lower parts of the Gus Seam, labelled CB1-L1, CMB-L1 and CB2-L1, respectively.

These samples were meticulously packed into clearly labelled sample bags for laboratory analysis (i.e., geochemical analyses, stubs preparation, and petrographic analyses), as summarised in Table 3.1.

Table 3.1: Description of the collected samples from the Uitkomst colliery.

S/N	Seam	Lab. No	Borehole/underground	Sampling depth (m)	Lithological description	Formation
1	Gus	CB1-L1	Underground (Upper)	68,00	Coal	Vryheid
2		CMB-L1	Underground (Middle)	69,00	Coal	Vryheid
3		CB2-L1	Underground (Lower)	80,00	Coal	Vryheid
4		CMB-L2	Underground (Middle)	81,90	Coal	Vryheid
5		CB1-L2	Underground (Upper)	80,50	Coal	Vryheid
6		CB2-L2	Underground (Lower)	82,40	Coal	Vryheid
7		CMB-D	Underground (Middle)	104,33	Coal	Vryheid
8		CB2-D	Underground (Lower)	105,50	Coal	Vryheid
9		CB2-S1	Underground (Lower)	116,00	Coal	Vryheid
10		CMB-S1	Underground (Middle)	117,48	Coal	Vryheid
11	Alfred	JCBH08A	Borehole (JCBH08)	106,70	Coal	Vryheid
12		JCBH08B	Borehole (JCBH08)	107,30	Coal	Vryheid

13		JCBH20	Borehole (JCBH020)	170,79	Coal	Vryheid
14		JCBH20A	Borehole (JCBH020)	171,16	Coal	Vryheid
15		JCBH20B	Borehole (JCBH020)	171,53	Coal	Vryheid
16	Fritz	AD3BH3A	Borehole (AD3BH3A)	34,72	Coal	Vryheid
17		AD3BH2	Borehole (AD3BH2)	27,30	Coal	Vryheid

3.1.3 Sample preparation

The samples were first sun-dried for two days to eliminate excess moisture. Thereafter, the samples were crushed to a particle size of approximately 4 mm using a roll, jaw, and cone crusher at the Bureau Veritas Coal Testing laboratory in Johannesburg. The 4 mm sample was split with a rotary splitter and half of it was stored as reference samples. Thereafter, the remaining half of the 4 mm sample was milled to 1 mm and 212 μm with a Retsch ZM200. The first split samples (1 mm particle size), weighing 2 kg each, are for petrographic and SEM analyses. After milling to 1 mm, these samples were sieved to eliminate particles smaller than 38 μm for better particle distribution appropriate for petrographic analysis. Polished blocks for petrography were produced at the University of Johannesburg (UJ) Department of Geology sample preparation laboratory, in accordance with SABS ISO 7404 Part 2. The polished blocks were made by mixing a representative split of 1 mm coal particles with a blend of epoxy resin and hardener. The mixture was then left to solidify overnight in a vacuum. After the blocks had been set, the samples were polished with a Struers TegraForce-1 polisher, using a 0.05 m OPS lubricant, in accordance with SABS ISO 7404 Part 2 standards to attain a scratch-free and relief-free surface. The polished mount blocks were utilized for both petrographic and scanning electron microscopy (SEM) studies.

To increase the conductivity of the samples for SEM, the samples were carbon coated using an Emitech K950X carbon coater at the Council for Geoscience SEM laboratory in Pretoria. Graphite rods were first sharpened using a drill, then sanded to ensure a smooth surface and proper fit into the electrodes of the Emitech K950X carbon coater. The rods were inserted into the electrodes, and the coating chamber was sealed. A vacuum pump

was used to evacuate air from the chamber and monitored until the turbine speed reached 100%, which took approximately five minutes. Before coating, the polished blocks were cleaned with ethanol and blown with air to remove any polishing chemicals or residual oil. Thereafter, the sample surface was coated using the Emitech K950X carbon coater, which electrically heated a narrow carbon rod in a high vacuum chamber. A coating thickness of 25 nm was indicated by a royal blue interference colour on the plate. Additionally, a polished brass plate was coated to serve as an indicator for the brass blue colour. After coating, the vacuum was gradually released, and the samples were carefully removed and stored in a desiccator to prevent contamination and oxidation until SEM analysis. This method ensured that the coal stubs were adequately conductive for high-quality SEM imaging and analysis (Figure 3.3). The carbon coating serves two purposes: it enhances conductivity and prevents surface charging during the SEM analysis. The second split was milled to 212 μm and each of the samples weighed 2 kg. These milled samples were divided with a splitter into four parts (500 g each) for X-ray diffraction (XRD), proximate, ultimate analysis, and inductively coupled plasma mass spectrometry (ICP-MS) analyses.

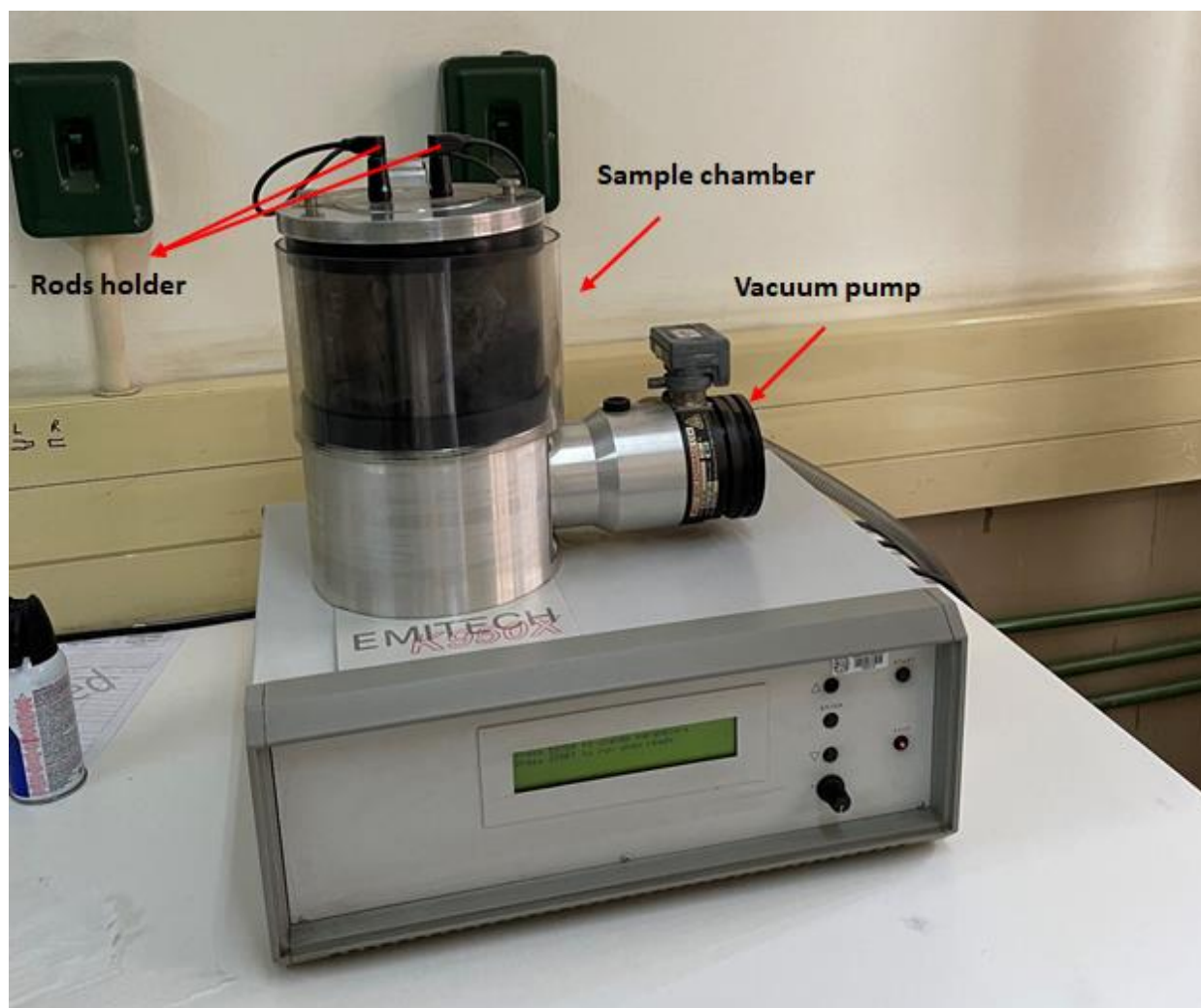


Figure 3.1: Photograph showing a carbon coater machine.

3.2 Coal petrographic analysis

The petrographic analysis was performed using a Zeiss Axio Imager reflected light petrographic microscope equipped with a Hilgers Diskus-Fossil system used for Vitrinite reflectance measurement (ISO 7404) at the University of Johannesburg. A comprehensive macerals analysis (following ISO 7404-5 standards) was performed at a magnification of $\times 500$ with oil immersion. The maceral groups, including vitrinite, inertinite, liptinite, and mineral matter, were distinguished based on their characteristics such as morphology, relative reflectance, shape, colour, polishing hardness and size. The Fossil software was employed for precise measurements and analysis. Sample stage

dimensions were set at 600 by 600 microns, with controlled movements at increments of X (32) and Y (32) to ensure thorough coverage. Each sample was labelled to maintain accurate documentation throughout the process. The investigation commenced with a systematic grid arrangement of 3 by 5, delineating macerals and minerals. Grain counting occurred under both white light and fluorescent lighting conditions to enhance visibility, especially for liptinite examination.



Figure 3.2: Photograph showing a zeiss Axio Imager M2 polarised reflected light microscope equipped with Hilgers diskus Fossil software.

To obtain the proportion of different macerals, a point count technique was employed. A total of 500 points were counted on the coal samples, mineral matter, and each maceral component. This point-counting method ensures a precise representation of the maceral composition of the coal samples. Microphotographs were also taken to show the visual characteristics of the macerals. Vitrinite reflectance ($R_{vmax\%}$, $R_o\%$) measurement, an important parameter for determining coal rank, was performed. The proportion of monochromatic greenish light with a wavelength of 546 nm that is reflected off well-polished vitrinite particles must be determined.

Reflectance analysis was also conducted; prior to analysis, the removal of dust or residue was undertaken. Then, the reflectance measurement system of the instrument was calibrated using the Yttrium-Aluminium Garnet (YAG) standard from Klein and Bekker, certified at 0.90 with a black hole precision of 0.01, and cross-verified using an internal standard. Calibration checks were performed after every third sample to ensure consistency and prevent any deviation. To better understand the distribution of reflectance values, histograms were drawn and the standard deviation was calculated. Apart from a few samples where adequate particles were not readily available, each sample received a total of 100 counts or measurements. To ensure representative measurements, semi-automatic readings were conducted on various vitrinite particles dispersed equally over the polished surface. The results of the petrographic analysis, including maceral composition and vitrinite reflectance, were reported on a percent (%) volume basis. To provide valuable information about the coal's rank and composition. Additionally, to establish the position of the coal sample, the results of the vitrinite reflectance analysis will be charted using the UN-ECE coal classification scheme.

3.3 Ultimate analysis

The ultimate analysis was performed in a controlled environment at the Bureau Veritas Testing and Inspections South Africa (Pty) Ltd, to obtain the elemental composition of a coal sample in addition to ash and moisture content. The major elements identified were carbon, hydrogen, sulphur, nitrogen and oxygen.

3.4.1 Carbon and hydrogen

The high-temperature combustion method of ISO 609:1996 standard was used in determining the hydrogen and carbon, which utilizes the combustion of a coal sample to gas, in a closed system (Francis and Peters, 1980). A coal sample weighing 0.5 g was heated with pure oxygen steam in a rapid current to a constant temperature of 1350 °C, to ensure complete combustion, the products were burned over copper oxide for the complete conversion of all carbon and hydrogen to CO₂ and H₂O. Chlorine was emitted in substantial amounts, as well as sulphur oxides, were typically eliminated from the combustion gases by passing them over lead chromate and silver, while nitrogen oxides were removed using manganese dioxide.

Solid anhydrous magnesium perchlorate was used to absorb the water, while soda-lime, contained in pre-weighed absorption vessels positioned downstream of the combustion tube, absorbed carbon dioxide. Followed by the moisture content determination, which aids in correcting the content of hydrogen incorporated as moisture. The tube was subjected to a 3-hour heating process within a cylindrical electric furnace, during which it should not undergo any discolouration or experience a weight change. This heating was conducted in an oxygen atmosphere at a temperature of 1350 °C. The apparatus is equipped with two flowmeters: one for measuring oxygen flow rates up to 300 ml/min and another for measuring air flow rates up to 250 ml/min. Then the carbon and hydrogen were calculated using the formulae (Francis and Peters, 1980):

$$C = \frac{0.273 (\text{increase in mass of soda lime tube})}{\text{mass of sample}} \times 100 \dots\dots\dots (1)$$

$$H = \frac{0.112 (\text{corrected mass of moisture retained by Mg(ClO}_4)_2)}{\text{mass of sample}} \times 100 \dots\dots\dots (2)$$

3.4.2 Sulphur

The Eschka technique based on the ISO 334:1992 standard was used to determine the sulphur content (Zhu, 2014; Francis and Peters, 1980). Using a porcelain crucible, 1 g of

coal was mixed with magnesium oxide (MGO) and anhydrous sodium carbonate (Na_2CO_3), which is a 2 by 1 mixture. The heat was gradually introduced until reaching a temperature of 800 °C, stirring in intervals until the whole sample was oxidated. The sulphur-bearing compound resulting from the combustion reacted with MGO and Na_2CO_3 and formed magnesium sulphate and sodium sulphate.

After cooling, the contents were transferred to a beaker, ensuring that the crucible was rinsed with distilled water. Before heating to a boil, 10 ml of a saturated bromine water solution was added. Once cooled, approximately 14 ml of concentrated HCl was added to dissolve any soluble substances introduced into the solution and boiled until all the bromine dissipated. Followed by filtering the mixture and washing the residue. The concentrated ammonia was used as a neutralizing agent and then 4 ml of concentrated HCl was added. Raised the temperature to a boil and gradually added a slight excess of 10% barium chloride solution. Boiled the mixture until the solid particles form a granular precipitate. The solution was allowed to cool before proceeding to filter it. It was then left to stand for 24 hours. Afterwards, it was filtered again and washed thoroughly until there were no more chloride residues. Incinerated the filter paper and the precipitate in a crucible that has been weighed and coated with tar. After cooling, the crucible and the contents were weighed again. Then, the sulphur content was calculated using the formula (Francis and Peters, 1980):

$$\% \text{ sulphur} = \text{wt of BaSO}_4 \times 100 \dots\dots\dots (3)$$

3.4 Proximate analysis

The proximate analysis was conducted using a Perkin-Elmer thermo-gravimetric analyser (TGA) housed at the Bureau Veritas Coal Testing Laboratory in Johannesburg. This analysis was carried out in accordance with the ASTM D-5142 standard method. The TGA proximate method measures the volatile matter, moisture, ash, and fixed carbon content in coal. Each sample, approximately 11.2 grams, is heated from 30 °C to over 900 °C. In the initial stage (30 °C-110 °C), the sample is dried in a nitrogen atmosphere, and moisture content is determined by the mass loss. As the temperature increases from

110°C to 700°C, the weight loss of the coal indicates its volatile content. In the last phase (700 °C - 900 °C). The transition from a nitrogen to an oxygen atmosphere enables the combustion of coal and the measurement of fixed carbon content. The ash content is calculated by introducing oxygen into the TGA furnace and burning the coal sample to a constant weight. The leftover residue, measured in weight, is referred to as ash. The data was analysed using the 2007 version of Pyris Software, generating a curve shown in Figure 3.5. Results are presented in weight percent (wt.%). Moisture content was determined by the weight loss from 30 °C to 110 °C, volatile matter from 110 °C to 700 °C, and fixed carbon from 700 °C to 900 °C. The ash was recalculated using the formula below:

$$\text{Ash} = 100 - (\text{volatile} + \text{moisture} + \text{fixed carbon}) \dots\dots\dots (4)$$

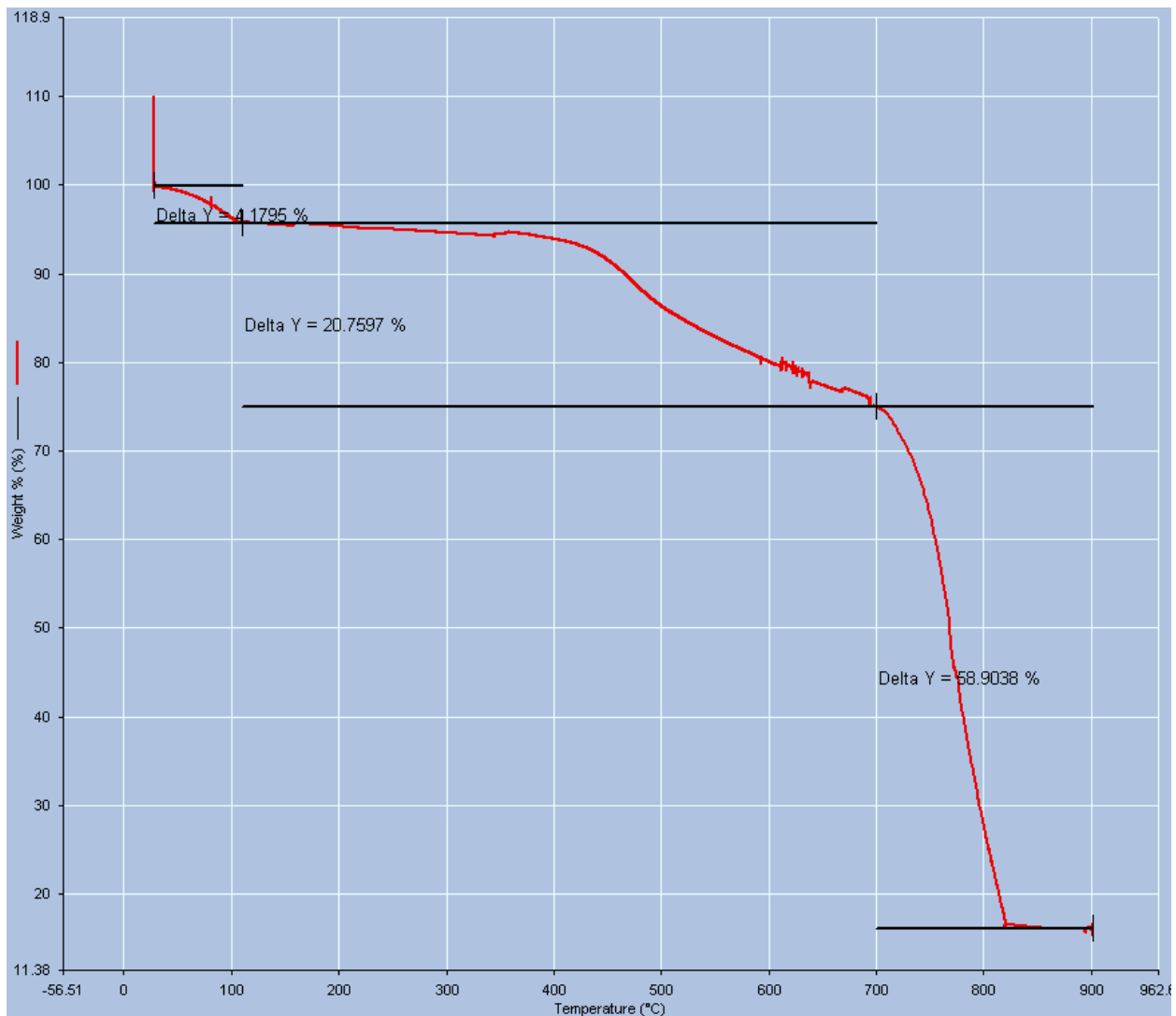


Figure 3.3: Proximate analysis curve showing weight loss in weight percentage (wt. %) against temperature (°C).

3.5.1 Inherent moisture

The inherent moisture was obtained by heating the coal at a 10 L/min flow rate in a nitrogen environment at a temperature of 107–110 °C for an hour and then the crucible was weighed using the loss in weight. The moisture content was calculated using the formula:

$$\% \text{ of moisture in coal} = \frac{W_{\text{moisture}}}{W_{\text{coal}}} \times 100 \dots \dots \dots (5)$$

3.5.2 Volatile moisture

In a nitrogen environment, the volatile matter was measured at a temperature between 107 °C and 950 °C, while being heated at a rate of 43 °C per minute and maintained at this temperature for seven minutes in the absence of air to avoid reduction in weight due to oxidation.

$$\% \text{ of volatile matter in coal} = \frac{W_{VM}}{W_{coal}} \times 100 \dots\dots\dots (6)$$

3.5.3 Ash content

This test involves heating the remaining sample in the crucible (i.e., uncovered container) in an environment of oxygen, first reaching 500 °C in half an hour, then progressing from 500 °C to 815 °C in a further 1 to 1.5 hours. It is then kept at 815 °C until no more weight loss is observed and the leftover residue provides the total ash content of the sample.

$$\% \text{ of ash content} = \frac{W_{ash}}{W_{coal}} \times 100 \dots\dots\dots (7)$$

3.5.4 Fixed carbon

The fixed carbon content was calculated as the remaining percentage after deducting the sum of ash, volatile matter, and moisture from 100% using the formula proposed by Zhu (2014) shown below:

$$\% \text{ of Fixed carbon in coal} = 100 - (\% \text{Moisture} - \% \text{Volatile matter} - \% \text{Ash}) \dots\dots\dots (8)$$

3.5 X-ray diffraction (XRD) analysis

The X-ray diffraction (XRD) analysis was conducted at XRD Analytical and Consulting in Pretoria, South Africa. A Malvern Panalytical Aeris diffractometer with PIXcel detector and fixed slits with Fe-filtered Co-K α radiation was used. This analysis was performed in accordance with the ASTM D-3682-13 method. The purpose of this analysis is to identify the presence of minerals known to host rare earth elements (REEs). The X-ray

diffractometer was set to operate at 40 kV and 40 mA for a duration of 2 hours. It employed a monochromatic anti-scatter slit, scanning over a 2θ range from 0° to 80° with a step size of 0.04. The coal samples were reduced to a size of 250 μm and lightly pressed into a metal ring. The ring containing the sample was then pressed on a flat surface, known as the sample preparation table. To ensure a uniform sample surface, any excess powder was carefully removed using a blade and brush. The prepared pellet discs were inserted into a sample holder inside the XRD machine. The samples were scanned preparing for XRD analysis using a backloading preparation method. When X-rays are directed at the powdered sample, the X-rays interact with each mineral phase present, producing a distinct diffraction pattern for each mineral due to its unique diffraction properties. The phases were identified using X'Pert Highscore Plus software, while the relative proportions of each phase (wt. %) were determined using the Rietveld method.

3.6 Scanning electron microscopy (SEM) with energy dispersive spectrometry

Scanning electron microscope using backscattered electron (SEM-BSE) and energy dispersive analysis (SEM-EDS) were conducted at the Council for Geoscience SEM laboratory. The prepared carbon-coated coal samples (stubs) were placed into the chamber, which takes up to 9 samples at a time (Figure 3.3). The SEM and computer were configured accordingly, SEM employs a focused electron beam to scan the sample in a rectangular pattern. As the result of the interaction of the electron beam and sample, it resulted in energy loss, which was consequently converted into the low emission of secondary electrons, x-ray emissions, or backscattered electrons (BSE). These emissions provided data on the sample's surface properties, such as topography, and composition. The SEM-BSE provided atomic number contrast, which aided in identifying the particles that are likely to contain rare earth elements (REEs). Multiple grey-scale images were taken to capture a comprehensive view of the particles of interest.

Selected images of the desired particles were subjected to EDS analysis. EDS allows for quantitative and qualitative spot analyses, providing information about the elemental composition of the particles. Additionally, element mapping was performed using the SEM-EDS to visualize the distribution of specific elements within the particles. A search

of the bright mineral phases was conducted to quantify the REE-bearing minerals (Table 3.4), and then backscattering electron (BSE) images were obtained from the bright particle search, this revealed vital information regarding the REE-bearing minerals in terms of their associations and distribution in coal.



Figure 3.4: Scanning Electron Microscopy fitted with Energy Dispersive X-ray Spectroscopy.

3.7 Inductively coupled plasma techniques (ICP-MS)

Microwave digestion followed by ICP-MS analysis was employed to effectively determine the occurrence of rare earth elements (REEs) in coal samples from the Utrecht Coalfield. A 0.1 g sample was placed in a Teflon vessel and digested with a mixture of 10 ml HNO₃ and 50 ml HF in a Mars 6 microwave oven for 30 minutes at 180°C. After digestion, the solution was filtered and transferred to a 50 ml volumetric flask, then filled with MilliQ water. This digestion method was validated using blank samples and a certified reference material (SARM 19). The coal samples for ICP-MS analysis were digested to convert them to a solution suitable for plasma aspiration as described in Section 3.8. The solution was subsequently analysed using the Perkin Elmer NexION 300 ICP-MS at the University of Johannesburg Spectrum Facility. Once in the plasma, the samples underwent processes such as desolvation, vaporization, atomization, and ionization. During these processes, atoms and ions absorbed energy from the plasma, which resulted in their electrons transitioning to higher energy levels (Figure 3.4). When the electrons return to their ground state, the excited atoms emit light at wavelengths characteristic of each element. The intensities of these emissions were then measured and compared to those of reference materials with known concentrations to determine the elemental concentration in each sample.

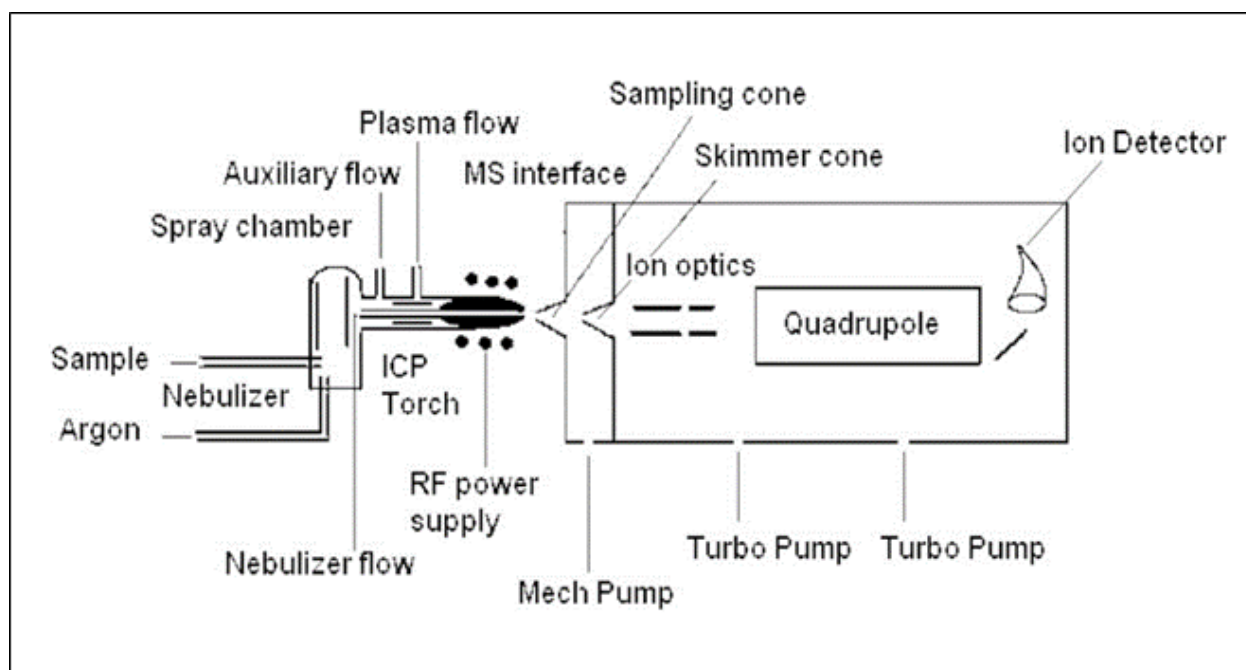


Figure 3.5: Schematic diagram describing the set-up of an ICP-MS instrument (Tyler and Jobin, 2003).

CHAPTER 4

RESULTS

4.1 Stratigraphy

The stratigraphy of the Vryheid Formation at the Uitkomst Colliery is shown in Figures 4.1-4.4. Four exploratory boreholes (AD3BH2, AD3BH3, JCBH08 and JCBH20) were drilled by MC Mining (Uitkomst Colliery) to different depths in order to target the coal seams in the area. The borehole AD3BH2 was drilled to a depth of 43.07 m, whereas the end of the hole for the borehole AD3BH3 was at 60.50 m. The two boreholes, JCBH08 and JCBH20, were drilled to depths of 124.94 m and 186.20 m, respectively. These boreholes intersected the rocks of the Vryheid Formation in the Eccra Group, whereas boreholes AD3BH2 and AD3BH3 showed an occurrence of dolerite intrusions at depths of 4.98 m and 3.09 m (Figures 4.1 and 4.2).

Generally, the stratigraphy of the Vryheid Formation in the Uitkomst Colliery mainly consists of sandstone and siltstone, with lesser amounts of mudstone, shale and coal seams (Figure 4.1-4.5). The seams intersected by the boreholes are Fritz, Alfred, Gus, and Elands seams. The Elands seam occurred at a depth of 16.45 m, and it was only intersected by borehole AD3BH2, while the Fritz seam was absent in boreholes AD3BH2 and JCBH08. The Fritz, Alfred and Gus seams were intersected at different depths. The Fritz seam was intersected at varying depths from 16.45 m to 161.05 m, whereas the Alfred seam occurred from 27.30 m to 170.79 m and the Gus seam occurred at depths from 40.25 m to 117.20 m in the boreholes. The average thicknesses of the seams are 0.21 m for Fritz seam, 1.12 m for Alfred seam and 1.26 m for Gus seam, whereas the Elands seam is 0.30 m thick (Figures 4.1-4.4) and the most economic seam of the operation in the Uitkomst Colliery is the Gus seam.

BHID: AD3BH2

Location: -27,58075995° S

30,09221272° E

Elevation: 1464.00

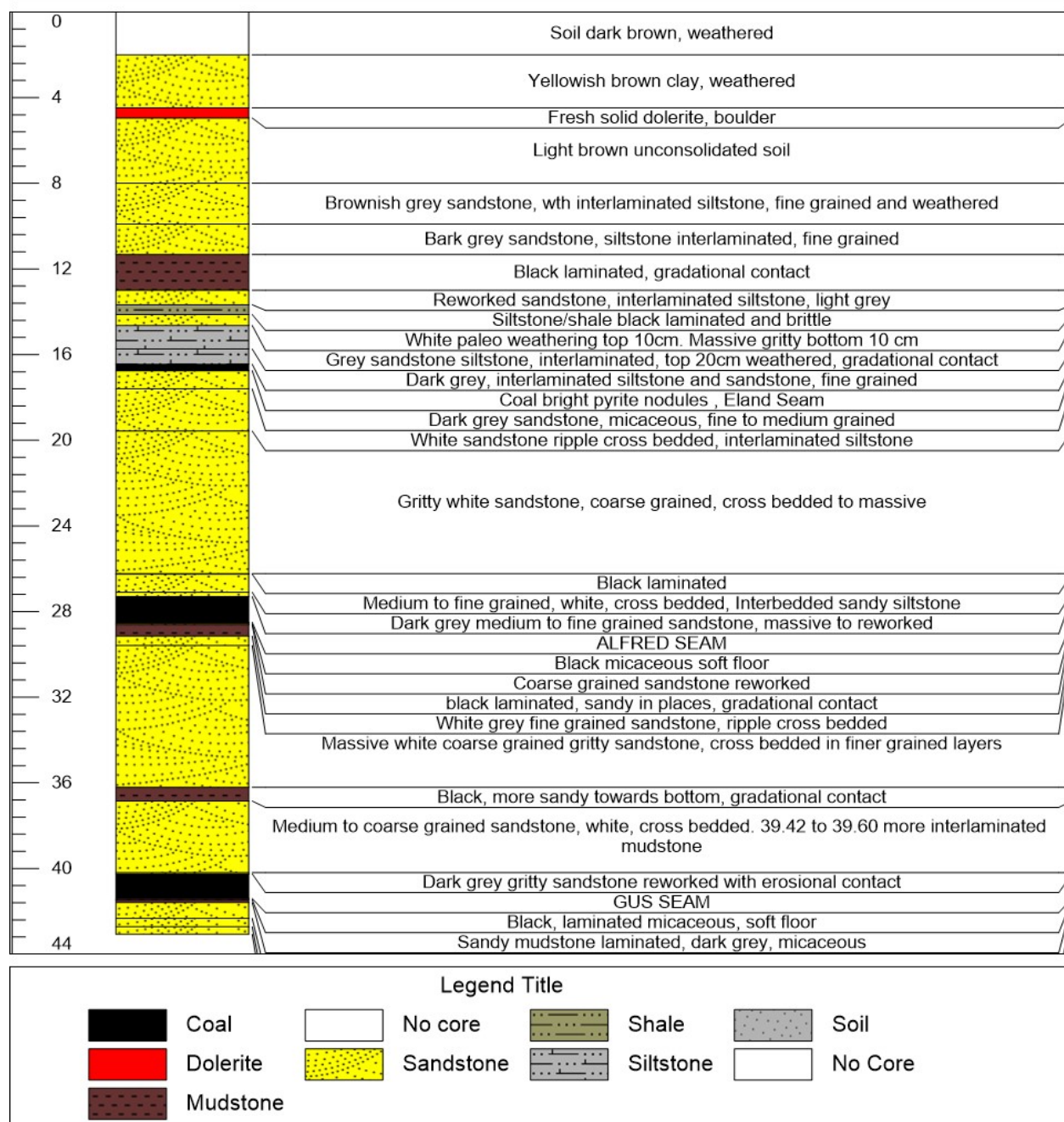


Figure 4.1: Stratigraphy of part of the Utrecht Coalfield in borehole AD3BH2.

BHID: AD3BH3

Location: -27,56105563° S
30,09547314° E
Elevation: 1464.00

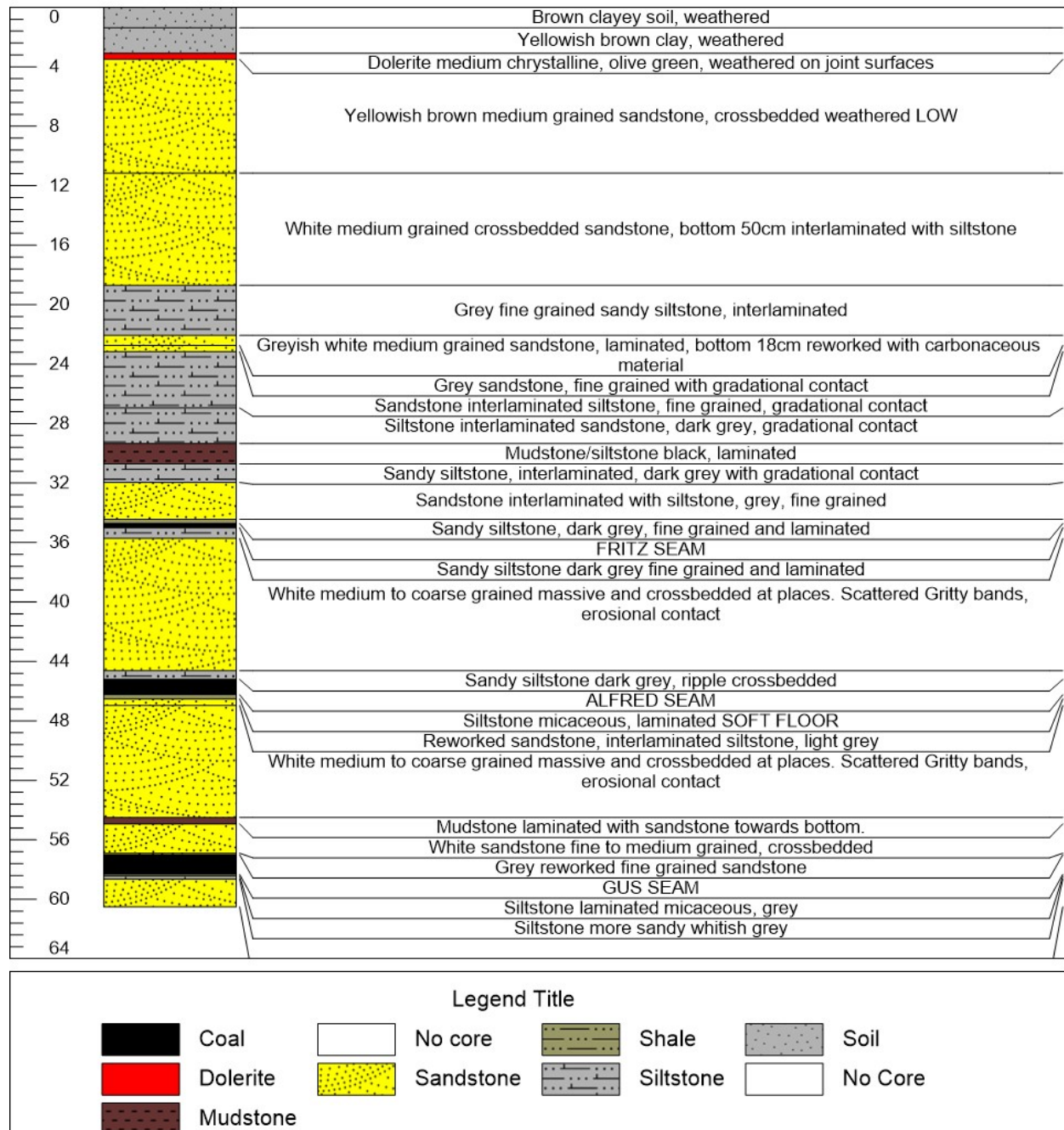


Figure 4.2: Stratigraphy of part of the Utrecht Coalfield in borehole AD3BH3.

BHID: JCBH08

Location: -27,57579571° S
30,10312938° E
Elevation: 1464.00

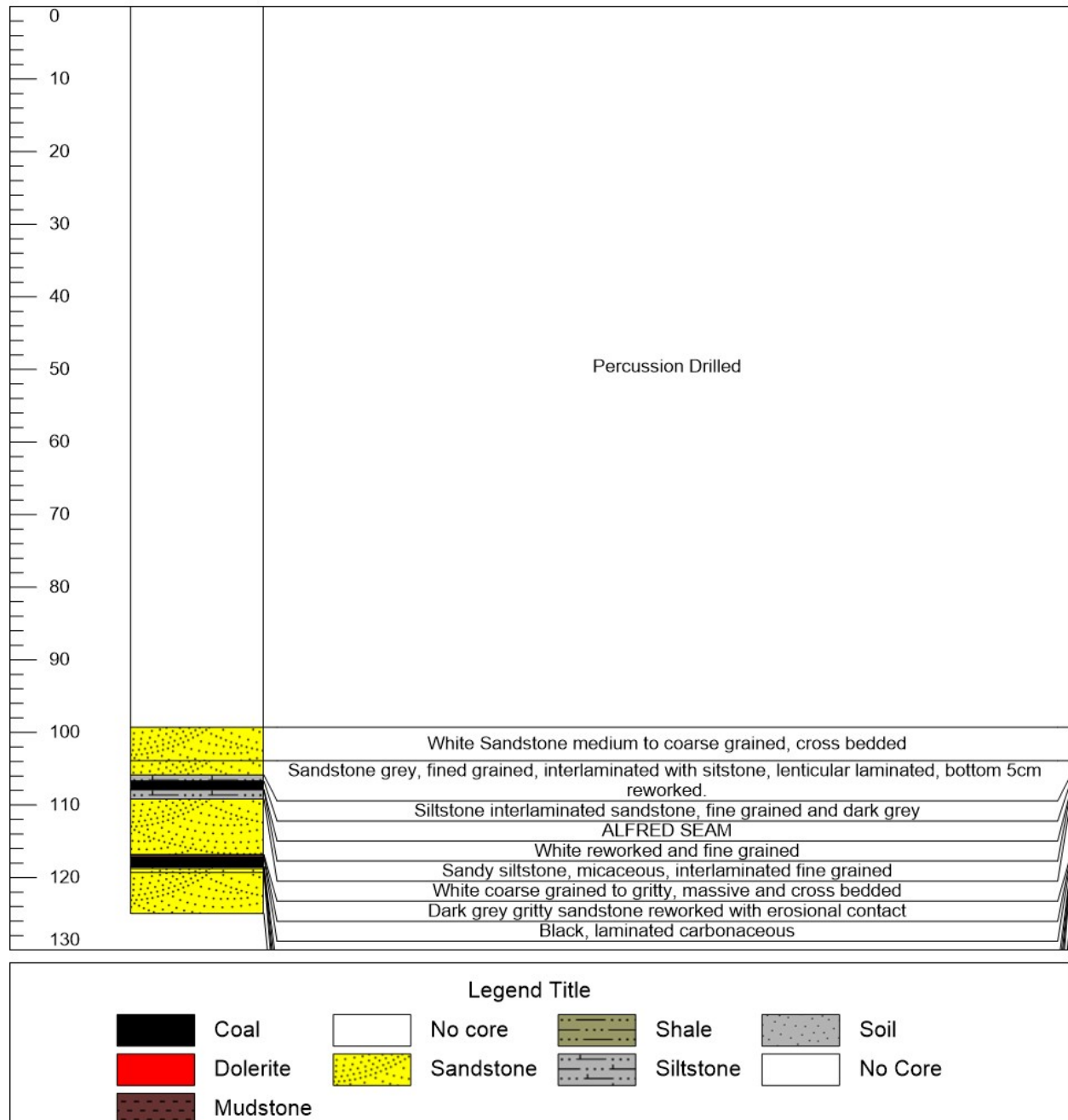


Figure 4.3: Stratigraphy of part of the Utrecht Coalfield in borehole JCBH08.

BHID: JCBH20

Location: -27,56371196° S
30,10435153° E
Elevation: 1464.00

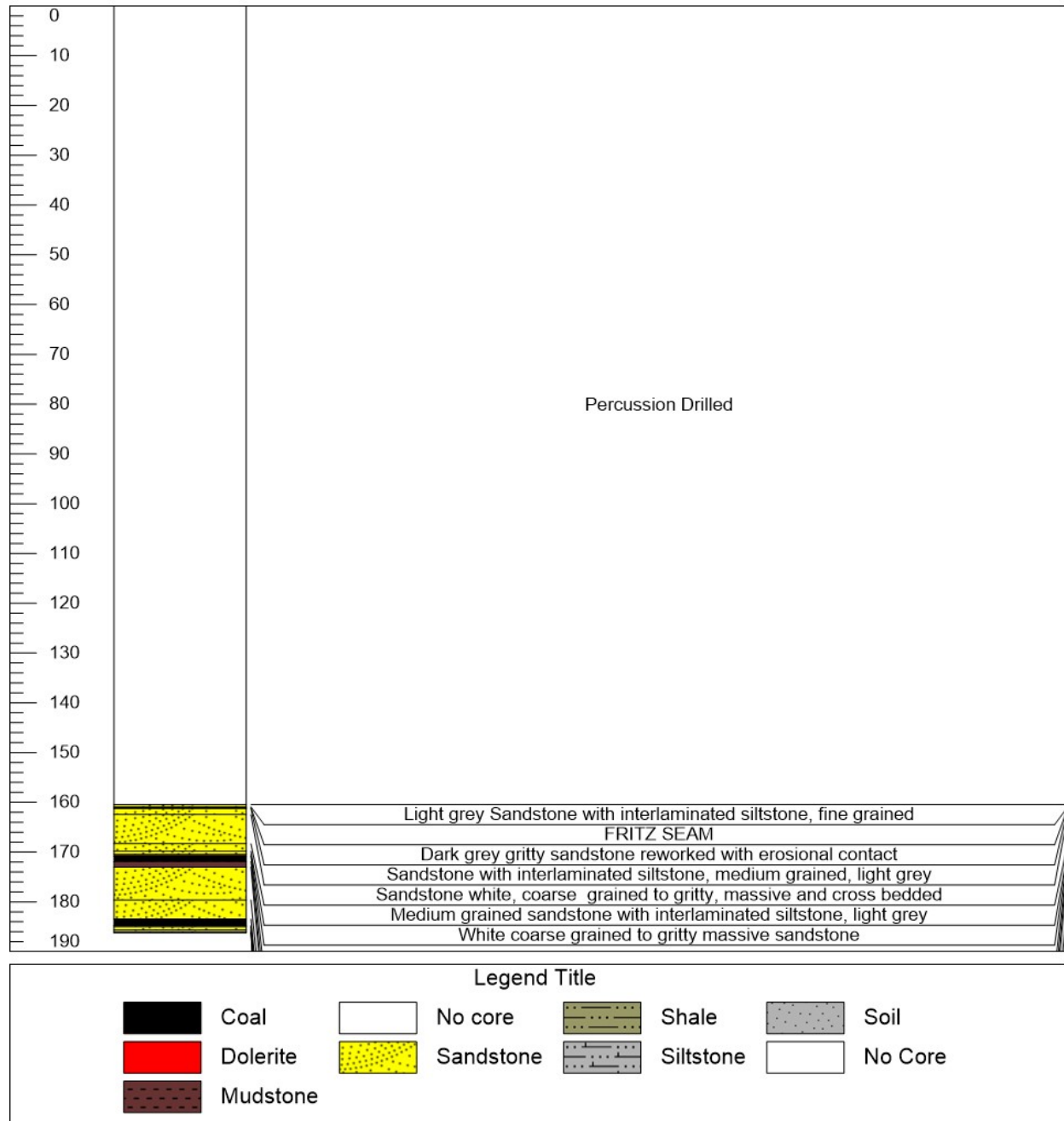


Figure 4.4: Stratigraphy of part of the Utrecht Coalfield in borehole JCBH20.

4.1.1 Stratigraphic correlation

The stratigraphic correlation of these seams across the four boreholes revealed significant variation in depth and thickness. The Gus and Alfred seams were observed in all four boreholes, showing lateral distribution across the entire area (Figure 4.5). The seams become deeply buried towards JCBH08 and JCBH20. The Fritz Seam was only observed in two boreholes (JCBH20 and AD3BH3), the seam is shallow in borehole AD3BH3 and becomes progressively deeply buried in JCBH20.

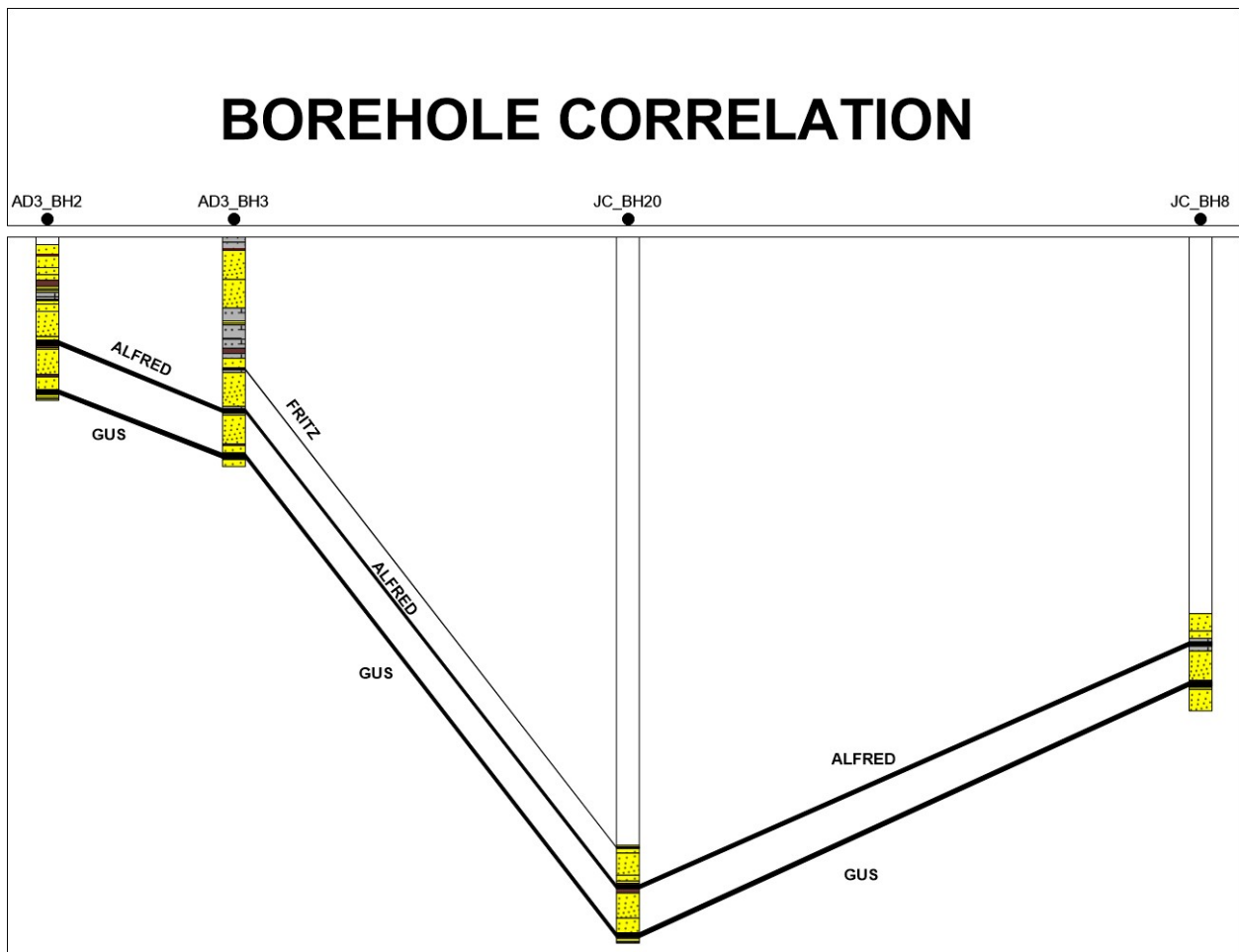


Figure 4.5: Stratigraphic correlation of boreholes AD3BH2, AD3BH3, JCBH08 and JCBH20.

4.2 Coal petrography

4.2.1 Vitrinite reflectance

Vitrinite analysis was performed to assess the coal rank (degree of coalification), focusing on reflectance measurements of collotelinite rather than pseudovitrinite. The average reflectance results can be found in Table 4.1. The random vitrinite reflectance (%RoVmr) of the Utrecht Coalfield ranges from 0.648 to 0.790. The vitrinite reflectance on samples that had an inertinite content greater than 80 vol.% (i.e., sample CMB-L2, CMB-D, CMB-S1, JCBH20A) could not be taken. According to the United Nations Economic Commissions for Europe (UN-ECE) coal classification standards on random vitrinite reflectance, the coal samples from the Utrecht Coalfield were classified as medium-rank C bituminous and ortho-bituminous (Figure 4.6; Table 4.1). The dominant vitrinite maceral was noted to be collotelinite while collodetrinite occurred in minor proportions, the dominant inertinite maceral was semifusinite with minor proportions of inertodetrinite. Sporinite was the dominant liptinite maceral detected in the samples.

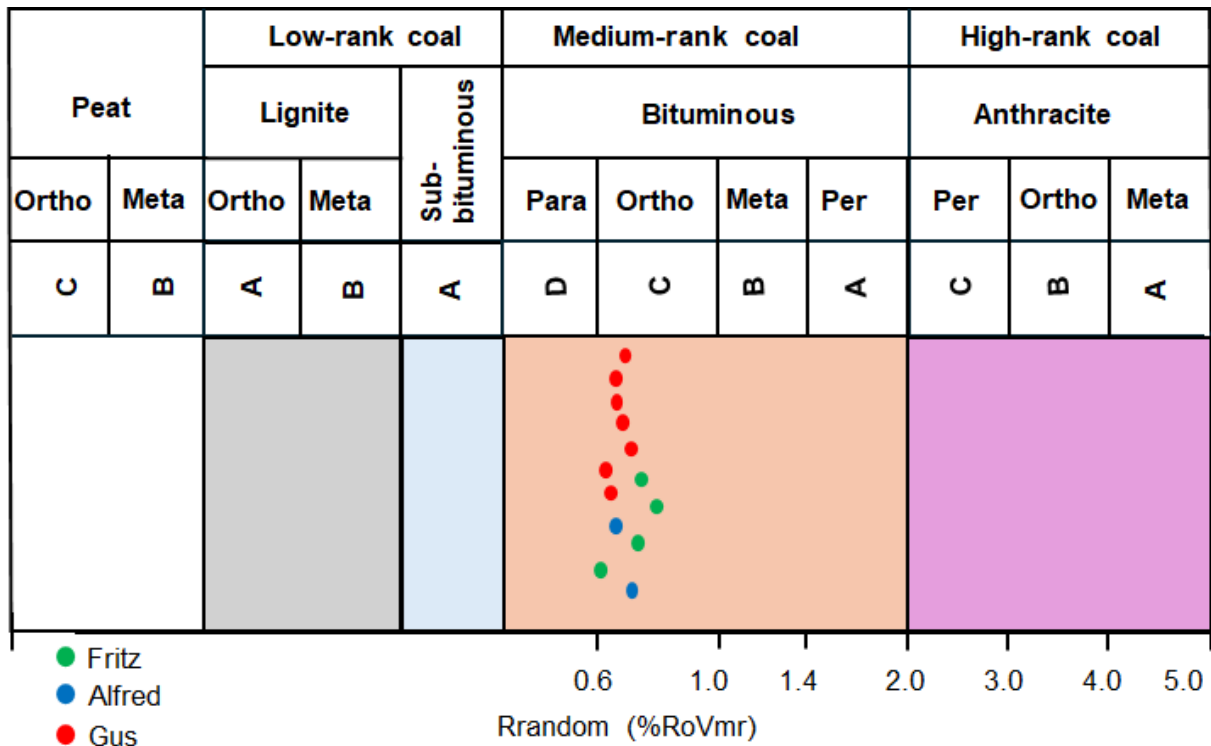


Figure 4.6: Classification of the analysed coal samples according to the UN-ECE standards.

Table 4. 1: Maceral group determination and vitrinite reflectance.

SEAM	SAMPLE	CONTENT		MACERAL GROUP			Vitrinite reflectance				RANK CATEGORY
				VITRINITE	LIPTINITE	INERTINITE	Rrandom	St. dev.	Maximum reading (RoV%)	Minimum reading	
GUS	CB1-L1	mmf	vol%	62.6	6	31.4	0.659	0.068	0.805	0.507	Medium-rank C
	CMB-L1	mmf	vol%	18.1	4.9	77	0.706	0.061	0.89	0.601	Medium-rank C
	CB2-L1	mmf	vol%	72.9	7.9	19.2	0.688	0.053	0.816	0.553	Medium rank C
	CMB-L2	mmf	vol%	9.3	1	89.7	n/a				n/a
	CB1-L2	mmf	vol%	65.6	8.7	25.7	0.669	0.053	0.81	0.553	Medium-rank C
	CB2-L2	mmf	vol%	68.8	4.5	26.7	0.671	0.048	0.76	0.55	Medium-rank C
	CMB-D	mmf	vol%	1.3	0.9	97.8	n/a				n/a
	CB2-D	mmf	vol%	37.1	2.4	60.5	0.689	0.068	0.88	0.526	Medium-rank C
	CB2-S1	mmf	vol%	62.7	5.8	31.5	0.648	0.059	0.794	0.508	Medium-rank C
	CMB-S1	mmf	vol%	3.8	1.8	94.4	n/a				n/a
ALFRED	JCBH08A	mmf	vol%	16.6	6.4	77	0.79	0.092	0.999	0.609	Medium-rank C
	JCBH08B	mmf	vol%	14.2	9.6	76.2	0.734	0.091	0.94	0.519	Medium-rank C
	JCBH20	mmf	vol%	49.8	15	35.2	0.606	0.06	0.814	0.475	Medium-rank C
	JCBH20A	mmf	vol%	7	6.1	86.9	n/a				n/a
	JCBH20B	mmf	vol%	14.1	7	78.9	0.743	0.091	0.969	0.543	Medium-rank C
FRITZ	AD3BH3A	mmf	vol%	35.2	12.7	52.1	0.713	0.061	0.87	0.569	Medium-rank C
	AD3BH2	mmf	vol%	31.5	6.8	61.7	0.674	0.067	0.841	0.535	Medium-rank C

4.2.2 Maceral group composition

A maceral point count was conducted on the samples to identify the composition of maceral and mineral matter; the results are reported as both including mineral matter (inc. mm) and mineral matter free (mmf) as presented in Table 4.1 and Appendix A. Averagely, the samples from Utrecht Coalfield are low in mineral matter and constitute less than 3%. There were a few samples that were noted to have a slightly higher content of mineral matter (i.e., sample CMB-D, JCBH2A, and JCBH20B), exceeding 16 vol.% (Appendix A). On average, the coal samples from the Utrecht Coalfield are enriched with inertinite with lesser amounts of vitrinites, while liptinites have the lowest vol.% (Table 4.1). On average (mmf), the inertinites constitute about 60.11 vol.%, vitrinites (33.56 vol.%) and liptinites (6.32 vol.%). The maceral analysis of coal samples from different seams (i.e., Fritz, Alfred, and Gus) revealed that the Fritz and Alfred seams are predominantly inertinite-rich, while the Gus seam exhibited more variability. Of the ten analysed samples from the Gus seam, five were vitrinite-rich and five were inertinite-rich, however, on average, the seam is inertinite-rich (Figure 4.7). Notably, the Upper and Lower Gus were predominantly vitrinite-rich, whereas the Middle Gus was dominantly inertinite-rich. The semifusinite and inertodetrinite were the dominant inertinite macerals detected during the petrographic analysis, whereas collotelinite, telinite and pseudovitrinite were the dominant vitrinite macerals, and lastly, sporinite was the most prevalent liptinite macerals detected in the samples.

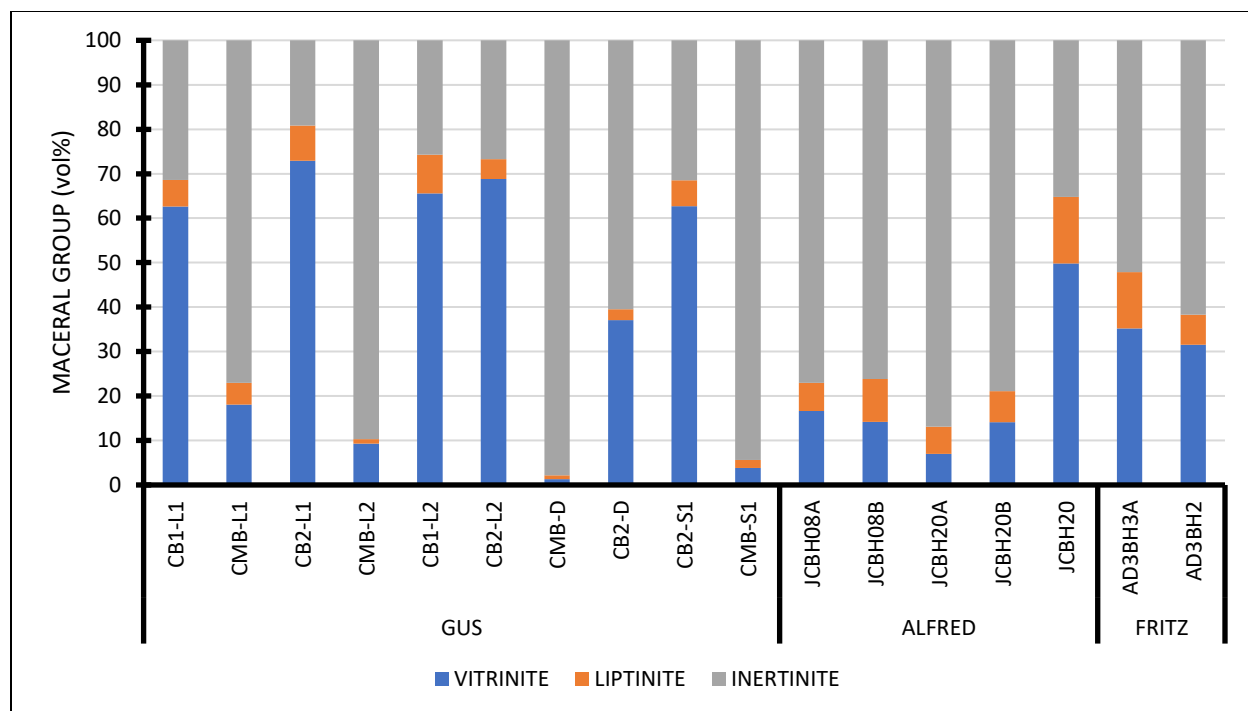


Figure 4.7: Bar chart showing the result of the maceral groups analysis.

4.2.2.1 Vitrinite

The vitrinite group has various shades of grey ranging from light to darker grey (the more frequent type). In the collected samples, different types of vitrinites were observed (Figure 4.8). Telinite is seen as very thin strands that run diagonally in the same parallel direction of the bedding plane and there are some observable cracks in the maceral (Figure 4.8a). Collotelinite has a smoother surface (Figure 4.8b). Gelinite displays a meandering shape through an inertinite that has some cracks in places (Figure 4.8c), while pseudovitrinite is seen with desiccation cracks and that lies both perpendicular and horizontal to the bedding plane (Figure 4.8d). Collodetrinite occurs in fine-grained vitrinite materials, while corpogelinite is combined with the darker telovitrinite (Figure 4.8e and f).

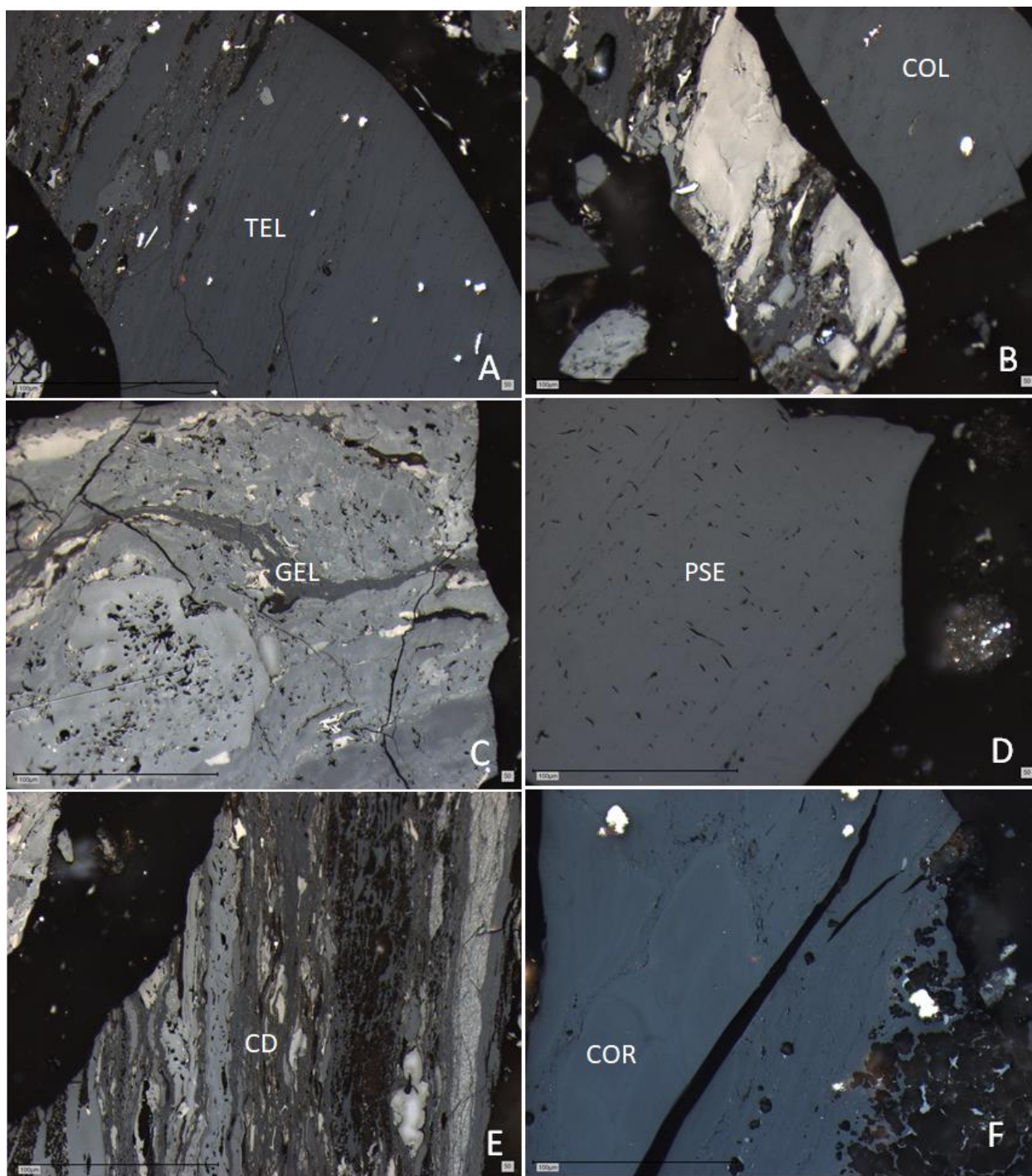


Figure 4.8: Photomicrographs of different types of vitrinite observed in the coal. a) Telinite (TEL); b) Collotelinite (COL); c) Gelinite (GEL); d) Pseudovitrinite (PSE); e) Collodetrinite (CD); f) Corpogelinite (COR).

4.2.2.2 Inertinite

Inertinite maceral group is seen by mostly a lighter shade of grey, except for the reactive and inert semifusinite, which are darker grey in colour (Figure 4.9). The different types of inertinite macerals have been detected in the samples. Fusinite occurs as thin lances and appears to have been fractured and sometimes filled in by mostly non-organic material (Figure 4.9a), as depicted by Figure 4.10, fusinite also exhibit a fractured boogen-like structure. Secretinite (SEC) has a sphere-shaped or oval structure, as shown in Figure 4.9d, minor cracks were observed. Semifusinites can be reactive semifusinite (RSF) or inert semifusinite (ISF). Both the ISF and RSF are characterised by having cell structures that are preserved poorly and most of them have cavities that have not been filled (Figure 4.9b, e and f). A variation of semifusinite is shown by the change in the shade of grey from the left to the right corner (Figure 4.9e). The inertodetrinite is a mixture of pieces of inertinites and vitrinites (Figure 4.9c and f). Other minerals may also be incorporated in the inertodetrinites, as depicted in Figure 4.9c, where there is the occurrence of pyrite (the very brightly coloured minerals) and clay minerals (Figure 4.9c), while others are fine-grained (Figure 4.9f).

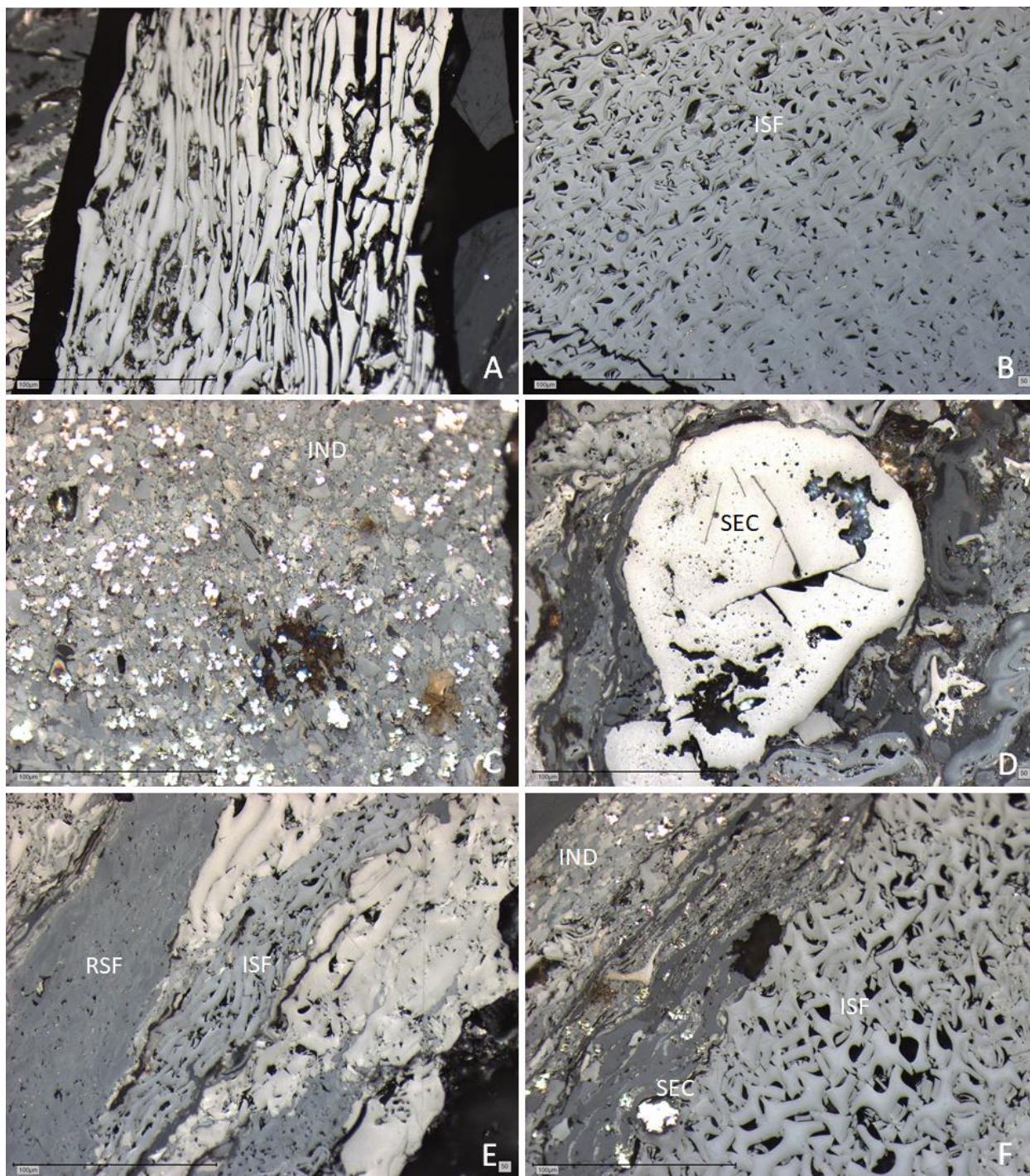


Figure 4.9: Photomicrographs showing inertinite macerals. a) Fusinite; b) Inert semifusinite (ISF); c) Inertodetrinite (IND); d) Secretinite (SEC); e) Reactive semifusinite (RSF); f) IND, SEC and ISF.

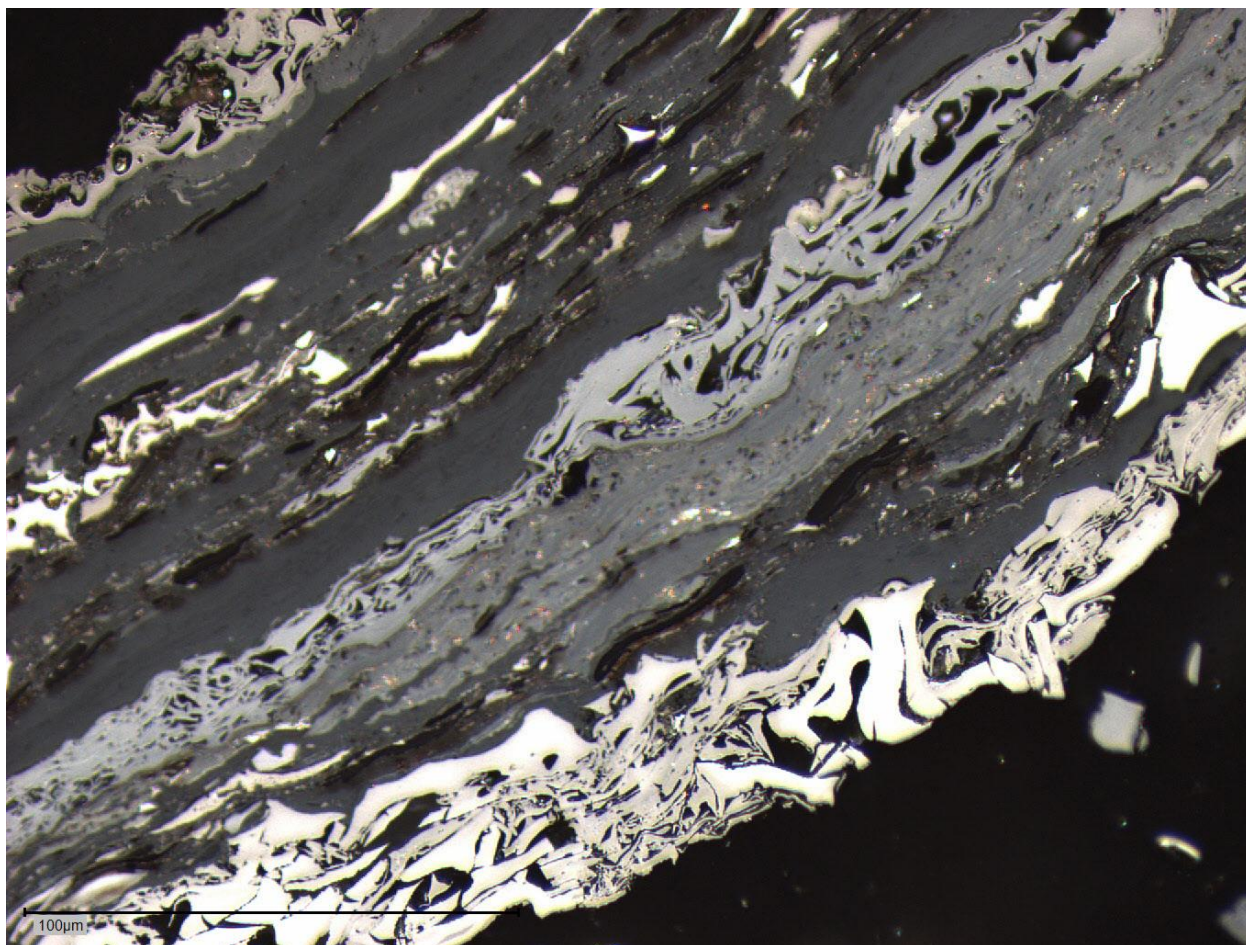


Figure 4.10: Photomicrograph of fusinite showing fractured boogen structures.

4.2.2.3 Liptinite

The liptinites group is not easily distinguishable from other mineral matter or macerals under white light (Figure 4.11a and b). However, liptinites exhibit fluorescence under fluorescent light and are noticeable by an orangish colour under fluorescent light (Figure 4.11c and d). The liptinites in the samples have fine-grained clay associations (Figure 4.11b). Sporinite is the most dominant type of liptinite observed in the Utrecht Coalfield, as shown in Figure 4.11c. There are also silicate (i.e., quartz and clay) mineral associations in the saccate pollens.

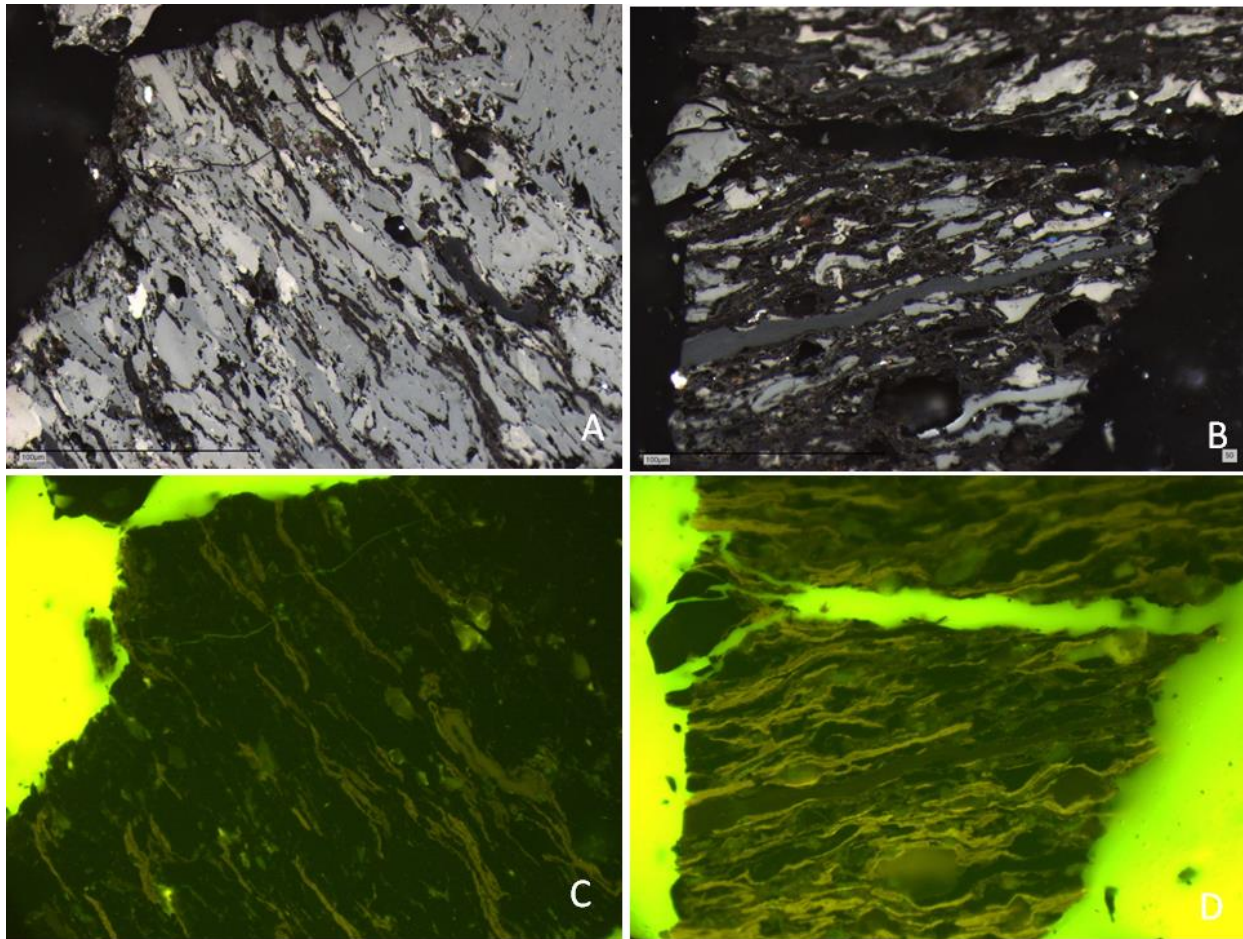


Figure 4.11: Photomicrograph showing liptinites under (a-b) white; (c-d) fluorescent lights.

4.2.3 Mineral matter

In addition to the different types of organic matter (macerals) identified in the coal samples of the Utrecht coalfield (Uitkomst Colliery), inorganic minerals are also found within or in the cleats between the organic matter. In the observed coal samples, the predominant mineral components were silicates with lesser sulphides and carbonate minerals.

4.2.3.1 Silicates

The main silicate minerals in the coal are clays and quartz minerals. The clays ranged from 0.2 vol.% to 19.2 vol.%, while quartz ranged from 0.2 vol.% to 31.2 vol%. The clay minerals in the samples occur as fine material dispersed in the coal samples, and the

structures of the cell walls are partially preserved in bands of clay infills (Figure 4.12a and b). Quartz is embedded in organic matter (Figure 4.12c) and large angular clastic quartz grains are observed in Figure 4.12d.

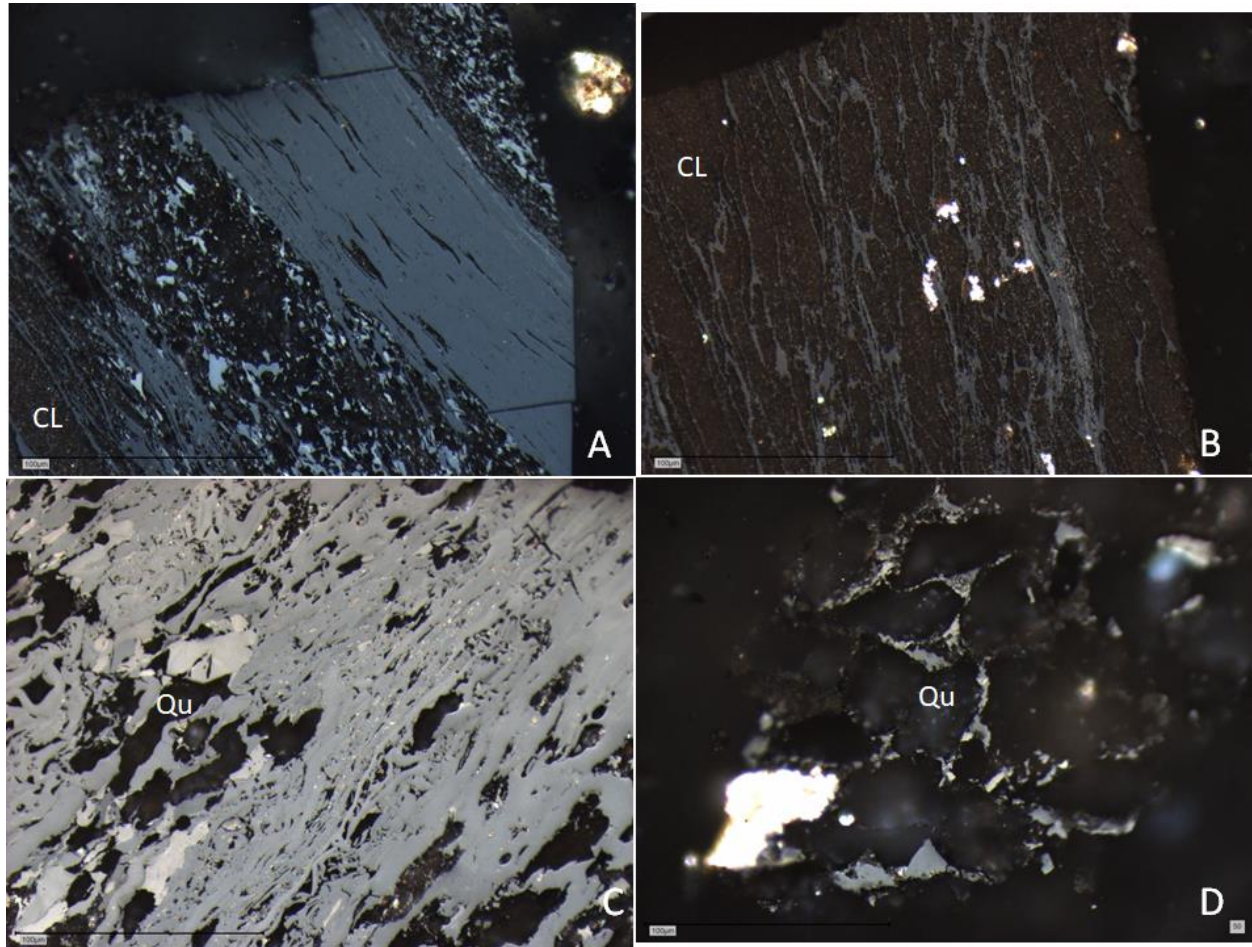


Figure 4.12: Photomicrographs showing silicate minerals a) clays in vitrinite; b) flocculated clays; c) quartz in inertidetrinite; d) clastic quartz.

4.2.3.2 Carbonates

Carbonate minerals, such as siderite and calcite were also detected in the samples and ranged from 0-3.8 vol% (Appendix A). Calcite has a sugary texture with a blue colour and is the dominant carbonate mineral observed, it occurs as infillings in cleats and fractures (Figure 4.13a), and large calcite grains were also observed (Figure 4.13b). Siderite has

a well-preserved structure resembling a flower or concentric structure; it was mostly observed to be associated with inertodetrinite (Figure 4.13c and d).

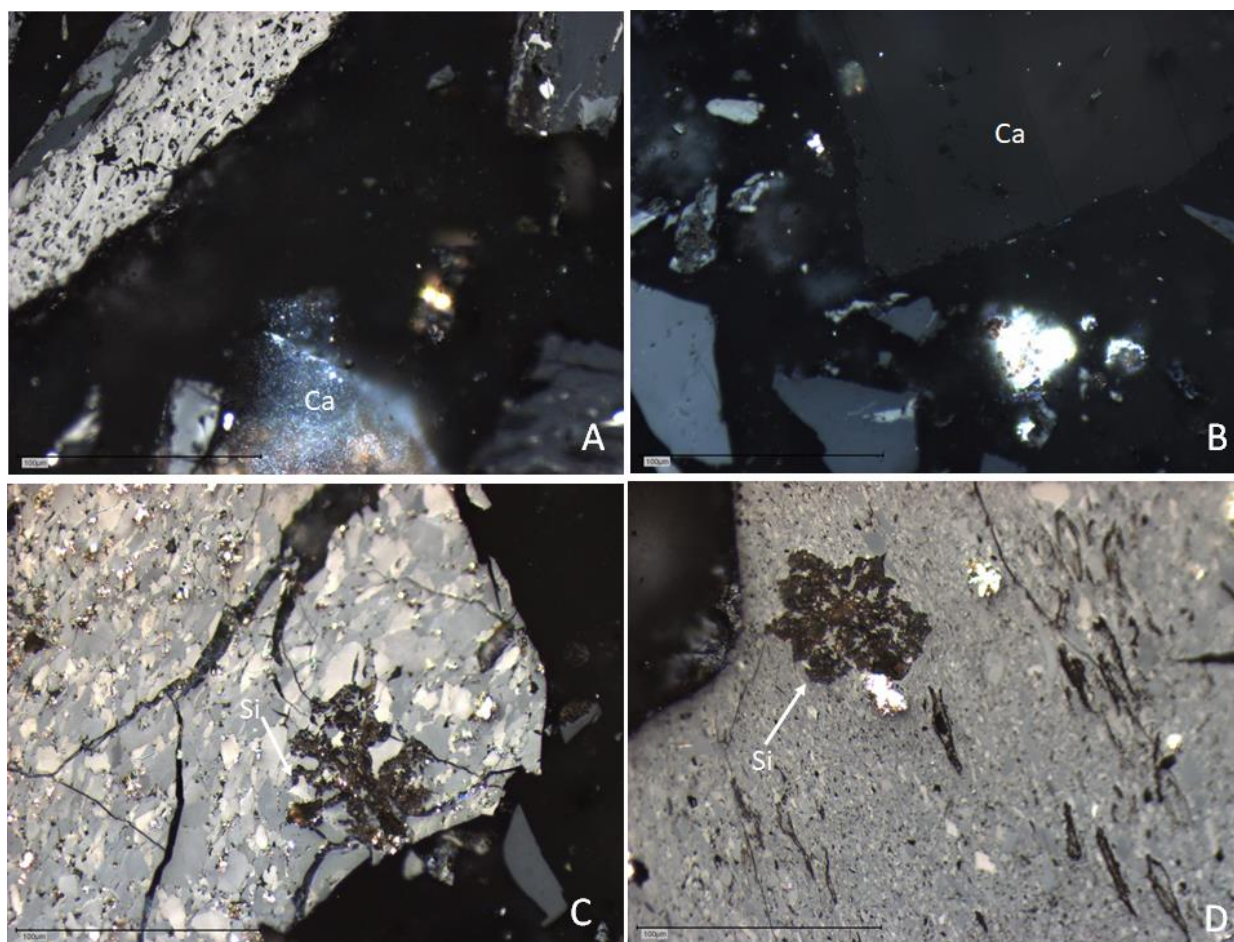


Figure 4.13: Photomicrograph showing carbonate minerals a) dispersed calcite; b) large calcite grain; c) siderite in a fractured inertodetrinite; d) siderite in an inertodetrinite with pyrite.

4.2.3.3 Sulphide

Sulphide, primarily in the form of pyrite is seen ranging from 0-8.5 vol%, pyrite was observed in the samples of the Utrecht coalfield, it has a very bright white-yellowish colour and as observed, it can be included in organic matter (Figure 4.14). Pyrite is also associated with inorganic matter, mostly clay minerals (Figure 4.14c). A diverse array of pyrite minerals were discerned, as illustrated in Figure 4.14. The detected pyrite is

observed to occupy pore spaces and cell structures, as depicted in Figure 4.14b and e. Furthermore, Figures 4.14a and c reveal instances where pyrite has undergone replacement processes, affecting organic and inorganic minerals (i.e., clays and vitrinite). The presence of larger euhedral pyrite grains forming clusters, as illustrated in Figure 4.14d, is notable. Additionally, framboidal pyrite clusters were observed, highlighting distinctive morphological features (Figure 4.14d). The study also identified instances of massive pyrite formations, as depicted in Figure 4.14f.

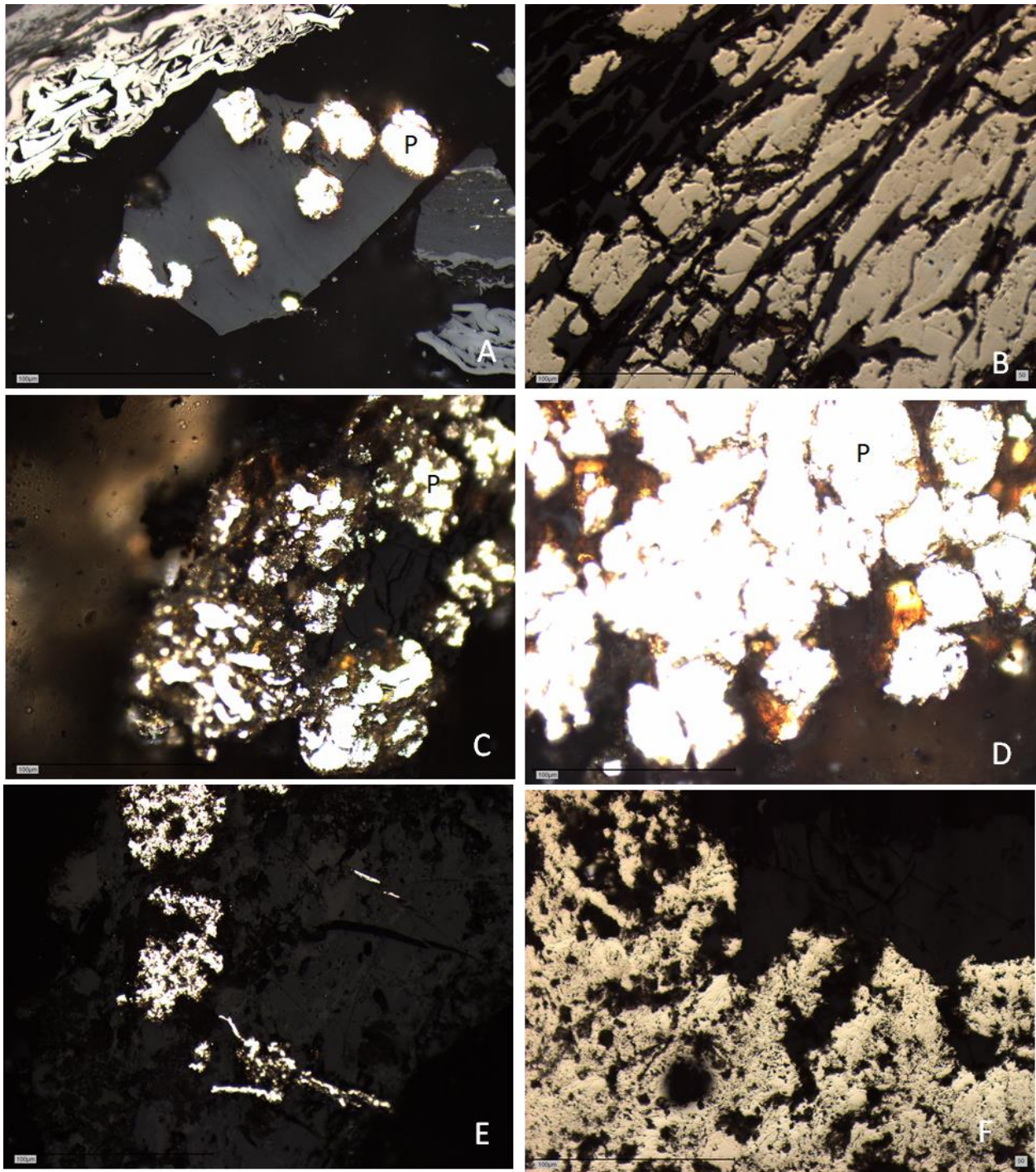


Figure 4.14: Photomicrographs showing sulphide mineral a) pyrite nodules in vitrinite; b) pyrite on organic matter; c) pyrite in clays; d) framboidal pyrite; e) pyrite in an inertodetrinite; f) massive pyrite.

4.2.4 Proximate analysis

The weight percentages of ash content, fixed carbon, volatile matter and inherent moisture of the coal from the Utrecht Coalfield are presented in Table 4.2 and are represented graphically in Figure 4.15. The proximate results show that the coal samples are characterised by a moisture content ranging from 1.5 to 3.3%, averaging 2.3%. The ash content of the samples varies from 5.8 to 48.5%, with an average ash content of 19.8%. The volatile matter ranges from 14.3% to 38.5%, averaging 26.7% (Table 4.2; Figure 4.15). Furthermore, the results show a fixed carbon content ranging from 35.7% to 62.6%, with an average of 51.2%.

The average content of the different coal seams (i.e., Gus, Alfred and Fritz) were also calculated. It is observed that the Fritz seam have the lowest average inherent moisture content of 1.8%, followed by the Gus seam having an inherent moisture content of 2.3%, and the Alfred seam with an inherent moisture content of 2.5% (Figure 4.15). The Alfred seam exhibits the highest average ash content of 29.9%, followed by the Fritz seam with an ash content of 18.4%, and the Gus seam with the lowest ash content at 14.9% (Figure 4.15).

The Gus seam has the highest average volatile matter content of 29.0%, followed by the Fritz seam at 27.3%, while the Alfred seam records the least volatile matter of 21.9% (Figure 4.15). In terms of fixed carbon content, the Gus seam exhibits the highest average content of 53.7%, followed by the Fritz seam at 52.5%, and the Alfred seam with a fixed carbon content of 45.2%. This analysis underscores the distinct characteristics of each coal seam, revealing variations in inherent moisture, ash, volatile matter and fixed carbon content.

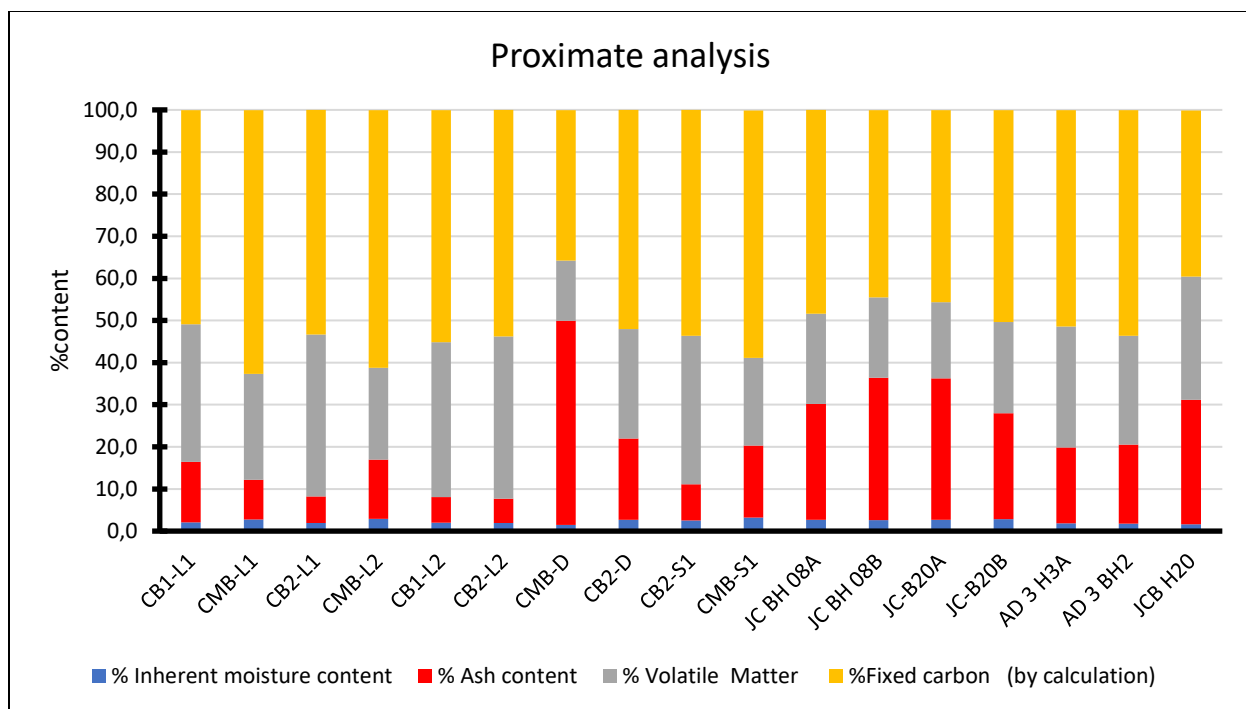


Figure 4.15: Bar chart showing the ash content, fixed carbon, volatile matter and inherent moisture of the coal from the Utrecht Coalfield.

Table 4.2: Proximate analysis results.

SEAM	Sample ID	% Inherent moisture content	% Ash content	% Ash content	% Volatile Matter	% Volatile Matter	%Fixed carbon (by calculation)
		(air-dried)	(air-dried)	(dry basis)	(air-dried)	(dry basis)	(air-dried)
GUS	CB1-L1	2.1	14.4	14.7	32.7	33.3	50.8
	CMB-L1	2.8	9.4	9.7	25.2	25.9	62.6
	CB2-L1	1.9	6.3	6.4	38.5	39.2	53.3
	CMB-L2	2.9	14.1	14.5	21.8	22.5	61.2
	CB1-L2	2.0	6.1	6.2	36.8	37.6	55.1
	CB2-L2	1.9	5.8	5.9	38.5	39.2	53.8
	CMB-D	1.5	48.5	49.2	14.3	14.5	35.7
	CB2-D	2.7	19.3	19.8	26.0	26.7	52.0
	CB2-S1	2.5	8.6	8.8	35.3	36.2	53.6
	CMB-S1	3.3	17.1	17.6	20.9	21.6	58.7
	Averages	2.3	14.9	15.3	29.0	29.7	53.7
ALFRED	JC BH 08A	2.7	27.5	28.3	21.4	22.0	48.4
	JC BH 08B	2.6	33.9	34.8	19.0	19.5	44.5
	JC-B20A	2.7	33.6	34.5	18.1	18.6	45.6
	JC-B20B	2.8	25.2	25.9	21.7	22.3	50.3
	JCB H20	1.7	29.6	30.0	29.3	29.7	39.4
	Averages	2.5	29.9	30.7	21.9	22.4	45.6
FRITZ	AD 3 H3A	1.9	18.0	18.3	28.8	29.3	51.3
	AD 3 BH2	1.8	18.8	19.1	25.8	26.3	53.6
	Averages	1.8	18.4	18.7	27.3	27.8	52.5

4.2.5 Ultimate analysis

The results of the ultimate analysis are shown in Table 4.3 and Figure 4.16. The sulphur content in the studied coals varies from 0.30 to 2.76%, with an average of 1.43%. The coal contains a higher proportion of carbon, ranging from 58.71-81.22%, and has an average carbon content of 70.25%, while the content of hydrogen ranges from 3.92-4.75%, averaging 4.23%. The content of nitrogen varies between 1.93% and 2.12%, with an average of 2.02%. The oxygen content ranges from 11.14–37.05% and has an

average of 22.06%. On average, the Fritz seam has the highest sulphur content of approximately 2.32%, followed by the Alfred seam at 1.49% and the Gus seam with the lowest sulphur content of about 1.3% (Figure 4.16). In terms of carbon content, the Gus seam has the highest at 73.79%, followed by the Fritz seam at 73.71% and the Alfred seam has the lowest average carbon content at 65.89%. The Fritz seam has the highest hydrogen content at 4.42%, followed by the Gus seam at 4.35%, with the Alfred seam having the lowest hydrogen content at 4.11%. Among the seams, the Alfred seam has the lowest nitrogen content at 1.98%, followed by the Fritz seam at 2.04%, and the Gus seam at 2.05%. With respect to the hydrogen content, the Alfred seam has the highest value at 26.52%, followed by the Gus seam at 18.51%, while the Fritz seam has the lowest hydrogen content at 17.53%.

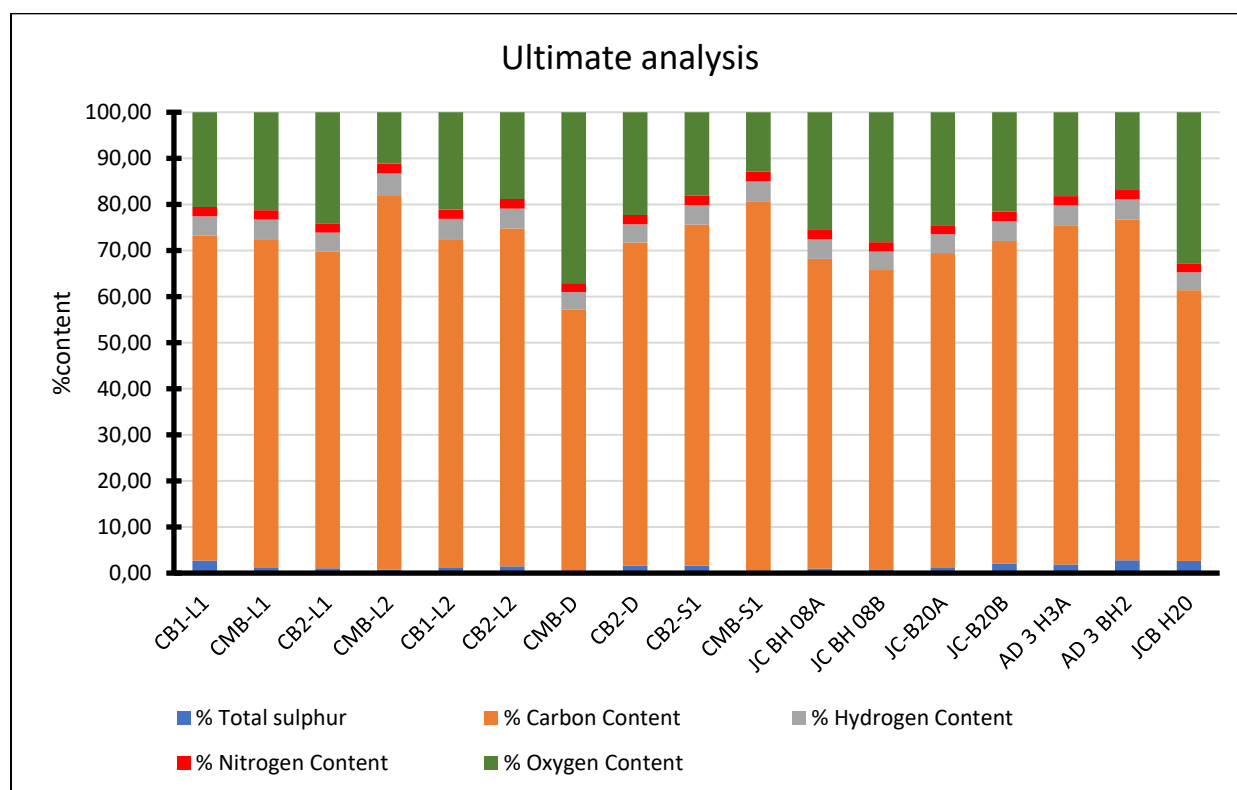


Figure 4.16: Bar chart showing the carbon, total sulphur, oxygen, hydrogen, and nitrogen content.

Table 4.3: Ultimate analysis results.

Seam	Sample ID	% Total sulphur	% Carbon Content	% Hydrogen Content	% Nitrogen Content	% Oxygen Content
		(air-dried)	(Determined)	(Determined)	(Determined)	(Calculated)
Gus	CB1-L1	2.7	70.6	4.1	2.1	20.5
	CMB-L1	1.1	71.2	4.4	2.0	21.3
	CB2-L1	1.1	68.8	4.1	2.0	24.1
	CMB-L2	0.8	81.2	4.8	2.1	11.1
	CB1-L2	1.3	71.0	4.6	2.0	21.1
	CB2-L2	1.5	73.3	4.3	2.0	18.9
	CMB-D	0.3	57.0	3.8	1.9	37.1
	CB2-D	1.6	70.1	4.0	2.0	22.3
	CB2-S1	1.6	74.0	4.2	2.1	18.1
	CMB-S1	0.4	80.2	4.4	2.1	12.9
	Averages	1.2	71.7	4.3	2.0	20.7
Alfred	JC BH 08A	1.0	67.2	4.3	2.0	25.5
	JC BH 08B	0.7	65.1	4.0	2.0	28.2
	JC-B20A	1.1	68.4	4.0	2.0	24.5
	JC-B20B	2.0	70.1	4.3	2.0	21.6
	JCB H20	2.6	58.7	3.9	1.9	32.8
	Averages	1.5	65.9	4.1	2.0	26.5
Fritz	AD 3 H3A	1.9	73.4	4.5	2.0	18.2
	AD 3 BH2	2.8	74.0	4.4	2.0	16.9
	Averages	2.3	73.7	4.4	2.0	17.5

4.3 Mineralogical composition

4.3.1 X-ray diffraction (XRD)

The XRD results reported as wt. % are presented in Figure 4.17 and Table 4.4. Kaolinite $[\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4]$ is the most abundant mineral with concentrations greater than 9 wt.% and quartz (SiO_2) being the second most abundant with concentrations ranging from 1.6 wt.% to 21.4 wt.% (Figure 4.17). Additionally, lesser amounts of pyrite (FeS_2) were found in proportions ranging from 0.1 to 6.4 wt.%, muscovite mica ($\text{KAl}_2(\text{AlSi}_3\text{O}_{10})(\text{OH})_2$), microcline feldspar (KAlSi_3O_8), analcime ($\text{NaAlSi}_2\text{O}_6 \cdot \text{H}_2\text{O}$), dolomite $[\text{CaMg}(\text{CO}_3)_2]$, calcite (CaCO_3) were also detected in amount lesser than 5 wt.%. Additionally, traces (<2 wt.%) of smectite $[(\text{Ca}, \text{Na})(\text{Al}, \text{Mg})_2(\text{Si}_4\text{O}_{10})(\text{OH})_2 \cdot n\text{H}_2\text{O}]$ and plagioclase feldspar $[(\text{Na}, \text{Ca})(\text{Al}, \text{Si})_4\text{O}_8]$ were detected, while traces of goethite $[\text{Fe}(\text{OH})\text{O}]$, were only observed in two samples. Most samples exhibited traces (<2 wt. %) of oxides, specifically magnetite (Fe_3O_4), while hematite (Fe_2O_3) was only detected in certain samples (Table 4.4). The detected minerals were also confirmed by the diffractograms (XRD) patterns, which substantiated the occurrence of kaolinite and quartz as the dominant minerals, followed by pyrite. The diffractograms of the samples from the Utrecht Coalfield have been included in Appendix C.

Table 4.4: Mineralogical composition of the coal.

Sample ID	Quartz (%)	Pyrite (%)	Kaolinite (%)	Plagioclase (%)	Siderite (%)	Microcline (%)	Muscovite (%)	Calcite (%)	Smectite (%)	Goethite (%)	Dolomite (%)	Apatite (%)	Analcime (%)	Magnetite (%)	Hematite (%)	Organic Carbon (%)
AD3 BH2	7.6	3.2	11.8	1.1	0	1	1.7	0	0	0	0	0	0.1	0.1	0	73.3
AD 3 H3A	6.1	2.4	13.8	1	0	0.9	1.4	1.3	0	0	0	0	0.3	0.1	0	72.7
CB1-L1	5	5.9	17.5	0.6	0	1	0	0	0	0	0	0	0	0	0	70
CB1-L2	1.6	6.4	11.3	1.3	0	4.1	2.2	0.3	0.3	0	0.5	0	2.6	0	0	69.3
CB2-D	9	2	15	0.6	0	0.6	1.6	0.4	0	0	0.5	0	0.1	0.1	0	70
CB2-L1	2.7	4	13	1.1	0	0.5	1.5	4.9	0.1	0	0.1	0	4.5	0	0	67.7
CB2-L2	1.5	5.7	9.3	1	0	5.6	1.8	0	0.1	0	0.2	0	2.1	0	0	72.7
CB2-S1	3.5	4.9	12	0.8	0	0.5	1.8	0.9	0.1	0.2	1.3	0	0.2	0.3	0	73.6
CMB-D	21.4	0	18.7	0.2	0	0.2	1.6	0	0	0.2	1	0	0	0.1	0.2	56.3
CMB-L1	4.4	2.9	13.1	1.1	0	1.8	3	0.1	0.1	0	2.5	0	0.6	0	0	70.2
CMB-L2	1.8	0.5	10.6	0.1	0	0.2	1.7	0.3	0	0	3	0	1	0.1	0	80.7
CMB-S1	2.4	0.1	11.2	0.4	0	0.3	1.2	1.5	0	0	3.3	0	0.1	0.1	0	79.4
JC BH-08A	12.2	0	15.3	0.2	0	0.2	2.1	1.8	0	0	0.8	0	0.5	0	0.4	66.5
JC BH-08B	13.4	0	17.1	0.3	0	0.1	2.4	0.6	0	0	1.4	0	0.3	0.1	0.3	64
JCB H2O	7.5	4.2	21.6	1.5	0	1.9	3.3	0	0.4	0	0	0	0.5	0.3	0	59
JC-BH20A	11.9	0.9	16.1	0.3	0	0.3	2.9	0.6	0	0	1.8	0	0.3	0.1	0.1	64.7
JC-B20B	6.9	3	14.9	0	0	0.6	0.9	1.5	0	0	3.1	0	0.6	0.1	0	68.5

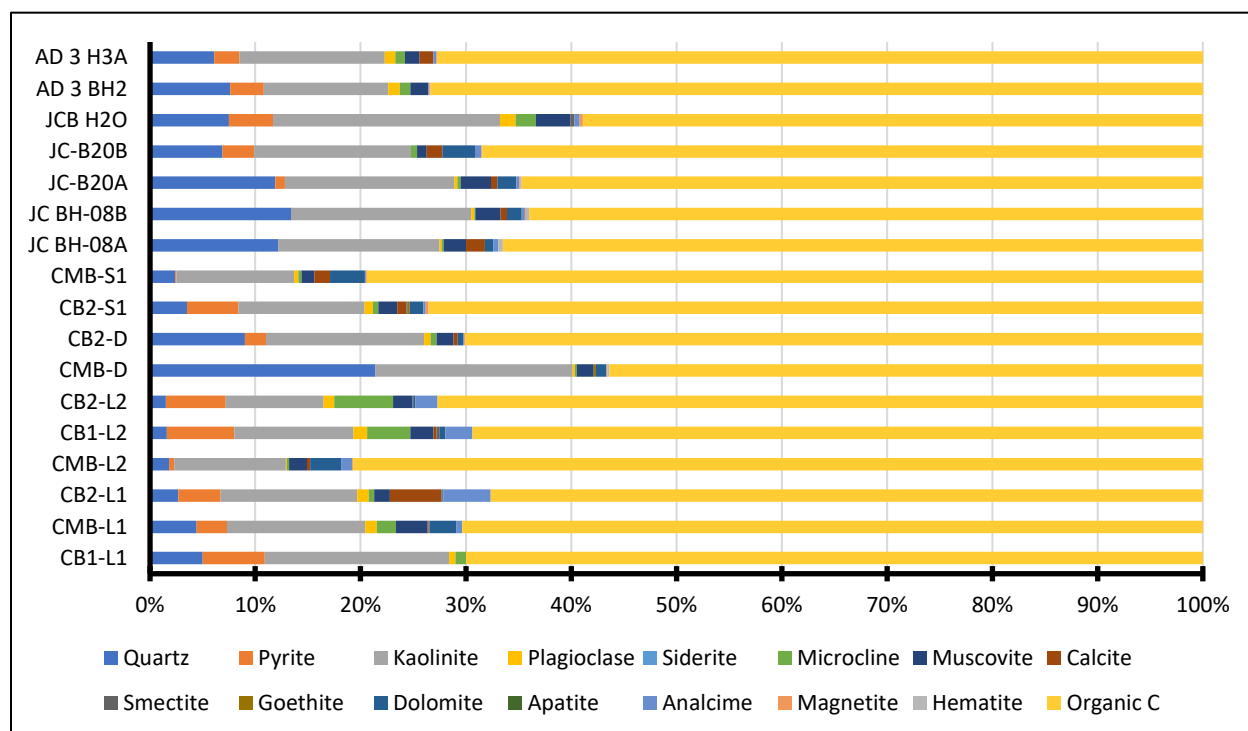


Figure 4.17: Bar chart showing the mineralogical results of all the samples.

4.3.2 Scanning electron microscopy (SEM)

The SEM results generally show that the dominant REE-bearing minerals in the coal are monazite and xenotime (Figures 4.18 - 4.22). As shown on the BSE images, the other minerals that were detected include clays (i.e., kaolinite), pyrite (Py), albite (Alb), rutile (Rut), and calcite (Ca) (Figures 4.18 - 4.21). These REE-bearing minerals are associated with clays and organic matter, as shown by the SEM-BSE photomicrographs (Figures 4.18 - 4.22). A search of the bright mineral phases was conducted to quantify the REE-bearing minerals (Table 4.4), which also revealed pyrite, barite, and chalcopyrite as the predominant bright phases. The monazite grains in sample AD3BH3A had a sub-angular to sub-rounded morphology with well-defined grain boundaries with some grains appearing to be elongated (Figure 4.18a-e). The grain sizes of monazite ranged from 8 to 30 microns (Figure 4.18a-e), whereas xenotime has a sub-angular morphology with a smoother surface and well-defined grain boundaries and the grain size is relatively less than 10 microns (Figure 4.18f). Monazite is associated with organic matter; it is worth

noting that the albite ($\text{NaAlSi}_3\text{O}_8$) grain appeared to be bent around monazite (Figure 4.18e), while xenotime was also associated with organic matter.

In sample CMB-L2, the grain sizes of monazite range from 4 to 20 microns with the surface of the grains having smoother surfaces (Figure 4.19a-c), the grain appears to be fractured in half and has a blocky texture (Figure 4.19b). The grains appear sub-angular to sub-round, whereas the monazite grain appear elongated as shown in Figure 4.19a, some of the grains exhibit well-defined boundaries whereas others do not, the monazite is mostly associated with organic matter but also observed to be associated with kaolinite (Figure 4.19b). Xenotime has an elongated morphology and sub-defined boundaries with a smoother surface, with the grain being approximately 7 microns, and is associated with organic matter (Figure 4.19e).

In sample JCBH20A, as observed in the BSE photomicrographs (Figure 4.20), the monazite does not have well defined grain boundaries as shown Figure 4.20a and has well-defined grain boundaries with a sub-angular morphology as shown in Figure 4.19b. The grain sizes of monazite range from 2-4 microns with smoother surfaces, and it is associated with both kaolinite and organic matter (Figure 4.20a and b). Xenotime is approximately less than 3 microns and does not have well defined grain boundaries (Figure 4.20c and d), and it mostly associated with kaolinite.

The EDS pattern unravelled the elemental makeup of the samples. In sample AD3BH3A from the Fritz seam, monazite occurred with and without thorium and was associated with organic matter (Figure 4.18). Additionally, it can be noted that the Ce peak in Figure 4.21d is indicative of a cerium-rich monazite. Cerium (Ce), lanthanum (La) and neodymium (Nd) were identified as the primary REEs within the Ce-rich monazite. Similarly, xenotime was found to be linked with the organic fraction of coal (Figure 4.22), exhibiting REEs such as Y, Er, Gd, Dy, and Yb.

In sample CMB-L2 from the Gus seam, where monazite was associated with the organic matter (Figure 4.19). Monazite in this sample was notably thorium-bearing, with identified REEs consisting of cerium (Ce), neodymium (Nd), lanthanum (La) and gadolinium (Gd)

(Figure 4.21e). Similarly, xenotime was observed to be associated with the organic carbon of coal (Figure 4.22), displaying REEs such as Y, Er, Gd, Dy, and Yb

The sample JCBH20A from the Alfred seam, was predominantly found in kaolinite and organic minerals (Figure 4.20a and b). Notably, the monazite was found to be associated with thorium and uranium. The rare earth elements (REEs) detected in this sample includes neodymium (Nd), cerium (Ce), lanthanum (La) and gadolinium (Gd). Conversely, xenotime was discovered within clay minerals mainly kaolinite (Figure 4.20c and d), with associated REEs such as yttrium (Y), erbium (Er), gadolinium (Gd), dysprosium (Dy) and Ytterbium (Yb) (Figure 4.22). The Nd peaks (Figure 4.21e and f) for both samples (JCBH20 and CMB-L2) are indicative of neodymium-rich monazite.

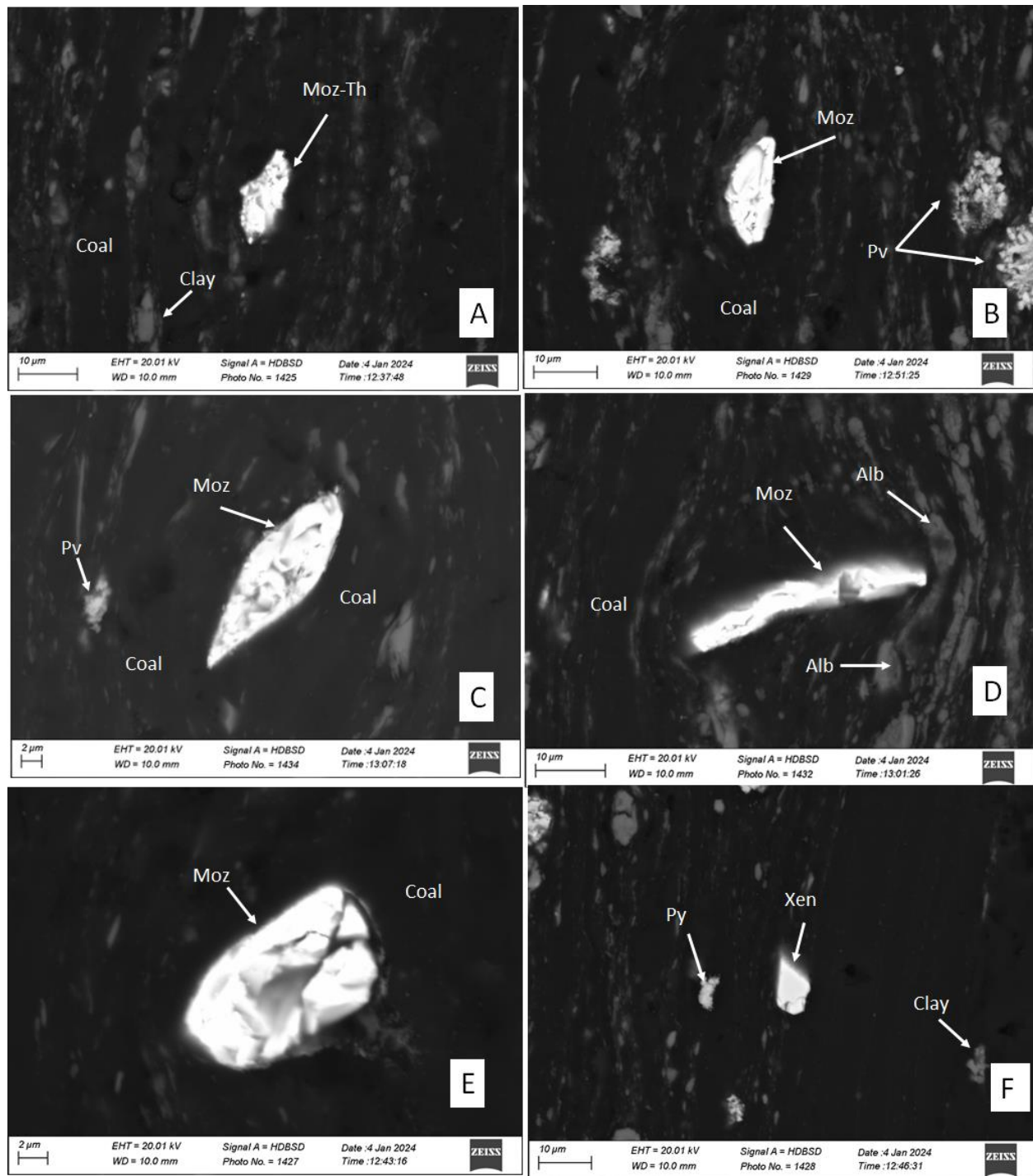


Figure 4.18: SEM (BSE) images of sample AD3BH3A showing a) monazite thorium associated with organic matter; b-c) monazite associated with organic matter with pyrite; d) elongated monazite bent around albite; e) blocky monazite in organic matter; f) xenotime in organic matter with clay and pyrite.

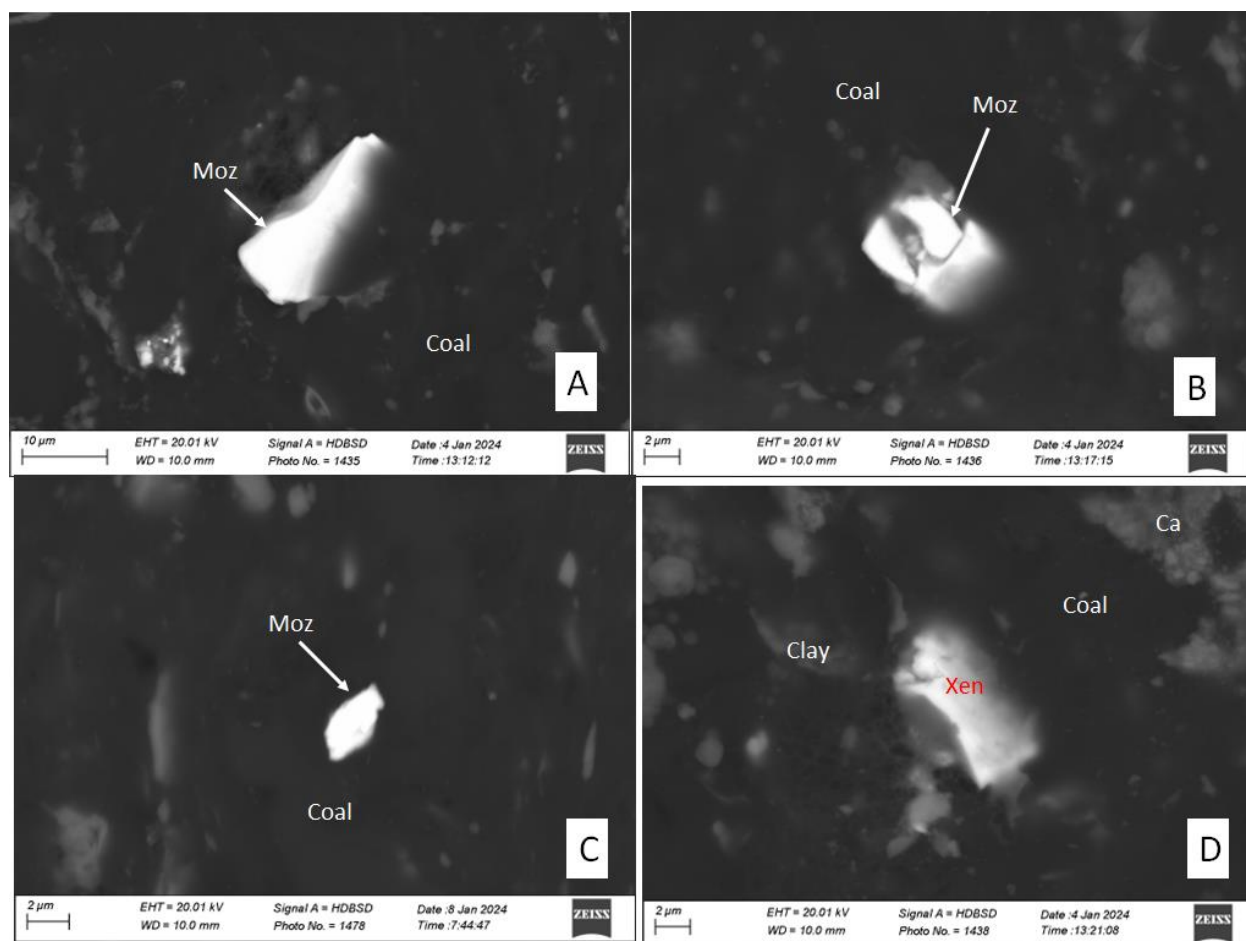


Figure 4.19: SEM (BSE) images of sample CMB-L2 showing: a) elongated monazite in organic matter; b) blocky monazite in clays; c) monazite in organic matter; d) xenotime associated with organic matter.

The SEM-EDS automated mineral and elemental mapping was employed to delineate and quantify the mineral phases inherent within the samples. Mineral compositions are reported in weight percentage (wt.%). The observed minerals include chalcopyrite, kaolinite, monazite, monazite-Ce (cerium-rich), monazite-Th (thorium-rich), pyrite, quartz, sphalerite, xenotime and zircon (Appendix B). Calcite was evident in samples JCBH20 and AD3BH3A, rutile in samples JCBH20A and CMB-L2, with sphene solely noted in sample JCBH20A. In addition, monazite-Nd (neodymium-rich) was discerned in samples AD3BH3A and CMBL2. The sub-microscopic, rare-earth element (REE)-bearing grains were identified, exhibiting grain sizes ranging from 0.50 to 2.51 μm for monazite and 0.02 to 2.48 μm for xenotime (Table B.1-B.3).

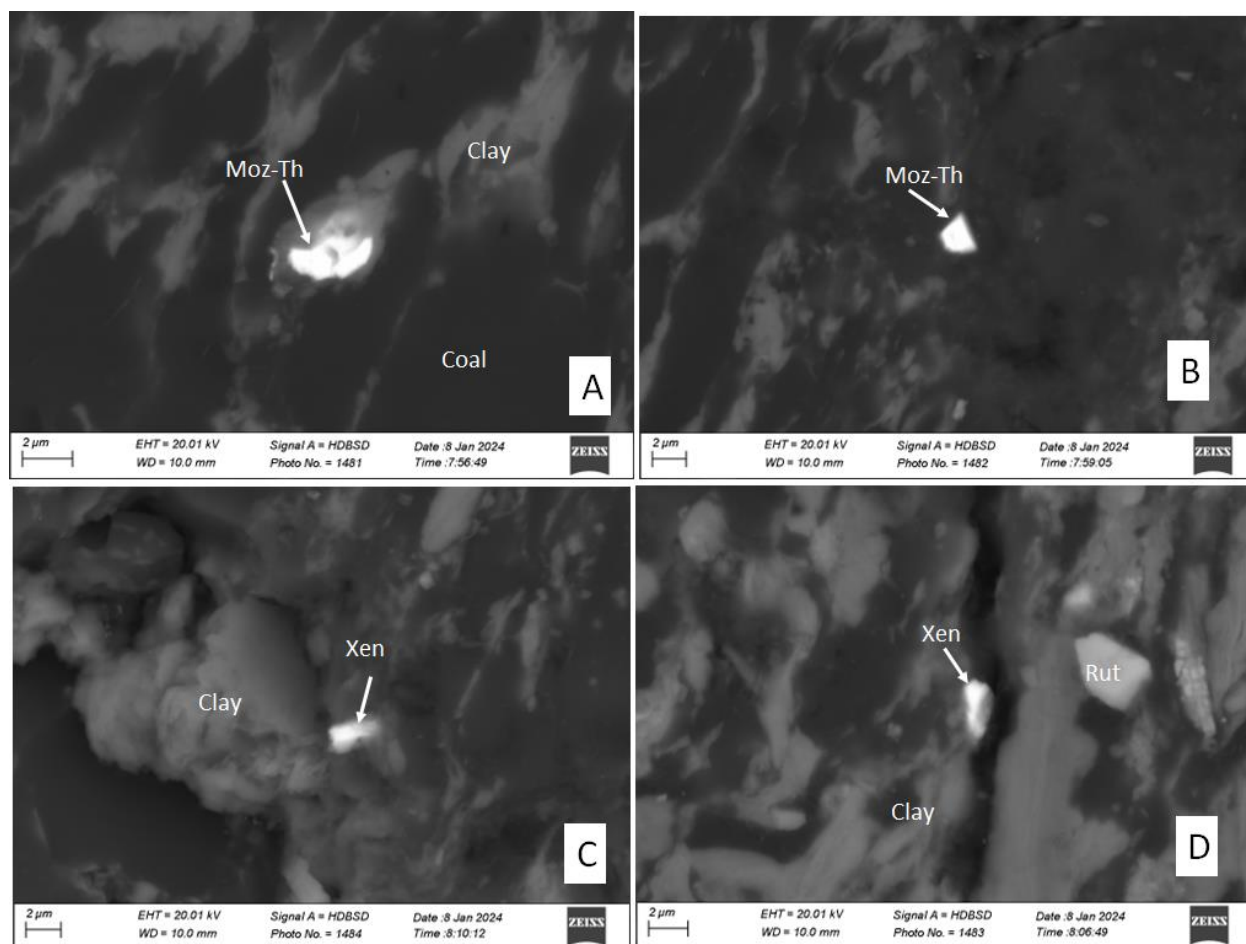


Figure 4.20: SEM (BSE) images of sample JCBH20A showing: a) thorium monazite in clays; b) thorium monazite in organic matter; c) xenotime in clays; d) xenotime in cleats of clays with rutile (Rut) occurrences.

During the elemental mapping, it was observed that in sample JCBH20A, monazite constituted approximately 1.66 wt.%, and xenotime 0.50 wt.%. In sample CMB-L2, monazite accounted for 27.94 wt.% and xenotime 6.72 wt.%. Lastly, in sample AD3BH3A, monazite constituted 54.68 wt.%, while xenotime constituted 5.71 wt.% (Appendix B).

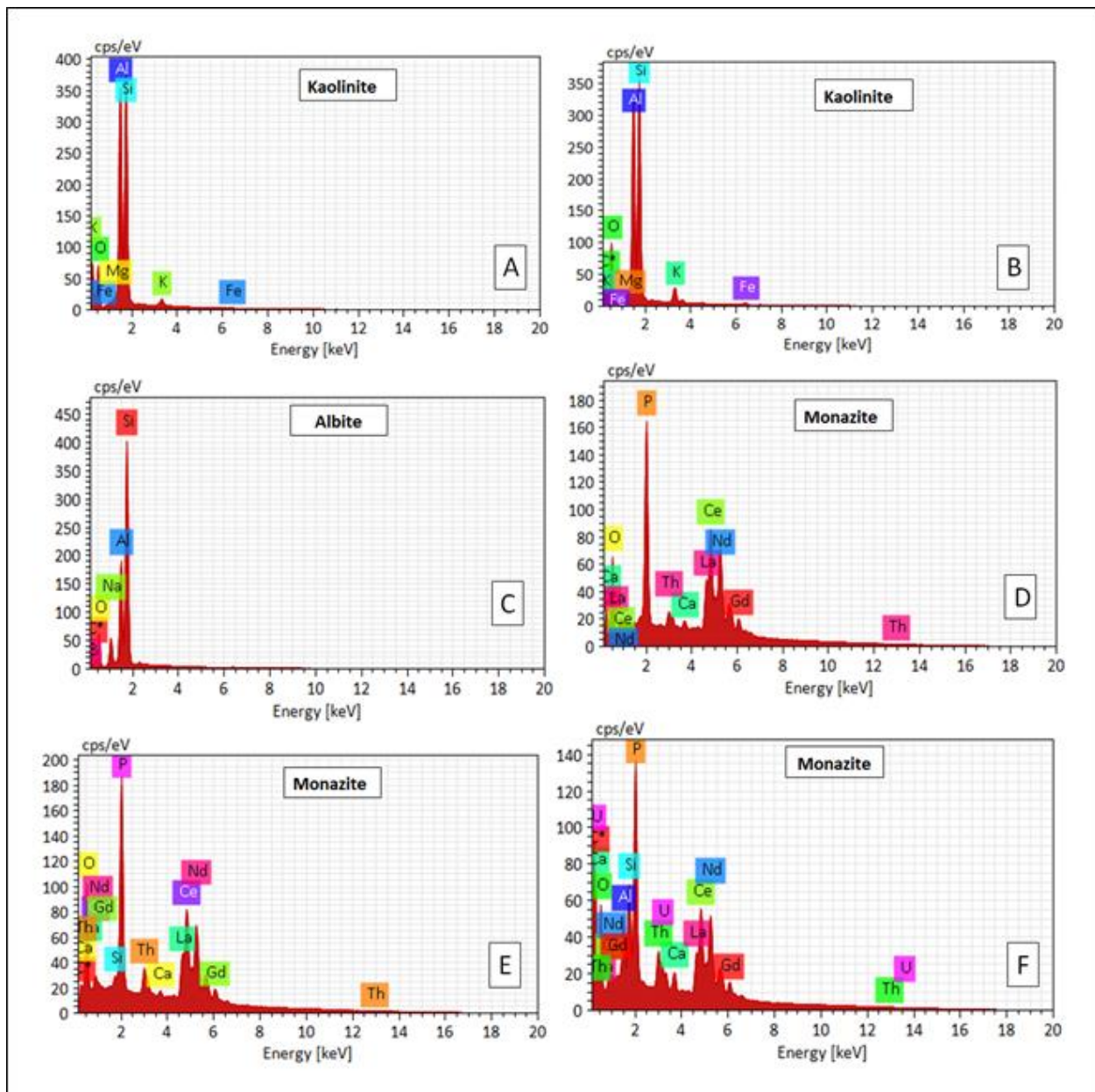


Figure 4.21: SEM-EDS pattern showing the elemental composition of a-b) kaolinite; c) albite; d) thorium-monazite in organic matter; e) thorium monazite in kaolinite; f) thorium-uranium monazite in kaolinite.

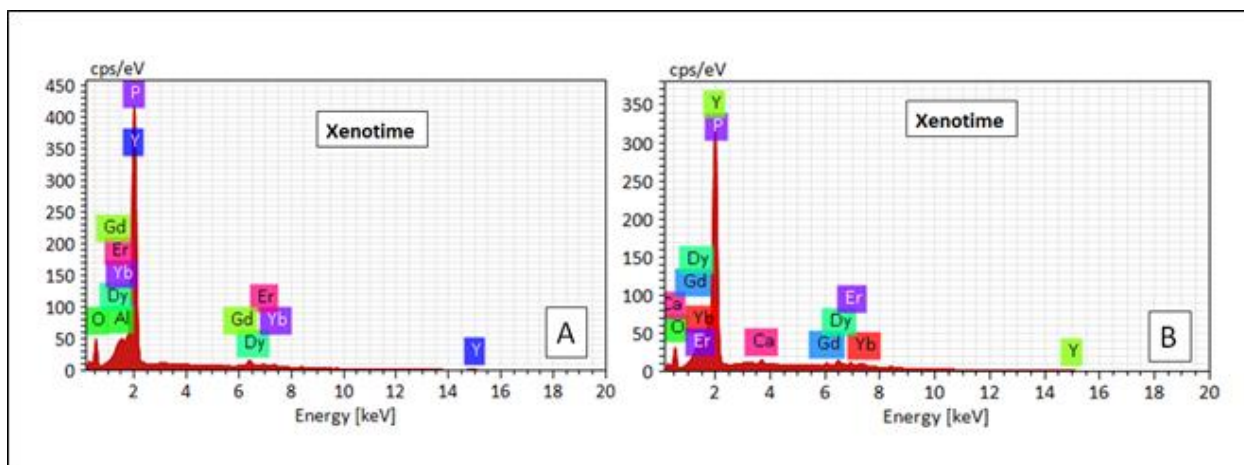


Figure 4.22: SEM-EDS pattern showing the elemental composition of a) xenotime in clays; b) xenotime in organic matter.

The conducted automated elemental mapping revealed the minerals hosting rare earth elements (REEs) to be monazite and which was associated with cerium (Ce), neodymium (Nd), gadolinium (Gd) and lanthanum (La). Meanwhile, xenotime was associated with yttrium (Y) and dysprosium (Dy). Furthermore, other minerals have been observed to contain REEs, which were not classified using the SEM-EDS. These unclassified minerals exhibit a diverse range of rare earth elements, including ytterbium (Yb), cerium (Ce), neodymium (Nd), yttrium (Y), lanthanum (La), dysprosium (Dy), erbium (Er), gadolinium (Gd) and praseodymium (Pr).

4.4 Elemental composition by inductively coupled plasma techniques (ICP-MS)

The elemental composition of the coal is presented in Table 4.5. The values determined for the Upper Continental Crust (UCC) as estimated by Taylor and McLennan (1985), together with the SARM 19 standard material have been included in the Table 4.5 for comparison purposes. The concentration of LREEs (i.e., La, Ce, Pr, Nd, and Sm) in the samples of the Utrecht Coalfield is higher than that of the MREEs and HREEs (Figure 4.23a). The following trend is observed in the abundance of REEs in the samples: $Ce > Y > La > Nd > Sc > Pr > Gd > Dy > Sm > Er > Yb > Ho > Eu > Tm > Lu$ (Figure 4.23b), with the concentration ranging from 0.05-64.67 ppm (Table 4.5). The total concentration of rare earth elements (TREEs) in the samples ranged from 23.2-173.5 ppm with the sample

JCBH08B having the highest concentration (Figure 4.24). Ce is the most enriched rare earth element in the samples (Figure 4.23a). The samples of the Utrecht Coalfield have an average TREEs of 101.4 ppm. The average sum of the TREEs of the Gus seam is 79.5 ppm, whereas the average sum of the TREEs of the Alfred seam is 137.6 ppm, and lastly 120.8 ppm for the Fritz seam.

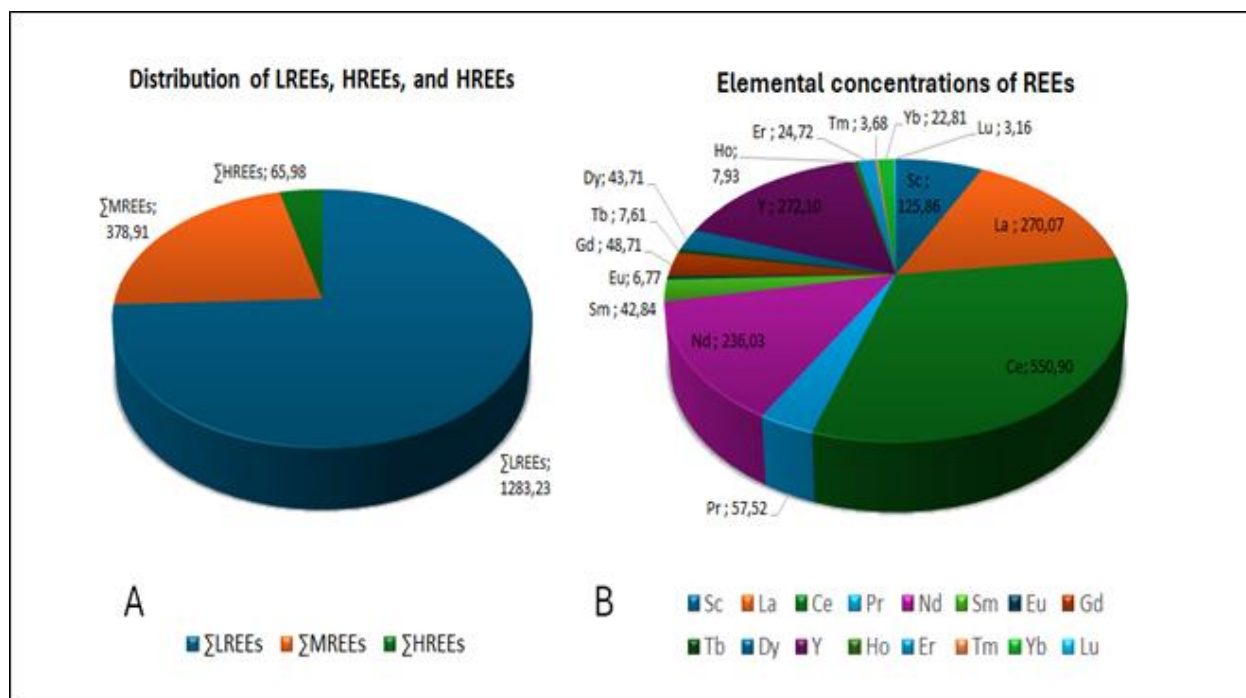


Figure 4.23: The pie charts illustrating: a) the distribution of LREEs, MREEs and HREEs; b) the variation of REEs in the samples.

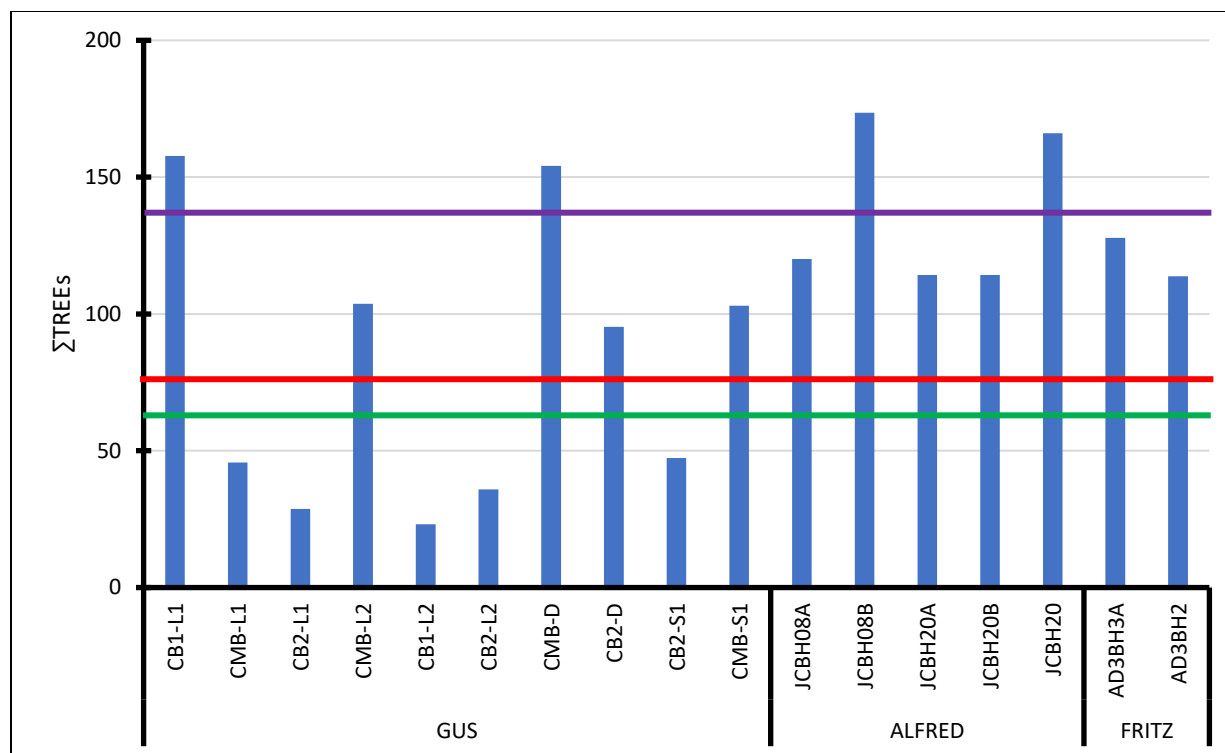


Figure 4.24: Bar chart showing the samples of the Utrecht Coalfield (TREES) results with averages from the USA (green line), World (red line), and Chinese (black line) coals.

Table 4.5: ICP-MS results for REEs contents and TREEs.

Seam	Sample Id	Sc	Y	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Σ TREEs	LREEs	HREEs
GUS	CB1-L1	13.0	29.4	18.3	48.8	4.9	20.5	4.2	0.7	4.6	0.7	4.4	0.9	3.1	0.5	3.2	0.5	157.7	96.67	19.08
	CMB-L1	2.4	7.3	6.9	14.9	1.6	7.2	1.2	0.2	1.3	0.2	1.0	0.2	0.6	0.1	0.7	0.1	45.7	31.74	4.41
	CB2-L1	2.7	5.2	4.9	7.8	0.8	3.8	0.6	0.1	0.9	0.2	0.8	0.1	0.4	0.1	0.4	0.0	28.8	17.95	3.03
	CMB-L2	4.0	14.1	17.6	36.2	3.8	16.3	2.9	0.4	2.8	0.4	2.1	0.4	1.2	0.2	1.1	0.1	103.7	76.86	8.83
	CB1-L2	1.9	3.7	4.2	6.7	0.6	3.5	0.4	0.0	0.7	0.1	0.6	0.1	0.3	0.0	0.3	0.0	23.2	15.44	2.18
	CB2-L2	4.9	8.5	4.5	8.1	0.8	4.6	0.8	0.1	1.2	0.1	1.2	0.1	0.2	0.1	0.4	0.3	35.9	18.83	3.68
	CMB-D	5.5	14.5	29.9	60.2	6.3	23.3	4.1	0.5	3.8	0.6	2.7	0.4	1.2	0.2	0.9	0.1	154.1	123.75	10.53
	CB2-D	4.5	12.9	16.5	33.2	3.4	13.8	2.5	0.3	2.6	0.4	2.4	0.4	1.2	0.2	0.9	0.1	95.3	69.35	8.68
	CB2-S1	1.3	6.7	7.0	18.0	1.9	7.5	1.1	0.1	1.3	0.2	1.0	0.2	0.5	0.1	0.5	0.0	47.4	35.49	3.96
	CMB-S1	5.8	17.3	17.0	33.3	3.4	13.4	2.6	0.4	3.0	0.5	2.9	0.5	1.4	0.2	1.2	0.1	103.0	69.67	10.50
ALFRED	JCBH08A	9.2	17.0	20.4	39.1	4.0	16.0	3.1	0.5	3.3	0.5	3.0	0.6	1.6	0.2	1.4	0.2	120.1	82.54	11.53
	JCBH08B	8.1	19.0	31.6	64.7	6.8	25.9	4.3	0.7	4.5	0.6	3.3	0.6	1.7	0.2	1.5	0.2	173.5	133.19	13.45
	JCBH20A	11.1	18.1	15.6	34.6	3.5	15.1	3.2	0.6	4.0	0.6	3.5	0.6	1.8	0.2	1.4	0.2	114.2	72.04	13.21
	JCBH20B	10.8	19.6	14.3	32.5	3.8	16.7	3.2	0.6	3.9	0.7	3.6	0.6	1.9	0.3	1.5	0.2	114.3	70.50	13.59
	JCBH20	18.5	29.9	23.9	45.7	5.1	20.3	3.9	0.7	4.5	0.7	4.6	1.0	3.1	0.5	3.1	0.4	166.1	98.90	19.19
FRITZ	AD3BH3A	10.3	25.8	20.4	36.8	3.7	14.7	2.6	0.5	3.2	0.5	3.5	0.7	2.3	0.3	2.2	0.3	127.8	78.12	13.91
	AD3BH2	11.9	22.9	17.1	30.3	3.2	13.6	2.3	0.4	3.0	0.5	3.0	0.7	2.2	0.3	2.2	0.3	113.8	66.34	12.97
	SARM 19	6.6	16.4	24.3	52.2	5.1	19.8	3.6	0.5	3.6	0.5	3.0	0.4	1.2	0.2	1.0	0.1			
	UCC	11.0	22.0	30.0	64.0	7.1	26.0	4.5	0.9	3.8	0.6	3.5	0.8	2.3	0.3	2.2	0.3			

CHAPTER 5

INTERPRETATIONS AND DISCUSSION

5.1 Petrography

The rank of the studied coal was determined to be medium-rank bituminous coal, which agrees with the study reported by Spurr et al. (1986), where it was observed that in the farm Utrecht Townlands and Tusschenbei 167, bituminous coal was extracted by several companies. Vitrinite reflectance for samples CMB-S1, CMB-D, CMB-L2 and JCBH20A could not be determined as the samples contained an inertinite content that is greater than 85 vol%, therefore, the samples lacked sufficient vitrinite particles needed for reflectance analysis. All the samples were classified as medium-rank C high volatile bituminous. In South African coals, liptinites rarely exceed 7 vol %, this was observed in most of the samples, although some of the samples (i.e., CB1-L2, CB2-L1, JCBH08B, JCBH20 and AD3BH3A) in the Alfred and Fritz seams exceeded 7 vol% (Kruszewska, 2003). The liptinite content on an average basis is lower than 7 vol %, suggesting that either spores or pollens were scarce, or the preservation conditions degraded the exines. Due to the fact that liptinites are hydrogen-rich with a high calorific value, coals with a high liptinite content tends to produce significant amount of tars and gases during the carbonisation process (Bottle and White, 2023).

According to Mokwena (2018), the Nongoma Coalfield is inertinite-rich with no liptinites, while there are variable amounts of vitrinite and minimal mineral matter. Furthermore, the rank of the coal in the Nongoma Coalfield is high-rank anthracite. This agrees with the results obtained in this study, as the coal is also inertinite-rich with lesser amounts of mineral matter. Moreover, liptinites are present in the Utrecht Coalfield and the rank of the coal, unlike the Nongoma Coalfield, is medium-rank high volatile bituminous coal, not anthracitic. According to several studies, including Falcon (1986), Cadle et al. (1993) and Wagner et al. (2018), South African coals in the Vryheid Formation are inertinite-rich. This also agrees with the results obtained in the Utrecht Coalfield, as the coal is dominantly inertinite-rich with lesser amounts of vitrinites and liptinites.

According to Ward (2016), the dominant carbonate minerals in coal samples are siderite, calcite, and dolomite. In this study, calcite and siderite were the dominant carbonate minerals in the coal, although dolomite was not observed petrographically. Siderite can be considered a syngenetic mineral and might have formed during the reworking of fusinite, which later formed inertodetrinite (Chitlango, 2023). In contrast, calcite, another carbonate mineral, has an epigenetic mode of occurrence as it is observed infilling the cracks and cleats of organic material.

Silicate minerals, particularly clay minerals, in the samples are fine-grained and are often associated with liptinites, similar observations were made by Wagner (2018). These clays are seen as infillings and occur at grain boundaries between macerals. Additionally, the clay minerals occurring as infills support an epigenetic mode of occurrence. As a result of the close association of the clay minerals with liptinites, some vitrinites and inertodetrinites the clay minerals are thought to have a syngenetic mode of occurrence and are consequently formed during the peatification stage of coal formation. Quartz in the studied samples presents angular to oval-shaped edges and is associated with liptinites, inertodetrinite and some vitrinites, indicating a detrital mode of occurrence which may suggest deposition in a reworked flood environment (Wagner et al., 2018).

The sulphide pyrite mineral was observed to have different morphologies that suggest different modes of occurrence. The framboidal pyrite has an authigenic mode of occurrence, while pyrite that is infilling the organic minerals, cleats and cracks have an epigenetic mode of occurrence. Figure 4.14 shows some particles where the cell lumina was previously infilled with pyrite and the pyrite was later leached out or removed, leaving a void in the pore. The mineral matter identified through microscopic analysis, which includes sulphide, carbonate, and silicate minerals, shows a strong positive correlation with the ash content of the coal samples. This is evidenced by the high r^2 value of 0.83, indicating that as the concentration of these mineral components increases, there is a corresponding rise in the ash content (wt. %). Such a relationship aligns with the expected trend, as higher levels of inorganic mineral constituents within the coal matrix typically contribute to an increase in ash yield upon combustion. The data presented in Figure 5.1

further supports this association, reinforcing the idea that mineral composition plays a significant role in influencing ash content.

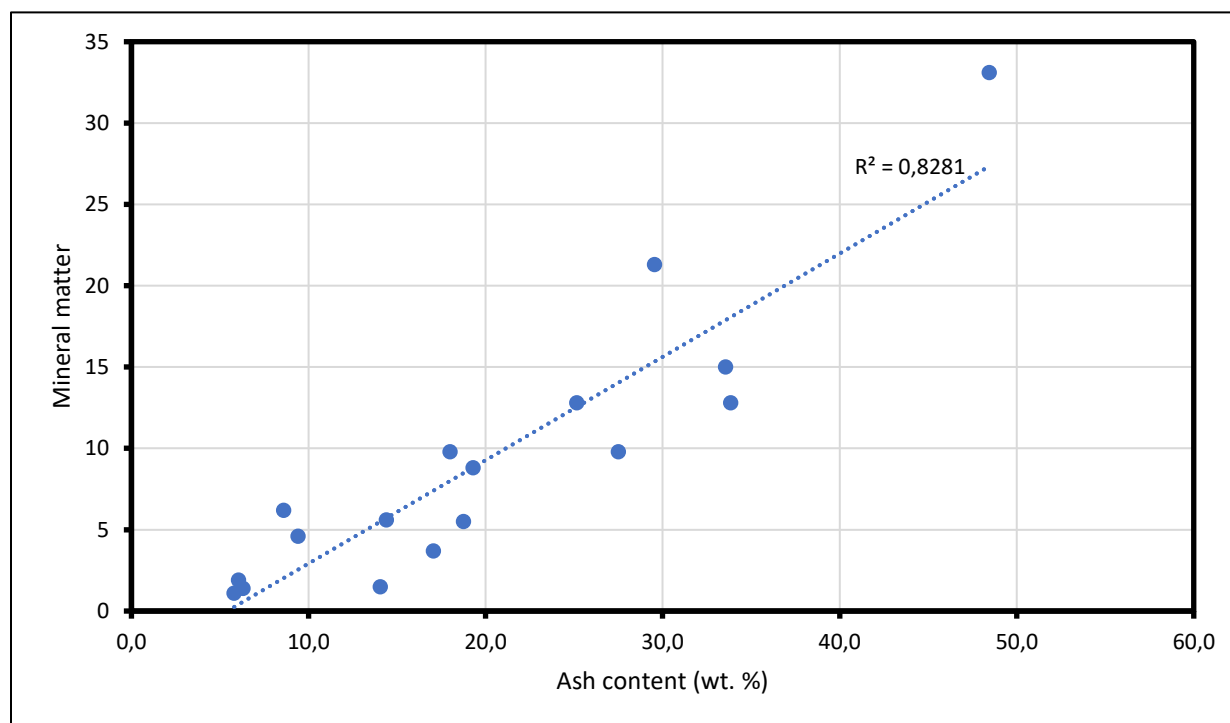


Figure 5.1: Binary plot showing the relationship between the ash content and the mineral matter.

5.1.1 Abnormal conditions

Cracks and fissures observed in some of the samples, perhaps indicate alteration due to weathering and oxidation. This alteration can be differentiated from pseudovitrinite by examining their irregular and discontinuous patterns (Wagner, 2018; Appendix A). Furthermore, the cracks from alteration often display a distinctive network-like structure, in contrast to the more uniform and glassy appearance typical of pseudovitrinite. The presence of stockpile mineral (i.e., iron oxide) in some of the samples occurred as a result of alteration (Appendix A). The alteration of the coal occurred due to the exposure of coal to weathering conditions (Wagner et al., 2018). Furthermore, these minerals are not typically observed in the fresh coal but rather in stockpiles. The results from this study agree with the observation made by Wagner et al. (2018), as alteration minerals were not

detected in the fresh samples. The occurrence of these minerals in the coal samples from the boreholes (i.e., JCBH20, AD3H3A, JCBH08B and JCBH08A) can be attributed to the lack of freshness in the coal. These boreholes were drilled by MC Mining and subsequently stored in a core yard, where exposure to alteration conditions may have led to the development of these minerals. In addition to weathering effects, some samples exhibited evidence of thermal alteration. In these cases, coal particles displayed higher reflectance, indicating devolatilization. This was particularly evident in the varied colouration of the coal particles, where thermally altered particles were lighter compared to the darker inertinite and vitrinite particles. This increase in reflectance is likely a result of devolatilization due to the influence of dolerite intrusions, as shown in the Appendix (Figure A.2). The effects of thermal alteration were not too extensive. However, the thermal influence of such intrusions could have caused significant physical and chemical transformations in coal, leading to changes in the optical properties and devolatilization of the coal.

5.2 Coal quality

According to Stach et al. (1982), coals with a relatively higher content of moisture are regarded to be lower ranks, while reduced moisture content is indicative of higher-rank coals. The studied coal samples have a lower moisture content, averaging 2.3%. On average, the Fritz, Alfred and Gus seams have moisture contents of 1.8%, 2.3% and 2.5%, respectively. The results obtained in this study differ from those of Spurr et al. (1986), who reported an average moisture content of 1.2% for the Alfred seam and 14% for the Gus seam. Furthermore, Spurr et al. (1986) reported the average volatile matter and ash content of the Gus seam to be 10.6% and 14.3%, respectively, while the Alfred seam had ash and volatile matter contents of 40.2% and 11.7%, respectively. In contrast, the present study found the Gus and Alfred seams to have ash contents of 16.8% and 29.9%, respectively, and volatile matter contents of 28.0% and 21.9%, respectively. The discrepancy might be due to the difference in the rank of the seams, the rank of the coal used in this study is bituminous while the other study was conducted on anthracitic coal. The observed elevated content of ash in the samples can be linked to the high inorganic

matter in the samples (Figure 5.1; Appendix A). Samples CMB-D, JCBH20, JCBH08A, JCBH20A and JCBH20B were observed to have ash contents greater than 25% and mineral matter of greater than 18.2%. The dolerite intruded coals had high ash content, which is common and consistent for contact-metamorphosed coals (Moroeng et al., 2024). High ash content in some samples can be attributed to the high mineral matter observed during microscopy and XRD analysis. This observation is supported by the positive correlation between ash content and mineral matter (Figure 5.1), this relationship aligns with the findings of Ward (2002) and Moorea and Esmaeilia (2012) who demonstrated that elevated concentrations of inorganic minerals significantly influence the ash content upon combustion. Furthermore, it was observed that as the ash content decreases, the volatile matter increases. According to Spurr et al. (1986), the elevated concentrations of ash content can be related to the mudstone associations with the coal seams.

Based on the coal grade classification (UN-ECE, 1992), the coal samples from the Fritz seam were classified as medium-rank coal, whereas the samples from the Alfred seam were classified as low to medium-grade coal (Table 5.1). The sample from the Gus seam showed variation, the samples from the lower Gus were classified as high to medium grade and the middle Gus samples were in the medium grade. The dyke intruded coal samples were classified as very low-grade coal (i.e., sample CMB-D) and medium grade coal (CB2-D).

Table 5.1: Classification of coal grades based on ash content (UN-ECE, 1998).

Grade	%Ash content
Rock	80-100
Carbonaceous rock	50-80
Very low-grade coal	30-50
Low-grade coal	20-30
Medium grade coal	10-20
High-grade coal	0-10

Volatile matter can be also used for coal rank classification based on the ASTM D 388-92 standards (Table 5.2). In this study, the Alfred seam was classified as medium to high volatile bituminous coal, the Fritz seam can be classified as high volatile bituminous coal whereas the Gus seam exhibited greater variation. The samples from both the upper and lower Gus were classified as sub-bituminous coal (i.e., sample CB1-L1, CB2-L1, CB2-L2, CB1-L2, and CB2-S1) whereas the samples from the middle Gus were classified as medium to high volatile bituminous coal (i.e., sample CMB-L1, CMB-S1, and CMB-L2). The two dyke intruded samples were classified as low volatile bituminous coal (i.e., sample CMB-D) and medium volatile bituminous coal (i.e., sample CB2-D). The observed trend is that there is an increase in volatile matter as the coal rank decreases (Bottle and White, 2023). Furthermore, volatile matter affects coke strength and yield by influencing the carbonisation behaviour of coal. In thermal coal, a higher volatile matter content improves the ignitability but will speed up the burning of the fixed carbon thereby affecting the burning efficiency of coal (Arisanti et al., 2018). Although this method can still be used to determine the coal rank, it should be noted that the most preferred and reliable method for coal rank determination is the vitrinite reflectance analysis as presented in Section 4.2.1 (Ward and Suárez-Ruiz, 2008).

Table 5.2: Coal rank classification based on the volatile matter (Bottle and White, 2023; UN-ECE, 1998; ASTM D 388-92).

Rank	%Volatile Matter
Peat	>60
Lignite	40-52
Sub-bituminous coal	31-40
High-volatile bituminous coal	22-31
Medium volatile bituminous coal	14-22
Low-volatile bituminous coal	8-14
Semi-anthracite	2-8
Anthracite	<2

Coal samples that were collected in proximity to the dolerite intrusions (i.e., samples CMB-D and CB2-D) show a decrease in volatile matter towards the intrusion. This observation is consistent with the findings of Murathi (2017), where it was reported that the reduction in volatile matter is a result of enhanced thermal maturity, due to the thermal influence of the igneous intrusion (Murathi, 2017). This can be attributed to the increased heat and pressure generated by the introduction of the dolerite intrusions, which can cause the coal to undergo thermal maturation, leading to a decreased volatile matter content (Chen et al., 2014; Dai and Ren, 2007). Volatile matter has a moderately negative correlation with vitrinite reflectance as shown by an r^2 value of 0.39, implying that as the degree of coalification increases the volatile matter decreases (Figure 5.2), similar observations were made by Dukta and Godyń (2021) in a different coalfield.

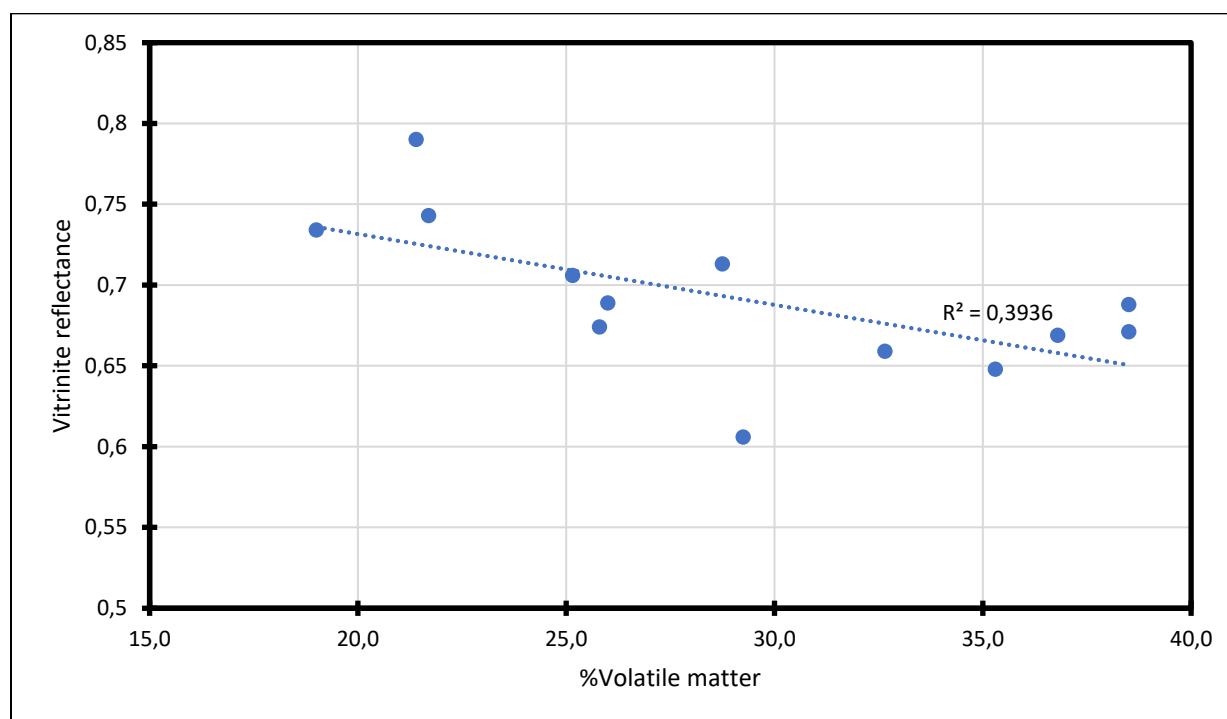


Figure 5.2: Binary plot showing the relationship between volatile matter and vitrinite reflectance.

As shown in Figure 5.3, there is a moderately negative correlation between fixed carbon and the ash content as depicted by the r^2 value of 0.68, indicating that as the ash content increases the fixed carbon content decreases resulting in lower energy yield. According

to Arnold (2013), the fixed carbon content increases as the coal rank increases. Additionally, Inherent moisture is considered to increase with the degree of coalification, the samples in the study area have a low inherent moisture content of 2.3% which is a characteristic of higher rank coals.

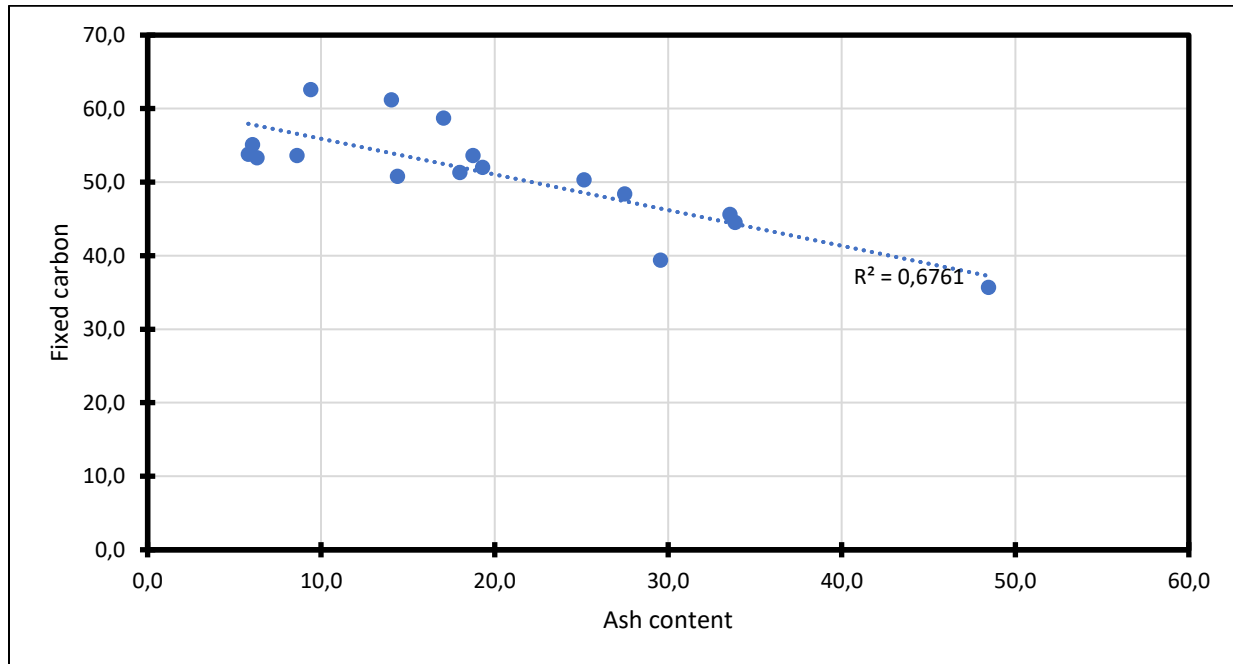


Figure 5. 3: Bivariant plot showing the relationship between fixed carbon and volatile matter.

5.3 Chemical analysis

A noticeable variation in the average sulphur content is observed among the different seams. The sulphur content decreases from the upper seam (Fritz) through to the deeper buried seam (Gus). The seams exhibit average sulphur contents of 2.3%, 1.43% and 1.23% for the Fritz, Alfred and Gus seams, respectively. The presence of sulphur in most of the samples can be associated with the presence of sulphur-bearing minerals, such as pyrite and chalcopyrite. According to Chou (2012), coal is classified as low sulphur (≤ 1 wt.%), medium sulphur (1 to 3%), or high sulphur ($\geq 3\%$). Based on this classification scheme, most samples from the Utrecht Coalfield are classified as medium sulphur coals, except samples JCBH20A, JCBH20B, CMB-S1, CMB-D, and CMB-L2, which can be classified as low sulphur coal. Sulphur in thermal coals speeds up boiler corrosion and

emits harmful sulphur dioxide during combustion (Bottle and White, 2023). The abundance of sulphur minerals in coal is influenced by factors such as seawater during peat formation and diagenesis after peat formation. It is worth mentioning that sample CMB-D which was collected close to dolerite intrusions had the lowest sulphur content of 0.98%.

The samples from this study have a high oxygen content which suggest an elevated content of fusinite macerals. Some fusinite are desirable for metallurgical applications, as it improves coke strength whereas others are not, fusinite macerals are undesirable in metallurgical applications due to their unreactive nature (Arnold, 2013). This agrees with microscopy examinations, as the dominant inertinite maceral was semifusinite. Lower-rank coals are considered to have a high hydrogen content (Rasheed et al., 2015), and the studied samples have a low hydrogen content ranging from 3.76 to 4.75. Furthermore, liptinite-rich coals generally are considered to have a higher hydrogen content. There is a strongly negative correlation between carbon and oxygen content as displayed by the r^2 value of 0.98, suggesting that as carbon increase the oxygen decreases, which satisfies the expected trend (Arnold, 2013; Figure 5.4).

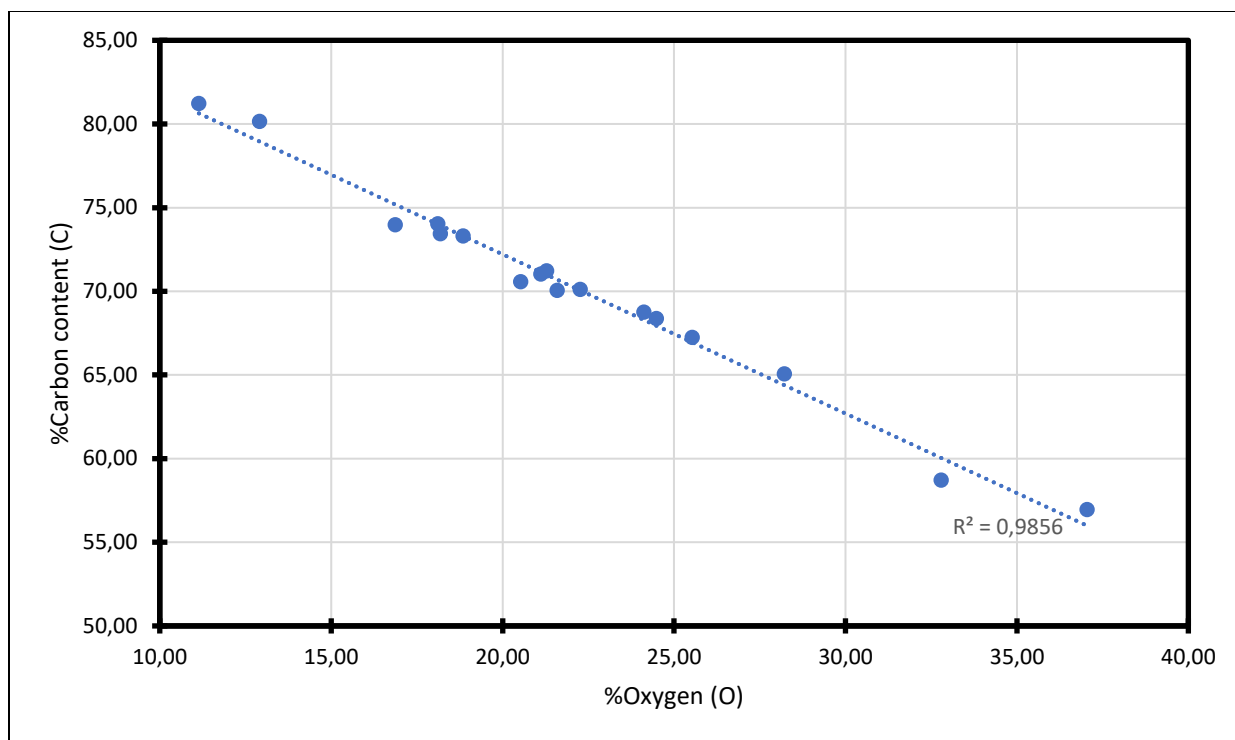


Figure 5.4: Binary plot showing the relationship between carbon and oxygen content.

The samples have a low nitrogen content ranging from 1.93-2.06%, which is considered characteristics of lower-rank coals. During the combustion of coal, nitrogen contributes to the formation of harmful emissions like nitrogen oxides (NO_x), which are one of the major pollutants (Liu et al., 2024). Carbon content is considered to increase with increasing coal rank in vitrinite-rich coals, however, there is no apparent correlation between carbon content and the vitrinite reflectance in the studied samples as shown by an r^2 value of 0.01 in Figure 5.5 (Arnold, 2023; Rasheed et al., 2015). This might be due to that, most of the samples in the study area are inertinite-rich.

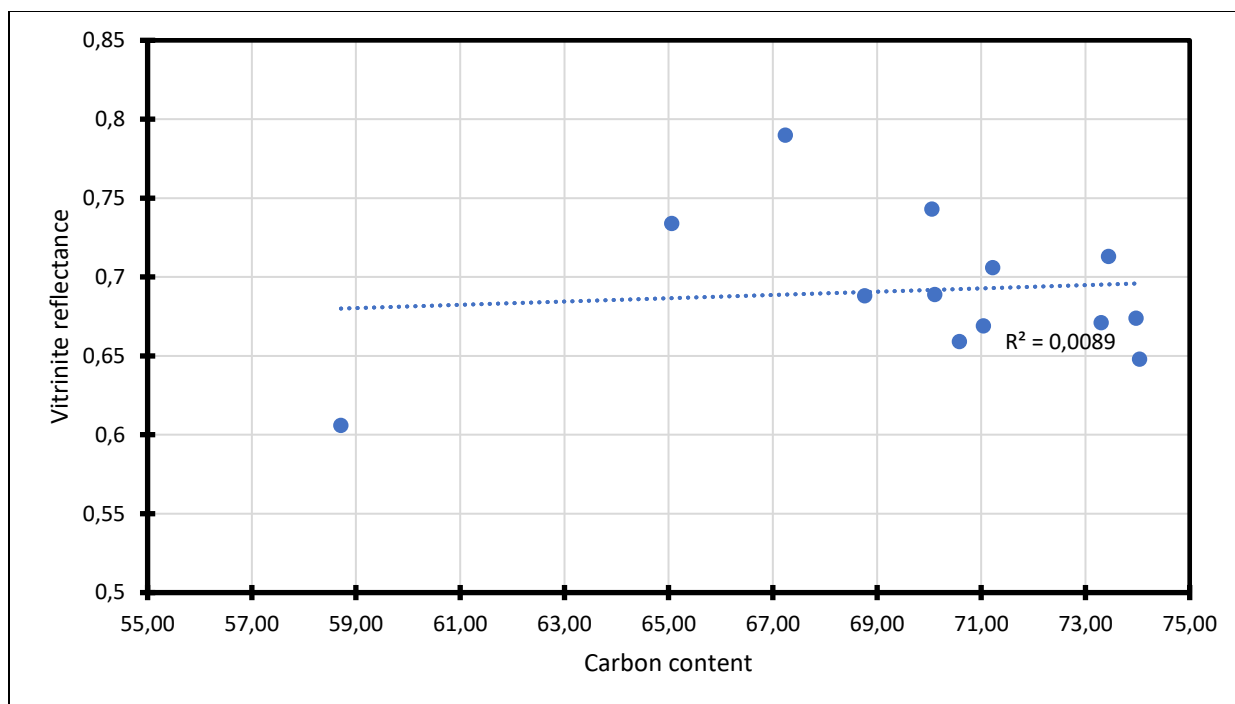


Figure 5. 5: Binary plot showing the relationship between the carbon content and vitrinite reflectance.

5.4 Mineralogy

The petrographic and XRD examinations show quartz, kaolinite, calcite, and muscovite as prevalent minerals in coal, with muscovite being relatively uncommon these observations are consistent with the findings of Xiuyi (2011). The high abundance of silicate minerals, particularly kaolinite and quartz as observed, and aligns with the mineral matter content summarized in Table A.1. As noted by Harrar (2022), the presence of aluminium silicate ($AlSiO_5$) polymorphs is responsible for the higher quantities of quartz and silica. The dolerite intruded coals recorded a maximum concentration of quartz to be 21.4%, which is nearly twice or even thrice as much as other samples. It was noted that the concentration of dolomite was very low, and this is not consistent with the study conducted by Moroeng et al. (2024), where carbonate minerals (i.e., dolomite) were observed to be higher in the dolerite intruded coals. Generally, the concentration of dolomite in the unaltered Gus coals is low, with an average concentration of 1.3%. Also,

the dolerite intruded coals have a low concentration of pyrite which is consistent with the study of Moroeng et al. (2024). The XRD was carried out to identify the REE-bearing minerals (i.e., monazite and xenotime), but due to the detection level of the analytical technique, the minerals were not identified. Although these minerals are known to be predominantly composed of REEs, monazite and xenotime are usually present in minimal amounts in coal (Ekmann, 2012). No REE-bearing minerals were identified by the XRD analysis, a study by Moorea and Esmaeilnia (2012) revealed an association between clay minerals and rare earth elements in coal.

5.5 Morphology and elemental composition (SEM-EDS)

The monazite and xenotime grains were sub-angular to sub-rounded with some grains having well-defined boundaries while others did not. There is a discrepancy between the grain sizes estimated using the scale bar on the photomicrographs, where the grain sizes were estimated to range from 2-30 μm and the results from the automated and elemental mapping. Given the precision of the automated grain size measurements, the SEM-EDS machine has determined that the monazite grain ranged from 0.50 to 2.51 μm , whereas xenotime ranged from 0.02 to 2.48 μm . Therefore, this study considers the grain sizes from the automated mineral mapping to be more accurate. The REE-bearing minerals in the samples of the Utrecht Coalfield are fine-grained, with sizes less than 3 microns, similar observations were made by Laudal (2017) in a different coalfield. As observed in Figure 4.18, the effects of compaction (a diagenetic process) caused by sediment loading, which resulted in the closed packing of grains, is observed in the albite mineral. It exhibits post-depositional (diagenetic) features, as it appears to be bending around a monazite grain. This may be indicative that the monazite was deposited before the feldspar (albite) grain, followed by mechanical deformation. Furthermore, the REE-bearing monazite might have been introduced during the early diagenetic processes or hydrothermal activities, whereas the formation of the albite grain is likely to have occurred during a later diagenetic stage.

The EDS analysis alone is insufficient for determining the elemental composition observed in the samples due to significant variations occurring in each elemental composition mapping. Consequently, some of the concentrations of the minerals were overestimated, the REE-bearing minerals (monazite and xenotime) are sub-microscopic and therefore, occur as traces in coal. Another reason for the overestimation might have occurred as a result of other minerals not being classified (Appendix B). Some of the minerals could be mostly clays (i.e., kaolinite) which were observed in both XRD and petrographic analysis. Rare earth elements (REEs) have been associated with clay minerals, organic matter, carbonates, and sulphur-bearing minerals (Seredin and Dai, 2012; Frinkelman, 1995). As denoted by Harrar et al. (2022), the REEs in the coal of the Waterberg Coalfield are associated with both organic and inorganic matter. Furthermore, the REEs are found in the cleats, and cracks or organic matrices. In the Utrecht Coalfield REEs bearing minerals are associated with both organic and inorganic minerals (Figure 4.18-20). The REEs in the samples from the Utrecht Coalfield are incorporated in authigenic kaolinite and organic matter. In sample AD3BH3A and CMB-L2, the LREES (Gd, Dy, and Y), MREES (La, Ce, and Nd), and HREES (Er, Yb) were associated with organic matter. Additionally, sample JCBH20A showed that the LREES (Gd, Dy, and Y), and MREES (La, Ce, and Nd) were associated with kaolinite and organic matter, whereas the HREES (Er, Yb) were associated with clays (i.e., kaolinite). Therefore, the samples have a mixed organic-inorganic association of REEs.

5.6 REEs distribution and geochemical insights

The average REEs concentration of the Upper Continental Crust (UCC) as determined by Taylor and McLennan (1985), is 168.4 ppm, while the average sum of REEs in the world coals is 68.5 ppm (Ketris and Yudovich, 2009; Figure 4.18). The Chinese coals were determined to have an average sum of REEs concentration of 137.9 ppm (Dai et al., 2008; Dai et al., 2012), and the average sum of REE concentration of the USA coals was determined to be approximately 62.1 ppm (Finkelman, 1993). The samples of the Utrecht Coalfield have an average sum of REEs concentration of 101.4 ppm, which is less than the UCC and Chinese coals, but it has an average REEs that is greater than

both the USA and Worlds coals, except for five samples from the Gus seam which have a TREEs concentration that is less than 48 ppm (Figure 4.21). The four samples (CB1-L1, CB2-L1, JCBH20B, and JCBH20) exceeded the TREEs concentration of the Chinese coals. Of the four samples, two are from the Gus seam and the other two are from the Alfred seam.

The Alfred seam has an average TREEs of 137.6 ppm, which is closer to that of the Chinese coals (Figure 4.21). All the seams have an average TREEs concentration that is greater than that of the Worlds, and USA coals. The seams are enriched with LHREE, this agrees with the general distribution of REEs in coals (Dai et al., 2008). The Alfred seam is relatively more enriched with REEs than the other two seams, followed by the Fritz seam (120.8 ppm) and the seam appears to be less enriched in REEs being the Gus seam (79.5 ppm). This follows the same pattern of the average ash content of the seams as observed in Section 4.2.4, suggesting that high ash content is associated with a higher concentration of REEs. The coal samples that are closer to the Karoo dolerites have concentrations of 154.1 ppm (CMB-D) and 95.3 ppm (CB2-D), the samples near the intrusions have TREEs concentrations higher than that of World's and USA coals, while the sample CMB-D has a concentration that is higher than that of Chinese coals (Figure 4.21). The TREEs concentration appears to increase towards the igneous intrusion; it was also observed that the ash content increased due to the coal-dolerite contact (Moroeng et al., 2024). In this study, the highest REEs concentration recorded was 172.3 ppm, which exceeds the 148 ppm reported for the main Karoo Basin (MKB) coals in South Africa by Wagner and Matiane (2018). However, it is lower than the 389 ppm, found in density-fractionated Waterberg coals by Chitlango et al. (2023).

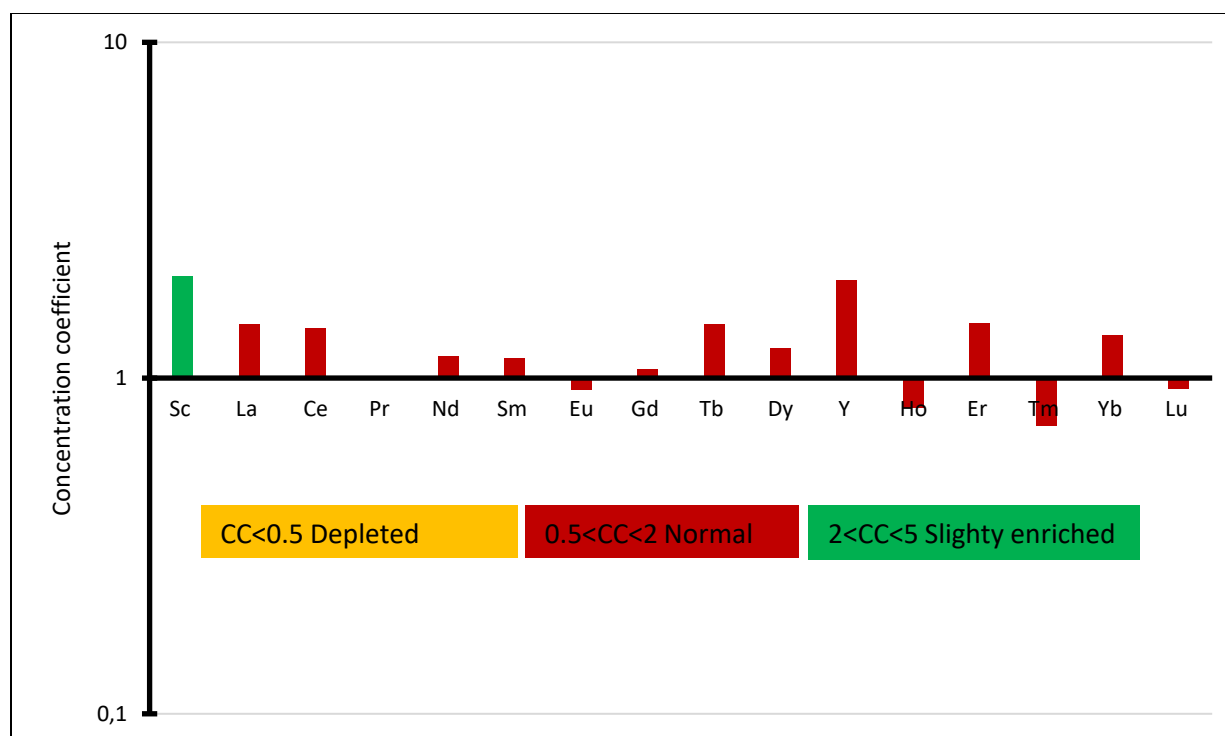


Figure 5.6: Average concentration coefficients (CC) of trace elements in coal samples of the Utrecht Coalfield.

Ketris and Yudovich (2009) and Dai et al. (2016) developed a classification system for trace elements in coal. This system is based on the concentration coefficient (CC), which compares the concentration of elements in a specific sample to the average concentrations of world hard coals (Ketris and Yudovich, 2009). As indicated, a CC value of less than 0.5 indicates depletion, while a CC between 0.5 and 2 is regarded as normal. Values between 2 and 5 suggest slight enrichment, those between 5 and 10 indicate enrichment, and values from 10 to 100 are classified as significant enrichment. A CC greater than 100 denotes unusual enrichment (Dai et al., 2016). The plot of the relative enrichment of trace elements of the studied coal samples on the classification system of Ketris and Yudovich (2009) and Dai et al. (2016) shows that the samples of the Utrecht Coalfield have normal enrichment of trace elements (REEs) relative to world coals, with average CC values ranging between 0.5 and 2 (Figure 5.6). Some samples exhibited slight enrichment of elements Sc, Y, Er, and Yb with $2 < CC < 5$ values (Figure 5.7).

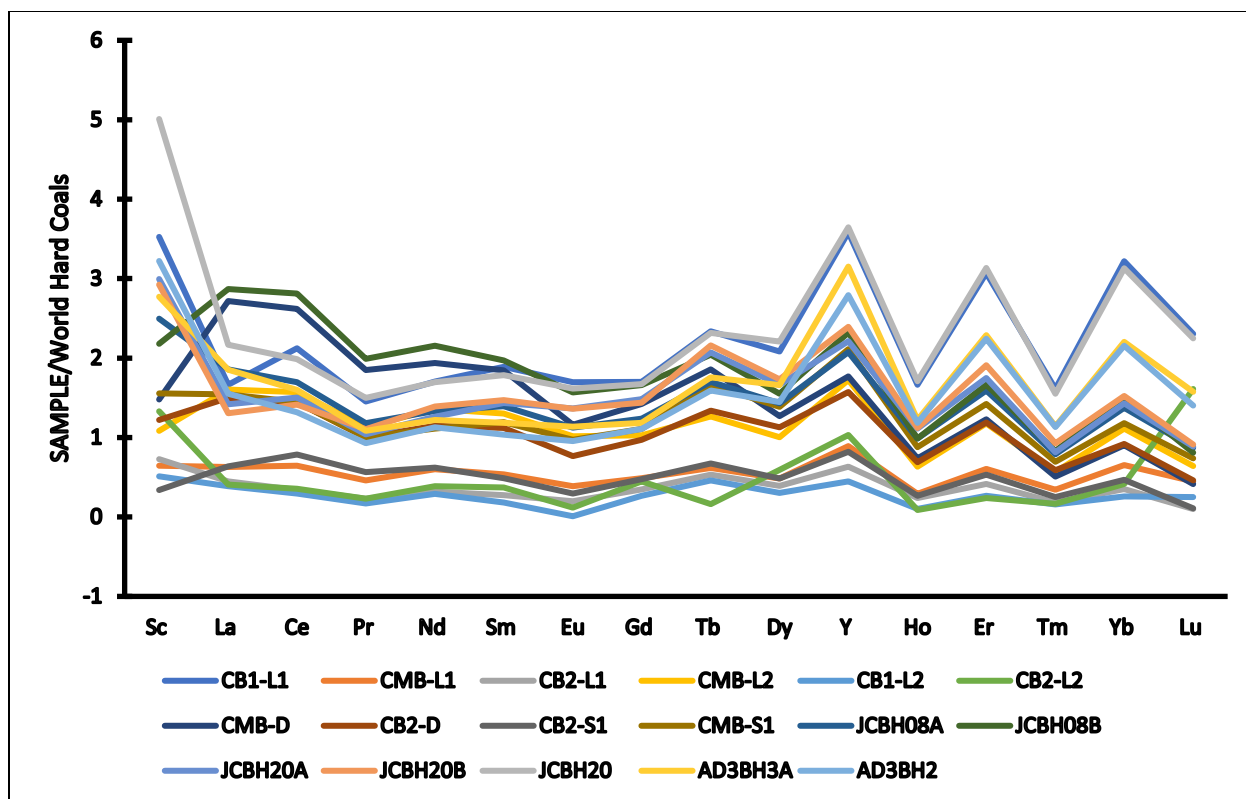


Figure 5.7: Concentration coefficients (CC) of all samples.

The ash content was plotted against the LREEs:HREEs ratio and the data shows that there is a weak positive correlation between the ash content and the ratio LREEs:HREEs. This is also revealed by the trendline with an r^2 value of 0.162, as shown in Figure 5.8. In addition, the binary plot of the TREEs concentration against the ash content shows that the TREEs concentration generally decreases as the ash content decreases. This is consistent with the trendline, showing a positive r^2 value of 0.613, suggesting that higher TREEs concentration is associated with elevated ash content in all the samples (Figure 5.9).

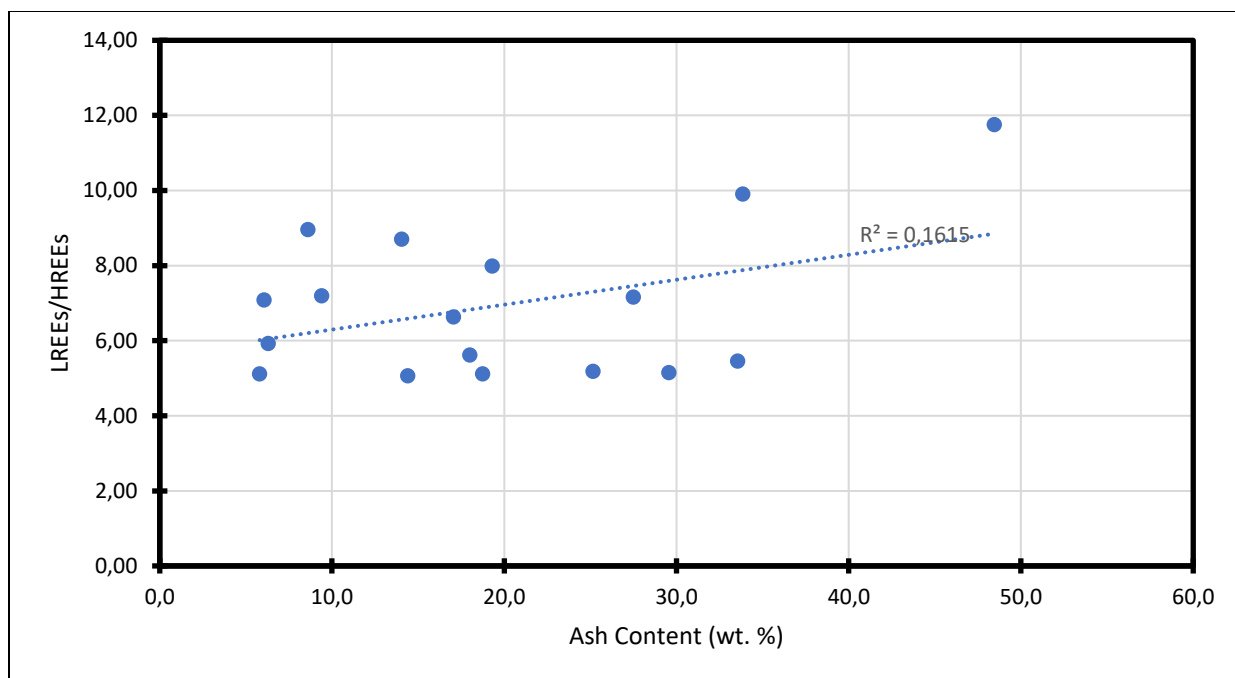


Figure 5.8: Binary plot of the ash content versus LREE/HREE for the studied samples.

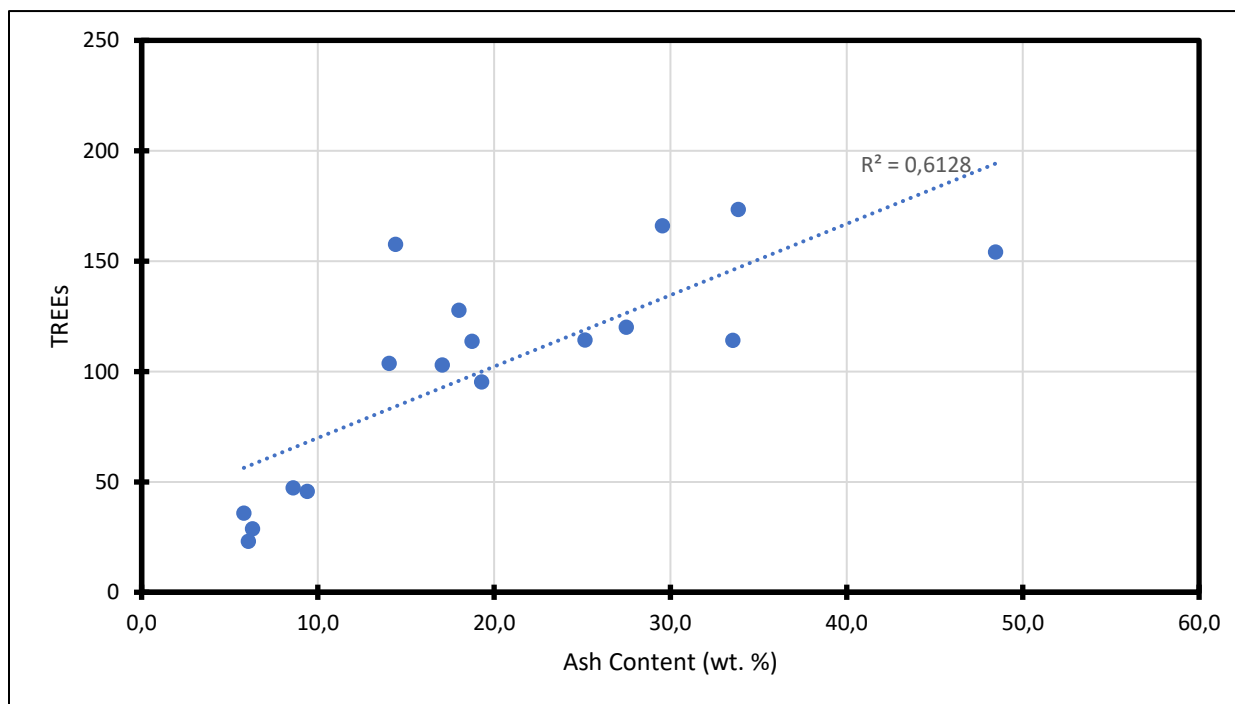


Figure 5.9: Binary plot showing the total REE (ash basis) versus ash content of the sample.

As observed in Figure 5.10, there is a statistical relationship between fixed carbon and the sum concentration of REEs (TREES), as depicted by an r^2 value of -0.4138. Similarly, there is a statistical relationship between volatile matter and TREES, as shown by the r^2 value of -0.4046 (Figure 5.11). This is indicative of a moderately negative correlation between volatile matter and fixed carbon, suggesting that the concentration of REEs increases as the concentration of volatile matter and fixed carbon decreases. There is no correlation between vitrinite reflectance and the concentration of REEs in the samples from the Utrecht Coalfield, with an r^2 value of 0.013, suggesting that there is no statistical relationship between the total concentrations of REEs and vitrinite reflectance (Figure 5.12).

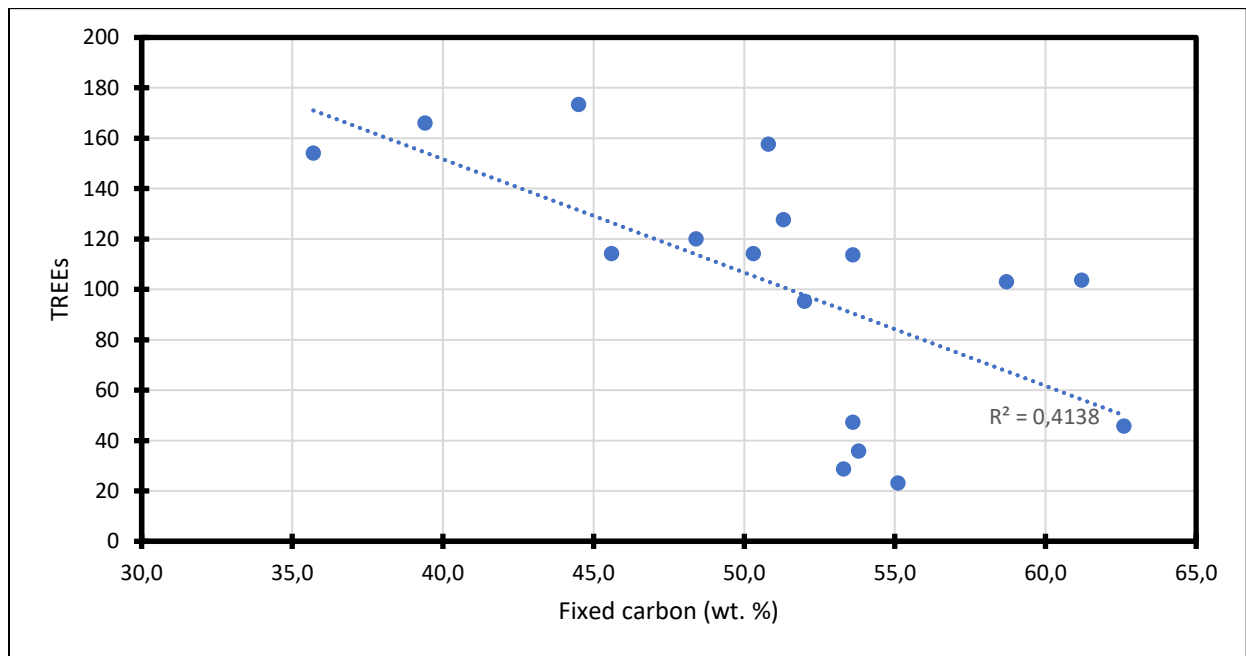


Figure 5.10: Binary plot showing the total concentration of REEs versus fixed carbon.

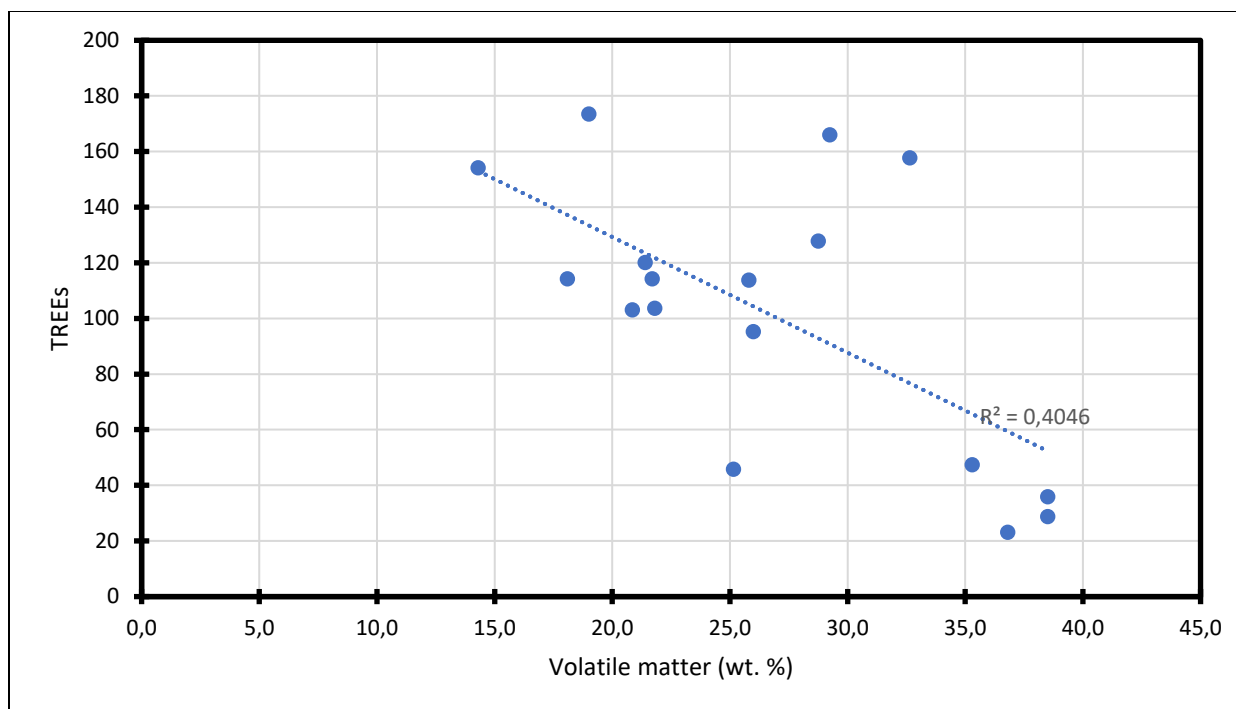


Figure 5.11: Binary plot showing the relationship between TREES and volatile matter.

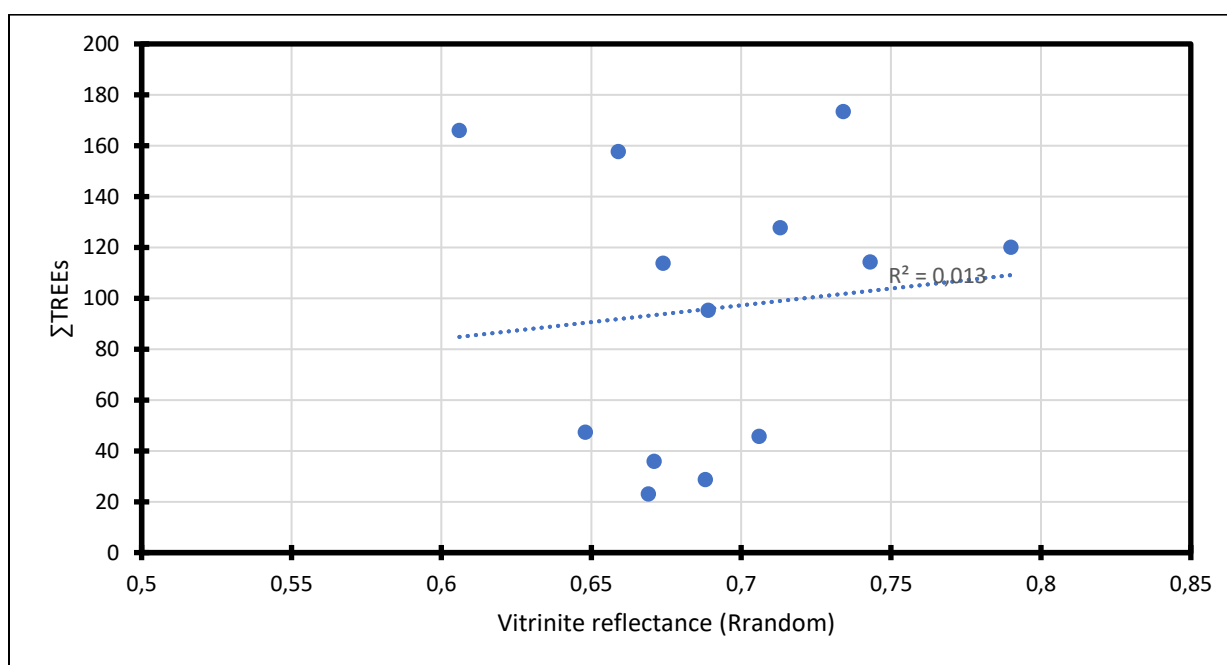


Figure 5.12: Binary plot showing the relationship between vitrinite reflectance and TREES.

5.6.1 Normalized Distribution patterns of REEs by zones

The concentration of REEs and distribution patterns in the coals are normalized to the Upper Continental Crust (UCC) for comparative purposes. The coals can be enriched or depleted with LREE, MREE and HREE when compared to the UCC (Ardakani et al., 2022). According to the REEs classification by Seridin and Dai (2012), three types of REEs enrichments aid in explaining the distribution patterns of REEs in coal. These types are the L-type distribution (LREEs; $La_N/Lu_N > 1$), M-type distribution (MREEs; $La_N/Sm_N > 1$ or $Gd_N/Lu_N > 1$) and H-type distribution (HREEs; $La_N/Lu_N < 1$) which are presented in Table 5.3. According to Harrar et al. (2022), these distribution patterns or ratios can provide information on the REEs during peatification. The coal samples from the Gus seam, CB1-L1, CMB-L1, CB2-L2, are characterised by the H-type and M-type distribution pattern, with sample CB1-L2 having only an H-type enrichment (Figure 5.13), whereas the samples CB2-L1, CMB-D, CB2-D are characterised by both the M-type and L-type distributions (Figure 5.14). The samples CMB-L2, CB2-S1 and CMB-S1 are characterised by L-type enrichment relative to the upper continental crust (UCC). The samples from the Alfred seam, JCBH08A and JCBH08B are characterised by L-type enrichment while samples JCBH20, JCBH20A and JCBH20B are characterised by H-type and M-type enrichment (Figure 5.15). Both samples from the Fritz seam are characterised as having an H-type enrichment (Figure 5.16)

Table 5.3: Anomalies and enrichment patterns for REEs in the Utrecht Coalfield.

SEAM	Sample ID	LaN/LuN	LaN/SmN	GdN/LuN	CeN	EuN	GdN	YN/HoN	CeN/LaN	Ce anomaly	$\delta\text{Ce}/\delta\text{Eu}$	LaN/YbN	LaN/YN (Chondrite)	REE deff, rel%	Coutlook
GUS	CB1-L1	0.42 H	0.66 M	0.84	1.17	0.84	1.14	1.13	1.25	0,08	1.40	5.72	3.56	37.25	1.09
	CMB-L1	0.82 H	0.88 M	1.23	1.03	0.69	1.21	1.60	1.01	-0,01	1.50	9.86	5.42	36.03	1.04
	CB2-L1	2.62 L	1.22	3.93	0.89	0.55	1.13	1.39	0.74	-0,12	1.60	12.25	5.44	36.50	1.26
	CMB-L2	1.46 L	0.93 M	1.82	1.00	0.79	1.18	1.43	0.96	-0,02	1.27	16.00	7.14	33.37	0.91
	CB1-L2	0.90 H	1.58	1.22	0.94	0.03	1.06	2.29	0.75	-0,12	29.27	14.00	6.59	35.43	1.16
	CB2-L2	0.15 H	0.82 M	0.32	0.98	0.39	2.85	6.16	0.86	-0,08	2.54	11.25	3.01	40.96	1.64
	CMB-D	3.85 L	1.11	3.91	1.00	0.63	1.12	1.26	0.94	-0,02	1.59	33.22	11.78	27.75	0.69
	CB2-D	1.91 L	1.00	2.40	1.01	0.64	1.12	1.20	0.94	-0,02	1.57	18.33	7.32	32.52	0.89
	CB2-S1	3.43 L	0.98 M	4.98	1.12	0.54	1.14	1.60	1.21	0,07	2.09	14.00	5.95	33.92	0.86
	CMB-S1	1.23 L	0.97 M	1.70	1.00	0.72	1.07	1.26	0.92	-0,03	1.38	14.17	5.61	34.90	1.02
ALFRED	JCBH08A	1.25 L	1.00	1.62	0.98	0.75	1.13	1.10	0.90	-0,04	1.30	14.57	6.86	32.16	0.93
	JCBH08B	2.08 L	1.09	2.33	1.01	0.79	1.20	1.23	0.96	-0,01	1.28	21.07	9.49	29.47	0.76
	JCBH20A	0.94 H	0.74 M	1.90	1.06	0.83	1.17	1.04	1.04	0,01	1.28	11.14	4.93	34.79	1.07
	JCBH20B	0.84 H	0.66 M	1.79	1.01	0.80	1.09	1.12	1.06	0,00	1.25	9.53	4.18	37.72	1.23
	JCBH20	0.57 H	0.91 M	0.85	0.94	0.83	1.14	1.12	0.90	-0,04	1.14	7.71	4.56	35.79	1.17
FRITZ	AD3BH3A	0.69 H	1.17	0.85	0.96	0.83	1.11	1.35	0.85	-0,06	1.15	9.27	4.51	37.03	1.17
	AD3BH2	0.65 H	1.12	0.90	0.93	0.79	1.15	1.23	0.83	-0,07	1.19	7.77	4.26	37.47	1.26

According to Seredin and Dai (2012), the L-type REEs distribution originates from terrigenous or tuffaceous origin, where the REEs input in the coal occurred during the early diagenetic stage or peatification. Conversely, REEs exhibiting the M-type distribution have various potential sources. However, Johannesson and Zhou (1999) constrained the source for the M-type REEs distribution to be acidic terrestrial waters, including hydrothermal solutions. The H-REEs distribution in coals is generally associated with neutral waters, which circulate within the coal-bearing basins (Seredin and Dai, 2012). The Utrecht Coalfield samples have mixed origins, as supported by the different distribution patterns (i.e., LREEs, MREEs, and HREEs) relative to the UCC, as tabulated in Table 5.1, only one seam, the Fritz seam had one origin depicted by the HREEs enrichment inferred to from neutral waters.

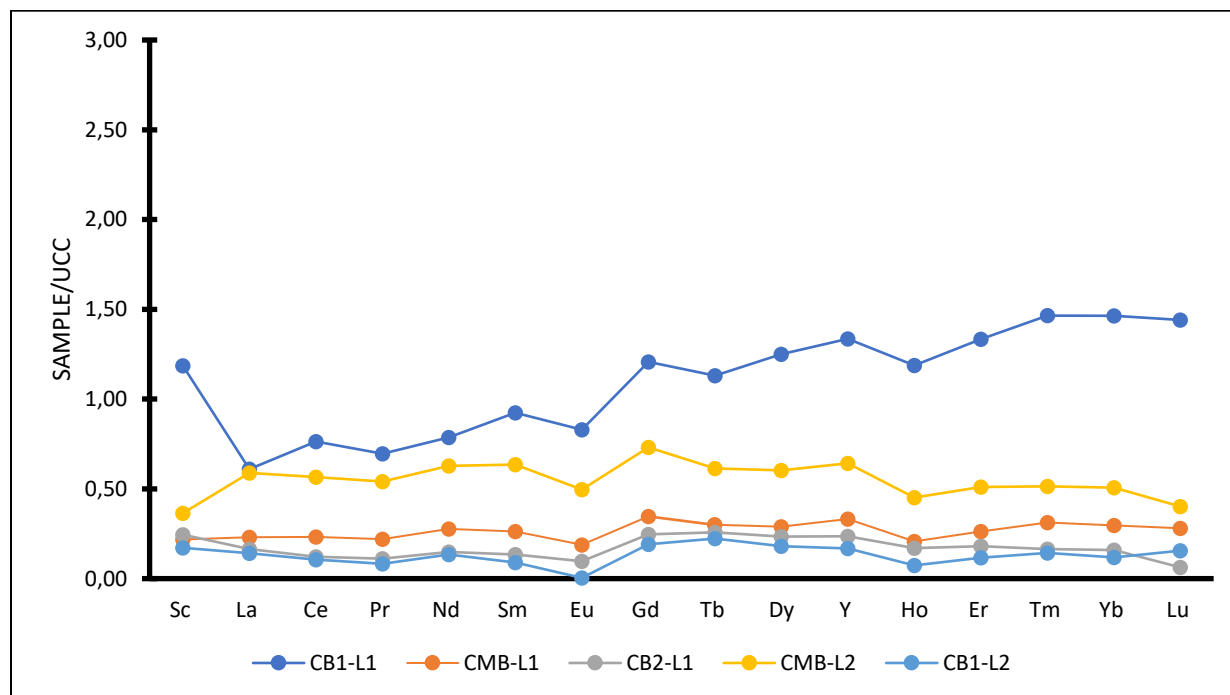


Figure 5.13: UCC normalized REEs distribution patterns of the Gus Seam.

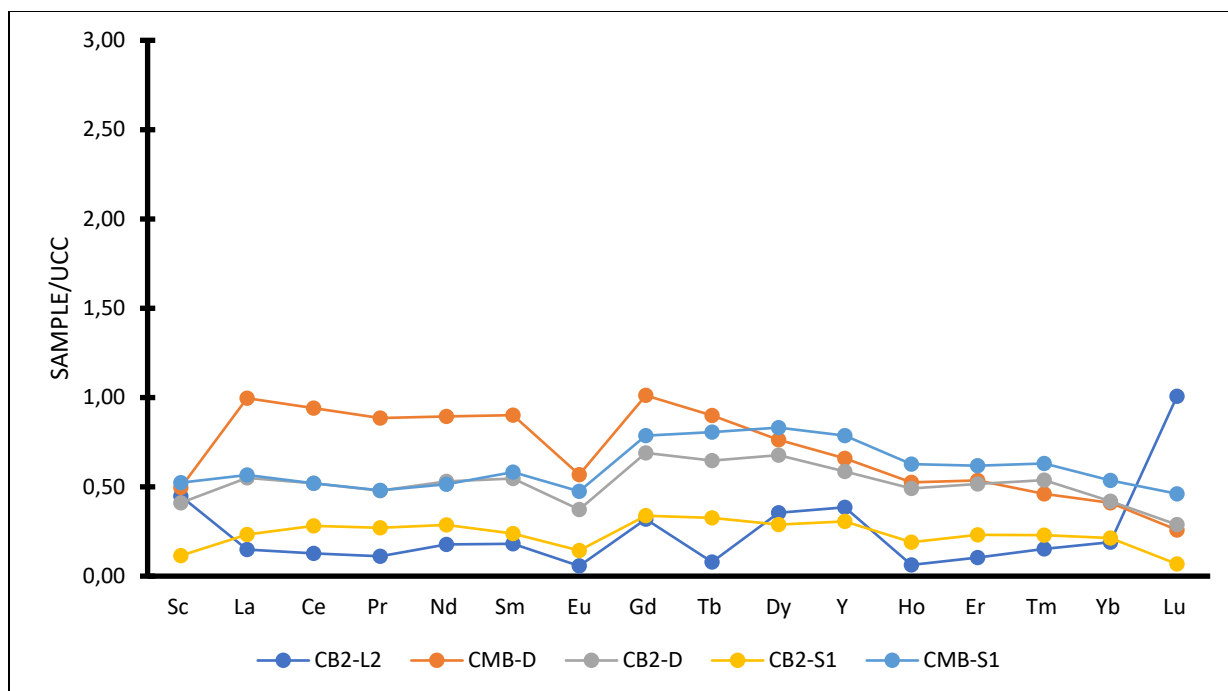


Figure 5. 14: UCC normalized REEs distribution patterns of the Gus Seam.

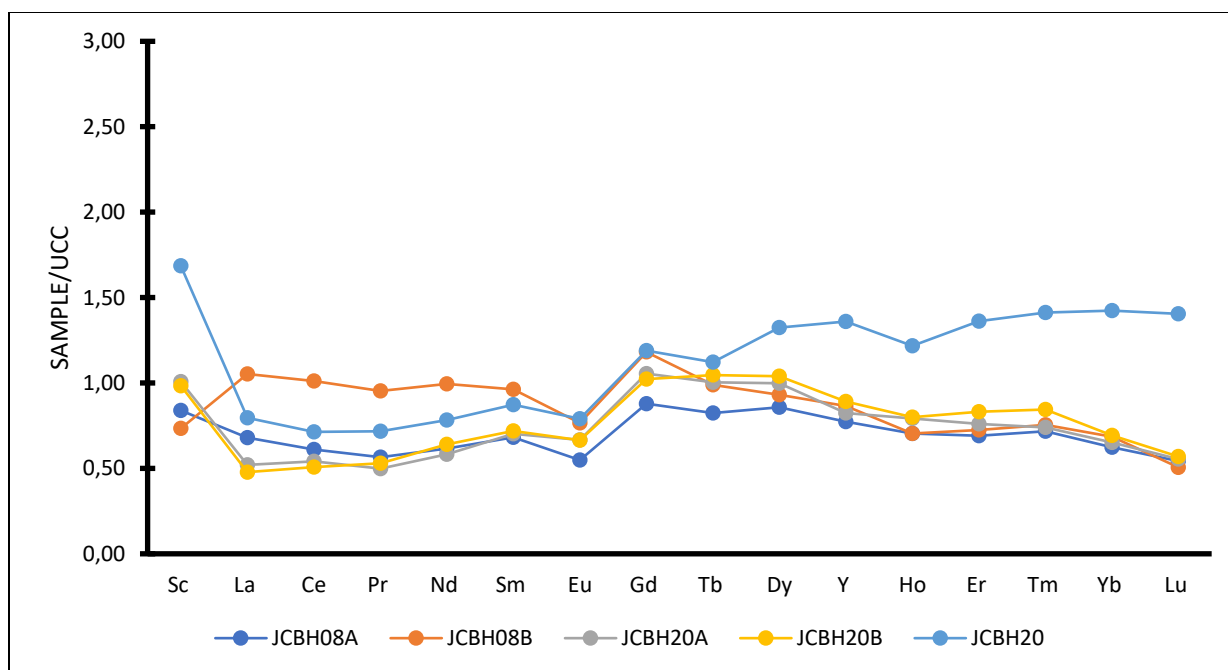


Figure 5. 15: UCC normalized REEs distribution patterns of the Alfred Seam.

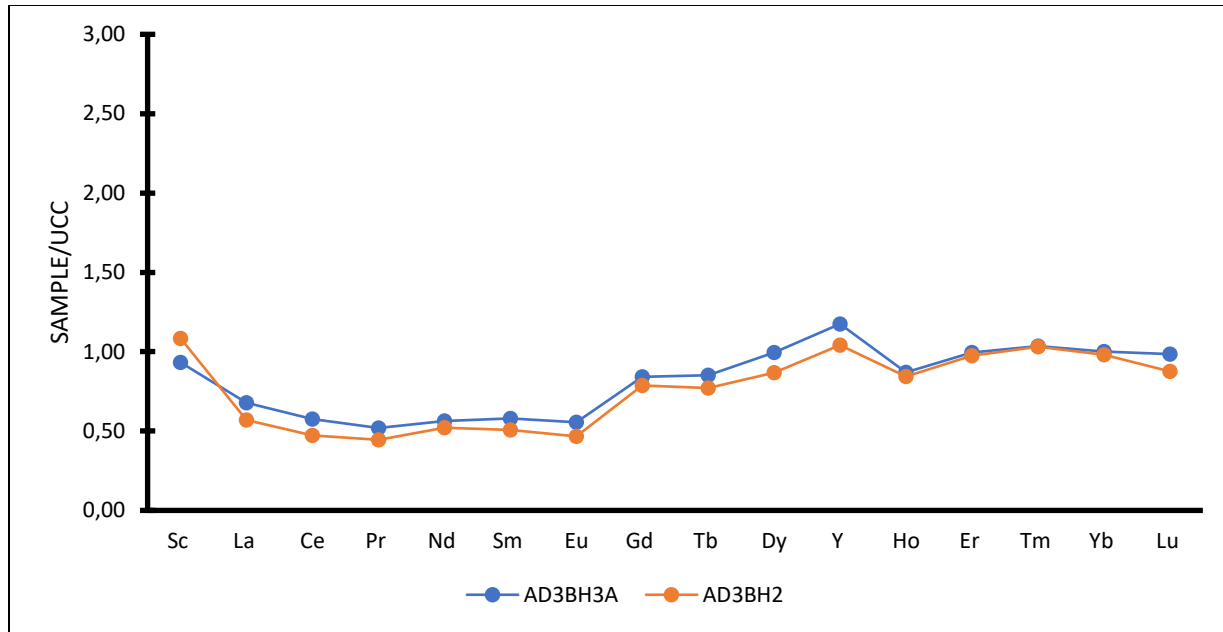


Figure 5.16: UCC normalized REEs distribution patterns of the Fritz Seam.

5.6.2 Sediment source region

The source region of the sediment, post-depositional, and depositional environment histories of coal-bearing sediments can be inferred by using the Ce, Eu, Gd and Y anomalies (Dai et al., 2016). Ce and Eu are redox sensitive, and their anomalies are commonly observed, whereas anomalies of non-redox sensitive elements (i.e., Y, La, and Gd) may also be observed (Hussain and Luo, 2020; Dai et al., 2016). To measure the separation of Eu, Gd, and Ce from other REEs and identify anomalies, values less than 1 indicate negative anomalies, whereas values greater than 1 indicate positive anomalies. The following equations were adopted from Dai et al. (2016):

$$\frac{Ce_N}{Ce_N} = Ce_N / (0.5La_N + 0.5Pr) \dots\dots\dots (8)$$

$$\frac{Eu_N}{Eu_N} = Eu_N / (0.67Sm_N + 0.33Tb_N) \dots\dots\dots (9)$$

$$\frac{Gd_N}{Gd_N} = Gd_N / (0.33Sm_N + 0.67Tb_N) \dots\dots\dots (10)$$

The Ce_N/Ce_N ratio of the samples ranges from 0.89-1.17. On average, the samples generally show no anomaly with an average Ce_N of 1.00 (Table 5.3). The samples from the Fritz seam exhibit a weakly negative cerium anomaly. The samples from the Alfred seam showed a weakly positive Ce_N anomaly, while some samples exhibited a weakly negative to no anomaly. The samples from the Gus seam show a weakly positive and negative cerium anomaly, with some samples having no anomalies. The cerium anomaly in the studied coal samples is controlled by the geochemical composition of the sediment source region (Dai et al., 2016). The different anomalies (i.e., weakly negative and positive) observed in the samples are indicative that the sediment source of the materials and epigenetic minerals are different. Furthermore, the sediment source regions that are dominated by mafic basalts exhibit no Ce_N anomalies, whereas the sediment source regions that are dominated by felsic-intermediate rocks are characterised by a negative cerium anomaly. The positive Ce_N anomalies are indicative that hydrothermal injections may be the sediment source region (Dai et al., 2016).

Most of the samples (normalized to the UCC) exhibited weakly negative Eu_N anomalies (Figure 5.13-5.16), whereas 4 samples exhibited strongly negative Eu_N anomalies. The Eu_N/Eu_N ratio ranges from 0.03-0.84. The sample CB1-L2 has a very strongly negative Eu_N anomaly. According to Dai et al. (2016) and Taylor McLennan (1985), Eu_N anomalies are generally not associated with the transportation or weathering processes of the sediment source region to the peat. Instead, Eu_N anomalies are inherited from the parent source rocks. Furthermore, coals from a felsic or felsic-intermediate terrigenous input material exhibit negative europium anomalies. The observed negative europium anomalies may also be a result of the alteration of k-feldspar during the kaolinization process to form kaolinite (Chitlango, 2023).

In addition, the studied coal exhibits a positive yttrium anomaly relative to the UCC. The occurrence of a positive Y_N anomaly in the samples could be explained by the presence of calcite in the coal samples. As reported by Chitlango (2023), the calcite in the studied coal often filling cleats and cracks of organic macerals. All hydrogenic deposits are thought to be having a negative Y_N anomaly (Ardakani et al., 2022). A weakly positive Y_N anomaly in coal is indicative of a basaltic sediment source region, while a felsic sediment

source region normally shows no or weak anomalies (Dai et al., 2016). The Gd_N/Gd_N ratio of the samples ranged from 1.06-2.85. Generally, the samples exhibit positive gadolinium anomalies, with sample CB2-L2 having a very strongly positive anomaly. A positive Gd_N anomaly occurs due to the influence of hydrothermal fluids and seawater (Dai et al., 2016).

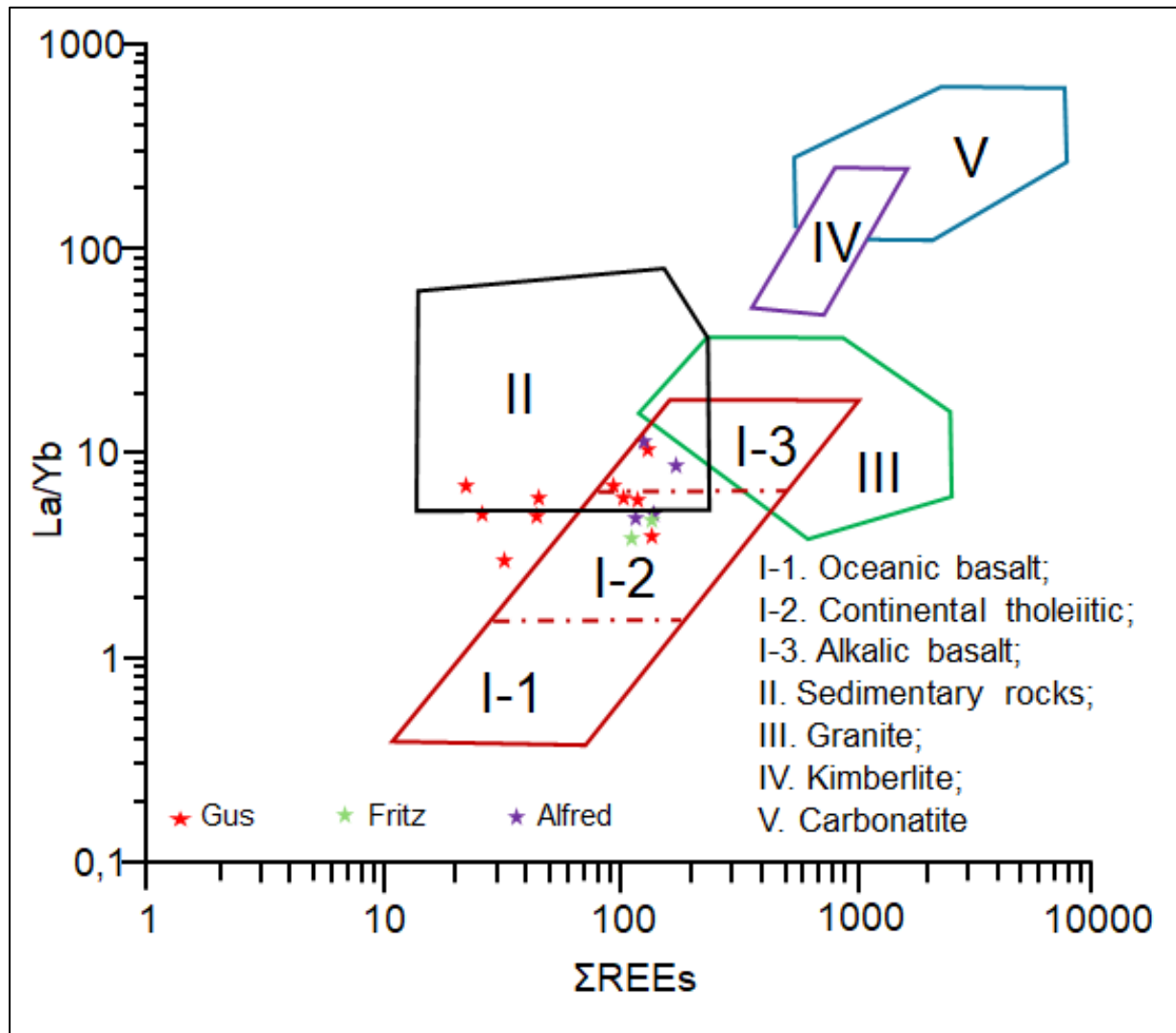


Figure 5.17: La/Yb-ΣREEs diagram normalized to chondrite (after Allegre` and Minster 1978).

In addition to REEs parameters (Ce_N/Ce_N , Eu_N/Eu_N , and Gd_N/Gd_N), provenance analysis was conducted using La/Yb- Σ REEs diagram (Figures 5.17 and 5.18). The concentrations of La and Y were normalized to chondrite values using the method of Allegre and Minster (1978) to show the characteristics of source rocks (Figure 5.17). Furthermore, the concentrations were normalised to the UCC (Figure 5.18). As shown in Figure 5.17, the samples from the Utrecht Coalfield plotted in the sedimentary rock area, continental tholeiitic, and alkalic basalt areas of the crossplot, whereas in Figure 5.18, the samples normalised to the UCC, plotted in the sedimentary rocks, continental tholeiitic, alkalic basalt and granite area of the crossplot.

The samples from the Utrecht Coalfield, when normalised to chondrite values, exhibit REEs distribution patterns similar to those of the upper continental crust (UCC). These patterns show an enrichment of LREEs compared to HREEs, which supports the idea that HREEs are more easily leached and transported by seawater, suggesting that the material likely originates from the UCC (Chunlan et al., 2022; Chen et al., 2017). The coal samples show characteristics of mixed provenance, as shown by the two crossplots, indicating a combination of sedimentary rocks, alkalic basalt, tholeiitic basalts, and granite signatures, suggesting a depositional environment influenced by both continental materials and input from igneous sources. The granites from the Namaqua Natal Mobile Belt and Pre-Karoo basement (i.e., Kaapvaal cratonic) rocks may have been one of the sources of felsic rocks, which resulted in the negative Eu_N/Eu_N anomalies leading to the enrichment of LREEs (Zho et al., 2019; Nethenzheni, 2016). The dolerite intrusions observed in the area could explain the no Ce_N/Ce_N anomalies and the samples that plotted in the tholeiitic and alkali basaltic areas of the crossplot, inferring a basaltic source region. According to Galerne et al. (2011), the Karoo dolerites predominantly consist of tholeiitic basalts to basaltic andesite.

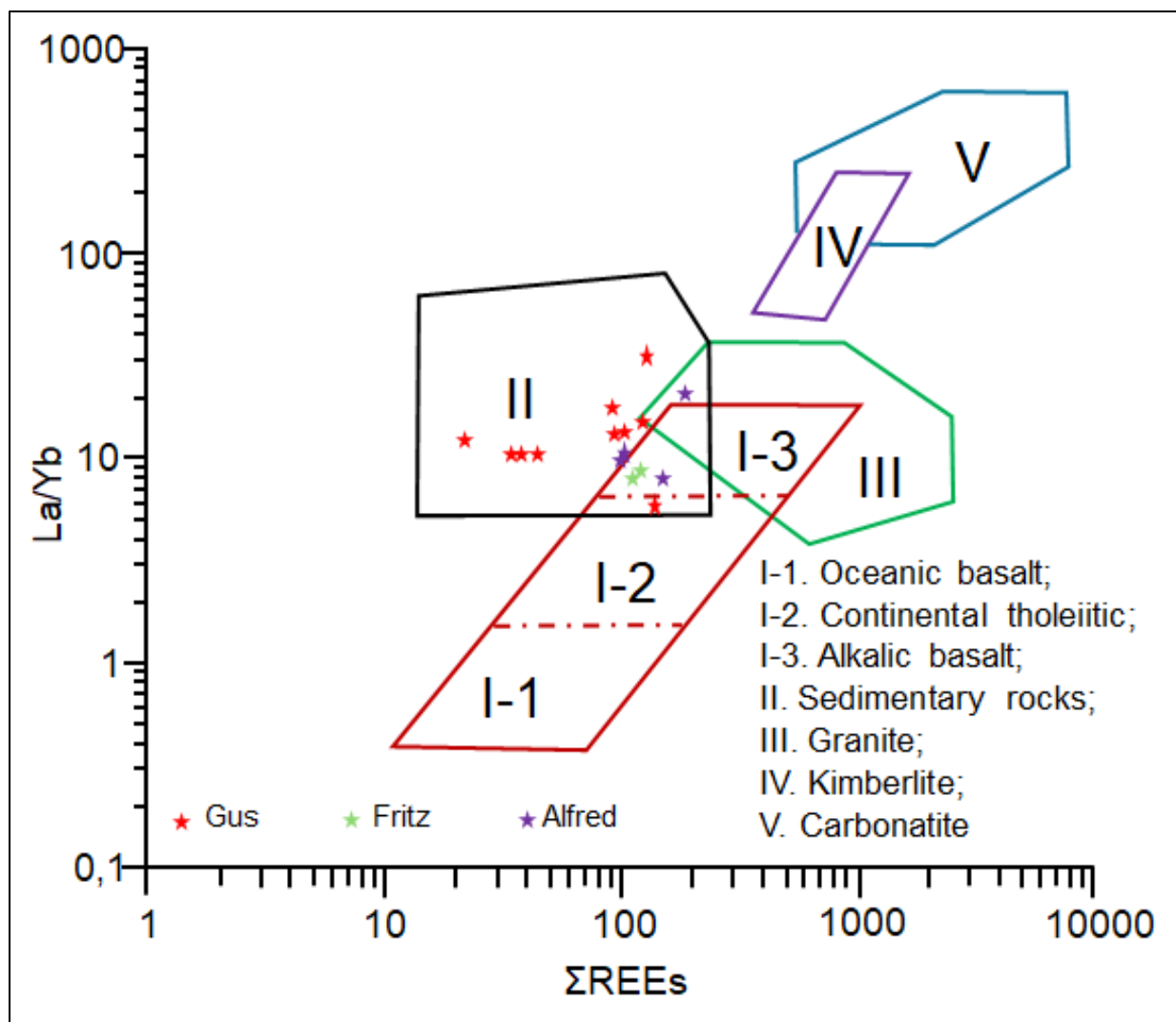


Figure 5.18: La/Yb-ΣREE diagram normalised to the UCC.

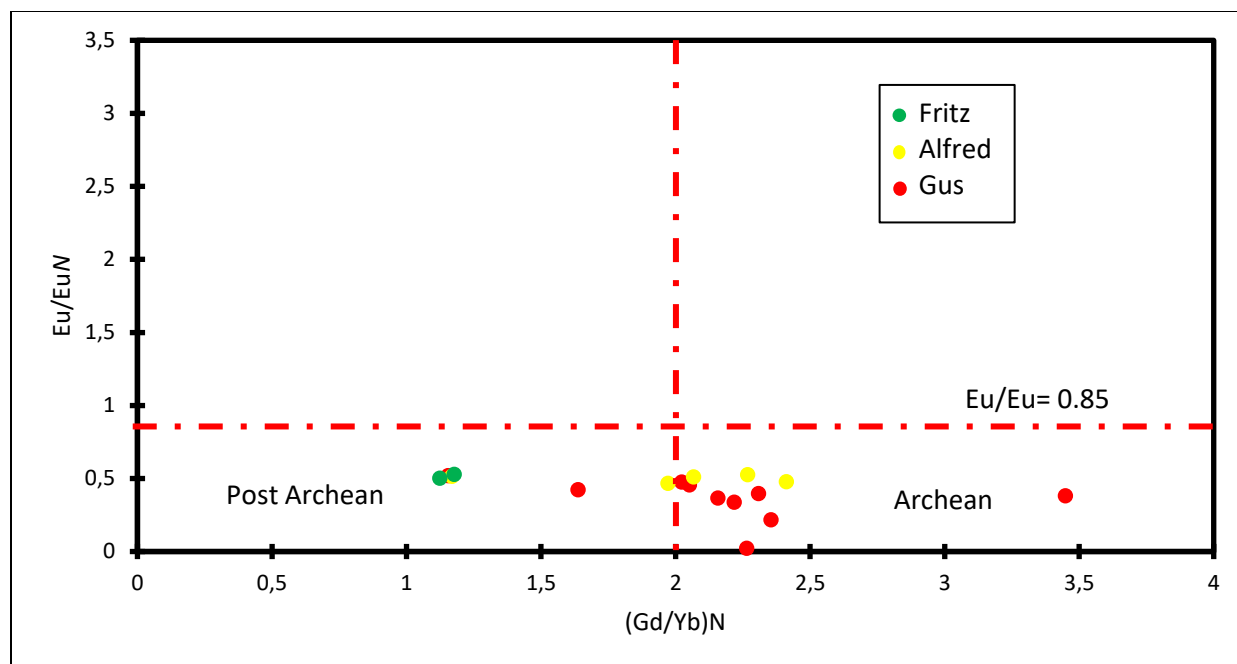


Figure 5.19: Diagram showing the relationship between Eu/Eu_N and $(\text{Gd}/\text{Yb})_N$ normalised to chondrite values.

The relationship between Eu/Eu_N and $(\text{Gd}/\text{Yb})_N$, normalized to chondrite values, was used to infer geological ages (Zhao, 2000). Samples from the Fritz seam plotted within the post-Archean field of the crossplot, while most samples from the Alfred and Gus seams plotted in the Archean field, with some also in the post-Archean. This distribution suggests that the source rocks include both Archean and post-Archean materials, supporting mixed provenance for the sediments.

5.6.3 Redox conditions

The crossplot of $\sum \text{TREEs} - \delta\text{Ce}/\delta\text{Eu}$ was used to determine the redox conditions of the coal seams during formation. Berry and Wilde (1976) investigated the relationship between water depth and redox conditions in formation water, suggesting that deeper water bodies tend to experience more reducing conditions due to limited oxygen penetration. According to Wen et al. (2024), if the $\delta\text{Ce}/\delta\text{Eu}$ value is less than 1, it suggests the presence of an oxidizing environment during coalification, whereas a value greater

than 1 indicates an acidic reducing environment. All the samples of the Utrecht Coalfield had a $\delta\text{Ce}/\delta\text{Eu} > 1$, suggesting that the environment during coalification was an acidic reducing environment (Figure 5.20).

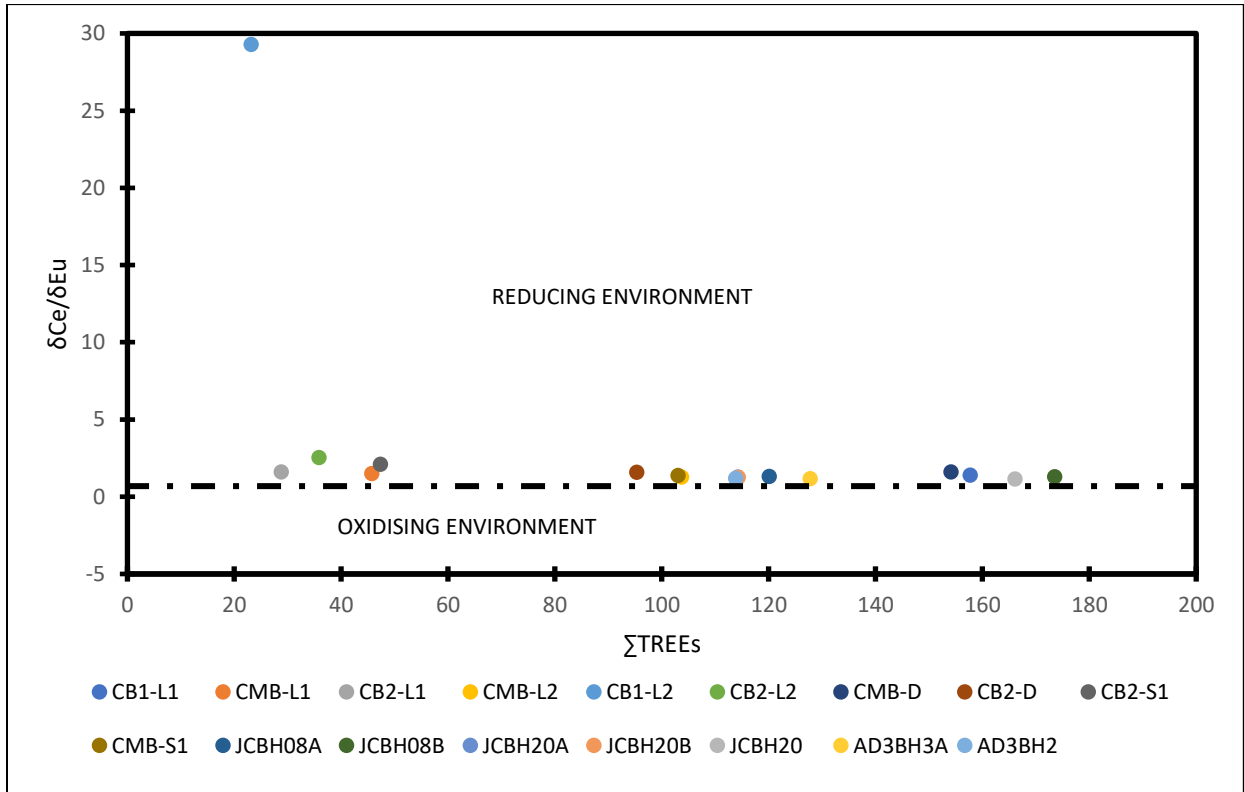


Figure 5.20: Relationship between $\delta\text{Ce}/\delta\text{Eu}$ and ΣREEs . Where $\delta\text{Ce} = \text{Ce}_N/\text{Ce}_N$ and $\delta\text{Eu} = \text{Eu}_N/\text{Eu}_N$.

According to Bao et al. (2011), Ce/La ratios can be used to infer environmental conditions. Furthermore, Ce/La values that are less than 1.5 indicate an oxygen-rich environment, while values between 1.5 and 2 suggest anaerobic conditions, and values above 2 represent a strongly anaerobic setting. In the Utrecht Coalfield, the Ce_N/La_N ratios range from 0.74 to 1.25, placing all the samples within an oxygen-rich environment. Furthermore, using the Ce anomaly (Ce_{anom}) calculation proposed by Elderfield and Greaves (1982):

$$Ce_{anom} = \log(Ce/(2La_N + Nd_N)) \dots\dots\dots (11)$$

Where $Ce_{anom} > -0.1$ signifies Ce enrichment and a reducing anoxic environment, and $Ce_{anom} < -0.1$ suggests a loss of Ce and an oxidising environment.

Most of the samples from the Utrecht Coalfield exhibit Ce_{anom} values greater than -0.1, ranging from -0.08 to 0.08, except for two samples (i.e., CB2-L1, CB1-L2) from the Gus seam having Ce_{anom} values of -0.12 which is lesser than -0.1. This indicates Ce enrichment and depletion in both reducing anoxic and oxidising environment. This places most of the samples reducing environment on the crossplot, suggesting that the environment was weakly reducing (Figure 5.21). Two samples from the Gus seam plotted in the oxidising environment area of the crossplot, suggesting that the environment was weakly oxidising. Therefore, both diagrams combined with the Ce/La ratios lesser than 1.5 (Figures 5.19 and 5.20) revealed that the coal-forming environment of the Uitkomst Colliery (Utrecht Coalfield) had a combination of weakly reducing and oxidising conditions, suggesting an environment with limited oxygen allowing the preservation of organic matter in sediments which is characteristic of swampy wetlands of the Main Karoo Basin observed during the coalification process (Catuneanu et al., 2005). According to Cairncross (2001) and Falcon and Snyman (1986), the elevated inertinite content in the coals of the Vryheid Formation implies periods of oxidation and microbial degradation during peatification, potentially due to intermittent exposure to atmospheric oxygen. In the Utrecht Coalfield, the presence of both inertinite- and vitrinite-rich samples also further supports a dynamic depositional environment, where oxidation and reducing conditions alternated.

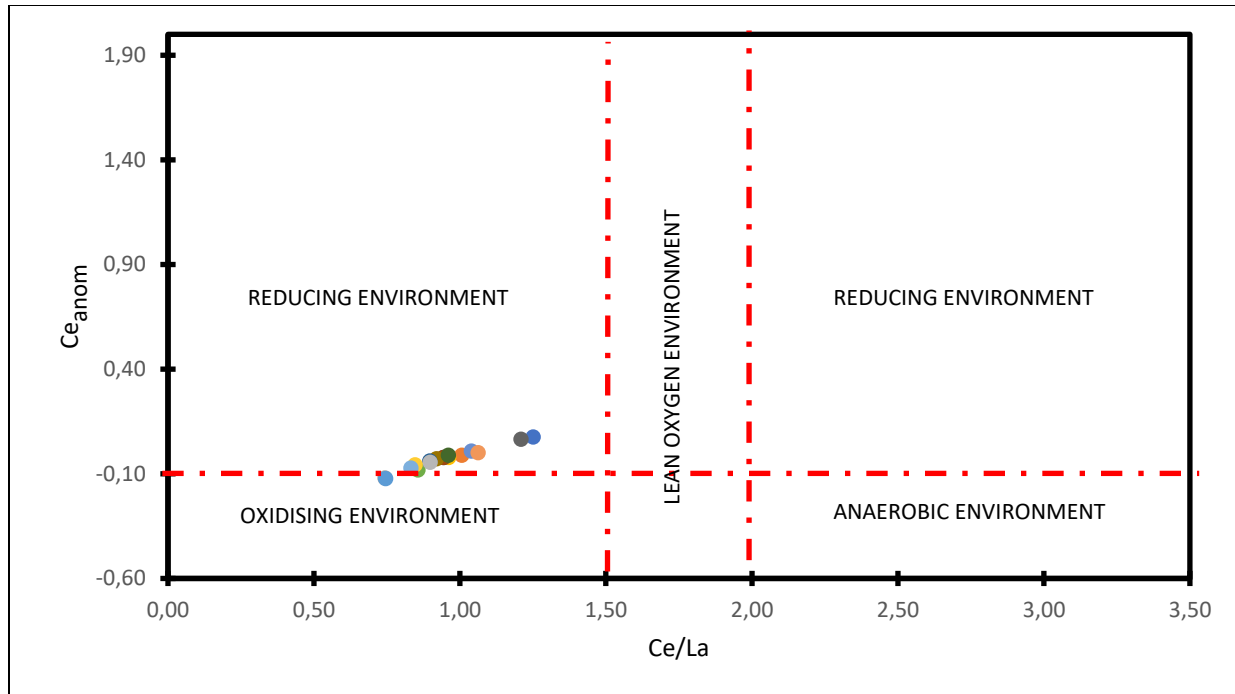


Figure 5.21: Relationship between Ce_N/La_N ratio and Ce_{anom} . Where $Ce_{anom} = \lg(Ce/(2La_N + Nd_N))$.

5.6.4 Potential economic viability of the REEs in the coal

The coefficient of outlook was employed to evaluate the economic potential of the coal samples from the Utrecht Coalfield. The outlook coefficient estimated as the proportion of critical REEs (CREEs) to excessive or uncritical REEs (UCREEs), is typically used to determine if ore containing REEs is economically feasible (Harrar et al., 2022; Perämäki et al., 2019; Zhang et al., 2015; Seredin and Dai, 2012). As stated by Seredin et al. (2016), the REEs deposit is considered promising if $0.7 \leq C_{outlook} \leq 1.9$ and highly promising if the outlook coefficient is greater than 2.5. The following equation was used (Seredin and Dai, 2012) to obtain the $C_{outlook}$:

$$C_{outlook} = \frac{Nd+Eu+Tb+Dy+Er+Y/\sum REEs}{Ce+Ho+Tm+Yb+Lu/\sum REEs} \dots\dots\dots (11)$$

The samples from the Utrecht Coalfield had a $C_{outlook}$ ranging from 0.69-1.26. Three samples (CB2-L1, CB2-L2, and AD3BH2) had a higher $C_{outlook}$ as compared to the other

samples (Figure 5.22). With the exception of sample CMB-D, all the other samples exceeded the cut-off grade of 0.7. All samples have a $C_{outlook}$ higher than that of world coals, estimated to be 0.64 (Ketris and Yudovich, 2009). In addition, the $C_{outlook}$ values of the samples from the Utrecht Coalfield were plotted on the % CREEs ($REE_{def, rel}$), which was developed by Seredin (2010). Furthermore, the plot can provide insight into the economic viability of the ore (Harrar et al., 2022). The classification is based on 3 categories: I-unpromising, II-promising and III- highly promising source (Seredin and Dai, 2012; Seredin, 2010). Almost all the samples of the Utrecht Coalfield plotted within the promising source category except for samples CMB-D and JCBH08B (Figure 5.22). The high $C_{outlook}$ in the samples is due to the elevated concentration of the critical rare earth elements, particularly Nd and Y. A larger outlook coefficient indicates that an ore is enriched in CREEs, suggesting more critical elements may be potentially extracted at a greater revenue (Harrar et al., 2022).

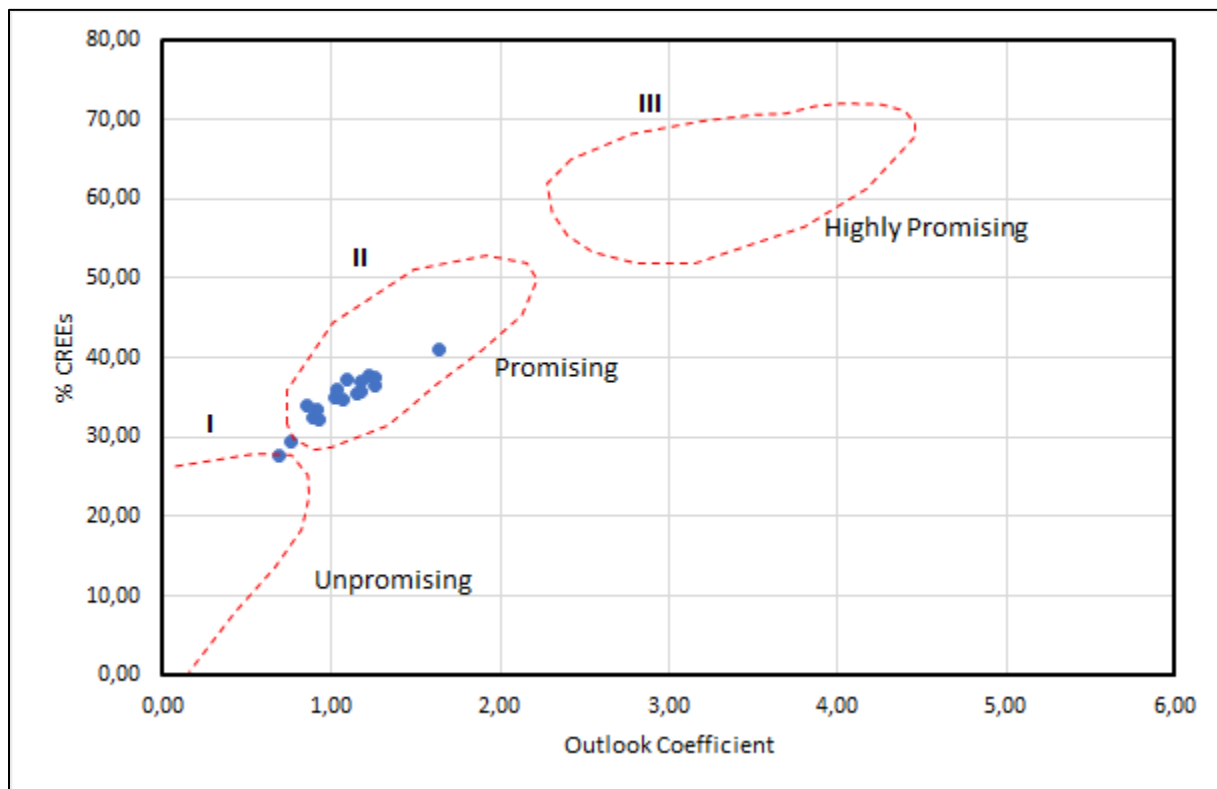


Figure 5.22: Bivariant plot for the classification of the samples from the Utrecht Coalfield using the $C_{outlook}$ and % CREEs ($REE_{def, rel}$) (After Seredin and Dai, 2012).

However, when the sum concentration of the REEs was plotted against Coutlook using the updated classification system by Dai et al. (2017), the samples plotted in the unpromising area. This suggests that, despite their promising classification on the previous classification, the Utrecht Coalfield samples are not economically viable for REEs extraction on a large scale (Figure 5.23).

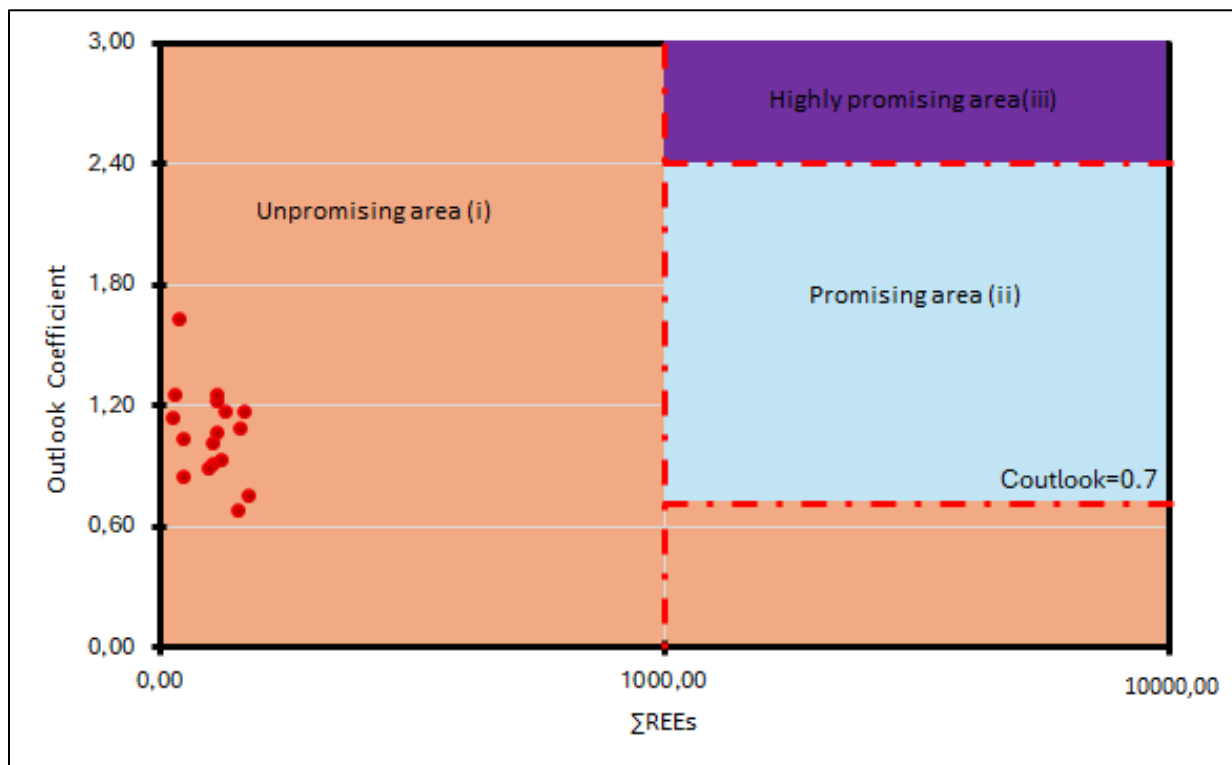


Figure 5.23: Bivariant plot showing the relationship between Coutlook and REEs (after Dai et al., 2017).

5.6.5 Pearson's correlation

In this study, Pearson's correlation was employed to investigate the relationship between the different properties of the samples relative to the REEs concentration or occurrence. Multiple correlations were investigated in an attempt to better understand the mode of occurrence of REEs in the coal samples. The REEs were correlated with inorganic minerals (kaolinite, pyrite, carbonates, clay, and quartz) and organic minerals (vitrinite,

inertinite, and liptinite) as shown in Table 5.4 and Appendix E. There are notable correlations between REEs and both organic and inorganic matter, indicating a combined inorganic-organic affinity (Figures 4.16-4.18). There is a weakly positive correlation (r ranging from 0.72 to 1.77) between REEs (La, Ce, Pr, Nd, Sm, Eu, Gd and Tb) and inertinite, whereas Sc, Y, Dy, Ho, Er, Tm, Yb and Lu had a weakly negative correlation. There is a weak to moderately positive correlation (r ranging from) between REEs (i.e., Sc, Y, Eu, Gd, Dy, Ho, Er, Tm, Yb and Lu) and liptinites. There is a strongly negative correlation (r ranging from 0.558 to 0.637) between the concentration of REEs (i.e., La, Ce, Pr, Nd and Sm) and vitrinite. This suggests that the REEs in the samples are not associated with vitrinite. Instead, the REEs are associated with inertinite and liptinite. According to Dai et al. (2021), a weak correlation may indicate a mixed organic-inorganic association.

The data shows a statistically significant (p -value <0.033) and strongly positive correlation (r ranging from 0.519-0.646) between kaolinite and REEs (i.e., Y, La, Pr, Nd, Ru, Gd, Tb, Dy, Ho and Er). Pyrite has a strongly negative correlation (r ranging from 0.476 to 0.674) with the REEs (La, Ce, Pr, Nd, Sm, Eu, Gd and Tb), whereas it had a weakly positive correlation with Lu, suggesting that the REEs are not associated with pyrite, which agrees with the SEM-EDS observations in Section 4.3.2. Pearson's correlation indirectly revealed associations of REEs containing both inorganic and organic matter in the samples of the Utrecht Coalfield. The association is with organic matter and kaolinite. The positive correlation of REEs with both organic and inorganic matter, as determined by Pearson's correlation method (Table 5.2), suggests that the REEs in the Utrecht Coalfield exhibit a mixed affinity for both organic and inorganic matter, which agrees with the SEM-EDS analysis in Section 4.3.2. This agrees with the findings that REEs in coal have a positive correlation with clay minerals (kaolinite in this instance) and organic matter (Dai et al., 2008; Finkelman, 1995; Dai et al., 2021; Chou, 1997).

Table 5.4: Pearson's correlation of TREES with other parameters.

		Vitrinite	Inerinite	Liptinite	Clay	Quartz	Pyrite	Carbonates	Σ TREES
Vitrinite	Pearson Correlation	1							
	N	17							
Inerinite	Pearson Correlation	-,860	1						
	Sig. (2-tailed)	<,001							
	N	17	17						
Liptinite	Pearson Correlation	,446	-,596	1					
	Sig. (2-tailed)	,073	,012						
	N	17	17	17					
Clay	Pearson Correlation	-,645	,257	-,147	1				
	Sig. (2-tailed)	,005	,319	,572					
	N	17	17	17	17				
Quartz	Pearson Correlation	-,464	,027	-,192	,645	1			
	Sig. (2-tailed)	,061	,917	,460	,005				
	N	17	17	17	17	17			
Pyrite	Pearson Correlation	,057	-,302	,419	,074	,184	1		
	Sig. (2-tailed)	,827	,239	,094	,778	,480			
	N	17	17	17	17	17	17		
Carbonates	Pearson Correlation	-,551	,510	,058	,339	-,031	-,147	1	
	Sig. (2-tailed)	,022	,037	,826	,183	,907	,573		
	N	17	17	17	17	17	17	17	
Σ TREES	Pearson Correlation	-,574	,325	,001	,477	,460	,289	,381	1
	Sig. (2-tailed)	,016	,202	,998	,053	,063	,260	,131	
	N	17	17	17	17	17	17	17	17

CHAPTER 6

CONCLUSIONS AND RECOMMENDATIONS

6.1 Conclusions

This study aimed to investigate the mineralogical and geochemical characteristics, and occurrence of REEs in the coal deposits at the Uitkomst Colliery (Utrecht Coalfield). Based on the results presented in this study, the following conclusions are made:

- The stratigraphy consisted of sandstone, siltstone, shale, and coal seams. The Alfred and Gus seams were laterally distributed across the four boreholes, whereas the Fritz and Elands seams pinched out.
- The petrographic examination revealed that the coals are characterised with high organic matter (vitrinite, inertinite, and liptinites) and a low mineral matter. The Alfred, Gus and Fritz seams are dominantly inertinite rich, while few samples are enriched with vitrinite. The dominant inertinite maceral was inertodetrinite and semifusinite, whereas the dominant vitrinite maceral was collotelinite, tellinite, and pseudovitrinite.
- The coal samples were categorised as medium rank C high volatile bituminous coal, with low sulphur, volatile matter and fixed carbon ranging between 0.3 to 2.8%, 14.3% to 38.5%, and 35.7-62.6%, respectively.
- The XRD detected kaolinite, quartz, pyrite, muscovite, microcline, dolomite, calcite, smectite, plagioclase and goethite. The REE-bearing minerals could not be detected due to the limited detection limit of the instrument.
- The SEM analysis revealed organic and inorganic associations of the REE-bearing minerals, which were noted to be clays (kaolinite) and organic matter. The detected REE-bearing minerals were xenotime and monazite. Monazite was observed to be bent around monazite, indicating an epigenetic origin.
- The REEs content in the samples was higher than that of the USA and Worlds coals, except for samples CMB-L1, CB2-L1, CB1-L2, CB2-L2, and CB2-S1, whereas the samples CB1-L1, CMB-D, JCBH08B, and JCBH20 was higher than that of Chinese Coals.

- The $C_{\text{CeN}}/C_{\text{CeN}}$ ratio, $E_{\text{uN}}/E_{\text{uN}}$ ratio, $G_{\text{dN}}/G_{\text{dN}}$ ratio and La/Yb- Σ REEs diagram suggests a mixed provenance, with the sediments being derived from sedimentary and igneous sources.
- The Pearson's correlation as an indirect method revealed that the REEs in the Utrecht Coalfield are associated with clay minerals and inorganic matter.
- Most of the Utrecht Coalfield samples were classified as a promising source based on their elevated Coutlook values and high concentrations of critical rare earth elements (CREEs). However, when plotted using the updated classification system, the samples were within the unpromising category, indicating limited economic viability for REEs extraction.

6.2 Recommendations

To further investigate the concentration and distribution of REEs in the Utrecht Coalfield and evaluate their economic viability, the following studies are recommended:

- Currently, only three seams have been analysed. It is advisable to assess the REEs concentrations in other seams within the Utrecht Coalfield to achieve a more comprehensive understanding of the distribution of REEs in the entire coalfield.
- Tescan integrated mineral analyser (TIMA) analysis be conducted to determine the mode of occurrence and distribution of REEs in relation to both mineral (inorganic) matter and maceral (organic) matter.
- Particle Size Analysis be conducted to examine the variation of REE concentrations with particle size.
- Determine the concentration of oxides and rare earth oxide (REO) and plot them as a function of C_{outlook} to better assess the commercial feasibility of the REEs in the Utrecht Coalfield, using the updated graph by Dai et al. (2017).
- Sample coal on both sides of the dolerite intrusions to assess its impact on REEs enrichment.

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APPENDICES

Appendix A: Petrographic analysis

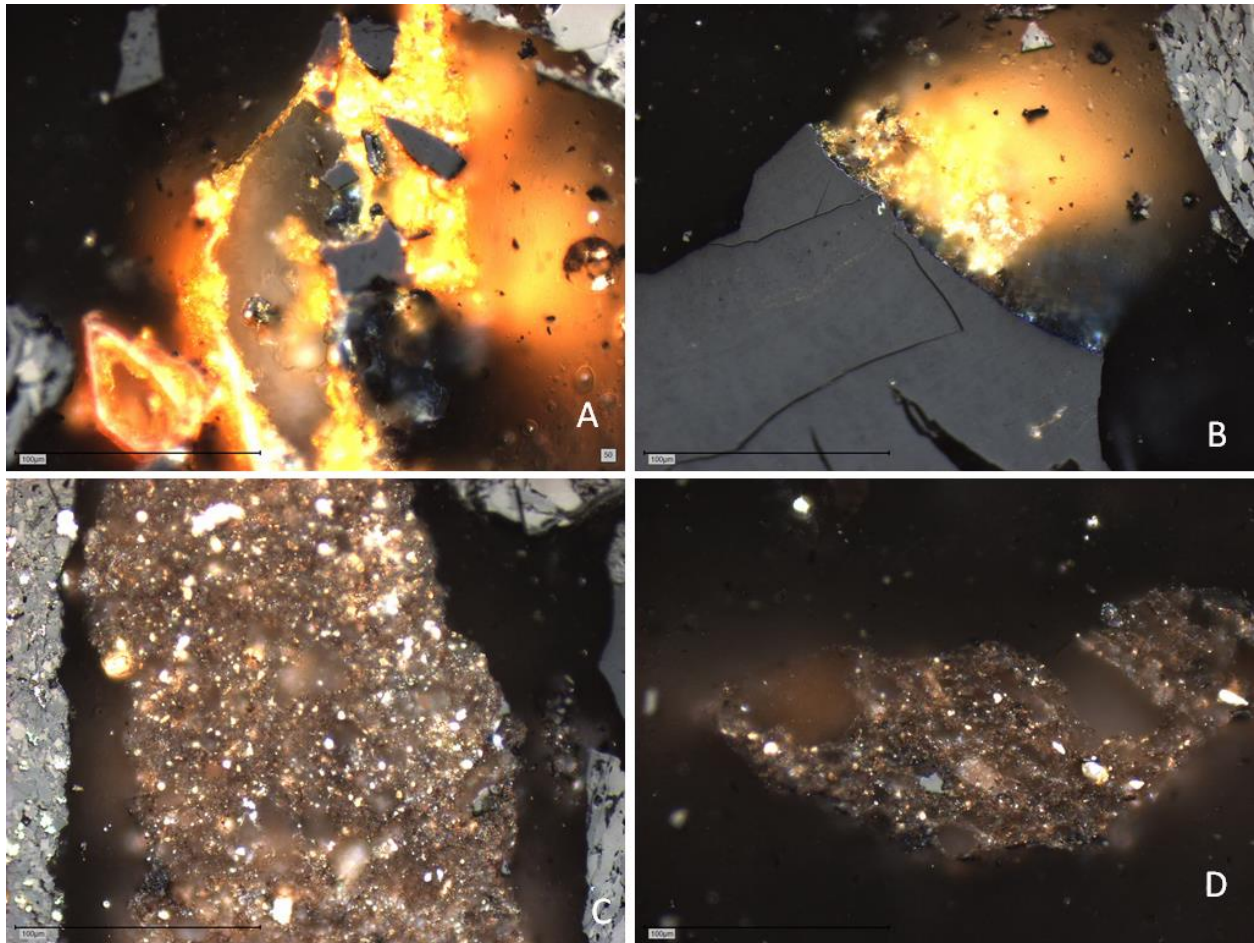


Figure A.1: Photomicrographs showing alteration minerals (stockpile minerals).

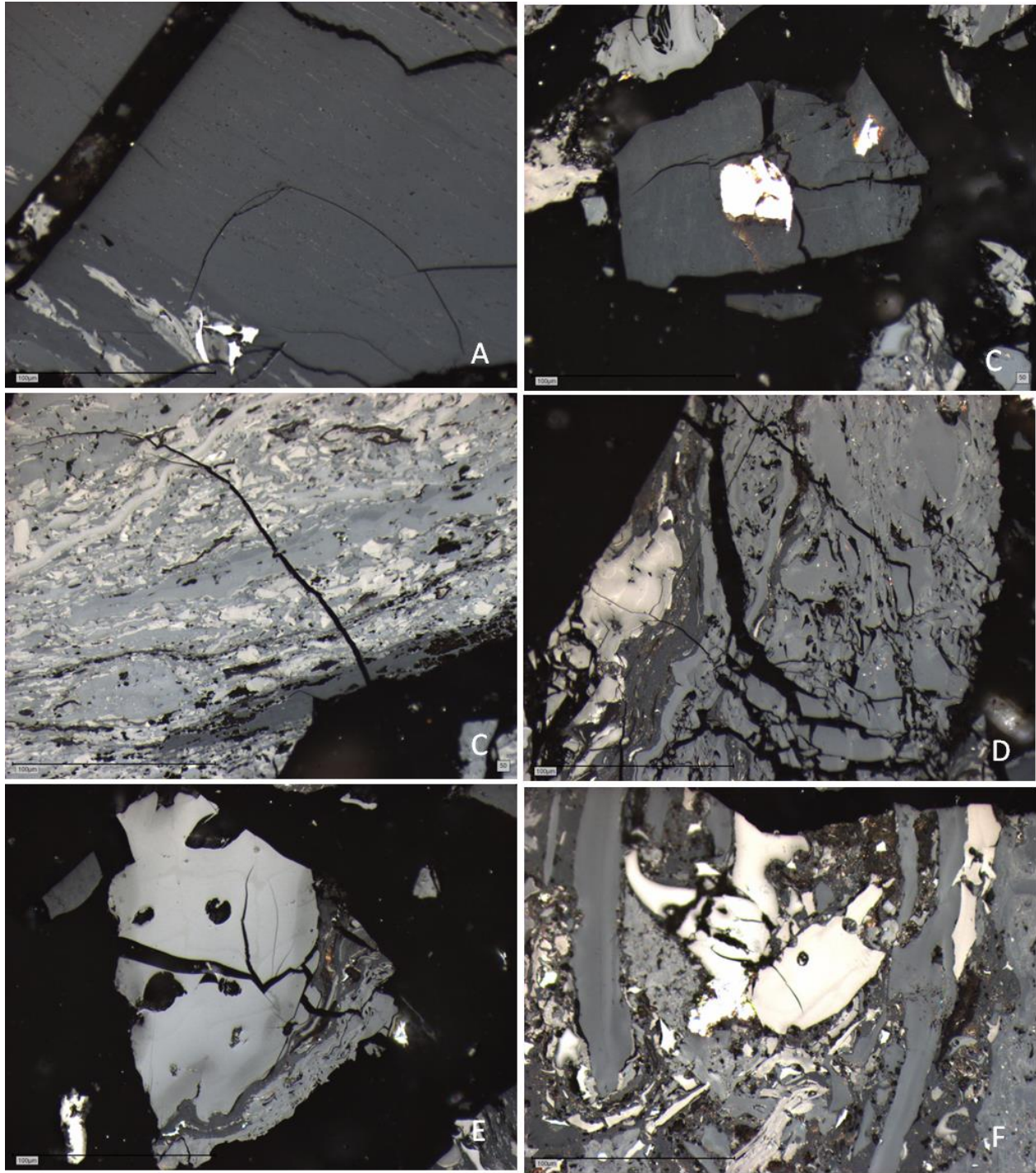


Figure A.2: Photomicrographs showing a-d) fracturing of organic minerals; e-d) effect of heat.

Table A.1: Maceral results.

SAMPLE	CONTENT		MACERAL GROUP			MINERAL MATTER				
			VITRINITE	LIPTINITE	INERTINITE	CLAY	QUARTZ	PYRITE	CARBONATE	OTHER MINERALS
CB1-L1	inc. mm	vol%	59	5.6	29.6	0.2	0.5	4.6	0.5	0
	mmf	vol%	62.6	6	31.4					
CMB-L1	inc. mm	vol%	16.8	4.6	71.6	2.4	1	1	2.6	0
	mmf	vol%	18.1	4.9	77					
CB2-L1	inc. mm	vol%	71.5	7.7	18.9	0.5	1.2	0	0	0.2
	mmf	vol%	72.9	7.9	19.2					
CMB-L2	inc. mm	vol%	8.9	0.9	86.2	2.3	0.2	0.4	0.9	0
	mmf	vol%	9.3	1	89.7					
CB1-L2	inc. mm	vol%	64.1	8.6	25.2	0.2	0.2	1.2	0.5	0
	mmf	vol%	65.6	8.7	25.7					
CB2-L2	inc. mm	vol%	68	4.5	26.4	0	0.2	0.9	0	0
	mmf	vol%	68.8	4.5	26.7					
CMB-D	inc. mm	vol%	0.7	0.5	53.1	12.6	31.2	1.4	0.5	0
	mmf	vol%	1.3	0.9	97.8					
CB2-D	inc. mm	vol%	32.9	2.1	53.6	2.6	4.5	2.4	1.9	0
	mmf	vol%	37.1	2.4	60.5					
CB2-S1	inc. mm	vol%	55.8	5.2	28	4.8	3.6	1	1.6	0
	mmf	vol%	62.7	5.8	31.5					
CMB-S1	inc. mm	vol%	3.5	1.6	85.8	5.4	0.2	0.5	3	0

	mmf	vol%	3.8	1.8	94.4					
JCBH08A	inc. mm	vol%	14.6	5.6	67.8	2.2	6.6	0.5	2.7	0
	mmf	vol%	16.6	6.4	77					
JCBH08B	inc. mm	vol%	11	7.4	58.8	10	8.4	0.6	3.8	0
	mmf	vol%	14.2	9.6	76.2					
JCBH20A	inc. mm	vol%	4.6	4	57.2	19.2	11.6	2	1.4	0
	mmf	vol%	7	6.1	86.9					
JCBH20B	inc. mm	vol%	10.8	5.4	60.6	10.4	6.2	4.6	2	0
	mmf	vol%	14.1	7	78.9					
AD3BH3A	inc. mm	vol%	28.8	10.4	42.6	8.4	4.6	2	3.2	0
	mmf	vol%	35.2	12.7	52.1					
AD3BH2	inc. mm	vol%	29.3	6.3	57.4	1.5	3.1	2.2	0	0.2
	mmf	vol%	31.5	6.8	61.7					
JCBH20	inc. mm	vol%	37	11.1	26.2	4.4	11.6	8.5	1	0.2
	mmf	vol%	49.8	15	35.2					

Appendix B: SEM

Table B.1: Mineral and elemental mapping for the sample JCBH20A.

Minerals	Number	Area %	Weight %	Grain Size (μm)	Grain Size Std Dev (μm)	Average Composition	Assigned Composition
Calcite	25	0,105	0,547	0,835	0,566	O 49.06; Ca 42.97; Fe 4.24; Mg 3.73;	O 49.06; Ca 42.97; Fe 4.24; Mg 3.73;
Chalcopyrite	6	0,393	3,165	3,793	1,544	Cu 36.24; Fe 32.74; S 31.02;	Cu 36.24; Fe 32.74; S 31.02;
Kaolinite	961	7,952	40,974	1,388	1,064	O 42.38; Si 31.23; Al 26.39;	O 42.38; Si 31.23; Al 26.39;
Monazite	2	0,029	0,319	2,128	1,303	Ce 24.48; O 21.83; P 18.73; Nd 12.09; Si 11.61; Al 10.11; Ca 1.14;	Ce 24.48; O 21.83; P 18.73; Nd 12.09; Si 11.61; Al 10.11; Ca 1.14;
Monazite-Ce	42	0,094	1,029	0,500	0,000	O 49.56; Si 21.84; Al 16.65; Ce 10.12; K 1.45; Ca 0.39;	O 49.56; Si 21.84; Al 16.65; Ce 10.12; K 1.45; Ca 0.39;
Monazite-Th	3	0,020	0,221	1,206	0,614	Ce 29.19; O 27.67; P 17.64; Si 12.77; Al 10.95; Ca 0.9; K 0.88;	Ce 29.19; O 27.67; P 17.64; Si 12.77; Al 10.95; Ca 0.9; K 0.88;
Pyrite	222	2,538	24,450	1,491	1,213	Fe 51.17; S 48.83;	Fe 51.17; S 48.83;
Quartz	157	3,552	18,096	1,959	1,587	Si 55.62; O 41.7; Al 2.02; Fe 0.54; K 0.12;	Si 55.62; O 41.7; Al 2.02; Fe 0.54; K 0.12;
Rutile	3	0,027	0,232	1,344	0,746	Ti 60.59; O 39.41;	Ti 60.59; O 39.41;
Sphalerite	2	0,308	2,417	7,870	9,422	Zn 65.54; S 33.94; Fe 0.53;	Zn 65.54; S 33.94; Fe 0.53;
Sphene	1	0,002	0,015	0,500	0,000	O 34.57; Ti 25.46; Ca 22.84; Si 17.13;	O 34.57; Ti 25.46; Ca 22.84; Si 17.13;
Titanomagnetite	2	0,004	0,044	0,500	0,000	Fe 81.79; O 13.21; Ti 5;	Fe 81.79; O 13.21; Ti 5;
Xenotime	18	0,049	0,482	0,606	0,248	O 40.1; Y 25.57; P 13.71; Si 10.74; Al 9.11; Dy 0.45; Ca 0.32;	O 40.1; Y 25.57; P 13.71; Si 10.74; Al 9.11; Dy 0.45; Ca 0.32;

Xenotime-H	1	0,002	0,022	0,500	0,000	O 37.41; Ti 17.21; Y 16.46; Ca 9.23; P 8.98; Si 6.98; Al 3.74;	O 37.41; Ti 17.21; Y 16.46; Ca 9.23; P 8.98; Si 6.98; Al 3.74;
Zircon	42	0,884	7,989	2,025	1,367	Zr 53.29; O 26.93; Si 17.05; Al 2.56; K 0.16;	Zr 53.29; O 26.93; Si 17.05; Al 2.56; K 0.16;
Not Analysed	1	0,002	0,000	0,500	0,000		
Not Classified	0	0,100	0,000	0,000	0,000	Si 40.37; Al 27.14; Ba 16.02; O 4.09; S 3.7; Fe 3.56; K 2.98; Ca 0.95; Ti 0.78; Er 0.3; Nd 0.1;	Si 40.37; Al 27.14; Ba 16.02; O 4.09; S 3.7; Fe 3.56; K 2.98; Ca 0.95; Ti 0.78; Er 0.3; Nd 0.1;
Unclassified	1401	83,938	0,000	3,531	2,047	O 21.55; Ba 20.8; Si 17.37; Al 12.24; Fe 11.82; S 10.12; Ca 1.75; K 1.62; Zr 0.88; Mg 0.54; Ti 0.42; Cr 0.27; Cu 0.1; Yb 0.1; P 0.09; Zn 0.06; Na 0.06; Sr 0.05; Ce 0.04; Y 0.03; Pb 0.01; U 0.01; Nd 0.01;	O 21.55; Ba 20.8; Si 17.37; Al 12.24; Fe 11.82; S 10.12; Ca 1.75; K 1.62; Zr 0.88; Mg 0.54; Ti 0.42; Cr 0.27; Cu 0.1; Yb 0.1; P 0.09; Zn 0.06; Na 0.06; Sr 0.05; Ce 0.04; Y 0.03; Pb 0.01; U 0.01; Nd 0.01;
Total	2889	100,000	100,000				

Table B.2: Mineral and elemental mapping for the sample AD3BH3A.

Minerals	Number	Area %	Weight %	Grain Size (µm)	Grain Size Std Dev (µm)	Average Composition	Assigned Composition
Calcite	7	0,043	0,152	0,904	0,517907	Ca 50.61; O 46.39; Fe 1.8; Mg 1.21;	Ca 50.61; O 46.39; Fe 1.8; Mg 1.21;
Chalcopyrite	1	0,012	0,067	1,618	0	Fe 34.29; Cu 33.12; S 32.59;	Fe 34.29; Cu 33.12; S 32.59;
Kaolinite	275	1,576	5,507	0,850	0,780756	O 42.09; Si 32.5; Al 25.41;	O 42.09; Si 32.5; Al 25.41;
Monazite	97	4,985	37,103	2,507	3,637294	Ce 40.76; P 18.29; O 16.09; Nd 15.59; La 4.82; Si 1.9; Al 1.75; Ca 0.8; Gd 0;	Ce 40.76; P 18.29; O 16.09; Nd 15.59; La 4.82; Si 1.9; Al 1.75; Ca 0.8; Gd 0;
Monazite-Ce	60	0,197	1,467	0,533	0,155862	O 26.16; Si 24.23; Ce 23.13; Al 17.55; P 4.88; La 2.24; Ca 1.19; K 0.38; Nd 0.24;	O 26.16; Si 24.23; Ce 23.13; Al 17.55; P 4.88; La 2.24; Ca 1.19; K 0.38; Nd 0.24;
Monazite-Nd	22	0,068	0,504	0,500	0	O 27.57; Nd 23.07; Si 19.53; Al 14.23; P 13.88; Ca 1.57; K 0.14;	O 27.57; Nd 23.07; Si 19.53; Al 14.23; P 13.88; Ca 1.57; K 0.14;
Monazite-Th	187	2,097	15,607	1,266	1,38095	Ce 45.67; P 18.03; O 16.46; La 8.25; Si 5.3; Al 4.65; Ca 1.56; Fe 0.07; Th 0.02; Gd 0.01; K 0;	Ce 45.67; P 18.03; O 16.46; La 8.25; Si 5.3; Al 4.65; Ca 1.56; Fe 0.07; Th 0.02; Gd 0.01; K 0;
Pyrite	328	3,362	21,958	1,163	0,924479	Fe 50.13; S 49.86; Pb 0.01;	Fe 50.13; S 49.86; Pb 0.01;
Quartz	32	0,486	1,680	1,513	0,816079	Si 56.15; O 40.41; Al 2.82; Fe 0.57; K 0.05;	Si 56.15; O 40.41; Al 2.82; Fe 0.57; K 0.05;
Sphalerite	12	1,481	7,877	3,287	3,434024	Zn 68.23; S 28.81; Fe 2.96;	Zn 68.23; S 28.81; Fe 2.96;
Titanomagnetite	1	0,003	0,020	0,500	0	Fe 85.36; O 12.86; Ti 1.79;	Fe 85.36; O 12.86; Ti 1.79;
Xenotime	29	0,871	5,793	1,394	2,37211	Y 43.17; O 27.89; P 24.39; Dy 2.03; Al 1.82; Si 0.59; Ca 0.11;	Y 43.17; O 27.89; P 24.39; Dy 2.03; Al 1.82; Si 0.59; Ca 0.11;

Zircon	22	0,369	2,264	1,645	1,066715	Zr 56.52; O 24.54; Si 17.12; Al 1.77; K 0.05;	Zr 56.52; O 24.54; Si 17.12; Al 1.77; K 0.05;
Not Analysed	1	0,003	0,000	0,500	0		
Unclassified	1203	84,445	0,000	3,415	2,242884	Ba 22.81; O 17.35; Fe 13.99; S 13.51; Si 12.2; Al 7.32; Ce 3.5; Ca 2.84; P 1.78; Na 1.08; Mg 0.77; Nd 0.75; Zr 0.64; Y 0.33; La 0.23; K 0.22; Ti 0.2; Cr 0.13; Cu 0.1; Sr 0.06; Yb 0.04; Zn 0.03; Pb 0.03; Dy 0.02; U 0.02; Er 0.01; Mn 0.01;	Ba 22.81; O 17.35; Fe 13.99; S 13.51; Si 12.2; Al 7.32; Ce 3.5; Ca 2.84; P 1.78; Na 1.08; Mg 0.77; Nd 0.75; Zr 0.64; Y 0.33; La 0.23; K 0.22; Ti 0.2; Cr 0.13; Cu 0.1; Sr 0.06; Yb 0.04; Zn 0.03; Pb 0.03; Dy 0.02; U 0.02; Er 0.01; Mn 0.01;
Total	2277	100,000	100,000				

Table B.3: Mineral and elemental mapping for the sample CMB-L2.

Minerals	Number	Area %	Weight %	Grain Size (µm)	Grain Size Std Dev (µm)	Average Composition	Assigned Composition
Chalcopyrite	68	32,009	55,560	3,867	1,11089	Cu 36.49; Fe 33.74; S 29.77;	Cu 36.49; Fe 33.74; S 29.77;
Kaolinite	121	4,333	4,810	1,086	0,707768	O 45.17; Si 30.61; Al 24.22;	O 45.17; Si 30.61; Al 24.22;
Monazite	28	9,055	21,420	2,319	4,184609	Ce 41.18; O 20.98; P 17.5; Nd 14.77; La 2.27; Si 1.48; Al 1.38; Ca 0.43;	Ce 41.18; O 20.98; P 17.5; Nd 14.77; La 2.27; Si 1.48; Al 1.38; Ca 0.43;
Monazite-Ce	10	0,165	0,390	0,550	0,158111	O 34.76; Si 24.76; Al 21.9; Ce 15.68; K 1.97; Nd 0.57; Ca 0.35;	O 34.76; Si 24.76; Al 21.9; Ce 15.68; K 1.97; Nd 0.57; Ca 0.35;
Monazite-Nd	5	0,090	0,213	0,600	0,223603	Nd 32.25; O 31.81; P 12.47; Si 11.19; Al 10.13; Ca 1.31; K 0.84;	Nd 32.25; O 31.81; P 12.47; Si 11.19; Al 10.13; Ca 1.31; K 0.84;
Monazite-Th	78	2,504	5,922	0,939	0,613073	Ce 44.98; O 22.17; P 18.02; Si 6.17; Al 4.81; La 3.09; Ca 0.63; K 0.13;	Ce 44.98; O 22.17; P 18.02; Si 6.17; Al 4.81; La 3.09; Ca 0.63; K 0.13;
Pyrite	3	0,060	0,124	0,667	0,288671	Fe 51.08; S 48.92;	Fe 51.08; S 48.92;
Quartz	8	0,165	0,181	0,702	0,409219	O 63.62; Si 34.68; Al 1.7;	O 63.62; Si 34.68; Al 1.7;
Rutile	1	0,060	0,112	1,618	0	Ti 65.48; O 34.52;	Ti 65.48; O 34.52;
Sphalerite	1	1,259	2,129	6,200	0	Zn 69.67; S 30.01; Fe 0.32;	Zn 69.67; S 30.01; Fe 0.32;
Xenotime	20	3,178	6,715	2,484	1,610072	Y 40.7; O 30.9; P 23.05; Al 2.33; Dy 1.96; Si 0.91; Ca 0.1; Tm 0.05;	Y 40.7; O 30.9; P 23.05; Al 2.33; Dy 1.96; Si 0.91; Ca 0.1; Tm 0.05;
Zircon	12	1,244	2,423	2,026	1,726692	Zr 55.07; O 29.87; Si 12.83; Al 1.89; K 0.32;	Zr 55.07; O 29.87; Si 12.83; Al 1.89; K 0.32;
Not Analysed	3	0,060	0,000	0,736	0,408242		

Unclassified	192	45,817	0,000	3,029	2,35152	O 27.28; Si 15.61; Al 11.35; Ce 9.47; P 7.45; Zr 4.65; Y 4.48; Fe 4.39; Ba 4; S 3.1; Nd 2.09; Ca 1.12; Ti 1.04; Cu 0.92; K 0.75; Na 0.66; Cr 0.41; Mg 0.33; Dy 0.29; La 0.27; Yb 0.12; Sr 0.06; Pb 0.05; Er 0.03; Gd 0.03; Zn 0.02; Pr 0.01; V 0.01; Hf 0.01;	O 27.28; Si 15.61; Al 11.35; Ce 9.47; P 7.45; Zr 4.65; Y 4.48; Fe 4.39; Ba 4; S 3.1; Nd 2.09; Ca 1.12; Ti 1.04; Cu 0.92; K 0.75; Na 0.66; Cr 0.41; Mg 0.33; Dy 0.29; La 0.27; Yb 0.12; Sr 0.06; Pb 0.05; Er 0.03; Gd 0.03; Zn 0.02; Pr 0.01; V 0.01; Hf 0.01;
Total	550	100,000	100,000				

Appendix C: XRD

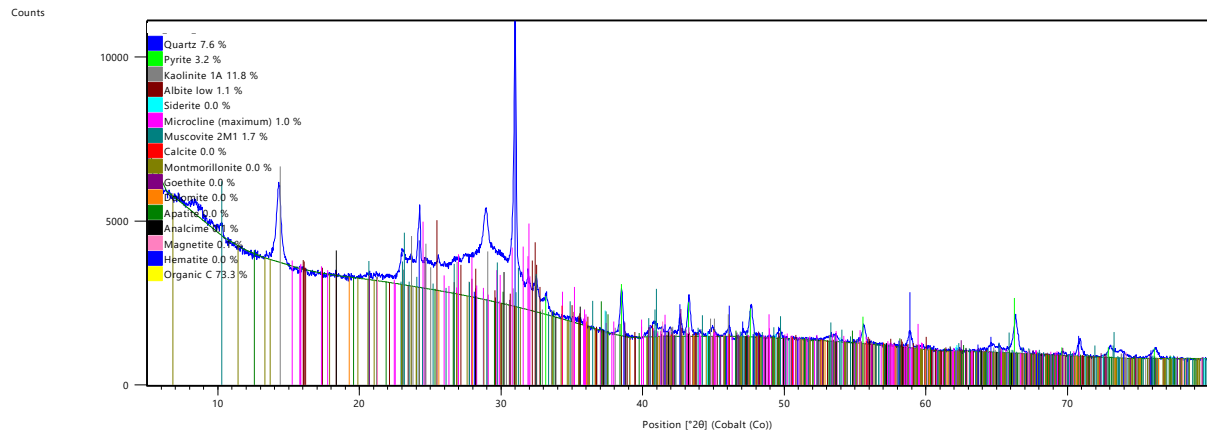


Figure C.1: X-ray diffraction patterns showing the mineral compositions of sample AD3BH2.

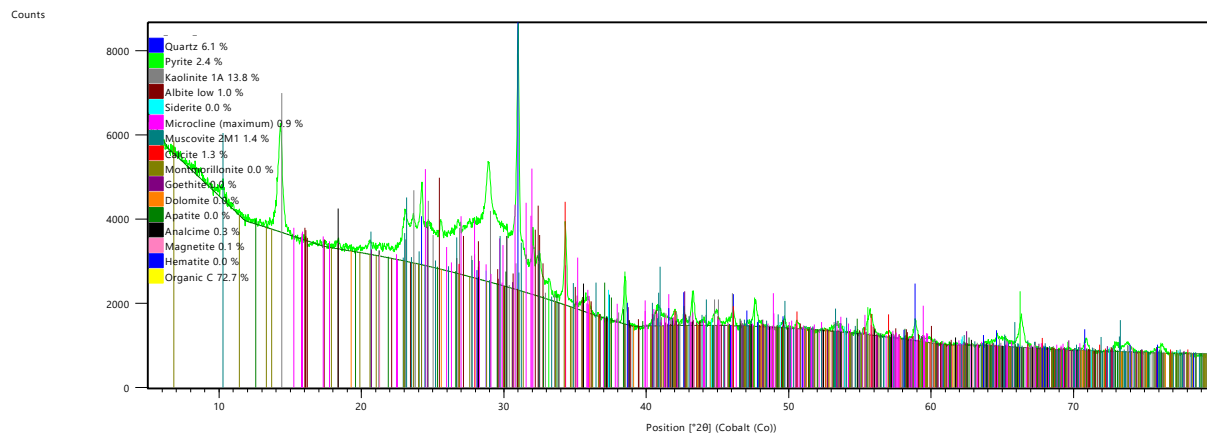


Figure C.2: X-ray diffraction patterns showing the mineral compositions of sample AD3BH3A.

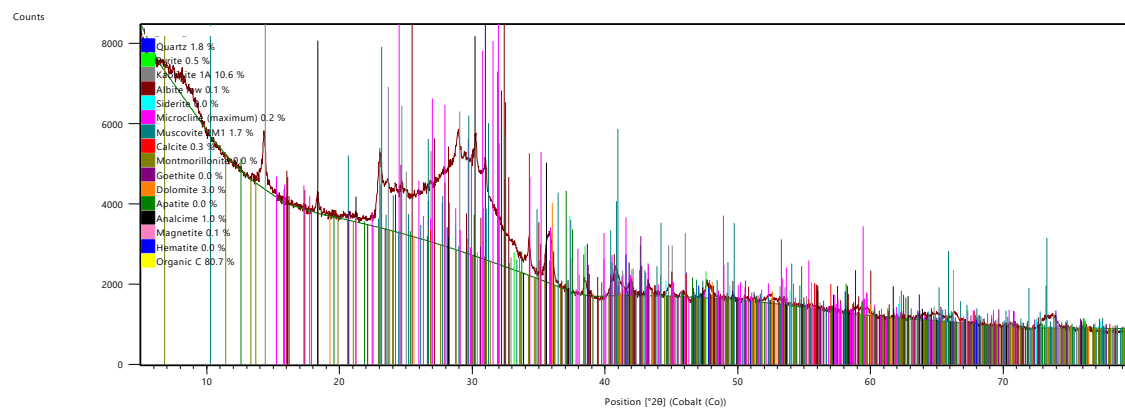


Figure C.3: X-ray diffraction patterns showing the mineral compositions of sample CMB-L2.

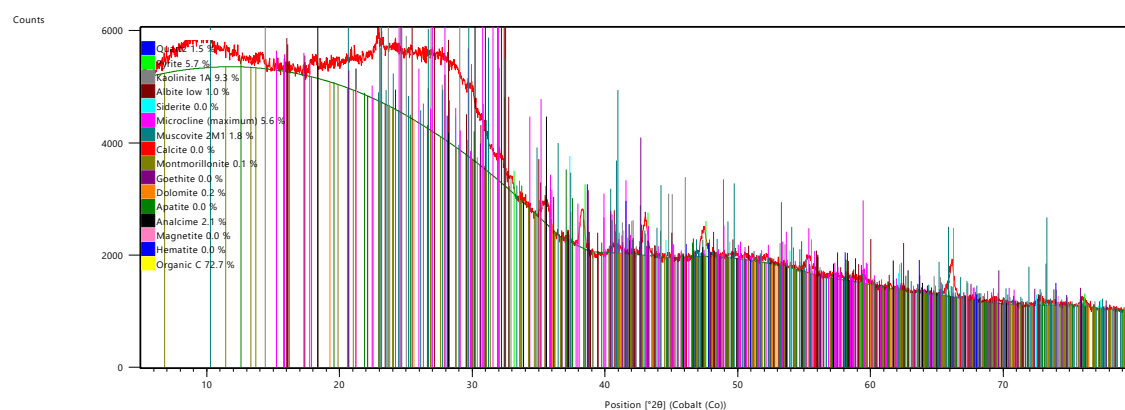


Figure C.4: X-ray diffraction patterns showing the mineral compositions of sample CB2-L2.

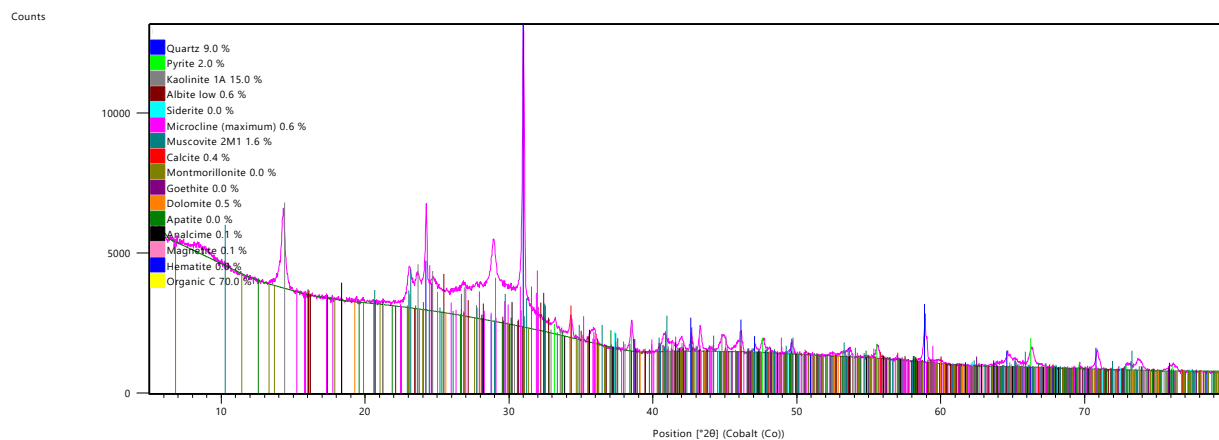


Figure C.5: X-ray diffraction patterns showing the mineral compositions of sample CB2-D.

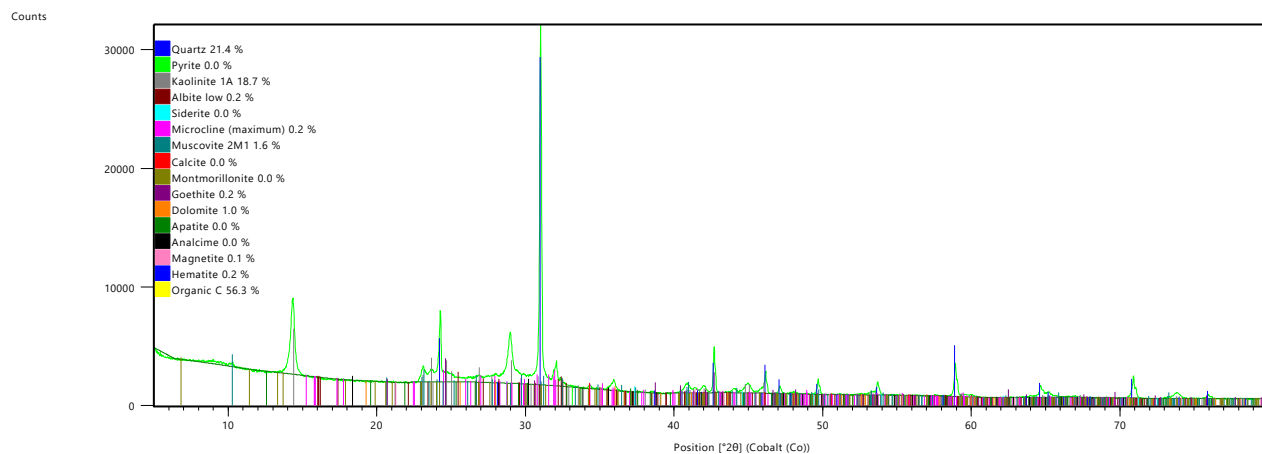


Figure C.6: X-ray diffraction patterns showing the mineral compositions of sample CMB-D.

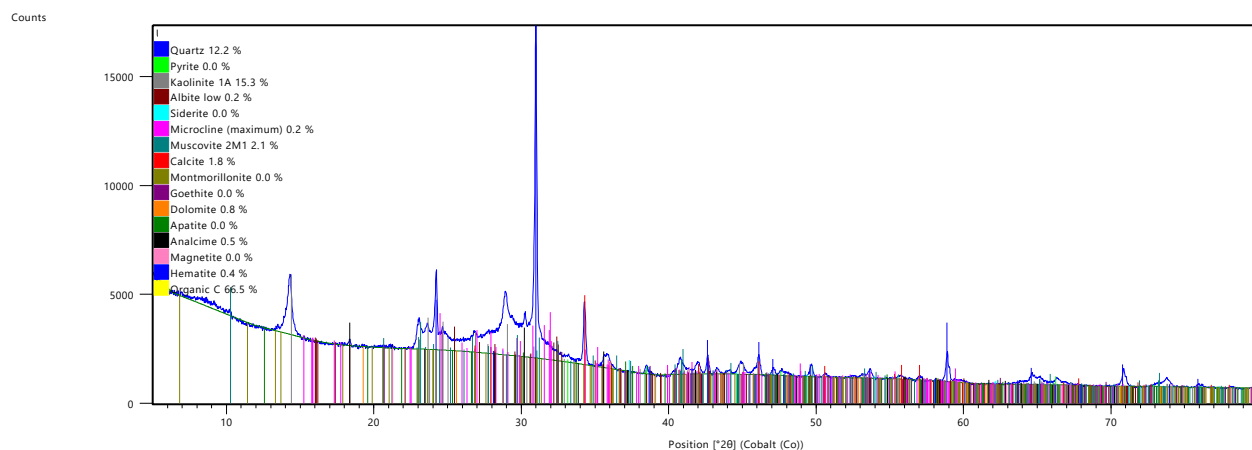


Figure C.7: X-ray diffraction patterns showing the mineral compositions of sample JCBH08A.

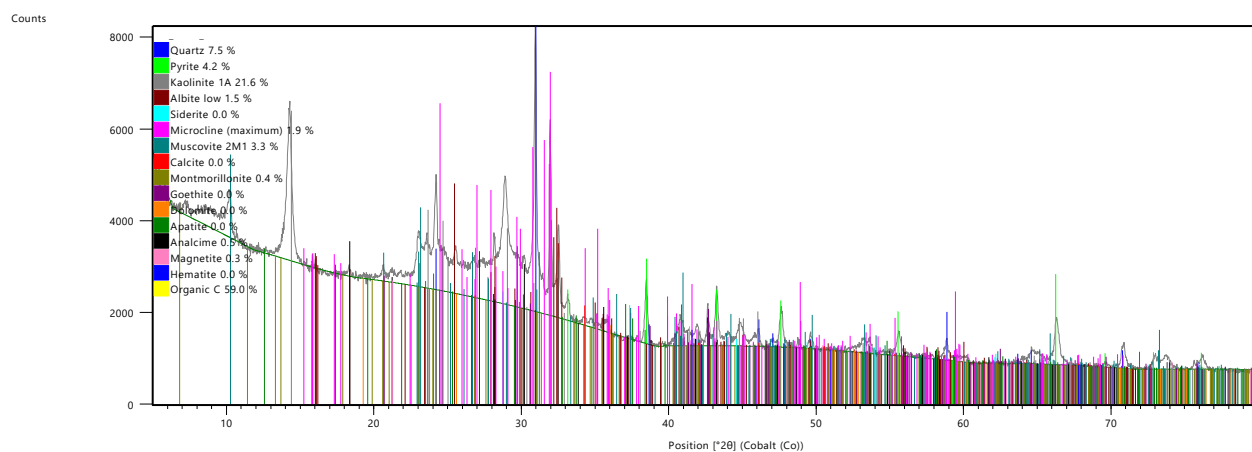


Figure C.8: X-ray diffraction patterns showing the mineral compositions of sample JCBH20.

Appendix D: Distribution patterns (Chondrite normalised)

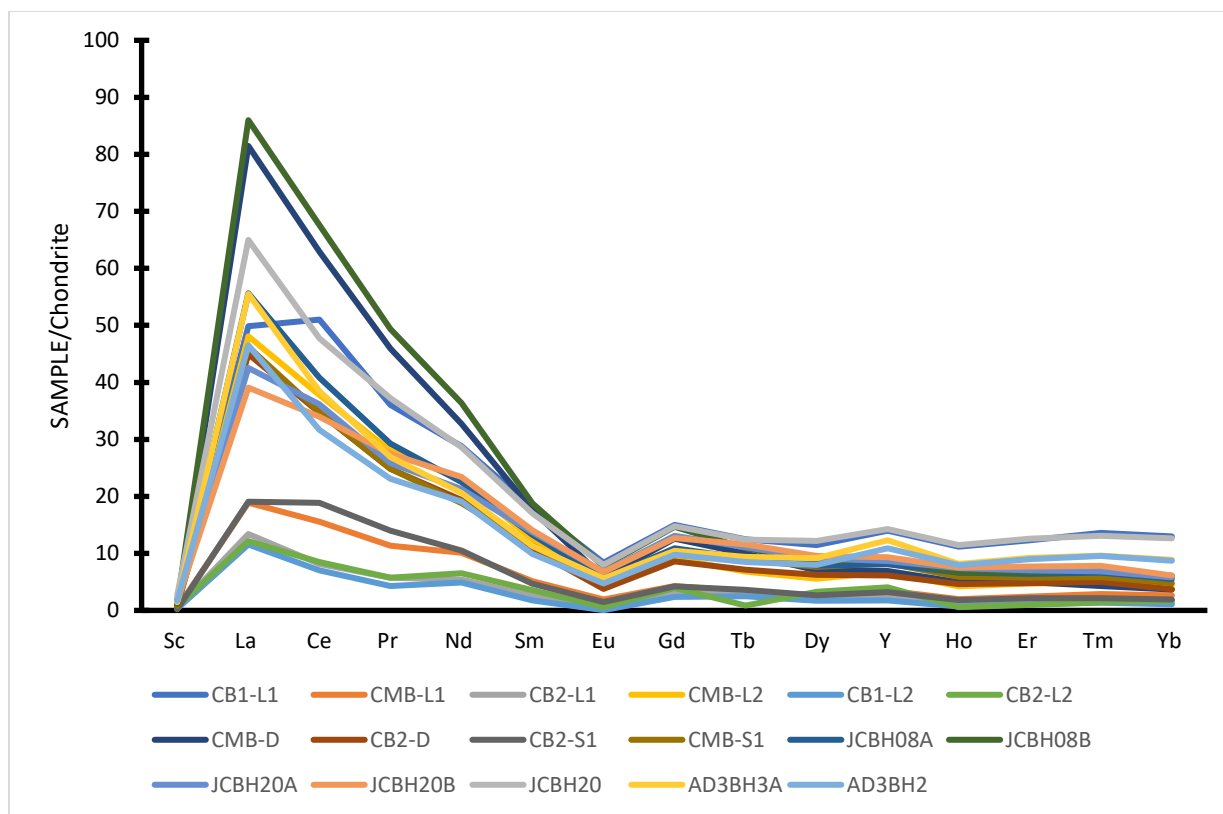


Figure D.1: Chondrite normalized REEs distribution patterns of the all the samples.

Appendix E: Pearson's correlation coefficient for various parameters with REEs concentrations

Correlations

		Sc	Y	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Vitrinite
Sc	Pearson Correlation	1																
	N	17																
Y	Pearson Correlation	,922	1															
	Sig. (2-tailed)	<,001																
	N	17	17															
La	Pearson Correlation	,538	,673	1														
	Sig. (2-tailed)	,026	,003															
	N	17	17	17														
Ce	Pearson Correlation	,543	,694	,975	1													
	Sig. (2-tailed)	,024	,002	<,001														
	N	17	17	17	17													
Pr	Pearson Correlation	,564	,701	,973	,997	1												
	Sig. (2-tailed)	,018	,002	<,001	<,001													
	N	17	17	17	17	17												
Nd	Pearson Correlation	,611	,737	,956	,989	,995	1											
	Sig. (2-tailed)	,009	<,001	<,001	<,001	<,001												
	N	17	17	17	17	17	17											
Sm	Pearson Correlation	,687	,794	,915	,962	,969	,984	1										
	Sig. (2-tailed)	,002	<,001	<,001	<,001	<,001	<,001											
	N	17	17	17	17	17	17	17										
Eu	Pearson Correlation	,806	,888	,828	,879	,890	,922	,964	1									
	Sig. (2-tailed)	<,001	<,001	<,001	<,001	<,001	<,001	<,001										
	N	17	17	17	17	17	17	17	17									
Gd	Pearson Correlation	,802	,871	,859	,905	,913	,940	,978	,990	1								
	Sig. (2-tailed)	<,001	<,001	<,001	<,001	<,001	<,001	<,001	<,001									
	N	17	17	17	17	17	17	17	17	17								
Tb	Pearson Correlation	,808	,877	,809	,851	,863	,889	,937	,977	,976	1							
	Sig. (2-tailed)	<,001	<,001	<,001	<,001	<,001	<,001	<,001	<,001	<,001								
	N	17	17	17	17	17	17	17	17	17	17							
Dy	Pearson Correlation	,917	,963	,732	,766	,777	,814	,881	,953	,951	,957	1						
	Sig. (2-tailed)	<,001	<,001	<,001	<,001	<,001	<,001	<,001	<,001	<,001	<,001							
	N	17	17	17	17	17	17	17	17	17	17	17						
Ho	Pearson Correlation	,928	,978	,676	,710	,720	,757	,824	,922	,902	,930	,977	1					
	Sig. (2-tailed)	<,001	<,001	,003	,001	,001	<,001	<,001	<,001	<,001	<,001	<,001						
	N	17	17	17	17	17	17	17	17	17	17	17	17					
Er	Pearson Correlation	,930	,985	,640	,672	,683	,721	,783	,887	,862	,889	,955	,992	1				
	Sig. (2-tailed)	<,001	<,001	,006	,003	,003	,001	<,001	<,001	<,001	<,001	<,001	<,001					
	N	17	17	17	17	17	17	17	17	17	17	17	17	17				
Tm	Pearson Correlation	,925	,980	,597	,634	,644	,685	,748	,859	,831	,855	,937	,981	,995	1			
	Sig. (2-tailed)	<,001	<,001	,011	,006	,005	,002	<,001	<,001	<,001	<,001	<,001	<,001	<,001				
	N	17	17	17	17	17	17	17	17	17	17	17	17	17	17			
Yb	Pearson Correlation	,917	,969	,561	,600	,608	,648	,710	,822	,791	,803	,904	,958	,983	,992	1		
	Sig. (2-tailed)	<,001	<,001	,019	,011	,010	,005	,001	<,001	<,001	<,001	<,001	<,001	<,001	<,001			
	N	17	17	17	17	17	17	17	17	17	17	17	17	17	17	17		
Lu	Pearson Correlation	,832	,821	,305	,335	,338	,387	,464	,568	,562	,511	,723	,738	,782	,813	,856	1	
	Sig. (2-tailed)	<,001	<,001	,234	,189	,184	,125	,060	,017	,019	,036	,001	<,001	<,001	<,001	<,001		
	N	17	17	17	17	17	17	17	17	17	17	17	17	17	17	17	17	
Vitrinite	Pearson Correlation	-,199	-,304	-,637	-,604	-,614	-,616	-,604	-,558	-,563	-,569	-,426	-,342	-,269	-,216	-,140	,113	1
	Sig. (2-tailed)	,445	,235	,006	,010	,009	,008	,010	,020	,019	,017	,089	,179	,296	,404	,592	,665	
	N	17	17	17	17	17	17	17	17	17	17	17	17	17	17	17	17	17

Correlations

		Sc	Y	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Inertinite
Sc	Pearson Correlation	1																
	N	17																
Y	Pearson Correlation	,922	1															
	Sig. (2-tailed)	<,001																
	N	17	17															
La	Pearson Correlation	,538	,673	1														
	Sig. (2-tailed)	,026	,003															
	N	17	17	17														
Ce	Pearson Correlation	,543	,694	,975	1													
	Sig. (2-tailed)	,024	,002	<,001														
	N	17	17	17	17													
Pr	Pearson Correlation	,564	,701	,973	,997	1												
	Sig. (2-tailed)	,018	,002	<,001	<,001													
	N	17	17	17	17	17												
Nd	Pearson Correlation	,611	,737	,956	,989	,995	1											
	Sig. (2-tailed)	,009	<,001	<,001	<,001	<,001												
	N	17	17	17	17	17	17											
Sm	Pearson Correlation	,687	,794	,915	,962	,969	,984	1										
	Sig. (2-tailed)	,002	<,001	<,001	<,001	<,001	<,001											
	N	17	17	17	17	17	17	17										
Eu	Pearson Correlation	,806	,888	,828	,879	,890	,922	,964	1									
	Sig. (2-tailed)	<,001	<,001	<,001	<,001	<,001	<,001	<,001										
	N	17	17	17	17	17	17	17	17									
Gd	Pearson Correlation	,802	,871	,859	,905	,913	,940	,978	,990	1								
	Sig. (2-tailed)	<,001	<,001	<,001	<,001	<,001	<,001	<,001	<,001									
	N	17	17	17	17	17	17	17	17	17								
Tb	Pearson Correlation	,808	,877	,809	,851	,863	,889	,937	,977	,976	1							
	Sig. (2-tailed)	<,001	<,001	<,001	<,001	<,001	<,001	<,001	<,001	<,001								
	N	17	17	17	17	17	17	17	17	17	17							
Dy	Pearson Correlation	,917	,963	,732	,766	,777	,814	,881	,953	,951	,957	1						
	Sig. (2-tailed)	<,001	<,001	<,001	<,001	<,001	<,001	<,001	<,001	<,001	<,001							
	N	17	17	17	17	17	17	17	17	17	17	17						
Ho	Pearson Correlation	,928	,978	,676	,710	,720	,757	,824	,922	,902	,930	,977	1					
	Sig. (2-tailed)	<,001	<,001	,003	,001	,001	<,001	<,001	<,001	<,001	<,001	<,001						
	N	17	17	17	17	17	17	17	17	17	17	17	17					
Er	Pearson Correlation	,930	,985	,640	,672	,683	,721	,783	,887	,862	,889	,955	,992	1				
	Sig. (2-tailed)	<,001	<,001	,006	,003	,003	,001	<,001	<,001	<,001	<,001	<,001	<,001					
	N	17	17	17	17	17	17	17	17	17	17	17	17	17				
Tm	Pearson Correlation	,925	,980	,597	,634	,644	,685	,748	,859	,831	,855	,937	,981	,995	1			
	Sig. (2-tailed)	<,001	<,001	,011	,006	,005	,002	<,001	<,001	<,001	<,001	<,001	<,001	<,001				
	N	17	17	17	17	17	17	17	17	17	17	17	17	17	17			
Yb	Pearson Correlation	,917	,969	,561	,600	,608	,648	,710	,822	,791	,803	,904	,958	,983	,992	1		
	Sig. (2-tailed)	<,001	<,001	,019	,011	,010	,005	,001	<,001	<,001	<,001	<,001	<,001	<,001	<,001			
	N	17	17	17	17	17	17	17	17	17	17	17	17	17	17	17		
Lu	Pearson Correlation	,832	,821	,305	,335	,338	,387	,464	,568	,562	,511	,723	,738	,782	,813	,856	1	
	Sig. (2-tailed)	<,001	<,001	,234	,189	,184	,125	,060	,017	,019	,036	,001	<,001	<,001	<,001	<,001		
	N	17	17	17	17	17	17	17	17	17	17	17	17	17	17	17	17	
Inertinite	Pearson Correlation	-,223	-,078	,147	,170	,182	,177	,130	,113	,072	,081	-,053	-,070	-,099	-,118	-,154	-,347	1
	Sig. (2-tailed)	,390	,765	,573	,513	,485	,498	,620	,667	,783	,757	,839	,790	,707	,652	,555	,173	
	N	17	17	17	17	17	17	17	17	17	17	17	17	17	17	17	17	17

		Correlations																
		Sc	Y	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Liptinite
Sc	Pearson Correlation	1																
	N	17																
Y	Pearson Correlation	,922	1															
	Sig. (2-tailed)	<,001																
	N	17	17															
La	Pearson Correlation	,538	,673	1														
	Sig. (2-tailed)	,026	,003															
	N	17	17	17														
Ce	Pearson Correlation	,543	,694	,975	1													
	Sig. (2-tailed)	,024	,002	<,001														
	N	17	17	17	17													
Pr	Pearson Correlation	,564	,701	,973	,997	1												
	Sig. (2-tailed)	,018	,002	<,001	<,001													
	N	17	17	17	17	17												
Nd	Pearson Correlation	,611	,737	,956	,989	,995	1											
	Sig. (2-tailed)	,009	<,001	<,001	<,001	<,001												
	N	17	17	17	17	17	17											
Sm	Pearson Correlation	,687	,794	,915	,962	,969	,984	1										
	Sig. (2-tailed)	,002	<,001	<,001	<,001	<,001	<,001											
	N	17	17	17	17	17	17	17										
Eu	Pearson Correlation	,806	,888	,828	,879	,890	,922	,964	1									
	Sig. (2-tailed)	<,001	<,001	<,001	<,001	<,001	<,001	<,001										
	N	17	17	17	17	17	17	17	17									
Gd	Pearson Correlation	,802	,871	,859	,905	,913	,940	,978	,990	1								
	Sig. (2-tailed)	<,001	<,001	<,001	<,001	<,001	<,001	<,001	<,001									
	N	17	17	17	17	17	17	17	17	17								
Tb	Pearson Correlation	,808	,877	,809	,851	,863	,889	,937	,977	,976	1							
	Sig. (2-tailed)	<,001	<,001	<,001	<,001	<,001	<,001	<,001	<,001	<,001								
	N	17	17	17	17	17	17	17	17	17	17							
Dy	Pearson Correlation	,917	,963	,732	,766	,777	,814	,881	,953	,951	,957	1						
	Sig. (2-tailed)	<,001	<,001	<,001	<,001	<,001	<,001	<,001	<,001	<,001	<,001							
	N	17	17	17	17	17	17	17	17	17	17	17						
Ho	Pearson Correlation	,928	,978	,676	,710	,720	,757	,824	,922	,902	,930	,977	1					
	Sig. (2-tailed)	<,001	<,001	,003	,001	,001	<,001	<,001	<,001	<,001	<,001	<,001						
	N	17	17	17	17	17	17	17	17	17	17	17	17					
Er	Pearson Correlation	,930	,985	,640	,672	,683	,721	,783	,887	,862	,889	,955	,992	1				
	Sig. (2-tailed)	<,001	<,001	,006	,003	,003	,001	<,001	<,001	<,001	<,001	<,001	<,001					
	N	17	17	17	17	17	17	17	17	17	17	17	17	17				
Tm	Pearson Correlation	,925	,980	,597	,634	,644	,685	,748	,859	,831	,855	,937	,981	,995	1			
	Sig. (2-tailed)	<,001	<,001	,011	,006	,005	,002	<,001	<,001	<,001	<,001	<,001	<,001	<,001				
	N	17	17	17	17	17	17	17	17	17	17	17	17	17	17			
Yb	Pearson Correlation	,917	,969	,561	,600	,608	,648	,710	,822	,791	,803	,904	,958	,983	,992	1		
	Sig. (2-tailed)	<,001	<,001	,019	,011	,010	,005	,001	<,001	<,001	<,001	<,001	<,001	<,001	<,001			
	N	17	17	17	17	17	17	17	17	17	17	17	17	17	17	17		
Lu	Pearson Correlation	,832	,821	,305	,335	,338	,387	,464	,568	,562	,511	,723	,738	,782	,813	,856	1	
	Sig. (2-tailed)	<,001	<,001	,234	,189	,184	,125	,060	,017	,019	,036	,001	<,001	<,001	<,001	<,001		
	N	17	17	17	17	17	17	17	17	17	17	17	17	17	17	17	17	
Liptinite	Pearson Correlation	,424	,284	-,059	-,116	-,103	-,097	-,096	,049	,015	,060	,176	,267	,317	,345	,382	,397	1
	Sig. (2-tailed)	,090	,270	,823	,658	,694	,712	,714	,851	,955	,820	,499	,301	,215	,175	,130	,114	
	N	17	17	17	17	17	17	17	17	17	17	17	17	17	17	17	17	17

		Correlations																
		Sc	Y	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Kaolinite
Sc	Pearson Correlation	1																
	N	17																
Y	Pearson Correlation	,922	1															
	Sig. (2-tailed)	<,001																
	N	17	17															
La	Pearson Correlation	,538	,673	1														
	Sig. (2-tailed)	,026	,003															
	N	17	17	17														
Ce	Pearson Correlation	,543	,694	,975	1													
	Sig. (2-tailed)	,024	,002	<,001														
	N	17	17	17	17													
Pr	Pearson Correlation	,564	,701	,973	,997	1												
	Sig. (2-tailed)	,018	,002	<,001	<,001													
	N	17	17	17	17	17												
Nd	Pearson Correlation	,611	,737	,956	,989	,995	1											
	Sig. (2-tailed)	,009	<,001	<,001	<,001	<,001												
	N	17	17	17	17	17	17											
Sm	Pearson Correlation	,687	,794	,915	,962	,969	,984	1										
	Sig. (2-tailed)	,002	<,001	<,001	<,001	<,001	<,001											
	N	17	17	17	17	17	17	17										
Eu	Pearson Correlation	,806	,888	,828	,879	,890	,922	,964	1									
	Sig. (2-tailed)	<,001	<,001	<,001	<,001	<,001	<,001	<,001										
	N	17	17	17	17	17	17	17	17									
Gd	Pearson Correlation	,802	,871	,859	,905	,913	,940	,978	,990	1								
	Sig. (2-tailed)	<,001	<,001	<,001	<,001	<,001	<,001	<,001	<,001									
	N	17	17	17	17	17	17	17	17	17								
Tb	Pearson Correlation	,808	,877	,809	,851	,863	,889	,937	,977	,976	1							
	Sig. (2-tailed)	<,001	<,001	<,001	<,001	<,001	<,001	<,001	<,001	<,001								
	N	17	17	17	17	17	17	17	17	17	17							
Dy	Pearson Correlation	,917	,963	,732	,766	,777	,814	,881	,953	,951	,957	1						
	Sig. (2-tailed)	<,001	<,001	<,001	<,001	<,001	<,001	<,001	<,001	<,001	<,001							
	N	17	17	17	17	17	17	17	17	17	17	17						
Ho	Pearson Correlation	,928	,978	,676	,710	,720	,757	,824	,922	,902	,930	,977	1					
	Sig. (2-tailed)	<,001	<,001	,003	,001	,001	<,001	<,001	<,001	<,001	<,001	<,001						
	N	17	17	17	17	17	17	17	17	17	17	17	17					
Er	Pearson Correlation	,930	,985	,640	,672	,683	,721	,783	,887	,862	,889	,955	,992	1				
	Sig. (2-tailed)	<,001	<,001	,006	,003	,003	,001	<,001	<,001	<,001	<,001	<,001	<,001					
	N	17	17	17	17	17	17	17	17	17	17	17	17	17				
Tm	Pearson Correlation	,925	,980	,597	,634	,644	,685	,748	,859	,831	,855	,937	,981	,995	1			
	Sig. (2-tailed)	<,001	<,001	,011	,006	,005	,002	<,001	<,001	<,001	<,001	<,001	<,001	<,001				
	N	17	17	17	17	17	17	17	17	17	17	17	17	17	17			
Yb	Pearson Correlation	,917	,969	,561	,600	,608	,648	,710	,822	,791	,803	,904	,958	,983	,992	1		
	Sig. (2-tailed)	<,001	<,001	,019	,011	,010	,005	,001	<,001	<,001	<,001	<,001	<,001	<,001	<,001			
	N	17	17	17	17	17	17	17	17	17	17	17	17	17	17	17		
Lu	Pearson Correlation	,832	,821	,305	,335	,338	,387	,464	,568	,562	,511	,723	,738	,782	,813	,856	1	
	Sig. (2-tailed)	<,001	<,001	,234	,189	,184	,125	,060	,017	,019	,036	,001	<,001	<,001	<,001	<,001		
	N	17	17	17	17	17	17	17	17	17	17	17	17	17	17	17	17	
Kaolinite	Pearson Correlation	,393	,525	,627	,646	,624	,608	,604	,597	,601	,620	,556	,545	,519	,482	,455	,229	1
	Sig. (2-tailed)	,119	,030	,007	,005	,007	,010	,010	,011	,011	,008	,021	,024	,033	,050	,066	,377	
	N	17	17	17	17	17	17	17	17	17	17	17	17	17	17	17	17	17

Correlations																		
		Sc	Y	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Pyrite
Sc	Pearson Correlation	1																
	N	17																
Y	Pearson Correlation	,922	1															
	Sig. (2-tailed)	<,001																
	N	17	17															
La	Pearson Correlation	,538	,673	1														
	Sig. (2-tailed)	,026	,003															
	N	17	17	17														
Ce	Pearson Correlation	,543	,694	,975	1													
	Sig. (2-tailed)	,024	,002	<,001														
	N	17	17	17	17													
Pr	Pearson Correlation	,564	,701	,973	,997	1												
	Sig. (2-tailed)	,018	,002	<,001	<,001													
	N	17	17	17	17	17												
Nd	Pearson Correlation	,611	,737	,956	,989	,995	1											
	Sig. (2-tailed)	,009	<,001	<,001	<,001	<,001												
	N	17	17	17	17	17	17											
Sm	Pearson Correlation	,687	,794	,915	,962	,969	,984	1										
	Sig. (2-tailed)	,002	<,001	<,001	<,001	<,001	<,001											
	N	17	17	17	17	17	17	17										
Eu	Pearson Correlation	,806	,888	,828	,879	,890	,922	,964	1									
	Sig. (2-tailed)	<,001	<,001	<,001	<,001	<,001	<,001	<,001										
	N	17	17	17	17	17	17	17	17									
Gd	Pearson Correlation	,802	,871	,859	,905	,913	,940	,978	,990	1								
	Sig. (2-tailed)	<,001	<,001	<,001	<,001	<,001	<,001	<,001	<,001									
	N	17	17	17	17	17	17	17	17	17								
Tb	Pearson Correlation	,808	,877	,809	,851	,863	,889	,937	,977	,976	1							
	Sig. (2-tailed)	<,001	<,001	<,001	<,001	<,001	<,001	<,001	<,001	<,001								
	N	17	17	17	17	17	17	17	17	17	17							
Dy	Pearson Correlation	,917	,963	,732	,766	,777	,814	,881	,953	,951	,957	1						
	Sig. (2-tailed)	<,001	<,001	<,001	<,001	<,001	<,001	<,001	<,001	<,001	<,001							
	N	17	17	17	17	17	17	17	17	17	17	17						
Ho	Pearson Correlation	,928	,978	,676	,710	,720	,757	,824	,922	,902	,930	,977	1					
	Sig. (2-tailed)	<,001	<,001	,003	,001	,001	<,001	<,001	<,001	<,001	<,001	<,001						
	N	17	17	17	17	17	17	17	17	17	17	17	17					
Er	Pearson Correlation	,930	,985	,640	,672	,683	,721	,783	,887	,862	,889	,955	,992	1				
	Sig. (2-tailed)	<,001	<,001	,006	,003	,003	,001	<,001	<,001	<,001	<,001	<,001	<,001					
	N	17	17	17	17	17	17	17	17	17	17	17	17	17				
Tm	Pearson Correlation	,925	,980	,597	,634	,644	,685	,748	,859	,831	,855	,937	,981	,995	1			
	Sig. (2-tailed)	<,001	<,001	,011	,006	,005	,002	<,001	<,001	<,001	<,001	<,001	<,001	<,001				
	N	17	17	17	17	17	17	17	17	17	17	17	17	17	17			
Yb	Pearson Correlation	,917	,969	,561	,600	,608	,648	,710	,822	,791	,803	,904	,958	,983	,992	1		
	Sig. (2-tailed)	<,001	<,001	,019	,011	,010	,005	,001	<,001	<,001	<,001	<,001	<,001	<,001	<,001			
	N	17	17	17	17	17	17	17	17	17	17	17	17	17	17	17		
Lu	Pearson Correlation	,832	,821	,305	,335	,338	,387	,464	,568	,562	,511	,723	,738	,782	,813	,856	1	
	Sig. (2-tailed)	<,001	<,001	,234	,189	,184	,125	,060	,017	,019	,036	,001	<,001	<,001	<,001	<,001		
	N	17	17	17	17	17	17	17	17	17	17	17	17	17	17	17	17	
Pyrite	Pearson Correlation	-,122	-,188	-,674	-,615	-,621	-,601	-,576	-,486	-,501	-,475	-,331	-,246	-,161	-,102	-,036	,213	1
	Sig. (2-tailed)	,642	,469	,003	,009	,008	,011	,015	,048	,040	,054	,195	,342	,538	,696	,890	,411	
	N	17	17	17	17	17	17	17	17	17	17	17	17	17	17	17	17	17