Rare Earth Elements enrichment in Triassic coals deposits and associated argillaceous rocks in Lesotho

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Abstract

The demand for rare earth elements has increased around the world due to their application in a variety of technological advancements. Previous studies have evaluated the potential of the rare earth elements and yttrium (REY) hosted within the Permian coal deposits of the main Karoo Basin (MKB) in Southern Africa. However, not a lot of scientific research has gone into the Triassic coal deposits. The Triassic coals in South Africa were the first coals to be exploited for their thermal use in the 1880s, but the discovery of the higher rank and more abundant Ecca coal deposits led to the Triassic coals remaining largely unexplored. The demand for rare earth elements has sparked interest in these coal deposits as potential sources for valuable minerals. Late Triassic coal deposits in Lesotho have previously not been well documented and these low-rank coals can be a potential source of rare earth elements. This study aims to characterize and evaluate the potential of REY in the Taung coal deposit, southwest of Lesotho. Coal and associated argillaceous samples from the Taung coal deposit were analyzed using microscopic petrography for coal characterization and an inductively coupled plasma mass spectrometry (ICP-MS) to determine the amount of rare earth elements. Taung coal is classified as middle medium rank D bituminous coal. The total REY content in Taung coal and its associated rocks range from 162.9 ppm to 855.1 ppm, which is significantly higher than the upper continental crustal (UCC) average. The average critical REY concentration of samples from the Taung coal deposit is 189.4 ppm, which is three times higher than that of the Chinese Bayan Obo deposit. Samples classified as very promising and promising because of their outlook coefficients, are found to contain up to 77% of critical REY. It is envisioned that the area could be a prime deposit for these REY.

Keywords

rare earth elements and yttrium (REY), low-grade coals, Triassic coals, Taung Lesotho

Introduction

The demand for rare earth elements and yttrium (hereafter referred to as REY) in the world has sharply increased because of their use in a variety of high technological applications (Seredin and Dai, 2012). They play a critical role for renewable energy as essential components of wind turbines and hybrid cars, which are essential as the world transitions to a more carbon neutral future (Balaram, 2019; Hower et al., 2016). Because of supply challenges, several countries and bodies have adopted policies in identifying REY as critical raw materials for which these policies intend to secure these materials through various geological sources (European Commission, 2023; U.S. Department of Energy, 2023). Naturally, rare earth elements are a group of 15 lanthanide elements identified by increasing atomic numbers from 57 (lanthanum) to 71 (lutetium); La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu (Damhus et al., 2005). Even though the atomic number of yttrium (Y) is 21, it is commonly added to the rare earth elements list and positioned between Dy and Ho on REY normalized plots (Bau, 1996). Geochemically, REY are classified as light REY (La, Ce, Pr, Nd, and Sm), medium REY (Eu, Gd, Tb, Dy, and Y), and heavy REY (Ho, Er, Tm, Yb, and Lu) (Seredin and Dai, 2012). Another significant classification of REY is associated with market considerations such as the ease or difficulty of supply and the demand of each element, where Nd, Eu, Tb, Dy, Y, and Er are recognized as critical REY, La, Pr, Sm, and Gd as uncritical REY, and Ce, Ho, Tm, Yb, and Lu as excessive REY (Kingsnorth, 2009).

The primary sources of REY ores are bastnasite, monazite, and xenotime minerals, for which viable deposits are associated with magmatic processes, and thus common in alkaline igneous rocks and carbonatites (Orris and Grauch, 2002). Secondary REY ores are found as placers, laterite deposits and the commonly economic ion-absorption in clay ore deposits (Suli et al., 2017). The challenge related to the availability of REY is based on mined conventional ore bodies not being able to meet the demand of

REY because their usage has been significantly increasing over the years (Scott et al., 2015). Another challenge is that most of these conventional deposits are in China, thus giving China leverage in terms of market considerations (Jowitt, 2022). The demand of REY, extraction efficiencies of REY from traditional ore bodies, and geo-politics have enabled unconventional sources like coal and coal derivatives such as fly ash to be considered as potential sources of these elements (Eterigho-Ikelegbe et al., 2021). Geological processes that are responsible for the accretion of REY in coal deposits include movement of natural leachates and volcanic ash (tuffaceous), interaction of hydrothermal fluids with coal, contact with aquifer waters (infiltration), and REY carried to coal depositional sites by surface waters (terrigenous) (Seredin and Dai, 2012).

Coal and coal fly ash have been explored extensively as alternative sources of REY (Chitlango et al., 2023; Dai et al., 2016; Finkelman, 1993; Mokoena et al., 2022; Wagner and Matiane, 2018). In coal fly ash, the REY are generally encapsulated in the glass matrix and extraction has proved to be a challenge with low yields recorded (Mokoena et al., 2022). In low-rank coals, REY can be hosted within the organic part (macerals) and are associated with various organometallic compounds, and side chain functional groups such as carboxylic acids (Dai et al., 2021). REY also occur within the inorganic component of coal as replacement minerals such as apatite, those absorbed by other minerals such as clays, the terrigenous primary REY minerals such as xenotime, and as ions being dissolved in pore fluids (Fu et al., 2022). To evaluate the potential of REY in coal, their dominance in either organic or inorganic components can have an impact on the success of their extraction using methods such as leaching (Finkelman et al., 2018). For example, studies have shown that methods such as sequential leaching have proven to be efficient (80% – 95%) in extracting REY from younger coals such as Fort Union lignite coal in North America, because these coals contain carboxylic acids, which are associated with the organic components of coal (Laudal et al., 2018). On the contrary, some studies have shown that extracting REY by sequential leaching method from the inorganic components of coal fly ash can be very challenging, as the majority of REY (70%) are locked within the structures of aluminosilicate glasses (Querol et al., 1996; Wang et al., 2019). Even though the volumes of fly ash produced in most coal-fired power stations are significant, extraction challenges have positioned low quality coals as an alternative source of REY. Using coal as a source of REY will always result in competing interests, where the temptation for thermal use will always outweigh REY extraction. However, poor quality coal can diminish this contradiction as there is less appetite for low-rank coal in the world market due to the associated high cost of beneficiation needed to meet the requirements of the end user.

The average sum of REY of the world-low-rank coals is 65 ppm, which necessitates enrichment of REY for these coals to be considered economic (Finkelman, 1993). There is substantial evidence that coals can be enriched in REY, such as the Pavlova lignite deposits of Russian Far East coal and Luizhi bituminous deposit in Guizhou China, with REY concentrations of 5952 ppm and 2491 ppm, respectively (Seredin and Dai, 2012). In South Africa, most of the coalfields being exploited are of a Permian age because they host good quality coal, leaving the generally low-quality Triassic coalfields under-utilized. Wagner and Matiane (2018) reported that the total REY range from 121 ppm to 150 ppm for the Permian coals, which are lower than the upper continental crustal (UCC) abundances, as determined by Taylor and McLennan (1985), but higher than the hard coals reported by Ketris and Yudovich (2009). A study by (Chitlango et al., 2023) on bituminous coal samples from the Waterberg Coalfield (Permian) reported concentration of REY ranging from 45.1 ppm to 389.2 ppm. Nonetheless, very little is known regarding the potential of REY in younger Triassic coals in South Africa, and more specifically in Lesotho. In this regard, the Triassic coals in South Africa and Lesotho are available in significant quantities because they are hosted within the Molteno Coalfield, which is the largest single coalfield in South Africa (Hancox and Götz, 2014). The quality of coal from the Molteno Coalfield is generally considered to be low quality (Hancox and Götz, 2014).

The aim of this study is to evaluate the REY concentrations in Triassic coals from the mountainous Kingdom of Lesotho. Coal deposits in this part of Southern Africa have not been reported previously and hence this study will add new insights into the coal deposits and their associated rocks in a new geographical area. Current Lesotho mining activity is primarily dominated by diamonds, which account for almost 98% of mining activities in the mountain kingdom (Lesotho Chamber of Mines, 2022). Exploring coal deposits could help Lesotho diversify their minerals industry.

Geological setting and background

The Molteno Coalfield is of a Triassic age (Figure 1) and is predominantly positioned in the Eastern Cape Province with an estimated surface area of 13 million hectares covering an extensive area in South Africa (Christie, 1986; Macdonald, 1993). This coalfield also extends northward into the southwestern parts of Lesotho, outcropping largely at Taung village (Nixon, 1971). Coal in South Africa was first discovered in the Molteno Coalfield with production beginning in the 1860s and ceasing during the late 1940s due to the relatively poor-quality coal and the discovery of good quality Permian coals in Mpumalanga Province (Hancox and Götz, 2014). There is a general increase of coal rank from the west (high volatile bituminous coal) to the east (low volatile bituminous to anthracite coals) of the Molteno Coalfield, with local variations in coal quality occurring because of the presence of nearby igneous intrusions (Saggerson, 1991).

The Molteno Coalfield is hosted within the sediments of the main Karoo Basin, which is an asymmetrical basin filled with mainly clastic sediments of the Karoo Supergroup (Johnson et al., 2006). The study area (Taung Coal) is situated in the southwestern corner of Lesotho on the southern boundary of the Kaapvaal Craton (Figure 2) and is part of the greater Molteno Coalfield, with intermittent coal seams hosted within the sediments of the Molteno Formation (Figure 3) (Hancox and Götz, 2014).

The Bamboesberg Member is thickest in the southern parts of the basin and is characterized by five stacked cycles of upward fining successions with sandstones at the base, followed by siltstones, mudstones, and coal (Christie, 1981). In addition, the Bamboesberg Member pinches out to the north, being absent in the northern parts of the Molteno Formation (Figure 2). The Bamboesberg Member hosts the economically significant Indwe and Guba coal seams, which occur as partitions of dull and bright bands of coal (Figure 3), interchanging with carbonaceous rocks (Hancox and Götz, 2014). The top of the Indwe and Guba seams consists of sandstone while the floor is characterized by the presence of shale/mudstone (Hancox and Götz, 2014). Analyses on the properties of the Indwe and Guba coals indicate high ash content (31%–51%), high inherent moisture (7%-11%), low volatile matter (7%–12%) according to Prevost (2002), a fixed carbon content between 30–41% (Macdonald, 1993), and a calorific value (CV) ranging from 23.9 MJ/kg to 25.9 MJ/kg (De Jager, 1983). These coals are of a poor quality when comparing them with other coalfields in South Africa, such as the Ermelo Coalfield (Vryheid Formation) with an average ash content (26.74%), inherent moisture (3.11%), volatile matter

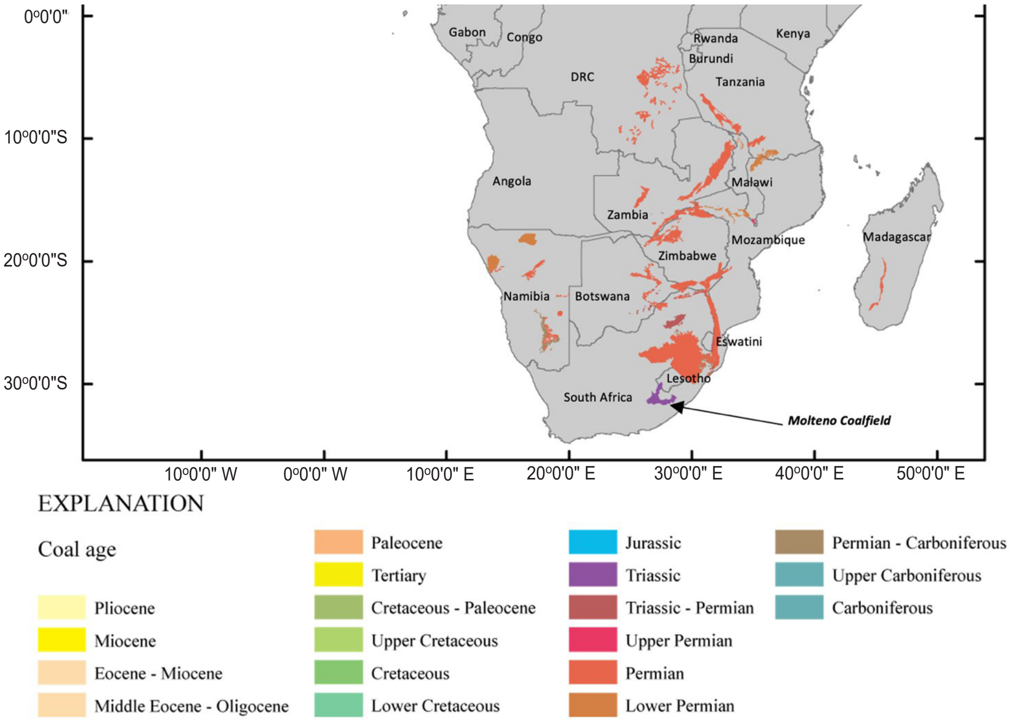


Figure 1—The distribution of Coalfields in the south of Africa with their associated ages (Merril and Tewalt, 2008)

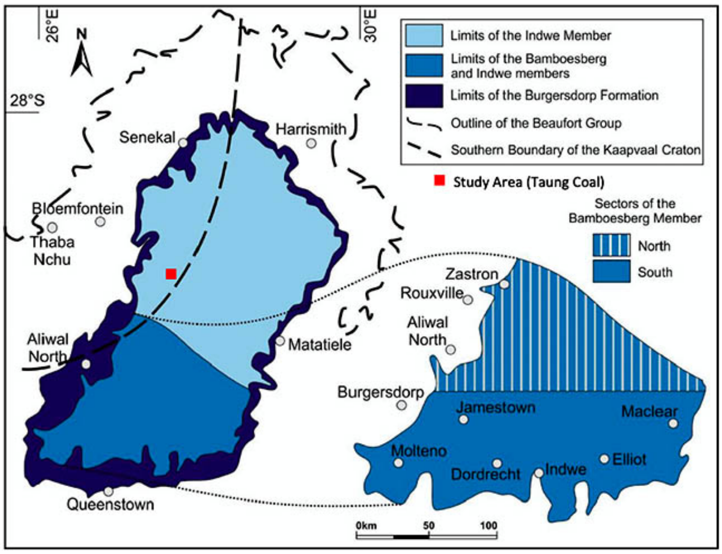


Figure 2—Geographical coverage of the Bamboesberg and Indwe Members of the Molteno Formation and the Burgersdorp Formation (Hancox and Rubidge, 2023). Note: Study area is located within the Indwe Member area within the Kaapvaal Craton

(23.64%), fixed carbon (46.72%), and a CV of 22.57MJ/kg (Wagner et al., 2018). The thicknesses of the Indwe and Guba seams fluctuate in relatively small distances, attaining maximum thicknesses of 4.5 m and 3 m, respectively (Christie, 1981, 1986). When reference is made to the name 'Indwe' when discussing Molteno Formation literature, it is worth mentioning that the Indwe Seam is not associated with the Indwe Member, as the former is hosted within the Bamboesberg Member (Christie, 1986).

The coal seams found within the upper stratigraphic units (Figure 3) identified by Christie (1981) are therefore important for this study because there is no evidence of coal occurrence in the lower Indwe Member. The Cala Pass/Molteno Seam is 2–3 m thick impersistent with poor-quality coal hosted within the argillaceous rocks at the top of the Mayaputi Member and comprises of carbonaceous shales with thin bands of bright coal (Christie, 1981; Turner, 1975). Gubenxa/Ulin Seam is made up of laterally intermittent bands about 1.7 m thick lenses of bright coal with coaly siltstones, mudstones, and shale, which are found within the sediments of the Qiba Member (Christie, 1981). The Umnachean and Offa Seams of the Loskop Member are the youngest seams of the Molteno Coalfield and have similar characteristics with Ulin coal, although they are thinner than the Ulin Seam (Christie, 1981). All these coal seams in the upper stratigraphic units are not well recorded in the northern parts of the Molteno Coalfield and this study will provide an insight on some coal properties, including REY potential, within these units.

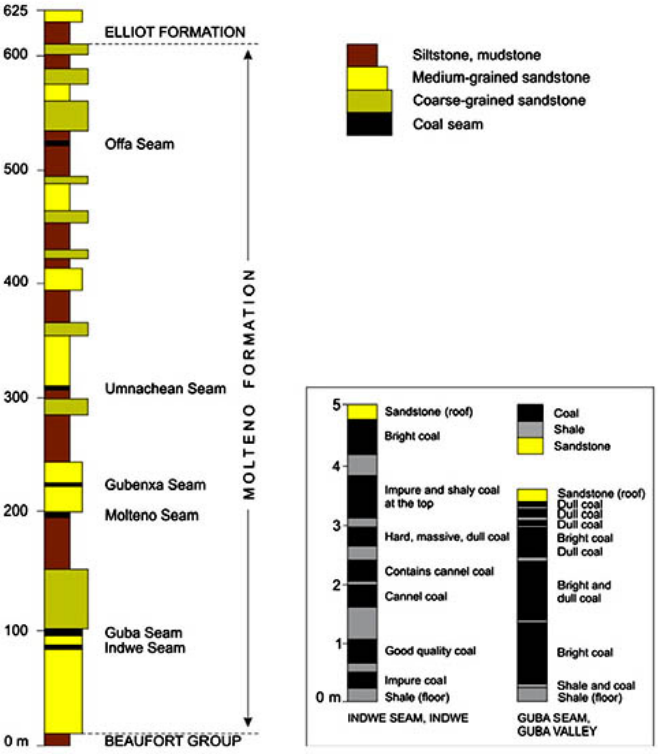


Figure 3—Stratigraphy of the Molteno Formation with relative coal seams in the southern part of the basin (Christie, 1986; Hancox and Götz, 2014)

Methodology

Sampling, preparation, and coal characterization

The sampling area comprises of coal outcrops with fissile, carbonaceous, dark grey rocks interlayered with argillaceous rocks, which are associated with the Cala Pass/Molteno Seams of the Molteno Coalfield (Christie, 1981). The coal and its associated argillaceous rock samples were collected from the outcrops exposed by weathering and erosion forming deep dongas (Figure 4). The geographical positions of all the sampling points are located within the Taung geological map (Figure 5). Well-labelled polystyrene bags were used to collect a total of 10 samples with an average weight of 2 kg per sample. The sample names were abbreviated as CPL denoting Coal Project Lesotho (CPL01 to CPL10). All descriptions of the properties of the samples and the sampling site were carried out in accordance with the best practices following the Australian Standard AS2916-1986. Sample preparation/handling was also done according to the SANS 18283 (2007).

Figure 4—Typical outcrop of Taung coal deposit exposed by weathering and erosion

Table I summarizes the methods and standards that were applied for coal characterization, which are all important in evaluating coal utilization capabilities. For example, calorific value (CV) is an important parameter as it measures the amount of heat per kilogram that coal can produce (a proxy of coal quality), which is critical for utilizing coal for producing thermal electricity. Besides thermal applications, coal can also be used as a potential source of REY through assessing the ash content in coal, as these minerals can be locked in the inorganic part of coal (ash) (Seredin et al., 2013). Proximate analysis (ash, moisture, volatile matter, fixed carbon) including CV and total sulphur (TS) were carried out at Eskom's central coal laboratory, which is accredited for all these methods. All the results for these methods were reported on an air-dry basis (a.r.).

Samples were sent to the University of Johannesburg for petrographic analysis. Here, the organic (maceral groups) and inorganic (mineral groups) components of coal were analysed through a technique as stipulated by SANS ISO 7407-2 (2015). This is important as low-rank coals are associated with REY concentrated within the organic component of coal (macerals) (Dai et al., 2021). Coal rank analysis reporting the random vitrinite reflectance (%RoV) was determined through a Zeiss Axio Imager microscope (reflected light) according to SABS ISO 7404-3 (2016).

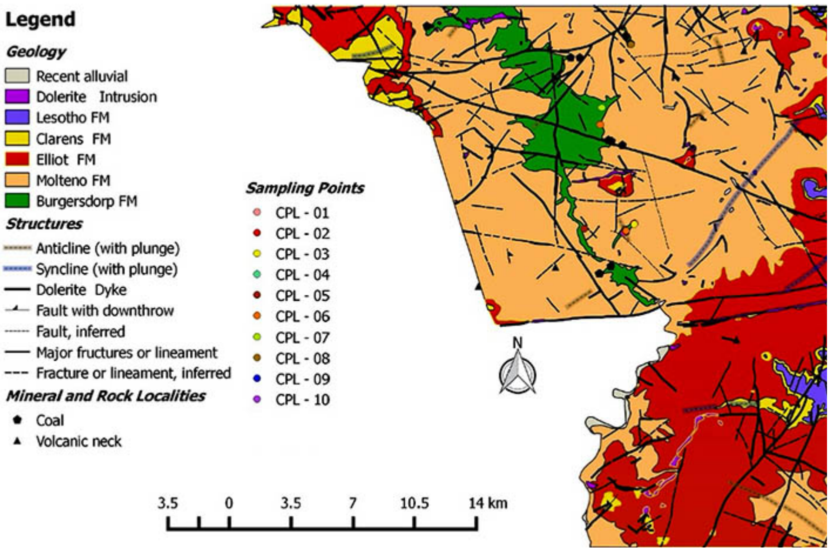


Figure 5—The geographical locations of the sampling points in the Taung area geological map

Table I

Coal analysis and corresponding standards

Analysis	Procedure/ Method
Sample preparation	SANS 18283:2007 / ISO 18283:2006
Proximate analysis - Ash content (mass%)	SABS ISO 1171:1997
Proximate analysis - Volatile matter content (mass%)	SABS ISO 562:1998
Proximate analysis - Moisture content (mass%)	SANS 5925:2007
Proximate analysis - Fixed carbon content (mass%)	By difference
Gross calorific value (MJ/kg)	SABS ISO 1928:1995
Total sulphur (mass%)	ISO 19579

Table II

Proximate analysis of the coal and argillaceous rocks samples (mass%)

SAMPLE ID	Ash (%)	Volatile matter (%)	Moisture (%)	Fixed carbon (%)	CV(MJ/kg)
CPL01	78	14.3	2.8	4.9	0.14
CPL02	93.1	4.6	3.2	0	0.2
CPL03	80.4	11.4	4.6	3.6	0.19
CPL04	92.6	4.9	3.7	0	3.53
CPL05	87.2	8.3	4	0.5	0.25
CPL06	85.6	7	1.3	6.3	3.02
CPL07	93.9	4.4	2.8	0	2.6
CPL08	79	14.6	3	3.4	0.14
CPL09	56.8	24.8	1.4	17	13.41
CPL10	57.2	27.2	2	13.6	13.2

Rare earth elements and yttrium (REY) analysis

Inductively coupled plasma mass spectrometry (ICP-MS) analysis is efficient in determining the concentration of trace elements, which include rare earth elements and yttrium. About 50 mg sample is weighed and digested in the microwave digester (MARS from CEM). The 50 mg sample is added to a Teflon vessel containing 6 ml of ultra-high Purity 2:1 HF: HNO_3 forming a mixture. The mixture is transferred inside a microvan that is set to a temperature of 180°C and pressure of 400 psi for 40 minutes. The sample is moved into a 15 ml savilex beaker, which is followed by thorough rinsing of the Teflon vessel. The savilex beaker containing the sample is closed and transferred to a hot plate set at 70°C for a duration of 24 hours to evaporate the acid. Approximately 2 ml of HNO_3 is added to the sample in in savilex beaker and returned to the same settings of the hot plate for another 24 hours. The same process of acid addition (HNO_3) and heating of the sample is repeated. The sample is removed from the hot plate and an additional 300 µl of HNO_3 is added to the sample that is ready for analysis. The sample is then transferred to the ICP-MS on a Thermo Scientific iCAP RQ, which is based at the University of the Witwatersrand, Earth laboratory.

Results and discussion

Sample characterization

Table II lists the results of proximate analysis of all the samples. The ash content in the samples range from 56.8 mass% to 93.9 mass%, which clearly indicates very high ash content (minerals) in these samples. Samples CPL09 and CPL10 have fixed carbon values at 17 mass% and 13.6%, respectively, while the rest of the samples have fixed carbon content lower than 6.5%, which is significantly lower than the Indwe and Guba Seams. The calorific values of these two samples (CPL09 and CPL10) are just above 13 MJ/kg while the other samples record CVs lower than 3 MJ/kg. The results indicate that all the samples have very low CVs compared to those of Indwe and Guba Seams, which range from 23.9 MJ/kg to 25.9 MJ/kg, respectively. (Rice, 1993).

Maceral analysis supports the proximate data, showing only sample CPL09 to contain less than 18 vol% of minerals while all samples, including CPL10, contain minerals more than 70 vol% (Figure 5). Because of the data presented by proximate analysis,

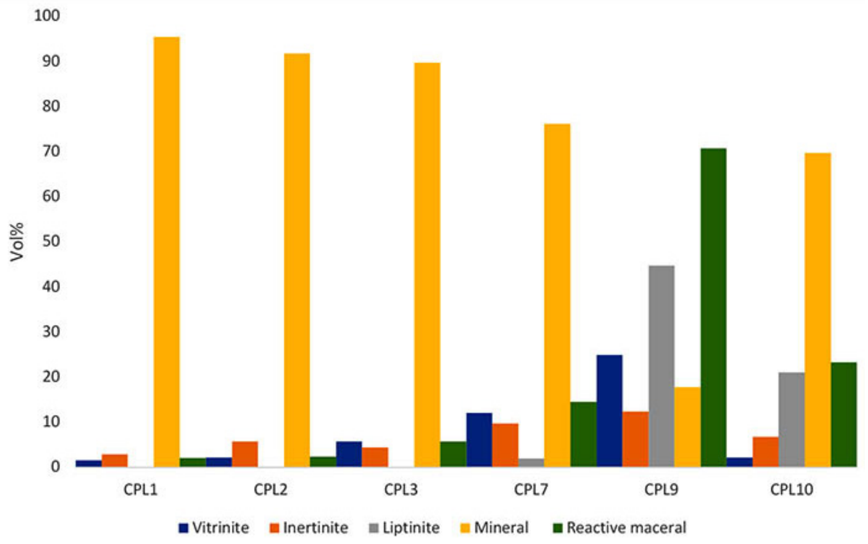
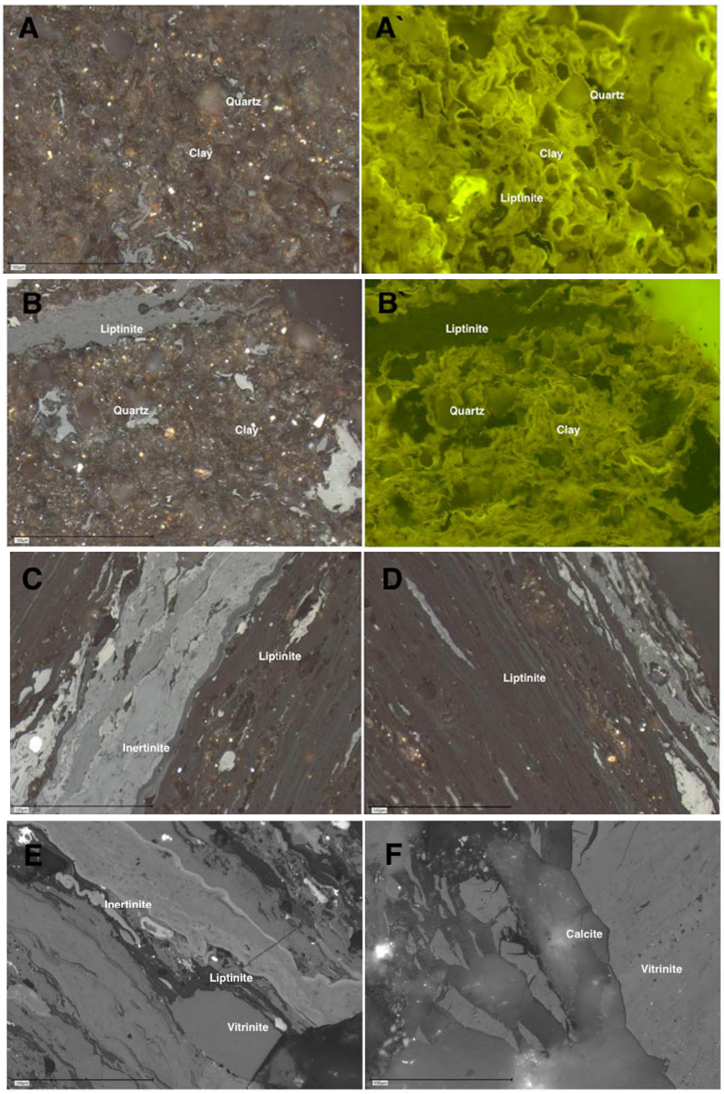


Figure 6—Maceral group analysis on selected samples of samples of the study area



L: white light image
R: fluorescent image of same field of view, showing extensive liptinite

L: white light image
R: fluorescent image of same field of view, showing extensive liptinite

L: banded coal – dark bands liptinite; light bands inertinite
R: Thick liptinite band – cutinite.

L: banded coal – dark bands liptinite, medium grey is vitrinite, lighter grey is inertinite
R: calcite cleats cutting through vitrinite.

Figure 7—Photomicrographs of macerals under reflected white light, x 500, oil immersion lens, scale bar = 100 μm, and fluorescent images from A to F of sample CPL 09

mineralogy, and maceral analysis, only sample CPL09 is classified as medium rank D bituminous coal borderline medium rank C, with a random reflectance (%RoV) of 0.6 (Figure 6A-F). This is a low-rank coal because it is very close to being lignite (%RoV of 0.5), which provides evidence of the overall low-quality nature of the coals from the Molteno Coalfield. All the other nine samples are argillaceous rocks, which are very common in proximity of Cala Pass/Molteno Coal Seam of the Mayaputi Member (Christie, 1981).

The mineralogical composition determined by petrography indicates that the inorganic component in coal for sample CPL09 is quartz (14.4 mass%), clay (2.8 mass%), and carbonate (0.4 mass%), with no presence of pyrite. In addition, CPL09 is dominated by the liptinite maceral group, especially cutinite (about 45 vol%), followed by vitrinite (~25 vol%) and inertinite (~12%) (Figure 6). This observation is unusual because Gondwana coals have been found to contain relatively small amounts of liptinite compared to the Northern Hemisphere coals (Wagner et al., 2018). Palynological studies for the high content of liptinite can provide more depth in terms of the original plant make-up of this coal, but they were not the scope of this study. The liptinite in this sample is associated with quartz included within it (Figure 7A-A). Petrography shows that sample CPL09 is a banded (humic) coal with dark bands made up of liptinite, medium grey bands as vitrinite, and lighter grey as inertinite (Figure 7C-D) (Hutton and Hower, 1999). Humic coals have fractures that are orientated parallel to the cleats (O'Keefe et al., 2013). This can be seen where calcite cleats are cutting through the vitrinite (Figure 7F). The quartz present within the structures of liptinite in the sample and the occurrence of calcite cleats on vitrinite is a clear indication that this coal has both syngenetic and epigenetic minerals.

Rare earth elements and yttrium (REY) distribution patterns in the samples

The results for rare earth elements and yttrium (REY) distribution in all the samples are from the ICP-MS analysis. The total content of REY in sample CPL09 (Taung coal) is 485.0 ppm, higher than the 472.3 ppm total average concentration of REY in the other argillaceous samples. The range of the argillaceous samples is from 162.9 ppm up to 855.1 ppm. The total REY concentration in all the samples, except CPL03 is above that of the UCC, with samples CPL02, CPL05, CPL06, CPL07, CPL09, and CPL10 above 400 ppm (Figure 8). Moreover, sample CPL05 is enriched with the LREY while both MREY and HREY are mostly enriched in samples CPL06, CPL07, CPL09, and CPL10. According to Ketris and Yudovich (2009), the average sum of the concentration of total REY in the world coals is roughly 68.5 ppm, while data from

Finkelman (1993) and Seredin and Dai (2012) for USA and China coals are 62.1 ppm and 137.9 ppm, respectively. The concentration of REY within the Taung coal is greater than the world coals, USA, and Chinese coals. Chitlango et al. (2023) reported a range from 45.1 ppm to 389.2 ppm of the total REY concentration within the Waterberg Coalfield samples, which is lower than the 485.0 ppm total REY content of the Taung coal.

The ICP-MS results of the Taung coal and argillaceous samples further present the distribution of REY within all the samples relative to the values of the upper continental crust (UCC) by Taylor and McLennan (1985), which normalizes the REY data (Figure 9A-B). The distribution patterns of REY in samples CPL03 and CPL01 show depletion of heavy REY and some weak enrichment in light REY (Figure 9A). All the other eight samples, including CPL09 (Taung coal), show patterns of enrichment of the heavy REY. Anomaly ratios of Ce, Eu, and Gd are significant in delineating depositional environments, fluid conditions, and sediment source-region of coal strata (Dai et al., 2016). The equations for calculating anomalies of these REY are presented in Equations [1] to [3]. For each equation, the ratio that equates to 1 indicates no anomaly, while greater or less than 1 is indicative of positive or negative anomalies, respectively. The calculations are summarized in Table III.

$$Ce_N \; / \; Ce_N = Ce_N \; / \; (0.5La_N + 0.5Pr_N) \qquad [1]$$

$$Eu_N/Eu_N = Eu_N/[(Sm_N \times 0.67) + (Tb_N \times 0.33)] \qquad [2]$$

$$Gd_N/Gd_N = Gd_N/[(Sm_N \times 0.33) + (Tb_N \times 0.67)] \qquad [3]$$

The $\mathrm{Ce_N/Ce_N}$ ratio for Taung coal (CPL09) is 0.95, which suggests a weakly negative anomaly. This observation is common for most coals although host rocks can sometimes display positive anomalies (Dai et al., 2016). The positive Ce anomalies are displayed by some Taung coal host rocks, such as samples CPL05 with $\mathrm{Ce_N/Ce_N}$ ratio of 1.19 and CPL05 at 1.07. The other argillaceous samples exhibit weakly negative to no anomalies of cerium, with ratios ranging from 0.92 to 1.01. Negative Ce anomalies are usually associated with a sediment source-region that is dominated by felsic to felsic-intermediate rocks (Dai et al., 2016). For example, the Guxu Coalfield, seam No. 25 from the Sichuan Province in China shows negative Ce anomaly, and its sediment source-region is attributed to the felsic-intermediate rocks (Dai et al., 2015).

Europium is a redox-sensitive element, and this enables it to decouple from other REY, which generates Eu anomalies in coal and its associated rocks (Elderfield, 1988). The $\mathrm{Eu_N/Eu_N}$ ratio for Taung coal is 1.00, indicating no Eu anomalies, which is also observed in Chinese coals and world low-rank coals (Figure 9B). The No Eu anomaly for Taung coal can be associated with possible interaction of high-temperature hydrothermal fluids, which shadow negative Eu anomalies sourced from felsic rich rocks (Dai et al., 2016). The $\mathrm{Eu_N/Eu_N}$ ratios for all the argillaceous samples range from 0.55 to 1.06 with an average of 0.94, indicating a range from a very strong negative anomaly to weakly positive anomaly. Strong negative Eu anomalies for host rocks such as CPL08, have been largely associated with rocks that have evolved through the fractional crystallization of feldspars, and therefore a felsic to intermediate-felsic sediment source-region (Cullers, 2000). High temperature hydrothermal fluids when interacting with coal strata can elevate the concentration of Eu and display weakly positive Eu anomalies such as sample CPL05, with $\mathrm{Eu_N/Eu_N}$ ratio of 1.06 (Bau, 1991).

Gadolinium is another REY of which its anomalies are used to determine the influence of various forms of fluids and/water in coal and its host rocks because of its ability to dissociate itself from other REY (Bau and Dulski, 1996). The $\mathrm{Gd_N/Gd_N}$ ratio for Taung coal is 1.11, while the rest of the argillaceous samples range from 1.09 to 1.19 with an average of 1.13, showing positive anomalies. A similar trend is observed in other coals such as the main Karoo Basin (MKB)-PS1 coal, Chinese coals, and world low-rank coals (Figure 9B). Injection of hydrothermal fluids is suspect to positive anomalies of Gd in Taung coal as evidence of interaction of these fluids can be inferred from the behavior of Eu anomalies in Taung coal. The ratio of $\mathrm{Y_N/Ho_N}$ is also useful in determining the yttrium anomalies, which provide insight into sediment-source region rock make-up (Dai et al., 2016). Taung coal $\mathrm{Y_N/Ho_N}$ ratio is 0.89, showing negative anomaly of Y while the argillaceous samples range from 0.85 to 1.33 with an average of 1.01, suggesting negative to strong positive Y anomalies. Sample CPL06 shows a $\mathrm{Y_N/Ho_N}$ ratio of 1.33, which indicates a strong positive anomaly that can be associated with a sediments-source region enriched with phosphate minerals (Dai et al., 2016). The high concentration of total REY (855.1 ppm) and the high proportion of medium REY (Eu, Gd, Tb, Dy, and Y) in sample CPL06 (Figure 8), could be the result of strong

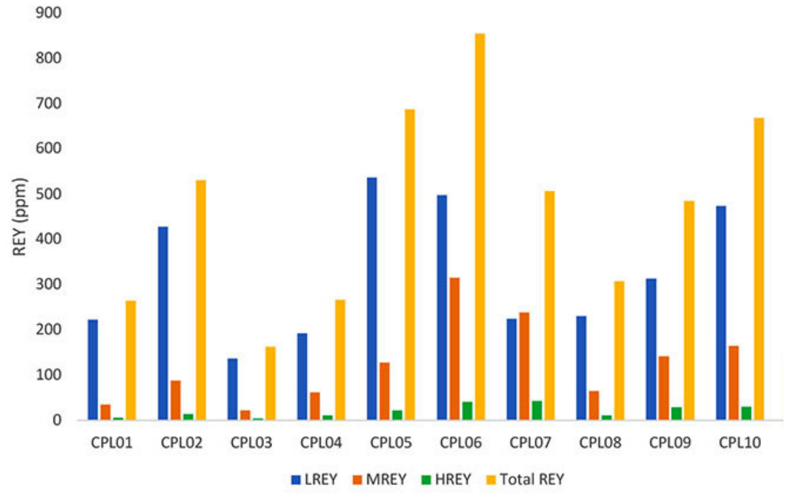


Figure 8—Distribution of REY in coal and argillaceous rocks samples with concentrations of the UCC as determined by Taylor and McLennan (1985)

positive Y anomaly in the sample. The provenance of Molteno Formation sediments is a south-east granitic region and the overall anomaly signature of Taung coal and some of its associated rocks does display a similar felsic type of sediment-source region (Eriksson, 1984; Turner, 1975).

Comparisons of the REY distribution pattern of the Taung coal with the world low-rank coals, Chinese coals, and main Karoo Basin (MKB) coal sample PS1 (South Africa), normalized by UCC as per Taylor and McLennan (1985) are presented in Figure 9B. The results show that the content of REY in CPL09 is significantly larger than the average REY content of the world low-rank coals and the Chinese coals, including the total REY content of the MKB (PS1) coal sample. Both the Chinese and MKB (PS1) coal samples are particularly enriched with the LREY and depleted in HREY.

Table III shows that Taung coal and most argillaceous samples have a higher concentration of the light REY than the heavy REY (HREY/LREY ratio less than 1.0) except sample CPL07 with HREY/LREY ratio of 1.3. There is a very weak/poor correlation between the HREY/LREY ratio of the samples and their ash content (Figure 10). Similarly, there is a very weak to no correlation between the ash content and the total REY content in the samples. This suggests that the distribution of REY in the samples is not necessarily associated with only the inorganic part of Taung coal and its associated rocks as observed in many coals. A strong negative correlation is displayed between the ash content and the calorific value, which is consistent with thermal characteristics of most coals.

It is also important to determine the enrichment types in coal relative to REY (Table III). There are three enrichment types and are normalized (N) to the upper continental crust by Taylor and McLennan (1985), which include the L-type (light-REY), the M-type (medium-REY), and H-type (heavy-REY) (Seredin and Dai, 2012). These enrichment types (Table III) are based on the ratios between La/Lu, La/Sm, and Gd/Lu with the following thresholds for each type: L-type ($La_N/Lu_N > 1$), M-type ($La_N/Sm_N < 1$, $Gd_N/Lu_N > 1$), and H-type ($La_N/Lu_N < 1$) (Seredin and Dai, 2012). The data clearly show that the enrichment type associated with sample CPL09 (Taung coal), is an H-type enrichment and therefore the coal is enriched mainly in heavy REY such as Ho, Er, Tm, Yb, and Lu. This observation is consistent with the UCC normalized distribution pattern of REY content in Figure 9A. The argillaceous samples CPL01 and CPL03 have L-type enrichment meaning that they are particularly depleted in HREEs, which is also evident from their REY distribution patterns. These samples contain the least total REY content (Figure 8) even though maceral analysis indicate ash concentrations above 90 mass% (Figure 6). Therefore, these samples represent the lowest grade of REY within the resource. The rest of the argillaceous samples belong to the M-type enrichment, which implies they are mostly enriched in the medium REY compared to other types.

Economic considerations

The coals around the world have variable concentrations of REY within the coal seams and their associated host rocks. Some coals have significantly high content of REY such as the Cenozoic Russian Far East coal deposit with REY content reaching as high as 1 000 ppm (Seredin, 1996) while considering that the world coal

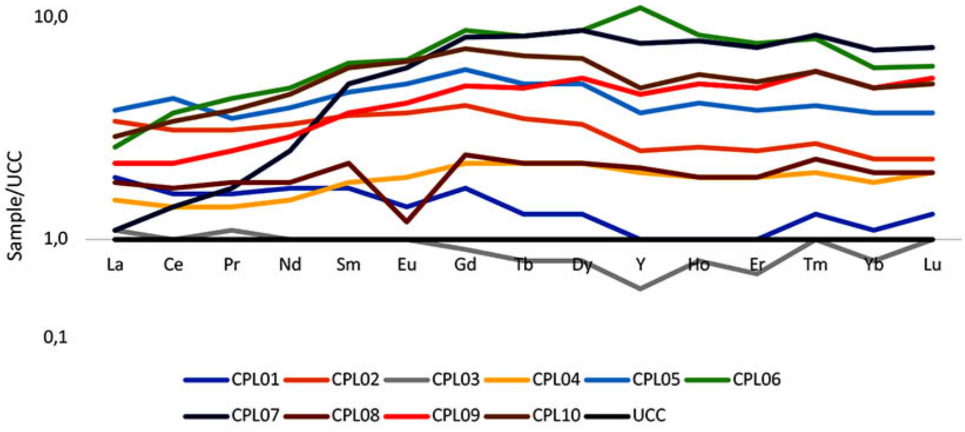


Figure 9a—REY distributions of Taung coal (CPL09) and argillaceous rock samples normalized to UCC (Taylor and McLennan, 1985)

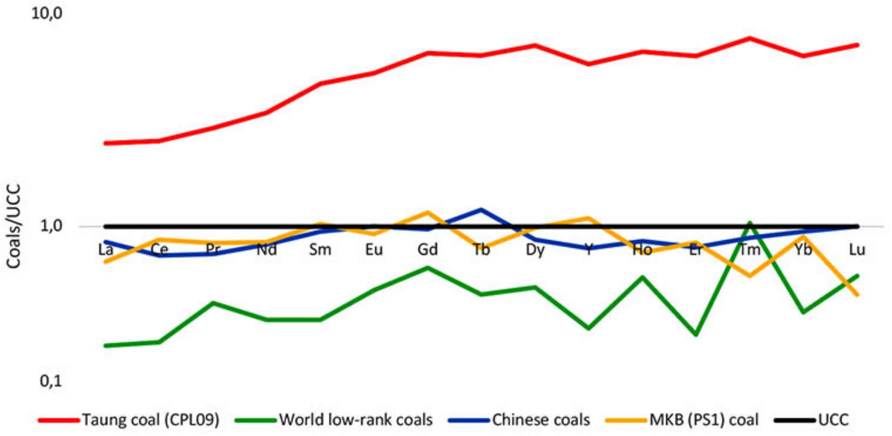


Figure 9b—REY distribution patterns in Taung coal (CPL09) compared to selected coals normalized to UCC (Taylor and McLennan, 1985)

Table III

REY enrichment trends and types in Taung coal and associated argillaceous rocks

Rock type	Sample	HREY/LREY	C_outl	La_N/Lu_N	La_N/Sm_N	Gd_N/Lu_N	Type	Ce_N/Ce_N	Eu_N/Eu_N	Gd_N/Gd_N	Y_N/Ho_N
Argillaceous	CPL01	0.19	0.7	1.41	1.09	1.28	L	0.93	0.91	1.17	1.02
	CPL02	0.24	0.8	1.47	0.94	1.73	M	0.96	1.02	1.13	0.97
	CPL03	0.19	0.7	1.13	1.08	0.95	L	0.92	1.03	1.05	0.85
	CPL04	0.38	1.0	0.76	0.82	1.11	M	0.96	0.97	1.07	1.05
	CPL05	0.28	0.7	1.03	0.83	1.58	M	1.19	1.06	1.19	0.90
	CPL06	0.72	1.6	0.44	0.43	1.45	M	1.07	0.94	1.16	1.33
	CPL07	1.25	2.4	0.16	0.23	1.11	M	1.00	0.98	1.14	0.98
	CPL08	0.33	0.9	0.88	0.78	1.20	M	0.95	0.55	1.09	1.12
	CPL10	0.41	1.1	0.59	0.50	1.43	M	1.01	1.03	1.12	0.87
Taung coal	CPL09	0.55	1.3	0.40	0.58	0.93	H	0.95	1.00	1.11	0.89

average sum REY concentration is considerably low (68.6 ppm) (Finkelman, 1993). Due to this REY disparity in coal resources, there is a need to estimate the economic potential of coal deposits if they are to be utilized as alternative sources of REY. There are a variety of tools that can be applied to evaluate the economic viability of coal deposits. Firstly, the concentration of critical REY (Nd, Eu, Tb, Dy, Y, Er) in coal deposits can be used as a proxy in understanding the economic importance of such deposits. This is because critical REY such as dysprosium (Dy) and neodymium (Nd) are very crucial for the development of permanent magnets used in wind turbines and many other industrial applications for which their demand is projected to grow by 2600% for Dy and 700% for Nd in the next two decades (Alonso et al., 2012). The results show that the total critical REY in samples CPL06, CPL07, CPL09, CPL10 is above 200 ppm and range from 208.6 ppm to 425.4 ppm (Figure 11). In addition, these samples have significantly higher (4 to 9 times) content of critical REY than the UCC, Chinese coals, and world low-rank coals. Moreover, the amount of critical REY on all the Taung coal deposits are still higher than some known operating mines, for example, the Bayan Obo mine located in northern China is the largest commercial mine in the world where REY are extracted from LREY-rich carbonatite hydrothermal related rocks (Lehmann, 2014). A geochemical background and dispersion study in the Bayan Obo region shows that the average sum of critical REY is 61.57 ppm (Zhou et al., 2020). The average sum content of critical REY in all the Taung coal deposit samples is 189.4 ppm, which is three times more enriched than those from the Bayan Obo region. Another example is that the average sum of critical REY in the Harmon-Hanson coal zone of the North Dakota lignite is almost half of that of the Taung coal (CPL09). The results also show that samples CPL06, CPL07, CPL09, CPL10 are enriched in Y, Dy, and Er (HREY) and Nd (LREY) and depleted in Tb (HREY) and Eu (LREY) of their critical REY. Overall, these results indicate that Taung coal and its associated argillaceous rocks can be a potential source of critical REY.

The outlook coefficient (C_{outl}) is one of the tools that is commonly used to appraise the economic potential of coal deposits. It calculates the ratio of critical REY in total REY and excessive REY in total REY in each sample (Seredin and Dai, 2012). This ratio is calculated by, (C_{outl}) = (Nd + Eu + Tb + Dy + Er + Y/Total REY)/(Ce + Ho + Tm + Yb + Lu/Total REY) where elevated values (C_{outl}) represent a promising potential source of REY (Dai et al., 2017). According to this evaluation scheme, the (C_{outl}) values greater than 2.4 are considered highly promising, (C_{outl})) values between 0.7 and 1.9 are regarded as promising, and those less than 0.7 as unpromising (Dai et al., 2017). The results for the outlook coefficient and the percentage of critical REY in total REY of the samples are presented in Figure 12. They show CPL07 as highly promising because of its (C_{outl}) being above 2.4 while all the other samples are indicated as promising, as they range from 0.7 to 1.9. The corresponding percentage of critical REY in total REY in the highly promising samples is 57% and ranges between 30% – 50% in the promising samples, followed by less than 31% locked within the unpromising samples. The results indicate that many of the samples including Taung coal, plot within the very promising and promising categories and contain up to almost 77% of the critical REY in total REY.

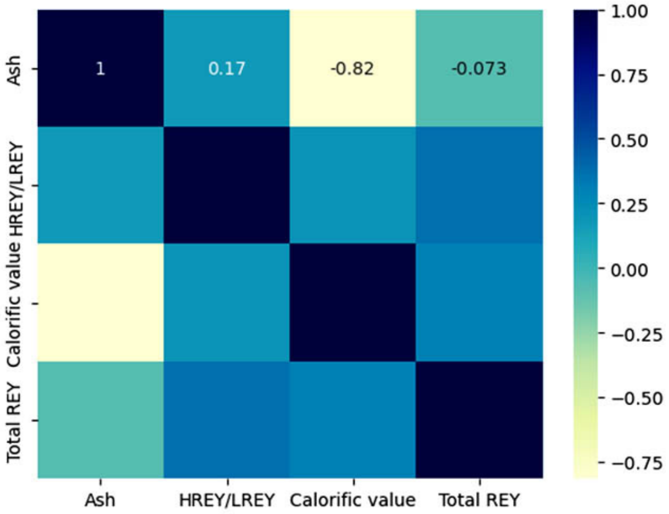


Figure 10—Correlation between ash content and HREY/LREY, calorific value, and total REY within the samples

To determine the industrial potential of recovering REY from coal resources, a cut-off grade of ≥ 1 000 ppm (0.1%) of REY oxide (REO) is required (Seredin, 2004). This cut-off grade evaluates various coal resources' potential of being an alternative source of extractable REY. The total REY in each sample is compared with the outlook coefficient of the corresponding samples in Figure 13. Here, the cut-off grade of REY ≥ 1 000 ppm influences if the samples plot on either the unpromising areas, or the very promising/promising areas of the plot. The results show that all the samples plot within the unpromising area, despite some having very high C_{outl} values because their individual total REY are below the 1 000 ppm threshold. Nevertheless, an increase in REY prices (supply and demand) and other geological considerations can

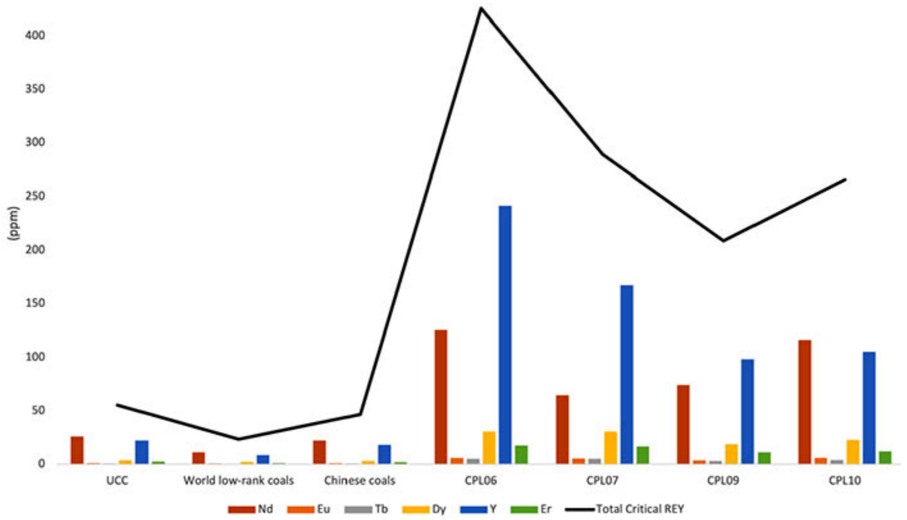


Figure 11—Enrichment of critical REY content in some Taung samples compared with selected coal deposits and the UCC (Taylor and McLennan, 1985)

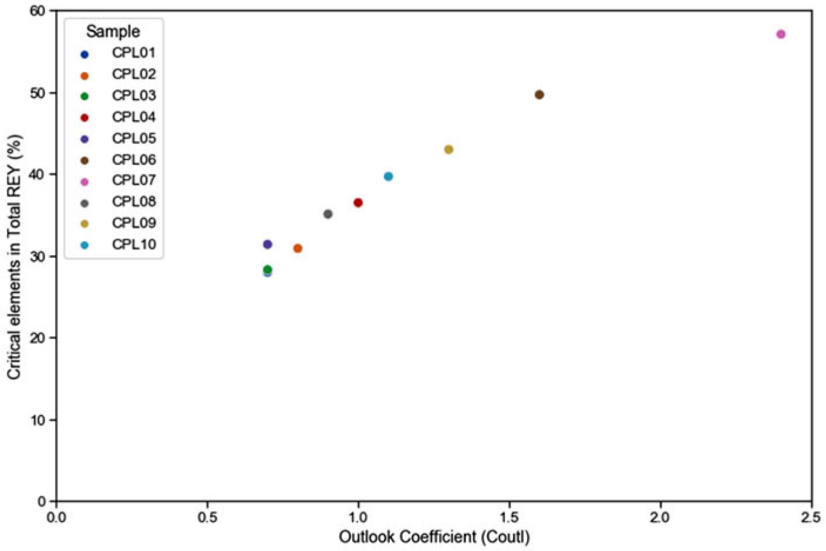


Figure 12—The outlook coefficient of the Taung coal and associated argillaceous samples relative to the percentage of critical REY in total REY

reduce the cut-off grade between 800 ppm to 900 ppm as the 1 000 ppm cut-off grade was determined a while ago (Seredin and Dai, 2012). This will render samples such as CPL07 plotting within the promising area of the total REY outlook coefficient diagrams and therefore a potential source of extractive REY.

Conclusions

This study provides an insight into the enrichment of REY in Triassic Taung coal and associated argillaceous rocks within the Molteno Coalfield. The following conclusions were drawn from this study:

A total of ten samples (coal and argillaceous material), were collected from the Taung coal deposit of the Molteno Coalfield. Taung coal is a low-quality coal and is categorized as medium rank D bituminous coal with a total REY content of 485.0 ppm. The average sum of REY in all the samples is 472.3 ppm, ranging from 162.9 ppm to 855.1 ppm. Most of the samples are enriched with critical REY, especially yttrium (Y) and neodymium (Nd). Market considerations for critical REY such as Nd, show a projected high future demand and therefore the Taung coal deposit can be a potential for these elements. The potential of the Taung coal deposit is also supported by the outlook coefficient trends, which place many of the samples within the promising area range from 0.7 – 1.9. The Ce, Eu, and Y anomalies for Taung coal and some samples suggest a felsic-intermediate source rock for the sediments that formed this deposit. To further understand the economic potential of this deposit, it is recommended that sequential leaching be used to determine the mode of occurrence of REY in all samples.

Authors' contribution

This research was conducted as part of a PhD degree in the Department of Geosciences at the University of the Witwatersrand under the supervision of Dr Lehlohonolo Mokhahlane. The research forms part of a broad study intended to evaluate the potential of rare earth elements and suitable extraction techniques within the Molteno Coalfield.
Hlajoane: Conducted sampling, analysis and interpreted the results, and wrote the manuscript.
Mokhahlane: Supervisor, defined and gave direction on the research, edited the manuscript.

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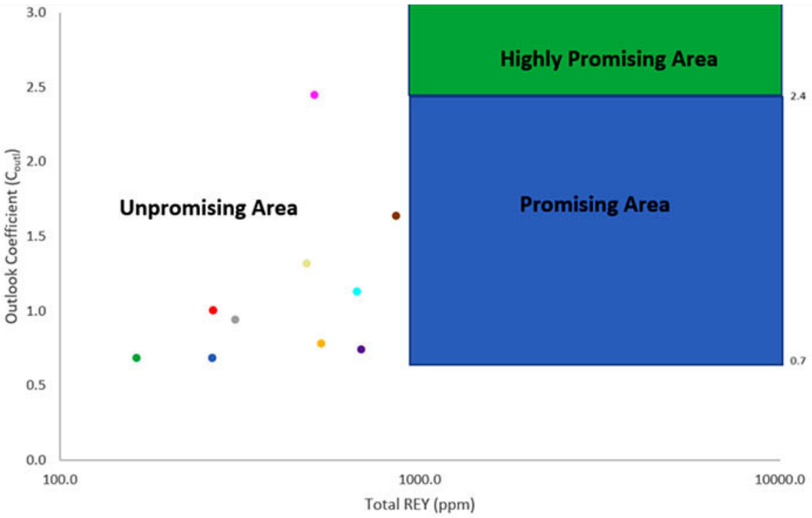

Figure 13—The total REY content with fields indicating the economic viability of Taung coal and argillaceous samples (Dai et al., 2017)

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