

Australian Journal of Earth Sciences

An International Geoscience Journal of the Geological Society of Australia

ISSN: 0812-0099 (Print) 1440-0952 (Online) Journal homepage: <https://www.tandfonline.com/loi/taje20>

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J. H. Hodgkinson & M. Grigorescu

To cite this article: J. H. Hodgkinson & M. Grigorescu (2020) Strategic elements in the Fort Cooper Coal Measures: potential rare earth elements and other multi-product targets, Australian Journal of Earth Sciences, 67:3, 305-319, DOI: [10.1080/08120099.2019.1660712](https://doi.org/10.1080/08120099.2019.1660712)

To link to this article: <https://doi.org/10.1080/08120099.2019.1660712>



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Published online: 24 Sep 2019.



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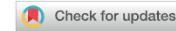
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Strategic elements in the Fort Cooper Coal Measures: potential rare earth elements and other multi-product targets

J. H. Hodgkinson^a and M. Grigorescu^b

^aCSIRO, Pullenvale, Qld 4069, Australia; ^bGeological Survey of Queensland, DNRME, Brisbane, Qld 4000, Australia

ABSTRACT

Mineral matter in coals has been found to host valuable elements including germanium, lithium and rare-earth elements (REE), but such content of Australian coals remains under-explored. The aim of this paper is to provide a proof-of-concept study that determines elemental concentrations in the mineral matter of the high-ash, Fort Cooper Coal Measures (FCCM), Bowen Basin, Queensland. Coal in the FCCM has good coking properties but has not been extensively explored owing to its high ash content. This study performs a preliminary assessment of the elements from the coal portion that would typically become waste after washing or combustion. Given that the needs for industrial extraction methods will change over time, cataloguing and documenting the elemental composition of coal may assist future development of multiple products for the benefit of both the coal and mineral industries. This preliminary study has revealed similar elevations of REE and higher-than-average crustal concentrations of lithium, bismuth and scandium in some of the samples. Further analyses will be required on a larger dataset to better understand elemental associations and explore spatial patterns of elemental content that may indicate localised enrichments. Understanding the potential of valuable elements in the FCCM may stimulate interest in multiple-product-coal (or elemental-coal) mining in this under-exploited resource and further encourage the reduction of waste from other Australian coals at the wash-plant stage.

ARTICLE HISTORY

Received 12 March 2019
Accepted 6 August 2019

KEYWORDS

coal; elements; mineral matter; high-ash; Fort Cooper Coal Measures; Bowen Basin; REE; lithium; waste

Introduction

As low-carbon energy sources become more widely adopted, coal use for power generation is expected to decline. Nevertheless, coal will continue to be mined for the foreseeable future, primarily used for electricity and heat (~75%; IEA, 2017) and steel making (~23%; IEA, 2017). While some power-station coal waste is used for construction materials such as cinder blocks, pavers and some cement production (e.g. Torkittikul, Nochaiya, Wongkeo, & Chaipanich, 2017), coal and its waste have other valuable uses (~2%) including chemicals and gases (Xie, Li & Zhao, 2010; Yang, 2017), electronics (He *et al.*, 2017; Keller, Ferralis & Grossman, 2016) and new materials such as graphene and polymers (Botte, 2015; Hu, Bian, Xue, Huang & Komarneni, 2017). ‘Other’ uses are growing (IEA, 2017).

Any elements in the Earth’s crust can be found, to varying degrees, in coal deposits, depending on the coal basin’s depositional and post-depositional environment (Hower, Granite, Mayfield, Lewis & Finkelman, 2016; Saxby, 2000). Elements and mineral matter found within coal measures may have originated from organic material (syn-genetic) or may have been added after deposition (Ward &

Dai, 2012). Minerals containing various elements are transported by wind or water to the basin during peat accumulation and can continue to accumulate through ongoing processes as the peat becomes buried, compressed and heated (coalified) and as groundwater passes through the formation (extraneous mineral matter). The accumulations of mineral matter can lead to concentrations that may be greater than normal background expectations in the upper crust (Raask, 1985).

Coal preparation processes aim to reduce the amount of mineral matter in coal to improve coal quality (Speight, 2015; Ward, 2016) for current coal uses, energy and steel making. If remaining material from coal preparation and post combustion contains deleterious elements it may constitute a pollutant residue potentially contains environmental pollutants. Alternatively, coal preparation and combustion could be considered as processes that produce mineral-rich materials (tailings or ash) (Swaine, 1990), which may be commercially attractive. With that view, a high-ash coal may be seen as a valuable multi-product resource, rather than a commercially unattractive resource. This preliminary investigation of a high-ash Australian coal’s elemental composition aims to provide a stimulus for industry

to further assess its potential as a valuable by-product of coal mining.

The terms 'mineral matter' and 'ash' are often used interchangeably in coal science but incorrectly so. The correct use of the term 'mineral matter' refers to the solid, inorganic material in coal (Speight, 2015). Whereas 'ash' refers to residue from the coal's total combustion (Speight, 2015), which may be termed 'fly ash', 'bottom ash' or 'slag' after industrial combustion of the coal. It may contain pre-existing mineral matter, or the result of the mineral matter having been heated (Speight, 2015). Further, in some cases such as the Fort Cooper Coal Measures (FCCM), some of the mineral matter within the coal originated as ash fallout from volcanic activity, so the pre-combustion coal's mineral matter contains volcanic ash-derived material (tuff), which may be confusing. Layers of tuffaceous material and ash fallout within the coal increase upwards through the Burngrove Formation of the FCCM (Ayaz, 2015). For the sake of clarity, we refer here to material in the 'high-ash' FCCM, Bowen Basin, Queensland as 'mineral matter' within which elemental content of interest may be located, assuming the mineral matter can be washed out and is not the result of the coal having been combusted; in the latter case, we use the term 'ash'.

Background

Mineral and elemental assessment of coal

Proximate, ultimate and ash analyses are routinely performed to determine the presence of elements that may impact on coal combustion and coking properties or those that may be corrosive, abrasive or impact on health and the environment through emissions or leaching to waterways (e.g. Dai *et al.*, 2012; Dale, 1995, 2006; Matjie, Li, Ward, Bunt & Strydom, 2016; Speight, 2015). Australian Standard 'AS 1038.10.0-2002—Coal and coke—Analysis and testing—Determination of trace elements—Guide to the determination of trace elements' (Dale, 2003) was developed by CSIRO and the Australian Coal Association Research Program, primarily aiming to determine elements that would be detrimental to health and the environment. Despite the current laboratory standards and capabilities available, analysis of strategic elements and minerals of economic interest in coal waste is not currently performed as a matter of course and thus valuable elements may have been easily overlooked. Full elemental content is presently unknown for many coals that are routinely mined, as is the elemental content of many coals believed to be uneconomic. For this reason, we analysed the FCCM coals and the main sedimentary rock types of the formation including its tuffaceous-rich layers unique in the Bowen Basin upper Permian sequence. Pre-Permian rocks that crop out to the west of the basin host a variety of ore deposits that may be a source of transition metals in younger rocks (von Gnielinski, 2017).

Element extraction from coal

Unutilised coal tailings and coal fly ash are often considered to be waste and may be later sold on to be used as construction material but may represent a potential source of rare earth and other strategic elements. Interest in exploring methods to extract elements from coal fly ash is growing. However, while the process of combustion liberates the non-combustibles and concentrates the elements, some elements may volatilise and be lost in the process of heating. Further, the high temperatures can cause some glassy ash particulates that entrap elements causing them to be unresponsive to acid digestion and other extraction processes (e.g. Peterson, Heinrichs, Glier, Lane & Taha, 2017). Low-temperature ashing can preserve some of the combustible elements and prevent to some degree the vitrification process but may not be possible in industrial boilers/furnaces. Coal tailings from coal preparation plants on the other hand, have not been heated and may be more amenable to element extraction.

Elemental recovery from coal typically occurs only when traditional raw-material sources have run low, such as when uranium was needed post WWII (Seredin, 2012) or when an increased surge in demand seeks additional sources, such as germanium that has been commercially extracted from coal since the 1950s. Some elements have been targeted over the past century and a few examples follow, and generally speaking, coal as a source of elements is starting to grow again as an area of commercial interest that had become subdued owing to costs. Some light rare earth elements such as La and Ce are currently considered to be in oversupply for global market needs but remain critical to existing and developing technologies; owing to their relatively stable value and availability, new uses are also being explored (Goodenough, Wall, & Merriman, 2018). Conversely, sources of some heavy rare earth elements (HREE) are scarcer and while their demand grows for use in a multitude of clean-energy technologies, uncertain long-term availability may control such demand as manufacturers seek solutions that utilise more reliable resource options (Pell, Wall, Yan & Bailey, 2019). The market for REEs may grow if availability can be more guaranteed as stated by Ayres (2019) '... the supply is limited because the market is limited because the supply is limited.'

Coal fly ash can be considered as a heterogeneous product that can be separated into distinct components (Blissett, Smalley & Rowson, 2014) that may have economic value rather than be considered waste. As coal washery waste contains up to 30 wt% aluminium oxides (Al_2O_3), aluminium extraction was explored to reduce waste and conserve the metal as a resource (Jenkins & Sinha, 1983). Many regions are known to host coal that is enriched in concentrations of elements, including REE, at levels higher than normal background levels, including USA, Russia and China (e.g. Hower *et al.*, 2016; Seredin & Finkelman, 2008; Zhao *et al.*, 2019). Zhao *et al.* (2019) cite multiple provinces across China for instance where coal-hosted ores are

sources of critical elements (Ge, Ga, Y and REE) typically owing to volcanic activity during coal development.

Despite their name, REEs are relatively abundant with a total of around 180–200 ppm (equivalent to $\mu\text{g/g}$, mg/kg or g/t) in average upper crustal material (Rudnick & Gao, 2003). However, they are rarely found in concentrated forms and need to be liberated from minerals making them difficult to be exploited (Jordens, Cheng & Waters, 2013). REE concentrations of economic potential in traditional mining scenarios can be between 1000 and 5000 ppm (Hower *et al.*, 2016). Concentrations of REE in coal tailings, fly ash and other coal waste may be lower but is material that has already been excavated, crushed and transported to a repository, providing cost benefits that will allow for lower concentrations to become economically viable. The fact that REE may exist in economic concentrations in coal waste was reported over 80 years ago (Goldschmidt & Peters, 1933). Dai, Graham and Ward (2016) concluded that a range of factors control REE and yttrium (Y) (or REY) anomalies in coal deposits, including geochemistry of terrigenous source material, hydrothermal fluid circulation and percolating water, volcanic ash and marine influences during peat formation. In some cases, the anomalies may be a result of more than two processes and would be indicators of different source regions and history of the coal during and after deposition. Specifically, they found that there are likely to be anomalies in coal related to redox-sensitive elements such as cerium (Ce) and europium (Eu) and non-redox-sensitive elements lanthanum (La), gadolinium (Gd) and yttrium (Y). Eu anomalies relative to REE are not uncommon and are typically attributed to preferential crystallisation of magma (Condie, 1993; Möller & Muecke, 1984).

Peterson *et al.* (2017) analysed coal mineral content to validate economic viability using a closed loop acid digestion process for samples with REE concentrations above 300 ppm. Ketris and Yudovich (2009) estimated global concentrations of REE in coal fly ash is on average 445 ppm and Franus, Wiatros-Motyko and Wdowin (2015) concluded that samples with REE content at that level should be considered for further examination. Pierave *et al.* (2017) were able to extract up to 99% of the REEs present in their coal fly ash samples that had concentrations from 200 to 700 ppm.

Economic viability of a rock to be mined depends on a wide range of factors, including deposit size, shape, accessibility and grade, value of product, demand, cost of labour and environmental constraints. The fact that the coal has already been excavated, crushed and partially processed (burned or washed) may change the stakes for evaluating the economic value of products within a coal waste resource.

While many Chinese coals have background values of most trace elements, some are significantly enriched in REE, lithium (Li), zircon (Zr), niobium (Nb), tantalum (Ta), hafnium (Hf), uranium (U), germanium (Ge) and thorium

(Th), owing to alkali volcanic ash deposits and circulation of low-temperature hydrothermal fluids. Extraction of gallium (Ga), aluminium (Al) and silicon (Si) from a Chinese coal in Inner Mongolia is providing environmental benefits (Dai *et al.*, 2012).

Jordens *et al.* (2013) investigated REE extraction potential of fly ash from USA coal samples that had concentrations of around two orders of magnitude less than those in a conventional ore of bastnäsite. They also reported that fly ash currently being produced in the USA would provide more than three times the REE mass per kilogram of total REE extracted from conventional ores making waste an attractive source, especially if the REE price of production per kilogram can match that from direct REE mining and, will increase as conventional REE deposits become exhausted (Jordens *et al.*, 2013). Kolker *et al.* (2017) examined REE distribution for devising effective extraction approaches and concluded that the aluminosilicate glass fraction in their samples would yield good REE volumes.

Blissett *et al.* (2014) reported that a rare-earth oxide content of 500 ppm in an 8000 t resource would yield $\sim \$163\text{ m}$ (2012 US prices). Emerging technologies will provide evolving chemical extraction methods that may improve economic feasibility of even lower concentrations. In a study to determine commercial viability of extracting REE from the Powder River Basin coal (USA), Taggart, Hower, Dwyer and Hsu-Kim (2016) reported up to 70% of REE content in fly ash was recovered using an existing heated nitric acid digestion process. REE have been found to be approaching commercially viable levels in some coal fly ashes from the UK, Russia's far-east and Siberia, Inner Mongolia and a number of southern and southwestern Chinese coal deposits, and eastern USA (Blissett *et al.*, 2014).

Based on research to date, the elements and metals in coal that are considered to have the best chance for economic recovery are: REE, silver (Ag), gold (Au), platinum group elements, beryllium (Be), selenium (Se), vanadium (V), gallium (Ga), antimony (Sb), scandium (Sc), molybdenum (Mo), tungsten (W), rhenium (Re), germanium (Ge), uranium (U), yttrium (Y), niobium (Nb), zirconium (Zr) and aluminium (Al) (Dai *et al.*, 2016; Seredin & Finkelman, 2008). While some elements, such as gold are only rarely found in anomalously high concentrations, their potential remains worth exploring. High gold concentrations have been found in brown coals and peat samples from Western Siberia (Arbuzov, Rikhvanov, Maslov, Arhipov & Belyaeva, 2006) and in India, some high sulfur coals have high gold concentrations (Baruah, Kotoky & Boarah, 1998). On the other hand, coal is a major source of germanium in Inner Mongolia and in Yunnan Province, China (Qi, Hu & Zhang, 2007), and the Novosjaktinskoye Mine in Russia has opened a plant to explore the micro-element composition of coal where the germanium content is more than 450 g/t (World Coal, 2019).

As potential economic targets, such elements can exist in coal mineral matter at concentrations similar to, or higher than, conventional economic deposits. Comparing values of potentially economic concentrations of elements in coal (and its waste) with those of traditionally mined ores and sources, however, is not straightforward. A cutoff grade for rare earth oxides from coal seams for example has been suggested as 800–900 ppm (Seredin & Dai, 2012); this does not consider mining cost reductions that are associated with the raw material (washery or burned waste), as there is for a conventional resource. While beneficiation costs may be high, extracted, crushed and concentrated material may provide a cheap feedstock for producing elemental co-products. Rozelle *et al.* (2016) were able to produce REE from poor coal waste that they considered to be economic simply owing to the ease of availability of the material, using an environmentally friendly inexpensive solvent (ammonium sulfate). A relevant cutoff grade for an economic concentration, therefore, may be much lower from a coal-waste source and processing for elemental liberation would only need to consider transport and treatment costs. Given that both industrial and technological resources and needs for extraction will change over time, cataloguing and documenting the elemental composition of coal in Queensland may assist future development of two products (coal and strategic elements) for the benefit of both the coal and mineral industries.

Investigated high-ash coal measures in the FCCM

While coal is present in every Australian state, the largest coal reserve is the intracontinental lower Permian to Upper Triassic Sydney–Gunnedah–Bowen Basin that extends from Batemans Bay in New South Wales in the south to northern Queensland. Measured and indicated coal resources in the Queensland section of this basin, the Bowen Basin are estimated at approximately 32 000 Mt (Blake, Green, McKillop & Coffey, 2018), while the deposits host more coal and other hydrocarbons that are not of current economic interest (Geoscience Australia, 2018).

The most widely mined coal measures in the Bowen Basin are the Rangal Coal Measures, Moranbah Coal Measures and German Creek Formation, whereas the FCCM, stratigraphically located between the Rangal and the Moranbah coal measures, have never been widely explored or analysed. This is primarily due to a historically accepted view of a high-mineral matter content (30–60 vol%), although these coal measures contain good-quality coking coal (Anderson, 1985; Grigorescu & Coffey, 2018; Matheson, 1990).

The FCCM lie within the northern Bowen Basin and consist of green-grey, tuffaceous, thinly interbedded lithic sandstones, siltstones and mudstones including carbonaceous shale, coal and cherty tuff (Grigorescu & Coffey, 2018). Towards the south, the FCCM grades laterally into an upper finer-grained formation, the Burngrove Formation

and a sandier lower unit, the Fair Hill Formation. Based on the solid geology map released by Sliwa, Hamilton, Hodgkinson and Draper (2008), the FCCM and correlatives have a spatial subcrop extent of around 8000 km² (Figure 1). The deposition of the FCCM in the late Permian (Lopingian epoch) coincided with regional volcanic activity that provided vast quantities of air-fall deposits, now found as tuffaceous material both within and between coal seams (Ayaz, Rodruiges, Golding & Esterle, 2016).

Typically, mining companies have preferred to extract the underlying low-ash Moranbah and German Creek coals, even though these seams are deeper and require underground mining. Although the high-ash content has been a deterrent for coal explorers for some time, FCCM is around 200–400 m in thickness, where it has been intersected fully, and extends over large areas from Collinsville to Springsure, resulting in large volumes of sediment and coal that may present a combined economic potential.

To date, exploration of the FCCM and its correlatives has been limited to a few projects (e.g. Curragh West, Washpool, Wilton, Comet Ridge) and their resources remain unmined at this time. Existing mines such as Hail Creek and Newlands have undertaken trials to assess the suitability of the FCCM coal for blending with coal mined from the overlying Rangal Coal Measures (Grigorescu & Coffey, 2018). Most recently, Metroof Minerals and Sojitz Coal have been awarded exploration authorities near Middlemount to develop the coal in the FCCM (Australian Mining, 2018).

In this context, the current investigation aims to test various coal seams and their sedimentary host rocks to determine the composition of FCCM mineral matter, providing support and impetus for further investigation of strategic elements in high-ash coal seams in the Bowen Basin.

Methods

Sampling

Core samples from coal exploration boreholes drilled by the Geological Survey of Queensland in the 1970s and 1980s, and stored at Queensland Government's Exploration Data Centre were collected for chemical analysis. The samples were collected from full-diameter core, which has been stored in covered core boxes under secure, controlled conditions by the Queensland Government. Alteration and precipitation of secondary minerals has been rarely observed and only in carbonaceous mudstones. Only well-preserved material has been selected for analyses.

A total of eight boreholes (Figure 1) were selected that represent a range of geological and structural conditions and provide spatial variation targeting coal and non-coal samples. In some cases, tuffaceous intervals were sampled at different depths in the same borehole (Table 1). Figure 2 shows the location of the FCCM stratigraphically in relation to other coal measures.

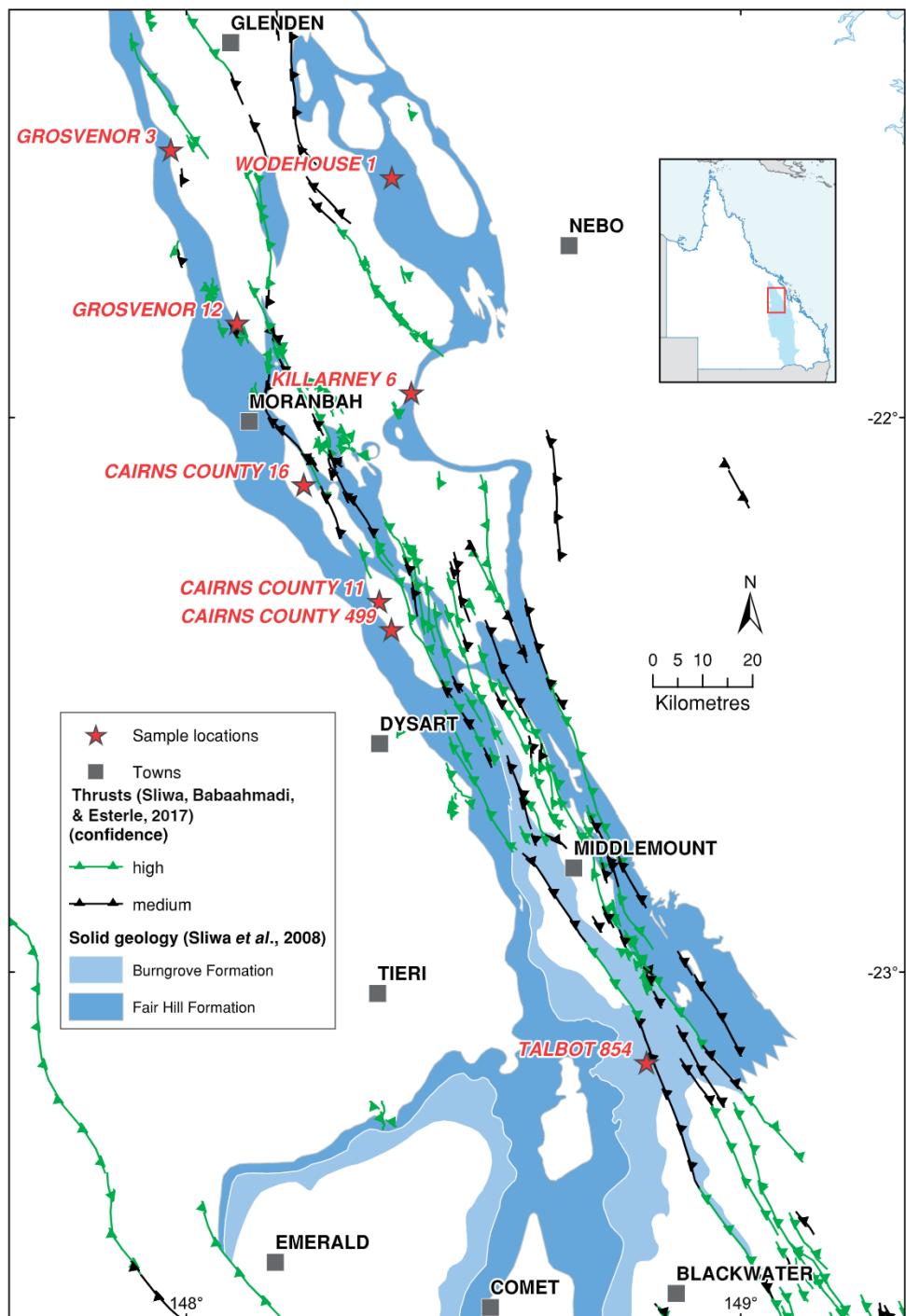


Figure 1. Sample locations in relation to faults and relevant solid geology. Detailed geological and structural information can be found in Grigorescu and Coffey (2018).

Sample naming convention is as follows: borehole code, sedimentary rock type and approximate depth in metres; for instance, GR3TF122 represents a tuffaceous sample collected from Grosvenor 3, from an approximate depth of 122 m (Table 1).

As shown in Table 1, the set of samples were collected from depths ranging from 36 to 453 m and included three coal samples and 20 non-coal samples: two heat-affected coals, eight tuffaceous siltstones and mudstones, four

carbonaceous mudstones, three mudstones and three siderite-rich samples.

Sample analysis

The samples were prepared and analysed for elemental content by Bureau Veritas, New South Wales, following Australian Standards for analytical methods appropriate for

Table 1. Sample characteristics.

Coal borehole	Samples
Grosvenor 3 (GR3)	GR3TF122, GR3CM124; GR3TF294
Grosvenor 12 (GR12)	GR12TF70; GR12C70; GR12TF200; GR12MD241; GR12TF331
Wodehouse 1 (WO1)	WO1CK36; WO1S57
Killarney 6 (KL6)	KL6C100; KL6TF38
Cairns County 16 (CC16)	CC16TF151; CC16CM161; CC16C172; CC16S187
Cairns County 11 (CC11)	CC11C296; CC11MD334; CC11CK452
Cairns County 499 (CC499)	CC499CM103; CC499TF109; CC499TF137; CC499S153
Talbot 854 (TA854)	TA854MD150; TA854CM194; TA854TF272

C, coal; CK, heat-affected coal; TF, tuffaceous-rich; MD, mudstone; CM, carbonaceous mudstone; S, siderite-rich siltstones.

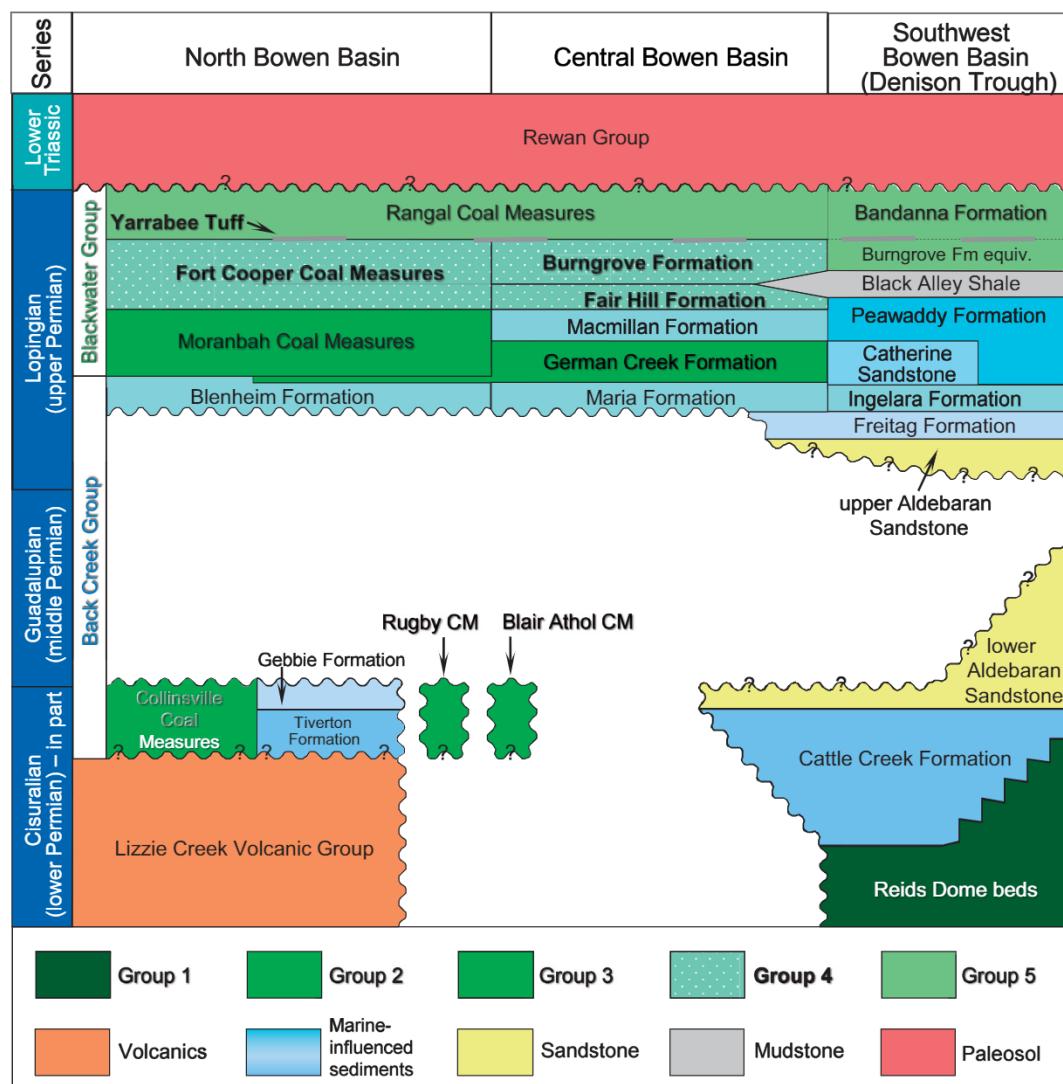


Figure 2. Stratigraphic column showing the location of the FCCM in relation to other coal measures (after Grigorescu & Coffey, 2018, figure 8).

the material types (coal and non-coal). Methods used and elements identified for each are summarised in Table 2. Coal samples were 'slow-ashed' to retain elemental content. This means that the coal samples were heated to 450°C and ashed slowly, overnight, to remove organic matter after which, the ashed sample was digested and results were converted back to the coal content using ash%.

Results

Elemental concentrations vs average crustal composition

Overall, the coal-associated samples, such as coal (C), heat-altered coal (CK) and the carbonaceous mudstone (CM) samples, have elemental concentrations below the average crustal composition (Table 3). Some coal samples are

Table 2. Analyses performed for elemental identification in non-coal and coal samples under Australian Standard AS 1038.10.0-2002.

Material	Method	Elemental assessment
Non-coal pulps	IC3E: Mixed acid digest, ICP-AES IC3E: Mixed acid digest, ICP-MS	Al (aluminium), Be (beryllium), Fe (iron), Li (lithium), Zn (zinc) Ag (silver), Ba (barium), Bi (bismuth), Cd (cadmium), Ce (cerium), Cs (caesium), Dy (dysprosium), Er (erbium), Eu (europium), Ga (gallium), Gd (gadolinium), Ge (germanium), Ho (holmium), In (indium), La (lanthanum), Lu (lutetium), Nb (niobium), Nd (neodymium), Pb (lead), Pr (praseodymium), Rb (rubidium), Re (rhenium), Sc (scandium), Sm (samarium), Sn (tin), Sr (strontium), Ta (tantalum), Tb (terbium), Te (tellurium), Th (thorium), Tl (thallium), Tm (thulium), U (uranium), W (tungsten), Y (yttrium), Yb (ytterbium)
	IC3E: Mixed acid digest, ICP-MS	Co (cobalt), Cr (chromium), Cu (copper), Mn (manganese), Mo (molybdenum), Ni (nickel), V (vanadium), Zr (zirconium)
Coal pulps, slow-ashed	AS1038.10.0: Trace elements by Fusion/Acid/ICP AS1038.10.0: Trace elements by acid digest/ICP-MS IC3E: Mixed acid digest, ICP-MS IC3E: Mixed acid digest, ICP-AES	Ba, Be, Co, Cr, Cu, La, Li, Mn, Mo, Ni, Sr, V, Y, Zn, Zr Ba, Ca (calcium), Ce, Cs, Ga, In, Nb, Pb, Rb, Sc, Ag, Sn, Ta, Te, Th, Ti, U, W Dy, Er, Eu, Gd, Ho, Lu, Nd, Pr, Re, Sm, Tb, Tm, Yb Al, Fe

Table 3. Composition of coal and associated samples (in ppm), in relation to average crustal concentrations.

Element	Symbol	Crust	KL6C100	CC16C172	CC11C296	WO1CK36	CC11CK452	GR3CM124	CC16CM161	CC499CM103	TA854CM194
Lithium	Li	21	5	nd	10	7	25	17	25	20	14
Rare earth elements	REE	184	150	178	144	38	58	79	86	205	104
Thorium	Th	11	14	9	5	1	2	1	6	17	3
Uranium	U	3	4	4	2	nd	1	nd	2	3	1
Zirconium	Zr	193	130	160	120	19	37	29	137	146	141
Vanadium	V	97	48	140	83	16	23	91	113	138	118
Niobium	Nb	12	8	32	6	1	2	2	5	11	4
Tantalum	Ta	1	1	1	0	0	0	0	0	1	0
Chromium	Cr	92	20	51	25	nd	nd	nd	8	18	7
Molybdenum	Mo	1	3	2	nd	1	1	1	1	3	0
Cobalt	Co	17	10	11	10	17	14	30	15	27	18
Nickel	Ni	47	13	34	5	nd	4	nd	2	40	3
Copper	Cu	28	29	28	30	9	19	5	36	70	25
Zinc	Zn	67	13	39	11	8	55	6	20	103	51
Gallium	Ga	17	24	21	7	3	10	1	13	25	7
Tin	Sn	2	4	3	nd	nd	4	nd	1	3	1
Lead	Pb	17	32	18	14	2	7	2	13	32	7
Bismuth	Bi	0.2	0.9	1.0	0.7	nd	0.2	0.1	1.2	0.9	0.3

REY (REE and yttrium) = yttrium, lanthanum, cerium, praseodymium, neodymium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium; nd, not detected; bold text, concentrations above crustal levels.

enriched in HREE with respect to the Post-Archean Australian Shale (Taylor & McLennan, 1985; Figure 3). Australian coal is typically considered to have low elemental concentrations. Our focus here, however, is on the elemental concentrations of the excavated material that would go to waste through either waste dump or wash-plant residues. Slightly elevated siderophile and chalcophile elements occur in some samples, but, owing to the limited number of samples, it is difficult to draw a conclusion on the causes of enrichment. Notable is the concentration of Bi, which is four to six times higher than the average crustal concentration (0.9–1.2 ppm) in five of the nine samples analysed. Similarly, Sc is elevated (19–27 ppm) in all the coal samples. Also remarkable is sample CC499CM103 (depth 103 m), a carbonaceous mudstone in CC499, which has elevated concentrations of REE and some transition metals, including Bi. This localised enrichment may be related to the presence of elevated iron, organic

compounds and the type of the clay matrix, which may have all preferentially adsorbed siderophile, chalcophile and REE, and caused concentrations higher than the background.

Siderite-rich siltstone (S) and mudstone (MD) intervals tend to be thick and a ubiquitous occurrence in the Fort Cooper seams. Although concentrations above background are rare in these intervals and do not exhibit a clear pattern of enrichment (Table 4), enrichment in HREE occurs in a few mudstone samples (Figure 4).

The tuffaceous-rich rocks (TF) are by far the most frequent occurrence in the Fort Cooper seams, as discrete or interfingered layers, and they are also likely to constitute the bulk of the coal mineral matter. TF are generally rich in clay minerals (predominately illite according to Fricker, 2018) and sometimes high in iron, in which case the tuffaceous material is slightly pink rather than fawn coloured as seen from our analyses. Tuffaceous rocks also contain

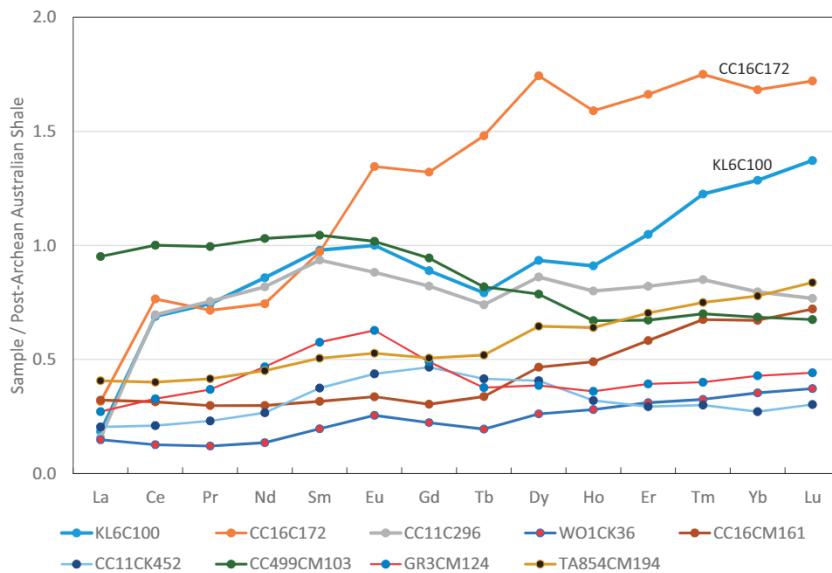


Figure 3. Post-Archean Australian Shale (PAAS; Taylor & McLennan, 1985) normalised REE concentrations. Enrichment in heavy REE is apparent in the coal samples collected from CC16 and KL6.

Table 4. Siderite-rich siltstones and mudstone elemental composition (in ppm), in relation to average crustal concentrations.

Element	Symbol	Crust	WO1S57	CC16S187	CC499S153	GR12MD241	CC11MD334	TA854MD150
Lithium	Li	21	8	28	12	15	13	27
Rare earth elements	REE	184	62	135	156	189	115	176
Thorium	Th	11	2	5	5	12	3	7
Uranium	U	3	1	1	2	3	1	2
Zirconium	Zr	193	43	99	141	243	59	116
Vanadium	V	97	101	83	81	38	225	84
Niobium	Nb	12	2	4	5	8	4	5
Tantalum	Ta	1	0	0	0	1	0	0
Chromium	Cr	92	nd	29	nd	nd	266	13
Molybdenum	Mo	1	1	1	0	1	0	1
Cobalt	Co	17	8	134	18	14	37	25
Nickel	Ni	47	nd	70	2	nd	73	10
Copper	Cu	28	78	42	12	10	109	49
Zinc	Zn	67	67	61	91	62	44	63
Gallium	Ga	17	8	13	19	22	16	12
Tin	Sn	2	nd	2	2	3	2	2
Lead	Pb	17	4	11	16	24	6	16
Bismuth	Bi	0.2	nd	0.2	0.2	0.3	nd	0.4

nd, not detected; bold text, concentrations above crustal levels.

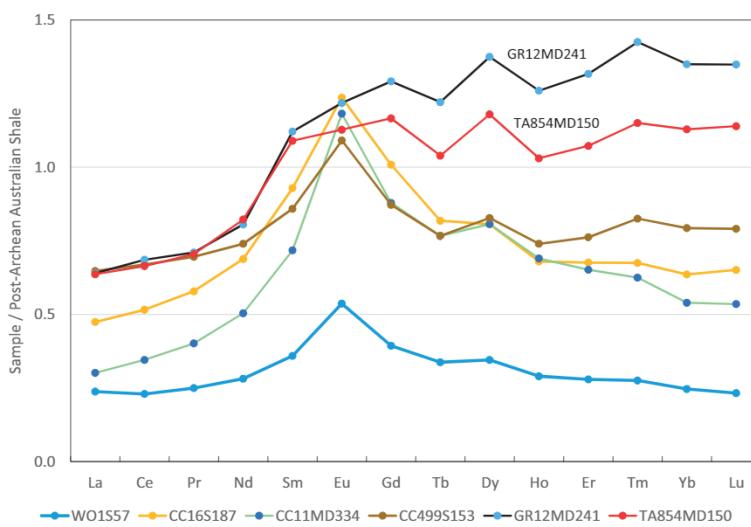


Figure 4. PAAS-normalised REE concentrations. Enrichment in heavy REE is apparent in mudstones collected from GR12 and TA854. Siderite-rich siltstones exhibit a positive Eu anomaly.

Table 5. Tuffaceous elemental composition (in ppm), in relation to average crustal concentrations.

Element	Symbol	Crust	KL6TF38	GR3TF294	GR12TF70	GR12TF200	CC16TF151	CC499TF109	CC499TF137	TA854TF272
Lithium	Li	21	5	7	105	7	21	7	5	15
Rare earth elements	REE	184	266	241	65	191	441	216	334	198
Thorium	Th	11	40	13	8	20	49	57	12	15
Uranium	U	3	7	4	4	4	12	7	5	3
Zirconium	Zr	193	151	282	50	83	189	104	157	214
Vanadium	V	97	nd	64	nd	51	nd	6	70	32
Niobium	Nb	12	13	10	9	4	18	11	10	2
Tantalum	Ta	1	1	1	1	1	2	1	1	1
Chromium	Cr	92	nd	nd	nd	nd	nd	nd	nd	nd
Molybdenum	Mo	1	0	1	1	5	0	nd	1	0
Cobalt	Co	17	8	4	14	4	10	19	10	5
Nickel	Ni	47	nd	nd	nd	nd	nd	nd	30	nd
Copper	Cu	28	1	5	1	11	1	6	5	8
Zinc	Zn	67	58	186	17	163	46	56	200	193
Gallium	Ga	17	29	35	34	37	33	23	32	35
Tin	Sn	2	6	4	7	4	7	11	4	4
Lead	Pb	17	62	34	83	75	70	49	41	27
Bismuth	Bi	0.2	0.8	0.3	1.1	0.7	1.2	0.9	0.3	0.4

nd, not detected; bold text, concentrations above crustal levels.

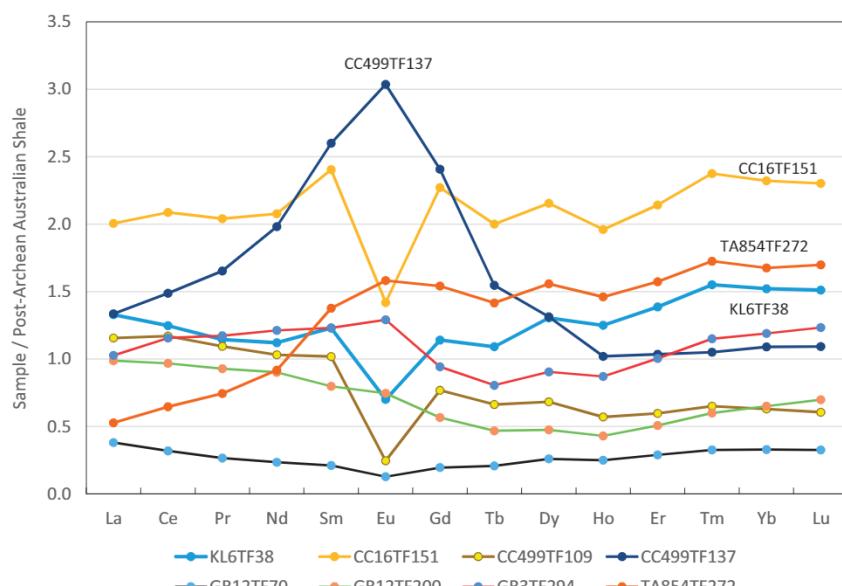


Figure 5. PAAS-normalised REE concentrations. Enrichment in heavy REE is observed in most of the tuff samples, which also present a variety of Eu anomaly patterns.

higher than crustal concentrations of various strategic elements (Table 5; Figure 5).

A sample from borehole GR12 is unusual as it contains five times the crustal concentrations of Li and Bi. The other tuffaceous rocks analysed are consistently higher than crustal abundance of REE and transition metals with affinity for Fe or Mn oxides.

The distribution and concentration of individual REE in tuffaceous-rich samples is presented in Figure 6. It must be noted that there are limited data to suggest spatial (including depth-related) correlations and we present this only as the first-representation of their spatial distribution. Most REE are above crustal concentrations in at least five of the eight samples analysed.

Clay minerals and iron and manganese oxides are known to adsorb or release chemical elements, depending on the pH and redox conditions of the environment. Such

secondary processes control the mobility and distribution of transition metals and REE and may explain localised enrichments (Bourg & Loch, 1995; Paterson, Goodman & Farmer, 1991; Reddy, Feijtel & Patrick, 1986). Using the Al, Fe and Mn concentrations as indicative of clay and oxide presence, the relationship between these minor elements and the lithological type of the analysed samples has been examined. As shown in Figure 7, heat-affected coal, mudstones and siderite-rich rocks tend to be high in Mn and Fe. Coal, tuffaceous rocks and some CMs are clay-rich and high in Al.

General findings

The heat-altered coal (Table 3; Figure 3) and the siderite-rich samples (Table 4; Figure 4) display the lowest elemental concentrations of interest of all samples. Although

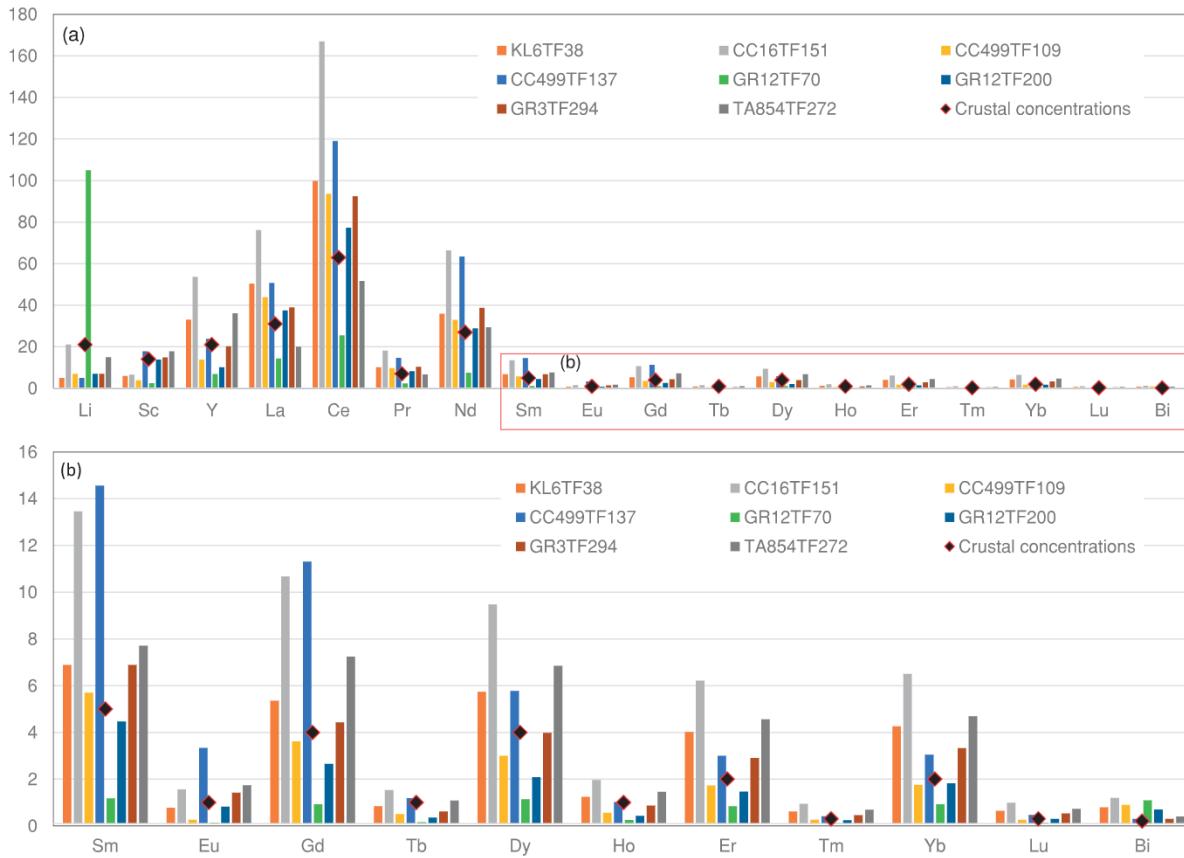


Figure 6. Lithium, REE and Bi concentrations (in ppm) in tuffaceous-rich samples.

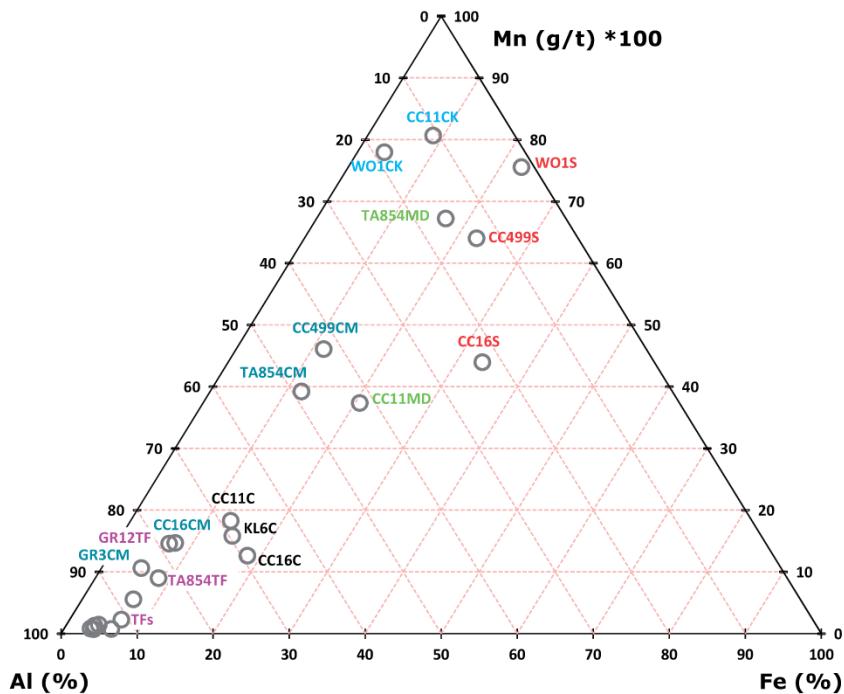


Figure 7. Relationship between minor elements and lithological type. Label colour: black, coal (C following borehole name); light blue, heat-altered coal (CK); dark blue, carbonaceous mudstone (CM); red, siderite-rich siltstone (S); green, mudstone (MD); purple, tuffaceous siltstone (TF).

devoid of most elements of interest, the coal samples are the only ones with Sc at a higher-than-average crustal concentration: CC16 at 172 m (27 ppm), CC11 at 296 m (20 ppm) and KL6 at 100 m (19 ppm). These three boreholes are located in relatively close proximity to one another, E–W across the basin. Scandium concentration is 21 ppm in a mudstone sample in borehole CC11 at 334 m depth but was not elevated in any of the other samples. The CMs are generally low in elemental concentrations, except for CC499CM103, which has some elevated REE and transition metals.

The tuffaceous-rich samples display a range of higher than crustal-average concentration elements (Table 5; Figure 5), such as Ce, Ga, La and Pb, and one sample (GR12TF70) also contains elevated concentration of lithium (105 ppm vs crustal average of 21 ppm). Four tuffaceous-rich samples display high Zn (CC499TF137, TA854TF27, GR12TF200 and GR3TF294), three have high Th (CC499TF109, CC16TF151, KL6TF38), and some have high Zr, Pr, Nd and Gd. Relative to crustal averages, concentrations of Ga, Nd, Pb, Sm and Th are elevated in tuffaceous-rich samples from all of the boreholes. Cerium, La and Pr are elevated in all of the boreholes except TA854 (Table 5; Figure 6). Bismuth is consistently high in 16 of the 20 samples analysed, with the coal and tuffaceous-rich samples containing three to six times the crustal averages (Table 5).

Spatial distribution

Grosvenor 12 is remarkable owing to its lithium concentration (Table 5), which is the highest of the dataset. Cairns County 16 and CC499 are located further south along strike and present elevated REE and some transition metals, in tuffaceous-rich and mudstone samples. TA854 is situated to the south of the other boreholes (Figure 1), proximal to a fault and has a different elemental signature in the tuffaceous-rich samples, specifically displaying a different association of elevated element concentrations, such as Y, Zn and Zr (Tables 3 and 5; Figure 6). The CM sample from TA854, for example, only has elevated V, whereas the carbonaceous mudstones in CC499 and CC16 have higher-than-average values for a range of other elements.

Variation in concentrations with depth seems to be rather related to sample lithology than depth. An example is borehole CC16 where the tuffaceous-rich sample collected from a depth of 151 m presents the highest concentration of REE of the dataset. Nearby carbonaceous mudstone at 161 m presents lower concentrations than the tuffaceous-rich samples, with the exception of Li and Sc, which are enriched in the mudstone (Figure 8).

A slightly different pattern can be observed further south in Cairns County 499, which is second highest in terms of REE concentrations, after CC16. The tuffaceous-rich sample (CC499TF109) underlying the carbonaceous mudstone (CC499MD103) does not contain REE concentrations higher than those found in the mudstone; however,

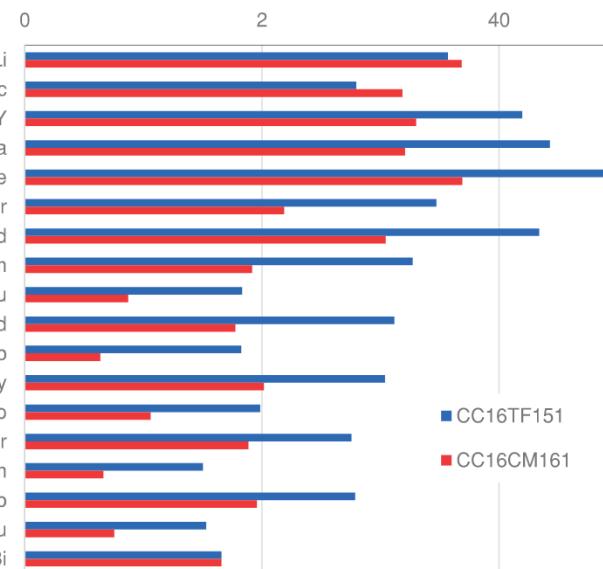


Figure 8. Comparative distribution of elemental concentrations, Cairns County 16, over 10 m. The bar chart compares a tuffaceous sample (TF) collected from 151 m depth and a carbonaceous mudstone (MD), from 161 m depth. The x-axis represents chemical concentrations in ppm. The tuff has higher elemental concentrations than the underlying carbonaceous mudstone.

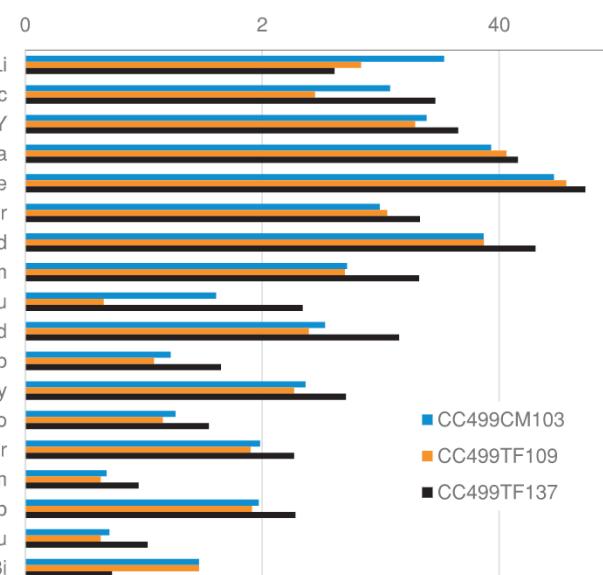


Figure 9. Comparative distribution of elemental concentrations, Cairns County 499, over 34 m. The bar chart compares a carbonaceous mudstone (MD, 103 m depth) and two tuffaceous samples (TF) collected from 109 and 137 m depth. The x-axis represents chemical concentrations in ppm. The tuffs have higher elemental concentrations than the underlying mudstone for most elements.

the deeper tuffaceous-rich layer (CC499TF137) has a higher REE concentration than both the overlying tuffaceous-rich samples and mudstone samples (Figure 9).

Discussion

The syn-depositional tuffaceous component of the FCCM, combined with complex post-depositional history,

including local igneous intrusions and faulting, has apparently provided suitable conditions for elevated elemental concentrations within coal intervals and interburden. In addition, the large sediment volume and the relative ease of access to the coal measures may justify the investigation of a potentially economic ash-derived by-product.

Lithium concentrations have been found to be high in the northern-most borehole and would be worthy of further investigation to discover the likely source and lateral extent of the anomaly. Although Li is a relatively abundant element in the Earth's crust, it is rarely found in concentrations sufficient to warrant mining owing to geological constraints (Kesler *et al.*, 2012). Qin, Zhao, Li and Zhang (2015) estimated that Li concentrations in coal should be at a minimum of 80 ppm and ideally 120 ppm to be of economic or industrial grade. Given that only one sample shows relatively high Li concentration (105 ppm), tuffaceous-rich tailings produced in the area should be analysed when available. It would also be valuable to analyse samples from the coal and waste from over- and underlying coal measures in that locality to determine whether Li content is consistently elevated, and whether it has been influenced by groundwater or hydrothermal circulation.

High concentrations (5–27 ppm) of scandium have been found in three relatively closely located boreholes, potentially emplaced post-depositionally. Swaine (1990) analysed Sc in New South Wales and Queensland coals and found levels to be typically at concentrations of 2–15 ppm. This is only slightly higher than the average concentration found in the upper continental crust (14 ppm). Sc concentrations in tailings are likely to be more elevated and should be explored when samples become available. Sc of over 45 ppm in coal tailings has been cited as recoverable (Texas Mineral Resources Corp, 2016), so further assessment of the FCCM mineral matter may be warranted.

The REE as a group occur at higher than average crustal concentrations in all of the tuffaceous-rich samples. It has been suggested that Ce can be used as a substitution for all the REEs (Blissett *et al.*, 2014). In the samples analysed in this study, Ce occurs in higher concentrations than any other REE and is also positively correlated with all of them, except Sc, which is elevated only in the coal samples. All the other REEs favour the tuffaceous-rich samples.

Normalisation against the PAAS confirms the enrichment of tuffs in comparison with the other sedimentary rocks analysed. Some of the coal, carbonaceous mudstones and siderite-rich siltstones present enrichment in heavy REE and positive Eu anomalies (**Figures 3 and 4**). The normalised concentrations of REE in the tuffs do not exhibit a similar pattern and the Eu anomaly is either positive or negative (**Figure 5**), suggesting mixed influences during the alteration of the original volcanic ash to tuffaceous siltstones. Dai *et al.* (2016) reported that positive Eu anomalies could possibly be caused by spectrometric interference with barium (Ba) during ICP-MS analysis. Consequently, Ba/Eu >1000 may suggest erroneous results of Eu and should be

treated with caution. In this study, only three of the 23 samples exhibit Ba/Eu ratios over 1000 (CC16CM161, KL6TF38 and CC499TF109). The samples were collected from different depths and different locations, suggesting that the high ratios may reflect local geological conditions.

The transition metals are present in all the types of sediments analysed; their most likely source is the pre-Permian rocks, cropping out to the west of the basin, known to host a variety of ore deposits. Patterns of distribution or enrichment could not be observed in this preliminary investigation, most likely owing to the limited number of samples. However, Bi is an exception, as concentrations higher than the average crust are consistent, similar to other Australian coals (Swaine, 1990). Volcanic activity is considered the main source of Bi in sediments (Swaine, 1990), so further investigation of volcanic-derived mineral matter, such as in the case of the FCCM, may be valuable.

Elements in coal mineral matter may have been part of the initial *in situ* sediment deposition or may be authigenic and post-depositional. Tuffaceous-rich layers may have been argillised, with mobilised clays having been redistributed by groundwater circulation. The elements may be of magmatic origin or a leached and redistributed product of hydrothermal alteration along faults, from magmatic intrusions or volcanic ash. Grosvenor 12 and Talbot 854 are proximal to faults and Killarney 6 is close to a very geologically disturbed area owing to intrusion of the Bundarra Granodiorite. Funding limitations meant that only half of the samples obtained have so far been analysed and presented here, hence we have been unable to test the hypothesis that known structures have an influence on elemental distribution. However, future work will endeavour to analyse this aspect. Better understanding of mineral origins within the samples, in association with local geological features (intrusions, faults, folds), will assist prediction and mapping of other elements that may be expected. Interpretation of element assemblages within the FCCM will require further sample analysis and consideration will also be given to the significance of heavy REE enrichment in some samples and of the Eu anomalies. Elemental identification is critical to determining whether further investigation is necessary. The next stage would naturally require detail on mineral phases present using for example petrographic assessment, quantitative X-ray diffraction or scanning electron microscopy such as those used by Zhao, Ward, French and Graham (2013) and others. Such methods will determine whether elemental association is suitable for economic extraction. For the purposes of this study, we have focussed on the first step only that is currently not considered for FCCM: elemental identification. This is the first investigation of its kind in Queensland and represents a stage of prospecting. The promising results have prompted further detailed analyses.

Global commitments to low-carbon energy sources may eventually change the role of the coal industry, with 'other uses' of coal, including chemicals, electronics and advanced

materials taking priority. Therefore, as coal will be mined, the value of every grain moved needs to be optimised. This could provide three advantages:

- improve economics of mining coal
- provide sources of sought-after elements for growing demand for new technologies
- reduce waste and improve energy use, together reducing the environmental footprint for mining.

Additionally, benefits of further investigations may be a potential driver for mining companies to consider mining a high mineral-matter coal such as the FCCM that may have additional commodities of interest. Further, it may drive research and development in mineral and element extraction technologies, to further improve environmental footprints and improve value for the industry.

If the value of the non-coal fraction could be defined by way of its elemental availability, higher-mineral-matter coal that has been traditionally avoided may have a future. Introduction of advanced elemental separation and extraction processes technologies or specialisation companies for such processing may help reduce waste and lead to improved value at current mining operations. Elements in slag and fly ash material destined for land-fill and mine back-fill could become mobilised through groundwater movement and lead to environmental harm (Madzivire, Ramasanya, Tlowana, Coetzee, & Vadapalli, 2018; Ward, French, Stephenson, Riley & Li, 2010). It may therefore be worth exploring currently mined coal and wash plant and post-use wastes for REE and other elemental concentrations prior to any other use and to prevent environmental contamination and avoid loss of value.

Based on its sheer volume and ease of access (in the case of the FCCM), the value of the coking coal content could become viable for mining, with improved wash-plant capabilities to deal with high clay contents and if the non-combustible fraction (clay speciation and its potential as a source of critical, strategic elements) can be better understood. This would be valuable for a multiple-product industrial conglomerate that may wish to mine the coal for all products. It may benefit from being seen as a 'mixed product' resource rather than 'product + waste'.

Conclusions

The aim of the study was to deliver preliminary results of an elemental assessment of Fort Cooper Coal Measure samples. Further, this study delivers a proof-of-concept assessment of the processes required to analyse elemental content in coal and identify its potential economic value. Findings suggest that, as greater than crustal-average abundances are evident in many of the samples selected, specifically in the tuffaceous component, further work would be warranted. Specifically, it would be valuable to explore associations between high elemental concentrations and local structural features. Additionally,

it would be useful to analyse more samples across the FCCM to improve the dataset, generally, to further understand elemental potential in addition to compare elemental concentrations of the FCCM and its correlatives with the Burngrove and other associated formations.

Although some of the elements may be difficult to liberate and extract using today's technology, knowledge of their presence may provide a stimulus for new technology development, if future extraction is deemed valuable.

Acknowledgements

The authors acknowledge the Geological Survey of Queensland for in-kind support and the Queensland Government Exploration Data Centre, in particular Chris Hansen for assistance with core viewing and sample collection. Additionally, David Coffey is thanked for assistance with core logging and sample selection. The CSIRO Coal Mining Research Program is acknowledged for strategically funding and approving publication, in particular Hua Guo and Marc Elmouttie for supporting this work. The authors would also like to thank Manoj Khanal, Phillip Ofori and Mark Maxwell, for their insightful comments. Joan Esterle and Ian Graham are gratefully acknowledged for their constructive reviews of the submitted manuscript. Finally, the authors acknowledge the work performed by Bob Morris and his colleagues at Bureau Veritas, New South Wales.

Funding

This project was a CSIRO Energy strategic project supported by the Coal Mining Research Group.

ORCID

J. H. Hodgkinson  <http://orcid.org/0000-0002-4031-3883>
M. Grigorescu  <http://orcid.org/0000-0002-6236-5158>

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