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Trace and heavy element distribution of the Hwange Coals in Zimbabwe: indicators of source rock chemistry, climatic conditions and deposition mechanisms during their formation in Southern Africa

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Abstract

The study of heavy metals in the Hwange coals enhances knowledge of both the geological evolution of the coal-bearing horizons and the climates that prevailed during their deposition, as well as indicating likely trace and heavy elements that would affect the health of the miners and the environment at large. The Main Coal Seam of the Hwange coals are bracketed by the Lower Wankie Sandstones of Carboniferous to Permian that were deposited during the Dwyka epoch and the Upper Wankie Sandstones of Permian age. The Hwange coals of Zimbabwe are inferred to have been deposited in swamps associated with fresh water lakes lying on either side of a great elevated tract of Archean and Proterozoic basement during the early Permian. Initially the lake was shallow, as observed from sedimentological data, and eventually the lake became deeper during the continuation of the Karoo period of southern Africa. The sedimentation in Zimbabwe began with the melting of the Carboniferous ice cap of the then south and central Africa. The Karoo succession in the Mid-Zambezi Valley suggests that climatic cycles of glacial to semi-glacial and finally to post-glacial nature occurred, followed by very hot, humid and arid conditions towards the end of the sedimentation period. Four sedimentary successions are reflected at Hwange, the first being fluvial-glacial beds, followed by flooding and deposition of the Lower Wankie Sandstones. At the end of this phase, there followed a general increase in flora and fauna, responsible for the formation of coal now preserved in the Main Coal Seam. Above this succession is the Lower Carbonaceous Mudstones of the Wankie succession. The unconformity of the Upper Wankie Sandstones with the Lower Mudstones marks the end of the coal-bearing horizons. Above the Upper Wankie Sandstones further flooding at a large scale occurred, which is thought to have been rapid, as no coal seams are associated with this mudstone in the whole of the Zambezi valley. A systematic study of heavy elements, ash, moisture content and arsenic, shows that during the deposition of the Hwange coals of the Main Coal Seam there were significant amounts of gallium, germanium, niobium, vanadium and chromium in the

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source areas, together with metals of felsic affinity such as strontium, tin and lithium. There is a systematic relationship between ash content and heavy mineral content in the coal. For coals with a high heavy metal content, their ash contents are low in some samples, whereas others demonstrate the reverse. While we can easily attribute the source of the felsic affliated elements to the basement granites, heavy metals are interpreted to have been fixed under anoxic conditions when the organic matter was being converted to coal. It is suggested that the heavy elements may have acted as catalysts in the coalification processes.

Keywords: Karoo heavy elements ash content glaciations climate gallium germanium lithophile chalcophile siderophile

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1 Introduction

Coal mines can be a source of deleterious elements for miners, such as at Hwange Mine in Zimbabwe, as these coals could contain appreciable amounts of heavy and trace elements such as arsenic. The mode and deposition of any coals directly links the health factors of the people mining the coals (Finkelman, 1994). The study of heavy metals in the Hwange coals enhances knowledge of both the geological evolution of the coal-bearing horizons and the climates that prevailed during their deposition, as well as indicating likely detrimental environmental factors during extraction and use of the coal (Lallier-Verges et al., 2008; Dai et al., 2008 a & b). The health of the people involved in the mining industry directly relates to the development and social well being of society. The town of Hwange in Zimbabwe is located at Latitude 18°1956S and Longitude 26°2506E, in the southwestern part of the Lower Zambezi Valley. The town of Hwange is located some 130 km south of Victoria Falls on the Zambezi River, Zimbabwe (Figs. 1 and 2). Hwange (formerly Wankie) is located in the Middle Zambezi Basin Coalfields, and constitutes the largest working coal mine in Zimbabwe. The mine also serves the main thermal electricity power stations of Zimbabwe and supplies coal to the Zimbabwe Steel Company, numerous ceramic companies and farmers around the country. The town name of Wankie was changed to Hwange at independence in 1980, however the geological formations in the area still retain their original stratigraphic names.

The presence of heavy metals in coals could be as a result of the quick intake of nutrients by plant material from the overlying soils and/or the derivation of heavy metals from the underlying rocks by weathering in oxic and anoxic conditions. The situation is best resolved by investigating the underlying rocks and inferred climatic conditions that prevailed during the deposition of the coal.

The geology of the Karoo deposits at Hwange has been discussed in detail by Bond (1952), Taverner-Smith (1958), Watson (1960), Falcon (1986) and Johnson et al. (1996). In this paper we focus on the Wankie Main Seam and the lithologies that immediately underlie and overlie the Main Seam at Hwange itself. No studies on the nature of heavy metals in coal from Hwange have been carried out in Zimbabwe, and thus this study serves as the first of its kind from these coals in the southern Mid-Zambezi Valley Basin. The characteristics of the ash contents, compared to those of other known coal fields around the world help to correlate the evolutionary history of the coal-forming conditions at Hwange during Karoo times (Late Carboniferous to Permian). It is the thrust of this paper to address these needs and to fill the gap on the Hwange coals.

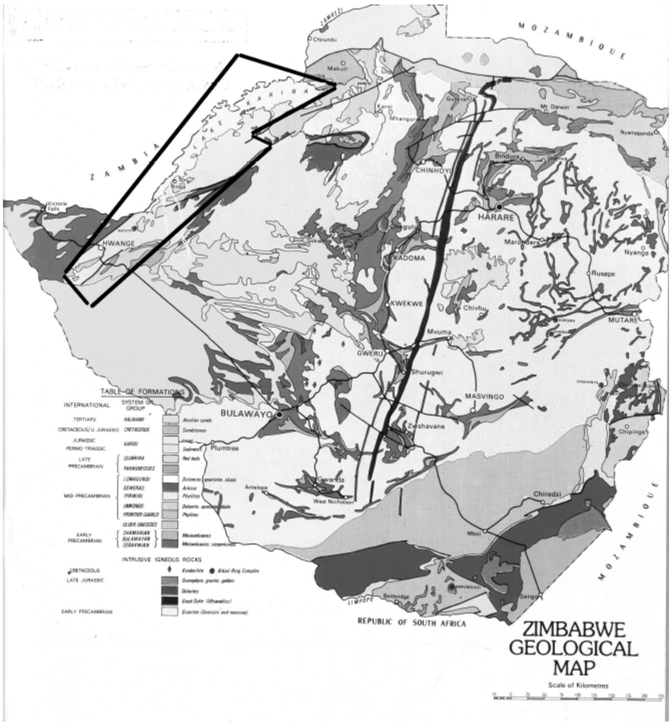

Figure 1: Geological Map of Zimbabwe, showing the location of the Lower Zambezi Valley that is enclosed in a polygon. The town of Hwange is shown in the north-west part of the Map, within the Lower Zambezi Valley.

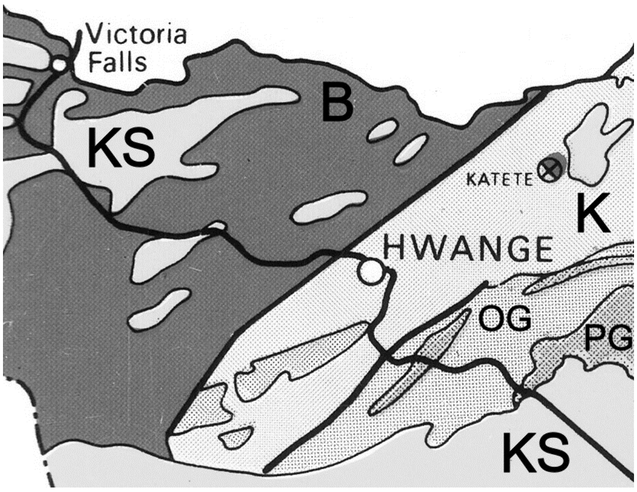

Figure 2: Detail of Geology around Hwange. All large capital letters refer to formations of the Karoo and younger, and the small capital letters refer to the Precambrian formations. K= Karoo Supergroup; B = Batoka Basalts; KS = Kalahari Sands; OG = Older gneisses; PG = paragneisses.

2 Geology of the Hwange coal field

In the Carboniferous to Early Permian times, Southern Africa was covered by an ice sheet that had a significant bearing on the development of the coal measures in the region. Similar coal fields developed in Inner Mongolia, China, with characteristics that are different from those at Hwange (Dai et al., 2003, 2008a). Johnson et al. (1996) have reviewed the stratigraphy of the Late Carboniferous to Middle Jurassic Karoo Supergroup in southern Africa, where they outline the nature of the basins and depositional environments. Late Palaeozoic glaciations of Gondwana comprised two short episodes in the Famennian and in the Visean, confined to Brazil and adjacent parts of the northwestern part of Africa (Nyambe, 1999a). These two were followed by a longer episode that started in the Mamrian of eastern Australia and Bolivia-Argentina, extending to cover much of Gondwana in the Stephanian-Asselian (Veevers and Powell, 1987). This Karoo glaciation therefore affected the manner in which sedimentation occurred, beginning with the melting of the ice sheets, leading to local flooding with resulting oxic to anoxic basin conditions. Falcon (1989) cites fluctuating pH and Eh factors in the basin in which peat had accumulated, and the influence of geothermal gradients as being partly responsible for the high inertinite values, reactive semi-fusinite in the colder-palaeoclimate Main Seam (due to glacial melts). Dewison (1989) attributes durain macerals and dull coals to the presence of hiatus during deposition, thus accelerating accumulation of extraneous inorganic and organic material whereas Dai et al. (2008b) cites influx of volcanic ash and or influx of salty/marine fluids in the basin.

It is now accepted that the basin in which the sediments of the Zimbabwean Karoo deposits accumulated was an extensional basin (Rust, 1975; Falcon, 1989; Nyambe, 1999a, 2000). Sedimentation in extensional basins is controlled by sediment input, faulting and block rotation, subsidence rates and climate affecting lake levels and preponderance of lacustrine facies, and they tend to be much more long-lived (up to 10s of millions of years) than pull-apart basins (Neugebauer, 1983; Nyambe, 2000). Thus the Ordovician-Jurassic Mid-Zambezi Valley Basin is interpreted to be a half graben with preserved sub-grabens. Most of the basin is filled by Karoo sediments, and Nyambe (1999a) estimates the volume of these sediments to be about 95% of the exposed rocks within the basin in the northern part of the basin in southern Zambia.

The surface upon which the Karoo sediments were deposited was a peneplain in the north (Drysdall and Weller, 1966) whereas in the southern basin, such as Hwange, it was more uneven (Bond, 1952). Sedimentation of the Karoo sediments in the Mid-Zambezi Valley appears to have consistently occurred in tandem with tectonic disturbances, and the surrounding land was still mature in relief (Bond, 1952; Drysdall and Weller, 1966; Tarverner-Smith, 1958). These factors led in general to the observed thin coals, with impersistent splitting of seams that are often dirty, and grade into mudstone (Watson, 1960; Drysdall and Weller, 1966; Tarverner-Smith, 1958, Nyambe, 2000). Such movements prevented the occurrence of a stable platform upon which a thick high quality coal formation would form, and instead, only in areas such as Hwange, Nkandabwe and Maamba, did localised stability allow sufficient accumulation of peat horizons. The Hwange Basin is underlain by a Pre-Cambrian basement of granitic and paragneissic units of the Magondi Mobile Belt of the Kamativi inlier, dated between 2000 and 1800 Ma (Stowe, 1989; Tennick and Leyshon, 1988) (Fig. 2). The Magondi gneisses are overlain by the Sijarira sandstones of Proterozoic age (Hanson et al., 2004, Dorland et al., 2006). The Sijarira Series are flaggy and hard red to brown sandstones, in places they are generally quartzitic and still preserve sedimentary structures. They are generally found capping the high hills of the Karoo floor (Table 1). Above the Sijarira there is an unconformity, which marks the beginning of Carboniferous times (Table 1).

Table 1: Summary of Geological Formations and thicknesses. (Revised after Watson, 1960).

	Period	Epoch	Formation	Thickness
Karoo	Jurassic	Stormberg	**Batoka Basalts**- Amygdaloidal lavas, with thin sediments between the flows.	300 m
			Unconformity	
Karoo	Triassic	Stormberg	Ripple-marked flagstones- Maroon shales at the base grading into grey flaggy ripplemarked siltstones with limestones.	182 m
Karoo	Triassic	Stormberg	Escarpment Grits- Coarse-grained white to grey grits, polymictic conglomerate.	61 m
			Unconformity	
Karoo	Permian	Beaufort	**Madumabisa Mudstones**- Grey mudstones, with occasional nodular limestones developed at the top. 60 m thick bedded limestones intercalated with grey mudstones at the bottom, which in places contains Tapinocephalus fossils, polymictic conglomerate.	363 m
Karoo	Permian	Ecca	**Upper Carbonaceous Mudstones**- Consists of 61 m of grey mudstones with impure carbonaceous bands, grading down into the main carbonaceous mudstones with numerous bands of coal.	120 m
Karoo	Permian	Ecca	**Upper Wankie Sandstones**- Coarse white feldspathic sandstones, with rare bands of mudstones that contains a middle Ecca flora.	33 m
Karoo	Permian	Ecca	**Lower Carbonaceous Mudstones**- Black carbonaceous mudstones, with numerous bands of coal up to 30 cm thick, locally and intermintently replaced by bands of fireclay. The lowest horizons contain the Main Wankie Coal Seam.	45 m
Karoo	Carboniferous to Permian	Dwyka	**Lower Wankie sandstone**- Coarse to fine-grained white sandstones. Lower horizons often missing, where present, they are argillaceous. Varved fluvio-glacial beds occasionally developed at the base.	61 m
			Unconformity	
Late Neoproterozoic			**Sijarira Sandstones**- Hard flaggy red-brown to purple quartzitic sandstones, overlying coarse white sandstones.	45 m
			Unconformity	
Paleoproterozoic			Granitic and paragneissic rocks forming the Pre-Karoo floor.	

Lower Paleozoic rocks from the Cambrian to the Devonian are not widespread in Zambia and Zimbabwe, and most southern African countries. Where present, the Devonian is represented as thin sequences such as the Sikalamba Formation in Zambia (Nyambe, 1999a). This gap suggests that sedimentation in the Palaeozoic began in this area with the melting of the large ice sheets that covered southern Africa in Late Carboniferous to Permian times.

The Lower Wankie Sandstones (Table 1) are characterised by fragments of gneiss and quartz from the pre-Karoo rocks. The basal part of the Wankie Sandstones contain varved clayey sandstones that occur as whitish arenites and dark grey carbonaceous shales. These reflect the initial waters of glacial origin in which the earliest sediments were deposited, in discontinuous lakes filling depressions on gently uneven surfaces (Watson, 1960), following the first flooding episode due to the melting of the ice sheet. Grain size progression from bottom to the top of the Lower Wankie Sandstone, shows that coarse-grained material became more widespread as lacustrine depressions filled up and sediment supply increased following glacial retreat, leading to the deposition of the main mass of the sandstones in glacial to peri-glacial environments.

The fine glacial detritus accumulated more distally, and as glaciers continued to retreat, transgressed above the Lower Wankie Sandstones to form the Lower Carbonaceous Mudstones (LCM) that contain the Main Coal Seam at their base, the main source of the coal at Hwange. The carbonaceous mudstone layers in the LCM alternate with thin coal layers, and eventually the coal seam replaces most of the mudstone to a thickness of 30 cm - 900 cm. Then it is called the "Main Coal Seam Formation", which is described separately in the following paragraph. Near the top of the Lower Carbonaceous Mudstones, there occurs locally a 100 cm thick coal seam, but it is not continuous.

The Main Coal Seam can reach a thickness of 12 m, but averages 9 m. Pyrite and calcite are found together with the coal. The ash content of the Main Coal Seam increases gradually from the bottom to the top (from 5-7% to 30%), until the zone is reached where it is no longer coal, but mudstone in the LCM (Table 2). Coal of 12.8% ash content and below is the best quality for coking purposes, whereas that between 12.8% and 30% is suited for burning, and that above 30% is not marketed at Hwange. The phosphorous content also increases from the footwall to the hanging wall, suggesting that there may have been a group of plants still growing just before the beginning of the coalification process, whose phosphorous was efficiently leached. The coal itself consists mainly of durain alternating with vitrain. Chemically the coal is classified as bituminous coking coal of class B.3 (International Classification of Coals). Table 2 shows some average analyses of the mined Hwange coals, whereas Table 3 shows the trace and heavy element contents analysed for this study. The coal that occurs at the base of the Main Seam, next to the footwall has low ash contents, low phosphorous contents, good swelling number, excellent agglutinating values and therefore form excellent coking coals. At the top of the seam the coals are opposite in character to those at the base, they possess high ash and phosphorous contents, low swelling numbers that drop down to zero, and poor agglutinating values. These high ash coals are best suited for industrial use, steam raising and gas production.

The Wankie Main Coal Seam, like the ones found in the Mid-Zambezi Valley, are all prone to spontaneous combustion when exposed to the air. This is partly due to their high sulphur contents and oxidation of pyrite. The Wankie Main Coal Seam is compositionally unlike the coal seams of the Northern Hemisphere that formed in Carboniferous times (Watson, 1960; Kandiyoti, et al., 2006; Yossifova, et al., 2007), and differs in character and ash content, being more of durain type than vitrain and has higher ash contents (Tables 2 and 3), suggesting different depositional condi-

Table 2: Average analyses of Hwange Coals.

Element/Material	Percentage(%)	Ash Analyses	Percentage(%)	Fuel Ratio
Fixed carbon	65.75	Fuel Ratio		2.8
Carbon	69.30	SiO_2	48.30	
Hydrogen	4.50	Fe_2O_3	1.16	
Nitrogen	1.70	Al_2O_3	29.82	
Ash	9.77	CaO	9.86	
Moisture	0.76	MgO	1.72	
Caloric Value (B.T.U)	13, 500	Alkalis	0.65	
Volatiles	23.77	Sulphur	0.85	
Vitrain	11	Water		
Durain	85			
Fusain	4			

tions. The ash contents of the Hwange coal, even those with the lowest amounts, do not compare with British coals, for example, whose values range between 1.2% to 7% (Kandiyoti, R, 2006). This is in keeping with the climatic conditions that prevailed during the coalification process. Whereas the Late carboniferous times were ice-free in the Northern Hemisphere, in the Southern Hemisphere, the continent was covered by an ice cap (e.g., Condie, 1996; Unrug, 1993). Fine dust particles can accumulate in ice over periods of thousands of years. We suggest that this could have happened during the Gondwana glaciation in the areas around Hwange.

The upper grey mudstones of the LCM (Table 1) are capped by the Wankie Fireclay, a brown to creamy mudstone, with a lenticular geometry. The Fireclay is mainly used for refractory bricks manufacture. The Fireclay averages 58% SiO2, 28% Al2O3 and 10% H2O. All the alkalis MgO (0.72%) (earth alkaline), CaO (0.30%), K2O (0.02) are fairly low. Inferred conditions of formation for the fireclay would suggest that feldspar was leached from source rocks of granitic composition and suspended in solution in the Madumabisa lake which was the depo-site of the Madumabisa Mudstone Formation of Beaufort age (Table 1). To leach feldspar, would require pH values of 3 to 7 (Mapani, 1995), which would then release trace elements that substitute for K. Humic acids in both oxidising and reducing conditions can also leach alkalis if weathering is thorough. At low pH values, alkalis are dissolved at source, but are transported at low to high pH conditions. Organic matter present in the Madumabisa lake would have been the ideal source of such humic acids. These factors would suggest that during the formation of the fireclay, the pH levels were low to neutral in the basin. The acidity would have been formed in the lake itself whilst the peat was being altered to coal, releasing a high volume of gases, such as hydrogen sulphide, nitrogen and oxygen in the lake. In other areas of the Mid Zambezi valley, no fireclay is developed where the coal quality is poor, such as at Maamba mine in southern Zambia (Nyambe, 1999b).

Above the Lower Carbonaceous Mudstones (LCM) and Fireclay, are the Upper Wankie Sandstones (UWS) that heralded the beginning of a new sedimentological milieu. In other parts of the Mid-Zambezi valley, there occurs an unconformity between the LCM and the Upper Wankie sandstones (Drysdal and Weller, 1966; Nyambe, 1999b, 2000). This is a much thinner unit in the succession at Hwange (Table 1). The UWS are composed of white coarse-grained feldspathic sandstones, with occasional thin grey and black interbedded shales. Within the argillaceous bands of UWS, Glossopteris and Sphenopteris fossils are found. Cement in the UWS is generally calcareous, to sideritic in places. During Upper Wankie sandstone times, transgression of the basin occurred for a second time on a large scale, and changed deposition of sediment from sandstone type to mudstones. This flooding induced the deposition of the Upper Carbonaceous Mudstones (UCM). The Lower Wankie Sandstones (LWS) and the Upper Wankie Sandstones (UWS) resemble each other in hand specimen, petrology and geochemistry, suggesting very similar climatic and deposition conditions. The distinguishing factor between the LWS and the UWS is the absence of pre-Karoo fragments of Sijarira and granitic basement in the latter. The UWS grade up into the Upper Carbonaceous Mudstones without a break (Table 1).

The Upper Carbonaceous Mudstones (UCM) are similar lithologically to the LCM. A ferruginous often nodular sideritic ironstone, suggesting oxidising conditions formed by the early post-depositional transformation of iron minerals, marks the base. Siderite would have precipitated due to diagenetic processes following compaction (e.g. Hubert and Reed, 1978). These nodular sideritic to ferruginous concretions may mark the sediment-water interface during deposition. Thin slivers of coal similar to those observed in the LCM are also present in the UCM. This unit sometimes has up to 150 cm of impure coal seam units. The main difference between the UCM and the LCM is the absence of a seam like the Main Coal Seam in the former.

The Madumabisa Mudstones Formation overlies the Upper Carbonaceous Mudstones, without a lithological break at Hwange, but a palaentological one is noted by Watson (1960). Within the Mid-Zambezi Valley in the northern half-graben in Zambia, an assemblage of ostracods, bivalves, gastropods and fish scale fossils are reported (Nyambe and Dixon, 2000), as well as to the east of Hwange, in Sebungwe (Bond, 1952, 1955; this study). The Madumabisa mudstones make up a 363 m thick succession of argillaceous beds, that comprise the bulk of the Karoo strata around Hwange. These mudstones attest to deposition in a large basin which covered the whole of the geographical extent of the Mid-Zambezi Valley (e.g., Nyambe, 1999). Similar fossils are reported in the Karoo of Botswana at Morupule Colliery and the mudstones are correlated to the Madumabisa Formation (Stephenson and McLean, 1999). At the peaks of flooding, heavy metals are expected to be present either as colloids or in solution. Chemical analyses reveal some patterns during the deposition events.

3 Analyses and Results

We present herein (Table 3) results of trace and heavy elements from three boreholes at Hwange, BH6254A (top), BH6254B (middle) and BH6254C (bottom), with sample numbers E202322 from the top of the Main Coal Seam, E202323 from the centre and finally E202324 from the base. The analyses were done by ICP-MS at the United States Geological Survey laboratories in Reston, Virginia.

The following elements were investigated, K, Li, Mg, Na, Ca, Al, P, Si, Ti, B, Ba, Zr, Ag, As, Au, Bi, Cd, Cs, Fe, Co, Cr, Cu, Ga, Ge, Mo, Mn, Ni, Zn, Pb, Se, Sc, Sr, Th, Y, Nb, Pb, Rb, Sb, Sn, Te, Tl, U, Cl, Hg, and S (Table 3). The specimen E202322 (top of the Main Seam) had the highest ash content from this analysis, and also from the general mine analyses (Table 2). Specimen E202323 had a lower ash value than E202322, and the bottom sample E2023324 had the lowest value of 6.5% (Table 3) corresponding to the general upward increase in ash contents in the Main Coal Seam. Arsenic values are not elevated, showing an enrichment factor of 3.1 above crustal abundances. This could in part perhaps be explained by the fact that plant material in this locale did not thrive on greenstones that posses more arsenic than granites.

Table 3: Trace and Heavy Element Data.

Sample	Ash	Moisture	Cl	Hg	Na_2O	Be	Co	Cr	Cu	Li	Fe_2O_3	Bi	Cd
Number	%	%	%	ppm	%	ppm	ppm	ppm	ppm	ppm	%	ppm	ppm
E-202322	36.7	0.48	0.02	<0.02	1.4	8.5	20.8	233	75.3	169	0.35	2	0.3
E-202323	27.6	0.33	0.03	0.15	1.4	7.0	29.8	210	132	103	3.2	3.1	0.67
E-202324	6.5	0.49	0.037	0.07	3.1	10.4	54.5	190	99.6	342	0.76	4.9	0.88

Sample	Mn	Ni	Sc	Sr	Th	V	Y	Zn	Al_2O_3	CaO	K_2O	Ga	Ge
Number	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	%	%	%	ppm	ppm
E-202322	29.6	42	49.5	154	57.1	148	55.4	50.2	33.5	0.07	0.46	27.4	5.5
E-202323	204	48.2	32.1	189	50.8	150	50	89.6	30.8	0.54	0.29	46.4	7.4
E-202324	106	248	26.3	1140	41.5	234	52.2	92.3	38.2	1.4	0.6	80.1	147

Sample	MgO	P_2O_5	SiO_2	SO_3	TiO_2	B	Ba	Zr	Ag	As	Au	Mo	Nb
Number	%	%	%	%	%	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
E-202322	0.15	0.06	56.5	0.04	1.9	138	150	492	<2	4.6	<10	2.4	20.8
E-202323	0.24	0.06	55.3	0.34	2.6	122	226	612	2.8	5.1	<10	3.1	40.1
E-202324	0.23	0.6	45.1	0.93	2.6	583	812	637	3.4	6.2	<10	11.7	52.6

Sample	Sb	Sn	Te	Tl	U	Se	S	Cs	Rb	Pb
Number	ppm	ppm	ppm	ppm	ppm	ppm	%	ppm	ppm	ppm
E-202322	1.1	17.6	1.8	0.15	9.2	0.86	0.235	31.2	31.6	40.8
E-202323	1.2	24.2	0.84	0.44	17.9	1.1	0.854	60.4	27.2	101
E-202324	1.9	35.6	0.72	0.89	18.8	0.23	0.935	94.5	61.3	108

	Sample	Hg	Be	Co	Cr	Cu	Li	Bi	Cd
	Number	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
	E-202322	<0.02	3.1	7.6	85.7	27.7	62.1	0.74	0.1
	E-202323	0.15	1.9	8.2	58	36.5	28.5	0.86	0.19
	E-202324	0.07	6.8	3.5	12.3	6.5	22.2	0.3	0.06
U.S. Ave		0.17	2.2	6.1	15	16	16	< 1	0.47

	Sample	Mn	Ni	Sc	Sr	Th	V	Y	Zn	Ga	Ge
	Number	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
	E-202322	10.9	15.4	18.2	56.6	21	54.4	20.4	18.5	10.1	2
	E-202323	56.4	13.3	8.9	52.2	14	41.4	13.8	24.8	12.8	2
	E-202324	6.9	16.1	1.7	74	2.7	15.2	3.4	6	5.2	9.5
U.S. Ave		43	14	4.2	130	3.2	22	8.5	53	5.7	5.7

	Sample	B	Ba	Zr	Ag	As	Au	Mo	Nb
	Number	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
	E-202322	50.7	55.1	181	<2	1.7	<10	0.9	7.6
	E-202323	33.7	62.4	169	0.77	1.4	<10	0.86	11.1
	E-202324	37.9	52.7	41.4	0.22	0.4	<10	0.76	3.4
U.S. Ave		49	170	27	< 0.1	24	< 0.1	3.3	2.9

	Sample	Sb	Sn	Te	Tl	U	Se	Cs	Rb	Pb
	Number	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
	E-202322	0.4	6.4	0.7	0.05	3.4	0.3	11.5	11.6	15
	E-202323	0.33	6.7	0.23	0.12	4.9	0.3	16.7	7.5	27.9
	E-202324	0.12	2.3	0.05	0.06	1.2	0.23	6.1	4	7
U.S. Ave		1.2	1.3	< 0.1	1.2	2.1	2.8	1.1	21	11

Table 4: Major elements and moisture.

Sample Number	Ash %	Moisture %	Cl %	Na_2O %	Fe_2O_3 %	Al_2O_3 %	CaO %	K_2O %	MgO %	P_2O_5 %	SiO_2 %	SO_3 %	TiO_2 %	Oxide	S %
E-202322	36.7	0.48	0.02	1.4	0.35	33.5	0.07	0.46	0.15	0.06	56.5	0.04	1.9	0	0.235
E-202323	27.6	0.33	0.03	1.4	3.2	30.8	0.54	0.29	0.24	0.06	55.3	0.34	2.6	0	0.854
E-202324	6.5	0.49	0.037	3.1	0.76	38.2	1.4	0.6	0.23	0.6	45.1	0.93	2.6	0	0.935

Nickel is an exception though, implying in part that there exists some biochemical mechanisms that enhance heavy metal concentrations in plants once they begin to decay. Germanium shows up to 98 times above crustal levels, while gallium only shows an enrichment factor of 11. Silver is highly elevated, higher than most Gondwana coals with enrichment factors of 34 times. Of the Gondwana coals, the New South Wales coals are some of the most enriched in heavy elements, but their silver values are enriched by a factor of 20, while the germanium enrichment factor is 330 (Swaine, 1962). Other indicator elements like Bi are enriched by a factor of 24.5 in the Hwange coals. The presence of such elements as gallium and germanium may be explained by the geochemistry of these elements in the source rocks. Gallium is generally camouflaged by aluminium in rock-forming minerals (Ga3+ 0.62, Al3+ 0.51) suggesting that Ga should be more abundant in later formed silicates during magmatism and crystallisation (Hll et al., 2007). Germanium (Ge4+ 0.53), on the other hand, replaces silicon (Si4+ 0.42) in silicates. In igneous differentiates, Ge increases in the late magmatic phases, together with Nb5+(0.64), Ta5+(0.64), Sn4+(0.69), W6+(0.64), U4+(1.00), Be2+(0.27), Cs+(1.70), Th4+(1.04), Li+(0.74) and Rb+(1.49), being concentrated during late stage granite crystallisation and in pegmatites (McDonough and Sun, 1995; Schnenberger et al., 2008) similar to those found in the basement inliers around Hwange.

Coals are known to accumulate heterogeneous groups of heavy and trace elements, both chalcophile and lithophile (Mason and Moore, 1982; McDonough and Sun, 1995; Thomas, 2002). Possibilities suggested for anomalous accumulation of trace and heavy elements in coals include (i) that the organic material was deposited together with the mineral matter, (ii) that the element accumulated as a result of the vital processes required for the parent plant matter, (iii) the element was precipitated from groundwater by adsorption or chemical reaction during coalification and (iv) that the climatic conditions were suitable for the speciation of that particular element during deposition or plant uptake. In the coals of the United Kingdom (Northern hemisphere coals), there is a predictable correlation between heavy element content of the coals and ash content (Kandiyoti et al., 2006). It is generally accepted that high ash content coals possess lower levels of heavy metals and trace elements, as opposed to low ash coals that have higher values (e.g. Mason and Moore, 1982) as a result of the plant metabolism during the uptake of the vital nutrients, nitrogen(N), phosphorus (P) and potassium (K). However the Hwange coals do not show that correlation for some of the elements analysed (Table 3), for example the coals at the bottom of the Main Coal seam have low ash contents, but still yielded low values of some heavy metals such as Sc, Cr, Te, Y.

Siderophile elements analysed consistently show high values for the bottom part of the Main Coal Seam and lower values at the top. Gold values are very low and therefore cannot be interpreted correctly. Nickel values are very enriched in comparison with other siderophile elements analysed. Uranium contents are used here as indicators of the capacity for the prevailing environment to be able to absorb a variety of cations in a stable state. The results for Hwange coals show uranium values that are 18.8 ppm at the bottom, to 17.9 ppm in the middle of the Main Coal Seam, and 9.2 ppm at the top. We interpret this result to imply that for the bottom part, the adsorption capacity was very high, and as basin subsidence increased, either there was less humus or there was intermittent flooding reducing the absorption of lithophile affiliated elements. All lithophile elements except Cr, Sc, Y and Al appear to obey this pattern (Table 3). However the values of Sr are extremely enriched at the base of the coal seam, in comparison to other elements. Such high values would require an alternative source in the basin. It is expected that all chalcophile elements would be enriched at the bottom of the coal seam, as it is the place where conditions were more reducing. All the elements analysed show this trend except for Te, Se and Cu.

4 Discussion

It has been shown that the Lower Coal seam is enriched in appreciable amounts of toxic elements such as arsenic, germanium, and nickel. This has necessitated the adoption of specific methods and standards of monitoring when the Lower Coal Seam is being mined. It has also led to the re-alignment of the uses of the Lower coal seam to be concentrated in industries with minimal human inhalation of toxic fumes. The study has directly contributed to the improvement of the social economic development of the workers and consumers on the downstream of coal usage.

The conditions that were imposed by the development of the lower coal seam stem from the geometry of the Lower Zambezi Valley. The Lower Zambezi Valley is asymmetric, it is deeper in the south around Hwange and shallower in the north around Maamba. The basin had a long axis roughly corresponding to that of the Zambezi River today (Gair, 1956; Watson, 1960; Drysdall and Weller, 1966; Nyambe, 1999b). Basin development evolved into a large floodplain, swampy in character with fauna and flora flourishing. Peat accumulated in such a manner that subsidence and flooding of swamps did not inundate the trees and other plants (Nyambe, 1999b). The Main Coal Seam contains some remains of glossopteris (Watson, 1960), which presumably played a major role in the Main Seams formation. The high durain content of the Main seam, may imply a detrital origin for the Main seam, however other characteristics of the seam such as a flora that required a long time to grow, would not drain its parent soil of nutrients such as alkalis, phosphorous, and metals as indicated by our results, and therefore would suggest an in situ origin for the coal. This suggestion is supported by some authors who have studied the subject from a sedimentological rather than heavy mineral chemistry emphasis (Watson, 1960; Rust, 1975; Nyambe, 1999b). Species such as brophates have been recorded from the Carboniferous times (Arnold, 1947), and the Hwange coal could have been developed from major flora as well as easily macerated mosses, favouring a climate such as that of the tundra regions of today, as an ice age had just ended.

The ash content of the Main Seam at Hwange as exemplified from our samples E202322 (top horizon), E202323 (middle horizon) and E202324 (bottom horizon) (Table 3) and those analyses from the mine (Table 2) show a systematic decrease of ash from top to bottom. This variation must also trace climatic changes during the coalification period. The early stages of coal formation generally involve the transformation of plant material into peat. The peat is less dense than coal by a factor of at least 0.33. It would take at least 4.5 m of peat to make 30 cm of good coal, and the abundance of good coal, points to an in situ origin. This has a bearing on the climatic conditions that prevailed during the period when plant debris was transformed to coal. Therefore the increase in weight of coal reflects the evolution pattern in the coalification process, where compression and organic transformation occurred. We thus suggest that the lower parts of the Main Seam with ash contents of 6.5% to 12.8 % must have formed from peat of around 4.5 to 9 % ash. Such ratios would favour an in-situ origin for the coals, and would in tandem require faunal and floral species that were excellent in accumulating heavy metals in their roots, bark or leaves. A detrital origin implies deposition of coal as a sediment, such that from the characteristics of the LCM, we should be able to decipher the climatic variations that took place in the basin. At Hwange, the Main Coal Seam truly grades into the carbonaceous mudstones or shales, which is undeniably a detrital material. The change from carbonaceous material (coal) formed in situ to carbonaceous material of detrital origin is gradual at Hwange, and probably this is in concert with the variations observed from bottom to top of the Main Coal Seam. What these observations imply is that the initial flooding following ice sheet retreat led to a more distal sedimentary system where coals accumulated within the basin centre, such that there was little extraneous matter mixed with the floral debris. However, as time progressed, and sediment sources became exposed with glacial retreat, more debris including organic matter was supplied to the basin, thus diluting the organic matter content of the seam at the top. This is shown in part to have been the case due to the presence of durain macerals (Dewison, 1989). Washouts occur in the Main Coal Seam, consisting of sub-angular grains of quartz and feldspar (Watson, 1960), suggesting drainage channels through the Main Seam, which would point to an in-situ origin of the coal.

Coals with high ash contents such as Hwange show lower values of heavy metals on average. However comparatively high values of gallium, germanium, vanadium and chromium can be explained in terms of changing climate and its effect on the crystalline basement. The effect of the ice cap on basement rocks during the Carboniferous times was to induce effective physical weathering of rock masses of granitic basement. This was quite effective because the observed material that makes up the Lower Wankie Sandstones is entirely that of granitic origin, together with detrital material from the Sijarira sandstones. Plant material that grew upon the Lower Wankie Sandstones and basal sections of the Lower Carbonaceous Mudstones as substrate was presumably able to efficiently extract the observed heavy elements. Most organic substances accumulate elements of low atomic number for their metabolic requirements, except in cases of pollution. Hutchinson (1943) plotted the concentration of elements of terrestrial plants in relation to elements in the crust, according to ionic potential; this showed in the first instance that more elements of lower ionic radius were found in plants, secondly that elements of higher ionic radii were also concentrated in plants but at lower levels. Bowen (1966) showed that terrestrial plants accumulate less of the same element in comparison to marine plants, in most cases by a factor of five to a hundred or more, with few exceptions such as for Cs, Al, Ca, Cd, Cu, Hg, Mn, Rb, and Zr. Except for the transition elements Cd, Cu, Hg and Mn, the other exceptions are all metals that are associated with granitoid type rocks, suggesting that plants growing on substrates with this type of rock chemistry tend to extract these elements effectively. The high contents or Ge, Ga, Nb, V, Sr and Li in the Hwange coals suggest that the depository in which the plant material of the mid-Zambezi Valley Basin grew during Karoo times was more salty than an ordinarily lacustrine environment. Thin limestone beds reported by Bond (1952) suggest that the basin had attained a large size, with lagoonal zones, that concentrated salts to make the waters not only brackish but salty, akin to sea water values. Such a scenario would allow for the development of plant species that are able to concentrate high values of heavy metals Ge, Ga, Nb, Ni and Cr without having a deleterious effect.

The stages at which heavy elements are introduced into coals can be linked to the coalification process. Peat formation begins as a biochemical process where microorganisms are active in reconstituting organic matter. The process begins by decomposition of organic matter in water soluble substances (Hoering and Abelson, 1963; Krauskopf, 1979; Mason and Moore, 1982; Thomas, 2002; Kandiyoti et al., 2006). At this stage, if the pH-Eh conditions are favourable, heavy elements become incorporated as organometallic compounds in the substance that evolves to become peat. This stage is followed by slow decomposition of cellulose (Hoering and Abelson, 1963; Mason and Moore, 1982; Thomas, 2002; Lallier-Verges et al., 2008), and if the decomposition is slow to very slow and complete, good coals result, with a high concentration of heavy metals, that acted as catalysts in transforming organic matter. Nitrogen from microorganisms is also involved in the decomposition mechanism together with bacterial activity (Hoering and Abelson, 1963; Mason and Moore, 1982; Thomas, 2002; Lallier-Verges et al., 2008). Once conditions become toxic or unsuitable for microorganic activity, the biochemical phase comes to an end, and the metamorphic process begins (Hoering and Abelson, 1963; Mason and Moore, 1982; Kandiyoti et al., 2006). If the biochemical process is interrupted by sedimentation or climate change, the coalification process is disturbed, and organic matter is not fully transformed; then the resulting coals are generally of poor quality due to extraneous material (ash) introduced into the basin (Hoering and Abelson, 1963). When the stage is reached where the metamorphic process goes to completion, then peat becomes coal of a certain rank, depending how well the metamorphic process occurred. Coal rank, indirectly measures the degree of metamorphism in coal basins. Heavy metal elements are actively involved in the transformation of organic matter into coal as is the case for V, Mo and nickel in petroleum (Hodgson, 1965, Philippi, 1974). They are present as synthesisers of organic matter into hydrocarbons. This process would explain their elevated levels in coal, however their ultimate source would have been the substrate upon which the plants grew, assuming an in situ development of the coals.

Coals are known to accumulate heterogeneous groups of heavy and trace elements, both chalcophile and lithophile (Mason and Moore, 1982; Kandiyoti et al., 2006; Yossifova et al., 2007). Anomalous accumulation of trace and heavy elements in the coals from Hwange, as discussed above, would favour element accumulation as a result of the vital processes required for the parent plant matter, element precipitation from groundwater by adsorption or chemical reaction during coalification, and prevailing climatic conditions that were suitable for the speciation of the observed particular elements during deposition or plant uptake. These conditions are especially applicable at the bottom of the coal seam.

We have shown that the Hwange coals were deposited in a reducing environment, where organic matter would be transformed into peat. These conditions are also ideal for the production of H2S, from the reduction of sulphur compounds in anoxic conditions. The H2S produced would also lead to the precipitation of such minerals as pyrite (which is common in the Main Coal Seam) and associated chalcophile elements found in the coals. This requirement also indirectly influences the quality of the coal. In the coals of the United Kingdom and Bulgaria (Northern hemisphere coals), there is a predictable correlation between heavy element content of the coals and ash content (Kandiyoti, 2006; Yossifova et al., 2007). High ash content coals possess lower levels of heavy metals and trace elements, as opposed to low ash coals that have higher values (e.g. Mason and Moore, 1982; Yossifova et al., 2007; Dai et al., 2008b). However the Hwange coals do not show that correlation for some of the elements analysed (Table 3), for example the coals at the bottom of the Main Coal seam have low ash contents, but still yielded low values of some heavy metals such as Sc, Cr, Te, Y. Uranium contents have been used in this paper as indicators of the capacity for the prevailing environment to be able to absorb a variety of cations in a stable state as mentioned above. The Hwange coals show uranium values that are 18.8 ppm at the bottom, to 17.9 ppm in the middle of the Main Coal Seam, and 9.2 ppm at the top. We interpret this result to imply that for the bottom part, the adsorption capacity was very high, and as basin subsidence increased, either there was less humus or there was intermittent flooding reducing the absorption of lithophile affliated elements. All lithophile elements except Cr, Sc, Y and Al appear to obey this pattern (Table 3). It is expected that all chalcophile elements would be enriched at the bottom of the coal seam, as it is the place where conditions were more reducing. All the elements analysed show this trend except for Te and Cu.

High levels of Ni together with Cr are toxic to plants as well as to humans. This is well observed on the Great Dyke in Zimbabwe, where only small shrubs and grasses are able to grow in areas that have high values of Ni (>3%) (Mapani, 2001). From an environmental point of view; workers in the steel factories of Gweru and Kwekwe in Zimbabwe are therefore exposed to these toxic elements by using this coal on a daily basis. The identification of the lower coal seam as being more enriched in heavy and toxic trace elements has led to adopting a more cautious manner of applied use and mining. From the scientific point of view, unless there was a certain species that grew in cold climes, and that species was able to concentrate these elements, the high levels of heavy metals can be explained in terms of gradual reduction, when organic matter was in the form of peat, with a differential settling of the heavy element fraction to the bottom during coalification. This is possible if the peat was consistently diluted by extraneous organic matter in the basin. The sedimentological pattern appears to validate this premise.

5 Conclusion

The identification of the lower coal seam as host to the most dangerous elements concentrated in some appreciable amounts that would cause a health problem is a success story in this study. This has directly improved awareness and also used in applications where human contact and inhalation of coal fumes is minimal.

The deposition of these coals follows two major transgressive episodes that occurred following the melting of the ice sheets of Gondwanaland. Each flooding episode was most likely related to glacial retreat and concomitant enhanced sedimentation rates from newly exposed source areas, and this spurred deposition of sediments in swamp and lake environments. The Hwange coals are inferred to have been deposited in these swampy and bog areas. The first flooding episode is associated with the Lower Wankie Sandstones and the overlying Main Coal Seam within the Lower Carbonaceous Mudstones. The second flooding likewise led to the deposition of the Upper Wankie Sandstones and Upper Carbonaceous Mudstones. These two flooding events bracket the period in which coal was formed at Hwange.

The heavy metals in the Hwange coals are as a result of: (a) the elements accumulating as a result of the vital processes required for the parent plant matter; (b) the elements being precipitated from groundwater by adsorption or chemical reaction during coalification; and (c) climatic conditions that were suitable for the speciation of that particular element during deposition or plant uptake. Although an in-situ origin for the Hwange coals is advocated, and heavy element data suggest that the basal and medial parts of the coal seam are indeed of in-situ origin, in contrast the top parts, and the small thin coal horizons found in the Lower Carbonaceous Mudstone and the Upper Carbonaceous Mudstones, may be detrital in origin. A detrital theory, would favour an occasion where plant intake of heavy metals is rapid over a short period of time to deplete the substrate. This is what is observed in the Upper Wankie sandstones. The Lower Wankie sandstones were more influenced by glacial climes, that were cold, and metabolic reactions were consequently relatively slow. Heavy elements act as catalysts in transforming organic matter into peat. Thus heavy elements incorporated by plants during their life become the agency required for peat formation. Lithophile elements concentrated in the coals have generally been sourced from the underlying rock units. Fauna and flora, at this time, must have accumulated these metals, during the flourishing conditions when the climate switched from cold tundra type, to humid tropical conditions. The switch in climatic conditions spurred plant growth in the mid-Zambezi Valley Karoo Basin. This was also a trigger for greater absorption rates of heavy elements, like the current sea plant materials of today.

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