

Development of a SEM-EDS-XRD Protocol for the Physicochemical and Automated Mineralogical Characterisation of Coal Dust Particles

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S1. Mineral and carbonaceous matter formulae used in study

To determine a relative estimate of the composition of the carbonaceous content in the coals, a general description of the variation on the properties of coal was consulted [68] (see Table S1). As the coal described in the study were all bituminous in rank, an empirical assessment of the element ranges was determined from those described in Figure S1. In doing so the composition of the carbonaceous matter defined in this study was broken down into “Dull coal” and “Bright coal” (represented in Table S2). As it was determined that mineral/CM mixtures may occur in the samples a “sub-bituminous” coal category was further defined to serve as a fixed composition by which to relate the relative contribution of CM to the mineral of interest (see Table S2).

Table S1. General classification of coal composition across coal rank, based on work described in [68].

Rank	Sub-bituminous	Bituminous
% Carbon	72–76	76–90
% Hydrogen	~4–3	~3–2
%Nitrogen	~1–2	~1–2
%Oxygen	~20–10	~10–1
%Sulfur	~0–4	~4–0

Table S2. Elemental composition of the different descriptions of carbonaceous matter outlined for this study.

Elements	Bituminous coal		
	CM: Dull coal (%)	CM: Bright coal (%)	CM: Sub-bituminous coal (%)
C	82	90	74
H	3	2	3
N	2	2	2
O	12	6	19
S	2	1	2

For the minerals identified, the compositions defined were sourced from [69,58] and are further presented in Table S3.

Table S3. Composition of minerals classified for the QEMSCAN measurement reports, extracted from [69,58].

Mineral Name	Mineral group	Composition (% element)
Kaolinite	Silicate	Al 20.90, H 1.56, O 55.78, Si 21.76
Quartz	Silicate	Si 46.74, O 53.26
Muscovite	Silicate	Al 20.30, F 0.95, H 0.46, K 9.81, O 47.35, Si 21.13
Zircon	Silicate	Zr 43.14, Hf 4.69, La 3.78, Si 14.76, O 33.63
Illite	Silicate	Al 9.01, Fe 1.43, H 1.35, K 6.03, Mg 1.87, O 55.06, Si 25.25
Talc	Silicate	Mg 19.23, H 0.53, O 50.62, Si 29.62
Szomolnokite	Sulfate	Fe 32.87, H 1.19, O 47.07, S 18.87
Rhombochase	Sulfate	Fe 17.40, H 2.83, O 59.80, S 19.97
Alunogen	Sulfate	Al 8.32, H 5.29, O 71.55, S 14.84
Coquimbite	Sulfate	Fe 19.87, H 3.23, O 59.78, S 17.12
Voltaite	Sulfate	Al 1.33, Fe 22.02, H 1.79, K 3.85, O 52.04, S 18.96
Hydronium-jarosite	Sulfate	Fe 34.85, H 1.89, O 49.92, S 13.34
Jarosite	Sulfate	Fe 33.45, H 1.21, K 7.81, O 44.72, S 12.81
Gypsum	Sulfate	Ca 23.28, H 2.34, O 55.76, S 18.62
Dolomite	Carbonate	Ca 21.73, Mg 13.18, C 13.03, O 52.06
Siderite	Carbonate	Fe 48.20, C 10.37, O 41.43
Ankerite	Carbonate	Ca 19.42, Fe 16.24, Mg 3.53, Mn 2.66, C 11.64, O 46.51
Calcite	Carbonate	Ca 40.04, C 12.00, O 47.96
Apatite	Phosphate	Ca 39.36, Cl 2.32, F 1.24, H 0.07, O 38.76, P 18.25
Pyrite	Sulfide	Fe 46.55, S 53.45
Pyrrhotite	Sulfide	Fe 62.33, S 37.67
Barite	Sulfide	Ba 58.84, O 27.42, S 13.74
Galena	Sulfide	Pb 86.60, S 13.40
Sphalerite	Sulfide	Fe 2.88, S 33.06, Zn 64.06
Chalcopyrite	Sulfide	Cu 34.63, Fe 30.43, S 34.94
Molybdenite	Sulfide	Mo 59.94, S 40.06
Bornite	Sulfide	Cu 63.31, Fe 11.13, S 25.56
Rutile	Oxide	Ti 59.94, O 40.06
Spinel	Oxide	Al 37.93, Mg 17.08, O 44.98
Hematite	Oxide	Fe 69.94, O 30.06
Goethite	Hydroxide	Fe 62.85, H 1.13, O 36.01
Gibbsite	Hydroxide	Al 34.59, H 3.88, O 61.53

S2. Wax block preparation: general casting methodology

As a standard methodology for block preparation, this study employed the following procedure: 100 g of dry Carnauba wax was weighed in a glass beaker and placed in a microwave to melt. Subsequently, 0.2 g of sample (coal dust particles) was weighed and placed in a 25 mm mould, after which ~ 8.5 g of the hot wax was added to the mould. Conventionally at this stage, powdered graphite would be used to aid in the deagglomeration of particles, however, due to the similarity in composition between graphite and the carbonaceous matter in coal, this step could not be done. To further assist in particle deagglomeration, a period of continuous stirring in a “figure of eight” motion was applied to provide thorough mixing before the block was allowed to cure in the oven at 60°C for approximately 40 minutes. Following this, the moulds were cooled and re-set under vacuum in a 30 mm mould with epoxy resin. After the resin has set, a three-stage polishing process was employed using employing three different types of silica sandpaper, where water was used as the polishing lubricant (stage 1: 1200 grit pad, stage

2: 2000 grit pad and stage 3: 4000 grit pad, all conducted for 10 second at 300 rpm). A final hand polishing stage using a special woven polishing pad and aluminium silicate is used as the lubricant is employed to finish the surface of the block. During each stage the blocks are checked under an optical microscope to inspect the consistency of the exposed surface due to the softness of the wax. After surface inspection, the blocks were then carbon coated and kept in a vacuum cupboard for at least two days to allow for the removal of any volatiles prior to loading them in the QEMSCAN.

S3. Particle breakdown methods

Upon receipt, the samples were coarse (ranging 5 cm to 180 μm) and thus required milling to reduce the particle size to the size range of dust. To achieve this, a process was developed to reduce the size of a representative aliquot of the coarse centimetre-sized samples to a size distribution of particles less than 100 μm in size. This involved the use of a jaw crusher (for particles > 1 cm), followed by a rod mill used to step down the particle size from less than 1 cm to approximately 100 μm in size. Such steps were taken to ensure that all samples had similar size distributions prior to the final size reduction step (using the pulveriser/ring mill). Prior to milling via the ring mill, the material was sub-sampled to 100 g aliquots using a large rotary sample riffler, before being dry screened to a final passing size of -25 μm . Dry screening was used throughout over wet screening to avoid the alteration of the particles.

S4. Ash methodology

Approximately 1 g (weighed to the nearest 0.1 mg) of the thoroughly mixed sample was transferred to a weighed capsule. After weighing the capsules were placed in a cold furnace and gradually heated so that the temperature reaches $500 \pm 10^\circ\text{C}$ at the end of 1 h. Continue heating the sample until the temperature rises from $500 \pm 10^\circ\text{C}$ to $750 \pm 15^\circ\text{C}$ at the end of another 1 hour. After this period continue to heat the capsules at the final temperature (750°C or 950°C) for an additional 2 hours. After this point the furnace is turned off and allowed to cool for 3 hours without opening the door. Subsequently, the capsules were removed from the muffle furnace and placed in a desiccator overnight to cool.

The two-stage ashing procedure allows pyritic sulfur to be oxidized and expelled before most metal carbonates are decomposed. An ample supply of air in the muffle furnace, “two to four volume changes per minute,” must be assured at all times to ensure complete oxidation of the pyritic sulfur and to remove the SO_2 formed.

To calculate the ash percent in the analysis sample as follows:

$$\text{Ash \% in sample} = [(A-B)/C] \times 100 \quad (\text{S1})$$

A = weight of capsule, cover, and ash residue, g,

B = weight of empty capsule and cover, g, and

C = weight of analysis sample used, g.

S5. XRF analysis information

The samples were crushed to a fine powder (particle size < 70 μm) with a jaw crusher and milled in a tungsten-carbide ring mill prior to the preparation of a fused disc for major and trace elements analysis. The jaw crusher and mill were cleaned with clean uncontaminated quartz between samples to avoid cross contamination. Glass disks were prepared for XRF analysis using 7 g of high purity trace element and Rare Earth Element-free flux ($\text{LiBO}_2 = 32.83\%$, $\text{Li}_2\text{B}_4\text{O}_7 = 66.67\%$, $\text{LiI} = 0.50\%$) mixed with 0.7g of the powder sample. A mixture of sample and flux were fused in platinum crucibles with a Claisse M4 gas fluxer at temp between 1100°C – 1200°C . Whole-rock major element compositions were determined by XRF spectrometry on a PANalytical Axios Wavelength Dispersive spectrometer at the Central Analytical Facilities, Stellenbosch University, South Africa.

The spectrometer is fitted with an Rh tube and with the following analyzing crystals: LIF200, LIF220, PE 002, Ge 111 and PX1. The instrument is fitted with a gas-flow proportional counter and a scintillation detector. The gas-flow proportional counter uses a 90% Argon-10% methane mixture of gas. Major elements were analyzed on a fused glass disk using a 2.4kW Rhodium tube. Matrix effects in the samples were corrected for by applying theoretical alpha factors and measured line overlap factors to the raw intensities measured with the SuperQ PANalytical software. The concentration of the control standards that were used in the calibration procedures for major element analyses fit the range of concentration of the samples. Amongst these standards were NIM-G (Granite from the Council for Mineral Technology, South Africa) and BE-N (Basalt from the International Working Group).