

Article

Preliminary XRF Analysis of Coal Ash from Jurassic and Carboniferous Coals at Five Kazakh Mines: Industrial and Environmental Comparisons

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Abstract: This study analyzes 105 coal ash samples from Jurassic and Carboniferous coals from five mines in Kazakhstan, Lenin, Saradyr, Bogatyr, Maikuben, and Shubarkol, focusing on the inorganic elemental compositions, their occurrence, and industrial and environmental implications. Methods include coal ash yield and volatile matter analysis, mineralogical characterization via low-temperature ash X-ray diffraction (LTA-XRD), and scanning electron microscopy with energy-dispersive X-ray spectroscopy (SEM-EDS). High-temperature ash (HTA) was analyzed using energy-dispersive X-ray fluorescence (EDXRF), highlighting XRF's potential for rapid multi-elemental analysis. Nine major elements (Al, Si, P, S, Fe, K, Ca, and Ti) and eleven trace elements (As, Cu, Cr, Zn, Pb, V, Ga, Mn, Ni, Y, Yb, and Zr) were identified in HTA samples through EDXRF. SEM and dendrogram analysis confirm their co-occurrence with quartz, kaolinite, pyrite, and accessory minerals such as chalcopyrite, zircon, rutile, and REE-bearing apatite. The elemental content of samples enhances industrial suitability by reducing emissions. Only Yb shows slight enrichment for economic benefits, along with La, Ce, and Nd, while concentrations of potentially toxic elements indicate minimal environmental risk. EDXRF demonstrates its efficiency for large-scale investigations, with all samples analyzed in a few days using automated overnight measurements. This approach shows promise for future studies focusing on trace elements, including REE.

Keywords: Kazakhstan; major elements; trace elements; coal; XRF



Citation: Junussov, M.; Mustapayeva, S. Preliminary XRF Analysis of Coal Ash from Jurassic and Carboniferous Coals at Five Kazakh Mines: Industrial and Environmental Comparisons. *Appl. Sci.* **2024**, *14*, 10586. <https://doi.org/10.3390/app142210586>

Academic Editors: Qingjie Gong and Ningqiang Liu

Received: 1 October 2024

Revised: 7 November 2024

Accepted: 12 November 2024

Published: 17 November 2024



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1. Introduction

Coal is a complex natural material with a diverse chemical structure, containing both organic and inorganic components. It includes all naturally occurring elements and over 200 minerals, each hosting one or more of these elements [1,2]. Major inorganic elements in coal exceed 0.1% by weight (e.g., Al, Si, Ti, Fe, and Ca), whereas trace elements (e.g., As, V, Cu, Zn, Pb, rare earth elements, and U) are typically present in concentrations below 0.1%, ranging from 1 ppb to several hundred ppm [2]. Understanding the occurrence of these elements is crucial as it provides insights into peat formation, coal diagenesis, and basin development. Practically, this knowledge affects coal mining, preparation, combustion, and utilization by helping to avoid technological issues (abrasion, corrosion, fouling, and slagging) and is crucial for evaluating environmental pollution control, health impacts, and its applications as an industrial raw material in cement manufacturing, wastewater treatment, and valuable element recovery [2–6].

Various analytical techniques, such as ICP-MS/AES, AAS, NAA, and DPASV, are employed to characterize coal combustion ash, each offering distinct advantages like low detection limits, high sensitivity, and wide dynamic ranges. Among these, X-ray fluorescence (XRF) techniques are particularly effective for simultaneous multi-element

analysis [4]. XRF techniques offer several benefits, including reduced sample preparation time, lower costs, and the avoidance of hazardous chemicals. In recent years, X-ray fluorescence has emerged as a powerful method for analyzing environmental samples, including coal ash. XRF instrumentation is advantageous due to its lower capital cost compared to Neutron Activation Analysis (NAA), faster analysis times relative to ICP-AES, and widespread availability [4]. In contrast, ICP-AES requires time-consuming dissolution procedures, which can lead to the loss of volatile elements such as As, Pb, Se, Sb, and Zn [7–9]. XRF is an effective method for rapid routine analysis of major and minor elements, offering a significant advantage due to its potentially wide application in industry settings for quick assessments [10].

The application of XRF for analyzing the chemical composition of coal and coal ash has been widely adopted in industrial, economic, and environmental studies across several countries, including Russia (28 studies), Australia (17), China (15), the USA (11), India (11), Mongolia (5), Portugal (5), the UK (4), Turkey (4), Spain (4), Austria (2), Canada (2), Kazakhstan (2), Poland (2), and others. Publications span various years: before 2000—6; 2001–2005—12; 2006–2010—11; 2011–2015—19; 2016–2020—31; and 2021–2023—13. More than half of the articles are concentrated in 8 journals, while the remainder are spread across approximately 30 other publications [11].

The major advantages of XRF analysis are as follows: (i) its versatility and wide availability as a common laboratory instrument; (ii) modern instruments often feature full automation for up to 50 samples; (iii) easy sample preparation, typically involving only pulverization and pelletization; and (iv) a broad concentration range from over 1 ppm to 100 wt%, with detection limits of 0.04 wt% for Al, 0.05 wt% for Si, 100 ppm for minor elements, and 20 ppm for trace elements [12,13]. XRF, in particular, is recognized as highly effective for analyzing high-temperature ash (HTA) to determine both major and trace elements [13–15]. HTA of coals is generally preferred for elemental analysis over fly ash or bottom ash derived from power plants, as HTA offers a more complete recovery of elements, particularly for coal and its ashes [16].

Recent studies on the inorganic geochemical characteristics of coal deposits in Kazakhstan, specifically in the Shubarkol coal deposit and Karagandy coal basin focusing on the k7 coal seam, highlight the potential for industrial extraction of rare metals from coal and coal waste, emphasizing coal's value as a source of critical elements [17–19].

However, comprehensive geochemical investigations of other coal deposits in central and northeast Kazakhstan remain limited. The coal deposits in this region are primarily found in Carboniferous coal basins, which include the largest in Kazakhstan: the Karagandy, Tenyz–Korzhinkol, and Ekibastuz basins, covering a combined area of 4155 km² and containing the region's largest coal reserves, totaling 54.4 billion tons [20,21]. The Carboniferous coals within these basins exhibit a wide range of total coal seams, varying from 6 to 80, with seam thicknesses ranging from 1.5 to 100 m. The Karagandy basin supports approximately 10 underground coal mines, including the active Lenin mine. In the southwest, the Ekibastuz basin produces coal from the Bogatyr mine, while the eastern Tenyz–Korzhinkol basin produces coal from the Saradyr mine [20–22]. Additionally, the Jurassic coals of this region, found in the Shubarkol and Maikuben coal basins (named after the mines), cover around 1470 km² and hold approximately 7.5 billion tons of coal reserves [21–23]. The Shubarkol mine contains two coal measures (Upper and Lower), with thicknesses ranging from 55 to 70 m. Meanwhile, the Maikuben mine within the Shoptkyol formation includes three coal measures (I, II, and III), with a total thickness of approximately 260 to 290 m [21–23]. The Carboniferous coals are predominantly classified as hard coals, distinguished by high ash content, relatively low volatile matter, and variable sulfur levels, and they frequently exhibit coking properties [21–23]. In contrast, Jurassic coals are characterized as brown coals and exhibit a lower ash yield and higher volatile matter. Petrographically, the coals from both Carboniferous and Jurassic periods show distinct variations, primarily consisting of vitrinite, liptinite (mainly sporinite), and inertinite. The thermal maturity of these coals, as evidenced by vitrinite reflectance measurements, ranges

from approximately 0.5% to 1.3% across the five coal mines, with potential variations observed across different zones, as discussed by various authors [21–23]. Coals from these mines are utilized for power and heat generation, as well as steel manufacturing.

These five coal mines are the primary focus of this study, aimed at a preliminary inorganic elemental assessment of coal, and will serve as the coal mines for more detailed investigations. This study presents the first report on the inorganic elemental composition of coal ash from five different coal deposits in Kazakhstan, dating to the Jurassic and Carboniferous periods. Although the results are preliminary and based on limited inorganic chemical analysis, they offer new insights into the distribution and modes of occurrence of major and trace elements. These insights could have potential industrial and environmental implications for the coals from these Jurassic and Carboniferous coal deposits.

The aims of the present study are as follows: (a) to determine the elemental content of coal ashes from Jurassic and Carboniferous coals sampled at five coal mines; (b) to compare the major and trace element concentrations in coal ash from the five coal mines with the Clarke values of the Earth's crust and global coal ash, aiming to determine the enrichment or depletion of elements and evaluate their potential as a secondary source for recovering valuable elements; and (c) to determine the mode of occurrence and origin of elements for their industrial and environmental implications.

2. Sampling and Methods

2.1. Mine Sampling Locations

The study area encompasses three major Carboniferous coal mines of Lenin, Saradyr, and Bogatyr in northeast Kazakhstan (see Figure 1A–C) and two Jurassic coal mines of Maikuben and Shubarkol (Figure 1D,E). Sampling at these mines was specifically chosen due to their status as the country's oldest and relatively young coal deposits, featuring extensive sedimentary deposition, various ash yield, substantial reserves, and significant mining activity, which makes them crucial for both industrial applications and environmental studies. A total 105 samples were collected and studied from working and exposed coal seams at the five active coal mines located in central and northeast Kazakhstan. Sampling was conducted across five operational coal mines of Lenin, Bogatyr, Saradyr, Maikuben, and Shubarkol (Figure 1A–E). A total of 105 grab samples were collected, with approximately 5 samples composited to form each of the 21 composite samples. Sampling was conducted at vertical intervals of 0.2–0.5 m for all mines, except at Bogatyr, where horizontal intervals were used due to mining area constraints. All samples were stored in plastic bags to minimize potential contamination and oxidation. The dataset includes 69 samples of Carboniferous hard coals obtained from three of these mines, and 36 samples of Jurassic brown coals sourced from the remaining two mines. Using a grab sampling method, samples were collected from active and mining coal seams at each mine and then combined through composite sampling to conduct a comprehensive analysis, which involved integrated inorganic geochemical investigations within general views of mineralogical content.

A total of 105 coal samples were selected: 26 samples from the workable coal seam № 6 within the Dolyn coal formation, collected from the underground Lenin mine (located in Shahtinsk town) at a depth of approximately 700 m, and 43 samples from the Saradyr (near Yerementau town) and Bogatyr (near Ekibastuz city) open-pit coal mines, at depths ranging from 140 to 260 m. Additionally, 36 Jurassic coal samples were collected from the Shubarkol (150 km northeast of Jezgazgan city) and Maikuben (160 km southwest of Pavlodar city, and 65 km southeast of the Bogatyr mine) open-pit mines, where coal production occurs at depths of around 150 m. The coal samples are labeled as DL and DU (from the Lower and Upper Dolyn seams) from the Lenin mine, B1, B2, and B3 (from three coal seams) from the Bogatyr mine, and S (from a single seam) from the Saradyr mine. For the Jurassic coals, samples are labeled SH and SP (from three coal seams in the western and central parts) from the Shubarkol mine, and M sample label (from the Shoptkykol coal formation) is from the Maikuben mine.

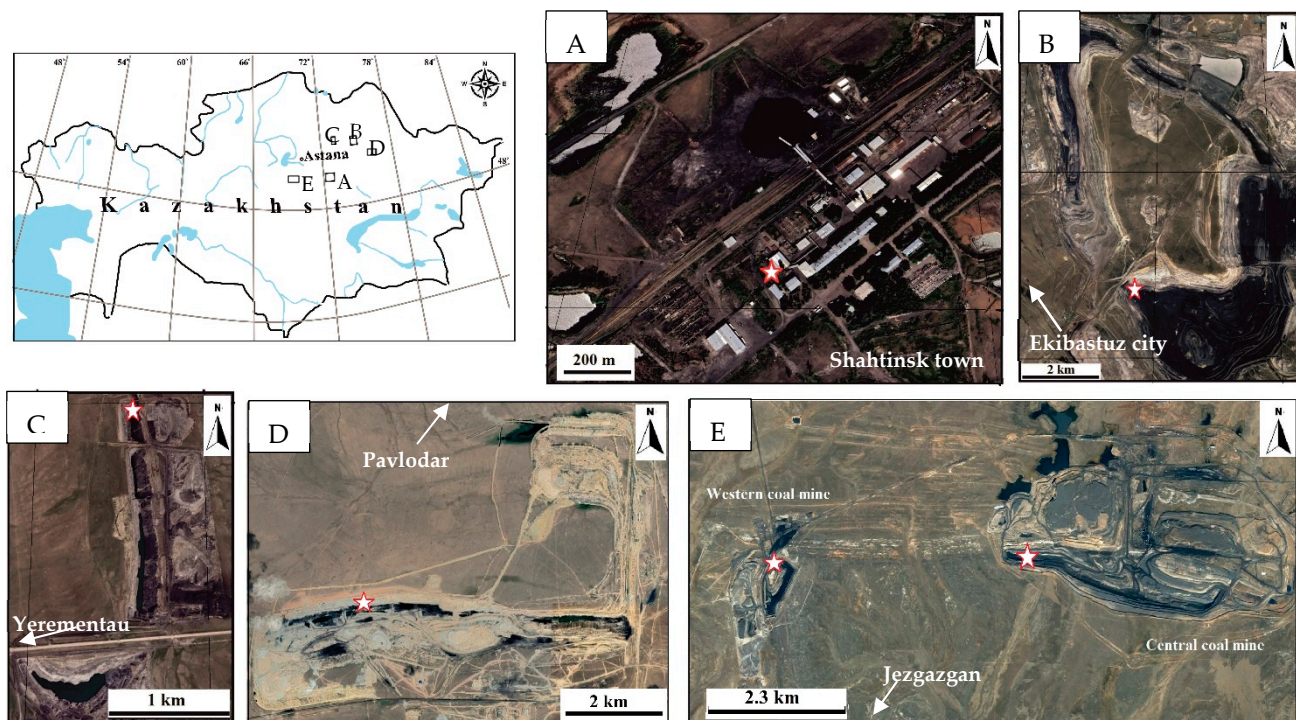


Figure 1. General overview map of three active coal mining areas: (A) Lenin underground mine (identified as Dolyn); (B) Bogatyr coal mine; (C) Saradyr coal mine; (D) Maikuben (identified as Shoptkyol); (E) Shubarkol. The star symbol denotes the locations where coal sampling took place (a satellite map, Google Earth Pro 7.3).

2.2. Analytical Methods

2.2.1. Sample Preparation

Two sample types were prepared as powdered coals (for further coal combustion residuals) and polished blocks from selected samples.

An amount of 2 g of each coal sample was weighed and crushed to particle sizes ranging from ~50 to 200 microns using an agate mortar and pestle. Powdered coal samples were used to determine ash yield and volatile matter in the coals.

The powdered coal samples were prepared for geochemical analysis using the standard coal sample preparation procedures as described in [24]. For the preparation of finely powdered coal samples, for high-temperature ash (HTA) and low-temperature ash (LTA): 1g of powdered coal was precisely weighed in a porcelain crucible to obtain coal ash and heated in an open muffle furnace (Carbolite ELF 11, Carbolite Gero, Sheffield, UK). This process for HTA for elemental analysis involved two phases: first at 500 °C for 30 min and then at 815 °C for 60 min, followed by cooling after removal from the muffle furnace (i); meanwhile, the preparation of LTA for mineralogical composition analysis was conducted at 150 °C for 60 min in the muffle furnace based on protocols described by various authors (ii) [25,26].

To obtain polished blocks, each sample underwent preparation based on [27], facilitating subsequent analysis through scanning electron microscopy.

2.2.2. Ash Yield and Volatile Matter

A proximate analysis was performed to determine ash yields and volatile matter content for all 105 samples. Ash yields and volatile matter were measured using a Simultaneous Thermal Analyzer (STA 6000, PerkinElmer, Waltham, MA, USA), in accordance with protocols described by several authors [28–30]. Both parameters were determined by heating the sample at 900 °C for 7 min in a covered crucible under a nitrogen atmosphere.

2.2.3. EDXRF

Energy dispersive X-ray fluorescence (EDXRF) was employed to measure major and trace elements for all 105 samples using an Epsilon 4 spectrometer (Malvern PANalytical, Malvern, UK, max 50 kV/2 mA/10 W). High-temperature coal ash samples were used for this analysis. The procedures followed [31], and the equipment's reliability has been discussed by [32].

XRF was selected as a rapid and routine method to process a large number of samples. After obtaining full data, further investigations are planned using long-term digestion experiments and advanced techniques to analyze individual elements from promising sample units.

2.2.4. LTA-XRD and SEM-EDS

Minerals in the coal were determined using five selected LTA (low-temperature ash) samples on a Rigaku SmartLab X-ray diffractometer (XRD) machine (Rigaku, Tokyo, Japan) with a Ni-filtered Cu K α X-ray source (energy 8.04 keV and X-ray wavelength 1.5406 Å) and the XRD pattern was recorded with a step size of 0.01°, over a 2 θ interval of 2.6–70° [33]. The XRD evaluation of the LTA was conducted at room temperature. The X-ray diffractograms were subjected to quantitative mineralogical analysis using Crystal impact software (Match), based on methods established in the literature [34].

Nine selected polished blocks were coated with carbon, and these samples were investigated under a scanning electron microscope in conjunction with energy-dispersive X-ray spectroscopy (SEM-EDS, Jeol JSM-IT200 LA, Jeol, Tokyo, Japan) to observe minor mineral characteristics and to determine elemental distribution in the coal samples. The operating parameters were set to 20 kV acceleration voltage and high vacuum mode.

3. Results

3.1. Results of Ash Yield and Volatile Matter

Results from the ash yield and volatile matter of all coal samples are presented in Tables 1 and 2. The coal samples from the Saradyr and Bogatyr mines exhibit relatively higher ash yields, averaging up to 31.9%, followed by the Lenin mine samples, with an average of 14.8%. Volatile matter content is nearly consistent across all three mines, averaging up to 21.8%. In contrast, the coal samples from the Maikuben and Shubarkol mines exhibit comparatively low ash yields, averaging between 2.7% and 8.8%, and higher volatile matter content, ranging from 40.9% to 46.6% on average.

3.2. EDXRF Results

Tables 1 and 2 present the concentrations of both major and trace elements in coal ash samples from the five coal mines. Mean values for all samples were calculated and are provided in Table 3 for comparison. The chemical compositions are compared with the compositions of the Clarke value of the crust (CVC) [35–38] and worldwide hard coal combustion (WHC) [38].

Table 1. Ash yield, volatile matter, and elemental composition (major and trace elements) of Carboniferous coal samples from three mines.

Samples	Ash (d, %)	VM (daf, %)	Major Elements (Unit: %)										Trace Elements (Unit: ppm)									
			Al	Si	P	S	Fe	K	Ca	Ti	Mn	Cu	Cr	Zn	Pb	V	Ga	As	Ni	Y	Yb	Zr
Saradyr mine																						
S1	19.3	24.7	1.4	5.1	0.06	0.6	0.1	0.5	0.06	0.3	n.a.	24.1	11.0	45.0	4.4	67.5	5.3	0.7	n.a.	n.a.	5.0	n.a.
S2	40.6	22.1	6.5	12.5	0.1	0.5	3.4	1.7	0.2	1.1	0.10	146.0	7.8	32.3	40.7	253.0	77.5	8.1	5.0	n.a.	3.7	n.a.
S3	18.7	28.6	7.3	17.3	0.1	0.06	11.5	1.2	0.4	0.7	0.31	162.0	n.a.	111.0	15.6	253.0	53.8	8.8	2.0	79.8	58.2	287.8
S4	39.1	8.8	5.6	18.6	0.1	n.a.	0.6	2.3	0.3	1.3	0.001	26.2	31.1	34.0	33.0	735	48.1	95.8	47.8	132.4	n.a.	0.1
S5	17.0	23.7	6.4	16.3	0.1	0.2	12.0	0.6	0.6	0.9	0.08	264.0	65.3	99.3	53.0	n.a.	61.5	39.9	n.a.	122.6	101.0	n.a.
Mean	26.9	21.5	5.4	13.9	0.1	0.2	5.5	1.2	0.3	0.9	0.1	124.4	23.0	64.3	29.3	261.7	49.2	30.6	10.9	66.9	40.2	57.5
Lenin mine																						
DU0	12.2	22.3	1.2	2.0	0.5	0.01	0.3	0.9	2.6	0.5	n.a.	0.4	0.1	0.3	0.04	2.2	0.09	0.7	0.1	0.3	0.03	0.4
DU1	21.9	22.6	1.5	2.8	0.1	1.9	2.5	0.2	1.1	0.5	0.05	213.5	11.3	112.7	13.5	398.3	31.1	5.6	n.a.	n.a.	63.5	n.a.
DU2	21.6	24.6	1.1	1.7	0.1	1.9	2.5	0.4	0.3	0.4	0.001	185.6	n.a.	76.0	11.0	n.a.	23.4	8.6	42.2	36.7	39.6	117.5
DU3	3.8	23.3	1.9	14.9	0.1	0.03	1.2	0.3	0.2	0.3	0.05	110.6	19.2	29.1	4.2	168.6	38.0	6.3	n.a.	31.0	4.8	389.6
DU4	6.1	22.6	2.2	3.2	0.05	0.03	0.9	0.3	0.1	0.1	0.002	27.0	n.a.	12.4	n.a.	n.a.	3.5	1.3	5.1	5.4	3.6	13.5
DU5	11.3	24.4	2.5	3.5	n.a.	0.6	4.8	0.1	8.8	0.3	0.02	60.8	18.5	231.8	1.4	199.4	9.6	2.1	12.8	36.8	19.4	72.2
DU6	6.6	19.8	7.4	9.2	2.1	0.02	1.2	0.4	5.3	2.4	n.a.	326.9	7.4	61.7	11.8	121	39.5	4.9	n.a.	95.8	n.a.	180.8
DU7	12.2	21.0	5.2	6.4	0.5	0.5	5.5	0.4	4.1	1.7	0.05	32.3	23.6	79.4	24.5	242.8	65.2	9.0	32.3	64.1	21.2	296.4
DU8	6.3	22.3	1.9	2.3	0.5	0.04	0.9	0.09	1.1	0.6	0.003	19.0	4.5	8.4	n.a.	132.5	5.9	n.a.	7.5	3.0	3.7	21.5
DU9	6.7	22.5	0.5	0.5	0.2	0.01	0.06	0.02	0.3	0.09	n.a.	6.1	n.a.	1.5	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	1.8
DU10	6.1	20.7	1.9	3.0	0.09	0.06	0.3	0.1	2.9	0.6	n.a.	80.5	8.7	20.1	4.5	346.9	19.3	2.4	30.8	38.2	n.a.	117.6
DU11	9.8	22.8	2.8	5.0	0.09	0.07	0.5	0.3	0.1	1.0	n.a.	201.5	78.2	64.9	43.5	100	45	5.5	39.7	49.4	n.a.	657.4
DU12	18.8	19.3	5.9	9.9	0.1	0.7	4.9	0.7	0.1	1.8	0.005	346	133.4	506	103.3	170	61.1	65.4	221.4	72.1	1.5	140
DU13	7.2	21.9	7.4	12.3	0.1	0.5	4.0	0.6	5.5	1.8	0.005	326.4	30.6	126.4	31.0	698	55.4	12.0	73.7	134.2	37.0	634
DU14	5.2	21.2	5.4	8.5	0.1	0.1	2.2	0.3	0.4	0.7	0.001	114.4	10.6	56.9	12.7	231.8	25.8	5.2	31.1	50.6	16.0	153.5
DU15	6.2	22.8	8.8	5.9	4.1	1.0	11.0	0.4	4.7	n.a.	0.04	212	n.a.	93.2	n.a.	n.a.	40.5	3.7	50.0	83.8	57.1	n.a.
DU16	8.9	20.4	6.9	8.8	1.0	0.05	2.8	0.4	2.4	1.0	0.005	181.1	n.a.	70.3	n.a.	366	34.3	n.a.	53.4	97.2	19.7	148.3

Table 1. Cont.

Samples	Ash (d, %)	VM (daf, %)	Major Elements (Unit: %)										Trace Elements (Unit: ppm)									
			Al	Si	P	S	Fe	K	Ca	Ti	Mn	Cu	Cr	Zn	Pb	V	Ga	As	Ni	Y	Yb	Zr
DU17	4.2	22.6	7.2	11.0	0.4	0.04	3.2	0.8	0.5	1.3	n.a.	212	20.8	194	18.4	768	35.9	9.3	50.3	50.6	16.2	175
DU18	6.0	23.2	8.7	10.9	1.0	0.6	6.0	0.7	5.4	1.3	0.02	180	29.5	84.6	17.9	407	57.8	4.1	73.1	50.9	17.8	307.8
DU19	4.6	22.4	0.6	1.0	0.01	0.04	0.3	0.07	0.1	0.08	n.a.	15.0	3.0	28.5	n.a.	50.1	1.4	n.a.	3.8	3.3	1.5	8.3
DL1	91.8 *	8.9	5.0	18.3	0.17	2.3	4.2	2.3	0.4	0.9	0.03	144.7	98.0	183.2	2.6	225.4	50.4	10.2	52.8	66.5	32.4	337.6
DL2	47.6	24.6	1.4	4.0	0.04	0.2	2.2	0.9	1.0	0.2	0.05	116.4	40.3	95.8	5.8	162.0	40.4	21.4	35.3	60.0	15.4	395.1
DL3	4.5	23.7	8.9	12.1	0.3	0.04	5.4	0.6	0.6	1.7	0.001	395.7	52.4	188.6	39.9	527.1	66.0	14.5	121.7	69.9	9.6	258.7
DL4	3.7	24.3	0.5	0.5	0.1	0.02	0.5	n.a.	0.1	0.04	0.007	11.2	n.a.	8.0	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	3.0	n.a.
DL5	43.0	20.4	9.2	12.2	0.1	0.1	16.2	0.5	1.0	3.1	n.a.	627.9	n.a.	216.0	22.6	487.4	109.6	25.9	6.6	80.5	101.5	312.6
DL6	9.7	22.5	9.3	10.9	1.1	0.1	18.7	0.3	4.4	0.7	n.a.	222.6	n.a.	250.5	n.a.	292.5	37.7	10.8	6.5	67.4	81.8	137.4
Mean	14.8	21.8	4.1	6.5	0.5	0.4	3.2	0.5	1.9	0.9	0.01	159.5	22.7	98.1	14.2	223.3	33.0	8.4	36.3	45.4	18.6	182.3
Bogatyr																						
B1/0	16.5	16.0	1.1	4.1	0.1	0.2	0.2	0.2	0.1	0.1	0.0003	21.9	n.a.	26.3	3.3	48.9	6.5	7.0	6.9	6.3	1.0	n.a.
B1/1	25.2	29.7	0.8	7.1	0.2	0.1	0.3	0.2	0.9	0.5	0.008	67.0	9.4	29.2	1.8	133.0	13.5	2.1	17.6	n.a.	0.6	n.a.
B1/2	24.9	21.0	4.2	20.2	0.1	0.03	1.5	1.0	0.2	0.6	0.02	209.0	45.3	51.4	13.9	430.0	49.8	11.8	47.2	54.0	12.5	n.a.
B1/3	29.7	19.3	4.1	20.2	0.1	0.06	3.8	1.1	0.2	0.6	0.06	144.0	20.4	100.2	15.3	161.5	39.5	6.4	21.8	43.8	26.1	223.8
B1/4	2.7	17.1	4.3	18.5	0.1	n.a.	0.38	0.9	0.1	0.6	0.007	107.5	11.5	27.6	9.3	177.0	29.0	2.6	6.5	16.4	6.6	72.5
B1/5	11.2	23.7	1.8	8.1	0.08	0.2	1.4	0.1	0.8	0.5	0.01	95.6	18.4	20.3	4.6	182.8	12.9	2.1	21.3	19.4	6.5	n.a.
B1/6	28.5	20.1	6.8	16.4	0.2	0.1	1.2	0.5	0.4	0.8	0.05	13.6	13.6	42.8	9.9	271.0	50.1	11.1	13.2	25.4	4.7	231.8
B1/7	24.3	23.1	5.4	16.0	0.2	0.01	0.72	0.5	0.2	1.6	0.01	410.0	51.3	43.0	n.a.	653	82.3	18.4	51.6	57.0	n.a.	n.a.
B1/8	16.6	23.1	5.9	20.1	0.2	0.06	6.1	0.5	0.2	0.8	0.01	263.0	50.7	64.2	9.3	469.0	52.1	16.1	44.0	42.3	25.4	245.7
B1/9	40.6	22.8	0.6	0.9	0.1	0.01	0.2	0.1	0.1	0.1	n.a.	16.9	n.a.	30.8	0.8	n.a.	n.a.	0.8	3.9	3.0	2.7	5.4
B2/1	56.8 *	13.7	17.6	0.1	0.1	n.a.	3.0	0.4	0.1	0.5	0.01	153.6	n.a.	23.6	45.7	213.2	40.3	32.4	21.6	40.2	27.1	323.0
B2/2	20.8	20.9	4.6	17.6	0.1	0.2	4.5	0.3	0.5	0.5	0.03	194.0	16.3	96.9	16.9	224.4	53.5	26.4	6.7	n.a.	21.4	116.1
B2/3	9.7	23.5	5.9	10.9	0.4	0.07	3.4	0.3	0.5	1.1	0.06	263.5	n.a.	212.2	n.a.	n.a.	60.7	39.1	74.2	34.8	n.a.	824
B2/4	12.0	22.3	5.5	17.5	0.2	0.04	9.8	0.4	0.2	0.9	0.04	292.6	27.2	122.7	19.2	360.8	64.8	37.1	19.8	90.5	41.4	476.8

Table 1. Cont.

Samples	Ash (d, %)	VM (daf, %)	Major Elements (Unit: %)										Trace Elements (Unit: ppm)									
			Al	Si	P	S	Fe	K	Ca	Ti	Mn	Cu	Cr	Zn	Pb	V	Ga	As	Ni	Y	Yb	Zr
B2/5	14.1	25.3	1.1	3.6	0.09	0.07	5.9	0.1	0.1	0.2	0.04	63.1	n.a.	77.9	1.5	109	12.3	15.7	11.6	16.7	21.2	129.3
B2/6	12.0	23.8	2.2	9.5	1.2	1.5	19.7	0.06	2.1	n.a.	0.06	133.4	n.a.	122.3	86	n.a.	10.8	n.a.	n.a.	93	69.6	n.a.
B2/7	34.5	18.9	3.2	10.7	0.1	0.08	0.6	0.5	0.2	0.4	0.008	84.9	3.6	289.3	9.0	123.0	26.3	5.3	2.3	18.4	7.0	168.9
B2/8	14.4	23.7	5.0	18.0	0.3	0.1	8.6	0.8	0.6	1.0	0.01	362.6	n.a.	79.6	n.a.	296.6	64.4	187	91.8	51.9	21.8	475.6
B2/9	15.4	20.2	3.4	15.4	0.3	0.1	0.9	0.4	0.2	0.7	0.01	208.9	n.a.	72.5	20.9	223.4	64.4	187	91.8	32.5	21.8	245.5
B2/10	30.8	20.2	3.1	16.2	0.1	0.8	3.0	0.8	0.2	0.7	0.05	197.7	n.a.	78.4	0.1	203.4	28.0	11.4	22.9	59.2	24.4	549.4
B2/11	26.0	23.8	4.7	15.5	0.1	0.1	4.8	1.0	0.3	0.8	0.03	360.1	18.9	124.5	20.5	314.3	43.1	17.8	31.8	75.3	21.9	389.4
B3/1	31.7	20.8	3.2	20.0	0.1	0.1	0.6	0.6	0.2	0.3	0.01	192.3	n.a.	44.2	9.4	100.9	22.8	6.6	8.0	48.7	6.6	145.1
B3/2	24.8	23.9	4.3	19.9	0.2	0.03	2.7	0.5	0.2	1.2	0.01	244.0	n.a.	57.9	15.9	307.7	43.9	36.4	38.6	53.9	11.4	416.9
B3/3	33.3	20.4	1.4	6.4	0.1	0.7	0.3	n.a.	3.2	0.4	0.01	66.9	10.4	52.5	8.9	129.6	16.0	12.0	n.a.	71.8	33.7	212.1
B3/4	53.5	16.1	6.6	17.4	0.1	0.06	0.2	0.5	0.3	1.5	0.008	88.4	8.2	11.2	16.9	253.4	69.1	14.3	n.a.	42.2	n.a.	266.6
B3/5	19.9	21.5	5.4	19.7	0.2	0.5	3.0	0.9	1.3	0.7	0.004	150.9	n.a.	38.3	15.7	343.6	52.8	46.5	33.2	120.8	28.2	285.0
B3/6	61.6	17.5	5.0	14.8	0.1	0.06	5.1	0.7	0.4	0.6	0.006	186.7	9.6	30.2	33.1	210.2	69.5	31.7	15.7	70.5	n.a.	1220
B3/7	39.1	15.9	5.7	18.3	0.2	0.05	4.9	0.7	0.4	0.67	0.006	179.7	13.3	63.9	27.7	193.6	58.0	27.2	21.3	52.4	34.4	908
B3/8	18.9	16.6	0.6	9.5	0.2	0.06	0.4	0.1	0.1	n.a.	0.01	85.3	n.a.	25.5	8.6	134	5.9	10.1	17.7	5.7	n.a.	68.4
B3/9	65.6	22.5	6.5	17.8	0.3	0.04	1.2	0.5	0.4	1.3	0.02	228.8	n.a.	99.5	40.8	238.8	73.9	52.6	13.7	57.2	3.5	457.5
B3/10	42.9	15.4	5.3	12.8	0.1	n.a.	0.6	0.4	0.1	1.1	0.009	92.0	n.a.	113.9	43.0	294.0	81.1	25.7	12.8	149.2	11.8	1160
B3/11	12.5	20.0	3.1	5.8	0.05	0.02	1.2	0.1	0.06	0.5	0.006	63.2	n.a.	58.1	12.5	n.a.	28.8	8.6	n.a.	22.8	13.6	n.a.
B3/12	37.4	17.0	6.5	19.1	0.2	0.05	3.1	0.4	0.2	0.8	0.01	135.9	n.a.	71.9	35.6	224.9	66.7	18.6	8.0	70.3	26.5	405.7
B3/13	52.5	20.8	8.3	15.8	0.2	0.1	2.1	0.4	0.2	1.0	0.01	84.4	n.a.	282.1	87.8	289.0	91.5	18.3	5.0	73.4	11.1	603.1
B3/14	62.5 *	14.9	6.5	17.3	0.1	0.1	26.3	0.3	0.3	0.5	0.05	226.6	n.a.	390.1	12.5	334.7	80.7	44.8	n.a.	102.8	116.8	586.3
B3/15	33.2	22.3	2.6	5.8	0.1	n.a.	0.4	0.1	0.07	0.6	0.003	20.9	2.9	128.3	114.2	138.7	62.7	n.a.	n.a.	90.8	n.a.	629.6
B3/16	65.1 *	14.4	5.2	11.2	0.1	0.02	0.5	0.1	0.08	0.7	0.007	25.4	5.1	19.2	7.4	111.3	50.4	5.9	n.a.	12.8	n.a.	144.3
B3/17	29.0	20.3	4.6	11.6	0.1	0.1	3.2	0.3	0.2	0.3	0.02	149.8	n.a.	341.4	24.2	128.4	36.7	36.3	7.9	99.8	29.9	345.3
Mean	31.9	20.8	4.9	13.7	0.2	0.1	4.2	0.4	0.4	0.7	0.02	166.7	7.7	104.0	24.2	258.9	49.2	31.3	21.5	56.3	20.1	376.1

Note: VM—volatile matter; d—dry basis; daf—dry and ash free. *—coal-bearing shale or rock samples.

Table 2. Ash yield, volatile matter, and elemental composition (major and trace elements) of Jurassic coal samples from two mines.

Samples	Ash (d,%)	VM (daf, %)	Major Elements (%)										Trace Elements (ppm)									
			Al	Si	P	S	Fe	K	Ca	Ti	Mn	Cu	Cr	Zn	Pb	V	Ga	As	Ni	Y	Yb	Zr
Maikuben																						
M1	4.1	44.7	2.5	3.9	n.a.	0.4	18.1	0.6	10.4	0.2	0.02	168.9	n.a.	192.5	n.a.	45.5	14.3	94.5	117.2	45.5	71.5	77.9
M2	1.9	52.4	3.1	5.3	n.a.	1.4	7.9	0.4	11.0	n.a.	0.03	146.5	88.8	187.1	1.1	n.a.	n.a.	59.3	107.5	23.5	n.a.	7.7
M3	2.6	45.1	4.2	1.4	n.a.	0.8	14.0	n.a.	18.5	0.3	0.01	319.2	n.a.	245.7	8.1	158.4	19.0	92.7	61.7	128.0	n.a.	66.3
M4	2.4	44.2	5.0	5.3	n.a.	1.1	14.6	0.4	18.8	0.1	0.01	243.8	107.9	157.4	n.a.	90.1	n.a.	36.9	64.1	61.1	n.a.	31.8
Mean	2.7	46.6	3.7	4.0	n.a.	0.9	13.6	0.3	14.6	0.1	0.02	219.6	49.1	195.6	2.3	73.5	8.3	70.8	87.6	64.5	17.8	45.9
Shubarkol																						
SH1	4.4	25.7	0.7	8.1	0.08	0.02	0.09	0.04	0.1	0.6	0.003	20.7	4.3	5.4	4.5	90.6	10.0	3.1	6.2	25.2	4.9	175.9
SH2	4.5	45.9	4.0	5.7	0.07	1.7	6.9	0.1	2.1	0.3	0.04	116.2	37.2	492.1	29.4	76.5	16.5	69.0	9.23	39.1	n.a.	87.8
SH3	12.8	33.8	3.2	5.2	0.05	0.1	0.4	0.2	0.4	0.3	0.006	126.6	50.1	109.2	14.8	270.7	18.5	11.8	30.1	52.3	2.3	78.0
SH6	5.5	41.4	1.4	2.7	0.1	0.04	3.4	0.3	0.5	0.3	0.01	144.1	150	336.4	54.3	109	68.6	191.3	134	39.6	n.a.	n.a.
SH8	1.9	43.8	0.6	0.6	0.02	0.7	0.1	0.08	0.6	0.05	0.007	13.2	n.a.	10.4	1.3	n.a.	n.a.	2.6	41.1	n.a.	n.a.	3.3
SH10	5.3	36.4	3.8	2.9	0.1	2.0	5.3	0.2	3.1	0.4	0.01	153.1	60.2	167.5	38.1	n.a.	13.8	115.1	51	44.8	n.a.	50.7
SH12	4.0	41.4	3.3	5.0	0.05	0.8	0.5	0.2	1.8	0.3	0.04	61.9	21.4	50.4	9.2	103.0	7.9	9.1	170.6	62.1	n.a.	40.0
SH13	1.9	41.8	3.9	3.1	0.1	1.5	0.6	0.1	2.9	0.3	0.01	105.8	175.6	33.8	15.3	617.8	12.0	17.1	382.8	n.a.	n.a.	33.8
SH15	11.2	37.7	4.7	8.3	0.1	1.3	3.2	0.7	2.9	0.8	0.06	169.5	114.8	184.3	107	373.9	33.2	44.3	121.6	n.a.	n.a.	218.8
SH16	10.6	44.1	2.3	5.5	0.1	1.0	5.6	0.4	0.9	0.3	0.09	91.3	43.5	222.8	38.4	n.a.	24.0	33.8	146.7	34.5	n.a.	133.0
SH18	12.6	40.6	1.0	2.8	0.06	1.7	2.1	0.5	1.3	0.07	0.09	59.0	n.a.	113.1	5.4	n.a.	n.a.	10.4	297.2	n.a.	n.a.	7.6
SH20	1.4	45.6	2.6	2.5	0.05	3.3	2.7	0.4	4.9	0.3	n.a.	81.4	n.a.	147.3	9.2	n.a.	n.a.	13.9	127	n.a.	n.a.	24.7
SH21	1.8	48.3	2.1	2.7	0.03	0.2	0.3	0.1	0.6	0.1	0.001	40.6	96.0	108.6	7.0	574.9	7.6	6.2	22.8	25.9	n.a.	28.0
SH23	1.1	42.8	1.3	0.8	0.01	1.6	1.8	0.08	1.6	0.08	0.03	38.3	n.a.	37.6	2.6	n.a.	n.a.	3.6	60.2	n.a.	2.1	8.0
SH24	3.4	44.3	2.5	2.6	0.1	3.1	15.4	0.3	2.8	0.2	0.01	119.1	n.a.	182.6	50.7	n.a.	6.7	60.1	207.1	n.a.	n.a.	59.8
SH26	2.7	40.7	6.2	4.0	n.a.	4.8	4.2	0.2	7.2	0.3	0.08	186.1	n.a.	121.7	23.5	n.a.	9.8	10.4	118	n.a.	n.a.	20.0
SH27	8.9	43.7	0.5	1.1	0.03	1.8	5.4	0.1	1.8	0.1	0.02	158.9	n.a.	93.7	n.a.	n.a.	n.a.	22.2	230.4	13.6	n.a.	26.9
SH28	1.3	41.7	1.6	0.9	0.04	0.7	0.4	0.07	2.1	0.08	0.007	27.8	17.7	22.1	4.9	n.a.	n.a.	6.2	24.3	20.0	3.4	10.8

Table 2. Cont.

Samples	Ash (d,%)	VM (daf, %)	Major Elements (%)										Trace Elements (ppm)									
			Al	Si	P	S	Fe	K	Ca	Ti	Mn	Cu	Cr	Zn	Pb	V	Ga	As	Ni	Y	Yb	Zr
SH30	1.3	42.1	1.6	2.8	0.08	3.2	0.9	0.1	3.7	0.2	0.01	69.5	18.4	137.1	7.1	223.5	n.a.	5.5	59.0	n.a.	12.3	27.9
SH31	2.5	38.3	8.2	11.9	0.1	0.3	1.3	0.9	2.0	0.5	0.008	314.6	376.3	102	48.7	n.a.	60.4	32.8	163.9	n.a.	36.4	n.a.
SP1	1.1	46.7	5.0	2.8	0.05	3.0	1.2	0.1	4.6	0.35	0.04	99.2	37.1	91.0	7.7	n.a.	11.9	9.3	40.2	n.a.	n.a.	13.9
SP2	2.1	44.8	2.3	2.1	0.04	3.1	2.8	0.3	3.4	0.4	0.03	172.2	60.4	n.a.	15.6	75.3	12.8	24.3	57.4	35.4	11.8	79.9
SP3	2.0	39.1	4.3	4.7	0.05	1.3	1.7	0.1	1.8	0.1	0.009	28.9	21.8	18.4	5.4	34.6	3.1	6.6	27.2	5.0	1.2	n.a.
SP4	1.7	44.6	3.0	1.6	0.03	3.0	0.8	0.2	3.4	0.2	0.02	74.1	18.5	38.3	1.5	n.a.	2.9	5.2	25.9	6.2	0.5	8.8
SP6	9.8	36.6	4.4	10.8	0.4	0.2	0.9	0.7	0.9	1.3	0.001	80.8	n.a.	30.1	9.9	n.a.	50.7	12.6	73.4	21.4	2.6	346.1
SP8	2.4	43.2	1.4	2.8	0.07	0.3	0.1	0.03	0.5	0.2	n.a.	27.0	10.5	21.4	5.5	n.a.	17.1	6.1	85.8	n.a.	n.a.	n.a.
SP9	1.0	43.6	2.2	1.8	0.08	2.3	0.9	0.09	2.3	0.2	n.a.	82.8	n.a.	55.6	8.7	n.a.	7.8	20.1	92.3	14.9	n.a.	31.5
SP14	5.0	35.8	1.5	4.5	0.04	0.8	0.4	0.1	1.1	0.6	0.004	56.9	n.a.	72.6	36.8	n.a.	22.0	10.0	88.1	n.a.	n.a.	n.a.
SP15	8.0	40.2	3.0	7.1	0.06	0.2	0.9	0.6	0.7	1.1	0.006	266.5	80.6	45.3	35.4	258.8	29.3	14.2	38.6	n.a.	n.a.	n.a.
SP16	12.3	37.4	3.5	5.6	0.2	0.2	0.4	0.4	0.6	0.3	n.a.	42.3	n.a.	19.0	18.7	n.a.	20.7	13.0	33.3	n.a.	3.3	249.8
SP17	5.2	40.2	6.2	9.2	0.4	0.5	1.1	0.6	1.7	0.5	0.003	145.0	107.2	51.7	57.5	n.a.	81.0	22.2	43.6	n.a.	n.a.	358.5
SP18	1.2	37.6	1.5	0.9	0.05	2.4	0.7	0.01	1.9	0.2	0.01	51.1	20.7	40.9	3.4	n.a.	n.a.	10.1	13.8	n.a.	n.a.	10.2
Mean	8.8	40.9	2.9	3.9	0.1	1.5	2.3	0.2	2.0	0.3	0.02	100.3	47.4	98.6	21.0	84.9	16.8	25.5	94.4	12.9	2.3	61.4

Note: VM—volatile matter; d—dry basis; daf—dry and ash free.

Table 3. Geochemical composition and comparison of mean major and trace element values in coal ash from the five coal mines in Kazakhstan, with enrichment factors normalized to CVC (Clarke value of the crust) and WHC (worldwide hard coal ash) values. Unit: ppm for trace elements.

№	Elements	Jurassic Kazakh Coal Ash (J)		Carboniferous Kazakh Coal Ash (C)		^a CVC	CVC vs. J and C		^b WHC	WHC vs. J and C	
		Range	Mean	Range	Mean	Mean	EF (J)	EF (C)	Mean	EF (J)	EF (C)
1	Al (%)	0.5–5	3.3	0.5–17.6	4.8	8.23	0.4	0.5	n.a.	n.a.	n.a.
2	Si (%)	0.9–11.9	3.9	0.1–20.2	11.3	28.1	0.1	0.4	n.a.	n.a.	n.a.
3	P (%)	0.01–0.08	0.05	0.01–2.1	0.2	0.10	0.5	2.6	0.15	0.3	1.7
4	S (%)	0.09–2.3	0.9	0.01–0.6	0.2	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
5	Fe (%)	0.09–18.1	7.9	0.06–26.3	4.2	5.63	1.4	0.7	n.a.	n.a.	n.a.
6	K (%)	0.03–0.7	0.2	0.02–1.7	0.7	2.09	0.1	0.3	n.a.	n.a.	n.a.
7	Ca (%)	0.1–18.8	8.3	0.06–8.8	0.8	4.15	2.0	0.2	n.a.	n.a.	n.a.
8	Ti (%)	0.3–0.6	0.2	0.04–3.1	0.8	0.57	0.3	1.4	0.53	0.3	1.5
9	Mn (%)	0.001–0.09	0.02	0.001–0.08	0.04	0.08	0.2	0.5	0.04	0.4	1.0
10	Cu	13.2–319	159.9	0.4–410.0	150.2	55	2.9	2.7	110	1.4	1.3
11	Cr	4.3–376.3	48.2	0.1–133.4	17.8	100	0.4	0.1	120	0.4	0.1
12	Zn	5.4–492.1	147.1	0.3–390.1	88.8	70	2.1	1.2	170	0.8	0.5
13	Pb	1.1–107.0	11.6	0.04–114.2	22.5	12.5	0.9	1.8	55	0.2	0.4
14	V	34.6–617.8	79.2	22–768.0	247.9	135	0.5	1.8	170	0.4	1.4
15	Ga	2.9–81.0	12.5	0.09–109.6	43.8	15	0.8	2.9	36	0.3	1.2
16	As	2.6–191.3	48.1	0.7–187	23.4	7.6	6.3	3.0	46	1.0	0.5
17	Ni	6.2–328.8	91.0	0.1–221.4	22.9	37	2.4	0.6	100	0.9	0.2
18	Y	5.0–128.0	38.7	0.3–134.2	56.2	29	1.3	1.9	57	0.6	0.9
19	Yb	1.2–71.5	10.0	1.0–116.8	26.3	2.0	5.0	13.1	6.9	1.4	3.8
20	Zr	3.3–358.5	53.6	0.1–657.4	205.3	165	0.3	1.2	230	0.2	0.8

Note: EF—enrichment factor (EF, J for Jurassic coal and EF, C for Carboniferous coal); ^a Clarke value of the crust (CVC) [35–38] and ^b worldwide hard coal ash (WHC) [38].

Figure 2 presents a comparison of the average concentrations of major and trace elements in Jurassic and Carboniferous coal ash with Clarke values of the Earth's crust (CVCs, [35–38]). The results indicate that the concentrations of major elements such as Al, Si, and K are generally lower than the CVC. In contrast, other major elements, including P, Ca, Ti, and Mn, as well as trace elements like Cu, Zn, Pb, V, Ga, As, Ni, Y, Yb, and Zr, are relatively higher than the CVC.

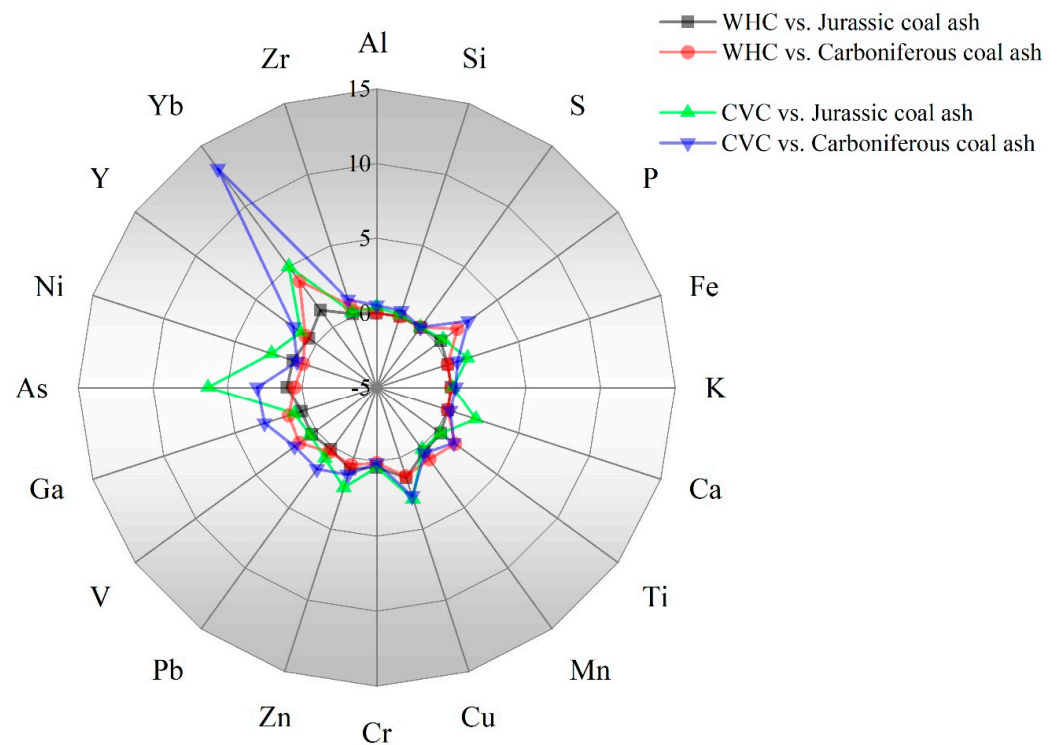


Figure 2. Spider plot of major and trace element concentrations in Jurassic and Carboniferous coal ash normalized to Clarke values of the Earth's crust (CVCs) [35–38] and worldwide hard coal ash (WHC) [38] values.

Figure 2 compares the average concentrations of major and trace elements in Jurassic and Carboniferous samples with the world hard coal (WHC) averages [38]. The results show that Yb averages 10 ppm in Jurassic samples and 26.3 ppm in Carboniferous samples, while Cu averages 159 ppm and 150 ppm, respectively. These values are higher than the WHC averages for these elements. In contrast, most other elements have lower averages compared to WHC, except for P (0.2%), Ti (0.8%), Ga (43.8 ppm), and V (247.9 ppm), which are higher than the WHC values and Jurassic samples. Notably, As (48.1 ppm) is higher in Jurassic samples compared to Carboniferous samples and WHC values.

3.3. XRD and SEM-EDS Results

Based on the results of XRD analysis (Figure 3 and Table 4) and SEM-EDS, the samples primarily consist of kaolinite, quartz, and pyrite. Additionally, SEM-EDS data also revealed the presence of accessory minerals such as apatite, chalcopyrite, and rutile. The mineralogical contents of the samples from the Carboniferous coal mines show slight variations compared to each other, but are generally comparable to those from the Jurassic coal mines. The differences in the Jurassic samples include the presence of apatite containing various rare-earth elements (REE with La, Nd, and Ce), pyrite with arsenic content filling the edges of sporinite macerals, and tiny rutile particles within woody fragments (Figures 4 and 5).

The dominant silicate mineral phases varied among the studied samples in the five coal mines, with quartz and kaolinite being particularly prominent. Quartz and kaolinite were identified as the most dominant minerals in all samples. Kaolinite is present as

pore and cell fillings within the coal, whereas quartz is observed as angular grains and occasionally as particles exhibiting good abrasion, appearing as subangular or angular quartz grains, as shown in Figures 4 and 5. Additionally, quartz and kaolinite were the only major minerals detected in a few samples by XRD. Accessory minerals, including chalcopryrite, rutile, and REE-bearing phosphate minerals, were detected in all samples, as identified during SEM-EDX studies. The accessory minerals, consistently found in association with kaolinite crystal grains, were identified through SEM-EDS analysis as cleat/pore-infilling minerals within the coal.

SEM-EDS analysis shows results from samples collected from Carboniferous coal mines: The samples from the Bogatyr mine the samples of Bogatyr (with B1/0 and B1/2) are mainly composed of quartz grains ranging in size from 5 to 10 μm . Additionally, kaolinite is distributed along the bedding planes and in the cleats of the coals within these samples. Minor amounts of pyrite are also present, occurring in two forms: euhedral (7 μm) and framboidal (10 μm). All minerals were identified as fracture-infilling minerals within the coals (Figure 4a,c). The samples of the Lenin mine (with DL4 and DU2) are enriched in quartz and kaolinite, with minor amounts of pyrite. Accessory minerals, such as apatite, were rarely observed in these samples (Figure 4c,d). Quartz occurs as grains of variable roundness (around 5–10 μm), kaolinite is mainly distributed along the bedding planes and in the cleats of the coals, while pyrite occurs as isolated euhedral pyrite particles with sizes ranging from 0.5 to 2 μm . The samples of Saradyr (S1 and S2) primarily consist of quartz grains and kaolinite distributed with a size of around 25 μm , along the bedding planes and in the cleats of the coals. Additionally, minor amounts of euhedral pyrite, with sizes of up to 10 μm , are observed in the samples. Within the kaolinite grains, accessory minerals such as chalcopryrite (10 μm) and rutile (4–5 μm) were identified within the coals (Figure 4e,f).

Jurassic coal mine samples show that the samples from Maikuben (M1) are enriched with quartz and kaolinite within coal fractures, with chalcopryrite (approximately 10 μm) present as an accessory mineral (Figure 5a,b). Shubarkol coal samples (SH1 and SH26) are primarily composed of quartz and kaolinite, along with apatites containing rare-earth elements (La, Ce, and Nd). Additionally, sporinite macerals are observed within vein-like pyrite structures that contain arsenic (Figure 5c,d).

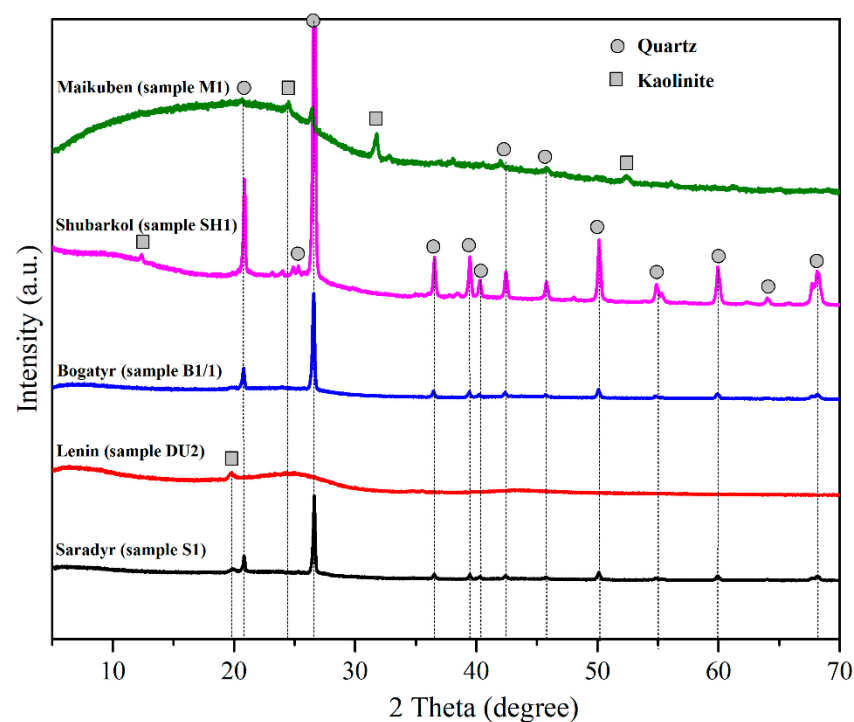


Figure 3. X-Ray diffraction (XRD) patterns of five coal samples from five active mines.

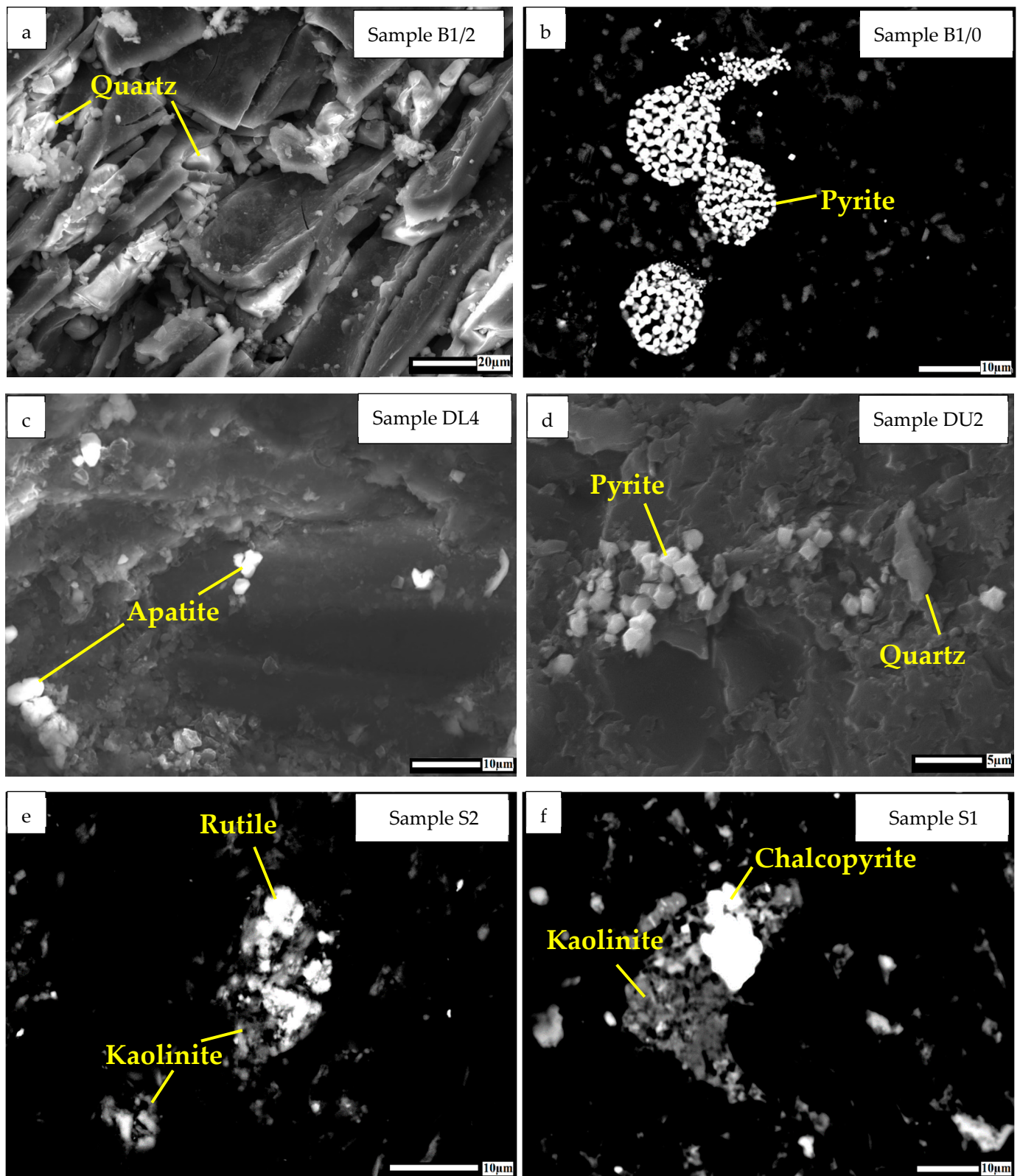


Figure 4. Selected SEM-BSE images of crystalline phases and EDS spectra of Carboniferous coal samples: (a) quartz growth occurring within coal fractures; (b) framboidal pyrite growth within coal matrix; (c) crystal growth of apatite among coal matrix; (d) euhedral pyrites associated with surrounding quartz; (e) individual crystals of rutile with kaolinite; and (f) chalcopyrite grains with kaolinite.

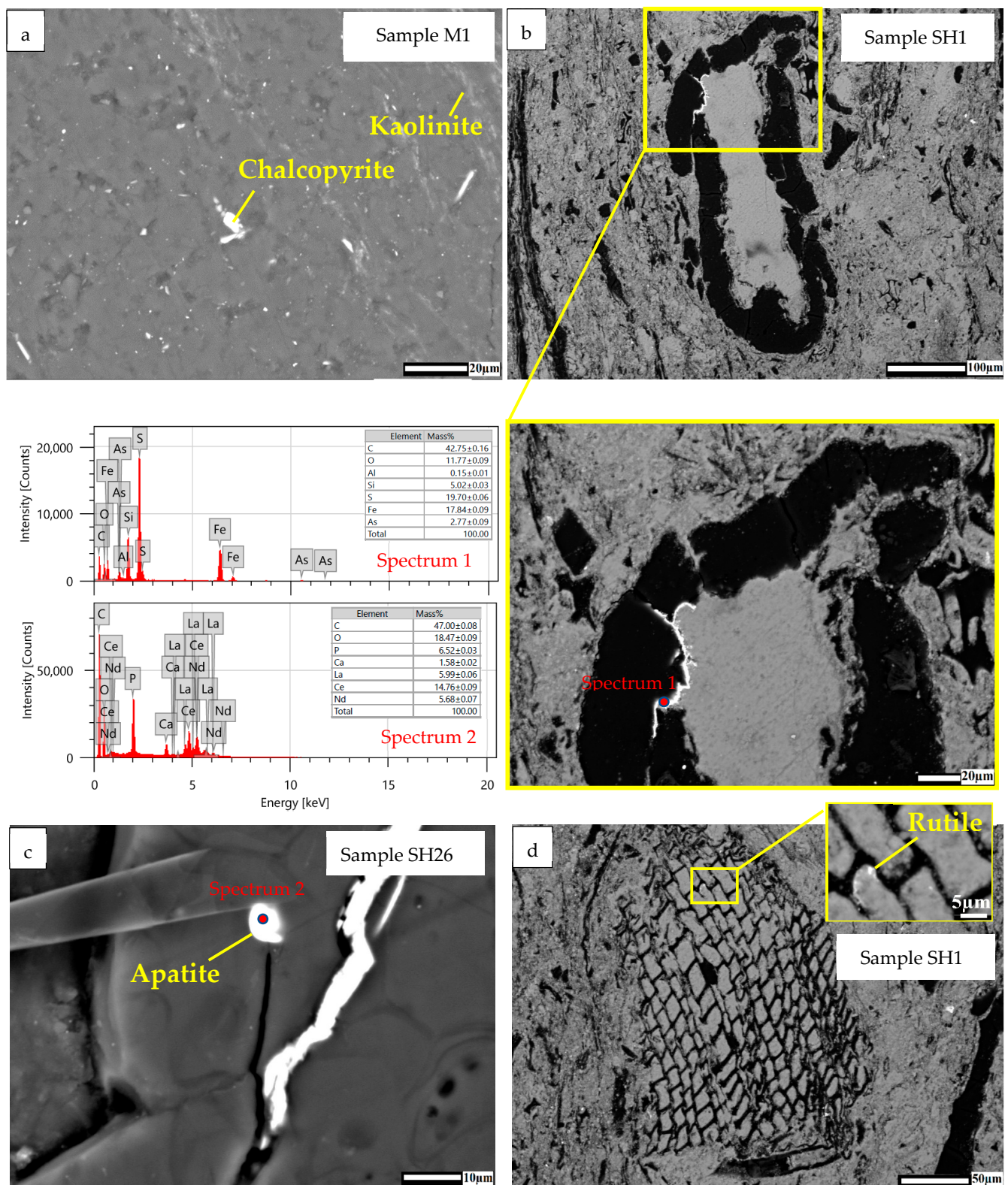


Figure 5. Selected SEM-BSE images of crystalline phases and EDS spectra of Jurassic coal samples: (a) chalcopyrite grains with kaolinite; (b) sporinite macerals observed within vein-like pyrite structures containing arsenic, with the EDS spectrum (1) showing elemental concentrations; (c) individual apatite crystals within coal fractures, with the EDS spectrum (2) showing rare-earth element concentrations (La, Ce, and Nd); and (d) rutile-filled primary organic matter pores in cellular woody material.

Table 4. Mineral contents in the five selected coal samples from the five coal mines measured by low-temperature ashing X-ray diffraction (LTA-XRD) and SEM (+++—dominant phase >20 wt%; ++—abundant phase 20–5 wt%; +—minor phase <5 wt%; and a—accessory mineral detected by SEM-EDS).

Minerals	Coal Mines				
	Lenin	Bogatyr	Saradyr	Maikuben	Shubarkol
Quartz	+++	+++	+++	+++	+++
Kaolinite	++	++	++	++	++
Pyrite	+	+	+	+	+
Chalcopyrite			a	a	
Rutile			a		a
Apatite	a				a

4. Discussion

4.1. Mode of Occurrence of Major and Trace Elements in Coals

Figure 6 presents the dendrogram analysis, which provides valuable insights into the clustering of elements based on their similarities, highlighting their modes of occurrence and affinities. The close association of Al and Si signifies their predominant presence in silicate minerals like quartz and clay minerals (kaolinite), illustrating their essential roles in aluminosilicate phases and emphasizing their strong inorganic affinity within mineral structures. Other authors [1,39,40] noted that Si and, to a lesser extent, Al are the most abundant elements in coal and primary components of its combustion products, identifying 63 silicate and aluminosilicate minerals, including quartz and clay minerals, among more than 200 total minerals.

Ti, Ga, and Cu are associated with accessory minerals, with titanium found in rutile and gallium substituting for Al in kaolinite minerals, and Cu prevalent in sulfide minerals such as chalcopyrite. Their clustering highlights shared associations with specific mineral phases, emphasizing their inorganic nature. As other authors have indicated, titanium is found in rutile, anatase, and other heavy minerals [41], and can also exist as Ti-gel-like phases within kaolinite particles [42]. Gallium is primarily associated with diaspore and kaolinite in coals [2], while copper exhibits a complex distribution in coals, occurring in carbonates, sulfides, silicates, and organic matter, with no single mode of occurrence predominating [43].

The grouping of V, Y, Zr, and K suggests their common occurrence in accessory minerals. This relationship indicates their contributions to the mineralogical complexity of environmental formations, supported by their inorganic affinities. Various authors indicate that Zr is almost exclusively found in zircons, while potassium is present in K-feldspars and clay minerals [41]. Additionally, V is primarily associated with clay minerals [44], and Y in coals is mainly linked to clay minerals and organic compounds [45].

S's central role in forming sulfide minerals demonstrates its critical interactions with metals like Pb and Fe, confirming its strong inorganic affinity. Pb and Fe's connection highlights their occurrences in sulfide minerals, with lead typically found in galena and iron in minerals like pyrite. This association is significant for understanding heavy mineral concentrations and sulfide mineralization, emphasizing their strong inorganic affinities. Many authors have noted that Fe in coal exhibits various modes of occurrence, including in sulfides, carbonates, oxides, chlorite, and Fe-bearing silicates [2]. Additionally, Pb has multiple inorganic associations, including carbonates, oxides, and sulfides, which can coexist in coal [46].

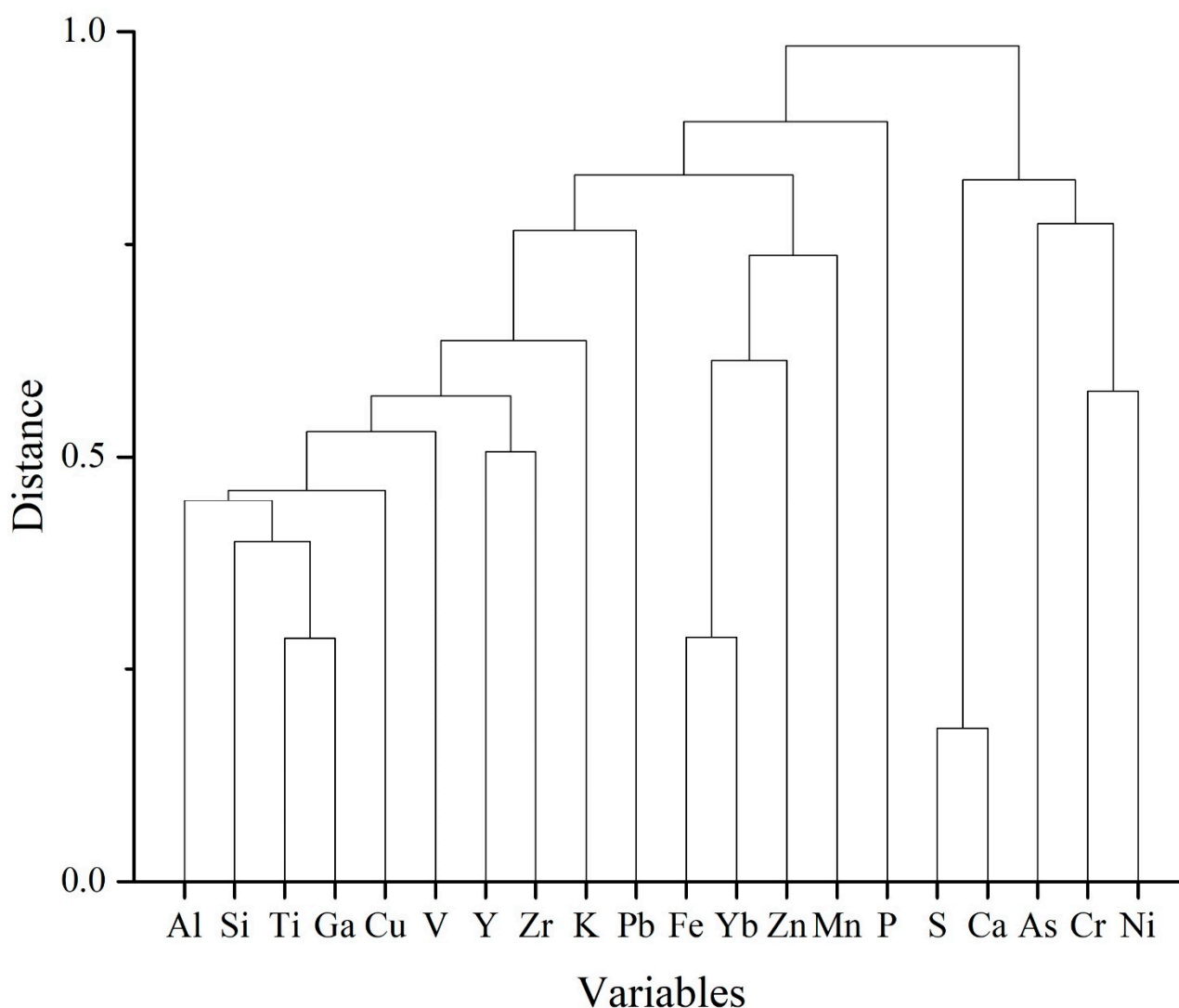


Figure 6. Dendrogram developed from cluster analysis on the elemental data of the complex Jurassic and Carboniferous coals from five coal mines.

Yb's link to rare earth elements emphasizes its presence in accessory minerals like apatite, with a distinct inorganic affinity that underscores its role in trace mineral phases. Zn and Mn are associated with sulfide and oxide minerals, reflecting their roles in less abundant mineral assemblages while maintaining strong inorganic affinities. Many authors emphasize that apatite, a common accessory mineral, is particularly important for hosting REE, especially Yb [47,48]. Mn in coal primarily occurs in carbonates and silicates [2], while Zn is mainly found as an accessory sulfide mineral [2]. Zn is associated with various mineral phases, including silicate-bound, sulfide-bound, and carbonate-bound fractions [49].

P is primarily found in phosphate minerals, and its occurrence in sediments highlights its importance in biogeochemical processes. Although it primarily shows an inorganic affinity, it may interact with organic matter in specific environments. Ward et al. (1996) [50] mentioned that P in coal occurs primarily as crystalline mineral particles, mainly apatite and aluminophosphates.

Ca is commonly found in carbonate minerals, phosphate, and silicates, emphasizing its widespread occurrence in geological settings and its strong inorganic affinity. As noted by Sánchez-Navas et al. (2013) [51], calcium (Ca) in coals is commonly found in carbonate, phosphate, and silicate minerals.

The grouping of As, Cr, and Ni indicates their associations with sulfide and oxide minerals, reflecting a shared inorganic affinity. While As primarily exhibits inorganic behavior, it may show organic affinity in reducing environments. The organic affinity of As, Cr, and Ni in coal varies by element and coal type, with studies suggesting moderate to strong organic associations for Cr and Ni, while As exhibits variable affinities, ranging from strong organic bonds [52,53] to inorganic associations [54], influenced by factors such as element abundance, properties, and coal-forming processes [53].

The analysis indicates that the elements in the dendrogram are predominantly associated with inorganic mineral phases, specifically silicates, oxides, sulfides, and phosphates. Although some elements may exhibit organic affinity under specific conditions, their primary associations are within inorganic mineral frameworks. The use of SEM-EDS further supports these findings, confirming the presence of various minerals, including aluminosilicates (clay minerals), oxides (e.g., quartz and rutile), sulfides (e.g., pyrite and chalcopyrite), and phosphates (e.g., apatite).

4.2. Technological Implications

Silicon (Si) and sulfur (S) can significantly impact coal utilization, primarily through their effects on combustion and ash behavior. Si in coals, as a major component of coal mineral matter, contributes to ash formation and slagging issues. S in coals, often present as pyrite, can react with silica during combustion to form clinkers, potentially inhibiting coal combustion [2,55].

While silicon (Si) in the form of quartz (hardness 7) causes significant abrasion to mining and grinding equipment, it also occurs in softer minerals such as clays and other silicates, which contribute less to abrasion [2]. In the studied samples, silicon content ranges from 0.9% to 11.9% (average 3.9%) in Jurassic coal, and from 0.1% to 20.2% (average 11.3%) in Carboniferous coal. The high silicon values of all samples may suggest a technological impact, but the effects may be mitigated by the presence of kaolinite, in addition to quartz, as observed through SEM analysis.

In the coal ash samples from the five coal mines, the average sulfur concentration is 0.9% in the Jurassic samples and 0.2% in the Carboniferous samples. According to [56], coal with sulfur levels ranging from 1.42% to 5.3% (average 3.36%) by weight is considered high-sulfur and low-quality. This indicates that the sulfur content in these samples is relatively low, which positively affects their technological suitability.

Research on high-ash coal combustion highlights complex interactions between coal properties and combustion efficiency. A higher volatile matter content reduces unburned carbon, facilitating easier ignition and more complete combustion. However, it can also increase emissions of elements like Hg, Pb, Zn, and Cd, which behave differently depending on furnace temperature [57,58]. Additionally, high-ash fusion temperatures and the presence of refractory minerals such as alumino-silicates, iron oxides, and titanium oxides impact combustion efficiency, as well as the potential for slagging and fouling [59]. Optimal combustion typically occurs with $25 \pm 1.75\%$ moderate volatile matter and 20–35% moderate ash content [60] is ideal for combustion because it provides efficient burning with fewer problems like emissions and slagging. The coal samples from the five mines show varying ash yields, with lower values in Jurassic samples and higher values in Carboniferous samples, along with higher volatile matter (Table 5). These differences may result in deviations from the optimal combustion range (20–35% ash yield) and the ideal volatile matter content (around 25%). This suggests that different combustion technologies may be needed for the coal from the five mines to handle these variations effectively.

Table 5. Comparison of ash yield, volatile matter, and inorganic sulfur content in coal samples from five mines with optimal combustion values [60] and impact sulfur level threshold [56].

Coal Mines	Coal Ash Yield (Dry Basis, Unit %)		Volatile Matter (Dry and Ash-Free Basis, Unit %)		Inorganic Sulfur (Dry Basis, Unit %)	
	Range	Average	Range	Average	Range	Average
Jurassic coals						
Maikuben	1.9–4.1	2.7	44.2–52.4	46.6	0.4–1.4	0.9
Shubarkol	1.1–12.8	8.8	33.8–45.6	40.9	0.02–3.1	1.5
Carboniferous coals						
Saradyr	17.0–40.6	26.9	8.8–28.6	21.5	0.06–0.6	0.2
Lenin	3.7–47.6	14.8	8.9–24.6	21.8	0.01–2.3	0.4
Bogatyr	2.7–42.9	31.9	13.7–29.0	20.8	0.01–0.8	0.1
OCV: range 20–35			OCV: 25 ± 1.75		IS range 1.42–5.3	

Note: optimal combustion values (OCVs); IS (impact sulfur).

4.3. Economical Implications

According to the method proposed by [61] for assessing the relative enrichment of trace elements, concentrations of trace elements in coal can be categorized into six groups: highly enriched ($CC \geq 100$, where CC represents the concentration coefficient, indicating the ratio of trace element concentrations in the samples being studied compared to the averages for WHC), significantly enriched ($10 \leq CC < 100$), enriched ($5 \leq CC < 10$), slightly enriched ($2 \leq CC < 5$), normal ($0.5 \leq CC < 2$), and depleted ($CC < 0.5$).

The concentration coefficient (CC) of P and Ti major elements and trace elements in our samples was determined by referencing the values established for world hard coal (WHC) by [38]. This CC helps ascertain whether elements are enriched or depleted by comparing the concentration of trace elements in our coal ash samples to the corresponding WHC values (Figure 3). While we aimed to calculate CCs for all major elements, most lacked corresponding WHC values for normalization. Consequently, we specifically measured the CCs for the major elements P, Ti, and Mn. The element P exhibits a CC ranging from 0.3 to 1.7 in Jurassic and Carboniferous coal ash samples, placing it within the normal concentration range. Similarly, Ti has a CC between 0.3 and 1.5, also falling within the normal concentration category. Mn has a CC of 0.4 in Jurassic samples, placing it in the depleted category, while in Carboniferous samples, its CC is 1.0, indicating a normal concentration.

Trace elements in the five mine samples, including Yb, have a CC ranging from 1.4 to 3.8 in Jurassic and Carboniferous coal ash samples, indicating they fall into the slightly enriched category. Other trace elements, such as Cu, As, and Y, with CC values ranging from 0.5 to 1.4, fall into the normal concentration category across the samples from the five coal mines. Elements such as Cr, Pb, V, Ga, and Zr in Jurassic samples have CC values below 0.5, placing them in the depleted category. Similarly, in Carboniferous samples, Cr, Zn, Pb, and Ni have CC values below 0.5 and are also categorized as depleted. However, in the same Carboniferous samples, V, Ga, and Zr have CC values greater than 0.5, placing them in the normal concentration category (see Figure 7).

The concentration coefficients (CCs) of certain elements in the studied coal ash samples provide insights into their potential economic value. Elements like Yb, slightly enriched across Jurassic and Carboniferous coal ashes, may attract economic interest due to their applications in high-tech industries. Although elements such as Cu, As, and Y fall within normal concentration ranges, they could still hold value depending on the feasibility of extraction. Conversely, the depleted levels of elements like Cr, Pb, V, Ga, and Zr suggest limited economic recovery potential from these samples. These findings highlight the selective recovery potential of specific trace elements, with implications for resource utiliza-

tion and potential economic benefits in targeting enriched or slightly enriched elements for extraction. Additional rare-earth elements, including La, Ce, and Nd, were identified through EDS analysis, indicating a promising economic presence of valuable elements as well. Yb was detected in coal ash samples using XRF, while La, Ce, and Nd were identified in unchanged coal matrices using SEM-EDS analysis, which allows for detailed elemental analysis of the coal structure without alteration. This distinction highlights the different analytical capabilities of XRF and SEM-EDS in characterizing rare-earth elements in coal and its by-products.

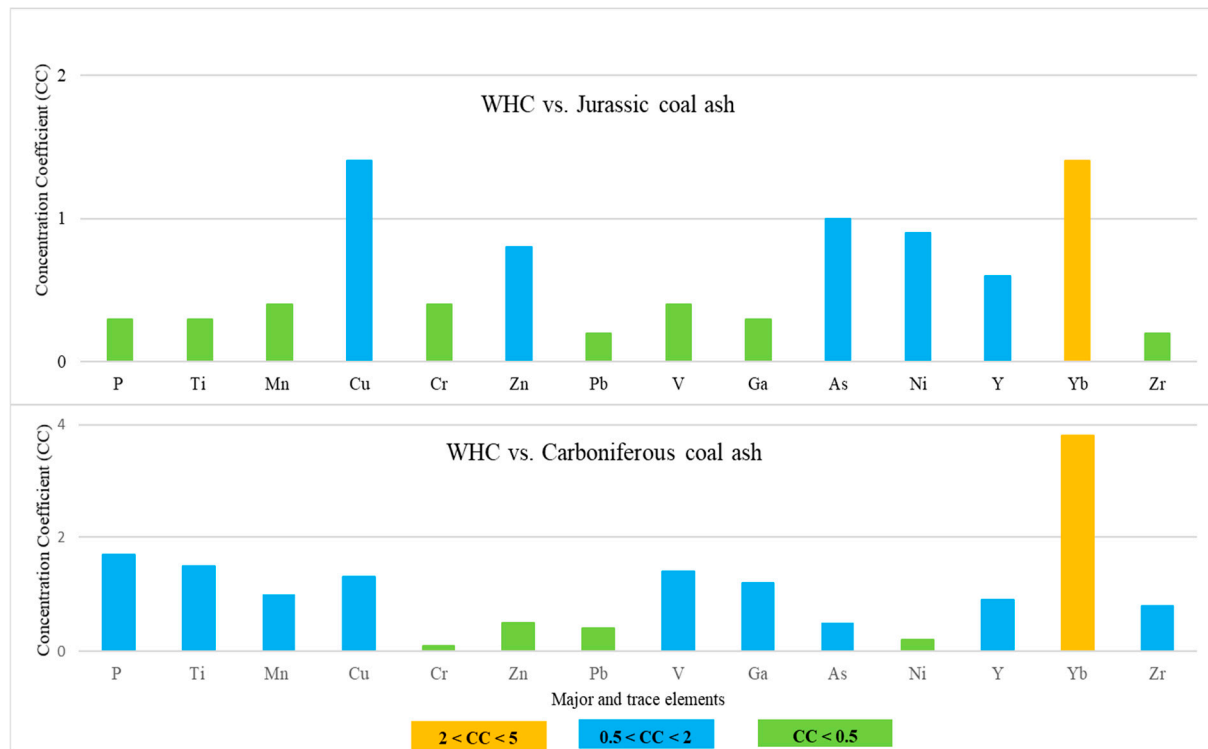


Figure 7. Concentration coefficient (CC) of major elements and trace elements in Carboniferous and Jurassic coal ash from five coal mines, normalized by the average concentrations of major/trace elements in world hard coal (WHC, [38]).

4.4. Environmental Implications

As [62–64] noted, the environmental impact elements associated with coals include As (100 ppm), Sb (45 ppm), Hg (1500 ppm), Pb (500 ppm), Cu (1–1.5%), Cd (0.1%), Bi (0.8%), Ag (1%), Zn (0.3–0.5%), Cr (0.5%), Mn (0.5%), and Ba (0.4%); shown in parentheses are the concentrations considered harmful to the environment. These chemical elements originate from both associated minerals and transformation processes during combustion [62]. It is well established that environmental impact elements in coal tend to be associated with mineral matter, particularly in high-ash coal containing significant amounts of heavy-metal-bearing minerals like pyrite, barite, and rutile/ilmenite. During coal combustion, ashes become enriched with trace elements, often reaching concentrations 3–10 times higher than those in the original coal. Remarkably, these elements are not released during combustion, as evidenced by the consistent concentration ratios found in both ash and original coal [64]. The comparison in Figure 8 illustrates the concentrations of trace elements in samples from three mines against standard harmful thresholds, based on protocols described in the literature [62]. The comparison of potentially toxic elements in ash samples from the five coal mines with harmful threshold standards suggests that the trace element-bearing coal ash poses minimal environmental impact. Potentially toxic elements such as As, Pb, Cu, Zn,

and Cr, including the highest concentration of Mn across all samples, exhibit concentrations below 433 ppm, which are ten times lower than harmful levels.

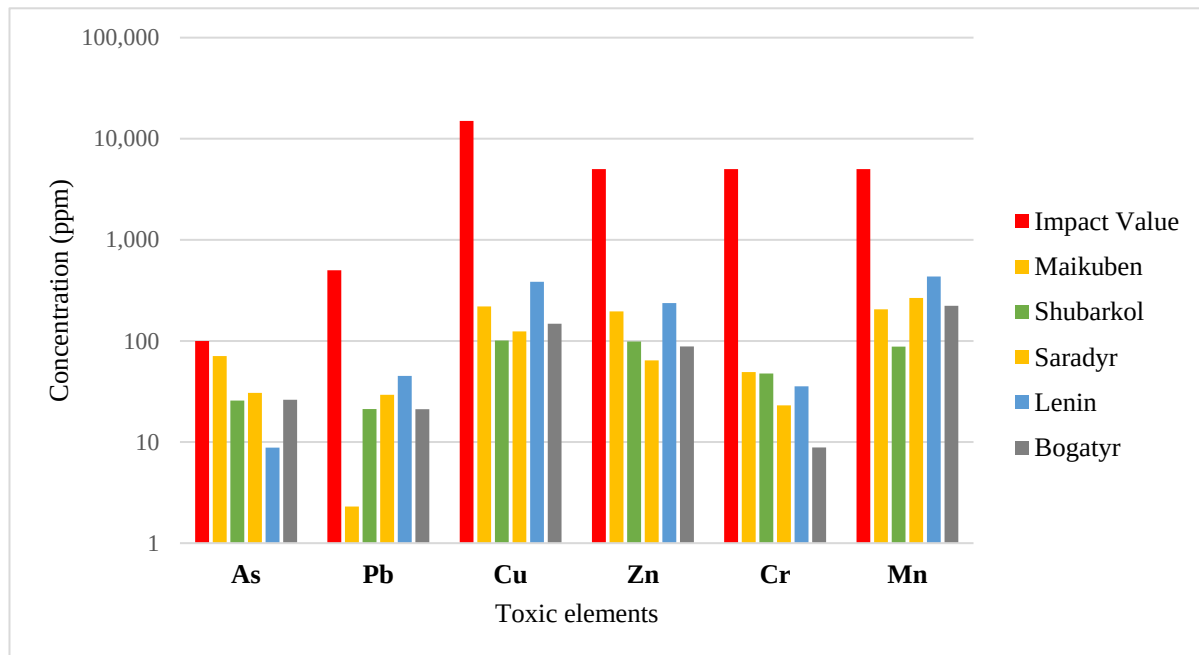


Figure 8. Comparative environmental impact assessment of selected potentially toxic elements in three coal mines against standard harmful thresholds (referred to as impact value) (impact value for comparison as per [62–64]).

5. Conclusions

XRF was selected as a fast and routine tool for analyzing 105 coal ash samples from Jurassic and Carboniferous coals sourced from five mines in Kazakhstan: Lenin, Saradyr, Bogatyr, Maikuben, and Shubarkol. A total of 20 elements were identified in the coal samples, including 9 major elements (Al, Si, P, S, Fe, K, Ca, and Ti) and 11 trace elements (As, Cu, Cr, Zn, Pb, V, Ga, Mn, Ni, Y, Yb, and Zr). Dendrogram analysis shows strong inorganic affinities, with Al and Si linked to aluminosilicates such as quartz and kaolinite, while Fe, Pb, Cu, Zn, and Mn are associated with sulfide minerals. Elements like Ti, Ga, Cu, Yb, V, Zr, and Y are found in accessory minerals, including rutile, zircon, and apatite, contributing to the mineralogical complexity alongside kaolinite. P and As may interact with organic matter. Quartz and kaolinite are the dominant minerals, with minor pyrite present in both euhedral and framboidal forms, accompanied by accessory minerals such as chalcopyrite, rutile, and REE-bearing apatite, as observed through SEM-BSE with EDS analysis.

Technological impacts arise from the significant variations in silicon and sulfur content in the coal samples from the five mines, affecting combustion and suitability for industrial use. High Si levels, particularly in Carboniferous coals, may cause abrasion and ash-related issues, though kaolinite could help mitigate these effects. The low S content improves the coals' suitability by reducing emissions. Variations in ash yield and volatile matter highlight the need for customized combustion technologies to optimize performance, minimize slagging, and improve efficiency for both Carboniferous and Jurassic coals.

The concentration coefficient (CC) analysis shows that most major elements, including P and Ti, fall within normal concentrations in both Jurassic and Carboniferous coal ash samples. Mn is depleted in Jurassic samples but normal in Carboniferous ones. Trace elements like Yb are slightly enriched, while Cu, As, and Y show normal levels. Elements such as Cr, Pb, and Zn are depleted in both coal types, highlighting differences in elemental distribution with potential environmental and industrial implications. Moreover, EDS anal-

ysis revealed additional rare-earth elements (La, Ce, and Nd), as identified in unchanged coal matrices using SEM-EDS, while Yb was detected in coal ash samples via XRF.

The comparison of trace element concentrations in coal ash samples from the five mines against harmful environmental thresholds suggests minimal environmental impact. Potentially toxic elements such as As, Pb, Cu, Zn, and Cr, including the highest levels of Mn, are found in concentrations significantly below harmful thresholds, often ten times lower. These findings indicate that the coal ash from the studied samples poses a low risk of environmental contamination.

XRF analysis may prove to be highly effective for large-scale studies involving multiple coal samples, as demonstrated by the successful analysis of 105 samples in 1.5 days using automated overnight measurements. This efficiency greatly exceeds that of traditional digestion-derived techniques, which require longer processing times. Additionally, the XRF results highlight the potential for further detailed investigations, particularly focused on trace elements, including REE.

Author Contributions: Methodology, M.J.; Investigation, M.J.; Resources, M.J.; Writing—original draft, M.J.; Writing—review & editing, M.J.; Visualization, M.J. and S.M.; Funding acquisition, S.M. All authors have read and agreed to the published version of the manuscript.

Funding: This study was supported by Satbayev University (Almaty, Kazakhstan), project no. AP14871618 “Major boundaries of the Lower Carboniferous in the sections of Central Kazakhstan: development of a zonal standard”.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Data is contained within the article.

Conflicts of Interest: The authors declare no conflict of interest.

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