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Individual Project

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Metalliferous coal and its economic importance: A case study of Molodezhny coal mine

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Dauren Zhanaidar

Professor: [Sebastianus Willem Josef Den Brok](#); [Medet Junussov](#)

Abstract

This study investigates the Molodezhny coal mine, located in the Osakarovsky District of the Karagandy Region, Kazakhstan, with the objective of identifying the occurrence of precious metals and rare earth elements (REEs) in coal and coal ash, and evaluating their economic and industrial potential. A total of 30 coal samples were collected from four stratigraphic horizons (C1, C2, C3, and N1) and analyzed using X-ray diffraction (XRD), X-ray fluorescence (XRF), Fourier-transform infrared spectroscopy (FTIR), inductively coupled plasma optical emission spectrometry (ICP-OES) following microwave-assisted acid digestion, as well as proximate and ultimate analyses.

The results indicate an average ash yield of 27.96% and an average carbon content of 18.67%, suggesting a moderate rank of coalification. Mineralogical analysis reveals that quartz is the dominant phase (37–46%), followed by kaolinite (17–23%), along with a significant amorphous component (28–33%). The analyzed trace elements include Ag, Au, Pr, Sc, Sm, Th, and Yb. Among these, gold exhibits a pronounced anomaly, with an average concentration of 17.5 ppm across all samples and an enrichment coefficient of 728 relative to world hard coal averages. Samarium shows moderate enrichment ($CC = 1.70$), whereas the remaining elements are generally depleted.

Provenance discrimination suggests a predominance of mafic to mixed intermediate source rocks. The calculated A–K index values (>80) indicate intense chemical weathering within the source area. From an economic perspective, the significant enrichment of gold highlights a potential for recovery from coal combustion residues. In addition, the mineralogical composition of the coal ash indicates favorable properties for industrial applications, including cement production, geopolymer synthesis, and ceramic materials.

The Molodezhny deposit demonstrates characteristics of a metalliferous coal system. However, further investigation is required to validate these findings. In particular, SEM–EDS analysis is recommended to confirm the occurrence and mode of REE and gold-bearing phases, repeated ICP-OES measurements under varying analytical conditions are necessary to verify the elevated concentrations of precious metals and REE, and an expanded sampling program is needed to better constrain their spatial distribution across different coal seams.

Table of contents

Abstract	2
1. Introduction	5
1.1 General information	5
1.1.1 Metalliferous Coals: Definition and Historical Background	5
1.1.2 Rare Earth Elements and Yttrium (REY): Significance and Demand	5
1.1.3 Critical and Strategic Elements in Coal	6
1.1.4 Gold and Its Emerging Applications	7
1.1.5 Environmental and Health Considerations	8
1.1.6 Coal Deposits of Kazakhstan	9
1.2 Aims and Objectives of the Study	9
2. Geological setting(geomorphology, local climate, stratigraphy and tectonics)	11
2.1 Geomorphology and local climate information of the study area	11
2.2 Geology, Stratigraphy and Tectonics of Molodezhny coal deposit	12
2.2.1 Geology of the Molodezhny Coal Deposit	12
2.2.2 Tectonic Setting and Magmatism	13
2.2.3 Magmatism	14
2.2.4 Structural Geology of the Molodezhny Deposit	15
2.2.5 Stratigraphy	15
3. Sampling and methods	17
3.1 Sampling procedure	17
3.2 Methods: Organic part – proximate and ultimate analyses	19
3.2.1 Proximate analysis (ash yield)	20
3.2.2 Ultimate analysis (organic elements CHNS)	22
3.3 Methods: Inorganic part - Mineralogical and elemental analyses	23
3.3.1 XRD analysis	24
3.3.2 XRF analysis	24
3.3.3 FTIR analysis	25
3.3.4 ICP-OES analysis and Microwave digestion	25
4. Results	25
4.1. Coal quality and characterization	25
4.1.1 Results of proximate analysis: Ash yield determination	25
4.1.2 Results of ultimate analysis: Organic elements of coal materials	28

4.2 Results of coal mineralogy and its inorganic geochemistry	31
4.2.1 Mineralogical content of coals	31
4.2.2 Elemental analysis (major and trace elements) using XRF and ICP-OES with microwave digestion	36
5. Discussion	42
5.1 Economic and Industrial Implications trace elements (Au, Ag, Th, Pr, Sc, Sm, Yb) from coal ash	42
5.2 Host phases and mineralogical controls of trace elements (Au, Ag, Th, Pr, Sc, Sm, Yb) in coal samples	48
5.3 Sediment provenance region for Au, Ag, Th and REE (Pr, Sc, Sm, Yb) in coal samples	50
6. Conclusion	53
Appendix A	56
Appendix B	57
References	59

1. Introduction

1.1 General information

1.1.1 Metalliferous Coals: Definition and Historical Background

Metalliferous coals are defined as coal deposits enriched in economically valuable trace elements and are commonly referred to as “mineralized” coals (Seredin and Finkelman, 2008). The term “metalliferous,” defined in the Glossary of Geology (1960) as “producing or containing metal; yielding metal,” is widely used in European coal literature and has also been adopted in studies of U.S. coals (Hower et al., 2000a, cited in Seredin and Finkelman, 2008). These coals are typically characterized by anomalously high concentrations of trace elements; however, no universally accepted threshold exists. In this study, coals with trace element concentrations exceeding ten times the global average for coal are considered metalliferous.

Interest in metalliferous coals dates back more than a century (Jenney, 1903; Stone, 1912, cited in Seredin and Finkelman, 2008), although their large-scale industrial utilization has historically been limited. Nevertheless, they have been locally exploited as sources of valuable metals. For example, coal deposits in Wyoming and Utah (USA) were used for gold and silver recovery during the late 19th and early 20th centuries (Jenney, 1903; Stone, 1912, cited in Seredin and Finkelman, 2008). Following World War II, metalliferous coals became an important source of uranium in both the USSR and the United States (Kislyakov and Shchetokin, 2000, cited in Seredin and Finkelman, 2008). In the early 1960s, they were also utilized for germanium extraction in the USSR, Czechoslovakia, the United Kingdom, and Japan (Swaine, 1990; Jandova and Vu, 2001, cited in Seredin and Finkelman, 2008). At present, metalliferous coals remain a significant source of germanium in Russia, Uzbekistan, and China (Seredin, 2006; Höll et al., 2007, cited in Seredin and Finkelman, 2008).

1.1.2 Rare Earth Elements and Yttrium (REY): Significance and Demand

In recent years, metalliferous coals have attracted increasing attention as potential alternative sources of rare earth elements and yttrium (REY; or REE when yttrium is excluded). REY in coal and coal ash are commonly divided into three groups: light (LREY: La, Ce, Pr, Nd, and Sm), medium (MREY: Eu, Gd, Tb, Dy, and Y), and heavy (HREY: Ho, Er, Tm, Yb, and Lu)

(Seredin & Dai, 2012). Countries such as the United States, China, Russia, India, South Africa, and Indonesia are actively investigating coal and coal ash for REY recovery. In Kazakhstan, REY-enriched coal has been identified in the Shubarkol deposit (Central Kazakhstan), with reported concentrations of Y (254 g/t), Nd (806 g/t), La (46 g/t), and Gd (335 g/t). Previously, the presence of REY in coal basins received limited attention due to the abundance of conventional REE deposits. However, since 2009, global concerns over REY supply have intensified, driven by geopolitical factors and rapidly increasing demand.

1.1.3 Critical and Strategic Elements in Coal

With the continued development of human society and economic growth, there is an increasing risk of depletion of various natural resources and mineral commodities. [As noted by Dai and Finkelman \(2017\)](#), coal remains a key resource predominantly used for energy generation, currently accounting for approximately 41% of global electricity production ([World Coal Association, 2017, cited in Dai and Finkelman, 2017](#)). In addition to its role in power generation, substantial quantities of coal are utilized in metallurgical processes, gasification, and the cement industry, as well as serving as a feedstock for activated carbon and a wide range of industrial chemicals. Coal also provides heat for sectors such as wallboard production, aluminum processing, and cement manufacturing.

Beyond its conventional applications, certain types of coal may be considered potential economic sources of critical and strategic elements. These include gold (Au) germanium (Ge), gallium (Ga), uranium (U), vanadium (V), selenium (Se), scandium (Sc), yttrium (Y), niobium (Nb), gold (Au), silver (Ag), platinum group elements (PGEs), and rhenium (Re), as well as base metals such as aluminum (Al) and magnesium (Mg). Modern global economies increasingly depend on such critical elements, which are essential for technological advancement and energy efficiency ([Massari and Ruberti, 2013; Hower et al., 2016c, cited in Dai and Finkelman, 2017](#)). However, the availability of these elements is becoming progressively constrained due to the depletion of conventional ore deposits and rapidly growing demand driven by their extensive industrial applications.

1.1.4 Gold and Its Emerging Applications

As Corti and Holliday (2004) notes gold is predominantly utilized as an electrical conductor in various applications. The most recent significant application of gold in industrial contexts was the introduction of gold bonding wire in the electronics sector approximately 30 years ago. Furthermore, the novel uses for gold that are beginning to surface predominantly rely on a chemical methodology for the production of beneficial goods, as opposed to the traditional materials or mechanical approaches. It is beneficial to examine some of these innovative applications. It is generally acknowledged that numerous applications fall within five market categories. The sectors are as follows:

- Technologies for pollution and emission control, including fuel cells.
- Innovative applications of gold in sophisticated electronics, electrical systems, and devices.
- Chemical processing of various bulk and specialty compounds utilizing gold-based catalysts.
- Sophisticated coatings utilizing the unique characteristics of gold, especially in nanoparticulate form.
- Novel biomedical applications of gold encompassing medicinal therapies, pharmaceuticals, implants, sensors, and devices.

And the more interesting is medical usage. As Vines et al. (2019) notes colloidal gold demonstrates localized plasmon surface resonance (LPSR), indicating that gold nanoparticles can absorb light at particular wavelengths, leading to photoacoustic and photothermal properties, thereby rendering them potentially advantageous for hyperthermic cancer therapies and medical imaging applications. Altering the shape and size of gold nanoparticles can modify their LPSR photochemical activities, thus affecting their photothermal and photoacoustic properties, which permits the use of various wavelengths of light, including near-infrared light. Manufacturing gold at the nanoscale enables passive distribution throughout the body, allowing localization in tumors, which possess permeable blood arteries, and safe excretion via the urine system. REY are essential for modern technologies and are widely used in electronics, renewable energy systems, electric and hybrid vehicles, magnets, lasers, and advanced materials. They also play critical roles in industries such as information technology, nanotechnology, medicine, and environmental

protection. As demand continues to rise, their economic importance has increased significantly, highlighting the potential of metalliferous coals as unconventional REY resources.

Moreover, the supply of many critical elements is geographically concentrated. For instance, China accounts for more than 85% of global rare earth element production ([U.S. Geological Survey, 2017, cited in Dai and Finkelman, 2017](#)). Similarly, China is the leading producer of germanium, with an annual production of approximately 120 tons in 2014–2015, representing about 73% of global output ([U.S. Geological Survey, 2016, cited in Dai and Finkelman, 2017](#)). These supply risks have stimulated a global search for alternative and unconventional sources of critical elements, particularly rare earth elements ([Barakos et al., 2016, cited in Dai and Finkelman, 2017](#)). In this context, coal and coal combustion products (CCPs, such as fly ash) have emerged as promising potential resources.

Coal-bearing sequences can host a wide range of resources, including solid (metals and non-metals), liquid, and gaseous phases. Therefore, their integrated development is increasingly viewed as a viable approach to transforming coal from a purely energy resource into a multifunctional raw-material platform, thereby enhancing resource efficiency and supporting the transition toward more sustainable energy systems.

1.1.5 Environmental and Health Considerations

However, the extraction and utilization of coal, including the recovery of valuable elements, are associated with significant environmental and health risks. As highlighted by [Gopinathan et al. \(2023\)](#), coal mining and combustion contribute substantially to air pollution and greenhouse gas emissions, thereby exacerbating climate change and negatively affecting both local communities and broader populations. The environmental impacts of coal extraction, transportation, and utilization include ecosystem degradation, water contamination, and deterioration of air quality. In addition, exposure to pollutants such as heavy metals, particulate matter, and volatile organic compounds poses serious health risks, particularly for populations living near coal mines and power plants. These exposures have been linked to respiratory diseases, cardiovascular disorders, and other adverse health outcomes, with vulnerable groups being disproportionately affected.

1.1.6 Coal Deposits of Kazakhstan

Kazakhstan, the 10th largest coal producer globally, comprises nine coal basins with estimated total reserves of approximately 150 Gt, of which 28.2 Gt are recoverable ([Ammosov et al., 1973](#); [Azizov and Vlasov 2013](#); [EIA report 2017](#)). The largest and economically viable reserves are typically Carboniferous in age. Recent studies report elevated levels of valuable metals in coal deposits across Central and Northeastern Kazakhstan. The Shubarkol coal deposit shows high concentrations of REE such as Y (254 ppm), Nd (806 ppm), La (46 ppm), and Gd (335 ppm), whereas earlier investigations in the Karagandy coal basin reported lower values (Y up to 54 ppm, Sc up to 43 ppm, U at 6.4 ppm, Th at 11.4 ppm) ([Amangeldikyzy et al., 2023](#); [Kopobayeva et al., 2024](#)). Coal from the Ekibastuz basin also contains elevated Ti and Zr (up to 1%), Y (up to 30 ppm), U (2.5 ppm), and Th (3.1 ppm) ([Ammosov et al., 1973](#); [Azizov and Vlasov 2013](#)).

Therefore, the determination of REY or other metals in coal and coal ash from different deposits in Kazakhstan is crucial for understanding the geological and geochemical processes controlling their distribution, as well as their modes of occurrence during coal formation. Such studies also provide insights into the provenance of REY and the depositional environment of coal-bearing basins, while supporting the evaluation of their economic potential. REY in coal typically exhibit relatively uniform distribution patterns and stable chemical properties, reflecting their specific geochemical behavior.

1.2 Aims and Objectives of the Study

The primary aim of this study is to determine the occurrence and concentration of precious metals and critical elements within the Molodezhny coal deposit, with particular emphasis on their socio-economic significance.

Firstly, from a socio-economic perspective, metalliferous coals represent a potentially valuable unconventional resource. As noted by [Bian et al. \(2025\)](#), concentrations of critical metals in coal ash may exceed established cut-off grades, indicating significant economic potential. At the same time, coal ash is often enriched in hazardous elements (e.g., Pb, Cr, Th, U) and contains nanoscale particles, posing environmental and human health risks. Therefore, the development of sustainable technologies for coal ash utilization as a secondary metal resource may mitigate these risks while contributing to a circular economy.

Secondly, from a scientific and geological perspective, coal-bearing sequences represent complex systems formed through the interaction of multiple geological processes. According to [Li et al. \(2022\)](#), coal measures host diverse solid, liquid, and gaseous resources, including metallic and non-metallic minerals, generated through processes of material formation, migration, and accumulation. These systems also preserve critical information on paleoenvironmental conditions, including organic carbon sequestration and atmospheric variations. The redistribution of elements during diagenesis and metamorphism results in variable enrichment patterns, making it essential to understand their occurrence and extractability.

Thirdly, the issue of supply risk for critical elements is of growing global importance. As highlighted by [Dai and Finkelman \(2017\)](#), the global supply of rare earth elements (REE) is highly concentrated, creating potential geopolitical vulnerabilities. In this context, coal and coal ash may serve as alternative and unconventional sources, contributing to supply diversification.

Fourthly, coal ash represents a significant environmental challenge. It is a major industrial waste that can negatively affect land, water, and air quality, particularly due to the dispersion of fine particles and the presence of toxic elements such as U and Pb. The recovery of valuable elements from coal ash could simultaneously reduce environmental impacts and generate economic value.

Fifthly, the study addresses the limited level of prior research in the region. Coals from Kazakhstan, and particularly the Molodezhny deposit, remain insufficiently investigated with respect to their content of critical and precious elements. This study therefore provides an initial assessment of its metalliferous potential.

Finally, this research aims to address a fundamental geological question regarding the mechanisms responsible for the enrichment of valuable elements in coal. Potential processes include hydrothermal activity, weathering, and syngenetic or epigenetic inputs. Understanding these mechanisms is essential for interpreting the genesis of the Molodezhny deposit and for advancing broader models of metalliferous coal formation.

2. Geological setting (geomorphology, local climate, stratigraphy and tectonics)

2.1 Geomorphology and local climate information of the study area

The point of interest is located in the Karagandy region. The Molodezhny (previously Borly) coal deposit is located in the steppes of the Osakarovsky District of the Karagandy Region, 116 kilometers from Karagandy. As [Kenetayeva et al. \(2021\)](#) noted the Karagandy region encompasses the highest central portion of the Kazakh hilly area, known as Saryarka, characterized by its unique and geomorphologically diverse, elevated landscape. The topography is characterized by shallow hummocks, river valleys, arid watercourses, depressions with exposed groundwater, closed basins, and lake basins. The overall area of the state forest fund in the Karagandy region is 269.6 thousand hectares. Elevated temperatures and insufficient precipitation during summer, coupled with extensive steppe regions, may result in wildfires from July to September. The Karagandy region serves as a significant industrial hub. Principal industries: mining (extraction of coal, ferrous and non-ferrous metal ores), ferrous and non-ferrous metallurgy, and the chemical sector. Processing firms constitute 80.1% of industrial production.

The deposits of the Akzhar Group are located in the Karagandy (Akzhar, Molodezhny), Akmola (Samaisor, Koytas, Tumenisor), and Pavlodar (Bayet) regions. The absolute elevations of the deposits' surfaces range from 400 to 500 m, those of the surrounding low-lying hills from 600 to 700 m, and those of the Ereimentau Mountains from 700 to 1,000 m. In terms of hydrology, the region is associated with the basins of the Olenti, Shiderti, and Akmurza rivers. The Irtysh–Karagandy channel runs through its territory. The region's climate is sharply continental, with an annual temperature range of 90° (from −49 to +41°C). The average annual precipitation is 311 mm.

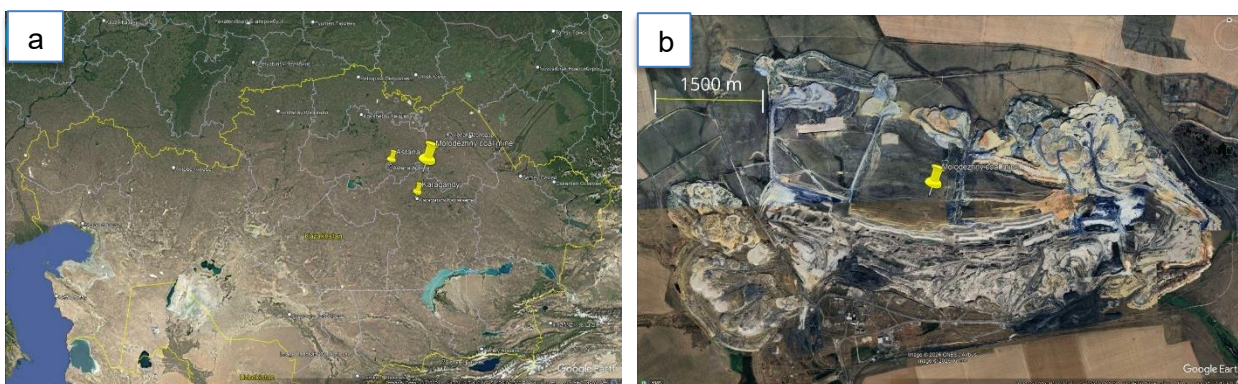


Figure 1. General view of Molodezhny coal mine from Google Earth Pro satellites: a) General view on the Kazakhstan map; b) General view of the Molodezhny coal mine from the satellite

2.2 Geology, Stratigraphy and Tectonics of Molodezhny coal deposit

2.2.1 Geology of the Molodezhny Coal Deposit

The Molodezhny coal deposit has been known since the last century. Until 1949, it was sporadically mined for local needs by a small quarry. The total volume of production by that time did not exceed 10,000 tons. The first geological exploration work at the deposit using drilling and mining operations began in 1949. Upon completion of this stage in 1956, the total coal reserves at the deposit were estimated at 203 million tons, of which 72 million tons were balance reserves. Given the low quality of drilling and the lack of logging in wells in previous years, exploration and evaluation work was carried out in 1972–1973, as a result of which the total coal reserves increased to 345 million tons. This work opened up new prospects for the Molodezhny coal deposit. The project carried out by the Karagandygiproshakht Institute in 1978, "Project studies for the development of the Molodezhny coal deposit," showed that an open-pit mine with a capacity of 8 million tons per year could be built there with good technical and economic indicators. The high assessment of the deposit's prospects led to the immediate conduct of preliminary exploration, which confirmed the favorable conditions for its development.

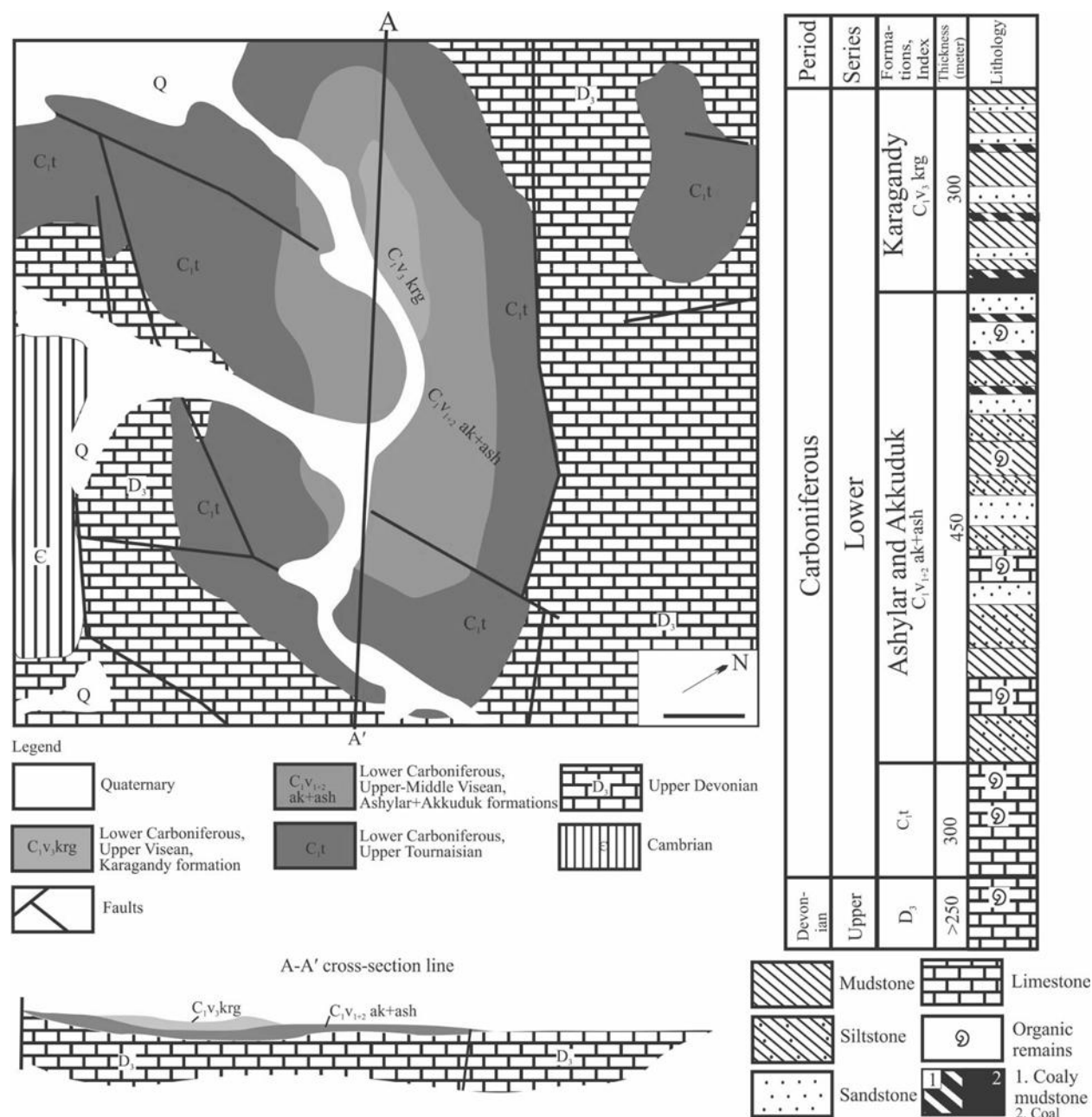


Figure 2. Geological map of Molodezhny coal mine

2.2.2 Tectonic Setting and Magmatism

As [Kopobayeva et al. \(2024\)](#) notes the Karagandy coal basin is situated in the western section of the Central Asian orogenic belt and corresponds to the central portion of the laterally extended synclinorium that holds a distinct place within the geological structure of Central Kazakhstan. The basin is situated in the region linking the Caledonian and Hercynian folds, namely

between the Hercynian Dzhungaro–Balkhash geosyncline to the south and the Caledonian solidification zone to the north. The Devonian fringe volcanogenic belt extends through this region, enabled by a network of deep-seated faults that induce twisting, fracturing, and schistosity in the rocks.

The Karaganda synclinorium is a complicated yet cohesive large laterally oriented synclinal structure composed of Devonian volcanogenic sedimentary rocks and Carboniferous coal-bearing sequences. Due to late Hercynian block movements, the Karaganda synclinorium was segmented along longitudinal faults into distinct blocks, which constitute graben synclines separated by highly eroded uplifts. The western section of the Karaganda synclinorium consists primarily of Devonian volcanogenic materials. The Karaganda coal basin developed within the Karaganda synclinorium due to significant downwarping of the southern border of the region during Hercynian tectogenesis ([Kopobayeva et al., 2024](#)).

The Dzhungaro–Balkhash geosyncline, located in the southwestern region of Central Kazakhstan, is delineated by two anticlinoria: the Spassk anticlinorium and the Tekturmass anticlinorium. The Spassk anticlinorium directly borders the basin to the south. The Tekturmass anticlinorium was developed during the early Givetian period as an advanced manifestation of Hercynian folded structures ([Kopobayeva et al., 2024](#)).

2.2.3 Magmatism

Magmatic rocks are extensively distributed within the geological framework of the basement and flanks of the Karaganda basin. They are characterized by intrusive complexes from the Ordovician (diabasic porphyry and quartz diorites) and Devonian (granodiorites, leucocratic granites, granosyenites, syenite porphyry, and granite porphyry), along with Devonian subvolcanic formations (dacitic porphyry). All Devonian formations belong to the volcanogenic formations of Coblentzian–Givetian age and typically constitute small bodies associated with the initial phase of Devonian magmatism ([Kopobayeva et al., 2024](#)).

Positive tectonic movements in the late Tournaisian and early Viséan epochs led to replacing the predominantly marine carbonaceous sediments of the upper Tournaisian with clayey deposits from the lower section of the Akkuduk series, which developed under lagoonal conditions. In the Dzhungaro–Balkhash geosyncline, this upheaval coincided with an intensification of

volcanic activity, evidenced by extensive thin interlayers of tuffs within the clayey sediments of lower Visean age, both inside and beyond the Karaganda basin.

2.2.4 Structural Geology of the Molodezhny Deposit

Geologically, the Molodezhny coal deposit is confined to the eastern part of the Olenty-Shiderty syncline, which stretches for 50 km in a latitudinal (east-west) direction. The western part of the syncline is represented by the Akzhar group of deposits. The Akzhar, Molodezhny, Samaysor, Koytas, and Tumenor deposits are associated with the Shiderti Synclinal System. The Akzhar and Molodezhny deposits are located within a single synclinal structure, in the central part of which two brachy-synclines (Akzhar and Molodezhny) are clearly distinguishable. The dip angles of the strata rarely exceed 15°. No major discontinuities in the coal-bearing strata were identified during exploration work at the Molodezhny deposit.

The degree of coal metamorphism in both regions was found to be similar. This is likely due to the elevated geothermal conditions of the region's subsurface, within which Late Paleozoic intrusions are widespread ([Kopobayeva et al., 2024](#)).

2.2.5 Stratigraphy

The Akzhar group deposits are confined to synclinal structures located within the development of volcanogenic-sedimentary formations of the Proterozoic and Lower and Middle Paleozoic. The structure of the synclinal wings includes variegated conglomerates, sandstones, and siltstones of the Givetian and Frasnian ages, as well as carbonate deposits of the Famennian–Tournaisian ages. Productive sediments of the Visean and Serpukhovian stages make up the inner parts of the synclines. Mesozoic and Cenozoic formations play a minor role in the structure of the deposit area. They usually lie on the eroded surface of the Paleozoic and have a local character of development, adapting to the lower parts of the ancient relief. Cenozoic formations are the most developed of these.

The description below is based on the unified stratigraphic scheme adopted for Central Kazakhstan at the Second Stratigraphic Conference in Almaty in 1971. According to this scheme, the Visean stage deposits are represented by the Akkuduk and Ashlyar horizons, corresponding to the lower and middle Visean substages respectively. The Karagandy horizon corresponds to the upper Visean substage, with its upper part extending into the Serpukhovian stage.

2.2.5.1 Proterozoic and Lower–Middle Paleozoic

Volcanogenic-sedimentary formations forming the basement of the synclinal structures.

2.2.5.2 Upper Devonian (D₃)

Upper Devonian deposits are part of the structure of the deposit's flanks. Lithologically, they are represented by organogenic argillaceous limestones of gray and dark-gray (almost black) color, with layers of polymictic fine-to-medium-grained sandstones and siltstones, richly characterized by brachiopod fauna, and more rarely, corals and crinoids. The deposits are assigned to the Famennian stage based on the brachiopod and ostracod assemblage. The thickness of the Famennian deposits ranges from 130 to 160 meters.

2.2.5.3 Lower Carboniferous (C₁)

Tournaisian (C_{1t}, 300 m): Represented by dense, highly silicified gray limestones containing cherty-argillaceous concretions and layers of calcareous siltstones and marls. Fauna includes brachiopods, corals, pelecypods, crinoids, and bryozoan imprints.

Visean Stage Akkuduk and Ashlyar horizons (C_{1v1-2} ak+ash, 450 m): Represented by undifferentiated Akkuduk and Ashlyar horizons, with a total thickness of up to 740 m. Four units are identified: First Unit (Lower, 200 m): Massive fine-grained calcareous siltstones and dark argillites with layers of greenish-gray siltstone-sandstones; contains no coal. Second Unit (180 m): Interbedded sandstones and siltstones with approximately 10 coal seams and carbonaceous layers. Third Unit (350 m): Calcareous siltstones and sandstones with layers of organogenic limestones and carbonaceous argillites; includes the a₂ marker bed. Fourth Unit (Upper, 90 m): Predominantly fine-to-coarse-grained sandstones and light-gray siltstones with rare layers of dark carbonaceous argillites and coal; includes the a₁ marker bed.

Visean – Serpukhovian Stages Karagandy horizon (C_{1v3} krg, 180–200 m): These deposits contain the main coal seams, with three coal horizons in the lower part. Host rocks include medium-to-coarse-grained sandstones and silicified siltstones with plant remains and ostracods.

2.2.5.4 Cenozoic Deposits

Carboniferous deposits are covered throughout by sandy loams and loams of Quaternary age, which have a brownish-gray color. In the floodplain of the Muzdybulak River, located in the

southeastern part of the area, gravels and sands with an admixture of clayey material are encountered. The thickness of the Quaternary deposits does not exceed 3.5 m, while in the river floodplain, it reaches 10–12 m. Neogene deposits occur mainly on the flanks of the syncline in its northwestern and northeastern parts. These deposits are represented by dense gypsiferous clays of reddish-brown to violet color. The thickness of the clays varies from 0 to 12 meters.

3. Sampling and methods

3.1 Sampling procedure

The coal samples used in this study were collected from the Molodezhny coal mine, located in the Karagandy region of central Kazakhstan, approximately 160 km north of Karaganda City within the administrative boundaries of the Osakarov District. The deposit is actively operated under a mining license owned by the Kazakhstani company Kazakhmys Coal. The mine represents an important part of the regional coal-bearing basin and provides access to multiple coal seams with distinct stratigraphic and lithological characteristics.

A total of 30 coal samples were collected in order to capture the vertical and lateral variability of coal composition across different stratigraphic levels of the deposit. The sampling strategy was designed to ensure representative coverage of both the middle and lower coal-bearing horizons, which are known to exhibit variations in organic matter composition, mineral content, and geochemical properties.

Based on stratigraphic positioning, the collected samples were divided into four groups: C1, C2, C3, and N1. The C-series samples represent the middle coal-bearing horizon, which is further subdivided into three distinct sub-layers. Specifically, C1 corresponds to the uppermost section of the middle horizon, C2 represents the intermediate layer, and C3 reflects the lower portion of the same middle coal-bearing sequence. In contrast, the N1 samples were obtained from the lower coal-bearing horizon, which lies stratigraphically beneath the C-series units and is considered geologically distinct in terms of depositional conditions and coalification processes.

The sampling distribution includes 7 samples from the C1 horizon, 7 samples from the C2 horizon, 3 samples from the C3 horizon, and 13 samples from the N1 horizon. This uneven distribution reflects both the accessibility of sampling points in the mine workings and the thickness and continuity of individual coal seams. Nevertheless, the overall dataset provides

sufficient coverage for comparative geochemical and mineralogical interpretation between the middle and lower coal-bearing horizons.

Field sampling was conducted using clean, non-contaminating tools to prevent cross-contamination between different coal layers. Each sample was carefully extracted from freshly exposed coal faces, ensuring that weathered surfaces and oxidized material were avoided as much as possible. After collection, all samples were immediately placed into pre-labeled, airtight polyethylene bags to preserve their in-situ physical integrity and to minimize exposure to atmospheric moisture and oxidation. Special attention was given to sample handling and storage conditions to maintain the original geochemical signature of the coal material. The sealed samples were transported to the laboratory under controlled conditions and stored in a dry environment prior to further preparation and analytical procedures. The sampling locations and procedures are illustrated in [Fig. 3](#), which provides a visual representation of the sampling design and stratigraphic framework of the study area. [Fig. 3a](#) shows open-pit mine and [Fig. 3b](#) and [Fig. 3c](#) show sampling process where we can see coal walls and horizontal strata, [Fig. 3d](#) shows total collection of all coal samples.



Figure 3. General view of Molodezhny coal mine: a) open-pit mine; b and c) sampling process; and d) total collection of all coal samples

Detailed sampling and analytical procedures for all sample types, conducted at the Core Facilities and laboratories of the School of Mining and Geosciences, Nazarbayev University (Astana, Kazakhstan), are provided in the following subsections.

3.2 Methods: Organic part – proximate and ultimate analyses

3.2.1 Proximate analysis (ash yield)

In this part, it was used 30 coal samples for the analysis. From this homogenized coal powder, two types of ash were produced under controlled laboratory conditions: high-temperature ash (HTA) and low-temperature ash (LTA). High-temperature ash was generated by combusting the coal powder at 815 °C for 4 hours in a muffle furnace, following standard procedures aimed at complete removal of organic matter and concentration of inorganic mineral residues. In contrast, low-temperature ash was produced at 350 °C for 24 hours, a condition selected to minimize thermal alteration of mineral phases and preserve more delicate or thermally sensitive mineral structures. For burning purposes we used furnace Carbolite ELF 11/6B at 6 block 139 lab in Nazarbayev University shown on the [Fig. 4](#). It is the laboratory furnaces that consist of three bench-mounted types intended for light-duty and general applications up to 1100 °C. These laboratory furnaces include a straightforward drop-down door and a top-mounted ceramic flue. The integration of low thermal mass insulation and freely radiating wire elements placed in the chamber walls facilitates efficient heating. Maximum working temperature of 1100°C. Drop-down door with an air gap to reduce exterior temperature. Furthermore, it is equipped with a Carbolite 301 controller, with a single ramp to the set-point and a process timer. On the [Fig 4a](#) we can see how the furnace looks like, having small display and two different colored indicators. On the [Fig 4b](#) we can see furnace part number, its model type and general characteristics. On the [Fig 4c](#) we can see raw coal samples before burning in the furnace, and on the [Fig 4d](#) we can see ash after combustion.



Figure 4. General view of Molodezhny coal mine: a) general view on the furnace b) Muffle furnace part number and model. c) coal sample in the muffle furnace d) high-temperature ash

The use of both HTA and LTA allowed for comparative evaluation of mineral transformations during combustion. Specifically, low-temperature ash (typically performed below 450–500 °C) is commonly used to preserve original mineralogical structures for more accurate phase identification, whereas high-temperature ash is more effective in eliminating organic components and concentrating stable inorganic phases for bulk geochemical assessment.

After we put the HTA sample into a plastic cylindrical container and added all acids listed previously, closed them with a thermo and protective case and then put in a digestion machine for 1h 29 minutes. It started to increase the temperature immediately until 230 degrees Celsius in the first 20 minutes, and then it was maintaining a stable temperature all the time. When digestion was completed we opened the containers, and added transferred the solution to new test tubes and then we added 6ml of H_3BO_3 and filled new test tubes until the edge of 50 mm. Produced solution had

very small particles that did not undergo digestion, so we used syringe filter and then after filtering the solution we gave them to the specialist who is responsible for the next steps.

After thorough analysis of the sample by the laboratory technician we got the data for all samples, and a blank sample too. Because there were not so many elements in the liquid, so there was not any dilution, and dilution coefficients were not applied of course. Correction to get real results were made through subtraction of element concentration with blank sample concentration, then this was divided by 20, and then by the mass of each HTA sample in the beginning. After that this value is multiplied by 1000000 times to get results in ppm or mg/kg.

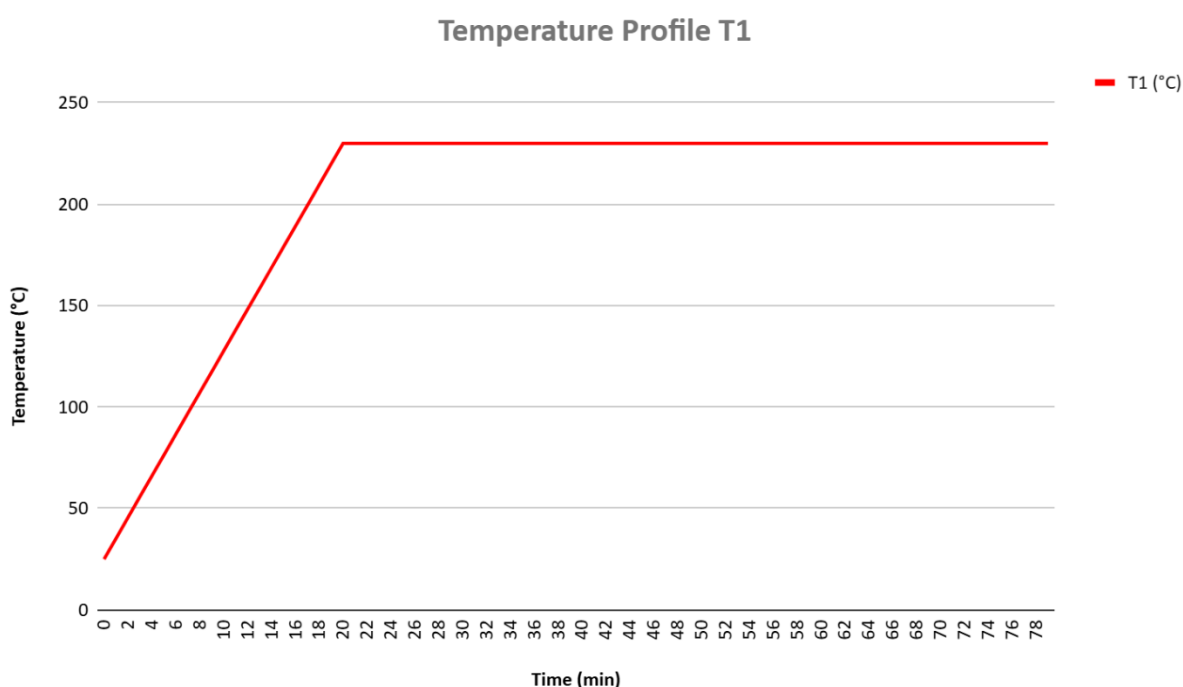


Figure 5. Digestion graph of microwave digestion of HTA samples

3.2.2 Ultimate analysis (organic elements CHNS)

CHNS analysis of coal samples was made on the CHNS-O Elemental Analyzer -by Unicube (Elementar). For all samples 2 measurements were made with the difference in 0.5 mg. Samples were packed into tin containers, and then they were put in the elemental analyzer.

3.3 Methods: Inorganic part - Mineralogical and elemental analyses

In this part, it was selected only 11 coal samples, subjected to controlled combustion and subsequent analytical procedures to support a multi-method geochemical and mineralogical investigation. The analytical workflow combined X-ray diffraction (XRD), X-ray fluorescence (XRF), microwave-assisted acid digestion coupled with inductively coupled plasma optical emission spectrometry (ICP-OES), organic elemental analysis, and Fourier-transform infrared spectroscopy (FTIR). Each method was selected to provide complementary information on mineralogical composition, bulk geochemistry, trace-element distribution, and organic matter characteristics of the coal samples.

XRD analysis was applied to identify and semi-quantify crystalline mineral phases present in the coal and ash residues. XRF was used to determine the bulk major and minor elemental composition of the samples, providing an overview of inorganic geochemical characteristics. ICP-OES was employed for multi-element determination of trace and rare elements at ppm-level concentrations, enabling reliable quantification of elements such as Au, Ag, REE, Sc, Th, and Yb. Prior to ICP-OES analysis, microwave-assisted acid digestion was performed to ensure complete decomposition of the sample matrix, particularly targeting resistant silicate and oxide phases, thereby improving the reliability and accuracy of elemental measurements. In addition, organic elemental analysis was conducted to determine the proportions of carbon, hydrogen, nitrogen, and sulfur, providing insight into the organic geochemical structure of the coal. FTIR spectroscopy was further applied to characterize functional groups and evaluate structural features of both organic matter and mineral-associated phases.

To support these analytical techniques, three types of sample materials were prepared from the collected coal specimens. The primary material consisted of finely ground coal powder with a particle size of approximately 5 μm . The coal was manually pulverized using an agate mortar and pestle until a uniform fine powder was achieved, confirmed when no grinding sound was observed, indicating sufficient comminution and homogenization.

However, during ash preparation, several methodological challenges were encountered. In particular, some samples produced very low ash yields, which limited the amount of material available for subsequent analytical procedures. As a result, additional combustion runs were

performed for selected samples to increase the total ash mass and ensure sufficient material for all planned analyses, including XRD, XRF, ICP-OES, and digestion-based measurements. These adjustments ensured analytical completeness while maintaining consistency across the dataset and minimizing potential bias introduced by insufficient sample quantities.

3.3.1 XRD analysis

The mineral composition of coal was analyzed via low-temperature ash (LTA) using a Rigaku SmartLab X-ray diffractometer (XRD) equipped with a Ni-filtered Cu K α source (energy 8.04 keV, wavelength 1.5406 Å). Diffractograms were recorded at room temperature over a 2θ range of 2.6°–70° with a step size of 0.01° (Yang et al. 2015). This technique has been widely applied to coal-related materials, as reported by several authors (Ward, 2002; Qi et al., 2021; Ward et al., 1999; Ruan & Ward, 2002). Quantitative mineralogical analysis of the XRD data was performed using Crystal Impact software (Match) following established procedures (Rietveld, 1969b).

3.3.2 XRF analysis

XRF was made in the same block of Nazarbayev university with HTA (high temperature ash). Maximum 10-14 samples could be loaded into the machine. And then the computer application shows approximate time to finish the measurement, and then we got the values of different chemical elements in the ppm or %. Then the correction of major elements, such as Si, Al, Fe, Ca, Mg, Na, K, Ti, P, Mn were made to get oxides of major elements. The formula of correction were $\text{Oxide} = \text{XRF value of element} \times (\text{molecular weight of oxide} / \text{atomic weight of element})$.

3.3.3 FTIR analysis

Fourier transform infrared (FTIR) analysis: Functional groups and mineral identification in the coal samples was carried out using a Nicolet iS10 FTIR spectrometer (Thermo Fisher Scientific, Madison, WI, USA) equipped with a diamond/ZnSe attenuated total reflectance (ATR) crystal. Spectra were recorded in the mid-infrared region in absorbance mode over the wavenumber range of 4500–450 cm^{-1} . The obtained FTIR spectra were used to identify both organic functional groups and inorganic mineral phases, including clay minerals and carbonates, based on characteristic absorption bands.

3.3.4 ICP-OES analysis and Microwave digestion

ICP-OES and Microwave digestion was made in the Core Facilities (Block C4). To digest we used 3ml of H_2SO_4 , 3ml of HNO_3 , 3ml of HF , and 1 ml of 3ml of H_2O_2 .

4. Results

4.1. Coal quality and characterization

4.1.1 Results of proximate analysis: Ash yield determination

A total of 31 representative coal samples were selected for ash yield determination in accordance with internationally recognized procedures, including ASTM International standard ASTM D3174 and the equivalent International Organization for Standardization method ISO 1171. These methods involve complete combustion under controlled conditions (typically $\sim 815^\circ\text{C}$) to remove organic matter and quantify the residual inorganic fraction.

The coal ash yield represents the proportion of inorganic residue remaining after complete combustion of coal. It is typically expressed as a percentage, using two formulas (1 and 2) shown below:

$$1) \quad \text{Ash Yield (\%)} = \frac{\text{Mass of ash after combustion}}{\text{Mass of original coal sample}} \times 100$$

2) Mass of ash after combustion = Mass of crucible – Mass of coal remains with crucible

The selected samples provide representative coverage of different coal seams, lithological variations, and mineralogical compositions within the study area. The sampling strategy was designed to include both low-ash and high-ash coals, ensuring that the full variability of mineral matter content is captured. The number of analyzed samples ($n = 30$) is considered adequate for statistically reliable interpretation and is consistent with standard coal quality assessment practices.

The ash yield values obtained range from 3.28% to 54.85%, with an average of approximately 27%, demonstrating substantial heterogeneity in inorganic matter content. The lowest ash yield was recorded in sample MD N1-6 (3.28%), whereas the highest value was observed in MD N1-7 (54.85%). Most samples fall within the moderate ash range (10–40%), indicating variable but generally moderate mineral matter abundance across the dataset.

This variability reflects differences in depositional environments, particularly the degree of clastic input during peat accumulation, as well as post-depositional processes such as diagenetic mineral formation and redistribution. Lower ash yields are characteristic of relatively pure organic coal with minimal detrital influence, whereas higher ash contents suggest significant contributions from mineral phases, including clays, quartz, and sulfide minerals.

Adherence to ASTM and ISO protocols ensures the accuracy, reproducibility, and comparability of the results. Consequently, the ash yield dataset provides a robust and standardized basis for further interpretation of coal quality, mineralogical composition, and the distribution of trace and critical elements within the coal and its combustion residues.

Table 1 Ash yield (%) of representative coal samples from the study area

Samples	Mass of crucible, g	Mass of original coal sample, g	Mass of coal remains with crucible, g	Mass of ash after combustion	Ash yield %
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MD C1-1	12.82	2.25	13.94	1.12	49.78
MD C1-2	15.46	2.12	16.03	0.57	26.89
MD C1-3	18.39	2.46	19.15	0.76	30.89
MD C1-4	13.17	2.27	13.67	0.5	22.03
MD C1-5	10.83	2.11	11.65	0.82	38.86
MD C1-6	10.23	2.22	11.15	0.92	41.44
MD C1-7	28	2.57	28.329	0.329	12.80
MD C2-1	12.79	2.33	13.76	0.97	41.63
MD C2-2	15.42	2.28	15.9	0.48	21.05
MD C2-3	36.6	4.38	37.02	0.42	9.59
MD C2-4	40.71	4.56	41.2	0.49	10.75
MD C2-5	18.35	2.81	18.82	0.47	16.73
MD C2-6	10.2	2.17	10.66	0.46	21.20
MD C2-7	28	2.15	29.17	1.17	54.42
MD C3-1	28	2.33	28.75	0.75	32.19
MD C3-2	18.35	2.35	19.07	0.72	30.64
MD C3-3	12.79	2.28	13.45	0.66	28.95
MD N1-1	10.18	2.43	11.14	0.96	39.51
MD N1-2	10.82	2.16	11.18	0.36	16.67
MD N1-3	13.15	2.27	13.54	0.39	17.18
MD N1-4	27.99	2.4	28.85	0.86	35.83
MD N1-5	15.42	2.74	16.18	0.76	27.74
MD N1-6	46.1	4.58	46.25	0.15	3.28
MD N1-7	13.15	2.37	14.45	1.3	54.85
MD N1-8	10.17	2.2	11.05	0.88	40.00

MD N1-9	36.84	4.73	37.41	0.57	12.05
MD N1-10	10.83	2.25	11.59	0.76	33.78
MD N1-11	27.99	2.53	28.5	0.51	20.16
MD N1-12	18.35	2.19	18.73	0.38	17.35
MD N1-13	15.42	2.12	16.07	0.65	30.66
Average of coal ash yield (%)					27.96

4.1.2 Results of ultimate analysis: Organic elements of coal materials

The results of the ultimate analysis for the 30 representative coal samples reveal notable variability in elemental composition, reflecting both organic matter characteristics and the influence of mineral impurities. The mean concentrations of the analyzed elements are 0.87% N, 18.67% C, 1.02% H, and 0.34% S, indicating generally low carbon content compared to high-rank coals and suggesting a relatively low degree of coalification or significant dilution by inorganic matter.

Nitrogen (N) contents range from 0.29% to 1.28%, with most samples clustering between 0.7% and 1.1%. The lowest value is observed in sample MD C1-1 (0.29%), whereas the highest occurs in MD C2-3 (1.28%). This relatively narrow range suggests a fairly consistent origin of organic matter, with nitrogen likely associated with organic macerals such as vitrinite and inertinite. Slight variations may reflect differences in depositional environments and the degree of microbial alteration.

Carbon (C) content shows a wider variation, ranging from 4.57% to 33.74%. The lowest value is recorded in MD C1-1 (4.57%), while the highest occurs in MD C2-1 (33.74%). Most samples fall within the range of 15–25%, indicating moderate organic carbon content. The relatively low carbon percentages across many samples are consistent with elevated ash yields observed in the same dataset, suggesting significant dilution of organic matter by mineral phases such as clays and quartz. Samples with higher carbon content likely represent cleaner coal intervals with reduced detrital input.

Hydrogen (H) concentrations vary between 0.47% and 1.73%, with a mean value of 1.02%. The lowest hydrogen content is observed in MD C1-1 (0.47%), whereas the highest is found in

MD C2-1 (1.73%). Hydrogen content generally correlates with the proportion of volatile matter and the type of organic constituents present. The relatively low hydrogen values across the dataset may indicate a predominance of more aromatized organic structures or the influence of mineral dilution.

Sulfur (S) content exhibits the most pronounced variability, ranging from 0.00% to 8.07%, with an average of 0.34%. Most samples contain very low sulfur concentrations (close to 0%), suggesting generally low sulfur coal. However, an anomalously high sulfur value is observed in sample MD C1-1 (8.07%), along with a moderately elevated value in MD N1-9 (0.74%). These elevated sulfur contents likely reflect localized enrichment of sulfur-bearing minerals, particularly pyrite, which is consistent with petrographic observations of sulfide mineralization. The overall low sulfur content in the majority of samples suggests deposition under relatively oxic to mildly reducing conditions, limiting extensive sulfur incorporation.

The observed variations in elemental composition are closely linked to the heterogeneity of the coal seams, including differences in depositional settings, organic matter input, and post-depositional processes. In particular, the inverse relationship between ash yield and carbon content highlights the significant role of inorganic matter in controlling bulk geochemical composition. Samples with high ash yields typically exhibit reduced carbon and hydrogen contents due to dilution by mineral phases.

The ultimate analysis data indicate that the studied coals are compositionally heterogeneous, with variable organic richness and localized sulfur enrichment. These characteristics are critical for understanding coal quality, combustion behavior, and the potential for trace and critical element enrichment, particularly in relation to mineral-associated phases such as clays and sulfides.

Table 2. Elemental composition (C, H, N, and S, in % unit) of coal samples determined by ultimate analysis

Samples	N	C	H	S
MD C1-1	0,29	4,57	0,47	8,07
MD C1-2	1,25	20,01	1,06	0,00
MD C1-3	0,88	17,59	0,89	0,04

MD C1-4	1,02	25,23	1,44	0,12
MD C1-5	1,14	17,89	1,02	0,00
MD C1-6	1,18	16,99	1,00	0,00
MD C1-7	0,98	24,43	1,36	0,30
MD C2-1	0,69	33,74	1,73	0,00
MD C2-2	0,98	21,60	1,21	0,14
MD C2-3	1,28	24,27	1,24	0,15
MD C2-4	0,96	23,97	1,30	0,16
MD C2-5	1,02	22,78	1,24	0,10
MD C2-6	0,85	20,73	1,08	0,00
MD C2-7	0,39	9,57	0,75	0,00
MD C3-1	0,82	18,04	0,92	0,07
MD C3-2	0,90	16,44	0,87	0,20
MD C3-3	0,60	18,27	0,96	0,00
MD N1-1	0,67	16,79	0,95	0,00
MD N1-2	1,10	19,77	1,04	0,01
MD N1-3	0,86	16,84	0,91	0,06
MD N1-4	0,78	15,60	0,86	0,00
MD N1-5	1,00	17,31	0,99	0,00
MD N1-6	0,83	23,17	0,87	0,03
MD N1-7	0,58	9,85	0,65	0,00
MD N1-8	0,96	14,30	0,77	0,00
MD N1-9	1,05	20,45	1,06	0,74
MD N1-10	0,83	16,40	0,87	0,00
MD N1-11	0,77	18,45	1,09	0,13

MD N1-12	0,78	19,94	1,15	0,00
MD N1-13	0,76	15,02	0,95	0,00
Average	0.87	18.67	1.02	0.34

4.2 Results of coal mineralogy and its inorganic geochemistry

4.2.1 Mineralogical content of coals

X-ray diffraction (XRD) analysis of eleven coal ash samples (Fig. 6; Table 3) reveals a broadly consistent and well-defined mineralogical assemblage, reflecting both the original detrital mineral input of the parent coals and their transformation during high-temperature combustion. The mineralogical composition is strongly dominated by quartz, which constitutes approximately 37–46 wt.%, indicating a high proportion of resistant siliceous material in the precursor coal. Quartz is identified by its characteristic intense reflection at $\sim 26.6^\circ 2\theta$, which remains sharp and well resolved across all samples, suggesting minimal structural alteration during combustion due to its high thermal stability.

The second most abundant phase is kaolinite, accounting for approximately 17–23 wt.%, representing the primary aluminosilicate component derived from clay minerals in the original coal. Although kaolinite is generally expected to undergo dihydroxylation during combustion, its presence in the ash indicates either incomplete transformation or partial preservation of relict clay structures under the applied combustion conditions. In several samples, kaolinite is associated with incipient formation of high-temperature aluminosilicate phases, suggesting progressive thermal evolution.

Feldspar minerals are present in subordinate amounts, ranging from ~ 5 –6 wt.%, and include both potassium- and sodium-bearing aluminosilicates. Their persistence in the ash indicates relatively low reactivity during combustion, as feldspars typically exhibit higher thermal stability compared to clay minerals but are less abundant in the original coal mineral assemblage. Iron-bearing oxide phases, estimated at ~ 3 –5 wt.%, are also consistently detected and are likely represented by hematite and magnetite formed through oxidation of iron sulfides such as pyrite

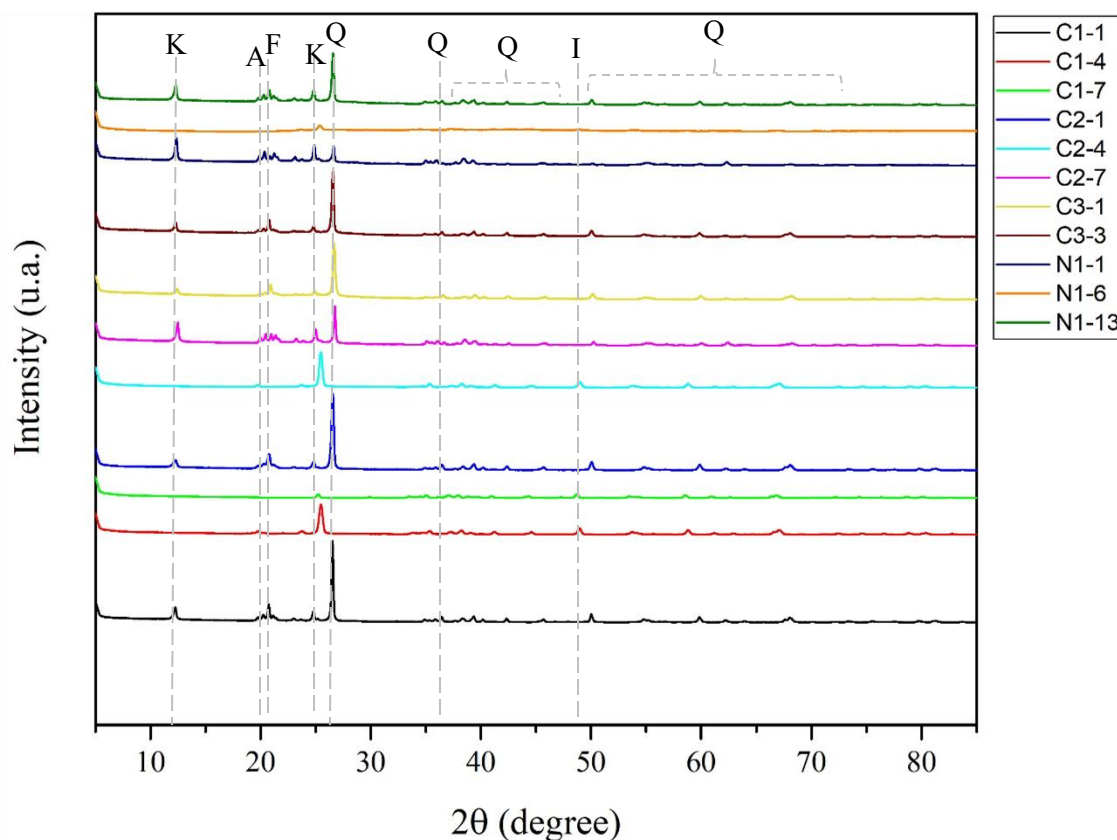
during combustion. The presence of these iron oxides reflects the transformation of sulfide-bearing phases into more stable oxide forms under oxidizing high-temperature conditions.

A notable feature of all samples is the presence of a substantial amorphous (non-crystalline) phase, estimated at approximately 28–33 wt.%, which constitutes a significant fraction of the bulk ash matrix. This amorphous material is primarily attributed to the rapid thermal decomposition of clay minerals (particularly kaolinite) and partial melting of aluminosilicate phases during combustion, leading to the formation of a glassy aluminosilicate matrix. This amorphous fraction plays a critical role in controlling the physicochemical properties of the ash, including reactivity, surface chemistry, and the potential immobilization or release of trace and critical elements.

Semi-quantitative comparisons among the eleven samples show only modest variations in the relative proportions of quartz, kaolinite, feldspar, and iron oxides. The quartz-to-kaolinite ratio remains relatively stable across the dataset, indicating that the overall mineralogical framework is largely consistent throughout the studied coal seams. This suggests that the observed mineral assemblages are primarily controlled by the original coal mineralogy rather than by variations in combustion conditions or analytical artifacts. In other words, the precursor sedimentary environment and detrital input appear to be the dominant factors governing ash mineralogy.

The occurrence of mullite reflections in the XRD patterns further confirms the high-temperature transformation of aluminosilicate phases during combustion, as mullite typically forms above ~950–1000°C from kaolinite-derived intermediates. Its presence, together with quartz persistence and amorphous phase development, indicates that the coal ash samples have undergone complete and effective combustion under controlled conditions. The coexistence of crystalline (quartz, feldspar, mullite, iron oxides) and non-crystalline phases reflects a typical thermally evolved coal ash system.

The coal ash samples are characterized by a relatively uniform mineralogical composition dominated by silica- and alumina-rich phases, with low variability among samples. The system can be classified as a silica–alumina dominated, low-calcium coal ash, which is typical of elastic-input-controlled coal deposits. This mineralogical consistency has important implications for



understanding ash behavior, including its geochemical stability, potential for trace element hosting, and suitability for further industrial or environmental applications such as geopolymer production or immobilization of hazardous elements.

Figure 6. X-ray diffraction (XRD) patterns of eleven coal samples. Abbreviations: Q-quartz; K-kaolinite; I-iron oxide, F-feldspar; and A-amorphous matter.

Table 3. Mineralogical compositions in eleven coal samples, measured by low-temperature ashing XRD (LTA-XRD)

Sample labels	Quartz	Kaolinite	Feldspar	Iron oxides	Amorphous matter
C1-1	42	18	6	4	30

C1-4	40	19	6	4	31
C1-7	38	20	5	4	33
C2-1	41	22	5	3	29
C2-4	39	23	5	3	30
C2-7	37	22	5	3	33
C3-1	45	17	6	3	29
C3-3	46	18	5	3	28
N1-1	43	18	5	4	30
N1-6	41	17	5	5	32
N1-13	39	18	5	5	33

The FTIR spectra of the eleven coal samples (C1–C3 and N1 series) collectively indicate a systematic evolution in organic structure and mineral contribution consistent with progressive coalification (see Fig.7). All samples display a broad O–H stretching band at $\sim 3400\text{--}3300\text{ cm}^{-1}$, attributed to phenolic and alcoholic hydroxyl groups as well as adsorbed moisture, which is more pronounced in the C1 and C2 samples and weakens toward the C3 and N1 series, reflecting a decrease in oxygen-bearing functional groups with increasing rank. Strong aliphatic C–H stretching bands at ~ 2920 and $\sim 2850\text{ cm}^{-1}$ ($-\text{CH}_2-$ and $-\text{CH}_3$) are clearly developed in the C1 and C2 coals but diminish progressively in the C3 and N1 samples, indicating shortening and loss of aliphatic side chains during maturation. The carbonyl C=O band near $\sim 1700\text{ cm}^{-1}$, associated with carboxylic acids, esters, and ketones, is evident mainly in the lower-rank C1–C2 samples and becomes weak or nearly absent in the higher-rank C3 and N1 coals due to decarboxylation processes. In contrast, aromatic C=C stretching vibrations at $\sim 1600\text{--}1500\text{ cm}^{-1}$ become sharper and relatively more intense from C1 to N1, demonstrating an increase in aromaticity and ring condensation. Aliphatic deformation bands at ~ 1450 and $\sim 1375\text{ cm}^{-1}$ decrease accordingly, further confirming the transition from aliphatic-rich to aromatic-dominated structures. The $1300\text{--}1000\text{ cm}^{-1}$ region shows composite absorptions related to C–O stretching in phenols, ethers, and alcohols, with additional contributions from mineral matter, particularly clay minerals (Si–O stretching around $\sim 1030\text{--}1100\text{ cm}^{-1}$). Mineral-related features are also suggested by bands near $\sim 915\text{--}950\text{ cm}^{-1}$ (Al–OH bending in clays), indicating the presence of silicate-bearing inorganic

phases within the coal matrix. Aromatic C–H out-of-plane bending vibrations in the 900–700 cm^{-1} region become better defined in the C3 and N1 samples, consistent with more ordered and condensed aromatic structures. Overall, the combined organic and mineral FTIR signatures demonstrate a clear coalification trend from the oxygen- and aliphatic-rich C1 coals through transitional C2 to the more aromatic, structurally ordered C3 and N1 coals, with clay minerals and minor carbonates constituting the dominant inorganic components.

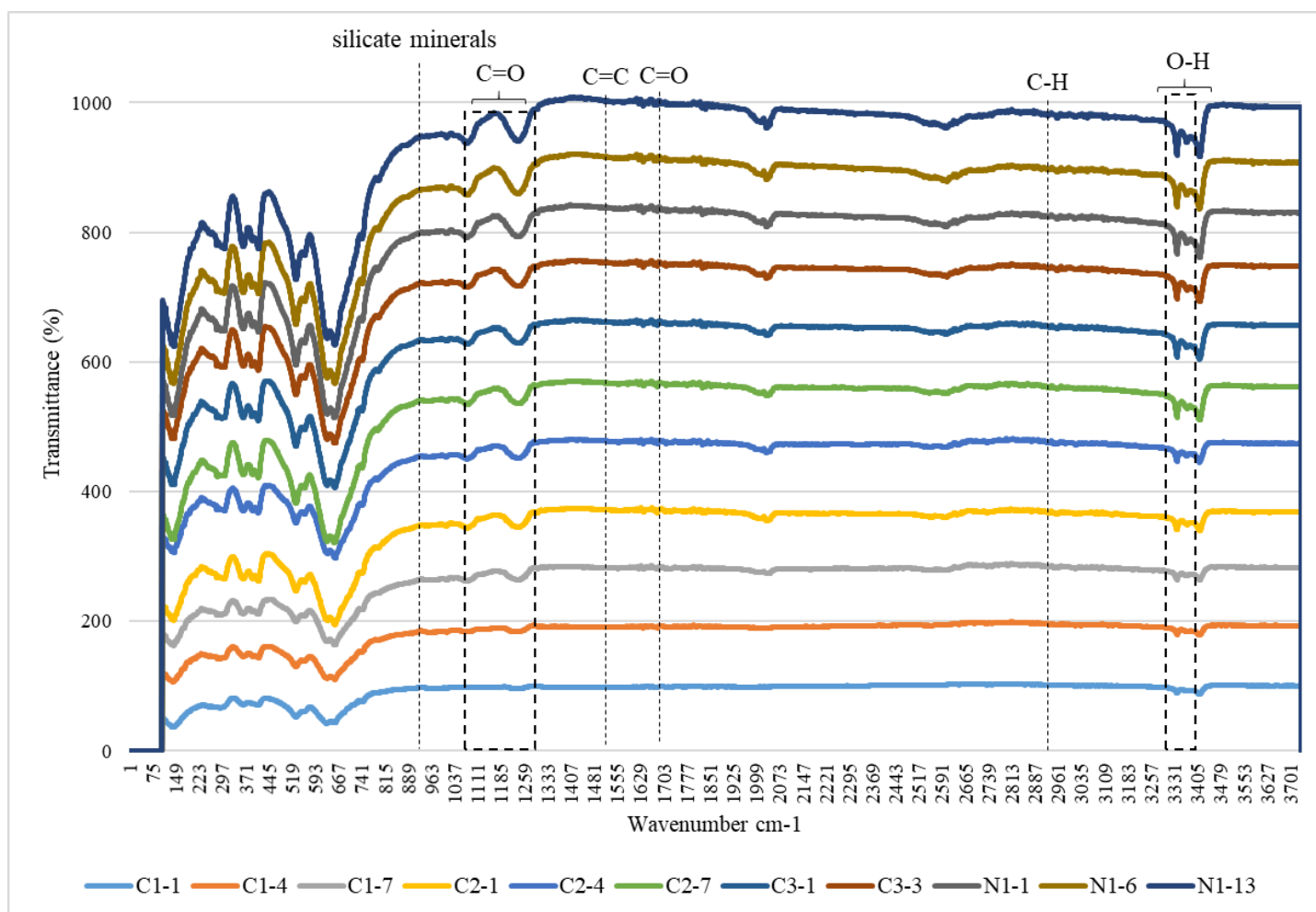


Figure 7. FTIR spectra of eleven coal samples

4.2.2 Elemental analysis (major and trace elements) using XRF and ICP-OES with microwave digestion

The results of XRF for the coal ash samples (see [Table 4](#) and [Fig. 8](#)) showing quantitative insight into the bulk major element composition, confirming a predominantly silicate-dominated geochemical system with subordinate contributions from aluminosilicate, iron-bearing, and minor accessory mineral phases.

Based on the XRF results, silicon dioxide (SiO_2) is the most abundant oxide, with concentrations ranging from 22.451 to 57.144 wt% and an average of 44.503 wt%. These high values clearly indicate that quartz is the dominant mineral phase in the ash samples. The wide compositional range reflects variable detrital input and differences in the proportion of quartz relative to other mineral constituents such as clay minerals and minor carbonates.

Aluminum oxide (Al_2O_3), determined by XRF to vary between 4.301 and 18.365 wt% (average 9.321 wt%), represents the second most abundant component. This oxide is primarily associated with aluminosilicate minerals, particularly kaolinite and, to a lesser extent, illite or feldspar. Elevated Al_2O_3 contents in samples such as N1-1 and C2-7 suggest enrichment in clay minerals, which may reflect enhanced weathering, sedimentary sorting, or increased input of fine-grained detrital material. The relationship between Al_2O_3 and SiO_2 further supports the dominance of mixed aluminosilicate phases.

Iron oxide (Fe_2O_3) concentrations obtained from XRF are relatively low, ranging from 0.223 to 2.267 wt% with an average of 0.756 wt%. These values indicate minor but consistent contributions from iron-bearing minerals. In coal ash systems, Fe_2O_3 is commonly derived from the oxidation of pyrite during combustion, as well as from the presence of iron oxides such as hematite. Slight enrichment in certain samples (e.g., C1-1) suggests localized accumulation of iron-bearing phases, possibly linked to primary pyrite distribution or diagenetic processes.

Calcium oxide (CaO) shows generally low concentrations in the XRF dataset, ranging from 0.0682 to 2.7886 wt%, with an average of 0.3446 wt%. The notably elevated CaO value in sample C1-7 suggests the presence of carbonate minerals such as calcite or Ca-bearing silicates. However, the overall low CaO content across most samples indicates minimal carbonate contribution, reinforcing the interpretation of a predominantly siliciclastic system.

Titanium dioxide (TiO_2), as determined by XRF, ranges from 0.444 to 3.244 wt% with an average of 1.322 wt%. This oxide is typically associated with resistant heavy minerals such as rutile, anatase, or ilmenite. Higher TiO_2 concentrations in samples like N1-1 and C2-7 may indicate enrichment in heavy mineral fractions or a stronger contribution from source rocks rich in titanium-bearing phases. Due to its relative immobility during weathering, TiO_2 also serves as a useful indicator of provenance.

Potassium oxide (K_2O) concentrations obtained from XRF range from 0.000 to 0.573 wt%, with an average of 0.273 wt%. K_2O is generally associated with K-bearing minerals such as illite and K-feldspar. The absence of detectable K_2O in samples N1-1 and N1-6 suggests a dominance of kaolinite or advanced leaching of potassium during weathering. Conversely, slightly higher K_2O values in samples such as C3-1 indicate minor contributions from illitic clays or feldspar components.

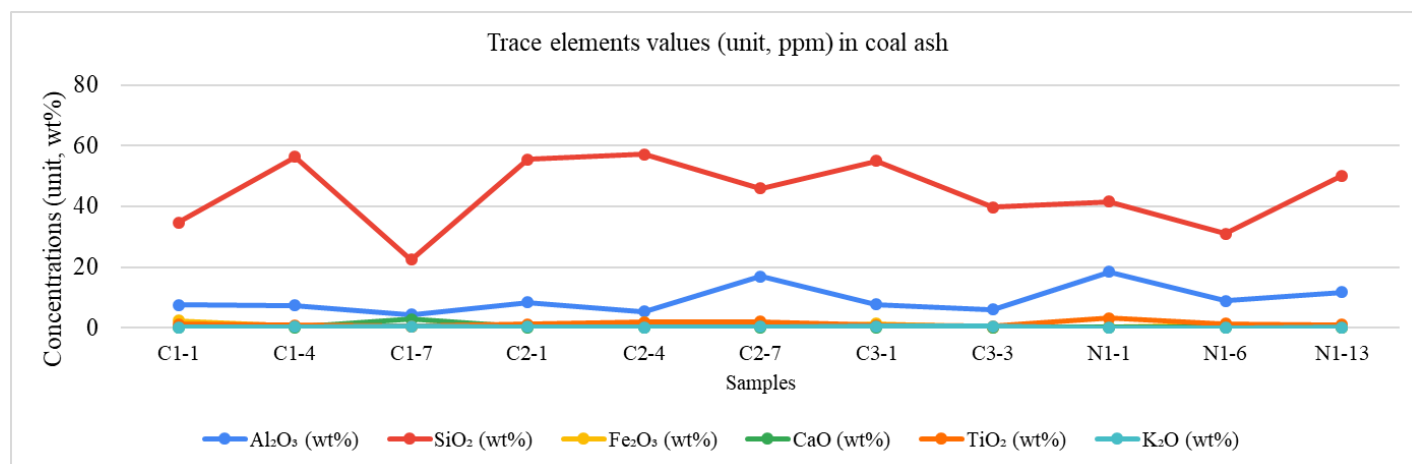
The XRF results confirm that the coal ash samples are characterized by high SiO_2 and moderate Al_2O_3 contents, indicating dominance of quartz and clay minerals, with minor contributions from iron oxides, carbonates, and accessory heavy minerals. The observed variability in oxide concentrations reflects differences in source material, sedimentary input, and post-depositional processes such as weathering and diagenesis. These geochemical characteristics are consistent with siliciclastic-dominated coal systems and provide a robust basis for interpreting mineralogical controls and element distribution in the studied samples.

Table 4. Major element composition (wt%) of coal ash samples determined by XRF, including minimum, maximum, and average values.

Sample	Al_2O_3 (wt%)	SiO_2 (wt%)	Fe_2O_3 (wt%)	CaO (wt%)	TiO_2 (wt%)	K_2O (wt%)
C1-1	7.498	34.730	2.267	0.0754	1.116	0.187
C1-4	7.358	56.212	0.522	0.1038	0.849	0.289
C1-7	4.301	22.451	0.343	2.7886	0.444	0.477
C2-1	8.407	55.489	0.244	0.1102	1.235	0.243

Sample	Al ₂ O ₃ (wt%)	SiO ₂ (wt%)	Fe ₂ O ₃ (wt%)	CaO (wt%)	TiO ₂ (wt%)	K ₂ O (wt%)
C2-4	5.380	57.144	1.611	0.0926	1.869	0.169
C2-7	16.910	45.939	0.347	0.1581	2.067	0.359
C3-1	7.706	55.033	1.317	0.1229	0.879	0.573
C3-3	5.996	39.751	0.237	0.1002	0.519	0.479
N1-1	18.365	41.607	0.326	0.0861	3.244	0.000
N1-6	8.817	31.012	0.884	0.0847	1.280	0.000
N1-13	11.796	50.160	0.223	0.0682	1.044	0.224
Minimum	4.301	22.451	0.223	0.0682	0.444	0.000
Maximum	18.365	57.144	2.267	2.7886	3.244	0.573
Average	9.321	44.503	0.756	0.3446	1.322	0.273

Note: Shown after oxide conversions. $\text{Oxide} = \text{Element} \times (\text{MW}_{\text{oxide}} / \text{AW}_{\text{element}})$. Factors: $\text{SiO}_2 \times 2.139$; $\text{Al}_2\text{O}_3 \times 1.889$; $\text{Fe}_2\text{O}_3 \times 1.430$; $\text{CaO} \times 1.399$ (Ca ppm $\rightarrow$ wt% before conversion);



$\text{TiO}_2 \times 1.668$; $\text{K}_2\text{O} \times 1.205$. Mg, Na, P, S, Mn not converted (trace or absent for oxide form). HTA = 815 °C, 4 h.

Figure 8. XRF results showing major oxide elements in coal ash samples from the Molodezhny coal mine

The trace element concentrations of the coal ash samples, determined by ICP-OES following microwave-assisted acid digestion, reveal significant variability and selective enrichment of precious metals, REE, and other trace constituents, using 11 samples (shown in [Table 5](#) and [Fig. 9](#)). This analytical approach ensures near-complete dissolution of the ash matrix, including resistant silicate and oxide phases, thereby providing reliable bulk concentrations of trace elements.

Microwave digestion plays a critical preparatory role by breaking down refractory minerals such as quartz and aluminosilicates using strong acid mixtures (commonly HNO_3 , HF, and HCl), allowing elements bound within crystalline lattices to be released into solution. This step is particularly important for coal ash samples, where trace elements may be encapsulated within glassy phases or tightly bound to mineral structures. The subsequent ICP-OES analysis enables simultaneous multi-element detection with good precision and sensitivity, making it suitable for quantifying both moderately abundant and trace-level elements.

Among the analyzed elements, gold (Au) exhibits consistently elevated concentrations across all samples, ranging from 10.22 to 23.64 ppm, with an average of 17.5 ppm. This relatively narrow range and consistently high values indicate a uniform enrichment of gold within the studied coal ashes. Such enrichment suggests that gold is likely associated with specific mineral phases, most plausibly sulfide minerals such as pyrite or related micro-inclusions.

Silver (Ag) shows a wider variability, with concentrations ranging from below detection (0.00 ppm) to 2.08 ppm, and an average of 0.4 ppm. While generally low, the elevated values in samples such as C2-4 and N1-13 indicate localized enrichment. This variability suggests that silver distribution is more heterogeneous compared to gold and may be controlled by discrete mineral phases such as sulfosalts or galena, or by micro-scale geochemical conditions during mineral formation.

The rare earth element praseodymium (Pr) displays moderate variability, ranging from non-detectable levels to 24.53 ppm, with an average of 7.4 ppm. The highest concentration observed in sample N1-1 suggests localized REE enrichment, potentially linked to adsorption onto clay minerals or association with phosphate or organic matter phases. The irregular distribution of Pr indicates that REE enrichment is not uniform and may depend on specific geochemical conditions.

Scandium (Sc) concentrations vary from 0.00 to 21.50 ppm, averaging 5.7 ppm. Elevated Sc values in certain samples (e.g., C2-4 and C1-1) suggest an association with aluminosilicate minerals, particularly clay phases or fine-grained detrital material. The absence of Sc in several samples may reflect either low original concentrations or analytical detection limits, as well as possible mineralogical controls on its distribution.

A particularly notable feature of the dataset is the highly variable concentration of samarium (Sm), which ranges from non-detectable levels to extremely high values of 193.52 ppm (N1-1), with an average of 23.9 ppm. Significant enrichment is also observed in samples C3-1 and C2-7. This strong variability indicates selective concentration of Sm in specific samples, likely controlled by REE-bearing mineral phases or adsorption onto clay minerals. Such high concentrations may point to localized enrichment zones or specific mineral hosts that preferentially incorporate middle REE.

Thorium (Th) concentrations range from 0.00 to 31.34 ppm, with an average of 12.2 ppm. Thorium is typically associated with resistant accessory minerals such as monazite, zircon, or xenotime. Elevated Th values in samples like N1-6 and C1-1 suggest the presence of such minerals, while its absence in some samples indicates heterogeneous distribution. The relatively high Th content in several samples may also have implications for radiogenic heat production and environmental considerations.

Ytterbium (Yb), representing heavy rare earth elements (HREE), shows concentrations between 0.00 and 33.13 ppm, with an average of 4.6 ppm. The exceptionally high value in sample C1-1 suggests strong localized enrichment, potentially linked to heavy mineral phases or specific adsorption processes. In contrast, most other samples exhibit low Yb concentrations, indicating limited HREE enrichment overall.

The ICP-OES results following microwave digestion demonstrate that the coal ash samples contain variable but locally significant concentrations of economically important trace elements, including Au and REE. The data indicate that element distribution is highly heterogeneous and strongly controlled by mineralogical hosts and geochemical processes. Gold shows relatively consistent enrichment, whereas REE (particularly Sm and Pr) and elements such as Th and Sc display pronounced variability, suggesting selective concentration mechanisms. These findings are consistent with the presence of mineral phases such as clay minerals, sulfides, and accessory REE-bearing minerals, which play a key role in controlling trace element behavior in coal ash systems.

Table 5. Trace element concentrations (ppm) of coal ash samples determined by ICP-OES after microwave-assisted acid digestion, showing the distribution of Ag, Au, Pr, Sc, Sm, Th, and Yb, with average values.

Elements	C1-1	C1-4	C1-7	C2-1	C2-4	C2-7	C3-1	C3-3	N1-1	N1-6	N1-13	Average
Ag	0.14	0.09	0.00	0.15	1.82	0.27	0.07	0.07	bdl	bdl	2.08	0.4
Au	15.02	13.84	15.46	19.72	23.40	18.47	23.64	13.40	10.22	20.23	18.91	17.5
Pr	0.00	5.94	7.70	10.03	7.86	0.00	0.00	4.80	24.53	11.08	9.22	7.4
Sc	14.06	6.87	11.72	2.93	21.50	0.00	0.00	5.12	0.98	bdl	bdl	5.7
Sm	bdl	bdl	bdl	bdl	bdl	28.33	40.59	0.00	193.52	bdl	bdl	23.9
Th	29.68	6.58	8.65	7.05	19.81	0.00	0.00	6.71	6.77	31.34	17.35	12.2
Yb	33.13	0.57	1.56	0.38	1.19	4.50	6.71	0.34	0.00	2.11	0.59	4.6

Note: bdl - below detection limit

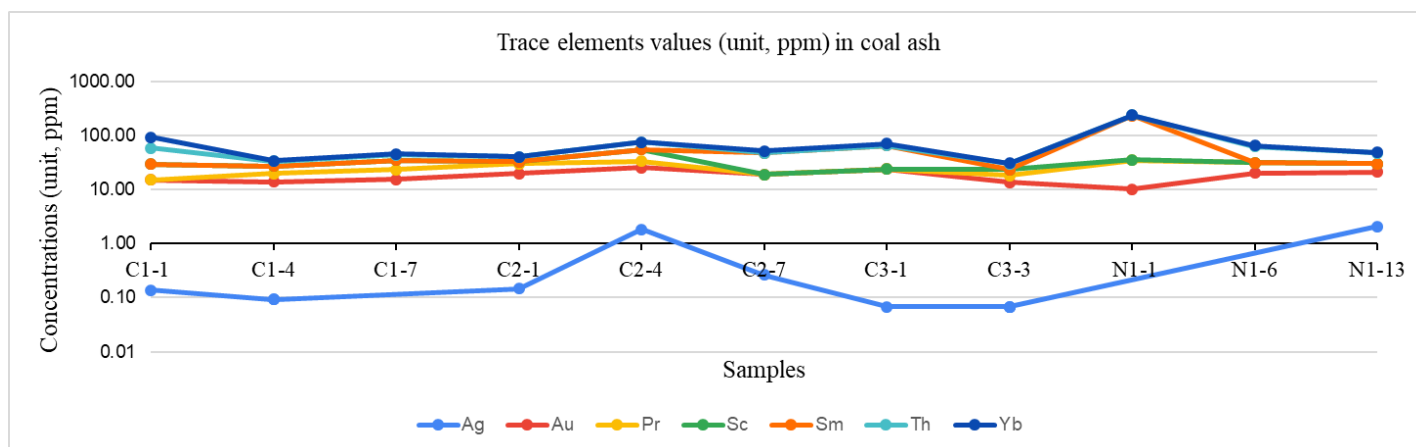


Figure 9. ICP-OES results showing selected trace elements in coal ash samples from the Molodezhny coal mine

5. Discussion

5.1 Economic and Industrial Implications trace elements (Au, Ag, Th, Pr, Sc, Sm, Yb) from coal ash

The trace element data (Au, Ag, Th, Pr, Sc, Sm, and Yb) in coal ash were evaluated for their economic implications using concentration coefficients (CC). The CC values, normalized to the average composition of world hard coal (WHC; Ketris and Yudovich, 2009), reveal a highly heterogeneous geochemical behavior characterized by extreme enrichment of gold and contrasting depletion–enrichment patterns among trace and REE (see Table 6 and Fig.10).

Table 6. Average concentrations of selected trace elements from 11 samples determined by ICP-OES, with mean values compared to world hard coal (WHC; Ketris and Yudovich, 2009).

Elements	Whole samples average	WHC	CC
Ag	0.4	0.63	0.67
Au	17.5	0.02	728.41
Pr	7.4	26.00	0.28
Sc	5.7	24.00	0.24
Sm	23.9	14.00	1.70
Th	12.2	23.00	0.53
Yb	4.6	6.90	0.67

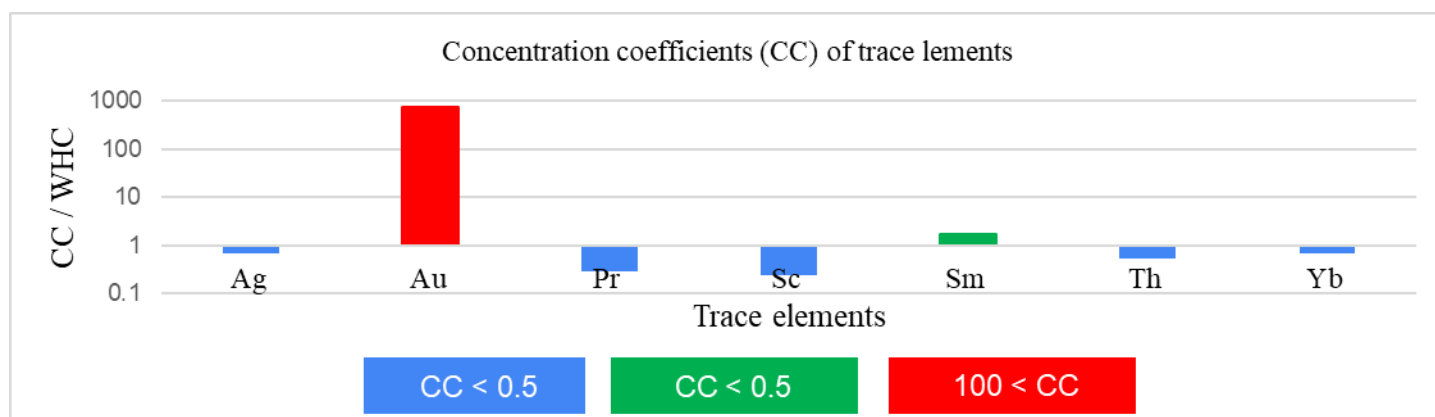


Figure 10. Concentration coefficients (CC) of trace elements in coal ash from Molodezhny coal mine, normalized by the average concentrations of trace elements in world hard coal (WHC, [Ketris Yudovich, 2009](#)).

Among all investigated elements, gold (Au; CC = 728.4) exhibits an exceptionally high enrichment relative to world hard coal averages. This magnitude of enrichment places Au in a highly anomalous geochemical category and strongly suggests the presence of concentrated auriferous phases within the coal matrix. Such extreme CC values are typically not explained by uniform lattice incorporation but instead indicate discrete mineral or sub-micron particulate hosts, including nano- to micro-sized native gold particles, gold-bearing sulfides (particularly pyrite and arsenopyrite), or organic-bound colloidal gold associations ([Finkelman, 1993](#); [Seredin and Finkelman, 2008](#)). In coal systems, Au enrichment of this magnitude is commonly interpreted as evidence of either hydrothermal input into the peat-forming environment or secondary redistribution and precipitation during diagenesis and coalification processes, where organic matter and sulfides act as strong geochemical traps for Au.

Gold mineralization in coal basins is not unique to this deposit. As [Parnell \(2019\)](#) noted, gold enrichment in organic-rich sedimentary formations is globally distributed and linked to Carboniferous Variscan cycling, with Central Asia specifically identified as one of the key regions where gold mineralization overlapped with coal deposition ([Figure 11](#)). In Kazakhstan specifically, gold occurs in carbonaceous sediments and is particularly concentrated near thrust surfaces, residing in pyrite and arsenopyrite at up to 150 ppm ([Levitan, 2008, cited in Parnell, 2019](#)). This

regional context supports the interpretation that the anomalous Au values observed at Molodezhny may reflect a real geological signal rather than analytical error.

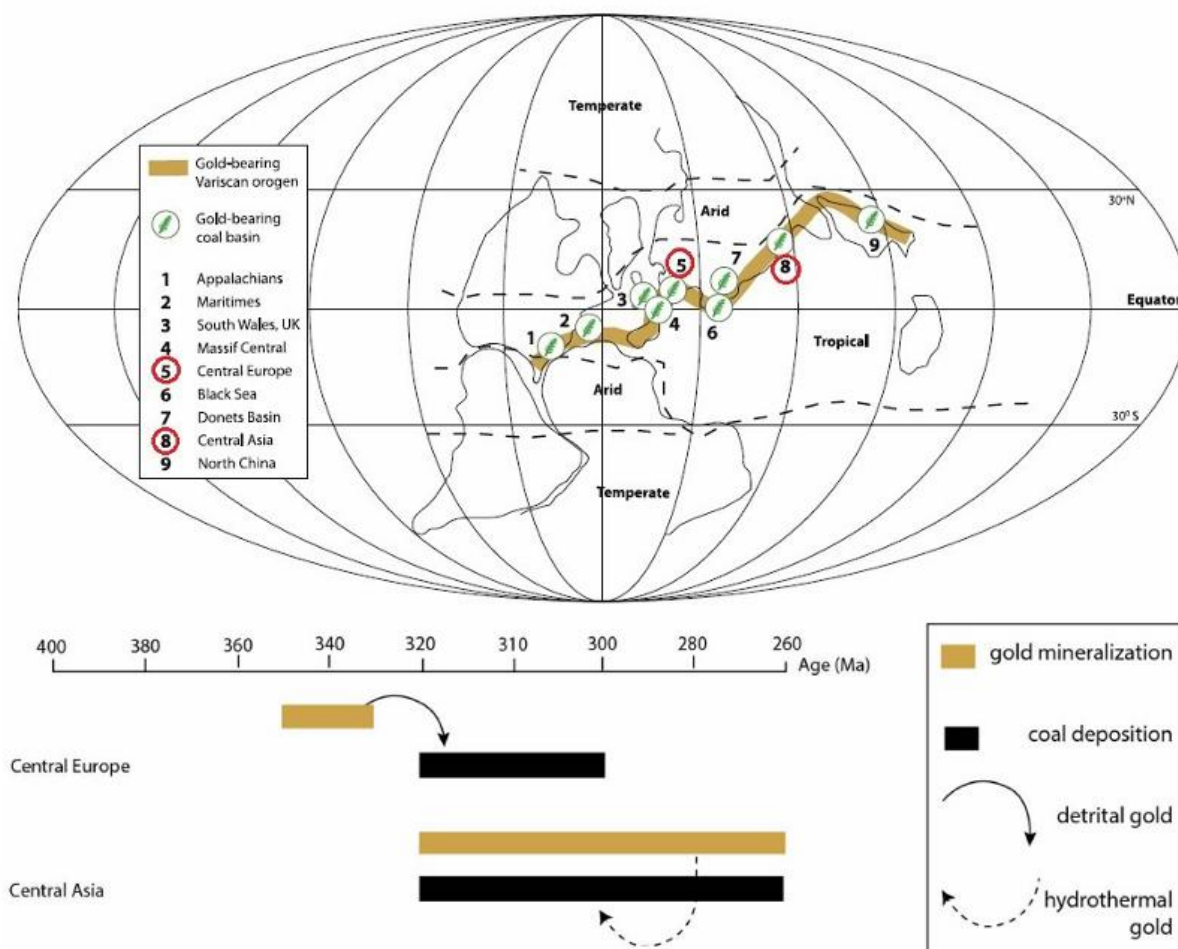


Figure 11. The Variscan orogenic belt is mineralized with gold deposits in a tropical climate zone during the Late Carboniferous, examining the correlation between gold mineralization and coal deposition along the Variscan Orogen, as well as the mechanisms of gold supply to coal (detrital and hydrothermal). (adapted from [Boucot et al., 2013](#); [Parnell, 2019](#)).

The extraordinarily high CC value further suggests that gold is not homogeneously distributed but is likely concentrated in “nugget-like” or localized mineralized domains, which become strongly concentrated in ash during combustion due to the removal of organic carbon. Pyrite-associated gold is particularly significant in such systems, as combustion collapses sulfide structures and enriches residual metallic phases in ash residues, thereby amplifying apparent

concentrations (Finkelman et al., 2002). Therefore, the Molodezhny coal appears to represent a highly gold-fertile system with strong metalliferous characteristics.

Several potential mechanisms may explain the gold enrichment observed at Molodezhny. As illustrated in Figure 12, organic matter in sedimentary systems can accumulate metals through multiple pathways, including hydrothermal mineralizing fluids, intrusion-related distillates, and oil migration processes (Parnell et al., 1993). Notably, hydrothermal deposits are associated with metals such as U, Ni, Co, and Bi, while radiation products are linked to U, Th, and REE. This is consistent with our findings where Th shows variable enrichment and gold may be linked to hydrothermal fluid activity in the Karagandy basin, given its complex Hercynian tectonic history

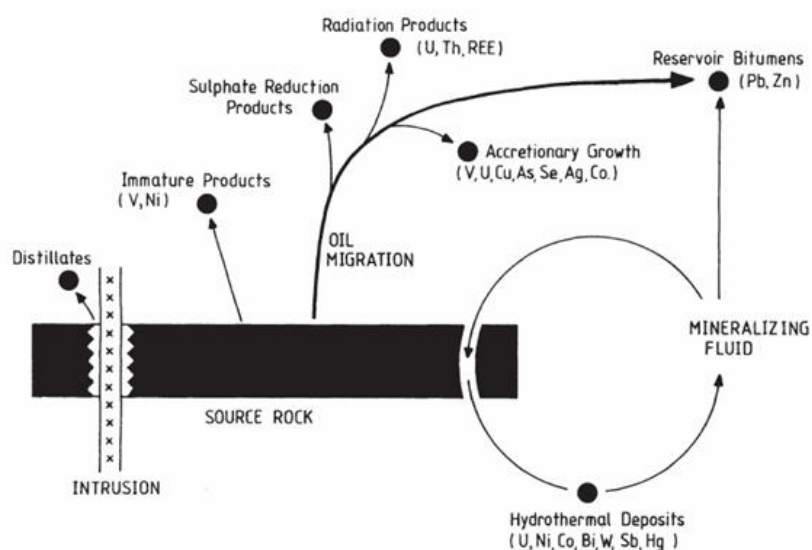


Figure 12. Diverse origins of organic matter (bitumens) relative to sedimentary source rock. (Parnell et al., 1993).

In contrast, silver (Ag; CC = 0.67) remains slightly depleted relative to WHC, despite its geochemical affinity with Au in sulfide systems. This decoupling between Au and Ag suggests differential partitioning behavior during mineralization, where gold is preferentially scavenged by organic matter or fine pyritic phases, whereas silver may remain more dispersed or partially volatilized during combustion. Ytterbium (Yb; CC = 0.67) similarly shows moderate depletion, indicating limited incorporation into resistant heavy rare earth element (HREE) mineral phases.

Thorium (Th; CC = 0.53) also shows depletion, reflecting its typical association with accessory minerals such as monazite and zircon, which appear to be either scarce or not effectively

concentrated in the ash matrix. This suggests a limited contribution from detrital heavy mineral assemblages in the parent sediment source.

A more pronounced depletion is observed for praseodymium (Pr; CC = 0.28) and scandium (Sc; CC = 0.24), indicating strong fractionation away from these elements during coal formation and combustion. The low Sc values suggest limited clay-mineral control or inefficient retention in aluminosilicate phases at high temperature, while Pr depletion reflects scarcity of LREE-bearing phosphates such as apatite or monazite in the original sedimentary system.

In contrast, samarium (Sm; CC = 1.70) shows clear enrichment relative to WHC. This selective enrichment indicates preferential retention of middle rare earth elements (MREEs), likely controlled by adsorption onto clay minerals or incorporation into resistant phosphate phases. Such fractionation patterns, where MREEs are relatively enriched compared to LREEs, are commonly reported in coal-hosted REE systems and are interpreted as the result of differential stability of REE-bearing minerals and surface-complexation processes during diagenesis and combustion ([Seredin and Dai, 2012](#)).

The CC distribution pattern from the Molodezhny coal ash is dominated by an extreme gold anomaly, combined with general depletion of most trace elements and selective enrichment of Sm. This suggests a geochemically complex system controlled by (i) hydrothermal or syngenetic Au introduction, (ii) strong affinity of Au with organic matter and sulfides, and (iii) limited availability of accessory heavy minerals and LREE-bearing phosphates. The resulting geochemical signature reflects both source-rock inheritance and secondary redistribution processes during coalification and combustion, emphasizing the metalliferous nature of the deposit and its potential significance as a gold-enriched coal system ([Ketris and Yudovich, 2009](#); [Finkelman et al., 2002](#); [Seredin and Finkelman, 2008](#)).

Industrial implications: The visual heterogeneity of the coal ash samples from the Molodezhny coal mine reflects variations in mineralogical composition, ash color, particle size distribution, and thermal transformation behavior. The lighter gray to whitish ashes indicate silica–alumina-dominated compositions typical of quartz-rich systems, whereas darker tones suggest a relatively higher contribution of Fe-bearing phases and partially transformed aluminosilicate residues. These macroscopic differences are directly relevant to downstream industrial utilization.

The relatively high proportion of coal ash (average 27.9 wt.%) in association with quartz significantly enhances the industrial potential of these samples. The material can be broadly classified as aluminosilicate-rich coal combustion residue, comparable to coal fly ash used in construction and cement industries (Sear, 2001; Heidrich, Feuerborn and Weir, 2013). This silica–alumina-rich composition places the material within the compositional range of widely used supplementary cementitious materials such as fly ash and metallurgical slags, supporting its suitability for construction and materials engineering applications.

From a construction materials perspective, the aluminosilicate-rich coal ash matrix provides the basis for pozzolanic and geopolymeric reactivity. Upon alkaline activation, the amorphous aluminosilicate fraction participates in the formation of sodium aluminosilicate hydrate (N–A–S–H) gels (Davidovits, 1991; Provis and van Deventer, 2009). Consequently, Molodezhny coal ash can be utilized as a supplementary cementitious material, improving mechanical strength and durability while reducing Portland cement consumption and associated CO₂ emissions. In addition, it serves as an effective geopolymer precursor for low-carbon binders and as a fine filler in concrete, enhancing particle packing and reducing permeability.

Quartz, although largely inert, plays a complementary role by enhancing mechanical strength and durability. Its high hardness and chemical stability make it suitable as a micro-aggregate in cementitious systems and as a stabilizing component in ceramic and refractory materials (Scrivener, Snellings and Lothenbach, 2016).

The quartz–coal ash association is particularly advantageous for ceramic applications. The coal ash fraction contributes to sintering behavior during processing, while quartz regulates drying shrinkage and thermal expansion. During firing, aluminosilicate phases may transform into mullite (Al₆Si₂O₁₃), a phase responsible for high mechanical strength and thermal resistance (Kingery, Bowen and Uhlmann, 1976). These characteristics support the use of Molodezhny coal ash in the production of bricks, tiles, and lightweight aggregates.

Beyond conventional uses, aluminosilicate-rich coal ash can be converted into advanced functional materials. Hydrothermal processing enables the synthesis of zeolites with high surface area, suitable for catalysis, ion exchange, and gas separation (Querol et al., 2007). Furthermore, the amorphous aluminosilicate fraction contributes to adsorption capacity, facilitating the removal of heavy metals and organic contaminants from aqueous systems (Bhatnagar and Sillanpää, 2010).

5.2 Host phases and mineralogical controls of trace elements (Au, Ag, Th, Pr, Sc, Sm, Yb) in coal samples

The correlation matrix (Fig. 13) provides clear evidence that the distribution of trace elements (Au, Ag, Th, Pr, Sc, Sm, Yb) in the studied coal samples is predominantly governed by mineralogical controls, with only selective and secondary influence from organic matter, consistent with established coal geochemical models (Swaine, 1990; Ward, 2002; Finkelman et al., 1994). A very strong coupling between gold (Au), ash yield, and scandium (Sc) (Au–ash = 0.98; Au–Sc = 0.97) indicates that Au is primarily hosted within the inorganic mineral fraction, most likely associated with aluminosilicate-rich and ash-forming phases, as commonly reported for mineral-associated noble metal occurrences in coal systems (Finkelman, 1995; Dai et al., 2012). This mineral affinity is further supported by positive correlations with Pr (0.85), Sm (0.64), and Th (0.57), reinforcing the interpretation that REE and actinide-like elements are partly co-enriched in detrital and authigenic mineral assemblages controlling ash formation (Seredin and Dai, 2012; Dai et al., 2016).

The association of gold with organic matter in coal systems has been widely reported. The so-called 'invisible gold' occurs as ionic gold in solid solution within arsenian pyrite, which is not detectable even by electron microscopy (Cook & Chrysosoulis, 1990). Gold content generally increases with arsenic content in the host mineral, since gold can substitute Fe in the arsenian pyrite lattice (Wu & Delbove 1989). Furthermore, organic matter can play a significant role in gold transport and deposition, as metal-organic compounds form when metal cations attach to organic ligands through oxygen, sulfur, and nitrogen bonds (Giordano & Kharaka, 1994). This is particularly relevant for the Molodetzny deposit, where the strong correlation between Au and ash yield ($r = 0.98$) suggests mineral-bound gold, while the possible organic association cannot be fully excluded without SEM-EDS analysis.

Scandium shows a similarly strong association with ash yield, confirming its robust partitioning into clay-rich and aluminosilicate minerals, which act as the principal host phases in coal systems (Ketriss and Yudovich, 2009; Ward, 2002). Within the rare earth element group, Pr and Sm exhibit strong mutual correlation (0.87) and significant association with Sc (0.77), suggesting a coherent mineral-controlled REE subsystem, typically linked to detrital clays, kaolinite, and other aluminosilicate phases (Seredin and Dai, 2012). Sm also maintains moderate

correlations with both Au and ash, indicating partial co-precipitation or adsorption onto mineral substrates during diagenetic processes.

In contrast, Yb and Th display more complex geochemical behavior, characterized by a strong inter-element correlation (0.85) combined with moderate positive relationships with organic carbon ($\text{Yb-C} = 0.74$; $\text{Th-C} = 0.46$). This dual behavior suggests mixed host-phase control, where these elements are partly incorporated into mineral lattices while also showing affinity for organic matter or organo-mineral complexes, likely through adsorption onto humic substances or association with finely dispersed mineral-organic interfaces (Hower et al., 2013; Dai et al., 2016).

Silver (Ag) shows comparatively weak and irregular correlations with the studied elements, including only a moderate relationship with Au (0.43) and Th (0.50), indicating a dispersed geochemical occurrence and weaker structural control by specific mineral phases. Such behavior is typical for Ag in coal systems, where it may occur in trace sulfide phases or be distributed among multiple minor host minerals (Swaine, 1990; Finkelman et al., 1994).

Ash yield emerges as the dominant controlling factor across the dataset, exhibiting exceptionally strong correlations with Au and Sc and significant relationships with most trace elements, confirming its role as a robust proxy for total mineral-bound elemental load (Ketris and Yudovich, 2009). Conversely, organic carbon shows predominantly negative correlations with most elements, reinforcing its role as a diluting phase for inorganic-associated elements, except in the case of Yb and Th where partial organic association is evident.

The geochemical relationships clearly demonstrate that trace element distribution in these coal samples is mainly controlled by mineralogical host phases—particularly aluminosilicate and ash-forming minerals—while organic matter plays a secondary but selective role in the uptake of specific elements such as Th and Yb, reflecting a complex interplay between inorganic mineral hosting and organo-mineral interactions (Ward, 2002; Seredin and Dai, 2012; Dai et al., 2016).

	Ag	Au	Pr	Sc	Sm	Th	Yb	Ash	C
Ag	1								
Au	0.434654	1						1	Strong Positive
Pr	0.100731	0.851247	1					0.5	Moderate
Sc	0.410066	0.971102	0.774836	1				0	No correlation
Sm	0.092715	0.635197	0.866743	0.466586	1			-0.5	Moderate Negative
Th	0.495263	0.572122	0.13909	0.639311	-0.11011	1		-1	Strong
Yb	0.128001	0.367224	0.123194	0.44297	-0.11197	0.851838	1		
Ash	0.533076	0.980235	0.738356	0.978694	0.495722	0.688302	0.433693	1	
C	-0.267	-0.22336	-0.33628	-0.13609	-0.43668	0.4627	0.735791	-0.15747	1

Figure 13. Pearson correlation coefficient matrix (r) between geochemical parameters for coal samples (Abbreviations: C - organic carbon; Ash -coal ash).

5.3 Sediment provenance region for Au, Ag, Th and REE (Pr, Sc, Sm, Yb) in coal samples

The geochemical ratios of major oxides in the Molodezhny coal high-temperature ash (HTA) samples were applied to reconstruct sediment provenance and evaluate weathering intensity of the source rocks, following established sedimentary geochemistry approaches (Nesbitt and Young, 1982; 1984; Hayashi et al., 1997; Junussov et al., 2025). These ratios are widely used because major immobile oxides such as Al_2O_3 and TiO_2 retain the geochemical signature of parent rocks during weathering, transport, and diagenesis, making them reliable tracers of provenance and chemical alteration processes (Young and Nesbitt, 1998; Taylor and McLennan, 1985).

The $\text{Al}_2\text{O}_3/\text{TiO}_2$ ratio is a robust provenance indicator because both Al and Ti are relatively immobile during surface processes, but are hosted in different mineral phases—Al predominantly in aluminosilicates (clays, feldspars), and Ti in resistant heavy minerals such as rutile and ilmenite. Therefore, variations in this ratio primarily reflect source lithology rather than post-depositional modification. According to Hayashi et al. (1997), $\text{Al}_2\text{O}_3/\text{TiO}_2$ ratios of 3–8 indicate mafic sources, 8–21 intermediate sources, and 21–70 felsic sources. In the Molodezhny HTA samples, the $\text{Al}_2\text{O}_3/\text{TiO}_2$ ratio ranges from 2.9 (C2-4) to 11.6 (C3-3), with an average of 7.9, indicating a transition from mafic to intermediate provenance. This suggests that the detrital material was derived from mixed mafic–intermediate igneous sources, likely related to the Carboniferous volcanic–sedimentary basement of the region, consistent with similar interpretations from adjacent coal basins in Kazakhstan (Junussov et al., 2025). The use of Al/Ti as a provenance proxy is further supported by its stability under chemical weathering conditions and its effectiveness in distinguishing igneous source types (Young and Nesbitt, 1998; Hayashi et al., 1997).

The $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio was used to evaluate mineralogical composition and weathering intensity, as it reflects the relative abundance of quartz versus clay minerals. Quartz enrichment increases $\text{SiO}_2/\text{Al}_2\text{O}_3$ values, whereas clay mineral dominance lowers it. This ratio is widely applied in sedimentary geochemistry because it captures variations in mineral assemblages more effectively than grain-size effects (Ruxton, 1968; Cox et al., 1995). In addition, chemical weathering progressively removes mobile elements such as Si, Na, and K, while relatively immobile Al accumulates in secondary clay minerals, thereby decreasing Si/Al ratios during advanced weathering stages (Nesbitt and Young, 1982; Liu et al., 2025). In the Molodezhny samples, $\text{SiO}_2/\text{Al}_2\text{O}_3$ ranges from 2.27 to 10.62 (mean 5.57), indicating significant heterogeneity in detrital input. Lower values (e.g., N1-1 = 2.27; C2-7 = 2.72) reflect clay-rich lithologies and stronger chemical alteration, whereas higher values (e.g., C2-4 = 10.62) indicate quartz-rich input and comparatively weaker weathering conditions. Such variability suggests non-uniform sediment supply and fluctuating depositional environments across coal-forming intervals. To further constrain weathering intensity, the A–K index was calculated using molar proportions following Nesbitt and Young (1982, 1984), expressed as:

$$A\text{--}K \text{ index} = \text{Al}_2\text{O}_3 / (\text{Al}_2\text{O}_3 + \text{K}_2\text{O}) \times 100$$

This index is particularly useful in this study because Na_2O was below detection limits in most samples, making traditional indices such as CIA less reliable. The A–K index is therefore applied as a Na-free weathering proxy to assess feldspar breakdown and clay mineral enrichment. High values indicate strong leaching of K-bearing feldspars and dominance of secondary Al-rich phases. All Molodezhny samples show values above 80, indicating intense chemical weathering conditions in the source region. The N1 horizon exhibits the highest values (98.0–99.4), suggesting extremely advanced weathering and/or sediment recycling. Such elevated values are consistent with intense feldspar decomposition and the formation of kaolinite-rich assemblages.

Mineralogically, these geochemical results are strongly supported by XRD data, which indicate kaolinite dominance (17–23 wt.%) and a near absence of feldspar (~5 wt.%). Kaolinite is a typical product of advanced chemical weathering under acidic, leaching-dominated conditions, further confirming the high A–K index values observed. The combined geochemical and mineralogical evidence therefore indicates that the Molodezhny source area experienced

prolonged and intense chemical weathering under conditions favorable for kaolinite formation and feldspar depletion (Nesbitt and Young, 1982; 1984; Taylor and McLennan, 1985; Liu et al., 2025).

The integrated application of $\text{Al}_2\text{O}_3/\text{TiO}_2$, $\text{SiO}_2/\text{Al}_2\text{O}_3$, and the A–K index demonstrates that the Molodezhny coal detrital material was derived from mixed mafic–intermediate sources and subjected to strong to extreme chemical weathering prior to deposition. These results are consistent with regional geological interpretations and support a model of variable sediment supply combined with intensive chemical alteration in the provenance area.

Table 7. Geochemical ratios for the coal samples

Sample	$\text{Al}_2\text{O}_3/\text{TiO}_2$	$\text{SiO}_2/\text{Al}_2\text{O}_3$	A-K index	Provenance ($\text{Al}_2\text{O}_3/\text{TiO}_2$)
C1-1	6.7	4.63	97.4	Mafic
C1-4	8.7	7.64	95.9	Intermediate
C1-7	9.7	5.22	89.3	Intermediate
C2-1	6.8	6.60	97.0	Mafic
C2-4	2.9	10.62	96.7	Mafic
C2-7	8.2	2.72	97.8	Intermediate
C3-1	8.8	7.14	92.5	Intermediate
C3-3	11.6	6.63	92.0	Intermediate
N1-1	5.7	2.27	99.4	Mafic
N1-6	6.9	3.52	98.6	Mafic
N1-13	11.3	4.25	98.0	Intermediate

6. Conclusion

This study presents a comprehensive geochemical and mineralogical characterization of coal samples from the Molodezhny coal deposit (Karagandy Region, Kazakhstan), with the aim of evaluating the distribution, enrichment, and economic potential of precious metals and critical elements in both coal and coal ash.

A total of 30 coal samples were collected from four stratigraphic horizons within the mine, where the N1 seam represents the lowest horizon and C1 the uppermost seam. The ash yield ranges from 3.28% to 54.85%, with an average value of 27.96%, indicating moderate mineral matter content. The average carbon content is 18.67%, suggesting an intermediate degree of coalification. Sulfur concentrations are generally low across the dataset, except for sample MD C1-1 (8.07%), which likely reflects localized enrichment associated with sulfide mineralization, particularly pyrite. Analytical methods included X-ray diffraction (XRD), X-ray fluorescence (XRF), Fourier-transform infrared spectroscopy (FTIR), inductively coupled plasma optical emission spectrometry (ICP-OES) following microwave-assisted acid digestion, as well as proximate and ultimate analyses.

Mineralogical characterization based on XRD and FTIR indicates that quartz is the dominant phase (37–46%), followed by kaolinite (17–23%), and a significant amorphous fraction (28–33%). FTIR spectra reveal a clear coalification trend from C1 to N1, expressed by an increase in aromatic structures and a concurrent decrease in aliphatic and oxygen-bearing functional groups. This trend reflects progressive thermal maturation with depth and is consistent with the burial and thermal history of the Karagandy Basin.

Geochemical data obtained from XRF and ICP-OES analyses show that SiO_2 and Al_2O_3 are the dominant oxides, indicating a typical silicate-dominated system. The most notable result is the exceptionally high enrichment of gold (Au), with a concentration coefficient (CC) of 728 and concentrations ranging from 10.22 to 23.64 ppm (average 17.5 ppm). Such values are highly anomalous and require careful interpretation. They may reflect analytical or sampling uncertainties; however, a geological origin cannot be excluded. Possible mechanisms include hydrothermal fluid activity and gold incorporation into sulfide phases. The complex tectonic evolution of the Karagandy Basin, particularly during Hercynian magmatism, along with the presence of deep-seated fault systems, could have facilitated hydrothermal fluid circulation and

metal enrichment during or after coal formation. Verification through scanning electron microscopy (SEM) and repeated ICP-OES analyses under varying digestion conditions is therefore essential.

Among the trace elements, samarium (Sm) exhibits moderate enrichment ($CC = 1.70$), whereas praseodymium (Pr), scandium (Sc), thorium (Th), silver (Ag), and ytterbium (Yb) are depleted relative to world hard coal averages. This suggests a limited contribution from heavy minerals and rare earth element (REE)-bearing phases in the source material.

Provenance analysis indicates a mixed mafic-to-intermediate source composition. The A–K index values exceeding 80 across all samples indicate intense chemical weathering, likely controlled by paleoclimatic and paleogeographic conditions. The predominance of kaolinite further supports prolonged weathering processes. These findings are consistent with the regional geological framework of Central Kazakhstan, where Devonian–Carboniferous volcanic-sedimentary complexes represent the primary source rocks.

The Molodezhny coal system is characterized by a silicate-dominated mineral assemblage and moderate ash yield. The principal finding of this study is the anomalously high gold enrichment, which represents the most significant and potentially economically relevant feature. Samarium shows moderate enrichment, whereas other trace elements are depleted. Elemental distribution is primarily controlled by mineralogical factors, particularly ash yield and kaolinite content. Provenance analysis indicates derivation from mafic to intermediate rocks subjected to intense chemical weathering. Collectively, these characteristics suggest that the deposit may be classified as metalliferous coal with potential economic significance.

From an industrial perspective, the coal ash exhibits favorable properties for utilization in cement production, geopolymers, ceramics, and zeolite synthesis. The high amorphous content enhances its suitability for geopolymer applications. If the elevated gold concentrations are confirmed, the deposit could represent a promising dual-purpose resource, combining energy production with the recovery of valuable metals, thereby contributing to the mining sector of Kazakhstan.

Future research should follow a systematic, multi-stage approach to validate and expand upon the present findings. First, SEM-based investigations are required to directly observe gold occurrences, including potential nanoscale particles, and to determine their associations with pyrite, organic matter, or other mineral phases. In contrast to XRD, which identifies bulk

mineralogy, SEM provides spatial and textural information, enabling precise localization of mineral phases such as kaolinite and iron oxides within the coal matrix. Second, ICP-OES analyses should be repeated under different digestion protocols to ensure the reliability of gold concentrations. Third, sampling should be extended to adjacent deposits within the Akzhar group to assess the regional consistency of gold enrichment. Finally, repeated ICP-OES measurements under different digestion conditions should be conducted to independently verify the anomalous concentrations of Au and other trace elements, as the current results particularly the exceptionally high gold enrichment coefficient require confirmation before definitive conclusions can be drawn. In addition, laser ablation ICP-MS should be applied to better constrain the mineralogical hosts and spatial distribution of REEs, particularly Sm. Together, these approaches will provide a robust basis for evaluating whether the Molodezhny deposit can be considered a viable resource for both energy production and critical raw material extraction.

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Appendix A

Progress report and work completion schedule. Actual information for 11 of December 2025.

Steps in preparation of Diploma work	Short Description	Status and Future Deadlines
1. Get samples from coal mine	-	Completed on 25th of October
2. Grinding of coal to 5 microns coal powder	Needed for other experiments, like FTIR, ICP MS, Microwave digestion, XRD,XRF.	Completed on 3rd on November
3. Muffle Furnace	Needed to make high and low temperature ash for experiments. High temperature ash conditions: 815 degrees of celsius for 4 hours. Low temperature ash conditions: 350 degrees of celsius for 24 hours.	Completed on 20th of November
4. XRF	Element analysis	Completed on 22th of November
5. XRD	Structural analysis	Completed on 5th of December
6. Microwave digestion and ICP MS	Element analysis	Completed on 1 st of February. Digestion is completed. There was a need in syringe filter. Procedure was made in the beginning of January.

7. FTIR	Determine functional groups	Completed on 1 st of February.
8. Thin section analysis	Description of coal sample	Was not started because of the results
9. Literature review	Collect necessary information and make a review on it	Started in February and ended on 18 th of April
10. Digitalization of different maps, and other info	-	Completed in January-February
11. Diploma preparation	Writing the paper including Abstract, Introduction, Geological info, Methods, Results + Discussion, and Conclusion + Presentation	Completed

Appendix B

As evidence of continued development in this research area, the author's recent publication is presented below.

The screenshot shows the De Gruyter Brill website interface. At the top, the navigation bar includes the De Gruyter Brill logo, links for 'For Authors', 'For Librarians', 'Our Subjects', 'Services', 'About Us', 'Search', and a 'Manage Access' dropdown. Below the navigation bar, a breadcrumb trail reads: 'Home > Geology and Mineralogy > Mineralogical and elemental analysis of Kazakh coals from three mines: Preliminary insights from mode of occurrence to environmental impacts'. The article title is prominently displayed in bold. Below the title, the authors are listed: Medet Junussov, Farkhad Tarikhov, Abaidildin Abildakhanov, Dauren Zhanaidar, Gulnur Mekenbek, and Aizada Assambayeva. The publication date is November 28, 2024. A 'Download Article (PDF)' button is visible. At the bottom, there is a section for 'Published by' with the De Gruyter logo, a link to 'Become an author with De Gruyter Brill' (including 'Submit Manuscript' and 'Author Information' links), and a 'From the journal' section for 'Open Geosciences' Volume 16 Issue 1, accompanied by a journal cover image.

Research Article

Medet Junussov*, Farkhad Tarikhov, Abaidildin Abildakhanov, Dauren Zhanaidar,
Gulnur Mekenbek, and Aizada Assambayeva

Mineralogical and elemental analysis of Kazakh coals from three mines: Preliminary insights from mode of occurrence to environmental impacts

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Abstract: This study aims to comprehensively characterize coal extracted from three active mines in northeastern Kazakhstan: Lenin, Saradyr, and Bogatyr. These mines exploit two Carboniferous coal-bearing formations, Dolyn and Karagandy. Dolyn, extracted by the Lenin underground mine at a depth of 700 m, contrasts with Karagandy, extracted at depths up to 260 m in Saradyr and Bogatyr. Six selected samples from the Lenin, Saradyr, and Bogatyr mines underwent various analyses, including proximate and ultimate analyses, elemental analyses (acid digestions with HCl + HNO₃ + HF, ICP-MS), and determination of mineral matter contents (XRD and SEM-EDS). This research aimed to understand the mode of occurrence of minerals and elements, technological and environmental implications of the coal seams extracted from these mines. Results indicate low sulfur and high ash content in the organic matter of all samples. Quartz and kaolinite dominate, with minor euhedral pyrite present in all samples. Framboidal pyrite, iron oxides, and rare earth element (REE)-bearing minerals are exclusively found in Saradyr and Bogatyr samples. Quartz and kaolinite likely

reached the peat swamp through detrital processes, while pyrite formation occurred through both syngenetic and epigenetic processes in the coal samples. Ratios like Ce_n/Ce_m, Eu_n/Eu_m, Y_n/Ho_m, and Gd_n/Gd_m suggest REE deposition in anoxic hydrothermal water environments, possibly indicating a tuffaceous origin for the coal samples. Examining the elements' mode of occurrence suggests their preferential association with mineral matter. Strong positive correlations among elements like Al, K, Na, Ti, Ba, Be, Ni, Cr, Co, Ga, Sc, V, As, Pb, Cu, Zn, and Zr, along with Eu and Sc of the REEs, suggest association with ash yield, consistent with kaolinite and accessory minerals. Comparative analysis of inorganic geochemical composition of coal worldwide reveals notable depletion of major, trace elements, and REEs in samples from all three mines, suggesting limited economic interest. Furthermore, coal samples containing trace elements pose minimal environmental impact.

Keywords: Karagandy, Bogatyr, Saradyr, trace elements, coals, enrichment factor

1 Introduction

Understanding coal mineralogy, and geochemistry is crucial for coal utilization and environmental management, impacting quality, processing methods, and resource exploration [1–3]. Coal is a complex mixture of both organic and inorganic components [4–6], formed through the diagenesis of organic matter, and characterized by a diverse range of minerals [7] and chemical elements [8–10]. Despite the inorganic fraction typically being a small part of coal, many challenges associated with coal are related to this component [11–14]. Inorganic materials in coal come from three main sources: a dissolved salt within the water-filled spaces (pores) in coals with a low rank, inorganic elements bound to organic compounds (into coal structures as a chelate), and mineral compounds [11,15–17]. Inorganic components provide geological insights into deposition and coal-bearing sequences [18], play a crucial role in

* **Corresponding author: Medet Junussov**, School of Mining and Geosciences, Nazarbayev University, Astana, 010000, Kazakhstan, e-mail: medet.junussov@nu.edu.kz

Farkhad Tarikhov: Core Facilities, Nazarbayev University, Astana, 010000, Kazakhstan, e-mail: farkhad.tarikhov@nu.edu.kz

Abaidildin Abildakhanov: School of Mining and Geosciences, Nazarbayev University, Astana, 010000, Kazakhstan, e-mail: abaidildin.abildakhanov@nu.edu.kz

Dauren Zhanaidar: School of Mining and Geosciences, Nazarbayev University, Astana, 010000, Kazakhstan, e-mail: dauren.zhanaidar@nu.edu.kz

Gulnur Mekenbek: Institute of Geology and Oil-gas Business, Satbayev University, Almaty, 050013, Kazakhstan, e-mail: mekenbekgulnur@mail.ru

Aizada Assambayeva: Committee of Geology of the Ministry of Industry and Construction of the RK, Astana, 010000, Kazakhstan, e-mail: aizada_Assambayeva@mail.ru

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