

## Article

# Experimental Investigation on Gallium and Germanium Migration in Coal Gangue Combustion

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**Abstract:** Gallium (Ga) and germanium (Ge) critical elements have a wide range of applications and market value. Extracting critical elements from coal gangue and combustion products can alleviate pressures on primary mining resources. Understanding the transformation behavior of Ga and Ge during coal gangue combustion processes is significant for resource utilization and environmental protection. Coal gangue from Xing'an League, Inner Mongolia, was chosen to explore how combustion temperatures (600 °C to 1000 °C) and particle sizes (50, 80, 10, 140, and 200 mesh) influence Ga and Ge migration during combustion. Techniques such as ICP-MS, XRD, XRF, SEM, TG-DSC, and sequential chemical extraction were employed to analyze the transformation of minerals and to quantify the contents and occurrence forms of Ga and Ge. Smaller gangue particle sizes were associated with higher concentrations of Ga and Ge. Approximately 99.19% of Ga and Ge in coal gangue were found in the residual, organic/sulfide-bound, and metal-oxide-bound modes. High temperatures promoted element volatilization and changed the reactions and interactions between elements and minerals. As combustion temperatures rose from 600 °C to 1000 °C, Ga and Ge contents in the products declined progressively. Under high temperatures, minerals like kaolinite, illite, and pyrite in gangue converted to silicate glass phases, mullite, and hematite. Minerals like kaolinite, calcite, and pyrite melted, leading to increased cohesion and agglomeration in the products. Over 90% of Ga and Ge in the combustion products existed in the residual, organic/sulfide-bound, and metal-oxide-bound forms. Moreover, Ga was enriched in combustion products, with its content exceeding critical extraction levels. The results may provide a useful reference for developing critical elements enrichment, extraction, and separation technologies from coal gangue.

**Keywords:** coal gangue; combustion; migration; gallium; germanium; enrichment



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## 1. Introduction

Coal gangue is a solid waste generated during coal mining and processing, containing energy components and critical elements [1,2]. Long-term storage of coal gangue occupies a substantial amount of land and may cause spontaneous combustion, leading to air and groundwater pollution [3]. Gallium (Ga) and germanium (Ge) are critical strategic elements for meeting the escalating demand for advanced energy-saving technologies and high-tech applications [4–6]. Ga and Ge are sparsely distributed in nature and are costly to extract traditionally. Therefore, it is urgent to find alternative resources to obtain Ga and Ge [7–9]. Coal gangue is a resource that can be used to recover coal, gallium, germanium, and other useful components [1,10]. The comprehensive utilization of coal gangue is an important part of resource utilization, reducing land occupation and environmental pollution while improving economic efficiency.

Many studies have demonstrated the remarkable enrichment of critical elements in coal gangue, including lithium (Li), gallium (Ga), germanium (Ge), and rare earth elements [2,11–13]. Limitations in extracting critical metals from coal gangue are the cost of extraction technology is high and the composition of the dissolved material is

complex [14,15]. The realization of multi-metal separation is also a technical difficulty and research hotspot. Alternative resources need to be explored to improve the recovery of these critical metals.

The recovery of Ga and Ge from combustion products has been widely used in industrial production and daily life [16]. The significant characteristics of specific coal mining regions lead to different gangue properties. The occurrence forms and structures of critical elements can be changed by chemical reactions and thermal conditions during coal gangue combustion [2,17,18]. The mineral composition of coal gangue is intricate. Ga can exist in both inorganic minerals and organic matter [19,20]. Ge is mainly associated with organic matter in both coal and coal gangue, although a small proportion of Ge is probably related to the inorganic matter in coal gangue [21]. Elevated temperatures facilitate element volatilization and modify their reactions and bindings with mineral components [22]. Critical elements deposited in organic matter tend to be more readily released, while those deposited in clay minerals (such as kaolinite and illite) or other inorganic components (such as aluminosilicate melt) pose greater challenges to release [23,24].

Researchers have made important research progress in the discovery of critical metal deposits in coal measures, the content and occurrence forms of critical elements, the source of ore-forming materials and the characteristics of migration and transformation, the evaluation of development and utilization, the research and development of detection technology, and the separation and extraction of critical elements [19,25–27]. These achievements are significant for promoting the sustainable development and utilization of critical metal mineral resources in China. However, the research on the migration and transformation characteristics of Ga and Ge during the combustion of coal gangue is not comprehensive enough. This study aims to address this gap by specifically investigating the migration and transformation characterizations of Ga and Ge during gangue combustion. Considering that the auto-thermal activation of gangue during combustion may trigger changes in the occurrence forms of Ga and Ge, this study offers new insights into the thermal behavior of critical metals, which has significant implications for the environmental management and recovery of critical metals from coal gangue.

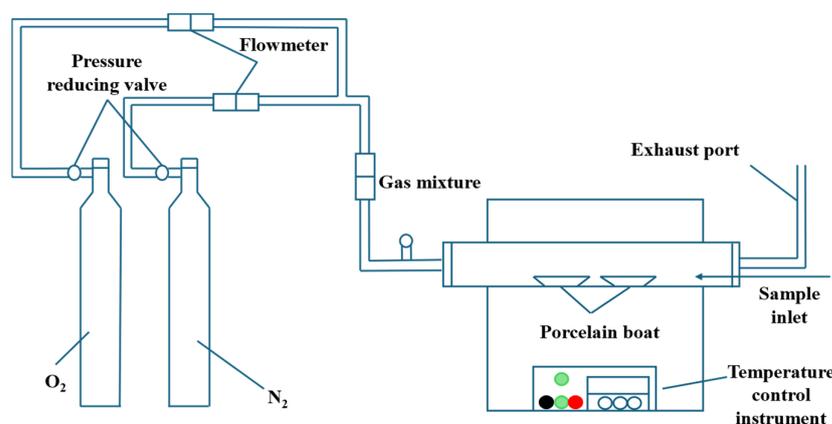
The study encompasses three primary objectives. It aims to address the following aspects: (1) elucidating the geochemical properties of Xing'an League region coal gangue; (2) investigating the migration and transformation characteristics of Ga and Ge during the combustion process of coal gangue; and (3) scrutinizing the enrichment behaviors exhibited by Ga and Ge throughout the combustion process of coal gangue. This research may provide a reference to innovations in the sustainable use of coal gangue resources.

## 2. Materials and Methods

Gangue samples were collected from the Xing'an League region of Inner Mongolia. To accurately represent the coal gangue under investigation, the samples were immediately sealed in plastic bags and numbered after collection to prevent contamination and weathering during transportation. The samples were dried naturally after mixing, then sampled by tetrad method, sieved to 50 mesh, 80 mesh, 100 mesh, 140 mesh, and 200 mesh sizes after grinding and finally stored in brown reagent bottles for subsequent analysis.

The experiment was conducted using a fixed-bed furnace. Figure 1 shows the BTF-1200 C tube furnace setup, which included an electrically heated tube furnace and a stainless-steel reactor containing porcelain boats for two sample placements. The quartz tube had a diameter of 80 mm and a length of 1 m. Before sealing the system and introducing gases at a specified pressure, the coal gangue was placed in the porcelain boat and inserted into the reactor from the right side. The tube furnace program entailed three phases: The heating rate was established at 10 °C/min to gradually elevate the temperature from ambient to the target combustion temperature. Combustion was then maintained at the target temperature for 2 h. The tube furnace was permitted to cool down naturally to ambient temperature. Combustion products were then stored in sealed bags for further analysis and testing. To

ensure precision and accuracy, three replicate samples of coal gangue, with each weighing 4.0 g, were prepared at different combustion temperatures.



**Figure 1.** The diagram of the tubular furnace setup.

A mixture of 21% O<sub>2</sub> and 79% N<sub>2</sub> simulated a conventional air atmosphere, aligning the experiments more closely with real-world applications and making them suitable for a wide range of combustion studies. A flow meter was utilized to monitor the gas flow, set at a rate of 500 mL/min. Before each experiment, the tube furnace was flushed with the gas mixture for 10 min to eliminate residual gases. Given that inorganic mineral decomposition typically initiates above 500 °C, six combustion points ranging from 600 °C to 1000 °C were established at 100 °C intervals [28]. This temperature range facilitated the investigation of migration, conversion, and enrichment characteristics of Ga and Ge during combustion.

In the pre-weighed crucible, the gangue sample (2 g) was accurately weighed, and the crucible containing the sample was placed in a muffle furnace (KHXL-1S, Keheng, Shanghai, China) with an initial temperature setting below 600 °C to avoid loss of the sample due to sudden combustion. The temperature was increased to 815 ± 10 °C, and the sample was incinerated for 2 h to eliminate all organic matter. The crucible was removed from the muffle furnace, placed on a clean rack to cool to room temperature and then weighed to calculate the ash content.

An appropriate amount of the ashed sample was analyzed using an X-ray fluorescence spectrometer (XRF-1800, Shimadzu, Kyoto, Japan) to determine the chemical composition and convert it to gangue samples. Coal gangue (1 g) was accurately weighed into a lidded porcelain crucible, which was then placed in a preheated muffle furnace at 900 ± 10 °C and heated in an oxygen-free environment for 7 min. The crucible was placed on a clean shelf to cool to room temperature and subsequently weighed to calculate the volatile fraction content. The morphology of samples was observed by scanning electron microscopy (SEM-Regulus 8230, Hitachi, Tokyo, Japan).

An elemental analyzer (Vario EL cube, Germany elemental, Shanghai, China) was used to determine the content of major elements such as carbon, hydrogen, sulfur, and nitrogen in coal gangue, and the mass percentage of elemental oxygen in samples was calculated. The mineralogical composition of the gangue and its combustion products was analyzed using an X-ray diffractometer (PANalytical X-Pert PRO MPD, PANalytical, Almelo, The Netherlands) with a Cu target. The speed of diffraction scanning was set at 2°/min, the angle of coverage was from 5° to 70°, and the diffractograms were analyzed using the Jade 6.0 software to characterize the diffraction patterns. Thermogravimetric analysis is the basic method for thermochemical analysis of samples. Based on the thermogravimetric analysis data, TG curves were plotted with the horizontal coordinate of the curve being temperature and the vertical coordinate being the mass fraction of the sample. DTG curves were plotted by solving the first-order differential equation of the TG curves against time. Based on the TG-DTG curve, the following combustion characteristic parameters (ignition temperature, burnout temperature, and maximum always rate) were

obtained to evaluate the combustion performance of the samples. The gangue sample (weight: 3.924 mg) underwent TG-DTG analysis using a STA449F5 simultaneous thermal analyzer (Netzsch, Selb, Germany) conducted in an air atmosphere (21% O<sub>2</sub>/79% N<sub>2</sub>). The temperature ranged from 25 °C to 1000 °C at a controlled heating rate of 10 °C/min. To eliminate systematic errors and buoyancy effects, a blank experiment was conducted before the test, and the results were obtained after deducting the baseline.

Referenced to the method of Tessier A [29], the occurrence forms of Ga and Ge in samples are categorized into five modes: ion exchange (F1), carbonate-bound (F2), metal-oxide-bound (F3), organic/sulfide-bound (F4), and residual (F5), and the detailed extraction steps are listed in Table 1. To ensure the reliability of the experimental data, blank experiments were performed. For test analyses, two parallel experiments were established, and the standard deviation was calculated to assess the consistency of results between the two determinations [30]. If within the error range, the results were expressed in the form of an average value, retaining two decimal places. If not within the error range, the results were re-determined.

**Table 1.** The sequential extraction procedure of coal gangue and combustion products [29].

Step	Extraction Procedure	Speciation
1	One gram sample was extracted with 10 mL 1.0 M MgCl <sub>2</sub> (pH = 7.0) under room temperature for 1 h, and the suspension was achieved by centrifugation at 3500 rpm for 20 min.	(F1) Ion exchange
2	The residual solid from step 1 was extracted with 10 mL 1 M sodium acetate (pH = 5.0) under room temperature and agitated continuously for 5 h. The suspension was achieved by centrifugation at 3500 rpm for 20 min.	(F2) Carbonate-bound
3	The residual solid from step 2 was treated with 20 mL 0.04 M NH <sub>2</sub> OH·HCl in 25% (v/v) under room temperature and agitated continuously for 6 h. The suspension was achieved by centrifugation at 3500 rpm for 20 min.	(F3) Metal-oxide-bound
4	The residual solid from step 3 was treated with 3 mL 0.02 M HNO <sub>3</sub> and 5 mL 30% H <sub>2</sub> O <sub>2</sub> (pH = 2.0) at 85 °C for 2 h. Another 3 mL aliquot of 30% H <sub>2</sub> O <sub>2</sub> (pH = 2.0 with HNO <sub>3</sub> ) was then added at 85 °C and agitated for 3 h. After cooling, 5 mL of 3.2 M NH <sub>4</sub> OAc in 20% (v/v) HNO <sub>3</sub> was added, and the sample was diluted to 100 mL and agitated continuously for 30 min.	(F4) Organic/ Sulfide-bound
5	The residual solid from step 4 was digested with an HCl–HNO <sub>3</sub> –HF mixture according to the procedure used for bulk samples.	(F5) Residual

Quality control during the experiment is a critical step in ensuring accurate and reliable results by adhering to operational standards in sample handling, reagent preparation, instrument usage, and data recording. To determine the Ga and Ge contents in coal gangue and combustion products, 0.1 g samples dissolved in a mixed acid medium (60 wt% HCl:20 wt% HNO<sub>3</sub>:20 wt% HF = 3:1:1, v/v) was conducted to microwave digestion at 210 °C for 60 min and then transferred to an electric heating plate to digest continuously for 90 min. After cooling to room temperature, the sample was diluted to 50 g with 5 wt% nitric acid then was determined by the ICP-MS (Agilent 7500, Santa Clara, CA, USA). Meanwhile, the 5 wt% nitric acid was the blank sample, and the standard samples were provided by the National Center for Standard Substances. Three parallel experiments were performed on each sample to ensure the accuracy of the results [31].

### 3. Results and Discussions

#### 3.1. Geochemical Characteristics of Ga and Ge in Coal Gangue

The proximate, ultimate, and chemical compositions of the coal gangue were examined by ASTM standards and are detailed in Tables 2 and 3. These observations enhance the understanding of coal gangue properties. The coal gangue in this region exhibited a water content of 1.19%, an ash content of 50.80%, and a total sulfur content of 0.53%. Table 3 shows that coal gangue contained SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>, accounting for 55.07% and 26.44%,

respectively. The other components were Fe<sub>2</sub>O<sub>3</sub>, K<sub>2</sub>O, TiO<sub>2</sub>, CaO, MgO, and P<sub>2</sub>O<sub>5</sub> in order of content. The concentrations of Ga and Ge in coal gangue are presented in Table 4. It is important to note that the selected coal gangue exhibited high concentrations of strategic metal elements, making them suitable as research subjects [32].

**Table 2.** The proximate and ultimate analysis of the coal gangue (wt.%).

The Proximate and Ultimate Analysis of Gangue (wt.%)					
Proximate analysis, dry basis	Moisture	Ash	Volatile matter	Fixed carbon	/
Coal gangue	1.19	50.80	18.38	29.63	/
Ultimate analysis, daf	C	H	N	O	S
Coal gangue	23.44	3.91	0.72	8.74	0.53

**Table 3.** The chemical composition of coal gangue (wt.%).

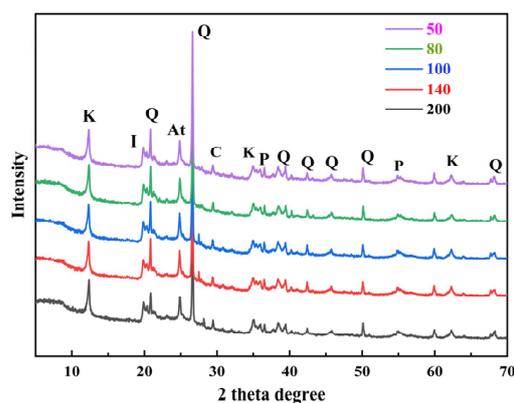
Chemical Composition	SiO <sub>2</sub>	TiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	MgO	CaO	Na <sub>2</sub> O	K <sub>2</sub> O	LOI <sup>a</sup>
Coal gangue	55.07	2.60	26.44	9.07	0.21	1.88	0.17	3.08	15.37

Note: <sup>a</sup>—Loss on ignition.

**Table 4.** The concentrations of Ga and Ge in coal gangue with different particle sizes (mg/kg).

Particle Sizes (Mesh)	50	80	100	140	200
Ga	85.09	88.40	91.03	92.53	94.80
Ge	10.60	11.59	13.02	14.87	15.66

Table 4 shows the concentrations of Ga and Ge in coal gangue with different particle sizes. In coal gangue, smaller particle sizes are associated with higher concentrations of Ga and Ge [33,34]. Figure 2 presents an investigation into the mineral composition of coal gangue. There was no difference in the mineral composition of coal gangues with different grain sizes. The coal gangue’s mineralogical composition comprised anatase, calcite, illite, kaolinite, pyrite, and quartz. Among them, SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> existed in the form of kaolinite, illite, and quartz, while Fe<sub>2</sub>O<sub>3</sub>, CaO, and TiO<sub>2</sub> existed in the form of pyrite, calcite, and anatase, respectively.



**Figure 2.** Mineral compositions of coal gangue with different particle sizes. The minerals identified were At representing anatase, C representing calcite, I representing illite, K representing kaolinite, P representing pyrite, and Q representing quartz.

Ga often substitutes for aluminum or iron in mineral structures due to its similar properties to aluminum. This substitution frequently occurs in aluminum or iron minerals present in the coal gangue [27,35]. Ga and Ge can be adsorbed onto the surfaces of minerals or incorporated into crystal lattices. Ga and Ge are mainly endowed in the glassy phase

in the form of the Si-Al lattice [36]. In this paper, Ga and Ge in gangue were commonly associated with calcite, with oxides of iron and manganese, and with organic matter and pyrite, and consisted mainly of kaolinite, illite, quartz, and other insoluble minerals [19,20]. Calcite is a common carbonate mineral that acts as a carrier for Ga and Ge in coal gangue. This association may take place through an ionic substitution mechanism in which Ga and Ge partially replace calcium (Ca) in the calcite structure [22]. Ga and Ge may substitute Fe or Mn in Fe-Mn oxides or adsorb on the surface of these minerals. Pyrite is a common sulfide mineral that may be associated with Ga and Ge through complex formation or direct adsorption. Kaolinite is an aluminum-containing silicate mineral. Kaolinite is more common in gangue and can be combined with Ga and Ge by physical adsorption or chemical bonding.

Critical elements bound to organic matter are often loosely held and can be easily liberated during combustion processes. Elements incorporated within the lattice structure of clay minerals or complexed with other inorganic compounds are more tightly bound, rendering them less susceptible to release [17,18]. This phenomenon can be attributed to the chemical nature of the critical element and the strength of the bond between the critical element and the other components. The mineral composition of coal gangue significantly influences the properties of its combustion products and the migration of elements [37]. At elevated temperatures, the decomposition of kaolinite may release metal ions previously bound within its structure, influencing the migration of Ga and Ge. The thermal stability of quartz at high temperatures is crucial for the transformation of silicon species in coal gangue [38]. Calcite decomposes into calcium oxide and carbon dioxide during combustion, potentially affecting the alkalinity of combustion products. The presence of pyrite could influence the migration of sulfur elements in combustion products [39,40].

The occurrence forms of critical elements were revealed through the sequential extraction procedure. Based on the mineral composition of coal gangue. The ion exchangeable mode (F1) represents the free form of metal cations, which can be easily exchanged with other ions. The carbonate-bound mode (F2) corresponds to minerals associated with calcite, which can be dissolved by acid treatment. The metal-oxidized mode (F3) refers to minerals in the form of iron and manganese oxides, which can undergo oxidation reactions. The organic/sulfide mode (F4) is present in organic matter and pyrite, where critical elements are bound to these compounds. Lastly, the residual mode (F5) includes clay minerals such as kaolinite and illite, quartz, and other insoluble minerals, where critical elements are retained [30].

Table 5 displays the occurrence forms of Ga and Ge in coal gangue with different particle sizes. Ga and Ge elements in coal gangue were mostly in the metal-oxide-bound, organic/sulfide-bound, and residual modes, accounting for more than 97% of the total proportion, and the proportions of Ga and Ge in the ion-exchange and carbonate-bound modes were tiny. The ion-exchanged and carbonate-bound Ga proportions were 0.03%–0.15% and 0.91%–2.15%, while metal-oxide-bound Ga accounted for 4.07%–6.47%. The ion-exchanged and carbonate-bound Ge proportions were 0.15%–0.35% and 1.15%–1.71%, respectively.

**Table 5.** The modes of occurrence of Ga and Ge in coal gangue with different particle sizes (%).

Particle Sizes (Mesh)	50	80	100	140	200	
Ga (%)	F1	0.03	0.09	0.16	0.07	0.15
	F2	0.91	1.43	2.15	2.01	1.80
	F3	6.23	6.47	4.07	5.89	5.31
	F4	8.95	9.06	5.74	7.97	6.21
	F5	83.88	82.95	87.88	84.06	86.53
Ge (%)	F1	0.18	0.15	0.35	0.33	0.16
	F2	1.34	1.43	1.71	1.17	1.15
	F3	6.78	7.96	7.93	12.13	10.26
	F4	22.23	23.79	27.49	26.51	25.22
	F5	69.47	66.67	62.52	59.86	63.21

### 3.2. The Redistribution Characterizations of Ga and Ge during Coal Gangue Combustion

The characteristic temperature point during combustion can be determined by analyzing the change characteristics of the coal gangue sample's mass [41,42]. Figure 3 presents the thermogravimetric (TG) and derivative thermogravimetric (DTG) curves obtained from thermogravimetric analysis of coal gangue under an air atmosphere. Based on the TG and DTG curves, the ignition temperature, the burnout temperature, and the maximum weight loss rate were obtained. The TG curve provided information about the weight loss of the sample as a function of temperature, revealing the various stages of coal gangue decomposition and combustion. Meanwhile, the DTG curve, derived from the TG curve, represented the rate of weight loss at various temperatures, allowing for the identification of peak decomposition and combustion rates.

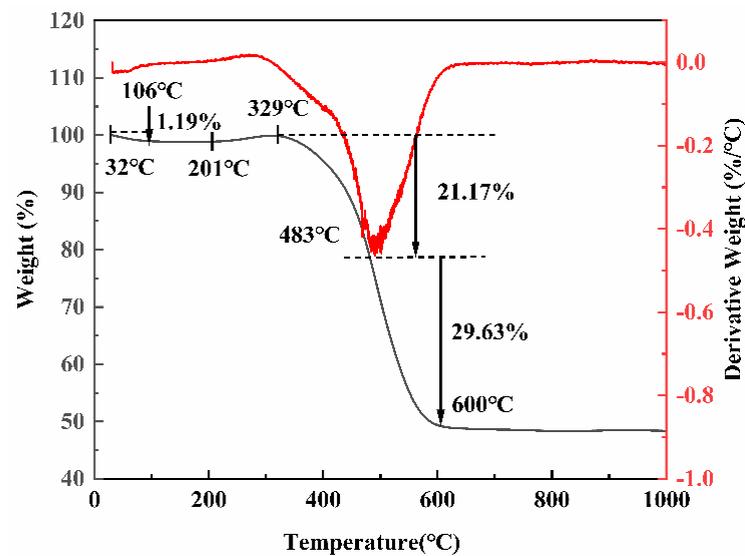
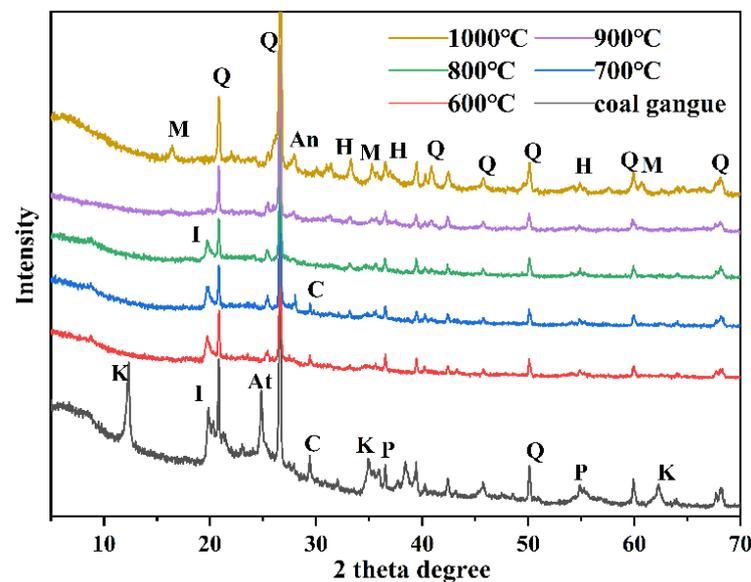


Figure 3. TG and DTG curves of coal gangue under an air atmosphere.

Based on the analysis of the TG curve of the coal gangue, different temperature ranges could be identified along with their corresponding processes. In the temperature range of 32–106 °C, the primary processes observed were the evaporation of water (free water and bound water) and gas desorption. This stage was referred to as the water evaporation stage, resulting in a minimal weight loss of only 1.19%. Moving on to the temperature range of 201–329 °C, a slight increase in weight was observed. This could be attributed to the fact that the oxidation absorption of coal gangue particles and the amount of absorption exceeded the amount of gas released in its pores before reaching the ignition point, known as the weight gain stage of oxygen absorption. When the temperature exceeded 329 °C, the coal gangue entered the combustion phase. From the combustion point temperature of 600 °C, the net weight loss was the most significant, accounting for 50.80% of the total weight loss. This weight loss was primarily caused by the breakdown of organic matter and clay minerals such as kaolinite and other minerals at elevated temperatures during the combustion process [43,44]. As the temperature continued to rise in the burnout stage, the weight of the coal gangue stabilized, ceasing to fluctuate. This stability was primarily due to the high thermal resistance of silicate, which made it resistant to further decomposition.

The mineral composition of coal gangue is complex and undergoes intricate reactions when exposed to elevated temperatures during combustion. Among these mineral phases, kaolinite, illite, and pyrite are present and can transform into different forms, such as silicate glass, and crystalline phases like mullite and hematite [45,46]. Importantly, the transformation of minerals can influence the migration behavior of Ga and Ge [30,47]. Understanding these intricate mineral reactions during coal gangue combustion is crucial for comprehending the behavior of critical elements.

The mineralogical characteristics of the coal gangue (100 mesh) combustion product are depicted in Figure 4. With increasing temperatures, the mineral composition of coal gangue underwent significant transformations. Minerals such as kaolinite, illite, pyrite, and calcite diminished, while mullite, hematite, anorthite, and other minerals emerged. When the combustion temperature was 1000 °C, quartz and anatase exhibited high thermal stability and remained intact. However, kaolinite and illite underwent partial conversion into mullite and other minerals, explaining the detection of the mullite diffraction peak in combustion products. The elevated temperatures induced the dehydration and dihydroxylation of clay minerals like kaolinite and illite, promoting the formation of amorphous silicate into a melt. The diffraction peak of kaolinite vanished at 600 °C, while that of illite disappeared at 900 °C, indicating the lower thermal stability of kaolinite compared to that of illite [40,48,49]. Under high-temperature combustion conditions, pyrite particles transformed pyrrhotite because of the intense heat generated during combustion. Pyrite fractures occurred, when the fissure expanded. As the combustion process progressed, the oxidized particles of pyrrhotite underwent further oxidation and eventually converted into hematite [50–52]. In laboratory simulation combustion experiments, it was observed that pyrite could be completely transformed into hematite when the coal gangue sample was burned for 2 h. As the temperature increased, the degree of crystallization of hematite also increased. Notably, the diffraction peaks of both pyrite and hematite disappeared at 600 °C. The transformation of pyrite into hematite could even occur at lower temperatures. At 700 °C, the diffraction peak of calcite disappeared. At this temperature, calcite decomposed into CaO and released CO<sub>2</sub>. Additionally, the presence of the diffraction peak of anorthite was detected in the combustion product at 1000 °C. This observation could be attributed to the decomposition reaction of calcite during the coal gangue combustion process and its interaction with the silica laminate melt, resulting in the formation of anorthite [40,48].



**Figure 4.** Mineralogical characteristics of coal gangue after combustion. The minerals identified were An representing anorthite, At representing anatase, C representing calcite, H representing hematite, I representing illite, K representing kaolinite, M representing mullite, P representing pyrite, and Q representing quartz.

Table 6 presents the contents of Ga and Ge in the combustion products across various particles. Table 7 provides the relative enrichment index (*REI*) values of Ga and Ge in combustion products. The relevant expression for calculating the *REI* was as follows:

$$REI = \left[ C_{product} / C_{gangue} \right] \times A_f \quad (1)$$

where  $REI$  is the relative enrichment index,  $C_{product}$  represents the contents of Ga and Ge in combustion products (mg/kg),  $C_{gangue}$  represents the contents of Ga and Ge in coal gangue (mg/kg), and  $A_f$  represents the ash yield of coal gangue [53]. Temperature plays a critical role in determining the release and migration characteristics of elements in coal gangue [54]. The content of Ga in the products was increased compared with coal gangue, surpassing the recommended economic critical level [53]. As the temperature rose from 600 °C to 1000 °C, the content of Ge in the combustion products gradually decreased. The content of Ge in the combustion product was the highest at 600 °C. As the temperature increased, the volatilization of Ge gradually increased, resulting in a decrease in the content of critical elements in the combustion product. Ga could replace Al in aluminiferous minerals and integrate into the lattice of aluminate melt as the temperature increased. The volatilization of Ga exceeded its incorporation, resulting in a relative decrease in Ga content [55–57]. As shown in Table 7, the  $REI$  was positively correlated with the content of critical elements in the products. The maximum enrichment indices of Ga and Ge in the product were 0.854 and 0.825, respectively.

**Table 6.** The contents of Ga and Ge in the combustion products at different temperatures (mg/kg).

Particle Size (Mesh)		50	80	100	140	200
Ga	600 °C	143.07	147.55	150.93	154.51	157.40
	700 °C	140.26	145.77	149.80	152.10	155.91
	800 °C	130.21	142.02	147.88	149.90	154.18
	900 °C	128.58	139.53	145.22	147.99	151.59
	1000 °C	126.36	129.84	134.67	136.92	143.11
Ge	600 °C	17.21	18.78	20.39	22.85	25.29
	700 °C	16.59	17.54	19.24	20.60	24.53
	800 °C	14.78	15.13	17.34	19.50	23.93
	900 °C	13.81	14.05	15.23	18.33	21.86
	1000 °C	12.00	13.20	14.11	16.15	20.43

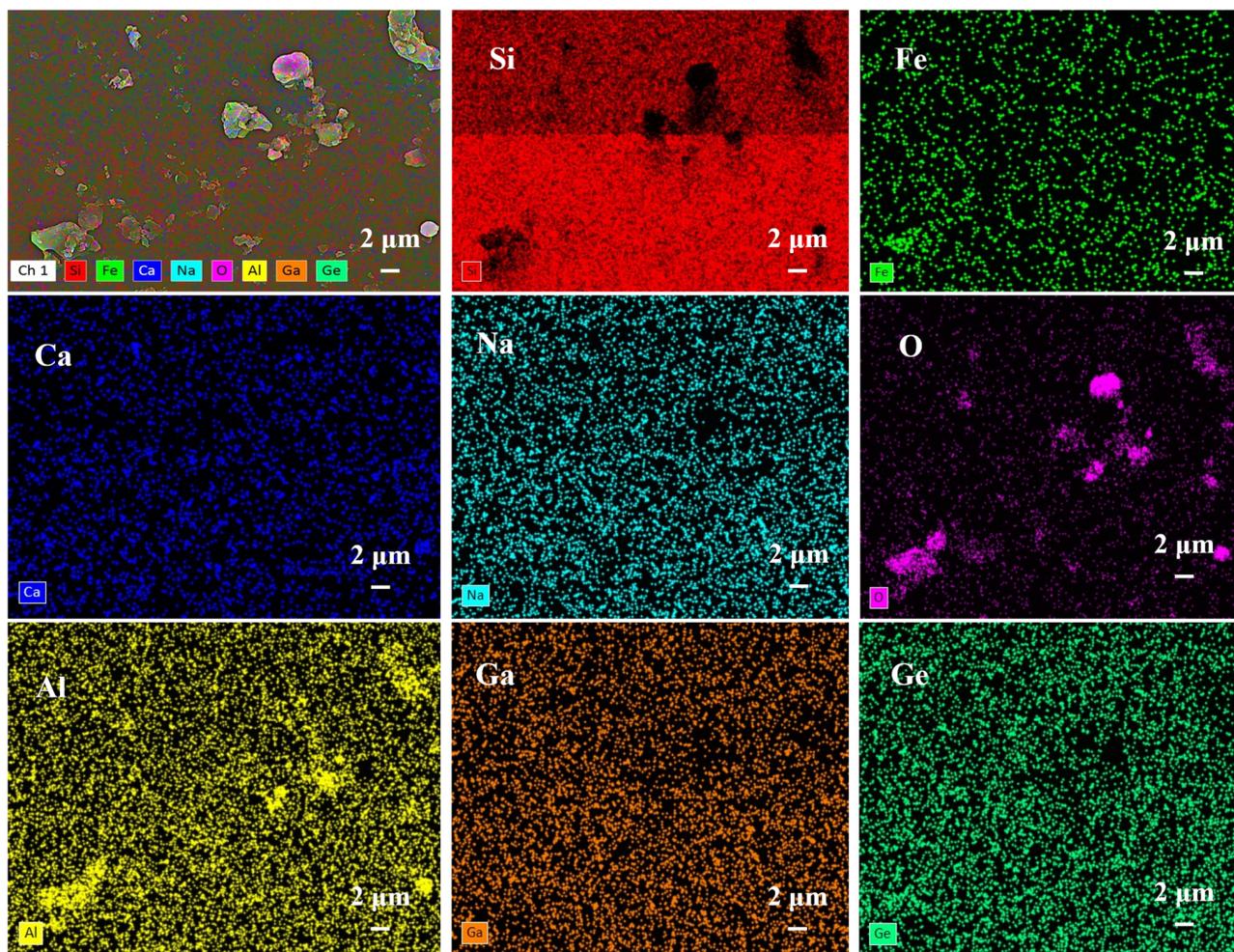
**Table 7.** The relative enrichment indices ( $REIs$ ) of Ga and Ge in the combustion products.

Particle Size (Mesh)		50	80	100	140	200
$REI$ (Ga)	600 °C	0.854	0.848	0.842	0.848	0.843
	700 °C	0.837	0.838	0.836	0.835	0.835
	800 °C	0.777	0.816	0.825	0.823	0.826
	900 °C	0.768	0.802	0.810	0.812	0.812
	1000 °C	0.754	0.746	0.752	0.752	0.767
$REI$ (Ge)	600 °C	0.825	0.823	0.796	0.781	0.820
	700 °C	0.795	0.769	0.751	0.704	0.796
	800 °C	0.708	0.663	0.677	0.666	0.776
	900 °C	0.662	0.616	0.594	0.626	0.709
	1000 °C	0.575	0.579	0.551	0.552	0.663

### 3.3. The Transformation Characterizations of Ga and Ge during Gangue Combustion

The SEM images of 100-mesh coal gangue and combustion products at 1000 °C are shown in Figures 5 and 6. As shown in Figure 5, the gangue was irregularly lumpy and sparsely distributed. As shown in Figure 6, the combustion product was bonded into larger lumps [27]. Si, Fe, Ca, Na, O, Al, Ga, and Ge were observed in both gangue and its products. Si, Al, and O were the most abundant elements in coal gangue and combustion products, which was consistent with their chemical compositions. Figure 5 illustrates the presence of Ga, Ge, Si, Al, and O, suggesting that Ga and Ge may be associated with aluminosilicate minerals present in the coal gangue [58]. The analysis further revealed that the elemental enrichment in the combustion products was significantly higher compared to those in the coal gangue, as shown in Figure 6. The presence of Ga and Ge in the combustion products implied their association with aluminosilicate minerals, along with Si, Al, and O, as their

distributions overlapped. Additionally, the conjunction of these elements with Na in the combustion products suggests the formation of complexes with alkali oxides during the combustion. Previous research has demonstrated that Ga exhibits a strong affinity for the inorganic fraction of coal gangue and has been identified as a substitute for aluminum within it [30]. As shown in Figures 5 and 6, silicate minerals such as kaolinite and quartz, carbonate minerals such as calcite, and minerals containing iron and sulfur such as pyrite were melted under high-temperature conditions [59].



**Figure 5.** The SEM images and distributions of elements of coal gangue.

Ga can exist in both inorganic minerals and organic matter and has a positive affinity to the inorganic fraction [49]. As depicted in Figure 7, Ga existed in coal gangue in three primary forms: residual, organic/sulfide-bound, and metal-oxide-bound modes. These forms accounted for 87.88%, 5.74%, and 4.07% respectively. After combustion, Ga was still mainly distributed in the above three combined modes, with the residual mode accounting for over 85% of its presence. The active mode consisted of three forms: ion exchange, carbonate-bound, and metal-oxide-bound. The occurrence form of Ge in all-hosted ore deposits was primarily an organic association [60]. According to the chemical extraction experiment, Ge was primarily found in the residue (62.52%), organic/sulfide-bound (27.49%), and metal-oxide-bound modes (7.93%). The proportions of carbonate-bound and ion-exchanged Ge were 1.71% and 0.35%, respectively.

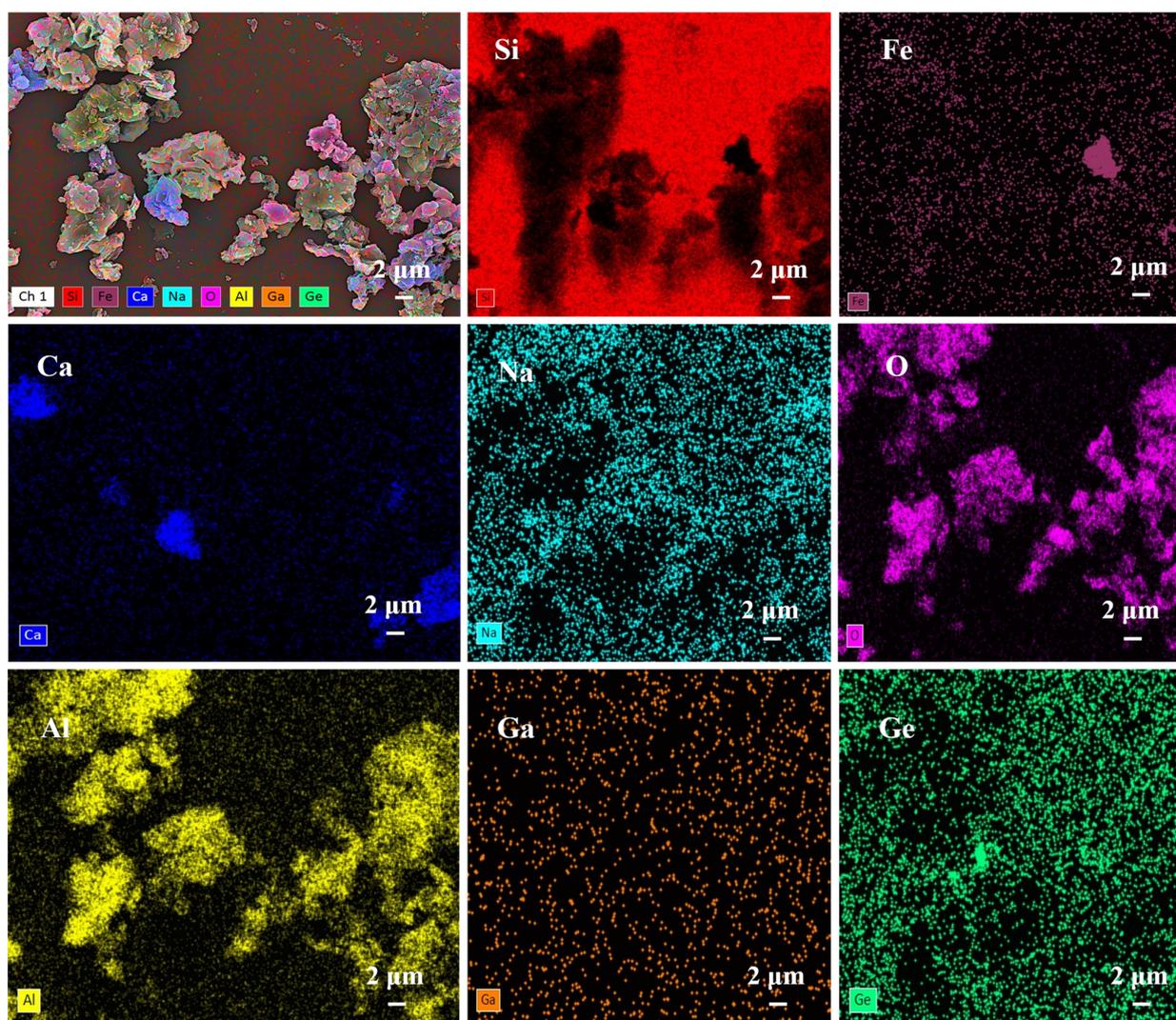


Figure 6. The SEM images and distributions of elements of combustion products at 1000 °C.

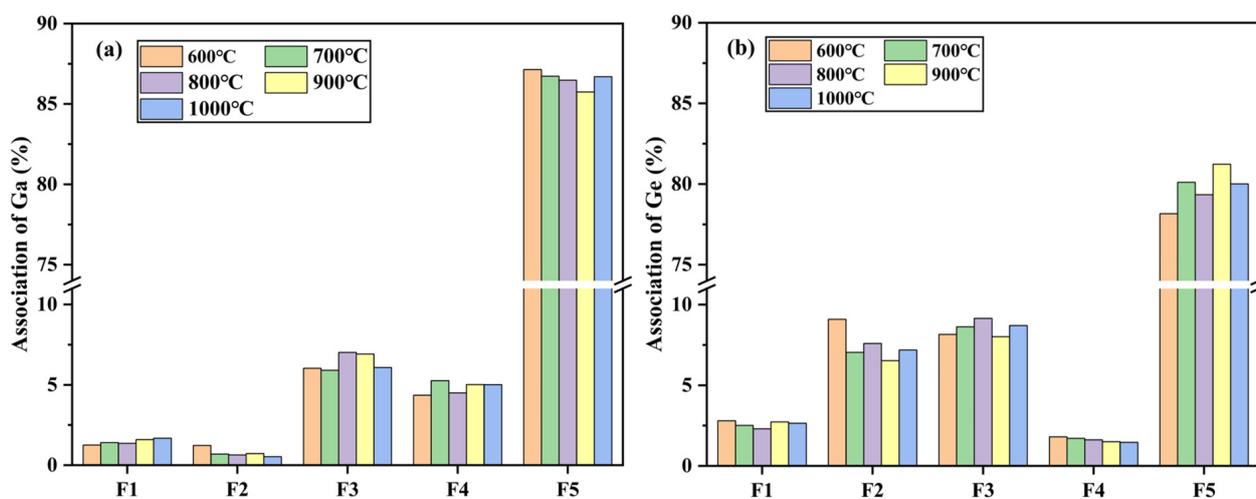


Figure 7. The occurrence forms (a) of Ga and (b) of Ge in combustion products at different temperatures. F1—ion exchangeable; F2—carbonate-bound; F3—metal-oxide-bound; F4—organic/sulfide-bound; F5—residual.

When the combustion temperatures were 600 °C and 700 °C, the proportions of active mode Ga were 8.51% and 8.01%, respectively. As the temperature rose to 800 °C and 900 °C, the proportion of active Ga slightly increased to 9.02% and 9.23%, respectively. Finally, at 1000 °C, the majority of Ga was stored in the molten aluminosilicates, accounting for up to 91.71%. After combustion, the proportions of carbonate-bound, organic/sulfide-bound, and residual Ga decreased, which were 0.53%–1.23%, 4.35%–5.26%, and 85.75%–87.14%, respectively. In contrast, the proportions of ion-exchanged and metal-oxide-bound Ga increased, which were 1.25%–1.68% and 5.91%–7.02%, respectively, indicating that other ions exchanged with Ga. Ga reacted with oxygen or other oxides to form metal oxide-bound Ga [30]. The organic/sulfide-bound Ge in the combustion products was significantly reduced, accounting for 1.46% to 1.80%. Organically bound forms of Ge and germanium-bearing kaolinite decomposed into germanium-bearing oxides (GeO<sub>2</sub>). Conversely, Ge in the residual, metal-oxide-bound, carbonate-bound, and ion exchangeable modes increased after combustion. Their proportions were 78.16%–81.23%, 8.01%–9.15%, 6.53%–9.09%, and 2.30%–2.80%, respectively. This indicates that the minerals present in organic matter and pyrite transformed [30,61].

The contents of Ga and Ge in coal gangue and their distributions post-combustion into ash and gaseous products are shown in Figure 8. For Ga, it started with a content of 91.03 mg/kg in the coal gangue. After combustion, the majority of Ga was found in the ash, with an increased concentration due to the loss of mass in other components of the gangue. A smaller portion of Ga transited to the gaseous phase, which suggests volatility or association with other volatile compounds during combustion. From the proportion of Ga and Ge in ash, most Ga and Ge exist in the form of the residual. The critical metals exist in the glass phase in the form of the Si-Al lattice and are extracted by strong acid and alkali solutions [30]. The extraction methods vary according to the different occurrence forms of Ga and Ge. Understanding the migration and transformation characteristics of Ga and Ge during coal gangue combustion is crucial for predicting the environmental impact of these processes and for the potential recovery of these elements from ash. The results of the study could provide a reference to subsequent gangue combustion processes to promote the targeted enrichment of critical elements into ash.

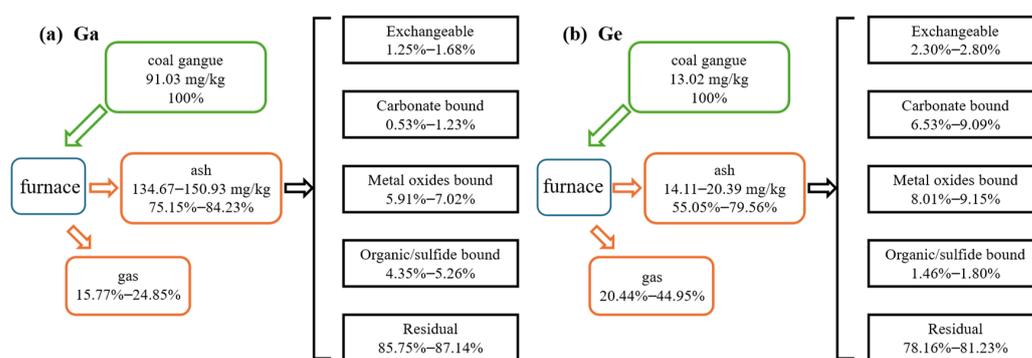


Figure 8. The mass balance diagram (a) of Ga and (b) of Ge elements migration.

#### 4. Conclusions

The contents of Ga and Ge in coal gangue were influenced by the particle size. Temperature was a crucial factor affecting the migration and transformation of Ga and Ge. The coal gangue’s mineralogical composition comprised anatase, calcite, illite, kaolinite, pyrite, and quartz. Ga and Ge bound to organic matter were easier to release, while elements bound to clay minerals or other inorganic components were more difficult to release. Most of Ga and Ge in coal gangue existed in the form of the residual, organic/sulfide-bound, and metal-oxide-bound modes.

As the temperature increased from 600 °C to 1000 °C, the contents of Ga and Ge in combustion products decreased and reached the maximum at 600 °C, which were

157.40 mg/kg and 25.29 mg/kg, respectively. Under elevated temperatures, kaolinite, illite, and pyrite transformed into silicate glass phases and crystalline phases such as mullite and hematite. The transformation of these minerals significantly impacted the migration of critical elements. After combustion, most of Ga and Ge existed in the form of the residual, organic/sulfide-bound, and metal-oxide-bound modes. These critical metals were in the glass phase as part of the Si-Al lattice. Most of Ga and Ge were found in the ash and existed in the form of the residual mode. As the temperature rose to 800 °C and 900 °C, the proportion of active (ion exchangeable, carbonate-bound, and metal-oxide-bound) Ga slightly increased to 9.02% and 9.23%, respectively. The majority of Ga was stored in the molten aluminosilicates, accounting for up to 91.71% at 1000 °C. The organic/sulfide-bound Ge in the combustion products was significantly reduced, accounting for 1.46% to 1.80%. Ge in the residual, metal-oxide-bound, carbonate-bound, and ion exchangeable forms increased after combustion. Their proportions were 78.16%–81.23%, 8.01%–9.15%, 6.53%–9.09%, and 2.30%–2.80%, respectively.

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