

Article

Enrichment of Trace Elements in the Early Carboniferous Coals from the Machala Mine in Eastern Qiangtang Basin, Eastern Tibet, SW China

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Abstract: The Machala Mine, which is located in the Eastern Tibetan Plateau, was one of the highest coal mines in the world, with an elevation of 5200 m. The Machala coals are rich in a variety of critical and harmful elements. However, the occurrence and enrichment mechanisms of these elements are not well understood, which hinders the assessment of their environmental impacts and recycling potential. Furthermore, the enrichment mechanism identified in the Machala coals is expected to extend our understanding of the simultaneous enrichment of multiple elements in coal. A total of 18 coal samples were collected from 14 coal (or carbonaceous mudstone) seams at the Machala open-pit mine for systematic analyses, including macerals, coal quality, minerals, trace, and major elements of coals. The results suggested that the coal seams in the Machala Mine were dominated by low-sulfur (mainly less than 1%), medium-to-low-ash (average: 18.15%), low-volatile (average: 16.01%), and medium-high-to-high-calorific (average: 27.23 MJ/kg) coals. The coal macerals were predominantly vitrinite, with the collodetrinite being the most abundant, followed by collotelinite and vitrodetrinite, while telinite was present in low amounts. The mineral compositions were mainly quartz and kaolinite, with average contents of 37.8% and 48.2%, respectively, which were followed by illite and smectite-mixed layers, with average contents of 4.7% and 3.3%, respectively. Other minerals, including plagioclase, pyrite, siderite, chlorite, and potassium feldspar, were present in low quantities. However, C3 coal seam was an exception, with a high pyrite content of 23.2% (low-temperature ash sample). The Machala coal seams were characterized by varying degrees of enrichment in Li, As, Pb, Hg, and Sn. Correlation analyses and energy spectrum analyses indicated that clays were their major host minerals. The enrichment of Li in the Machala Coal Mine was mainly attributed to volcanic ash during the sedimentation period, while As, Pb, Hg, and Sn were primarily sourced from hydrothermal fluids in the late stages.

Keywords: the Machala Mine; coal geochemistry; metal elements in coal; the early Carboniferous period; the Tibetan Plateau



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1. Introduction

The presence of trace elements in coal and their subsequent impact on the ecological environment have garnered significant attention in the fields of geology and environmental science for many years [1,2]. As global demand for critical metal resources escalates, research into the enrichment characteristics of trace elements in coal, which represents a pivotal potential source of these metals, has received increasing scrutiny. Indeed, some critical metals in coal have already been extracted and utilized [3–8]. The Qinghai–Tibet Plateau, renowned as one of the world’s highest regions, presents exceptional conditions conducive to the enrichment of trace elements in coal, owing to its unique geological structure and evolutionary history. A hallmark of coals sourced from the Tibetan Plateau is the enrichment of multiple elements. Notably, it has been documented that the Jurassic coal from the Muli Coalfield is abundant in phosphorus, fluorine (F), strontium (Sr), and barium (Ba), whereas the Triassic coal from the Tumen Coal Mine is enriched with arsenic (As), mercury (Hg), lead (Pb), and selenium (Se) [9,10]. Given the fragile ecological environment of the Qinghai–Tibet Plateau, previous studies have emphasized that the enrichment of environmentally unfriendly elements in this region is a common feature highlighted in the existing literature [3]. The enrichment of these toxic and harmful elements has significantly hindered the exploitation and utilization of coal resources in the Qinghai-Tibet Plateau.

The Machala Coal Mine, located in Eastern Tibet, was historically the highest mine in the world, with an elevation of 5200 m [11]. The coal resources from the Machala coal mine played a crucial role in the local energy supply during the 20th century and have attracted significant attention due to their unique coal-bearing deposition and tectonic evolution. The North Qiangtang Block, where the Machala Coal Mine is located, is part of the Gondwana continent [12], and the eastern Tibet region has been tectonically and magmatically active since the Mesozoic [13–15], which provides favorable conditions for metal mineralization. The enrichment of Nb-Zr-REE-Ga in Late Permian coals in Western Guizhou is a typical example for multiple elements gathering, which was revealed to be attributed to tuff input [16,17]. While tuff is present in the lower coal-bearing strata of the Machala coal mine, the precise characteristics and mechanisms underlying the multi-element enrichment in its coal remain elusive. This research endeavors to elucidate the enrichment patterns of trace elements in coal extracted from the Machala mining area, with a particular emphasis on those critical metal elements that not only pose significant environmental risks but also exhibit substantial resource development potential. Ultimately, the objective is to provide novel insights and guidance for the exploitation and utilization of coal resources in Eastern Tibet and adjacent regions.

2. Geological Settings

The Machala Mine is located at the northeastern edge of the Shuanghu–Lancangjiang belt in the Southeastern Qiangtang Basin (Figure 1a), which is a part of the North Qiangtang Block. The coal-bearing strata are the Lower Carboniferous Machala Formation, and the coal seams are mainly formed in the peat swamp sedimentary environment that transitions from marine to continental environments [18]. The North Qiangtang Block, a micro-block within the Paleo-Tethys Ocean, has undergone a series of tectonic events from the Late Paleozoic to the Mesozoic. These events include the northward drift initiated in the Southern Hemisphere, convergence with the South Qiangtang Block to the south, convergence with the Songpan–Ganzi Block to the northeast, and the uplift of Tibetan Plateau in Cenozoic [12,19–21]. These processes have resulted in the strong deformation of the Machala coals. The Machala Mine is positioned in an anticline with a north-south axial trend (Figure 1b), surrounded by Late Triassic rhyolite and Yanshanian felsic intrusive rocks. These rocks follow a north-south axis trajectory and are situated between faults.

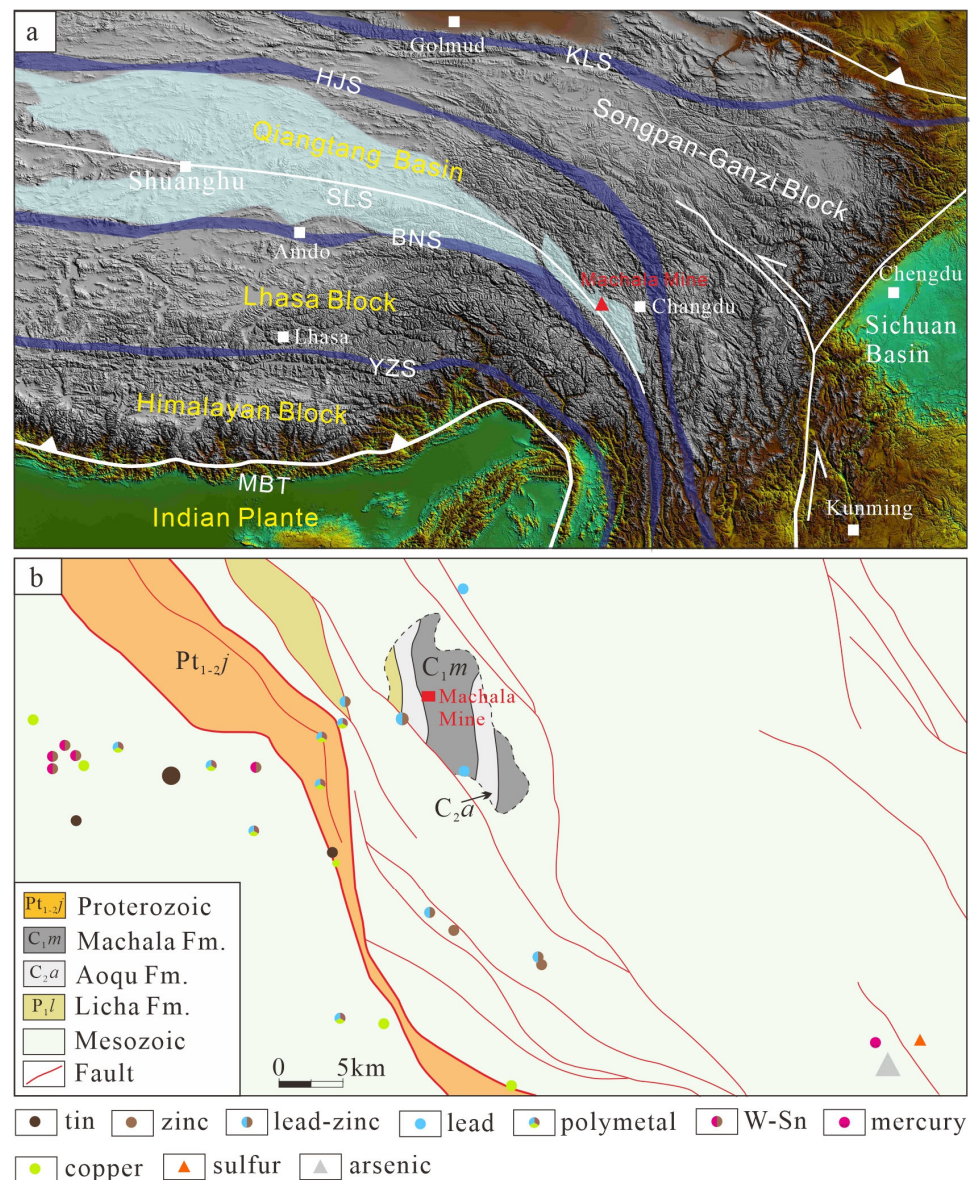


Figure 1. (a) Tectonic location of the study area; (b) geological map of minerals in and around the Machala Mine.

The coal-bearing Machala Formation, with a thickness over 500 m, is generally divided into a lower clastic section and an upper carbonate section based on lithology (Figure 2). The upper carbonate section is mainly composed of biological limestone, with quartz sandstone also present in several outcrops. The lower coal-bearing clastic rock section mainly consists of gray-black mudstone, black shale, and interbedded fine quartz sandstone of different thicknesses. The Machala Mine contains over 20 coal seams, ranging from 0.2 m to 0.6 m in thickness, with the thickest seam reaching 1.2 m. Tectonic activities have significantly deformed these coal seams, imparting them with distinctive sliding characteristics and irregular thicknesses distributions.

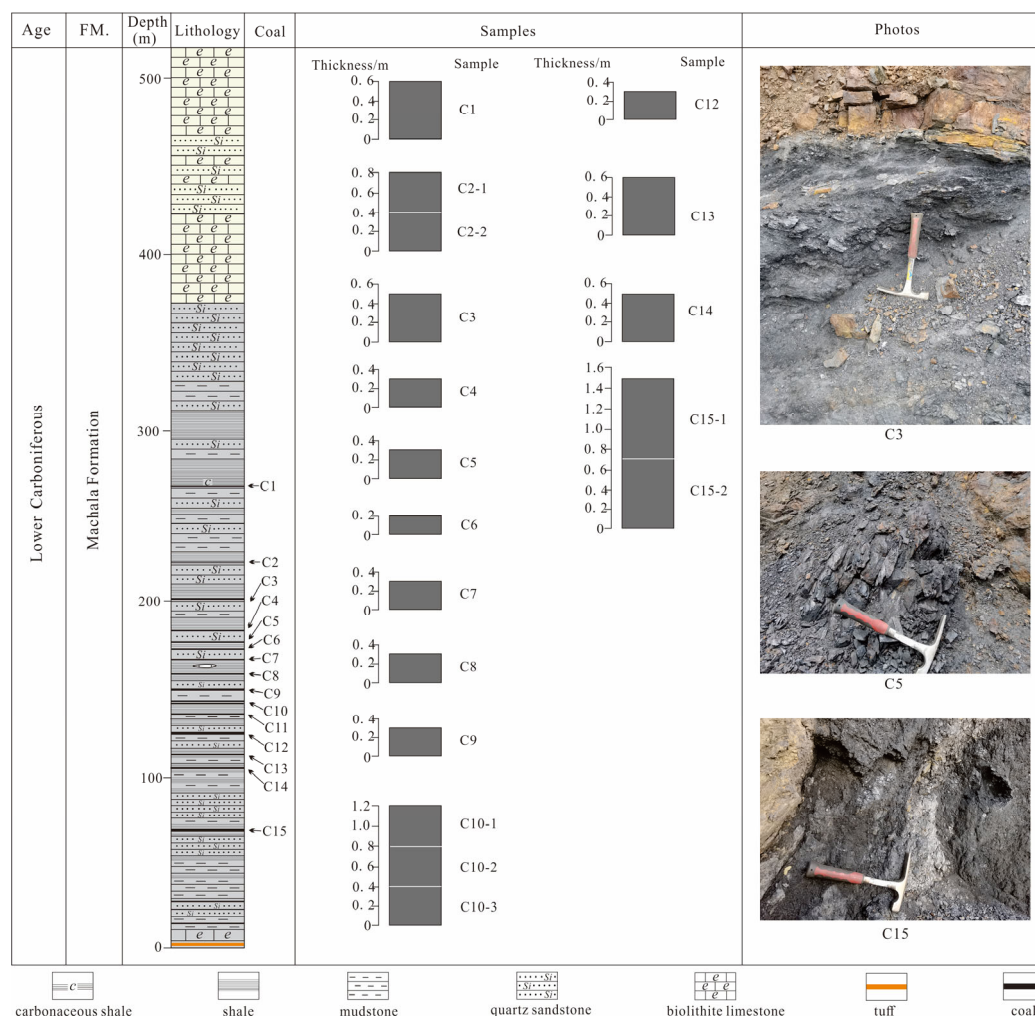


Figure 2. The generalized stratigraphic section of the Machala Formation and the sampling sections of the Machala Coals.

3. Samples and Analytical Methods

Samples were taken from an open pit at the Machala Mine using a channeling sampling strategy from top to bottom of the Lower Machala Formation. A total of 18 coal samples were collected from 14 coal seams. One sample was collected from a coal seam with a thickness of less than 0.6 m, while multiple samples were collected at equal intervals from top to bottom in coal seams with a thickness exceeding 0.6 m.

Proximate analysis was performed in accordance with ASTM Standards (2011) [22–24], while the total and morphological sulfur analyses were performed according to ASTM Standard D3177-02 (2007) [25]. The contents of elements C, H, and N were determined using the Chinese-made K1100/K1100F fully automatic Kjeldahl nitrogen analyzer (Hanon Group, Guangzhou, China) and the CTCH500 semi-automatic carbon and hydrogen analyzer (Xuzhou Terry Instrument And Equipment Co., Ltd., Beijing, China) according to the Chinese National Standard GB/T 30733-2014 [26]. The content of element O was calculated. Maceral identification of the samples was performed using a Leica-BMRXP microscope (LEICA Camera microscope, Wetzlar, Germany) under oil-immersion reflected light according to the ICCP System 1994 [27,28].

The major and trace elements were analyzed after the raw coal sample was crushed to 200 meshes. Major elements were tested following the ashing of the powder coal sample at 815 °C using an X-ray Fluorescence Spectrometer (XRF, Malvern Panalytical, Shanghai, China), which provided an error value ranging between 0.12% and 0.20%. In

contrast, trace elements were analyzed through an ICAP-Qc inductively coupled plasma-mass spectrometry (ICP-MS, Thermo Fisher Scientific, Beijing, China), which provided a detection limit of 0.1–0.5 ppm. X-ray diffraction analysis was carried out on 200 mesh pulverized coal samples after low-temperature ashing. Coal samples were ashed at a low temperature (<150 °C) for XRD using a Quorum K1050X. The instrument used for X-ray diffraction was the D8 Discover, manufactured by Bruker, Ettlingen, Germany. The scanning condition was $\pm 0.05^\circ$ (2 θ), with a 2 θ angular accuracy of 0.01°. The scanning range for the whole rock was 3° to 45°, while the three scanning ranges for the clay minerals were 2.5–15°, 2.5–30°, and 3–15°. Scanning electron microscopy (SEM, HITACHI, Beijing, China) and energy spectrum analysis were performed on 80 mesh coal powder samples after low-temperature ashing and on samples after gold spray treatment under a scanning electron microscope (FE-SEM; SIGMA 300, Carl Zeiss Jena, Guangzhou, China). The energy spectrum analysis had an element detection limit of approximately 0.01% wt.

4. Results

4.1. Coal Characteristics

Proximate analysis results of the 18 coal samples (Table 1) showed that the coal ash yields for samples C3 and C5 exceeded 50%, classifying them as carbonaceous mudstone. The coal ash yields for the remaining samples ranged from 8.49% to 40.26%, with the majority falling below 25%, and an average value of 18.15%. This demonstrated that the coal falls into the category of medium to low ash coal according to Chinese Standards GB/T 15224-2010 [29]. The volatile yields of the coals ranged from 10.18% to 22.32%, with an average of 16.01%, which is indicative of low-volatile coals according to the ASTM classification D388-12 (2012) [30]. The total sulfur content of the coal was generally less than 1%, classifying it as low-sulphur coals according to Chinese Standards GB/T 15224-2010 [31]. Organic sulfur was the predominant form of the sulfur, with the pyrite sulfur being the secondary sulfur form in coal. Notably, the pyrite sulfur content in the C3 carbonaceous mudstone sample reached 9.06%, indicating unique sedimentary characteristics compared to other coal seams. The calorific values of the coal seams ranged from 18.80 to 31.96, with an average of 27.23 MJ/kg, which is indicative of medium-high to high calorific values according to GB/T 15224-2010 [32]. In general, the coal seams in the Machala Mine were dominated by low-sulfur, medium-low ash, low-volatile, and medium-high calorific coals.

Table 1. Proximate and ultimate analyses of the samples in the Machala Mine.

Samples	C1	C2-1	C2-2	C3	C4	C5	C6	C7	C8	C9	C10-1	C10-2	C10-3	C12	C13	C14	C15-1	C15-2
Thickness (m)	0.6	0.4	0.4	0.5	0.3	0.3	0.2	0.3	0.3	0.3	0.4	0.4	0.4	0.3	0.8	0.7	0.7	0.8
Moisture (% ad)	1.12	0.89	0.72	0.77	2.56	1.57	2.80	1.45	1.03	0.60	2.84	1.54	3.11	1.38	0.65	0.52	0.69	0.66
Ash (% d)	55.96	19.34	22.74	22.61	24.30	53.72	11.82	19.40	37.92	40.26	13.74	8.49	11.42	9.18	12.06	8.96	11.02	17.19
Volatile matter (% daf)	24.91	13.45	14.82	18.02	22.32	29.48	16.79	16.22	20.28	15.78	20.31	16.35	21.50	14.59	11.89	10.18	11.06	12.68
Total sulfur (% d)	0.33	0.87	1.03	16.73	0.64	0.41	0.88	0.97	0.60	1.57	0.84	1.02	1.24	1.10	1.03	1.29	1.05	0.83
Pyrite sulfur (% d)	0.03	0.18	0.21	9.06	0.05	0.04	0.06	0.04	0.00	0.34	0.00	0.00	0.39	0.00	0.05	0.09	0.03	0.10
Sulphate sulfur (% d)	0.02	0.08	0.12	0.77	0.02	0.04	0.02	0.32	0.16	0.38	0.00	0.01	0.02	0.28	0.08	0.16	0.20	0.02
Organic sulfur (% d)	0.28	0.61	0.70	6.90	0.56	0.33	0.80	0.61	0.43	0.85	0.84	1.01	0.83	0.81	0.90	1.04	0.82	0.70
Oxygen (% daf)	15.38	6.83	7.04	0.46	11.73	16.84	8.12	7.59	11.12	9.43	9.71	7.04	8.96	6.30	5.44	4.34	4.82	6.61
Carbon (% daf)	79.49	88.07	87.46	74.41	83.49	77.76	86.68	87.05	83.53	83.43	85.24	87.57	85.70	88.07	89.12	89.96	89.82	88.17
Hydrogen (% daf)	3.67	3.33	3.49	2.79	3.23	3.73	3.29	3.17	3.42	3.74	3.27	3.44	3.22	3.56	3.50	3.53	3.46	3.50
Nitrogen (% daf)	0.69	0.70	0.68	0.73	0.72	0.79	0.91	0.98	0.98	0.77	0.80	0.84	0.72	0.87	0.78	0.75	0.72	0.72
R _{o,max}	1.93	2.19	2.33	2.10	2.21	1.99	2.35	1.52	1.54	2.17	2.21	2.01	2.14	1.95	2.38	2.37	2.35	2.36
Q _{b,ad} (MJ/kg)	12.98	27.20	26.10	25.81	22.96	13.12	28.56	26.27	19.47	18.86	27.09	30.38	27.84	30.90	30.22	31.96	31.18	28.38
Q _{net,d} (MJ/kg)	12.72	26.74	25.58	23.91	22.92	12.88	28.58	25.96	19.13	18.33	27.11	30.03	27.91	30.48	29.62	31.28	30.60	27.83
Q _{gr,d} (MJ/kg)	13.08	27.32	26.15	24.38	23.48	13.28	29.25	26.52	19.59	18.80	27.76	30.71	28.57	31.18	30.27	31.96	31.25	28.44

Ad, as determined; d = dry; daf, dry, ash-free basis; R_{o,max}, vitrinite reflectance (%; mean maximum); Q_{b,ad}, bomb calorific value, air-dried basis; Q_{net,d}, net calorific value, dry basis; Q_{gr,d}, gross calorific value, dry basis.

Elemental analyses revealed that the samples from the 14 coal seams contained relatively consistent contents of O, C, H, and N. The average contents of these elements were

8.30%, 85.11%, 3.40%, and 0.79%, respectively. The Machala coal was distinguished by its high carbon content and low hydrogen and oxygen contents.

4.2. Coal Macerals

Coal macerals are presented in Table 2. The organic fractions in each coal seam consisted of vitrinite and inertinite, with liptinite not being identified. The vitrinite-to-inertinite ratios ranged from 0.8% to 14.3%, with an average of 5.5%. Generally, the lower coal seams exhibited a higher vitrinite content than the upper coal seams.

Telinite, collotelinite, collodetrinite, and vitroderinite (Figure 3C,D,F) were detected within vitrinite. Collodetrinite had the highest content, followed by collotelinite and vitroderinite, with the telinite being the least abundant. The inertinite consisted of fusinite, semifusinite, and inertodetrinite (Figure 3A,B,D), in which the content of semifusinite was slightly higher than those of the other two. There was minimal variation in maceral content among vertical coal seams.

Table 2. Maceral analysis of the samples in the Machala Mine (vol.%).

Maceral Group	Maceral	C1	C2-1	C2-2	C3	C4	C5	C6	C7	C8	C9	C10-1	C10-2	C10-3	C12	C13	C14	C15-1	C15-2
Vitrinite	Telinite	4	3	1		1			1		2				1	1	1	2	4
	Collotelinite	2	8	6	12	3	2	7	3	3	8			5	26	16	17	22	16
	Collodetrinite	13	47	45	45	43	29	65	46	26	37	57	51	54	49	55	54	56	44
	Vitroderinite	3	4	5	6	4	3	6	1	0	5	17	24	12	11	14	14	8	11
Inertinite	Fusinite	3	6	5	4	8	3	3	6	4	4	2	4	5	1		1		3
	Semifusinite	18	10	15	9	15	4	6	22	26	6	7	4	8	2	2	3	3	4
	Macrinite									0				<1					
	Inertodetrinite	6	6	5	3	6	8	3	9	2	3	5	5	7	3	5	4	3	4
Totals	Total Vitrinite	22	62	58	63	51	35	77	52	28	51	76	81	70	87	85	86	87	75
	Total Inertinite	27	22	24	16	29	15	13	38	32	13	14	12	22	7	7	8	6	11
	Total Liptinite																		
	Total Minerals	51	16	18	21	19	50	10	11	38	36	10	7	8	6	9	6	7	14

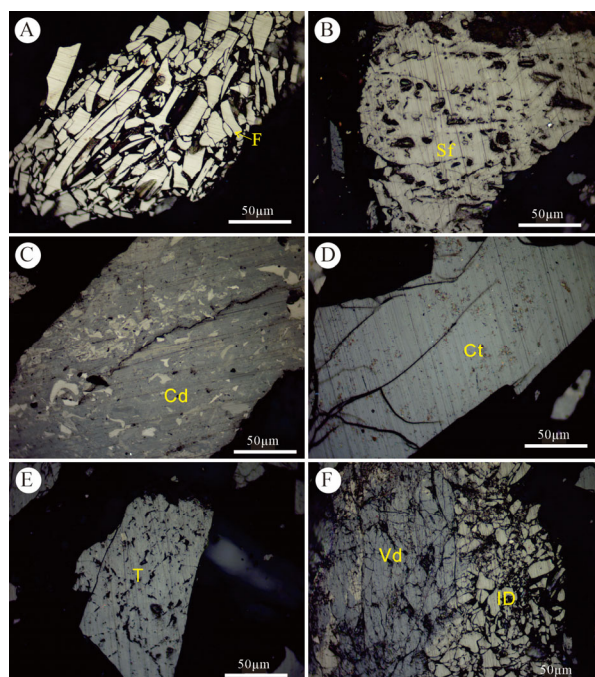


Figure 3. Macerals in the Machala coals. (A) fusinite, from sample C10-3; (B) semifusinite, from sample C2-1; (C) collodetrinite, from sample C2-2; (D) collotelinite, from sample C10-1; (E) telinite, from sample C12; (F) inertodetrinite and vitroderinite, from sample C12.

4.3. Coal Mineralogy

Microscopic examination showed that the total mineral content of low-temperature ashed samples ranged from 7% to 50%, with the upper coal seams exhibiting significantly higher mineral content than the lower coal seams (Table 2). The semi-quantitative analysis of X-ray diffraction (Table 3) indicated that the mineral composition of the coal was predominantly composed of quartz and kaolinite, with average contents of 37.8% and 48.2%, respectively. Illite-and-smectite-mixed layers were present at secondary levels, with average contents of 4.7% and 3.3%, respectively. Other minerals, including plagioclase feldspar, pyrite, siderite, chlorite, and potash feldspar, were detected in low concentrations. The C3 coal seam was distinctive, with a pyrite content of 23.2%, which aligned with its high total sulfur value.

SEM and energy spectrum analyses of low-temperature ashed coal sample provided further evidence of the high quartz content and clay mineral content within the coals. Moreover, these analyses identified a variety of pyrite types in the Machala coals, including irregular massive pyrite, clumped massive pyrite, strawberry pyrite, grid pyrite, oolitic pyrite, and cube pyrite (Figure 4).

Table 3. Mineral contents in low-temperature ashed Machala coals detected by X-ray.

Samples	C1	C2-1	C3	C4	C5	C6	C7	C8	C9	C10-2	C12	C13	C14	C15-1	C15-2
Quartz (%)	48.9	39.1	32.2	34.6	50.4	39.4	42.6	39.2	54.8	11.1	36.9	29.5	41.6	30.2	47.7
Feldspar (%)					0.8										
Plagioclase (%)	1.8	1.3	1.3					1.3							
Pyrite (%)			23.2						0.7				3.7		3.4
Siderite (%)	0.9						5.3	2.2							
Kaolinite (%)	16	40.5	24.5	52.6	33.8	46.9	44.8	35	41.8	88	61.8	52.1	52	55.8	44.5
Chlorite (%)					1.3			0.8				4			
Illite (%)	16.5	6.6	7.7	3.9	2.9	4.2	3.6	10.3	2.2	0.9	1.3	5.6	2.7	11.2	2.9
Illite/Smectite (%)	16.1	8.2	8.1	4.5	8.1	4.7	2.6	6.3				4.1			

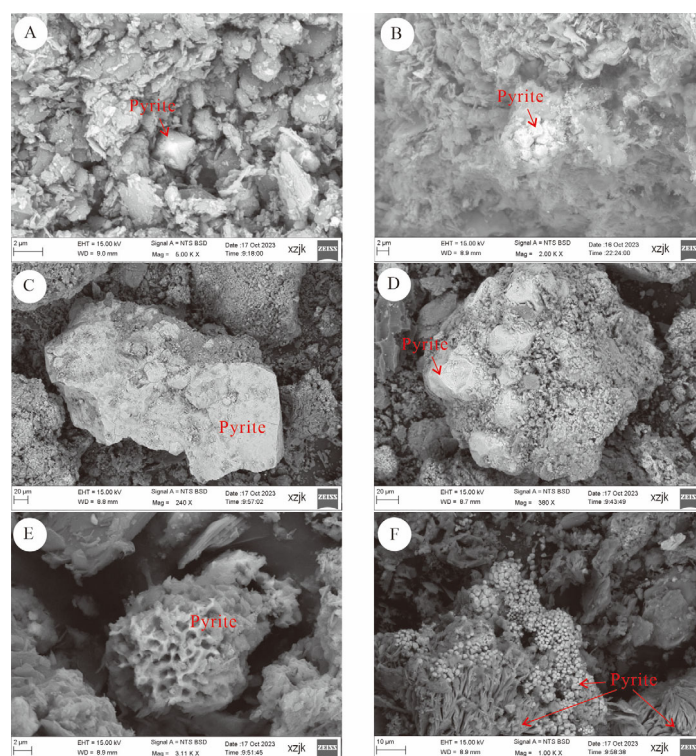


Figure 4. Different types of pyrite in the Machala coals: (A) cube pyrite, from sample C3; (B) strawberry pyrite, from sample C3; (C) clumped massive pyrite, from sample C3; (D) irregular massive pyrite, from sample C5; (E) grid pyrite, from sample C5; (F) oolitic pyrite from sample C5.

4.4. Elemental Abundance

The major elements in Machala coal and carbonaceous mudstone samples are presented in Table 4. The major elements in Machala coals were mainly SiO_2 and Al_2O_3 , with concentrations ranging from 2.74% to 27.37% (average value: 9.29%) and from 1.84% to 10.34% (average value: 4.31%), respectively. The value of $\text{SiO}_2/\text{Al}_2\text{O}_3$ ranged from 1.25 to 2.97, with an average of 2.09, which indicated a high quartz content in the Machala coal. The concentration coefficient (CC) was employed to characterize the degree of mineral and element enrichment in coal [33]. Compared with typical Chinese coal [34], the concentrations of SiO_2 and K_2O (average: 0.31%) in Machala coal exceeded the average value of Chinese coal, with CC values being 1.1 and 1.6, respectively. The concentrations of other major elements were lower than the average value of Chinese coal, with CC values ranging from 0.4 to 1.0.

Table 4. Oxides of major elements in samples (% , based on a SO_3 -free and ash basis).

Samples	C1	C2-1	C2-2	C3	C4	C5	C6	C7	C8	C9	C10-1	C10-2	C10-3	C12	C13	C14
SiO_2	50.35	10.16	6.25	5.10	12.64	27.10	7.35	13.42	27.37	5.20	5.14	3.92	2.74	4.54	10.15	4.73
TiO_2	0.74	0.19	0.19	0.08	0.30	0.49	0.12	0.19	0.42	0.07	0.17	0.05	0.16	0.13	0.30	0.14
Al_2O_3	17.79	4.83	4.43	2.13	6.44	9.47	4.08	4.51	10.34	1.89	3.61	3.13	1.84	2.36	5.59	2.33
Fe_2O_3	0.89	3.39	10.59	2.70	0.13	5.70	0.30	1.64	1.81	0.23	0.12	0.01	0.01	0.63	0.97	0.22
MgO	0.43	0.14	0.07	0.10	0.12	0.15	0.13	0.21	0.25	0.08	0.14	0.09	0.11	0.07	0.11	0.07
CaO	0.23	0.10	0.07	0.09	1.07	1.02	1.00	2.78	0.48	0.09	1.70	0.59	1.62	0.63	0.43	0.10
Na_2O	0.17	0.08	0.06	0.05	0.06	0.09	0.06	0.08	0.10	0.07	0.06	0.06	0.05	0.04	0.07	0.06
K_2O	3.19	0.45	0.06	0.27	0.39	0.61	0.24	0.52	1.59	0.06	0.16	0.07	0.03	0.05	0.39	0.07
MnO	0.00	0.01	0.03	0.00	0.00	0.01	0.00	0.14	0.01	0.00	0.02	0.01	0.02	0.00	0.01	0.00
P_2O_5	0.07	0.04	0.05	0.02	0.02	0.11	0.19	0.05	0.04	0.02	0.13	0.03	0.07	0.05	0.11	0.11
LOI	25.98	80.48	78.05	89.31	78.69	55.14	86.31	76.25	57.49	92.25	88.63	91.90	93.10	91.31	81.66	91.94
SUM	99.84	99.87	99.85	99.87	99.86	99.89	99.79	99.80	99.89	99.96	99.87	99.85	99.76	99.82	99.79	99.78

The results of the whole-rock trace element analysis for Machala coal and carbonaceous mudstone samples are detailed in Table 5. When compared to world hard coal [35], the degree of elemental enrichment varied among different coal seams. As illustrated in Figure 5, the elements that exhibited significant enrichment ($\text{CC} \geq 10$) in the C5 sample are Li, Pb, and As, with CC values being 18.0, 11.2, and 21.1, respectively. Elements with moderate enrichment ($5 \leq \text{CC} < 10$) included Pb and Hg in the C3 sample, Li in the C4 sample, Hg and Sn in the C5 sample, Cs in the C8 sample, Li and Sn in the C13 sample, and As in the C14 sample. The aforementioned elements were also rich in other coal seams in the Machala coal. For example, Li was slightly enriched ($2 \leq \text{CC} < 5$) in the C2, C6, C8, C10, C12, and C15 coal seams. Pb was slightly enriched in the C2, C4, C6, C8, and C13 coal seams. As was slightly enriched in the C2 coal seam, Hg was slightly enriched in the C2, C4, C6, C8, C13, C14, and C15 coal seams. Sn was also enriched or slightly enriched in other coal seams, with the exception of the C7 coal seam. In addition, elements such as V, Sr, Zr, Hf, and Th were enriched or slightly enriched in some coal seams.

Table 5. Trace elements of the coal samples (ppm; on a whole-coal basis; air-dried).

Element	C1	C2-1	C2-2	C3	C4	C5	C6	C7	C8	C9	C10-1	C10-2	C10-3	C12	C13	C14	C15-1
Li	125	60	72	24	93	252	46	21	51	22	63	59	27	34	81	22	34
Be	2.3	2.5	3.4	2.4	2.7	1.2	4.6	2.9	2.5	3.2	2.4	0.5	1.1	1.3	1.5	4	5.5
Sc	8.9	7.1	8.2	9	6.7	8.1	9.7	7.6	9.3	6.3	5.5	6.7	4	6.5	5.9	4.8	8.4
V	143	51	17	27	88	94	51	50	97	24	40	33	17	20	39	19	26
Cr	69	22	14	18	26	44	21	33	45	15	23	20	14	20	27	17	21
Co	2.5	4.1	8.2	2.5	1.1	3.2	2.7	26.8	3.4	1.1	6	2.4	2.6	3.3	2	0.78	1.6
Ni	7.4	15	24	10.3	9.4	13	17	36	7	5	13	6.6	10	15	8.7	4.5	5.7
Cu	4.1	5.4	11	9.4	2.6	16	3.1	10	9.5	1.8	1.8	1.4	2	17	8.2	4.6	8.2
Zn	15	30	56	14	8	15	9	60	15	23	17	6.8	7.2	7.1	12	11	14
Ga	22	5.8	4	3.8	10	13	8.2	5.6	12.4	3.4	5.2	4	2.7	4.3	8.1	3.3	4.9
Rb	163	22	2.7	13	19	30	12	23	66	2.5	6.6	2.8	1.5	1.9	20	3	7.7
Sr	142	75.9	94.8	53.5	33.3	129	498	62	71	44.9	358	48.6	187	142	262	193	305
Y	29.9	12.4	12.2	16.9	15.3	20.2	14	15.2	21.4	11.7	15.7	11.3	9.5	10.7	14.7	13.5	20.6
Zr	160	67.3	35.4	66.4	88.9	139	158	86	97	27.8	40.8	36.4	29.1	65.3	69.5	39.5	38.1
Nb	17.4	4.4	2.56	3.21	6.35	12.9	6.23	5.02	10.63	1.16	3.62	3.32	2.59	4.78	6.19	2.72	3.04
Mo	2.79	1.43	1.16	1.54	1.51	3.72	1.72	0.69	0.8	0.82	1.78	1.12	0.73	0.7	0.92	0.57	0.67
Cd	0.057	0.04	0.025	0.073	0.023	0.046	0.022	0.27	0.078	0.02	0.061	0.015	0.02	0.045	0.033	0.018	0.018
Cs	11.7	1.91	0.18	1.06	1.66	2.97	0.92	1.75	7.26	0.15	0.52	0.19	0.087	0.14	1.88	0.2	0.72
Ba	403	154	79	90	127	174	253	68	197	62	356	63	156	84	243	172	274
La	41	13	8.2	7.5	12	19	23	13	22	4.2	22	7.4	8.6	11	23	11	18
Ce	77	23	18	16	25	34	42	21	43	6.9	41	17	17	23	43	21	37
Pr	9.1	2.6	2.5	1.9	2.9	3.7	4.4	2.7	5.4	0.7	4.2	2.1	2.1	2.5	4.4	2.7	4.1
Nd	35	10	11	9	11	13	17	11	20	2.7	17	8.5	8.1	10	18	11	16
Sm	6.6	2.2	2.2	2.2	2.5	2.5	3.5	2.2	4	0.6	3.3	2.2	2	1.9	3.6	2.9	3.5
Eu	1.2	0.5	0.53	0.48	0.52	0.5	0.78	0.44	0.82	0.14	0.7	0.44	0.42	0.36	0.67	0.63	0.85
Gd	5.7	2.5	2.8	2.6	2.5	2.7	3.9	2.6	3.9	1	3.2	2.2	2.2	2	3.3	3.1	4.1
Tb	0.85	0.4	0.43	0.43	0.43	0.47	0.63	0.7	0.62	0.23	0.5	0.36	0.31	0.31	0.5	0.45	0.62
Dy	4.8	2.1	2.3	2.8	2.4	3.1	3.2	2.5	3.4	1.8	2.5	2.1	1.5	1.8	2.6	2.2	3.5
Ho	0.98	0.41	0.43	0.52	0.5	0.65	0.51	0.45	0.68	0.4	0.47	0.4	0.28	0.33	0.49	0.38	0.58
Er	2.9	1.3	1.2	1.6	1.5	2	1.3	1.3	2.1	1.1	1.4	1.1	0.8	1	1.5	1.1	1.6
Tm	0.42	0.18	0.17	0.22	0.22	0.31	0.17	0.19	0.33	0.16	0.19	0.15	0.12	0.15	0.21	0.14	0.23
Yb	2.8	1.2	1	1.3	1.4	1.9	1.1	1.2	2.1	1	1.2	0.9	0.7	0.9	1.3	0.9	1.2
Lu	0.42	0.18	0.15	0.2	0.21	0.29	0.16	0.17	0.3	0.13	0.17	0.12	0.11	0.13	0.2	0.12	0.19
Hf	4.3	1.5	0.8	1.4	2.1	3.3	2.6	1.8	2.7	0.6	1.1	0.8	0.8	1.3	1.7	0.8	1
Ta	1.2	0.24	0.14	0.14	0.36	0.78	0.2	0.27	0.74	0.079	0.3	0.083	0.18	0.24	0.47	0.21	0.24
W	3	1	0.76	1.3	0.63	1.9	0.72	0.42	0.99	0.48	1.4	1.2	0.47	0.89	0.89	0.45	0.58
Tl	1.23	0.17	0.075	0.32	0.23	0.7	0.18	0.2	0.62	0.041	0.22	0.079	0.055	0.061	0.28	0.31	0.1
Pb	115	17	35	70	20	101	36	17	35	9	20	5.8	6.6	8.1	34	24	9.2
Th	16	3.7	1.6	2.2	5	9.8	3.6	4.1	10.1	2.4	4.8	2.2	2.8	4.2	7.1	3.6	4.7
U	3.8	1.3	0.92	0.85	1.5	2.4	1.9	1.4	3.9	1.5	1.6	1	0.7	1.5	1.7	1	1
As	9.7	8	62	9.6	7.2	190	10	8	10	1.9	6.6	4	4	0.9	12	63	8.9
Hg	0.44	0.18	0.25	0.71	0.28	0.71	0.28	0.17	0.26	0.17	0.38	0.11	0.11	0.05	0.31	0.27	0.2
Se	1.98	0.49	0.61	0.88	0.47	1.81	0.5	0.61	0.48	0.43	1.35	1.26	0.86	0.87	3.69	0.47	1.11
B	147	28	11	16	29	51	18	18	46	11	26	11	13	12	33	10	19
Sn	5.9	6	5.1	5.1	6.1	12.1	4.9	2.7	4.4	5.4	6.5	5.1	6	5.9	7.2	4.8	7.1
REY	219	71	63	63	79	104	115	74	130	33	113	56	54	66	117	72	112

The degree of enrichment of REY (the lanthanides and Y) was consistent across all studied coal seams. According to the tripartition classification [4], REY can be categorized into light rare earth elements (LREY), medium rare earth elements (MREY), and heavy rare earth elements (HREY). The Upper Continental Crust (UCC)-standardized distribution pattern of REY in Machala coals can be classified into four types [36]. The first type, termed the normal type, exhibited a pattern nearly parallel to the horizontal axis (Figure 6A), which suggested that its REY content was comparable to that of the UCC. The second type was the MREY-enriched type, characterized by a pattern that was high in the middle and low at both ends (Figure 6B), suggesting a deficiency in LRY and HRY, while MRY was relatively enriched. The third type was identified as the LREY-depleted type, characterized by a pattern that was low in the LREY region but normal in the MREY and HREY regions (Figure 6C), suggesting that the LREY content was lower than that of the UCC, while MREY and HREY remained comparable. The fourth type, referred to as the LREY significantly depleted type, displayed a pattern where LREY was much lower than both MREY and HREY (Figure 6D), indicating a significant depletion of LREY.

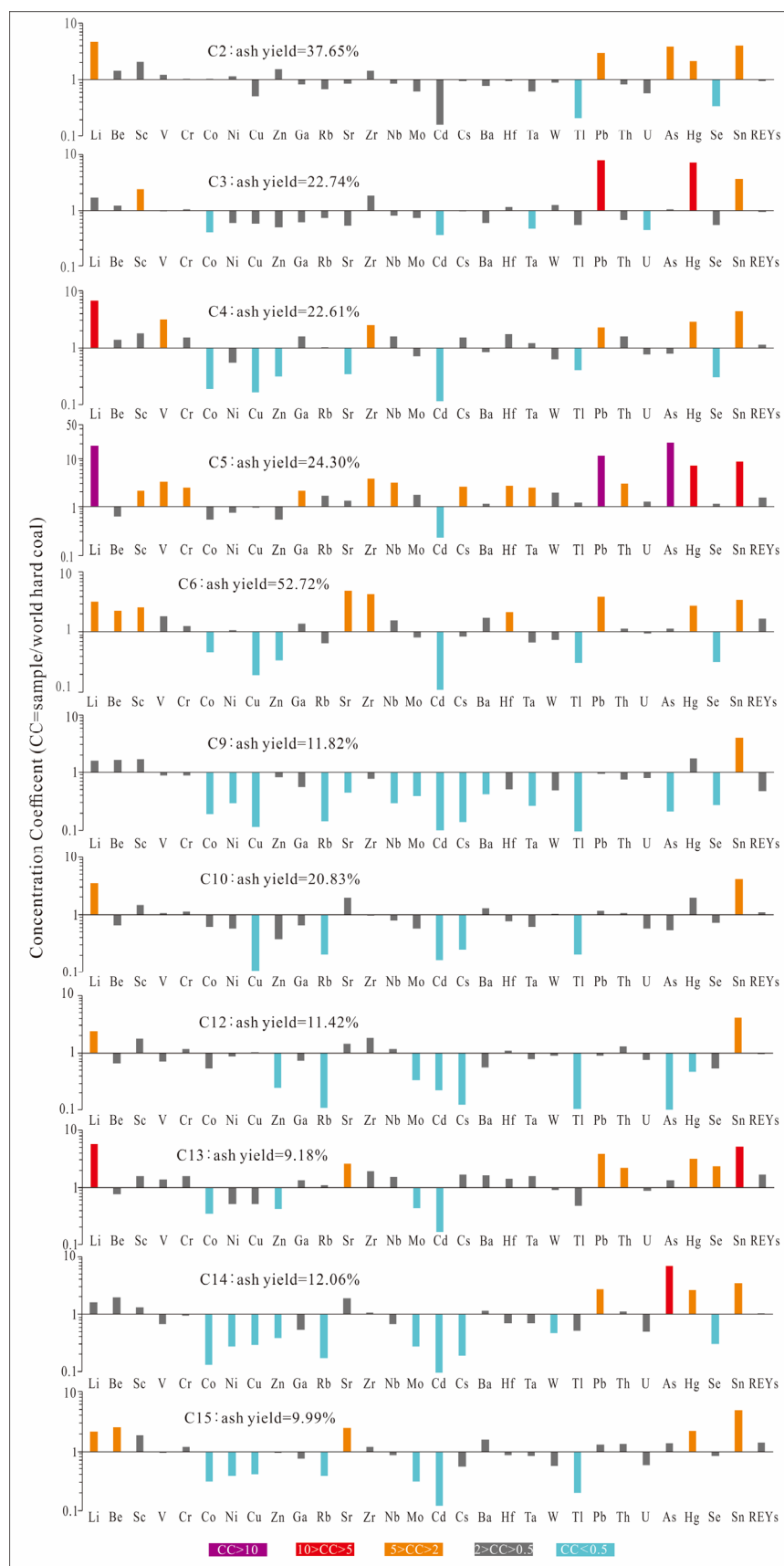


Figure 5. Concentration coefficients of trace elements in the Machala coals, normalized by average trace element concentrations in world hard coals.

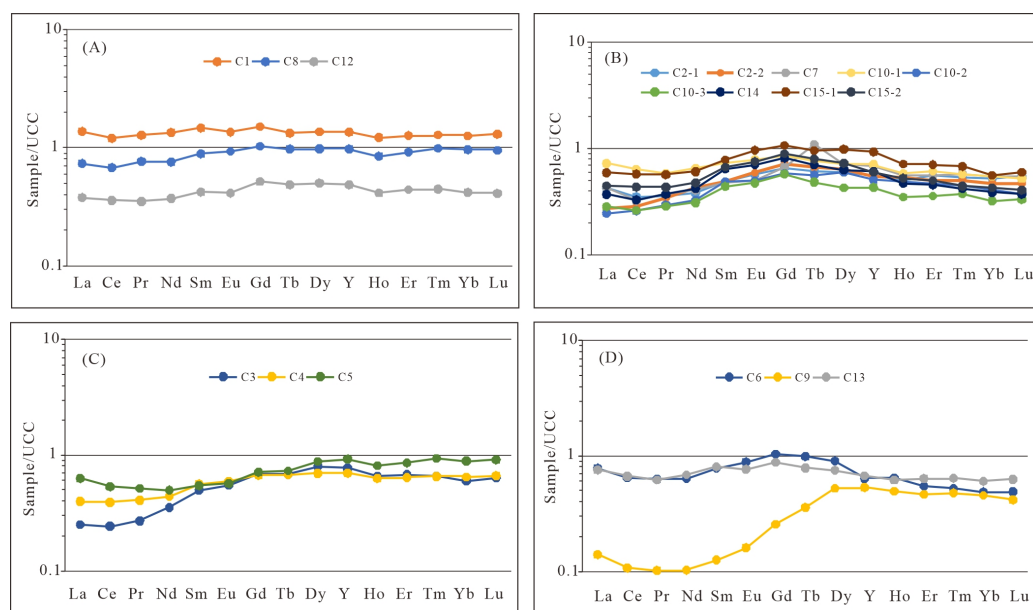


Figure 6. REY distribution patterns of the Machala coal samples, normalized by the Upper Continental Crust (UCC): (A) normal; (B) MREY-enriched; (C) LREY-depleted; (D) LREY-depleted and HREY slightly depleted.

5. Discussion

5.1. Occurrence Mode of the Enriched Elements

5.1.1. Li

Lithium is a critical rare metal. China takes 0.2% of the associated Li_2O in coal ash as the standard for industrial utilization [37]. In addition, some researchers have proposed a recovery threshold of 120 $\mu\text{g/g}$ in coal [38]. According to these standards, most of the coal seams in the Machala Mine do not meet the criteria for industrial utilization, although they are generally rich in Li. Notably, the Li concentration in the C5 coal seam reaches 252 $\mu\text{g/g}$, indicating a significant recycling potential.

Previous studies extensively examined the enrichment of Li in coal and revealed that the majority of Li is found in silicate minerals, particularly in kaolinite, cookeite, and chlorite [39–42]. Lithium enrichment has been particularly noted in kaolinite, with chlorite also reported as a significant source. For example, chlorite (chamosite) is a primary Li-bearing mineral in Guanbanwusu coal [34], while kaolinite serves as the major host mineral of Li in Jincheng and Zhina coals [41,43]. In addition, the smectite-mixed layer is identified as a potential Li-enriched clay [44]. Correlation analyses demonstrated a strong positive correlation between Li concentration in Machala coals and the presence of SiO_2 , Al_2O_3 , and TiO_2 , indicating that Li predominantly occurred in silico-aluminate minerals. This finding is consistent with the established knowledge that Li commonly occurs in clay minerals (Figure 7). X-ray diffraction analysis showed that the clay minerals in Machala coals were primarily kaolinite, followed by illite, with only minor amounts of the smectite-mixed layer and chlorite. In the Li-enriched samples C4, C5, and C13, the chlorite content measured by XRD was generally below the detection limit, with a maximum value of 1.3%. Moreover, chlorite was not detected in several samples with slight Li enrichment, so chlorite was excluded as the main Li-bearing mineral in Machala coals. Given the low content of chlorite and smectite-mixed layer in the coal, along with the observed Li enrichment in several coal seams, it was inferred that kaolinite is likely the major host mineral of Li in Machala coal.

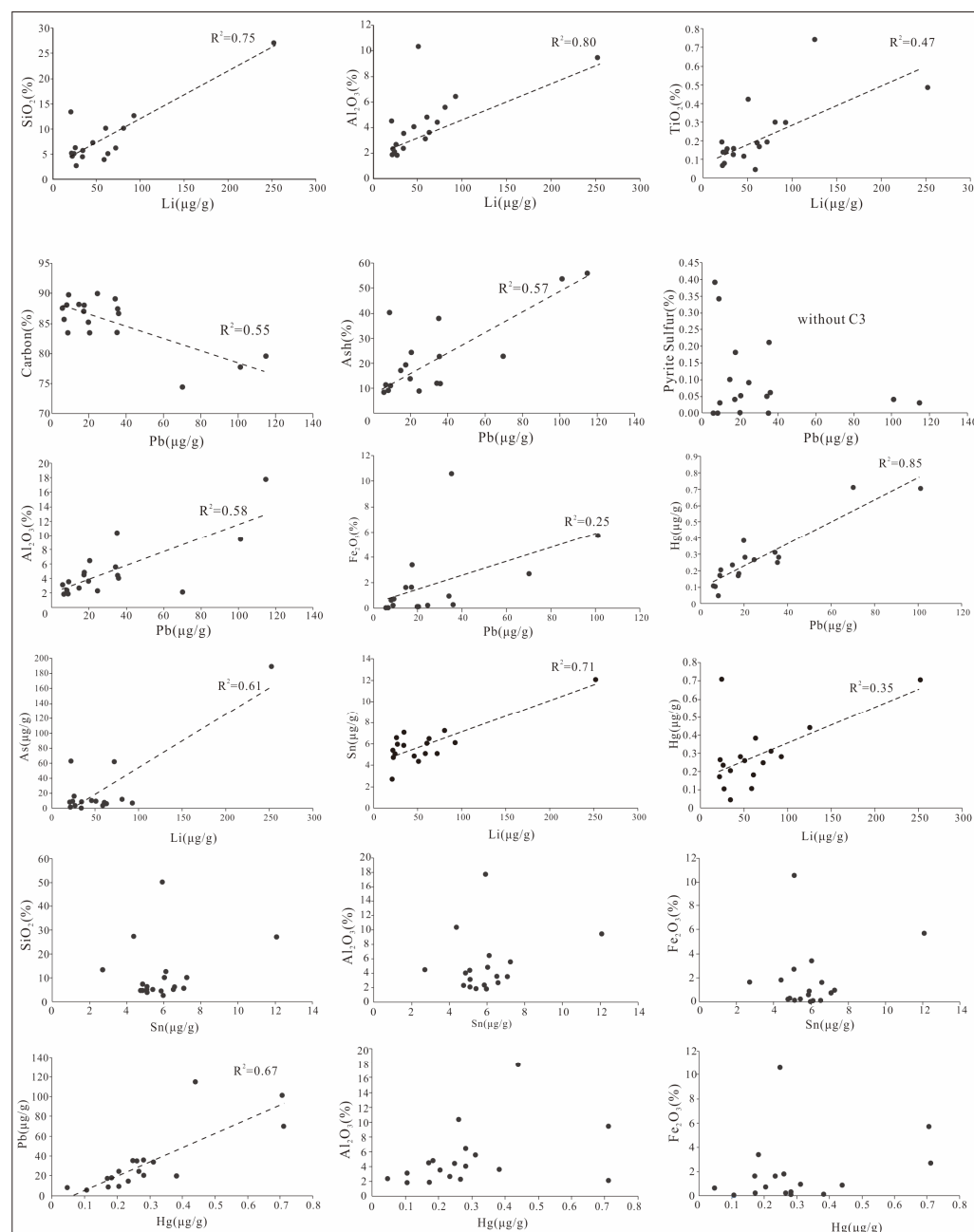


Figure 7. Correlation analyses of main enriched elements Li, As, Pb, Sn, and Hg in Machala coal and other indexes.

5.1.2. Pb

Pb, a typical heavy metal, exists in various forms in nature, including sulfide-bound, silicon–aluminum compound-bound, carbonate-bound, and organic forms. Previous studies indicated that Pb in coal is primarily associated with sulfides and silica-aluminates [45]. Hower and Robertson (2003), Hou et al. (2023), and Dai et al. (2006) [46–48] identified clausthalite in coals in the U.S., in Yangquan coals in China, and Se-galena in Junger coals from Inner Mongolia, China, respectively. In coal, galena typically occurs as large secondary mineral crystals in fissures or as tiny particles within pyrite. In the absence of sulfide such as galena, Pb primarily exists within the macromolecular structure of coal and within the lattice of clay minerals [49]. Correlation analysis revealed that the Pb content in Machala coal is negatively correlated with carbon content and positively correlated with ash yields, indicating that Pb mainly occur in inorganic minerals. Pb content in coal was negatively

correlated with pyrite sulfur content and positively correlated with Al_2O_3 . Correlation analysis showed that pyrite may not be the major host mineral of Pb in Machala coals, but clay may be the major host mineral.

However, the correlation analysis of mineral content from X-ray diffraction revealed a poor correlation between kaolinite and illite. In the four samples where pyrite was detected, the Pb content was highly positively correlated with the pyrite content. SEM and energy spectrum analysis identified a small amount of Pb in nodular pyrite (Figure 8C). In contrast, no Pb was detected in other forms of pyrite, such as strawberry pyrite, oolitic pyrite, and massive pyrite (Figure 8A,B,D). This suggested that while some Pb in Machala coal was associated with pyrite, it was limited to a specific type. A small amount of Pb was also detected in some clay minerals, indicating that some Pb also exists within these minerals.

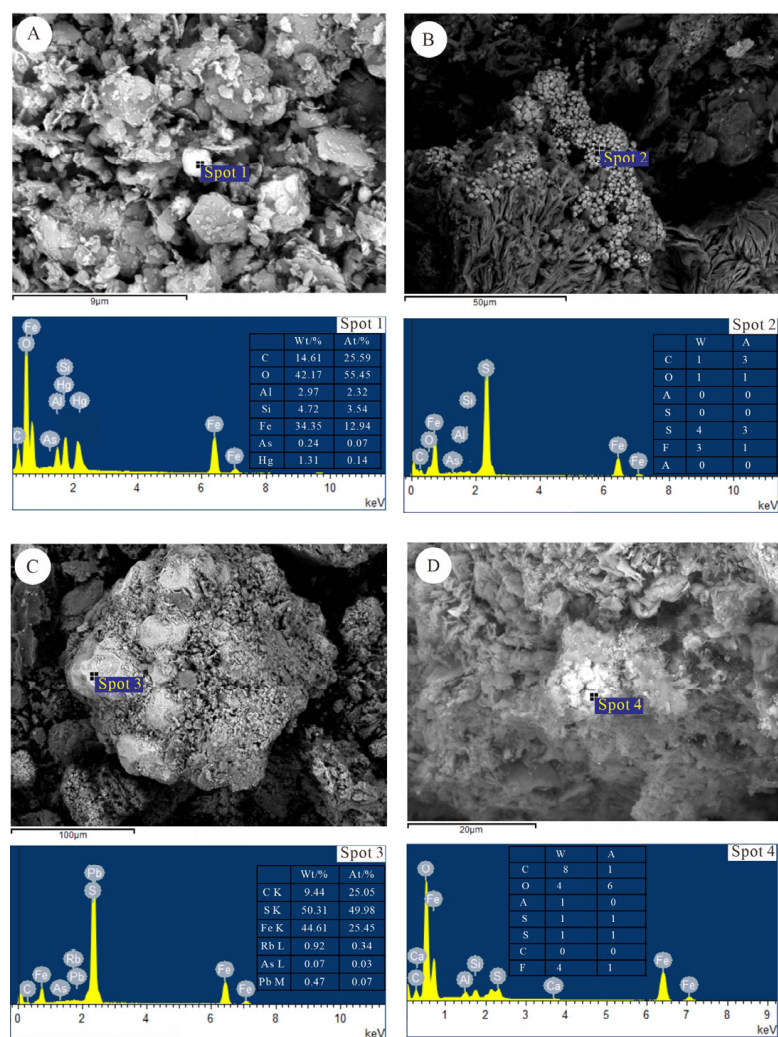


Figure 8. Enrichment of Pb, Hg, and As in iron-bearing minerals in low-temperature ashed samples from sample C5 (A,D) and from sample C3 (B,C).

5.1.3. As

Arsenic is a toxic element and is one of the most harmful elements in coal [50,51]. Numerous studies have demonstrated that As exists in various forms within coal, but it is primarily related to pyrite. Some of it exists in the form of arsenides (such as arsenopyrite and realgar) or organic matter. It may also be linked to carbonate, sulfate, and silicate minerals [52,53]. Furthermore, Getchellite, a very rare As-bearing mineral, was identified in coals from Xingren, Guizhou, Southwest China [54]. High arsenic concentrations were found in the organic matter of the late Permian coals in this region [55]. Correlation

analysis showed that As exhibited a low correlation with other elements or oxides, a high positive correlation with Li (Figure 7) and a weak positive correlation with SiO_2 and K_2O . Energy spectrum analysis identified a small amount of As in siderite, oolitic pyrite, nodular pyrite, massive pyrite, and other iron-bearing minerals; however, the As was not detected in strawberry pyrite. In addition, a small amount of As was detected in illite, kaolinite, and other clay minerals (Figure 9), indicating a diverse occurrence of As minerals in Machala coal.

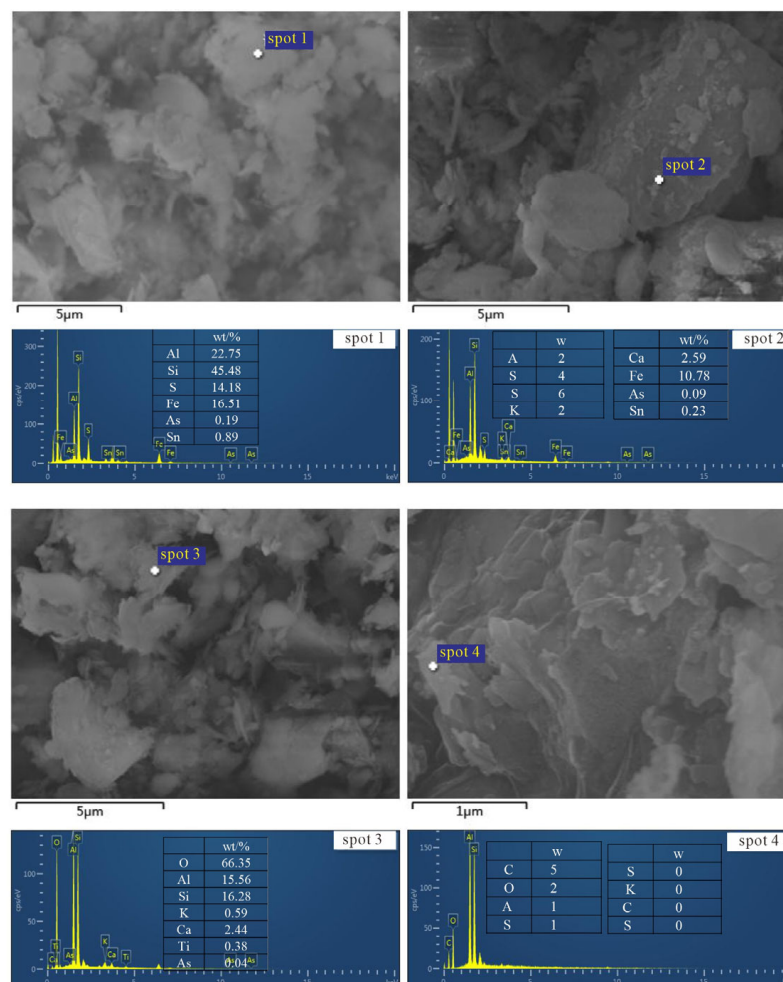


Figure 9. SEM images and energy spectra of some clay minerals in low-temperature ashed sample C5, where As and Sn were detected by energy spectra.

5.1.4. Hg

Previous statistical studies indicated that mercury in coal primarily occurs within pyrite, although some research confirmed that Hg in coal exists in an organic complex state [5]. Correlation analysis showed that Hg contents in Machala coals were positively correlated with Pb contents, indicating that some types of pyrite may served as an essential host mineral of Hg. However, energy spectrum analysis revealed that Hg was not detected in all forms of pyrite; on the contrary, a small amount of Hg was detected in siderite, indicating that siderite may also be the host mineral of Hg in Machala coals. The thermal stability of Hg varied in different minerals, among which the sulfide bond state was relatively stable, with a low-temperature ashing threshold below 150 °C, which did not reach the temperature required for Hg release [56]. Therefore, it could be inferred that the absence of Hg detection in pyrite via energy spectrum analysis reflected the actual conditions of the raw coal.

5.1.5. Sn

Tin in coal is present in various forms and is mainly associated with silicoaluminate and cassite. It is also possibly related to carbonate minerals and pyrite [5,57]. Correlation analysis indicated that Sn content in Machala coal showed a poor correlation with SiO_2 and Al_2O_3 but exhibited a strong positive correlation with Li. This indicated that Sn is likely to occur in clay minerals. SEM and energy spectrum analysis identified a small amount of Sn in illite and kaolinite (Figure 9). The absence of Sn in various forms of pyrite and siderite further supports the inference that clay minerals, particularly illite and kaolinite, are the main host minerals of Sn in the Machala coal.

5.2. Factors Influencing Li, Pb, As, Hg, and Sn in Coal

The sources and influencing factors of enriched elements in coal were mainly categorized into four aspects: sediment provenance, short-term transgression, volcanic ash, and fluid activity.

5.2.1. Sediment Provenance

Mineral analysis showed that quartz and clay minerals were the predominant constituents of Machala coal, with SiO_2 exhibiting the highest concentration, followed by Al_2O_3 . This suggested that the sediment source significantly influenced the contents of major elements in coal. The content of trace elements was also likely affected by the provenance. The composition characteristics of rare earth elements serve as an important means to analyze sediment sources [58]. La/Yb and REEs intersection maps are commonly employed to reflect the types of sediment source rocks [59]. As illustrated in Figure 10, the Machala coal samples all fell near the sedimentary rock region, indicating that the Machala Formation is primarily composed of recycled sedimentary rock minerals. The sandstone minerals within the Machala Formation were mainly quartz, exhibiting high composition maturity and structural maturity. The minerals supplied by the material source in Machala coal were mainly quartz, along with a small amount of feldspar. By comparing the host minerals with those supplied by the sediment provenance, it was inferred that the contribution of sediment provenance to the enrichment of Li, Pb, As, Hg, and Sn in Machala coal may be limited.

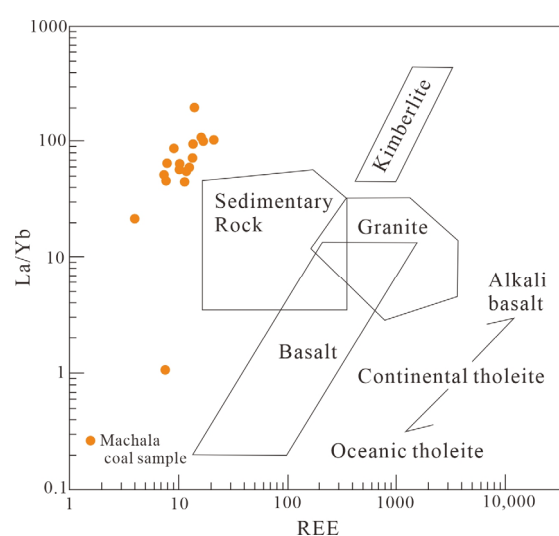


Figure 10. Cross plot of La/Yb – ΣREE in Machala coal samples.

5.2.2. Short-Term Transgression

The concentration of many elements in seawater is higher than that in freshwater, so that the depositional environment of swamps during coal deposition affects the content

of elements in coal. The Machala Formation is primarily situated in the supratidal zone, with occasional short-term transgression during the sedimentary period indicated by the presence of lenticular limestone. Generally, high-sulfur coal (especially high organic sulfur) is affected by transgression [60,61]. The total sulfur content of the C3 coal seam was as high as 16.73%, and the contents of pyrite sulfur, organic sulfur, and sulfate sulfur were 9.06%, 6.90%, and 0.77%, respectively. This indicated that the sedimentation period of the C3 coal seam was affected by seawater. Previous studies demonstrated that Li is more likely to be enriched in reducing brackish water environments [62], and temporary transgression is a key factor contributing to Li enrichment in Permian coal in Ningwu Basin, North China. Seawater facilitates the formation of pyrite, which serves as the primary source for several elements. In the C3 coal seam, both Pb and Hg were enriched, while the degree of enrichment of Li was normal. The sulfur content in other coal seams was relatively low, with organic sulfur content ranging from 0.28% to 1.01%, suggesting these coal seams were not significantly affected by transgression. Transgression may play a limited role in the enrichment of Li, As, Pb, Hg, and Sn in these low-sulfur coal seams.

5.2.3. Volcanic Ash

Volcanic ash serves as an important source of enriched elements, such as Li, in the coals of Southwest China [63]. The presence of volcanic tuff at the base of the Machala Formation indicated that the tectonic conditions conducive to volcanic eruption existed in the Early Carboniferous period within the study area (Figure 2). The hydrolysis of volcanic ash leads to the formation of kaolinite in the clay mineral composition [12,13]. X-ray diffraction analysis showed that kaolinite was the predominant clay mineral in Machala coal, with its content typically exceeding 70% of the total clay minerals in all samples. In specific samples, C9, C10-2, C12, C14, and C15-2, kaolinite constituted more than 90% of the total clay minerals, which suggested that these clay minerals were probably mainly formed from the alteration of volcanic ash [64–67]. Due to the relative stability of Al and Ti, $\text{Al}_2\text{O}_3/\text{TiO}_2$ is commonly used for determining the source rock type of volcanic ash [68–70]. The $\text{Al}_2\text{O}_3/\text{TiO}_2$ values of 3–8, 8–21, and 21–70 indicated that the source rock types were mafic, intermediate, and felsic igneous, respectively. $\text{Al}_2\text{O}_3/\text{TiO}_2$ values in Machala coal were approximately 21 (Figure 11), indicating that the source rocks were mainly medium and felsic. Li was slightly enriched in several coal seams in the Machala Mine, but it was significantly enriched in C5 coal seam. Volcanic ash was considered the fundamental source of the Li (Figure 12), and groundwater leaching might further enhance its accumulation in the coal.

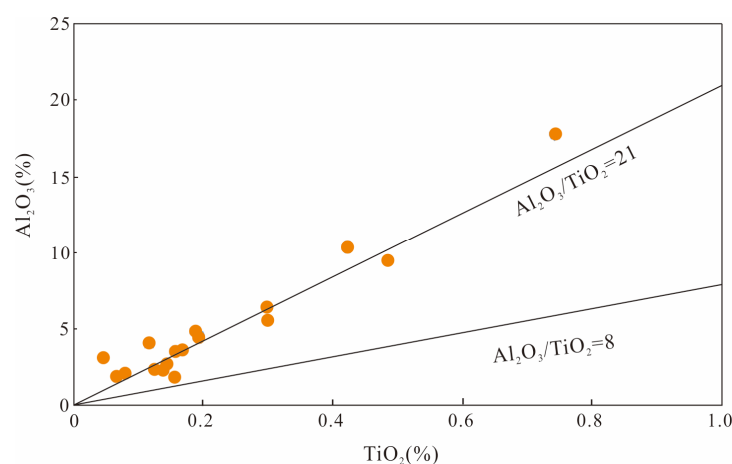


Figure 11. Relationship between Al_2O_3 and TiO_2 in Machala coal samples (the $\text{Al}_2\text{O}_3/\text{TiO}_2$ values of 3–8, 8–21, and 21–70 indicated that the source rock types were mafic, intermediate, and felsic igneous rocks, respectively).

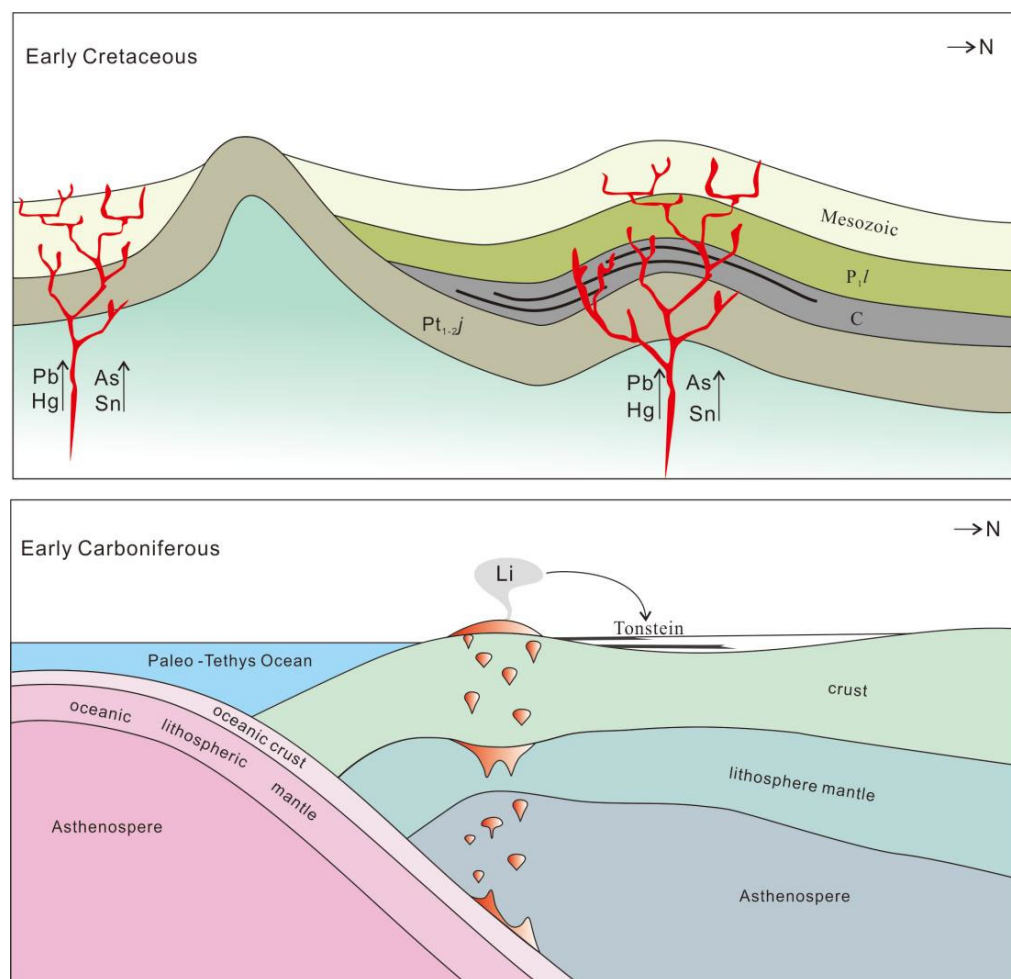


Figure 12. Mode of Li, Pb, As, Hg, and Sn enrichment in the Machala Mine.

5.2.4. Hydrothermal Fluids

Regional geological surveys around the Machala Mine have reported various mineralization points [71], including arsenic, lead-zinc, tin, sulfur, copper, and other types (Figure 1). These mineralization types are generally reflected as sulfurophilic [9,72] and are mainly distributed around fault zones. Their formations are believed to be controlled by hydrothermal activities. The Machala Mine is situated between two structurally severe faults, resulting in significant structural deformations within the Machala Formation, which allows the coal seams to be influenced by hydrothermal fluid. The rare earth element pattern serves as an important indicator of fluid transformation [69,73]. The samples collected from C2, C7, C10, C14, and C15 coal seams in the Machala Mine indicated a relative enrichment of the MREY, particularly Gd, and a relative loss of both the LREY and HREY (Figure 5). These rare earth element patterns confirmed that the Machala coal indeed underwent fluid transformation [74–76]. Based on the extensive distribution of mineralization points in the adjacent sedimentary rocks in the Machala Mine, it was inferred from that the hydrothermal fluid may be an important source of enriched elements such as Pb, As, Sn, and Hg in the Machala coal (Figure 12). Fluid activity may also contribute to the further differentiation and enrichment of Li within the Machala coals.

6. Conclusions

Through the proximate analysis, maceral analysis, major and trace element analysis, and mineralogical analysis of coals from multiple coal seams in the Machala Mine, the following conclusions can be drawn:

- (1) The coal seams in the Machala Formation are dominated by low-sulfur, medium-low ash, low-volatile, medium-high calorific coals.
- (2) The primary enriched elements in Machala coals include Li, As, Pb, Hg, and Sn. C5 coal seam exhibits the highest degree of enrichment, in which Li, Pb, and As are highly enriched.
- (3) Minerals present in Machala coals primarily include quartz, kaolinite, feldspar, pyrite, siderite, illite, and so on. Kaolinite is the major host mineral of Li in the Machala coal, which was mainly formed from the alteration of volcanic ash. Clay minerals and specific type of pyrite are the host minerals of As, Pb, Hg, and Sn in Machala coals, and hydrothermal fluids are their major source.

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