ISSN 2642-1550, Volume 5, 2023

Gallium and Germanium in Pennsylvanian Coals, Shales, and Paleosols in Indiana

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E-mail: mmastale@indiana.edu
Received 07/25/2023
Accepted for publication 11/06/2023
Published 12/13/2023
Suggested citation: Mastalerz, M., and Roden, N., 2023, Gallium and germanium in Pennsylvanian coals, shales, and paleosols in Indiana: Indiana Geological and Water Survey, Indiana Journal of Earth Sciences, v. 5. doi: 10.14434/ijes.v5i1.36455

SUMMARY

Gallium (Ga) and germanium (Ge) are two elements of high industrial interest, included in the current United States and European Union lists of critical raw materials. This paper compares Ga and Ge concentrations between coals and associated paleosols and shales in Indiana. In addition, we include Ga and Ge data on the coal waste from coal preparation plants (coal tailings) to evaluate the coal tailings as potential sources of these elements.

Paleosols have an average Ga content of 26.70 ppm, more than shales with an 18.77 ppm average, and coals with a 4.61 ppm average. The Springfield coal tailings average 15.60 ppm of Ga and the Brazil and Staunton Formation coal tailings average 31.90 ppm. For Ge, the coals have the highest average concentration (6.46 ppm), then shales (1.36 ppm), and paleosols (0.96 ppm). In coal tailings, the average Ge concentration is 13.90 ppm for the Springfield and 47.70 ppm for the Brazil and Staunton Formation coal waste.

For Ga, a very strong positive correlation was obtained with aluminum (Al) in paleosols (R^2=0.89) and coal tailings. A strong correlation was also obtained for shales (R^2=0.86), together indicating that Al content is a great predictor of Ga concentrations in these materials. For Ge, there seems to be a tendency of decreasing Ge concentration with an increase in Al content in coals, suggesting an organic and not mineral association for this element. The organic association is also supported by a strong negative correlation between Ge and ash yield in coal tailings.

INTRODUCTION

Gallium (Ga) and germanium (Ge) are two elements of high industrial interest, included both in the United States and European Union lists for critical raw materials (Burton, 2022; European Commission, 2020). Gallium is a soft metal similar in appearance to aluminum. Its main uses are in the electronic industry; having a similar structure to silicon, Ga is used as a silicon substitute. It is an important component of many semiconductors, used in products ranging from mobile phones to solar powered technologies. The United States does not produce any Ga, totally relying on imports from China (53 %), Germany and Japan (13 % each), Ukraine (5 %), and other countries (16 %) (USGS, 2022a). U.S.-reported consumption is close to 20,000 kg of Ga per year. Most Ga is produced as a byproduct of bauxite processing, and some is produced from zinc-processing residues. The average Ga content of bauxite is 50 ppm. U.S. bauxite deposits are not considered to be a good source of Ga because of their high silica content. Some U.S. zinc ores contain up to 50 ppm of Ga and could potentially be a significant resource (USGS, 2022a).

Primarily, germanium is used in electronic and solar applications, fiber optic systems, and polymerization catalysts. China is a leading global producer and exporter of Ge, and the U.S. is one of the main importers (USGS, 2022b). The estimated consumption of Ge in the U.S. is ~30,000 kg annually. The available resources of Ge are associated with some zinc and lead-zinc-copper sulfide ores. Substantial U.S. reserves of recoverable Ge are contained in zinc deposits in Alaska, Tennessee, and Washington. It is estimated that U.S. reserves of zinc may contain as much as 2,500 metric tons of Ge. On a global scale, only 3 % of Ge contained in zinc concentrates is recovered. Some coal ashes are also considered to be potential sources of Ge.

Gallium occurs in most rocks. In sedimentary clay-rich rocks, its content averages ~30 ppm, whereas in sandstones and carbonate rocks, the concentration is 12 and 4 ppm, respectively (Turekian and Wedepohl, 1961), compared to the average concentration in the lithosphere of 17 ppm. In coals, Swaine (1990) gave a Ga range of 1 to 20 ppm, with an average of 5 ppm, whereas Ketris and Yudovich (2009) calculated 2.0 and 2.4 ppm as Ga Clarke values (average worldwide concentrations) for brown and hard coals, respectively. Gallium is generally considered to be associated with clay minerals (Finkelman, 1993; Zhuang and others, 2007). The dimorphous aluminum hydroxide oxide minerals [AlO(OH)] boehmite (Dai and others, 2008) and diaspore (Dai and others, 2011) are common hosts of Ga in coal. For some Chinese coal deposits, Dai and others (2008) suggested that Ga came from weathering products and was transported into the peat mire along with aluminum hydroxide as a colloid. Other studies, however, showed that the Ga content in coal could be higher than in the adjacent claystone (Bouška and others, 1963), suggesting some organic association. In general, a review of the previous studies suggests that Ga can be bound either to mineral components or the organic fraction (Dai and others, 2023), but the association with mineral matter appears to be more common than with the organic fraction.

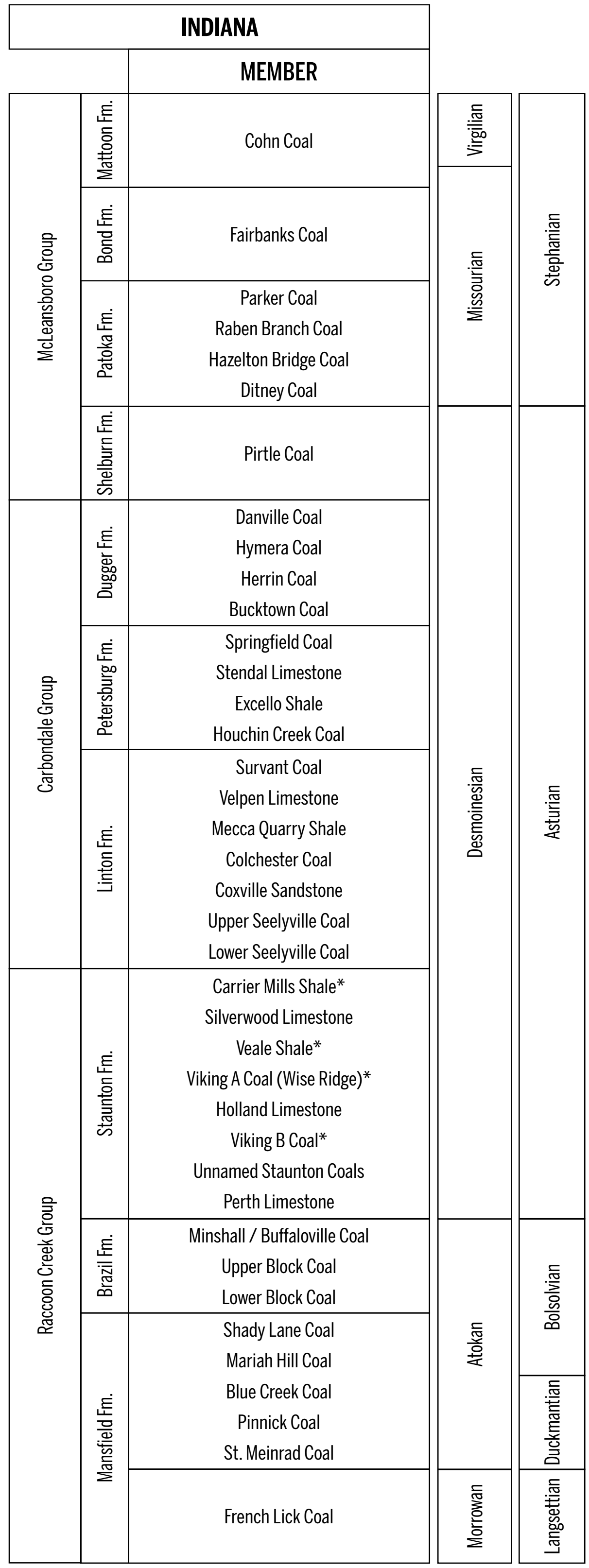


Figure 1. Stratigraphic column of the Pennsylvanian coal-bearing strata in Indiana. (*) Indicates informal names.

Germanium in coals has been shown to be associated dominantly with the organic fraction (e.g., Admakin, 1975; Bouška, 1981; Breger and Schopf, 1955; Eskenazy, 1996; Vassilev and others, 1995) and rarely occurs in silicate and sulfide (sphalerite) associations (Finkelman, 1982). Dai et al (2023) states that "germanium is the only element that is almost 100 % organically associated with coal. No Ge minerals have been found in coal." Germanium plays an important role in biochemical life of plants (Asai, 1980), and in coal, a large proportion of Ge comes from the original biomass. In addition to its original organic association, Ge in coal can also come from a variety of outside sources, including leaching of muscovite-bearing granitic rocks (Zhuang and others, 1998), hydrothermal and volcanic activity (Eskenazy, 1996; Vassilev and others, 1995), and deposition from alkaline waters and volcanogenic fluids (Seredin and Danilcheva, 2001). These outside sources are usually responsible for large enrichments of Ge in coals (e.g., Eskenazy and others, 1994; Hallam and Payne, 1958). Generally, Ge appears to be concentrated at the top and the bottom of coal seams (e.g., Admakin, 1975; Breger and Schopf, 1955; Hower and others, 2002) and is typically more concentrated in thin seams (Eskenazy, 1996; Kulinenko, 1976).

In Indiana, the Ga and Ge distribution was studied in two Pennsylvanian, high-volatile bituminous coals: the Springfield Coal Member of the Petersburg Formation and the Danville Coal Member of the Dugger Formation (Table 1; Mastalerz and Drobniak, 2012; see fig. 1). Gallium concentration in the Springfield and Danville Coals shows similar ranges, from 1.70 to 8.90 ppm (averaging 5.06 ppm) for the Danville Coal, and 1.40 to 12.30 ppm with an average of 3.39 ppm for the Springfield Coal. For Ge, these ranges are 2.50 to 26.70 ppm (average 14.19 ppm) for the Danville Coal and 1.54 to 38.0 (average 9.40 ppm) for the Springfield Coal. In the vertical section, Ga showed a symmetric distribution with the lowest values in the middle part of the seam in the Springfield Coal and an asymmetric distribution (increasing or decreasing upward) in the Danville Coal (Mastalerz and Drobniak, 2012). In these coals, Ga appears to be dominantly associated with mineral matter, and clay minerals in particular. Germanium shows a symmetric distribution with the largest enrichment in the topmost and the basal benches of the coal. It appears to be associated with either mineral matter (dominantly clays, occasionally pyrite) or organic matter.

The overall aim of this study is to expand our understanding of Ga and Ge concentrations in Pennsylvanian coals and associated clastic sediments in Indiana. The more specific objectives are to: 1) compare Ge and Ga concentrations between coals and the associated paleosols and overlying shales; 2) examine the controls on Ga and Ge distribution to identify parameters that can be used to predict their concentrations; and 3) discuss shale/coal/paleosol sections as potential Ga and Ge sources. In addition, including Ga and Ge data on coal tailings allows for the evaluation of coal waste as potential sources of these elements.

Table 1. Comparison of Ga and Ge contents of selected coals and associated rock (from Mastalerz and Drobniak, 2012) to the Upper Continental Crust (UCC) values (Rudnik and Gao, 2003). Coal Clarke value refers to the average worldwide concentration of the elements in the coals of all ranks.

	Ga (ppm)	Ge (ppm)
Upper Continental Crust	17	1.13
Coal Clarke Value	5.8	2.4
Illinois Basin coal	4.83	14.57
Powder River Basin coal	3.04	2.62
Danville Coal, Indiana	1.7-8.9 (average 5.06)	2.5-26.7 (average 14.19)
Clastic partings in Danville	15-45 (average 27.73)	1.50-51.0 (average 11.93)
Springfield Coal, Indiana	1.4-12.3 (average 3.39)	1.54-38 (average 9.4)
Shale above Springfield	16-43 (average 26.6)	1.5-7.8 (average 4.0)
Clastic partings in Springfield	20-45 (average 34.85)	1.5-50 (average 6.07)
Paleosol under Springfield	22-49 (average 33.15)	1.5-12 (average 7.38)

DOI 10.14434/ijes.v5i1.36455

METHODS

Shale, coal, and paleosol samples were collected from cores at 11 locations in Indiana (fig. 2). In total, 39 shale samples, 29 coal samples, and 84 paleosol samples were analyzed. Coal tailing samples were collected from two deposits in Indiana: one in Greene County (19 samples) and one in Pike County (19 samples).

Trace elements, and major elements in coal, paleosol, and shale samples, were provided to us by the USGS as part of the Earth Mapping Resources Initiative (Earth MRI). Trace elements and major elements in coal tailings were analyzed at the University of Kentucky's Kentucky Geological Survey (KGS) and the Center for Applied Energy Research (CAER) in Lexington,

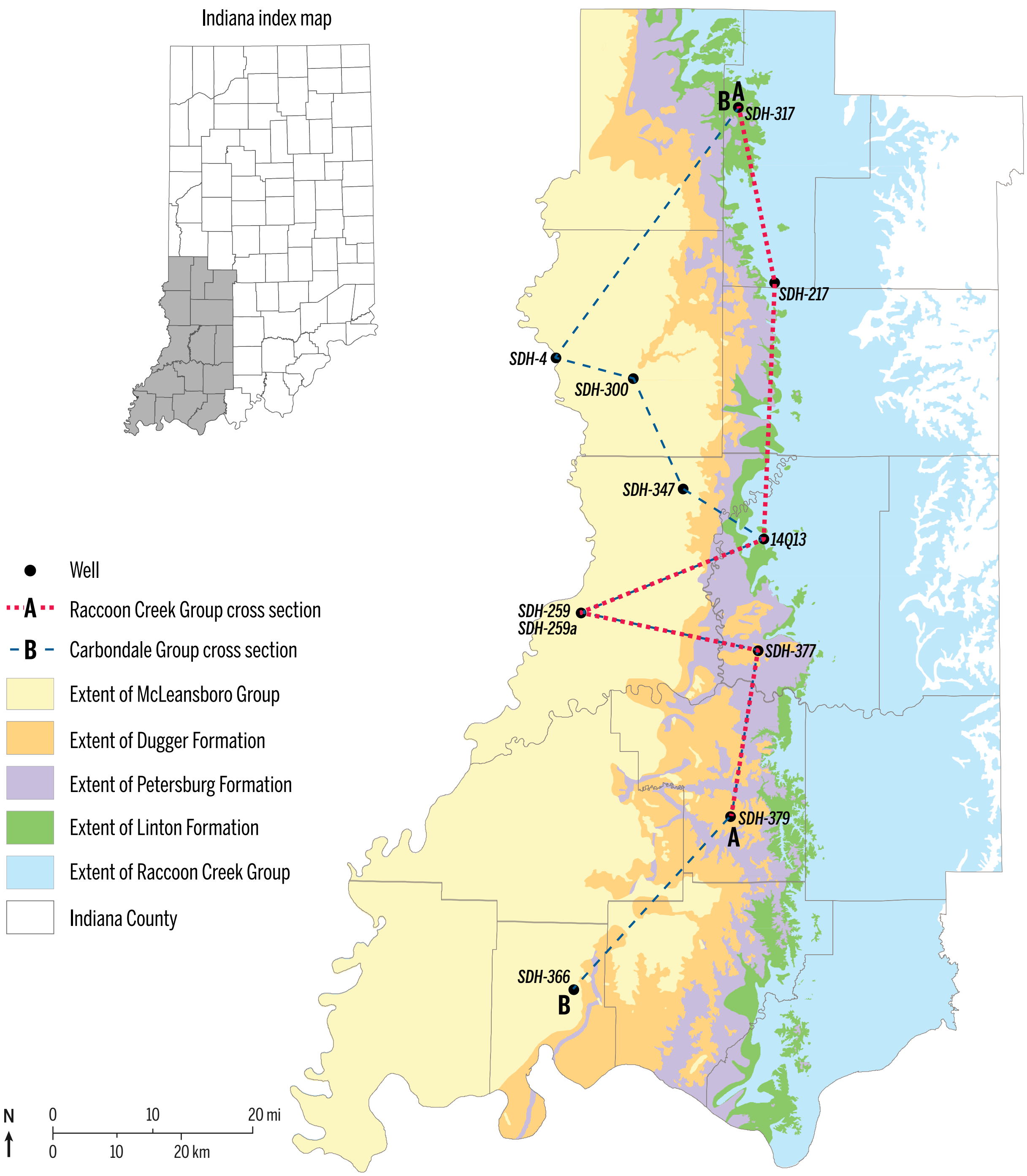


Figure 2. Map showing the locations of boreholes in southwest Indiana where paleosol, coal, and shale samples were collected. Stars mark the locations of two coal tailing deposits studied. For stratigraphic position of the groups and formations, see figure 1.

Table 2. Gallium and germanium in shale, coal, and paleosol samples studied.

	Average (ppm)	Min (ppm)	Max (ppm)	Number of samples
Gallium				
Shale	18.77	2.19	28.80	39
Coal	4.61	1.30	12.80	29
Paleosol	26.76	9.42	43.50	84
Germanium				
Shale	1.31	<1	5.00	39
Coal	6.46	<1	56.00	29
Paleosol	0.96	<1	2.00	84

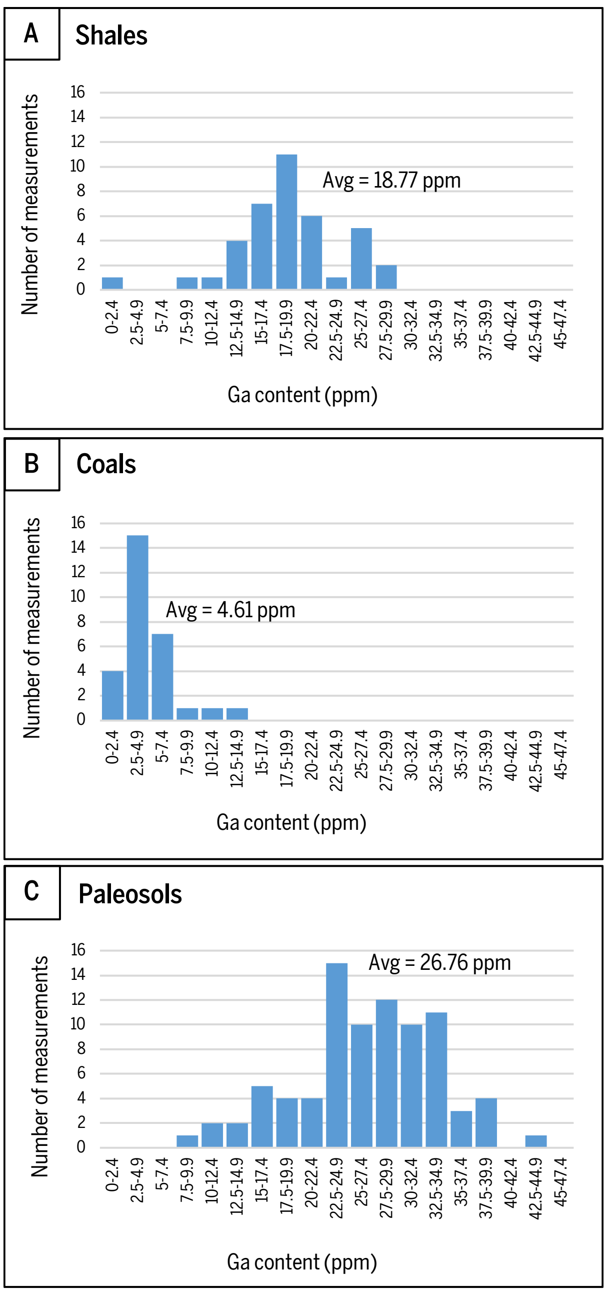


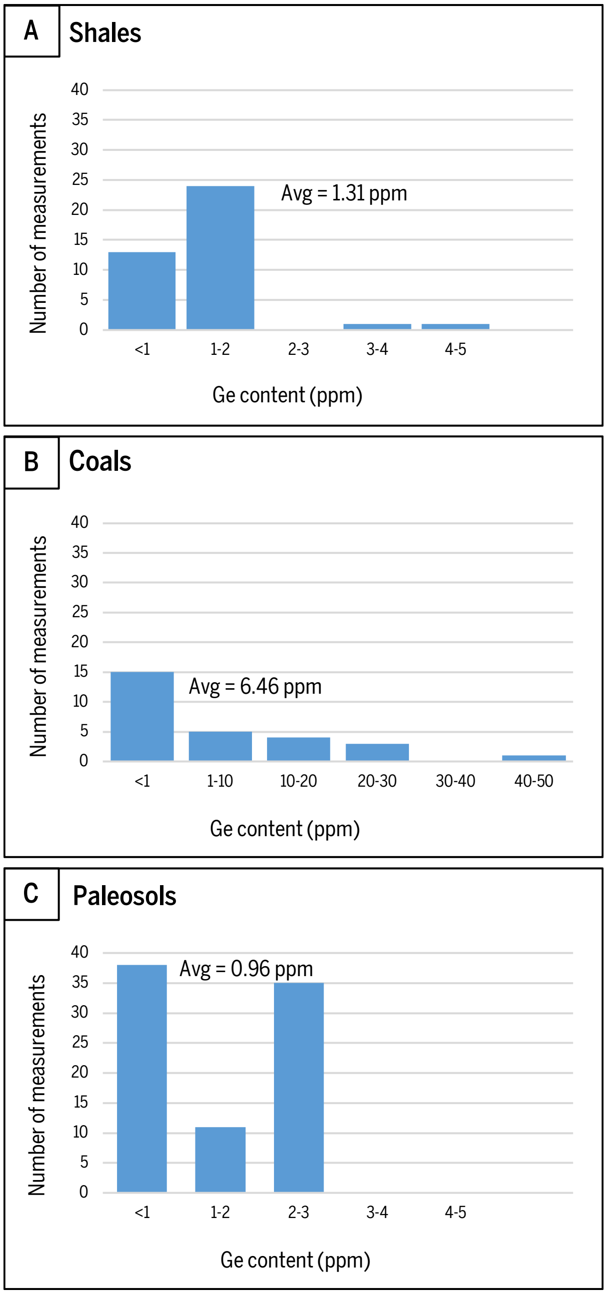
Figure 3. Bar graphs showing the frequency distribution of Ga concentrations in shales (A), coals (B), and paleosols (C).

Kentucky. Trace elements and REE were analyzed by the inductively coupled plasma–optical emission spectrometry–mass spectroscopy (ICP-OES-MS) method, and major elements were determined by the wavelength dispersive X-ray fluorescence (WDXRF) technique.

RESULTS AND DISCUSSION

The paleosols studied have an average Ga content of 26.76 ppm and ranged from 9.42 to 43.50 ppm, comparing favorably to shales (18.77 ppm average, 2.19 to 28.80 ppm range) and coals (4.61 ppm average, 1.30 to 12.8 ppm range) (Table 2). A closer analysis of the distribution (fig. 3) confirms that among the three lithologies, paleosols are indeed the most rich in Ga, with a large proportion of values above 20 ppm and a modal class of 22.5 to 25 ppm. For shale, the modal class is 17.5 to 20 ppm, whereas for coals the modal class is 2.5 to 5 ppm.

For Ge, coals have the highest average concentration (6.46 ppm), then shales (1.31 ppm), and paleosols (0.96 ppm) (Table 2). The maximum value for coal samples was 56.00 ppm, much higher than the 5.00 ppm for shales and the 2.00 ppm for paleosols. In many samples for all lithologies, Ge was below the detection limit. Frequency distribution results (fig. 4 A-C) show that Ge concentrations above 20 ppm are present in some coal samples. In an earlier study of Indiana coals, Mastalerz and Drobniak (2012) suggested that the Indiana coals might be good sources of Ge, and this study supports that suggestion.



Ga and Ge concentrations were compared with major elements such as aluminum (Al), silicon (Si), and sulfur (S) to investigate whether these routinely analyzed elements can be used as proxies. For Ga, a very strong positive correlation was obtained with Al in the paleosols (R^2=0.89, fig.5A). A strong correlation was also obtained with Al for shales (R^2=0.86, fig. 5B). These results show that for paleosols and shales, there is a high possibility that if Al content >7 %, Ga will be enriched compared to the Upper Continental Crust (UCC) value of 17 ppm. Gallium concentrations of 34 ppm (twice the UCC value) and higher can be expected when Al content is above 12 %. Indeed, Al content is a great predictor of Ga concentrations in these two lithologies. For coals, there is a tendency of increasing Ga with Al content, but the correlation is much weaker (fig. 5C). Consequently, for coal, Al content is not as diagnostic as for the associated shales or paleosols. A positive correlation also has been revealed for Ga and Si in shales (R^2=0.50, fig. 5D); this relationship is much weaker in coals (fig. 5E), and no relationship was determined for the paleosols There is no relationship between S and Ga for any of the three lithologies, but there is a negative relationship between Ga and carbon (C) content (fig. 5F). All these correlations suggest that Ga is associated with clays, and this association is especially strong for paleosols and shales, and less so in coals. Compared to the average Ga content of the world coals (5.8 ppm, Ketris and Yudovich, 2009), most of the coals studied here oscillate around this value and only rarely show enrichment. Considering the Chinese standard of 30 ppm as the industrial grade of Ga deposit (Dai and others, 2012), no coal samples studied here would qualify (fig. 3B). However, large proportions of the paleosol samples would meet this requirement (fig. 3C), suggesting that Pennsylvanian paleosols should be investigated as a possible source of Ga. Comparison of individual paleosol horizons with regard to Ga content (Table 3) shows that the most

Figure 4. (AT LEFT) Bar graphs showing the frequency distribution of Ge in shales (A), coals (B), and paleosols (C).

Table 3. Gallium concentrations in Pennsylvanian paleosols in Indiana.

Paleosol under	Min (ppm)	Max (ppm)	Average (ppm)	Number of samples
Wise Ridge	32.5	43.5	36.4	7
Viking B	30.1	37.9	32.7	4
Danville	19.3	34.4	29.5	13
Upper Block	19.3	37.6	29.5	6
Hymera	22.5	32.9	27.7	2
Colchester	24.1	29.0	26.2	5
Seelyville	18.3	32.4	25.3	9
Houchin Creek	14.8	33.7	24.5	11
Lower Block	15.8	27.3	22.1	3
Springfield	10.1	33.0	20.5	8

DOI 10.14434/ijes.v5i1.36455

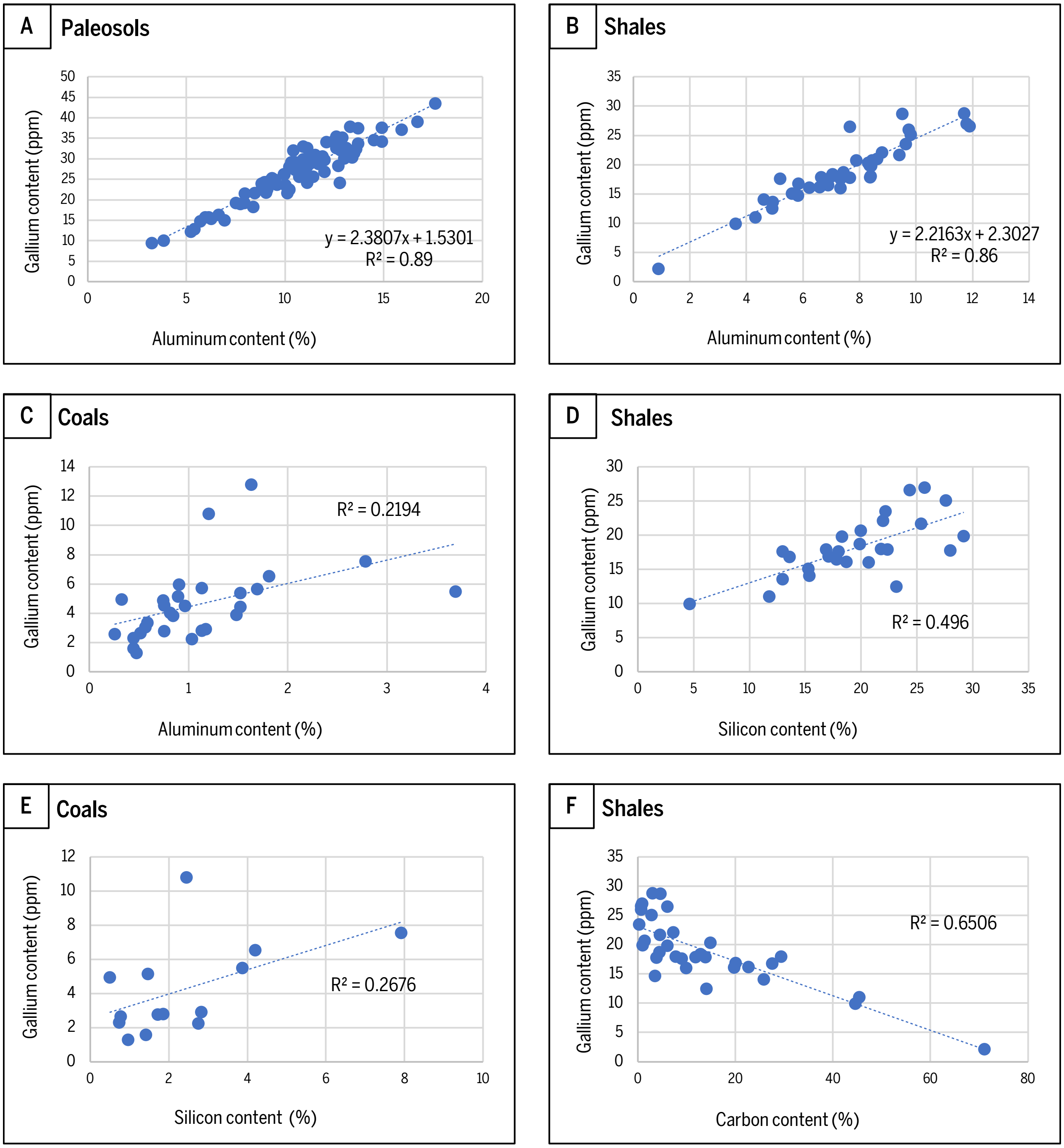


Figure 5. Scatter plots with linear regressions showing relationships of Ga with Al in paleosols (A), Al in shales (B), Al in coals (C), Si in shales (D), Si in coals (E), and C in shales (F).

Ga-enriched paleosols are those located under Staunton Formation coals (informally known in Indiana as Wise Ridge and Viking B coals, Mastalerz and others, 2022), and the Upper Block and the Danville Coal Members (fig. 2). However, we note that the number of samples available for individual paleosols varied, making the comparison preliminary and in need of confirmation by further studies.

For Ge, no clear relationships with the major elements were found for paleosols and shales. In coals, there seems to be a tendency of decreasing Ge concentration with an increase in Al content (fig. 6A) and with Si content (fig. 6B), testifying against Ge association with Al- and Si-rich inorganic fractions. In previous studies of coals from Indiana, Mastalerz and Drobniak (2012) suggested that organic matter in coal was an effective

Table 4. Gallium and Germanium in coal tailing deposits. Both the Springfield Coal waste and the Brazil and Staunton Formations' coal waste are based on 19 samples. Average values for the Springfield Coal in Indiana (in brackets) from Mastalerz and Drobniak (2012) are included for comparison.

	Ga (ppm)	Ge (ppm)
Springfield Coal tailings		
Min	7.8 (1.4)	3.6 (1.54)
Max	26.5 (12.3)	30.5 (38)
Average	15.6 (3.39)	13.9 (9.4)
Brazil and Staunton Formations' coal tailings		
Min	15.9	3.0
Max	43.7	148.5
Average	31.9	47.7

scavenger of Ge from circulating fluids, and the negative correlation with Al and Si in this study supports that suggestion. Among the coals studied, the Wise Ridge Coal has the largest average Ge content (28 ppm, max 56 ppm, Table 2). The average for other coals is below 20 ppm. Mastalerz and Drobniak (2012) recorded 9.4 ppm as the average Ge concentration in the Springfield Coal and 14.2 ppm in the Danville Coal.

To investigate whether there is an increase in the concentration of these two elements in coal waste from coal preparation plants, we analyzed two coal tailing deposits: one that comes from the processing of the high-sulfur Springfield Coal (Pike County), and the other from lower-sulfur Brazil and Staunton Formation Coals (Greene County). For the Springfield Coal tailings, the average Ga content is 15.6 ppm, much larger compared to the average value of 3.39 ppm of the Springfield Coal (Table 4). Because Ga in coal is dominantly associated with clay minerals, it would be expected that Ga is more concentrated in the material that is inorganic-enriched matter, such as coal tailings. This inorganic association of Ga is also confirmed by a strong correlation with Al in coal tailings (fig. 7A).

For Ge, even though the average content in coal tailings (13.9 ppm) is higher than the 9.4 ppm average for the Springfield Coal (Table 4), comparison of the minimum and maximum values put Ge enrichment in coal waste under question. Because the dominance of Ge in coal is thought to be associated with the organic fraction, the same association was expected in the coal waste, a suggestion strongly supported by a negative correlation between Ge and ash content (fig. 7B). Consequently, since coal waste has less carbon than the coal itself, the enrichment of Ge in coal tailings compared to the coal was not expected. However, in the coal tailings there is a positive (not as strong as for Ga) correlation between Al and Ge (fig. 7C), suggesting that the inorganic fraction can also host some Ge. For the Springfield Coal waste, both Ga and Ge showed a general trend of decreasing concentrations with an increase in sulfur content (fig. 7D). For Ga especially, sulfur content of less than 5 % is typically associated with Ga concentrations above 20 ppm. Altogether, these results suggest that high Al and low S zones of coal waste could be potential sources for both Ga and Ge.

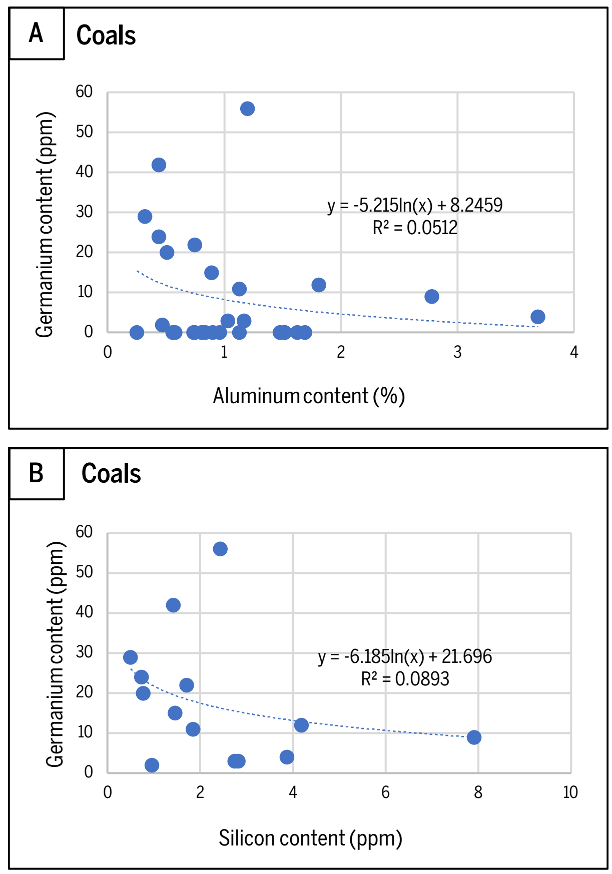


Figure 6. Scatter plots and fitted regressions showing the relationship between Ge and Al (A) and Si (B) in coals.

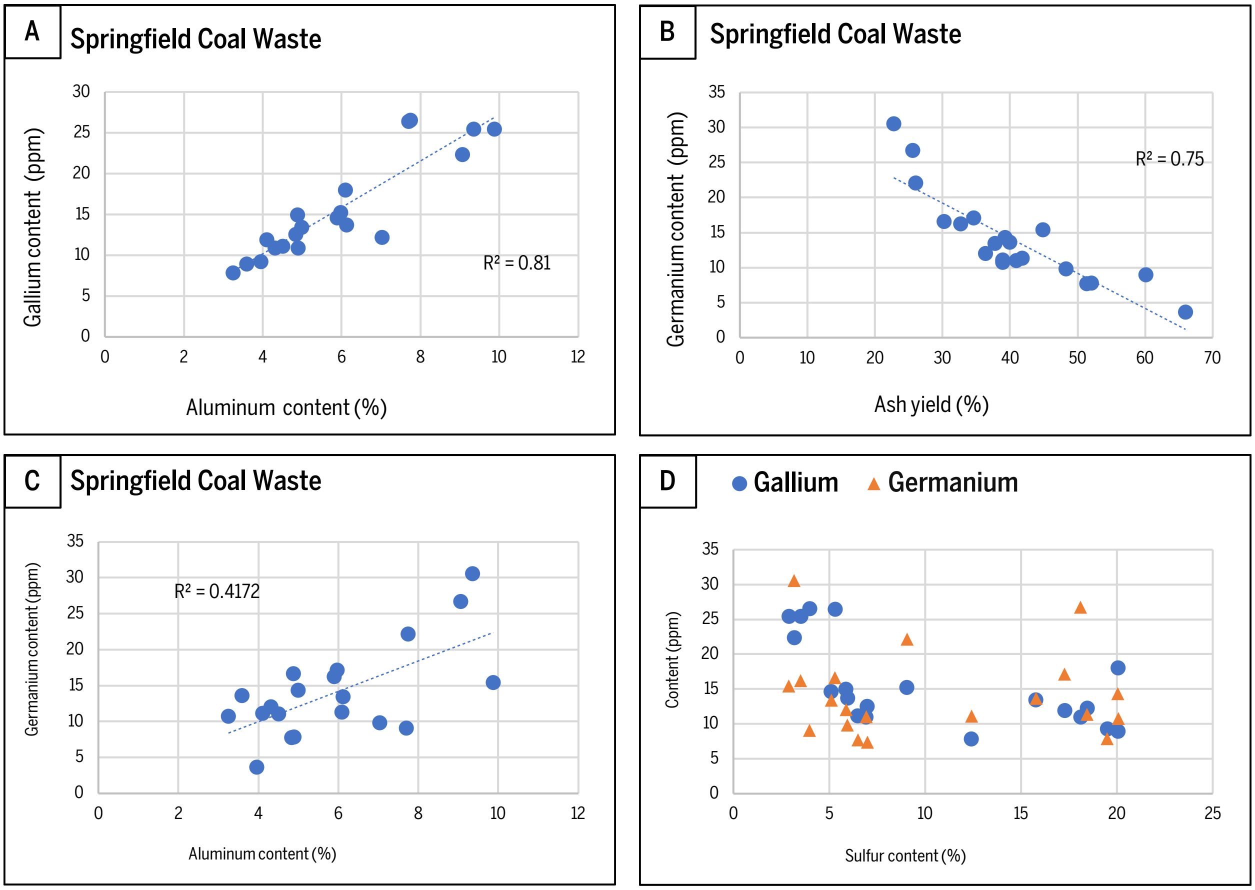


Figure 7. Scatter plots and linear regressions showing relationships between Ge content and Al (A), ash yield (B), Ge and Al (C), and S versus Ga and Ge (D) in the Springfield Coal tailings.

Compared to the Springfield Coal tailings, the Brazil and Staunton Formations' coal tailings are enriched in both Ga and Ge, with an average of 31.9 ppm for Ga and 47.7 for Ge (Table 4). Similar to the Springfield Coal waste, there is a distinct positive correlation between Al and Ga (fig. 8A), supporting the inorganic association. For Ge, there is a negative correlation with the ash yield (fig. 8B), supporting organic association of Ge. In contrast to the Springfield Coal tailings, there is a tendency of increasing Ge with an increase in S content (fig. 8C).

In addition to the concentrations/enrichments of Ga and Ge, the feasibility of technical and economic extraction of these elements is the other critical consideration while considering potential sources. Globally, most Ga is produced as a byproduct of processing bauxite and from zinc (Zn)-processing residues (Sverdrup and others, 2017; USGS, 2022a). As mentioned earlier, recovery of Ga from U.S. bauxite deposits is unlikely because of their high silica content. Out of the materials studied here, paleosols and coal tailings (and those of the Brazil and Staunton Formation coals in particular) are the best potential sources of Ga. Similar to bauxite, paleosols and coal tailings are rich in Al. The association of Ga with clays could make it suitable for using physical separation/mineral processing to preconcentrate and upgrade the material; this would be especially suitable for coal tailings which contain variable grain sizes and fragments of variable densities. In general, not much information has been published about the recovery of Ga from mining waste. In México, Ceniceros-Gomez and others (2018) found that Ga could be recovered from iron non-oxidized tailings and that extraction and separation of Ga from other elements would be relatively easy using hydrometallurgical methods (Mihaylov and Distin, 1992; Macías-Macías, 2017).

The available world resources of Ge are primarily associated with Zn and complex Pb–Zn–Cu ores, but significant amounts of Ge are also produced from coal combustion products (Sverdrup and others, 2017; Haghighi and others, 2018; USGS, 2022b). Among shales, paleosols, and coals, coals appear to be the best source of Ge. In fact, Ge has been commercially extracted from some Ge-enriched (hundreds to thousands of ppm) coal deposits in Russia and China since the late 1950s (Dai and others, 2023). The cut-off grade of Ge in coal ash is suggested at 300 ppm. Although the extraction processes are typically complex, high extractabilities of Ga and Ge were obtained from sulfuric acid (H_2SO_4) treatments of metallurgical slags (Ettler at al., 2022). Controlled H_2SO_4 treatment could also be used to extract Ga and Ge, as documented in a study by Harbuck (1992). Diverse separation methods, including tannin precipitation and solvent extraction, have been used to recover Ge from aqueous solution, and solvent extraction seems to be especially effective (Tao and others, 2021).

CONCLUSIONS

This study investigates Ga and Ge distribution in coals, shales, paleosols, and coal tailings in Indiana as potential sources of these elements. The main conclusions are as follows:

1. Paleosols and coal tailings are promising sources of Ga. Having an average concentration of 26.78 ppm in paleosols and 31.9 ppm in tailings from the Brazil and Staunton Formation coals, they compare favorably to coals (4.6 ppm) and shales (18.77 ppm). Among paleosols, those under the Staunton Formation coals (Wise Ridge and Viking B) have the largest Ga concentrations. The very strong correlation between Ga and Al makes Al an effective predictor of Ga concentrations. Specifically, when Al content is above 12 %, Ga concentrations of 34 ppm (twice the UCC value) and higher can be expected.

2. Positive correlations between Ga and Al in paleosols and shales suggest that Ga is associated with clays, in agreement with previous studies.

3. Indiana coal appears to be a promising source of Ge; the average content of the coals studied here is 6.45 ppm and the maximum is 56 ppm. The Wise Ridge Coal has the largest Ge concentrations (28 ppm on average). Considering the cut-off grade of Ge in coal ash at 300 ppm, the coal samples having Ge concentration above 30 ppm on a whole-coal basis could make that cut.

4. A trend of decreasing Ge concentration with an increase of Al and ash yield suggests the organic association of Ge, supporting previous studies on coals. The organic association for Ge explains why much lower Ge concentrations are found in paleosols and shales that are much leaner in organic matter than coal.

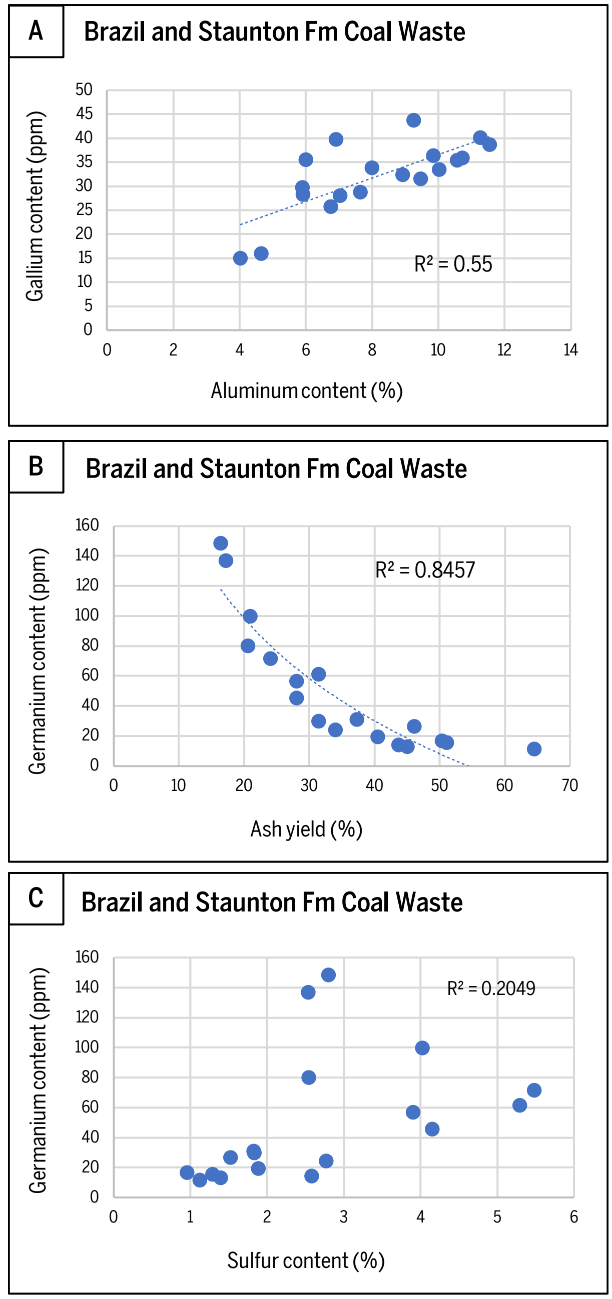


Figure 8. Scatter plots and regressions showing the relationships between Ga and Al (A), Ge and ash yield (B), and Ge and S (C) in the tailings of the Brazil and Staunton Formation coals.

ACKNOWLEDGEMENTS

Gallium and Germanium data on coal, paleosols, and shales came from a project performed under the USGS Earth Mapping Resources Initiative (Earth MRI). Data on coal tailings are part of the U.S. DOE-sponsored CORE-CM project. The support of N. Roden comes from a grant to Assistant Professor Shelby Rader of the Department of Earth and Atmospheric Sciences at Indiana University.

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