

Mercury Isotopic Evidence for Multiple Mercury Sources in Coal from the Illinois Basin

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S Supporting Information

ABSTRACT: Coal combustion is the largest source of anthropogenic mercury (Hg) emissions to the atmosphere and, thus, has vast environmental implications. Recent developments in Hg stable isotope geochemistry offer a new tool for tracing sources and chemical transformations of anthropogenic Hg in the environment. We present here the first isotopic study of mercury in organic and inorganic constituents of four Pennsylvanian-age coal seams in the Illinois Basin, one of the main coal-producing areas in the USA. We report mass dependent isotopic variations relative to the NIST 3133 standard as $\delta^{202}\text{Hg}$ and mass independent fractionation as $\Delta^{199}\text{Hg}$ and $\Delta^{201}\text{Hg}$ values. The data for Illinois coals show a wide range of $\delta^{202}\text{Hg}$ (-0.75 to -2.68%), $\Delta^{201}\text{Hg}$ (0.04 to -0.22%), and $\Delta^{199}\text{Hg}$ (0.02 to -0.23%). In contrast, vein pyrite from two coal seams is isotopically unfractionated relative to NIST 3133. Collectively, these data suggest that isotopically distinct Hg sources contributed to the organic and inorganic fractions of Illinois coals. The $\Delta^{201}\text{Hg}/\Delta^{199}\text{Hg}$ ratio of Illinois coals is 1:1, consistent with isotopic fractionation by photochemical reduction of Hg^{2+} prior to deposition in coal-forming environments. The isotopic composition of Hg in pyrite is more likely derived from hydrothermal fluids that precipitated reduced sulfur in Illinois coal seams. These results demonstrate, for the first time, the potential of Hg isotopes to discriminate between syngenetic (depositional) and epigenetic (hydrothermal) sources of Hg in coal. Our findings may be useful in distinguishing among various geological processes controlling the distribution of Hg in coal and monitoring the fractions of Hg in emissions associated with organic versus inorganic components of coal.

INTRODUCTION

Mercury (Hg) pollution poses global human health and environmental risks.^{1,2} While Hg is naturally present in the environment,^{3–5} human activities have increased the amount of Hg cycling through the atmosphere–ocean–terrestrial system by a factor of about three.⁶ The largest source of anthropogenic Hg is currently coal combustion, responsible for releasing 810 Mg yr⁻¹ of Hg into the atmosphere.⁶ In addition, coal mining and coal ash disposal may contribute substantial amounts of Hg to the environment by processes other than combustion.^{6,7}

Although coal generally has relatively low Hg abundances, with typical levels of 0.02–1.0 $\mu\text{g/g}$,⁸ Hg emissions from coal induce a significant environmental impact because of the large amounts that are burned worldwide to generate electricity.⁶ In spite of recent advances, our knowledge about many details of Hg occurrence and distribution in coal is still rather poor. Current debate centers on the processes and pathways by which Hg accumulates in coal,^{9,10} as well as uncertainties in identifying the primary sources and geological factors controlling Hg distribution.^{8,11} Consequently, there is a mounting need for new approaches geared toward better understanding of geochemical and mineralogical controls on the abundance of Hg in coal both at regional and global scales.

Hg stable isotope geochemistry has recently undergone rapid development and has become a critical tool for unravelling the complex web of inorganic and biological processes that characterize the Hg cycle in the environment.¹² Hg has seven stable

isotopes (196–204 amu) that span a relative mass difference of $\sim 4\%$. In addition to kinetic and equilibrium processes that result in mass-dependent fractionation (MDF), significant mass-independent Hg isotope fractionation (MIF) of the odd isotopes ¹⁹⁹Hg and ²⁰¹Hg has also been observed in both natural samples and laboratory experiments.^{13–21} Large Hg odd-isotope MIF effects have been observed in Hg reservoirs that have undergone photoreduction.^{13,14,21} The mechanism thought to produce large MIF of Hg is the magnetic isotope effect,²² which influences radical pair reaction pathways.^{13,20,21} Hg MDF (reported as $\delta^{202}\text{Hg}$, the ‰ variation in the ²⁰²Hg/¹⁹⁸Hg ratio relative to NIST SRM-3133) and Hg MIF (reported as $\Delta^{199}\text{Hg}$ and $\Delta^{201}\text{Hg}$, the ‰ deviation in ²⁰¹Hg/¹⁹⁸Hg and ¹⁹⁹Hg/¹⁹⁸Hg relative to values predicted for MIF from $\delta^{202}\text{Hg}$) both span a reported range of $>6\%$.¹² Large positive Hg MIF has been observed in freshwater and marine fish,¹³ and smaller positive and negative Hg MIF has been measured in lichens,¹⁸ moss, peat, coal, soil, sediments, and precipitation.^{14,15,23,24} In laboratory experiments large Hg MIF was observed during photoreduction reactions^{13,19} and smaller Hg MIF was observed during phase changes accompanying evaporation and dark reduction.^{16,20} $\Delta^{201}\text{Hg}/\Delta^{199}\text{Hg}$ ratios characteristic of MIF-inducing reaction pathways involving photoreduction of inorganic Hg^{2+} are typically ~ 1.0 , while photoreduction

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of methyl-Hg (MeHg) results in distinctly different $\Delta^{201}\text{Hg}/\Delta^{199}\text{Hg}$ ratios of ~ 1.3 .¹²

Until recently, Hg research on coals has mainly focused on Hg concentration distributions in organic and inorganic constituents from micro- to basin-scale.^{8–11,25,26} The results have shown that the majority of Hg residing in coal is associated either with (1) organic matter, where it binds strongly to reduced-sulfur groups,^{9,27} or (2) sulfide minerals, where it is incorporated within the mineral structure.^{9–11} To date, only a small number of coal samples worldwide have been measured for their Hg isotopic composition. Biswas et al.¹⁴ observed a 3‰ range in $\delta^{202}\text{Hg}$ MDF and a 1‰ range in $\Delta^{201}\text{Hg}$ and $\Delta^{199}\text{Hg}$ MIF for coal samples collected from the U.S., China, Russia, and Kazakhstan. They suggested that the combination of Hg MDF and MIF signatures could be employed as a diagnostic tool useful for “fingerprinting” anthropogenic Hg from different coal sources.

This study reports, for the first time, Hg isotope data for organic and inorganic constituents of four Pennsylvanian bituminous coal seams from the Illinois Basin. Our results show that the Hg isotopic composition of Illinois coal constituents is controlled by a combination of at least two sources: (1) syngenetic Hg present during deposition and (2) epigenetic Hg delivered by hydrothermal Hg-bearing fluids.

MATERIALS AND ANALYTICAL METHODS

Representative coals were channel sampled following the ASTM D4596²⁸ standard in production areas from four coal beds in the southern part of the Illinois Basin. Samples were collected from the Pennsylvanian-age, high volatile bituminous²⁹ Herrin (No. 6) and Springfield (No. 5) coal members of the Carbondale Formation and the Murphysboro and Mt. Rorah coal members of the Spoon Formation. Upon return to the laboratory, the mineral-free organic fraction was separated from each raw coal sample. The fracture-filling pyrite was handpicked to obtain separates for Hg analysis. Subsequently, the organic fractions were crushed, sieved to <50 mesh fraction, and analyzed for Hg concentration and isotopic composition.

Hg was separated from coal by combustion and Hg vapor trapping into a potassium permanganate solution following methods of Biswas et al.¹⁴ Hg isotope measurements were carried out on a Nu Instruments multicollector ICP-MS at the University of Michigan by continuous flow cold vapor generation, using a Tl internal standard and standard sample bracketing for mass bias correction (see the Supporting Information for details of methodology). Hg isotopic variations are reported in delta notation in units of permil (‰) referenced to the NIST SRM-3133 Hg standard.³⁰ We report values for mass dependent fractionation (MDF) as $\delta^{202}\text{Hg}$. For odd-numbered isotopes (^{199}Hg and ^{201}Hg), we first derive $\delta^{199}\text{Hg}$ and $\delta^{201}\text{Hg}$ values for the predicted mass-dependent values based on $\delta^{202}\text{Hg}$ using a kinetic mass-dependent fractionation law.¹³ We then calculate $\Delta^{xxx}\text{Hg}$ (or deviation from mass dependency, in ‰), as the difference between the measured and predicted $\delta^{199}\text{Hg}$ and $\delta^{201}\text{Hg}$ values.¹⁴ Details of the long-term external reproducibility of Hg isotopic compositions and equations used to calculate Hg isotopic values are given in the Supporting Information.

RESULTS AND DISCUSSION

1. Hg Concentrations of Coal and Pyrite. We measured the Hg concentration and Hg isotopic composition in twenty-five coal samples and three pyrite samples from four major coal seams

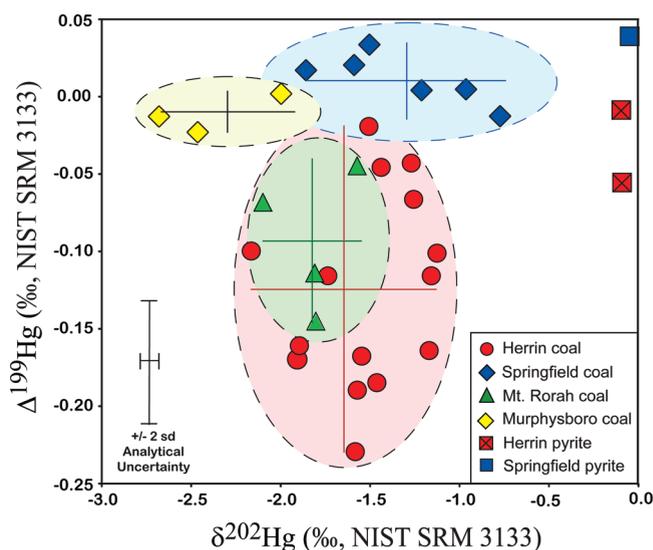


Figure 1. $\delta^{202}\text{Hg}$ vs $\Delta^{199}\text{Hg}$ for coal and pyrite samples from the Illinois Basin ($n = 31$). Analytical uncertainty (2SD error bar) reflects the expanded scale on the y-axis. $\delta^{202}\text{Hg}$ shows a $\sim 2\text{‰}$ range (-0.75 to -2.68‰), and $\Delta^{199}\text{Hg}$ shows a $\sim 0.25\text{‰}$ range down to values of -0.23‰ in coals. Pyrite samples have $\delta^{202}\text{Hg} \approx 0\text{‰}$ and no MIF ($\Delta^{199}\text{Hg} = 0.00 \pm 0.05\text{‰}$). Average and 2SD ranges for each coal seam are also shown. On the basis of $\delta^{202}\text{Hg}$ and $\Delta^{199}\text{Hg}$ values, these coal seams appear to be isotopically distinct (see text).

from the Illinois Basin (Table S1 of the Supporting Information). Hg concentrations in coals ranged from 28 to 371 ppb (average value of 102 ppb). Pyrite from Herrin and Springfield coal seams contained 3500 and 7600 ppb Hg, respectively, indicating much higher Hg content in vein pyrite than host coal (Table S1 of the Supporting Information). No systematic spatial patterns in Hg abundances were observed in any of the coal beds. Replicate Hg concentration measurements of three coal samples were reproducible to within 7%, while a single pyrite replicate analysis was reproducible to within 14% (Table S2 of the Supporting Information). Six combustions of the NIST 1632c bituminous coal standard reference material (SRM) by AAS averaged 88 ± 5 ppb compared to the certified NIST value of 94 ± 4 ppb (Supporting Information), resulting in average calculated Hg recoveries of $\sim 93\%$ during combustion, trapping, transfer, and AAS analysis of coal samples in advance of isotopic analysis (Table S2 of the Supporting Information).

2. End-Member Hg Isotopic Signatures in Coal and Pyrite.

A prominent feature identified by our investigation is a distinct Hg isotopic difference between organic and inorganic constituents of Pennsylvanian coals in the Illinois Basin (Figure 1). The coal samples have a $\sim 2\text{‰}$ range in $\delta^{202}\text{Hg}$ values (-0.75 to -2.68‰) (Figure 1), and many samples show negative $\Delta^{201}\text{Hg}$ and $\Delta^{199}\text{Hg}$, with values as low as -0.23‰ (Figures 1 and 2). In contrast, the pyrite samples have $\delta^{202}\text{Hg}$ close to 0‰ with no evidence of significant MIF (Figures 1 and 2). This data strongly suggest that Hg from sources with distinct Hg isotopic signatures was incorporated into Illinois Basin coal and associated sulfide phases.

The Hg isotope values in coals from the Illinois Basin overlap those of other coal samples worldwide¹⁴ and include some of the most negative $\delta^{202}\text{Hg}$ values yet measured for coals (Figure 3). Within the Illinois Basin, several of the coal seams appear to be isotopically distinct from each other using $\delta^{202}\text{Hg}$ and $\Delta^{199}\text{Hg}$ values (Figure 1). In particular, the Murphysboro, Springfield,

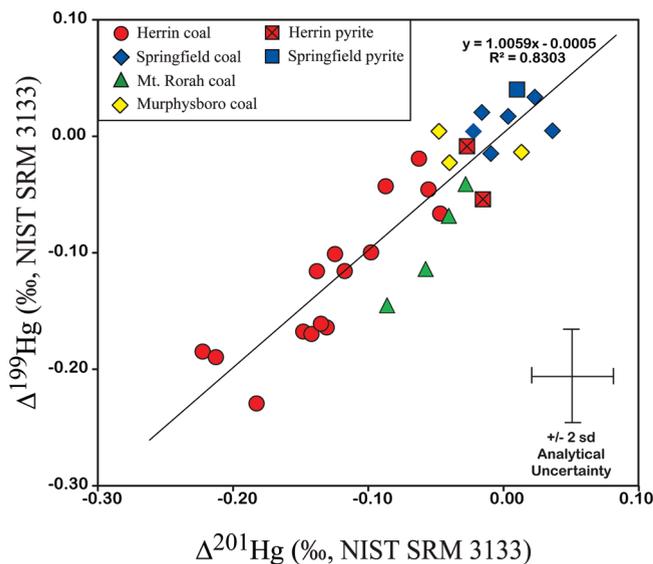


Figure 2. $\Delta^{201}\text{Hg}$ vs $\Delta^{199}\text{Hg}$ of coal samples and pyrite from the Illinois Basin. The relation between $\Delta^{201}\text{Hg}$ and $\Delta^{199}\text{Hg}$ for Illinois coals is linear, and most data points fall on a 1:1 reference line of $y = 1.0059x - 0.0005$ with an r^2 of 0.8303. Analytical uncertainties for MIF are defined by the long-term average (2SD) of the Almaden reference isotopic standard run at a 5 ppb Hg solution concentration by MC-ICP-MS.

and the combined Mt. Rorah and Herrin coals can be distinguished from each other on this basis; however, the Mt. Rorah and Herrin coals are indistinguishable from each other (Figure 1). The presence of significant negative Hg MIF (expressed in both $\Delta^{199}\text{Hg}$ and $\Delta^{201}\text{Hg}$) is established here as an important feature of some Illinois coals, with the most negative values observed in Herrin coals (Figure 1). In contrast, our samples of Springfield and Murphysboro coals did not reveal any measurable Hg MIF (Figure 1). The Herrin data set shows reproducible negative $\Delta^{201}\text{Hg}$ and $\Delta^{199}\text{Hg}$ down to -0.23‰ (Figure 2). Significantly, for the entire Illinois coal data set, the relation between $\Delta^{201}\text{Hg}$ and $\Delta^{199}\text{Hg}$ is linear with most data points defining a 1:1 reference line (Figure 2).

3. Hg Isotopes and Coal-Forming Environments. Ancient coal-forming environments, with their water-saturated, partially anaerobic soils, were important sites for Hg accumulation. Pennsylvanian-age (about 300 Ma) coastal swamps, deltas, and floodplains of the Illinois Basin coal-producing region³¹ would have received Hg from primary geological sources such as emissions from volcanoes and hydrothermal systems, as well as secondary emissions from ocean and land areas naturally enriched in Hg.^{4,5} The lush vegetation in Pennsylvanian mires³² would have sequestered Hg complexed with organic matter. Available data from modern peat-forming environments indicate that terrestrial vegetation, with an average Hg concentration of ~ 20 ppb,⁸ accumulates Hg from several atmospheric sources, including gaseous Hg and Hg from wet and dry deposition, and stores it within the plant tissues.³³ Therefore, it is likely that Hg originally incorporated into plant tissues is preserved within the peat and coal structure. Recent studies have shown that mosses and lichens in modern ecosystems typically have a large range of negative MDF values ($\delta^{202}\text{Hg} = 0$ to -3‰) and significant negative MIF ($\Delta^{201}\text{Hg} = 0$ to -1‰),^{14,15,18} which overlaps but extends beyond the Hg isotopic compositions of Illinois coals (Figure 3).

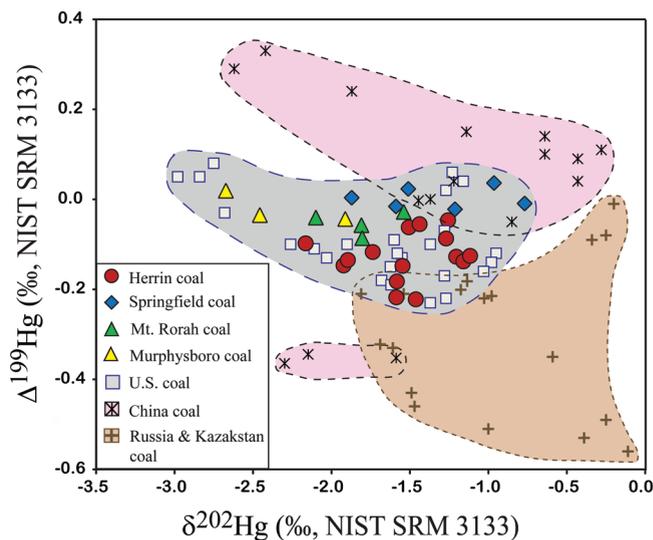


Figure 3. $\delta^{202}\text{Hg}$ vs $\Delta^{199}\text{Hg}$ for Illinois coals compared with coal samples from the United States, China, Russia, and Kazakhstan (data from this study and Biswas et al.¹⁴). The range of Hg isotopic compositions of Illinois coals largely overlaps that of other coal samples worldwide (see text).

Peat, the organic material resulting from partially decayed plant matter and the precursor to coal formation, generally contains about an order of magnitude higher concentration of Hg than plants.⁸ This significant Hg enrichment in peat has been explained by addition of Hg from other sources such as surface waters,³⁴ volcanic and geothermal activity,³⁵ and local Hg enrichment during organic matter decomposition in peat bogs.³⁶ Estimates of Hg fluxes suggest that the amount of preindustrial atmospheric Hg deposition to land and to the ocean was probably $\sim 1/3$ of the present-day deposition.^{4,5} In peat, as well as soil humus, Hg bonds strongly with thiols and other reduced sulfur groups associated with organic matter.²⁷ Recent studies of modern peat deposits report negative MDF of Hg.^{14,15,18} Microbial reduction is known to produce $\text{Hg}(0)$ with significantly lower $\delta^{202}\text{Hg}$ values than the original Hg^{2+} .³⁷ Additionally, inorganic processes, such as photochemical reduction of Hg^{2+} ,^{13,19,20} volatilization,¹⁶ and adsorption-desorption processes³⁸ can produce MDF. Overall, the photochemical reduction of both Hg^{2+} (and to a lesser extent MeHg) in the presence of organic matter is a key process in producing significant Hg isotopic contrasts because the volatile $\text{Hg}(0)$ can escape into the atmosphere producing isotopic fractionation of Hg that is later deposited to the surface environment.

Similar to modern plants, and relevant to this study, peat has negative MIF anomalies with a $\Delta^{199}\text{Hg}/\Delta^{201}\text{Hg}$ ratio of ~ 1.0 .^{14,15} Such a 1:1 relationship was observed during Hg^{2+} photochemical reduction experiments^{13,21} and suggests that much of the Hg in the modern peat-forming ecosystem was either photoreduced from aquatic systems and redeposited to peat or is the residual Hg remaining after loss of $\text{Hg}(0)$ by photoreduction. Our observation that the Illinois coals have negative MIF anomalies with $\Delta^{201}\text{Hg}/\Delta^{199}\text{Hg}$ ratios that fall close to 1 indicate that similar to modern ecosystems, photoreduction of Hg was important in the Pennsylvanian mires.

Paleoecological studies in the Illinois Basin have revealed that peat surfaces in Pennsylvanian mires ranged from continuously flooded to exposed, with extensive subaerial decay of organic

matter.³² The pathways of Hg to the mires possibly varied from atmospheric-dominated pathways to mixed atmospheric–terrestrial pathways in areas subject to flooding from streams.³² The wide range of depositional conditions and complex biogeochemical processes in the Pennsylvanian mires probably played a critical role in setting Hg isotope values of Illinois coals, much as they do in modern peat-forming environments.

Coalification processes during burial compaction result in significant physical reduction in volume and loss of water and organic matter.²⁹ During coalification, some weakly bonded Hg can be lost through volatilization,²⁵ and this process might potentially be capable of altering the Hg isotope signature of coal. However, the Illinois coal samples considered in this study have comparable rank (high volatile bituminous B and C) and were probably affected to similar degrees by the coalification processes.

4. Hg in Hydrothermal Solutions and Isotopic Composition of Sulfides. Additional Hg input to Illinois Basin coals could have come from hydrothermal solutions. In coal seams, Hg enrichments have previously been described in association with epigenetic hydrothermal fluids.^{8–11} In U.S. coals, late-stage, fracture-filling pyrite associated with structurally disrupted coal was found to be the dominant reservoir of epigenetic Hg.^{8,9,11} In contrast, Hg concentrations are much lower in all other generations of pyrite.^{9,11} The coal organic matrix can also be enriched in epigenetic Hg. Diehl et al.,⁹ found that in coal samples affected by Hg-bearing fluids there was a direct correlation between Hg and S and an inverse correlation between Hg and Fe concentrations and suggested that in the coal matrix epigenetic Hg was trapped by the carbon-bonded sulfhydryl groups in coal (thiols) and not by sulfide minerals. In Illinois coals, nearly all of the Hg associated with mineral matter is stored in pyrite and other metallic sulfides with Hg most likely present in solid solution.^{11,25} Sulfide minerals, for which Hg has a high affinity,³⁹ have great potential for Hg immobilization. Hydrothermal pyrite is a natural and perhaps dominant sink for Hg in Illinois coal.

A few studies have explored the isotopic signature of Hg in various crustal and mantle sources^{23,35} of hydrothermal fluids. Typical crustal rocks have $\delta^{202}\text{Hg}$ values of $-0.6 \pm 0.2\text{‰}$ with no evidence of MIF.²³ Marine hydrothermal deposits and ores display a $\sim 7\%$ range of $\delta^{202}\text{Hg}$ values and $\Delta^{201}\text{Hg}$ values close to 0‰.¹² The significant range of $\delta^{202}\text{Hg}$ values are interpreted to result mostly from the volatilization of isotopically light Hg(0),³⁵ in agreement with experimental results.¹⁶ The Hg isotopic values of Illinois Basin pyrite have heavier $\delta^{202}\text{Hg}$ than those reported from typical crustal samples but otherwise fall within the Hg isotopic range of ocean basin and continental hydrothermal deposits.

Hydrothermal solutions are often enriched in Hg,⁹ and therefore, it seems likely that hydrothermal fluids could have affected the Hg concentrations and isotopic compositions of Illinois coal seams. The linear trend of $1/\text{Hg}$ versus $\Delta^{199}\text{Hg}$ observed in Figure 4 could be explained by a mixture of two main Hg sources: (1) Hg with an MIF signature associated with coal depositional processes and (2) Hg without significant MIF associated with hydrothermal processes. Our observation that Herrin coals with the lowest Hg content retain the largest $\Delta^{199}\text{Hg}$ anomalies, whereas Springfield coals with highest Hg content have the lowest $\Delta^{199}\text{Hg}$, is suggestive of varying degrees of interaction between Hg-bearing hydrothermal solutions and the Hg-bearing organic components in Illinois coal seams (Figure 4). A regional hydrothermal flux involving multistage fluid migration that affected Hg distribution in Illinois Basin coals is consistent with

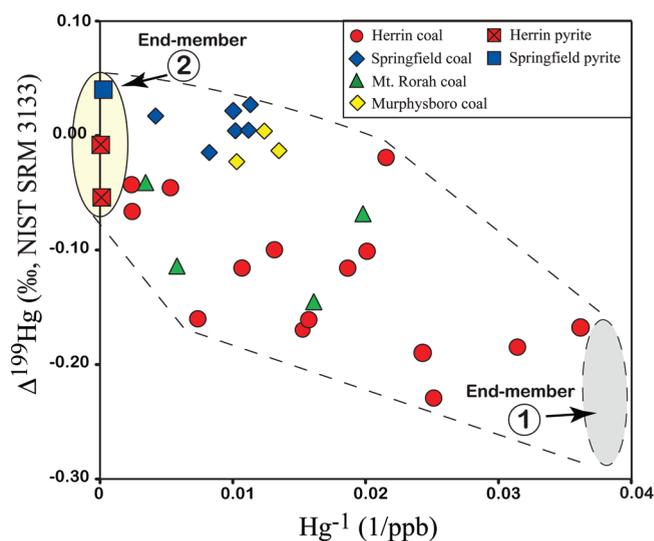


Figure 4. $1/\text{Hg}$ concentration (ppb) vs $\Delta^{199}\text{Hg}$ for coal and pyrite samples from the Illinois Basin. Distinct Hg content and Hg isotopic values for coal and pyrite samples strongly suggest that Hg from multiple sources was incorporated into the organic and inorganic fractions of Illinois coal seams. The two end-member sources of Hg in Illinois coal described in the text are (1) syngenetic (depositional) and (2) epigenetic (hydrothermal).

previous studies indicating a complex hydrothermal origin for Permian-age MVT mineralization in the Illinois Basin.^{40–42} Hg-bearing fluids originating as basinal brines could therefore have precipitated Hg-rich vein pyrite in Illinois coals.^{41,42}

Springfield coal, which has no Hg MIF, has high ash yields and elevated total sulfur, metals, and other trace elements and was greatly affected by mineralizing hydrothermal solutions.⁴³ In contrast, Herrin coal, which has large Hg MIF, the main minable coal seam in the Illinois Basin, is known for its low ash yield and low sulfur and trace metal content,⁴³ suggesting less of a hydrothermal imprint. Therefore, it is tempting to consider the degree of Hg MIF in Illinois Basin coals as a proxy for the degree of geochemical interaction between hydrothermal solutions and coal. However, given limited current knowledge of the processes controlling the Hg isotopic values of potential Hg end-members, it is not yet possible to satisfactorily quantify the overall Hg input from different sources to the Illinois coal and pyrite samples that we analyzed. For a Hg hydrothermal mixing model to be valid, the processes controlling the $\delta^{202}\text{Hg}$ values in the coals would need to be decoupled from the $\Delta^{199}\text{Hg}$ and $\Delta^{201}\text{Hg}$ signatures, as there is no correlation between Hg MIF and MDF (Figure 1). $\delta^{202}\text{Hg}$ values are likely shifted by fractionation through exchange during hydrothermal transport and by pyrite precipitation,³⁵ whereas $\Delta^{199}\text{Hg}$ and $\Delta^{201}\text{Hg}$ signatures are only expected to be imparted to coals prior to coalification by photochemical processes acting in surface environments. The 1:1 $\Delta^{199}\text{Hg}/\Delta^{201}\text{Hg}$ ratio evident in Figure 2 is, therefore, perhaps best interpreted as a dominantly photochemical isotopic signature retained by the organic-bound Hg in coals, with additional overprint by hydrothermal processes that shifted isotopic compositions in coals toward the origin (e.g., pyrite compositions).

5. Environmental Implications. This study demonstrates for the first time the potential of Hg isotopes to discriminate between the syngenetic (depositional) and epigenetic (hydrothermal) sources of Hg in coal from the Illinois Basin, leading to an

enhanced understanding of the processes by which Hg is accumulated in coal. Emissions of Hg from coal-fired power plants are a global transboundary issue and an ongoing challenge. The observed variations in $\delta^{202}\text{Hg}$ and $\Delta^{199}\text{Hg}$ values in coals can be used to isotopically distinguish different coal seams and may possibly aid in “fingerprinting” Hg isotope signatures of Illinois coals and allow differentiation from regional and global atmospheric Hg background.²⁴ Finally, the differences in isotopic composition found here between the organic and inorganic components in coal may find important future applications for monitoring Hg control strategies during pre- and post-combustion of coal,⁴⁴ with the ultimate goal of reducing Hg emissions to the environment.

■ ASSOCIATED CONTENT

S Supporting Information. Sample locations and detailed experimental data, including sample treatment prior to analysis, analytical methods, data treatment, and delta value calculations. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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