Clausthalite in coal

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Abstract

A lead selenide mineral, tentatively identified as clausthalite (PbSe) based on optical microscopy, scanning electron microscopy with energy-dispersive X-ray (EDAX), electron microprobe, and scanning proton microprobe (SPM), has been described in a number of coals. While clausthalite has been mentioned as a possible source of Se in coal, it is present in such small quantities and sizes, that the mineral identification has not been absolutely confirmed. The mineral specimens examined in this study would contribute, not only to the Pb and Se concentrations in the coal, but also, in at least one case, to Hg concentrations.
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1. Introduction

Clausthalite (PbSe) has been considered to be a host of Se in coal, but, generally being small and in trace quantites, mineral identification is difficult to confirm (Finkelman, 1981). Other sources of Se, both inorganic and organic, are possible. For example, Minkin et al. (1984) and Kizil'shtein and Shokina (2001), among others, called for a sulfide association of Se.

Clausthalite is the most common selenium mineral (Picot and Johan, 1977; Ramdohr, 1980; the following information on clausthalite is from the latter sources).

The mineral has an isometric (hexoctahedral) crystal structure, a 53.1% reflectance in air at 540 nm, and a density of 7.8–8.2. In metasomatic vein deposits, clausthalite occurs with tiemannite (HgSe), berzelianite (Cu_2Se), klockmannite (CuSe), umangite (Cu_2Se_2), gold, Co-selenides, and stibiopalladinite (Pd_5Sb_2). Maucher and Rehwald (1961) have also noted the association of clausthalite with gold, calcite, and naumannite (Ag_2Se). They illustrated one example from Cordeck, Waldeck, Germany, in which clausthalite migrated out of calcite of the same age, forming crusts surrounding idiomorphic calcite crystals. Pitchblende (gel form of uranite, UO_2 to UO_3) is also known to occur with clausthalite.

Coal combustion is a major source of Se in the environment (Lakin and Davidson, 1973; Swaine, 1990, p. 151). Coal combustion, among other emission sources, is also a source of Pb. Sloss and Smith

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(2000) discussed a number of factors governing the emission of trace elements from coal combustion. Among the studies discussed was that of Stewart and Walker (1997), who estimated Se emissions of 7.1–28.9 μg/MJ and Pb emissions of 53.1–216 μg/MJ from the combustion of European bituminous coal, 24.8 MJ/kg average heating value, in boilers without flue-gas desulfurization.

Combustion of Se-rich coals can be a factor in human health. In consideration of endemic selenosis in southwestern China, Zheng et al. (1999) recommended abandoning the practice of drying soil using high-Se coal as a fuel, using ventilated furnaces, and abandoning the mining and utilization of known high-Se coal. They reported Se concentrations in excess of 8000 μg/g (?) for carbonaceous shales used as fuel. US Se values are substantially lower. US, Eastern Kentucky, and Western Kentucky average Se and Pb concentrations are shown in Table 1 (data from Bragg et al., 1998), with the caveat that the values represent coal collected at the mine face or from core with the exclusion of >1 cm partings. Coal collected in this manner approximates a clean coal product, but, in reality, the average of coals actually shipped to utilities will likely differ from the published values. Se in fly ash has also been linked to numerous health problems in fish (Lemly, 2002).

Swaine (1990, p. 151) noted that ... "A feature of the environmental behaviour of Se is that the difference between a concentration causing deficiency and what may be harmful is relatively small." At the extremes of Se intake and nutritional utilization, selenosis is a disease caused by a high concentration of Se in the diet (Swaine, 1990, p. 153; Zheng et al., 1999), while Keshan disease and Kashin-Beck disease are caused by Se deficiencies (Swaine, 1990, p. 153). The US (National Research Council, 1989) recommended daily allowance for Se is 55–70 μg/day for adult women and men, respectively, while the recommended limit is 400–450 μg/day based on Se toxicity at levels as low as 600 μg/day (Rayman, 2000).

In this paper, we discuss the further evidence, based on specimens from several locations, for clausthalite as a host of Se and Pb in coal and, consequently, as a source of Se and Pb in emissions from coal combustion.

2. Procedure

2.1. Optical and electron microscopy

Optical microscopic examination was conducted at the Center for Applied Energy Research (CAER). Specimens of PbSe minerals (clausthalite?) were initially viewed using a Leitz Orthoplan microscope with either a $50 \times$ air objective Leitz (NPl $50 \times$/0.85 P ∞/0) or a $50 \times$ oil immersion objective (Leitz Oel $50 \times$/0.85 P ∞/0). In both cases, we employed reflected light, polarized at $45°$, with the analyzer out of the plane of the reflected light. Cargille Type A immersion oil (formula code 1248) with $n_D = 1.5150 \pm 0.0002$ at $23 °C$ was used for oil immersion observation.

Initial confirmation of the bulk elemental composition of selected specimens was made on a Hitachi S-2700 scanning electron microscope with a PGT EDS energy-dispersive X-ray (EDAX) at the CAER and on an ARL-SEMQ electron microprobe in the University of Kentucky Department of Geological Sciences.

2.2. Scanning proton microprobe (Micro-PIXE)

Scanning proton microprobe (Micro-PIXE; SPM) analysis of a specimen was conducted in the University of Guelph (Ontario) Scanning Proton Microprobe Laboratory. Discussion of the Guelph facility can be found in Campbell et al. (1992). The sample was viewed with a television camera connected to the microscope equipped with a $300 \times$ objective. The micro-PIXE analyses were carried out using a 2.9-MeV proton beam at an intensity of 3–5 nA and a

Table 1
Se and Pb concentrations (μg/g, whole coal basis) in United States (including Kentucky), Eastern Kentucky (part of the Appalachian coal fields), and Western Kentucky (part of the Illinois Basin) (data from Bragg et al., 1998)

	Mean	S.D.	Min	Max	N
Se					
all US (including Kentucky)	21.6	18.1	0	330	7431
Eastern Kentucky (Appalachians)	4.2	2.3	0	18	780
Western Kentucky (Illinois Basin)	3.2	2.1	0.8	12	125
Pb					
all US (including Kentucky)	10.5	36.2	0	1900	7431
Eastern Kentucky (Appalachians)	9.1	7.8	0	78	780
Western Kentucky (Illinois Basin)	22.8	22.9	0.8	120	125

total charge/sample of 4 °C. The proton beam was focused via a miniature air-cooled magnetic quadrupole doublet and was incident on the sample at an angle of 45° with respect to sample normal. The X-rays emitted were measured with an 80-mm^2 Si(Li) detector with a full-width half-maximum resolution of 140 eV at the manganese K_Υ X-ray. The intensity of low-energy X-rays and background Bremsstrahlung radiation was reduced by placing a 128-μm-thick Mylar and 250-μm-thick aluminum absorber in front of the detector. Data analysis was performed using the GUPIX software package (Maxwell et al., 1994). A discussion of the accuracy and precision of PIXE measurements in coal can be found in the article by Wong and Robertson (1993).

3. Results

3.1. Optical and electron microscopy

In optical examination, particularly when the coal petrographer's emphasis is on macerals, not minerals, clausthalite can easily be mistaken for pyrite. Both pyrite and clausthalite are bright, opaque minerals, and the reflectances are similar, 53.8% for pyrite versus 51.3% for clausthalite (both in air at 540 nm; Picot and Johan, 1977). Unassisted by a photometer, the difference between pyrite and clausthalite reflectances, particularly when compared to the much lower reflectance of bituminous macerals, would not be particularly discernable. Clausthalite has a much
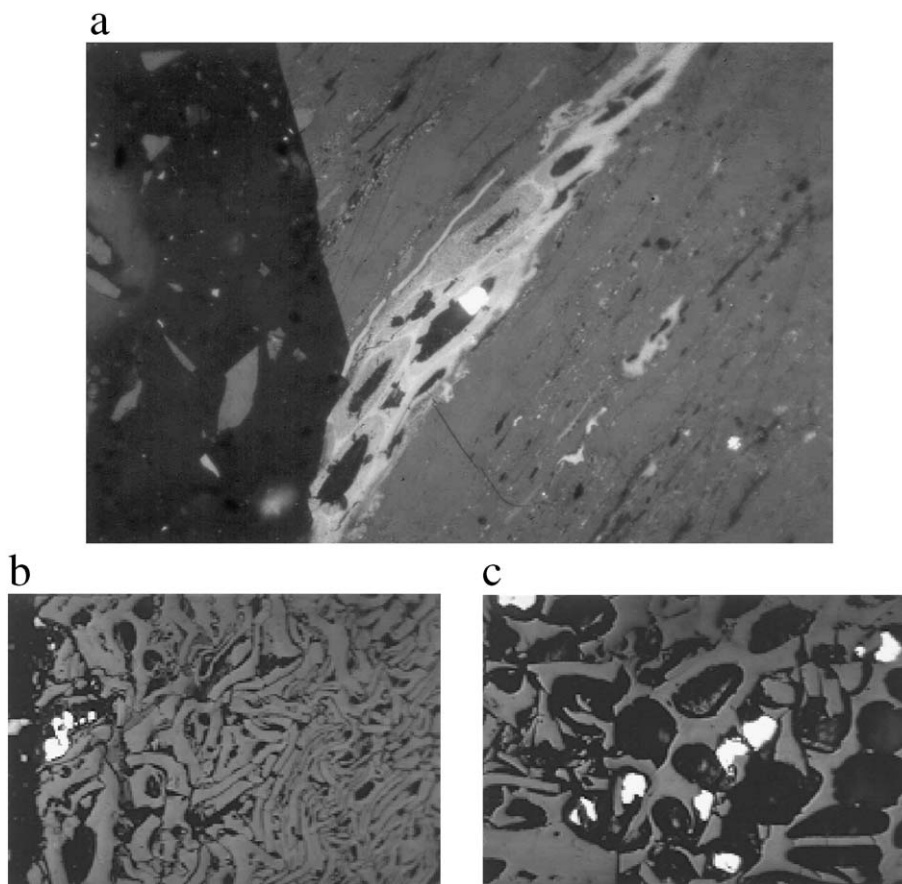

Fig. 1. (a) Mineral grain used in micro-PIXE characterization. Mineral is in semifusinite within vitrinite. Manchester coal bed, Clay County, Kentucky. Field of view is about 250 μm on long axis of photo. (b and c) Mineral grain in inertinite. Unnamed coal, Union County, Kentucky. Field of view is about 250 μm on long axis of photo.

higher reflectance than galena (42.4% in air at 540 nm for galena; Picot and Johan, 1977), making confusion between galena and clausthalite less likely than confusion between clausthalite and pyrite. Clausthalite, however, has a bluish tint in reflected light, in contrast to the yellow to bronze tint of pyrite. The difference can be subtle, but once observed, clausthalite can be distinguished from pyrite. Petrographic characteriza-
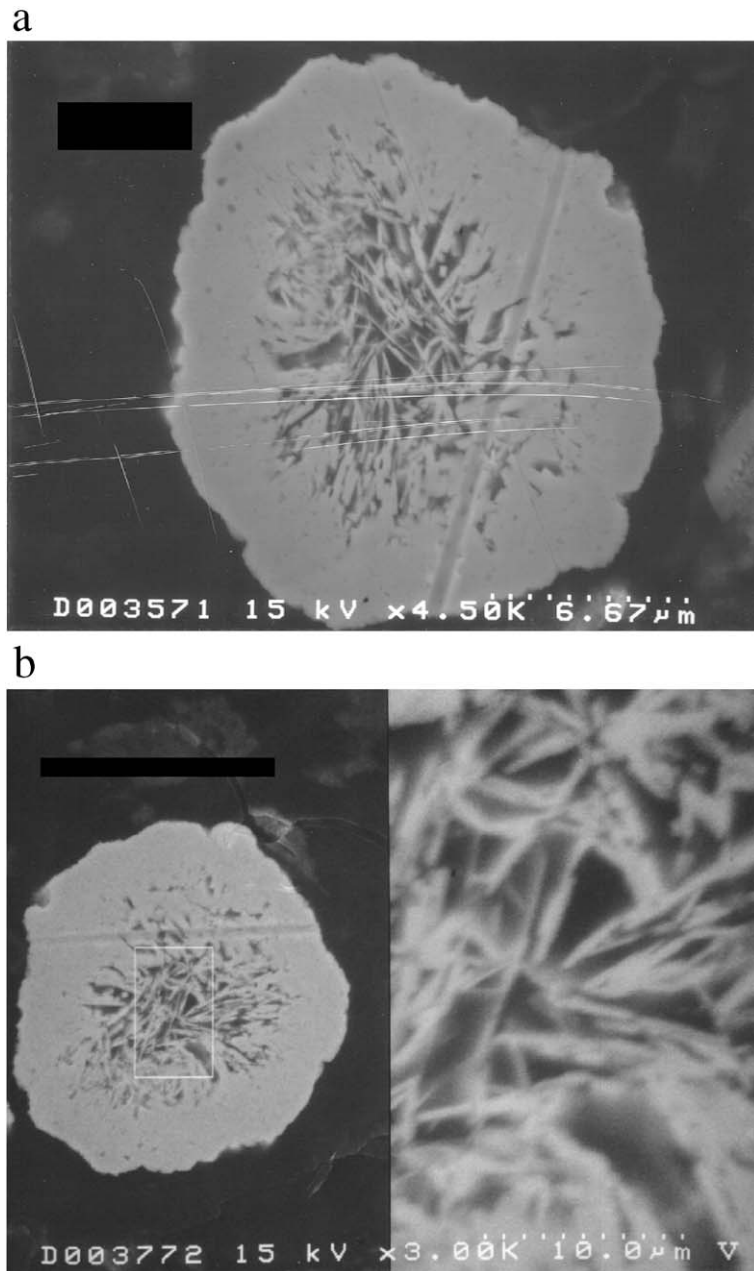

Fig. 2. Scanning electron microscopy image of mineral from Uinta Basin coal. (a) Image of cross section of mineral. Scale at lower right of image. (b) Expanded view of center of mineral. Scale refers to image of the entire cross section on left side.

tion of clausthalite is further complicated by the fact that it is rarely present in coal in grain much larger than 3 μm in diameter (Finkelman, 1985).

In our studies, the mineral identified as clausthalite has generally been observed as a secondary mineral filling fusinite and semifusinite lumens. Examples of clausthalite from two Kentucky coals are shown on Fig. 1. Fig. 1a illustrates a grain, also used for the micro-PIXE study (below), from the high volatile A bituminous Pennsylvanian Manchester coal bed in Clay County, eastern Kentucky (Sakulpitakphon et al., submitted for publication). The clausthalite occurs within a semifusinite lumen. The remainder of the lumen is occupied by carbonate. Fig. 1b and c illustrate clausthalite grains from a Pennsylvanian coal of uncertain correlation in Union County, Western Kentucky. The high volatile A bituminous coal bed is severely brecciated and recemented by a carbonate-dominated mineral assemblage (Hower et al., 2001). Similar to Fig. 1a, these clausthalite grains are found in inertinite lumens. In both cases, there is a possibility that the mineralization had a hydrothermal component, fluids expelled in the emplacement of the Pine Mountain thrust sheet in the eastern Kentucky example and fluids related to the fluorite, lead, zinc, and barite mineralization in the Illinois–Kentucky Fluorspar District in Western Kentucky. Further discussion of the mineralization is found in the cited papers and will not be repeated here.

All of the clausthalite observed in the Kentucky coals had a solid structure. In contrast, a specimen from the Uinta Basin (specific age and location is proprietary) was observed to have bladed-to-platy crystals of clausthalite within a solid, albeit pitted, sphere of the same mineral (Fig. 2). The crystals appear to be several microns in the longer dimensions, up to 4 μm in the dimension visible, and about 100 nm in thickness.

Confirmation of the chemistry of the mineral grains was accomplished by EDS or microprobe. In all cases, no elements other than Pb and Se appeared in the spectra.

3.2. Scanning proton microprobe (Micro-PIXE)

The results of the micro-PIXE analysis of the Manchester coal bed clausthalite are shown in Table 2. A key advantage of the proton microprobe over the

Table 2
Element composition of "clausthalite" grain from micro-PIXE analysis

Element	Concentration[a] (μg/g)	LOD[b] (μg/g)	Element	Concentration (μg/g)	LOD (μg/g)
Fe	1162 ± 4	23	Se	1131 ± 1	3
Co	94 ± 13	17	Br	26 ± 7	3
Ni	94 ± 6	5	Sr	16 ± 9	2
Cu	34 ± 9	2	Hg	47 ± 22	5
Zn	17 ± 19	1	Pb	6020 ± 1	32
Ga	34 ± 9	7			

[a] The uncertainty is based upon the statistical uncertainty in a single measurement in the area of the X-ray peak.
[b] The 95% confidence interval calculated on the basis of three standard deviations of the background area over one full-width half-maximum of the principal X-ray peak centroid.

electron microprobe in these measurements is the ability to observe and quantify trace metals that are below the detection limit of an electron microprobe. The X-ray absorption filters used for the micro-PIXE measurements were selected to enhance the detection limits for mercury and other heavy elements. As a result, chromium was the lightest element measured. The measurements revealed the presence of not only Pb and Se, but also Ga, Fe, Co, Ni, Cu, Zn, Br, Sr, Se, and Hg. Br may be a remnant of the immersion oil used in the initial optical examination of the specimen. As an example of possible associations among the other elements, Ga can form compounds with Se: GaSe, Ga_2Se, and Ga_2Se_3, none of them named minerals. The proton beam was larger than the clausthalite grain, about 10 μm × 30 μm compared to about 10 μm for the mineral, opening the possibility that the Ga was lodged in the adjacent carbonate (note that Ca could not be detected with the filter configuration employed), although there are no known Ga-bearing carbonates, or in the surrounding macerals. With the exception of Sr and Br, all of the other elements detected have mineral associations with Se. Fe, however, could be associated with the carbonate mineral sharing space with the clausthalite in the semifusinite lumen.

Clausthalite contains 27.59% Se by weight. The Se/(Se + Pb) ratio according to the micro-PIXE measurement is 15.82%, leaving some Pb unaccounted for in an ideal clausthalite formulation. There is a possibility that some of the Pb is in a sulfide association (note that S could not be detected with the filter

configuration employed), which could also account for the occurrence of the other chalcophile elements detected. Se can certainly occur in other associations, as well. For example, Tewalt et al. (2001) noted a mercury selenide mineral in the Ione (California) lignite.

The occurrence of Hg in the mineral specimen is worth noting. The coal sample has 0.52 ppm Hg, above average for US coals (based on averages from Bragg et al., 1998). Considering the elements *detected* in the mineral grain, Hg accounts for 0.54% of the total, four orders of magnitude greater than in the whole coal. At this level, minor minerals can account for the whole-coal Hg concentration. This particular grain was one of two minerals, of 23 sulfides and selenides examined, the remainder being pyrite and marcasite, which contained Hg at levels at least three times the 5-µg/g limit of detection of the micro-PIXE measurement.

4. Summary

Are the mineral specimens observed in the coals actually clausthalite? One missing piece of the puzzle is X-ray diffraction analysis. Attempts were made to isolate a single grain for X-ray diffraction analysis. Unfortunately, the attempt was not successful and the grain was lost. The chemistry of the specimens does suggest a lead selenide mineral, although not necessarily to the exclusion of other elements. Micro-PIXE analysis indicated that a number of other elements, primarily chalcophile elements, were potentially present in the specimen examined, with the caveat that the area of analysis was larger than the mineral grain. EDAX and microprobe analyses of single grains did not show any elements other than Pb and Se, eliminating the possibility of a sulfide association.

In any case, PbSe minerals, clausthalite or not, are present in coal. They are a significant source of Se in coal and an important source of Pb.

Acknowledgements

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