LA-UR -82-113

MASTER

CONF-820409--2

Los Alamos National Laboratory is operated by the University of California for the United States Department of Energy under contract W-7405-ENG-36.

TITLE: RELATIONSHIP BETWEEN PYRITE FORMATION AND ORGANIC SULFUR
CONTENT OF COAL AS REVEALED BY ELECTRON MICROSCOPY

AUTHOR(S): Robert Raymond, Jr. and Roland C. Hagan

LA-UR--82-113

DE82 010417

SUBMITTED TO: Scanning Electron Microscopy Conf.,
Anaheim, CA, April 19-23, 1982

Los Alamos

Los Alamos National Laboratory
Los Alamos, New Mexico 87545

FORM NO. 836 R4
ST. NO. 2629 5/81

Title: RELATIONSHIP BETWEEN PYRITE FORMATION AND ORGANIC SULFUR CONTENT OF COAL AS REVEALED BY ELECTRON MICROSCOPY

Running head: Pyrite Formation vs Coal Organic Sulfur Content

Authors: Robert Raymond, Jr. and Roland C. Hagan
Geochemistry Group - Earth and Space Sciences Division
Los Alamos National Laboratory

Contact: Robert Raymond, Jr.
ESS-2, MS 978
Los Alamos National Laboratory
Los Alamos, NM 87545
(505) 667-4580

home:
121 Piedra Loop
Los Alamos, NM 87544
(505) 672-1321

Key Words: Pyrite, Organic Sulfur, Coal, Electron Microscopy, Elemental Line Profiles, Elemental X-ray Maps,

RELATIONSHIP BETWEEN PYRITE FORMATION AND ORGANIC SULFUR CONTENT OF COAL AS REVEALED BY ELECTRON MICROSCOPY

Abstract

There are a large number of questions concerning the mode of occurrence of organic sulfur in peat, and what, if anything, alters its occurrence during and after coalification. The formation of pyrite during periods of peatification and coalification has been hypothesized to have a great effect on the organic sulfur content of organic material surrounding the pyrite. Measurement of organic sulfur contents at different distances from pyrite particles would serve as direct experimental proof for or against this hypothesis. A combination of _in situ_ EDS line profiles, EDS x-ray maps, and WDS analyses across pyrite/coal interfaces in a variety of coals shows unequivocally that formation of pyrite does not alter the organic sulfur contents of the surrounding coal macerals.

Introduction

Research on the occurrence and form of sulfur in peat continues to offer new insights into the occurrence of various sulfur forms in coal. Some of the best work on sulfur in peats has been by Casagrande et al. (1977) where they investigated a variety of sulfur forms in peats including hydrogen sulfide, sulfate, carbon-bonded sulfur, ester-sulfate, total sulfur, elemental sulfur and pyritic sulfur. The ester-sulfate and carbon-bonded sulfur make up what is commonly referred to as organic sulfur. Casagrande et al. (1977) were not able to conclusively state how organic sulfur is incorporated or formed in peats. However, they were able to show that plants from different peat sites contain similar organic sulfur contents. Furthermore, they showed that in marine environments there appeared to be an overall increase in sulfur during the transition from plant samples to peat. Much smaller increases and even decreases occurred in entirely freshwater environments. For the purpose of this paper, the initial organic sulfur contents of the plants will be called primary organic sulfur. Any enrichment of the primary organic sulfur content during or after peat deposition will be considered secondary organic sulfur.

Depending on specific geochemical factors during peatification and/or coalification, a variety of chemical reactions may occur leading to the formation of pyrite. It is not the place of these authors nor the purpose of this paper to discuss these reactions in detail, but rather to note that as Yurovskii (1974) had pointed out, the combination of $FeSO_4$ and H_2S leads not only to formation of pyrite but also to release of elemental sulfur. Elemental sulfur in turn may be utilized in pyrite formation by reacting with FeS or may react with organic constituents to become organic sulfur (Casagrande, et al., 1977). Yurovskii (1974) suggested that free sulfur liberated during pyrite formation quickly reacts with organic coal-forming matter and forms the major part of secondary organic sulfur in coal seams. As a means of testing his hypothesis, Yurovskii took heavy coal fractions (sp.gr. > 2.80), and after almost complete removal (by leaching) of pyritic sulfur and mineral matter, measured the organic sulfur content of the remaining material. Additional analyses were run on small coal fractions associated with very fine concretions of pyrite containing traces of aluminosilicates. (These fine concretions are most probably what are now commonly referred to as framboids.) For the coals of the Donbas coal field, from which his samples were taken, Yurovskii felt that any organic sulfur content in excess of 0.3-0.5 wt%, which was the minimal content for the field and represented the primary organic sulfur content of the peat, was the result of secondary enrichment. In both of the above analyses, the organic material analyzed had been in contact with or in close proximity to pyrite, and therefore, by Yurovskii's reasoning, should have contained high organic sulfur contents resulting from the elemental sulfur liberated during the pyrite formation. In these two cases Yurovskii reported 15.29 wt% and 24.33 wt% organic sulfur respectively. As a result of this data, Yurovskii stated

> "Pyrite concretions in coals are surrounded by coal layers richer in organic sulfur which decrease as the distance from the center of the pyrite concretion increases. The higher sulfur concentrations in the direct vicinity of the pyrite concretion can be attributed to higher concentration of elemental sulfur that was set free while the pyrite center was being formed. The concentration of elemental sulfur" (and

> therefore secondary organic sulfur) "should decrease as the distance from the pyrite center increases." (pg. 116)

Yurovskii further stated

> "Separation and investigation of thin coal layers situated at different distances from a pyrite concretion would have served as direct experimental proof of the view expounded upon above, but it is hardly possible to carry out such an experiment." (pg. 117)

Yurovskii's work, which was translated into English in 1974, was originally published in Russian by the Academy of Sciences of the USSR in 1960. At that time there was no known method to measure organic sulfur contents of thin coal layers at different distances from a pyrite concretion. Such measurements are now possible using the electron probe microanalyzer (EPM) (Neavel, 1966; Raymond and Gooley, 1978). Furthermore, using a scanning electron microscope (SEM) equipped with an energy dispersive spectrometer (EDS), both line profiles and x-ray maps for sulfur can be made which differentiate explicitly any variations in organic sulfur in the vicinity of pyrite particles. The purpose of this paper is to report on the distribution of organic sulfur with respect to pyrite occurrence as determined by electron microanalysis.

Materials and Methods

Many well-documented coal samples for basic coal research at Los Alamos were provided by the Pennsylvania State University Coal Section. These samples include 29 coal seams from 19 states within the contiguous United States, range in rank from subbituminous C to low volatile bituminous, and contain sulfur contents that range from 0.28 to 8.60 wt% (dry). The major premises stated in this paper are based predominantly on observations made on these coals. The Americana coal from Alabama, used as an example in this paper, is from this group. This sample had been ground by the Pennsylvania State University Coal Section to -20 mesh size. Upon receipt, the sample was split, potted in epoxy, and made into a polished 2.5 cm round, approximately 120 microns thick. The round was mounted on a glass slide and carbon coated for conduction during electron bombardment. The Lower Kittanning coal sample was collected by the authors outside of Kittanning, Pennsylvania. Sample preparation followed that as discussed for the Pennsylvania State University coal sample. The Lower Freeport coal from Pennsylvania and the Illinois #6 coal from Illinois were provided by the Pittsburgh Mining Technology Center as finished polished rounds in conjunction with another research project. These rounds needed only to be mounted on glass thin sections and carbon coated for microanalysis.

A Cameca model MBX EPM was used to make quantitative measurements of organic sulfur in coal matter surrounding pyrite particles. In each case the reported values are the mean of five analyses. Standardization datum for EPM analysis is determined as an average of seven background and matrix corrected x-ray intentsities on a recently developed petroleum coke standard. X-ray intensity of iron is continually monitored during analysis and any intensities in excess of background levels are assumed to result from contamination by pyrite, so those results are rejected. At the same time, an EDS system is monitored for any elements that might suggest the presence of other sulfide or sulfate minerals.

An ISI model DS-130 SEM was used to locate and photograph particular areas containing a variety of pyrite/coal interfaces. A combination of backscattered and secondary imaging was used depending on whether organic matter or pyrite was being differentiated. Accelerating voltage was mostly kept at 15 kV to enhance imaging and x ray generation, though 9 kV was used to differentiate electron scattering effects as mentioned later in Discussion. A Kevex EDS system was used to generate the sulfur and iron line profiles and the sulfur x-ray maps.

The data shown in this paper are essentially elemental line profiles and x-ray maps shown in conjunction with scanning electron micrographs of the same areas. In figures with line profiles, the profile represents the relative concentration of the element of interest at the horizon noted by the continuous straight line. X-ray maps showing elemental distribution over the entire photograph are based on x-ray output less background measurements.

Results

Pyrite in coal seams occurs as 1) primary pyrite -- that which is deposited syngenetically with the peat and prior to coalification, 2) secondary pyrite -- that which forms during or after coalification as fracture and cell fillings, and 3) a combination of the two -- that which results from a recrystallization of the primary pyrite or from secondary pyrite deposition at a site already containing primary pyrite. The organic sulfur content in surrounding material could be altered differently in each of the above three cases by the pyrite formation. Therefore each case will be addressed separately.

Figure 1 demonstrates the sensitivity of the line profile technique. Figure 1a shows small particles of coal within an epoxy matrix. The boxed area, which is magnified in Figure 1b, cuts across three coal maceral types as noted in the Figure (V = vitrinite, considered to result from degradation of woody material; S = sporinite, formerly a spore in the peat environment; and F = fusinite, material similar to charcoal). EPM analyses of the macerals show the vitrinite contains 1.1 wt% organic sulfur, the sporinite 2.1 wt% organic sulfur, and the fusinite 0.6 wt% organic sulfur. Even though there is a great deal of fluctuation in the sulfur line profile, the profile demonstrates the minor variations between the three maceral types and ensures that we will see gradations in organic sulfur content if they exist in the organic coal matrix surrounding pyrite particles.

In Figure 2a we show two forms of primary pyrite within a coal matrix composed predominantly of vitrinite (organic sulfur content of

1.4 wt%). On the left of the figure is a cluster of pyrite framboids. Each framboid, approximately 15-20 microns in diameter, is composed of pyrite crystallites less than one micron in size. Framboidal pyrite has been shown to develop in peat depositional environments (Caruccio et al., 1977) and is considered to be a primary rather than secondary form of pyrite. On the right of the figure is a large crystal of pyrite, now somewhat dissolved. Its euhedal shape and the fact that its presence has not visibly altered the stratification in the surrounding organic matrix supports its primary (syngenetic) emplacement within the peat.

A sulfur x-ray map of the same area is shown in Figure 2b. There is no obvious gradation in sulfur concentration surrounding either of these 2 primary forms of pyrite. Looking at sulfur line profiles crossing the pyrite/coal interfaces in each of the above cases, as seen in Figures 3a and 4a which are magnified views of the boxed areas in Figure 2a, we see that there is no organic sulfur increase until approximately 3-5 microns from the pyrite/coal interfaces, where a minor increase in x-ray intensity is present. In Figures 3b and 4b, iron line profiles across the same area show absolutely no increase, suggesting that the small increase in the sulfur scans is not due to the presence of sulfide particles hidden beneath the surface of the coal but still within excitation range of the electron beam.

Two forms of secondary pyrite are shown in Figures 5a and 6a. In the first, an irregular, scorpian shaped fracture in vitrinite (organic sulfur content of 2.7 wt%) has been filled with pyrite. In the second, pyrite fills cells within a fragment of fusinite (organic sulfur content of 0.2 wt%). Sulfur line profiles across the interfaces in the boxes in Figures 5a and 6a are shown respectively in Figures 5b and 6b. No sulfur gradation is present in Figure 5b, while a strong increase in sulfur x-ray intensity begins approximately 3 microns from the pyrite/coal interface in Figure 6b.

In Figure 7a we show the presence of pyrite framboids within a vitrinite matrix (organic sulfur content of 1.1 wt%) that have either been recrystallized or have had secondary pyrite precipitated between all the primary pyrite crystallites. The sulfur line profile shown in Figure 7b and the sulfur x-ray map shown in Figure 7c indicate unequivocally that in this case there is no gradation in organic sulfur content surrounding a pyrite particle resulting from both primary and/or secondary deposition.

Discussion

The sulfur x-ray maps in Figures 2b and 7c show that there are no widespread gradations in organic sulfur contents surrounding primary and secondary pyrite particles. That the sulfur line profiles show an increase in x-ray intensity 2-3 microns distance from the pyrite/coal interfaces in Figures 3a and 4a while no such increase is seen in the iron line profiles in Figures 3b and 4b suggests there may be an increase in organic sulfur content in the coal material "directly" surrounding the pyrite particles. Such a potential increase could best be supported by the line profile in Figure 6b where a strong increase in sulfur x-ray intensity is present approximately 3 microns from the secondary pyrite cell filling. But if secondary organic sulfur is enriched in the fusinite in Figure 6b due to the emplacement of the secondary pyrite, why don't we see enrichment in Figures 5b and 7b where again we observe secondary pyrite/coal interfaces?

In Figure 6b the coal matrix surrounding the pyrite is fusinite, which is composed essentially of carbon. In Figures 5b and 7b, the coal matrix surrounding the pyrite is vitrinite, which contains approximately 80% carbon and an abundance of hydrogen, oxygen, nitrogen, and sulfur. Goldstein (1975) has shown that the scattering effect on an electron beam will allow excitation of elements in a volume surrounding where the beam has been focused. This volume of excitation from the beam center is dependent on a variety of parameters. One possible variable could be a more crystalline structure of the fusinite, being composed essentially of pure carbon, compared to a more amorphous structure of the vitrinite. If this is the case, we might expect to see a greater area of scattering occurring within the sample in Figure 6b, due to the fact that the coal material is more crystalline, than in the other samples.

During scattering, electrons will lose energy as they travel through the matrix (Goldstein, 1975). As a result, the electron beam scattering will have less effect on sulfur and iron x-ray intensities the further the beam is away from the pyrite/coal interface. Furthermore, since the energy of the electrons will be less following scattering, they will have less effect on iron x-ray intensities than on sulfur x-ray intensities. Such may be the case in Figures 3b and

4b where no apparent increase in iron x-ray intensity is present near the pyrite/coal interface as it is for the sulfur.

A test that would show the effect of the electron beam scattering is to reduce the accelerating voltage of the beam from 15 keV to 9 keV. The distance over which scattering will have an effect on x-ray intensity will be reduced. Figures 8 and 9 show the results of such a reduction in accelerating voltage. In both cases the sulfur x-ray intensities do not appear to increase until the electron beam is situated much closer to the pyrite/coal interface, compared to their respective 15 keV counterparts in Figures 6b and 3a. Though we can only hypothesize on why we have variations in scattering between fusinite/pyrite and vitrinite/pyrite, it appears that the increase in sulfur x-ray intensities near the coal/pyrite interfaces in Figures 3a, 4a, and 6b are in fact due to a scattering phenomenon.

Conclusions

It has been shown unequivocally for the 4 coals used as examples in this paper that emplacement of pyrite, whether primary or secondary, has no effect on the organic sulfur contents in the surrounding coal. Indeed, the effect on the sulfur line profiles due to electron beam scattering is greater than any resulting from the pyrite formation. Our experience dealing with a large variety of coals has provided no evidence different from that presented in this paper. Unless the Donbas coal field samples, on which Yurovskii (1974) made his measurements, are different from any North American coals we studied, it appears that the high organic sulfur values reported by Yurovskii (1974) in fact result from an analytical technique that erred determining organic sulfur content by difference. The potential for error in chemical analysis for organic sulfur in coal is quite real, as discussed in a review by Raymond and Gooley (1978). Until secondary enhancement of organic sulfur can be shown by some microanalytical technique _in situ_ to result from the emplacement of pyrite, it is our judgement that emplacement of secondary organic sulfur early in the peatification stages is a much more viable alternative. Due to the high moisture content and high permeabiltiy of the peat at that time, such an emplacement would provide a relatively uniform distribution of organic sulfur within local areas of a coal seam.

References

Caruccio, F. T., Ferm, J. C., Horne, J., Geigle, G. and Baganz, B. (1977). Paleoenvironment of coal and it's relation to drainage quality, Interagency Energy Environmental Research and Development Progress Report, EPA-600/7-77-067, published by EPA, Cincinnati, Ohio, 108 pgs.

Casagrande, D. J., Siefert, K., Berschinski, C., and Sutton, N. (1977). Sulfur in peatforming systems of the Okefenokee Swamp ar Florida Everglades: Origin of sulfur in coal, Geochim. et Cosmochim. Acta, v. 41, pp. 161-167.

Goldstein, J. I. (1975). Electron beam-specimen interactions, in Practical Scanning Electron Microscopy, Goldstein and Yakowitz (eds.)Plenum Press, New York pgs. 49-94.

Neavel, R.C. (1966). Sulfur in coal. Its distribution in the seam and in mine products, Ph.D. Thesis, The Pennsylvania State Univ.

Raymond, R. Jr. and Gooley, R. (1978). A review of organic sulfur analysis in coal and a new procedure, Scanning Electron Microsc. 1978; I, pgs. 93-107.

Yurovskii, A. Z. (1974). Sulfur in Coals, Bureau of Mines Publication, Washington DC, NSF C466, 459 pgs. Translated from a Russian 1960 publication of the Academy of Sciences of the USSR, Institute of Mineral Fuels.

Figure Captions

Figure 1. (a) Secondary electron micrograph of a polished fragment of coal from the Lower Kittanning seam. (b) Secondary electron micrograph and 15 keV sulfur line profile of boxed area in Figure 1a. Note the highest sulfur x-ray intensity in the sporinite (S), the next highest is in the vitrinite (V), and the lowest is in the fusinite (F). (scale bars in microns)

Figure 2. (a) Secondary electron micrograph of a polished surface of a piece of Americana coal containing two forms of primary pyrite: framboidal (on the left) and euhedral (on the right). (b) Sulfur x-ray map of the same area showing no gradation in organic sulfur contents surrounding the areas of primary pyrite. (scale bars in microns)

Figure 3. (a) Backscattered electron micrograph and 15 keV sulfur line profile across area (A) shown in Figure 2a. (b) Backscattered electron micrograph and 15 keV iron line profile across the same area. (scale bars in microns)

Figure 4. (a) Backscattered electron micrograph and 15 keV sulfur line profile across area (B) shown in Figure 2a. (b) Backscattered electron micrograph and 15 keV iron line profile across the same area. (scale bars in microns)

Figure 5. (a) Secondary electron micrograph of a polished fragment of Illinois #6 coal containing an irregular, scorpian-shaped piece of secondary pyrite. (b) Secondary electron micrograph and 15 keV sulfur line profile across the boxed area shown in Figure 5a. (scale bars in microns)

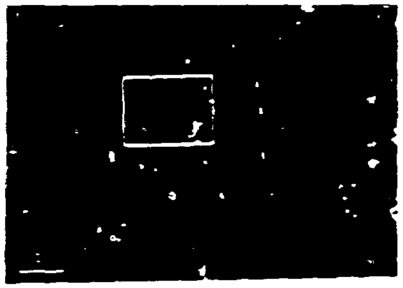
Figure 6. (a) Secondary electron micrograph of a polished fragment of Lower Freeport coal containing a piece of fusinite in which the cells have been filled with secondary pyrite. (b) Secondary electron micrograph and 15 keV sulfur line profile across the boxed area shown in Figure 6a. (scale bars in microns)

Figure 7. (a) Secondary electron micrograph of a polished fragment of Lower Kittanning coal containing framboidal pyrite that has either been recrystallized or altered by secondary pyrite precipitation. (b) Secondary electron micrograph and 15 keV sulfur line profile across the boxed area shown in Figure 7a. (c) Sulfur x-ray map of the same area showing no gradation in organic sulfur content surrounding the pyrite particles. (scale bars in microns)

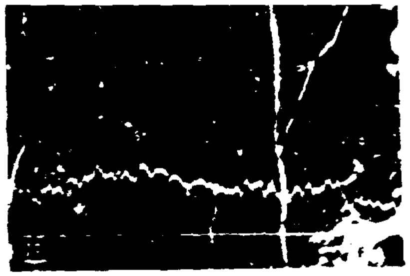
Figure 8. Secondary electron micrograph and 9 keV sulfur line profile of the same area shown in Figure 6b. (scale bar in microns)

Figure 9. Backscattered electron micrograph and 9 keV sulfur line profile of the same area shown in Figure 3a. (scale bar in microns)

1a



1b

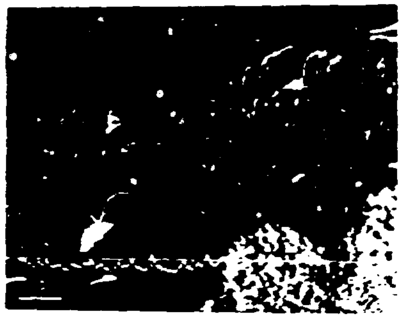


2a

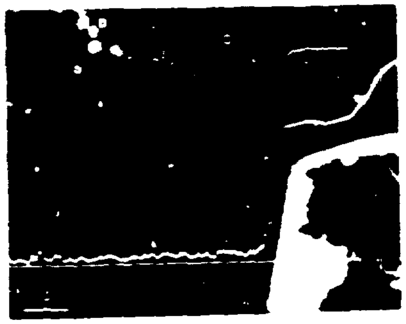
2b

3a

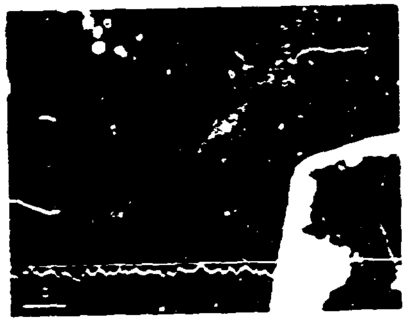
3b



4a

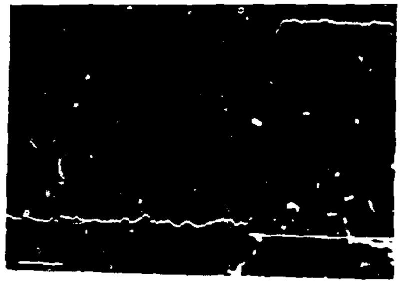


4b

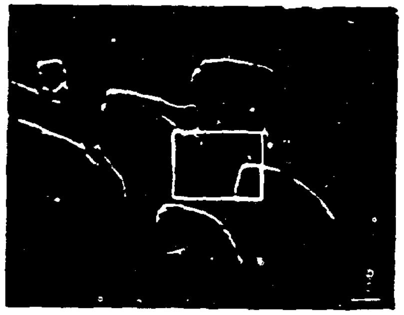


5a

5b

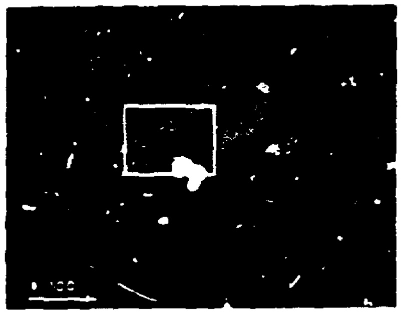


6a



6b

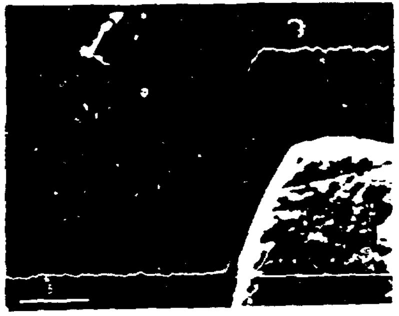
7a



7b

7c

8



9