

FINAL TECHNICAL REPORT
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Project Title: Location of Isotopically Characterized Coal Samples
ICCI Project Number: 86-87/3.3A-2
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ABSTRACT

The primary goal of this project is to locate a coal sample with unique sulfur isotope compositions which could be utilized by CRSC studies. Since the forms of sulfur in coal may be changed during thermal and chemical processing, methods of following the mobility of each original form independently are highly desirable. Through the application of stable sulfur isotope tracing it is possible to determine the quantity of both original pyritic and original organic sulfur which remain in a thermally and chemically treated coal product, regardless of the final form either type of sulfur has acquired. Hence, locating a coal that has a large natural difference between the isotopic compositions of the different sulfur forms and making it available for desulfurization studies would be beneficial to many coal researchers.

Approximately 120 coal samples have been collected from several locations with different roof rocks in the Herrin No. 6 coal seam. Three sites show promising results for producing a coal sample which could be used for stable isotope tracing during desulfurization studies. These sites have several adjacent samples that exhibit large isotopic differences between the organic and pyritic sulfur indicating that it may be possible to collect a relatively large sample having suitable isotopic characteristics. Of these three sites one in particular has excellent potential of producing a large coal sample which would be useful for stable isotope tracing purposes. Isotopic differences on the order of 20 to 30 per mil have been observed between the organic and pyritic sulfur for many of the small samples collected at this site. A 70 lb coal sample taken from this site has also yielded favorable isotopic results. A larger coal sample could be collected from this site immediately if there is a demand for it by the CRSC researchers.

The roof rock of the two sampling sites that exhibit the best potential for producing an isotopically useful coal sample is channel fill material. The pre-erosional roof rock at these two sites was Anna shale. The other site that showed fairly good potential for yielding an isotopically useful coal sample is overlain by Anna shale. Those sites that showed extreme inconsistencies in the isotopic composition of the pyritic and organic sulfur appear to have Brereton limestone in close proximity to the top of the coal seam. Based on the isotopic results of the six sites studied in this project the areas in Herrin No. 6 coal beneath channel fill material have the best potential of yielding coal samples with large isotopic differences between the pyritic and organic sulfur.

EXECUTIVE SUMMARY

There were two principle objectives for this project, the first and primary objective was to locate coal samples that had large isotopic differences between the organic and pyritic sulfur. Such coal samples could be used by CRSC researchers for stable sulfur isotope tracing during their desulfurization studies. Since the forms of sulfur in coal may be changed during thermal and chemical processing, methods of following the mobility of each original form independently are highly desirable. Through the application of stable sulfur isotope tracing it is possible to determine the quantity of both original pyritic and original organic sulfur which remain in a thermally and chemically treated coal product, regardless of the final form either type of sulfur has acquired. The second objective was to learn more about the relationships of the geological setting and the isotopic compositions of the pyritic and organic sulfur in the coal. Information gained about the geological parameters which control the stable isotopic composition of the sulfur in coal will facilitate the task of locating isotopically appropriate coal samples in the future. If such samples were located, many researchers could benefit from utilizing the samples in their research to monitor the behavior of the major forms of sulfur.

Approximately 120 coal samples have been collected from several sites with different roof rocks in the Herrin No. 6 coal seam. One site in particular has been located which has very good potential of producing a relatively large coal sample which would be useful for stable isotope tracing purposes. Isotopic differences on the order of 20 to 30 per mil have been observed between the organic and pyritic sulfur for several of the small samples collected at this site. Approximately a 70 lb coal sample has been taken from this site and has also yielded very favorable isotope results. It is believed by the investigators that a larger sample could be collected from this site immediately if the demand for it is present.

Two other sites show promising results for producing a coal sample which could be used for stable isotope tracing during desulfurization studies. These sites also have several adjacent samples that exhibit large isotopic differences between the organic and pyritic sulfur indicating that it may be possible to collect a relatively large sample that has suitable isotopic characteristics.

The other three sites do not show very good potential for yielding a coal sample which would be useful for the stable isotope tracing technique. Two of these sites have a few samples with large isotopic differences between the pyritic and organic sulfur but the trend is not maintained for adjacent samples.

The roof rock of two of the sampling sites that exhibit the best potential for producing an isotopically useful coal sample is channel fill material. The pre-erosional roof rock at these two sites was Anna shale, a marine shale. The third site that exhibited potential for producing an isotopically useful coal sample is overlain by a relatively thick Anna shale. The sites that show extreme inconsistencies in the isotopic composition of the pyritic and organic sulfur appear to have Brereton limestone in close proximity to the top of the coal seam.

OBJECTIVES

The first objective and primary goal of this proposed project was to locate coal samples that could be used for stable sulfur isotope tracing during desulfurization studies. The natural sulfur isotope variations observed in coals can be employed as efficient chemical tracers capable of monitoring the behavior of pyritic and organic sulfur during desulfurization processes.

The second objective of this project is to learn more about the geological parameters and the coal seam characteristics which appear to have influenced the isotopic compositions of the two major forms of sulfur in the coal. Information gained about the parameters which control the stable isotopic composition of the sulfur in coal will facilitate the task of locating isotopically appropriate coal samples in the future. To help accomplish this objective the Herrin No. 6 coal seam has been sampled both vertically and horizontally at five different sites under different roof rock lithologies.

INTRODUCTION AND BACKGROUND

During this project we completed three sampling trips to three coal mines in central and southern Illinois. The mines were selected based on previous results of sulfur isotope studies on coals in the Illinois Basin. A description of the local geology including the type of roof rock and characteristics of the coal seam was made at each sampling site. A total of 120 small samples of coal have been taken.

The majority of coal samples collected have been analyzed using the quick screening method developed in our laboratory under previous CRSC contract (Liu et al., 1986). The isotopic results from the quick screening analyses are very encouraging. Of the six sites sampled three sites appear to have the potential of yielding coal samples that could be useful for stable sulfur isotope tracer studies in coal desulfurization research. One site in particular has very good potential for yielding a relatively large coal sample that could be useful for applying the stable sulfur isotope tracing technique.

Monitoring the sulfur behavior during coal desulfurization by the use of stable isotopes is a unique and novel approach. An advantage of this technique is that no special treatment or additives to the coal are necessary to establish the "tracer" prior to desulfurization processes; the isotopic difference observed between the pyritic and organic sulfur is a natural, inherent property of the coal. In addition it is not necessary to separate the forms of sulfur in the desulfurized products and hence one can avoid the questions of reliability which arise when the sulfur extraction techniques developed for untreated coals are applied to chemically or thermally altered coals. Using stable isotope ratio analysis makes it possible to determine the original form of sulfur which remains in a thermally and chemically cleaned coal, regardless of its present form. This allows one to monitor the behavior of organic and inorganic sulfur individually in a desulfurization process and to optimize the method for removal of each sulfur form.

Previous results obtained from the use of the stable sulfur isotope tracing technique on pyrolyses studies have demonstrated the usefulness of the technique for (1) comparing the reactivity of the different forms of sulfur during pyrolysis, (2) directly monitoring the mobility and redistribution of sulfur during pyrolysis, and (3) optimizing thermal, physical, and chemical conditions for the ultimate goal of producing a clean, low sulfur solid fuel (Coleman et al., 1985; Liu et al., 1987). The stable isotope tracer technique has been successfully applied to thermal desulfurization studies and one super critical desulfurization technique.

Since the stable sulfur isotope tracing method has proven to be successful for increasing our understanding of sulfur mobility during charring we thought it would be very beneficial to have the capability of locating additional coal samples which could be used for sulfur isotopic tracing. Previously we were not able to predict where these isotopically suitable samples would be located in a coal seam. Thus a systematic study of the geological setting and coal characteristics which are associated with large isotopic differences between the organic and pyritic sulfur in the coal was needed.

EXPERIMENTAL PROCEDURES

Approach

Coal samples have been collected at six different locations in the Herrin No. 6 seam with different roof rock lithologies at nearly each site. The isotopic compositions of the pyritic and organic sulfur were roughly determined by the quick screening method described below. The isotopic characteristics at each site were compared to the type of roof rock lithology to determine if some general correlation can be made. If a correlation between the roof rock and isotopic characteristics of the coal seam can be established this will facilitate the task of locating additional isotopically appropriate coal samples in the future.

Once a potential site was located a return trip for additional sampling was made. Several more samples were taken adjacent to the original set of samples to determine if the favorable isotopic characteristics extended beyond the initial sampling area. Once a good potential coal sample has been identified in the seam it will have to be extracted from the seam, homogenized, fully characterized both chemically and isotopically, and then made available to other CRSC researchers. This will be done with the cooperation of the Illinois Basin Coal Sampling Program after it is determined whether CRSC researchers are interested in using an isotopically characteristic coal sample.

Methods

We began this project by collecting several reconnaissance samples in the Herrin No. 6 coal seam under different roof rocks in mines where previous sulfur isotope studies have yielded significant differences between the $^{34}\text{S}/^{32}\text{S}$ ratios of the organic and pyritic sulfur. The samples were collected using portable cordless electric drills fitted with 1 5/16" hole saws which enabled us to accurately pinpoint our samples both vertically and horizontally in the coal seam.

Each sampling site was marked in case a return trip was needed. Upon returning to the laboratory the samples were crushed and analyzed as quickly as possible. The vertical isotopic compositions are known to vary widely within a coal seam (Price and Shieh, 1979; Westgate and Anderson, 1984; Hackley and Anderson, 1986). Thus, two columns of vertical samples were taken at each site location so that if a suitable sample is identified the extent of the preferred sample can be evaluated.

To expedite the search for appropriate coal samples the "quick screening" method, developed in the isotope geochemistry laboratory (Liu et al. 1986), was employed. This screening technique significantly reduces the time it takes to tell whether there is a significant difference between the isotopic compositions of the organic and pyritic sulfur. Once a sample was selected a full chemical analysis was performed.

Isotope Screening Analysis

The initial screening analyses consisted of running a 450°C pyrolysis followed by a post-pyrolysis oxidation on each sample. Our previous research has shown that the sulfur driven off with the volatiles at 450°C is virtually all organic sulfur and the sulfur removed with post-oxidation is predominantly pyritic sulfur. Using this method we can quickly determine whether a coal sample has the potential of containing a large isotopic difference between its organic and pyritic sulfur. More detailed isotopic analyses were made for the site that showed the best potential. The different forms of sulfur are quantitatively separated using analytical techniques similar to those described by Price and Shieh (1979) and Westgate and Anderson (1982).

Briefly, the more detailed sulfur analyses consist of an initial acid leach followed by the extraction of pyritic sulfur using the lithium aluminum hydride (LAH) method. After the LAH extraction the organic sulfur is collected by a modified ASTM high temperature combustion method.

Many other isotope laboratories use a CrCl_2 extraction method rather than the LAH method we are currently using. Because the CrCl_2 method takes less time and is safer to handle we looked into the possibility of adopting the CrCl_2 method. Before changing to a new extraction procedure, however, we decided to compare the results of our LAH method with the CrCl_2 method as well as the ASTM nitric acid method used in most analytical coal laboratories. The results and a description of the procedures to the pyritic sulfur extraction methods are given in the Appendix.

Once the different species of sulfur are separated from the coal they are converted to SO_2 on a high vacuum line using methods described by Fritz et al. (1974) and Halus et al. (1982). The isotopic composition of the SO_2 for each sample are analyzed on a Nuclide 6-60 ratio mass spectrometer.

Sulfur Isotope Notation

Sulfur occurs in nature as four stable isotopes ^{32}S , ^{33}S , ^{34}S , and ^{36}S ; the relative abundances are 95.02%, 0.75%, 4.21% and 0.02% respectively (Hoefs, 1980). The ratio between the two most abundant isotopes ($^{34}\text{S}/^{32}\text{S}$)

is measured to determine isotopic variations among different geological materials. Isotopic ratios are expressed in a delta-notation as the permil (‰) difference between the $^{34}\text{S}/^{32}\text{S}$ ratio of a sample and the $^{34}\text{S}/^{32}\text{S}$ ratio of a standard;

$$\delta^{34}\text{S} = \frac{{}^{34}\text{S}/{}^{32}\text{S}(\text{smp1}) - {}^{34}\text{S}/{}^{32}\text{S}(\text{std})}{{}^{34}\text{S}/{}^{32}\text{S}(\text{std})} \times 1000$$

All delta values are reported with respect to the international sulfur standard, Canyon Diablo Troilite (CDT).

RESULTS AND DISCUSSION

Coal samples from six different locations have been analyzed by the quick screening method to determine whether there is a significant difference between the isotopic compositions of the organic and pyritic sulfur. Differences on the order of 5 ‰ or more between the volatile "organic" sulfur (450° N₂) and the oxidized "pyritic" sulfur (450° ox) are considered significant. When a site has several adjacent samples with approximately a 5 ‰ or more difference between the volatile ("organic") and oxidized ("pyritic") sulfur then that site has the potential of producing appropriate samples for stable isotope tracing purposes. The isotopic results are summarized in bar graphs shown in Figures 1-6 for the six sampling sites. The bar graphs show the isotopic differences between the "pyritic" and "organic" sulfur for one full set of samples taken from the top to the bottom of the seam at each site. So at a glance we can quickly determine whether a site has the potential of yielding useful samples. Tables I-XV contain all the isotopic and analytical results including the extra samples collected during return trips to some sites. The tables also include the type of roof rock at each site and the depth from the top of the seam for each sample.

The isotopic results from the screening analyses are very encouraging. Three of the six sites (CR-II-A, CR-III-A, and CR-II-B) show promising results for producing a sample which could be used for stable sulfur isotope tracing during desulfurization studies. Several adjacent samples in the lower half of the seam of these three sites exhibit isotopic differences between the "organic" sulfur and the "pyritic" sulfur on the order of 5 ‰ or greater (see Figures 1-3 and Tables I-III). The fact that such samples are grouped in these sites in the middle and lower half of the seam should make it easier to extract a useful sample for the Illinois Basin Coal Sample Program. CR-II-A exhibits the most consistent difference between the "pyritic" and "organic" sulfur.

Figure 7 is a diagram of the vertical column of coal sampled at site CR-II-A. Included in Figure 7 is the sampling pattern and a brief description of the significant partings observed in the seam (descriptions taken from P. DeMaris' field notes, 1986). The samples in the lower half of the seam were analyzed in more detail at this site to determine the actual organic and pyritic isotopic compositions. These isotopic results are also shown in Figure 7 to the right of the coal column. The

difference (Δ) between the $\delta^{34}\text{S}$ of the organic and pyritic sulfur for most of the samples is on the order of 20 to 30 ‰. Such large isotopic differences between the pyritic and organic sulfur is very good for the stable isotope tracer method. The sensitivity of the stable isotope tracing technique is enhanced by large differences between the isotopic compositions of the pyritic and organic sulfur in a coal sample.

The sampling pattern shown in Figure 7 is representative of the sampling pattern used at each site. The horizontal distance between the pair of sample columns is approximately one foot. Thus the large isotopic difference between organic and pyritic sulfur exists not only vertically in the lower half of the seam at site CR-II-A but also exists in the horizontal direction.

Another positive aspect about site CR-II-A is that the organic sulfur isotopic compositions are pretty similar between the 8 samples representing the lower half of the seam at site CR-II-A (Figure 7). The pyritic sulfur isotopic compositions do vary somewhat but are consistently much more positive than the corresponding organic sulfur $\delta^{34}\text{S}$ values, with the exception of only one sample (A_2-7). This one exception is not enough to decrease the potential of this site for producing an isotopically appropriate sample for stable isotope tracer studies. Quantitative chemical analyses were also done for the organic and pyritic sulfur at site CR-II-A. The quantitative analyses show that the organic and pyritic sulfur for the lower half of site CR-II-A are quite consistent (Table IV). These quantitative results along with the isotopic results are good evidence that site CR-II-A will produce a relatively large coal sample with fairly uniform isotopic and chemical sulfur compositions.

A return sampling trip was made to CR-II-A. During the trip another set of small coal samples were collected one foot to the right of the first two columns, samples of the major partings and cleat pyrite were taken and a large coal sample (approximately 70 lbs) was also collected from the bottom 3 1/2 feet of the seam just to the left of the original two sample columns. The isotopic results for the new column of samples taken at site CR-II-A again show good potential for this site.

According to the quick screening results the isotopic spread between organic and pyritic sulfur is consistently large in the lower half of the seam Table V. These samples collected on the return trip agree quite well with the earlier samples collected from this site. Table VI is a comparison of the quick screening results obtained from the initial sampling trip at site CR-II-A (columns A_1 and A_2) and the results obtained from the return sampling trip (column AR).

The isotopic results obtained from the pyrite in the cleats and major partings for site CR-II-A are shown in Table VII. Unfortunately the isotopic composition of the pyrite in the cleats and major partings from site CR-II-A are quite different from the pyrite intimately associated with the coal. This means that if a large sample is taken from this site it will probably have to be tabled to separate most of the massive pyrite.

Two representative samples were taken from the 70 lbs of coal collected during the return trip to site CR-II-A. One "clean" sample which excludes the massive cleat and parting pyrite and a second sample which

includes the cleat and parting pyrite (except the large clay band known as the Blue Band). The chemical composition for these samples are shown in Table VIII. Both of these samples were analyzed by the quick screening method. The isotopic results again show a large isotopic difference between the "pyritic" and "organic" sulfur for both the clean sample and the more representative sample of the 70 lbs (Table IX). These results are very encouraging and mean that the isotopic compositions of the pyritic and organic sulfur are fairly consistent for a relatively large area at this site. The lower isotopic difference observed between the "pyritic" and "organic" sulfur from the representative sample is attributed to the more negative isotopic composition of the massive pyrite present in this sample.

Site CR-III-A is a site with a similar type of roof rock as site CR-II-A and also shows good potential of yielding an isotopically useful coal sample. As shown in Figure 3 large isotopic differences between the "pyritic" and "organic" sulfur are observed for the middle and lower half of the seam at site CR-III-A. Table II shows that the isotopic composition of the "organic" sulfur appears to be quite consistent for most of the seam. However, the isotopic differences between the "pyritic" and "organic" sulfur are not as consistent as observed at site CR-II-A.

The lower half of the coal seam at site CR-II-B had also shown potential for yielding a coal sample with a large difference between the organic and pyritic sulfur Table III. So we returned to site CR-II-B and took two more vertical columns of samples, consisting of 5 samples each, from the lower portion of the seam. The columns were spaced laterally about one foot apart. The isotopic results from the quick screening tests for these second set of samples are shown in Table X. According to the quick screening results large isotopic differences exist between the pyritic and organic sulfur for most of the samples. However, the isotopic differences are not as consistent down the seam as observed in site CR-II-A. For example the "pyritic sulfur" in B-R4 and B-R9 have significantly lighter $\delta^{34}\text{S}$ values compared to the other samples collected at site CR-II-B. The "organic sulfur" in sample B-R6 is quite different from the organic sulfur of the surrounding samples. Such differences in the organic sulfur could create problems for isotopic tracing applications. Table XI compares the initial isotopic results obtained from the first sampling trip to site CR-II-B (columns B₁ and B₂) to the results obtained from the return trip to site CR-II-B (columns BR). Note that in the right hand column (B₂) none of the samples tested exhibit a very significant difference between the "organic" and "pyritic" sulfur. It was also found that the pyritic sulfur content for these two columns at site CR-II-B are not that consistent (Table XII). The inconsistent pyritic sulfur contents may help explain why the isotopic composition is not consistent between the two columns as well as vertically in a single column of samples. In spite of the problems mentioned here, site CR-II-B does have some potential of yielding a suitable for isotope tracing purposes but it is not as favorable a site as CR-II-A.

Two of the other sites (CR-II-C and RK-I-B) also have several samples with large isotopic differences between the "pyritic" and "organic" sulfur but the trend is not maintained over several adjacent samples (Figures 4 and 5, Tables XIII and XIV). The two samples at the top of site CR-II-C exhibit very large differences between the "pyritic" and "organic" sulfur according to the screening tests but, unfortunately, the differences are very inconsistent. The "pyritic" sulfur in CR-II-C₂-1 is 16 ‰ more negative than the corresponding "organic" sulfur while in the next sample down the "pyritic" sulfur is at least 19 ‰ more positive than the "organic" sulfur. Even the "organic" sulfur is very inconsistent at the top of this site. The isotopic differences observed in the bottom foot of column 1 is significantly large but this trend did not carry over to column 2 (Table XIII). Such inconsistent isotopic compositions would not be good for stable isotope tracing studies. Thus CR-II-C is not a good potential site for yielding a useful sample for stable isotope tracing purposes.

Site RK-I-A (Figure 6 and Table XV) does not show very significant differences between the $\delta^{34}\text{S}$ of the "organic" and "pyritic" according to the quick screening tests. Thus, this site is not a good potential site for yielding a sample useful for stable isotope tracing applications.

Of all the sites analyzed CR-II-A shows the most potential for yielding a coal sample with suitable isotopic characteristics to be used in stable isotope tracing studies for coal desulfurization research. The roof rock at site CR-II-A is channel fill material. The channel eroded away Anna shale and laid down siltstone directly upon the coal seam (DeMaris, 1987). Site CR-III-A is also overlain by channel fill material and is also a good potential site for yielding suitable isotopic coal sample. The third site that showed potential for yielding an isotopically useful sample was CR-II-B which is overlain by Anna Shale. Those sites that show extreme inconsistencies in the isotopic composition of the pyritic and organic sulfur appear to have Breerton limestone in close proximity to the top of the coal seam.

CONCLUSIONS AND RECOMMENDATIONS

We have located one site (CR-II-A) that has consistently shown very good potential for yielding an isotopically suitable sample for stable isotope tracer applications. Many of the small samples collected at this site have isotopic differences on the order of 20 to 30 per mil between the pyritic and organic sulfur. It is believed that a relatively large (approximately 200 lb) coal sample could be collected immediately from this site if there is a demand for it by the CRSC researchers. It should be noted that after December of this year (1987) we will not be able to get back to this site. The mine will be closing this section off at that time. Thus if a large sample from site CR-II-A is desired it will have to be collected before December 1987.

Two other sites have also shown potential of yielding an isotopically suitable sample for stable isotope tracer applications, sites CR-III-A and CR-II-B. These two sites have several adjacent samples that exhibit large isotopic differences between the pyritic and organic sulfur indicating that it may be possible to collect a relatively large sample

suitable for isotope tracer studies. Site CR-III-A is the better of these two sites since it has a larger area that exhibits the desired isotopic characteristics.

The other three sites do not show very good potential for yielding a coal sample which would be useful for the stable isotope tracing technique. Two of these sites have a few samples with large isotopic differences between the pyritic and organic sulfur but the trend is not maintained for adjacent samples.

The roof rock of the two sampling sites that exhibit the best potential for producing an isotopically useful coal sample is channel fill material. The pre-erosional roof rock at these two sites was Anna shale. The other site that showed fairly good potential for yielding an isotopically useful coal sample is overlain by Anna shale. Those sites that showed extreme inconsistencies in the isotopic composition of the pyritic and organic sulfur appear to have Brereton limestone in close proximity to the top of the coal seam. Based on the isotopic results of the six sites studied in this project the areas in Herrin No. 6 coal beneath channel fill material have the best potential of yielding coal samples with the desired isotopic characteristics suitable for stable isotope tracer studies.

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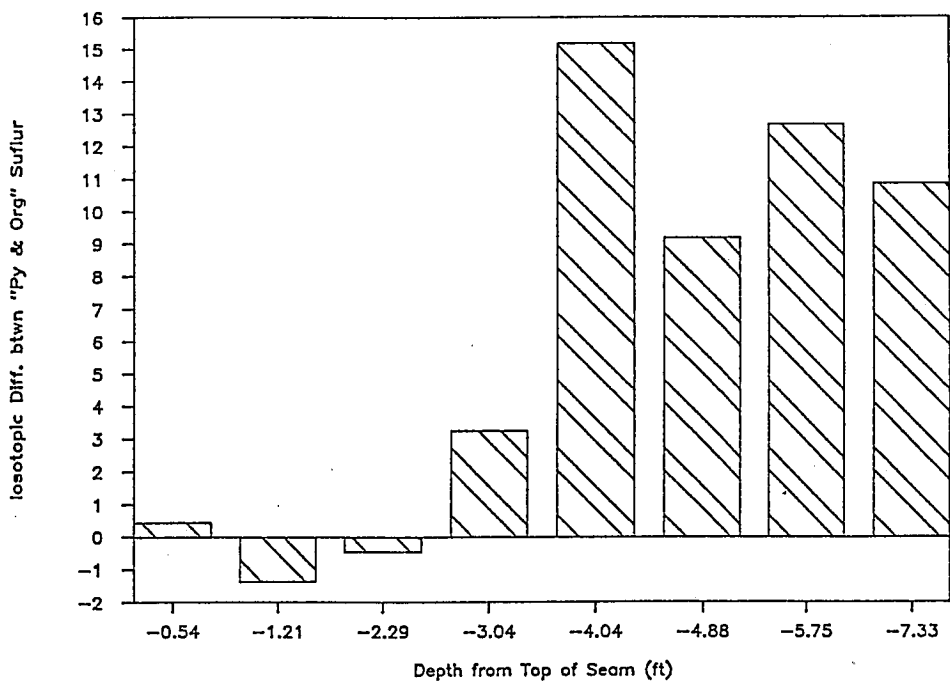


Figure 1. Summary of isotopic results for site CR-II-A (Column A₁).

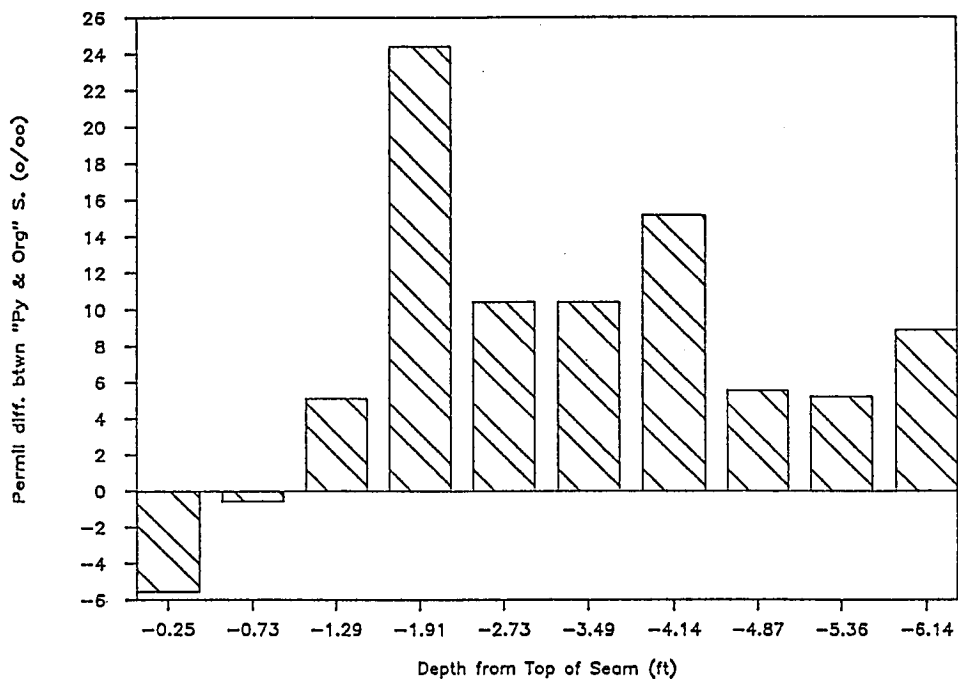


Figure 2. Summary of isotopic results for site CR-III-A (Column A₁).

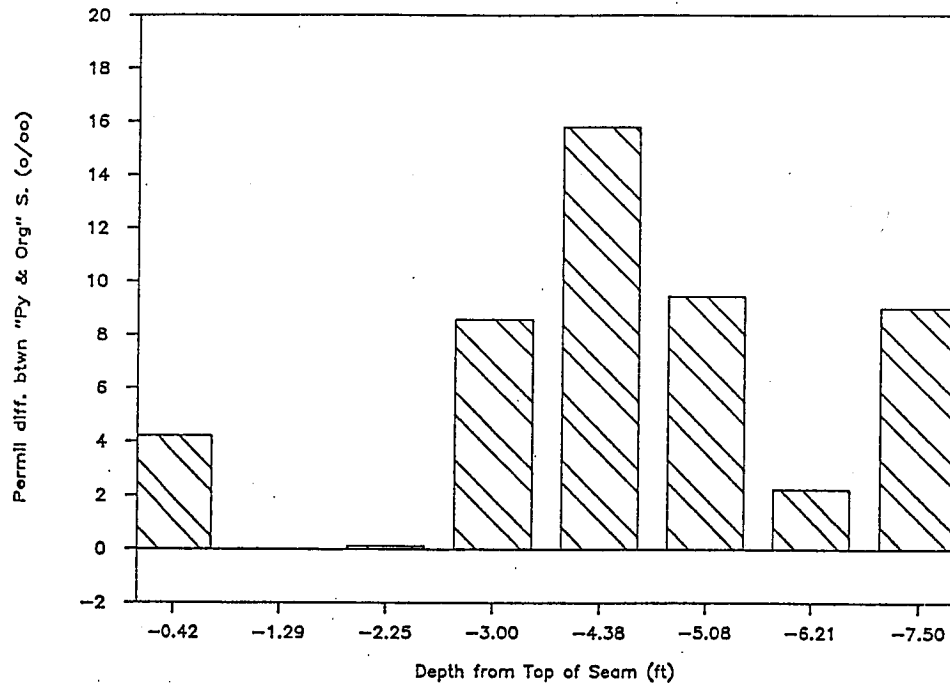


Figure 3. Summary of isotopic results for site CR-II-B (Column B₁).

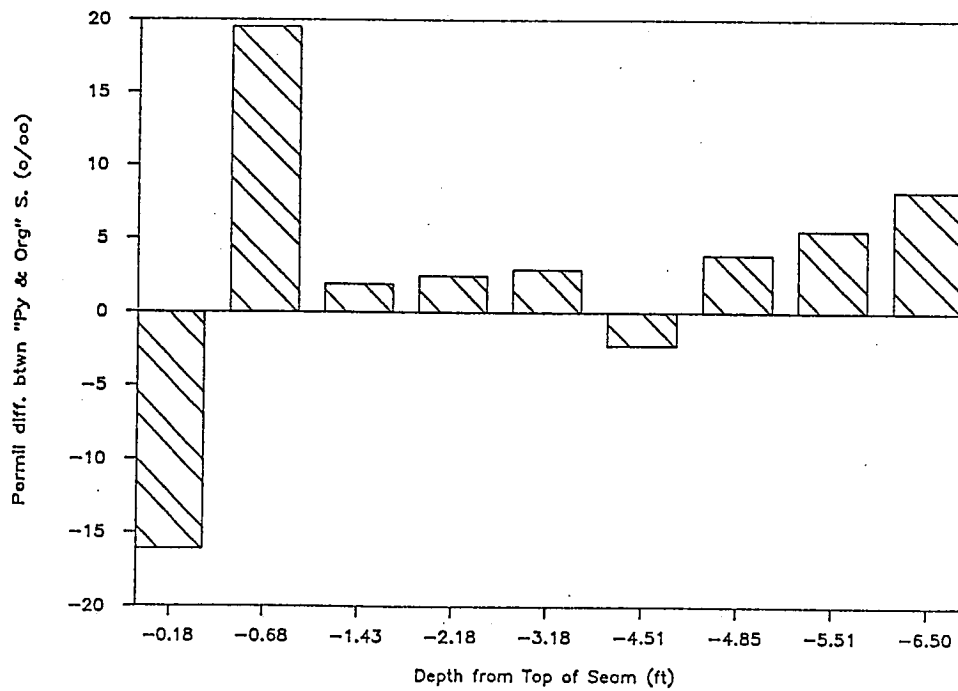


Figure 4. Summary of isotopic results for site CR-II-C (Column C₁).

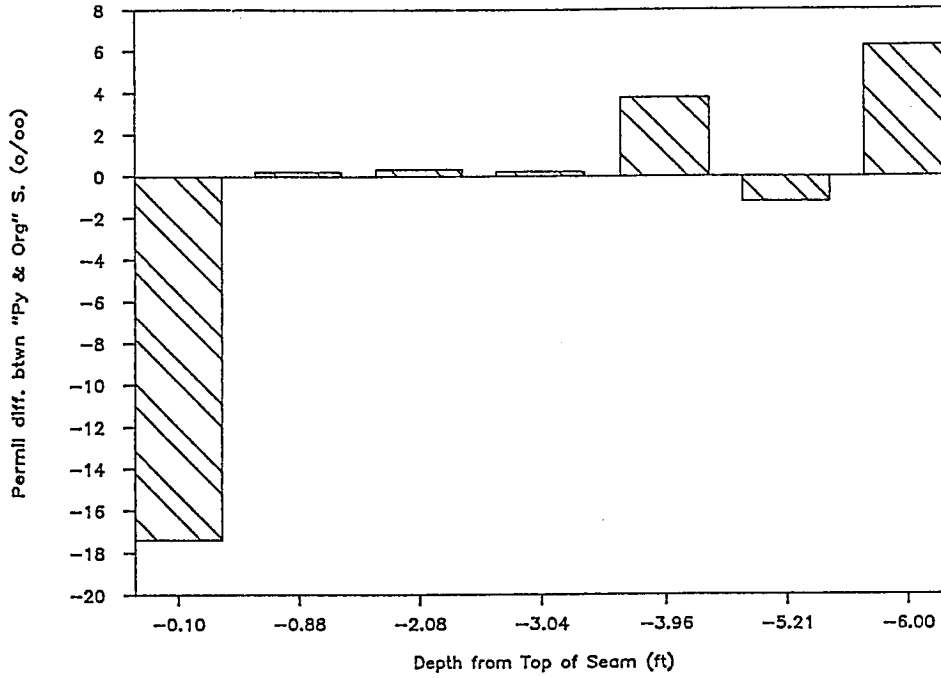


Figure 5. Summary of isotopic results for site RK-I-B (Column B₁).

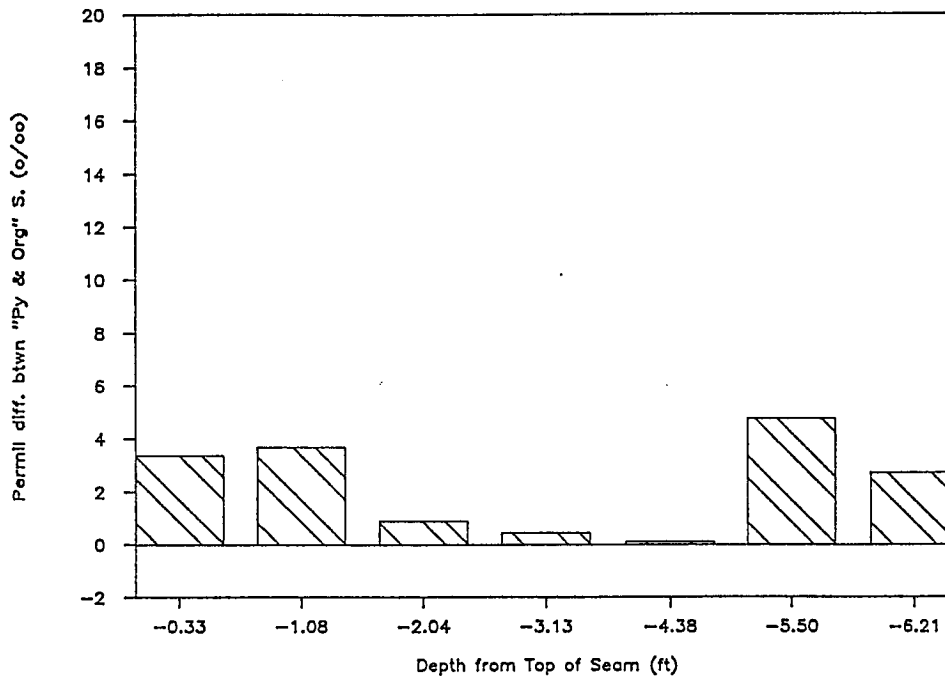


Figure 6. Summary of isotopic results for site RK-I-A (Column A₁).

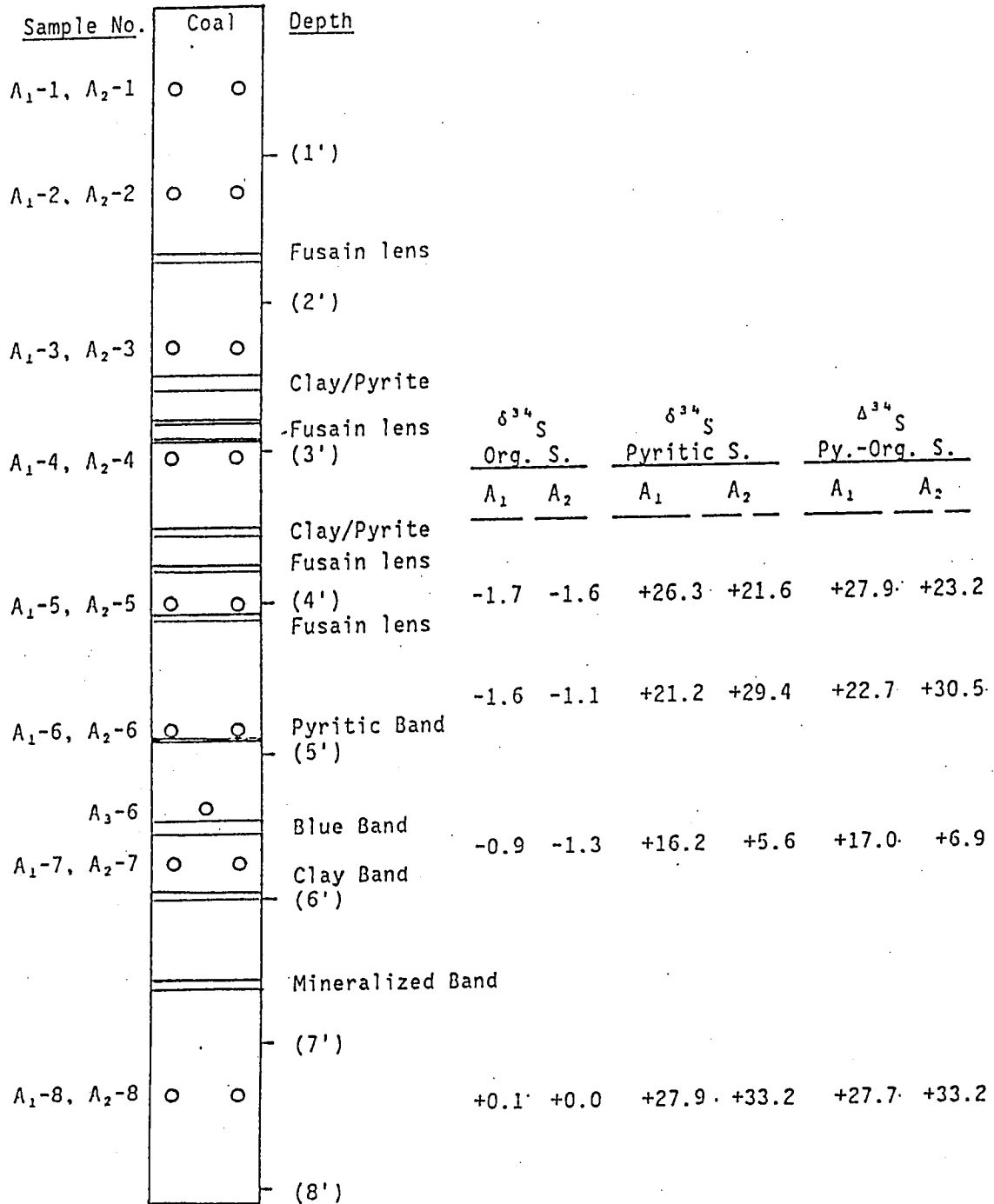


Figure 7. Sample site CR-II-A showing the vertical column of coal, the sampling pattern and the significant partings observed in the seam. The isotopic compositions of the pyritic and organic sulfur for the lower part of the seam is shown to the right of the column.

Table I. Sulfur isotope results obtained from the quick screening analysis of coal samples from site CR-A.
Roof: Erosional channel fill, pyritic siltstone and gray silty shale. Anna Shale was pre-erosion roof rock.

Sample No.	Depth from Top of Seam (ft)	$\delta^{34}\text{S}_{\text{CDT}}_{450 \text{ N}_2}$ (‰)	$\delta^{34}\text{S}_{\text{CDT}}_{450 \text{ Ox}}$ (‰)	* $\Delta^{34}\text{S}$ "Py-Org" (‰)
A ₁ -1	.54	-1.61	-1.16	+0.45
A ₁ -2	1.21	-0.14	-1.51	-1.37
A ₁ -3	2.29	-2.05	-2.51	-0.46
A ₁ -4	3.04	-1.48	+1.81	+3.26
A ₁ -5	4.04	-2.05	+13.14	+15.19
A ₁ -6	4.88	-1.25	+7.93	+9.18
A ₁ -7	5.75	-1.37	+11.32	+12.69
A ₁ -8	7.33	+0.22	+11.09	+10.87
A ₂ -5	4.04	-2.26	+4.20	+6.46
A ₂ -6	4.88	-1.82	+9.07	+10.89
A ₂ -7	5.75	-1.82	+2.60	+4.42
A ₂ -8	7.33	+0.22	+19.82	+19.62

* $\Delta^{34}\text{S}$: Isotopic difference between the sulfur released at 450°C under N₂ ("Org.S") and the sulfur collected at 450°C under partial oxidation ("Py.S").

Table II. Sulfur isotope results obtained from the quick screening analysis of coal samples from site CR-III-A.
Roof: Erosional channel fill.

Sample No.	Depth from Top of Seam (ft)	$\delta^{34}\text{S}_{\text{CDT}}_{450 \text{ N}_2}$ (‰)	$\delta^{34}\text{S}_{\text{CDT}}_{450 \text{ Ox}}$ (‰)	* $\Delta^{34}\text{S}$ "Py-Org" (‰)
A ₁ -1	0.25	-1.98	-7.53	-5.55
A ₁ -2	0.73	-2.64	-3.20	-0.56
A ₁ -3	1.29	-0.65	+4.47	+5.12
A ₁ -4	1.91	-2.87	+21.55	+24.42
A ₁ -5	2.73	-3.98	+6.46	+10.44
A ₁ -6	3.49	-3.30	+7.12	+10.42
A ₁ -7	4.14	-3.42	+11.77	+15.19
A ₁ -8	4.87	-3.10	+2.46	+5.56
A ₁ -9	5.36	-2.98	+2.25	+5.23
A ₁ -10	6.14	-0.65	+8.24	+8.89

* $\Delta^{34}\text{S}$: Isotopic difference between the sulfur released at 450°C under N₂ ("Org.S") and the sulfur collected at 450°C under partial oxidation ("Py.S").

Table III. Sulfur isotope results obtained from the quick screening analysis of coal samples from site CR-B.
Roof: Anna Shale.

Sample No.	Depth from Top of Seam (ft)	$\delta^{34}\text{S}_{\text{CDT}}_{450 \text{ N}_2}$ (‰)	$\delta^{34}\text{S}_{\text{CDT}}_{450 \text{ Ox}}$ (‰)	* $\Delta^{34}\text{S}$ "Py-Org" (‰)
B ₁ -1	0.42	-2.45	+1.79	+4.24
B ₁ -2	1.29	-2.00	-2.00	0.0
B ₁ -3	2.25	-1.57	-1.46	+0.11
B ₁ -4	3.00	-1.70	+6.9	+8.6
B ₁ -5	4.38	-1.77	+14.05	+15.82
B ₁ -6	5.08	-2.33	+7.14	+9.47
B ₁ -7	6.21	-2.57	-0.33	+2.24
B ₁ -8	7.50	-1.22	+7.82	+9.04

* $\Delta^{34}\text{S}$: Isotopic difference between the sulfur released at 450°C under N₂ ("Org.S") and the sulfur collected at 450°C under partial oxidation ("Py.S").

Table IV. Chemical analysis of the organic and pyritic sulfur for the lower half of site CR-II-A, columns A₁ and A₂*.

Sample No.	% Organic Sulfur		% Pyritic Sulfur	
	A ₁	A ₂	A ₁	A ₂
CR-II-A5	2.95	2.38	0.93	0.45
CR-II-A6	2.80	2.89	0.32	0.31
CR-II-A7	2.73	2.72	0.72	0.62
CR-II-A8	2.63	2.60	0.39	0.39

* Sulfur analyses are reported on a moisture free basis.

Table V. Sulfur isotope results obtained from the quick screening analysis of coal samples collected during the return trip to Site CR-II-A

Sample No.	Depth from Top of Seam (ft)	$\delta^{34}\text{S}_{\text{CDT}}_{450 \text{ N}_2}$ (‰)	$\delta^{34}\text{S}_{\text{CDT}}_{450 \text{ Ox}}$ (‰)	* $\Delta^{34}\text{S}$ "Py-Org" (‰)
A-R1	4.04	-1.11	+16.30	+17.41
A-R2	4.88	-0.66	+11.15	+11.81
A-R3	5.33	-0.88	+10.04	+10.92
A-R4	5.75	+1.12	+13.72	+12.60
A-R5	6.74	+1.12	+13.17	+12.05

* $\Delta^{34}\text{S}$: Isotopic difference between the sulfur released at 450°C under N₂ ("Org.S") and the sulfur collected at 450°C under partial oxidation ("Py.S").

Table VI. A comparison of the sulfur isotope results obtained from the three columns of coal samples taken in the lower half of the seam at site CR-II-A. (The three columns are spaced approximately one foot from each other.)

Sample No.			Depth from Top of Seam (ft)	* $\Delta^{34}\text{S}$ "Py-Org" ‰		
A ₁	A ₂	AR		A ₁	A ₂	AR
5	5	1	4.04	+15.19	+6.46	+17.41
6	6	2	4.88	+9.18	+10.86	+11.81
-	-	3	5.33	-	-	+10.92
7	7	4	5.75	+12.69	+4.42	+12.60
-	-	5	6.74	-	-	+12.05
8	8	-	7.33	+10.87	+19.62	-

* $\Delta^{34}\text{S}$: Isotopic difference between the sulfur released at 450°C under N₂ ("Org.S") and the sulfur collected at 450°C under partial oxidation ("Py.S").

Table VII. Isotopic composition of pyritic sulfur in partings and cleat near CR-II-A.

Sample Type	Depth from Top (Ft)	$\delta^{34}\text{S}_{\text{CDT}}$ (%)
Steel Band	-4.94	-2.68
Cleat Py	-5.12	-2.42
Blue Bnad Mass.	-5.45	-2.68
Blue Bnad Shale	-5.45	+4.90
Parting	-5.93	-0.86

Table VIII. Chemical composition of the two samples representing the 7016 coal sample collected from the lower half of site CR-II-A*.

	Clean Sample Excluding Mass. Py.	Representative Including Mass. Py.
Moisture	(8.7)	(8.5)
Volatile Matter	40.0	39.6
Fixed Carbon	50.7	50.8
H-T Ash	9.3	9.6
Sulfate Sulfur	0.066	0.175
Pyritic Sulfur	0.79	1.49
Organic Sulfur	2.68	2.39
Total Sulfur	3.54	4.05

* All values are reported on a moisture free basis except for moisture.

Table IX. Isotopic results of coal representing 70 lbs (Site CR-II-A).

Sample Descript.	$\delta^{34}\text{S}$ 450° N ₂ (%)	$\delta^{34}\text{S}$ 450° Ox (%)	$\Delta^{34}\text{S}$ "Py-Org" (%)
Clean	-0.65	+12.48	+13.13
W/mass Py	-0.21	+9.80	+10.01

Table X. Sulfur isotope results obtained from the quick screening analysis of coal samples collected during the return trip to site CR-II-B.

Sample No.	Depth from Top of Seam (ft)	$\delta^{34}\text{S}_{\text{CDT}}$ 450 N ₂ (‰)	$\delta^{34}\text{S}_{\text{CDT}}$ 450 ^{ox} (‰)	* $\Delta^{34}\text{S}$ "Py-Org" (‰)
B-R1	4.38	-1.77	+26.08	+27.85
B-R2	5.08	-0.43	+26.09	+26.52
B-R3	6.21	-2.22	+16.50	+18.72
B-R4	6.90	-4.21	-3.32	+0.89
B-R5	7.50	-2.88	+3.13	+6.01
B-R6	4.38	+4.24	+22.73	+18.49
B-R7	5.08	-2.44	+22.28	+24.72
B-R8	6.21	-2.43	+6.02	+8.45
B-R9	6.90	-1.99	+0.68	+2.67
B-R10	7.50	-0.65	+14.72	+15.37

* $\Delta^{34}\text{S}$: Isotopic difference between the sulfur released at 450°C under N₂ ("Org.S") and the sulfur collected at 450°C under partial oxidation ("Py.S").

Table XI. A comparison of the quick screening sulfur isotope results obtained from the three columns of coal samples taken in the lower half of the seam at site CR-II-B. (The four columns are spaced approximately one foot from each other.)

Sample No.				Depth from Top of Seam (ft)	* $\Delta^{34}\text{S}$ "Py-Org" ‰			
Br	Br	B ₁	B ₂		BR	BR	A ₁	A ₂
-	-	4	-	3.00	-	-	+8.6	-
6	1	5	5	4.38	+18.49	+27.85	+15.82	-2.90
7	2	6	6	5.08	+24.72	+26.52	+9.47	+2.01
8	3	7	-	6.21	+8.45	+18.72	+2.24	-
9	4	-	-	6.90	+2.67	+0.89	-	-
10	5	8	8	7.50	+15.37	+6.01	+9.04	+2.68

* $\Delta^{34}\text{S}$: Isotopic difference between the sulfur released at 450°C under N₂ ("Org.S") and the sulfur collected at 450°C under partial oxidation ("Py.S").

Table XII. Chemical analysis of the organic and pyritic sulfur for the lower half of site CR-II-B, columns B₁ and B₂*.

Sample No.	% Organic Sulfur		% Pyritic Sulfur	
	B ₁	B ₂	B ₁	B ₂
CR-II-B5	2.96	2.71	0.44	7.68
CR-II-B6	2.98	2.74	0.46	0.37
CR-II-B7	2.82	2.37	1.77	0.99
CR-II-B8	3.08	2.84	1.03	0.36

* Sulfur analyses are reported on a moisture free basis.

Table XIII. Sulfur isotope results obtained from the quick screening analysis of coal samples from site CR-II-C.
Roof: .92' Anna Shale, Brereton lms (rolly and knobby).

Sample No.	Depth from Top of Seam (ft)	$\delta^{34}\text{S}_{\text{CDT}}^{450\text{N}_2}$ (‰)	$\Delta^{34}\text{S}_{\text{CDT}}^{450\text{OX}}$ (‰)	* ^{34}S "Py-Org" (‰)
C ₂ -1	0.18	-16.09	-32.17	-16.08
C ₁ -2	0.68	-4.46	+15.07	+19.53
C ₁ -3	1.43	-4.23	-2.34	+1.91
C ₁ -4	2.18	-2.45	+0.01	+2.46
C ₁ -5	3.18	-3.91	-1.00	+2.91
C ₁ -6	4.51	-3.78	-6.02	-2.24
C ₁ -7	4.85	-3.22	+0.68	+3.90
C ₁ -8	5.51	-2.23	+3.35	+5.58
C ₁ -9	6.50	-1.56	+6.70	+8.26
C ₂ -2	0.68	-5.13	-1.56	+3.57
C ₂ -8	5.51	-2.90	-3.34	-0.44
C ₂ -9	6.50	-2.68	-1.34	+1.34

* $\Delta^{34}\text{S}$: Isotopic difference between the sulfur released at 450°C under N₂ ("Org.S") and the sulfur collected at 450°C under partial oxidation ("Py.S").

Table XIV. Sulfur isotope results obtained from the quick screening analysis of coal samples from site RK-I-B.
Roof: 0.2' of clod with >3' of Brereton lms above clod.

Sample No.	Depth from Top of Seam (ft)	$\delta^{34}\text{S}_{\text{CDT}}$ 450 N ₂ (‰)	$\delta^{34}\text{S}_{\text{CDT}}$ 450 _{ox} (‰)	* $\Delta^{34}\text{S}$ "Py-Org" (‰)
B ₁ -1	Top	-20.27	-37.66	-17.39
B ₁ -2	0.88	-6.90	-6.68	+0.22
B ₁ -3	2.08	-3.00	-2.67	+0.33
B ₁ -4	3.04	-2.45	-2.22	+0.23
B ₁ -5	3.96	-1.22	+2.57	+3.79
B ₁ -6	5.21	-1.33	-2.56	-1.23
B ₁ -7	6.00	-0.44	+5.81	+6.25

* $\Delta^{34}\text{S}$: Isotopic difference between the sulfur released at 450°C under N₂ ("Org.S") and the sulfur collected at 450°C under partial oxidation ("Py.S").

Table XV. Sulfur isotope results obtained from the quick screening analysis of coal samples from site RK-I-A.
Roof: 2 1/2' of Anna Shale w/Brereton above the shale.

Sample No.	Depth from Top of Seam (ft)	$\delta^{34}\text{S}_{\text{CDT}}$ 450 N ₂ (‰)	$\delta^{34}\text{S}_{\text{CDT}}$ 450 _{ox} (‰)	* $\Delta^{34}\text{S}$ "Py-Org" (‰)
A ₁ -1	0.33	-3.39	-0.01	+3.38
A ₁ -2	1.08	-3.35	+0.35	+3.70
A ₁ -3	2.04	-2.03	-1.13	+0.90
A ₁ -4	3.13	-1.47	-1.02	+0.45
A ₁ -5	4.38	-0.45	-0.33	+0.12
A ₁ -6	5.50	+1.47	+6.24	+4.77
A ₁ -7	6.21	+1.82	+4.54	+2.72

* $\Delta^{34}\text{S}$: Isotopic difference between the sulfur released at 450°C under N₂ ("Org.S") and the sulfur collected at 450°C under partial oxidation ("Py.S").

APPENDIX

Methods Study: Comparison of the LAH, CrCl₂ and HNO₃ Methods of Pyrite Extraction

In sulfur isotopic studies, this laboratory uses lithium aluminum tetrahydride (LAH) reduction of sulfide to recover disulfide sulfur. We are one of the few laboratories using this technique while others use a variety of other chemical procedures particularly nitric acid and chromous chloride methods. To ascertain whether these methods of disulfide extraction are comparable, both in regards to yield (disulfide-sulfur) and isotopic composition of sulfur recovered, we have analyzed a series of splits of coals and shales using these three methods. In addition, we have used different size fractions of each split to find the maximum particle size for complete disulfide reduction.

Coals have two major sulfur species; disulfide and organic sulfur. Marine shales commonly have a significant amount of pyritic sulfur but often contain only small amounts of organic sulfur. The chemical techniques mentioned above are designed to attack only the disulfides allowing separate analyses of sulfur species in a sample. The coals chosen for this study are characterized by variable pyrite and organic sulfur contents and isotopic compositions. We hope to show by isotopic analysis whether the chemical techniques are disulfide specific or whether some of the organic sulfur is released during the chemical reaction.

From earlier studies the LAH method of disulfide reduction has proven reliable with virtually complete reduction of disulfide sulfur in coal (Kuhn et al., 1971; Price 1977; Westgate and Anderson 1982). The method is, however, time consuming and potentially dangerous. The sample is boiled with LAH, dissolved in an organic solvent (tetrahydrofuran) for an hour during which the metal-sulfur bond of the disulfide is broken and the sulfur is reduced. To liberate the sulfide sulfur as H₂S gas, water and then HCl is added to the reaction vessel. As LAH reacts violently with water, this step is done very slowly adding water drop by drop with the reaction flask in an ice bath. After the HCl has been added the reaction flask is again heated and the sample is boiled for three hours to allow sufficient time for complete disulfide reduction. The H₂S generated is trapped in cadmium acetate as cadmium sulfide which can then be converted to silver sulfide and weighed. The silver sulfide is later converted to sulfur dioxide gas for isotope analysis. The chemical procedure requires about seven hours.

The chromous chloride (CrCl₂) method of disulfide extraction has recently gained popularity for isotope analysis of pyrite in sediments and shales (Canfield et al., 1986). The CrCl₂ method is considerably faster than the LAH method and does not require the use of explosive or dangerous chemicals. The procedure requires similar glassware as the LAH method with the exception that CrCl₂ is easily oxidized and must be handled carefully and not exposed to oxygen. The coal or shale sample is wetted with ethanol in a sealed reaction flask under nitrogen gas flow. CrCl₂ is extracted from an airtight storage flask with a syringe

and, along with HCl, is added to the reaction flask through a self-sealing serum cap. As with the LAH method, the disulfide-sulfur is reduced producing an acid soluble monosulfide and sulfur ions in solution. These react with HCl producing H₂S gas. For complete reaction the sample is boiled with the CrCl₂ for two hours. The H₂S is swept out of the reaction flask by N₂, trapped in cadmium acetate, converted to silver sulfide, and weighed. The entire procedure takes about 3 1/2 hours.

The nitric acid method (HNO₃) is an ASTM method and involves the dissolution of pyrite in nitric acid. This method has been commonly used on coals to assess pyrite content by measuring the amount of iron in solution subsequent to pyrite dissolution. To recover pyritic sulfur for isotopic analysis requires precipitation of barium sulfate by the addition of barium chloride subsequent to removal of iron and nitrates from the solution (Thode et al., 1958). The removal of iron and nitrates from the nitric acid solution is very time consuming and takes several hours to complete. Bromine water was added to the acid solution and boiled for 15 min. The solution was then carefully evaporated to dryness, concentrated HCl was added and the solution was evaporated to dryness again. Finally dilute HCl was added, iron was precipitated with ammonium hydroxide and filtered. The sulfur was precipitated as barium sulfate by the addition of barium chloride.

As discussed above, the CrCl₂ technique is the most efficient and least dangerous of the methods. If the method proves comparable to the LAH method in both amount of disulfide sulfur recovered and in its isotopic composition we will adopt this method of disulfide sulfur extraction.

Summary of Results

Results have shown that the LAH and CrCl₂ methods yield similar amounts of disulfide sulfur from coals and shales when the sample particle size is less than 63 μm (<230 mesh). There appears to be a greater degree of variability between the amount recovered by these two methods in the coals. The CrCl₂ method removed slightly less disulfide sulfur than the LAH method for the two coals with greater amounts of pyrite RK-83B-2 and CR-83B-6. There was also a greater variation in the amount of pyritic sulfur removed by the CrCl₂ method.

Only samples ground to (250 μm) <60 mesh were used to test the HNO₃ method as described by ASTM. The amount of pyritic sulfur recovered by this technique sometimes varied from the amount recovered by the other methods. The HNO₃ determination of pyritic sulfur in the shales was generally less than that determined by LAH and CrCl₂. The determination of pyritic sulfur by HNO₃ was similar to that determined by LAH for the coals with large amounts of pyritic sulfur (RK-83B-2 and CR-83B-6). However, for the two coals with only a few tenths of a percent pyritic sulfur the HNO₃ determination of pyritic sulfur was greater than that determined by LAH and CrCl₂.

The isotopic compositions of disulfide sulfur recovered by the CrCl₂ and LAH methods are similar, although the sulfur extracted by CrCl₂ is consistently enriched in the heavier isotope. However, the isotopic

composition of sulfur extracted by HNO_3 dissolution of pyrite is isotopically much lighter than the pyritic sulfur extracted by the other two methods. This is especially true for the coals with less pyritic sulfur. The lighter isotopic composition is probably a result of some organic sulfur extracted along with the pyritic sulfur by the HNO_3 method. The isotopic composition of the organic sulfur of all four coals is quite negative and ranges between -4.0 ‰ to -5.5 ‰. The HNO_3 disulfide extraction method is obviously not a good method for stable sulfur isotope studies.

Conclusion

Currently the LAH method appears to be the better method to use for stable sulfur isotope studies. However by changing our reaction apparatus so that the N_2 purging gas is bubbled through the CrCl_2 reaction instead of passing over the reaction we can probably improve the recovery yields and repeatability of the CrCl_2 method (personal communication Dr. Chusak Chaven).

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Table A1. Comparison of isotopic and analytical data obtained from the LAH, CrCl₂ and nitric acid methods for shales and coals.

Sample	Mesh Size	Isotopic Composition			% Sulfide Sulfur		
		LAH	CrCl ₂	HNO ₃	LAH	CrCl ₂	HNO ₃
S000037 (Shale)	60.00	2.35	2.57		2.40	2.71	2.16
	120.00	1.57	1.79		2.62	2.58	
	230.00	1.35	2.02		2.71	2.53	
	325.00	1.71	1.71		2.80	2.71	
S00002 (Shale)	60.00	-18.28	-17.35		1.81	2.48	3.46
	120.00	-18.28	-17.87		3.34	3.74	
	120.00	-18.02	--		3.66	--	
	230.00	-17.91	-17.57		3.94	3.72	
	325.00	-17.57	-17.57		3.76	3.83	
	325.00	-18.02	--		3.94	--	
S00349 (Shale)	60.00	6.26	7.14		2.06	1.22	2.00
	120.00	4.91	5.58		2.26	2.25	
	120.00	5.14	5.36		2.29	2.12	
	230.00	--	--		2.44	1.35	
	230.00	--	4.69		--	2.13	
	325.00	4.91	5.36		2.47	2.33	
	325.00	4.69	5.36		2.31	2.09	
NW Albany (Shale)	60.00	-0.20	0.03		1.95	1.60	
	120.00	0.31	0.47		1.97	1.42	
	230.00	-0.41	0.25		2.05	1.97	
	325.00	-0.20	0.91		2.06	1.92	
RK-83B-2 (Coal)	60.00	-0.67	-0.43	-1.11	2.94	2.28	3.80
	60.00	--	0.25		--	2.86	
	230.00	-1.33	--		3.74	2.85	
	230.00	--	0.23		--	3.13	
	325.00	-0.88	-0.43		3.50	2.57	
	400.00	-0.43	-0.21		3.53	3.25	
CR-83B-4 (Coal)	60.00	--	10.91	-0.89	0.14	0.19	0.38
	230.00	10.49	10.93		0.26	0.25	
	230.00	--	--		0.29	--	
	325.00	10.27	12.05		0.26	0.23	
	400.00	--	--		0.31	0.25	
CR-83B-6 (Coal)	60.00	2.02	3.80	1.12	1.74	1.70	2.30
	60.00	--	4.24		--	1.58	
	230.00	2.47	3.58		2.20	1.83	
	325.00	2.47	3.58		2.09	1.77	
	325.00	--	--		1.89	--	
RK-83A-4 (Coal)	60.00	8.25	9.55	2.46	0.39	0.40	0.88
	60.00	--	10.45		--	0.46	
	230.00	8.43	9.78		0.49	0.49	
	230.00	8.45	--		0.48	--	
	325.00	8.66	9.55		0.43	0.36	
	325.00	--	--		0.48	--	