

BORON AND SULFUR ISOTOPIC FRACTIONATION
IN THE COAL COMBUSTION SYSTEM

by

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TABLE OF CONTENTS

	Page
LIST OF ILLUSTRATIONS	7
LIST OF TABLES	9
ABSTRACT	10
1. INTRODUCTION	11
1.1 Description of Problem	11
1.2 Previous Work	12
1.2.1 Isotopic Signatures and Fractionation Factors	12
1.2.2 Fractionation Processes	15
2. SAMPLE DESCRIPTION AND ANALYTICAL METHODS	20
2.1 Introduction	20
2.2 Description of Samples	20
2.3 Boron Extraction Procedures	25
2.3.1 Water-soluble Coal and Soil	25
2.3.2 Fly Ash and Bottom Ash	27
2.3.3 Ion Exchange Resins	29
2.3.4 Methyl Borate Distillation	29
2.4 Sulfur Extraction Procedures	30
2.4.1 Coal	30
2.4.2 Fly Ash	36
2.5 Boron Isotopic Analysis	37
2.6 Sulfur Isotopic Analysis	37
3. COAL COMBUSTION CHEMISTRY	39
3.1 Introduction	39
3.2 Coal Chemistry	39
3.2.1 Mineral Content	39
3.2.2 Organic Phases	43
3.3 Coal Combustion	44
3.3.1 Combustion Processes	44
3.3.2 Combustion Products	49
3.3.3 Combustion Systems	54

TABLE OF CONTENTS--Continued

		Page
4.	BORON ISOTOPIC PARTITIONING IN COAL AND COMBUSTION PRODUCTS	55
	4.1 Boron Sources in Coal	55
	4.2 Boron Isotopic Partitioning	56
	4.2.1 Coal	56
	4.2.2 Fly Ash	56
	4.2.3 Gas Emissions	57
5.	SULFUR ISOTOPIC PARTITIONING IN COAL AND COMBUSTION PRODUCTS	59
	5.1 Sulfur Sources in Coal	59
	5.1.1 Organic Sulfur Formation	60
	5.1.2 Pyrite Formation	60
	5.2 Sulfur Isotopic Partitioning	61
	5.2.1 Coal	61
	5.2.2 Fly Ash and Gas Emissions	63
6.	RESULTS AND DISCUSSION OF COAL AND FLY ASH SAMPLES	66
	6.1 Introduction	66
	6.2 Isotopic Results of Coal and Fly Ash Samples	66
	6.3 Discussion of Boron Isotopic Data	68
	6.3.1 Boron Incorporation into Coal	68
	6.3.2 Boron Combustion Behavior	71
	6.4 Discussion of Sulfur Isotopic Data	73
	6.4.1 Sulfur Incorporation into Coal	73
	6.4.2 Sulfur Combustion Behavior	76
7.	ISOTOPIC CONTENT OF SAMPLES FROM A COAL-FIRED POWER PLANT	80
	7.1 Introduction	80
	7.2 General Description of Study Area	80
	7.2.1 Hydrogeology	80
	7.2.2 Site Description and Sample Locations	83
	7.2.3 Chemical Data	88
	7.3 Preliminary Geochemical Modeling	92
	7.4 Discussion of Isotopic and Chemical Data	92

TABLE OF CONTENTS--Continued

	Page
8. SUMMARY AND CONCLUSIONS	95
APPENDIX A: ANALYTICAL DATA OF MINOR AND TRACE ELEMENTS OF COAL SAMPLES ..	98
REFERENCES	103

LIST OF ILLUSTRATIONS

Figure		Page
1.1	Selected values for $\delta^{11}\text{B}$ for natural materials indicated by large circles, less reliable values generally with large standard deviations are presented as small circles (Bassett, 1990).	18
1.2	$\delta^{34}\text{S}$ values for natural materials (Krouse, 1980).	19
2.1	Apparatus for the extraction of water-soluble boron in coal and soil.	26
2.2	Methyl borate distillation apparatus.	31
2.3	Extraction apparatus used in the lithium aluminum hydride (LAH) method for sequentially extracting the various forms of sulfur.	34
3.1	Schematic diagram of the constituents and reaction processes of a coal particle during pyrolysis and combustion.	46
3.2	Oxidation reactions in the immediate vicinity of a burning coal particle (Berkowitz, 1985).	48
3.3	Generalized path of combustion products at a typical power plant (Roy et al., 1981).	50
3.4	Mineral matter changes that occur during coal combustion due to increasing temperatures (based on Mitchell and Gluskoter, 1976).	52
6.1	The relationship observed between the boron concentration as a function of the $\delta^{11}\text{B}$ of the water-soluble boron for four coal samples.	70
6.2	Boron combustion behavior illustrated by the $\delta^{11}\text{B}$ of the fly ash leachate verses the $\delta^{11}\text{B}$ of the water-soluble boron for three Illinois coal samples.	72
6.3	The relationship observed between the $\delta^{34}\text{S}$ of organic sulfur as a function of the organic sulfur content for four coal samples.	74
6.4	The relationship observed between the $\delta^{34}\text{S}$ of pyritic sulfur as a function of the pyritic sulfur content for four coal samples.	75

LIST OF ILLUSTRATIONS--Continued

Figure		Page
6.5	Generalized flowchart summarizing the sources and methods of sulfur incorporation into coal (after Price and Shieh, 1979). ..	77
6.6	Sulfur combustion behavior illustrated by the $\delta^{34}\text{S}$ of fly ash leachate verses the $\delta^{34}\text{S}$ of the total sulfur content for four coal samples.	78
7.1	Site location map of the Coronado Generating Station located near St. Johns, Arizona.	81
7.2	Vicinity map of the Coronado Generating Station showing locations of evaporation reservoir and ash disposal area.	84
7.3	Site plan of the Coronado Generating Station showing locations of canals, ponds, reservoirs, and storage areas.	85
7.4	Location map of ground water, reservoir, and soil samples and geologic cross section (A-A')	86
7.5	Geologic cross section (A-A') across the SRP site.	87
7.6	Graphic representation of the boron and sulfate concentration increase in the evaporation reservoir from 1980-1989.	90

LIST OF TABLES

Table		Page
1.1	Relative abundance of sulfur and boron isotopes.	13
1.2	Isotopic fractionation factors for the exchange reaction between SO ₂ and SO ₃ (Sakai, 1957).	15
2.1	Analysis of IBCSP and SRP coal samples.	22
2.2	Mineral composition (wt. % coal) of IBCSP coal samples.	23
2.3	Oxide content of high temperature (750 °C) ashes of IBSCP samples.	24
2.4	Boron concentration and percent soluble boron from the hot water extraction method for four coal samples.	27
2.5	Boron concentrations of fly ash leachates.	28
3.1	Common coal minerals (Renton, 1982).	42
6.1	Boron isotopic results of coal and fly ash samples.	67
6.2	Sulfur isotopic results of coal and fly ash samples.	69
7.1	Summary of chemical and isotopic analyses of SRP field samples.	89
7.2	1984 water chemistry data.	91

ABSTRACT

The boron and sulfur isotopic ratios of four coal samples and corresponding fly ash leachates provide explanations for boron and sulfur incorporation into coal and behavior during combustion. Fractionation processes occur during coal formation and during the combustion of coal as some of the boron and sulfur is concentrated on the ash, and some escapes into the atmosphere as flue gas.

Water-soluble boron in coal is extracted using a modified soil technique. Boron is isolated from solution using Amberlite IRA-743 resin and concentrated by methyl borate distillation with no isotopic fractionation observed. The forms of sulfur in coal are extracted sequentially using the lithium aluminum hydride (LAH) method.

The isotopic content of samples from a coal-fired power-plant are used to determine if waste water has impacted a shallow aquifer system. No indication of mixing between waste water and ground water was observed.

CHAPTER ONE

INTRODUCTION

Coal is a complex, heterogeneous solid originating from plant material, and contains almost all of the elements normally found in the earth's crust. The elements of coal are mobilized upon combustion to bottom ash, fly ash, or gases before being discharged into the environment. Two of the many contaminants resulting from coal combustion include boron and sulfur.

Boron is concentrated on fly ash and is readily leached into the ground water system in the form of boric acid, $B(OH)_3$, and as the borate anion, $B(OH)_4^-$. Leachate from coal-fired power plants contains boron in the milligram/liter (mg/l) range and can result in environmental problems due to boron's toxicity to many plants at concentrations above 1 mg/l (Bassett, 1980).

Sulfur has become the most publicized and studied element associated with coal, because of its widespread environmental significance. Sulfur in coal exists in several chemical forms including sulfates, iron sulfides, organic sulfur, and elemental sulfur. Approximately 85% of the sulfur in coal is converted to sulfur oxides (SO_2 or SO_3) during combustion while the remaining sulfur is concentrated on the fly ash as sulfate (Shobert, 1987). Environmental problems associated with sulfur and coal combustion include acid atmospheric precipitation and elevated sulfate concentrations in ground water near coal-fired power plants (Unites et al., 1985; Sirmsiman et al., 1987).

1.1 Description of the Problem

Over 60% of the electrical power in the United States is produced from burning coal

(Muraka, 1982). An understanding of the path of the resulting coal constituents is important in developing effective techniques for solving the resulting environmental problems. The application of boron and sulfur isotope chemistry to the coal combustion system is a proposed method in this study.

The purpose of this study was to determine the boron and sulfur isotope ratios of three Illinois coal and corresponding fly ash samples to observe the isotopic fractionation. As stable isotopes of boron (^{11}B and ^{10}B) and sulfur (^{34}S and ^{32}S) have relatively large mass differences, isotopic fractionation favoring either the heavy or light isotope is likely to occur during phase changes.

The boron and sulfur isotopic contents of samples from a coal-fired power plant were also determined. Samples included coal, fly and bottom ashes, two soil samples, a sample from the evaporation pond, and three ground water samples. The resulting boron and sulfur isotopic ratios were then used to speculate how the observed fractionation from different parts of the coal combustion system could be used to determine if proper containment of waste water is being achieved. If leachate from the fly ash or the plant waste water has a different isotopic signature than the background water, then boron and sulfur isotopes could be utilized as convincing monitoring tools to assess contamination.

Additional objectives included (1) testing a method for extracting the water-soluble boron from coal, and (2) applying an extraction method and preparation procedure for boron isotopic analysis using a boron-selective ion-exchange resin and methyl borate distillation.

1.2 Previous Work

1.2.1 Isotopic Signatures and Fractionation Factors

The relative abundances of the stable isotopes of sulfur and boron are given in

Table 1.1. The ratios between the two most abundant isotopes ($^{34}\text{S}/^{32}\text{S}$ and $^{11}\text{B}/^{10}\text{B}$) are measured to determine isotopic variations. Isotope ratios are reported in the del notation in parts per thousand (per mil or ‰) using the difference between a standard and a sample.

The equation used to calculate the per mil of a sample containing boron is:

$$\delta^{11}\text{B} = \frac{[(^{11}\text{B}/^{10}\text{B})_{\text{sample}} - (^{11}\text{B}/^{10}\text{B})_{\text{std}}]}{(^{11}\text{B}/^{10}\text{B})_{\text{std}}} \times 1000 \quad (1)$$

Likewise, $\delta^{34}\text{S}$ values are reported from $^{34}\text{S}/^{32}\text{S}$ ratio measurements. Therefore, a sample with a $\delta^{11}\text{B}$ value of +10 is enriched in ^{11}B by 10 per mil, or one percent, relative to the standard while a negative $\delta^{11}\text{B}$ value signifies the sample is depleted in the heavy isotope.

The internationally accepted reference standard for sulfur is troilite (FeS) from the Canyon Diablo iron meteorite (Hoefs, 1973). For boron isotopes, no international standard is recognized. However, most studies after 1970 have consistently used the National Bureau of Standards, Standard Reference Material No. 951 boric acid (NBS SRM-951) (Bassett, 1990). This standard was also chosen for this study.

Table 1.1 Relative abundance of sulfur and boron isotopes.

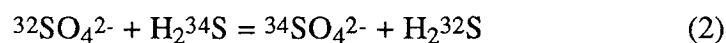
	<u>Abundance, ‰</u>		
	<u>Sulfur</u> ¹		<u>Boron</u> ²
^{32}S	95.0	^{10}B	18.98
^{33}S	0.75	^{11}B	81.02
^{34}S	4.21		
^{36}S	0.02		

¹Krouse, 1980.

²Bainbridge and Nier, 1950.

Isotopes of a particular element have the same number of protons, but a different number of neutrons; therefore, isotopes of the same element will behave similarly in chemical reactions, but differ in their masses. These minute differences in mass are more pronounced among isotopes of the lighter elements such as boron and sulfur, because the difference in mass is a significant fraction of the total mass of the atom. Variations in mass cause isotopic fractionation, which is by accepted definition, any process that causes the isotopic ratios in particular phases or regions to differ from one another (Drever, 1982). For example, Harrison and Thode (1957) studied the reduction of SO_4^{2-} to H_2S and found that $^{32}\text{SO}_4^{2-}$ is reduced 2.2 percent faster than $^{34}\text{SO}_4^{2-}$, because of mass differences.

The isotope exchange reaction between sulfate and sulfide may be written:



The equilibrium constant for equation (2) is:

$$K = \frac{[^{34}\text{SO}_4^{2-}][\text{H}_2^{32}\text{S}]}{[^{32}\text{SO}_4^{2-}][\text{H}_2^{34}\text{S}]} \quad (3)$$

The isotopic fractionation factor (α) for reaction (3) is:

$$\alpha(\text{SO}_4^{2-} - \text{H}_2\text{S}) = \frac{(^{34}\text{S}/^{32}\text{S})_{\text{SO}_4^{2-}}}{(^{34}\text{S}/^{32}\text{S})_{\text{H}_2\text{S}}} \quad (4)$$

which equals the equilibrium constant, K , of equation (3). In terms of quantities measured by mass spectrometry (δ values) this expression for sulfur isotopes becomes:

$$\alpha(\text{SO}_4^{2-} - \text{H}_2\text{S}) = \frac{(1000 + \delta^{34}\text{S}(\text{SO}_4^{2-}))}{(1000 + \delta^{34}\text{S}(\text{H}_2\text{S}))} \quad (5)$$

As ^{34}S bonds are stronger than ^{32}S bonds, the chemical properties of two species (i.e. H_2^{34}S and H_2^{32}S) are different; therefore, K and α generally do not equal unity. For example, for the isotopic exchange reaction in equation (2), α equals 1.075 at 25°C ; therefore, sulfides are depleted in ^{34}S by amounts of up to 75 ‰ relative to sulfates (Hoefs, 1973).

As the temperature of a system involving two species decreases, the fractionation factor of the two species increases. As the temperature increases, α approaches unity resulting in no isotopic fractionation. At low temperatures ($< 25^\circ\text{C}$) $\ln \alpha$ is inversely proportional to absolute temperature, T , while at higher temperatures $\ln \alpha$ is inversely proportional to T^2 (Pearson and Rightmire, 1980). For example, the isotopic fractionation factors between SO_2 and SO_3 increase with decreasing temperatures (Table 1.2). In addition, pressure effect upon α is negligible (Clayton et al., 1974).

Table 1.2 Isotopic fractionation factors for the exchange reaction between SO_2 and SO_3 (Sakai, 1957).

Temperature ($^\circ\text{C}$)	25	50	100	500	1000
α ($\text{SO}_3 - \text{SO}_2$)	1.020	1.016	1.015	1.003	1.003

1.2.2 Fractionation Processes

Isotopic variations in nature are caused from either isotope exchange reactions or from mass-dependent fractionations that accompany physical and chemical processes. These variations are governed by equilibrium exchange and/or unidirectional kinetic processes.

Physical fractionation processes include evaporation, diffusion, and adsorption. Evaporation and diffusion are kinetic processes and are explained by the different

translational velocities of isotopic molecules moving through a phase or across a phase boundary. Mass differences between the isotopes accounts for the varying velocities where the lighter isotope is preferentially enriched in the products of the reaction. The diffusive uptake of soluble species by plants is known to enrich the lighter isotope in the plant material. For example, plant assimilation of sulfur involves a minor depletion (1 to 3 ‰) of the heavy isotope (^{34}S) relative to the dissolved sulfate source (Nielson, 1976). Adsorption is also related to mass differences between the isotopes. For example, a study by Nriagu (1974) on the sediment adsorption of sulfate showed the lighter $^{32}\text{SO}_4^{2-}$ concentrated in the sediment leaving the sulfate in solution enriched in $^{34}\text{SO}_4^{2-}$. In addition, boron is adsorbed by clay minerals such that the light isotope (^{10}B) is preferentially incorporated into the adsorbed phase (Palmer et al., 1987). These isotopic fractionations are the result of equilibrium processes rather than kinetic isotope effect. According to Palmer et al. (1987), boron fractionation on clay is also dependent on pH with less fractionation occurring at higher pH values. In general, physical fractionation processes account for no appreciable fractionation of sulfur compounds in nature, while for boron the isotopic effects are greater.

Chemical fractionation processes are responsible for the large variations in sulfur isotope ratios in nature and can be divided into sulfur reduction and sulfur oxidation. Sulfur reduction takes place by either inorganic or organic mechanisms. Inorganic sulfur reduction requires high temperatures ($>250\text{ }^\circ\text{C}$) to overcome strong bond energies in oxidized sulfur compounds (Ries, 1982); therefore, reactions are restricted within the earth's crust. Fractionations from these high-temperature inorganic processes are in the 25 ‰ or less range (Harrison and Thode, 1957).

Bacterial sulfate reduction is one of the most important sulfur fractionating processes. The largest natural sulfur isotope fractionations are caused by the sulfate-

reducing bacteria *Desulfovibrio* which enzymatically lower the sulfur-oxygen threshold bond energy (Pearson and Rightmire, 1980). As ^{34}S bonds are stronger than ^{32}S bonds, the bacteria will preferentially reduce the lighter $^{32}\text{SO}_4^{2-}$ to $^{32}\text{H}_2\text{S}$ producing fractionations ranging from zero to 55 per mil (Pearson and Rightmire, 1980). From laboratory and field data, bacterial reduction tends to divide sulfur into an isotopically "heavy" sulfate fraction and an isotopically "light" sulfide mineral fraction.

Sulfur oxidation processes are minor contributors to sulfur isotopic variations. Smejkal (1978) studied the oxidative weathering of sulfides and found no major fractionation of sulfur isotopes with δ values for pyrite and sulfate of +16.4 ‰ and +15.2 ‰, respectively. Therefore, sulfate from oxidized sulfide minerals tend to be lighter than sulfate dissolved from evaporite deposits (+20 ‰). In addition, bacterial oxidative fractionation occurs, but is usually much smaller than bacterial reductive fractionation.

The fractionation processes described above have selectively distributed boron and sulfur isotopes in nature. The boron and sulfur isotopic distributions in naturally occurring compounds are provided in Figures 1.1 and 1.2, respectively. Additional information on boron isotopes can be obtained from Bassett (1990) who provides a detailed evaluation of available boron isotopic measurements from the literature.

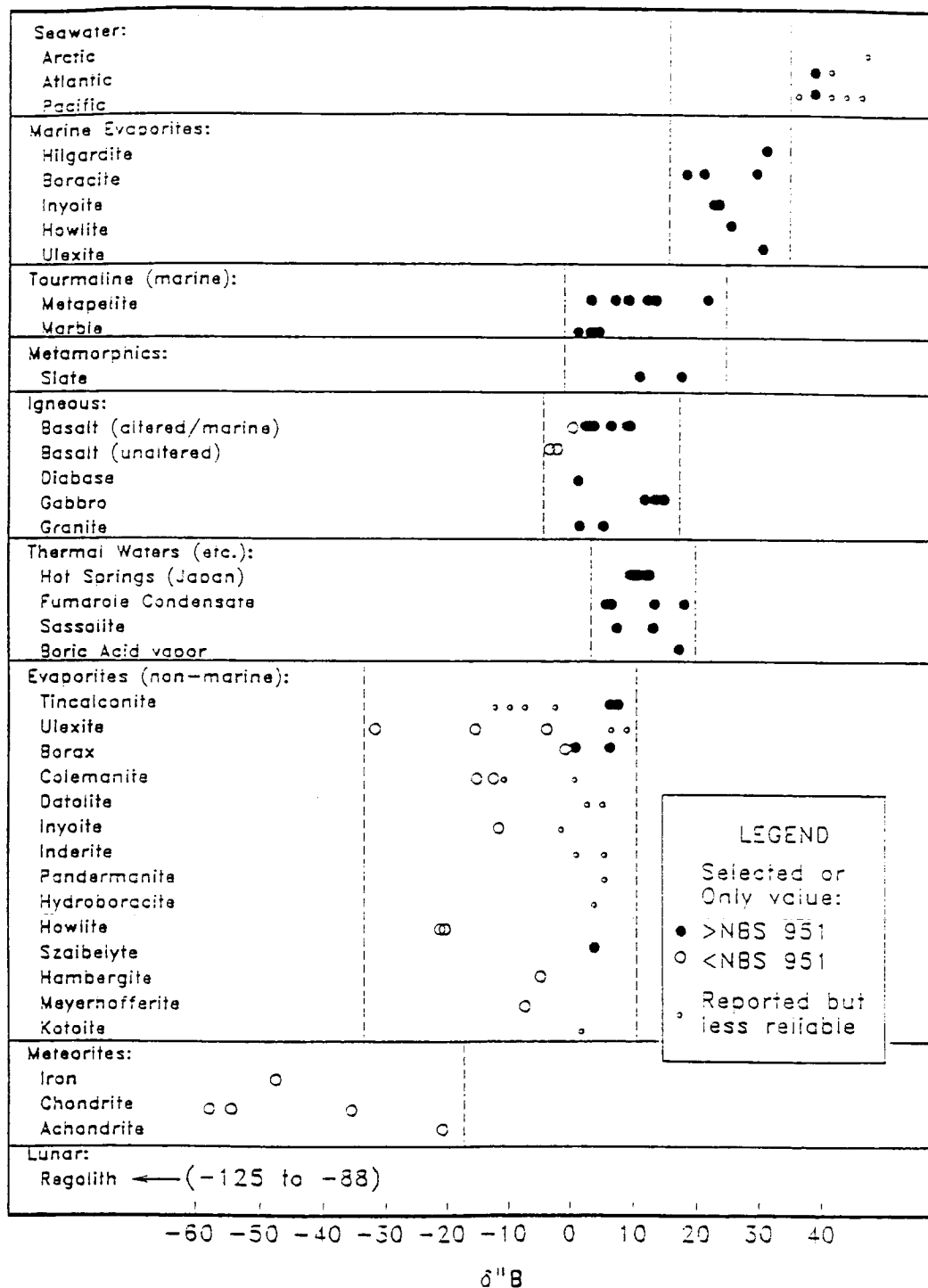


Figure 1.1 Selected values $\delta^{11}\text{B}$ for natural materials indicated by large circles, less reliable values generally with large standard deviations are presented as small circles (Bassett, 1990).

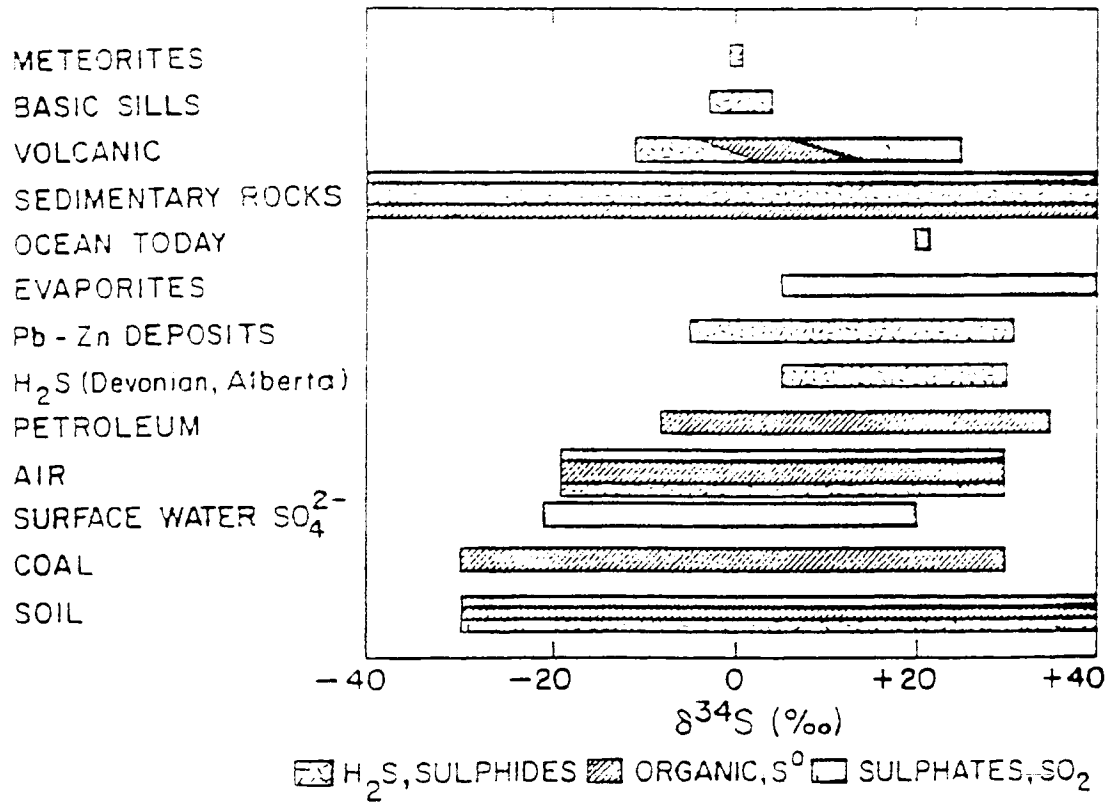


Figure 1.2 $\delta^{34}\text{S}$ values for natural materials (Krouse, 1980).

CHAPTER TWO

SAMPLE DESCRIPTION AND ANALYTICAL METHODS

2.1 Introduction

This chapter gives complete descriptions of all analytical methods used in this study. The first section provides sample descriptions which include chemical analyses and mineral content of the coal samples. The second and third sections provide detailed accounts of boron and sulfur extraction procedures for coal and its combustion products. In the last two sections, isotopic analyses are briefly discussed.

To ensure the accuracy of the experimental work, care was taken when preparing and storing reagents, standards, and experimental solutions. New Nalgene plastic bottles were used, and all standard and cleaning solutions were prepared in deionized water passed through a Millipore, four chambered Milli-Q water purification system.

2.2 Description of Samples

Three Illinois Basin coal samples were provided by the Illinois Basin Coal Sample Program (IBCSP) at the Illinois State Geological Survey (ISGS). One coal sample was obtained from the Coronado Generating Station which is operated by the Salt River Project (SRP).

The following descriptions of the Illinois Basin coal samples were provided by IBCSP. Sample IBC-101 is a Herrin (Illinois No. 6) coal obtained in 1983 from a commercial preparation plant in west central Illinois, and has a low pyritic sulfur value for a conventionally-washed coal. Sample IBC-102 is a Colchester (Illinois No. 2) coal obtained in 1983 from a western Illinois preparation plant at a mine which was closed after

the sample was obtained. This coal is low in organic sulfur and high in pyritic sulfur. Its pyrite is oxidized to sulfate when exposed to air at unpredictable rates. High sulfate sulfur, 0.2 to 0.3%, has been observed after overnight drying in air. The $\delta^{34}\text{S}$ of any remaining sulfide will be unaffected isotopically. Sample IBC-107 is a Herrin (No. 5) coal that has a significant difference in the $^{34}\text{S}/^{32}\text{S}$ ratios in the organic and pyritic forms of sulfur. This sample was taken from a central Illinois underground mine at a location where this large isotopic difference occurs naturally.

The SRP coal sample was obtained in January 1989 from the Coronado Generating Station which is located near St. Johns, Arizona. The utility plant has been supplied with coal from a mine in northwestern New Mexico for at least the past five years (Shirley, 1990).

The results of several standard analytical tests for the coal samples are given in Table 2.1 along with total boron concentrations. Additional data on minor and trace elements in the coal samples are in Appendix A. Also, mineral compositions of the IBCSP coal samples are provided in Table 2.2.

Fly ash samples from the IBCSP coals were obtained from burning each coal separately in a batch furnace at 800°C until combustion was complete. This was conducted at the Coal Research Center at Southern Illinois University under the direction of Dr. John Mead. Table 2.3 provides information on work conducted at the ISGS on the oxide content of high temperature (750°C) ashes of the IBCSP samples. The SRP fly ash sample was taken directly from the Coronado Generating Station in January 1989. No information was provided on the burning and furnace conditions at the plant.

The remaining descriptions of the field samples obtained from the Coronado Generating Station are provided in detail in Chapter 7.

Table 2.1 Analyses of IBCSP and SRP coal samples.

Percent	¹ IBC-101	¹ IBC-102	² IBC-107	³ SRP
Moisture	14.7	14.2	9.3	6.22
Volatile Matter	40.5	39.8	40.5	-
H-T Ash	10.5	6.9	11.5	16.21
Carbon	69.2	73.9	68.1	-
Hydrogen	5.1	5.3	5.0	-
Nitrogen	1.3	1.5	1.2	-
Oxygen	9.5	9.0	10.6	-
Sulfate Sulfur	0.05	0.06	0.26	<0.01
Pyrite Sulfur	1.27	2.29	0.48	0.15
Organic Sulfur	3.00	0.94	2.94	0.51
Total Sulfur	4.32	3.29	3.67	0.66
Boron (ppm)	193	109	102	200

¹Data obtained from Harvey and Kruse (1988).

²Data obtained from Kruse (1989).

³SRP coal analysis conducted at Hazen Research, Inc., Golden, CO (Appendix A).

Table 2.2 Mineral composition (wt% coal) of IBCSP coal samples.

¹ Mineral (%)	² IBC-101	² IBC-102	³ IBC-107
quartz	2.6	0.6	2.7
calcite	0.5	2.7	1.5
pyrite	2.1	4.0	0.9
kaolinite	3.3	1.0	1.2
illite	2.4	0.8	1.2
expandable	2.1	0.9	1.4
total mineral matter	13.0	10.0	13.9
⁴ Other minerals (minor or trace)	marcasite anhydrite szomolnokite	marcasite coquimbite	marcasite anhydrite coquimbite

¹Low temperature ash (140°C). Mineral values are normalized to this value.

²Data obtained from Harvey and Kruse (1988).

³Data obtained from Kruse (1989).

⁴Refer to Table 3.1 for chemical formulas of listed minerals.

Table 2.3 Oxide content of high temperature (750°C) ashes of IBSCP samples.

Oxide (%)	¹ IBC-101	¹ IBC-102	² IBC-107
SiO ₂	49.22	32.80	51.01
Al ₂ O ₃	17.30	15.45	19.00
Fe ₂ O ₃	17.00	40.57	11.78
CaO	4.85	2.83	5.22
MgO	0.96	0.66	1.00
K ₂ O	2.16	1.88	2.39
Na ₂ O	1.38	0.38	1.20
TiO ₂	0.95	0.93	0.89
P ₂ O ₅	0.18	0.11	0.04
MnO	0.04	0.04	0.07
SrO	0.04	0.02	0.04
BaO	0.05	0.05	0.05
SO ₃	4.34	2.36	5.85
Total	98.47	98.08	98.53
Ash	10.67	7.30	12.01

¹Data obtained from Harvey and Kruse (1988).

²Data obtained from Kruse (1989).

2.3 Boron Extraction Procedures

2.3.1 Water-soluble Coal and Soil

Although boron concentrations in coal have been analyzed for years using emission spectrographic analysis (Gluskoter, 1975; Dreher and Schleicher, 1975; Peterson and Zink, 1963), no work has been done on the extraction of boron from coal for isotopic analysis. A modified soil technique for determining boron by hot water extraction was used for both the coal and soil samples (Sabbe, 1980). Further work needs to be conducted on methods of extracting the insoluble boron fraction and total boron content in coals for isotopic analysis.

Water-soluble boron was extracted from four individual coal samples plus one duplicate using the hot water extraction procedure. 5.0 g of coal that had been ground to pass a 230 mesh (62.5 μm) sieve was mixed with 100 ml of deionized water. The mixture was placed in a 1000 ml three-neck round-bottom flask connected to a reflux condenser (Figure 2.1) and was allowed to boil for 15 minutes. The resulting solution was then immediately filtered using a vacuum flask and 0.45 μm filter and stored in a clean Nalgene bottle for boron concentration analysis. The percent soluble boron obtained from each extraction is given in Table 2.1 and was calculated from the total boron concentration in the coal. It is suspected that the low boron percentage computed for the SRP sample is the result of the reported boron concentration of the coal being too high. In addition, some of the soluble boron may adsorb to the coal before filtration causing all boron concentrations to be lower than actual values.

Two soil samples were also extracted for water-soluble boron. 50.0 g of soil that was ground to pass a 10 mesh (2 mm) sieve was mixed with 500 ml deionized water and was boiled for 15 minutes as described for the coal samples. The solutions were then

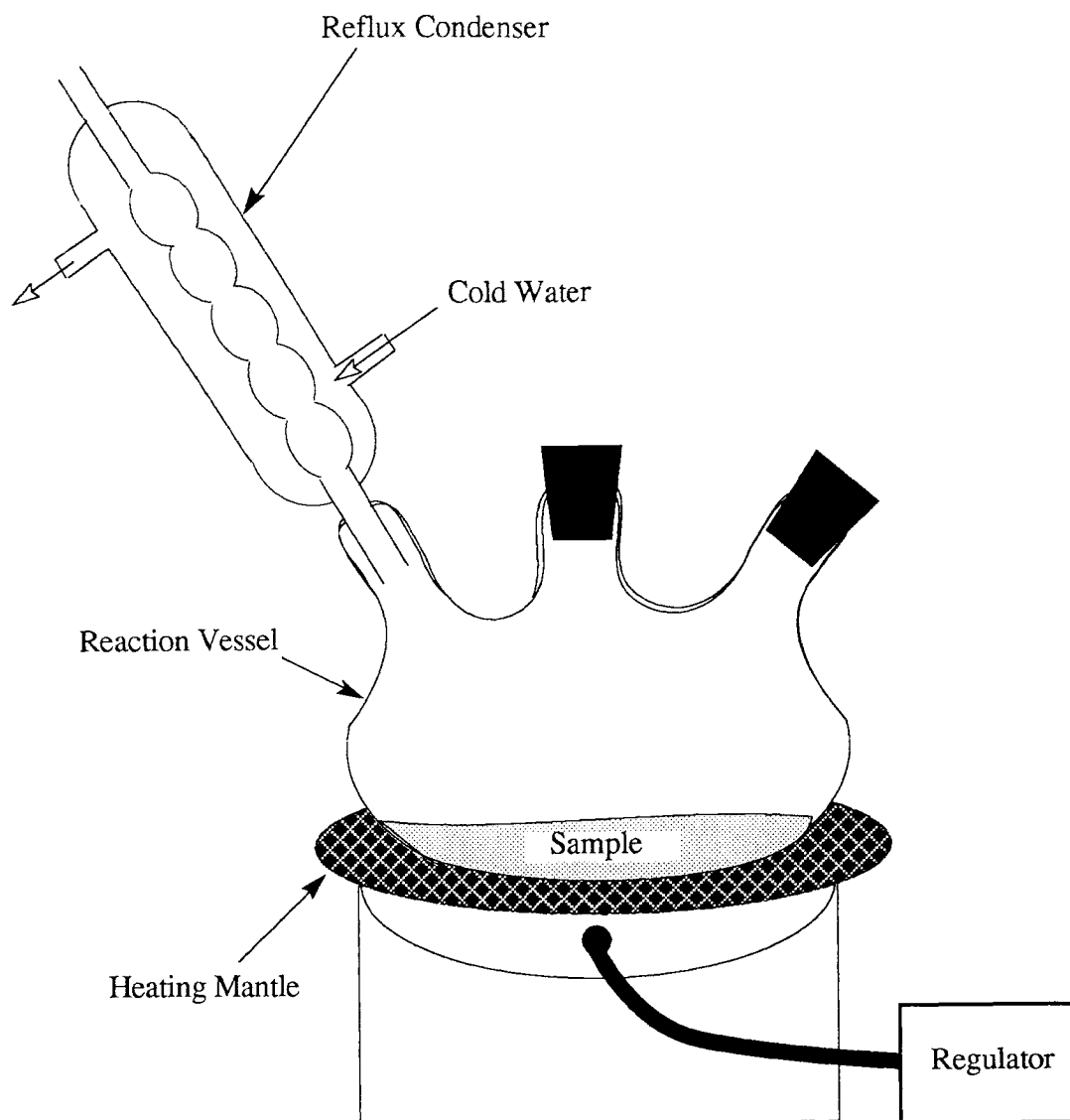


Figure 2.1 Apparatus for the extraction of water-soluble boron in coal and soil.

centrifuged before filtering because of the high sediment load. The resulting solution from the Chinle #40 soil sample was difficult to filter due to the probable presence of humic organics. Soluble boron percentages were not calculated, because the total boron content of the soils was not available.

Table 2.4 Boron concentration and percent soluble boron from hot water extraction method for four coal samples.

<u>Sample</u>	<u>*Boron Concentration (mg/l)</u>	<u>% Soluble Boron</u>
IBC-101	2.3	23.8
IBC-102	1.8	33.0
IBC-107	2.4	47.0
IBC-107-Dup	2.5	49.0
SRP	0.3	0.03

* analysis done by Skyline Labs, Inc.; Tucson, Arizona.

2.3.2 Fly Ash and Bottom Ash

Boron release from fly ash solid waste by leaching has been the subject of many studies. The solubility of boron from fly ash in water is primarily dependent on coal combustion temperatures. Ashing temperatures of greater than 1200°C and less than 800°C have produced ashes with solubilities of less than 10% and almost 100%, respectively (Cox et al., 1978; Mackay, 1978). In addition, the percent boron leached does not systematically increase with the total boron content in the fly ash (Pougnnet et al., 1990). Therefore, several mechanisms such as desorption of highly soluble borate minerals control the solubility of boron from fly ash.

Studies on the rate of desorption of boron from fly ash, reported in the literature, contain variable results. Although all authors have reported rapid initial dissolution,

contrasting results are given for the point of complete dissolution. Cox et al. (1978) reported complete dissolution of soluble boron within 15 minutes, while Halligan and Pagenkopf (1980) reported that steady state was achieved in 30 days. Davidson (1989) also reported desorption to be very rapid, with greater than 50% of the equilibrium concentration present in solution within 5 minutes, and over 80% within 30 minutes for all but one of the 24 hour desorption experiments for four fly ash samples.

Boron in bottom ash has been found to be almost totally insoluble (Cox et al., 1978). This was also confirmed in this study. Leaching 30.0 g of SRP bottom ash with 500 ml of deionized water for 30 minutes resulted in no boron above the analytical detection limit of 0.1 ppm.

A similar procedure to that used by Davidson (1989) was adopted for the leaching of four fly ash samples. 10.0 g of fly ash was weighed in a 1000 ml Nalgene beaker containing a teflon coated stirring bar. The slurry was stirred continuously for 30 minutes, and then allowed to settle for about one and a half hours. The solution was filtered using a vacuum flask and a 0.45 μm filter, and then stored in 1 L Nalgene bottles for subsequent extraction as discussed below. Boron concentrations from the fly ash leachates are given in Table 2.5.

Table 2.5 Boron concentrations of fly ash leachates.

<u>Sample</u>	<u>Boron Concentration (mg/l)</u>
101-Fly Ash	4.6
102-Fly Ash	8.1
107-Fly Ash	5.7
SRP-Fly Ash	0.55

2.3.3 Ion Exchange Resins

Boron must be extracted from solution for preparation of the sample for stable isotope analysis ($^{11}\text{B}/^{10}\text{B}$). Care must be taken to avoid fractionation of the isotopes by improper loading on the ion exchange column. Amberlite IRA-743 boron-selective ion-exchange resin, developed by Rohm & Haas Corp., has been used effectively for isolating boron from solution (Duchateau et al., 1986; Davidson, 1989). The resin forms complexes with the borate anion at pH above 4, and has a theoretical capacity of 5.7 mg of boron per cm^3 of resin (Rohm & Haas Corp., 1980). Davidson (1989) provides a detailed description of the resin chemistry. In general, ion exchange resins were used in this study for concentrating boron from sample solutions with concentrations below 0.5 ppm.

The procedure used in this study was based on sample procedures obtained from Bassett (1991). After aqueous samples were measured for boron content with inductively coupled plasma (ICP), the boron was extracted using an ion exchange resin column containing Amberlite IRA-743 resin. Sample volumes and subsequent elutions were passed through the columns at a rate of approximately 1 ml/min using a peristaltic pump with multi-tube apparatus. The maximum capacity of the resin for the sample volumes used was determined to be below two ml of resin. Before each extraction, the resin was cleaned with two rinse cycles of 50 mls of 2 N HNO_3 , 20 mls of NaOH , and 50 mls of Milli-Q water. After sample volumes were passed through the columns, each column was eluted using 0.1 N HNO_3 . The eluate containing boric acid was then evaporated in teflon beakers at temperatures $<75^\circ\text{C}$ to boron concentrations of greater than five ppm.

2.3.4 Methyl Borate Distillation

The methyl borate extraction distillation procedure has been found to be an accurate quantitative method for extracting boron from aqueous solution without fractionation

(Kanzaki et al., 1979; Spivak and Edmond, 1986; Land and MacPherson 1989). Boron is effectively and selectively volatilized as methyl borate, $B(OCH_3)_3$, during distillation leaving behind matrix solutes and acids.

The methyl borate extraction apparatus is shown in Figure 2.2. Care must be taken to perform the distillation in a dust-free environment to avoid collection of impurities in the receiving beaker. Seventy-five ml of Optima-grade (99.9%) methanol was measured into the distillation vessel which was in a 70-80°C water bath. After connecting the funnel, 15 ml of methanol was allowed to distill in a waste container to ensure boron-free methanol. Up to 3 ml of sample solution containing 15 to 20 µg of B was rapidly added through the funnel to the methanol. The distillate was collected in 50 ml of Milli-Q water in a Teflon 100 ml beaker at a rate not exceeding 0.75 ml/min (Spivack and Edmond, 1986). This solution was evaporated to dryness in Teflon vials at about 70°C and saved for mass spectrometric analysis.

2.4 Sulfur Extraction Procedures

2.4.1 Coal

Sulfur is present in coal in several chemical forms which can include sulfates, iron sulfides, and organic sulfur. Therefore, an analytical method is preferred which incorporates quantitative, sequential extraction of sulfur without causing isotopic fractionation in the remaining sulfur. The order in which sulfur was extracted in this study was fracture-coating pyrite, acid-soluble sulfides and sulfates, disseminated pyrite, and organic sulfur.

The reductive lithium aluminum hydride (LAH) method allows for the extraction of disseminated pyrite without reaction with the remaining organic fraction. LAH reduces the

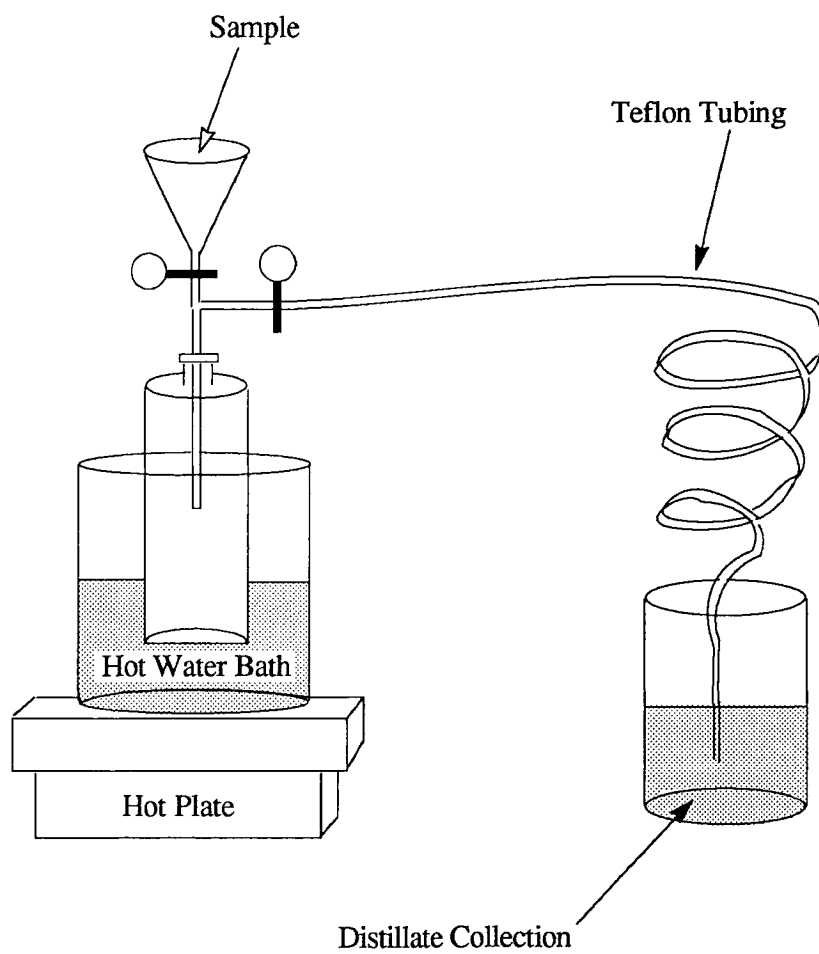


Figure 2.2 Methyl borate distillation apparatus.

pyrite releasing the sulfides as H_2S upon the addition of concentrated HCl . When passed through cadmium acetate solution, the H_2S containing the pyritic sulfur is precipitated as CdS . The remaining organic fraction in the coal residue is oxidized to sulfate by combustion with 3 parts, by weight, of MgO and 2 parts Na_2CO_3 . Kuhn et al. (1973) give a complete discussion of the LAH reduction method in comparison to other oxidation and reduction methods in determining the forms of sulfur in coal. In addition, Price and Shieh (1979) report that more than 94% of the disseminated pyrite is recovered from <230 mesh (63 μm) coal by LAH treatment. Therefore, cross contamination of disseminated pyrite and organic sulfur is negligible using the LAH method.

Extraction procedures for isolating the various forms of sulfur in coal used in this study were modified from those described by Westgate and Anderson (1982) who developed a complete extraction procedure by combining several standard techniques. Their procedure has been used successfully in several investigations on sulfur isotopes in coal (Price and Shieh, 1979; Westgate and Anderson, 1984; Hackley and Anderson, 1986).

Sulfur extractions for isotopic analysis were conducted on four coal samples, one in duplicate. Prior to beginning chemical extractions of the various forms of sulfur, any pyrite that was visible to the eye was hand-picked from 20.0 g of coal and was called fracture-coating pyrite. No massive pyrite was observed. Sample IBC-102 was the only coal that had appreciable visible fracture-coating pyrite. Samples of fracture-coating pyrite were concentrated by using a scalpel to flake portions from the coal. The remaining coal was ground to less than 230 mesh (63 μm) and dried at 60°C to constant weight.

The next step involved removing acid-soluble sulfides and sulfates by a hot acid treatment. 10.0 g of dried, 230 mesh coal sample was placed in a 1000 ml three-neck-round-bottom flask. One hundred ml of 4.8 M HCl was added, and the flask was attached

to the extraction apparatus (Figure 2.3). The mixture was heated using a heating mantle and rheostat, and was maintained at just below boiling for at least one hour under a constant flow of N_2 (g) at 0.5 L/min. Any acid-soluble sulfides were liberated as H_2S (g) and precipitated as CdS (s) in the cadmium acetate solution (Figure 2.3). However, during all treatments no CdS was ever observed during this step. In addition, because of the insignificant amount of sulfates in all of the coal samples, sulfate sulfur determinations were not performed. After the hot acid treatment was completed, the residual solids remaining in the flask were filtered and rinsed with 35 ml of 0.5 M HCl. The solids were washed with deionized water until the filtrate reached pH 4. The residue was dried at $60^\circ C$ to constant weight and saved for the next step. The filtrate was discarded.

Sulfur in the form of disseminated pyrite was then extracted using the LAH method. Special care was used in handling the unstable LAH by weighing the material into vials in a N_2 (g) filled glove bag. After being vacuum dried at $60^\circ C$ for two hours, 5.0 g of acid-leached coal was placed into the reaction flask connected to the extraction apparatus. 1.5 g of LAH was carefully added to the coal sample after starting the flow of N_2 (g) as described previously. (1.5 g of LAH is capable of reducing up to 200 mg of pyrite (Westgate and Anderson, 1982)). Seventy-five ml of treated tetrahydrofuran (THF) which was dried over 3 angstrom molecular sieves before use, was slowly added to the coal-LAH mixture using a 125 ml addition funnel. The mixture was heated to $85^\circ C$ for 45 minutes. To ensure proper refluxing in the system, an ice bath was used for a constant discharge of cold water through the condenser. After heating, the traps were removed from the condenser and the heating mantle was replaced with an ice bath. The condenser was then reconnected to the traps and 1.0 ml of deionized water was slowly added dropwise to the coal-LAH mixture using a micropipet. After quenching was complete, 75 ml of deionized water was slowly added using the addition funnel. Next, 75 ml of concentrated

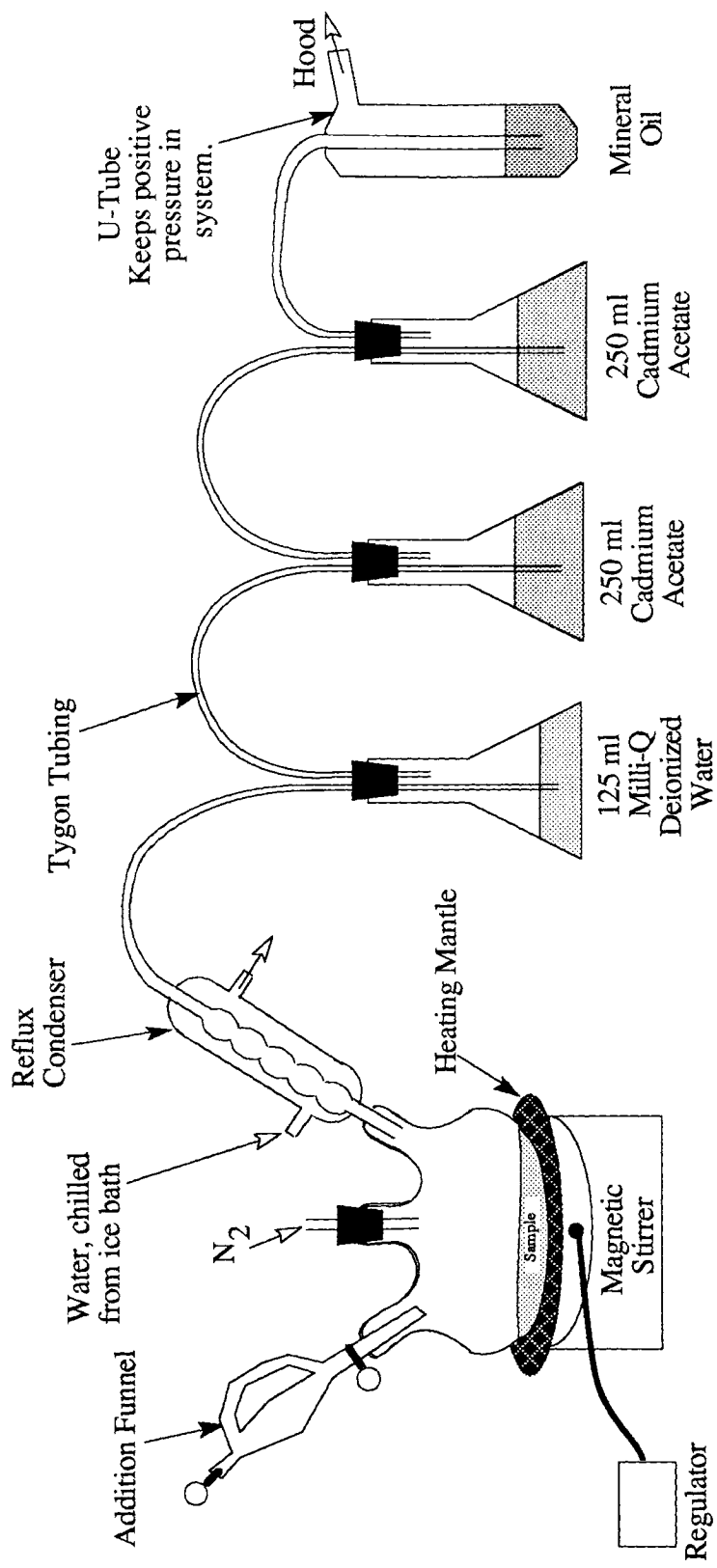


Figure 2.3 Extraction apparatus used in the lithium aluminum hydride (LAH) method for sequentially extracting the various forms of sulfur.

HCl was also added through the addition funnel, and the ice bath was replaced by the heating mantle. The mixture was heated to 90°C for about three hours. The CdS precipitate in the cadmium acetate solution was allowed to settle over night, decanted, and finally dried and stored for direct isotopic analysis. The coal-LAH residue was filtered, thoroughly rinsed with deionized water, and dried to constant weight at 60°C. This residue was saved for the extraction of organic sulfur.

The remaining organic sulfur fraction in the coal residue was oxidized to sulfate by combustion with Eschka compound (3 parts, by weight, of MgO and 2 parts Na₂CO₃) based on the American Society of Testing Materials (ASTM) method D3177 (1990). 2.0 g of coal-LAH residue was thoroughly mixed with 6.0 g of Eschka compound. Additional Eschka compound was used so that no coal remained exposed. The crucible was then placed in a Thermolyne Type 6000 Programmable Ashing Furnace and was slowly heated to 800°C which was maintained for 1.5 hr. The sample was allowed to cool overnight in the furnace. The solids from the crucible were then put into a beaker that contained 150 ml of hot deionized water. The beaker was covered with a watch glass and heated to below boiling for 30 minutes. This solution was then filtered, and the solids were rinsed with additional deionized water. The filtrate containing the soluble sulfates was saved for barium sulfate (BaSO₄) precipitation while the solids were discarded. In addition, the total sulfur was also obtained by the same procedure described for organic sulfur except that a freshly ground (230 mesh) coal sample was used.

Finally, the filtrates containing the total and organic sulfur were precipitated as BaSO₄. A pH below 2 was obtained for each filtrate using 2 N HCl and samples were then warmed on a hot plate. Twenty ml of BaCl₂ (100 g/l) was added, and the mixture was heated to just below boiling for two hours. The solution containing the BaSO₄ precipitate was allowed to settle overnight, decanted, and then evaporated to dryness. As the resulting

product did not have the appearance of pure BaSO_4 , an acid rinse was performed. Fifty ml of 2 N HNO_3 was placed in a beaker with the BaSO_4 and heated at a moderate temperature for one hour. The solution was then filtered using a 0.45 μm filter and vacuum flask and thoroughly rinsed with deionized water. Finally, the filter containing the BaSO_4 was placed on a watch glass and dried at 105°C. The BaSO_4 was scraped into a labeled vial and stored for isotopic analysis.

2.4.2 Fly Ash

Methods for sulfur extraction of fly ash were based on a study by Elsewedi et al.(1980). They discovered that elements of low to moderate solubility such as sulfate showed greater dissolution when water to fly ash ratios were increased. For example, 0.2% and 15.3% of sulfate was extracted when 5 ml/g and 80 ml/g, respectively, of fly ash was used. They concluded that the low solubility of sulfate was caused by the inability of water to extract gypsum encased in insoluble ash material. No further attempt was made to study the desorption characteristics of sulfate in fly ash.

A preliminary investigation using SRP fly ash (20 ml/g) was conducted to determine the equilibrium state and rate at which sulfate is removed from fly ash under atmospheric conditions. If sulfur removal from fly ash does not reach an equilibrium state, isotopic fractionation processes such as diffusion, dissolution, and adsorption may be active in the system. This would cause difficulty in using sulfur isotopic ratios accurately to identify ground water mixed with leachate, because of varying $^{34}\text{S}/^{32}\text{S}$ ratios through time. Results indicated that desorption of sulfate is rapid in the first 30 minutes with equilibrium reached in 24 hrs. These results agreed with the method described by Elsewedi et al.(1980) who also leached their fly ash samples for 24 hrs.

Water to fly ash ratios were increased for the leaching of the Illinois fly ashes to 50

ml/g. 10.0 g of fly ash along with a teflon coated stirring bar were placed into a 1 L Nalgene bottle. Five hundred ml of deionized water was added, and the mixture was allowed to stir continuously for 24 hr. with the caps secured. After settling for about one hour, the solution was filtered using a vacuum flask and 0.45 μm filter. A small amount of deionized water was used to rinse the ash for any remaining sulfate. The resulting leachate was precipitated for BaSO_4 as described in the previous section.

2.5 Boron Isotopic Analysis

Boron isotope ratios ($^{11}\text{B}/^{10}\text{B}$) were measured using thermal ionization mass spectrometry in the positive ion mode at the University of Arizona under the direction of Dr. R. L. Bassett. Bassett (1991) provides a full description of procedures used for sample loading and analysis and is summarized as follows. The distilled boric acid from the methyl borate distillation is evaporated to dryness and resolubilized in 4 microliters of a sodium carbonate solution to produce a 1:1 mass ratio of B:Na. The boric acid/sodium carbonate solution is placed onto a Ta filament reaching a minimum 5 μg boron loading. The beads are then heated to dryness in a filament loader at 0.6 A and flashed to about 1.0 A until the bright white solid phase sodium borate is visible.

2.6 Sulfur Isotopic Analysis

Isotope ratios of $^{34}\text{S}/^{32}\text{S}$ were measured by Dr. C. J. Eastoe at the Laboratory of Isotope Geochemistry at the University of Arizona. Analytical precision based on repeated measurements on a lab standard is $\pm 0.3\text{‰}$ (2σ). Sulfate in BaSO_4 was converted to SO_2 by heating with SiO_2 and Cu_2O for 15 minutes at 1100°C (Coleman and Moore, 1978).

Sulfide in CdS was converted to SO₂ by heating with Cu₂O at 950°C for 10 minutes (Robinson and Kusakabe, 1975). The spectrometer takes alternate measurements of a reference standard and the unknown sample to obtain an average for calculating the values.

CHAPTER THREE

COAL COMBUSTION CHEMISTRY

3.1 Introduction

A discussion of the coal combustion chemistry is provided to establish sufficient background in coal chemistry and combustion theory. The first section deals with basic coal chemistry and focuses on the initial mineral and organic phases in coal. In the second section, coal combustion processes are described using a simplified model of what happens to a coal particle upon combustion. In addition, explanations of the chemical changes which occur in the mineral and organic phases in coal during combustion are provided based on solid waste products and gas emissions. A brief discussion of various combustion systems and their effects on combustion products is also provided. Chapters Four and Five give more detailed information on the boron and sulfur isotopic partitioning in coal and its combustion products.

3.2 Coal Chemistry

3.2.1 Mineral Content

Mineral matter in coal is defined in various ways in the coal literature. Some authors limit the definition to include only distinct mineral grains such as quartz and clay minerals that are embedded within the organic matrix. Other authors extend this definition to also include all elements except organically derived or organically bound C, H, N, O, and S (Gluskoter, 1975). For the purpose of this study, the latter definition will be used.

On the basis of origin, coal minerals are subdivided into three categories as detrital, vegetal, and chemical. A detrital origin is a source external to the peat-forming swamp where particulate matter is transported into the swamp by wind but primarily by water. Minerals of vegetal origin are derived from the inorganic constituents of swamp plants. All plants contain inorganic material (Conner and Shacklette, 1975) such as alumina and silica. The abundance and composition of this inorganic material depends upon the plant species, the type of plant tissue, the climate, and the soil-bedrock geology of the site. In general, woody tissue which composes most of the organic component of coal contains lower concentrations of inorganic material than bark and leaves (Renton, 1982). Finally, minerals of chemical origin were formed by direct chemical precipitation from aqueous solutions or from chemical reactions between these solutions and inorganic or organic materials already present in the peat or the coal. Sources for solutes include weathering of rocks and decomposition of plant material.

The emplacement of mineral matter in coal occurs throughout the history of the coal. The time of emplacement is generally divided into either syngenetic or epigenetic phases.

Syngenetic mineral emplacement occurs during diagenesis, and includes all minerals incorporated into coal from the earliest peat-accumulation stage to the beginning of the metamorphic stage. By this definition, most minerals in coal are syngenetic. Syngenetic emplacement is divided into early and late phases.

The minerals emplaced during early syngenetic phases or peat-accumulation stages are from detrital, vegetal, or chemical origins. During the initial composition of plant debris, silica and alumina amorphous materials contained within the plant tissues are released into the peat, where they later form silicate minerals. In addition, chemically precipitated disulfides in the form of pyrite are commonly found in recently formed peat (Renton, 1982). Finally, any minerals of detrital origin would also be introduced into the peat at this

stage.

The later syngenetic phase of mineral emplacement begins after burial of the peat and during humification-gelification stages of coalification (Renton, 1982) which are described in more detail in the next section. The minerals of the late syngenetic phase are entirely chemical in origin, because further addition of materials of detrital and vegetal origins is excluded upon burial of the peat. Minerals formed during this stage are from ions released into solution as a result of the chemical decomposition of basic molecules of both the peat and the already present coal. Minerals emplaced into coal at this time are carbonates, disulfides, and clay minerals.

The second phase of mineral emplacement is epigenetic emplacement which includes minerals incorporated into coal during metamorphism. Major fractures in the coal beds allow for the movement of groundwater solutions containing mineral-forming ions through the coal bed. Mineralization occurs along these fractures.

Minerals commonly found by X-ray diffraction analysis of low-temperature ash from various grades of coal are given in Table 3.1. The silicate minerals represent 80-90% of the total mineral content in coal (Renton, 1982), with the clay minerals being the most abundant. Of the clay minerals, kaolinite and illite are the most abundant and are usually found in association with each other. Both kaolinite and illite form during syngenetic mineral emplacement and are found concentrated along bedding planes. In addition, kaolinite is also a common epigenetic mineral, and is found in natural fractures in the coal. The second most abundant silicate mineral in coal is quartz having an average content of 20-30% (Mitchell and Gluskoter, 1976). Rarely found in epigenetic occurrences, quartz is a syngenetic mineral and can be of detrital, vegetal, or chemical origin.

After the silicate minerals, the remaining assemblage is dominated by carbonates and disulfides. The carbonate minerals, of which calcite is the most abundant, are of chemical origin formed during the late syngenetic and epigenetic phases of mineral

Table 3.1 Common coal minerals (Renton, 1982).

Major	Silicates	Clay minerals	Kaolinite	$\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$
			Illite	"
			Mixed layer	"
			Chlorite	$(\text{MgFeAl})_6(\text{SiAl})_4\text{O}_{10}(\text{OH})_2$
			Quartz	SiO_2
		Carbonates	Calcite	CaCO_3
			Dolomite	$\text{Ca} \cdot \text{Mg}(\text{CO}_3)_2$
			Ankerite	$\text{Ca}(\text{FeMg})\text{CO}_3$
			Siderite	FeCO_3
			Disulfides	Pyrite
Marcasite	FeS_2 (orthorhombic)			
Minor		Sulfates	Coquimbite	$\text{Fe}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$
			Szomolnokite	$\text{FeSO}_4 \cdot \text{H}_2\text{O}$
			Gypsum	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$
			Bassanite	$\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$
			Anhydrite	CaSO_4
		Feldspars	Jarosite	$\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6$
			Plagioclase	$(\text{NaCa})\text{Al}(\text{AlSi})\text{Si}_2\text{O}_8$
		Sulfides	Orthoclase	KAlSi_3O_8
			Sphalerite	ZnS
			Galena	PbS
Trace		Pyrrhotite	FeS	
		Trace minerals		

^a Illite has a composition similar to muscovite— $\text{KA}l_2(\text{Si}_3\text{Al})\text{O}_{10}(\text{OH})_2$ —except for less K^+ and more SiO_2 and H_2O .

^b Mixed layered clays are usually randomly interstratified mixtures of illitic lattices with montmorillonitic and/or chloritic lattices.

emplacement. The disulfides, predominately pyrite and marcasite, form during both the syngenetic and epigenetic phases. Compared to early syngenetic mineral deposits, pyrite emplaced in the late syngenetic and epigenetic stages are characterized by more massive morphological occurrences i.e. filling cavities and fractures, overgrowing previously formed disulfides, and replacing coal macerals.

Sulfates are common in most coals, having the highest concentrations in coals with high disulfide contents (Renton, 1982). Bassanite is the most common and gypsum is the least abundant of the calcium sulfates, while szmolnokite is the more common iron sulfate.

In contrast to the major and minor minerals, trace minerals in coal are generally present in concentrations not exceeding a few percent, with many mineral phases in the ppm range. Trace mineral content in coal allows for a better understanding of the trace element distribution. According to Gluskoter et al. (1977), most trace elements in coal have associations with inorganic matter with the exception of beryllium, boron, and germanium which are predominately combined with the organic coal substance.

3.2.2 Organic Phases

Almost all organic matter in coal is classified as macerals. Macerals are the organic remains of plant debris that were altered to peat upon decomposition, and were then further converted into coal by increased temperature and pressure through time. Comprising the combustible fraction of coal, macerals account for >50 wt. % of the coal mass (Schopf, 1956), with the total amount depending upon the mineral content of the coal.

Macerals are divided into three major groups as exinite, vitrinite, or inertinite on the basis of differing optical properties. Exinites are derived from spore and pollen coats, cuticles, resins, and other fatty secretions. Vitrinites, which compose most of the coal, originates from decomposed woody tissue. Finally, inertinites are derived mainly from partial carbonization by fire of various plant tissues in the peat swamp stage.

The following is a brief account of the history of organic phase incorporation into coal. During early syngenetic and peatification stages, less-resistant plant tissues are decomposed by microbial activity and converted into gases and water. More-resistant plant tissues, such as lignin and cellulose, survive and become concentrated in the peat. Upon burial of the peat, the lignin and cellulose are oxidized and converted into humic acids by the process of humification. The humic acids then complex with cations such as calcium, aluminum, and iron. These products of humification are then further modified as the coalification process continues by gelification where fundamental structural changes occur within the organic material. These changes include the loss of various functional groups, the decomposition of carboxylic acid groups with the formation of CO₂, and the conversion of organic materials into complex organic molecules known as humins which are the precursors to vitrinite macerals. In addition, elements originally held in organometallic complexes are released into solution, water is expelled through desiccation, and the organic material becomes more aromatic in character. By the time the epigenetic phase begins, the geochemical coalification process has proceeded to the point where the organic portion of the coal has become relatively inert. Therefore, the organic phase of the coal is no longer a major source of ions to the surrounding ground water or able to react with ground-water solutions.

3.3 Coal Combustion

3.3.1 Combustion Processes

Coal combustion is a complicated process due to the complexity of the physical and chemical properties of coal. In general, combustion produces heat by oxidizing the organic phase of coal to carbon dioxide and water, while the nonvolatile inorganic constituents are

transformed into coal ash residues. In more general terms, combustion involves a wide variety of reactions among reactants, intermediates, and products. The reactions can occur simultaneously and consecutively in forward and reverse directions, and may even approach equilibrium conditions. During the heating and burning processes, the physical and chemical structure of the coal particle transforms continuously, resulting in an extremely complex system.

An understanding of coal transformations during pyrolysis, ignition, and burning was developed along with descriptions of oxidation processes on the surface and vicinity of the coal particle. To accomplish this task, a simplified, conceptual model of the combustion process using a single coal particle was used. More detailed and technical information on coal combustion processes can be obtained from the coal literature (Speight, 1983; Berkowitz, 1985; Smoot and Smith, 1985).

A schematic diagram of a coal particle with constituents and reaction processes is given in Figure 3.1. Coal reactions can be divided into four stages based on transformations resulting from pyrolysis. Pyrolysis is the process involving extensive thermal decomposition of the coal structure through progressive oxidation. The initial constituents of the coal particle consist of moisture, raw coal, and ash or mineral matter. The first stage, condensation reactions, occurs at 175-200 °C and accounts for only limited thermal alteration of the original molecular structures (Berkowitz, 1985). Moisture in the coal is vaporized into steam and some condensible hydrocarbons such as tar are expelled. During the second stage, massive thermal decomposition characterizes the devolatilization of the raw coal particle when temperatures reach between 350-550 °C (Berkowitz, 1985). Coal volatiles and heavy tarry substances are emitted in amounts varying from a few percent up to 70-80% of the total particle weight (Smoot and Smith, 1985). This entire process can occur in a few milliseconds or several minutes depending on coal size and type, and on temperature conditions. The residual mass contains ash and char which is

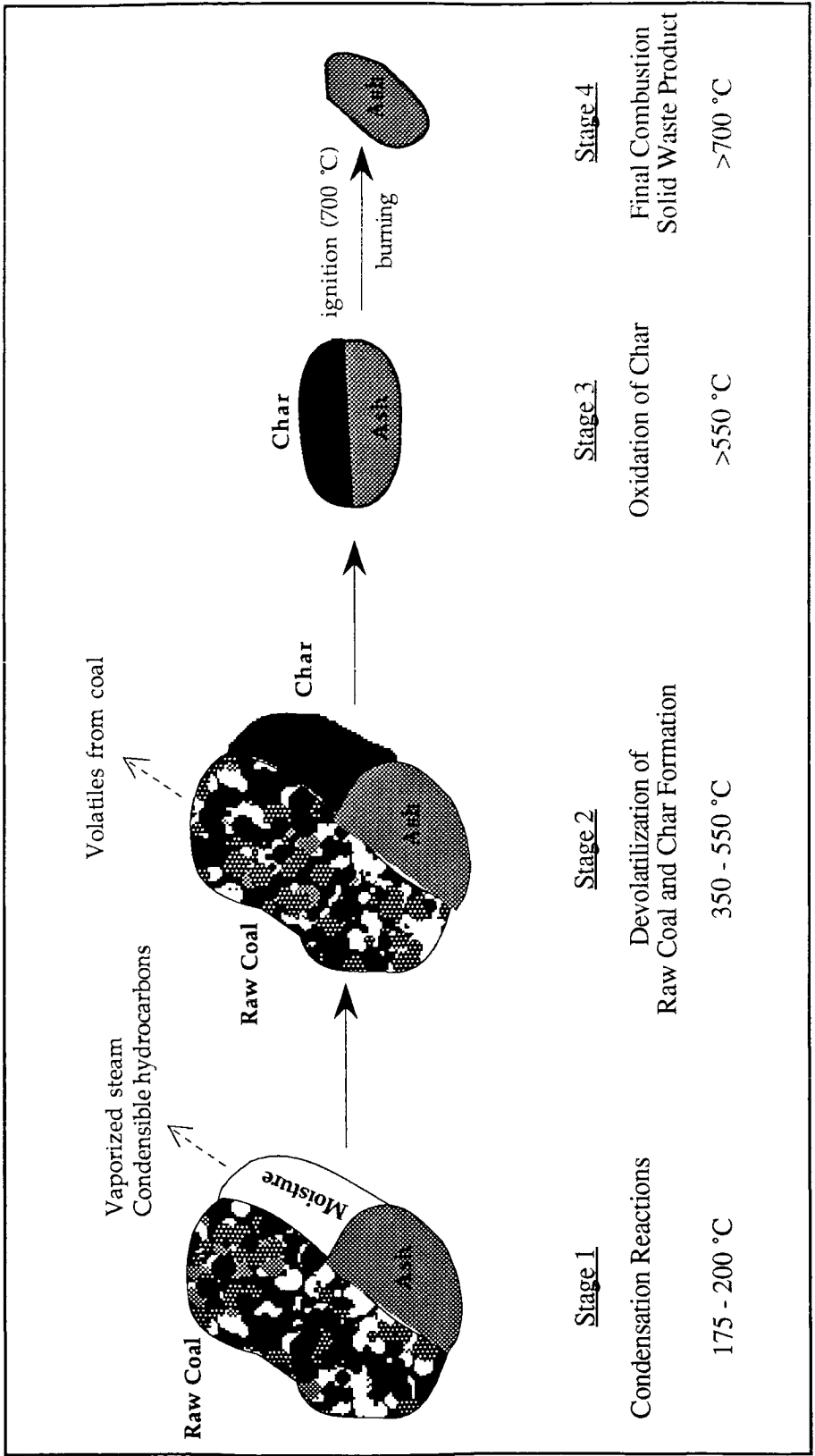


Figure 3.1 Schematic diagram of coal particle with constituents and reaction processes during pyrolysis and combustion.

altered raw coal enriched in carbon and depleted in oxygen and hydrogen. Char also contains some nitrogen and sulfur. Oxidation of the residual char happens in the next stage at temperatures greater than 550 °C (Berkowitz, 1985). The residual char particles are then oxidized to primarily elemental H₂ and CO or burned away by direct contact with oxygen after ignition which usually occurs at 700 °C (Speight, 1983). The final, noncombustible product is a crystalline material or ash which is the remains of the mineral matter.

Occurring on the surface and in the vicinity of the coal particle, oxidation processes are an integral part of the coal combustion system. Oxidation reactions in the immediate vicinity of a burning coal particle are shown in Figure 3.2. During the first stage of pyrolysis, oxygen adsorbs onto the surface of the raw coal particle, and reacts quickly with the hydrogen forming elemental hydrogen and water. With increasing temperatures, the carbon oxidizes producing carbon dioxide and carbon monoxide. In addition, sulfur oxides are volatilized along with the hydrogen and carbon to surround the coal particle with a vapor cloud. This vapor cloud can control the access of oxygen to the surface of the coal particle, and is also a zone of secondary oxidation and reduction reactions.

Ignition of a coal particle is determined by competition between pyrolysis and surface oxidation, and is dependent upon the volatile matter content, heating rate, and particle size. If the particle is small and heats rapidly, massive release of volatiles is delayed causing the combustion of vaporized hydrocarbons and solid carbon to proceed simultaneously. However, if heating rates are excessive or if the particle is large, the discharging volatile matter will block oxygen from reaching the particle surface and delay ignition until volatiles are consumed by combustion.

When a coal particle is oxidized, the result is heat, combustion products (CO₂ and water vapor), and pollutants. The volatile pollutants of the greatest environmental concern are the sulfur oxides. Sulfur oxides emitted from coal combustion are a function of the

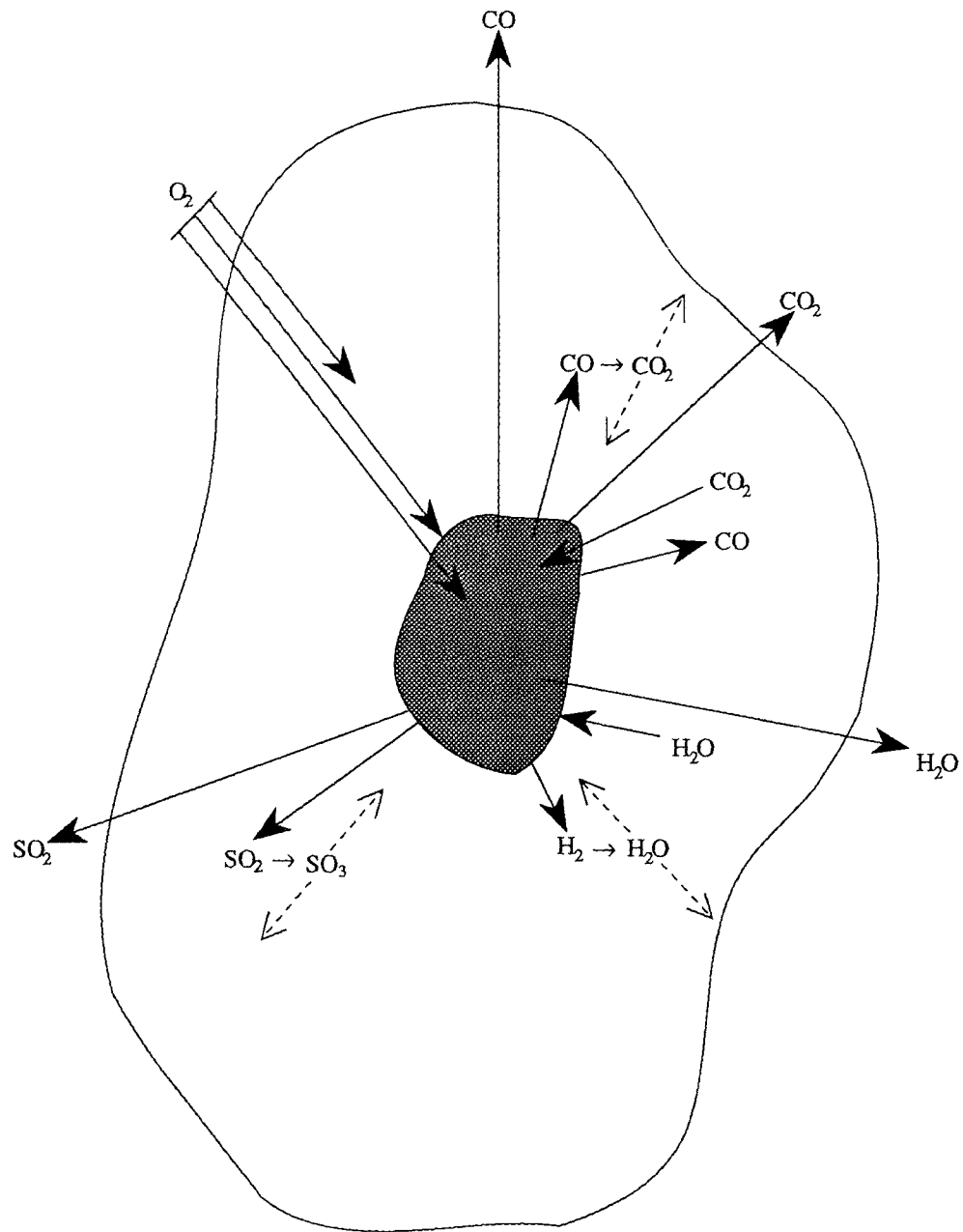


Figure 3.2 Oxidation reactions in the immediate vicinity of a burning coal particle (Berkowitz, 1985).

sulfur and ash composition of the coal. According to Levy et al. (1981), alkaline oxides (CaO, MgO, K₂O, and Na₂O) which may constitute 5-30% of the ash, will capture as much as 60% of the sulfur due to the alkaline content. The remaining sulfur in the coal is emitted as SO₂. During combustion processes, one to two percent of the SO₂ produced is converted to SO₃ (Levy et al., 1981).

3.3.2 Combustion Products

The combustion of coal results in the formation of a variety of pollutants including particulates, gases, volatile organics, and trace elements. The path of these pollutants in a typical power plant is illustrated in Figure 3.3. During combustion, coal is separated into bottom ash or flue gas which contains suspended fly ash and volatile elements or compounds. Bottom ash is angular and mostly noncrystalline material that accumulates in the boiler as the coal melts to a viscous liquid. Periodically quenched with water, bottom ash is flushed from the boiler and then sluiced to settling ponds for disposal (Figure 3.3). Meanwhile, the flue gas is forced through mechanical collectors where particles (>10 μm) are removed and routed to the disposal area (Roy et al., 1981). Using blowers, the flue gas carrying the remaining fly ash particles are passed through either an electrostatic precipitator or a wet scrubber or both. The fly ash collected from these devices, which have a total efficiency of 99.5% (Roy et al., 1981), is also routed to the disposal area. Volatiles and any remaining fine, fly ash particles are discharged into the atmosphere through the stacks.

The elemental composition of fly ash is variable and is directly related to elemental variations in the parent coals. Elemental partitioning behavior during combustion is dependent upon the initial state of the element in the coal. The following is a summary of a scheme proposed by Klein et al. (1975) that outlines the origins and transformations of

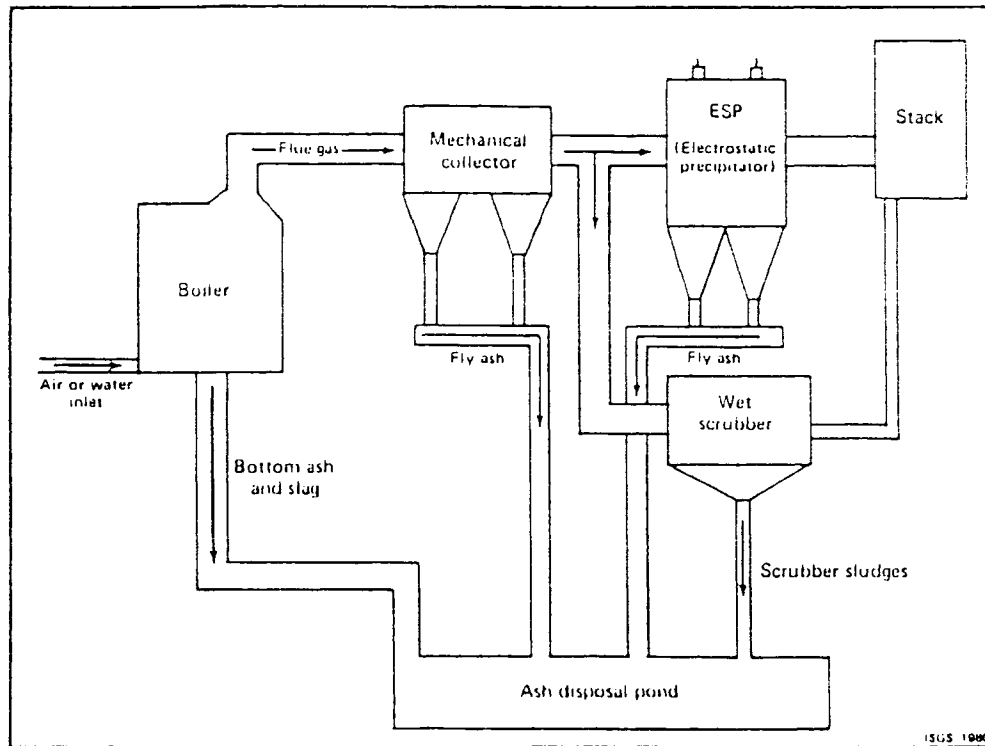


Figure 3.3 Generalized path of combustion products at a typical power plant (Roy et al., 1981).

elements and minerals during combustion:

(1) Trace elements in coal are present in aluminosilicates, as inorganic sulfides, or as organic complexes.

(2) Upon combustion, the aluminosilicates are not decomposed, but rather melt and coalesce to form the bottom ash and fly ash.

(3) During the initial stages of combustion, the conditions in a coal particle and within its immediate vicinity are probably reducing. Under these conditions, the chemical bonding between metallic elements and sulfur in sulfide minerals or between the elements and the organic matrix is broken, and these elements form volatile species. If the elements are dispersed in the coal organic matrix, they become initially dispersed in the gas stream when the coal is burned. Therefore, even those elements that are not as stable as the vapor at the combustion temperature, initially enter the flue gas stream.

(4) The elements initially volatilized into the flue gas stream may then be oxidized to form less volatile species which may then condense or be adsorbed on the fly ash as the temperature of the flue gas drops.

(5) Since the bottom ash is in contact with the flue gas for a short time and at a high temperature compared to the fly ash, condensation of volatiles on the bottom ash is minimal.

The above scheme illustrates the fact that elements tend to be more enriched on fly ash than bottom ash, because of the longer contact time of the fly ash with the flue gas stream. Another factor is the relationship between decreasing particle size and increasing elemental concentrations (Davison et al., 1974; Roy et al., 1981). When elements or compounds are volatilized during coal combustion, they either condense or adsorb onto entrained particles. Therefore, the mass deposited is greatest per unit weight for the smallest particles i.e. fly ash.

The chemical composition of fly ash is also directly related to the mineral and organic phase changes produced by heating. As coal is a complex system involving mixtures of silicates, sulfides, sulfates, carbonates, etc., it is beyond the scope of this study to explain fully all the reactions involved. However, some comments are provided from Mitchell and Gluskoter (1976) on several of the mineral alterations which are also summarized in Figure 3.4. Quartz is the most persistent of the coal minerals being an important constituent at temperatures as high as 1100°C. Illite and mixed-layer clays are

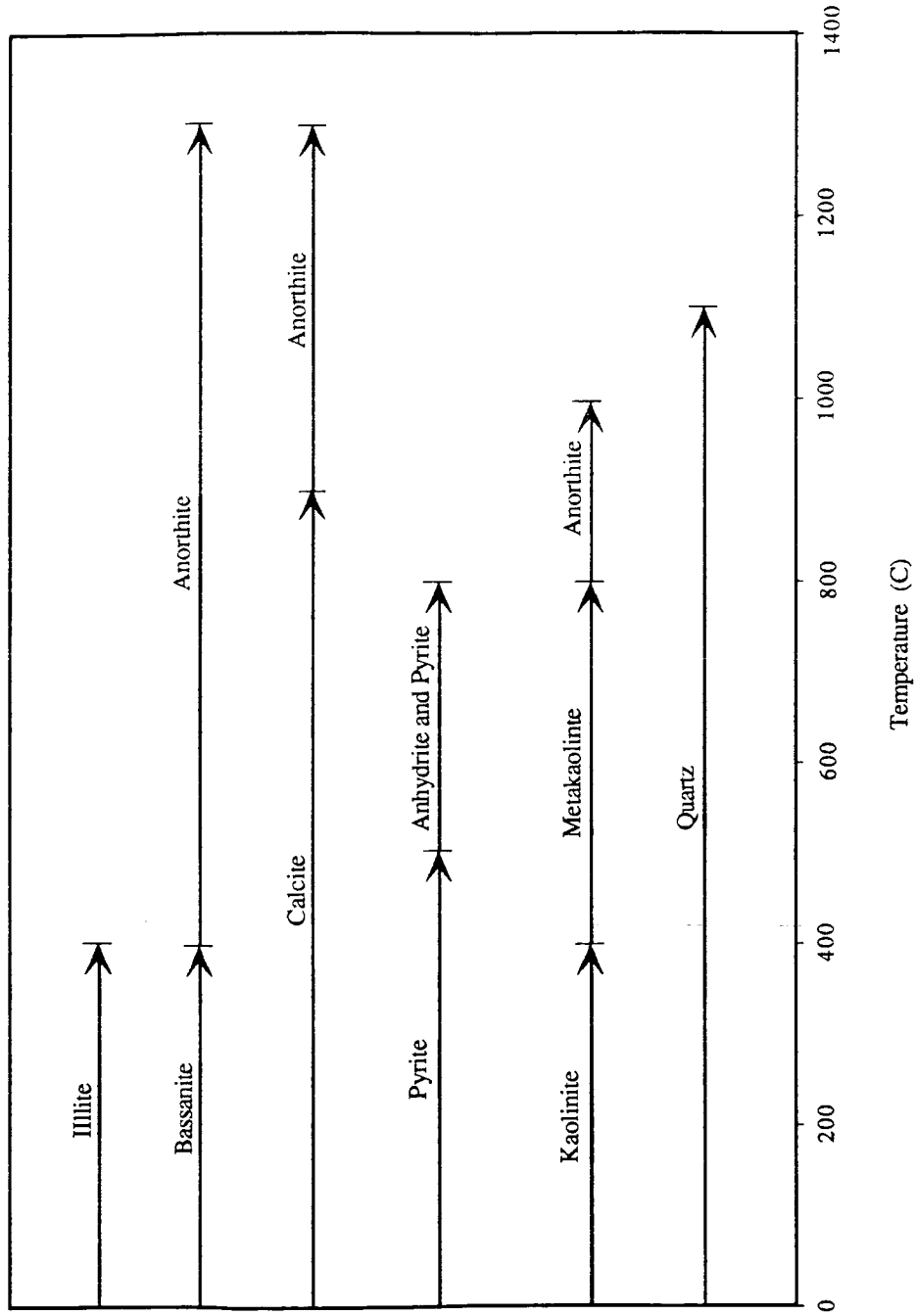


Figure 3.4 Mineral matter changes that occur during coal combustion due to increasing temperatures (based on Mitchell and Gluskoter, 1976).

found present in coal heated to 400°C. Like illite, kaolinite is only present up to 400°C when metakaolinite forms through 800°C. In addition, some of the aluminum from the original kaolinite may be in anorthite which begins to form between 800 and 1000°C. Mullite is a major phase in ash subjected to temperatures greater than 1000°C. At 500°C, hematite forms from the oxidation of pyrite and remains stable until 800°C. Another product of pyrite oxidation is sulfate which is the dominant sulfur species in fly ash. Stable up to 400°C, bassanite is formed by the partial dehydration of the original gypsum. Anhydrite develops above 400°C by reactions between bassanite and clay minerals, and is detected from 800-1300°C. In summary, although amorphous material can predominate in the fly ash matrix to more than 85% (Hurst and Styron, 1979), minerals are found including quartz, hematite, magnetite, calcite, anhydrite, mullite, and gypsum (Schuller et al., 1979; Page et al., 1979). In addition to these minerals, trace amounts of boron species including borax, rhodium boride, boron arsenite, and boron phosphate have been detected in fly ash (Adriano et al., 1980).

Although most of the original organic phase in coal is volatilized during combustion, trace organic constituents are also present in the fly ash matrix. Organics identified in fly ash include dimethyl and monomethyl sulfate (Lee et al., 1980) and some polycyclic aromatic hydrocarbons (Masek, 1976). According to Roy et al. (1981), fly ash concentrations of total hydrocarbon contents are less than 10 mg/kg and total polycyclic aromatic hydrocarbon concentrations are less than 0.2 mg/kg based on available analyses. More work needs to be conducted on characterizing the organic compounds in fly ash.

Gaseous combustion products include CO, NO_x, SO₂, SO₃, and volatile organics. Emissions of CO and hydrocarbons are generally low and are the result of incomplete combustion. Few coal-fired power-plant boiler furnaces emit more than 100 ppm CO (Meyers, 1981). Nitrogen oxides are produced during combustion by the conversion of

organic nitrogen compounds in the coal to NO_x , and by thermal fixation of nitrogen from combustion air. According to Meyers (1981), twenty-five to forty percent of the organic nitrogen in coal is converted to NO_x under normal combustion conditions. Finally, sulfur oxides are generated from the oxidation of pyrite and organic sulfur.

3.3.3 Combustion Systems

The characteristics and operational procedures at individual power plants are major factors in determining the elemental composition of the fly ash generated. Three categories of boiler are commonly used at power plants; namely, stoker-fired boilers, cyclone furnaces, and pulverized-coal-fired furnaces. Based on the furnace configuration, each type of boiler produces different amounts and compositions of bottom ash and fly ash due to differences in coal size, supply of air, combustion conditions, and temperature rates. According to Bern (1976), pulverized-coal-fired furnaces produce the highest percentage of fly ash (75-80%) in comparison to the stoker-fired boilers and cyclone furnaces (15-55%) which both produce higher amounts of boiler slag due to larger particle sizes and higher temperatures. More detailed information on combustion systems can be obtained from Meyers (1981) and Speight (1983).

CHAPTER FOUR
BORON ISOTOPIC PARTITIONING IN COAL
AND COMBUSTION PRODUCTS

4.1 Boron Sources in Coal

Boron is among the elements in coal with the highest organic affinities, and is almost entirely associated with the organic fraction in coals (Gluskoter et al., 1977). Boron was incorporated into the coal matrix by the accumulation of boron in plants. Soluble forms of boron are easily available to plants which take up undissociated boric acid and boron species in the ambient solution. At concentrations <0.5 ppm B, absorption is metabolically controlled, while at higher concentrations uptake is diffusive increasing rapidly with concentration (Oertli, 1963). In addition, plants take up boron that is adsorbed on the surface of clay minerals, especially montmorillonite and illite (Kabata-Pendias and Pendias, 1984). Therefore, the total amount of boron accumulated by plants is dependent upon the concentration and flow of water, soil pH and type, and plant species. Once boron has been incorporated into the plant structure, boron remains relatively immobile and fixed in plant tissues even upon decomposition.

In general, boron is more concentrated in Illinois coal than coals from the eastern and western United States, because of different depositional environments. According to Gluskoter et al. (1977), marine sediments generally contain more boron than non-marine sediments; therefore, higher salinity waters covered the coal swamps in the Illinois Basin. Paleosalinity studies have been conducted using boron content where boron concentrations of 200 ppm were found in illite overlying Illinois coals, indicating brackish environments (Boher and Gluskoter, 1973).

4.2 Boron Isotopic Partitioning

The complex nature of coal formation and coal combustion produces likely environments that are conducive to boron isotopic fractionation. The following is an attempt at describing how and when these fractionations occur in coal, fly ash, and gas emissions based on available data and speculation.

4.2.1 Coal

No published data were found on the boron isotopic content in coal. However, speculations can be made based on how boron was incorporated into coal and the possible fractionation processes involved. The diffusive uptake of boron by plants at high concentrations would tend to favor the lighter isotope, ^{10}B , because of mass differences. Similarly, boron that is adsorbed on clay surfaces has already undergone isotopic fractionation with ^{10}B being preferentially incorporated into the adsorbed phase (Palmer et al., 1987). Therefore, based on how boron was incorporated into coal, one would expect that boron in coal is depleted in the heavy isotope.

Although isotopic fractionation during boron incorporation is expected to occur, additional fractionation during final coalification stages is probably minimal due to the lack of boron going into or out of the coal. In addition, as the temperature of a system increases, fractionation factors decrease while approaching unity; therefore, during coalification one would assume that little to no additional fractionation occurs.

4.2.2 Fly Ash

During coal combustion, boron is partitioned between bottom ash, fly ash, and flue gas with distributions of 12.1, 83.2, and 4.7%, respectively, of the total boron concentration based on one coal study (Schwitzgebel et al., 1975). Boron can be

concentrated in fly ash to levels up to 2000 ppm which is a higher concentration than the original coal (James et al., 1982).

Elements having high organic affinities such as boron become preferentially enriched in the fly ash (Gladney et al., 1978), because of the high degree of volatility of organic matter. During the initial stages of combustion, boron in the organic matrix is volatilized and is dispersed in the gas stream. As the temperature of the flue gas decreases, some of the volatilized boron may condense or be adsorbed on fly ash entrained in the gas stream while the remaining boron is released into the atmosphere. No fractionation is expected to occur in the gas stream due to high temperatures as indicated in chapter one (Table 1.2).

The solubility of boron from fly ash has been the subject of many studies where >50% of the boron on the fly ash was found to be water soluble (Cox et al., 1978; Halligan and Pagenkopf, 1980). Davidson (1989) leached four fly ash samples and obtained $\delta^{11}\text{B}$ values ranging from -22.7 to -0.7 ‰. The leachate values were then compared with the isotopic content of the background water which was found to be enriched in ^{11}B up to 25 per mil.

4.2.3 Gas Emissions

No publications have been found at this time which report boron isotopic content of gas emissions from coal combustion. The best available data are based on studies of atmospheric boron concentrations at and near coal-fired power plants. Fogg and Rahn (1984) report that boron concentrations in the stacks were 10^4 times higher than ambient levels and concluded that coal combustion is a major anthropogenic source of atmospheric boron near coal-fired power plants. In addition, they reported that boron concentrations from rain sampled near the coal-fired power plants were higher than

expected and indicative of a higher gas-phase emission.

The total amount of boron that is volatilized during combustion ranges between 20-80% based on several studies (Gladney et al., 1978, Fogg and Rahn, 1984; Fogg and Duce, 1985; Ten Brink et al., 1987). As stated in the previous section, no boron isotopic fractionation is expected to occur in the gas stream.

CHAPTER FIVE
SULFUR ISOTOPIC PARTITIONING IN COAL
AND COMBUSTION PRODUCTS

5.1 Sulfur Sources in Coal

Sulfur was incorporated into coal when sulfate-rich waters entered the coal swamp, and remained fixed in the peat/coal matrix by the chemical precipitation of calcium sulfates from ions in solution or by the in situ production of reduced sulfur species (i.e. HS⁻, H₂S, and S⁰). Reduced species are produced by plants which reduce sulfate to sulfide in their leaves (Pale, 1965), or by microbes which produce reduced sulfur species that then react with the organic and inorganic compounds in the peat/coal. Therefore, the initial sulfate concentration entering the coal swamp determines the maximum amount of sulfur that can be reduced.

For example, a marine system with an average [SO₄²⁻] = 2700 mg/kg (Goldberg, 1963) would produce a high-sulfur coal while a freshwater system having an average [SO₄²⁻] = 8.25 mg/kg (Meybeck, 1979) would produce a lower-sulfur coal. The marine/brackish environment of the Florida Everglades contains peat with a sulfur content which resembles that of high-sulfur coals (Casagrande and Price, 1981). Peat in the freshwater Okefenokee swamp has a sulfur content lower than marine peat (Casagrande et al., 1977). However, comparing the sulfur content of coal and modern peats may be invalid, because no further addition of sulfur after deposition is assumed.

Sulfur incorporated during deposition and accumulation of the peat will be referred to as primary sulfur, while secondary sulfur will be the sulfur addition during post-depositional stages. Sources of secondary sulfur include overlying sediments and ground

waters containing sulfate that permeated the coal beds after deposition. Coals in the Illinois Basin overlain by thick nonmarine sediments have lower sulfur contents than coals overlain by marine sediments (Gluskoter and Simon, 1968). A similar relationship was reported by Williams and Kieth (1962) who studied the organic sulfur content of a freshwater coal in Pennsylvania and depositional environment of the overlying sediments. Therefore, the total sulfur content of a coal is not only dependent on the original peat, but also may be influenced by the depositional environment of the overlying sediments.

5.1.1 Organic Sulfur Formation

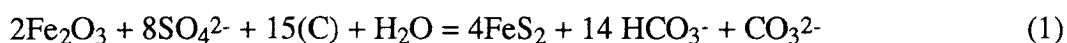
Primary organic sulfur in coal is either derived from organically bound sulfur preserved from plant material or from reactions of reduced sulfur from microbial processes with the organic debris in the peat (Westgate and Anderson, 1984). Uptake of sulfur in plants in general is an assimilatory process that reduces sulfate to sulfide and incorporates the sulfur into amino acids (Chambers and Trudinger, 1979). The plant sulfur is combined with the peat as plants decompose, although some sulfur may be lost from the system. In contrast, sulfur-reducing bacteria reduce sulfate from the swamp waters via dissimilatory processes (Westgate and Anderson, 1984). Dissimilatory processes involve the removal of the reduced sulfur species from the organism causing the sulfur to be either lost from the system or to react with organic compounds in the peat matrix.

Secondary organic sulfur is a function of the chemical reactivity of the peat and the extent of bacterial sulfate reduction after deposition. The formation of secondary sulfur is primarily caused by the release of sulfides by sulfate-reducing bacteria; the sulfides react with the organic and inorganic components of the coal (Casagrande et al., 1979).

5.1.2 Pyrite Formation

Pyrite in coal varies in morphology, size, and mode of occurrence depending on the

different periods of mineral formation. The sulfur sources for pyrite formation are the same as those for organic sulfur. The amount of pyrite found in coal is dependent upon the availability of iron under suitable conditions (Eh, pH) for its precipitation and upon sufficient organic matter for sulfate reduction. The resulting sulfide species will react with any reactive iron-containing minerals present to form solid sulfides which are generally transformed to pyrite (FeS₂). The overall reaction is represented by the equation:



where (C) represents metabolizable organic matter (Drever, 1982). In addition, many coal seams contain massive pyrite crystals in their fractures, cleats, and bedding planes implying secondary pyrite formation (Gluskoter and Simon, 1968). This occurs when iron-organic compounds are transported into the coal seam by infiltrating waters and when iron is desorbed from clay particles.

5.2 Sulfur Isotopic Partitioning

5.2.1 Coal

The processes described for the incorporation of sulfur into coal cause isotopic fractionation. The following is a brief discussion of the possible fractionation processes occurring during coal formation.

The largest and most diverse isotopic effect in the sulfur cycle is caused by bacterial sulfate reduction (Chambers and Trudinger, 1979) which produces all of the pyritic sulfur and some of the organic sulfur during the early stages of coal formation. Fractionation of sulfur isotopes between sulfide and sulfate from dissimilatory paths have been reported to

range from -22 ‰ to -74 ‰ (Harrison and Thode, 1957, 1958; Kaplan et al., 1960; Nakai and Jensen, 1960, 1964; Kaplan and Rittenberg, 1964; Kemp and Thode, 1968; Trudinger and Chambers, 1973; McCready et al., 1974; McCready, 1975). The degree of isotopic fractionation is dependent upon the rates of sulfate metabolism and the physiological environment. In contrast to bacterial sulfate reduction, the sulfur isotope effect for the sulfur incorporation into coal via assimilatory processes in plants appears to be minimal. Plants show only a slight enrichment of ^{32}S in organic sulfide relative to the sulfate source (Kaplan and Rittenberg, 1964; McCready et al., 1974; Chambers and Trudinger, 1979). Finally, fractionation by equilibrium exchange reactions between sulfides and sulfates during coal formation is unlikely, but may occur between sulfur species in similar oxidation states (Westgate and Anderson, 1984).

The first detailed study of sulfur isotopes in coal was published by Smith and Batts (1974). They reported that coals from Australia containing less than 1 wt. percent of total sulfur had $\delta^{34}\text{S}$ values for organic sulfur generally between +5 and +7 ‰. Smith et al. (1982) reported similar organic sulfur values (+2 to +8 ‰) of coals from Australia, New Zealand, and South Africa. In addition, the $\delta^{34}\text{S}$ values for organic sulfur of coals from the Illinois Basin that contain less than 0.8 wt. percent organic sulfur also have similar values (Price and Shieh, 1979; Westgate and Anderson, 1984). Therefore, based on these results, the isotopic composition of organic sulfur in low-sulfur coals is representative of primary plant sulfur which appears to be isotopically homogeneous. However, Hackley and Anderson (1986) who studied low-sulfur coals in the Rocky Mountain region suggested that the isotopic composition of organic sulfur in low-sulfur coals may not always be representative of original plant sulfur. They discovered isotopic evidence of bacterial influences during the incorporation of organic sulfur in two coals sampled.

In contrast to low-sulfur coals, high-sulfur coals from the regions described above

were more variable and usually more negative, suggesting major contributions from the bacterial reduction of sulfate to sulfide. In addition, isotopic compositions of pyrite from these coals were even more variable, and is probably caused by the occurrence of several generations of pyrite from varying sources and mechanisms (Price and Shieh, 1979; Westgate and Anderson, 1984).

5.2.2 Fly Ash and Gas Emissions

Sulfur in coal is partitioned during combustion primarily between fly ash and flue gas with approximate distributions of 15 and 85%, respectively (Shobert, 1987). While many volatilized elements condense onto the fly ash, the most volatile ones such as sulfur do not completely condense and pass through the particulate control devices partially in the vapor state as SO_2 or SO_3 . The sulfur retained on the fly ash is in the form of sulfate.

Although separate studies have been conducted on sulfur isotopes in coal and on atmospheric sulfur, few single publications have been found at this time which report the use of sulfur isotopes throughout the coal combustion system i.e. coal, fly ash, and flue gas. The closest work found was an investigation by Nakai and Jensen (1967) who determined the isotopic content of three coal samples from Japan along with the corresponding fly ash and flue gas samples from their laboratory burning experiments. From their quantitative and isotopic results, they concluded that the SO_2 gas produced was always enriched in ^{32}S while the soluble sulfate in the ash was enriched in ^{34}S in reference to the total sulfur of the original coal samples. These results were consistent with their comparisons of sulfur in precipitation near industrial and non-industrial areas. In non-industrial areas, $\delta^{34}\text{S}$ values ranged from +12.3 to +19.0 ‰, while precipitation at industrial sites varied from +3.2 to +7.3 ‰ (Nakai and Jensen, 1967). Therefore, based on this study, the lighter isotope composition of atmospheric sulfur in industrial areas is

caused predominantly from atmospheric oxidation of isotopically light SO_2 emitted by industrial activities.

Although no further sulfur isotopic data were found for fly ash, numerous studies have been conducted on atmospheric sulfur emissions near industrial areas. Types of samples used for assessing isotopic values for gas emissions besides direct analysis include rain, ground water, vegetation, and soil samples near the site. Isotopic results vary greatly from site to site. In agreement with Nakai and Jensen (1967) who concluded that precipitation from industrial areas are more enriched in ^{32}S than that from non-industrial areas, rain samples from Graceland, New Zealand contained sulfur enriched in ^{32}S by 20 ‰ relative to the sulfur in sea water sulfate (Mitzutani and Rafter, 1969). In contrast, Ludwig (1976) reported that the $\delta^{34}\text{S}$ values of aerosol and cloud droplet samples collected in unpolluted marine air near San Francisco Bay were lower than those from the adjacent and more polluted urban areas. Similar results were obtained by Nriagu and Coker (1978) who studied the isotopic composition of sulfur in precipitation within the Great Lakes Basin. They concluded that precipitation samples at urban sites were enriched in ^{34}S compared to samples at rural and remote locations. In addition, Ostland (1959) analyzed precipitation samples collected at several locations in North America and Scandinavia during 1957-58 and found no variation in $\delta^{34}\text{S}$ values with sample location.

Isotopic and chemical data from soil, ground water, and vegetation samples are also useful tools in determining the fate of industrial gas emissions. Robertson et al. (1989) reported that peak ground water sulfate concentrations coincided with reported peak anthropogenic sulfur emissions at a nickel-copper smelting operations near Sudbury, Ontario. They concluded that the sulfate in the ground water originated from the atmosphere rather than solid phase material in the surrounding sediments. In contrast, Krouse and Case (1981) concluded that sulfur in the environment surrounding the Teepee

Creek gas plant in Alberta, Canada was dominated by sources other than plant emissions. They reported that the atmospheric sulfur compounds due to sour gas processing were enriched in ^{34}S (+24 ‰), while the soil and vegetation had mean values of -8 ‰.

CHAPTER SIX

RESULTS AND DISCUSSION OF COAL AND FLY ASH SAMPLES

6.1 Introduction

If isotopic fractionation occurs during coal formation and combustion, the resulting isotopic ratios from the various coal fractions and corresponding fly ash would differ depending on the dominant fractionation processes. This chapter describes the results of the boron and sulfur isotopic analyses of coal and fly ash, and discusses the significance of the measured values in explaining boron and sulfur incorporation into coal and behavior during combustion. Chapter Seven provides a full discussion of the field samples from the SRP site.

It should be noted that conclusions were based on a small data set (four samples) and that fly ash samples actually represent the average isotopic value of burning a much larger amount of coal and not the exact same coal analyzed. In addition, the homogeneity of the coal burned to produce the fly ash sample is not known when compared to the corresponding coal sample.

6.2 Isotopic Results of Coal and Fly Ash Samples

The four coal samples described in chapter two (Table 2.4) that were extracted for water-soluble boron, and the four leachate samples from the corresponding fly ash samples (Table 2.5) were analyzed for their boron isotopic ratios using thermal ionization mass spectrometry in the positive ion mode. Table 6.1 reports the results for each sample

Table 6.1 Boron isotopic results of coal and fly ash samples.

<u>Sample</u>	<u>$\delta^{11}\text{B}$ (‰)</u>
101-WSB*	+10.2
101-FLY ASH	+4.3
102-WSB	+6.4
102-FLY ASH	+1.9
107-WSB	+5.9
107-DUP-WSB	+5.3
107-FLY ASH	+2.4
SRP-WSB	+11.7
SRP-FLY ASH	-6.6

as the $\delta^{11}\text{B}$ from the NBS SRM-951. In addition, the sulfur isotopic ratios were determined for the pyritic, organic, and total sulfur of the same four coal samples (Table 2.1) as well as the resulting fly ash leachates described in section 2.4.2. Table 6.2 provides the sulfur isotopic results. Full analysis procedures for the boron and sulfur extractions are discussed in detail in chapter two.

6.3 Discussion of Boron Isotopic Data

6.3.1 Boron Incorporation into Coal

Although only four coal samples were analyzed for boron isotopes, generalized statements were made on boron incorporation into coal based on boron concentration and isotopic content of the coal. Figure 6.1 illustrates the $\delta^{11}\text{B}$ of the water-soluble boron in coal as a function of the total boron concentration of the coal sample. Lower boron content coal samples (102 and 107) were enriched in ^{10}B in comparison to the higher boron content coal samples (101 and SRP). Enrichment of the lighter isotope, ^{10}B , is indicative of processes that favor the lighter isotope. These processes may include the adsorption of boron from clays and the uptake of boron by plants during coal formation. In contrast, the higher content boron coal samples were more enriched in the heavier isotope, ^{11}B , possibly due to more contact with saline waters during coal formation. This agrees with conclusions found in the literature where marine sediments tend to contain higher concentrations of boron than non-marine sediments (Boher and Gluskoter, 1973; Gluskoter, 1977). In conclusion, one would expect the water-soluble boron in coal to be more enriched in the lighter isotope, ^{10}B , unless additional processes occurred during coal formation that introduced a source of isotopically heavy boron. This study only focused on the water-soluble boron fraction in coal. Therefore, more work needs to be

Table 6.2 Sulfur isotopic results of coal and fly ash samples.

COAL					
<u>Chemical Analysis (%)</u>	<u>101</u>	<u>102</u>	<u>107</u>	<u>107-DUP</u>	<u>SRP</u>
pyritic sulfur	1.27	2.29	0.48	0.48	0.15
organic sulfur	3.00	0.94	2.94	2.94	0.51
total sulfur	4.32	3.29	3.67	3.67	0.66
<u>Isotopic Composition (‰)</u>					
pyritic sulfur ¹	15.3	8.2	30.3	28.2	ND ²
organic sulfur	2.7	12.5	6.8	7.2	13.8
total sulfur	4.1	9.3	10.0	9.8	12.8
<u>Mass Balance ($\delta^{34}\text{S}_{\text{TS}}$)</u>					
calculated value ³	6.4	9.3	9.4	9.4	--
measured value	4.1	9.3	10.0	9.8	12.8
FLY ASH					
<u>Isotopic Composition (‰)</u>					
fly ash leachate	5.1	13.5	11.1	--	4.9 4.6

¹The isotopic values for pyritic sulfur are disseminated pyritic sulfur values. Massive pyrite was visibly observed only in 102. A δ value of +7.6 ‰ was determined which was similar to the disseminated pyrite value for 102.

²No detection. Calculated pyritic value using the mass balance equation is +9.4 ‰.

³Mass balance equation:

$$\delta^{34}\text{S}_{\text{TS}} = \frac{x_{\text{p}}(\delta^{34}\text{S}_{\text{p}}) + x_{\text{or}}(\delta^{34}\text{S}_{\text{or}})}{x_{\text{TS}}}$$

$\delta^{34}\text{S}_{\text{TS}}$ =isotopic composition of total sulfur; $\delta^{34}\text{S}_{\text{p},x_{\text{p}}}$ =isotopic composition and per cent pyritic sulfur; $\delta^{34}\text{S}_{\text{or},x_{\text{or}}}$ =isotopic composition and per cent organic sulfur; and x_{TS} =per cent total sulfur.

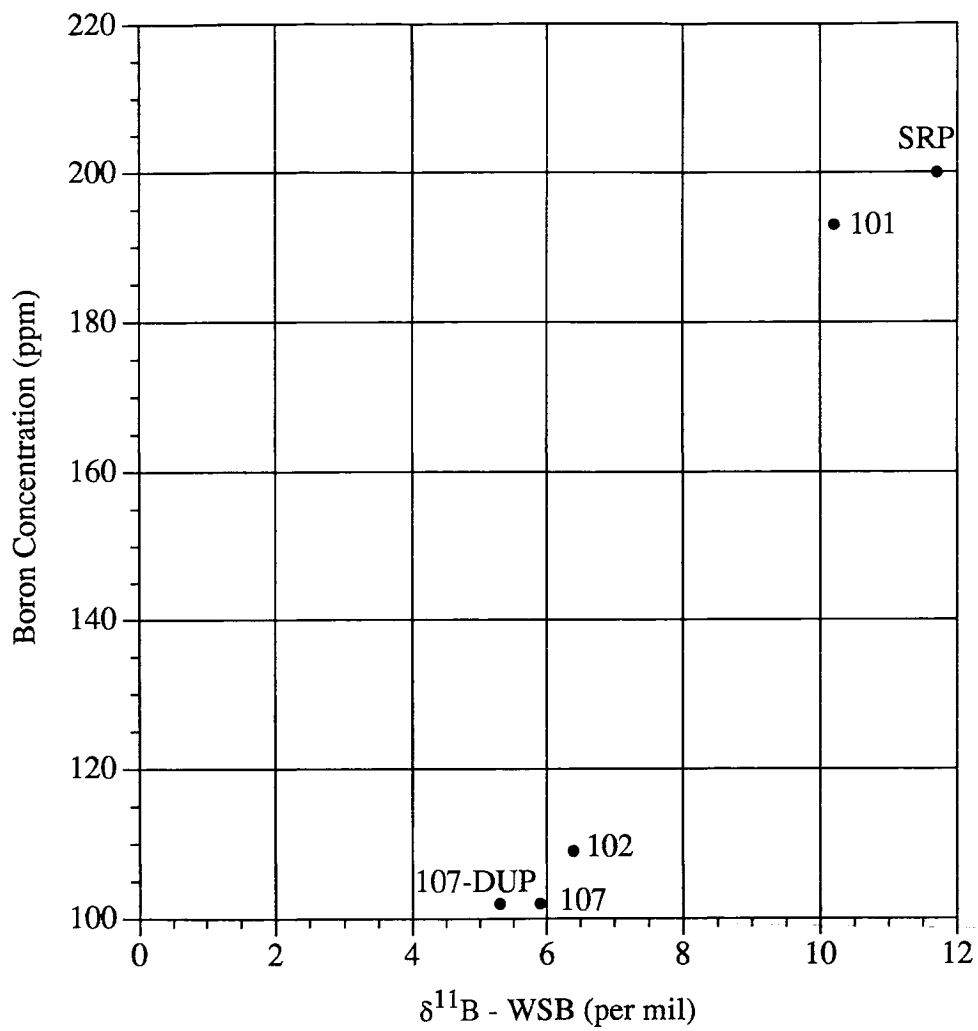


Figure 6.1 The relationship observed between the boron concentration as a function of the $\delta^{11}\text{B}$ of the water-soluble boron for four coal samples.

conducted on the isotopic total organic and inorganic boron fractions of coal before conclusive statements concerning boron incorporation into coal can be made.

6.3.2 Boron Combustion Behavior

Statements made concerning behavior of boron during combustion were based on isotopic data from coal and corresponding fly ash leachate samples. Resulting flue gas emissions would have provided more conclusive statements, but were not obtained for analysis.

Figure 6.2 illustrates the relationships observed between the $\delta^{11}\text{B}$ of the fly ash leachate and the $\delta^{11}\text{B}$ of the water-soluble boron in coal. Results of the SRP sample were analyzed separately, because of different burning conditions. Overall, the Illinois fly ash samples were only slightly depleted in ^{11}B compared to the original coal sample (3.5 to 5.9 ‰ $\delta^{11}\text{B}$ shifts). In addition, fly ash δ values appear to be dependent on the initial boron concentration in the coal. Higher boron content coals (101) produced fly ash leachates more enriched in the heavy isotope.

The isotopic data obtained from this study suggests that boron isotopic fractionation may occur during coal combustion and/or leaching processes. As mentioned in chapter four, no isotopic fractionation is expected to occur in the gas stream during coal combustion.

The SRP fly ash and coal leachate exhibited a significantly greater ^{11}B difference (18.3 ‰ $\delta^{11}\text{B}$ shift) when compared to the Illinois samples (Table 6.1). Reasons for this include: 1) the SRP coal sample was obtained from a more heterogeneous coal source producing varying fly ashes; and 2) different combustion conditions will result in different isotopic fly ash values i.e. temperature, incomplete combustion, and kinetic effects causing varying rates of adsorption. For example, it would be expected that under

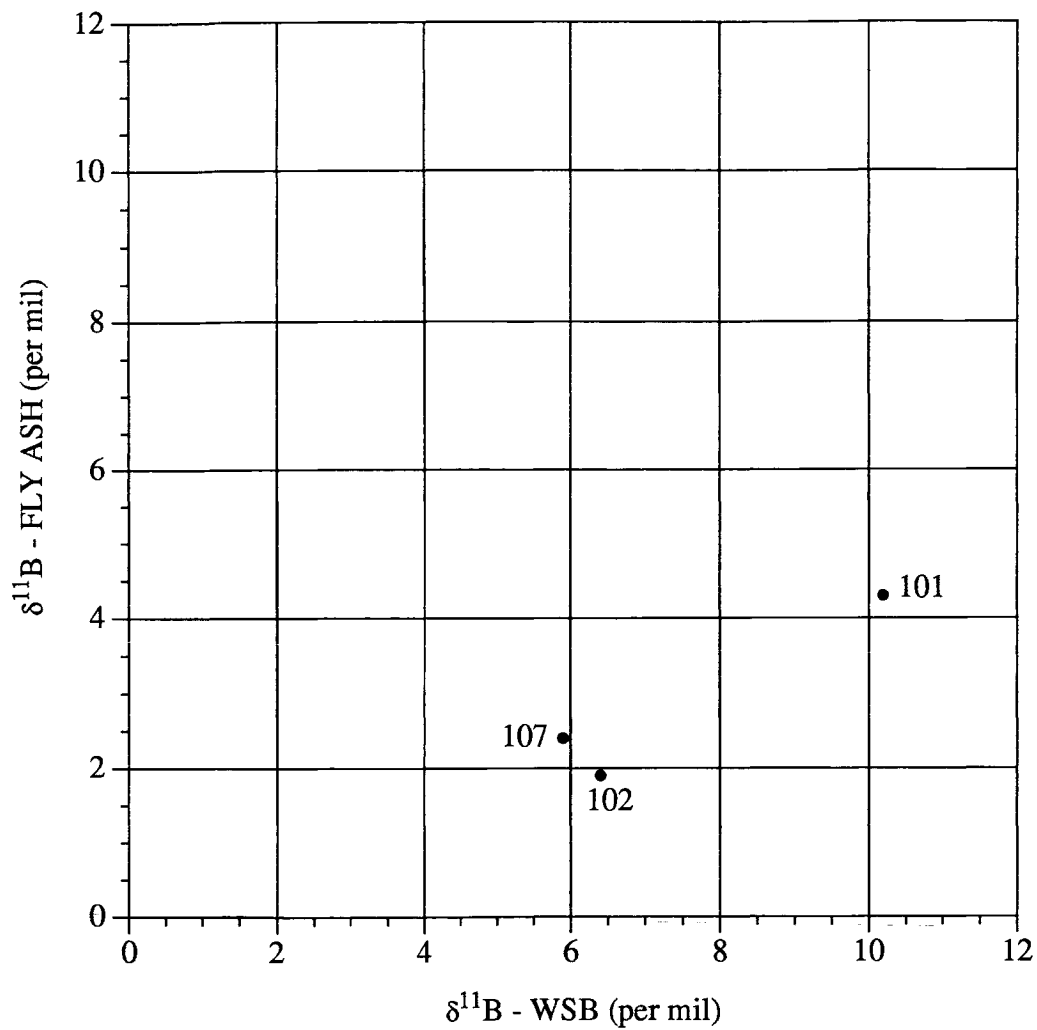


Figure 6.2 Boron combustion behavior illustrated by the $\delta^{11}\text{B}$ of the fly ash leachate versus the $\delta^{11}\text{B}$ of the water-soluble boron for three Illinois coal samples.

field burning conditions, the entrained fly ash has a longer contact time with the flue gas through the exhaust path of stacks than that of a laboratory burning apparatus constructed for a minimum amount of coal. Therefore, under field conditions, more contact time is available for adsorption processes to occur enriching the resulting fly ash with ^{10}B .

6.4 Discussion of Sulfur Isotopic Data

6.4.1 Sulfur Incorporation into Coal

Several conclusions were made on sulfur incorporation into coal based on the isotopic results from the different coal fractions. These observations were in agreement with a similar study by Price and Shieh (1979).

Organic and pyritic sulfur isotopic data were plotted against the organic and pyritic sulfur content, respectively (Figures 6.3 and 6.4). The trend from the data suggests the mixing of two isotopically distinct sources of sulfur in the coal samples. The negative slopes observed in both figures indicate that the light sulfur source, ^{32}S , is directly related to higher organic and pyritic sulfur content coal samples. Smith and Batts (1974) suggested that the organic sulfur in low sulfur coals was obtained from the initial plant material, while in high sulfur coals a significant fraction of sulfur was introduced into organic matter from hydrogen sulfide formed by bacterial reduction of sulfates. In addition, higher content sulfur coals tend to show a wider range of organic sulfur isotope ratios, while lower content sulfur coals have a more narrow range. Therefore, low content sulfur coals represent an isotopically homogeneous sulfur source i.e. primary plant sulfur.

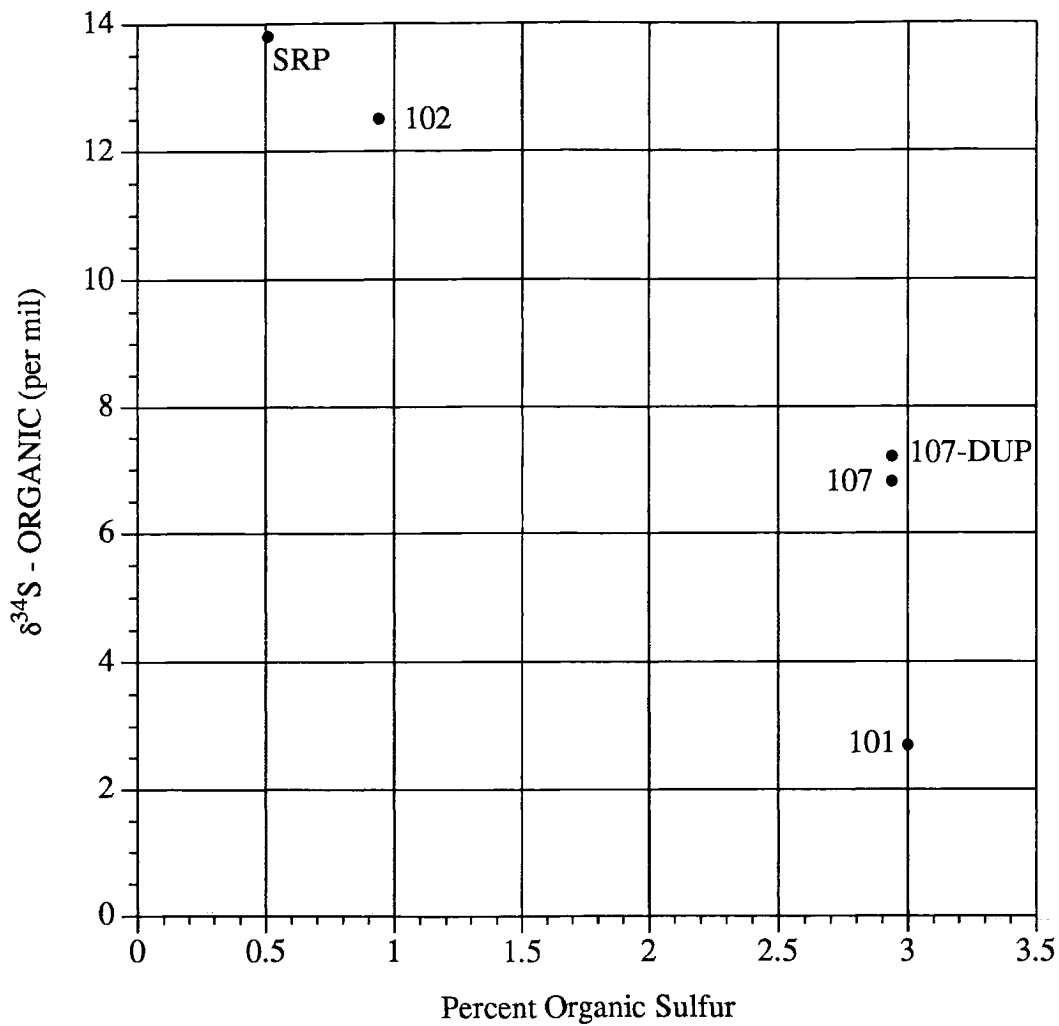


Figure 6.3 The relationship observed between the $\delta^{34}\text{S}$ of organic sulfur as a function of the organic sulfur content for four coal samples.

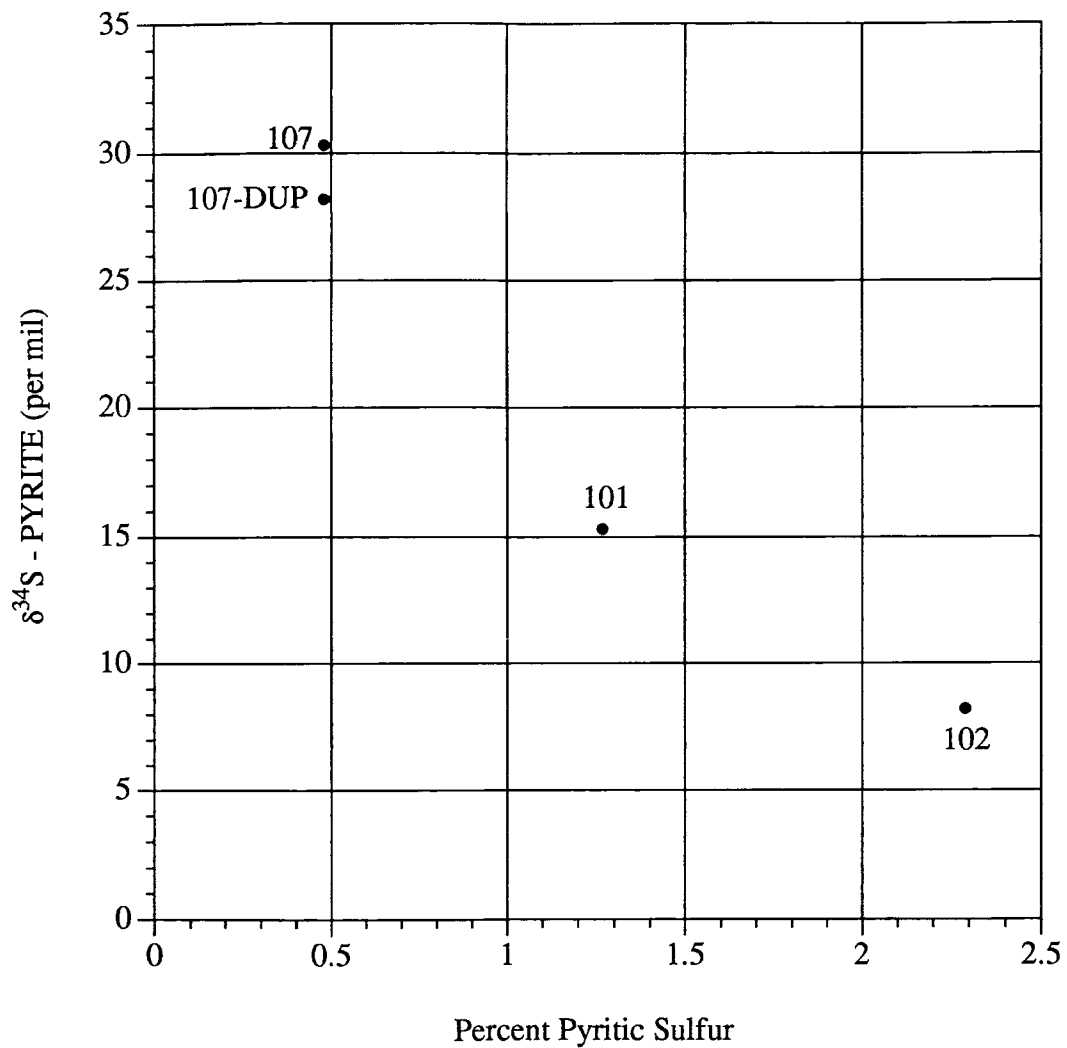


Figure 6.4 The relationship observed between the $\delta^{34}\text{S}$ of pyritic sulfur as a function of the pyritic sulfur content for four coal samples.

In conclusion, organic sulfur originates from two major independent sources of sulfur: 1) sulfur assimilated by living plants in the coal swamp; and 2) sulfur from bacterial reduction of dissolved sulfate in water. A generalized flow chart summarizing the sources and methods of sulfur incorporation into coal is provided in Figure 6.5 (Price and Shieh, 1979). Different sources of sulfur should produce isotopically different values. In addition, one would expect isotopic ratios of massive pyrite and organic sulfur originating from the same H₂S source to have similar values unless the pyrite undergoes additional fractionation after deposition. The varying organic and pyritic isotopic sulfur values from the coal samples in this study indicate that additional fractionation of the pyritic fraction occurred after deposition.

6.4.2 Sulfur Combustion Behavior

Figure 6.6 shows the relationship observed between the $\delta^{34}\text{S}$ of the fly ash leachate and the $\delta^{34}\text{S}$ of the total coal sulfur. The Illinois high sulfur coals (>1% total sulfur) became slightly enriched on fly ash in comparison to the total isotopic content of the original coal. This conclusion agrees with the laboratory results of Nakai and Jensen (1967) who determined the $\delta^{34}\text{S}$ of three high sulfur coal samples to be +23.5, +11.9, and +22.1 ‰ and the corresponding fly ash leachate values as +24.8, +12.8, and +25.1 ‰, respectively. In contrast, the low sulfur SRP coal sample resulted in a slight depletion of ³⁴S on the fly ash in comparison to the total isotopic content of the original coal sample. As with the boron results, the Illinois samples exhibited only minor δ shifts from the coal to fly ash values (1.0 to 4.2 ‰ $\delta^{34}\text{S}$ shifts) in comparison to the 8.2 ‰ shift of the SRP samples.

The following provides an explanation of the observed sulfur isotopic behavior of low and high sulfur coals during combustion. Two major fractionation processes for

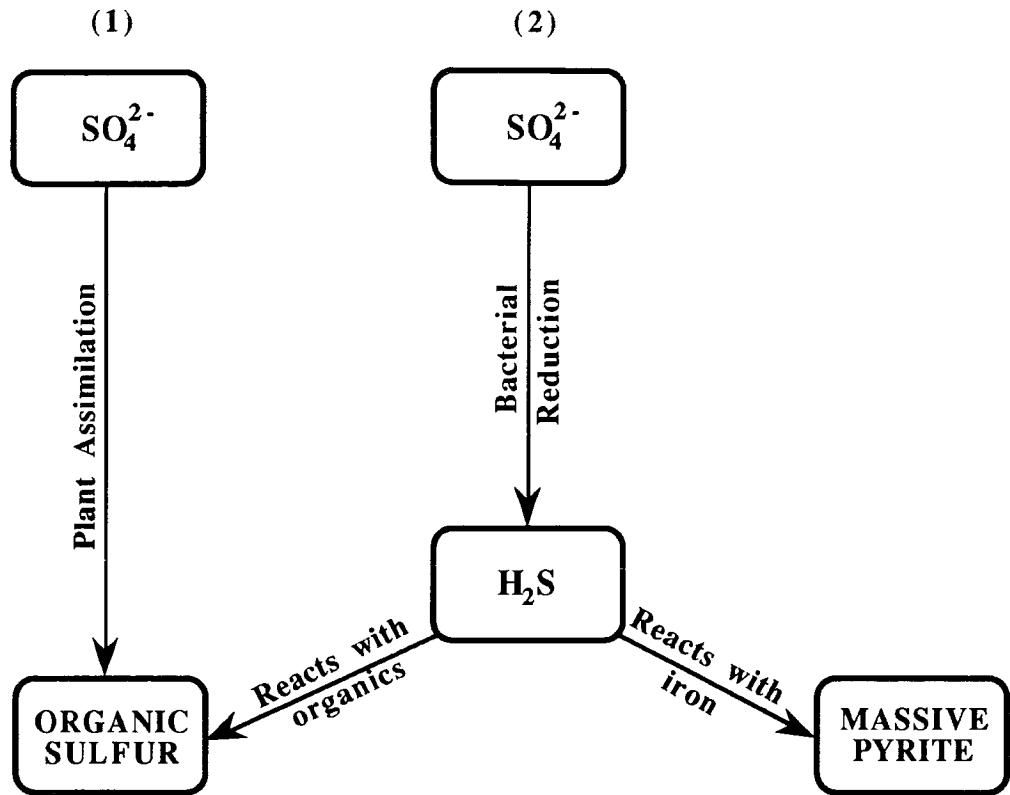


Figure 6.5 Generalized flowchart summarizing the sources and methods of sulfur incorporation into coal (after Price and Shieh, 1979).

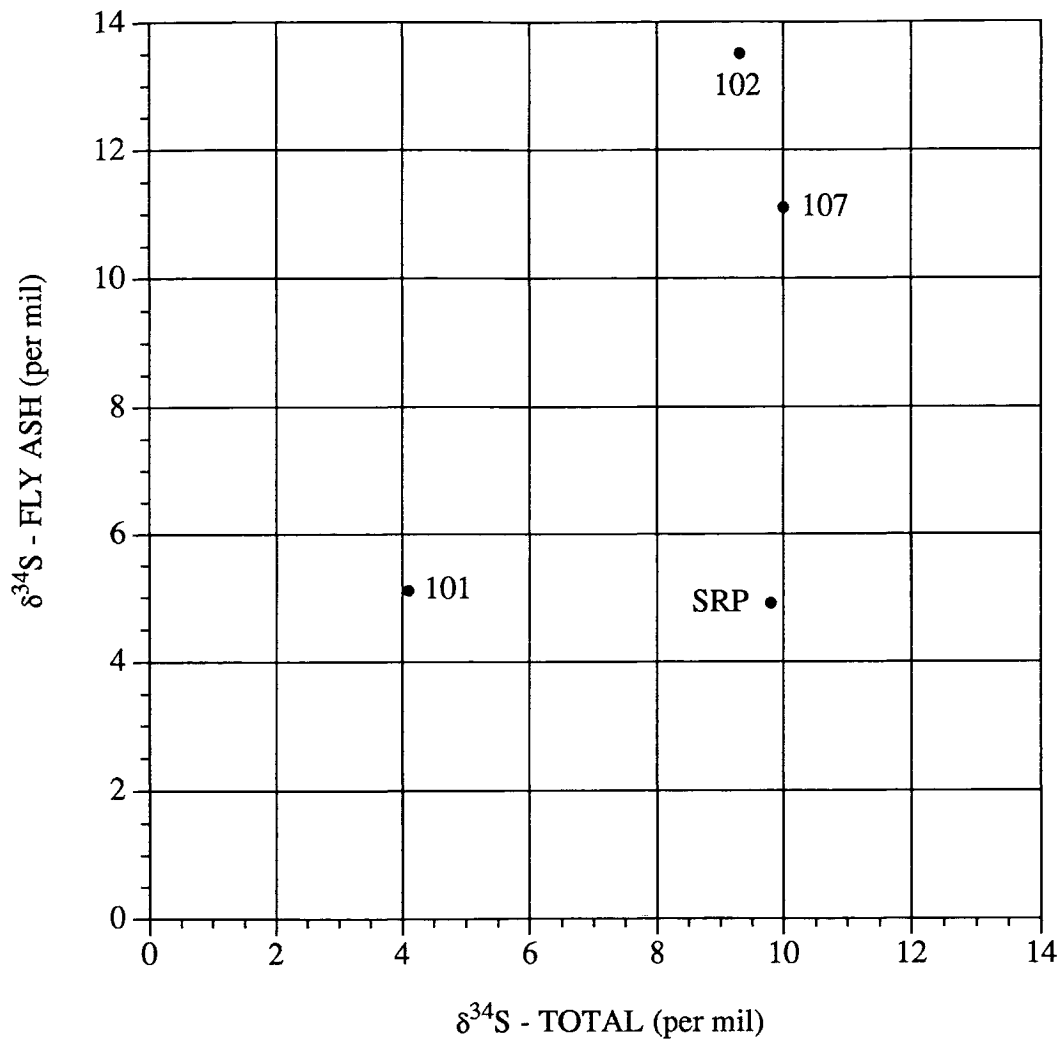


Figure 6.6 Sulfur combustion behavior illustrated by the $\delta^{34}\text{S}$ of fly ash leachate versus the $\delta^{34}\text{S}$ of the total sulfur content for four coal samples.

sulfur partitioning during coal combustion include the volatilization of organic sulfur phases and the oxidation of sulfides to sulfates. Low sulfur coals (<1 % total sulfur) consist primarily of organic sulfur. During combustion this organic material is volatilized with some condensation and then adsorption onto the entrained fly ash particles. The resulting sulfate on the fly ash is depleted isotopically which is similar to boron isotopic behavior. In addition to the organic sulfur phase, high sulfur coals may contain a significant percentage of sulfides that are oxidized to sulfates during combustion. Smejkal (1978) studied the oxidative weathering of sulfides to sulfates and discovered only a minor depletion from pyrite to sulfate (1.2 ‰ $\delta^{34}\text{S}$ shift). Although this does not fully explain the enrichment of ^{34}S in the fly ash of high sulfur coals, the overall depletion is less for high sulfur coals than for low sulfur coals where most of the sulfate originates from volatilized organics. Therefore, other processes must also be occurring to explain the slight enrichment in the high sulfur coals. In addition, coal samples in this study contained isotopically heavy pyritic sulfur values which would result in relatively heavy sulfate values for the fly ash leachate when compared to the total sulfur isotopic value.

CHAPTER SEVEN
ISOTOPIC CONTENT OF SAMPLES
FROM A COAL-FIRED POWER PLANT

7.1 Introduction

This chapter describes the work done on samples from the Salt River Project (SRP) Coronado Generating Station located near St. Johns, Arizona (Figure 7.1). The objective of the study was to determine the boron and sulfur isotope ratios on samples from the site and speculate how the observed fractionation for different parts of the coal combustion system could be used to determine whether proper containment of waste water was being achieved. Samples used in this study included coal, fly and bottom ashes, two soil samples, a sample from the evaporation pond, and three ground water samples.

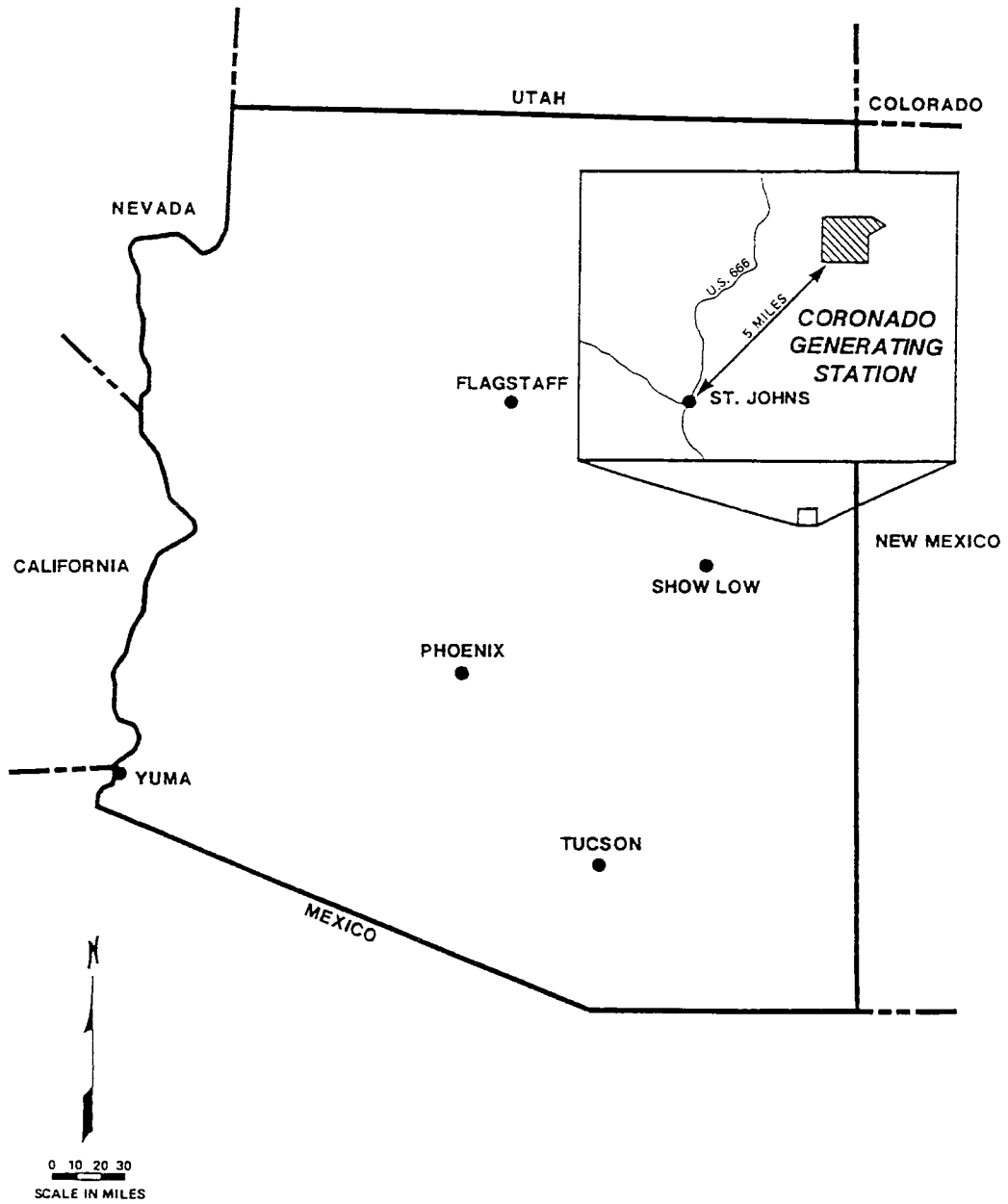
The first section provides a general description of the study area based on limited information provided by SRP (Shirley, 1989). The second section discusses the results from preliminary solution modeling conducted on two wells using the geochemical model PHREEQE to determine water-rock interactions in the system. The final section provides isotopic results and potential applications for the use of boron and sulfur isotopes for coal combustion systems.

7.2 General Description of Study Area

7.2.1 Hydrogeology

The Coronado Generating Station (CGS) is located near the southern margin of the Colorado Plateau which is characterized by laterally continuous sedimentary units. Surface features include broad, rolling terrain and minor, isolated rock outcrops. Rock formations

Figure 7.1 Site location map of the Coronado Generating Station located near St. Johns, Arizona.



of hydrologic interest in the vicinity of the site include the Supai, Coconino, Kaibab, Moenkopi, Chinle, and Bidahochi Formations. The Bidahochi and Chinle Formations are the only outcrops near the station.

The deepest units of hydrologic interest are the Permian age Supai, Coconino, and Kaibab Formations. The Kaibab Limestone is the uppermost formation occurring at a depth of about 700 feet in the CGS area. These formations form the Coconino aquifer which is the major water supply for this region. The aquifer is confined in some areas by the overlying siltstone and mudstone beds of the Moenkopi and Chinle Formations.

The potentiometric head in the Coconino aquifer near the plant is at a depth of about 250 feet based on measurements taken in December 1985. In comparison, the unconfined Bidahochi aquifer in the same area contains water depths at about 150 feet indicating a considerable gradient between the two aquifers. However, no known hydrologic connection exists between the two groundwater systems in the vicinity of the CGS. Isotopic results should help to support this statement.

Yielding small quantities of poor quality water, the Triassic age Moenkopi Formation consists of mudstones and siltstones ranging in thickness from about 60 to 100 feet in the area. The Moenkopi Formation contains evaporite deposits which may be the cause of the water quality degradation. Although not considered a usable water supply in general, the formation contains discontinuous sandstone and conglomerate units which supply domestic water in the St. Johns area.

The Triassic age Chinle Formation is characterized by granular volcanic ash, siltstone, and claystone which contain thin, localized beds of sandstone and conglomerate. The sandstones and conglomerates occasionally contain small quantities of poor quality water, and are not considered a usable water supply. The mudstone and siltstone units of this formation underlie the entire plant area forming a nearly impermeable layer. The entire thickness of the Chinle Formation is about 400 feet near the station.

The Tertiary age Bidahochi Formation forms the ground surface at the CGS and ranges from 0 to 250 feet of loosely consolidated sand, silt, and clay. The unconfined Bidahochi aquifer consists of the Bidahochi Formation and the upper part of the Chinle Formation in the CGS area. As mentioned previously, ground water occurs at a depth of about 150 feet in this system, and is only of local extent. Water in the system is not utilized to a significant degree due to low well yields and poor quality. In general, ground water movement in the Bidahochi aquifer is to the north-northwest.

7.2.2 Site Description and Sample Locations

A map of the CGS and vicinity is provided in Figure 7.2. Fifteen water conveyance or storage structures are located at the station including canals, ponds, and reservoirs (Figure 7.3). The reservoirs may contain raw water, surface runoff, treated sewage effluent, process water, and/or waste water.

The primary purpose of retention ponds 26, 105, and 106 is the capture of natural runoff, although 105 and 106 can receive small amounts of process water or waste water from reservoirs 107 to 110. Waste water reservoir 108 and blowdown reservoir 107 are the only impoundments of the site that contain significant amounts of waste water. The remainder of the impoundments contain plant process water, raw well water, or domestic sewage effluent. The major waste water impoundment at the CGS site is the evaporation reservoir which is southwest of the plant.

Samples from the site were obtained in January 1989 and included water samples from the evaporation reservoir, monitoring wells 30 and 45, and Kaibab/Supai ground water from a flowing well in the Salado Springs area. Chinle soil samples were taken near monitoring well 40 and near Highway 666 north of St. Johns. The well and soil sampling locations and a cross-section provided by SRP are given in Figures 7.4 and 7.5 to show the relative locations of the water and soil samples to the evaporation reservoir. In

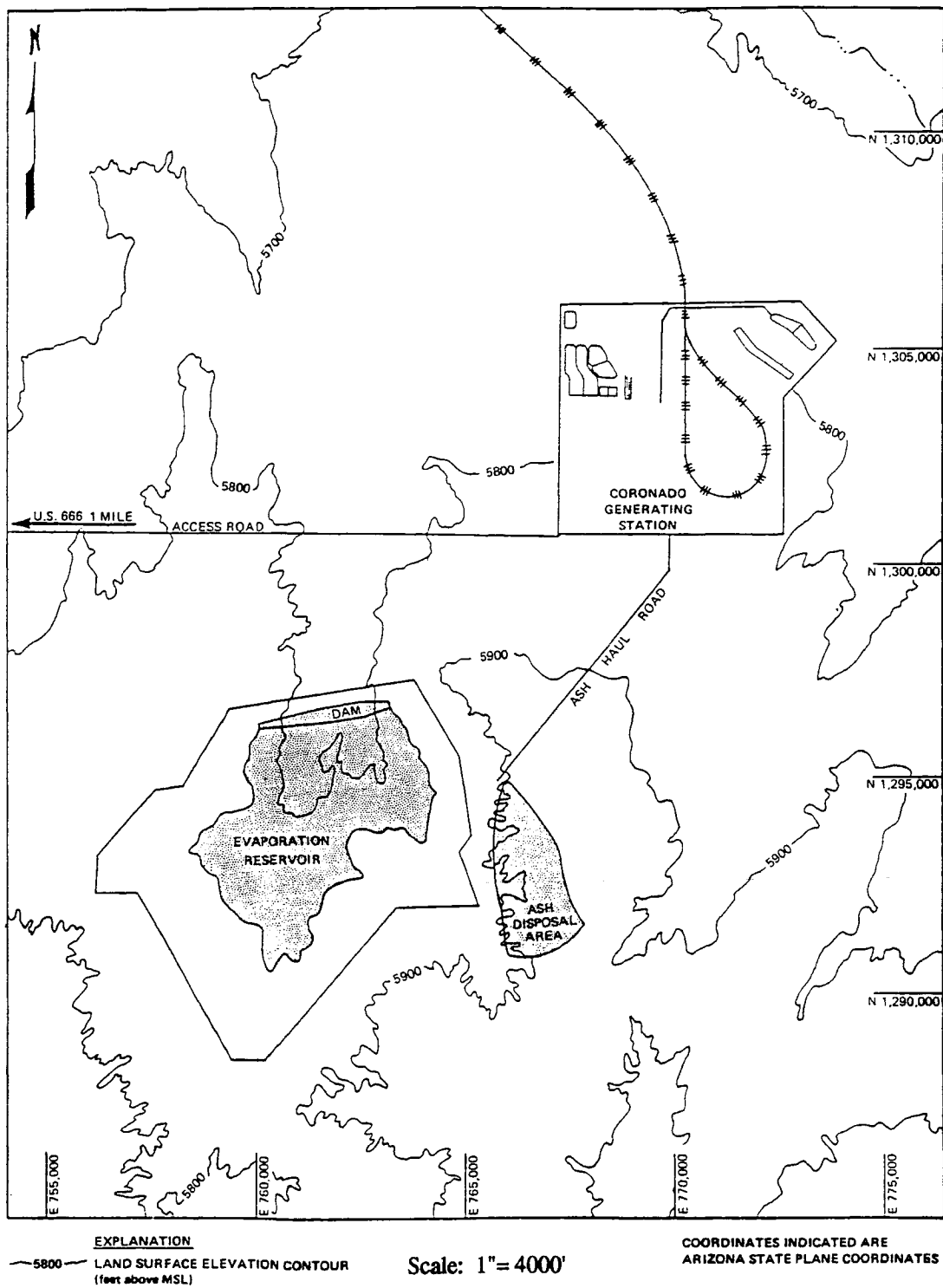


Figure 7.2 Vicinity map of the Coronado Generating Station showing locations of evaporation reservoir and ash disposal area.

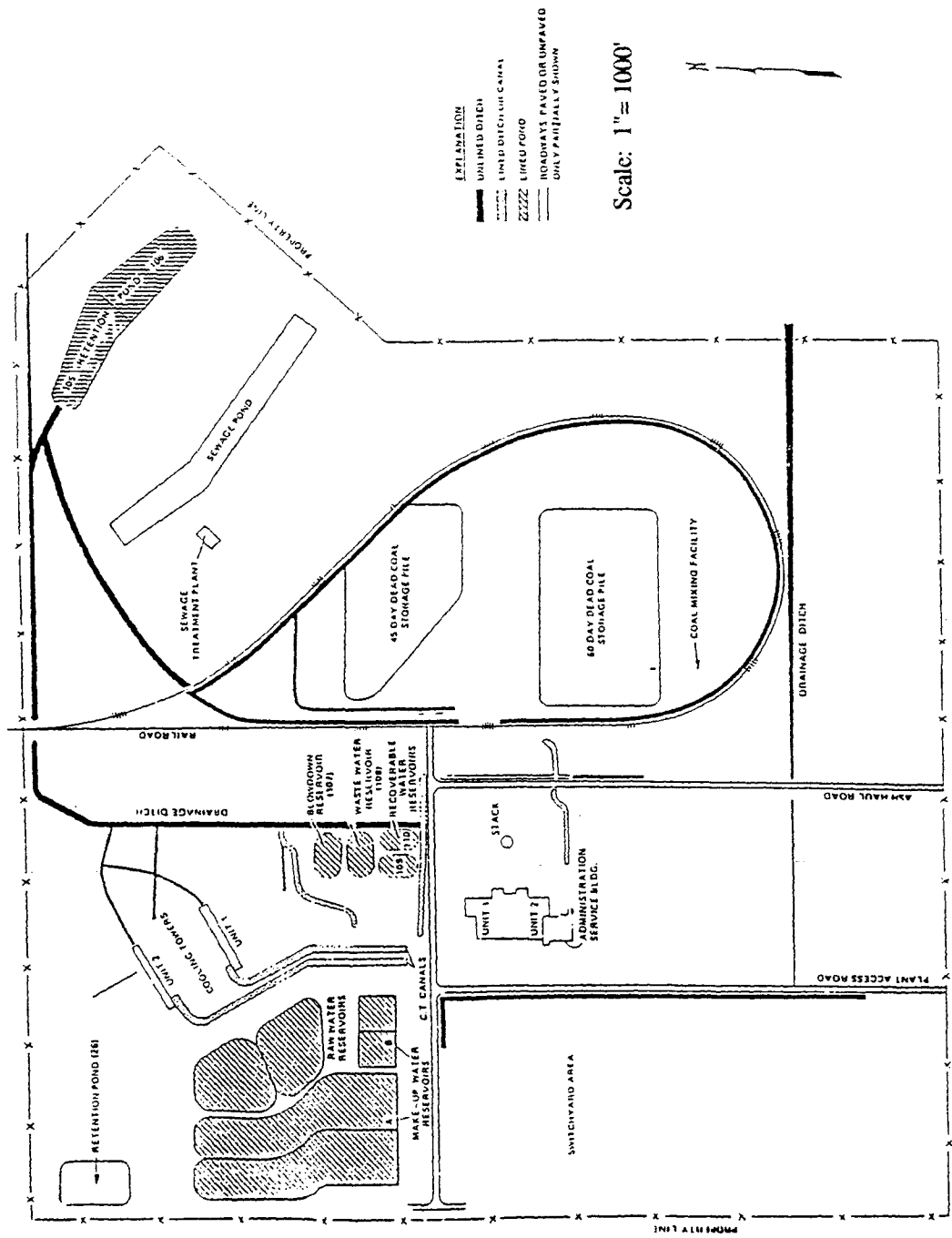
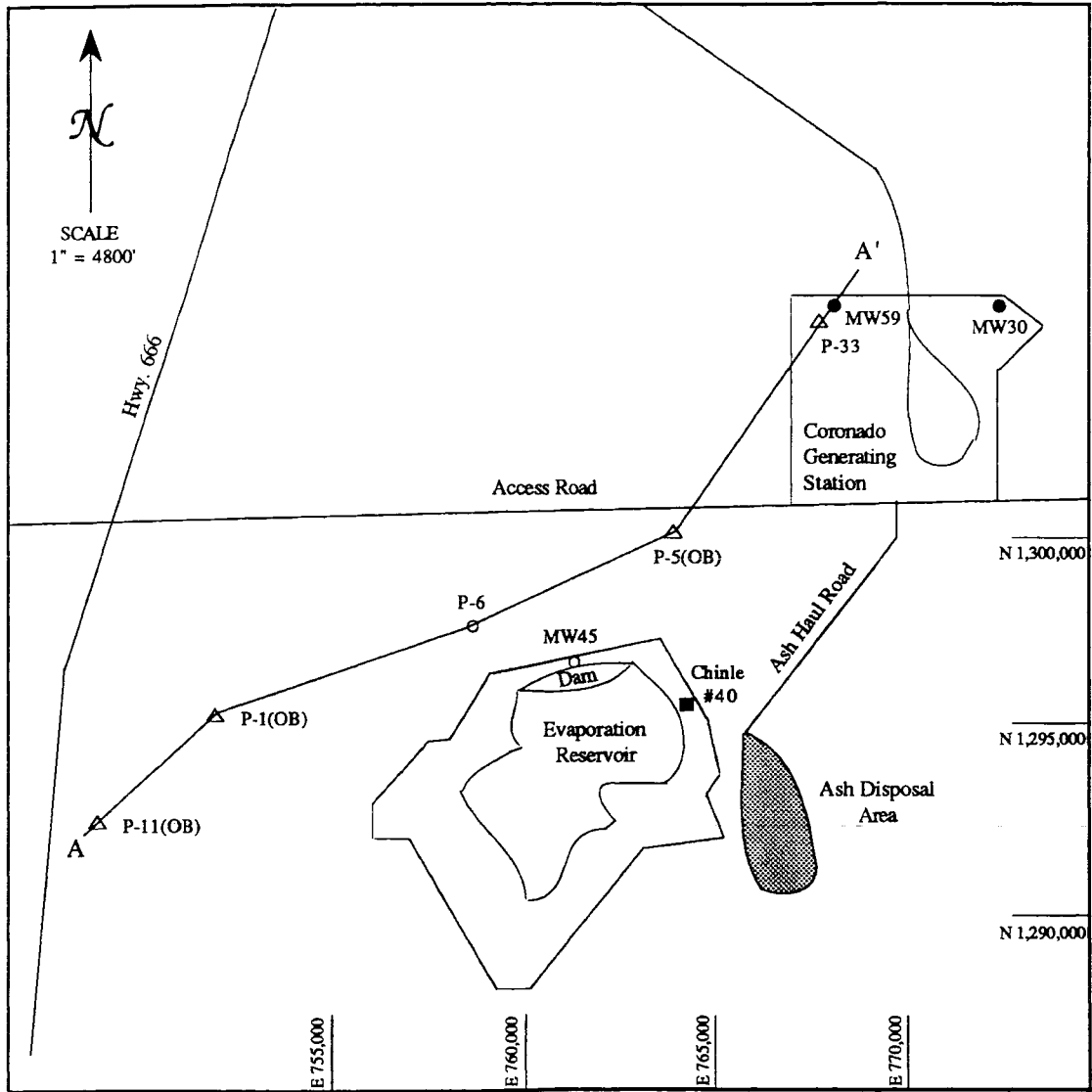


Figure 7.3 Site plan of the Coronado Generating Station showing locations of canals, ponds, reservoirs, and storage areas.

Figure 7.4 Location map of ground water, reservoir, and soil samples and geologic cross section (A-A').



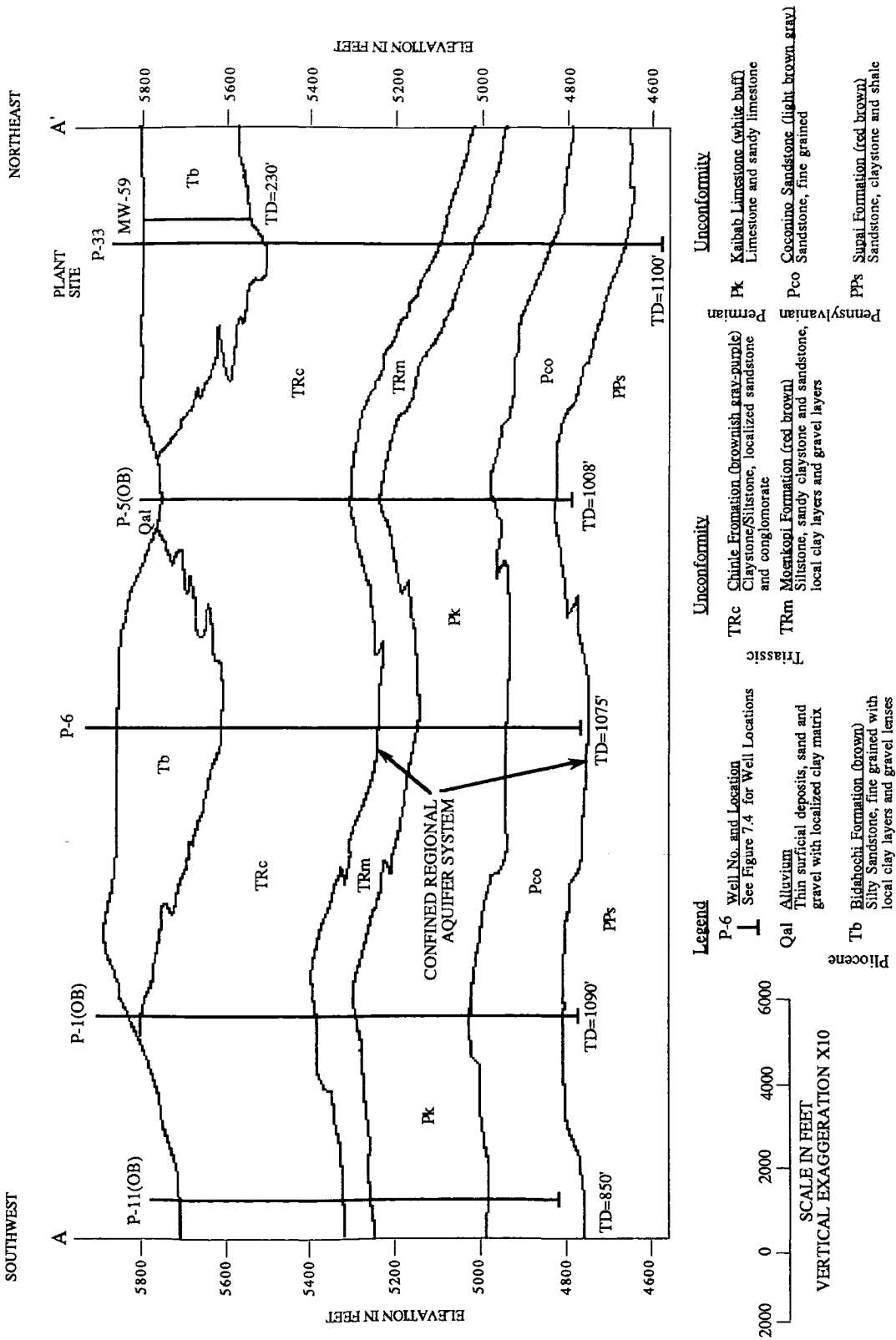
Coordinates indicated are Arizona state plane coordinates

Explanation

- Monitoring Well (Bidahochi)
- Monitoring Well (Chinle-Chinle/Moenkopi)
- △ Monitoring Well (Kaibab-Coconino)
- Soil Sample Location
- A-A' Cross Section Location

NOTE: (1) Kaibab spring located approximately ten miles southwest of the evaporation reservoir. (2) Chinle St. Johns soil sample taken at an outcrop near Highway 666 north of St. Johns.

Figure 7.5 Geologic cross section (A-A') across the SRP site.



addition, coal, fly ash, and bottom ash samples were received at this time. No information was provided on the furnace configuration and conditions at the plant.

7.2.3 Chemical Data

The water, coal, and fly ash samples were analyzed for boron and sulfate concentrations as well as for boron and sulfur isotope ratios as described in Chapter Two. The two soil samples were only analyzed for boron concentrations and isotopic ratios. In addition, the bottom ash sample was also leached, but the boron concentration in the bottom ash sample was too low for boron isotopic analysis. Isotopic work was also discontinued on the Kaibab ground water sample and the Chinle #40 soil due to unsuccessful boron isotopic runs on the thermal ionization mass spectrometer. The soil sample failure was associated with high organic content which caused difficulty in separation procedures. Chemical data and isotopic results are provided in Table 7.1.

To supplement the isotopic work, a review of the water chemistry data provided was conducted. In general, native ground water is characterized as sodium bicarbonate type while plant process water is a sodium sulfate type. The highest ion concentrations in the on-site reservoirs are in the cooling tower canals, contaminated waste water reservoir 108, blowdown reservoir 107, and retention pond 105. Water from these impoundments is of sodium sulfate type. The evaporation reservoir contains the highest ion concentrations at the CGS. Water in the reservoir is a sodium sulfate type with mean TDS content of 15,900 mg/l for 1989. As this impoundment serves as the final waste water repository for the plant, ion concentrations are increasing over time. Figure 7.6 illustrates the significant boron and sulfate concentration increases from 1980 to 1989. In addition, major cation and anion data are also listed in Table 7.2 based on 1984 stiff diagrams for MW30 and MW45 and 1984 chemical analysis for the evaporation reservoir.

According to Shirley (1989), two principal areas at the CGS contain altered

Table 7.1 Summary of chemical and isotopic analysis of SRP field samples.

Chemical Analysis (mg/l)	Evaporation Reservoir	MW-30	MW-45	Kaibab	Chinle St. Johns	Coal	Fly Ash Leachate
B	16.67	0.35	0.30	0.64	0.04	200 ppm	0.55
SO ₄	9,708	853	338	471	--	Pyritic=0.15% Organic=0.51% Total=0.66%	--
Isotopic Analysis (‰)							
$\delta^{11}\text{B}$	+3.1	+17.1	+31.2	--	+10.7	+11.7*	-6.6
$\delta^{34}\text{S}$	+6.0 +5.7	-9.2 -11.0	+21.6 +21.7	+20.6 +20.2	--	**Pyritic=+9.4 Organic=+13.8 Total=+12.8	+4.9 +4.6

*value obtained from the water-soluble boron of the coal sample.

**pyritic sulfur isotope value determined from mass balance calculations.

Figure 7.6 Graphic representation of the boron and sulfate concentration increase in the evaporation reservoir from 1980 to 1989.

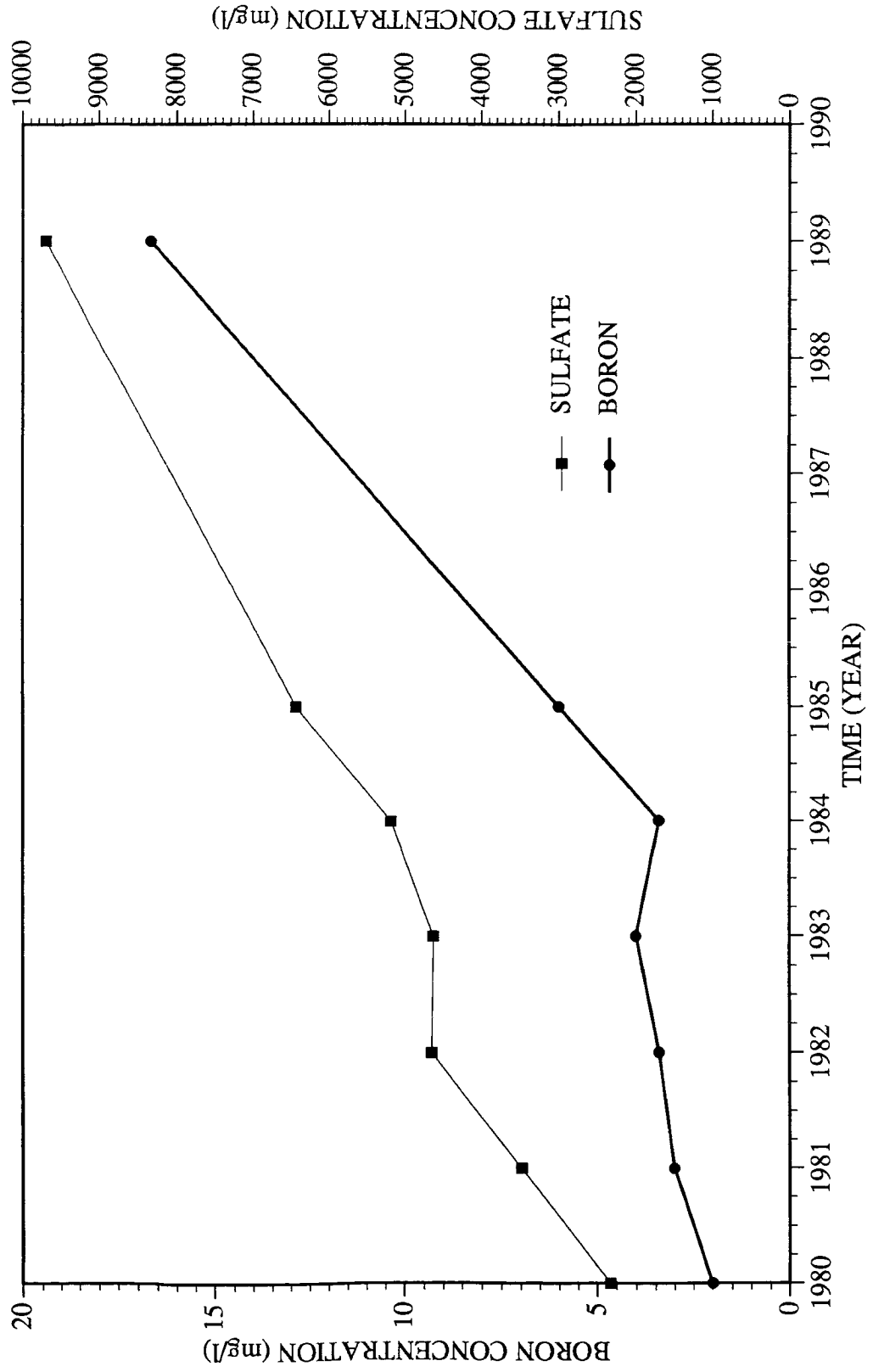


Table 7.2 1984 water chemistry data.

<u>Constituent</u>	<u>Evaporation Reservoir</u>	<u>MW30</u>	<u>MW45</u>
Na	2,311	550	1,330
Ca	649	180	160
Mg	315	40	50
Cl	1,743	250	1,420
HCO ₃	124	790	430
SO ₄	5,180	770	1,100
B	3.4	--	--
pH	7.9	7.7	7.6
TDS	10,386	1,683	4,860

Chemical data obtained from Shirley (1989). MW30 and MW45 data measured from stiff diagrams.

ground water in comparison to past native conditions on the indication of ion concentrations and TDS results. These areas include the northern perimeter of the site (MW30) and just north of the evaporation pond (MW45). Correlations were produced by SRP that suggested that percolation of plant process/waste water is occurring with potential sources including seepage from reservoirs, cooling tower canals, and retention ponds. However, as isotopes are used to determine ground water sources on the basis of distinct, isotopic signatures from various origins, isotopic results coupled with chemical data and geochemical modeling should provide the final evidence if there has been mixing of the process/waste water with ground water.

7.3 Preliminary Geochemical Modeling

The geochemical model PHREEQE (Parkhurst et al., 1980) was used to conduct solution modeling on MW45 and MW30 in order to determine water-rock interactions in the system. Results should provide useful information in assessing equilibrium processes and origin of dominant species in the system.

Chemical constituent values for both MW45 and MW30 were obtained from 1984 stiff diagrams and are listed in Table 7.2. As these values are only rough estimates of the actual chemical conditions, conclusive statements cannot be made until accurate chemical analyses are provided. However, preliminary results show that equilibrium is being approached with respect to calcite and gypsum indicating water-rock interactions rather than anthropogenic sources are dominant in the system.

7.4 Discussion of Isotopic and Chemical Data

On the basis of different isotopic values, the evaporation reservoir does not appear to be contaminating the surrounding area. Conclusions and recommendations were based

on the following observations.

The boron and sulfur concentrations and stable isotope ratios for boron and sulfur for both laboratory generated fly ash leachates and the evaporation pond sample are distinctly different from the monitoring wells. Therefore, no indication of mixing of the waste water with ground water was observed. In addition, preliminary geochemical modeling, coupled with boron and sulfur isotope results for MW45, indicate that the water composition is indigenous to the aquifer, and results from natural dissolution of minerals encountered along the flowpath. For example, the sulfur isotope value is consistent with sulfur derived from evaporite deposits containing anhydrite and gypsum as opposed to being derived from sulfide oxidation in the coal burning process. This is also confirmed by the similar sulfur isotope value of the Kaibab ground water sample. The computer model also predicts that the ground water in MW45 is in equilibrium with gypsum which is a likely scenario for water derived from such an aquifer.

The source of the sulfur detected in MW30 is distinctive of sulfur derived from a sulfide source, because the values are so depleted in the heavier isotope. Possible sulfide sources include pyrite within coal piles on the surface, or sulfide minerals within the Bidahochi Formation itself. The sulfur is not originating from the waste water because the sulfur isotopes ratios are significantly different. Based on the calculated SRP pyritic sulfur value ($\delta^{34}\text{S} = +9.4 \text{ ‰}$) which is significantly heavier in ^{34}S than MW30, it was concluded that the sulfur source is sulfide in the Bidahochi Formation rather than pyrite within the coal piles.

MW45 and MW30 were both enriched in ^{11}B . The large differences between the boron isotopic values of the evaporation pond, fly ash leachate, and two monitoring wells again confirm that no mixing of waste water with ground water has occurred. The boron isotope values are indicative of boron derived from marine shales (Figure 1.1).

Before conclusive statements can be on the boron isotopic value of the Chinle St. Johns soil sample, more soil samples would need to be analyzed from the site.

Significant changes in the water chemistry of the evaporation pond have occurred over the past decade where the concentration of boron in the water is now greater than 16 mg/l. The tolerance level for most agriculturally related plants is approximately 1 mg/l (Bassett, 1980); consequently it is becoming much more important that the water from the evaporation pond not be allowed to reach the ground water.

In conclusion, isotopic and chemical data have provided evidence that waste water at the Coronado Generating Station is not impacting the shallow aquifer system. The ubiquitous nature of boron and sulfur in the natural environment has provided a useful monitoring tool to observe if mixing of waste water and natural water has occurred by comparing their isotopic ratios.

CHAPTER EIGHT

SUMMARY AND CONCLUSIONS

Boron and sulfur are found in varying concentrations in coal. Boron is incorporated into the coal matrix by the accumulation of boron in plant tissue while sulfur incorporation is primarily caused by the in situ production of reduced sulfur species by microbial processes. While isotopic fractionation occurs during uptake into plant tissue and by microbial processes in the coal swamp, further fractionation is likely to occur during the combustion of the coal as some of the boron and sulfur is concentrated on the ash, and some escapes into the atmosphere as flue gas. The results of this study provides explanations for boron and sulfur incorporation into coal and behavior during combustion.

The processes that occur during boron incorporation into coal tend to deplete the heavier isotope, ^{11}B , and include the adsorption of boron from clays and diffusive uptake of boron by plants. Unless additional processes occur during coal formation that introduces a source of isotopically heavy boron, one would expect water-soluble boron in coal to be more depleted in ^{11}B .

The isotopic data obtained from this study show that fly ash leachate becomes depleted in ^{11}B when compared to the original coal sample. No boron isotopic fractionation is expected to occur in the gas stream during coal combustion. In addition, fly ash δ values appear to be dependent on the initial boron concentration of the original coal where higher boron content coals produced fly ash leachates more enriched in the heavy isotope than those with lower boron concentrations in coal.

Several conclusions were made on sulfur incorporation into coal on the basis of isotopic results from the different coal fractions coupled with results found in the literature. Organic sulfur originates from two major independent sources: 1) sulfur assimilated by

living plants in the coal swamp; and 2) sulfur from bacterial reduction of dissolved sulfate in water. In addition, organic sulfur in low-sulfur coals (< 1% total sulfur) is indicative of the original plant material.

Different combustion behaviors were observed between the high and low-sulfur coals analyzed in this study. The high-sulfur coals became slightly enriched in ^{34}S in comparison to the total isotopic content of the original coal, while the low-sulfur coal resulted in a slight depletion of ^{34}S on the fly ash. The behavior of the low-sulfur coal was similar to that described for boron isotopic behavior. Low-sulfur coal consists primarily of organic sulfur. During combustion this organic material is volatilized with some condensing and then adsorbing onto the entrained fly ash particles. The resulting sulfate on the ash particle is depleted isotopically. In addition to the organic sulfur phase, high-sulfur coals may contain a significant percentage of sulfides that are oxidized to sulfates during combustion. Although there is a minor depletion when sulfides oxidize to sulfates, the overall depletion is less for high-sulfur coals than for low-sulfur coals where most of the sulfate originates from volatilized organics. Therefore, other processes must also be occurring to explain the slight enrichment in ^{34}S in high-sulfur coals.

The isotopic content of samples from a coal-fired power-plant were also determined. Samples included coal, fly and bottom ashes, two soil samples, a sample from the evaporation pond, and three ground water samples. The resulting boron and sulfur isotopic ratios were then used to speculate how the observed fractionation from different parts of the coal combustion system could be used to determine if proper containment of waste water was being achieved. On the basis of isotopic results from the various samples, no indication of mixing of the waste water with ground water was observed. The boron and sulfur concentrations and stable isotope ratios for boron and sulfur for both laboratory generated fly ash leachates and the provided evaporation pond sample were distinctly

different from the monitoring wells. In addition, preliminary geochemical modeling, coupled with boron and sulfur isotope results for a monitoring well just north of the evaporation pond, indicate that the water composition is indigenous to the aquifer resulting from natural dissolution of minerals encountered along the flow path. A similar conclusion was also reached for a second monitoring well analyzed. The source of sulfur detected was distinctive of sulfur derived from a sulfide source, because the values were so depleted in the heavier isotope. As the pyritic isotopic value determined for the coal used in this power plant was significantly heavier in ^{34}S than the monitoring well, it was concluded that the sulfur source must originate from sulfide within the geological formation underlying the site rather than pyrite within the coal piles.

Boron and sulfur isotopic analyses could provide an invaluable tool in better understanding coal combustion behavior. The use of boron and sulfur isotopes has proven to be a successful application in this study for determining if waste water has impacted a shallow aquifer system.

APPENDIX A**ANALYTICAL DATA OF MINOR AND TRACE ELEMENTS
OF COAL SAMPLES**

Appendix A Minor and trace elements of the Illinois coal samples (ppm, dry basis).

<u>Element</u>	<u>101*</u>	<u>102*</u>	<u>107**</u>
Ag	<1	<1	<1
As	2	32	0.6
Ba	32	14	55
Be	1.4	3.3	<1
B	193	109	102
Br	6	3	<1
Cd	1.1	0.8	<0.4
Ce	6	2	7.7
Co	3	6	2.8
Cr	31	7	12
Cs	1.1	0.8	1.3
Cu	9.7	21.9	7.6
Dy	0.6	1.5	-
Eu	0.2	0.2	0.13
F	63	26	-
Ga	3	3	3
Ge	<5	30	<5
Hf	0.4	0.2	0.6
La	4	2	4.8
Li	11.3	18.1	5.2
Lu	0.1	0.1	0.08
Mn	31	16	42
Mo	15	4	<5
Ni	11	22	5
Pb	8	149	11
Rb	9	5	15
Sb	0.2	3.4	0.11
Sc	2.1	2.1	2.0
Se	1.5	1.3	1.2
Sm	0.9	0.9	0.7
Sn	<1	<1	<5
Sr	25	12	35
Ta	0.1	0.1	0.11
Tb	0.1	0.2	0.10
Th	1.2	0.7	1.7
Tl	<2	<2	<1
U	<2	<1.5	<0.7
V	25	22	16
W	<0.5	<0.5	<0.4
Yb	0.4	0.6	0.2
Zn	172	99.8	21.9
Zr	16	13	23

*Harvey and Kruse, 1988.

**Kruse, 1989.



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 FAX: (303) 278-1528

DATE October 3, 1990
 HRI PROJECT 002-64-X
 HRI SERIES NO. 44599-A
 DATE RECD. 9/10/90
 CUST P.O.# C-62332

University of Arizona
 Linda Lerner
 Department of Hydrology
 Tucson, Arizona 85721

REPORT OF ANALYSIS

 SAMPLE NO. 44599-1
 SAMPLE IDENTIFICATION: SRP Coal Sample

Total Moisture, %	6.22
As Received Ash, %	15.20
As Received Total Sulfur, %	0.62
As Received Sulfate Sulfur, %	<0.01
As Received Pyritic Sulfur, %	0.14
As Received Organic Sulfur, %	0.48
Dry Ash, %	16.21
Dry Total Sulfur, %	0.66
Dry Sulfate Sulfur, %	<0.01
Dry Pyritic Sulfur, %	0.51
Dry Organic Sulfur, %	0.15

By: 
 Coal Laboratory Manager



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DATE October 3, 1990
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 HRI SERIES NO. 44599-B
 DATE RECD. 9/10/90
 CUST P.O.# C-62332

University of Arizona
 Linda Lerner
 Department of Hydrology
 Tucson, Arizona 85721

QUALITATIVE/SEMI-QUANTITATIVE EMISSION SPECTROGRAPHIC ANALYSIS

SAMPLE IDENTIFICATION: SRP Coal Sample

ELEMENT	DETECTION LIMIT	UNITS	ANALYSIS RESULT
Aluminum	(0.01)	%	15
Silicon	(0.01)	%	G(50)
Sodium	(0.1)	%	0.7
Potassium	(0.1)	%	N
Iron	(0.05)	%	3
Magnesium	(0.02)	%	0.5
Calcium	(0.05)	%	3
Titanium	(0.002)	%	0.7
Manganese	(10)	PPM	150
Silver	(0.5)	PPM	0.5
Arsenic	(200)	PPM	N
Gold	(10)	PPM	N
Boron	(10)	PPM	200
Barium	(20)	PPM	3000
Beryllium	(1)	PPM	3
Bismuth	(10)	PPM	N
Cadmium	(20)	PPM	N
Cobalt	(5)	PPM	20
Chromium	(10)	PPM	15
Copper	(5)	PPM	50

By: 

Robert Rostad
 Laboratory Manager

G denotes greater than value shown. H denotes interference
 L denotes detected but below detection limit shown. N denotes not detected.

Results reported on an ash basis.



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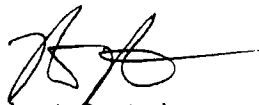
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QUALITATIVE/SEMI-QUANTITATIVE EMISSION SPECTROGRAPHIC ANALYSIS

SAMPLE IDENTIFICATION: SRP Coal Sample

ELEMENT	DETECTION LIMIT	UNITS	ANALYSIS RESULT
Lanthanum	(20)	PPM	50
Lithium	(100)	PPM	N
Molybdenum	(5)	PPM	5
Niobium	(20)	PPM	20
Nickel	(5)	PPM	30
Lead	(10)	PPM	50
Antimony	(100)	PPM	N
Scandium	(5)	PPM	20
Tin	(10)	PPM	N
Strontium	(100)	PPM	1000
Thorium	(100)	PPM	N
Vanadium	(10)	PPM	150
Tungsten	(50)	PPM	N
Yttrium	(10)	PPM	50
Zinc	(200)	PPM	N
Zirconium	(10)	PPM	150

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