Short communication

Chemistry and petrology of paired feed coal and combustion ash from anthracite-burning stoker boilers

James C. Hower ¹, Madison M. Hood ¹, Ross K. Taggart ², Heileen Hsu-Kim ²

¹ University of Kentucky, Center for Applied Energy Research, 2540 Research Park Drive, Lexington, KY 40511 (corresponding author: Hower: 1-859-257-0261, james.hower@uky.edu; Hood: madison.hood@uky.edu)

² Duke University, Department of Civil & Environmental Engineering, Durham, NC 27708 (Taggart: ross.taggart@duke.edu; Hsu-Kim: hsukim@duke.edu)

Abstract

The feed coal and corresponding ash from a series of stoker boilers burning Pennsylvania anthracite were investigated for their petrographic and chemical characteristics. The coals have low-S and moderate-ash contents with similar major oxide and minor element compositions. The volatile minor elements, such as Zn and As, decrease in concentration from the feed coal to the stoker ash (comparisons on the ash basis). The light rare earth elements (La through Sm) decrease in concentration relative to the heavy rare earth elements (Eu through Lu) from the coal ash to the stoker ash.

Keywords: rare earth elements; arsenic; unburned coal

1. Introduction

While there is a great deal of knowledge concerning chemical, mineral, and petrographic transitions from low rank and bituminous coals to solid combustion products, anthracites have not been the subject of nearly as many studies. Suárez-Ruiz et al. (1), Ribeiro et al. (2-3), and Silva et al. (4) investigated the fly ash from pulverized-fuel combustion of Spanish, Portuguese, and Chinese anthracites, respectively. Investigations of the behavior of anthracite in fluidized bed combustion (FBC) are more common, as in Duan et al.'s (5) study of minor element partitioning in circulating FBC (CFBC) combustion of anthracite and of bituminous coal.

Pennsylvania anthracite is generally used for home heating, in industrial and institutional boilers, and for specialty uses, such as for coal-fired pizza ovens. Utility usage of anthracite has, in recent years, largely been confined to CFBC boilers burning the culm (coal plus rock) from pre-reclamation-law mining and beneficiation. The use of limestone in the CFBC process complicates interpretations of the transition from the coal petrology and coal mineralogy and chemistry to the combustion ash chemistry and petrology.

In this study, the ash from the combustion of known feed coals in several stoker boilers was investigated. The stoker ash generally resembles a bottom ash, with some slag-like fragments, from a pulverized coal boiler. No culm was part of the fuel, meaning that no extraneous rock other than mineral matter included with the

beneficiated coal was included in the stoker feed. Therefore, this investigation provides the opportunity to study the products of anthracite combustion without the interference of CFBC-produced sulfates. Nevertheless, the study is limited in the comparisons to bituminous coal combustion since most of the latter have dealt with the bottom ash and fly ash from pulverized-fuel combustion.

2. Methods

Feed coal and stoker ash were collected on five days at five different industrial stoker boilers in Pennsylvania's Eastern Middle Anthracite Field (Table 1). In all cases, the feed coal was sampled in the morning and the stoker ash was sampled in the afternoon in an attempt to ensure, given the time lag between combustion and the passage of the ash to the sampling point, that the stoker ash was reasonably representative of the feed coal. Samples were crushed to ca. 6-mm top size. A fraction of the coal and stoker ash from each day were split off to build a composite sample. Representative splits of each of the samples were crushed to -20 mesh (840 μm) for petrology and to -60 mesh (250 μm) for chemistry.

Proximate and ultimate analyses, sulfur forms, and heating value were conducted at the University of Kentucky Center for Applied Energy Research (CAER) following ASTM D7582 15, ASTM D3176 15, ASTM D2492-02(2012), and ASTM D5865 13, respectively. Major oxides and minor elements concentrations were quantified by X-

ray fluorescence (XRF) at the CAER following procedures outlined by Hower and Bland (6). The rare earth elements + yttrium (REY) were extracted from the high-temperature (750°C) ash samples (as prepared for the XRF analyses) by heated digestion with a 1:1 HF:HNO₃ acid mixture followed by analysis by inductively couple plasma atomic absorption spectroscopy at the CAER (based on published procedures (7)).

Both coal petrology and stoker ash petrology were performed on epoxy-bound pellets prepared to a final 0.05-μm-alumina polish. The petrographic studies used 50x, reflected-light, oil-immersion optics on Leitz Orthoplan microscopes at the CAER. Vitritite reflectance was measured with the incoming light polarized at 45° and the reflected light passing through a 546-nm bandwidth filter on the path to the photomultiplier. The photomultiplier was standardized using glass standards of known reflectance. Vitritite reflectance procedures followed ASTM D2798-11a. The maceral analysis followed nomenclature outlined by the ICCP (8-9). The ash petrology followed procedures described by Hower (10).

3. Results and discussion

3.1 Coal and ash chemistry

The feed coal has moderate ash yield content (about 8-12%, as-received basis) and low sulfur content (Table 2). The major oxide and minor element content is relatively consistent between the samples. The total REY (rare earth elements [REE] +

Y) content, 595-695 ppm (ash basis), is within the range of other Appalachian coals (11-12) and similar to the values found in sized coals from anthracite breakers (preparation plants) (13). In addition to the standard REE values, the rare earth element concentrations normalized for the values in the Upper Continental Crust are included (14). The formulas for the normalized Eu, Ce, and Gd (15-16), below, are used to decouple the respective elements from the other normalized REE in the distribution patterns:

$$Eu_N/Eu_N^* = Eu_N / (0.67Sm_N + 0.33Tb_N) \quad (1)$$

$$Ce_N/Ce_N^* = Ce_N / (0.5La_N + 0.5Pr_N) \quad (2)$$

$$Gd_N/Gd_N^* = Gd_N / (0.33Sm_N + 0.67Tb_N) \quad (3).$$

The stoker ash shows the expected loss of volatile elements from the ash-basis coal to the ash. This is evident in the drop in SO₃ among the major oxides, but also in the decrease in concentration of As and Zn, and, to a lesser extent, Cu and Pb, from the feed coal to the ash. The REY in the coal and stoker ash are similar in concentration to the levels found in many Central Appalachian coals (11-12). The REY show a slight increase in concentration (ash basis) from the coal to the stoker ash, likely owing to the loss of volatile elements. The light REE elements (La through Sm) decrease in concentration relative to the heavy REE (Eu through Lu), as seen in the average coal LREE/HREE of 9.80 vs. the stoker ash LREE/HREE of 9.42 with a the increase in LREE of

550 ppm (ash basis) in the coal to 603 ppm (ash basis) in the stoker ash being offset by the increase in HREE. The Ce_N/Ce_N^* decreases (3.68 to 3.48) while the Gd_N/Gd_N^* (1.95 to 2.10) increases from the coal to the stoker ash, also indicative of the shift in LREE and HREE distributions between the coal and the stoker ash. Heavy REE tend to have an affiliation with the organic structure of coal, at least in low-rank coals (17-24). If this association is retained at the anthracite rank, as chelated elements and/or, probably more likely, as fine minerals formed from elements previously in chelate association at a lower coal rank, it could contribute to the differences in behavior of the subsets of the REE suite. It is certainly possible that more complete combustion of the feed coal and a more complete vitrification of the aluminosilicate minerals would have led to a different distribution of the REE in the stoker ashes.

3.2 Coal petrology

The coals are dominated by vitrinite group macerals, mainly telovitrinite, with lesser amounts of fusinite and other inertinite macerals (Table 3). Liptinite group macerals are likely to be present, sporinite was noted in sample 94008 and liptinites have been observed in other Pennsylvania anthracites (13), but the convergence of vitrinite and liptinite reflectances makes liptinite detection difficult.

Anthracite is a metamorphic rock. While some minerals, quartz, for example, will persist across the rank range, the clays of the bituminous precursors to the

anthracite were transformed to other minerals by the metamorphism of the coal. This will be discussed further in section 3.3. Despite the metamorphism of some clay minerals to micas and other phyllosilicates, for convenience, we will refer to all aluminosilicates observed in the coal by optical petrology as “clay”. The mineral assemblages are dominated by clays (Figure 1A) with lesser amounts of siderite (Figure 1B-C), pyrite (Figure 1C), and sphalerite (Figure 1D). Further investigation of anthracite petrology, some of it from coals similar to the ones studied here, can be found in Hower and Dai (13).

Coal rank within the Pennsylvania anthracite coalfields increases from west to east (25-26). As such, the higher vitrinite maximum reflectance feed coals, samples 93998 and 94000, have a greater proportion of the feedstock from the easternmost mines in the Eastern Middle Anthracite Field.

3.3 Stoker ash petrology

The stoker ash petrology is dominated by glass with significant amounts of unburned or partially burned coal and lesser amounts of rock fragments, mullite, spinel, sulfate and/or other oxidized minerals, and other less common mineral and carbon forms (Table 4).

Anthracite, particularly anthracite approaching meta-anthracite rank as with the feed coals in this study, is not going to melt and repolymerize, as would be the case

with the Appalachian-sourced bituminous caking coals commonly used in eastern US power plants. In the pulverized-fuel combustion of anthracites, the carbons can appear as intact or charred particles (1, 4). Some of the coal in the stoker ash appears to have been unburned (Figure 2A-B). Considering that the coal was crushed to obtain the size preferred for petrology, such observations may actually be of the unburned interiors of much larger particles. More common are occurrences such as seen in Figures 2C-D where the effects of heating are visible as eroded and darker edges and voids within the coal particles. Along with the unburned coal, rock fragments are a sign of less efficient heating (and combustion) associated with the stokers. The rock fragments (Figure 3) show a baked, but not vitrified, interior with a vitrified, glassy rim.

Spinel minerals (Figure 4), including magnetite along with a number of other Ni-, Cr-, Al- bearing and other spinel varieties, represent the thermal degradation of sulfides and other Fe-bearing minerals in the feed coal. The minerals can occur in coarse to sub-micron sizes, usually in a glassy matrix. Some of this complexity is seen in Figure 4A-C, all of which seem to represent welded particles (in particular, Figure 4C) with some growth of larger crystals between spinel-bearing spheres (Figure 4A). Dendritic development of the minerals is seen in Figures 4A (upper left), 4B (left center), and 4C. Figure 4D is an example of the coarse, complex grains observed in these ashes and in fly ashes and bottom ashes from pulverized-fuel combustion. The red oxidation rims surrounding the welded spheres in Figure 4C and on the left side of the Figure 4D

particle are common features on many spinel and glass grains in these stoker ashes and in the broader universe of fly ash and bottom ash.

As noted, glass, with and without fine mineral inclusions, is the most abundant constituent of the stoker ash. Since the glass is also representative of the most abundant minerals in the feed coal, it is worth noting that the mineralogy of an anthracite and the bounding and interburden rocks is not necessarily the same as in a bituminous or lower rank coal. Shale mineral assemblages in the Anthracite Fields are dominated by K- and NH_4 -illites, kaolinite, pyrophyllite, quartz, and Fe-rich chlorite with mixed-layer chlorite/smectite and illite/smectite with minor to trace amounts of Na-rich illite (brammallite) and paragonite (27-32). With an increase in rank, and our coals are at the high end of the regional rank series, kaolinite contents decrease and illite and pyrophyllite contents increase. The mineral transformations have an impact on the melting behavior of the rock fragments in the boiler with kaolinite, melting in the 450-700°C range (33-34), being replaced by assemblages of illite (>1400°C melting T, depending on the chemical composition (35)), mullite (stable high-T mineral forming at 980°C in transformation from metakaolinite (36)), pyrophyllite, and paragonite. Studies of metamorphic rocks show that pyrophyllite transitions to cristobalite and mullite at 1200°C (37) and paragonite transitions to albite and andalusite at about 500°C and to sillimanite at about 840°C (38).

As a short step beyond the rock fragments discussed above, Figure 5A shows a glass fragment with an internal structure reminiscent of shale. Figure 5B shows a variety of glass forms, from glass with included minerals (upper left) to glass with no apparent inclusions (diagonal from upper right to center) to glass with Fe-oxides. The inclusion of Fe-oxides in glass is also seen in Figure 5C and in the rim surrounding the glass + minerals sphere in Figure 5D. Transitions in the density of mineral inclusions are seen in Figure 5E. In this case, the glass + bladed mineral assemblage of the left half of the image gives way to a denser packing of mineral in the right third of the image. A 5-10- μm rim seems to have either no inclusions or, more likely, much finer inclusions than the mineral-rich assemblage to its left. The structure of the rim is likely a function of the more-rapid cooling of the rim versus the interior of the particle. The structure of the interior is a function of the cooling history and the chemistry of the melted slag. Figure 5F shows glass, possibly with mineral inclusions, with a structure reminiscent of vermicular kaolinite.

4. Summary

Combustion ash sourced from known anthracite blends in several stoker boilers was investigated. The feed coals are moderate ash (8-12%, as-received basis) with low sulfur. The coal petrology is dominated by vitrinite group macerals, primarily telovitrinite, with lesser amounts of fusinite. Clays and their metamorphic products

dominate the minerals in the coal, with lesser amount of pyrite, sphalerite, and siderite. The fly ash petrology is dominated by glass with significant amounts of unburned and partially burned coal. Rock fragments, usually rimmed by glass, are minor constituents in the ash. Sulfur (measured as S and SO₃) decreases from the coal to the ash. Among the minor elements, As, Zn, Cu, and Pb decrease from the coal ash to the stoker ash. Comparing the coal ash versus the stoker ash, the concentration of light REE's decreases relative to the heavy REE's.

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Figure captions

1. Minerals in coal.

A/ Clay (c) in fusinite lumens. Image 94006 01.

B/ Siderite (s). Image 94006 03.

C/ Pyrite (py) in siderite (s). Image 94008 05.

D/ Sphalerite (arrow). Image 94008 04.

2. Coal in stoker ash.

A/ Vitrinite (v), secretinite (sc), and fusinite/semifusinite (f). Image 94001 03.

B/ Vitrinite (v), micrinite (mi), and inertodetrinite (id)/ Image 94003 04.

C/ Vitrinite with indications of heating, as seen in the darker regions along edge of particle. Image 94003 11.

D/ Vitrinite with indications of heating, as seen in the darker regions along edge of particle and in the center of the image. Image 94007 07.

3. Rock fragments.

A/ Rock fragment (r) with glassy rim. Image 93999 01.

B/ Rock fragment (r) in glass (g). Image 94001 12.

4. Spinel.

A/ Spinel in glassy matrix. Image 94007 06.

B/ Spinel in glassy matrix. Image 94001 04.

C/ Spinel in glassy matrix; note red oxidation rim around edge of spheres. Image 94003 02.

D/ Spinel in glassy matrix; note red oxidation rim around edge of particle. Image 94001 16.

5. Glass and included minerals.

A/ Glass with banding reminiscent of layering of clays in shale. Image 93999 06.

B/ Three forms of glass: upper left – glass with bladed mineral inclusions; upper right and center across diagonal – glass with no apparent inclusions; and lower left – glass, apparently with oxidized Fe minerals. Image 94001 13.

C/ Glass, apparently with oxidized Fe minerals. Image 94009002.

D/ Glass with bladed crystals and red oxidation rim. Image 94001 07.

E/ Glass on left with included bladed minerals. Denser packing of minerals in right third of image. Image 94009003.

F/ Glass with banding reminiscent of vermicular kaolinite. Image 94009 09.

392 Table captions

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394 1. Sample numbers for coal and ash along with the stoker type.

395

396 2. Coal and ash chemistry. As-received ash, Moisture, volatile matter, fixed carbon,
397 ultimate analysis (C, H, N, S, O), sulfur forms, heating value (MJ/kg); major oxides (wt.
398 %, ash basis); Cl (wt. %, whole coal); minor elements, Sc, Y, rare earth elements (ppm;
399 ash basis); total rare earths + Y (REY); total rare earths (REE); light REE; heavy REE;
400 ration of LREE to HREE.

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402 3. Whole-coal and mineral-free maceral and mineral composition (vol. %) and vitrinite
403 maximum and random reflectances (and standard deviations) for each of the daily coal
404 samples and the composite sample.

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406 4. Fly ash petrology (vol. %) for each of the daily ash samples and the composite
407 sample.

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Table 1

Key #	KCER#	MA#	Type	Stoker Type
1	93998	75706	Coal	EFM
1	93999	75712	Ash	
2	94000	75707	Coal	Baeromatic
2	94001	75713	Ash	
3	94002	75708	Coal	Harman
3	94003	75714	Ash	
4	94004	75709	Coal	Harman DVC 500
4	94005	75715	Ash	
5	94006	75710	Coal	Harman
5	94007	75716	Ash	
composite	94008	75711	Coal	
composite	94009	75717	Ash	

coal composite represents 1/8th of each daily coal sample

ash composite represents 1/4th of each daily ash sample

Table 2 part 1

MANumber	SampleID	material	key	Ash	Mois	VM	FC	C	H	N	S _{total}	S _{py}	S _{sulf}	S _{org}	O
75706	93988	coal	1	10.65	2.91	5.42	81.02	81.60	2.48	0.76	0.62	0.13	0.03	0.46	3.89
75707	94000	coal	2	8.07	5.37	5.09	81.47	79.68	2.70	0.69	0.58	0.06	0.01	0.51	8.28
75708	94002	coal	3	9.94	5.57	5.50	78.99	81.52	2.55	0.71	0.63	0.12	0.02	0.49	4.65
75709	94004	coal	4	12.09	3.69	5.57	78.65	78.67	2.51	0.70	0.64	0.16	0.02	0.46	5.39
75710	94006	coal	5	9.91	5.40	5.64	79.05	79.96	2.59	0.64	0.63	0.13	0.01	0.49	6.27
75711	94008	coal	comp.	10.14	4.68	5.36	79.82	80.16	2.53	0.65	0.67	0.13	0.01	0.53	5.85
75712	93999	ash	1	60.92	0.38			39.39	0.52	0.09	0.17				dl
75713	94001	ash	2	60.88	4.15			35.24	0.73	0.07	0.14				2.94
75714	94003	ash	3	59.54	0.43			39.04	0.46	0.12	0.33				0.51
75715	94005	ash	4	59.38	0.56			39.19	0.48	0.16	0.22				0.57
75716	94007	ash	5	64.56	0.44			35.58	0.42	0.10	0.11				dl
75717	94009	ash	comp.	61.38	0.86			36.87	0.47	0.09	0.14				1.05

MANumber	SampleID	material	key	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O	P ₂ O ₅	TiO ₂	SO ₃	Cl
75706	93988	coal	1	51.85	33.60	8.02	0.70	0.94	0.21	2.18	0.17	2.49	0.21	0.16
75707	94000	coal	2	50.18	34.55	6.66	0.78	0.86	0.28	2.27	0.31	2.49	0.21	0.14
75708	94002	coal	3	51.20	33.68	7.21	0.63	0.90	0.25	2.36	0.21	2.51	0.19	0.14
75709	94004	coal	4	51.64	32.53	7.32	0.57	0.94	0.26	2.42	0.17	2.46	0.17	0.15
75710	94006	coal	5	50.95	33.76	7.57	0.66	0.90	0.23	2.29	0.22	2.52	0.18	0.14
75711	94008	coal	comp.	51.45	32.86	7.04	0.64	0.87	0.24	2.27	0.21	2.47	0.22	0.13
75712	93999	ash	1	50.48	33.86	7.06	0.84	0.87	0.27	2.26	0.27	2.41	0.14	
75713	94001	ash	2	51.33	33.12	7.23	0.53	0.98	0.28	2.35	0.11	2.41	dl	
75714	94003	ash	3	51.22	34.19	6.79	0.75	0.90	0.24	2.19	0.27	2.53	dl	
75715	94005	ash	4	51.55	33.17	7.72	0.76	0.88	0.29	2.33	0.29	2.31	0.03	
75716	94007	ash	5	51.59	33.69	7.07	0.76	0.91	0.24	2.19	0.28	2.43	0.05	
75717	94009	ash	comp.	51.90	33.51	6.94	0.72	0.90	0.26	2.30	0.25	2.48	0.02	

Table 2 part 2

MANumber	SampleID	material	key	V	Cr	Mn	Co	Ni	Cu	Zn	As	Rb	Sr	Zr	Mo	Cd	Sb	Ba	Pb
75706	93988	coal	1	728	227	415	96	157	205	109	22	371	278	344	167	dl	9	1128	76
75707	94000	coal	2	765	247	337	86	147	199	121	30	357	487	354	192	dl	8	1281	76
75708	94002	coal	3	711	227	348	93	159	235	154	28	362	339	337	184	dl	9	1168	77
75709	94004	coal	4	675	216	405	82	142	194	162	33	344	303	337	181	dl	8	1138	79
75710	94006	coal	5	723	229	380	101	164	202	119	29	355	371	341	171	dl	8	1184	79
75711	94008	coal	comp.	702	226	341	92	151	219	112	28	366	344	342	195	dl	8	1178	75
75712	93999	ash	1	719	241	330	79	132	131	48	dl	490	361	301	118	dl	4	1230	65
75713	94001	ash	2	652	208	358	81	139	37	34	dl	496	173	267	91	dl	2	1146	68
75714	94003	ash	3	727	234	346	86	141	166	64	dl	480	392	328	152	dl	6	1229	63
75715	94005	ash	4	692	226	357	76	131	161	70	dl	487	437	324	160	dl	8	1281	61
75716	94007	ash	5	719	237	325	86	138	170	63	dl	486	368	318	149	dl	6	1198	62
75717	94009	ash	comp.	716	231	318	83	140	127	48	dl	481	419	344	177	dl	8	1223	60

MANumber	SampleID	material	key	Sc	Y	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
75706	93988	coal	1	40	41	94	217	24	241	15	3	19	7	11	dl	14	dl	7	2
75707	94000	coal	2	40	36	84	191	20	225	14	3	16	6	10	dl	12	dl	7	1
75708	94002	coal	3	41	41	93	210	23	242	15	3	18	6	11	dl	13	dl	7	2
75709	94004	coal	4	35	32	79	181	20	234	13	3	16	5	8	dl	12	dl	6	1
75710	94006	coal	5	34	29	74	176	19	232	13	3	15	6	9	dl	12	dl	6	1
75711	94008	coal	comp.	35	30	75	176	18	215	12	3	15	5	9	dl	12	dl	6	1
75712	93999	ash	1	45	48	98	212	23	250	15	3	19	6	12	dl	14	dl	8	2
75713	94001	ash	2	40	48	94	207	23	253	15	3	19	6	12	dl	15	dl	8	2
75714	94003	ash	3	44	48	103	221	26	264	16	4	19	6	12	dl	14	dl	8	2
75715	94005	ash	4	41	41	93	206	24	235	14	3	19	6	11	dl	13	dl	7	dl
75716	94007	ash	5	45	48	103	219	25	259	16	3	20	7	13	dl	14	dl	8	2
75717	94009	ash	comp.	43	26	99	214	23	257	15	3	19	7	12	dl	14	dl	9	2

MANumber	SampleID	material	key	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
*				30	64	7.1	26	4.5	0.88	3.8	0.64	3.5	0.8	2.3	0.33	2.2	0.32
75706	93988	coal	1	3.13	3.39	3.38	9.27	3.33	3.41	5.00	11.67	3.14		6.09		3.18	6.67
75707	94000	coal	2	2.80	2.98	2.82	8.65	3.11	3.41	4.21	10.00	2.86		5.22		3.18	3.33
75708	94002	coal	3	3.10	3.28	3.24	9.31	3.33	3.41	4.74	10.00	3.14		5.65		3.18	6.67
75709	94004	coal	4	2.63	2.83	2.82	9.00	2.89	3.41	4.21	8.33	2.29		5.22		2.73	3.33
75710	94006	coal	5	2.47	2.75	2.68	8.92	2.89	3.41	3.95	10.00	2.57		5.22		2.73	3.33
75711	94008	coal	comp.	2.50	2.75	2.54	8.27	2.67	3.41	3.95	8.33	2.57		5.22		2.73	3.33
75712	93999	ash	1	3.27	3.31	3.24	9.62	3.33	3.41	5.00	10.00	3.43		6.09		3.64	6.67
75713	94001	ash	2	3.13	3.23	3.24	9.73	3.33	3.41	5.00	10.00	3.43		6.52		3.64	6.67
75714	94003	ash	3	3.43	3.45	3.66	10.15	3.56	4.55	5.00	10.00	3.43		6.09		3.64	6.67
75715	94005	ash	4	3.10	3.22	3.38	9.04	3.11	3.41	5.00	10.00	3.14		5.65		3.18	
75716	94007	ash	5	3.43	3.42	3.52	9.96	3.56	3.41	5.26	11.67	3.71		6.09		3.64	6.67
75717	94009	ash	comp.	3.30	3.34	3.24	9.88	3.33	3.41	5.00	11.67	3.43		6.09		4.09	6.67

* correction for concentration in upper continental crust (after ref. 14)

Table 2 part 3

MANumber	SampleID	REY	LREE	HREE	LREE/HREE	EuN/EuN*	CeN/CeN*	GdN/GdN*
75706	93988	695	591	63	9.38	0.24	3.68	1.97
75707	94000	625	534	55	9.71	0.26	3.67	1.85
75708	94002	684	583	60	9.72	0.25	3.62	2.01
75709	94004	610	527	51	10.33	0.29	3.66	2.09
75710	94006	595	514	52	9.88	0.28	3.78	1.81
75711	94008	577	496	51	9.73	0.31	3.78	2.05
75712	93999	710	598	64	9.34	0.25	3.50	2.12
75713	94001	705	592	65	9.11	0.25	3.54	2.12
75714	94003	743	630	65	9.69	0.31	3.43	2.04
75715	94005	672	572	59	9.69	0.26	3.52	2.20
75716	94007	737	622	67	9.28	0.23	3.42	2.01
75717	94009	700	608	66	9.21	0.24	3.51	1.97

* correction for concentration in upper continental crust (after ref. 14)

Table 3

sample	93998		94000		94002		94004		94006		94008	
key	1		2		3		4		5		comp.	
telinite	11.0	12.2	19.6	20.5	9.6	10.2	7.4	7.8	9.9	10.5	15.6	17.0
collotelinite	58.2	64.4	55.7	58.1	51.8	54.5	61.9	65.1	50.0	53.3	55.5	60.5
<i>total telovitrinite</i>	<i>69.2</i>	<i>76.6</i>	<i>75.3</i>	<i>78.5</i>	<i>61.4</i>	<i>64.6</i>	<i>69.3</i>	<i>73.0</i>	<i>59.9</i>	<i>63.8</i>	<i>71.1</i>	<i>77.5</i>
vitrodetrinite	4.1	4.6	5.7	5.9	11.1	11.7	6.2	6.5	8.2	8.7	5.9	6.4
collodetrinite	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
<i>total detrovitrinite</i>	<i>4.1</i>	<i>4.6</i>	<i>5.7</i>	<i>5.9</i>	<i>11.1</i>	<i>11.7</i>	<i>6.2</i>	<i>6.5</i>	<i>8.2</i>	<i>8.7</i>	<i>5.9</i>	<i>6.4</i>
corpogelinite	0.8	0.9	0.6	0.7	0.6	0.6	0.3	0.3	0.7	0.7	0.6	0.6
gelinite	0.0	0.0	0.3	0.3	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
<i>total gelovitrinite</i>	<i>0.8</i>	<i>0.9</i>	<i>0.9</i>	<i>1.0</i>	<i>0.6</i>	<i>0.6</i>	<i>0.3</i>	<i>0.3</i>	<i>0.7</i>	<i>0.7</i>	<i>0.6</i>	<i>0.6</i>
<i>total vitrinite</i>	<i>74.2</i>	<i>82.1</i>	<i>82.0</i>	<i>85.5</i>	<i>73.1</i>	<i>76.9</i>	<i>75.9</i>	<i>79.8</i>	<i>68.7</i>	<i>73.2</i>	<i>77.6</i>	<i>84.6</i>
fusinite	15.1	16.7	13.0	13.5	20.2	21.2	18.0	18.9	24.1	25.7	13.0	14.1
semifusinite	0.8	0.9	0.3	0.3	0.6	0.6	0.6	0.7	0.7	0.7	0.3	0.3
micrinite	0.3	0.3	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
macrinite	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
secretinite	0.0	0.0	0.6	0.7	1.2	1.2	0.6	0.7	0.3	0.4	0.6	0.6
funginite	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
inertodetrinite	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
<i>total inertinite</i>	<i>16.2</i>	<i>17.9</i>	<i>13.9</i>	<i>14.5</i>	<i>21.9</i>	<i>23.1</i>	<i>19.2</i>	<i>20.2</i>	<i>25.2</i>	<i>26.8</i>	<i>13.9</i>	<i>15.1</i>
sporinite	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.3	0.3
cutinite	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
resinite	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
alginite	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
liptodetrinite	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
suberinite	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
exsudatinite	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
<i>total liptinite</i>	<i>0.0</i>	<i>0.0</i>	<i>0.0</i>	<i>0.0</i>	<i>0.0</i>	<i>0.0</i>	<i>0.0</i>	<i>0.0</i>	<i>0.0</i>	<i>0.0</i>	<i>0.3</i>	<i>0.3</i>
silicate	9.3		3.8		5.0		4.6		5.8		8.0	
sulfide	0.3		0.3		0.0		0.0		0.0		0.0	
carbonate	0.0		0.0		0.0		0.0		0.3		0.3	
other	0.0		0.0		0.0		0.3		0.0		0.0	
<i>total mineral</i>	<i>9.6</i>		<i>4.1</i>		<i>5.0</i>		<i>5.0</i>		<i>6.1</i>		<i>8.3</i>	
Rmax	5.65		5.78		5.31		5.05		5.26		5.35	
st dev	0.47		0.40		0.62		0.43		0.42		0.63	
Rrandom	4.73		4.92		4.63		4.40		4.50		4.67	
st dev	0.41		0.45		0.52		0.42		0.43		0.65	

Table 4

sample	93999	94001	94003	94005	94007	94009
key	1	2	3	4	5	comp.
glass	61.1	64.9	70.8	67.2	71.6	63.1
mullite	2.5	2.6	0.3	0.3	0.0	0.3
spinel	t	1.2	1.8	0.3	2.5	1.7
quartz	0.7	0.0	0.0	0.0	0.0	0.0
sulfide	0.0	0.0	0.6	0.0	0.0	0.0
sulfate	1.8	0.9	0.6	0.0	0.3	0.0
rock fragment	2.5	2.6	2.4	0.3	0.3	0.9
isotropic coke	0.4	0.6	0.0	0.0	0.0	0.3
anisotropic coke	0.0	0.0	0.0	0.3	0.0	0.0
inertinite	0.7	0.0	0.3	0.0	0.0	0.0
unburned coal	30.5	27.2	22.8	31.5	25.3	33.8