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TRACE ELEMENTS *in* COAL

Volume I

Vlado Valković

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Author

Vlado Valković

Institute Ruder Bošković
Zagreb, Yugoslavia

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PREFACE

Coal has been widely used as a principal energy source since the 18th century. It is believed that coal was the main driving force behind the Industrial Revolution; for the first time in history, a truly cheap metal, iron, was made available. By the end of the 19th century coal surpassed wood as the main energy source in the U.S. (see Figure 1, Chapter 1, showing projections of the U.S. Energy Information Administration). Since then it has been used as the principal fuel for heating of buildings, manufacturing processes, and electrical power generation. For a long time coal was king.

Then, at the beginning of the 1950s it was dethroned by petroleum with the help of attacks by environmentalists. The problems of energy and environment were brought together. In order to maintain or increase the standard of living, an increase in the development of energy sources is required. So, to preserve the quality of life, the production of energy in an environmentally acceptable manner is required. So far, energy has been extracted from coal by direct combustion in steam boilers and generation of electricity. This results in damage to the environment, with the worst offender probably being sulfur in the coal.

With the predictable exhaustion of oil reserves and the finite amounts of deposits of some elements, attention is again being focused on coal. There have been some very important developments in coal utilization technology in the areas of coal liquefaction, coal gasification, and advanced methods of coal combustion to generate electric power. It may turn out to be equally important that coal combustion produces an ash which may offer an economical raw material for resource recovery. It has been generally accepted that coal technologies (unlike nuclear technologies, for example) can proceed in a largely empirical way. However, recently the need to accelerate the transition from experience-based technology to science-based technology has been recognized. This new approach can produce more efficient and cleaner technologies.

Coal has been described as a "bridge to the future". It is the most plentiful fossil fuel in the world, and it has a potential for filling a growing proportion of the demand for energy. It is found around the globe, but three countries (the U.S. the U.S.S.R., and China) own nearly two thirds of all known coal reserves. At present rates of consumption, these reserves would last the world more than 200 years, according to conservative estimates. Furthermore, geologists think the world probably has 15 times this much coal.

Developments in the U.S. are of great interest. The goal of the U.S. government to reduce dependency on imported fossil fuels, as well as some other factors, is moving the U.S. toward an economy based on coal as the primary fossil fuel. The use of coal as fuel is expected to triple in the period 1975 to 2000, from approximately 10 quads (1 quad $= 10^{15}$ Btu) to 30 quads (see Figure 1, Chapter 1). Electric power utilities are the major users of coal, and most of the projected increase will also be for the generation of power. Minor increases in coal use as a chemical feedstock to replace petroleum sources is anticipated, but not in the next few years. The use of coal in coking will probably remain at about the present level.

Because of the way it was formed, coal may contain every naturally occurring element. Early chemical analyses of coal and its ashes were limited to the major elements (C, H, O, N, S, Si, Fe, Al, K, Ca, and Mg). Trace elements is often defined as any element whose concentration in coal is 1000 ppm (0.1%) or less. However, elemental composition is very variable, and for the sake of completeness, major elements should be included in discussions on elemental composition of coals.

The first trace element analyses of coal were performed in the 1930s. In the U.S., an ongoing program for the sampling and analysis of coal for trace elements began in 1948. At that time the lack of trace element analysis resulted from the difficulty of applying the classical wet chemistry methods of analysis to trace constituents. However, the advent of newer techniques of instrumental analysis has made analysis of trace elements more feasible. In recent years, general interest in chemical analysis of coal and coal related materials has significantly increased to the state where adequate analytic procedures and suitable standards are currently available for many trace elements. The number of complete modern analyses for trace elements in coal has increased greatly in recent years. As of 1979, the largest accumulation of these data, on 3700 samples of U.S. coal, is publicly available from the data bank of the U.S. Geological Survey in its National Coal Resources Data System.

The main emphasis of this book is on the occurrence and distribution of trace elements in coal. Nature and mode of occurrence of trace elements, variations in distributions, and concentration levels in ash are discussed in detail. The accumulated knowledge about all elements detected in coal is summarized. Special attention is paid to rare and uncommon elements and to radionuclides. Trace elements distribution in different phases of coal utilization processes is discussed next. Possibilities of trace element recovery from coal and coal ash are elaborated.

Environmental considerations are of great importance for the acceptance of coal-utilization techniques. Trace element contaminants from coal-fired power plants are studied by many researchers. The effects of radionuclides released in the environment are critically summarized.

Methods for the measurements of trace elements concentration in coal and its ash are described in the last chapter of Volume II. Optical methods, X-ray analysis, and nuclear methods are presented, in addition to classical chemical methods.

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THE AUTHOR

Vlado Valković, Ph.D., is presently Scientific Advisor at the Institute Ruder Bošković, Zagreb, Croatia, Yugoslavia.

Dr. Valković graduated in 1961 from the University of Zagreb, with a B.A. degree in experimental physics and obtained his M.A. degree in nuclear physics in 1963 and his Ph.D. degree in 1964. The thesis title was "Nuclear Reactions with 14.4 MeV Neutrons on Light Elements".

Dr. Valković has been associated with two institutions during all his professional career — one in the U.S., one in Yugoslavia. The institutions are the Institute Ruder Bǒsković in Zagreb and the T. W. Bonner Nuclear Laboratories at Rice University, Houston, Texas.

Dr. Valković is a fellow of the American Physical Society, a member of the European Physical Society, Yugoslav Physical Society (Croatian section), Society for Environmental Geochemistry and Health, and other professional and honorary organizations.

His research has been done on both sides of the Atlantic: in the U.S. as well as in a number of laboratories in Europe.

Dr. Valković has published more than 100 research papers on nuclear physics and applications of nuclear techniques to the problems in biology, medicine, environmental research, and trace element analysis. He is the author of five additional books: *Trace Element Analysis* (Taylor and Francis, London, 1975), *Nuclear Microanalysis* (Garland, New York, 1977), *Trace Elements in Human Hair* (Garland, New York, 1977), *Trace Elements in Petroleum* (Petroleum Publishing, Tulsa, 1978),and *Analysis of Biological Material for Trace Elements Using X-ray Spectroscopy* (CRC Press, Boca Raton, 1980). His current major research interests include the study of the role and movements of the elements in nature.

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Chapter 1

COAL — ORIGIN, CLASSIFICATION, PHYSICAL AND CHEMICAL PROPERTIES

I. COAL ORIGIN

Coal is one of the fossil fuels found on our planet. It represents the accumulation of organic materials in sedimentary strata. The basic difference between coal and other fossil fuels (oil and gas) is in the fact that coal does not migrate but it undergoes *in situ* compaction with time, to form various ranks of coal. In many cases coal still contains recognizable source material and is composed chiefly of compressed and altered remains of terrestrial plant material such as wood bark, roots, leaves, spores, and seeds.

The results of accumulation of *in situ* residues and important debris in swamps leads to the formation of peat. After peat has accumulated for a period, it must be buried under mineral sediment, generally clay, silt, and sand. In time, the peat forms beds of coal that range from a few centimeters to many meters in thickness. The coal is often interbedded with shale, sandstone, and other sedimentary rocks. A single stratigraphic sequence may include several coal beds. Coal-bearing strata may include alternating marine and nonmarine beds. The coal beds are in the nonmarine parts of the section and are of brackish water or freshwater origin, though some peat swamps received occasional marine incursions.

In terms of biogeochemical cycles, coal represents the fixation of carbon from atmospheric carbon dioxide by plant growth over extensive geologic time. The release of all this accumulated fixed carbon into the atmosphere as carbon dioxide may result in an unbalanced biogeochemical carbon cycle. In the long term, the consequences of this imbalance may be the most significant impact of coal utilization, and these are currently under study by many scientists. Other elements will be mobilized to a far less dramatic level but in sufficient quantities to warrant concern (see References 1 to 27).

Van Krevelen[27] gives the following account of the processes involved in coal bed formation: during the period of coal formation lasting from the lower Carboniferous to the Permian, uninterrupted swamps covered large areas of the Northern Hemisphere. Due to the great depth of Carboniferous coal formations, it seems likely that these swamps underwent a process of subsidence that was largely balanced by sedimentation. Such sunken areas, called geosynclines, are usually formed by strong lateral, compressive forces acting on the crust of the Earth. The geosynclines probably did not sink at a constant rate, but alternated between periods of rapid and slow subsidence. During the periods of slow subsidence, shallow lagoons formed and sedimentation occurred at a more rapid rate than did the sinking, resulting in luxuriant growth of aquatic plants. The plant debris settled to the bottom and was acted upon by microorganisms to form peat deposits, which grew until the rate of subsidence increased again. Eventually, the swamp was submerged and covered by sediment, and a coal seam was formed. The pattern was probably the one most often followed in formation of coal deposits; however, some coal seams were probably formed by the build-up of silt in deeper waters.

It is generally accepted that there were at least two stages of coal formation from plant material: (1) the biochemical period of accumulation and preservation of plant material as peat and (2) the geochemical period of conversion of peat to coal. Although most coal researchers accepted this theory, agreement on the details of the actual chemical and physical changes that occurred in the process is not so widespread.[28]

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Spackman[29] states that coal seams are laminar, sedimentary rock bodies ranging in thickness from a centimeter to several hundred meters. Most of the economically significant seams of the U.S. are 6 cm to 7 m thick, a few being as thick as 25 m. A seam may consist of a number of layers (lithobodies), and these layers may contain different mixtures of macerals and minerals, giving them different characteristics. Although the classification of coal components, macerals and minerals, will be discussed later, here we shall summarize van Krevelen's[27] description of the formation of major lithotypes.

Fusain was formed under very dry conditions. Many researchers feel that, because of its similarity to charcoal, fusain may have formed as the result of forest fires caused by lightning. Another theory suggests that it was produced by some exothermic microbial process.

Vitrain was formed more slowly under semidry conditions, as in a swamp where the groundwater level was just under the surface. The dead plant material sunk into the wet humus soil and was preserved. Because the stagnant water contained little oxygen, aerobic decomposition was inhibited, and the lignified material, which was also relatively resistant to anaerobic decay, was preserved. Under true wet swamp conditions, decay of plant material was carried out to a much higher degree, resulting in only the most resistant fragments being left, thus forming durain.

Clarain is believed to have been formed under conditions between the relatively dry environment of vitrain and fusain and the true wet swamp environment of durain. It is characterized by a relatively high vitrinite content. The woody tissue was evidently macerated before burial because clarains contain spores and other materials embedded in a matrix of vitrinite.[30]

Cannel coal was probably formed in lakes and pools where spores accumulated by wind and water were deposited in the muck on the bottom.

Boghead coal is very similar to cannel coal, but it originated from different material. It consists mainly of algae that died and settled into the mud.[27]

The U.S. Bureau of Mines system of classification of coal types is slightly different. Comparison of the international and the U.S. Bureau of Mines terminology used for basic coal types is shown in Table 1.[29]

Because of the inclusion of this sediment and waterborne dissolved elements, coal beds will contain all the elements found in the eroded rocks from which the sediments are derived. A coal bed could therefore contain all the naturally occurring elements. Additional elements can be introduced into the coal after burial by infiltrating groundwater, either precipitating as minerals or through ion exchange in the clays or organic matter.

According to Zubovic,[31,32] the ability of any particular element to form from chemical emplacement processes in the coal-forming swamp is regulated by several geological processes in the source area. Rapid and extensive uplift of the source areas would tend to reduce the length of time necessary for chemical weathering and would result in a greater influx of clastic materials and a smaller amount of soluble inorganic matter into the depositional basin. Under these conditions, a larger amount of the trace elements would be associated with the nonauthigenic mineral matter of coal and a lesser amount with the organic fraction.

Tectonic and climatic activity in the depositional basin must maintain conditions for the accumulation of organic matter. If subsidence is too rapid, little or no vegetation will be able to grow and clastic materials will dominate the depositional sequence. If little or no subsidence takes place, the biochemical cycle will be essentially completed and most of the vegetative organic matter will be oxidized. For organic matter to accumulate in significant quantities, an optimum balance of tectonic and climatic conditions must exist.

The rate of accumulation of organic matter is important in determining the concen-

Table 1
COMPARISON OF INTERNATIONAL AND U.S. BUREAU OF MINES TERMINOLOGY USED FOR BASIC COAL TYPES[9]

International	U.S. Bureau of Mines
Humic coals	Banded coals
Fusain (charcoal-like)	Bright (<20% opaque matter)
Vitrain (black, vitreous)	Semisplint (20 to 30% opaque matter)
Clarain (striated, glossy)	Splint (>30% opaque matter)
Durain (nonstriated, matte)	
Liptobiolithic coals	Nonbanded coals
Cannel	Cannel (abundant spore remains)
Boghead	Boghead (abundant algal remains)

After Spackman, W., Paper presented at Short Course on Coal Characteristics and Coal Conversion Processes, Pennsylvania State University, University Park, October 29 to November 2, 1973.

tration of trace elements in the resulting coal. If the availability of trace elements from a source area remains constant, then the concentrations that will result in the organic matter will be inversely proportional to the rate of accumulation of the organic matter.

In addition, if the areal extent of organic deposition is large, then low concentrations of trace elements will result. This is why generally thick widespread coal beds have low trace-element concentrations and, conversely, why thin-bedded coals have high concentrations.

During the initial phase of organic accumulation in a basin, the trace elements may be obtained by the plants from the underlying soil profile. When the peat accumulates to a point where the root systems are within the peat, then the dominant source becomes the elemental flux from the surrounding borderland. The mineral matter that makes up the soil most probably also had its origin in the same area.[31,32]

The age of a coal seam is important because coal constitutents vary according to the different materials found in plant matter, and these change during the evolution of the plants. Spackman[29] cites as an example the difference in exinite content of coals formed before and after the Tertiary period. During the Jurassic and Cretaceous periods, the dominant plant group was the gymnosperms, which are today represented by pines, fir, spruce, etc. In their reproductive cycle, gymnosperms produced and released large numbers of spores into the air. These spores were in such abundance during the dominant period of the gymnosperms that they constituted a large proportion of a hydroaromatic plant component of coal called exinite. Angiosperms are plants that appeared during the Cretaceous period and are today the dominant plant group. These plants evolved in embryo sac retained in an ovule on the sporophyte generation of the plant, and spores were no longer produced in such great abundance. Thus, one of the coal types common in the older coals is relatively rare in tertiary coals.

Geological and geochemical differences also influenced the production and composition of coal seams. For example, Illinois seams in the U.S. developed in close association with marine water, producing large concentrations of pyritic and organic sulfur in the coal, whereas coals that developed in parts of the Dakotas (U.S.) experienced minimal marine water influence and contain small concentrations of sulfur.[33]

The important role of microorganisms during coal formation is discussed in detail by Parks[28] and Given.[34,35] Microorganisms were essential to the early stages of the coalition process because they performed the function of converting dead plant material to the partially decayed organic matter called peat. Reasons for partial rather than

Table 2
REMAINING COAL RESERVES IN THE WORLD

Continent and country	Productible coal 10^9 metric tons	Percent of continental total	Percent of world total
Asia			
U.S.S.R.	600	52.3	25.8
China	506	44.1	21.8
India	32	2.8	1.4
Japan	5	0.4	0.2
Others	4	0.4	0.2
Total	1147	100.0	49.4
North America			
U.S.	753	94.4	32.5
Canada	43	5.4	1.8
Mexico	2	0.2	0.1
Total	798	100.0	34.4
Europe			
Germany	143	47.5	6.2
U.K.	85	28.2	3.7
Poland	40	13.3	1.7
Czechoslovakia	10	3.3	0.4
France	6	2.0	0.3
Belgium	3	1.0	0.1
Netherlands	2	0.7	0.1
Others	12	4.0	0.5
Total	301	100.0	13.0
Africa	35	—	1.5
Australia	29	—	1.3
South and Central America	10	—	0.4
World Total	2320		100.0

After Meyers, R. A., Coal Desulfurization, Marcel Dekker, New York, 1977.

total decay of the plant material are still somewhat open to debate; however, studies of present peat deposits in Florida (U.S.) indicate two important factors, the inherent resistance of certain plant materials such as lignins to decay and the chemical condition of the swamp water. For example, the pH, oxygen content, and mineral matter would have determined whether the dominant bacterial population of the water was aerobic or anaerobic and thus would have controlled the rate of decomposition.

II. COAL DEPOSITS AND RESERVES

On a global scale coal deposits are much more uniformly distributed than oil and gas reserves. Remaining coal reserves of the world by region and principal coal producing countries are shown in Table 2. Table 2 indicates the big reserves in the U.S.S.R., China, and the U.S., which together comprise 80% of the world total. Europe, another big energy consumer, has 13% of the world total. Obviously, these figures should be taken with some caution, and they might be subject to some changes. For example, the U.S. coal resources were estimated in 1974 at 3.6 × 10^9 metric tons.[37] The 1974 estimate of the amount of coal that can be mined economically was 0.396 × 10^9 metric tons. These reserves will be sufficient to satisfy projected energy requirements in the U.S. (see Figure 1).

Coal-bearing rocks underlie about 14% of the land area of the contiguous U.S.

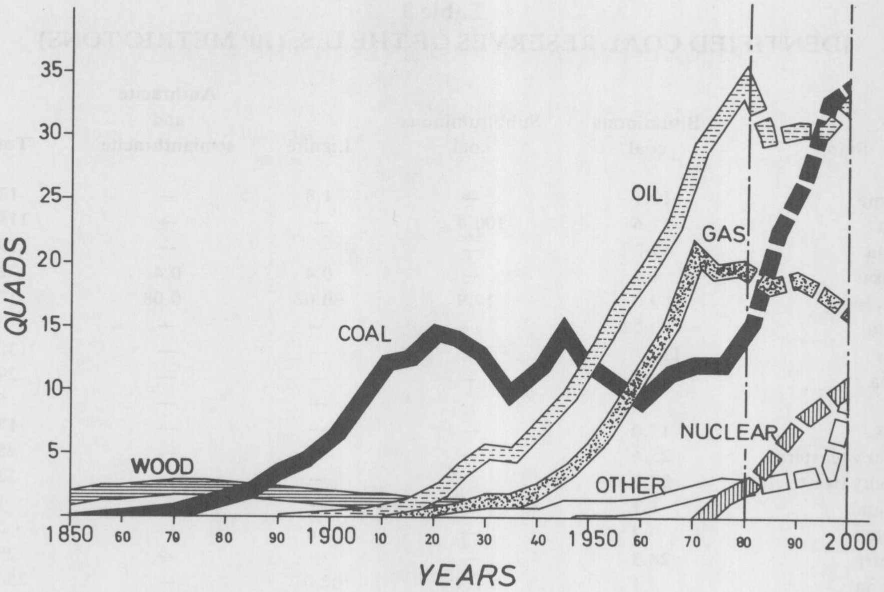

FIGURE 1. Different types of energy supply in U.S. projections from Energy Information Administration.

According to Averitt[37] bituminous, subbituminous, lignitic, and anthracitic coals represent 43.1, 28.1, 27.7, and 1.1%, respectively, of the identified U.S. coal resources in 1974. Geographical distribution of these reserves is shown in Table 3.

Reserves of bituminous coal, as estimated by the U.S. Geological Survey, generally are categorized according to coal thickness. Coals having a thickness of 14 to 28 in. are classified as thin, of 28 to 42 in. as intermediate, and of more than 42 in. as thick.

In this text coal of different U.S. regions will be mentioned many times. Table 4 shows a geological classification of the U.S. coals by rank and their distribution by regions.[30] Coals of the western and central states were formed about 150 million years later than those of the eastern and southeastern states; therefore, the plants that provide the organic material for these coals were different. Because the locations were different, the coals were also exposed to greatly differing geological conditions. Thus, it is not surprising that the coals of Appalachia differ greatly from those of the Dakotas. Basically, there are three differences between the coals of the eastern and western U.S. (1) The coals of the western regions were formed much more recently than the eastern coals and are thus generally of much lower rank; (2) the difference in geological location resulted in different mineral distribution between coals of the two regions, e.g., eastern coals generally have a higher sulfur content; and (3) both the difference in geologic time and location resulted in the appearance of different plants, so that different plant materials were incorporated into each of the coal.[33]

III. CHARACTERIZATION OF COAL

Many authors have tried to define coal; the definition of Schopf[38] seems acceptable. Coal is defined as a readily combustible rock containing more than 50% by weight and more than 70% by volume of carbonaceous material. This carbonaceous material resulted from the accumulation and slow decay of plant remains under water. Coal is formed through an apparently continuous series of alterations: living material > peat > lignite > subbituminous coal > anthracite. This succession of changes in the proper-

Table 3

IDENTIFIED COAL RESERVES OF THE U.S. (10^9 METRIC TONS)

State	Bituminous coal	Subbituminous coal	Lignite	Anthracite and semianthracite	Total
Alabama	12.1	—	1.8	—	13.9
Alaska	17.6	100.4	—	—	118.0
Arizona	19.2	—	—	—	19.2
Arkansas	1.5	—	0.4	0.4	2.3
Colorado	99.0	17.9	0.02	0.08	117.0
Georgia	0.02	—	—	—	0.02
Illinois	132	—	—	—	132
Indiana	29.8	—	—	—	29.8
Iowa	5.9	—	—	—	5.9
Kansas	17.0	—	—	—	17.0
Kentucky (eastern)	25.6	—	—	—	25.6
Kentucky (western)	32.7	—	—	—	32.7
Maryland	1.1	—	—	—	1.1
Michigan	0.2	—	—	—	0.2
Missouri	28.3	—	—	—	28.3
Montana	2.1	160.4	102.0	—	264.5
New Mexico	9.8	45.9	—	0.004	55.7
North Carolina	0.10	—	—	—	0.10
North Dakota	0	—	318.0	—	318
Ohio	37.4	—	—	—	37.4
Oklahoma	6.4	—	—	—	6.4
Oregon	0.05	0.25	—	—	0.30
Pennsylvania	58.0	—	—	17.1	75.1
South Dakota	0	—	2.0	—	2.0
Tennessee	2.3	—	—	—	2.3
Texas	5.5	—	9.3	—	14.8
Utah	21.0	0.2	—	—	21.2
Virginia	8.3	—	—	0.3	8.6
Washington	1.7	3.8	0.1	0.005	5.6
West Virginia	91.0	—	—	—	91.0
Wyoming	11.5	111.7	—	—	123.2
Other states	0.5	0.03	0.05	—	0.5
Total	677.7	440.4	433.7	17.9	1569.7

Note: Data as of January 1, 1974. Some figures shown in this table were rounded off to the nearest first or second decimal place and may therefore be slightly different from the original source. Dashes indicate that tonnage is too small to make a noticeable contribution and/or is included under other ranks.

Data from Averitt, P., Coal Resources of the United States, Bull. 1412, U.S. Geological Survey, Reston, Va., January 1, 1974.

ties and structure of coal is called metamorphism. The degree of metamorphism is called "rank".[39]

Transformation of the vegetable matter into peat and then into coals of different rank was the result first of decomposition due to bacterial action, then of dehydration, devolatization, and densification due to chemical and geodynamic processes. Heat, pressure, and long periods of time were required for the slow progressive change in rank from peat to lignite to subbituminous coal to bituminous coal. Strong folding apparently is necessary to produce anthracite, a higher rank of coal.[40]

According to Teichmuller and Teichmuller[41] time is an important factor in bringing about advances in the rank of coals. Pressure effects upon coal formation are related

Table 4
DISTRIBUTION OF COALS BY REGION IN THE U.S.

	Appalachian	Interior	North Great Plains	Rocky Mountain	Pacific	Gulf	Alaska
States	Pennsylvania, Ohio, Virginia, West Virginia, E. Kentucky, Alabama, Tennessee	East coast region, Indiana, Illinois, W. Kentucky, West coal region, Oklahoma, Missouri, Kansas, Arkansas	North and South Dakota, Montana, NE Wyoming	Many distinct basins of different geological history in SW Wyoming, Colorado, Utah, New Mexico, Arizona	Washington, Oregon, California	Parts of Arkansas, Texas, Louisiana, Mississippi, W. Alabama	Alaska
Age[a]	Carboniferous (300)	Carboniferous	Some Cretaceous, mostly early Tertiary (100—50)	Mostly Cretaceous, early Tertiary (130—60)	Tertiary (60—15)	Tertiary (70—30)	Cretaceous and early Tertiary (100—50)
ASTM rank	Principal deposits of high-volatile A and B, medium-volatile, and low-volatile bituminous anthracite	Principal deposits of subbituminous, high-volatile A, B, and C; minor deposits of low-volatile bituminous and anthracite	Principal deposits of lignite and subbituminous	Principal deposits of subbituminous and high-volatile A, B, and C bituminous; minor deposits of medium-volatile bituminous and anthracite	Principal deposits of lignite, subbituminous and high-volatile A, B, and C bituminous; minor deposits of anthracite	Principal deposits of lignite	Principal deposits of subbituminous and high-volatile A, B, and C bituminous

[a] Numbers in parentheses represent millions of years.

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