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The Principal Geological, Chemical and Physical Factors Controlling the Mineral Content of Coal

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Coal is essentially a near end-member of a homologous series with 100 percent carbonaceous matter at one end of the series and with 100 percent mineral matter at the other end. This is tacitly recognized by chemists in their common usage of the mineral-matter-free basis for treatment of coal analyses in experimental work and in process industries.

Whenever classification of coal has been subject for discussion or study (1,2,3)*, the mineral matter content of coal is mathematically removed from consideration--and rightly so for such a purpose. But mathematical elimination of mineral matter does not eliminate the fundamental problem of mineral matter in coal.

Minerals are an integral part of a coal bed. Once this fact gains general acceptance the genetic relations of the minerals found in coal can be properly appreciated. Many papers on the kinds of minerals (4,5,6,7), the distribution of minerals(8,9), and the mode of occurrence of minerals (10) in coal have been published. The biochemical and geochemical origins of ash forming ingredients in coal, the fate of mineral elements leached from degraded plants, and the origin of minor elements in coal are the subject of a previous paper (11). The present paper discusses the interrelationships of the geological, chemical, and physical factors which control the mineral content of coal.

Coal is a rock which is of great economic value and its grade is largely determined by the percentage of minerals present. Most persons concerned with coal are familiar with the mineral matter content of coal only through the residue remaining after combustion. But geologists are concerned with coal as a rock as well as its value as a commodity, and in mapping coal formations throughout the world they are faced with the problem of whether what appears to be coal should be called coal or something else. In such a situation Schopf's (12) definition of coal becomes very important. Here is his definition:

> "Coal is a readily combustible rock containing more than 50 percent by weight and more than 70 percent by volume of carbonaceous material formed from compaction or induration of variously altered plant remains similar to those in peaty deposits. Differences in the kinds of plant materials (type), in degree of metamorphism (rank) and range of impurity (grade) are characteristic of varieties of coal."

On a weight basis, Schopf extends the definition of coal to include one half of the homologous series discussed at the beginning of this paper. The lateral gradation of a coal seam with only a relatively small percentage of mineral matter into a carbonaceous shale is not uncommon in Cretaceous and later coal beds of the western United States. Many thinly bedded deposits are not considered to be coal beds nor would they be included as such according to Schopf's definition, yet these kinds of deposits probably contain a far greater

*Figures in parentheses refer to references listed at end of paper.

geologic reserve of carbonaceous material than do the coal beds now included in reserve data compiled by the U. S. Geological Survey (13).

Geological factors of sedimentation are the primary controls of the mineral content of coal beds. Purely chemical control of mineral deposition problably occurs only during the peat stage and during the early diagenetic stages of the coalification process. During the subsequent history of a coal bed certain physical factors become important in controlling mineral deposition--but these operate directly in conjunction with chemical processes.

GEOLOGICAL FACTORS

The accumulation of peat in sufficient quantities to permit the ultimate formation of a coal bed of commercial importance requires a degree of stability short of equilibrium. Organic material must accumulate at a rate somewhat greater than that at which complete degradation occurs. But minerals are continuously being supplied to the swamp, and with only a relatively small percentage of organic matter accumulating a carbonaceous shale forms, rather than a coal bed. A coal swamp, throughout its life, is a basin of deposition into which minerals are being brought by water and wind. These are mainly hydromica and kaolin minerals with minor amounts of quartz and traces of resistant accessory detrital minerals such as zircon, garnet, tourmaline, and other minerals as reported by Gauger, Barrett, and Williams (7).

The clay minerals that occur as persistent partings in so many coal beds are typical of the geological control of sedimentation operating on a very large scale. The so-called "coal balls," which are large masses of limestone or dolomite found in great abundance within certain coal beds owe their presence in coal to geological controls.

Once again it must be emphasized that geological conditions and geological processes are the primary controls in establishing the grade of an incipient coal bed. But even beyond this first stage of development of coal, beyond the purely sedimentary stage, geological factors have an influence on the chemical and physical controls which are to be discussed.

CHEMICAL FACTORS

The chemical environment of the coal swamp can be effective in modifying the composition of minerals.

The acidity of swamp waters is certainly an important factor in influencing the ultimate disposition of the suspended and detrital mineral matter brought into the peat bog. The acidity of 64 samples of peat taken 0.5 foot below the surface in 15 Minnesota peat bogs had an average pH of 4.2. The pH data are given in Table I and are taken from Passer's report (14).

These data are probably typical for most peat bogs not located in limestone or dolomite terranes. The high acidity of these peat bogs is probably surprising to most chemists and this is why these data have been presented. Coastal swamps, which may be brackish or which may alternate between fresh water and marine water environments must have an entirely different range of acidity but pH data are lacking for such swamps.

Generally, the pH of samples from any given peat profile will decrease from a minimum value near the top to a maximum at or near the soil base. One example is a peat profile from Rice Lake Bog in St. Louis County, Minnesota, where the pH varies from 3.6 to 5.5 as indicated in Table II.

TABLE I. pH OF 64 SAMPLES TAKEN FROM 15 MINNESOTA PEAT BOGS LOCATED IN FIVE COUNTIES (14)

PEAT BOG	COUNTY	NO. SAMPLES	pH (0.5 ft below surface)
Rice Lake	St. Louis	17	3.8, 3.6, 3.3, 3.9, 3.4, 3.3, 3.4, 3.2, 3.2, 3.1, 3.3, 4.0, 3.9, 3.4, 3.5, 5.3
Floodwood State	St. Louis	8	4.1, 4.4, 4.6, 5.1, 4.3, 5.1, 4.0, 4.2
Corona	Carlton	5	3.0, 4.1, 4.1, 3.4, 3.4
Cook	St. Louis	3	3.9, 3.8, 3.9
Cusson	St. Louis	1	4.0
Big Falls	Koochiching	3	5.3, 5.3, 5.5
Red Lake 1	Beltrami	6	5.2, 5.2, 5.8, 4.7, 4.8, 5.5
Red Lake 2	Beltrami	2	5.5, 3.5
Rapid River	Lake of the Woods	3	4.5, 4.9, 5.2
Canyon	St. Louis	3	5.6, 5.6, 5.4
Elmer	St. Louis	3	4.6, 3.8, 3.9
Zim	St. Louis	3	4.4, 5.4, 4.8
Cotton-Shaw	St. Louis	3	3.3, 3.1, 3.0
Payne	St. Louis	3	4.7, 5.8, 5.1
Prosit	St. Louis	1	4.8

TABLE II. PROFILE OF pH AT POSITION CV, RICE LAKE BOG ST. LOUIS COUNTY, MINN. (Ref. 14, p.4)

DEPTH	pH
0.5	3.6
1.5	3.5
2.5	3.5
3.5	4.1
4.5	4.0
5.5	3.9
6.5	4.1
7.5	4.4
8.5	4.5
9.5	4.4
10.5	5.1
11.5	5.0
12.5	5.5

A relatively low pH may be an important factor in altering the character of the clay minerals deposited in a coal swamp. Grim (15) believes that the leaching of alkalies and alklaine earths under such circumstances may account for the dominance of kaolinite in fresh water lake sediments. The intense acid leaching of clays associated with coal beds may well account for the origin of the high grade fire clays so commonly found with coal beds. Carroll (16) experimented with precisely this type of system in the laboratory and found that under anaerobic conditions in fresh water as much as 62 percent of the ferric oxide present on the clay minerals tested were removed in only 23 days. By the action of anaerobic bacteria the pH generally was reduced 2 units or more. This demonstrated that by chemical activity the character of the sedimentary minerals may be changed and iron made available for further chemical reaction.

Bacteria are factors in the chemical control of mineral matter in coal. Sulfide minerals, and especially pyrite and marcasite, are among the most important minerals to be found in coal. The roles of these minerals in affecting the utilization of coal are too numerous to be mentioned in this paper. Bacteria are active in two ways here--one group of organisms will attack the protein in the plants and as a consequence of that activity will ultimately release hydrogen sulfide; while yet another group of bacteria, the Desulfovibrios of Zobell and Rittenberg (17), reduce sulfate ions to sulfide ions. Quantitatively the contribution of sulfide ion from reduced sulfate is far more important and has previously been discussed by Deul (18). Even insofar as the composition of surface waters entering a peat swamp is concerned there are geological overtones. In basins of limited extent geological controls are effective determinants of the chemical nature of the surface waters in a drainage area. An outstanding example is given by Davis (19) in a discussion of the geologic control of the mineral composition of surface waters of the Southern Coast Ranges of California. Davis shows that the ratio of bicarbonate to sulfate concentrations are related to the lithology of the rocks exposed in the tributary drainage area and that the ratio may vary from 0.8 to 6. (dominantly bicarbonate) to a ratio of 0.02 to 0.7 (dominantly sulfate).

The nature of the minerals deposited in the peat swamp and the chemical modification of these sedimentary minerals have been briefly discussed. It is now necessary to consider the interaction of physical and chemical forces in further transformations which may take place subsequent to the peat stage. When equilibrium is interrupted and a peat is buried under an increasing load of sediment, water is squeezed out of the peat and from the underlying sediments. The expelled water migrates either laterally or vertically upward under the compressive forces. During this stage of burial and compaction, called the early diagenetic stage, chemical conditions are constantly changing. The expelled waters probably are concentrated in iron, silica, and in sulfide ions as compared with water in a peat swamp. Replacement of organic structures by pyrite and quartz may well take place at this stage. Replacement phenomena are far too complex to discuss in the light of present knowledge but the fact of replacement as a process cannot be denied.

PHYSCIAL FACTORS

Once a coal has been formed and the bed moisture is reduced to below 20 percent, as in a subbituminous rank coal, cleating of coal becomes a prominent physical feature. Cleats are closely spaced parallel vertical joints; their origin is attributed to pressure phenomena, to tectonic forces, and to forces of contraction following devolatilization (20). These cleat surfaces are often coated with thin layers of mineral matter. Regardless of the mode of origin suggested for the cleats in coal all observers agree that cleating occurs late in the history of a coal bed. Cleating is a physical phenomenon and only after cleats have formed can minerals be deposited in the voids formed by fracturing. In these voids are deposited minerals of a high degree of purity and whichcan be easily identified. Pyrite, kaolinite, calcite, gypsum and halite are minerals which have been found on cleat surfaces of coal. Their origins obviously are similar despite the great difference in composition of the minerals. Pyrite and kaolinite were formed by recrystallization from solution of minerals already present in the coal beds; calcite, gypsum, and halite were in part formed from ions migrating through the coal from outside the coal bed.

Erosion, a geological factor, may expose a coal bed to the atmosphere, and under such conditions cleat fractures in coal may be enlarged by physical forces. Weathering processes now impose an entirely new set of chemical conditions upon the coal bed. Atmospheric oxidation and the action of ground waters effect changes in the mineral matter of coal which are even more startling than the changes in the organic matter. Whole new suites of minerals are formed while pyrite may be completely destroyed. Minerals like gypsum, jarosite, melanterite, copiapite and many other sulfate minerals are formed from the oxidation products of pyrite. Allophane, an amorphous clay mineral which is chiefly a hydrous mixture of alumina and silica, may be an extreme alteration product of clay minerals within the coal and in the overlying sediments (21).

SUMMARY AND CONCLUSION

Geological controls are the primary factors in determining the grade of coal insofar as the mineral content is concerned. These primary controls, operative in the geologic past, have influenced current practices in coal utilization. The chemical environment of the coal swamp certainly has played a role in modifying the minerals deposited in the swamp, which has acted as a reaction vessel within which pyrite and marcasite could form. Under changing physical conditions during burial and compaction, and later, if subjected to erosion and exposure to circulating ground water and air, physical factors become dominant in controlling the chemical transformationsthat occur.

Perhaps it would have been more precise to discuss the factors which control the mineral content of coal all under only one classification--geochemical factors. In a broad sense geochemistry is concerned with all the changes by which the chemical composition of earth systems are modified. Sedimentation, a geological process, is itself controlled by diastrophic forces which are initiated by major geochemical forces. In every stage of coalification, from the first accumulation of plant debris to the ultimate exposure and oxidation of a coal bed, geochemical transformations are occurring.

However, such broad concepts, unless one is accustomed to thinking in such terms, do not convey to the fuel chemist the idea that the variable mineral content of coal is dependent upon a relatively few fundamental processes. Therefore, an attempt has been made to weave into the discussion of chemical and physical factors the continuous thread of dependence upon geological control--and this, in essence, makes the controls geochemical.

The mineral content of coal is a natural consequence of its mode of deposition and its subsequent geological history, and is not due to capricious causes. It is common knowledge that the mineral content of coal influences its utilization, often in a deleterious manner. Coal preparation as now practiced, can effectively reduce the mineral content of almost any coal. With a better understaanding of how minerals in coal are formed, and how they occur, the technology of coal preparation can be further improved.

REFERENCES

(1) A.I.M.E. Tech. Pub. No. 156, 'Classification of Coal.' Papers and discussions presented at the New York meeting, Feb. 1928, 103 pp.

(2) Rose, H. J., 'Classification of coal,' Chemistry of Coal Utilization, Vol. I (Edited by H. H. Lowry), p. 25, John Wiley and Sons, New York, 1945

(3) Flint, D., 'The total mineral matter in coal and its influence on coal classification.' B.C.U.R.A. Mon. Bull. 17 (1953) p. 133.

(4) Nelson, J. B., 'Assessment of the mineral species associated with coal.' B.C.U.R.A. Mon. Bull. 17 (1953) p. 41.

(5) Mackowski, M. T., 'Moglichkeiten zur Kennzeichnung der Mineralverteilung in Kohlen.' Proc. Int. Comm. Coal Petrology, 2 (1956) p. 31.

(6) Parks, B. C., 'Mineral matter in coal.' Second Conf. on the origin and constitution of coal, Crystal Cliffs, Nova Scotia (1952) p. 272.

(7) Gauger, A. W., Barrett, E. P. and Williams, F.J., ' Mineral matter in coal--a preliminary report.' A.I.M.E. Trans. 108 (1934) p. 226.

(8) Ball, C. G., 'Mineral matter of the No. 6 Bed Coal at West Frankfort, Franklin County, Illinois.' Illinois State Geol. Sur. Report Inv. No. 33 (1935).

(9) Sprunk, G. C. and O'Donnell, H. J., 'Mineral matter in coal.' U. S. Bureau of Mines T. P. 648 (1942).

(10) Juranek, G., Kirsch, H., Nemetschek, Th., and Schliephake, R. W. 'Contribution à la connaissance des substances minérales et en particulier des minéraux argileux que l'on recontre dans les charbons et dans les épontes du bassin de la Ruhr.' (Colloque International de Pétrologie Appliquée des Charbons). Revue de L'Industrie Minérale. Special Number, page 41,(July 1958).

(11) Deul, M., 'Biochemical and geochemical origins of ash-forming ingredients in coal.' Preprints of papers presented at Chicago, Ill. American Chem. Soc., Div. Gas and Fuel Chem. (1958) p.169.

(12) Schopf, J. M., 'A definition of coal.' Economic Geology, 51 (1956) p. 521.

(13) Averitt, P., Berryhill, L. R., and Taylor, D. A. 'Coal resources of the United States.' U. S. Geological Survey Circular 293 (1953).

(14) Passer, M. 'Peat samples from Minnesota bogs.' Report No. 16, Dept. of Chemistry, U. of Minn., Duluth Branch (1957).

(15) Grim, R. E., 'Clay mineralogy.' McGraw-Hill Publishing Co., New York, 1953.

(16) Carroll, D. 'Role of clay minerals in the transportation of iron.' Geochimica et Cosmochimica Acta, 14 (1958) p 1.

(17) Zobell, C.E. and Rittenberg, S.C. 'Sulfate-reducing bacteria in marine sediments.' Sears Foundation Jour. of Marine Research, 7 (1948) p. 602.

(18) Deul, M., 'Origin and mode of occurrence of fine-grained disseminated pyrite in coal.' (abs) Geol. Soc. America Bulletin 69 (1958) p. 1553.

(19) Davis, G. H., 'Geologic control of mineral composition of surface waters of the Southern Coast Ranges, California.' (abs) Geol. Soc. America Bulletin 69 (1958) p. 1680.

(20) Stutzer, O. and Noe, A.C. 'Geology of coal.' Univ. Chicago Press, 1940.

(21) Breger, I. A., Deul, M., and Rubinstein, S., 'Geochemistry and mineralogy of a uraniferous lignite.' Economic Geology 50 (1955) p. 206.