INORGANIC SULFUR IN COAL

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INTRODUCTION

Sulfur is a necessary element for the sustenance of all living systems. It is therefore not at all surprising that sulfur is found in abundance in coal, a rock composed primarily of organic detritus.

The forms of sulfur in coal as reported by chemical analyses (ASTM 1974) are: organic sulfur, pyritic or sulfide sulfur, and sulfate sulfur. The last two are inorganically combined within the coal and will be discussed here. Other analytical techniques have been used to identify native or elemental sulfur in coals (Yurovski, 1940; Berteloot, 1947) and also in modern peats (Casagrande, *in* Spackman et al., 1974, p. 63, 219). The amounts of elemental sulfur that have been reported are small and would not be significant in coal utilization.

Sulfate sulfur is also generally of only minor importance in fresh coal samples and except in rare instances occurs in significant amounts only as the coals oxidize (weather). Organic and pyritic sulfur comprise essentially all of the sulfur found in most coals. Yancey and Geer (1968) list analyses of these two forms of sulfur in various coals of the world and these range from a low of 0.44 percent to a high of 9.01 percent total sulfur. Only rarely would one expect to find coals in which the percentage of sulfur would not be included in that range. The organic sulfur content of the coals listed by Yancey and Geer ranged from 11.4 percent to 97.1 percent of the total sulfur. Gluskoter and Simon (1968) reported a mean value of 1.56 for the ratio of pyritic to organic sulfur in 473 face-channel samples of Illinois coals.

SULFUR BEARING MINERALS IN COAL

Iron Sulfides—Pyrite is the dominant sulfide mineral found in coals. Marcasite has also been found in many coals and may be the dominant form in some coals of lower rank (Kemežys and Taylor, 1964). Pyrite and marcasite are dimorphs, minerals that are identical in chemical composition but differ in crystalline form. Pyrite is cubic and marcasite is orthorhombic. The two minerals cannot generally be differentiated in coals except by determining their crystalline structures, usually by X-ray diffraction methods. The term "pyrite" is often used to refer to the undifferentiated iron disulfide minerals in coals.

Rather extreme variations in morphology, size, and mode of occurrence characterize the iron sulfide minerals in coals. These variations arise because of the different geochemical environments in which the minerals were formed and the time of their genesis. Some sulfides were formed contemporaneously with the coal in a peat swamp and are therefore syngenetic. The syngenetic pyrite includes submicrometer-sized particles and also some nodules with diameters as large as a meter. These syngenetic sulfides are the response to the geochemical environment during or immediately following the peat formation, which was approximately 300 million years ago for the coals of carboniferous age. Other of the sulfides are epigenetic; they formed within the coal seam subsequent to the first stages of coalification. The most common form of epigenetic iron sulfide in coal is pyrite deposited along vertical fractures (cleat). I am not aware of any report of marcasite as an epigenetic mineral in bituminous coals of North America, but a mixed marcasite-pyrite cleat filling in a subbituminous coal from Wyoming is shown in Plate 1. Other epigenetic and syngenetic sulfides are shown in scanning electron photomicrographs in Plate 1.

Other Sulfide Minerals—A number of sulfide minerals other than iron sulfides have been reported in coals, including galena (PbS), chalcopyrite ($CuFeS_2$), arsenopyrite (FeAsS), and sphalerite (ZnS). These generally occur only in small amounts. However, coals from northwestern Illinois that contain as much as 5350 ppm zinc and up to 1 percent sphalerite have recently been described by Ruch et al. (1974) and Miller (1974). The sphalerite occurs as a cleat filling up to 10 mm in width (Plate 2).

Sulfate Minerals—Gypsum ($CaSO_4 \cdot 2HO$) and barite ($BaSO_4$) have both been identified as cleat-filling minerals or in nodules in unweathered coals (Plate 2). However, their occurrences are rare and sulfate minerals do not generally comprise a significant portion of the total sulfur in coal.

Because pyrite and marcasite oxidize rapidly when exposed to moist air, a number of different phases of ferrous and ferric sulfates may form. The following have been identified as oxidation products of iron sulfides in Illinois coals (Gluskoter and Simon, 1968): Szomolnokite ($FeSO_4 \cdot H_2O$), rozenite ($FeSO_4 \cdot 4H_2O$), melanterite ($FeSO_4 \cdot 7H_2O$), coquimbite ($Fe_2(SO_4)_3 \cdot 9H_2O$), roemerite ($FeSO_4 \cdot Fe_2(SO_4)_3 \cdot 12H_2O$), and natrojarosite ($(Na_2K)Fe_3(SO_4)_2(OH)_6$). Although these are not present in fresh coals they can become abundant in weathered, oxidized coal samples. The amount of sulfate sulfur reported in the chemical analyses of many coals is a function of the length of time since the fresh sample was collected and of the manner in which it was sorted. Several iron sulfates are shown in Plate 2.

ACKNOWLEDGEMENTS

The research reported upon was sponsored in part by Grant No. R800059 and Contract No. 68-02-0246 from the U.S. Environmental Protection Agency, Demonstration Projects Branch, Control Systems Laboratory, Research Triangle Park, North Carolina. All of the scanning electron photomicrographs were taken with the equipment of the University of Illinois Center for Electron Microscopy.

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ILLUSTRATIONS

Plate 1. Pyrite in Coals: Scanning Electron Photomicrographs
- A. Framboids in low-temperature ash of a sample from the DeKoven Coal Member (bituminous), southern Illinois
- B. Octahedra in low-temperature ash of a sample from the DeKoven Coal Member (bituminous), southern Illinois
- C. Epigenetic cleat filling in a sample of the Opdyke Coal Member (bituminous), southern Illinois
- D. Cast of plant cells from the low-temperature ash of a sample from the Colchester (No. 2) Coal Member (bituminous), northern Illinois
- E. Epigenetic pyrite along inclined shear surface in a sample of lig-lignite, North Dakota
- F. Epigenetic cleat filling in a sample from the Colchester (No. 2) Coal Member (bituminous), northern Illinois

Plate 2. Sulfide and Sulfate Minerals in Coals: Scanning Electron Photomicrographs
- A. Marcasite, epigenetic, along cleat in a sample from a sub-bituminous coal, Wyoming
- B. Sphalerite (ZnS), along cleat in a sample from the Herrin (No. 6) Coal Member (bituminous), northwestern Illinois
- C. Barite ($BaSO_4$) with marcasite and pyrite in a sample from a sub-bituminous coal, Wyoming
- D, E, and F. Iron sulfates which formed on bituminous coal samples subsequent to their having been collected from fresh exposures. X-ray diffraction analyses of these samples identified melanterite ($FeSO_4 \cdot 7H_2O$) and coquimbite ($Fe_2(SO_4)_3 \cdot 9H_2O$).

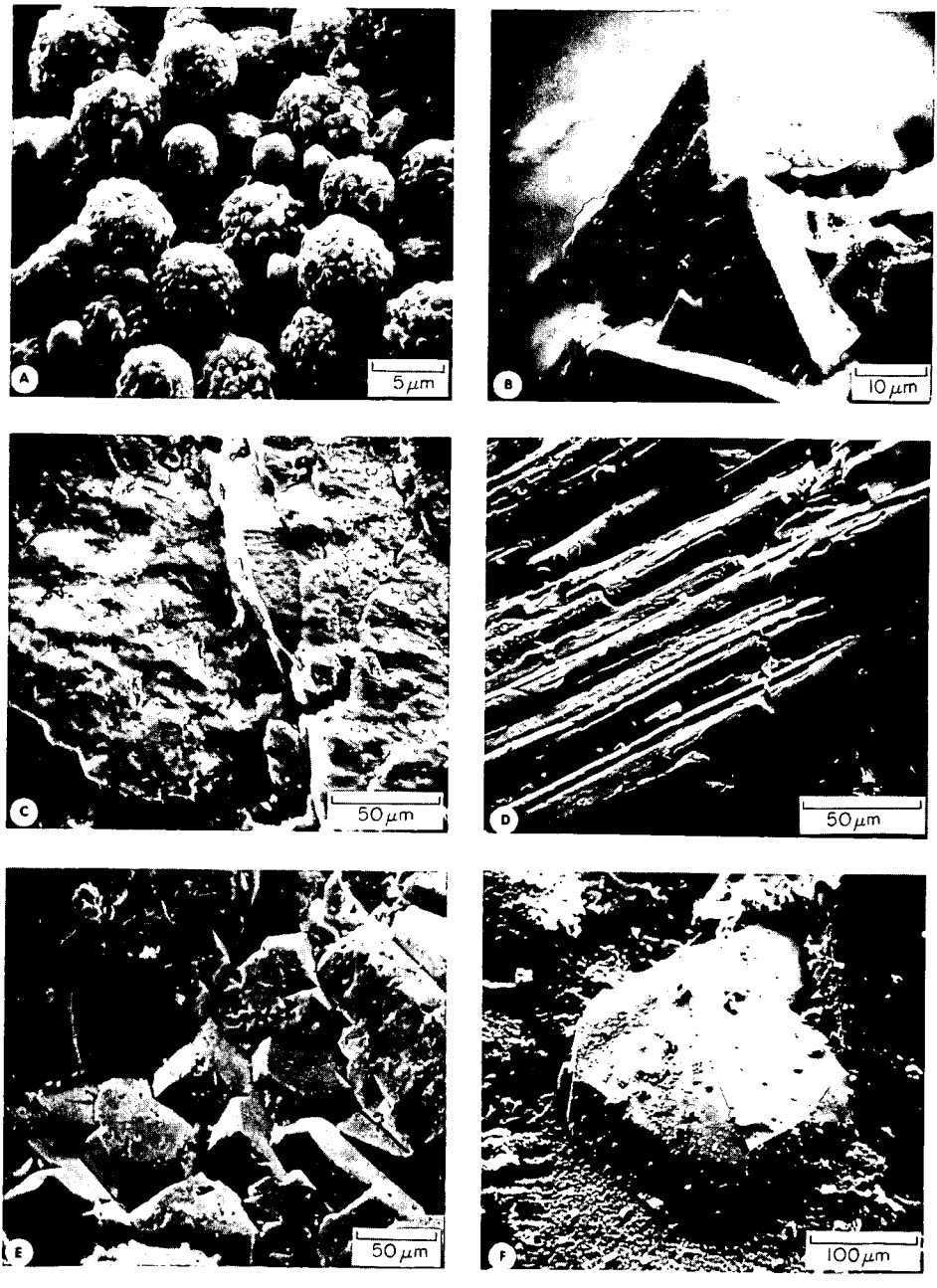

Plate 1. Pyrite in Coals

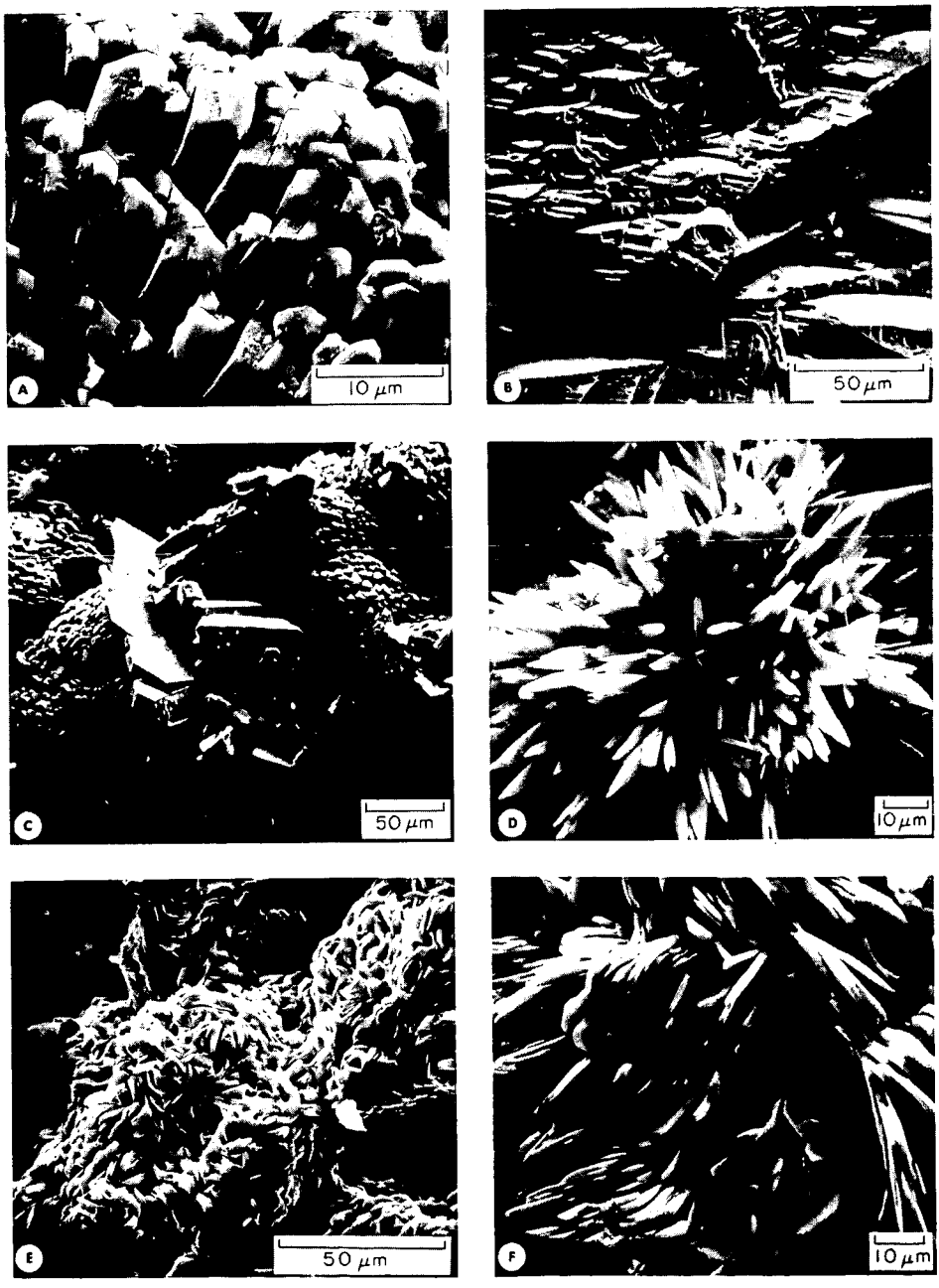

Plate 2. Sulfide and Sulfate Minerals in Coals