Chapter 8

INFLUENCE OF GEOLOGY ON POSTMINING WATER QUALITY: NORTHERN APPALACHIAN BASIN

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Summary

Mining accelerates the weathering of coal overburden. The weathering products of two minerals groups, iron sulfides and calcareous carbonates, dominate the chemical characteristics of postmining water. These minerals need only be present in an abundance of a few percent or less to be significant. By comparison the other 95% or so of overburden minerals play a minor role. The most important factor as to whether or not a site will produce alkaline drainage is the presence or absence of calcareous minerals. Pyrite, although necessary for acid formation, is of secondary importance, because if sufficient carbonates are present postmining water will be alkaline.

The coal-bearing rocks in Pennsylvania are from the Pennsylvanian and Permian? Periods of geologic time. The rocks of the Bituminous Coal Field of western Pennsylvania are divided, from oldest to youngest, into the Pottsville, Allegheny, Conemaugh, Monongahela, and Dunkard Groups. The majority of mineable coal occur in the Allegheny and Monongahela Groups. Several lithologic trends can be observed in this sequence of rocks. The clay/shale content increases upward from a low of about 25% in the Pottsville Group to highs of 70 to 80% in the Dunkard Group. In general there is a inverse relationship with sandstone, with sandstone increasing from ~20% or less in the higher Groups to a high of 50% in the Pottsville. The percentage of calcareous rocks increases upward. The Pottsville Group has less than 1% calcareous rock. The lower Allegheny is less calcareous (6%) than the upper Allegheny Group (14%). Rocks of the Casselman Formation in the Conemaugh Group and higher are greater than 50% calcareous. The percentage of sandstone that is calcareous generally reflects the percentage of overall rock that is calcareous. The uppermost Dunkard Group rocks contain the least amount of siderite, whereas over 20% of the strata in the Allegheny Group and Glenshaw Formation contain siderite. Within the Allegheny and Pottsville Groups sideritic rocks are more abundant than calcareous rocks.

The important depositional environments, from a mine drainage standpoint, are the location of marine zones and distribution of calcareous rocks. The marine rocks are frequently associated with high-sulfur strata, but can also have calcareous zones. Brackish rocks tend to have high sulfur and lack calcareous minerals. Marginally brackish (paralic) rocks frequently have less sulfur than their marine and brackish counterparts. Truly freshwater sediments tend to have calcareous minerals and limestone.

The strata in the Anthracite Region are divided, from oldest to youngest, into the Pottsville and Llewellyn Formations. The Pottsville Formation is entirely of a nonmarine depositional environment. As in western Pennsylvania, the dominant lithology of the Pottsville is sandstone and conglomerate, although the Pottsville of the Anthracite Region contains significant pebble conglomerates. The Pottsville contains up to 14 coal beds, but most are not mineable. The Llewellyn Formation consists predominantly of sandstone, but also contains conglomerates, plus lesser amounts of finer-grained rocks and coals. There are up to 40 mineable coals in the Llewellyn, the thickest and most persistent occur in the lower part of the formation. The Llewellyn and Pottsville Formations are believed to be nonmarine with the exception of the Mill Creek marine zone in the Northern Field. In addition to this marine zone, other calcareous rocks have also been found in the Northern Field. Some of the water quality reflects this source of alkalinity. Although stratigraphic studies have not yet identified calcareous rocks in the Southern and Western Middle Fields, highly alkaline mine waters imply that calcareous rocks exist. The lack of alkaline drainage in the Eastern Middle Field suggests a dearth of calcareous strata in this anthracite field.

Pleistocene glaciation came as far south as the northwestern corner of Pennsylvania's bituminous coal field. Tills, where calcareous, can contribute significantly to the alkalinity of postmining water quality. Tills in the Northern Anthracite Field are not calcareous and do not contribute alkalinity to water.

Sulfur in sedimentary rocks occurs in three forms: sulfide (e.g., pyrite), sulfate, and organic. The oxidation of pyrite results in the formation of sulfuric acid and iron. This acid can dissolve other minerals, releasing other ions such as aluminum, manganese and magnesium. Sulfate minerals are typically weathering products of pyrite oxidation. Frequently these sulfate salts are essentially stored acidity and will produce acid when dissolved in water. Organic sulfur is generally assumed to produce little acid.

The most reactive carbonates in terms of their ability to neutralize acid are calcite and dolomite. The iron-carbonate, siderite, is a common mineral throughout the Pennsylvanian and Permian? strata of Pennsylvania, but it does not generate alkalinity. Calcite and dolomite not only neutralize acidity, but it appears that they can also contribute to the inhibition of acid production.

The presence or absence of calcareous minerals and pyrite is a function of several geologic processes. The paleodepositional environment and paleoclimate during the Pennsylvanian Period were important in determining the original mineralogic composition of strata. Paleoclimate influenced pyrite and carbonate concentrations for terrestrial rocks. For example, wet climates typically yielded less pyrite than dry climates and dry climates favored deposition of freshwater limestones. Rocks deposited in marine environments often have high sulfur and high neutralization potential. Brackish environments generally produce high sulfur with no calcareous minerals, although siderite can be present. High sulfur occurs in marine and brackish environments because of abundant sulfate ions in marine waters. This sulfate served as the source of pyritic sulfur. Marginally brackish environments are generally lower in sulfur and have little neutralization potential. Freshwater (terrestrial) deposits are often calcareous and frequently contain limestones. More recent geologic processes such as glaciation and surficial weathering have also influenced the mineralogy of coal overburden. Tills, if calcareous and of sufficient thickness, can contribute alkalinity to mine waters. Weathering by oxidation removes pyrite and by dissolution removes carbonates The relative depth of removal of these two mineral groups can be an important factor in determining the water quality potential of a mine site.

The geologic controls on coal overburden that have and are operating in Pennsylvania have resulted in overburden that can contain a wide range of concentrations of pyrite and calcareous minerals. Mine drainage quality reflects this variable mineralogy; water can be significantly alkaline to severely acidic.

Within Pennsylvania's Bituminous Coal Field, mine drainage problems differ by stratigraphic horizon and geographic region. Acid problems are more significant in the lower Allegheny Group than in higher strata. Regional variations are often due to paleodepositional environment. For example, lower Allegheny overburden deposited in marine, brackish-marine, to marginally-brackish environments, will differ in the amount of pyrite and amount and type of carbonates present. The highest alkalinities are associated with the thick freshwater limestone sequences of the Pittsburgh Formation (Monongahela Group) in the southwestern corner of Pennsylvania, the thick marine Vanport limestone of the lower Allegheny Group in the central to northwestern area of the bituminous region, and the freshwater limestones of the upper Allegheny Group in areas where these limestones and associated calcareous shales are abundant. In addition, significant alkalinity concentrations occur in the Conemaugh Group where marine limestones are present, and the lower Allegheny Group mines in northwestern Pennsylvania where the overburden includes calcareous tills.

The highest acidity concentrations are associated with overburden: (a) of the Clarion and lower Kittanning coals, particularly where black brackish shales and thick marine shales predominate in the overburden, (b) in the Pittsburgh Coal and Waynesburg Coals of the southwestern portion of the bituminous region, ir areas where the carbonate strata are absent or lack appreciable thickness, and (c) of Allegheny Group coals where sandstone predominates. The wide rang of pH and the range in alkalinity and acidity concentrations for each stratigraphic group documents that some strata within each group has the potential to pr duce alkaline and acidic drainage.

Overall, mine water in the anthracite and bituminous regions has a bimodal distribution of pH. Wat is either acidic or circumneutral. This is because Pennsylvanian Period rocks, at least in western Penn sylvania, can have significant concentrations of pyrit and calcareous carbonates. Calcareous overburden

produces alkaline drainage and pyrite-rich and carbonate-poor overburden produces acidic drainage in the absence of appropriate pollution prevention techniques.

Regional-scale water quality variations are seen in the Anthracite Region. The most obvious being an absence of alkaline discharges in the Eastern Middle Field. The Eastern Middle Field also lacks severely acidic mine drainage. The Northern Field has proportionally more water with a pH above 5, than below 5. This is consistent with the finding of calcareous rocks in the Northern Field. The Western Middle and Southern Fields show a wide range of pH values. Combined data for all the anthracite fields display a bimodal distribution for pH similar to that for the Bituminous region.

An understanding of mine site geology is necessary for developing a representative drilling program, for providing information as to the acid or alkaline producing potential of strata, and for design of a groundwater monitoring program. Also, knowledge gained from these geologic factors can be used in developing site specific pollution prevention techniques such as material handling and calculation of alkaline addition rates. Geologic information is essential for determining the economic feasibility of a proposed mine site.

Introduction

Geologic factors play a major role in the kind of water quality produced by a surface coal mine. This chapter examines those geologic factors with respect to the northern Appalachian Basin. Surface mining accelerates weathering by exposing fresh rock surfaces which contain minerals not at equilibrium with the newly mined environment. The two most important groups of minerals, in terms of postmining water quality impacts, are carbonates and sulfides. Weathering of the carbonates produces alkalinity and weathering of sulfides produces acidity. Other major ions can be calcium, sulfate, and iron. The weathering of other minerals also contributes to the composition of mine drainage, especially under low pH conditions. Some of these ions include manganese, magnesium and aluminum. The minerals available for weathering, and the resultant water quality, is to a large extent a function of geology. Some minerals were present at the time of deposition of the coal and enclosing sediments, while others are the result of more recent processes. More recent processes include near-surface weathering and effects from Pleistocene glaciation, such as deposition of till and glacial erosion.

Although acid mine drainage (AMD) is not unique to the northern Appalachians, the problem is more severe in this region than in any other coal producing region of the United States. Within Pennsylvania mine drainage problems differ by geographic region and stratigraphic horizon. Over the years some rules of thumb have been developed relating regional and stratigraphic geology to postmining water chemistry in Pennsylvania. An understanding of mine site geology is important in developing a representative drilling program, for providing information on the acid or alkaline producing potential of strata, and for design of a groundwater monitoring program. Also, knowledge gained from these geologic factors can be used in developing site-specific pollution prevention techniques, such as overburden handling and calculation of alkaline addition; in any case this geologic information is a necessary part of economic determinations.

All mine drainage prediction tools, and some of the prevention tools, in one way or another, require an understanding of the site's geology. For example, many of the factors pertaining to the proper interpretation of previous mining as a prediction tool (Chapter 9) are related to an understanding of geologic similarities and differences between mine sites. Premining groundwater quality (Chapter 10) is dependent on the mineralogy of the rocks through which the water flows. Strategies to obtain representative samples for acid-base accounting (Chapters 6 and 11) and kinetic tests (Chapter 7) require an understanding of lateral and vertical facies changes of rock units and an understanding of the depth of weathering. Special handling (Chapter 14) requires a knowledge of the site stratigraphy and alkaline addition (Chapter 13) requires a knowledge of the relative amounts of pyrite and carbonates.

Pennsylvania During the Pennsylvanian Period

Pennsylvania during the Pennsylvanian Period was part of the "supercontinent" called Pangea. The equator was just north of present-day Pennsylvania (Edmunds, et al.,1998) (Figure 8.1), and the climate was tropical (Cecil et al., 1985). A mountain range existed in present-day New Jersey and southeastern Pennsylvania, which was the result of the converging African and North American continental plates and collisions of micro-continents with the North American plate (Faill, 1997b). A further consequence of the convergence and collisions was the formation of an ever deepening

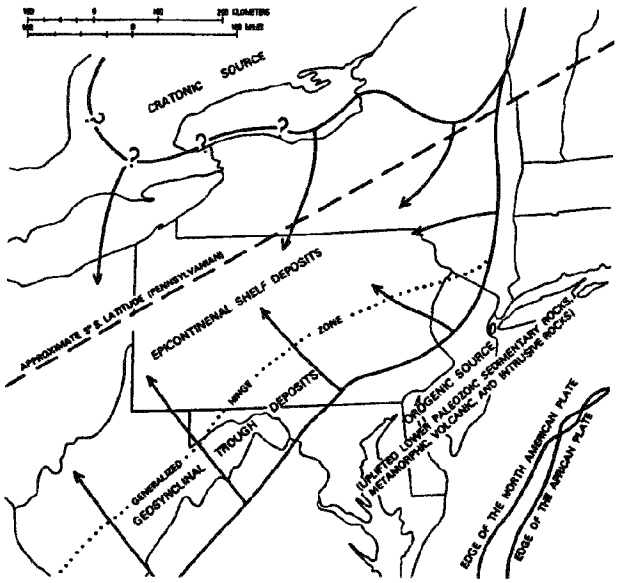

Figure 8.1 Generalized paleogeographic map of the Pennsylvanian depositional basin and source areas. Modified from Edmunds, et al. (1979).

foreland basin. This foreland basin is preserved as the present Appalachian basin. Sediments, eroded from mountains to the east and highlands to the north, were deposited in the basin (Figure 8.1) and became the coal and associated rocks of the coal fields of Pennsylvania (Figure 8.2).

Cyclicity in Pennsylvanian Period strata is a common phenomena in the United States (Cecil and Edgar, 1994). This cyclical pattern has been termed a "cyclothem" (Wanless, 1931). The "ideal" cyclothem is illustrated in Figure 8.3. The "ideal" cyclothem is a rare phenomena in Pennsylvania. Despite this, an overall cyclicity seems to be present. For example, in the Allegheny Group, the major coals are typically separated by ~50 ft (15 m) of sediments. The stratigraphic sequences associated with some of the Conemaugh marine invasions (e.g., Brush Creek and Ames) are most similar to the "ideal" cyclothem.

Figure 8.2 (Figure is in pocket at back of book). Generalized stratigraphic section of the bituminous coal field of western Pennsylvania showing stratigraphic nomenclature, positions of principal coals, marine zones, and major freshwater limestones. Also shown are distributions of rock types and carbonates that can influence mine drainage quality.

There appear to have been two major controls on regional cyclicity. One of these was basin subsidence due to collision between the North American and African plates. A second factor was climatic controls on sea level. Although, during the Pennsylvanian, the area of present day eastern North America was located near the equator and had a tropical climate, the southern polar regions of Pangea were experiencing widespread glaciation (Crowell, 1978; Veevers and Powell, 1987). Waxing and waning of continental glaciers resulted in episodic sea level changes, similar in amplitude to those during the Quaternary (~100 m; Heckle, 1995). Klein and Willard (1989) evaluated the relative impacts from these two mechanisms on the Pennsylvanian Period coal basins of the United States. They attribute the control of cyclothems in the Western Interior Basin to repeated transgressions and regressions of a mid-continent sea. These changes in sea level were caused by glaciation. Klein and Willard conclude, based on the more clastic nature of Appalachian sediments and the deeper basin warping, that the Appalachian Basin was affected most by tectonic controls. They also invoke a combination of transgressive-regressive cycles and tectonism as controls on cyclicity in the Illinois basin.

Two more factors have been proposed to explain the distribution of coals and intervening sediments. These are the "deltaic" model of Ferm (1970, 1974) and Donaldson (1969, 1974, and 1979) and the "climatic" model of Cecil et al. (1985) and Donaldson et al. (1985). The deltaic model accounts for rapid facies changes that occur over very short horizontal distances. These rapid changes are due to repetitive channel switching, as in the modern Mississippi delta. The climatic model explains the marked vertical stratigraphic, sedimentological, and mineralogic variations from the beginning to end of Pennsylvanian sedimentation, throughout the Appalachian Basin, and explains chemical and physical changes in coals through time. For example the red beds found in the Conemaugh Group are attributed to dry conditions. The widespread freshwater lake deposits of the upper Allegheny and Monongahela Groups are also indicative of dry conditions (Cecil et al., 1985). Skema and Lentz (1994) contend that deposition during the Pennsylvanian, within the region of present-day Pennsylvania, was complex. They conclude that multiple factors were at work. For example, Cecil et al.'s climatic model explains the widespread development of redbeds and freshwater limestones, and the glacial-eustatic model is consistent with widespread marine deposits in the lower Allegheny Group and Glenshaw Formation. The discontinuous nature of non-marine beds and abrupt facies changes imply more localized control, which Skema and Lentz (1994) attribute to "deposition

Table 8.1 Tabulation of stratigraphic horizons that were evaluated for construction of Figure 8.2. X indicates complete section was represented in the drill core; * indicates a portion of the section was represented.

Core No.	C1	C2	C3	C4	C5	C6	C7	C8	C9	C10	C11	C12	C13
Dunkard	X	X							*				
Monongahela	X	X							X				
Conemaugh	X	X	X	X	*	X		*	X				
Allegheny	X	X	X	X	X	X	X	X		X	*	X	X
Pottsville	X	X	X			X	X	X		X	X		X

on a fluvially prograding coastal plain" (p. 33). This process along with compactional subsidence explains much of the abrupt lateral stratigraphic changes observed in coal overburden. In summary, sedimentation in the northern Appalachians was complex and controlled by both basin-wide and local factors.

Pennsylvanian and Permian(?) Stratigraphy of Western Pennsylvania

A generalized stratigraphic column of the Pennsylvanian and Permian(?) units of western Pennsylvania is depicted on Figure 8.2. Shown are the groups and formations, principal coals, marine zones, and major freshwater limestones. Additionally, lithologic information that is important to mine drainage quality is portrayed.

The lithologic descriptions of Figure 8.2 are based on an examination of 13 core logs in the files of the Pennsylvania Geologic Survey. Figure 8.4 shows the locations of the cores and Table 8.1 shows the formations that occurred within each core. The core logging was very detailed, with stratigraphic units as thin as 0.05 ft (1.5 cm) identified. For the purposes of this study, lithology was simplified to clay, shale, siltstone, sandstone, limestone, coal, and boney coal. Particular attention was paid to units that were calcareous and

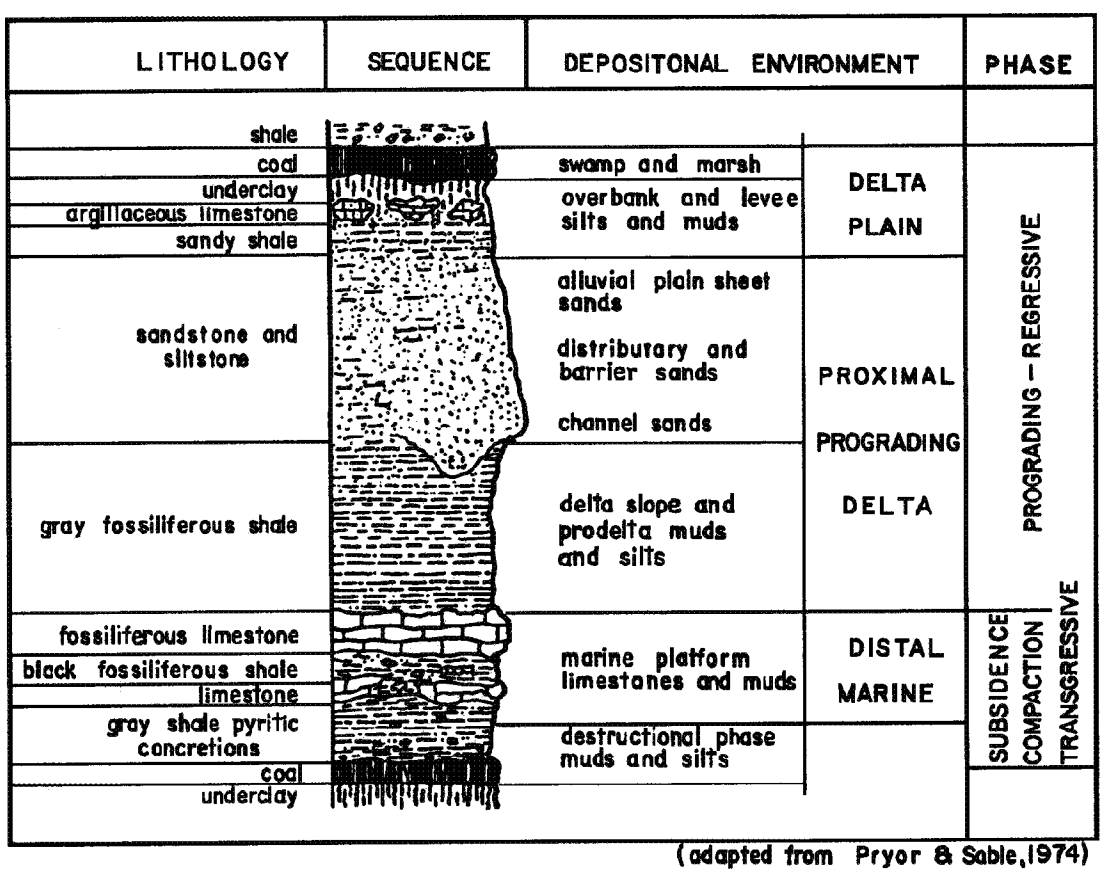

Figure 8.3 "Ideal cyclothem." Modified from Pryor and Sable (1974).

DISTRIBUTION OF PENNSYLVANIA COALS

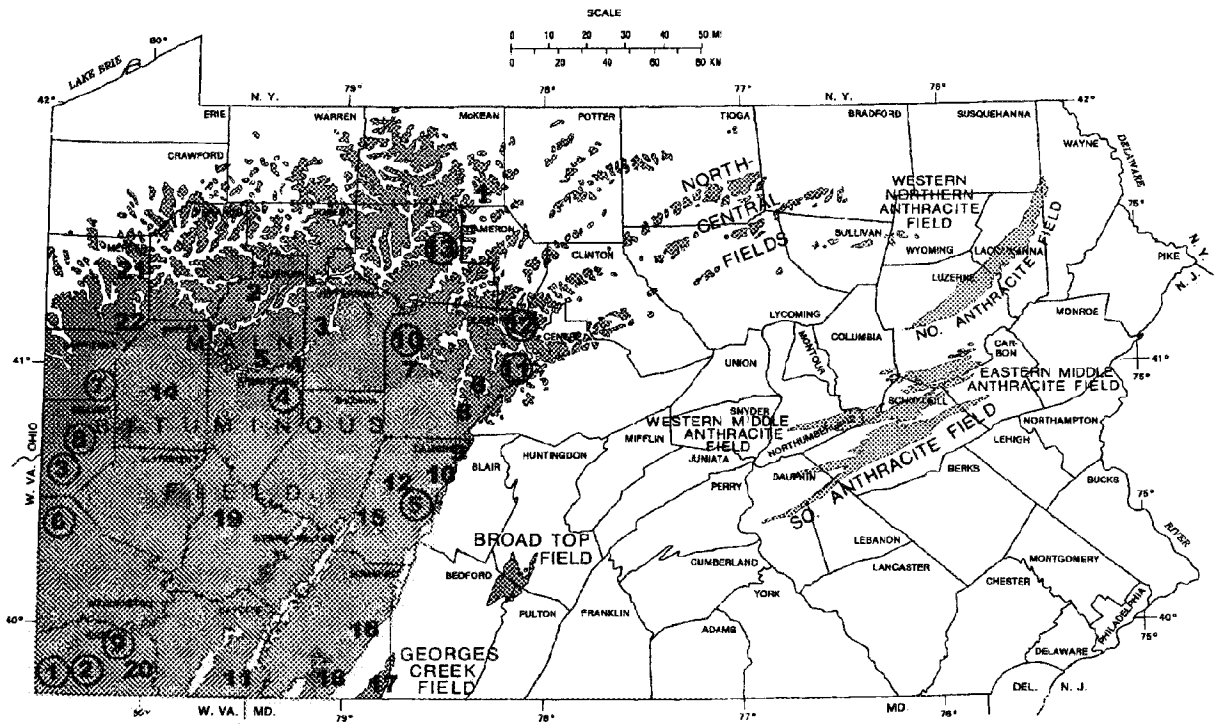

Figure 8.4 Map showing the locations of cores used in construction of Figure 8.2 (circled) and sites of overburden drill holes used in the figures displaying overburden chemistry (not circled) throughout this chapter. Site numbers correspond to those shown in figures of overburden chemistry.

sideritic. Percentages of select lithology and calcareous and sideritic attributes are depicted by group or formation. In some instances, such as the Allegheny Group and Waynesburg Formation, these have been subdivided to provide more detail because of known differences in stratigraphy within the group/formation. The histograms should be viewed as semi-quantitative.

In addition to the core holes, overburden analysis drill holes with percent sulfur and neutralization potential (NP) were obtained from the permit files of the Department of Environmental Protection's District Mining Offices. Percent sulfur furnishes an indirect estimate of pyrite content and neutralization potential furnishes an indirect estimate of calcareous carbonates (e.g., the minerals calcite and dolomite). NP in some instances may also reflect siderite. Pyrite and calcareous carbonates are the minerals that have the greatest influence on mine drainage quality. Examples are provided for all the major coals and some of the minor coals mined in Pennsylvania. The figures depicting stratigraphic logs show only total percent sulfur values greater than 0.25 percent, and neutralization potential (NP) values greater than 15 parts per thousand (ppt) $CaCO_3$. This has been done for clarity of the figures and because lower values typically have minimal influence on water quality. A key to these logs is shown in Figure 8.5.

Figure 8.5 Key to drill logs depicted in this chapter, showing lithologic symbols. Figures also show sulfur values greater than 0.25 percent sulfur (on left) and neutralization potentials above 15 ppt $CaCO_3$ (on right).

Glass et al. (1977) dedicated their report to George Hall Ashley (1866-1951) a former State Geologist of Pennsylvania and "life-long combatant with the perplexing rocks of southeastern Clearfield County." They point out that their work is built upon his foundation and that "(t)he geology was not as difficult as you thought, Dr. Ashley - it was worse!" The stratigraphy of the Pennsylvanian of Pennsylvania is not as simple as is often assumed. For most of the past 150 years stratigraphic correlations were made using the coal seams. The group-level boundaries are based on coal seams. The Allegheny Group, for example, was designed to contain all the mineable coals within that section of the Pennsylvanian, and the Pittsburgh coal defines the base of the Monongahela Group. Many coal seams are not continuous over large areas, some are only local. A good example is the Brookville coal, which marks the base of the Allegheny Group. This coal can only be precisely defined in the area where it was first described. Readers of this chapter will hopefully get some feel for the fact that the real world is not simple. Recent work by the Pennsylvania Geologic Survey has relied on laterally persistent units such as marine zones for correlation. This has proven to be much more reliable. As will be shown, many of these marine zones are quite extensive.

Whether to refer to the Pottsville and Allegheny as formations or groups is still in dispute and is not consistent in the literature. We have, for the most part, used the term "group." Resolution of which is the proper designation must be left to others. For a broader discussion of the Pennsylvanian stratigraphy, consult Edmunds et al. (1998). The quotes below from Edmunds et al. have had metric conversions added.

Pottsville Group

The Pottsville Group is variable in thickness. It is dominated by sandstone, and the coals are discontinuous. Because of the discontinuous nature of these coals, and the fact that they are often split with numerous partings, mining is not common in the Pottsville Group. The principal coal that is mined is the Mercer. This is actually a coal zone rather than a single coal. The Mercer clay, below the Mercer coal, has also been mined in some areas.

Edmunds et al. (1998) discuss the Pottsville of western Pennsylvania in terms of strata below the Mercer coal and above the Mercer coal.

> "The Pottsville Formation in western Pennsylvania ranges from 20 ft (6 m) to at least 250 ft (75 m) in thickness. Its basal contact is apparently everywhere disconformable and from south to north overlies increasingly older Mississippian and possibly uppermost Devonian rocks....The base of the Brookville coal marks the upper boundary of the Pottsville Formation" (Edmunds, et al., 1998, pp. 150-151).

> "In some places, the Pottsville is particularly thin, mainly because of depositional overlap... (which) is believed to reflect trends in the topographic relief of the pre-Pottsville erosion surface" (Edmunds, et al., 1998, p. 152).

V. Skema (Geologist, PA Geol. Survey, 1997, personal communication) has observed a complete absence of Pottsville rocks on areas of pre-Pottsville topographic highs in portions of Clinton County.

Edmunds, et al. (1998) state that

> "In Pennsylvania, the pre-Mercer Pottsville is entirely nonmarine. Its thickness varies from 0 to as much as 175 ft (53 m).... The upper part of the Pottsville Group, commencing with the lowest Mercer coal or its underclay, is a very complex highly variable sequence between 20 (6 m) and approximately 80 feet (24 m) thick.... (I)n Mercer and adjacent counties, it contains two marine limestones. Shales containing marine or brackish-water fauna occur widely, if irregularly, throughout western Pennsylvania" (p. 153).

Figure 8.6 shows examples of Mercer coal overburden from Clarion and McKean Counties, PA. The Clarion County drill holes (DH 201-1, 201-2, and 201-3) are from the same mine site and all within a hundred or so acres (~40 ha). These holes illustrate the lateral and vertical variation of the Mercer coal zone. For example in hole DH 201-3 there are three coals, in DH 201-1 the zone is represented by six coals. The lateral correlation of any single coal can not be assured from drill hole to drill hole. The acid-base accounting data shows no significant calcareous strata (i.e., no NP > 30 ppt $CaCO_3$), but there are frequent high sulfur (sulfur > 0.5%) strata. As with the coals, the high sulfur rock units are not laterally continuous and they vary greatly in thickness. Discontinuous units, such as those shown in Figure 8.6 create problems for coal reserve studies because it is difficult to determine the lateral extent or thickness of a particular coal. Similarly, this geologic complexity makes overburden sampling very difficult.

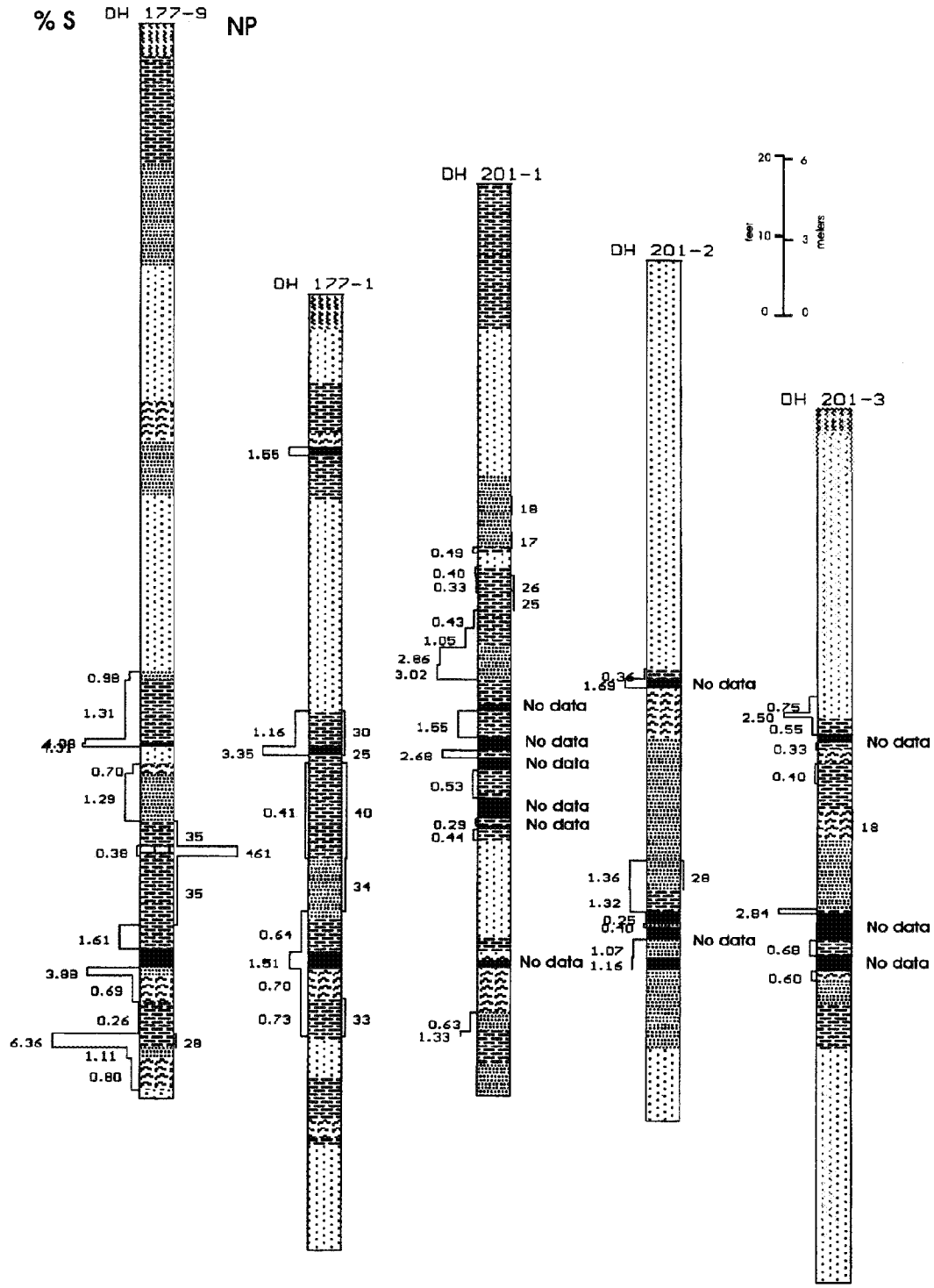

Figure 8.6 Overburden analyses of the Mercer coal zone. Location 1: DH 177-9 and DH177-1, Norwich Township, McKean County; and Location 2: DH 201-1, -2, and -3, Elk Township, Clarion County. Site locations shown on Figure 8.4.

A thorough understanding of mine site geology is necessary to insure that representative samples are selected. Complex stratigraphy can also make mine drainage prevention plans, such as special handling and alkaline addition, hard to design and implement.

Drill hole DH 177-9, from McKean County (Figure 8.6) contains one of the Mercer marine zones. This zone has a NP of 461 ppt $CaCO_3$. The two McKean County holes show more lateral continuity of the coals than did the Clarion County site. The marine zone, however, occurs in only the one hole. It is unknown whether the NPs from 30 to 40 ppt $CaCO_3$ equivalent are calcareous minerals or siderite.

Figure 8.2 shows the unconformable nature of the Pottsville Group. The Pottsville is dominated by sandstone, and is marked by a near absence of calcareous strata. Siderite occurs in about 13% of the strata. This lack of calcareous strata probably accounts for acid mine drainage problems that are often associated with mining of Pottsville coals and underclays.

Table 8.2 (Located in pocket at back of book). Postmining water quality of Pennsylvania Bituminous Coal Region by stratigraphic interval.

Typical examples of mine drainage quality of Pottsville Group coals and most other coal-bearing stratigraphic sections of the bituminous coal region of western Pennsylvania are shown in Table 8.2 (located in pocket at back of book). The water quality data contained in Table 8.2 were obtained from the surface mine permit files of the Department of Environmental Protection's District Mining Offices. Whenever possible, the water quality data were obtained from the same permit files as the overburden analysis data shown on the drill logs in the figures contained in this chapter. This enables a direct comparison of the percent sulfur and NP data used to predict mine drainage quality, with the actual water quality monitored at the mine site. In some cases where during-mining and postmining water quality data were lacking for a site, the water quality data were obtained from nearby sites on the same coal seams. The relationships between the stratigraphic data described in this section and the mine drainage data contained in Table 8.2 and related tables are more fully described later in this chapter.

Allegheny Group

The Allegheny Group is one of two groups within the Pennsylvanian that contains the majority of economically mineable coals. For the purpose of discussion, the Allegheny has been divided into the upper and the lower Allegheny. The lower Allegheny extends from the base of the Brookville coal to the base of the Johnstown limestone (or upper Kittanning coal where the limestone is absent). The upper Allegheny extends from the base of the Johnstown limestone to the top of the upper Freeport coal. This division is made because "marine units occur only below the upper Kittanning underclay"... "and, with minor exceptions, nonmarine limestones occur only at or above that unit" (Edmunds, et al., 1998, p. 154). This distinction of "marine" and "nonmarine" is to a large extent based on the work of Williams (1960). Williams defined four faunal groups, inferred as "fresh-water", "restricted marine or near-shore marine", and two marine groups, one having a more diverse fauna than the other. Williams also relied on the geochemical investigations of Degens et al. (1957, 1958) in defining his depositional environments.

Williams (1960) interpreted the rocks in the Allegheny Group above the upper Kittanning coal (and including the Johnstown limestone below the coal) to be freshwater. This interpretation was based on fossil Esterids (now referred to as conchostracans or "clam shrimps"). Conchostracans are found above the upper Kittanning, lower Freeport, and upper Freeport coals (e.g., Williams, 1960; Edmunds, 1968). New analysis and interpretations of the ecology of conchostracans during the Pennsylvanian Period support a marginally-brackish environment. Thus, conchostracan-bearing sediments are not completely devoid of marine influence and therefore some marine sulfate would be available for reduction to sulfide sulfur (and pyrite). This is consistent with the sulfur content of the upper Kittanning and Freeport coals and roof rocks. The assignment of conchostracans as an indicator of freshwater depositional environments was debated at the time Williams wrote his paper, and is acknowledged by Williams. A detailed discussion of this topic is found at the end of this chapter in the Appendix.

Although conchostracan-bearing sediments apparently had some marine influence, it was less than that of brackish or truly marine sediments and this is often reflected in the lesser amount of sulfur and the thinner sequences of high-sulfur strata associated with conchostracan-bearing rocks. Marginal-brackish facies would be exposed to saline influences for less time during transgressive-regressive cycles than marine or brackish sequences; thus the thinner zone of high sulfur rock.

According to Edmunds et al. (1998) the Allegheny Group:

"was specifically defined to include all of the economically significant coals present in that part of the Pennsylvanian sequence. The thickness of the formation is between 270 (82 m) and 330 feet (100 m) in Pennsylvania, and there is no obvious regional trend. The Allegheny Formation is a complex, repeating succession of coal, limestone, and clastics, ranging from claystone or underclay to coarse sandstone....No individual bed or lithosome is universally persistent, but some coals, marine shales, and limestones seem to be fairly continuous over thousands of square miles (thousands of square kilometers). The group is fairly uniform in its lithologic diversity... The Allegheny Formation contains six major coal zones. The coal in each zone may exist as a single, more-or-less continuous sheet, as a group of closely related individual lenses, or as a multiple-bed complex in which the various beds can be separated by tens of feet or merge into a single thick coal" (pp. 153-154).

Because the Allegheny Group is extensively surface mined, and some portions of and areas within this formation have created acid mine drainage, the Department has an extensive database of acid-base accounting data for the Allegheny Group. For the purposes of simplifying discussion, the overburden above the upper Freeport, although part of the Glenshaw Formation of the Conemaugh Group, is included in the discussions as part of the upper Allegheny Group.

Lower Allegheny -The base of the lower Allegheny is defined as the base of the Brookville coal. This is not a useful working definition because the Brookville coal is not always present so that the base of the Allegheny may be difficult or impossible to define. What is often called the Brookville is probably often correlative with a lower Clarion coal. Thus, the base of the lowest Clarion coal often substitutes as a working definition. The Clarion and Brookville coals are not differentiated in this discussion.

Marine units occur over large areas and at several stratigraphic horizons within the lower Allegheny Group. The paleoenvironment of the marine zones can vary regionally and vertically. A good example of this is the Vanport horizon which occurs above the Clarion coal. The marine limestone facies covers an area of at least hundreds of square miles (km^2) and is over 20 ft (6 m) thick in the center of the basin. A maximum thickness of over 40 ft (12 m) has been recorded for a small area in northeastern Lawrence County. Core logs in the files of the PaGS were examined to determine the extent of the Vanport zone south of the area mapped by Williams and Keith (1963). The presence of the Vanport marine horizon cannot be confirmed for the southwestern corner of the state because sandstone typically occupies this horizon. This sandstone may indicate non-deposition of limestone and the presence of distributary channels that emptied into the Vanport sea. Alternatively, but less likely, the sandstone may occupy channels that cut through and removed the limestone.

Clarion Coal Overburden and the Vanport Limestone - Where present, the Vanport can be a nearly pure limestone. Figure 8.7 shows the Vanport limestone in drill hole DH 23-6. Site locations for the drill logs with overburden chemistry are shown in Figure 8.4. The Vanport in DH 23-6 has a NP of 999 ppt $CaCO_3$. The Vanport in DH-4 in Figure 8.39 (presented in the section on glacial sediments) is greater than 920 ppt $CaCO_3$. The rocks below the Vanport are high sulfur (up to 4.1 % in DH 23-6 and up to 5.2% in DH-4). The high sulfur strata are 10 to 30 ft (3 to 10 m) thick. These high sulfur units are associated with NPs that are typically less than 35, but as high as 73 ppt $CaCO_3$. These low NPs may be due to siderite. These two logs represent, from the coal to the limestone, a transgressive sequence. The lower shale units have marginal marine (brackish) or shallow marine fossils and the limestone represents maximum transgression in Appendix for description of faunal facies). In drill hole DH 23-6 the high sulfur strata are associated with marine fossils. The strata for a drill hole in Black Lick Township, Indiana County (logged by Al Glover and Vic Skema, Pennsylvania Geological Survey) nicely show this transgressive sequence from brackish to marine conditions. Glover found *Lingula* and *Dunbarella* fossils immediately above the Clarion coal. These are indicative of brackish waters and represent the earliest portion of the marine transgression. Above this is a sandier zone that is bioturbated with siderite-filled burrows, typical of marine or brackish environments. Marine fossils and siderite concretions occur near the top of this unit. The next unit upward contains marine brachiopods, some of which are pyritized. This unit is overlain by the Vanport limestone which contains crinoids, an indicator of deeper, less muddy and consistently saline marine water.

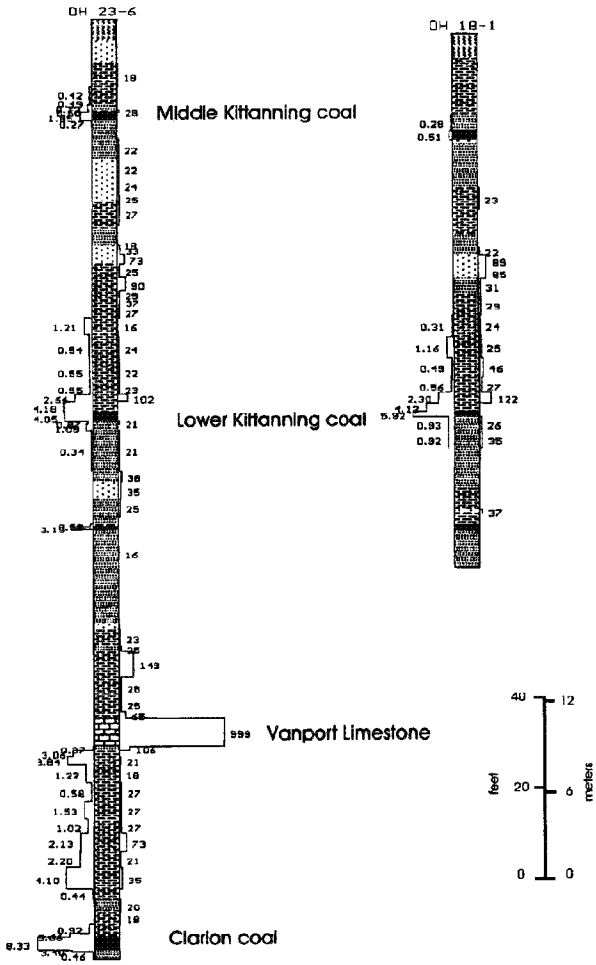

Figure 8.7 Stratigraphy at Location 3, Porter Township, Clarion County. Interval is from the Clarion coal through middle Kittanning overburden. The overburden above all three coals is marine.

The Vanport horizon, which occurs above the Clarion coal, is often laterally (and vertically) transitional from marine to brackish conditions. Figure 8.8 and Figure 8.9 show regional changes in thickness of the Vanport limestone and the location of other contemporaneous facies in a portion of western Pennsylvania. In Butler County, where the Vanport is thick and in close proximity to the coal (Figure 8.9), mining of the Clarion coal will result in alkaline drainage. Where the Vanport-equivalent facies are brackish shale and the shale lacks calcareous minerals, such as in Clearfield County, the mine water is typically acidic. Figure 8.10 shows the distribution of pH for Clarion coal mine drainage from areas with and without the Vanport limestone. Median pH for areas without the limestone is 3.6 and with limestone is 5.0. Many of the mines were probably "pre-Act" and unreclaimed, and thus may be producing poorer quality water than would be produced by modern mining methods.

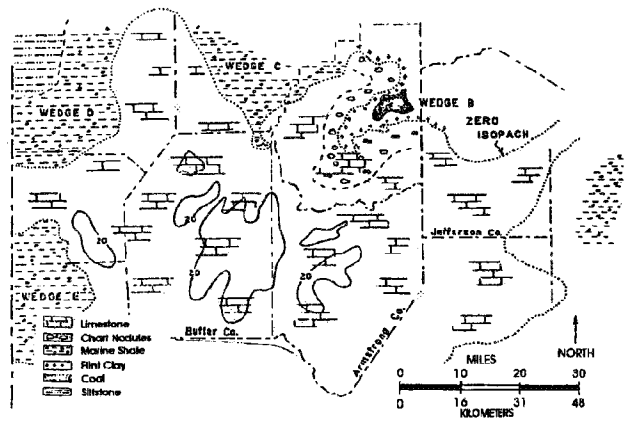

Figure 8.8 Generalized isopach map of the Vanport limestone and lateral facies for a portion of western Pennsylvania. Figure from Bergenback (1964).

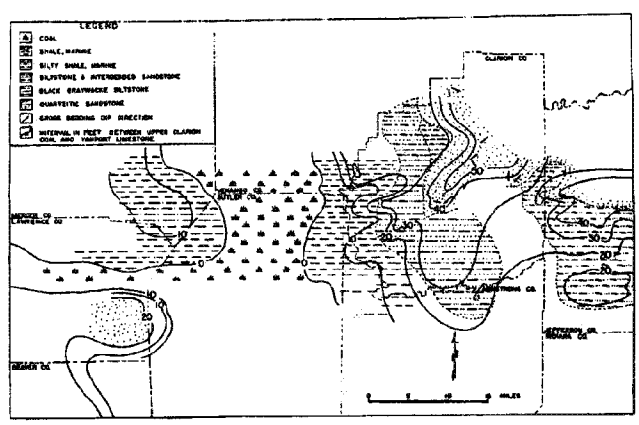

Figure 8.9 Isopach map showing the thickness of rock between the Vanport limestone and the upper Clarion coal, and the rock types/facies occurring directly below the limestone. The Vanport rests directly on the coal in northern Butler and southern Venango counties. Figure from Williams et al. (1964).

Lower Kittanning to Middle Kittanning Interval - Williams (1960) and Williams and Keith (1963) determined, using fossils, that the lower Kittanning (LK) was overlain by rocks deposited under marine, brackish (marginal marine) and freshwater depositional environments. The marine and brackish rocks are formally referred to as the Columbiana shale. They published maps showing the distribution of LK paleoenviron-

ments. A revised map is presented in Figure 8.11. This map was derived from more recent published and unpublished studies by the Pennsylvania Geologic Survey (PaGS), and discussions with PaGS geologists (in particular, V. Skema and J. Shaulis), and BMR studies. The locations of LK drill holes discussed below are shown on this map. The faunal facies used to construct Figure 8.11 are discussed in the Appendix. The drill holes provide examples of sulfur and neutralization potential for coal and overburden deposited under different depositional environments.

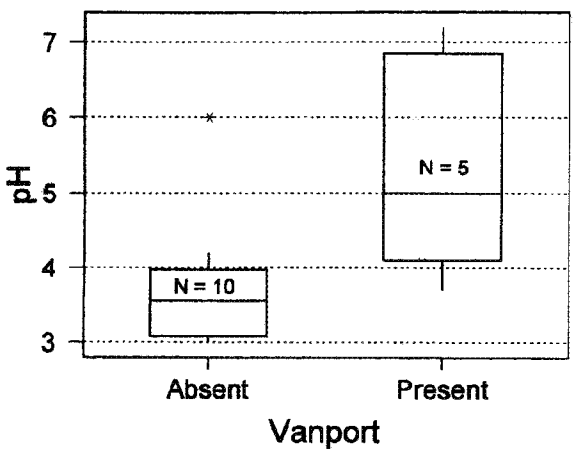

Figure 8.10 Boxplots of pH of surface mine water from mines on the Clarion coal in areas where the Vanport limestone is present and in areas where it is absent. Lower boundary of the box represents the 25th percentile, the upper boundary represents the 75th percentile. The line between the two is the median. "Whiskers" indicate the range of data. Data are from Williams et al. (1982).

Figure 8.7 shows overburden of marine origin. Drill cores DH 23-6 and DH 18-1 contain marine brachiopods (e.g., *Mesolobus*) in the black carbonaceous shale overlying the lower Kittanning coal. The carbonate minerals siderite, dolomite and calcite were all identified within this zone at this site (Cravotta et al., 1994). High sulfur, identified as pyrite by Cravotta et al., is associated with the brachiopod-bearing rocks. The drill cuttings analyzed by Cravotta et al. did not encounter the highest NP zone located a few feet above the lower Kittanning coal. This zone with NP's over 100 ppt $CaCO_3$ is probably calcite or dolomite. The alkaline postmining water quality confirms that calcareous minerals are present.

The lower Kittanning overburden is also marine in northeastern Armstrong County and southern Jefferson County (Figure 8.12). The drill logs show 30 or more feet (10+ m) of rock with over 0.5 % sulfur (2.37 % maximum). They also show NP's in the range of 15 to 40 ppt $CaCO_3$. X-ray diffraction analyses indicate that calcite is the only carbonate present (R. Smith, PaGS, personal communication, 1996). The water associated with lower Kittanning mines in this area is alkaline despite the high sulfur overburden.

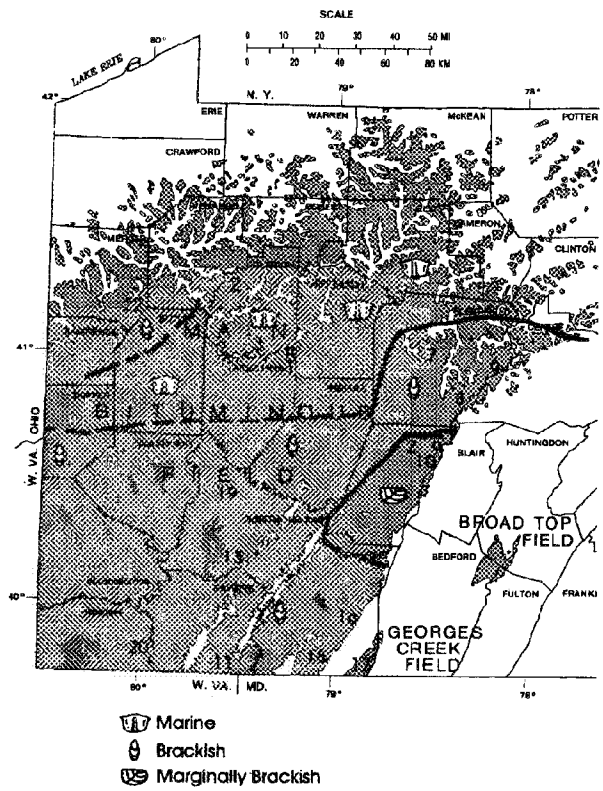

Figure 8.11 Tentative paleodepositional environment map for the rock above the lower Kittanning coal. Dashed line indicates uncertainty as to the actual location of the boundary between depositional environments; solid lines indicates that good paleontological control was available and boundary location is better known. Numbers identify locations of sites discussed in text and shown in figures. Fossil symbols are used to identify the area of a depositional environment and do not necessarily indicate that fossils occur at the location of the symbol. Sources used in the construction of this map: drill logs and site locations shown on Figure 8.4 and Table 8.1, Glass (1972), Edmunds (1968), Edmunds and Berg (1971), Berg and Glover (1976), Glover and Bragonier (1978), Williams and Keith (1960), personal observations by K. Brady, and insights gained from conversations with V. Skema, J. Shaulis and C. Dodge, all with the PaGS.

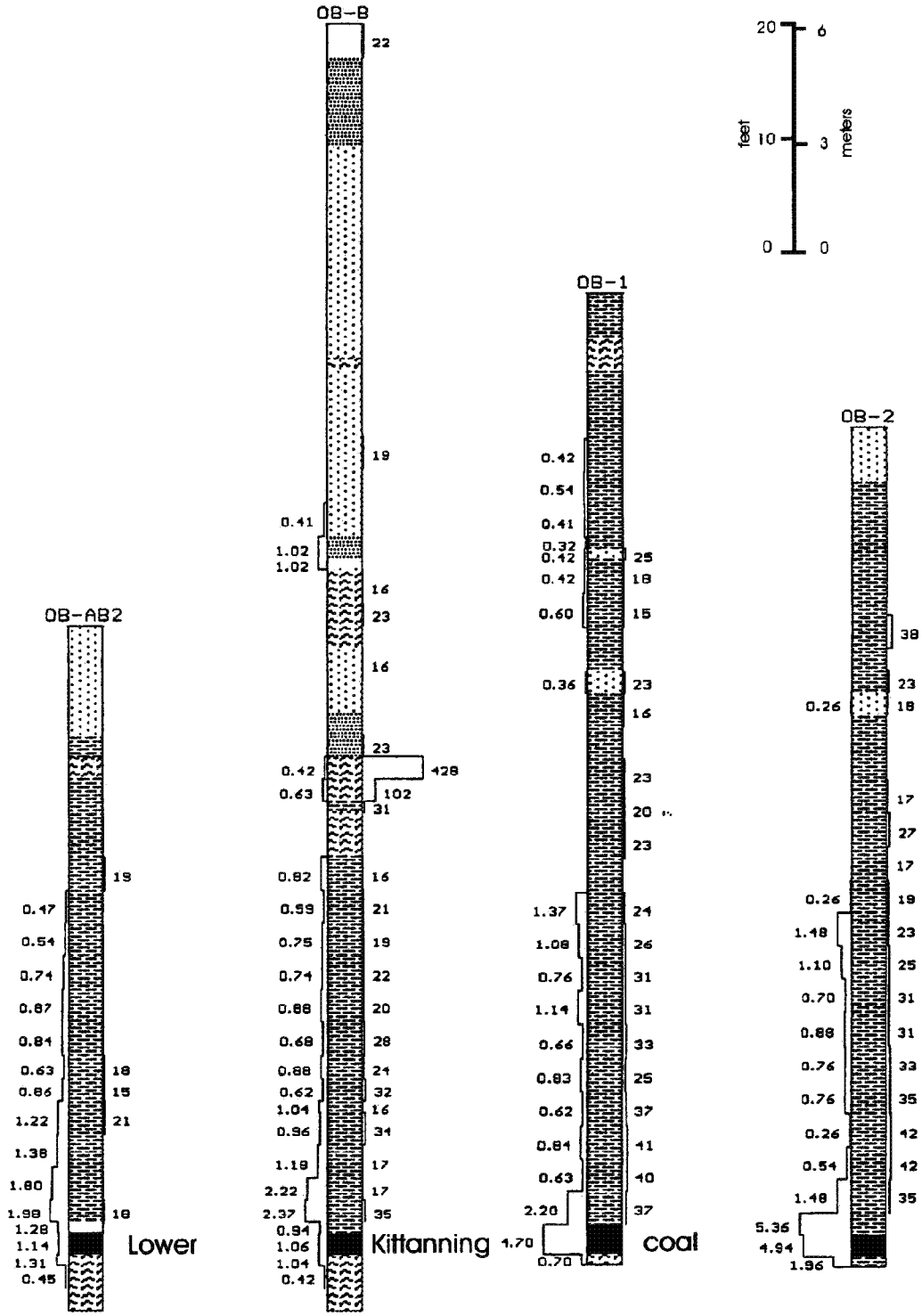

Figure 8.12 Drill logs showing lower Kittanning overburden chemistry where the roof rock was deposited in a marine environment. Drill logs OB-AB2 and OB-B are from Site 4 in Rose Township, Jefferson County. Drill logs OB-1 and OB-2 are from Site 5 in Redbank Township, Armstrong County.

Figure 8.13 and Figure 8.14 show sulfur and NP for the lower Kittanning in Clearfield County where the overburden was deposited in a brackish depositional environment. Typically the shale above the coal is high in sulfur. Guber (1972) found that the high sulfur rocks often contain the brachiopod *Lingula*. Guber's findings are discussed in more detail in a later part of this chapter. *Lingula*, as discussed in Williams (1960), is indicative of brackish environments. Geologic reports for the areas of the drill holes shown in Figure 8.13 and Figure 8.14 describe brackish fossils above the lower Kittanning coal (Glen Richey Quadrangle, Edmunds, 1968; Luthersburg Quadrangle, Edmunds and Burg, 1971; Ramey Quadrangle, Glass, et al., 1977). The high sulfur zones shown in Figure 8.13 near the middle of the shale above the LK coal in holes OB-1 (0.92 % S), OB-4 (4.4 % S) and near the top of the shale unit in A-8 (1.15 % S) contain *Lingula*. The NP that is present is probably due to siderite, the exception being the base of the sandstone and immediately adjacent shale in A-8, which is likely calcareous. LK mines in the brackish areas of Clearfield County are notorious for producing acid mine drainage.

Williams (1960) shows a small portion of the LK roof rock in northeastern Cambria County as having been deposited in what he defined as a freshwater depositional environment, based on the presence of conchostracans. Recent investigations by J. Shaulis and V. Skema (personal communication, 1997) have confirmed the presence of conchostracans in extreme northern Somerset County. Fossil fauna however are rare (Figure 8.11). LK overburden chemistry in this region does appear to be different from the other areas discussed above (Figure 8.15). Sulfur is seldom above 0.5 percent. The small amount of NP (between 15 and 36) may be siderite because the postmining water is not alkaline. Mines from these areas tend to produce mild acid mine drainage, with pH ~4 and acidity ~100 mg/L.

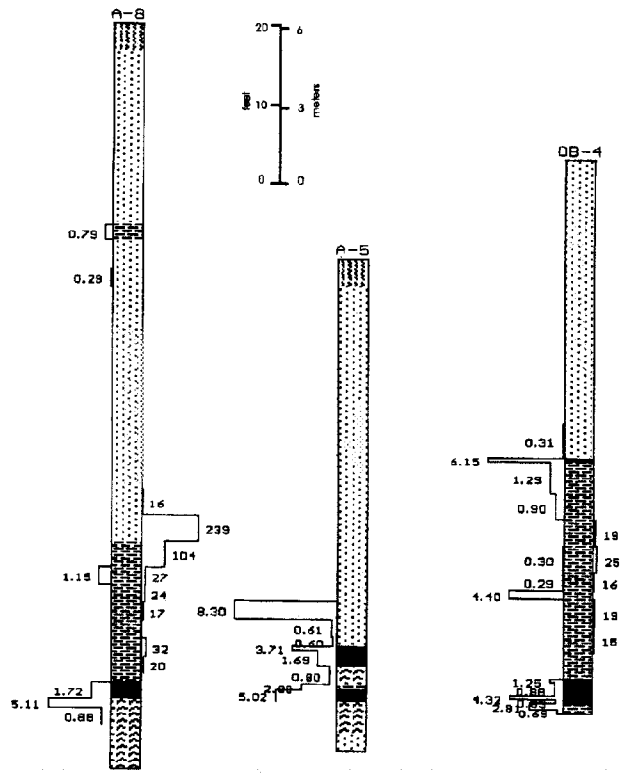

Figure 8.13 Drill logs showing lower Kittanning overburden chemistry where the roof rock was deposited in a brackish environment. All examples are from Clearfield County. Logs are from the Kauffman site in Boggs Township. The sandstone occurs in place of the shale units to varying degrees. The sandstone is of a fluvial origin.

Middle Kittanning to Johnstown Limestone Interval - The middle Kittanning (MK) coal is overlain by marine or brackish sediments over most of Pennsylvania's bituminous coal field. The exception is an area around Cambria County where the MK overburden has conchostracans or no fossil fauna. The marine zone is formally referred to as the Washingtonville Shale. Figure 8.16 is a map of paleodepositional environments for the rocks overlying the middle Kittanning coal. The northern portion of this map is from Williams (1960) and the southern portion is derived from drill hole data made available by the PaGS and PaGS publications. This MK horizon, in a PaGS drill hole in northwestern Washington County, is represented by a coquina limestone. This was probably the deepest part of the MK "basin" in what is now Pennsylvania. Faunal facies used to construct this map are discussed in the Appendix.

The "MK" is a coal zone in many areas rather than a distinct coal seam. Over much of Clearfield County there are typically two to four "splits" of the MK. For example, in the Hazen, Reynoldsville, Falls Creek, and DuBois quadrangles the MK consists of a "middle Kittanning" that is typically two feet (0.7 m) thick and up to 42 inches thick (1.1 m) (Glover and Bragonier, 1978). This is the MK coal that is mined locally. This however is not the coal that the marine zone overlies. The marine zone overlies a "middle Kittanning rider" coal and the marine zone is about 30 ft (10 m) above

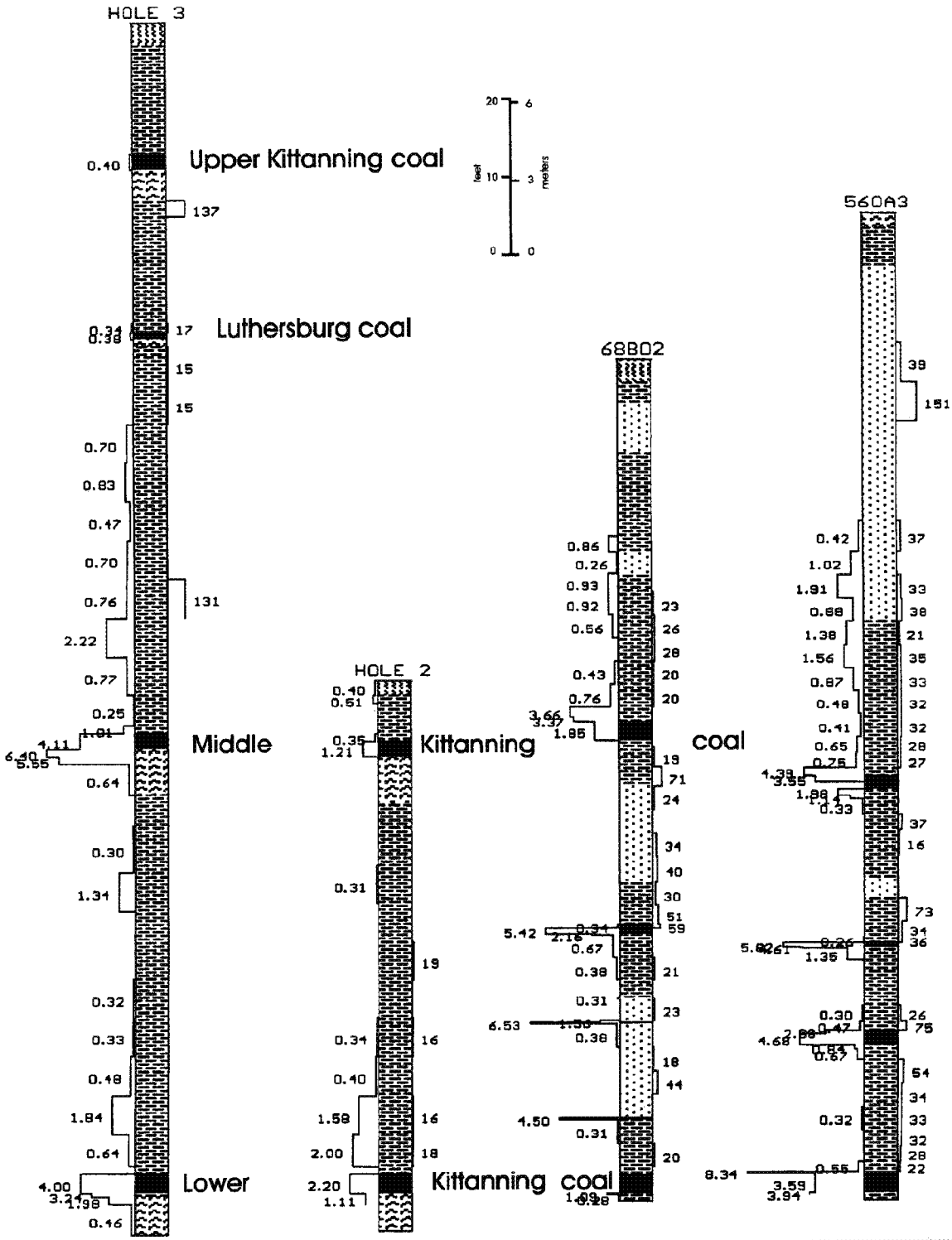

Figure 8.14 Lower Kittanning overburden deposited under brackish conditions. Hole 3 and Hole 2 are from Union Township, Clearfield County (Location 7, Figure 8.4). Logs 68BO2 and 56OA3 are from Bigler Township, Clearfield County (Location 8). The middle Kittanning overburden is also brackish.

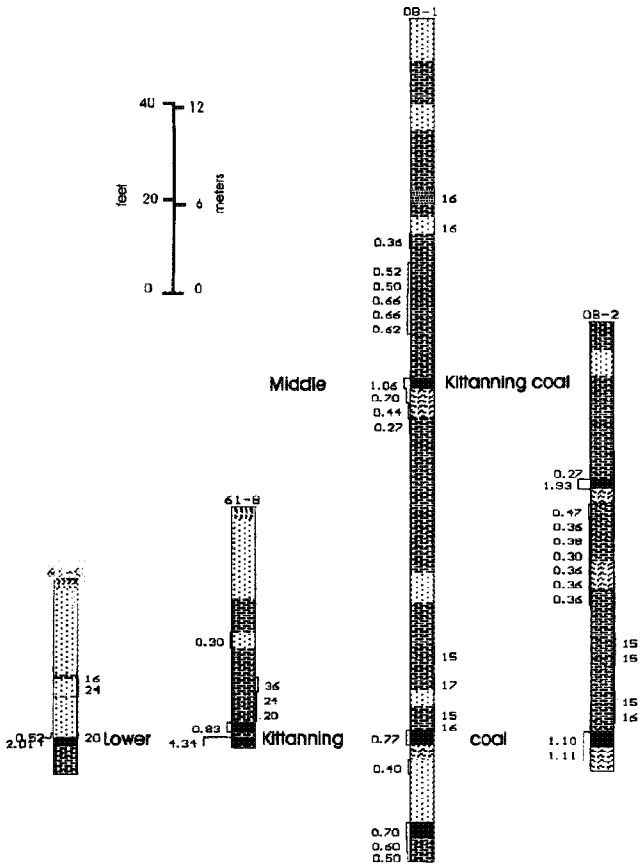

Figure 8.15 Drill logs depicting lower Kittanning overburden in the area of Cambria County that Williams and Keith (1963) indicated finding conchostracans. Holes 61-C and 61-B are in Reade Township, Cambria County (Site 9) and holes OB-1 and OB-2 are in Dean Township, Clearfield County (Site 10).

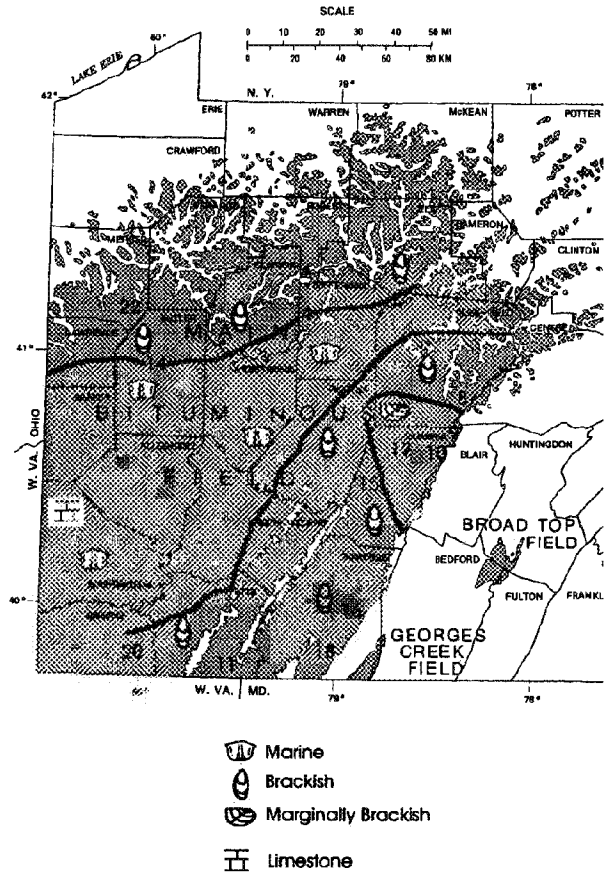

Figure 8.16 Tentative paleodepositional environment map for the rock above the middle Kittanning coal. Good paleontological control was available for construction of this map. Fossil symbols are used to identify the area of a depositional environment and do not necessarily indicate that fossils occur at the location of the symbol. The northernmost line showing the division between brackish and marine environments is essentially that of Williams and Keith (1963). Work for this chapter agreed with the location of this boundary. Other sources used for the construction of this map were: drill logs and site locations shown on Figure 8.4 and Table 8.1, Glass (1972), Edmunds (1968), Edmunds and Berg (1971), Berg and Glover (1976), Glover and Bragonier (1978), Williams and Keith (1960), personal observations by Keith Brady, and insights gained from conversations with V. Skema, J. Shaulis and C. Dodge, all with the PaGS.

the "middle Kittanning" that is mined. This raises the likely prospect that the "middle Kittanning" seam being mined in one area may be a different split than that being mined in another area.

Holes showing the results of NP and percent sulfur above the MK coal (Figure 8.7, and Figure 8.14) were drilled in areas that are marine or brackish environments (Figure 8.16). The MK at Area 5, in the area of marine deposition, occurs beneath shallow cover which is probably weathered and therefore not very revealing for determining depositional controls on overburden mineralogy. Locations 7 and 8 (Figure 8.14; and see Figure 8.4 map for site locations) occur in the area of brackish overburden. The three holes with significant overburden (Hole 3, 68B02, and 560A3) have 30 to 40 ft (10 to 12 m) of high sulfur overburden overlying the coal. X-ray diffraction analyses reveal that the carbonate present over the MK at Location 7 is siderite. It is uncertain whether the zone with a NP of 131 is siderite or a calcareous carbonate. X-ray diffraction showed strata from other holes with NP as high as 75 contained siderite and no detectable calcite. The high sulfur and abundance of siderite for brackish overbur-

den is similar to that observed above the LK. The zone with an NP of 151 in the sandstone of drill log 560A3 is probably calcareous.

Figure 8.15 shows the MK in the area of the Figure 8.16 map where the MK is overlain by conchostracan-bearing shales. The highest sulfur in the overburden in drill log OB-1 is only 0.66 percent. This low sulfur is consistent with sulfur values from the conchostracan-bearing depositional environment for the LK coal. Further work needs to be done to establish relationships between concentrations of sulfur and carbonate minerals and depositional environment.

Upper Allegheny - The base of the upper Allegheny, as defined for this chapter, is the bottom of the Johnstown limestone. It is realized that this "limestone" is often transitional with the sediments below and does not occur everywhere, although it is remarkably persistent over much of the Bituminous Region and can be a good stratigraphic marker bed. Where the Johnstown limestone does not occur the base of the upper Kittanning coal substitutes as the base of the upper Allegheny. The reason for this stratigraphic break in the Allegheny is that this sequence includes nearly all the freshwater limestone units in the Allegheny Group. Fauna in the freshwater limestones is generally dominated by ostracods, *spirorbis,* and fish remains. This fauna is completely different from the fossils found in upper Allegheny coal-roof rock. Typically the only fossil fauna found in the rock above the coals in the upper Allegheny are conchostracans. The separate depositional environments of the roof-rock and the freshwater limestones is evidenced not only by the different faunas, but also by position and composition. The freshwater limestones are usually found below the coals, whereas the conchostracan-bearing rocks are above the coals. The "limestones" are highly calcareous and lack carbonaceous material, whereas the roof-rocks may not be calcareous at all and are often black due to abundant carbonaceous matter. It would appear that during the time of deposition of the upper Allegheny, coal deposition was followed by a marginally brackish transgression. Eventually truly freshwater sediments were deposited, including the freshwater limestones.

The Johnstown limestone is shown in Figure 8.17 and Figure 8.18. The Johnstown limestone has NP greater than 900 ppt $CaCO_3$ in LH-3 and 700 or greater in the other two drill holes in Figure 8.18. The high NP values are in the range of those of the marine Vanport limestone for "purity." Sometimes the Johnstown horizon is not a true limestone, but a calcareous claystone or shale (e.g., the zone just below the upper Kittanning coal in OB-9, Figure 8.17). Hole #101 in Figure 8.19 does not show a calcareous zone below the UK. This may simply be because the Johnstown limestone occurs below the bottom of this drill hole. The drill logs in Figure 8.20 are from an area where the Johnstown limestone does not occur. The limestone does occur, however, about a mile (1.6 km) west of these drill holes.

The interval between the UK coal and the lower Freeport (LF) coal often includes a calcareous zone beneath the LF coal. Where this zone is a limestone, it is referred to as the lower Freeport limestone. The interval between the LF and upper Freeport (UF) is similar to that of the underlying UK-LF interval. A widespread limestone or calcareous shale/claystone unit also lies beneath the UF coal. The rocks between the UK and LF, and LF and UF, as well as the overburden above the UF are portrayed in Figure 8.17, Figure 8.18, Figure 8.19, Figure 8.20, and Figure 8.21. The fauna of the Johnstown limestone, and LF and UF limestones are interpreted as freshwater in origin.

The lateral distribution of individual freshwater limestones in the Allegheny Group can be quite extensive, covering hundreds of square miles. The limestone is variable in thickness, and frequently there are areas where the limestone is absent. One freshwater limestone, the upper Freeport limestone, has been studied by Williams et al. (1968) and Weedman (1988). This limestone occurs between the lower and upper Freeport coals. Their findings illustrate the variability in thickness and distribution of an upper Allegheny limestone. Williams et al. (1968) looked at an area of approximately three 7.5 minute quadrangles in Clearfield County, and Weedman (1988) studied an area which covered slightly more than four 7.5 minute quadrangles in Indiana county. Observations by the authors confirm that this limestone is present, and persistent, between their two study areas. In Clearfield County, the thickness ranged from absent (where replaced by channel sandstone) to greater than 4 ft (1.2 m). Figure 8.22 shows the area studied by Weedman. The isopach map shows the variability in thickness that is typical of the upper Freeport limestone. Williams et al. (1968) indicate that the limestone in rare instances approached 100% calcium carbonate. Our experience is that these limestones are often "dirty" with a high component of clay and silt. At places this stratigraphic interval is represented by calcareous rocks with less than 50%

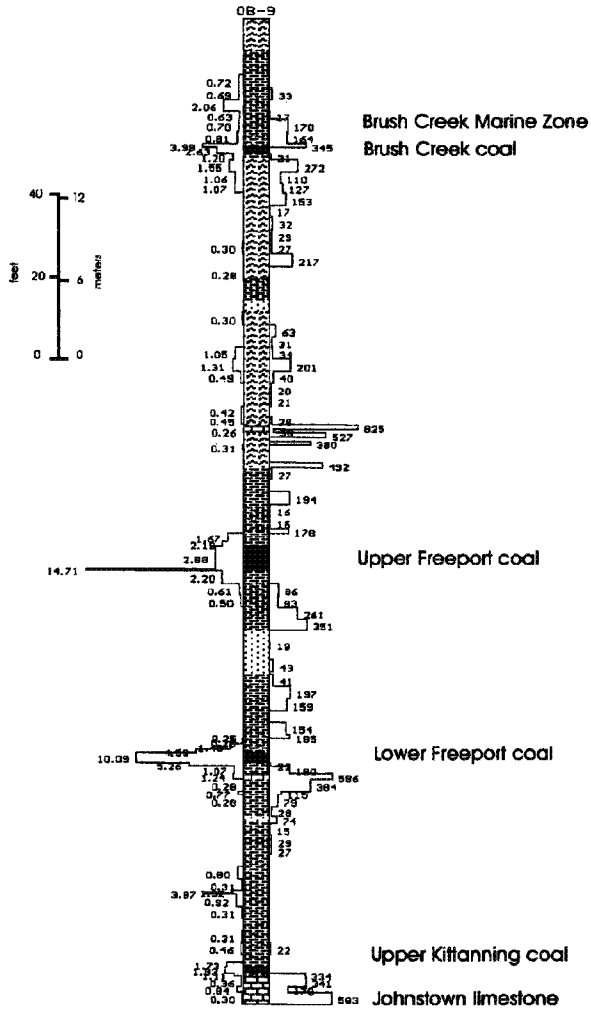

Figure 8.17 Overburden and chemistry of the interval from the Johnstown limestone to the Brush Creek marine zone. The overburden exhibits the calcareous nature of the upper Allegheny Group. High sulfur is typically restricted to the coal and immediately adjacent rock. This hole was drilled at Site 15 in Jackson Township, Cambria County.

calcium carbonate, and therefore by definition not a limestone, although they are often referred to as limestones on drillers' logs.

In addition to freshwater limestones, the upper Allegheny Group frequently contains an abundance of calcareous claystones, mudstones and siltstones. Figure 8.20 shows a stratigraphic section in Fayette County, between the upper Kittanning and lower Freeport coals. Much of this interval is calcareous (NP > 100; i.e., >10% $CaCO_3$), but only small portions could be classified as limestone (> 50% $CaCO_3$).

Conemaugh Group

The Conemaugh Group "is stratigraphically defined as the rocks lying between the upper Freeport coal horizon and the Pittsburgh coal. The thickness of this interval ranges from 520 feet (158 m) in western Washington County to 890 feet (270 m) in southern Somerset County. A gradual eastward thickening of the Conemaugh is apparent" (Edmunds et al., 1998, p. 154). The Conemaugh is subdivided into a lower formation called the Glenshaw, and an upper formation called the Casselman. The division is made at the top of the Ames marine limestone. Mineable coals are uncommon in the Conemaugh.

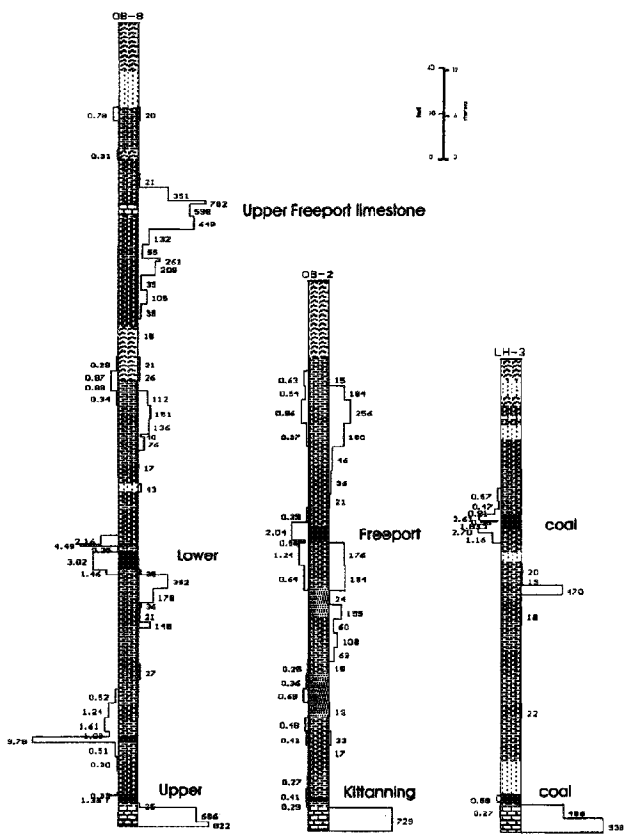

Figure 8.18 Upper Kittanning and lower Freeport overburden and chemistry for three drill logs at Site 15 in Jackson Township, Cambria County. The overburden exhibits the calcareous nature of the upper Allegheny Group. High sulfur is typically restricted to the coal and immediately adjacent rock.

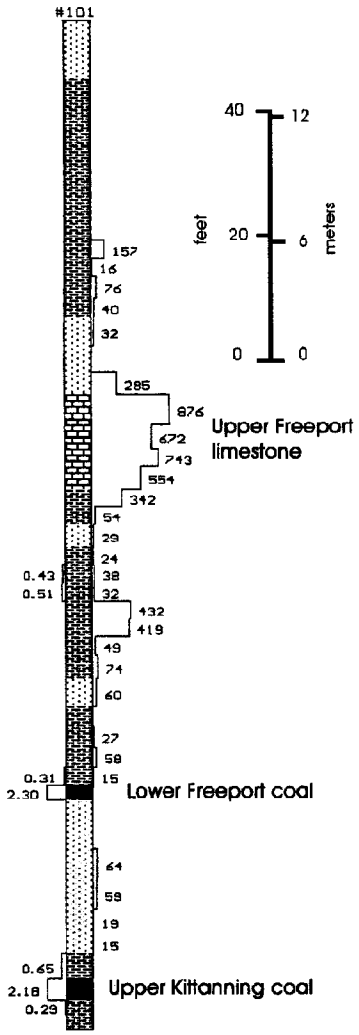

Figure 8.19 Upper Allegheny Group overburden and chemistry at Site 12 in West Carroll Township, Cambria County. Note the thick freshwater limestone with NP's over 500 ppt $CaCO_3$ above the lower Freeport coal.

Glenshaw Formation - The Glenshaw contains several widespread marine zones (see Figure 8.2). There are possibly as many as seven marine zones within the Glenshaw (Skema, personal communication, 1997). The Glenshaw is thickest in Somerset and southern Cambria counties, where it reaches 400 to 420 ft (122 to 128 m). It is thinnest near the Ohio border where it is about 280 ft (85 m) thick (Edmunds et al., 1998).

The Brush Creek limestone facies is present within most of its outcrop belt in western Pennsylvania. An area of more clastic shale and siltstone occupies the limestone horizon in Washington, southern Allegheny, northern Westmoreland, southern Indiana, and Cambria Counties (Skema et al., 1991). The Brush Creek coal, which occurs below the marine zone, is typically thin and not mined over much of western Pennsylvania. The coal is sometimes mineable in portions of the south-central and southeastern sections of the bituminous coal fields of Pennsylvania. Figure 8.23 shows Brush Creek overburden from Wharton Township, Fayette County and Figure 8.24 and Figure 8.17 show overburden from Jackson Township, Cambria County. The rock above the coal, in each area, has relatively high sulfur (> 0.5%) and relatively high NP (> 30 ppt $CaCO_3$). A true limestone is not present in any of these holes, the highest NP being 345 ppt $CaCO_3$ in OB-9 from Cambria County. Because the limestone or a calcareous facies is typically present where the Brush Creek coal is of mineable thickness, the drainage is generally alkaline.

Figure 8.25 shows overburden for the lower and upper Bakerstown coals. The Woods Run marine zone overlies the lower Bakerstown coal, although in Somerset County it is poorly developed and is represented by a brackish facies containing *Lingula* and *Dunbarella* (J. Shaulis, personal communication, 1997). Just below the upper Bakerstown coal a freshwater limestone sometimes occurs. This is evident in DH-12. The upper Bakerstown coal is commonly overlain by a black shale with abundant conchostracans in Somerset County (Shaulis, personal communication, 1997). This zone is the stratigraphic equivalent of the Noble marine zone, which is a restricted marine to brackish shale in some other portions of the bituminous field (Edmunds, et al., 1998).

The overburden above the lower Bakerstown coal is similar to lower Allegheny coal overburden with a brackish depositional environment. It is characterized by sulfur greater than 0.5 percent and NP generally 30 ppt $CaCO_3$ or less. The zones with higher NP, above the brackish zone, may be freshwater calcareous zones related to the freshwater limestone. Unfortunately it is hard to evaluate the overburden above the upper Bakerstown. The upper Bakerstown coal in Hole 11 F is only about 10 ft (3 m) below the surface. Holes DH-3 and DH-12 have sandstone and shale, respectively, above the coal. Both show some zones with elevated sulfur, but the sulfur in these drill holes is always less than 1.0 percent. NP is negligible. More comparisons need to be made, but this overburden looks similar to the lower Kittanning overburden in eastern Cambria County where conchostracans occur.

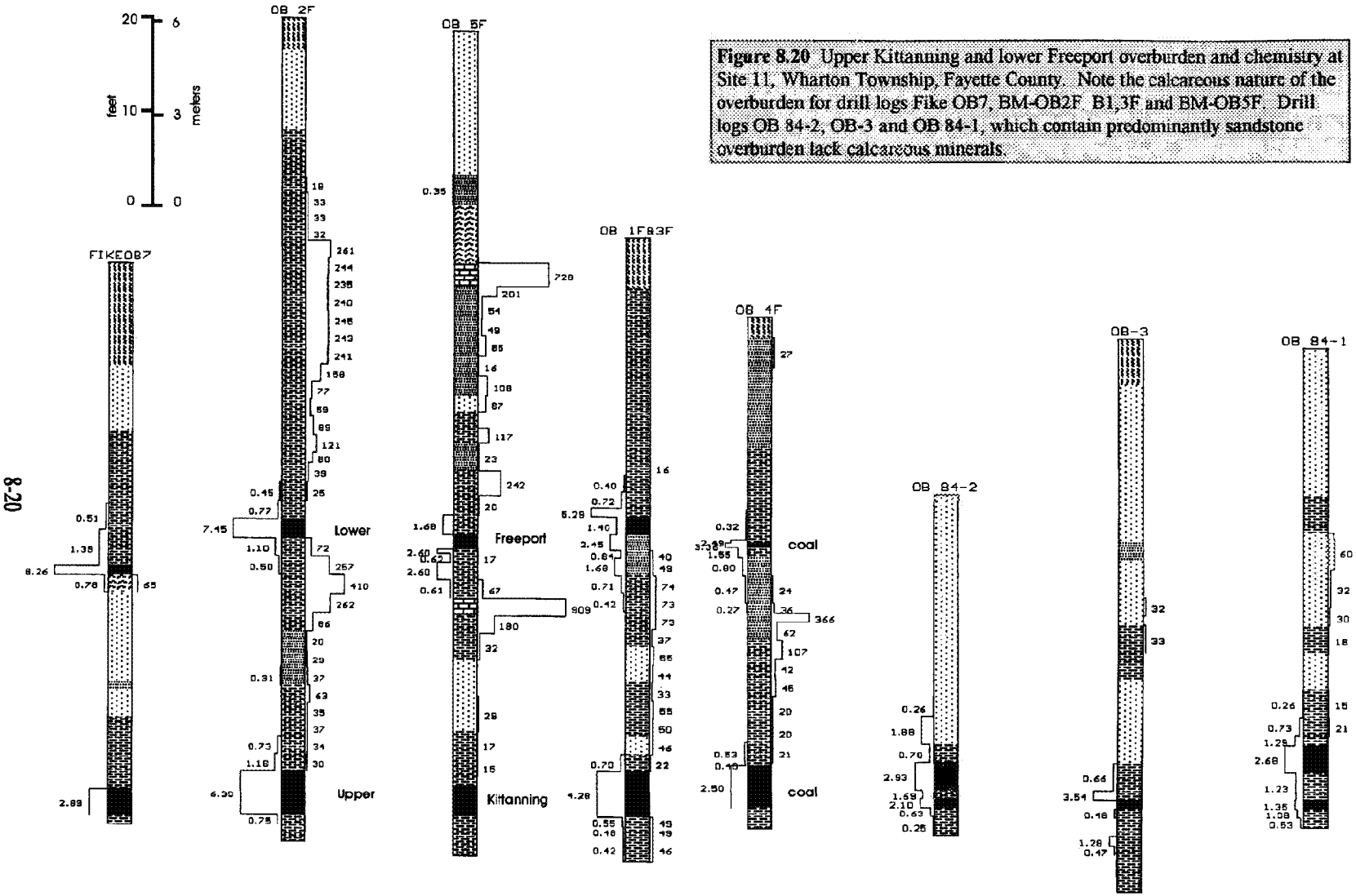

Figure 8.20 Upper Kittanning and lower Freeport overburden and chemistry at Site 11, Wharton Township, Fayette County. Note the calcareous nature of the overburden for drill logs Fike OB7, BM-OB2F B1,3F and BM-OB5F. Drill logs OB 84-2, OB-3 and OB 84-1, which contain predominantly sandstone overburden lack calcareous minerals.

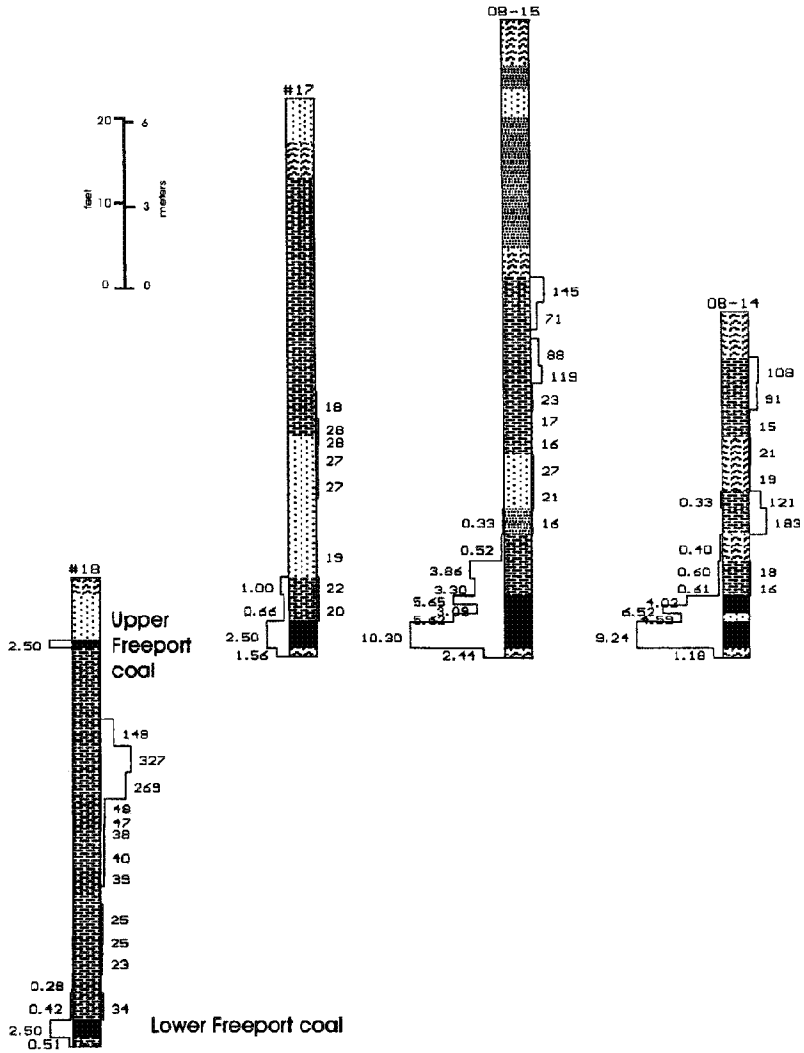

Figure 8.21 Lower and upper Freeport overburden and chemistry. Drill logs #17 and #18 are from Site 13 in Mt. Pleasant Township, Westmoreland County, and drill logs OB-15 and OB-14 are from site 14 in Clay Township, Butler County.

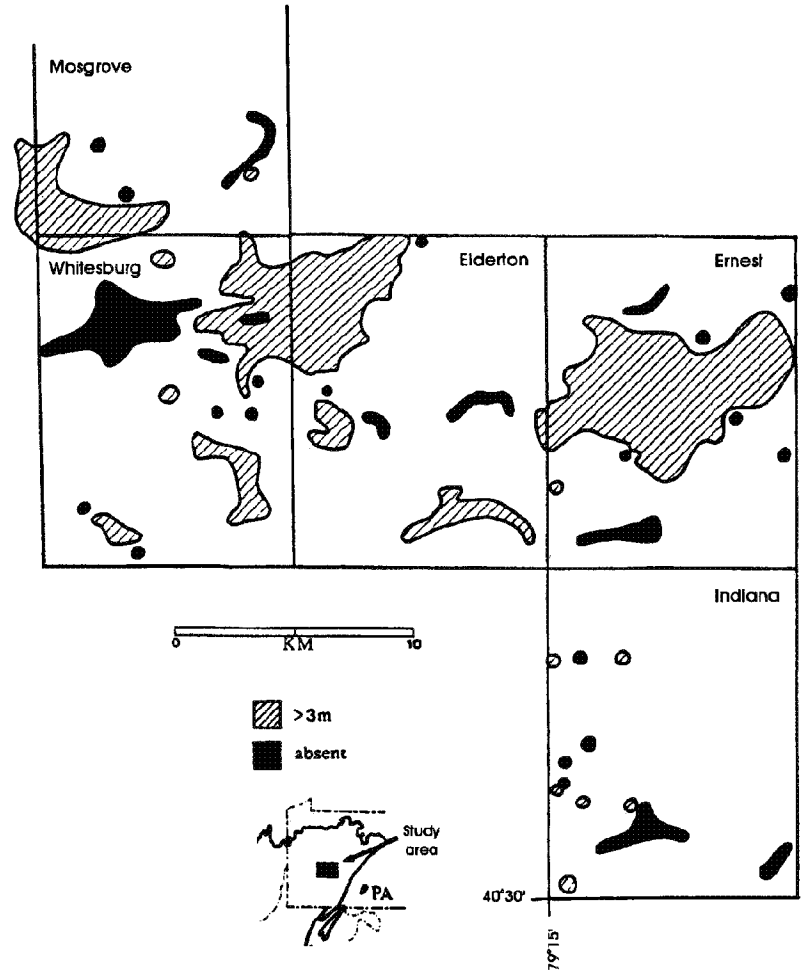

Figure 8.22 Isopach map of the limestone that occurs between the upper Freeport coal and the next lower coal. Areas of zero occurrence and greater than three meters are contoured. Areas with three meters or more of limestone were probably the deepest parts of the freshwater lake into which the limestone was deposited. Figure modified from Weedman (1989).

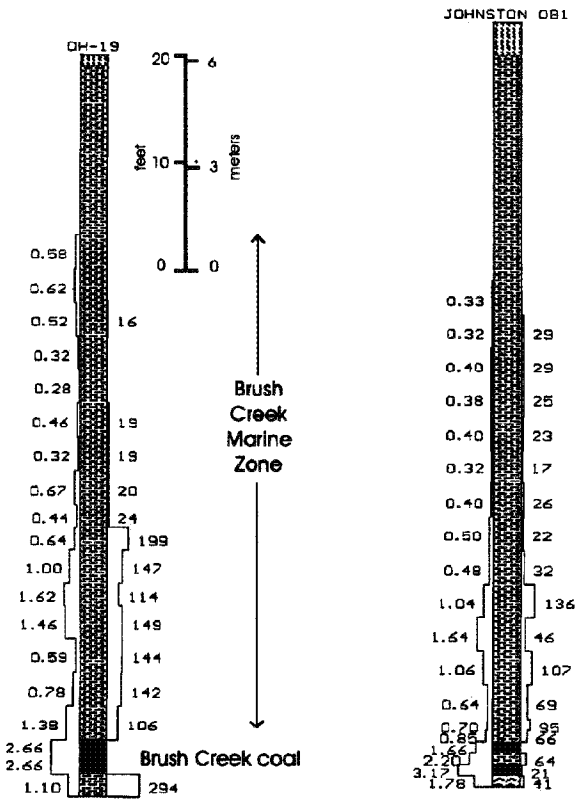

Figure 8.23 Brush Creek coal and overburden at Site 11 in Wharton Township, Fayette County. The overburden is of marine origin.

Casselman Formation - "The thickness of the Casselman Formation ranges from 230 feet (70 m) in the extreme western part of the Appalachian Plateaus province to 485 feet (148 m) in southern Somerset County" (Edmunds, et al., 1998, p. 156). With the exception of the marine shales above the Ames limestone, and the Skelly horizon, which occurs about 30 to 60 ft (9 to 18 m) above the Ames marine zone, the Casselman is made up of exclusively fresh water rocks. Redbeds, which are regionally discontinuous, are scattered throughout the Casselman in the western portion of Pennsylvania. "Eastward they become thinner and fewer in number. This trend continues into eastern Somerset and Cambria Counties, where large areas of the Casselman Formation are completely devoid of red beds. Conversely, coals are nearly absent or very thin in the west but increase in quantity eastward. In Somerset County, a few coals are thick enough to mine" (Edmunds, et al., 1998, p. 156).

Very little coal is mined in the Casselman Formation. Figure 8.25 shows overburden for the Wellersburg coal which is of mineable thickness only in the Wellersburg syncline of Somerset County (equivalent to the Georges Creek Field in Maryland). Although the overburden contains some strata with sulfur greater than 0.5 percent, the overburden is largely calcareous. Figure 8.26 displays chemical data for overburden above and below the Morantown coal, the uppermost coal in the Casselman. This coal is only mined in Somerset County. Shaulis (1993) feels the Morantown is actually a lower split of the Pittsburgh coal, which would place the coal in the Monongahela Group. One of the reasons cited for this stratigraphic placement is the presence of the freshwater limestone below the Morantown. This limestone occurs in OB-A in Figure 8.26 with an NP of 524. Whatever the stratigraphic position, the overburden in the two examples from Somerset County exhibits low sulfur and some neutralization capability. The Morantown, when it is present, is mined in conjunction with the Pittsburgh coal.

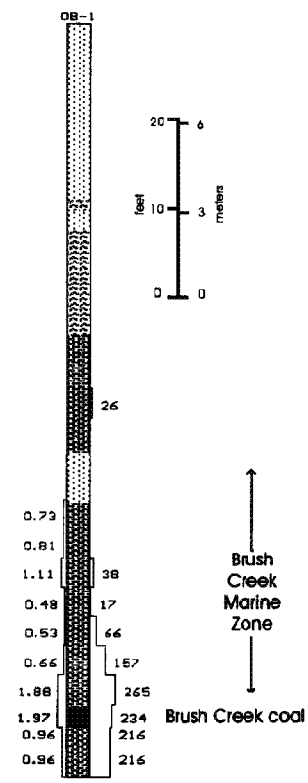

Figure 8.24 Brush Creek coal and overburden at Site 15 in Jackson Township, Cambria County. The overburden is of marine origin.

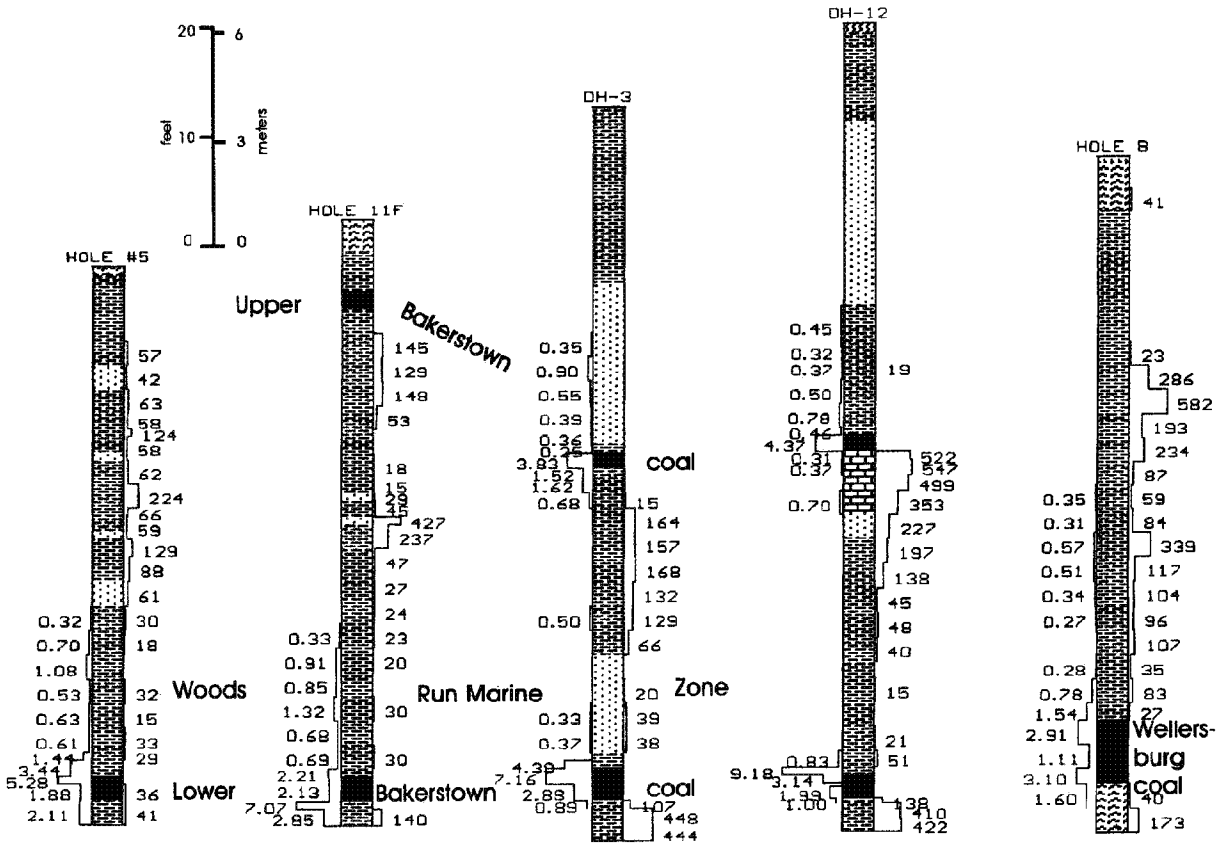

Figure 8.25 Upper and lower Bakerstown coals and Wellersburg coal overburden in Somerset County. Bakerstown coal Hole #5 and Hole 11F are at Site 16 in Brothersvalley Township, and DH-3 and DH-12 are at Site 17 is in Southampton Township. The Wellersburg coal Hole 8 is also from Site 17 in Southampton Township.

Monongahela Group

"The Monongahela Group extends from the base of the Pittsburgh coal to the base of the Waynesburg coal. It is divided into the Pittsburgh and Uniontown Formations at the base of the Uniontown coal. The group is about 270 to 400 feet (82 to 122 m) thick in Pennsylvania, increasing in thickness irregularly from the western edge of the state to western Fayette County....It is entirely nonmarine" (Edmunds, et al., 1998, p. 156).

The Monongahela Group is

"...dominated by limestones and dolomitic limestones, calcareous mudstones, shales, and thin-bedded siltstones and laminites... The only sandstone of significant thickness within the formation lies directly above the Pittsburgh coal complex. A major fluvial channel system, flowing north to northwest through what is now Greene and Washington Counties, deposited an elongate sandstone body up to 80 feet (24 m) thick and several miles (kms) wide" (Edmunds, et al., 1998, pp. 156-157).

This sandstone channel is shown in Figure 8.27. The mineable coals in the Monongahela Group are restricted to the lower portion of the group. The number of mine sites with overburden data for the Monongahela Group in the files of the Department of Environmental Protection are few in number. This is not because the Monongahela coals are rarely mined, it is because mining almost always produces alkaline drainage, and water quality from previous mining is used as the prediction tool.

Pittsburgh Formation - The lower half of the Pittsburgh Formation contains the majority of mineable coals in the Monongahela Group. The Pittsburgh coal,

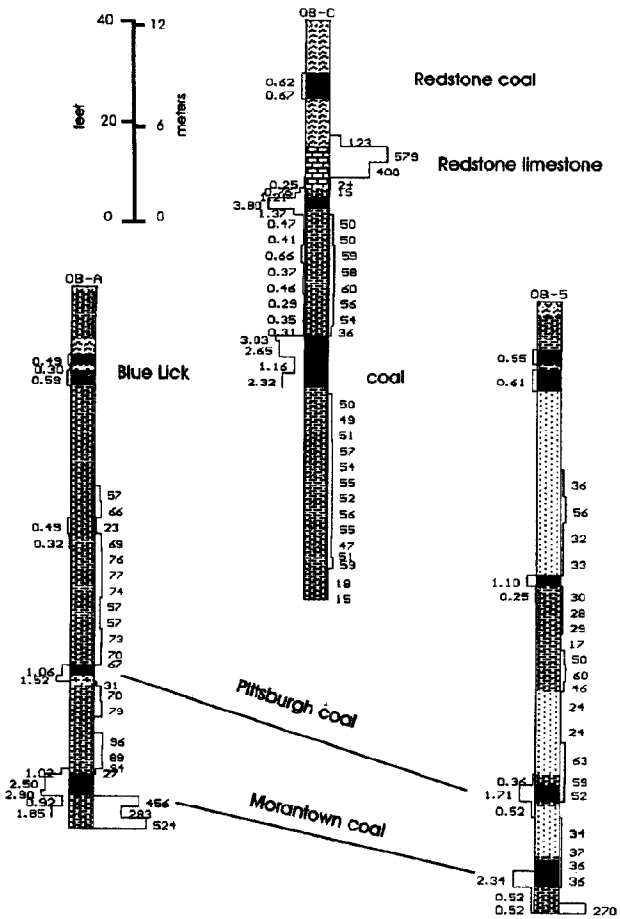

Figure 8.26 Overburden and chemistry of coal and rocks from the Morantown to the Redstone coals at Site 16 in Somerset County. This interval is considered to have been deposited entirely in a freshwater environment. Relationship to paleogeography at time of deposition of Pittsburgh overburden is shown on Figure 8.28.

which defines the base of the formation and group is unusually continuous, covering thousands of square miles (km^2) and is unusually thick (5 to 10 ft; 1.5 to 3 m) for a coal of western Pennsylvania. The other major coals are the Redstone and Sewickley. In Somerset County an additional coal, the Blue Lick, occurs between the Pittsburgh and Redstone coals. Shaulis (1993) believes the Blue Lick coal is a split of the Pittsburgh coal.

Pittsburgh Coal to Redstone Coal Interval - Pittsburgh coal overburden varies from sandstone to limestone to shale. Figure 8.28 is a reconstruction of paleodepositional environments during the time of deposition of the Pittsburgh coal overburden.

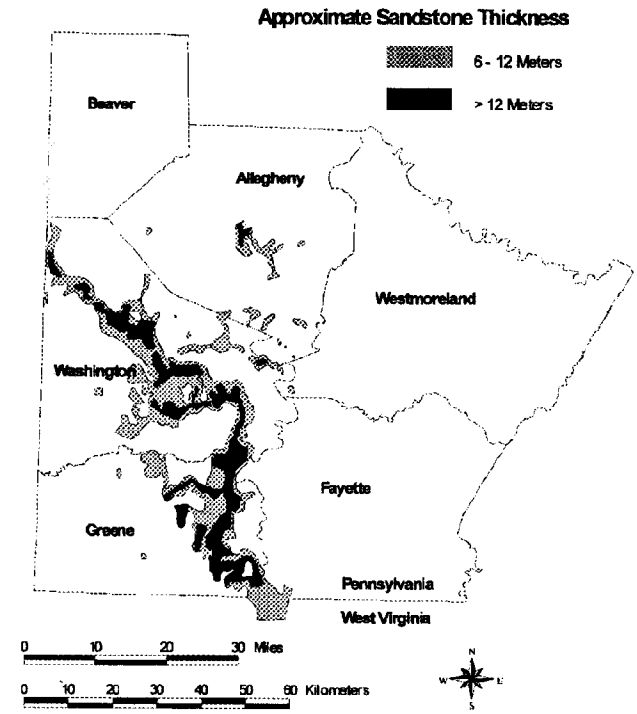

Figure 8.27 Location, geometry and isopach map of a sandstone channel above the Pittsburgh coal in Green and Washington Counties. Isopach map modified from Donaldson (1979).

Sandstone was deposited in the distributary channel running through the southwestern corner of Pennsylvania. An isopach map of the thickness of this channel is shown in Figure 8.27. Limestone or shale was deposited in the lakes and on the mud flats. Some examples of the distribution of Pittsburgh Formation limestones in Greene County, PA and northern West Virginia, are illustrated by Figure 8.29, Figure 8.30, and Figure 8.33. Figure 8.29 is an isopach map of the Redstone limestone. Figure 8.30 is a cross-section of the Pittsburgh/Redstone interval. This cross-section is oriented east-west and approximately parallels the Pennsylvania-West Virginia border shown on Figure 8.29. The Redstone limestone is "patchy", which may simply be due to variable carbonate content of the lake-deposited sediments. The intervening shales may be a lateral, less calcareous, facies of the freshwater limestone. The drill logs shown in Figure 8.31 are from an area east of the major channel shown in Figure 8.27 (isopach map of Pittsburgh sandstone), but they show the nature of the Pittsburgh overburden when it is sandstone. It is characterized by some high sulfur strata, especially the shale portions of OB-2, and some calcareous zones within the sandstone (e.g., the zone in

OB-1 with a NP of 115 ppt, and the zone in OB-2 with a NP of 122 to 169 ppt). The overburden in Somerset County (Figure 8.26) is shale in holes OB-A and OB-C, and a mixture of sandstone and shale in OB-5. The overburden is slightly calcareous with NP's commonly in the range of 30 to 70 ppt. This is true whether the overburden is sandstone or shale. The overburden from the Somerset County sites is lower sulfur than that in Westmoreland County. Pittsburgh coal mines can produce acid and alkaline water (see Table 8.2).

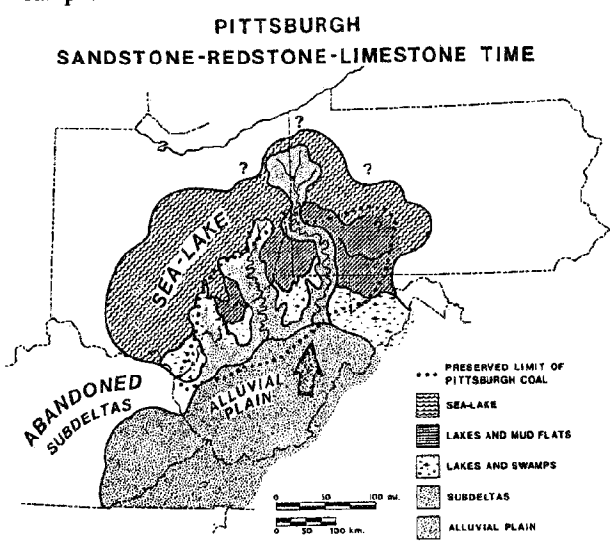

Figure 8.28 Paleogeographic reconstruction of the Pittsburgh sandstone and Redstone limestone time. The river in the southwestern corner of Pennsylvania is the sandstone channel shown in Figure 8.27. The Redstone limestone was deposited in freshwater lakes (see Figure 8.29). The shale overburden above the Pittsburgh coal shown in Figure 8.26 would have been deposited on "mudflats." From Donaldson and Shumaker (1979).

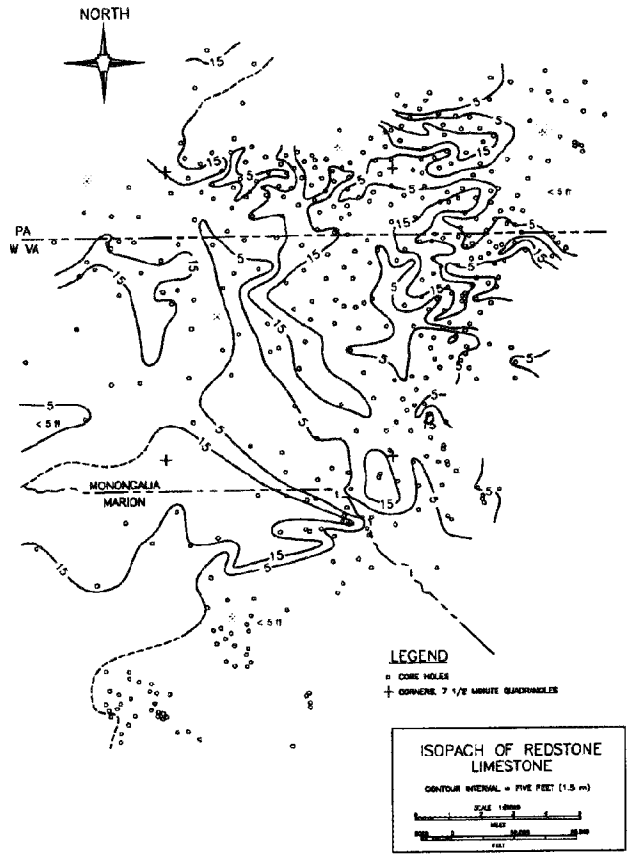

Figure 8.29 Isopach map of Redstone limestone in southern Pennsylvania and northern West Virginia. From Linger (1979).

Blue Lick Coal to Sewickley Coal Overburden - The Pittsburgh coal often has a rider coal positioned approximately 5 to 50 ft (1.5 to 16 m) above it. This rider coal is usually thin and not economically significant. However, in Somerset County the coal at this stratigraphic horizon, named the Blue Lick, attains mineable thickness. The Blue Lick coal is usually overlain by calcareous units and produces alkaline drainage. Blue Lick coal overburden NP values are shown in OB-C, Figure 8.26. OB-C shows only a small amount of strata with sulfur greater than 0.5 percent. There is a zone of calcareous rock, including limestone, above the Blue Lick rider coal.

The Redstone/Sewickley interval is shown in Figure 8.32. This zone contains strata with sulfur greater than 0.5 percent, however, abundant limestone and other calcareous rocks are present. Although limestone occurs above the Sewickley in OB-3, this log is not typical of overburden further west in Pennsylvania. To the west this interval is typically occupied by a very thick limestone, known as the Benwood. The Benwood is the thickest limestone in the Monongahela Group and can be 60 or 70 ft (18 to 21 m) thick. Figure 8.33 is a facies map showing the Benwood interval at 55 feet (16.8 m) above the Sewickly coal.

Pittsburgh Formation Limestones - Figure 8.33 illustrates the lateral persistence that many Monongahela lacustrine limestones exhibit. The lakes in which these laterally extensive limestones were deposited had to have been very large. For example the Benwood limestone above the Sewickley coal covers more than 4,000 square miles (10,000 km^2) (Berryhill, et al.,), and Eggleston (1993) notes that the Redstone limestone

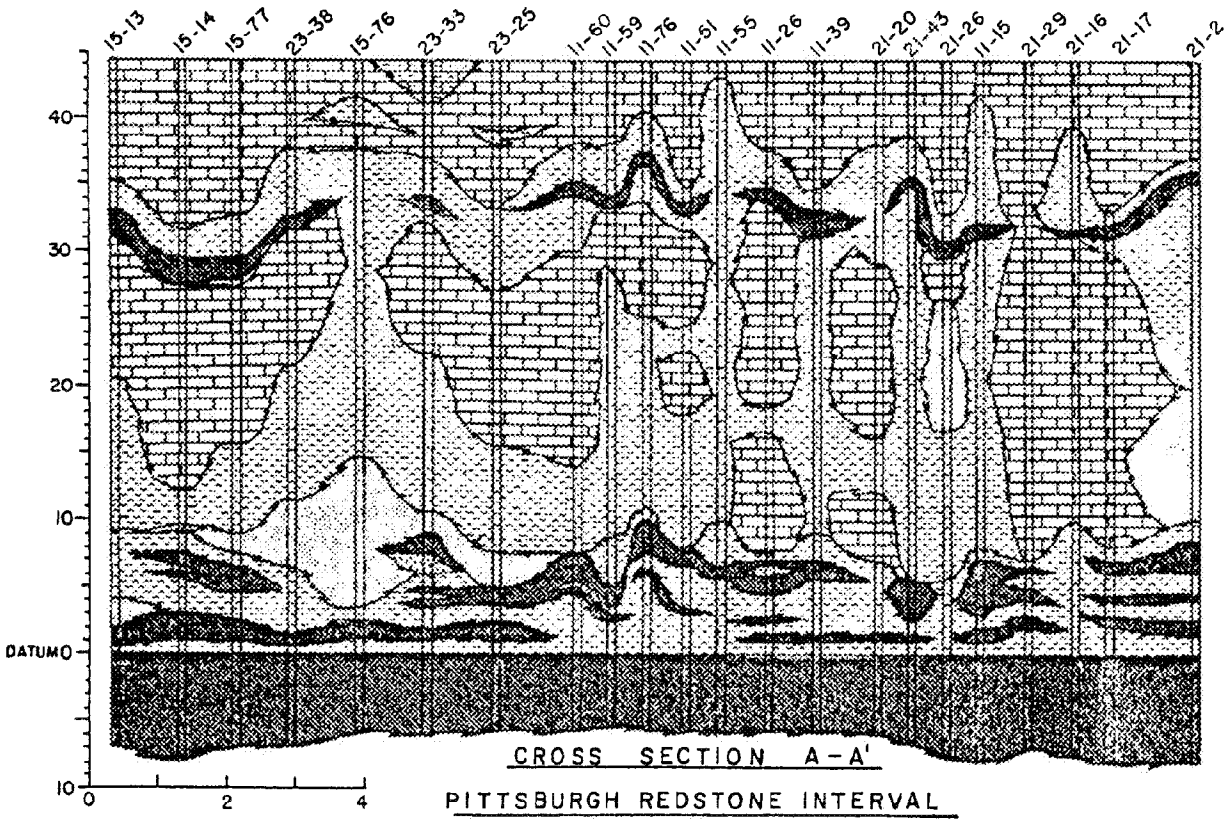

Figure 8.30 Cross-section of the Pittsburgh-Redstone coal interval oriented east-west near the Pennsylvania/West Virginia border shown on Figure 8.29. Vertical exaggeration is approximately 1000 times the horizontal. From Linger (1979)

extends from Somerset County, PA to as far south as Cabell County, WV, and as far west as Morgan County, OH. Figure 8.32 illustrates the NP for the Redstone and Fishpot limestones, and an unnamed limestone above the Sewickley coal. The highest NP for the Fishpot in OB-3 is 735 ppt.

Eggleston (1993) concludes that the Redstone limestone was deposited in a "very shallow lake that was subject to periodic subaerial exposure during drier periods." As evidence of drying she refers to desiccation breccia, root traces, and lack of original bedding. Evidence of shallow depositional conditions include rounded intraclasts, broken and nested shells, and bioturbated limestone. Berryhill et al. (1971) arrived at similar conclusions, using similar evidence, concerning the depositional environment of other limestones in the Monongahela and Dunkard Groups. Berryhill et al. suggest that the limestones were deposited in shallow lakes, where water depth "probably never exceeded a few feet" and that "(n)either fossil evidence nor physical properties of the rocks indicates any influence of marine conditions" (Berryhill et al., 1971, p. 34). In addition to the limestones, the sandstones and shales of the Monongahela Group are also often calcareous (Figure 8.2). The environmental interpretations of Eggleston (1993) are consistent with the paleoclimatic interpretations of Cecil et al. (1985) and Donaldson et al. (1985) for this stratigraphic interval.

Berryhill et al. (1971, p. 16) found that of 50 limestone samples from the Monongahela and Dunkard Groups, 34 were classified as limestone or magnesium limestone (< 10% dolomite, > 90% calcite), 13 were dolomitic limestone (10% to 50% dolomite, remainder being calcite) and three were calcitic dolomite (50% to 90% dolomite). The clay content is generally greater than 10%, thus the limestones are classified as marly. The ratio of calcium to magnesium varies both from bed to bed and also vertically and laterally within a single bed.

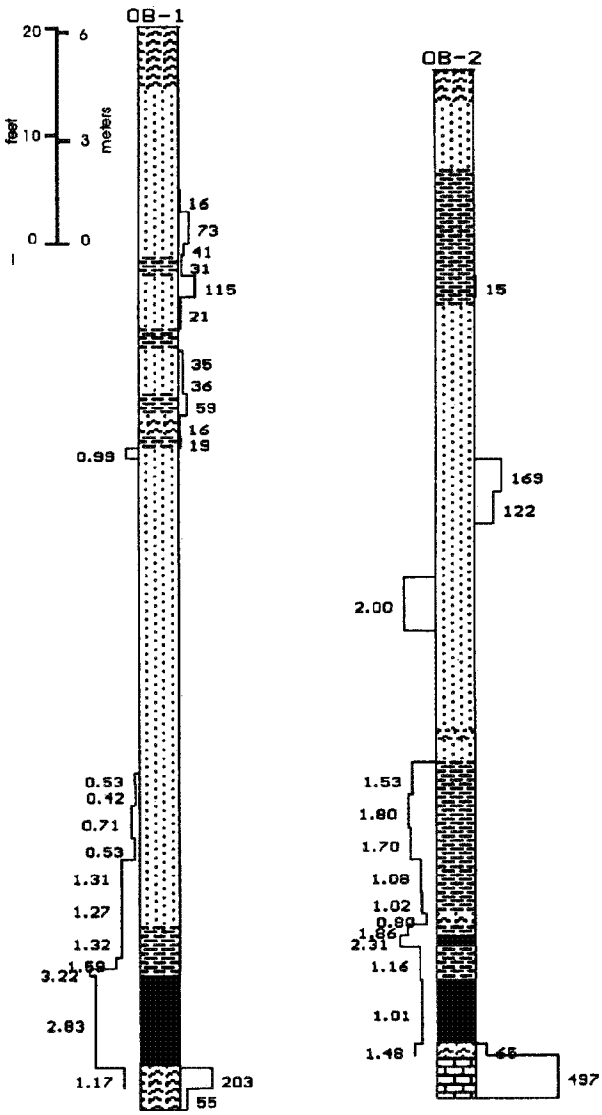

Figure 8.31 Logs and chemistry of Pittsburgh overburden at Site 19 in Salem Township, Westmoreland County. Relationship with paleogeography is shown on Figure 8.28.

Dunkard Group

The Dunkard Group is found only in the most southwestern corner of Pennsylvania in Greene and Washington Counties. It is made up of Waynesburg, Washington and Greene Formations (Berryhill et al., 1971). The Dunkard reaches a maximum thickness of about 1120 ft (340 m) in Greene County and the upper surface is the modern day erosional surface. The lower boundary of the Dunkard Group is defined as the base of the Waynesburg coal, which is the only coal routinely mined in the Dunkard.

The Dunkard is generally composed of fine-grained clastics which are frequently calcareous. Thick lacustrine limestones are especially prevalent in the Washington Formation. The only significant interval with sandstone is above the Waynesburg coal (Figure 8.2). This sandstone is often, but not always, calcareous. The Dunkard Group data represented in Figure 8.2 is all from Greene County. A comparison of this data with the study by Berryhill et al. (1971) for Washington County shows some differences in abundance of lithologies. For example Berryhill et al. show that 33% of the Group is limestone, whereas this study found only 6.2% limestone. This is probably largely attributable to a facies change between Washington and Greene Counties. Skema (personal communication, 1997) reports that the Upper Washington and Lower Washington Limestones, which are thick in Washington County are barely present in Greene County.

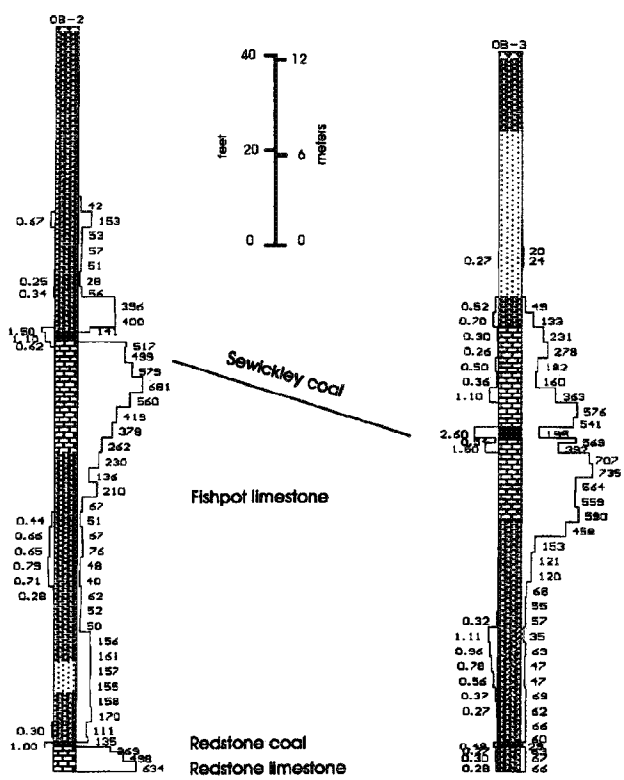

Figure 8.32 Overburden and chemistry of the Redstone and Sewickley interval at Site 18 in Elklick and Summit Townships, Somerset County. Note the presence of freshwater limestones and abundant calcareous shales.

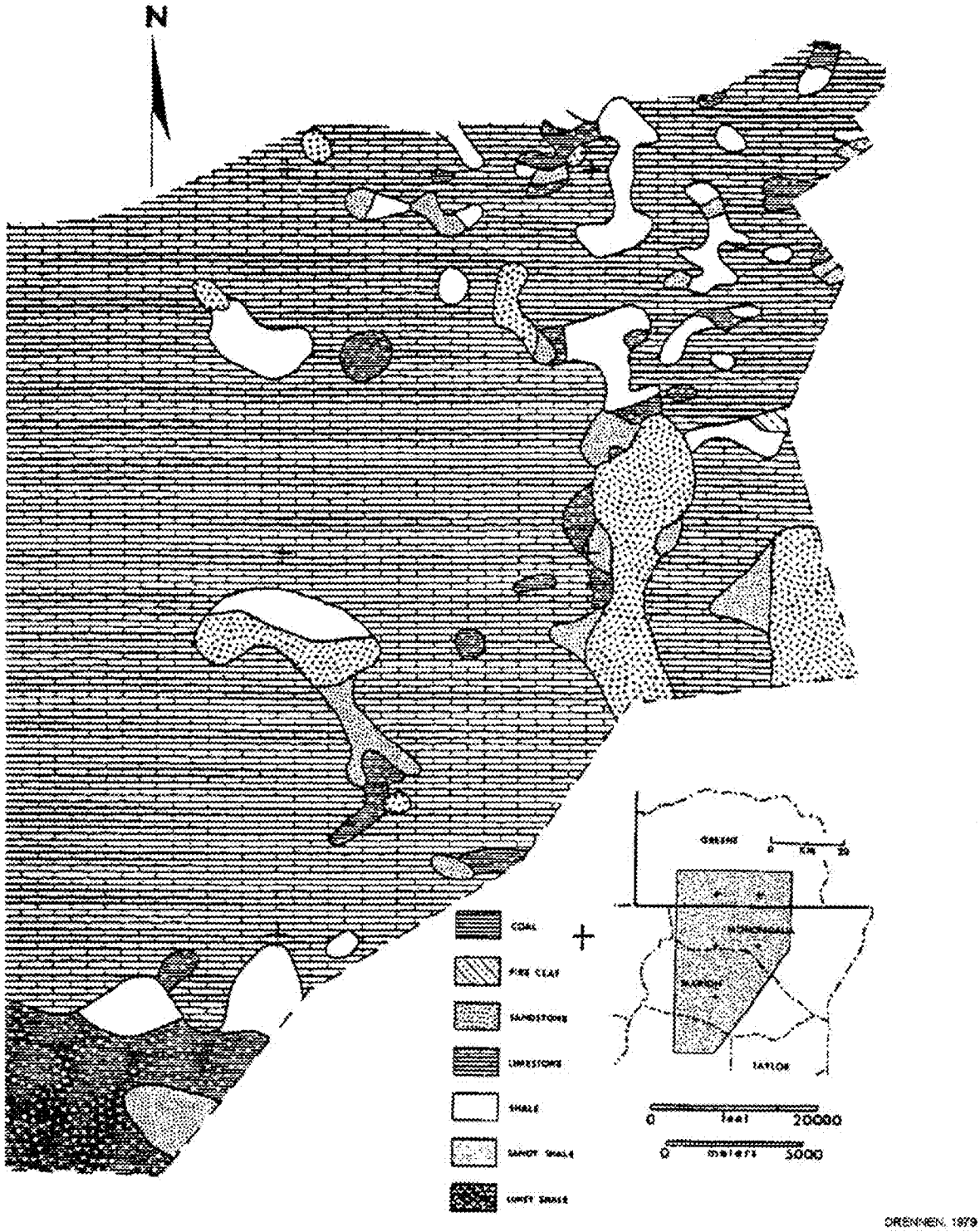

Figure 8.33 Facies map 55 ft (17 m) above the Sewickley coal (Benwood limestone horizon). At this interval the limestone is predominant. Although not indicated as such (with the exception of "limey shale"), the other facies are probably calcareous. The area shown is in northern West Virginia and southwestern Pennsylvania. From Linger (1979).

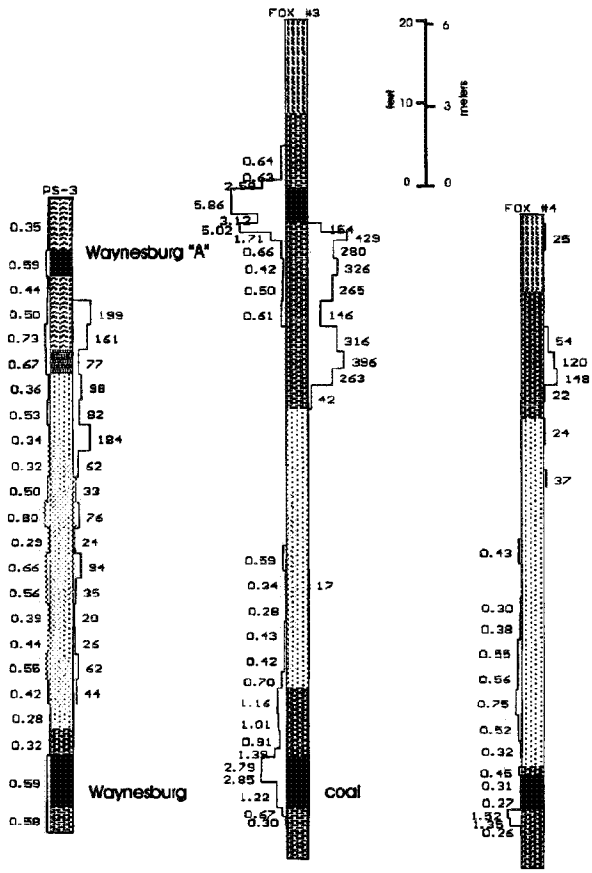

Figure 8.34 Overburden and chemistry of the Waynesburg and Waynesburg 'A' coals at Site 20 in Greene Township, Greene County. Note the variability in NPI within the sandstone.

As mentioned, the only coal routinely mined in the Dunkard is the Waynesburg. For purposes of this study the Waynesburg Formation has been divided into upper and lower members. This is because in recent years mining has generally been restricted to only the Waynesburg, thus not disturbing strata above the Waynesburg 'A' coal. Also, the Waynesburg overburden is lithologically different. As shown in Figure 8.2, much of the Waynesburg overburden is sandstone, and much of this sandstone is calcareous. The Waynesburg 'A' and its overburden are notorious for producing poor quality water. Figure 8.34 shows the Waynesburg coal overburden. The shale above the coal can be high sulfur as illustrated in drill hole Fox #3. The three drill logs in Figure 8.34 illustrate the variability in overburden chemistry for this unit. Of the three holes, the sandstone is only calcareous in PS-3. The finer-grained calcareous zones, near the tops of drill holes Fox #3 and Fox #4, would not be encountered unless more than 50 or 60 ft (15 or 20 m) of cover is mined. Where the sandstone is calcareous, mines produce alkaline drainage, where it is not calcareous mining results in acid mine drainage.

Pennsylvanian Stratigraphy of Pennsylvania's Anthracite Region

The stratigraphy of the anthracite region of eastern Pennsylvania has not been studied as extensively as that of Pennsylvania's bituminous coal region. Geologic and mining engineering work done in the anthracite region over the past 150 years, however, documents some significant stratigraphic differences between the anthracite and bituminous coal regions. The anthracite region is comprised of four coal fields as shown on Figure 8.4: The Northern Field, the Eastern Middle Field, the Western Middle Field, and the Southern Anthracite Field.

The four anthracite coal fields are located within the Valley and Ridge Physiographic Province and the orogenic activity in this province since the Pennsylvanian Period has resulted in: (a) the increase in rank of the coals due to metamorphism (as compared to time-equivalent coal beds in the Appalachian/Allegheny Plateau Province of the bituminous region), and (b) the preservation of the anthracite coal fields within synclinal basins which are essentially surrounded by sandstone/conglomerate ridges that are more resistant to erosion than the coal and associated finer-grained sedimentary rocks. A comprehensive description of the geologic history of the north-central Appalachians, is contained in Faill (1997a, 1997b, 1998a, 1998b). The most recent orogenic episode, the Alleghenian, commenced in the Early Permian (Faill, 1997b). Faill (1997a, p. 552) states that "(l)ate in the Allegheny orogeny, rock thrust northward over the Carboniferous rocks in the Anthracite region of northeastern Pennsylvania caused anthracitization of the underlying coals."

Much of the Southern and Western Middle Fields has been geologically mapped by Wood and associates (e.g., the Minersville Quadrangle, Wood, et al., 1968, and related cross sections). The maps depict the synclinoria and other complex geologic structures. The geologic structure and stratigraphy of the Southern Anthracite Field are described in Wood et al. (1969) and the depositional and structural history of the entire Anthracite Region are presented in Wood et al. (1986). The complexity of the geologic structure, resulting in nearly vertical beds of coal and other rocks in some areas of the anthracite fields, has impeded the acquisition

of stratigraphic data from routine exploration drilling. Detailed mine maps of the abandoned underground mines and cross-sections through vertical shafts and nearly horizontal tunnels have added to the understanding of the structure and stratigraphy of the anthracite coal fields, however most stratigraphic efforts have been directed toward coal seam delineation.

The Pennsylvanian age rocks of the anthracite region of Pennsylvania have been divided into two major formations, the Pottsville and the Llewellyn. Generalized columnar sections of the Pottsville and Llewellyn Formations are shown on Figure 8.35.

Pottsville Formation

The Pottsville Formation ranges in thickness from a maximum of approximately 1600 ft (490 m) in the Southern Field to less than 100 ft (30 m) in the Northern Field. The Tumbling Run and Schuylkill Members of the Formation are not present in the Northern Anthracite Field (Wood et al., 1969, 1986; Meckel, 1967, 1970; and Edmunds et al. 1979, 1998).

The Pottsville Formation contains up to 14 coal beds in some areas, but most are relatively discontinuous and only a few persist outside of the Southern Field (Edmunds et al. 1998). Figure 8.35 shows the mineable coals of the Pottsville Formation. The Lykens Valley Coal Numbers 4 through 7 are within the Tumbling Run Member; the Lykens Valley Coal Numbers 1 through 3 are within the Schuylkill Member; and the Scotty Steel and Little Buck Mountain Coals are within the Sharp Mountain Member of the Pottsville Formation (Figure 8.35). The base of the Buck Mountain Coal is considered the top of the Pottsville Formation in eastern Pennsylvania; however, the Buck Mountain coal is generally correlated with the lower Kittanning Coal within the lower Allegheny Group in western Pennsylvania (see Edmunds et al., 1998). The type section of the Pottsville Formation (located near Pottsville) is described by C.D. White (1900) and more recently by Wood et al. (1956) and Levine and Slingerland (1987).

The Pottsville Formation in eastern Pennsylvania is entirely of a nonmarine depositional environment (Edmunds et al., 1998). As in western Pennsylvania, the dominant lithology of the Pottsville Group is sandstone and conglomerate; but the Pottsville Formation of the Anthracite region contains significant pebble conglomerates derived from an orogenic source area to the southeast (Meckel, 1967, 1970; Edmunds et al. 1998; and Faill, 1997b). The Tumbling Run Member is composed of approximately 55% conglomerate and conglomeratic sandstone, about 30% fine- to coarse-grained sandstone, and about 15% shale and siltstone. Conglomerate and conglomeratic sandstone comprise about 50% of the Schuylkill Member, and the sandstone in the member ranges from very fine to very coarse, constituting approximately 30% of the member. The Sharp Mountain Member in most of the Southern Anthracite Field is composed of about 45% conglomerate, 25% conglomeratic sandstone, 15% sandstone, 5% siltstone, 9.5% shale, and 0.5% anthracite (Wood et al. 1969, 1986). The carbonate content of the rocks has not been determined.

Llewellyn Formation

The Llewellyn Formation is as much as 3500 feet (1050 m) thick. The maximum known thickness of the

Pennsylvanian in Pennsylvania is approximately 4400 ft (1340 m) near the town of Llewellyn in Schuylkill County (Edmunds et al., 1998). The Llewellyn Formation contains up to 40 mineable coals (Edmunds et al., 1998), most of which are shown on Figure 8.35. The thickest and most persistent coals occur in the lower part of the Llewellyn Formation, particularly the Mammoth coal zone. The Mammoth coal zone typically contains 20 ft (6 m) of coal and thicknesses of 40 ft to 60 ft (12 to 18 m) are not unusual. A local thickness of greater than 125 ft (38 m) has been reported in the Western Middle Field. This was attributed to structural thickening in the trough of the syncline. The nomenclature and stratigraphy of the coal bearing rocks of the Llewellyn Formation in the Northern Anthracite Field are different than in the Southern and Middle Fields (Figure 8.35).

The dominant lithology of the Llewellyn Formation is sandstone, including conglomerate units, as in the Pottsville Formation. According to Edmunds et al. (1998, p. 159): "Lithologically, the Llewellyn is a complex, heterogeneous sequence of subgraywacke clastics, ranging from conglomerate to clay shale and containing numerous coal beds. Conglomerates and sandstones dominate". The Llewellyn Formation in the Southern and Middle Fields is believed to be entirely continental in depositional environment (i.e., lacking any marine beds). The Llewellyn Formation in the Northern Field, however, contains one known marine bed, the Mill Creek Limestone (Figure 8.35). I.C. White (1903) suggested that the Mill Creek was correlative with the Ames limestone of western Pennsylvania. This belief is generally held to the present. The

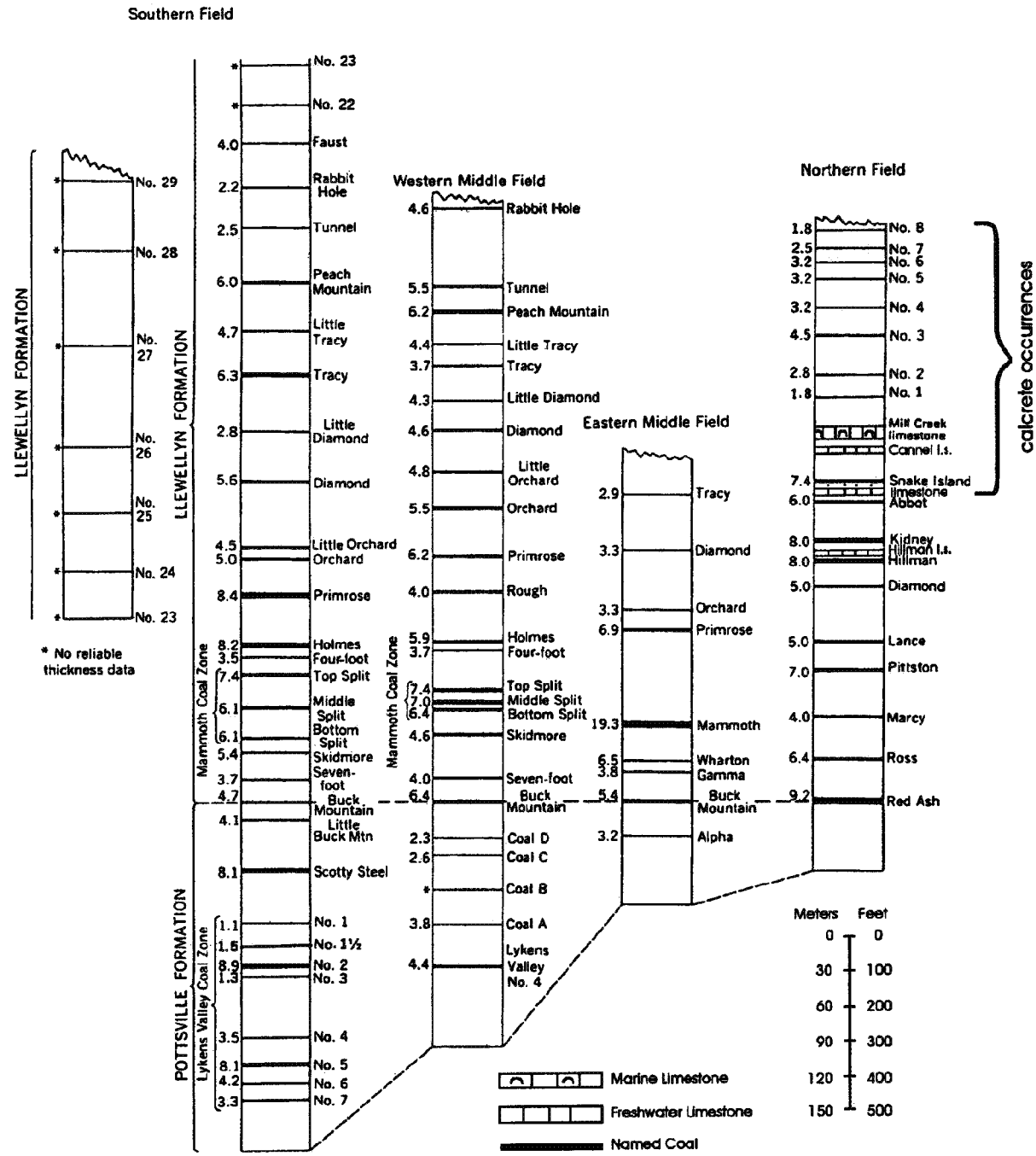

Figure 8.35. Generalized columnar sections showing names, average thickness of coals (in ft), and intervals between coal beds in the Pennsylvania Anthracite fields. Figure is primarily from Wood et al. (1986). Information on calcareous zones in the Northern Field has been supplemented by data from Edmunds et al. (1998) and Inners and Fabiny (1997).

Mill Creek Limestone is a one- to three-ft (0.3 m to 1 m), richly fossiliferous marine limestone (Chow, 1951). The Llewellyn Formation contains several other nonmarine limestones in the Northern Field including the Cannal and Hillman limestones (Chow, 1951, and Edmunds et al., 1998). Additionally, Inners and Fabiny (1997) have identified calcareous paleosols ("calcrete") in the uppermost Llewellyn Formation in the Northern Field. They have tentatively correlated this portion of the stratigraphy with the Conemaugh of western Pennsylvania. The calcretes are indicative of "seasonally semi-arid conditions" (Inners and Fabiny, 1997, p. 85). The calcretes are often associated with siderite. Kochanov (1997) has found calcareous sandstones in the lower part of the Llewellyn in the Northern Field. Siderite nodules are also common in the lower Llewellyn (Kochanov, 1997, personal communication).

The identification and mapping of limestone and other calcareous rocks in the Southern and Middle Fields have not been reported in the literature; however, some large mine pool discharges such as the Wadesville Colliery (see Table 8.14), have alkalinity of several hundred milligrams per liter, which must be attributed to some carbonate minerals in the overburden. Discharges in the Eastern Middle Field have little if any alkalinity (see Table 8.14). This strongly suggests a lack of calcareous rock in this coal field. Study of carbonate minerals and identification of calcareous lithologic units in the Southern and Middle Fields is needed.

Pleistocene Sediments

Based on permits issued by the Department of Environmental Protection in glaciated regions in northwestern Pennsylvania, glacial sediments are most likely to be encountered where mining of the Brookville/Clarion, lower Kittanning and middle Kittanning coals takes place. These sediments affect mine water quality because they contain calcareous clasts. Lower Freeport permits have also been issued in glaciated regions. For Clarion/Brookville coal mines, it can be difficult to assess the impact of glacial sediments on postmining water quality because the Vanport limestone is often part of the overburden. Figure 8.36 shows the area of overlap of glacial sediments, Vanport limestone, and coal areas. The Vanport limestone becomes thinner and more discontinuous near its northern limit.

Glacial overburden in surface coal mines can exert a different influence on mine drainage quality than does bedrock. The texture, composition (mineralogy), and structure of glacial overburden differs from that of bedrock. Much information on the glacial geology and sediment composition exists for northwestern Pennsylvania.

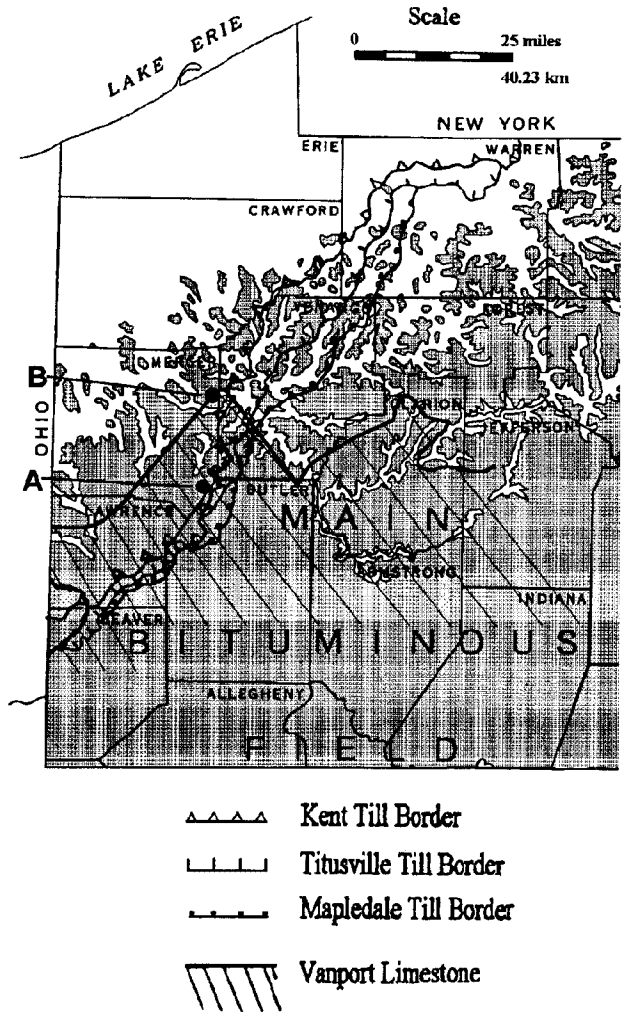

Figure 8.36 Map showing the locations of glacial borders, Vanport limestone, and Pennsylvanian Period rocks and location of sites with glacial overburden that are discussed in the text.

Because of a lack of carbonate source rock, glacial sediments in northeastern Pennsylvania are typically low in carbonate. The only exception is in an area near the Delaware River, east of the anthracite fields (William D. Sevon, personal communication, 1994; Epstein, 1969). Several overburden holes have encountered till in the semi-anthracite Bernice Basin,

Sullivan County. The till ranges in thickness from 0 ft (m) to 32 ft (9.8 m). The highest NP and sulfur (out of 32 samples) was 3 ppt $CaCO_3$ and 0.04 percent respectively, i.e., negligible. There are no overburden analyses of glacial sediments in the anthracite coal fields. Duane Braun (Bloomsburg University, personal communication, November 18, 1997) has done field work in the northern Field and has not observed any till reacting visibly to HCl. Available data suggests that glacial sediments are generally not a source of NP in northeastern Pennsylvania. Therefore, glacial sediments in northeastern Pennsylvania will not be discussed further.

Northwestern Pennsylvania has been glaciated a number of times during the Pleistocene. At least 8 tills have been identified on the Appalachian Plateau of northwestern Pennsylvania (White and others, 1969) and northeastern Ohio (White, 1982) (Table 8.3). The glaciations range in age from pre-Illinoian (> 500,000 ya) to late Wisconsinan (about 15,000 ya). Generally, each advance was less extensive than the previous. The last glacier to advance into Pennsylvania, the Ashtabula advance, stopped at the northwestern edge of the Appalachian Plateau, just south of Lake Erie. The Titusville glaciation deposited the bulk of the glacial sediment in northwestern Pennsylvania. Stacking of multiple Titusville sheets makes up the bulk of the main end moraine, the Kent Moraine (White and others, 1969; White, 1982).

Table 8.3 Pleistocene tills, from youngest to oldest and carbonate content in the clay fraction of those tills in northwestern Pennsylvania. Data from White and others (1969) and White (1982).

Till	Carbonate Content
Ashtabula	Calcareous. Oxidizes dark brown
Hiram	Total carbonate up to 17%
Lavery	Total carbonate > 10%
Kent	Calcite = 1.4% Dolomite = 1.8%
Titusville	Calcite = 1.1% Dolomite = 1.3%
Keefus (NE Ohio)	Not quantified, but highly calcareous
Mapledale	Calcite = 0.7% Dolomite = 0.6%
Slippery Rock	Unknown - all samples weathered and leached

Individual tills in northwestern Pennsylvania are generally only a few feet (~1 m) to a few tens of feet (10s of m) thick, but can be over 100 feet (30 m) thick (White, 1982). Multiple tills of different composition may be encountered in the overburden during mining. White et al. (1969) show this for the Ambrosia mine near Grove City, PA (Figure 8.37). The Mapledale, Titusville, Keefer and Kent tills are present. The upper portion of the Mapledale and Titusville tills are leached of carbonates, where the unweathered portions contain

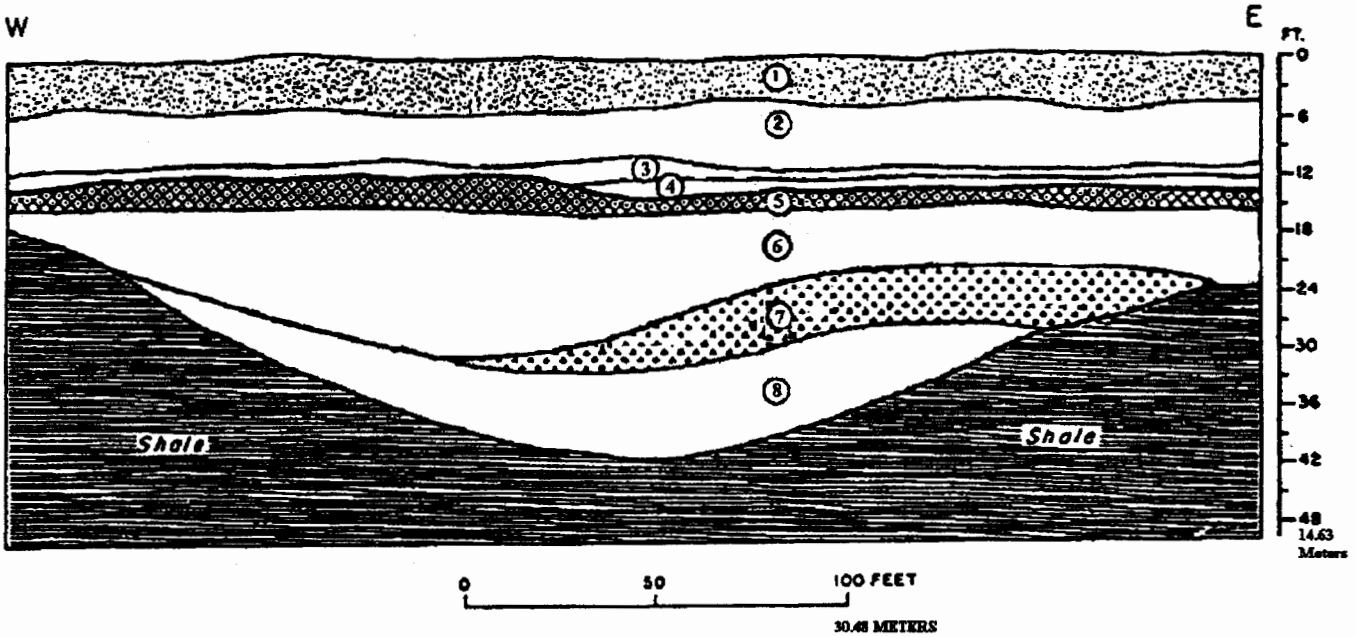

Figure 8.37 Sketch of overburden in Ambrosia strip mine near Grove City. 1. Soil in till and colluvium, noncalcareous. 2. Kent Till, calcareous. 3. Kent Till, calcareous. 4. Sand, calcareous. 5. Keefus Till, calcareous. 6. Titusville Till, noncalcareous. 7. Titusville Till, calcareous. 8. Titusville Till, calcareous. 10. Mapledale Till, noncalcareous. 11. Mapledale Till, noncalcareous. 12. Mapledale Till, slightly calcareous. Site is located at "A" on Figure 8.36.

calcareous minerals. Figure 8.38 shows the variable carbonate contents of tills in mines near the Ambrosia site.

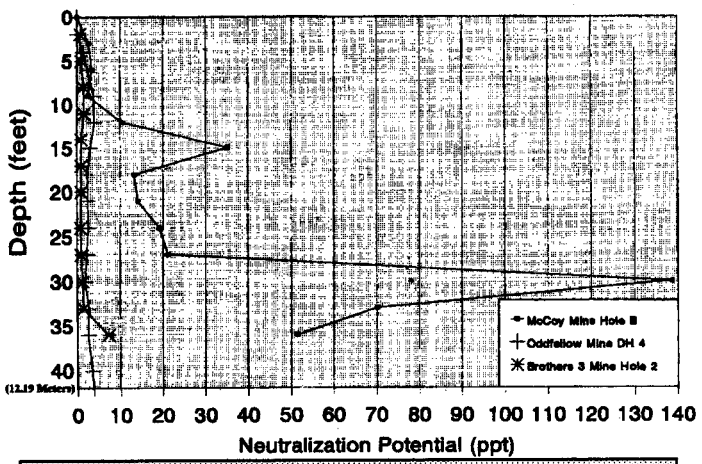

Figure 8.38 Distribution of neutralization potential for glacial overburden from mine sites southeast of Grove City. Sites are located at "A" on Figure 8.36.

Geochemistry of Glacial Sediments

The compositions of sediments from different glaciations are determined by the source materials eroded by the glacier and incorporated into the sediments. Glaciers advancing into northwestern Pennsylvania advanced from the Lake Erie basin. The bedrock in the basin, which was the source for the glacial sediments, consists of a large amount of limestone and dolomite. Therefore, the sediment contained in the glaciers was high in carbonate minerals (calcite and dolomite) when it entered Pennsylvania. Early glaciers advanced far to the south of the Lake Erie basin over a surface of weathered siliceous bedrock and soil, resulting in dilution of the carbonate rich sediment by carbonate poor sediment. The resulting glacial deposits are relatively low in carbonate. Later glaciers advanced less far out of the Lake Erie basin over unweathered bedrock (the weathered horizons having been removed by previous glaciations), and over previously deposited glacial sediments. These glacial sediments were diluted less by the siliceous bedrock south of the Erie basin and are relatively high in carbonate, more characteristic of the source limestone and dolomite rocks in the Lake Erie basin (White, 1982).

Till in the coal fields, near the glacial margins, is probably lower in carbonate content than the average for that till. Because of the difference in source materials for succeeding glaciations, carbonate content generally increases from older tills to younger tills (White et al., 1969) (Table 8.3).

The Mapledale Till is the only till that has such a low carbonate content that unweathered till will not act visibly with dilute hydrochloric acid. It is completely leached of carbonates in the clay fraction in outcrop area (Gross, 1967). Unfortunately, from a surface mining standpoint, only the older glaciations mainly the Mapledale, Titusville, and Kent, advance far enough to reach the coal fields of Pennsylvania. The higher carbonate tills (Ashtabula, Hiram) occur mainly in Crawford and Erie Counties (Figure 8.36). Although the Kent and Titusville Tills, in addition to the Mapledale Till, occur beyond the Kent Moraine, little neutralization benefit will be realized from glacial sediments beyond the Kent Moraine because they are all thin, discontinuous, and weathered. Fortunately, overburden data suggests that the amount of iron sulfide in glacial sediments is negligible (Figure 8.39), thus enabling the till to contribute a generally net positive influence on mine water quality. The highest sulfur in any of the tills is 0.38% in OB 3-Spag. All of till samples had less than 0.25% sulfur.

By comparison, in the Illinois Basin, most of the coal field is within the glaciated region and the bulk of the tills have carbonate contents greater than 10% in the clay fraction, and up to 64% in the coarse sand fraction (Fleeger, 1980), similar to the Pennsylvania tills near Lake Erie. The presence of glacial deposits is much more significant to the coal mining industry for the prevention of AMD in Illinois than in Pennsylvania. Although coal and associated strata in the Illinois Basin are high sulfur (Maksimovic and Mowrey, 1993), acid streams (pH < 6) were only identified south of the glacial border (Hoffman and Wetzel, 1993, 1995).

Tills have characteristic grain size distributions (Shepps and others, 1959). All have a significant amount of fine-grained material, that is, sand size and smaller. Groundwater movement through glacial sediments differs from that through consolidated bedrock in the Appalachian Plateau. The majority of groundwater movement through bedrock is along fractures and bedding planes. In glacial sediments, much more of the groundwater movement is intergranular, although some movement does occur through fractures in dense tills. The small grain size, poor sorting, and lack of fractures and bedding planes in tills results in low permeability. Water moves through tills very slowly, increasing the amount of time that the groundwater remains in contact with the mineral grains. Like the increased surface area, the increased residence time

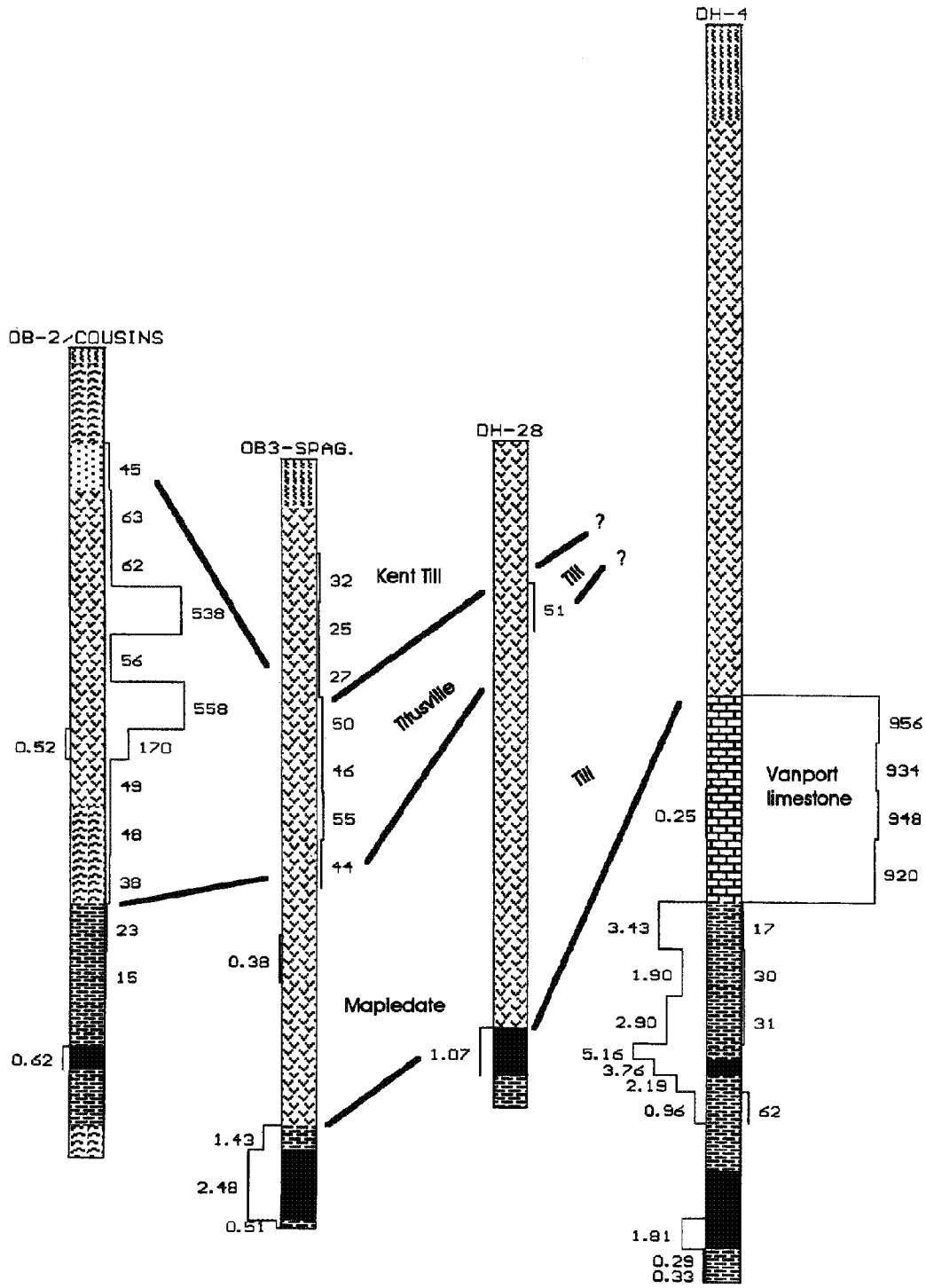

Figure 8.39 Till overburden above the Brookville/Clarion coal at Sites 21 in Millcreek Township (OB1-SPAG and OB3-SPAG) (site B on Figure 8.36) and Site 22 in Pine Township (DH-28 and DH-4) (site A on Figure 8.36), Mercer County. Probable till correlations are shown. This figure shows the variable thickness of tills that can occur within the same mine, wide variation in neutralization potential of tills and differences in the amount of erosion of underlying bedrock.

Table 8.4 Water quality parameters at the Spagnolo and Owens Mines. The unit for specific conductance is µS/cm, and units for other parameters, with the exception of pH, are in mg/L.

	N	Lab pH	Specific Conductance	Alkalinity	Acidity	Fe	Mn	Al	SO_4
Spagnolo Pre-mining	9	6.5	94	29	2	0.98	0.09	0.34	17
Spagnolo During-Mining	9	6.78	100	34	3	0.33	0.09	0.15	20
Owens Postmining	10	7.13	391	110	0	0.19	0.04	0.39	122

allows for greater reactivity in tills than in shallow, fractured bedrock.

The neutralizing capability of a till varies considerably and is reported in the literature in various ways. Published carbonate values for tills of northwestern Pennsylvania are for the clay fraction only, and not representative of the till as a whole. In addition, the carbonate content of any size fraction varies areally due to dilution by local bedrock, and vertically due to dilution and weathering (White, 1969). The published mean carbonate contents for the clay fraction of tills likely to be encountered in mines in northwestern Pennsylvania are based on limited numbers of sample analyses (3 Kent, 9 Titusville, and 9 Mapledale) (Gross, 1967). For these reasons, converting published carbonate values for tills in northwestern Pennsylvania into NP values is not valid, and site-specific testing and analyses are required.

Four mines near Grove City in Mercer County (Location A on Figure 8.36), including the Ambrosia mine, demonstrate the variability that till can have. All are within the Kent Moraine. All mined the Brookville/Clarion coals. About 50% of the glacial overburden in the Ambrosia Mine (Figure 8.37) is calcareous. Two nearby sites, Oddfellow Mine (Figure 8.36 and Figure 8.38) and Brothers 3 Mine (Figure 8.37), have very little NP > 30, even though the depth of the glacial overburden is up to 60 feet (18 m). The fourth site, McCoy Mine (Figure 8.38), did have significant NP in the glacial overburden.

Carbonate minerals in tills with NP less than 30 ppt CaCO3 can probably dissolve to produce alkalinity. Calcareous minerals in till probably react more completely than those in bedrock because of the greater surface area of particles in till. Because of the source area (Erie Basin) the NP of glacial sediments is less likely to be complicated by siderite, and reflects actual neutralizing potential.

Importance of Glacial Sediments in Mine Drainage Water Quality

The overlap of the main bituminous coal field and glaciated region is mainly in Beaver, Lawrence, Butler, Mercer, and Venango Counties (Figure 8.36). The Slippery Rock, Mapledale, Titusville, and Kent Tills are present in these areas. Rare thin patches of Lavery Till may also be encountered in northwestern Lawrence County.

In glaciated areas of Pennsylvania, postmining water quality is frequently good, presumably due to the carbonate content of glacial sediments. Overburden for the Spagnolo mine is shown in Figure 8.39, and the location of this and the Owens mine are shown in Figure 8.36. Water quality at the Spagnolo Mine, at the time of this writing, has not changed significantly from the premining background quality Table 8.4. However, the Spagnolo Mine reclamation was completed about the time this was written. Thus, there has not been sufficient time to collect and evaluate the postmining water quality.

The Owens Mine, about 6,000 feet (1,830 m) from the Spagnolo Mine (Location B on Figure 8.36) was mined in the late 1960's and early 1970's, and left partially unreclaimed. No acid-base accounting data are available for this site. Its geology, however, is likely similar to the Spagnolo Mine, although, as has been previously shown at Grove City, there can be rapid lateral variability in the mineralogy of glacial sediment. Both are located within the Kent Moraine, have similar drift thickness (Schiner and Kimmel, 1976), and mine the same coal. Postmining water from the Owens mine in 1990 was higher in specific conductance, alkalinity, and sulfates than the pre- or during-mining water from the Spagnolo site Table 8.4. The Owens water is characteristic of neutralized mine drainage. Other parameters are largely the same as the Spagnolo site water quality. Not all mines in glacial overburden will have alkaline drainage. Older tills, especially in their outcrop area, are low in carbonate and may not exert much neutralization effect.

In summary, glacial overburden can be beneficial in preventing acid mine drainage if it is calcareous. Because of the small grain size, unlithified nature, and the source of carbonates in glacial sediments, the NP determinations of glacial overburden probably more accurately reflect the ability of the glacial sediments to prevent and neutralize acid mine drainage than is sometimes the case with bedrock overburden. Site specific data are required to determine the NP of glacial sediments because of their variability in the texture and composition due to dilution and weathering.

Discussion on Stratigraphy

Several lithologic and mineralogic trends for the coal-bearing rocks of western Pennsylvania are evident from examination of Figure 8.2. The clay/shale content increases upward from a low of about 25% in the Pottsville Group to highs of 70 to 80% in the Dunkard Group. In general, there is a reverse relationship with sandstone, with sandstone increasing from ~20% or less in the higher Groups (with the exception of the lower Waynesburg Formation) to a high of 50% in the Pottsville. The percent calcareous rocks increases upward. The Pottsville Group has less than 1% calcareous rock. The lower Allegheny is less calcareous (6%) than the upper Allegheny Group (14%). Rocks of the Casselman Formation and higher are greater than 50% calcareous. The percentage of sandstone that is calcareous is generally similar to the percentage of overall rock that is calcareous. The uppermost Dunkard Group rocks contain the least amount of siderite, whereas over 20% of the rocks in the Allegheny Group and Glenshaw Formation are sideritic. Within the Allegheny and Pottsville Groups sideritic rocks are more abundant than calcareous rocks (Figure 8.2).

Some stratigraphic trends are also worth discussing. The Allegheny Group was divided into upper and lower Allegheny based on the presence of marine and brackish zones below the Johnstown limestone and the occurrence of freshwater limestones in the upper Allegheny, which are rare or absent in the lower Allegheny. The Conemaugh Group, like the Allegheny is divided such that the Glenshaw Formation contains most of the marine rocks, whereas the Casselman is primarily of freshwater origin. Mineable coals are generally restricted to the Allegheny and Monongahela Groups, although coals in the other groups are occasionally mineable.

The important geologic relationships, from a mine drainage standpoint, are the location of marine zones and distribution of calcareous rocks. The marine rocks are frequently associated with high sulfur strata, but can also have calcareous zones. Brackish rocks tend to have high sulfur and a lack of calcareous minerals. The conchostracan-bearing rocks frequently have less sulfur than their marine and brackish counterparts. Truly freshwater sediments tend to have calcareous minerals and limestone. These topics are discussed below in detail.

Little is known about the overburden mineralogy of the anthracite region. The Llewellyn Formation of the Northern Field is known to contain calcareous rocks. Some of the water quality reflects this source of alkalinity. Although stratigraphic studies have not yet identified calcareous rocks in the Southern and Western Middle Fields, highly alkaline mine waters imply that calcareous rocks exist. The lack of alkaline drainage in the Eastern Middle Field suggests a dearth of calcareous strata in this anthracite field.

Pleistocene glaciation in the bituminous coal field only came as far south as the northwestern corner of the field. Tills, where calcareous, can contribute significantly to the alkalinity of postmining water quality. Tills in the Northern Anthracite Field are not calcareous and would not contribute alkalinity to water.

The only places where the stratigraphy is important from a mining standpoint is where these strata will be disturbed by surface mining. Ultimately, postmining water quality is related to the mineralogy of these rocks.

Mineralogy of Mine Site Overburden

Coal overburden is composed of many different minerals in varying abundance. As mentioned previously, mining accelerates the weathering of these minerals by exposing fresh rock surfaces, and from a mine drainage or soil reclamation standpoint, two groups of minerals are overwhelmingly important. These are the acid-forming iron sulfides and the acid- neutralizing carbonates. The weathering of these two groups of minerals dictate whether the mine spoil will produce alkaline or acidic water. These minerals need only be present in an abundance of a few percent or less to be significant. By comparison the other 95% or so of overburden minerals play only a minor role.

Iron sulfide (pyrite) oxidizes and dissolves to create acidic water. Calcareous minerals (Ca-rich carbonates, such as calcite) can dissolve to neutralize and inhibit acid production (Chapter 1). The inhibitory effect is probably due to neutral pH conditions reducing the

catalytic effects of pyrite oxidizing bacteria, and the virtual elimination of pyrite oxidation by Fe^{+3} because of low solubility at near neutral pH. An example of the interaction between pyrite and a calcareous mineral (calcite) can be represented by:

$$FeS_2 + 2\ CaCO_3 + 3.75\ O_2 + 1.5\ H_2O \Rightarrow Fe(OH)_3 + 2\ SO_4^{2-} + 2\ Ca^{2+} + 2\ CO_{2(g)} \quad (8.1)$$

In the above equation the acid generated by the pyrite is neutralized by the calcite. The ultimate products of this reaction are iron hydroxide, sulfate, calcium and carbon dioxide gas. Other equations can be written and other products produced, and these are discussed in Chapter 1. For the present chapter it is simply necessary to recognize that weathering of pyrite makes acid, and dissolution of calcareous minerals will neutralize acid and possibly inhibit pyrite oxidation.

Pyrite, Other Forms of Sulfur, and Acid Production

In this section we will discuss the influence of forms of sulfur, pyrite morphology, and pyrite genesis as they relate to the production of acid-sulfate weathering products. Forms of sulfur that occur in coal overburden are sulfide, sulfate and organic. As discussed above, iron sulfide minerals (principally pyrite) are the culprit in the formation of acid mine drainage. Pyrite occurs in several crystal morphologies, ranging from micron-size framboids to millimeter (or larger) size euhedral crystals and coatings. Pyrite genesis has been suggested as a factor influencing pyrite reactivity, for example sedimentary pyrite is more reactive than hydrothermal pyrite (Hammack et al., 1988). Pyrite associated with Pennsylvania's bituminous coal seams and overburden is sedimentary in origin.

Chemical Forms of Sulfur (Sulfur Mineralogy) in Overburden Rock - When overburden is analyzed, weight percent total sulfur is generally determined as a means of estimating pyritic sulfur and thus the acid-producing potential of the rock. Forms of sulfur can be determined as described in Noll et al. (1988), however because of difficulties with analytical methods, added cost of analysis, and the fact that most sulfur in overburden rock is pyritic, typically only total sulfur is determined.

Although pyrite may comprise only a few percent, or even a fraction of a percent, of the overburden rock, its importance to postmining water quality far outweighs its seemingly minor presence. An overburden that averages just a fraction of a percent sulfur, in the absence of neutralizing rocks, can create significant postmining water quality or revegetation problems if not dealt with properly.

Sulfide Sulfur - Two iron-sulfide minerals occur in bituminous coal and overburden. They are pyrite and marcasite. Both have the chemical formula FeS_2 and are 53.4 percent sulfur with the remainder being iron, but the two minerals have different crystallinity. For simplicity we will refer to iron sulfide minerals as pyrite.

The oxidation of pyrite results in the production of sulfuric acid and iron. This acid can dissolve other minerals and thus release undesirable ions such as aluminum and manganese. The oxidation and acid-weathering processes are discussed in Chapter 1. A summary equation for the process can be described as follows:

$$FeS_2 + 3.75\ O_2 + 3.5\ H_2O \Rightarrow Fe(OH)_3 + 2\ SO_4^{-2} + 4\ H^+ \quad (8.2)$$

As seen above, one of the products of pyrite oxidation is aqueous sulfate. Under evaporative conditions sulfate minerals can form.

Sulfate Sulfur - Sulfate minerals are generally secondary weathering products of pyrite oxidation. Nordstrom (1982) shows the sequence by which these minerals can form from pyrite (Figure 8.40). Many sulfate minerals have been identified in Pennsylvania overburden (Table 8.5). They are divided into acid-producing and non-acid-producing. These minerals (with the exception of barite) are typically very soluble and transient in the humid east. They form during dry periods and then are flushed into the groundwater system during precipitation events. The phases that contain aluminum or iron are essentially stored acidity and will produce acid when dissolved in water. Gypsum, which is not acid forming, is relatively uncommon in Pennsylvania, whereas other sulfate minerals such as pickeringite and halotrichite occur more commonly.

The dissolution of coquimbite will be given as an example of how dissolution of sulfate minerals can create acid:

$$Fe_2^{3+}(SO_4)_3 \cdot 9H_2O \Rightarrow 2Fe(OH)_3 + 3\ SO_4^{2-} + 3\ H_2O + 6\ H^+ \quad (8.3)$$

Furthermore, Cravotta (1991, 1994) showed how the dissolution of roemerite could oxidize pyrite in the absence of oxygen, and thus create acid.

$$FeS_2 + 7\ Fe^{2+}Fe_2^{3+}(SO_4)_4 \cdot 14H_2O \Rightarrow 22\ Fe^{2+} + 30\ SO_4^{2-} + 16\ H^+ + 9\ H_2O \quad (8.4)$$

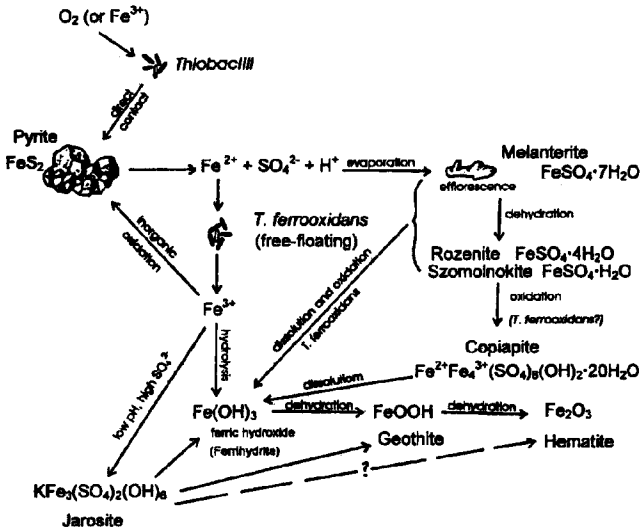

Figure 8.40 The overall sequence of mineral reactions for pyrite oxidation showing the relationships between oxidizing agents, catalysts and mineral products. From Nordstrom (1982).

The bottom line is that in Pennsylvania sulfate sulfur should be assumed to be acid producing unless the mineral can be verified as a non-acid producing one.

No systematic work has been done in Pennsylvania on pyrite weathering products, so the list in Table 8.5 is by no means exhaustive. Sulfate minerals are common to coal mine environments and have been reported from (among other places) Texas (Dixon et al., 1982) and Indiana (Bayless and Olyphant, 1982). Dixon et al. (1982) provide a list of 26 sulfate minerals "related or potentially related to lignite mine spoil..." A more complete list for Pennsylvania coal overburden would likely include most of the same minerals.

Organic Sulfur - Organic sulfur is sulfur that is tied up in organic molecules. This sulfur can originate by two processes. It can be associated with the original plant material, and it can be complexed with organic molecules during diagenesis. Casagrande et al. (1989) concluded that organic sulfur is not acid forming. Harvey and Dollhopf (1986) concluded that some forms of organic sulfur are acid producing, although the amount of acid produced in two leaching tests showed that organic sulfur contributed only 6 and 19 percent of total acidity. They showed, however, that theoretically some forms of organic sulfur should be capable of creating more acid than pyrite, whereas other forms are comparatively inert. Few, if any, other studies have been conducted on acid potential of organic sulfur.

Table 8.5 Secondary sulfate minerals identified in western Pennsylvania mine spoil and overburden. (Minerals from L. Chubb and R. Smith (PA Geologic Survey, personal communications, various years), Cravotta (1991, 1994), and observations by the authors. Mineral chemistries are from Roberts et al. (1990).

Acid-Producing

Pickeringite:	$MgAl_2(SO_4)_4 \cdot 22\ H_2O$
Halotrichite:	$Fe^{+2}Al_2(SO_4)_4 \cdot 22\ H_2O$
Alunogen:	$Al_2(SO_4)_3 \cdot 17\ H_2O$
Copiapite:	$Fe^{2+}Fe^{3+}(SO_4)_6(OH)_2 \cdot 20\ H_2O$
Copiapite Group:	aluminocopiapite with magnesium?
Coquimbite:	$Fe_2(SO_4)_3 \cdot 9\ H_2O$
Roemerite:	Fe2+Fe23+$(SO_4)_4 \cdot 14$ H2O
*Jarosite:	$KFe_3^{+3}(SO_4)_2(OH)_6$

Non-Acid-Producing

Gypsum:	$Ca(SO_4) \cdot 2\ H_2O$
Epsomite:	$MgSO_4 \cdot 7\ H_2O$
Barite:	$BaSO_4$

*Jarosite is less soluble than the other acid-producing sulfate minerals.

One factor complicating organic sulfur estimates is that organic sulfur is usually determined by "difference" (Noll et al., 1988). That is, total weight percent sulfur minus pyritic sulfur and sulfate sulfur. If pyritic sulfur or sulfate sulfur are incorrectly determined during analysis, organic sulfur will also be incorrect. In any event, acid production from organic sulfur is probably much smaller than from sulfide or sulfate sulfur.

It might be expected that rocks with high organic content would have greater amounts of organic sulfur compared with rocks with lesser amounts of organic matter. This appears to be true for coals, but not so for other rock types. A study by Brady and Smith (1990) examined the percentage of pyritic sulfur in relation to total sulfur for various rocks. Carbonalith (i.e., an organic-rich rock) did not have significantly different pyritic sulfur in relation to total sulfur than other rock types such as shale, sandstone and clay. The lack of higher amounts of organic sulfur in organic-rich rocks may be allied to the relationship between organic matter and pyrite formation, which is discussed below.

Pyrite Morphology - A considerable effort has been expended over the years looking at pyrite morphology and attempting to relate this to acid mine drainage generation. Some of the earliest work is by Caruccio (e.g. 1970), however numerous other individuals have also examined this issue. This seems like a logical thing to

look at because pyrite is what causes acid mine drainage.

Morrison (1988) defined nine "classes" of pyrite morphology, end members being framboids and euhedral crystal structures. Framboids tend to be small (< 1 micron size), and euhedral are generally larger (tens to thousands of microns). For any given percentage of sulfur, framboids would have a proportionally larger surface area than euhedral crystals. Other classification systems have also been discussed (e.g., Arora et al., 1978; Hawkins, 1984). Caruccio (1970) and Morrison (1988) found a relationship between relative surface area and acid production, with the small particles more reactive than large particles. Hornberger and associates (1981,1985) found a statistically significant difference in the abundance of framboidal pyrite (i.e. framboids and framboidal clusters <10 microns) in lower Kittanning coal samples from marine and freshwater paleoenvironments. There were almost no discrete framboids in point counts of the freshwater samples, but the marine samples had many. However, some of the freshwater samples produced as much acidity and sulfate in leaching tests as the marine samples. One LK sample from a brackish paleoenvironment produced by far the highest acidity and sulfate of all of the LK coal samples tested, despite having a dearth of framboids (and total and pyritic sulfur contents similar to the marine samples). It seems reasonable that surface area would have an effect on reactivity, but it is not by any means the only factor controlling reactivity.

Discussion on Sulfur Minerals and their Relation to Acidic Water - Typically in Pennsylvania determination of total sulfur will adequately serve as a proxy for acid potential. This is because it includes the sulfur from acid-generating sulfide and sulfate minerals and typically the amount of organic sulfur in overburden rock is insignificant. In locations where gypsum, and other sulfur-bearing non-acid-forming materials are abundant, accurate determination of sulfide sulfur should provide a better prediction of acid potential.

Formation of Pyrite

This section will discuss the factors involved in the formation of pyrite. These factors are responsible for the amount of pyrite present in a stratigraphic interval, and thus that rock's acid-producing potential. Pyrite consists of iron and sulfur, so clearly these ingredients are required. Other factors that influence the creation of pyrite are the presence of organic matter decomposable by sulfate-reducing bacteria (essential for creating reducing conditions), sedimentation rate and bioturbation.

Sulfur and Iron - Sulfate, the typical aqueous form of sulfur, is the source of sulfur in most sediments. The sulfur in sulfate is oxidized and must be reduced to sulfide to become part of pyrite. Ocean water contains about 2700 mg/L SO_4. Freshwater, on the other hand, is typically low in sulfate. An average river transports about 8 mg/L sulfate (Hem, 1985), although rivers draining arid and semi-arid regions can have much higher sulfate (hundreds of mg/L). Another source of sulfate that has been suggested as a source of sulfur for pyrite is sulfate from eroded evaporites. Erosion of upstream evaporites containing gypsum has been espoused by Querol et al. (1991) as the source of sulfur for some high sulfur coals in Spain and by Gibling et al. (1989) for high sulfur coals in the Maritime basin of Canada. Most studies of sulfur in rocks have dealt with marine sediments, where the water column provides a nearly unlimited supply of sulfate sulfur. Few studies are available for freshwater rocks and the formation of pyrite. The few that do exist seem to indicate that sulfur is low in freshwater sediments.

The concentration of iron in ocean water is very low (<.01 mg/L), whereas iron associated with fresh water is comparatively high (~0.7 mg/L average) (Hem, 1985). Iron can also be transported as detridal iron-bearing minerals (e.g., iron oxides) and bound to clay minerals. Thus iron can be transported into a marine or marginal marine environment by iron-bearing water and sediments.

It has been suggested that the most optimum environment for pyrite formation would be a brackish environment, where freshwater high in iron mixes with marine water high in sulfate (Guber, 1972). The subject of paleoenvironmental controls on pyrite formation are discussed later in this chapter.

Organic Carbon and its Relationship to Sulfur - Sulfate can only be reduced to sulfide in sediments by bacterial activity in the absence of oxygen. The bacteria oxidize organic carbon to provide energy for their metabolic processes and sulfate is the terminal electron accepting reactant. The sulfate is reduced to sulfide. Suitable reducing environments are typically found below the sediment-water interface. Although pyrite is the end product, intermediate iron sulfide minerals are created first (e.g., mackinawite (FeS); greigite (Fe_3S_4)). A schematic of this process is shown in Figure 8.41 (Goldhaber and Kaplan, 1982). Pons et al. (1982)

have described this process with the following overall equation (CH_2O represents organic matter):

$$Fe_2O_3 + 4\ SO_4^{2-} + 8\ CH_2O + \tfrac{1}{2}\ O_2 \Rightarrow 2\ FeS_2 + 8\ HCO_3^- + 4\ H_2O \qquad (8.5)$$

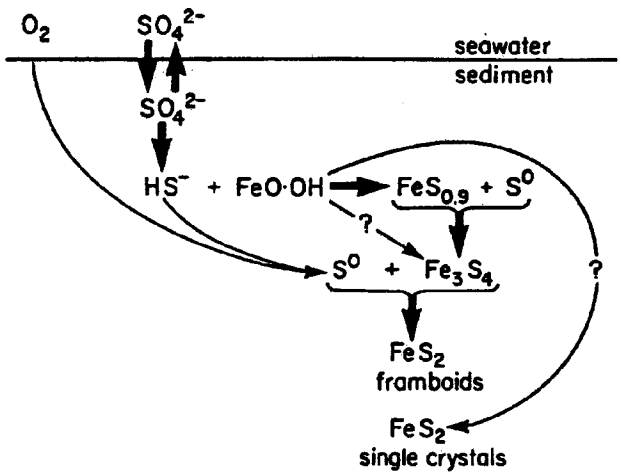

Figure 8.41 Pathway of sedimentary pyrite formation. From Goldhaber and Kaplan (1982).

A positive linear relationship has been shown between percent organic carbon and percent sulfur for Recent and Pleistocene marine sediments (Goldhaber and Kaplan, 1982; Raiswell and Berner, 1986). Fairly strong positive linear relationships exist for marine sediments back in time to at least the Jurassic (Holocene and Pleistocene, correlation coefficient (r) = 0.95; Upper Cretaceous, r = 0.73; Jurassic, r = 0.91), but more random scatter seems to be the case during the lower Carboniferous of Europe (Mississippian Period in the US) with r = 0.39 (Raiswell and Berner, 1986). The reason for the poor correlation between carbon and sulfur during the Carboniferous is not discussed. But the correlation coefficient of 0.39 indicates that carbon abundance explains only 15% of the variation in sulfur, while carbon explains 90% of the variation of sulfur in the Holocene and Pleistocene samples.

Despite the importance of pyrite and the abundance of organic matter in coal-bearing rocks of Pennsylvanian age, studies of the relationship between organic carbon and sulfur in these rocks are rare. No studies are known from Pennsylvania. Gilb (1987) looked at the relationship between organic carbon and sulfur in the Pennsylvanian Breathitt Formation of eastern Kentucky. Gilb separated the lithologies into carbonaceous shale (organic carbon between 5 and 30%), mudrock with calcareous concretions, and mudrock without calcareous concretions. Chesnut (1981) concluded that mudrocks with calcareous concretions were of marine origin. Gilb proceeded on this assumption, plus the assumption that the mudrocks lacking concretions are freshwater. The carbonaceous shale shows a positive relationship (slope = 0.13) between percent sulfur and percent organic carbon (% Org. C), with a correlation coefficient (r) of 0.60. The mudrocks with calcareous concretions also have a positive slope (0.6) and r = 0.72. The relationship between sulfur and organic carbon in mudrocks not having calcareous concretions is essentially random. Of 38 samples, all but four are less than 0.4% sulfur and most are less than 0.1% sulfur. It must also be remembered that these rocks were defined as "freshwater" based on negative evidence (lack of calcareous concretions), so the few high sulfur rocks (and perhaps some of the low sulfur rocks) may have a marine origin. Some of the samples Gilb included in his study had carbon less than 1%. Berner (1984) cautions that the use of sulfur to carbon ratios as a paleoenvironmental indicator should only be used for sediments with organic carbon greater than 1%.

Studies of pyrite formation in freshwater sediments are few in number. Most suggest that sulfur values will be low because sulfate availability is limited to only a small percentage of that present in marine waters (e.g., Berner and Raiswell, 1984; Davison, 1988). Berner and Raiswell (1984) have suggested that the carbon to sulfur ratio (C/S) can be used as a means of distinguishing freshwater from marine sediments. They found that marine rocks are characterized by C/S values of 0.5 to 5 and that freshwater rocks had C/S values >10 (Figure 8.42). This difference is attributed to the low sulfate levels of freshwater being limiting on pyrite production. They cautioned that this method should (1) only be applied to rocks with greater than 1% organic carbon, (2) not be applied to nearly pure limestones because low amounts of iron probably limited pyrite formation and (3) not be applied to coal because organic sulfur could be mistaken for pyritic sulfur in total sulfur analyses and the "superabundance of organic matter" would create a situation where pyrite formation becomes limited by iron availability. Also "...at such high organic-carbon concentrations, high C/S ratios can result even at high salinities." Gilb (1987) adds a further caution regarding the use of C/S ratios for coal. He points out that many swamp environments have low pH. This is not conducive to sulfate-reducing bacteria, which prefer neutral water conditions. "Therefore peat deposited in swamps hav-

ing low pH may form low sulfur coal regardless of sulfate and iron availability" (p. 13). It would be interesting to see the results of a study of C/S for Pennsylvania's Pennsylvanian rocks and compare these results with the other studies.

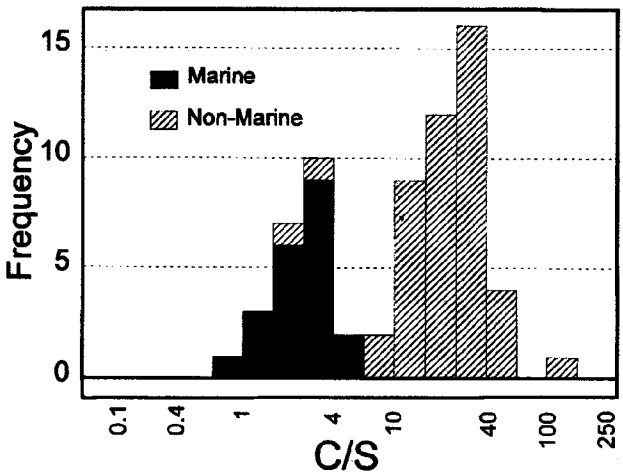

Figure 8.42 Frequency distribution of C/S weight ratios (plotted on a logarithmic X-axis) for British Carboniferous siltstones, mudstones and shales that were determined to be marine or non-marine by independent means. From Berner and Raiswell (1984).

The Berner and Raiswell (1984) study included modern freshwater lake sediments and British Carboniferous freshwater sediments. The freshwater sediments (modern and ancient) were, with few exceptions, low in sulfur (<0.5%). This fact differs from what we see in Pennsylvania, where presumed "freshwater rocks," especially organic-rich rocks, frequently exceed 0.5 % sulfur (for example see Figures 8.15, 8.17, 8.18, 8.19, 8.20, 8.21, 8.26, and 8.31). As discussed earlier, the upper Allegheny "freshwater rocks" are believed to have been deposited in a slightly-saline, marginally-brackish environment. For a comparison with marine and brackish rocks from the Allegheny and Conemaugh Groups, see Figures 8.7, 8.12, 8.13, 8.14, 8.23, and 8.24. It does appear, however, within the Allegheny Group and Conemaugh Group that high-sulfur, marginally-brackish strata overlying coals are typically not as thick as the high-sulfur strata associated with brackish and marine environments. For example the high sulfur (>0.5% S) associated with the UK, LF and UF in Figures 8.15, 8.17, 8.18, 8.19, 8.20, 8.21, and 8.26 is one to 5 ft (0.30 to 1.5 m) thick, whereas the thickness of the high-sulfur strata in marine and brackish environments (Figures 8.7, 8.12, 8.13, 8.14, 8.23, and 8.24) can be up to 30 ft (10 m). Freshwater rocks associated with coals of the Monongahela and Dunkard Groups (Figures 8.31, 8.32, and 8.34) seem to have thicker sequences of high-sulfur strata than the Allegheny overburden. Since there seems to be no evidence of marine influence within this section, this may be due to more arid conditions resulting in higher sulfate levels in surface water and groundwater. A modern relationship between aridity and high dissolved solids, including sulfate, has been noted in the arid and semi-arid western United States. Hem (1985) notes that in semi-arid regions, the amount of sulfate is large in proportion to the water volume in which it is carried away, thus elevated sulfate.

Sedimentation Rate and Bioturbation (Open vs. Closed System) - Sedimentation rate and bioturbation can influence whether the sediment just below the sediment/water interface is an open or a closed system with respect to sulfate in the overlying water column. Bloch and Krouse (1992), studying rocks of the Cretaceous period in western Canada, found the highest sulfur concentrations (>2.75%) associated with bioturbated marine mudstones and siltstones, when compared to mudrocks that were not bioturbated (0.1 to ~2%). Bioturbation irrigated the upper portions of the sediment with sulfate from the overlying water column, thus creating an open-system source of sulfur. They also suggested that some of the low sulfur sediments were due to fast sedimentation rate, resulting in a more closed system where sulfate would be limited to that entrapped within the sediment pore-water. Bloch and Krouse calculated, assuming a porosity of 75% for the original sediment and 100% retention of sulfur (from sulfate) within the sediment, that a closed marine sediment would be limited to 0.1% sulfur. Berner (1970, p. 2) gives a higher figure, saying that "simple burial of sea water and reduction of all included sulfate can provide only about 0.3 percent pyrite sulfur..." For this to be true, the porosity of the sediment would be around 90%. Another important factor is that pyrite sulfur probably only represents a small fraction of the total hydrogen sulfide, H_2S, produced by sulfate reduction (Dean and Arthur, 1989). Jorgensen (1977) in studying a marine sediment in the coastal waters of Denmark found that only 10% of H_2S was fixed as iron sulfide, the remainder was lost by diffusion and reoxidation. The point Berner (1970) and Bloch and Krouse (1992) make is that for sulfur to be higher than a few tenths of a percent, diffusion and/or irrigation by burrowing organisms must occur to permit sufficient sulfate into the sediment to achieve high sulfur values. Movement of H_2S away from sites with high organic matter to other sites with available iron could result in

pyrite formation in the absence of organic matter. This may explain the high sulfur in some sandstones that "cut" down to the coal and overlay the coal. Typically the high sulfur zones occur near the base of the sandstone. Drill Hole A-5 and OB-4 in Figure 8.13 are examples of such a sandstone. The bottom 5 ft (1.5 m) of the sandstone in A-5 has greater than 0.5% S, with the interval from 3 to 5 ft (1 m to 1.5 m) above the coal having greater than 8% S. The base of the sandstone in OB-4 has 6.15% S.

Goldhaber and Kaplan (1982) also recognize the potential importance of bioturbation to increase the amount of sulfate available for reduction. They, however, present an extended argument to show that sulfate reduction rates are greater at higher sedimentation rates. Higher sedimentation rates tend to help preserve organic carbon, a component necessary for bacterial conversion of sulfate to sulfide. Their comparisons of sedimentation rate showing higher sulfide with higher sedimentation rates, are made with H_2S and "acid volatile" sulfides, not pyrite. Goldhaber and Kaplan do not discuss how these rates correspond to final pyrite concentrations. Berner (1984) concluded that "rapid burial enables relatively reactive (organic) compounds and more organic matter in general to become available for bacterial sulfate reduction at depth...These considerations help to explain why there is a crude correlation between sedimentation rate on the one hand, and organic matter and pyrite contents on the other" (p. 607).

Curtis and Spears (1968) looked at iron minerals, principally pyrite and siderite, in sediments of the Carboniferous Period coal measures and of the Jurassic Period in England. Pyrite and siderite both require reducing conditions. In the Carboniferous and Jurassic sediments they observed that pyrite and siderite were not randomly distributed in the sediment, but that siderite-bearing mudstones occurred above shales and mudstones containing pyrite. They concluded that slow sedimentation rates in marine sediments favored pyrite formation (more availability of sulfur) and fast rates favored siderite formation.

It is obvious from the conflicting conclusions that more work on the subject of pyrite formation as a function of sedimentation rates is warranted. High sedimentation rates would tend to create a "closed" system which, in the absence of bioturbation, would result in little input of sulfate from the overlying water column, and limited sulfate available for additional sulfate reduction. High sedimentation rates, however, preserve organic matter that is necessary for bacterial reduction of sulfate. In any event, it appears that bioturbation is important in irrigating the sediment such that additional sulfate is available for reduction.

Discussion on Formation of Pyrite - Although there is a clear positive relationship between percent organic carbon and percent sulfur in Recent and Pleistocene marine sediments, the relationships between these parameters (plus percent iron) in older marine sediments is complex. Raiswell and Berner (1986) examined British Carboniferous marine sediments and found that there was considerable scatter and a low correlation coefficient for C/S ratio. They however suggest that the overall C/S ratio remained relatively constant from the Devonian to Tertiary (~2). It is somewhat higher in more recent sediments (~2.8), and lower (<1.0) in older Paleozoic sediments.

Gild's (1987) findings on the relationships between organic carbon and sulfur are similar to those by Berner and Raiswell (1984). Even though no studies relating sulfur to organic carbon have been performed on Pennsylvanian rocks in Pennsylvania, the general findings of Gilb (1987) and Berner and Raiswell (1984) are probably applicable. Typically there will be a relationship between percent organic carbon and percent sulfur for marine rocks; higher sulfur values will be found in marine mudstones than in freshwater mudstones; and carbonaceous rocks will typically contain more pyrite than noncarbonaceous rocks for any given paleoenvironment. More discussion on paleoenvironmental and rock-type controls on sulfur will be presented later.

The higher the content of organic matter the darker the rock tends to be. If a mudstone is known to be of marine or brackish origin and it is dark in color, there is a good chance that it is also high in sulfur. Carbonaceous rocks (> 5% organic carbon) may be high in sulfur, at least relative to other rocks, regardless of paleoenvironment. This can be useful in helping to identify potentially high sulfur rocks in the field or in drill cuttings/cores.

Alkalinity Producing Minerals: The Carbonates

Carbonate minerals play an extremely important role in determining postmining water chemistry. They not only neutralize acidic water created by pyrite oxidation, but as discussed above, there is evidence that they also inhibit pyrite oxidation (Hornberger et al., 1981; Williams et al., 1982; Perry and Brady, 1995). These processes are discussed more fully in Chapters 1 and 11. Brady, et al. (1994) determined that the pres-

ence of as little as 1% to 3% carbonate (on a mass weighted basis) on a mine site can determine whether that mine produces alkaline or acid water. Although pyrite is clearly necessary to form acid mine drainage, the relationship between the amount of pyrite present and water quality parameters (e.g., acidity) is only evident where carbonates were absent. Neutralization potential, a measure primarily of the carbonate content of the overburden, relates positively to the alkalinity of postmining water.

A knowledge of the distribution, amount, and type of carbonates present on a mine site is extremely important in predicting the potential for postmining problems and in designing prevention plans.

Carbonate Mineralogy - The most common carbonate minerals found in coal mine overburden are listed in Table 8.6. Carbonate minerals are often not "pure" end members, but form solid solution series with cation substitution.

Table 8.6 Common Carbonate Minerals in Mine Overburden, listed in descending order of their capability to neutralize acid.

Mineral	Chemistry
Calcite	$CaCO_3$
Dolomite	$CaMg(CO_3)_2$
Ankerite	$Ca(Fe,Mg)(CO_3)_2$
Mn-Siderite	$(Fe, Mn)CO_3$
Siderite	$FeCO_3$

The above minerals, with the exception of siderite, will neutralize acid generated from pyrite oxidation. An example of this neutralization process is:

$$CaCO_3 + 2H^+ \Rightarrow Ca^{2+} + CO_2 + H_2O \qquad (8.6)$$

Not all carbonates are created equal when it comes to neutralization of acid. Calcite is more soluble than dolomite although the overall dissolution is similar to that shown for calcite (Geidel, 1982). Both calcite and dolomite will neutralize acid, and potentially inhibit pyrite oxidation. Siderite is less soluble than calcite and dolomite, and its role as an acid-neutralizer is either limited or non-existent as discussed below.

Siderite is a very common mineral in coal measures (e.g., Texas - Senkayi et al. 1986; and Japan - Matsumoto, 1978), including those in Pennsylvania (Morrison et al, 1990a, 1990c; and Figure 8.2). Siderite will form preferentially to calcite where iron is abundant (Blatt et al., 1972). It forms under reducing conditions where sulfur availability (as sulfate) is limited (e.g., Curtis and Spears, 1968; Postma, 1982). Where reduced sulfur is abundant, pyrite will form in preference to siderite. Dissolution of siderite can create weakly acid conditions in a closed system (Barnes and Romberger, 1968; Cravotta et al., 1990):

$$FeCO_3 + 0.25\ O_2 + 2.5\ H_2O \Rightarrow Fe(OH)_3 + H_2CO_3 \qquad (8.7)$$

Even in an open system, the weathering of siderite, because of the hydrolysis of iron, has no net neutralizing effect. As discussed in Chapter 6 (see also Skousen et al., 1997), tests for neutralizing potential can give misleading results if siderite is present. Siderite may cause the test to appear positive for neutralizers. Additionally, siderite can contribute iron to water, and is probably responsible for at least some, and possibly much of the Mn observed in some mine waters. Mn is a common substitute for iron in siderite (Morrison, et al., 1990c).

Curtis and Spears (1968) attributed whether pyrite or siderite formed to the relative anion concentrations. A factor that may contribute to the bicarbonate ion concentration is that bicarbonate is produced during sulfate reduction (equation 8.5). Presley and Kaplan, (1968) observed an increase in bicarbonate with a corresponding decrease in sulfate in some modern nearshore marine sediments. Under reducing conditions and a more or less closed system, sulfate reduction would occur first with iron fixed as pyrite; once the sulfate was consumed, and assuming iron is available, siderite could form. A variety of factors may result in no clear relationships between the relative amounts of pyrite and siderite. For example, pyrite forms under slightly acidic to alkaline conditions, thus bicarbonate may have been present in the pore waters even before sulfate reduction. Also, Presley and Kaplan (1968) found more biogenically produced bicarbonate than could be explained solely by sulfate reduction. They attributed this to other biologic processes such as fermentation. The potential loss of sulfide due to oxidation or diffusion and the presence of preexisting bicarbonate may also result in a lack of relationships. No work similar to that by Curtis and Spears (1968) has been done in the Pennsylvanian of Pennsylvania.

The presence of siderite does not by itself reflect a particular depositional environment. Siderite occurs in sediments of freshwater, brackish, and marine origin (Matsumoto, 1978; Mozley, 1989; Morrison, 1988). Siderite is normally an early diagenetic mineral, formed below the sediment-water interface. Siderite can also

form in terrestrial soil forming processes and is associated with some underclays (Gardner et al., 1988).

Mozley (1989) looked at compositional variabilities of siderite from marine and freshwater sediments. He found that marine siderite is impure with no more than 90 mole percent (mol %) $FeCO_3$. It can have Mg substituting up to 41 mol %, and Ca up to 15 mol % in the siderite crystal lattice. Freshwater siderite is commonly very pure (> 90 mol % $FeCO_3$), and can have higher Mn concentrations compared to marine siderite. Unfortunately Mozeley did not discuss siderite from brackish environments, and did not study "(s)iderite from complex depositional sequences with intercalated marine and nonmarine strata (e.g., coal-measure siderite)...", because of the possible early mixing of pore waters from different paleoenvironments. No efforts similar to Mozley's have been conducted in the Pennsylvanian of Pennsylvania. It would be interesting to see if siderite composition varied by paleoenvironment. A better understanding of siderite composition would be useful for a variety of purposes. First, impure siderite may offer some neutralizing capacity; second, it would be a step in determining to what extent siderite contributes to Mn in mine waters; and third it may offer insight into paleodepositional environments.

Distribution of Carbonates in the Pennsylvanian of Western Pennsylvania - Within the Allegheny Group in Pennsylvania, siderite is the most common carbonate mineral (Morrison, 1988; and Figure 8.2). It occurs throughout the Pennsylvanian of Pennsylvania, regardless of paleoenvironment (Figure 8.2). An important aspect of siderite, in terms of mine drainage, is that it is the only carbonate that normally occurs in brackish sediments (see Table 8.15 in Appendix). This, coupled with the high sulfur content of brackish rocks, often leads to poor quality water from mines developed in brackish sediments.

Calcite and dolomite occur in the freshwater limestones of the Allegheny, Conemaugh, Monongahela, and Dunkard Groups. Additionally, in the Monongahela and Dunkard Groups, calcite and dolomite are the most common carbonate minerals present in other rock types (Figure 8.2). Marine limestones and associated rocks (Allegheny and Conemaugh Groups) can have a high carbonate content. As shown previously the Vanport limestone can be over 90% $CaCO_3$.

Chemical composition data for the Vanport limestone and other Pennsylvanian limestones and dolomites are shown in Table 8.7. Data from a few Cambrian and Ordovician limestones and dolomites, including the Valentine limestone from Centre County are included for comparison, as these high-calcium limestones are well known for their purity and industrial significance (see chemical composition data and additional discussion in O'Neill, 1964, 1976; Rones, 1969; and Chapter 7 in this volume). Table 8.7 shows that some marine and freshwater limestones of the Pennsylvanian Period exceed 90% calcium carbonate, which is also evident from NPs exceeding 900 ppt on Figures 8.7, 8.18, 8.20, and 8.39. Chemical composition data for the freshwater Fishpot, Redstone and upper Freeport limestones are shown in Table 8.7. These freshwater limestone samples typically have lower calcium carbonate contents than the Vanport limestone samples included in Table 8.7. NPs in the range of 500 to 875 ppt $CaCO_3$ for some of these stratigraphic intervals are also shown in Figures 8.17, 8.18, 8.19, 8.20, 8.25, 8.26, and 8.32. The origins of limestones and other calcareous rocks will be discussed in more detail in a following section of this chapter.

Not much is known about limestones and other calcareous rocks of the Anthracite Region. As mentioned earlier and shown on Figure 8.35 one marine limestone and several freshwater limestones occur in the northern field. No analyses of these limestones are known. Siderite, at least in the form of nodules, is fairly common in the Anthracite Region. Another possible source of calcite is secondary mineralization along fractures.

Other Neutralizing Minerals and Processes

The most effective minerals, in terms of acid neutralization, are the carbonates. Some other minerals, however, can also neutralize acid. For example silicate minerals can neutralize acid, but the reaction rates at near neutral pH tend to be slow. Quartz, the most common silicate, is for all practical purposes inert. Many of the other silicate minerals, however, can provide buffering at low pH's (Stumm and Morgan, 1981; Lapakko, 1992). The following example shows how anorthite can neutralize acid.

$$\underset{\text{(anorthite)}}{CaAl_2Si_2O_{8\,(s)}} + 2\,H^+ + H_2O \Rightarrow Ca^{2+} + \underset{\text{(kaolinite)}}{Al_2Si_2O_5(OH)_{4\,(s)}} \qquad (8.8)$$

Another source of neutralization is cation exchange on clay particles. Clay particles tend to have negative charges at their surfaces. These attract positively charged ions. Thus, H^+ can adhere to the clay surfaces and raise the pH of the solution.

Table 8.7 Chemical composition of limestones and dolomites from Pennsylvania.

Limestone/Dolomite Name	Geologic Period	Formation	County	$CaCO_3$	$MgCO_3$	SiO_2	Al_2O_3	Fe_2O_3	R_2O_3	Insol.	S	Year of analysis	Source
Upper Washington	Permian	Washington	Washington	72.9	3.8				2.9	17.4	0.16	1876	1
Benwood	Upper Penn	Monongahela	Westmoreland	85.8	2.3	6.4	1.0	1.4				1925	1
Fishpot	Upper Penn	Monongahela	Somerset	67.7	12.3					15.6		1997	2
Redstone	Upper Penn	Monongahela	Somerset	69.4	11.5					13.4		1997	2
Redstone	Upper Penn	Monongahela	Somerset	86.6	6.2					4.0	0.09	1879	1
Upper Freeport	Middle Penn	Allegheny	Westmoreland	71.6	1.7					24.8		1997	2
Upper Freeport	Middle Penn	Allegheny	Westmoreland	68.5	1.7					27.2		1997	2
Upper Freeport	Middle Penn	Allegheny	Indiana	84.4	2.8				2.1	9.2	0.20	1878	1
Upper Freeport	Middle Penn	Allegheny	Jefferson	90.0	2.9				1.3	3.5		1946	1
Upper Freeport	Middle Penn	Allegheny	Jefferson	66.5	12.4	12.7						1946	1
Vanport	Middle Penn	Allegheny	Armstrong	94.2	1.4	1.4	0.4	1.4				1934	1
Vanport	Middle Penn	Allegheny	Armstrong	93.4	2.0	1.2	0.4	1.1			0.05	1927	1
Vanport	Middle Penn	Allegheny	Butler	94.9	1.5	1.5	1.0	0.7				1934	1
Vanport	Middle Penn	Allegheny	Butler	95.8	1.8	1.6			2.2			1934	1
Vanport	Middle Penn	Allegheny	Clarion	91.7	1.6	3.9	2.7					1963	1
Vanport	Middle Penn	Allegheny	Lawrence	95.0	0.9	2.2	1.5	0.6			0.05	1929	1
Vanport	Middle Penn	Allegheny	Lawrence	94.6	1.4	2.1	0.6	0.7			0.03	1963	1
Valentine	Ordovician	Benner	Centre	98.5	1.1	0.6	0.3	0.1			0.04	1955	1
Valentine	Ordovician	Benner	Centre	97.2	1.1	0.8	0.3	0.1		0.6	0.00	1963	1
Valentine	Ordovician	Benner	Centre	98.6	0.3	0.6			0.5			1955	1
Valentine	Ordovician	Benner	Centre	96.9	1.8	0.9			0.4	0.6		1963	1
Ledger	Cambrian	Ledger	Chester	52.9	43.7	1.4	0.5	0.3		0.6	0.00	1963	1
Ledger	Cambrian	Ledger	Chester	51.4	42.9	3.7			2.0			1959-60	1
Ledger	Cambrian	Ledger	Montgomery	53.8	44.5	1.1	0.2	0.5				1963	1
Kinzers	Cambrian	Kinzers	York	93.0	6.5	0.5			0.4	0.6	0.00	1963	1
Kinzers	Cambrian	Kinzers	York	99.2	0.4	0.2			0.2			1934	1

* 1=O'Neill, 1964, PA Geological Survey Report M 50

2=R.C. Smith II, PA Geological Survey, unpublished data

Silicates neutralize acid by dissolving (often incongruently, as in the above example). This dissolution releases elements such as aluminum and magnesium, to name two of the more common elements seen in mine drainage. Thus, although their role may not be significant at near neutral pH, at low pH they can also contribute to the dissolved solids content of the mine water and provide some buffering. The role of silicate neutralization may explain why overburden that is low in percent sandstone and therefore high in finer-grained sediment (and feldspar and clay minerals) frequently produce alkaline drainage. This subject will be discussed more fully in the section relating lithology to water quality.

Geologic Controls on Overburden Mineralogy in the Appalachian Basin

The Appalachian Regional Commission (1969) and Wetzel and Hoffman (1983, 1989) observed that acid mine drainage was a regional problem, and upon closer inspection they determined that it is most prevalent within the Allegheny Group. Figure 8.43 illustrates the distribution of pH and sulfate problems for surface waters in the Appalachian basin. Although these maps show in a general way the distribution of water quality problems, some caution must be used in their interpretation. For instance, it must be kept in mind that some watersheds are much more intensely mined than other watersheds, and some watersheds on the periphery of the basin may have little or no coal. Some general statements can be made. The West Branch Susquehanna River has the highest percentage of streams with pH less than 6.0 (56 %). This watershed has a correspondingly high percentage of streams with sulfate above 75 mg/L, thus indicating that the proportionally low pH is mining influenced. The other two watersheds with greater than 35% of the streams having a pH less than 6.0 occur where mining would have encountered the Allegheny Group. The watersheds with greater than 35% of streams with sulfate greater than 75 mg/L in southern West Virginia and Kentucky illustrate that high sulfate does not necessarily correspond with low pH. None of the sampled streams have a pH less than 6.0. Figure 8.43 would be made more useful if bedrock geology and the percentage of each watershed that has been disturbed by mining could be plotted. Because of the limitations, Figure 8.43 should only be used to discern broad trends.

Although there is a general relationship between geology and mine drainage quality, no comprehensive study relating geology and coal mine drainage quality has been attempted for the entire Appalachian basin. An examination of geologic studies suggests some significant differences in mineralogy for the southern Appalachian (Pottsville) strata and the northern Appalachian (Allegheny through Dunkard) strata (e.g., Cecil et al., 1985; Donaldson et al., 1985a). Several geologic processes have contributed to the variability of coal properties and the chemistry/mineralogy of intervening strata. These processes are paleoclimate, paleodepositional environment, and recent surface weathering. The discussions below will attempt to address the geologic factors that contribute to water quality differences.

The paleoclimatic and paleodepositional environmental influences on rock chemistry in the northern Appalachians resulted in the formation of coal overburden with greatly variable sulfur content (0% to >10% S) and calcareous mineral content (0% to >90% $CaCO_3$). The wide variations in rock chemistry contribute to the wide variations in water quality associated with Pennsylvania's surface coal mines. Figure 1.2 in Chapter 1 shows the frequency distribution (i.e., range) of pH and net alkalinity of mine discharges in western Pennsylvania.

Conventional wisdom, and early research in the northern Appalachians, has suggested that high sulfur coal and rocks are associated with marine environments (Williams, 1960; Guber, 1972). Coals in the northern Appalachians are higher in sulfur than those in the central Appalachians (Cecil, et al., 1985). This difference in coal composition can not be due simply to paleodepositional environment. Marine sediments in the southern Appalachian (Pottsville) rocks are very common. Chestnut (1981), for example, identifies 49 marine zones in the Lee and Breathitt Formations of Kentucky. As a comparison, the number of recognized marine and brackish zones in the Pennsylvanian of Pennsylvania is ~13 (Skema, personal communication, October 13, 1995). If depositional environment was controlling sulfur content in the southern Appalachian coals and rocks, the sulfur should be high, but it is not. Also, acid mine drainage typically is less of a problem in the southern Appalachians than in the northern Appalachians (Figure 8.43) (Wetzel and Hoffman, 1983; Appalachian Regional Commission, 1969).

One aspect of southern Appalachian geology that seems to have received little attention is that calcareous marine zones occur within the Pennsylvanian in Kentucky and southern West Virginia. Chestnut (1981) in discussing marine units in Kentucky with calcareous

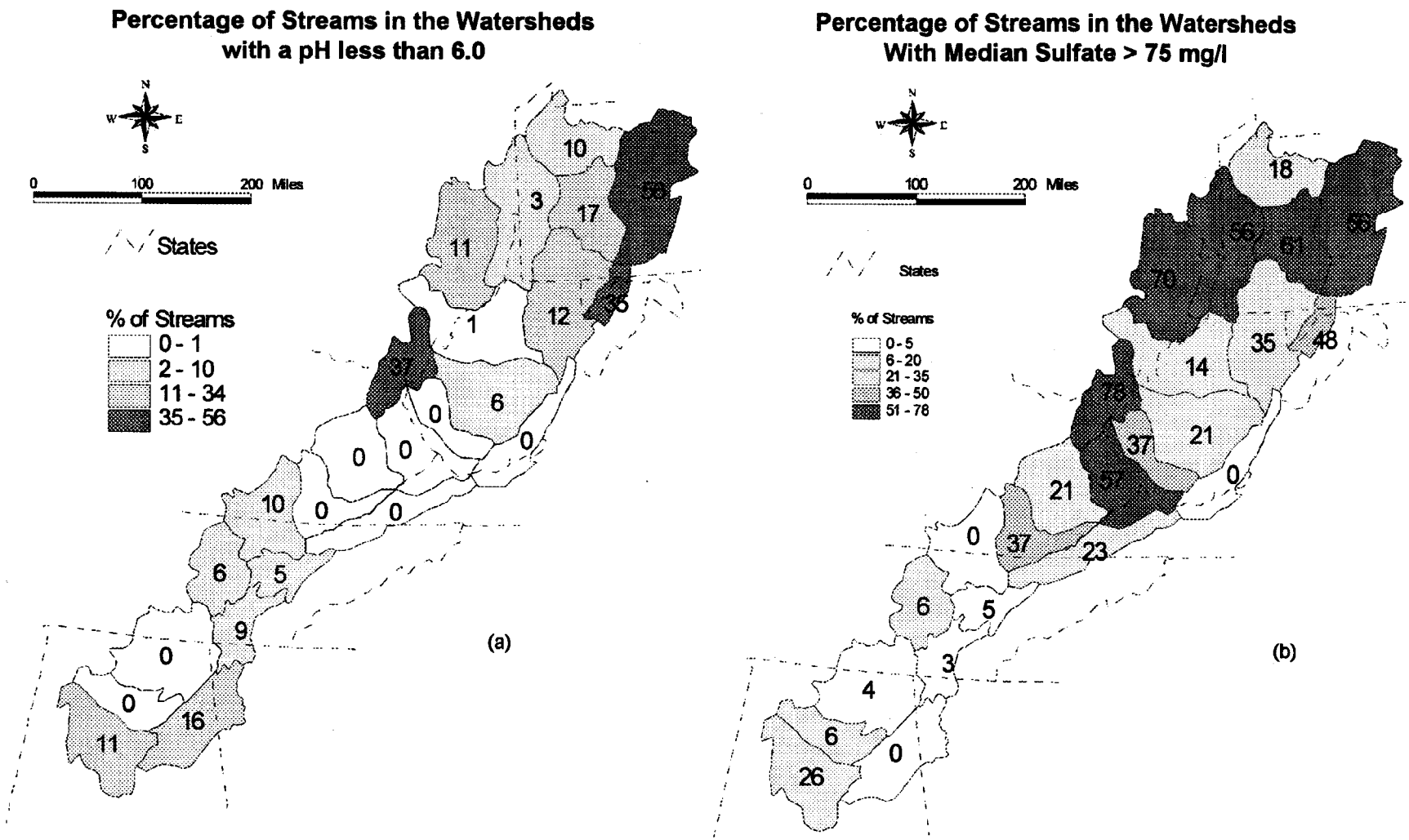

Figure 8.43a and b Percentage of surface water sample stations that had pH < 6.0 (figure a) and sulfate greater than 75 mg/L (figure b) for 24 watersheds in the Appalachian Basin. Data are from Wetzel and Hoffman (1983).

calcareous concretions says "(c)alcite is often in great enough proportion to classify the rock a limestone..." Martino (1994) refers to several calcareous marine zones in southern West Virginia.

Cecil et al. (1985) indicate that sandstones with calcareous cement are absent in the central Appalachians. More recent studies of central Appalachian sandstones indicate otherwise. Englund et al. (1986) describe the sedimentology of the lower Pennsylvanian Pocahontas Formation in southwestern Virginia and southern West Virginia. They indicate that 70 percent of the formation is sandstone which is "in part, calcareous." Chesnut (1992) also identifies calcareous sandstones and siltstones in the Breathitt Group of Kentucky. Powell and Larson (1985) likewise indicate that "calcite is present as a cement and as clasts in some of the sandstone" in the Norton Formation of Virginia. The literature does show that calcareous rocks are present in the southern and central Appalachian Pottsville Group. These calcareous strata along with the low concentrations of sulfur probably explain the lower abundance of acid mine drainage problems in the southern Appalachians.

Paleoclimatic Influences on Terrigenous Rock Mineralogy

Various attempts have been made to reconstruct the paleoclimate of the northern and central Appalachian Basin during the Pennsylvanian. Donaldson et al. (1985a) and Cecil et al. (1985) interpreted paleoclimate from the depositional characteristics and the chemistry of terrigenous sediments within the coal-bearing stratigraphic sequence of the central and northern Appalachians. Phillips et al. (1985) and Winston and Stanton (1989) derived their interpretations of climate from vegetational changes. Figure 8.44 shows a side by side comparison of these various climatic interpretations. As can be seen, there is less than a consensus, especially within the Pottsville Group. We will, however, only concern ourselves with the uppermost Pottsville and higher strata; that is, the strata that occurs in Pennsylvania. The four models differ as to how wet or dry the upper Pottsville was, but they agree that at the time of deposition of the Allegheny Group, the climate was moderately wet, although drying upward. All models agree that during deposition of the Conemaugh Group, it was dry. The base of the Monongahela was wet, and probably became drier higher up in the section. Cecil et al. (1985) and Donaldson et al. (1985a) concluded that the period during which the Dunkard was deposited was comparatively dry.

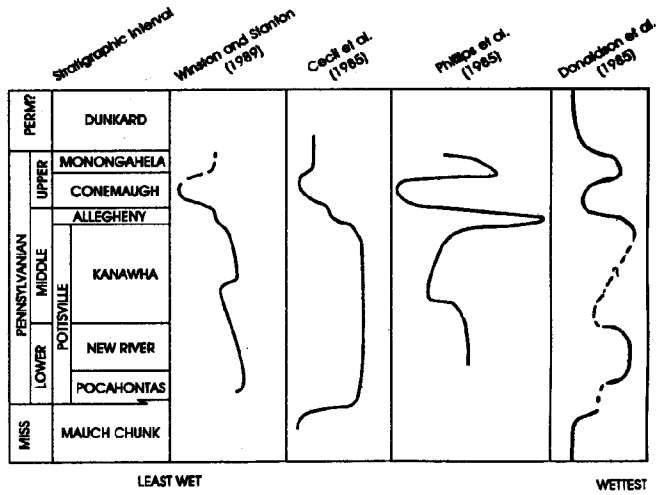

Figure 8.44 Comparison of paleoclimatic interpretations during the late Mississippian through Permian? from four studies. Curves show relative wetness. Wetter periods were probably "ever-wet", i.e., wet year-round (Pottsville time in southern Appalachians), the driest period (Conemaugh time) was probably semi-arid, and in-between curves represent yearly climate that was seasonally wet and dry. Sedimentological features in the Monongahela and Dunkard Groups also indicate periods that were semi-arid. Each curve is relative only to itself. The Cecil et al. and Donaldson et al. curves are based on sedimentological characteristics, and the Phillips et al. and Winston and Stanton curves are based on paleobotanical interpretations.

Cecil et al.'s (1985) interpretation was that the climate was an "ever-wet" tropical one during deposition of the early Pennsylvanian Pottsville Group (the Kanawha, New River, and Pocahontas Groups of southern West Virginia), but was more seasonally "wet-dry" in the stratigraphically higher sections. Cecil et al. (1985) suggest that climate affected the shape of the peat deposit, which in turn affected the chemistry of the swamp (and ultimately the chemistry of the coals). During the early Pennsylvanian (Pottsville Group coals), the ever-wet conditions resulted in domed peat swamps which had rainfall as their source of water. The swamp water would be low in dissolved solids, and nutrients and the low pH (<4) conditions would not be conducive to pyrite formation or accumulation of solids (ash). During the middle and later Pennsylvanian (Allegheny, Conemaugh, and Monongahela coals) the swamps were planar and water entered the swamp from ground and surface sources. This resulted in a swamp with higher pH (4 to ~7), more dissolved solids, and greater availability of nutrients (Cecil et al., 1985). Additionally, periodic dry conditions would allow the surface of the peat to dry, oxidize and de-

grade, thus increasing ash content. These conditions, taken together would result in higher sulfur and ash in the northern Appalachian coals. Cecil et al. use this theory to explain why the coals of the southern Appalachian Pottsville Group are lower in sulfur (typically <1% sulfur) and ash (typically lower than 10% ash) than the younger coals of the northern Appalachians (typically >1% sulfur and >10% ash) (Figures 8.45 and 8.46, and Table 8.8).

Sulfur in Pennsylvania's anthracite is much lower than in coals of the bituminous region. On average the sulfur is about 0.8% (Wood et al., 1986).

As with coal quality, Cecil et al. (1985) and Donaldson et al. (1985) conclude the associated terrigenous rocks are also influenced by paleoclimate. Figure 8.47 (Cecil et al., 1985) and Figure 8.48 (Donaldson et al., 1985a) show the distribution of important rock types and minerals throughout the Pennsylvanian and lower Permian. The drier conditions during the Upper Pennsylvanian (upper Allegheny and younger strata) resulted in the common occurrence of freshwater limestones, calcareous cements, and calcareous concretions in nonmarine sandstones and shales.

Figure 8.49 presents plots of percent sulfur in roof rock and floor rock as functions of percent sulfur in coal for 12 coal seams from four different coal fields.

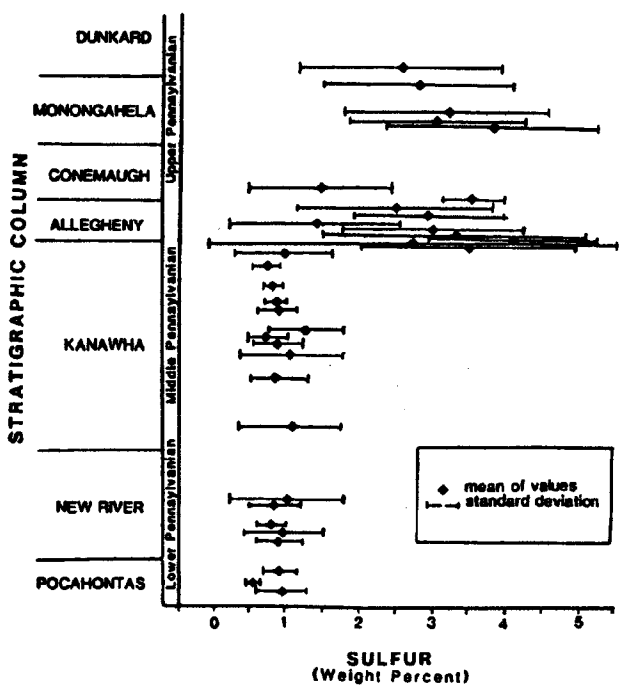

Figure 8.45 Stratigraphic variation of sulfur content of 34 coal beds of the central Appalachians, including Pennsylvania. Figure from Cecil et al. (1985).

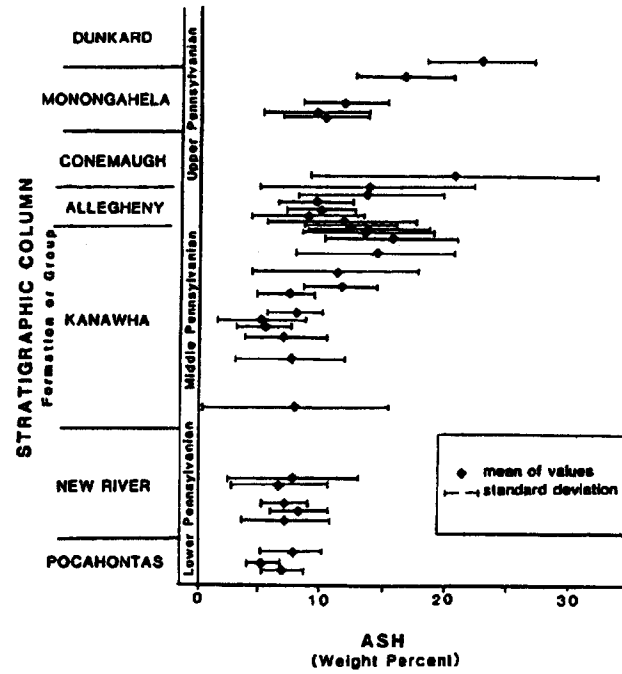

Figure 8.46 Stratigraphic variation of ash content of 34 coal beds of the central Appalachians, including Pennsylvania. Figure from Cecil et al. (1985).

Table 8.8 Means (x) and standard deviations (sd) for coals by formation/group in the Pennsylvanian of the northern Appalachian Basin. (Adapted from Cecil et al., 1985).

		Total Sulfur		Ash	
Formation	**Number of Samples**	**x**	**sd**	**x**	**sd**
Monongahela	159	3.4	1.4	10.8	4.2
Conemaugh	8	2.2	1.3	18.1	10.6
Allegheny	296	2.9	1.5	11.2	5.5
Kanawha	73	0.9	0.5	9.2	5.3
New River	74	0.9	0.4	7.1	3.5
Pocahontas	21	0.8	0.3	6.8	2.1

Although the sample is small, the data from the Appalachian Basin is consistent with the findings of Cecil et al. (1985) in that pyrite is rare in the older sediments of the southern Appalachians, but common in the younger sediments of the northern Appalachians (Figure 8.47). For comparative purposes, data from the Powder River Basin and the Illinois Basin are also shown in Figure 8.49. The low sulfur of the freshwater-deposited Powder River Basin sediments and the high sulfur of the mostly marine-deposited Illinois Basin sediments are consistent with paleodepositional models, which will be discussed in the next section. Assuming the data in Figure 8.49 is representative, it appears that low-sulfur coals, such as in the southern Appalachian and Powder

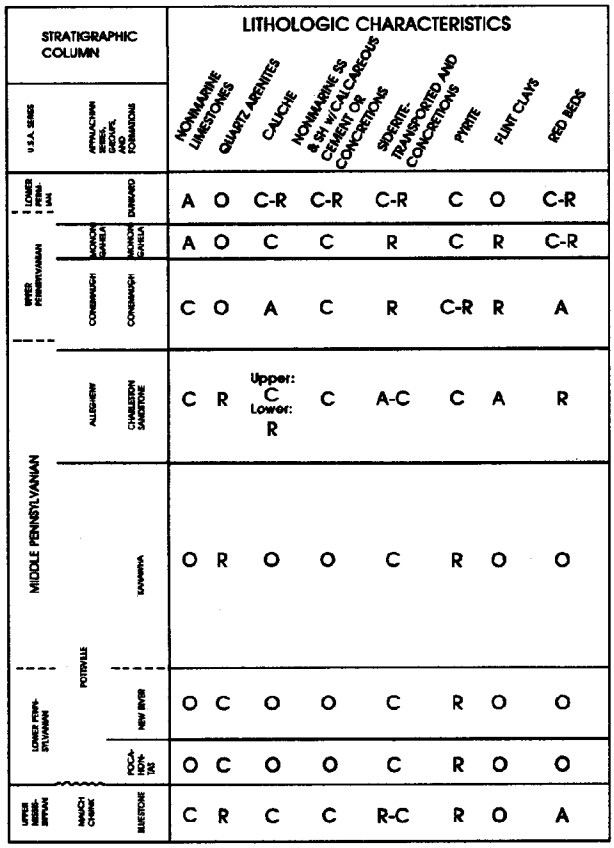

Figure 8.47 Characteristics of lithologies from strata in the central Appalachian Basin, including Pennsylvania (A = abundant; C = common; R = rare; O = absent). Figure from Cecil et al. (1985).

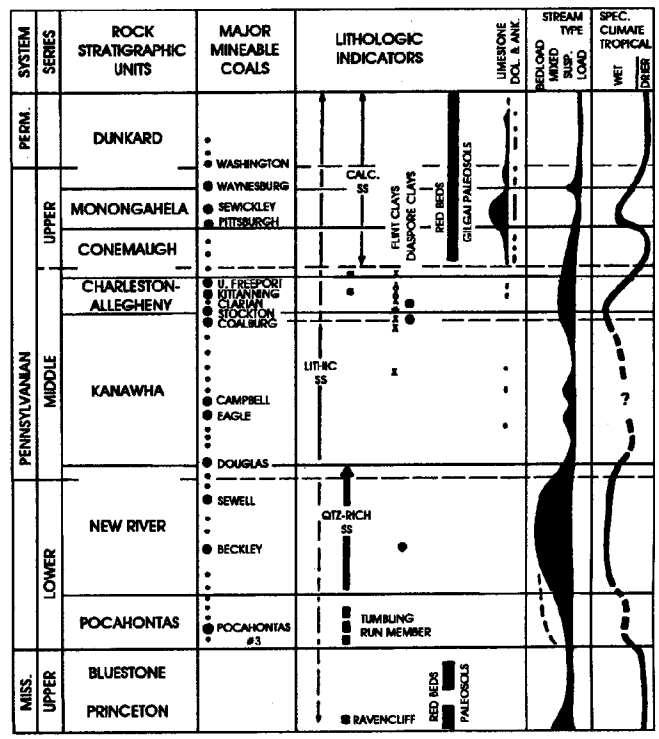

Figure 8.48 Lithologic indicators of paleoclimate in the Appalachian basin, including Pennsylvania. Modified from Donaldson et al. (1985).

River Basins, are associated with low-sulfur roof and floor rock. High-sulfur coals, such as those in the northern Appalachian and Illinois Basins, may or may not have high sulfur roof and floor rocks.

Paleodepositional Environmental Influences on Rock Mineralogy

A second category of geologic processes that influenced the chemistry and mineralogy of Pennsylvanian Period coal-bearing sediments, including the distribution of calcareous and pyritiferous rocks, was paleodepositional environment. Typically, within the Pennsylvanian of Pennsylvania, paleoenvironment is classified into three categories (Williams, 1960): freshwater, brackish, and marine. These three categories are not evenly distributed geographically or stratigraphically. Figure 8.2 shows that marine and brackish units are restricted to the upper Pottsville/ lower Allegheny and lower Conemaugh Groups. Freshwater limestones are principally found above the middle of the Allegheny Group. As discussed in the section on the Allegheny Group, conchostracans probably represent marginal brackish, rather than continental (fresh-water) conditions. These paleoenvironmental influences are only important, from a mine drainage standpoint, where there are economic coals; i.e., the Allegheny and Monongahela Groups (Figure 8.2). Figure 8.50 is a schematic showing "rule-of-thumb" trends in stratigraphy, and acid-potential, of the lower Allegheny and upper Allegheny strata. In general, the lower Allegheny becomes more marine influenced to the west.

Many researchers (Hornberger et al., 1981; Williams et al., 1982; diPretoro, 1986; Brady et al., 1994; and Perry and Brady, 1995) have concluded that the key factor regarding the prediction of mining-associated water quality is the amount of calcareous material encountered. The amount of sulfur (pyrite) present is of secondary importance. Paleoenvironment is an important control on the distribution of carbonates and pyrite. Marine limestones, such as the Vanport and Brush Creek can have significant alkalinity generating capability, and mines that encounter these limestones generally produce alkaline drainage. Freshwater limestones are common in the upper Alle-

gheny and Monongahela Groups. Mines that encounter these limestones, likewise, routinely produce alkaline drainage. Brackish environments typically lack calcareous minerals, with siderite being the only carbonate present. Coal overburden of marine and brackish origin often have much greater thicknesses of high sulfur strata than overburden of "freshwater" origin. Brackish environments therefore frequently have the unfortunate attributes of high sulfur rock with a lack of calcareous minerals, which often results in acid mine drainage. These paleoenvironmental influences on the distribution of carbonates and sulfur (pyrite) will be examined in detail below.

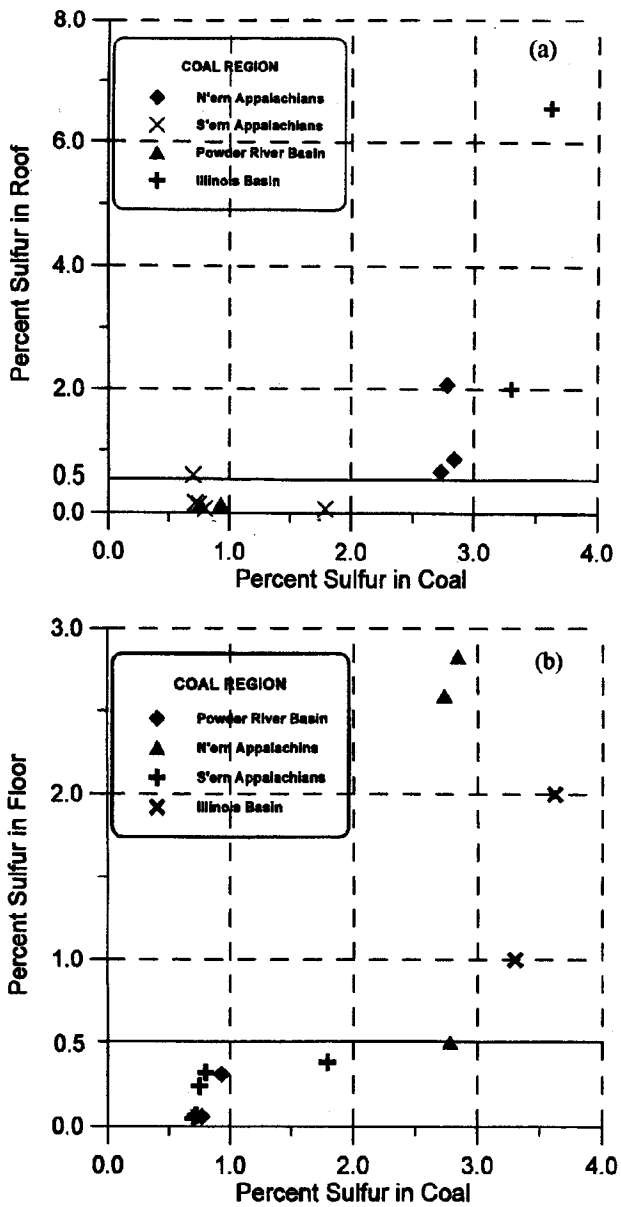

Figure 8.49 Plots of sulfur in coal and sulfur in roof rock (figure a) and floor rock (figure b) for the northern Appalachian, southern Appalachian, Powder River, and Illinois Basin coal fields. The 0.5% sulfur line that intercepts the Y-axis divides "high-sulfur" from "low-sulfur" rock. Data are from Maksimovic and Mowry (1993).

Depositional Environments of Carbonate Minerals - Carbonate minerals form under marine and freshwater environments. Both environments are represented in Pennsylvania's Pennsylvanian stratigraphy.

Marine Carbonates - The climatic models of Cecil et al. (1985) and Donaldson et al. (1985a), discussed above, only consider terrigenous sediments. Marine environments are likewise important in contributing to overburden mineralogy. The formation of limestone, or other calcareous rocks, under marine conditions may have little or nothing to do with climate, but can play a significant role in preventing acid mine drainage in Pennsylvania and elsewhere in the Appalachian Basin. Marine limestones significantly contribute to the alkaline water of the Illinois Basin and the Western Interior Coal Province.

As discussed previously and shown in Figures 8.2, 8.7, and 8.12, marine rocks can be an important component of coal overburden in Pennsylvania. Marine sediments are also very common in the southern Appalachian (Pottsville) rocks [see for example: Alabama - Horsey (1981), Pody (1987), and Demko and Gastaldo (1996); Tennessee - Dorsey and Kopp (1985); Kentucky - Chestnut (1981); and southern West Virginia - Martino (1994, 1996)].

Marine rocks in Pennsylvania occur principally in the lower Allegheny Group and the Glenshaw Formation (Figure 8.2). The rocks represent open marine to marginal marine (brackish) conditions. The open marine facies are frequently limestone or calcareous shales. Brackish facies often lack alkalinity generating calcareous minerals, although siderite ($FeCO_3$) can be abundant. Conchostracans probably represent a marginal brackish environment with some marine influence. If marginal-brackish environments are included, some marine influence is present in Pennsylvanian Period rocks in Pennsylvania from the Pottsville Group through at least the Skelly horizon of the Glenshaw Formation.

The Allegheny Group Vanport member is a good example of the nature of marine limestones. The Vanport horizon, which occurs above the Clarion coal, is often transitional laterally (and vertically) from marine

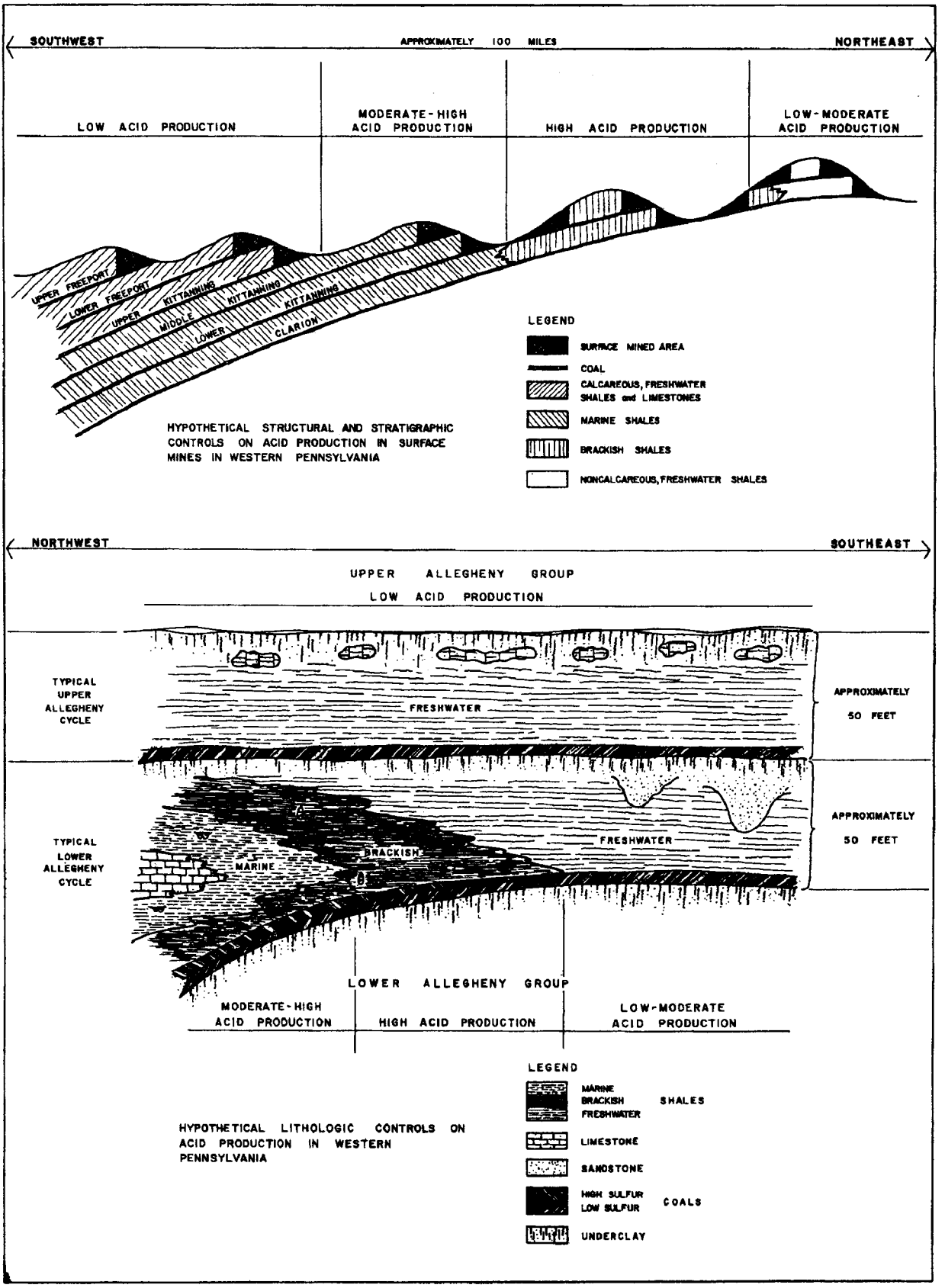

Figure 8.50 Schematic summary of hypothetical lithologic stratigraphic and structural controls on acid mine drainage production for the upper and lower Allegheny Group. From Hornberger (1985).

to brackish conditions. Figure 8.8 shows regional changes in thickness of the Vanport limestone.

Skema et al. (1991, and personal communication, 1997) discussed the facies distribution of the Conemaugh Group Brush Creek marine zone. The Brush Creek Marine zone is present almost everywhere within its outcrop belt. Because the limestone or a calcareous facies is typically present where the Brush Creek coal is of mineable thickness, the drainage is typically alkaline.

In addition to limestones, other marine sediments are often calcareous. This is illustrated by NPs above 30 ppt $CaCO_3$ in Figures 8.7 and 8.12 for marine-deposited lower Allegheny rocks.

Freshwater carbonates - Freshwater calcareous rocks, including lacustrine limestones, occur in the upper portion of the Allegheny Group and throughout the Monongahela and Dunkard Groups (Figure 8.2). The extensive lateral distribution of some of these limestones was discussed in the stratigraphy section of this chapter. These limestones, and other calcareous rocks, are responsible for the alkaline nature of many of the mining associated discharges within these stratigraphic horizons. Freshwater calcareous rocks also occur in the Conemaugh Group, and are important when they occur above the upper Freeport coal. Higher in the section they are typically less important in terms of mine drainage quality because Conemaugh coals are rarely mined. Additionally, they often occur below the coals and can be thin and discontinuous. The discontinuous nature is evident by comparing drill holes DH-12 and DH-3 in Figure 8.25. Both holes were drilled at the same mine site. DH-12 shows the freshwater limestone below the upper Bakerstown coal. The limestone is absent in DH-3. Our experience is that these "limestones" are often "dirty" with a high component of clay and silt. At places this stratigraphic interval is represented by calcareous rocks with less than 50% calcium carbonate, and therefore by definition not a limestone.

In addition to freshwater limestones, the upper Allegheny Group frequently contains an abundance of calcareous claystones, mudstones and siltstones. Figure 8.20 shows a stratigraphic section in Fayette County, between the upper Kittanning and lower Freeport coals. Much of this interval is distinctly calcareous (>10% $CaCO_3$), but only small portions could be classified as limestone (> 50% $CaCO_3$).

As discussed earlier, the Monongahela and Dunkard Groups have numerous thick, laterally persistent, lacustrine limestones. Figure 8.2 shows that >50% of the rocks of the Monongahela and Dunkard Groups are calcareous.

Depositional Environments of Iron Sulfides - Much research on the relationship between sulfur and depositional environment has been done on coal because of its economic importance. Comparatively little research, however, has been done on the paleodepositional relationships to sulfur in the rocks associated with coal, despite its importance in the production of acid mine drainage. The following discussion is based upon work with modern sediments, the few studies that have been done on coal associated rocks, studies of sedimentary rocks that are not coal bearing, and our own observations of coal-bearing rocks. Sulfur in coal will be discussed in most detail because of the plethora of studies on this subject.

Marine, Brackish and Freshwater Environments - Coal swamps and associated sediments form under a variety of depositional environments. These environments include alluvial plain, upper delta plain, lower delta plain, marginally brackish, transitional (brackish), and marine environments.

Guber (1972) found that the highest sulfur in rocks overlying the lower Kittanning coal in north-central Pennsylvania was associated with sediments deposited under brackish conditions (identified using the phosphatic brachiopod *Lingula*). Paleoenvironmental determinations were based on the paleontological work of Williams and Keith (1963) which was supplemented by geochemical studies by Degens et al. (1957). At one location the lower Kittanning coal was directly overlain by shale with conchostracans, and the conchostracan-bearing rock was low sulfur. Guber (1972) also studied a section containing the Brush Creek (Glenshaw Fm.) marine zone. The outcrop had calcareous marine fossil-bearing rocks and brackish *Lingula*-bearing rocks. The brackish rocks were higher in sulfur than the marine rocks. He concluded that a brackish environment provides optimum conditions for pyrite formation, with sulfate derived from the brackish water and iron from the nearby terrestrial sources. These sources, coupled with high organic content, provide optimum conditions for pyrite formation; that is, a reducing environment with an ample supply of sulfur and iron.

A relationship between depositional environment and sulfur in coal has been demonstrated for many ar-

eas. Williams and Keith (1963) in their classic study of sulfur in the lower Kittanning coal of Pennsylvania, demonstrated that the sulfur in the coal was related to the paleodepositional environment of the roof rock. Brackish and marine roof rocks overlay high sulfur coal, whereas non-fossiliferous and conchostracan-bearing rocks [what Williams (1960) referred to as "freshwater"] overlay lower-sulfur coal (Table 8.9). The mean sulfur for coal overlain by marine rocks was 3.15%, for brackish (transitional) rocks 2.45%, and for freshwater (continental) rocks 1.73%. The upper Freeport coal which is overlain entirely by unfossiliferous (no fauna) or conchostracan-bearing rocks was used as a control. It did not show any significant regional differences in percent sulfur. The average percent sulfur for the upper Freeport coal was 2.09%, which is intermediate between the freshwater and brackish values for the lower Kittanning coal. It is interesting to note that at one standard deviation the average sulfur for the upper Freeport shown in Table 8.9 overlaps with the average sulfur for the lower Kittanning. Also the upper Freeport average sulfur is higher than the "freshwater" portion of the lower Kittanning. As stated above, it is not the sulfur content that makes the water associated with the Freeport coals of better quality than lower Allegheny County, but the presence of freshwater calcareous rocks. Our experience has shown that the lower Kittanning overburden even where it is conchostracan-bearing (such as in northeastern Cambria County) lacks calcareous strata and produces moderately acidic drainage.

Table 8.9 Summary statistics of sulfur in the lower Kittanning and upper Freeport coals in the northern bituminous coal field of Pennsylvania. Adapted from Williams and Keith (1963).

SAMPLING UNIT	N	x	s
L. Kittanning coal - total area	255	2.64	1.16
- marine area	71	3.15	1.17
- brackish area	48	2.45	1.03
- freshwater area	125	1.73	0.81
U. Freeport coal - total area	183	2.09	0.85

When Williams and Keith (1960) did their field work, good stratigraphic correlations across the state were lacking. Work by the Pennsylvania Geological Survey from the late 1960's to the present has helped to clarify many correlation problems. Detailed mapping in Clearfield County that post-dated Williams' work was used in the construction of Figure 8.11. Although Figure 8.11 shows somewhat different facies boundaries compared to the map by Williams and Keith (1963), their conclusions are probably still largely correct. Irrespective of correlation mistakes, Williams' conclusions regarding the relationship of roof-rock facies to coal chemistry should be valid, in other words, even if the correlations were incorrect (for example, Clarion or middle Kittanning sampled instead of lower Kittanning), marine-, brackish-, and conchostracan-roofed coals and their respective coal analyses would have been compared and used in the compilation of Table 8.9. Also, it appears from examples in this chapter that shales from the conchostracan-bearing areas have lower sulfur than shales from areas of marine or brackish environments, although a larger sample population is needed to quantify this.

Relationships between sulfur and depositional environment for coal have also been documented in Texas and Australia. The Eocene coals of Texas typically have highest sulfur (1.5 to 2%) associated with coals deposited in marine and brackish lagoonal environments, while alluvial plain coals exhibit the lowest sulfur values (< 1%). Deltaic coals are intermediate in sulfur (1 to 1.5%) (Kaiser 1974, 1978). Permian coals in Australia deposited in lower delta plain facies usually contain > 0.55% sulfur, whereas those associated with braided fluvial facies found further inland, usually on alluvial plains, contain < 0.55% sulfur. Upper delta plain coals, which are located between the lower delta plain and the alluvial plains, are typically of intermediate sulfur (Hunt and Hobday, 1984).

Various studies have looked at the relationship between the distance from the coal to overlying marine rocks. The Pennsylvanian Period Herrin (No. 6) coal in Illinois is high sulfur (>2.5%) where overlain by the marine Brereton Limestone, however where the coal is separated from the limestone by the crevasse-splay deposited Energy Shale the sulfur is lower (<2.5%) (Figure 8.51) (Gluskoter and Hopkins, 1970). Figure 8.52 shows the relationships between the contemporaneous sandstone channel, coal and Energy Shale, and the marine Brereton Limestone. A study of Paleogene coals in Japan similarly shows a relationship between the amount of pyrite present in the coal and the thickness of freshwater sediments separating coal from overlying marine sediments (Figure 8.53) (Shimoyama, 1984). Numerous studies in the Illinois Basin, for various coal seams, relate low sulfur coal to freshwater shale roof-rock (e.g.: Murphysboro coal - Jacobson, 1983; Springfield coal - Eggert, 1984; Herin No.6 coal

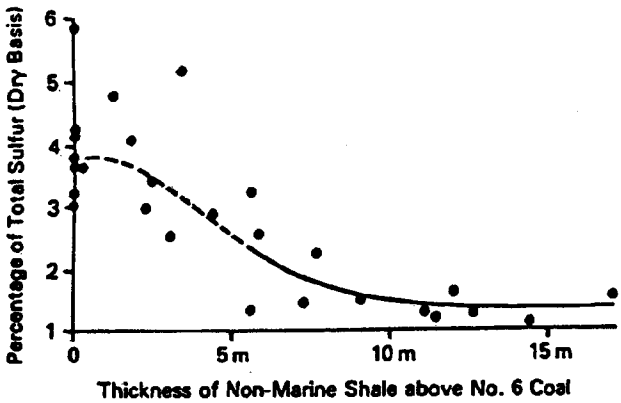

Figure 8.51 Relationship of total sulfur content of the Herrin (No. 6) coal with thickness of non-marine shale which separates the coal from overlying marine sediments. See Figure 8.52 for a cross-section showing relationships between the coal, non-marine Energy shale, and the marine Brereton limestone. After Gluskoter and Hopkins (1970) from McCabe (1984).

- Gluskoter and Hopkins, 1970, Kravits and Crelling, 1981, and Burk, et al., 1987).

The high sulfur (>5%) in Pennsylvanian Period coal in Atlantic Canada (Gibling et al., 1989) and Cretaceous coal in Spain (Querol et al., 1991, 1992) have been attributed to erosion of older upstream evaporite sediments containing gypsum; the sulfate from the gypsum providing the source of the sulfur in the coals. There are Spanish coals with clearly associated marine strata that have lower sulfur than the evaporite influenced coals lacking marine affinities. These studies suggest that dissolved sulfate sulfur eroded from upstream sources can contribute to the sulfur in coal. The high sulfur of the Canadian coals may have another explanation. It was assumed until only recently, after 150 years of research, that because of their association with freshwater biota and alluvial sedimentary

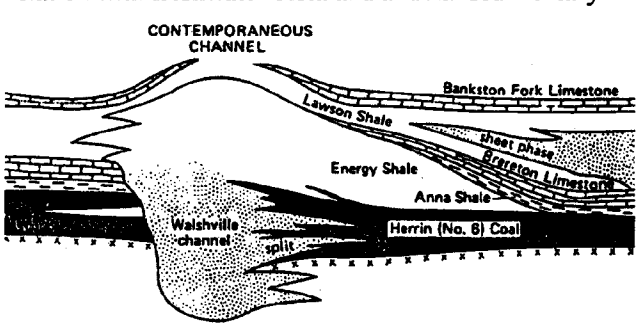

Figure 8.52 Cross-section showing the relationships between the Herrin (No. 6) coal, the contemporaneous Walshville channel, the Energy shale, and Brereton limestone. Modified from Nelson (1983).

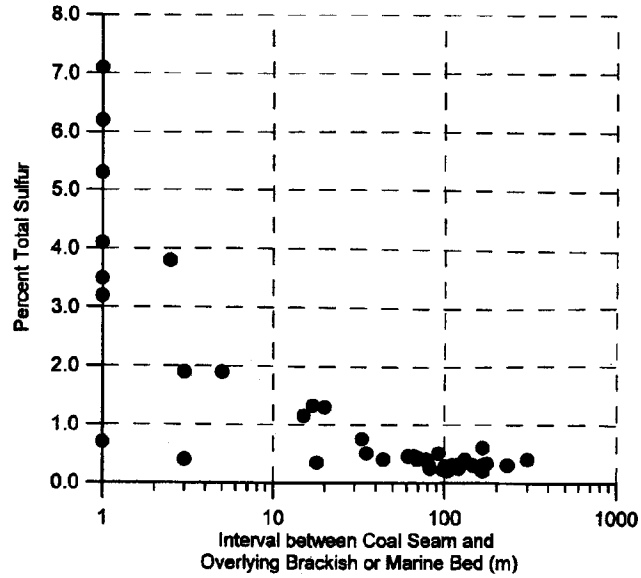

Figure 8.53 Relation of the total sulfur concentration in the main Japanese Paleogene coals to the interval between coal beds and the overlying marine or brackish-water horizons. Modified from Shimoyama (1984).

features that the Atlantic Canada coals were associated with freshwater depositional environments. Wightman, et al. (1993), however, have concluded that deposition took place on a coastal platform, and not the fluvial and lacustrine environments previously proposed. This conclusion was based on the finding of agglutinated foraminifera, which are indicative of marginal marine, tidal-marsh, conditions. These foraminifera are constructed of detrital grains and can remain where calcareous fossils have dissolved. It may be profitable to search for these critters in rocks associated with some of Pennsylvania's high-sulfur "freshwater" coals.

Englund et al. (1986) noted that sulfur in the Pottsville Group Pocahontas No. 3 coal in southern West Virginia and western Virginia was highest at the margins of the deposit (0.9 %) and lowest away from the margins (0.4 %). Two studies of the Allegheny Group upper Freeport coal in southwestern Pennsylvania show similar trends. Skema et al. (1982) found that coal near the margins contained 4 to 5 % sulfur, while coal toward the center of the deposit had 1 to 2 % S. Sholes et al. (1979) found that coal near the margins had 5 to 6 % S, and 3 % or less in the center. In all cases cited above, the coal thins to 0 ft (m) at the margins (i.e., "pinches out"). Thus the thin coal has the highest sulfur. Cheek and Donaldson (1969) also noted an increase in sulfur with decreasing thickness of the upper Freeport coal in northern West Virginia. The upper Freeport coals were deposited in a freshwater (or

more likely a marginal brackish) depositional environment. A couple of factors may contribute to this distribution of sulfur. The margins of the peat swamp would have more access to dissolved solids (e.g., sulfate) carried by streams or estuaries draining the swamps, whereas away from the margins the water would be primarily from precipitation. A second factor is that the margins probably maintained a higher pH due to influence from stream or estuary water compared to the lower pH of the swamp interior. Higher pH is more conducive to pyrite formation (Cecil et al., 1985).

Sulfur in Pennsylvania's anthracite is much lower than in coals from the bituminous region. On average the sulfur is 0.48% organic sulfur, 0.35% pyritic sulfur, and 0.02% sulfate sulfur (Wood et al., 1986). Sulfur generally increases to the west and north, and is highest in the northern field (Figure 8.54). Wood et al. proposed a couple of explanations for the low sulfur. One was that metamorphism may have somehow reduced the sulfur. Another was that the coals, and associated rock, were deposited on an alluvial plain, with virtually no marine influence and therefore away from a source of sulfur. The Mill Creek limestone of the northern field is the only known marine unit. Marine waters may have had more influence in the Northern Field, thus higher sulfur coals.

Some of the examples cited above show well documented relationships between sulfur in coal and paleodepositional environment. However, even where present, the relationships between sulfur and paleodepositional environment are region specific. For example, sulfur in the Eocene Texas coals and Permian Australian coals for a given paleodepositional environment are lower in sulfur than comparable Allegheny Group coals in Pennsylvania. Also, marine rocks commonly overlie coals of the southern Appalachians, but the sulfur is generally lower in these coals than in freshwater coals of the northern Appalachians. The examples from Atlantic Canada and Spain, with a possible upstream source of sulfate, reveal further complexities that may be involved. Therefore, the use of "high" and "low" sulfur as a predictive tool for paleodepositional environment should be used with extreme caution. Only affirmative paleontological and sedimentological evidence should be used to determine paleodepositional environment, and even this can be problematic. It took geologists 150 years to find evidence of marine influence on coals of Maritime Canada (Wightman, et al., 1993) and conchostracans, the "freshwater" indicator in Pennsylvania, are probably marginal-brackish.

Vertical Distribution of Sulfur within a Coal Seam - Changes in percent sulfur have been observed at a more local level than discussed above. Here we will examine vertical variations in sulfur content in coals and the factors which may control this variation.

Shimoyama (1984), in a study of Japanese Paleogene (early Tertiary) coal seams, related depositional environment of roof strata and floor strata with the percent sulfur at the top and bottom of coal seams. Coal seams overlain by marine roof strata had high percentages of sulfur at the top of the seam, and coals underlain by marine sediments had high sulfur at the base of the coal. Coal associated with freshwater deposits had uniform and comparatively low sulfur throughout the coal. Although this may explain the Japanese coals examined, high sulfur at the top and bottom of a coal seam appears to be very common regardless of paleodepositional environment.

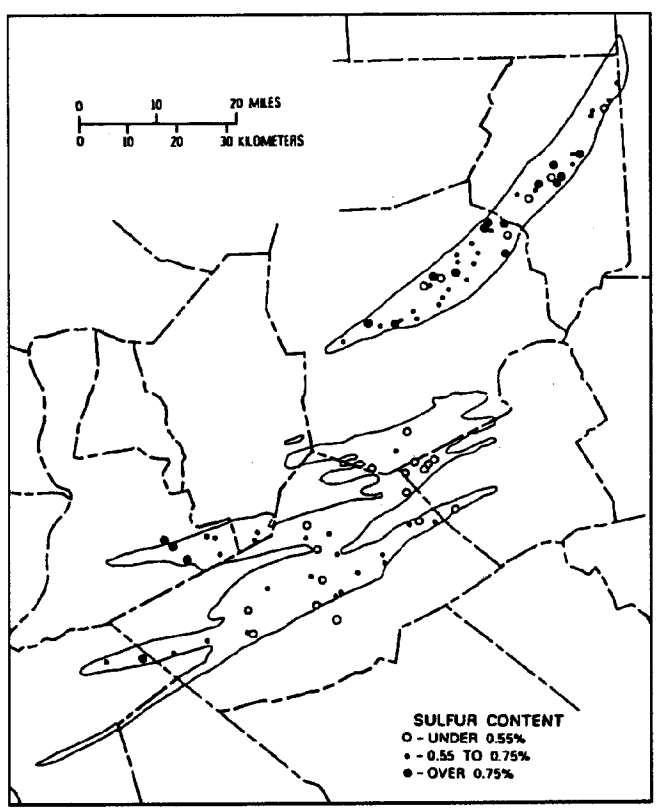

Figure 8.54 Percentage of sulfur in anthracite samples from the Pennsylvania Anthracite region (from Wood et al., 1986).

Numerous studies of the vertical distribution of sulfur in coal have been done for coals around the world, encompassing various geologic periods and coal rank. Increased sulfur at the top and bottom of coal seams appears to be the rule rather than the exception. Suggate (1995) in a study of subbituminous Miocene Epoch coal in New Zealand observed that sulfur content decreased from roof to floor, with a minor increase near the floor. The percent sulfur at the top of coal varied from > 6% to < 2%, however the sulfur in the middle of the coal seam was always 1.5 to 2.0% less. A study of New Zealand Cretaceous coals deposited under marine conditions (Sherwood et al. 1992) also noted higher sulfur at the top of the seam. A bituminous coal of Cretaceous Period from Alberta, Canada averaged only 0.3% sulfur, and the coal was deposited "well removed from marine clastic influences" (Langenberg et al. 1992). This coal showed sulfur elevated at the base and to some extent at the top. The Tertiary "Big George" coal deposit in the Powder River Basin of Wyoming is a 200-ft (60 m) thick subbituminous coal associated with freshwater depositional environments. This coal has total sulfur typically below 0.3%, however the bottom 0.6 ft (0.2 m) has over 1% sulfur (Kent, 1986). The trend of higher sulfur in the upper and lower portions of a coal seam have also been observed in the Eocene lignite coal deposits in Texas (Arora et al. 1980).

Another example in the literature of high sulfur at top and bottom of coal is a coal in the Cherokee Group (Pennsylvanian) in southeastern Iowa (Biggs and Bruns, 1985). The upper 28% of the coal contained 67% of the pyrite, the middle 47% contained 19% of the pyrite and the lower 25% contained 14% of the pyrite. The coal was bounded top and bottom by pyrite-rich shales. The paleoenvironment is not discussed, but most coals in this part of Iowa have associated marine sediments (Howes, 1990).

Similar trends to those described above have been observed in coal seams of the northern Appalachian basin. Reidenour et al. (1967) found higher sulfur at the top and (sometimes) bottom of Clarion and lower Kittanning coals in Clearfield County that have roof rocks that were deposited in a brackish depositional environment. Appalachian coals interpreted to have been deposited in a freshwater depositional environment also show high sulfur at the top and bottom of the seam. This has been observed for the Pittsburgh (Donaldson, et al., 1979) (Figure 8.55), Redstone (Hawkins, 1984), and Waynesburg (Donaldson et al., 1985b) (Figure 8.56) coals of northern West Virginia and southwestern Pennsylvania. High sulfur has also

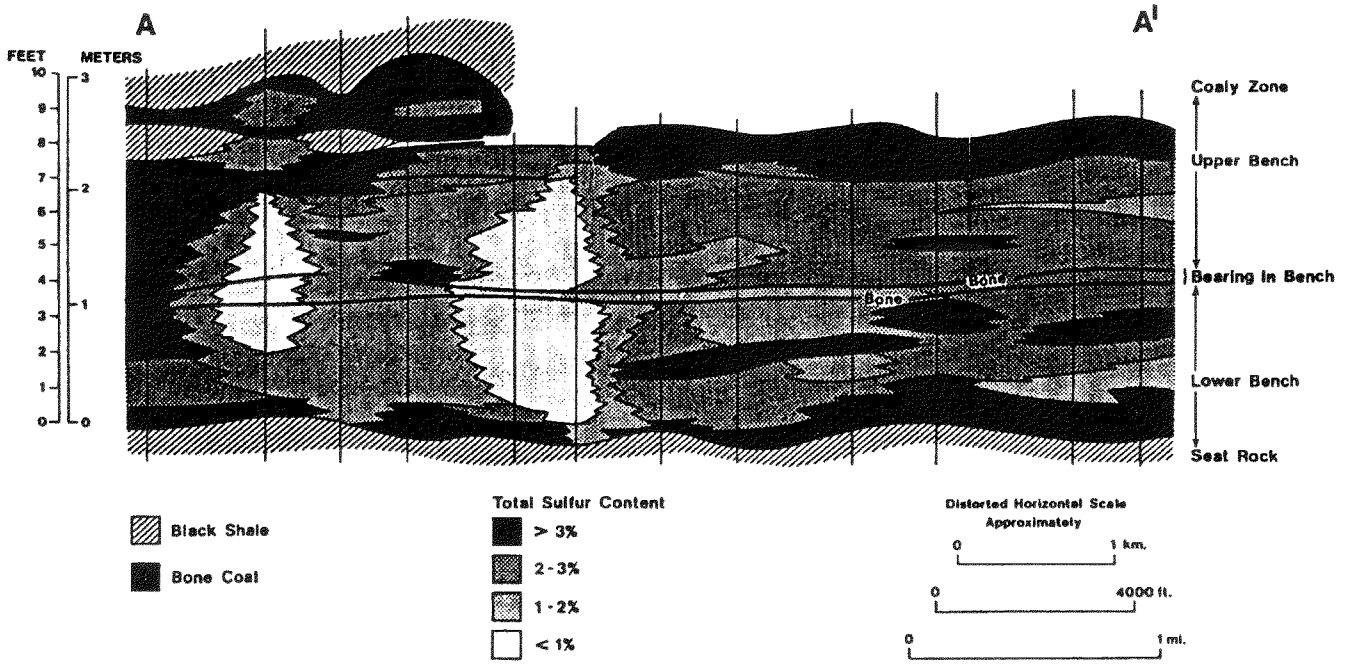

Figure 8.55 Stratigraphic cross-section of total sulfur facies in the Pittsburgh coal. Cross-section is oriented approximately north-south and is located in northern West Virginia and southwestern Pennsylvania. Precise location is not given. Note that the highest sulfur is at the top and bottom of the coal seam. From Donaldson et al. (1979).

been observed at the top and bottom of the upper Freeport coal by Cheek and Donaldson (1969) in northern West Virginia.

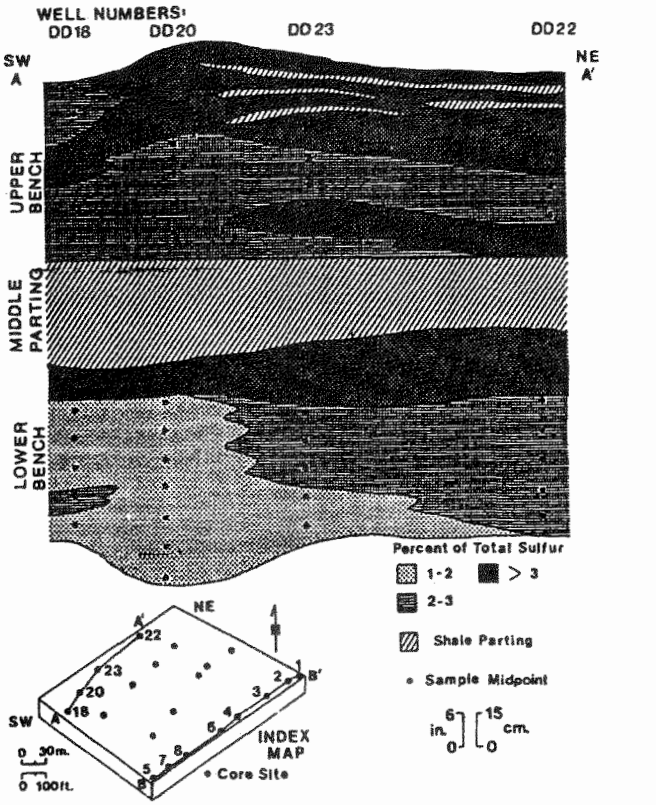

Figure 8.56 Cross-section showing total sulfur content of the Waynesburg coal in a strip mine in northern West Virginia. Note that the highest sulfur is at the top of each of the two benches of coal. From Donaldson et al. (1979).

The findings for vertical variations in sulfur concentration within a coal seam are consistent with the distribution of sulfur in modern thick peat deposits. Modern peat deposits frequently show high sulfur at the base of the deposit, for example Staub and Esterle (1994) attribute the high sulfur at the base of a peat deposit on Sarawak, East Malaysia to initial conditions being "mangrove and *Nipa* vegetation" growing on a mudflat under brackish to marine conditions with waters rich in sulfate. This organic rich environment would have near neutral pH and abundant iron, conditions favorable for pyrite formation. Neuzil et al. (1993), likewise found the highest sulfur in the bottom of the peat in the Riau and West Kalimantan provinces of Indonesia. Sulfur values for the basal peat were ~0.3 % (with a high of 0.56 %), whereas the upper peat was less than 0.2 %. The underlying sediments were of marine origin and the authors suggest this may have supplied sulfur to the lowest peat horizons. Esterle and Ferm (1994) looked at thick peat deposits at Sarawak, Malaysia, and Sumatra, Indonesia. Sulfur in the basal one meter of the deposit was 2.4 to 4.5%, and was 0.3% or less above this zone.

It can not be assumed that high sulfur in the upper portion of a coal bed, or high sulfur within a coal bed, are evidence of marine influence. Paleoenvironmental interpretations using sulfur alone, may not be valid. The fact that high sulfur is frequently found at the top and bottom of coal seams, regardless of paleoenvironment, is important from a mining standpoint. The top and bottom of a coal seam are the most likely to be left behind on the mine site as "pit cleanings" because of high sulfur or ash, or as coal that is not recoverable in the mining process. The acid potential from this source must be considered in any evaluation of potential acid-materials problems.

Surface Weathering

All of the discussions so far have involved geologic processes that occurred hundreds of millions of years ago, during the Pennsylvanian. These include the controls that paleoclimate and paleodepositional environment had on overburden mineralogy. This section will deal with a much more recent geologic process, the near surface physical and chemical weathering of rock which has occurred within the past million or so years. The significance of this influence on the distribution of carbonate and sulfide minerals (pyrite) can be as great as those that occurred in the more distant past. The discussion will look at weathering south of the glacial margin and within the glaciated portion of the Appalachian Plateau. Weathering results in the near surface removal of carbonates and sulfide minerals; carbonates by dissolution and sulfides by oxidation. This zone is usually recognizable by the yellow-red hues (indicative of oxidized iron) of the rocks. Generally, in the unglaciated portions of the Appalachian Plateau, the intensely weathered zone extends to 20 to 60 ft (6 to 20 m) below the surface.

Weathering of Bedrock on the Appalachian Plateau

Chemical weathering of bedrock is enhanced by physical factors such as stress-relief fracturing on hill slopes and bedding-plane separations due to unloading. Clark and Ciolkosz (1988) have suggested that periglacial conditions during the Pleistocene contributed to the shattering of near-surface rock. Kirkaldie (1991), in a study of weathering of bedrock on the northern Appalachian Plateau, observed that the maximum thickness of weathered bedrock beneath glacial deposits was similar to the maximum thickness of

weathered bedrock in unglaciated regions. The distribution of thickness of the weathered zone beneath the glacial deposits, however, was different, with less weathered rock typically beneath glaciated areas (Figure 8.57). This is attributed to erosion of much of the weathered surface material by glaciers. The findings of Kirkaldie suggest that (1) the bedrock weathering occurred prior to the last glacial period, or that (2) in the non-glaciated areas the rate of weathering has been balanced by the rate of erosion. No studies of weathering rates have been done for the Appalachian Plateau, so the second theory has not been tested. Whatever the method, and whatever the duration of time, shattering of rock increases surface area and thus provides greater area for contact with water and air, and weathering is accelerated. These processes acting together also increase the permeability of the weathered zone. As discussed in Chapter 10 the ground water associated with the weathered zone is dilute, in terms of dissolved solids, because readily soluble products have been removed by chemical weathering.

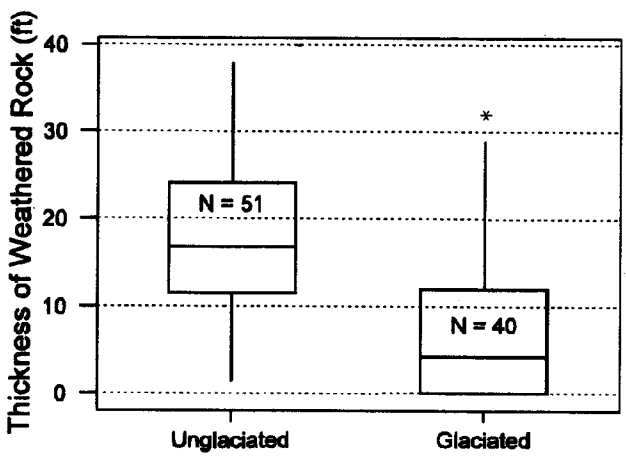

Figure 8.57 Distribution of the thickness of weathered bedrock in glaciated and unglaciated portions of the Appalachian Plateau in Pennsylvania. The large box encloses the 25th and 75th percentiles. The horizontal line within the box is the median, the "whiskers" indicate the range of data. Data are from Kirkaldie (1991).

Chemical weathering is also influenced by lithology. Coarser, more permeable lithologies may allow oxidation to extend to a greater depth. Kirkaldie (1991) measured the depth of the highly weathered zone, noting the type of cover, amount of cover, lithology, and topographic position. In unglaciated terrain, he noted that the maximum thickness of highly weathered rock was 28.9 ft (8.8 m) in sandstone, and only 11 ft (3.3 m) in shale. However, the lithologic difference was not the only variable.

This weathered-rock zone exists throughout the Appalachian Plateau. In spite of this it has been little studied. Smith and colleagues (Grube et al., 1972; Smith et al., 1974; and Singh et al., 1982) investigated the effects of weathering on the Mahoning sandstone in northern West Virginia, and noted a "pyrite-free weathered zone approximating 20 feet (6 m) of depth below the land surface..." (Smith et al., 1974, p. 3). Singh et al. (1982), in addition to noting the pyrite-free zone, also note a loss of "alkaline earth" elements within 20 ft (6 m). This is illustrated for calcium in Figure 8.58. The loss of calcium is best explained by a loss of calcareous minerals (calcite and dolomite). Brady et al. (1988; 1996) in a study of the upper Kittanning and lower Freeport overburden in Fayette County, PA noted a similar loss of calcareous rocks in the near-surface weathered zone to about 7 m depth. Hawkins et al. (1996) noted weathering to depths of 30 to 60 ft (10 to 20 m). The loss of carbonates due to weathering is also discussed in Chapter 10.

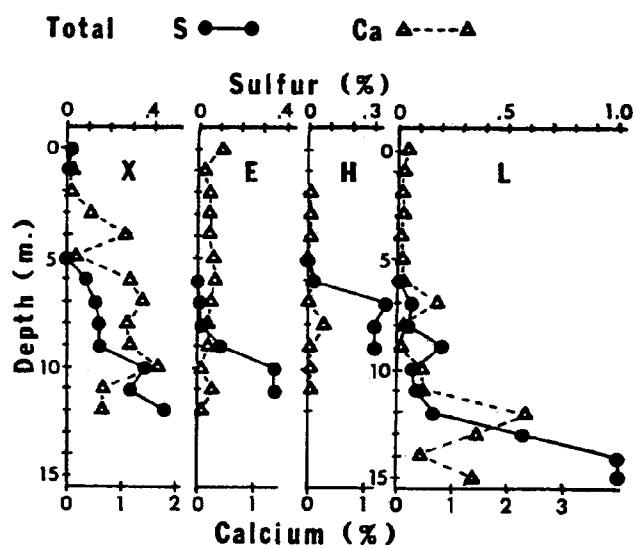

Figure 8.58 Total sulfur and total calcium in sandstone overburden, as a function of depth below the surface, for four sites in Preston County (northern), West Virginia. From Singh et al. (1982).

A weathering profile is evident at the top portion of most drill logs shown in this chapter. It is hard to determine precise rules of thumb for the depth of leaching of carbonates and oxidation of pyrite because these minerals can only occur where they were originally present (before weathering). If no pyrite was ever present within a stratigraphic horizon, its absence is not due to weathering, but to the fact that it was never there in the first place. The same is true for calcareous strata. It is evident from the stratigraphic figures that

rarely do NPs greater than 30 ppt $CaCO_3$ or sulfur greater than 0.5% occur within 20 ft (6 m) of the surface. A good example of this effect is the Blue Lick coal in Figure 8.26. Where the coal is under shallow cover it has less than 0.7 percent sulfur, however, in OB-C where the coal occurs under about 60 ft (20 m) of cover the coal averages over 2 percent sulfur. Most of the exceptions are where a horizon equivalent to a limestone, or strongly calcareous zone lies close to the surface. Some drill holes that encounter this zone at less than 20 ft (6 m) may still contain carbonates. The same is true for very high sulfur zones.

Figure 8.59 shows the effects of weathering on the sulfur content of the upper Freeport coal and the roof rock (shale) in an area of Fayette County. There is a clear loss of sulfur at shallow depth (17 to 20 ft; 5 to 6 m) in both the coal and the shale.

An accurate knowledge of the extent (depth) of the weathered zone is important from an overburden sampling standpoint. Overburden sampling should be done to the extent that it adequately represents the weathered zone and unweathered bedrock. This will entail drilling overburden analysis holes at maximum cover to be mined and at lesser cover. Weathering is also discussed in Chapter 9.

An understanding of the effects of weathering on the distribution of pyrite, sulfate salts, and carbonates is important in (1) accurately defining their distribution within unmined overburden, (2) being able to design a mine plan to prevent postmining problems, and (3) accurately predicting postmining water quality. An understanding of the weathering profile is just as important as understanding the lateral and vertical distribution of strata and their pyrite (sulfur) and carbonate content.

Glacial deposition was discussed earlier. Glaciers not only deposit, but can also erode. Erosion can include previously deposited glacial sediment, bedrock, and soil. Weathered bedrock is easily erodible and tends to be thinner in glaciated regions because of removal by glacial erosion. This is illustrated in Figure 8.57 where the median thickness, as well as the interquartile range of weathered bedrock is lower for areas that have been glaciated than for areas that have not been glaciated.

Weathering of Glacial Sediments in Western Pennsylvania

As with bedrock, the weathering of tills and other glacial sediments results in a change in the geochemistry and therefore in their effect on water quality. Weathering produces a vertical mineralogical gradation within tills. Leighton and MacClintock (1930, 1962) described the weathering of tills by dividing them into five horizons (Figure 8.60). Horizon 5 is unweathered till. It is still its original color (usually a shade of gray in northwestern Pennsylvania) and carbonates are still

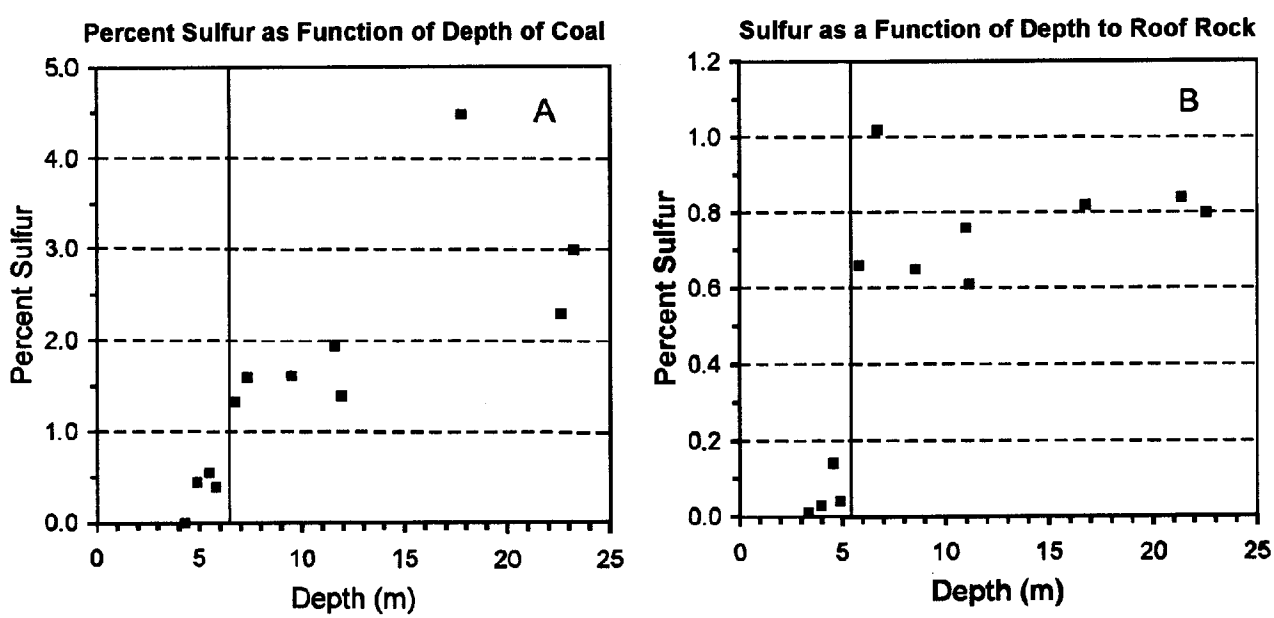

Figure 8.59 Percent sulfur in the upper Freeport coal (figure A) and 5 to 7 ft (1.5 to 2 m) of roof rock (figure B) as a function of depth below the surface. The mine is in Saltlick Township, Fayette County.

present. In horizon 4, pyrite, and other iron minerals, are oxidized. A till's characteristic oxidized color, a shade of yellow, brown, or red, is caused by iron oxide (such as hematite) or hydrous iron oxide (such as goethite and limonite) replacements of iron magnesium silicates and iron sulfides (Hallberg, 1978). Oxidation of manganese minerals (Hallberg, 1978) generally produces a darker brown color. Tills high in carbonate also tend to oxidize to a darker brown compared to low carbonate tills (White, 1982). Carbonate minerals are still present in horizon 4.

In horizons 3, 2, and 1, till is oxidized and totally leached of carbonates. Horizon 2 is chemically decomposed till. Silicates have been degraded. It is still recognizable as till. Horizon 1 is the A and upper B horizons of the soil where major leaching, added organic material, and addition of iron oxide and clay have modified the composition and texture. The parent material is no longer recognizable.

Horizons 4 and 5 are those of benefit in the prevention of acid mine drainage. Carbonate minerals are still present in those horizons, although partial leaching may have occurred. Horizon 4 may be partially leached in the coarse sand fraction (Hallberg, 1978) before leaching is apparent in the clay fraction.

Weathering begins immediately upon deglaciation. A later glacial advance over the existing till may erode

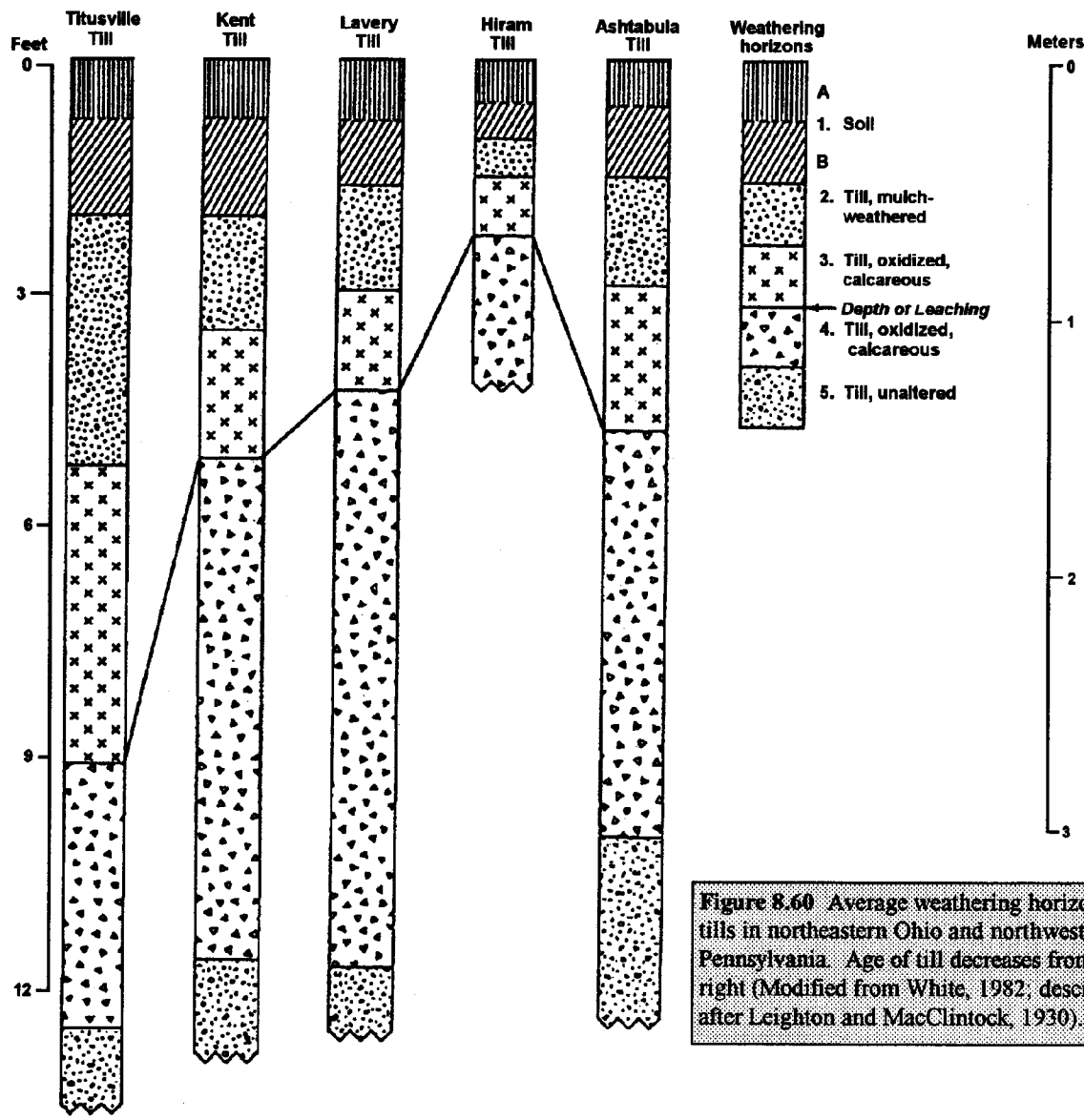

Figure 8.60 Average weathering horizons of tills in northeastern Ohio and northwestern Pennsylvania. Age of till decreases from left to right (Modified from White, 1982; descriptions after Leighton and MacClintock, 1930).

part or all of the weathered horizons of the preexisting till. If multiple tills are encountered during overburden removal, a buried soil or weathered horizon, with carbonate minerals leached, may exist between two calcareous zones. Figure 8.37 illustrates this situation. Unit 6 is a weathered, leached zone between calcareous zones 4 or 5 and 7. Units 10 and 11 are again a leached zone between the calcareous units 9 and 12. In Figure 8.38 and Figure 8.61, the NP distribution with depth at the McCoy and Spagnolo mines show low NP zones between high NP zones. These are partially leached weathering zones at the top of older, buried tills.

Likewise, if a till is thin and overlies another weathered till (a likely scenario in the glaciated coal region), leached zones of both tills may be superimposed, resulting in an excessive depth of leaching. Figure 8.62 illustrates this situation with three tills. Over most of the exposure, calcareous till is not encountered until the third till is reached (unit 6).

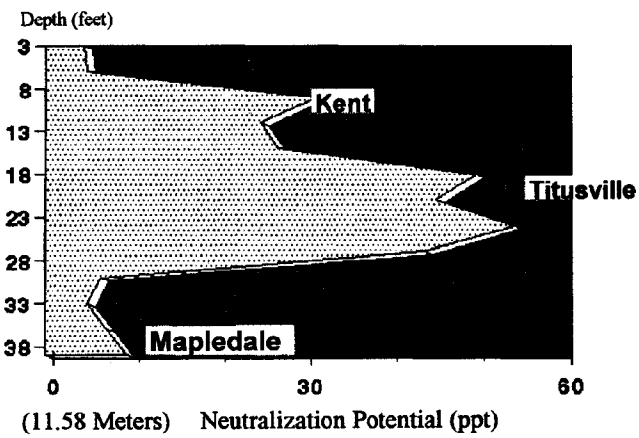

Figure 8.61 Distribution of NP for till stratigraphy at the Spagnola mine, Mill Creek Township, Mercer County. Mine site is at location "B" on Figure 8.36.

Each till has a characteristic average depth of leaching (Figure 8.60), providing no erosion of till has occurred since the beginning of weathering, and no other sediment has been deposited on top to halt the weathering process. The carbonate content of the Mapledale Till is so low that weathering horizon 4 cannot be determined in the field, and the depth of leaching is difficult to determine. The Mapledale Till is oxidized to a depth of 10 to 16 feet (3 to 5 m) (White et al., 1969).

Because a number of factors control the depth of leaching (and other weathering characteristics), the same till may be leached to different depths in different locations. All other factors being equal (which they usually aren't), older tills are leached of carbonates to a greater depth than younger tills. The nature of the parent material affects the rate of weathering. Coarser, more permeable sediments allow greater penetration of weathering agents (Hallberg, 1978). Landscape position can affect runoff vs. infiltration. Also, on steep slopes, erosion may proceed at a rate equal to weathering and a weathering profile may not develop.

Weathering in the Anthracite Region

Many of the weathering processes described above for western Pennsylvania are relevant to the Anthracite Region because the paleoclimate and present climate for both regions were/are essentially the same. The geologic structure of the Anthracite Region, however, as part of the Ridge and Valley Physiographic Province, is dramatically different than the flat-lying rocks

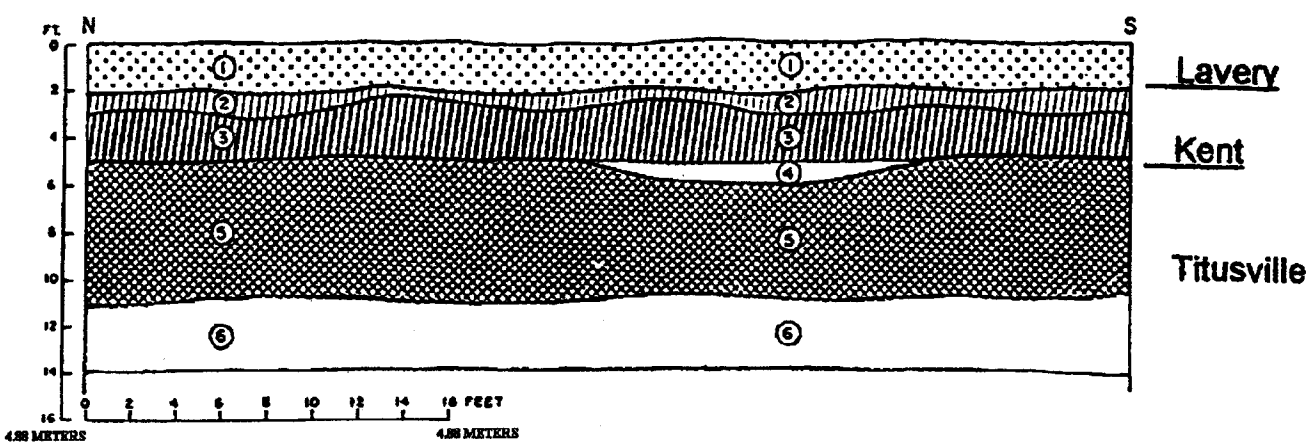

Figure 8.62 Sketch of glacial deposits exposed in an excavation in Mercer County. The tills are essentially devoid of calcareous material above unit 6. Horizon numbers are those used in Figure 8.60. Modified from White et al. (1969). Excavation at location "C" on Figure 8.36.

of the Appalachian Plateau. Due to the combined effects of the folded and faulted geologic structure and the resistance of the sandstone lithologic units to erosion, the weathering processes have formed a different topographic expression in the Anthracite Region.

Classic and recent works on weathering in the Ridge and Valley Province have concentrated on topographic development and glacial and periglacial features. In the first issue of National Geographic, Davis (1888) discussed the geologic structure, erosional history and topography of valleys and ridges of central Pennsylvania and the "dissected plateau further west" (p. 14). A later more detailed discussion of the subject is in Davis (1909). Descriptions of Appalachian slope form development are contained in Hack (1960, 1979). Additional information on weathering in the Ridge and Valley is found in Thornburry (1965, 1969), Clark and Ciolkosz (1988), and Sevon (1989). The four anthracite fields are preserved in synclinal basins that are essentially surrounded and "defended" by sandstone ridges. These ridges are more resistant to erosion than the shales and coals of the Pottsville and Llewellyn Formations. The slope forms of the ridges are typically mature (i.e., convexo-concave), but some free faces occur, such as the Harveys Creek water gap in the Northern Field.

The Pleistocene glaciation and climate left several features that can be observed today. These include till deposited in the Northern Anthracite Field (Hollowell, 1971, and Braun, 1997), and periglacial effects which extend south to the other anthracite fields. Periglacial activity has, in most places, lowered ridge tops as much as a few tens of meters (Braun, 1989). As a result, earlier weathering horizons have been removed, leaving a very small depth of weathered rock. Some of this weathering has resulted in the deposition of colluvium on the lower slopes. Colluvium in the Ridge and Valley province ranges in thickness from one meter on the upper ridge slopes, to 30 meters at the base of the slopes and in valleys. Twenty-seven percent of the soils in the Ridge and Valley province are colluvial, versus only 13 percent in the Plateau (Ciolkosz, 1978). Ridge tops have little or no weathered material. The lower one-half to three-fourths of the ridge slopes are colluvial. Residual soils occupy valley floors (Ciolkosz and others, 1979). In most places in Pennsylvania, at least two ages of colluvium are present, which includes reworked older regolith (Braun, 1989; Sevon, 1989). There is rarely any residual weathered bedrock beneath colluvium or glacial sediments in the Ridge and Valley (W. Sevon, personal communication, 1997), and where present, it is only a few feet thick (Hoover and Ciolkosz, 1988).

Because the bedrock, as far as is known, is low in pyrite and the tills lack carbonates, the effects of weathering in the Anthracite Region on mine drainage is probably not as significant as in the bituminous region.

Lithologic Factors Affecting Postmining Water Quality

Lithology is controlled by geologic factors such as paleoclimate and paleo-depositional environment. Sandstones are deposited in high energy environments, whereas shales and siltstone are deposited in quieter environments. Donaldson et al. (1985a) report the presence of several types of sandstones throughout the Pennsylvanian: lithic, calcareous, and quartz-rich (Figure 8.48). Quartz-rich sandstone is found predominantly in the lower Pennsylvanian Pottsville Group formations, but also occurs in the Allegheny and lower part of the Conemaugh, decreasing in frequency upward (Skema, personal communication, 1998). Lithic sandstones are found throughout the section. Calcareous sandstone is common from the middle of the Conemaugh through the Dunkard. Sandstone can form in a variety of environments, including

Table 8.10 Mean values for select water quality parameters demonstrating differences of water quality with different overburden lithology. "Group" numbers refer to specific lithologic sections shown on Figure 8.63 and Figure 8.64. Data are from Williams et al. (1982).

	Kittanning/Clarion Lithologies						Freeport Lithologies			
Group	**1**	**2**	**3**	**4**	**5**	**6**	**1**	**2**	**3**	**4**
pH	6.2	*3.2	*6.2	3.3	6.9	*6.2	*6.1	2.3	6.2	6.8
Acidity	5	410	*~10	330	*35	*0	*12	1230	26	*10
Sulfate	369	950	132	914	256	19	*25	1987	26	*110
Specific Conductance	*600	*2000	*650	*1500	*480	*65	*800	1455	200	*180

*Estimated from Figures 55, 56, 57, 58, 60, 61, and 62 in Williams et al. (1982). The other values are from the text in Williams et al. (1982).

alluvial and distributary (deltaic) channel sands, and marine barrier-bar sands. Typically sandstone is composed of quartz with varying amounts of feldspar, mica, and organic debris. Frequently they contain a high concentration of quartz because of this mineral's resistance to mechanical and chemical weathering. In this section we will examine the relationship between rock type and water quality. Abundant sandstone relative to finer-grained rock types, such as shale and siltstone, has been linked to acid mine drainage in the Allegheny Group. We will also examine what, if any, relationships exist between rock type and water quality in the other coal-bearing stratigraphic Groups of western Pennsylvania.

Sandstone and Postmining Water Quality

Many published studies of Allegheny Group mines with abundant sandstone overburden attest to a problem with water quality. Examples of Allegheny Group mine sites with sandstone overburden that produced acidic drainage are: Clarion coal (Dugas et al., 1993; Cravotta, 1991; Site 9 in Brady, et al., 1990; Henke, 1985; J.H. Williams et al., in press); lower Kittanning coal (Guo et al., 1994; Durlin and Schaffstall, 1993); upper Kittanning coal (Brady et al., 1988) and upper Freeport coal (Kania et al., 1989).

Williams et al. (1982) did an analysis of the geologic controls on water quality within the lower Allegheny (Kittanning/Clarion "formations") and upper Allegheny (Freeport "formation") for, primarily, the northern portion of the bituminous coal field. Figure 8.63 is the model for the Kittanning/Clarion, showing six different lithologic (overburden) relationships. Table 8.10. Mean values for select water quality parameters demonstrating differences of water quality with different overburden lithology. "Group" numbers refer to specific lithologic sections shown on Figure 8.63 and Figure 8.64. Data are from Williams et al. (1982).

These models, and accompanying water quality as displayed in the above table, show the important influence of marine and freshwater limestones and calcareous rocks on postmining water quality. They also show the effects of predominantly sandstone overburden, especially for the Freeport sites (Model 2) which typically produce acidic drainage. Comparatively, sites with little or no sandstone typically produce alkaline drainage (Models 1, 3, and 4). Williams et al. (1982) found that the "role of sandstone as an acid-producer cannot be determined from this Kittanning study, due to accompaniment of either acid-producing, high-sulfur shale, or limestone" with the sandstone. Kittanning/Clarion models 2 and 4 are both acid producing. Model 2 represents primarily brackish shales in the absence of calcareous strata. Model 4 represents the sandstone overburden, with acid-producing shale below. Model 3 is similar to situations where the marine Vanport limestone overlies the Clarion coal. Models 5 and 6 include freshwater limestone, such as the Johnstown limestone that occurs below the upper Kittanning coal, thus the alkaline water. The non-marine portion of the Kittanning model is very similar to the Freeport model.

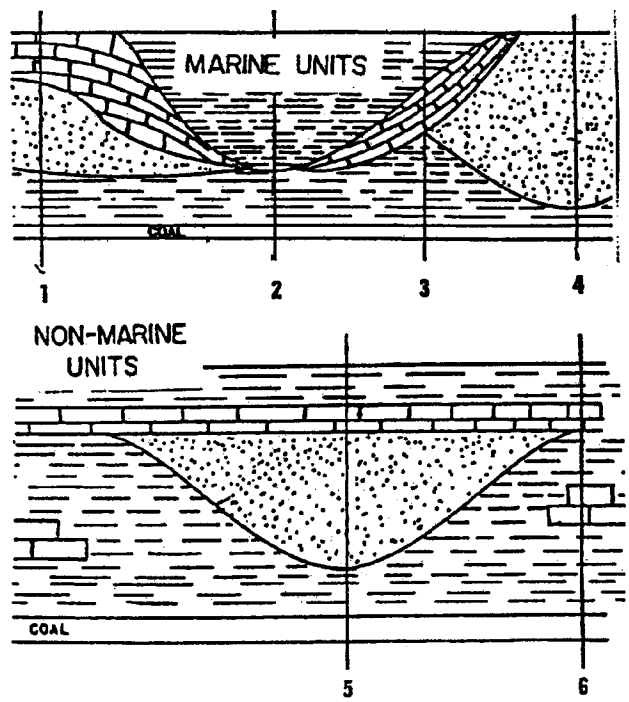

Figure 8.63 Schematic diagram representing the Kittanning/Clarion model of Williams et al. (1982). From Williams et al. (1982).

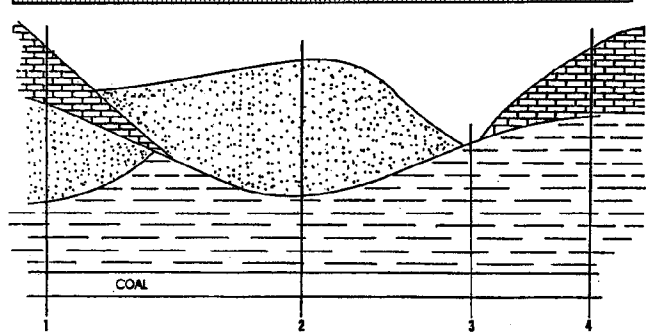

Figure 8.64 Schematic diagram representing the Freeport model of Williams et al. (1982). From Williams et al. (1982).

The work of Brady et al. (1988) is consistent with Williams et al.'s (1982) upper Allegheny "Freeport" model. Brady et al. looked at the overburden above the upper Kittanning coal in the Stony Fork watershed in Fayette Co., PA. Mine sites with predominantly channel sandstone overburden produced acidic drainage. The sandstone lacked calcareous minerals or cements. Overburden in areas away from the sandstone channels contained calcareous shales and muddy limestone, and mining in these areas resulted in alkaline drainage. The mines and resulting water quality in the Stony Fork watershed are discussed in detail in Chapter 9.

Typically sandstone is low in sulfur, even when acid producing. Channel sands can contain eroded material, including ripped up mats of peat (present day "coal spars") and lag deposits consisting of fossilized, and often coalified, logs. Individually these coal inclusions can be high in sulfur, but during typical overburden sampling this high sulfur is diluted by the surrounding inert quartz and other minerals that compose the sandstone. Thus these sandstones may contain acid-forming material (coal spars), but the samples have low overall sulfur concentrations. Occasionally there are pyrite-rich sandstones. Some of these are black and high in organic carbon, still others are light in color, but high in sulfur. The light-colored high-sulfur sandstones seem to occur just above coal or organic-rich shale. An example of this was shown in Figure 8.13, hole A-5.

Within the Allegheny and Pottsville Groups, sandstones generally contain low concentrations of calcareous minerals. There are some (rare?) exceptions to this however. Figure 8.13 shows two drill logs with calcareous sandstone in the lower Kittanning overburden, drill logs A8 and OB-1 from the Kauffman site in Clearfield County. The calcareous minerals are present as cement in the channel bottom deposits. Examination of thin sections reveals that minor amounts of siderite occur with calcite in the interpore cement (V. Skema, 1996, personal communication). Some calcite at the Kauffman site is also associated with fractures. Most of the sandstone at this mine, however, is not calcareous. Sandstones in the Conemaugh, Monongahela, and Dunkard Groups frequently contain calcareous minerals (Figures 8.2, 8.26, 8.31 and 8.34). Some sandstones have lost their carbonates through weathering.

diPretoro (1986) found a relationship between postmining net alkalinity and percent sandstone. All but one mine site within his study area (northern WV) containing greater than 63% sandstone produced negative net alkaline (i.e., acid) drainage. Sixty-seven percent of sites with less than 30% sandstone had positive net alkalinity (Figure 8.65). All but one of the sites with high percent sandstone were Allegheny Group coal mines. All but one of the Dunkard Group (Waynesburg coal) mines were alkaline. Many of the Waynesburg sites were less than 50% sandstone (in contrast to Waynesburg mines in Pennsylvania, where sandstone is the major overburden lithology, Figure 8.2 and Figure 8.34). Figure 8.66 shows a comparison of net alkalinity, for upper Freeport mines in West Virginia, with <50% sandstone and those with >50% sandstone. Median net alkalinity for sites with less than 50% sandstone is 105 mg/L, and for sites with more than 50% sandstone it is -172 mg/L.

An examination of 41 mine sites in western Pennsylvania by the Department of Environmental Protection (DEP) and the Office of Surface Mining (OSM) also shows relationships between percent sandstone and water quality (Figure 8.67). This data is somewhat biased in that, for the most part, it represents sites that were predicted to produce alkaline drainage (in theory acid-producing sites would not have been issued because of regulatory requirements), therefore acidic sites are probably underrepresented. Acidic sites are

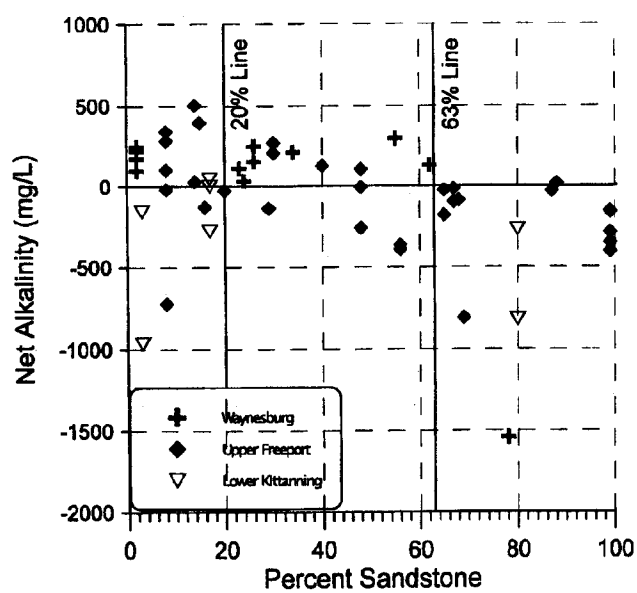

Figure 8.65 Net alkalinity as a function of percent sandstone for surface mines that encountered the Waynesburg, upper Freeport and lower Kittanning coals. Sites are in Preston County (northern), West Virginia. Most sites with greater than 63% sandstone are acidic, and most sites with less than 20% sandstone are alkaline. Data are from diPretoro (1986).

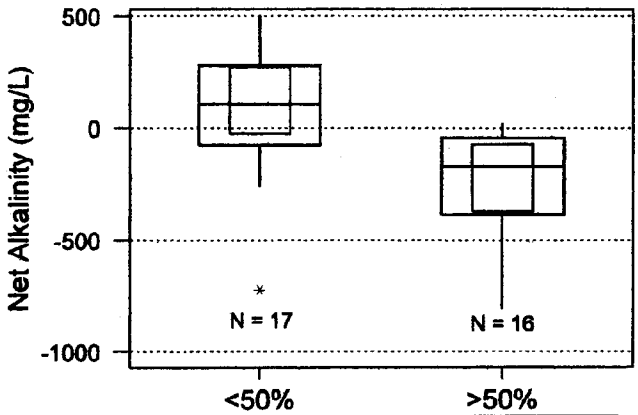

Figure 8.66 Distribution of net alkalinity as a function of percent sandstone for the upper Freeport mines in Preston County, West Virginia. The outer box brackets the 25th and 75th percentiles, the horizontal line is the median, the inner box represents the 95% confidence interval around the median. The two populations are statistically significantly different. Data are from diPretoro (1986).

present however, and make up 36% of the mines studied. Despite this bias toward "good" mines, we feel several observations can be made. Twelve of 13 (93%) mines with less than 20% sandstone are alkaline. Five of 8 mines with greater than 63% sandstone have net alkaline water, which is in contrast with diPretoro's findings where nearly all sites with >63% sandstone produced acidic water. A reason for this difference is that four of the alkaline, high-percent sandstone sites in the DEP/OSM study are in the Monongahela and Dunkard Groups. As Figure 8.2 shows, calcareous sandstones occur in this stratigraphic interval, but are generally lacking in the Allegheny Group. The DEP/OSM data underrepresents high percent sandstone Allegheny Group sites, because experience has shown that they frequently produce acidic drainage, thus the permits were not issued.

The data from the two studies (diPretoro, 1986; and the DEP/OSM study) have not been combined into one data set because they employed different methods of "weighting" to determine percent sandstone. Separation of the studies allows comparison of data from two adjacent, but separate areas. Both studies show that when there is a low percentage of sandstone the mine drainage is generally alkaline (Figure 8.65 and Figure 8.67). Analysis of the DEP/OSM data suggests this is not related to higher NPs in the finer-grained rocks, nor to lower sulfur in these rocks. Some of the low-percent sandstone overburden, in fact, has higher sulfur than the high percent sandstone overburden (Figure 8.68).

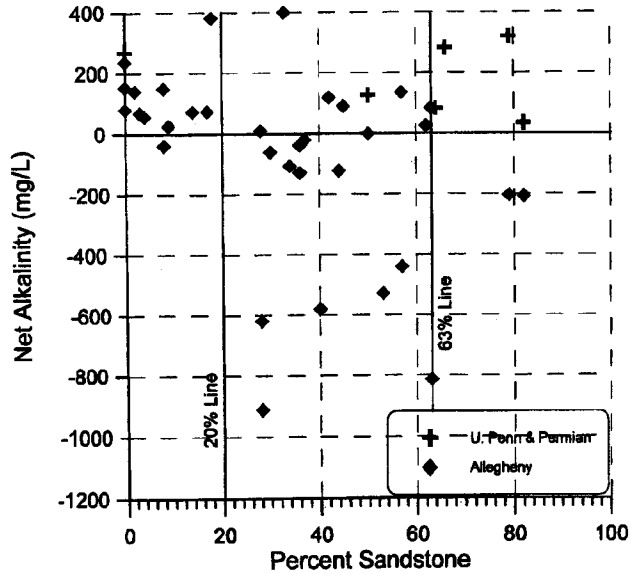

Figure 8.67 Net alkalinity as a function of percent sandstone for 41 surface mines in western Pennsylvania. Mines in the Conemaugh, Monongahela and Dunkard Groups are all alkaline, regardless of percent sandstone. Most sites with less than 20% sandstone are alkaline.

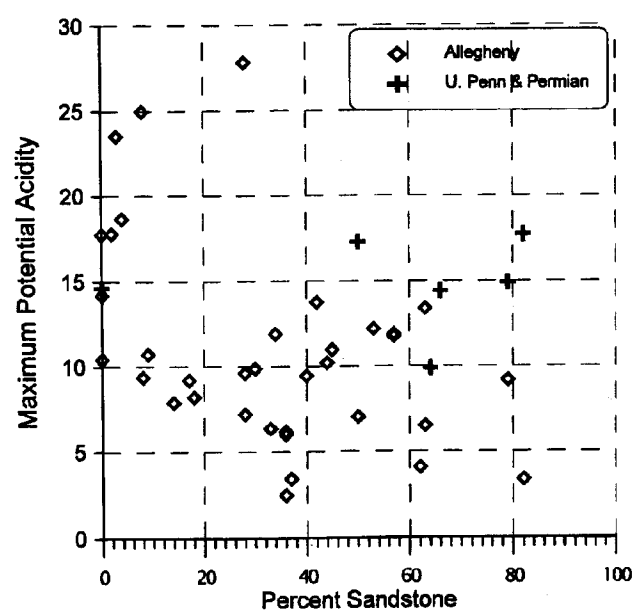

Figure 8.68 Maximum potential acidity as a function of percent sandstone. There is essentially no relationship between the two variables, with the possible exception of higher MPA at low percent sandstone. Data are from 41 surface mines in western Pennsylvania.

Also there is no relationship between net neutralization potential and percent sandstone (Figure 8.69). The finer-grained rocks would contain more clay minerals

than sandstone and these clay minerals may contribute to acid neutralization through silicate weathering, ion exchange, and adsorption of H^+ on negatively charged clay surfaces, thus better quality water.

There are probably several reasons Allegheny Group overburden with a high sandstone content produces acidic drainage. As mentioned, sandstones in the Allegheny group typically do not contain calcareous cements or minerals. This is probably related to paleoenvironmental influences that were not conducive to calcareous mineral deposition. Sandstones, which are composed largely of quartz, lack any appreciable ion exchange capacity and any ability to neutralize acid that would be generated by this process, and thus lack acid-buffering capability. Massive sandstones can have small discrete zones with high pyrite content (such as coal stringers) that may be important in acid mine drainage (AMD) generation. The importance of these zones may be missed in a sulfur analysis of the rock due to dilution of the zone by the surrounding "inert" sandstone. diPretoro (1986) suggested that low pH water generated by sandstones is favorable for AMD catalyzing bacteria, and sandstone, which during mining breaks into large blocks, allows greater permeability to air and water. The greater permeability to air by sandstone overburden is verified by Guo and Cravotta (1996). A site with blocky sandstone had a minimum O_2 in spoil gas of 18 volume percent (vol %). A second site with shale overburden had a minimum O_2 in spoil gas of less than 2 vol %. The minimum values for both sites were measured at ~10 m below the surface. Another way sandstone can affect overburden is where noncalcareous channel sandstones cut out and replace calcareous strata (Brady et al. 1988). As discussed above, the Monongahela and Dunkard Group sandstones are frequently calcareous.

Although there are certain rules of thumb regarding the relationship between sandstone and mine drainage quality, site-specific information is necessary to accurately predict water quality from a particular mine site. For example, sandstone above the lower Kittanning in Clearfield County is normally not calcareous, but some can be on rare occasions; and the sandstone above the Waynesburg coal which though situated in a dominantly calcareous part of the section is not necessarily calcareous. Sandstone and its relationship to mine drainage quality is stratigraphically specific and may be regionally specific. It would be interesting to compare the findings discussed above for the northern Appalachians with other coal-producing regions.

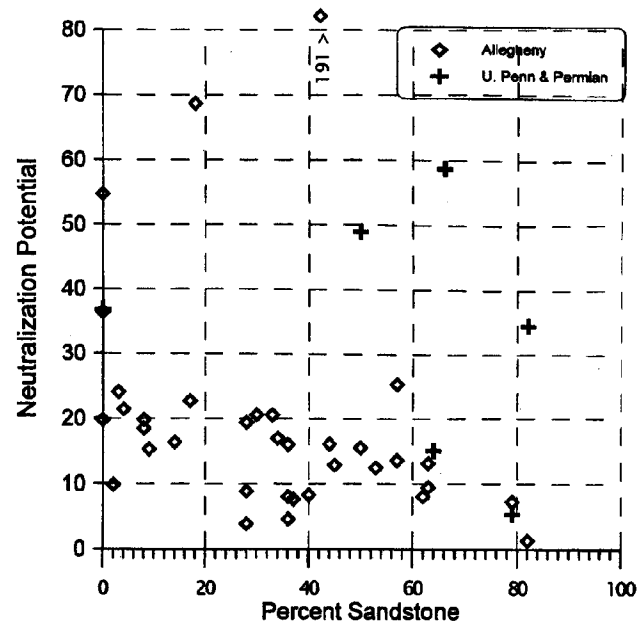

Figure 8.69 Neutralization potential as a function of percent sandstone. Data from 41 surface mines in western Pennsylvania.

Distribution of High-Sulfur Rocks

Frequently the highest sulfur strata are coals, boney coals, and other organic-rich rocks. Typically these organic-rich rocks are immediately above, below, or within a coal seam (e.g., a parting). Figure 8.49 shows sulfur content of roof and floor rocks compared to sulfur in the adjacent coal. Low-sulfur coals, such as those in the Powder River Basin and the southern Appalachians, have low-sulfur roof and floor. High-sulfur coals, such as occur in Pennsylvania and the Illinois Basin, may or may not have high-sulfur roof and floor. The sulfur in the associated rocks in some instances is higher than the sulfur in the coal.

Maksimovic and Mowrey (1993) examined the characteristics of the floor and roof materials from over 450 underground and surface coal mines across the US. The majority of immediate roof rocks were fine-grained sediments, shale, limestone, and fireclay. Sandstone only made up a minor fraction of the immediate roof rock. Sandstone was more significant a component in the main roof, making up 50% of deep mine roofs, but only 29% of surface mines. This difference may possibly be because deep mines are preferentially developed where the roof is sandstone because of more stable roof conditions, whereas surface mines may avoid areas with massive sandstone bodies because of increased mining costs. In all cases, the immediate floor is largely composed of fine-grained

sediments. The fine-grained rocks associated with the coal, whether roof rock, floor rock, or a parting, are often transitional between coal and the rock types above and below the coal. This transitional nature resulted in rocks that are high in organic matter, and probably formed in a higher pH environment than existed in the coal swamp. These conditions, as previously discussed, can be conducive to pyrite formation, since organic matter is a necessary ingredient for sulfate reduction.

The proximal relationships between high-sulfur strata, and coal or rider coal seams can be seen in virtually all the drill logs depicted in this chapter that show sulfur data. An exception to the high sulfur occurring immediately above the coal can be seen in Figure 8.13, where the highest sulfur interval occurs 3 ft (1 m) or more above the low sulfur overburden which overlies the coal. The high-sulfur zone (1.15% in A-8, 0.92% in OB-1, and 4.4% in OB-4) is associated with the brackish fossil *Lingula*. This is consistent with the work of Guber (1972) who found that shales and siltstones overlying the lower Kittanning coal containing the phosphatic brachiopod *Lingula* had higher sulfur than rocks not having *Lingula* (Table 8.11). Morrison (1988) also found on average that brackish shales had higher sulfur (2.40%) than marine (0.95%) or freshwater (0.15%) shales. Our experience confirms that brackish shales are typically high in sulfur.

Table 8.11 Contingency table of observed frequencies of *Lingula*- and non-*Lingula*-bearing rocks by three sulfur classes. The rocks are from the interval above the lower Kittanning coal, Clearfield County. Data are from Guber (1972).

Sulfur Content	Lingula-bearing	Non-Lingula-bearing	Totals
Low 0.0 - 0.5%	11	59	70
Medium 0.5 - 1.5%	49	22	71
High >1.5%	35	2	37
Totals	95	83	178

High-sulfur strata are also associated with marine shales such as the lower Kittanning and Brush Creek overburdens shown in Figures 8.11, 8.12, 8.23 and 8.24. Many of these same shales are calcareous. The top and bottom of some of these shale facies may be brackish. The thickness of high-sulfur zones in marine and brackish environments is often greater than that in the conchostracan-bearing overburden. It is important to accurately account for this high-sulfur material when designing plans to prevent acid drainage problems, and when predicting postmining water quality.

Relationships Among Mineralogy, Stratigraphy, and Regional and Local Variations in Postmining Water Chemistry

Four geologic processes account for overburden mineralogy. Two of these, paleoclimate and paleodepositional environment, date back hundreds of millions of years to the Pennsylvanian Period. The other two, surface weathering and glaciation, are more recent, occurring within the past few million years. Paleoclimate can account for the mineralogy of some terriginous rocks, but probably has little, if anything, to do with the paleodepositional controls that influenced pyrite and carbonate content of marine/brackish sediments. Weathering can reduce the original carbonate and sulfur content of rocks by dissolution and oxidation processes respectively. Glaciation can influence overburden by erosion of weathered bedrock and by the deposition of calcareous tills. The mineralogy of the rocks, particularly the presence of carbonates and pyrite, ultimately influences postmining water quality.

Importance of Carbonates

Earlier discussions argued that the calcareous carbonates are more important in controlling water quality from surface mines than is pyrite. The presence of only 1 to 3% carbonate minerals can influence whether acidic or alkaline drainage is produced (Brady et al., 1994; and Perry and Brady, 1995). The amount of sulfur present is not directly related to acid production except in the absence of calcareous strata.

Despite early recognition of the importance of calcareous strata (Leitch et al., 1932 and Crichton, 1923), most subsequent research has concentrated on studying the reactivity of various forms and features of pyrite. This seemed logical, because pyrite is required for the formation of acid mine drainage. The number of studies on pyrite reactivity is in the hundreds if one includes kinetic (leaching) tests. A few representative examples on relative pyrite activity are Caruccio's studies of pyrite morphology (1970) and trace element content (1972), Hammack et al.'s (1988) studies of pyrite origins (genesis); and Scheetz's (1992) investigations of pyrite molecular structure. Chapter 7 lists hundreds of references for various studies on "kinetic" tests. Few comparable studies have been done on the role of carbonates on mine drainage neutralization and inhibition, despite the clear role they play.

The complexity of carbonate mineralogy, with extensive solid solution substitution, and the role of this variable on resultant mine drainage chemistry is poorly

understood. It is known that the NP test (see Chapters 6 and 11) does not adequately distinguish forms of carbonates (Skousen et al., 1997b). The iron carbonate "siderite" may be temporarily alkalinity producing, but with oxidation and precipitation of the iron component, it is ultimately not alkalinity producing (Cravotta et al., 1990). Possible exceptions are where significant solid solution substitution for the iron, by Mg or Ca occur, or where siderite is mixed with a calcareous carbonate. A revised NP procedure reduces the falsely high readings for NP when siderite is present (Skousen et al., 1997b). The work by Skousen et al. is a follow-up of studies done by Morrison et al. (1990a; 1990b; 1994). The field studies by Brady et al. (1994) and Perry and Brady (1995), as well as references contained therein, suggest that not only do calcareous minerals neutralize mine drainage, but they also inhibit pyrite oxidation. Laboratory studies are consistent with these findings (e.g., Williams et al., 1982). The role of carbonate mineralogy on mine water chemistry is clearly a subject deserving more study.

Others factors, in addition to mineralogy, such as mining methods, mine site hydrology, and controls on spoil pore gas composition can also significantly influence postmining water quality. The role of these variables (and others) is discussed in Chapters 1, 3, 12, 13, 14, 15, 16, and 17.

Stratigraphic Relationships to Water Chemistry

Several studies have examined water quality as it relates to stratigraphic position of coal seams. Most surface mines in Pennsylvania have extracted coals in the Allegheny and Monongahela Groups. Table 8.12 shows comparisons of pH for upper Pennsylvanian (Conemaugh and Monongahela Groups, plus the Permian? Dunkard Group) coal mines, and the upper Allegheny and lower Allegheny Group. Two of these studies looked at water quality from deep mines in Pennsylvania four studies looked at water quality from surface mines in Pennsylvania and West Virginia, and one study included water quality from both surface and deep mines. The last line of Table 8.12 is the mine drainage quality data from Table 8.2 which have been adapted and summarized for comparison with the other studies. Samples of streams and water supply wells have been deleted from our summary.

Deep mines, as discussed in Chapter 9, can produce poorer quality water than surface mines on the same coal seam, if they are "free draining." The deep mines included in these studies are "pre-Act" and mostly up-dip mines. The study by diPretoro (1986) had the lowest percentage of alkaline sites from the upper Allegheny. This is probably because a high percentage of these sites had predominantly sandstone overburden. The DEP/OSM study and this study have the highest percentage of alkaline sites for the Lower Allegheny mines. This is probably because these studies include a bias toward sites that would produce acceptable water quality, bad permits being denied (and thus no postmining water quality). As a generality, the upper Pennsylvanian and upper Allegheny mines in Pennsylvania produce more alkaline drainage than lower Allegheny mines.

As discussed above, the water quality reflects the geologic processes that have been at work. The upper Pennsylvanian/Permian? strata has freshwater limestones and calcareous shales. The upper Allegheny, with the exception of northern West Virginia, generally has calcareous shales and freshwater limestones. The lower Allegheny is frequently marine or brackish, and

Table 8.12 Median pH from mines in the upper Pennsylvanian (Conemaugh, Monongahela, and Dunkard Groups), upper Allegheny (upper and lower Freeport, and upper Kittanning overburden), and lower Allegheny (middle and lower Kittanning, Clarion/Brookville overburden) Groups in northern West Virginia (WV) and western Pennsylvania (PA). ---- indicates data not provided.

		Upper Penn & Permian			Upper Allegheny Group			Lower Allegheny Group			
Location	Type of Mines	No. of Sites	Median pH	Percent Alkaline	No. of Sites	Median pH	Percent Alkaline	No. of Sites	Median pH	Percent Alkaline	Reference
WV & PA	Deep & Surface	40		52%	20	----	75%	17	----	29%	Bituminous Coal Research (1977)
PA	Deep	0			24	6.2	56%	31	3.3	8%	Hornberger (1985)
PA	Deep	117		30%	347	----	32%	199	----	20%	Emrich and Thompson (1968)
PA	Surface	0			26	5.7	50%	29	4.0	21%	Williams et al. (1982)
PA	Surface	6	7.0	100%	10	6.4	60%	19	6.0	52%	DEP/OSM (unpublished)
WV	Surface	16	7.1	88%	51	3.7	26%	8	2.9	11%	diPretoro (1986)
PA	Surface	18	6.8	72%	13	7.1	85%	21	4.8	52%	This study

often lacks calcareous strata. The Emrich and Thompson (1968) study also tried to look at regional trends in water quality by coal seam. They found that lower Kittanning deep mines in Armstrong and Jefferson Counties frequently produced alkaline drainage. We have found that surface mines in this same area also generally produce alkaline drainage (area of Figure 8.12), and this is discussed in Chapter 9.

A side by side comparison of Figure 8.2 and Table 8.2 (both in pocket at rear of book) shows the relationships between stratigraphic intervals and water quality of the bituminous coal region of Pennsylvania. Table 8.2 can also be compared to total sulfur and NP data of drill holes shown in Figure 8.4 through Figure 8.34, for a more detailed evaluation of the relationships between stratigraphic characteristics of specific surface mine sites and the postmining water quality of those sites. Alkalinity greater than 100 mg/L and acidity greater than 100 mg/L are shown in bold, thus highlighting water samples and stratigraphic intervals with high alkalinity and acidity. The remaining paragraphs of this section describe the relationships from the Waynesburg Formation of the Dunkard Group down to the Pottsville Group, as the data is presented in Table 8.2.

Dunkard Group - The only coal commonly mined in the Dunkard Group is the Waynesburg coal. The postmining water quality from surface mining of the Waynesburg Formation can be highly variable (Table 8.2; in pocket at back of book). The water samples of the Waynesburg interval (Table 8.2) are from D.S. Jones and P. Cestoni (1991, DEP hydrogeologists, personal communication). Samples are from a 2 x 2.5 mile (12.8 km^2) area in Greene County. Most samples were collected at the Susan Ann site, and represent water before, during and after surface mining activities. Surface mining began in 1980 and was completed in 1991. The first two samples, collected prior to mining, have alkalinity of 379 mg/L and 340 mg/L, and are from low flow seeps (<1 gpm; <4 L/min). These emanate from a small abandoned deep mine (DM-2) on the Waynesburg coal. The next two samples (Table 8.2) have acidity of 1500 mg/L and 306 mg/L. These are from low flow seeps adjacent to the sealed entry of DM-2 and were collected during mining. The fifth sample, from the same location, has alkalinity of 92 mg/L, iron of 18 mg/L and manganese of 29.4 mg/L. This sample was collected after backfilling and revegetation in 1991. The next sample in Table 8.2 is from a small underground mine (DM-1). It has an alkalinity of 142.0 mg/L and significantly lower metals concentrations then the preceding sample. The flow was ~5 gpm (~19 L/min.) The two samples labeled "F" in Table 8.2 have high alkalinity, relatively high metals concentrations and emanate from spoil. The remaining Dunkard Group samples are from tributary streams. All have alkalinity greater than 250 mg/L.

The relationship between lithology and water quality of the Waynesburg Formation is evident from a comparison of Table 8.2 to Figure 8.34. Data in Figure 8.34 are from the Susan Ann mine and a nearby site called Fox. There are significant thicknesses of calcareous sandstones, siltstones and shales with NP values greater than 50 ppt. These account for the high alkalinity concentrations in postmining water quality. There are also significant amounts of strata with high sulfur (>0.5%). These include the Cassville shale above the Waynesburg coal (e.g., 1.39% S in Fox # 3) and the high-sulfur sandstone in hole PS-3. These strata account for the high acidity and metals concentrations in some mine discharges.

Monongahela Group - The water quality of the Monongahela Group is shown in Table 8.2. The lithologic and geochemical characteristics of the Group are depicted in Figures 8.2, 8.26, 8.31 and 8.32. Freshwater limestones including the Benwood, Fishpot, and Redstone, and other calcareous strata are abundant in the Monongahela. For example, Figure 8.32 shows drill holes with thick limestones and other high NP strata associated with the Sewickley and Redstone coals. As would be expected from the abundance of carbonate strata, the water quality associated with all but the lowest part of the Pittsburgh Formation is highly alkaline with relatively low metals concentration (Table 8.2). In fact, the sample from Upper Tyrone Township, Fayette County of a spring near the cropline of the Redstone coal has an alkalinity of 626 mg/L, the highest of any samples found in DEP permit files. While the metals concentrations of this sample are relatively low, the sulfate concentration is 1440 mg/L, making it the dominant anion, rather than bicarbonate.

The abundance of carbonate strata in the overburden of the Redstone coal, along with the high alkalinity in natural background water, and the ubiquity of alkaline mine drainage associated with this seam in southwestern Pennsylvania has resulted in overburden analysis rarely being needed to make permit decisions. Thus acid-base accounting data for the Redstone are rare.

Farther east, in Somerset County, the geologic structure and stratigraphic correlations become more complex, and overburden analysis data from the Monongahela Group is more common. For example, the Blue Lick Coal is routinely mined in Somerset County. This is a split or rider of the Pittsburgh seam which is not mineable in counties to the west (Shaulis, 1993). The generally high alkalinity of the Blue Lick 3 and Krause sites (Table 8.2) are representative of the postmining water quality of the Morantown to Sewickley coal overburden in this area. Drill holes OB-A, OB-C, and OB-5 in Figure 8.26 are examples of the overburden for this interval in Somerset County.

Some active and abandoned, surface and underground mining activities on the Pittsburgh coal have produced serious acid mine drainage problems (see water samples from Allegheny and Westmoreland Counties in Table 8.2). This scenario occurs in areas where the Pittsburgh coal is mined alone (see OB-1 and OB-2, Figure 8.31). There are a few calcareous strata in these drill holes, but the high-sulfur (> 1%) shales and sandstones overlying the coal apparently overpower the calcareous strata, thus the production of AMD. This type of AMD scenario also occurs where calcareous Redstone and Sewickley strata are present, but mining does not encounter them. For instance, where deep mines only disturb high-sulfur strata adjacent to the coal, or where a surface mine disturbs only low cover strata that have had the carbonates removed by weathering. A classic example of where a remining operation was able to improve water quality by mining a greater amount of cover and thus encountering calcareous strata, and improve mine drainage quality, is the Solar site discussed in Chapter 9 (and in Skousen et al 1997a). The discharge from a large Pittsburgh deep mine improved from a pH of 2.5 prior to remining to a pH of 7.5 following remining.

Conemaugh Group - The postmining water quality of surface mines within the Conemaugh Group is shown in Table 8.2. The lithology and geochemistry of the overburden are depicted in Figure 8.24 and Figure 8.25. The earlier discussion of Conemaugh stratigraphy documented that this thick sequence of rocks is generally "barren" of mineable coals. Few coals are mined in the Casselman Formation. The only part of the bituminous region where these coals reach mineable thicknesses is in extreme eastern Somerset County. The coals that have been mined are the Morantown (which is actually a split of the Pittsburgh coal and thus in the Monongahela Group), the Wellersburg coal (Figure 8.2 and Figure 8.25), the Barton, and Federal Hill coals. The last two are rarely mineable. Postmining water quality for the Wellersburg overburden is shown on Table 8.2. The alkaline nature of the water is consistent with the calcareous nature of the overburden depicted in Figure 8.25.

The Glenshaw Formation contains several mineable coals and numerous marine and freshwater limestones (Figure 8.2). The principal coals mined are the upper and lower Bakerstown and the Brush Creek, and the water quality associated with surface mines for these coals in Somerset and Fayette Counties are shown in Table 8.2. Drill holes DH-3 and DH-12 in Figure 8.25 are from Southampton Township, Somerset County and water from the same mine is shown in Table 8.2. Three samples of lower Bakerstown pit water and two samples of upper Bakerstown pit water are included in Table 8.2. All have alkalinity greater than acidity (the most alkaline of these is 118 mg/L from a lower Bakerstown pit pool). A postmining discharge from the Stateline site has alkalinity as high as 210 mg/L and a pH of 8.1. This demonstrates that the thick calcareous strata shown above the lower Bakerstown in DH-12 and DH-13 (Figure 8.25) are capable of producing alkaline postmining water quality, despite the presence of some high sulfur coal and shale (e.g. 9.18% in DH-12). Drill holes 5 and 11F in Figure 8.25 are from nearby Brothersvalley Township. The four water samples from the Brothersvalley site are of preexisting discharges with moderate acidity and considerable manganese and aluminum concentrations. These samples were collected prior to the remining operations on the site. These water samples show that acid discharges can occur on some mines where the overburden quality is generally good (Drill Holes 5 and 11F). It is not known whether the water quality following remining improved.

The last six water samples from Conemaugh strata in Table 8.2 are from two sites in Wharton Township, Fayette County where the Brush Creek coal has been surface mined without postmining water quality problems. These samples are from the same site as Drill Holes DH-19 and OB1 in Figure 8.23.

Allegheny Group - The postmining water quality characteristics of surface mine sites in Allegheny Group strata are represented by approximately 100 samples in the bottom half of Table 8.2. The coals of the Allegheny Group are the most extensively mined seams of western Pennsylvania and consequently more is known about the relationships of the stratigraphy,

lithology, mineralogy, and postmining water chemistry of this stratigraphic interval, from published geologic reports and unpublished data in DEP permit files, than any other coal-bearing stratigraphic interval in Pennsylvania.

The areal extent of mining of the upper Freeport and lower Kittanning coals in western Pennsylvania is large. The magnitude of permit file data for this area can be estimated from DEP data bases: (1) mylar map records, (2) a computer system which tracks all permitting, inspection, compliance, and enforcement actions for all mines active since 1985, and (3) an overburden analysis database that contains rock chemistry analyses for permits issued since 1993, plus some historical records. The computer tracking system includes 1594 mines on the upper Freeport coal (from 1985 to November 1997), for a total of 339,018 permitted acres. The lower Kittanning coal was permitted for 1142 mines covering 305,187 acres (M. Klimkos, 1997, DEP, personal communication). The overburden analysis database contains 291 drill logs with chemical data for the upper Freeport overburden and 336 drill logs for lower Kittanning overburden.

The following description of upper and lower Allegheny Group water quality will be brief and broad-brush. Table 8.2 provides details for water samples from specific mine sites. The postmining water quality characteristics of some Allegheny Group surface mines has also been described in detail in Chapters 9, 10, and 18 of this book.

Upper Allegheny - There is a relationship between the stratigraphy and postmining water quality of the upper Allegheny Group (stratigraphy shown in Figures 8.2, 8.17 through 21, and water quality shown in third panel from the bottom of Table 8.2). The three freshwater limestones of the upper Allegheny (Johnstown limestone, lower and upper Freeport limestones) and associated coal, calcareous shales, siltstones, sandstones, and underclays are shown in these drill holes with relatively high NP values. Most of the water samples for this stratigraphic interval in Table 8.2 have alkalinity concentrations greater than 100 mg/L and several samples are greater than 300 mg/L. For example, the Laurel Hill # 1 and # 2 sites in Jackson Township, Cambria County are the same sites as the four drill holes shown in Figures 8.17 and 8.18, and the toe of spoil seep with a pH of 8.1 has an alkalinity of 484 mg/L. The Shero site in West Carroll Township, Cambria County, has postmining water quality with an alkalinity of ~375 mg/L. This site is in close proximity to the Fisanick site shown in Figure 8.19. The Fruithill, Witherow, Beaver # 1, and Fink/Mays surface mine sites from Clearfield County also exhibit relatively high postmining alkalinity for seeps, spoil discharges, and abandoned deep mines that are hydrologically connected to the surface mines, and in headwater tributary samples. The Nashville site in Indiana County and the Schmunk and Rennie sites from Fayette County in Table 8.2 have similar alkalinity and low metal concentrations in postmining seeps, springs, and tributary samples for the upper Allegheny Group strata. However, the Chanin, Morrison, and Stuart sites in Fayette County, particularly in the upper Kittanning coal, exhibit dramatic variations from high alkalinity to high acidity postmining discharge (Table 8.2) corresponding to facies changes where the typically calcareous overburden strata are replaced by thick channel sandstones lacking carbonate minerals. The Morrison and Stuart sites are in the same vicinity of Wharton Township, Fayette County. The dramatic difference is overburden quality is depicted in Figure 8.20 where drill holes BM-OB2F and BM-OB5F from the Morrison site possesses high NP overburden strata, while the drill holes from the Stuart site are generally lacking high NP strata, especially drill holes GBS-DH2, which is entirely sandstone overburden with total sulfur as high as 2.6%.

Lower Allegheny - The relationships between the stratigraphy and postmining water quality of the lower Allegheny Group can be determined by comparing the second panel from the bottom of Table 8.2 with Figures 8.2, 8.7, 8.12, 8.13, 8.15 and 8.39. The lower Allegheny lacks the freshwater limestones and associated calcareous shale which are characteristic of the upper Allegheny; therefore the postmining water quality of the lower Allegheny is often more acidic as displayed in Table 8.2. However, the marine Vanport limestone in the lower Allegheny Group is the thickest and most commercially significant limestone unit in the Pennsylvanian rocks of the state, and in the counties where it is of appreciable thickness (e.g. Armstrong, Butler, Clarion, Lawrence and Mercer, see Figure 8.8), high alkalinity concentrations occur in mine drainage, springs, wells and streams as shown in Table 8.2 (e.g., Graff and Wilson sites).

The water quality associated with the surface mining of the MK coal reflects the transition in stratigraphy from the lower to the upper Allegheny Group (see analyses in Table 8.2). The overburden strata between the MK and UK coals typically includes the Washing-

tonville shale overlying the MK coal which is stratigraphically the highest marine or truly brackish bed in the formation, and the Johnstown limestone underlying the UK coal, which is stratigraphically the lowest freshwater limestone in the formation. In a multiple seam mining operation having a bench for each coal, the MK pit water may have considerable alkalinity because the Johnston limestone is the dominant influence on water quality, overwhelming the acid from the acidic shales and siltstones (Figures 8.13 and 8.15).

Lower Kittanning overburden contains no true limestones. The characteristics of the overburden chemistry and postmining water quality of this stratigraphic interval are quite variable as shown in Figure 8.12 through Figure 8.15 and Table 8.2. More is known about paleoenvironmental and mine drainage quality variations for this interval than for any other coal in Pennsylvania. This is due to the large amounts of data in DEP permit files and numerous geologic studies (e.g., Williams, 1960; Williams and Keith, 1963;, Guber, 1972; Hornberger et al., 1981, 1985; Williams et al., 1982; and Morrison et al., 1990a). In some areas where the lower Kittanning overburden was deposited in a marine environment as shown in Figure 8.12, the mine drainage can exhibit appreciable alkalinity. For example, the Snyder site in Table 8.2 is the same site as drill holes OB-1 and OB-2 in Figure 8.12, and the pit water had an alkalinity of 114 mg/L, despite the presence of sulfur content greater than 1% in several shale strata. (The Snyder site is also featured in Chapter 18 of this book). Additional mine drainage data from a marine environment is contained in Table 8.2 for the Shannon site in Clarion County. The lower Kittanning overburden from brackish environments is generally characterized by black shales overlying the coal. These shales can have very high sulfur content, for example 8.34% in drill hole 560A3 in Figure 8.13. Similar holes were drilled on the Kauffman site in Figure 8.13 (e.g. drill holes OB-1 and OB-4). Comparable acidic postmining water is shown in Table 8.2 for the adjacent Betty site. Water data from the Kauffman site was not used because site reclamation is incorporating imported alkaline material, thus postmining water from it is not necessarily representative of the overburden. Additional postmining discharges with high acidity, metals and sulfate concentrations from brackish environments of the lower Kittanning are shown for the Albert #1 and Kelce sites in Clearfield County. Geologic description and water data for brackish sites in the Luthersburg area of Clearfield County are presented in Chapter 9.

Lower Kittanning overburden from a "freshwater" paleoenvironment (probably marginally brackish) is depicted in drill holes 61-B and 61-C in Figure 8.15. Postmining seeps from the Swiscambria site have moderate acidity and metals concentrations. These LK "freshwater" environment sites (also drill holes OB-1 and OB-2 in Figure 8.15), often have shales with lower sulfur contents than the marine and brackish shales, but these sites still tend to produce water with acidity greater than alkalinity. Finally, some lower Kittanning sites may have overburden strata principally comprised of thick channel sandstones. These often produce drainage with high acidity and metals (e.g., Lawrence site from Fayette County; Table 8.2).

Postmining water quality variations of surface mines on the Clarion coals are probably the most complex of any coal mined in Pennsylvania because three of the four geologic factors that account for overburden mineralogy (i.e., paleoenvironment/stratigraphy, glaciation, and surface weathering) can be operative and significant within the same county (e.g., Clarion County). The result is good and poor quality mine drainage in the same vicinity. Stratigraphic correlations and nomenclature of these lower Allegheny coals can be confusing as discussed earlier.

Often the total sulfur content of the Clarion coals and the overlying shales are high, as shown in drill holes DH23-6 (8.33%) and DH18-1 (5.92%) in Figure 8.7 and drill hole DH-4 (5.16%) in Figure 8.39. Other Clarion coal overburden analyses in DEP files (not included in these figures) commonly have total sulfur greater than 8%. Discharges with >1,000 mg/L acidity related to this type of Clarion overburden strata are common. Examples shown in Table 8.2 are the Old 40 and Zackerl sites in Clarion County, the Orcut site in Jefferson County, and the Philipsburg site in Centre County. Where the Vanport limestone is present, the mine drainage quality can be dramatically different as discussed earlier and shown in Figure 8.10.

The influence of unweathered and weathered glacial tills upon overburden mineralogy and mine drainage quality of Clarion coal surface mines is shown in Figures 8.39 and 8.60 and Tables 8.2 and 8.3. Drill hole OB-2 in Figure 8.39 from the Cousins site in Lawrence County is an example of an unweathered till zone (i.e., zone 5 in Figure 8.60) with NP values > 500 ppt $CaCO_3$. These high values are due to clasts of the Vanport limestone. The pit water sample from the Cousins site on Table 8.2 has an alkalinity concentration of 130 mg/L, while spring samples from the site

(Table 8.2) have higher alkalinity concentrations. Drill hole OB-3 - SPAG (Figure 8.39) is from the Spagnolo site shown in Table 8.3. This drill hole encounters till with several zones of NP greater than 30 ppt. This is indicative of zone 4 (oxidized, calcareous till) in Figure 8.60 and the water quality at the Spagnola site has a pH greater than 6.5 and an alkalinity of approximately 30 mg/L (Table 8.3). Most of the glacial till shown in DH-4 and DH-28 from the Pike Township site in Figure 8.39 appears to be weathered and non-calcareous (see Zones 2 and 3), but the thick Vanport limestone below the till would promote alkaline water at this site without influence from the till.

Pottsville Group - The Pottsville Group coals are generally thin and discontinuous. While generalized columnar sections of the Group show the Sharon, Quakertown and Mercer coals, the only Pottsville Group coal that is mined to any reasonable extent in the bituminous region is the Mercer coal zone. A few surface mines in Somerset County are mining a coal labeled the Quakertown but the correlations are tenuous or doubtful. Recent surface mining of the Mercer coals is largely restricted to an area of northwestern Pennsylvania including portions of Clarion, McKean, Lawrence and Mercer Counties. Since there has been so little mining activity on Pottsville Group coals, very little useful data exists. Consequently the description of the relationships between Pottsville Group overburden chemistry and water quality characteristics has been reduced to a comparison of the drill logs for two proposed mine sites that were not mined, (shown in Figure 8.6), to some background water samples from that area, plus some recent and abandoned mine drainage samples of Pottsville Group mines shown in the bottom panel of Table 8.2.

The five samples of old mine discharges for the Mercer coal site in Norwich Township, McKean County are from the same site as drill holes DH 177-1 and DH 177-9 shown in Figure 8.6. The highest alkalinity for these samples is 7 mg/L, and the highest acidity is 73 mg/L; some of these samples have nearly equal acidity and alkalinity values. The two water samples in Table 8.2 from the Mine #201 site, are from the same site as drill holes DH 201-1, DH 202-2 and DH 201-3 in Figure 8.6. These samples are background (premining) springs off the Mercer coal outcrop and exhibit similar alkalinity, acidity, and sulfate concentrations to the Mine #177 background samples described above. The four pit water samples of the Matthews site on the Mercer Coal in Mahoning Township, Lawrence County, have significant alkalinity concentrations (e.g. 206 mg/L) and relatively low metals concentrations. However, the high alkalinity is chiefly attributed to carbonate minerals in the till overburden.

The mildly acidic to highly alkaline water quality available from the recent Mercer coal sites may tend to deceive some readers because it does not represent the full range of mine drainage quality emanating from the Mercer coal zone in Pennsylvania. Therefore, the abandoned mine discharges from the Horseshoe site in Cambria County were included in Table 8.2 to represent the significant acidity and metals concentrations that are possible from Mercer coal mine discharges. The Louden (MP-29 and MP-22) and Page (MP-65) discharges are from large abandoned underground mine complexes on the Mercer coal near Altoona, PA. The Louden discharge has acidity and iron as high as 1835 mg/L and 194 mg/L respectively. The Quakertown coal pit water sample from an active surface mine in Somerset County, at the bottom of Table 8.2, is the only water sample found in DEP files for this interval.

Regional and Local Variations in Postmining Water Quality

Following is a summary of postmining water quality variations in Pennsylvania attributable to geologic factors. Regional- and local-scale variations in postmining water quality for the bituminous and anthracite mining regions are evident in data from this study and previous studies.

A bimodal distribution of coal mine drainage pH has been observed within both the bituminous and anthracite regions (Figure 8.70a and Figure 1.2, Chapter 1, for bituminous coal mine drainage and Figure 8.70b for anthracite mine drainage). Brady et al. (1997) state: "Although pyrite and carbonate minerals only comprise a few percent (or less) of the rock associated with coal, these acid-forming and acid-neutralizing minerals, respectively, are highly reactive and are mainly responsible for the bimodal distribution.... Depending on the relative abundance of carbonates and pyrite, and the relative weathering rates, the pH will be driven toward one mode or the other." Chapter 1 discusses the pH distribution for the bituminous region.

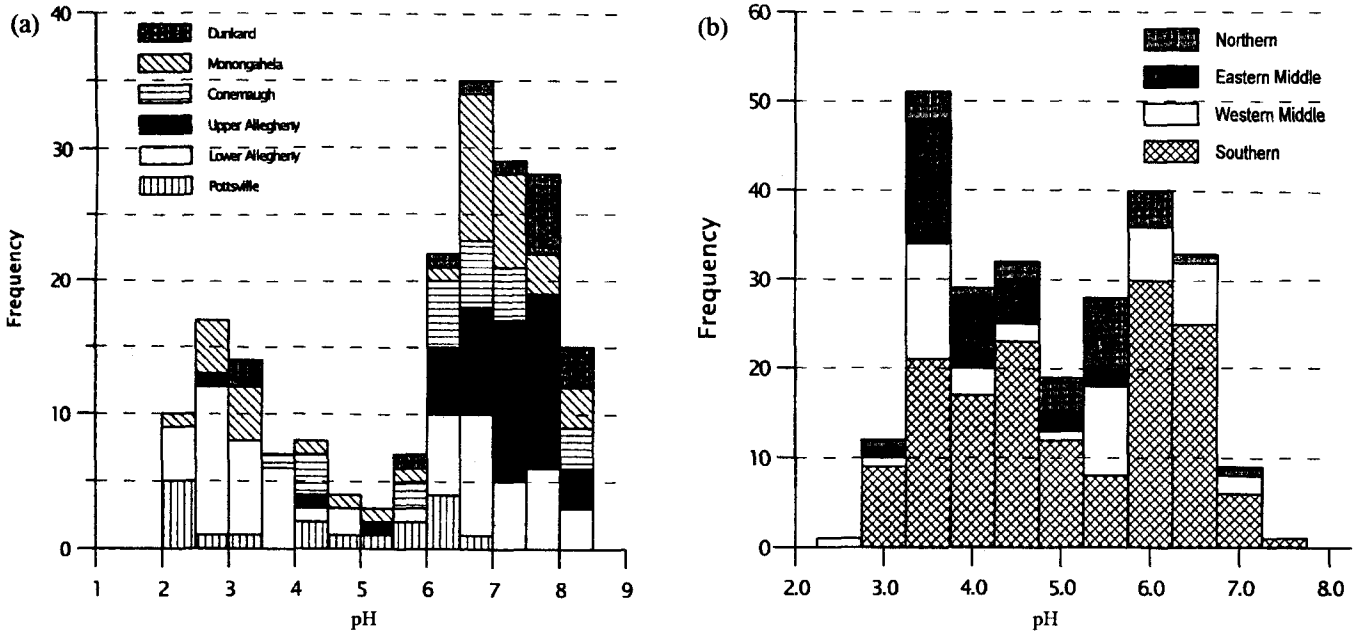

Figure 8.70a and b Bimodal distribution of pH for (a) bituminous mines and (b) anthracite mine discharges in Pennsylvania. Bituminous data are from Table 8.2 and anthracite data are from Growitz et al. (1985). Bituminous data is displayed by stratigraphic group and anthracite data by coal field.

Water Quality in the Bituminous Coal Region - The large-scale variations in water quality within the Bituminous Coal Region are principally related to the outcrop patterns of the Pottsville, Allegheny, Conemaugh, Monongahela and Dunkard Groups, and to paleoenvironmental changes of specific stratigraphic intervals at a regional scale. The large-scale water quality variations are chiefly attributable to the presence or absence of calcareous rocks. A good example of delineating mine drainage quality by outcrop area is the Monongahela Group. Surface mining most Monongahela Group seams results in alkaline drainage (an exception is acid problems from some Pittsburgh deep mines). The alkaline drainage occurs because of the abundance of thick freshwater limestones that are encountered during mining. Good examples of regional-scale paleoenvironmental variations occur within the lower Allegheny Group. Some examples are where: (1) the marine Vanport limestone is thick and overlays the Clarion coals, as opposed to areas where the Vanport limestone is absent; and (2) marine shales overlying the lower Kittanning coal to produce alkaline mine drainage, as opposed to lower Kittanning shales that are of a brackish or "freshwater" environment resulting in acidic drainage.

By comparing Table 8.2 to Figure 8.2 (both in pocket at back of book), relationships between the geology and water quality of the bituminous region can be discerned. The highest alkalinities in Table 8.2 are associated with: (1) the thick freshwater limestone sequences (e.g., the Redstone limestone) of the Pittsburgh Formation in the southwestern corner of Pennsylvania, (2) the thick marine Vanport limestone of the lower Allegheny Group in the central to northwestern area of the bituminous region, and (3) the freshwater limestones of the upper Allegheny Group (i.e., Johnstown, lower and upper Freeport Limestones) in areas where these limestones and associated calcareous shales are abundant, such as portions of Clearfield, Cambria, Indiana, Westmoreland, and Fayette Counties. In addition, significant alkalinity concentrations in Table 8.2 occur in: (1) the Conemaugh Group where the marine Brush Creek and Woods Run limestones are present, and (2) the lower Allegheny Group mines in northwestern Pennsylvania where the overburden includes significant thickness of calcareous glacial till.

The highest acidity concentrations in Table 8.2 are associated with: (1) the Clarion and lower Kittanning coals, particularly where black brackish shales and thick marine shales predominate in the overburden, such as Clarion, Clearfield, and Centre Counties, and (2) in the Pittsburgh coal and Waynesburg coals of the southwestern portion of the bituminous region, in areas where the carbonate strata are absent or lacking appreciable thickness. Significant acidity concentrations are also shown in Table 8.2 where local facies changes occur, such as in the upper Allegheny Group in areas of

Fayette County, where the channel sandstones occur instead of freshwater limestone and calcareous shales.

The medians and ranges of pH, alkalinity, acidity and sulfate concentrations of the major stratigraphic intervals of the bituminous region are shown in Table 8.13. This table has been constructed using data in Table 8.2. Most stream samples were not included from Table 8.2, unless the water reflected drainage from the mine site (e.g., headwater streams during baseflow conditions). Well samples were also deleted, unless they were monitoring wells within mine spoil. Where multiple samples of the same mine discharge point occur in Table 8.2, a median was computed for inclusion in Table 8.13. Unrepresentative premining samples were also deleted. The number of samples (N) shown in Table 8.13, is the number of mine discharge locations used to compute the medians and ranges shown.

Comparison of median pH values in Table 8.13 shows a lower pH for the lower Allegheny Group than for the stratigraphically higher strata. The median pH values for the upper Allegheny, Conemaugh, Monongahela, and Dunkard Groups are within the upper mode of the bimodal frequency distribution for pH shown in Figure 8.70a. These pH values are reflective of the importance of carbonate strata in controlling mine drainage quality. The wide range of pH values and the range of alkalinity and acidity concentrations for the intervals document that some strata within each major interval have the potential to produce alkaline and acidic drainage. The relatively higher median sulfate concentration for the lower Allegheny Group, indicates that this strata has a greater potential for acid production. That is consistent with the extreme acidity and sulfate concentrations in lower Allegheny Group samples in Table 8.2. Many of these samples are also marked by high concentrations of iron, manganese, aluminum, and sulfate.

Anthracite Region Water Quality - Regional variations in mine drainage quality of the Anthracite Region are shown in Table 8.14. The relationships between the postmining water quality and specific stratigraphic intervals of the Anthracite Region are much less well known than those of the Bituminous Region for at least two reasons: (1) the complexity of the geologic structure has impeded the acquisition of stratigraphic data from routine exploration drilling and made correlations of units and associated mine drainage difficult; and (2) a large portion of the mining hydrology of the four anthracite fields is controlled by large-volume, mine pool discharges. The mine drainage from gangways developed in multiple coal beds is commingled in rock tunnels (that crosscut the geologic structure and strata) which interconnect the mine workings. Thus discharges are often a composite water representing multiple coal seams throughout a large mine complex. Despite this, some significant regional variations in mine drainage quality are evident for the anthracite fields (Figure 8.71). These are probably related to mineralogic differences between the fields.

Some Northern Anthracite Field mine waters have significant alkalinity (e.g., Plains Borehole, Table 8.14). This may be attributable to the presence of marine and freshwater limestones and other calcareous rocks in the Northern Field. A few postmining discharges of the Northern Field have low pH and high acidity (Loomis Bank discharge), although high acidity discharges are relatively rare in the anthracite fields. Many large volume discharges of the Northern Field have circumneutral pH with nearly equal concentrations of acidity and alkalinity (e.g., Jermyn Outfall,Table 8.14). Although cirumneutral, some of these discharges have relatively high concentrations of iron, manganese or aluminum, and because of large flows they have high pollution loads.

Table 8.13 Median and range of mine drainage quality of the Bituminous Region of Pennsylvania (adapted from Table 8.2). N = number of samples.

GROUP	N	pH		Alkalinity mg/L		Acidity mg/L		SO_4 mg/L	
		median	range	median	range	median	range	median	range
Dunkard	10	7.75	3.35 - 8.03	251.5	0 - 359	0.0	0 - 903	171.3	124 - 1869
Monongahela	26	6.75	2.45 - 8.30	92.0	0 - 338	0.0	0 - 2851	481.4	39 - 2701
Conemaugh	17	6.40	3.56 - 8.10	24.0	0 - 210	5.1	0 - 168	272.0	22 - 881
Upper Allegheny	31	7.11	2.80 - 8.10	114.8	0 - 484	0.0	0 - 1290	211.0	12 - 1467
Lower Allegheny	41	4.80	2.20 - 8.10	8.0	0 - 310	43.5	0 - 10000	957.5	32 - 14000
Pottsville	15	5.60	2.20 - 7.30	2.0	0 - 206	5.0	0 - 2070	165.0	5 - 3250

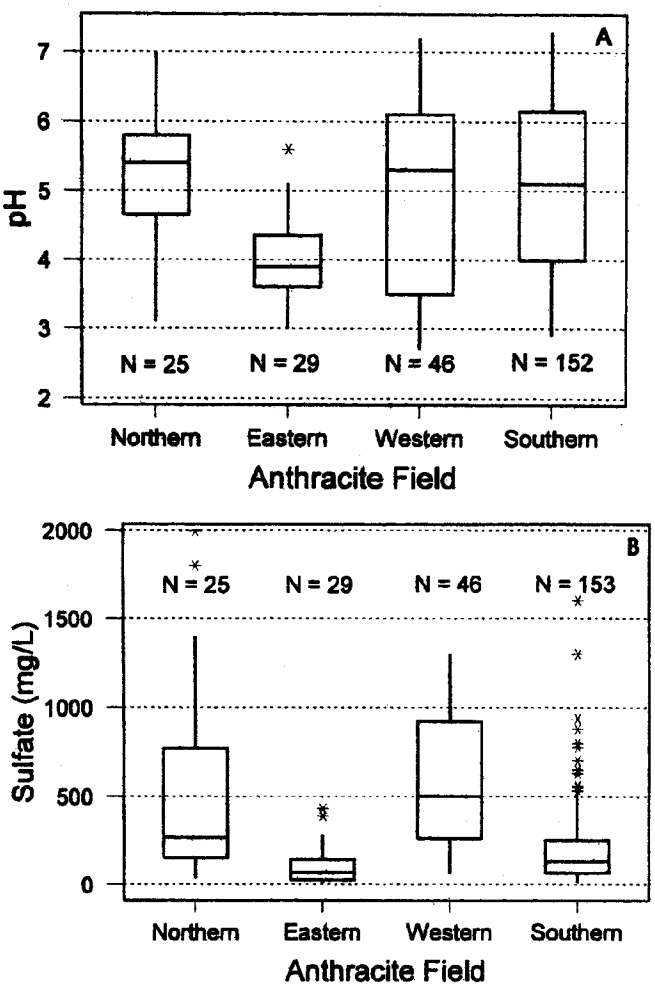

Figure 8.71 Boxplots showing differences in (A) pH and (B) sulfate for discharges from the four anthracite fields in eastern Pennsylvania. The box is bounded by the 25th and 75th percentiles and the median is represented by a horizontal line within the box. "Whiskers" and "*" (outliers) define the range. Data are from Growitz et al. (1985).

There are 14 major discharges in the Eastern Middle Field. Mine drainage from four of these are shown in Table 8.14. There is no significant alkalinity in any of the discharges. As far as is known, there are no limestones or other calcareous strata in this region. The highest alkalinity is 13.8 mg/L and the highest acidity concentration is 194 mg/L. No severe AMD (pH < 3.0, acidity > 1000 mg/L) is known in the Eastern Middle Field. The Eastern Middle Field appears to lack both calcareous rocks and high-sulfur rocks. The Jeddo Tunnel discharge, in the Eastern Middle Field, is the largest mine discharge in the state (Table 8.14), and generally has an acidity concentration >100 mg/L and a flow >50,000 gpm (>190 m^3min^{-1}). Though the acidity concentration is not "high," because of the flow the acid load is large.

The water quality of the postmining discharges of the Western Middle and Southern Anthracite Fields is somewhat more mysterious than that of the Northern and Eastern Middle Fields. Some discharges have significant alkalinity, but no carbonate stratigraphic units have been reported in these fields. The Packer V discharge in the Western Middle Field has alkalinity of 160 mg/L and iron of 20.9 mg/L in Table 8.14. The Richards discharge near Mt. Carmel has a pH of 3.7 and an acidity of 70 mg/L. Other discharges of the Western Middle Field exhibit circumneutral pH, with iron concentrations of 10.6 to 30.5 mg/L in Table 8.14. Because some of these discharges drain large interconnected underground mines spanning square miles, various anthropogenic sources may also contribute to water quality. However the North Franklin and the Doutyville tunnel discharges are located in a mostly rural area.

Several mine discharges of the Southern Anthracite Field have significant alkalinity concentrations, including the Wadesville, Eagle Hill, and Kaska discharges (Table 8.14)). In fact the water pumped from the Wadesville shaft has an alkalinity of 414 mg/L. This is one of the most alkaline mine waters found in Pennsylvania. It is almost certain that a detailed study of stratigraphy in this area would reveal calcareous strata or calcareous secondary mineralization. Several Southern Field discharges have significant acidity concentrations (Bell, Newkirk, Porter Tunnel and Markson discharge, Table 8.14). A study by C.R. Wood (1996) shows that many abandoned underground mine discharges in the anthracite fields have improved in water quality between 1975 and 1991.

A final factor that may affect the relationships between postmining water quality and stratigraphy in the Anthracite Region is the stratification of mine pool water. The mine pools consist of water accumulated in void spaces within abandoned underground mines, and deep pools or lakes in abandoned surface mines that are hydrologically connected to abandoned underground mines. These mine pools typically are chemically stratified into "top water" and "bottom water." The stratification of anthracite mine pools is discussed in Barnes (1964), Erickson et al. (1982) and Ladwig et al. (1984). Additional discussions on the areal extent, volume of impounded water, and interconnections (breeches) between mine pools are contained in a series of studies by Ash (e.g., 1949, 1954).

Table 8.14. Mine drainage quality for the four anthracite fields. N = Northern Field, EM = Eastern Middle Field, WM = Western Middle Field, and S = Southern Field

Site Name	County	Coal Field	Sample Date	pH	Alkalinity mg/L	Acidity mg/L	Iron mg/L	Mn mg/L	Al mg/L	SO_4 mg/L	TSS mg/L	Flow (gpm)
Old Forge Borehole	Lackawanna	N	11/1/85	6.0	80	12	28.0			518		
Duryea Ditch	Lackawanna	N	11/1/85	5.9	90	2	35.2			464		11,670
Jermyn Outfall	Lackawanna	N	3/22/91	6.4	10	4	1.0	0.6	0.1	150	5	8,976
Loomis Bank	Luzerne	N	2/27/95	2.6	0	760	34.0	29.2	94.6	1,975		
Hudson Anthracite	Luzerne	N	4/23/90	2.7	0	1,960	105.0	22.9	242.0	1,782	4	
Plains Borehole	Luzerne	N	3/9/94	6.5	122	0	45.1	3.3	< 0.5	491	< 3	
Alden Strip #2	Luzerne	N	7/28/92	7.1	168	7	0.9	0.3	< 0.5	628	22	
Jeddo Tunnel	Luzerne	EM	10/24/96	4.3	6	104	7.2	4.5	11.1	346	22	50,150
Owl Hole	Luzerne	EM	9/30/96	3.5	0	194	1.3	4.6	30.9	225	12	757
Oneida #3	Schuylkill	EM	12/30/96	4.7	9	26	0.1	0.3	1.1	22	< 2	7,415
Pond Creek	Luzerne	EM	2/15/97	4.7	14	10	0.2	0.5	0.4	33	4	128
Packer V	Schuylkill	WM	7/29/97	6.4	160	0	20.9	7.8	0.1	597	30	Ave= 1,200
Richards	Northumberland	WM	8/19/97	3.7	0	70	7.5	2.5	4.8	82	2	1,672
Scott Overflow	Columbia	WM	8/19/97	5.9	54	68	28.3	4.1	0.3	254	2	4,386
Stirling	Northumberland	WM	6/4/97	6.0	68	52	30.5	3.4	0.3	310	8	4,830
North Franklin	Northumberland	WM	6/10/97	5.6	26	24	10.6	2.4	0.9	287	16	2,097
Doutyville	Northumberland	WM	6/10/97	4.4	6	28	3.0	1.5	2.2	150	20	1,645
Bell	Schuylkill	S	6/18/97	3.9	0	110	11.7	3.0	9.4	294	26	75
Porter Tunnel	Schuylkill	S	12/2/81	2.8	0	802	159.0			1,056		253
Porter Tunnel	Schuylkill	S	4/24/97	3.3	0	98	14.8	3.8	4.3	267	3	4,039
Newkirk	Schuylkill	S	8/12/97	3.6	0	84	4.3	2.4	9.3	97	2	176
Goodspring #1	Schuylkill	S	9/27/95	6.2	66	0	15.2	2.5	0.0	112	6	127
Goodspring #3	Schuylkill	S	9/27/95	6.0	54	32	22.2	3.4	0.0	323	26	516
Markson	Schuylkill	S	9/27/95	3.4	0	82	18.3	5.6	1.6	491	4	844
Kaska	Schuylkill	S	8/12/97	6.3	100	0	18.7	3.0	0.2	194	6	25
Eagle Hill	Schuylkill	S	8/14/97	6.7	268	0	11.7	1.9	0.4	276	24	646
Wadesville	Schuylkill	S	5/19/86	7.1	330	0	1.9	2.6	< 0.50	1,164	14	

The top water discharges are typically of circumneutral pH, although some samples in Table 8.14 may have elevated iron, manganese, or aluminum. Top water is believed to reflect shallow groundwater systems, with relatively short residence times, where most of the flow is confined to the upper part of the mine pool. The bottom water typically has higher concentrations of acidity, metals, and sulfate than the top water of the same mine pool. Bottom waters are indicative of longer residence times, less circulation (and less oxygen). For example, the Markson and Good Spring No. 1 mine pool discharge samples shown in Table 8.14 are from adjacent collieries within the Donaldson Syncline in the Southern Anthracite Field. The mine maps of these two collieries indicate that the coal seams mined, mining engineering factors, and geologic conditions of the collieries are essentially the same; yet the Good Spring No. 1 discharge has a pH of 6.2 (and sulfates of 112 mg/L) and the Markson discharge has a pH of 3.4 (and sulfates of 491 mg/L) (Table 8.14). The Good Spring No. 1 discharge is top water and the Markson discharge is bottom water with a distinct hydrogen sulfide aroma. The samples of the Markson and Good Spring No. 1 mine pool discharges were collected on the same date in relatively low flow conditions and are within a few mg/L of the average sulfate values from five years of monthly samples.

Figure 8.71a depicts variations in the pH of mine discharges for the four anthracite fields. The Eastern Middle Field has the lowest median pH and the least variability in pH, consistent with an absence of carbonate strata. Figure 8.71b shows that the Eastern Middle Field discharges also have the lowest sulfate concentrations and the least variability in concentration. The other fields show a wider range in pH and sulfate, although the Southern Field typically has lower sulfate than the Northern and Western Middle Fields.

Local-Scale Variations in Water Quality of the Bituminous and Anthracite Regions

For purposes of this discussion, local-scale variations in geology and mine drainage quality are those which occur within a single mine site, or between adjacent mine sites, or within a relatively small geographic area. These local-scale variations are much more prevalent and explainable in the Bituminous region, although distinct differences in mine drainage quality have been reported from adjacent active underground

mines in the Anthracite region. There are at least four types of local-scale variations in geology that account for differences in mine drainage quality: (1) abrupt facies changes where freshwater calcareous strata (i.e., from a lacustrine or upper delta plain paleoenvironment) are replaced/cut out by channel sandstones, (2) more subtle facies/depositional environment changes occur where the thickness and purity of carbonate strata or the presence and thickness of high sulfur zones, within the coal seam or overlying shales, can very within a mine site, (3), weathering of bedrock which results in loss of carbonate and sulfur minerals, and (4) variations in the thickness and depth of weathering of glacial tills which result in loss of carbonate minerals.

An example of the effects of abrupt facies changes is shown in Figure 8.20 and reflected in the water quality from the neighboring Morrison and Stuart surface mines (Table 8.2). The mines extracted the upper Kittanning coal in Wharton Township, Fayette County. The calcareous overburden strata of the Morrison site is reflected in the alkaline nature of the seep (pH 7.0, alkalinity 308 mg/L and low metals concentrations). The Stuart site overburden was principally channel sandstones. The postmining seepage from this site is acidic (pH 2.8, acidity 1290 mg/L and high metals concentrations).

The more subtle local variations in facies, carbonate mineral, and sulfur content of overburden strata cannot be readily seen in Table 8.2. However the ranges and medians of acidity, alkalinity, and pH values from Table 8.2, summarized in Table 8.13, demonstrate that low pH and circumneutral pH, and alkaline and highly acidic values occur in all of the major stratigraphic groups in the bituminous region. The high acidity concentrations in generally alkaline stratigraphic sequences may appear anomalous, but they probably represent local variations where significant pyrite is present and carbonate minerals are lacking.

Geologic variability in portions of Lawrence, Venango, and Mercer Counties illustrate some of the reasons for local variations in mine drainage quality. The water quality differences result from differences in thickness and weathering depth of tills, and abundance of carbonate and sulfide minerals in till and bedrock. Mine drainage quality in Table 8.2 for the Cousins site on the Clarion coal in Hickory Township, Lawrence County show the influence of calcareous till (alkalinity of 130 mg/L in pit water), as does the Mathews site on the Mercer coal in Mahoning Township, Lawrence County (pit water alkalinity as high as 206 mg/L). This is consistent with the alkaline nature of till on the Cousins site (with NP > 500 ppt). Drill hole OB3-SPAG in Figure 8.39 from the Spagnola site in Millcreek Township, Mercer County contains a few zones with NP > 50 ppt. This calcareous overburden resulted in alkaline drainage. By contrast, the Oddfellow site in Pine Township, Mercer County, with a lack of calcareous rock, produced acidic drainage. Drill hole DH-28 from the Oddfellow mine shows thick till (and essentially no bedrock) overlying the Clarion coal, with only one zone with NP greater than 50 ppt; while DH-4 exhibits equally thick till with no zones of NP greater than 30 ppt, but the till is underlain by ~15 ft (5 m) of Vanport limestone with NP values from 920 to 956 ppt. A surface mine on the Clarion/Brookville coal with no evidence of thick till or Vanport limestone in the overburden, is the old Riddle site from Mineral Township, Venango County. An unnamed tributary to Sulphur Run receiving water from the Riddle site has a pH of 3.0 and an acidity of 240 mg/L (Table 8.2).

Worst case examples of acidity, metals, and sulfate concentrations that can be produced from Clarion coal overburden, without the benefits of Vanport limestone or calcareous tills on site, are the Old 40 and Zacherl sites in Table 8.2, located a short distance to the southeast in Clarion County. These two sites have the highest acidity concentrations of the any stratigraphic interval shown in Table 8.2. Thus, the importance of carbonates in controlling mine drainage quality is evident in both local and regional water quality for the bituminous and anthracite fields of Pennsylvania.

APPENDIX

Fossil Fauna and Paleosalinity

This Appendix proposes a revision of Williams (1960) "Environmental Faunal Classification" by reexamining the paleoecology of conchostracans, a fossil used by Williams (1960) to define freshwater depositional environments, and by adding an additional faunal group.

Williams (1960) pioneered the use of fossil fauna as a paleosalinity indicator in the Pennsylvanian of Pennsylvania. Table 8.15 is a list of faunal facies. Faunal Groups 1 through 4 are from Williams. Faunal Group 5 has been added by the authors. Faunal Group 4 was interpreted as "Fresh-water" by Williams. A reexamination of what is known about the most abundant fossil Order in Faunal Group 4, conchostracans, suggests

that this group lived in a marginally brackish, not freshwater, environment. This is important from an overburden chemistry standpoint. As discussed in the body of the text, ocean water is high in sulfate and freshwater contains very small amounts of sulfate. Sulfate, through reduction, supplies the sulfur that forms pyrite. Where sulfate is low it can limit the amount of pyrite that is formed. Thus salinity can control the amount of sulfur available for the formation of pyrite.

Faunal Groups 1 through 3 retain the same interpretations that Williams gave them. Faunal Group 1, which is often associated with limestone, was probably deposited in deeper water than Faunal Group 2. Crinoids, which are stenohaline (i.e., not tolerant of brackish conditions or variable salinity) have been added to Faunal Group 1.

Tasch (1969) has an extensive discussion on "Ecology and Paleoecology" of conchostracans. Most modern conchostracans live in "small, temporary, alkaline, inland ponds," although they have also been reported "on coastal salt flats" and "(s)ome living species are known from both fresh and brackish water environments" (Tasch, p. R146-R147). Tasch goes on to say "...living conchostracans can withstand brackish water and it is in zones of brackish-water deposits that the mixture of the fresh-water and marine [fossil] forms in question probably occurred" (p. R149). Tasch adds that "(p)resent evidence suggests transition from an original marine to a fresh water environment during the Carboniferous" (p. R149). Thus, at a minimum, Pennsylvanian conchostracans are not conclusively representative of a freshwater depositional environment, and in fact during the Pennsylvanian they most likely lived in a marginally-brackish environment.

The marginally brackish environment may have been "paralic." Paralic is defined as "pertaining to intertongued marine and continental deposits laid down on the landward side of a coast or in shallow water subject to marine invasion, and to the environments (such as lagoonal or littoral) of the marine borders" (Bates and Jackson, 1987). Skema (1997, personal communication) has suggested the term "marginally-brackish" because it infers salinity (of interest to overburden chemistry), whereas paralic infers geographic position. The evidence for conchostracans occupying a marginally-brackish environment during the Pennsylvanian, in addition to the comments by Tasch, include the following:

(1) Progressions from one paleoenvironment to another, such as those found in the rocks above the lower and middle Kittanning coals, are completely transitional. The transition is from truly marine conditions such as Williams' Faunal Group 1, which has a wide variety of marine fauna, to a more restricted fauna in Faunal Group 2, to the brackish fauna of Group 3, to the conchostracan-bearing Group 4. This transition can be lateral or vertical. The paleoenvironmental maps (Figure 8.11 and Figure 8.16) show this lateral transition. Skema (1997, personal communication) has seen conchostracan-bearing strata grade vertically into *Lingula*-bearing strata, and back to conchostracan-bearing strata.

(2) The faunal groups can interfinger laterally. An excellent illustration of this is the cross-sections in Plate 2 of Glass et al. (1977). The cross-sections show conchostracans and *Lingula* occurring at the same stratigraphic horizon above the middle Kittanning coal only a few miles (km) apart.

(3) Many of the rocks and coals associated with conchostracan fossils are high in sulfur (>0.5%). The sulfur content of the upper Kittanning, lower and upper Freeport coals and overlying strata are higher than typical for freshwater coals and sediments. This is consistent with some marine influence.

Table 8.15 Faunal groups showing typical fossils for specific depositional environments. Salinity increases downward in the table. Also shown are the carbonates that are typically associated with the rocks from these faunal groups.

Faunal Group	Index Fossils	Depositional Environment	Most Common Carbonates
5	Ostracods, *Spirorbis*, fish remains	Freshwater Lakes	Calcite, Dolomite
4	Conchostracans	Paralic with marginally brackish water	Siderite?
3	Phosphatic brachiopods (*Lingula*), and pectenids (*Dunbarella*, *Aviculopecten*), and *Orbiculoidea*	Marginal marine with brackish water	Siderite
2	Calcareous brachiopods (*Chonetes*, *Marginifera*, *Composita*)	Shallow marine with sea water	Calcite, Siderite
1	Calcareous brachiopods (greater diversity than in Faunal Group 2), cephalopods, crinoids, bivalves, gastropods	Deeper marine, with sea water and stenohaline organisms	Calcite

(4) Conchostracan-bearing rocks occur at the same stratigraphic positions as known marine horizons. This is true from at least the lowest Allegheny marine/brackish zone to the Skelly horizon of the Casselman Formation (Skema, 1997, personal communication). The Freeport roof rocks, which are entirely within Faunal Group 4 in Pennsylvania, grade laterally into marine or brackish rocks in Ohio (Sturgeon and Hoare, 1968).

(5) Convincingly freshwater deposits, such as the freshwater limestones that occur in the upper Allegheny and younger strata, have a very different suite of fossils composed of Faunal Group 5. Also, these strata can not be followed laterally into marine or brackish zones.

With the inclusion of marginally brackish environments, some marine influence is present in Pennsylvanian Period rocks in Pennsylvania from the Pottsville Group through at least the Skelly horizon of the Glenshaw Formation. The importance of this reinterpretation of Faunal Group 4 is that the higher than freshwater salinity that influenced the faunal facies would also influence the amount of sulfate available for pyrite formation. The marine influence present for Faunal Group 4 was less than that of brackish or truly marine sediments. This is reflected in the generally thinner sequences of high-sulfur strata associated with conchostracan-bearing rocks. Marginally brackish facies would be exposed to marine influence for less time, from transgressive to regressive portions of a cycle, than more fully marine sequences, and the shallower depths of water allowed for less sediment deposition. Thus the thinner zone of high sulfur rock.

Acknowledgments

This chapter has benefited from the input of many individuals. Vic Skema and Jim Shaulis, of the Pennsylvania Geologic Survey, have patiently answered numerous questions about the stratigraphy of western Pennsylvania and have generously provided unpublished data. Bob Smith, also with the PaGS, has kindly provided unpublished mineralogic data on limestones of Pennsylvania and X-ray diffraction data on rocks. Particular debt is owed to many DEP District Mining Operations hydrogeologists for contributions of data. We thank them all and in particular Joe Tarantino, Scott Jones, Tim Kania, and Dave Bisko. Steve Ebersole, Bob Weir, Michael Klimkos and Ray Roy helped with the figures. Stacy Thorne improved the manuscript in innumerable ways.

An embryonic form of this chapter began as a session for the Office of Surface Mining's Acid-Forming Materials course back in 1989. This course allowed Keith Brady to be exposed to mine water chemistry and coal geology outside of Pennsylvania. He would like to thank Ann Walker, course coordinator, for the opportunity to broaden his horizons.

We thank our reviewers Dr. Arthur Rose and Joel Morrison, Penn State University, and Viktoras Skema, Pennsylvania Geologic Survey. Your comments improved the accuracy and readability of the text. As always, any shortcomings are those of the authors.

Several figures appearing in this chapter were taken or modified from figures appearing in the International Journal of Coal Geology, Vol. 5 (1985). These include Figure 8.45, 8.46 and 8.47 and Table 8.8 which are from Cecil et al. (1985). They originally appeared on pages 210, 205, 212, and 210 respectively of that journal. Figure 8.48 appeared in Donaldson et al. (1985) on page 189 of the same journal. Climate curves used in the construction of Figure 8.44 are from Cecil et al. (1985) on page 224 and Donaldson et al. (1985) on page 189 in Vol. 5 of the same journal, and the curve from Philips and Peppers (1984) appeared on page 230 of Vol. 3 of the International Journal of Coal Geology. The above cited figures from the International Journal of Coal Geology are used with the kind permission of Elsevier Science - NL, Sara Burgerhartstraat 25, 1055 KV Amsterdam, The Netherlands.

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