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Preliminary Lithogeochemical Map Showing Near-Surface Rock Types in the Chesapeake Bay Watershed, Virginia and Maryland

By

John D. Peper[1], Lucy B. McCartan[1], J. Wright Horton, Jr.[1], and James E. Reddy[1]

[1]U.S. Geological Survey
Reston, Virginia

Prepared in cooperation with
Virginia Division of Mineral Resources
Maryland Geological Survey

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FRONTISPIECE

LITHOGEOCHEMISTRY

(On initiation of the Chesapeake Bay Watershed lithogeochemical assessment)

Resonate, my soul, with the million themes,
Of all of God's creation.
Yea!, hear the lark's clear clarion call;
The swift's singular elation.
And yet the many, and the twain,
And yea the one and only,
Are set upon life's diverse stage,
Amongst earth's verdant cacophony.
Is it by want, or is it by chance,
Or is it by one who ordains?
For simple measures, simple rules,
Identify the strains
Key-minerals' crumbling, deep 'neath our feet,
Sweeten smog-polluted rains !

J.Peper, 1997

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ABSTRACT

This preliminary experimental lithogeochemical map shows the distribution of rock types as lithogeochemical units in the Virginia and Maryland parts of the Chesapeake Bay watershed, and small flanking areas in western Maryland and eastern Virginia. Earlier studies by others in some parts of the map area have related some solute loads in ground and stream waters to some aspects of rock type. The map was produced digitally by classifying geologic-map units according to composition, mineralogy, and texture, rather than by age and stratigraphic relationships as shown on traditional geologic maps. This map differs from most lithologic maps in that the lithogeochemical unit classification distinguishes rock units with key water-reactive minerals that may induce acid neutralization, or chemical reduction, of hosted water at the weathering interface. The bulk chemical composition of these rock units, however, is independent of suggested water chemistry. The rock units are derived from geologic maps and rock descriptions. Areas of high soil carbon content, and sites of sulfide deposits (metallic ore deposits) are also shown.

Water-reactive minerals and their weathering reactions are grouped as five classes of lithogeochemical units: 1) carbonate rocks and calcareous rocks and sediments, the most acid-neutralizing; 2) carbonaceous-sulfidic rocks and sediments, likely to be oxygen-depleting and reducing; 3) quartzofeldspathic rocks and siliciclastic sediments, mostly relatively weakly reactive with water; 4) mafic silicate rocks and sediments, likely to be oxygen consuming and high solute-load delivering; and, 5) the rarer calcareous-sulfidic (carbonaceous) rocks, that may be neutralizing and reducing. Preliminary statistical testing of relationships among four of the classes of mapped lithogeochemical units and ground-water chemistry in the Mid-Atlantic area using this map, is consistent with the suggested nitrate-reducing and acid-neutralizing properties of some rock types. Additional testing of relationships among the lithogeochemical units and aspects of ground and surface water chemistry could help to refine the lithogeochemical classification of this map. The testing could also improve the qualitative and quantitative usefulness of the map for assessing aquifer reactivity and the transport properties of reactive contaminants such as acid rain, and nitrate from agricultural sources, in the Chesapeake Bay watershed.

INTRODUCTION

A preliminary lithogeochemical map (Plate 1) shows the distribution of near-surface rock types as lithogeochemical units. This map classifies and groups geologic units shown on State geologic maps of Maryland (Cleaves and others, 1968) and Virginia (Virginia Division of Mineral Resources, 1993; Rader and Evans, 1993) according to rock types and descriptions of general composition, mineralogy, and texture (Appendix 2). The design of the map is similar to that of other lithologic maps (e.g., Berg and others, 1984) except that key water-reactive mineral components of potential interest for hydrology were emphasized in the lithogeochemical classification and coloring scheme, as explained below.

The lithogeochemical unit classification for the southern part of the Chesapeake Bay watershed (see map explanation) is similar to the one applied in New England by Robinson (1997) and Robinson and others (1999), that was taken cognizance of by Grady and Mullaney (1998) in their grouping and testing of water quality samples to assess natural and human factors affecting water quality in surficial aquifers in the Connecticut, Housatonic, and Thames River

basins. Modifications to the original scheme accommodate differences in some rock types in the New England and Mid-Atlantic areas. This scheme reduces the 451 geologic map units on the state maps to only 25 lithogeochemical units. Although not shown on this map, the original geologic map-unit boundaries are retained in the database for possible future use. The correspondence of any lithogeochemical unit to the original state geologic map unit may be queried directly, at any location on the map, from the dataset.

In addition to these lithogeochemical units, a black-line overprint symbol shows areas of high soil carbon content from U. S. Department of Agriculture (1994), and a symbol shows sulfide metal ore deposits from the USGS Mineral Resources Data System (MRDS) (Mason and Arndt, 1996).

This map is intended for use by hydrologists to extensively evaluate the possible regional relationships between rock types, ground-water aquifer reactivity, and ground and surface water quality. The validity of the lithogeochemical units, however, is independent of any relationships between rock composition and water chemistry, because the units are derived from geologic maps and rock descriptions. Relationships between each lithogeochemical unit and water chemistry in the map area are generally untested at the scale of this map, except for broad categories of lithology (Langland and others, 1995; Ator and Ferrari, 1997), but some have been documented locally (e.g., Bricker and Rice, 1989; Webb and others, 1994, Bohlke and Denver, 1995; Senior, 1996), and many verified by general class of lithogeochemical unit (Table 1 on map, and McCartan and others, 1998).

Refinement of the lithogeochemical classification by geologists, in response to such testing by hydrologists, may lead to cooperative development of a geographic information system (GIS) layer for rock types for the entire Chesapeake Bay watershed. This GIS layer potentially would be more informative and useful for water-quality assessments and models than that based on the current four-fold classification (siliciclastic, carbonate, crystalline, unconsolidated) presently used in the Chesapeake Bay watershed (Langland and others, 1995, fig. 7; Ator and Ferrari, 1997, fig. 2). In addition, an existing ground and surface water simulation model for the Chesapeake Bay watershed uses geographically-referenced databases, having layers for sub-watersheds, soils, and land use, to group ground and surface water-monitoring samples according to environmental settings that may pertain to water quality (Donigian and others, 1994, 1995; Bicknell and others, 1993). Host-rock composition data, which may influence water quality, are generally lacking in the present version of that model for the Chesapeake Bay watershed.

GEOLOGIC SETTING: PHYSIOGRAPHIC PROVINCES

The physiographic provinces in the Virginia and Maryland Chesapeake Bay watershed are, from northwest to southeast: the Appalachian Plateau, Valley and Ridge, Blue Ridge, Piedmont, and Atlantic Coastal Plain (Langland and others, 1995, fig. 6). Each province has related distinctive rock types, land forms, soils, hydrogeologic settings, natural resources, and associated patterns of land use and land cover. Examples of these relationships in central Pennsylvania and northern Maryland are given in Risser and Siwiec (1996, p. 10-20).

The Appalachian Plateau is a dissected plateau of flat-lying and gently folded sandstone, shale, and limestone. Soils under mixed forest cover are mostly brown podzols of temperate climate, whereas soils on steep slopes are typically thin and stony or absent. Parts of major

valleys may be densely settled. Broad areas of table lands may be forested public land or may be extensively stripped for coal.

The Valley and Ridge is intricately folded and faulted. Forested ridges are commonly underlain by resistant sandstone. Intervening valleys are typically underlain by limestone and shale. Sandy soils are found on the ridges whereas thicker, clayey and silty soils generally overlie shales in the valleys. Farmed thin red soil overlies most of the carbonate rocks in the valleys.

The Blue Ridge, a belt of valleys and easternmost highland ridges in Maryland and Virginia, comprises a belt of gneiss, schists, and metamorphosed granitic rocks. The overall structure is that of an anticlinorium, with the oldest, highest-grade metamorphic rocks in the core, and ridge-forming stratified metasedimentary and calcareous, mafic metavolcanic rocks on the flanks. The granites and metamorphic rock weather to thick red-yellow podzol soils. Sandy colluvial fans dot the lower parts of the flanking ridges. Valleys are farmed, extensive forested uplands are public lands.

The Piedmont is underlain by highly varied metamorphic and igneous rocks, which occur in distinctive belts. Residual soils vary considerably according to parent rock types. Block-faulted Mesozoic basins trend northeastward and contain stratified shale, sandstone, arkosic conglomerate, local limestone-pebble conglomerate, and basalt flows and intruded diabase. Silisiclastic rocks weather to soils which are mostly iron- and manganese-rich sands and silts over sandstone and shale. Soils are thin clay over basalt and diabase. Land use is dominantly urban and suburban along the northeastern and southeastern edge of the province, varying to forested and agricultural land along its western and southern margins.

The Atlantic Coastal Plain surface is relatively flat and slopes gently southeastward. The province contains unconsolidated to partly consolidated river, estuary, and marine deposits: gravelly sand, silt, peat, muck, and clay. Gravelly terrace and colluvial deposits typically blanket upland parts of the interfluves. These upland flats may be current or previous extensive areas of intensive farming, particularly on the Virginia “necks” and on the Delmarva “eastern shore”.

The aquifer characteristics of ground and surface waters differ markedly in the five physiographic provinces. For example, ground water occurs primarily in fractured bedrock in the Blue Ridge and Piedmont with relatively short flow paths (< l-2 km) from recharge to discharge areas. In contrast, ground water occurs in fractured bedrock in the Valley and Ridge and Plateau with relatively longer (<2-4 km) flow paths from recharge to discharge areas. Ground water in the Coastal Plain area flows, in some cases, for long distances through a gently-seaward dipping, multilayered sediment sequence of aquifers and aquitards. These hydrogeologic settings, illustrated with aquifer maps and characteristic cross-sections, are described in Trapp and Horn (1997).

The rock types on the surface at any given location might not be the rock types of an aquifer at depth from which a well draws water. This consideration applies both to fractured bedrock and unconsolidated aquifers, and is potentially most important in the Plateau and Coastal Plain provinces, where geologic strata are nearly flat-lying. The lithogeochemical classification of subsurface units, such as those shown on cross-sections for aquifers at depth, can be found by looking at the surface expressions of the same units on the lithogeochemical map, or by looking up the geologic map unit in the table of lithogeochemical codes (Appendix 2).

PREVIOUS STUDIES RELATING ROCK TYPES AND WATER CHEMISTRY

General Statement

Previous investigations by others related local rock type to local water chemistry and suggested to us that a lithogeochemical map, such as this one, might be useful as a generalized areal overview of, and surrogate for, eH and pH of ground and stream waters. Proposed as a factor extension of existing "hydrogeomorphic regions" (HGMRs, Focazio and others, 1997, fig. 2), the lithogeochemical map might prove a more powerful areal discriminant, useful for interpreting and grouping water quality data, analyzing reactive contaminant transport, and assessing potential aquifer reactivity. For example, in southeastern Pennsylvania and Delaware, Senior (1996, p. 42-71) found that "differences among ground water in eight lithologic groups were statistically significant for specific conductance; total dissolved solids; pH; alkalinity; corrosivity index; and dissolved calcium, magnesium, chloride, nitrate plus nitrite, sulfate, silica, iron, barium, lithium, copper, and radon-222" (Senior, 1966, p. 43). Results of other investigations, discussed below, indicate that maps of rock types may be useful for regional extrapolation of local information about transport properties and fate of reactive contaminants such as acid rain and agricultural nitrate in the Chesapeake Bay watershed.

Acid Neutralization

The Virginia Trout Stream Sensitivity Survey (VTSSS, still on-going) encompassed a variety of rock types in upland, mostly forested watersheds of the Appalachian Plateau, Valley and Ridge, and Blue Ridge provinces (Webb and others, 1994). For the most part, these were small, first or second-order stream basins in areas of high relief where the small streams flowed on or near fractured bedrock and were recharged directly by ground water from the fractured bedrock aquifer. In this setting there is little opportunity for extensive bank-storage and recharge from older stream terrace or modern alluvial stream deposits. The stream-water chemical concentrations from about 70 sites were used to differentiate among waters from the different types of rocks in the catchment basin of the stream. Significant statistical differences in acid neutralization capacity (ANC) among the rock types were used to assign each rock type to one of three response classes of acid deposition sensitivity (high, medium, and low). For example, acid deposition sensitivity of a stream basin, which is equal to 1/ANC, is low for limestone and higher for siliciclastic rocks. An acid-deposition sensitivity map of the southern Appalachian region was generated from a digital lithology map by assigning rock types to the three response classes (Peper and others, 1995).

In an earlier pioneering study, Bricker and Rice (1989) related the chemistry of low-flow stream waters to catchment basin rock types in Frederick County, Maryland. Their study found that limestones in the Frederick Valley had the highest acid-neutralizing capacity (ANC), followed by Catoctin Formation metabasalt. Intervening phyllite and quartzite were shown to be more weakly reactive with acidic precipitation.

Nitrate Reduction

Preliminary evidence for regional relationships between lithology and aspects of water chemistry pertinent to acid neutralization and nitrate reduction (Langland and others, 1995; Ator

and Ferrari, 1997; McCartan and others, 1998) is limited but encouraging. Using a fourfold classification of rock types as carbonate, crystalline, unconsolidated, and siliciclastic, in a study of ground water throughout the Mid-Atlantic region, Ator and Ferrari (1997) demonstrated that nitrate concentrations in ground water are highest in carbonate rocks, followed by crystalline rocks, then siliciclastic rocks, and unconsolidated materials. They also concluded that the concentration of nitrate in ground water is related to both rock type and land cover. In a similar study of surface water throughout the Chesapeake Bay watershed, Langland and others (1995) correlated annual nutrient yields with land use, physiography, and rock type. They found that the greatest nitrate yields were from agricultural land underlain by carbonate rock.

In the Coastal Plain of eastern Maryland, Bohlke and Denver (1995) documented the local reduction of agriculturally-loaded nitrate, in shallow ground water and base-flow stream waters by unweathered glauconitic greensands in the area of the Nanjemoy Formation of the 1968 Maryland State geologic map, more recently logged locally as Aquia and Hornerstown Formations. In this area the greensands occurred near valley bottoms, and discharge to the streams was upward through weathered and unweathered greensands. It was suggested that oxygen reduction and denitrification were coupled with oxidation of pyrite, glauconite, and organic carbon in the aquifer.

Testing the Relationships between Map Units and Water Chemistry

McCartan and others (1998) describe a preliminary statistical comparison of some aspects of the chemistry of ground water in 246 shallow wells in the map area, with four of the five classes of rock types shown in Table 1. For this comparison of water chemistry with lithology, they used water chemistry data from the EPA Mid-Atlantic Integrated Assessment (MAIA) database (Ator and Ferrari, 1997, and references therein). They used this map database, identifying the location of sampled shallow wells within lithologic units on the map, and assigning the lithologic units to one of the four sampled unit classes (Table 1). Tukey tests and Kruskal-Wallis multiple contingency table analyses (Helsel and Hirsch, 1992) indicate regional-scale relations between lithology and aspects of water chemistry pertinent to acid neutralization and nitrate reduction. They considered: dissolved oxygen, pH, dissolved ammonia + organic nitrogen, nitrate +nitrite, dissolved organic carbon, calcium, bicarbonate, sulfate, iron, and aluminum. They also discuss similar comparisons of rock type with baseflow stream water chemistry with selected examples from 66 stream reaches in the map area.

CHEMICAL FACTORS IN ROCK-WATER INTERACTIONS

Chemical Reactions in the Weathering of Rocks

Rocks weather, in part, by reacting with acidic rain and ground water. Most of the acid is dilute carbonic acid from the dissociation of atmospheric carbon dioxide in solution, although sulfates and/or nitrates may be significant components of rain and fog at higher altitudes downwind from certain sources of pollution (U.S. National Park Service, 1997), or in ground water beneath agricultural and urban lands (Ator and Ferrari, 1997). Most silicate minerals are dissoluble; they alter structure and gain or lose new metal ions. Quartz, alkali feldspars, and clay minerals, and many metal oxides, are designated as resistates (relatively insoluble, and abrasion resistant). The less-soluble components of weathered rock are sand-to clay-sized residuum accumulated in situ (such as saprolite), or are transported, are sorted by grain-size, resistate characteristics, and densities; and come to rest in depositional basins. Most of the Coastal Plain

is made of the weathered remnants of the progenitors of the crystalline rocks of the Piedmont and the Blue Ridge.

Weathering, erosion, and sedimentation redistributes and reconcentrates the elements of the source rock. Silica is concentrated as resistate quartz in sand and sandstone. Alumina is concentrated in clay and shale. Iron is concentrated in hydroxylates limonite and hematite (Mason, 1958). Calcium and magnesium are dissolved.

The lithogeochemical classification scheme is designed to distinguish water-reactive mineral components of rocks. Acid neutralization reactions and reducing reactions are most important. Most rain, pH 4.1 - 4.3 (Executive Council on Environmental Quality, 1981, map, p. 284) that falls in the Mid-Atlantic region is acidic, and it contains dilute carbonic, sulfuric, and nitric acids. Natural ground waters are less acidic, as a result of the acid-neutralization reactions of water with minerals in soils and rocks. Effects of these mineral reactions may be modified or obscured by land use and human activities.

Acid neutralization is accomplished by rocks reacting with water in two important ways: a) carbonate mineral dissolution, and, b) silicate mineral dissolution which along with weathering forms bicarbonate ions (Bricker and Rice, 1989). In the general case for the dissolution and weathering of carbonate and silicate minerals by carbonic acid, hydrogen ions are consumed. Two moles of bicarbonate are produced for each mole of calcite consumed, and generally only one mole of bicarbonate is produced for each mole of species silicate consumed, thus, carbonate is the more potent acid-neutralizer.

The relevant reactions for bicarbonate productions are (Bricker and Rice, 1989):

a. $CaCO_3 + H_2CO_3 = Ca^{+2} + 2HCO_3^-$; and/or
(calcite) (acid) (solute) (bicarbonate)

b. primary silicate + H_2O + H_2CO_3 = M^{+n} + secondary silicate mineral + silica + HCO_3^-
(water) (acid) (bicarbonate)

where M is Na, K, Fe, Mg, Ca, etc.

For a specific silicate weathering example:

$2NaAlSi_3O_8 + 2H_2O + 2H_2CO_3 = 2Na^+ + Al_2Si_2O_5(OH)_4 + 4H_4SiO_4 + 2HCO_3^-$
(albite) (solute) + (kaolinite) + (dissolved silica) + (bicarbonate)

Oxygen depletion and reduction is accomplished by carbonaceous and sulfidic rocks; and possibly to some minor, but important extent by weathering of complex mafic silicate minerals (Drever, 1997). Examples of possible reactions are:

a. $(C) + 2H_2O = CO_2 + 4H^+ + 4e^-$

b. $4Fe^{+3} + 4e^- = 4Fe^{+2}$

c. $FeS_2 + O_2 + 2H_2O = Fe^{+2} + 2H_2SO_4$
(pyrite) (sulfuric acid)

d. $2Fe^{+2} + 1.5O_2 + H_2O = 2FeOOH$
(limonite)

e. primary ferrous- or ferric-iron-rich mafic silicate + water + CO_2 + O_2 = secondary silicate + silica + bicarbonate + solutes + iron oxide.

As an example of a field-tested and balanced weathering reaction of a complex mafic silicate mineral, as in e. (above), the following biotite weathering reaction was derived and restored from mass-balance considerations by Bricker and others (1968), in an intensive and

focused chemical study of stream water solutes on fresh and weathered rock in a small Maryland Piedmont catchment basin:

$$1.18K_{0.84}Mg_{1.40}Fe_{1.35}Al_{1.63}Si_{2.69}O_{10}(OH)_2 + 7.97\,H_2O + 4.29CO_2 + 0.71O_2 =$$
(biotite) + (water)+(carbon dioxide)+(oxygen) =

$$0.96\,Al_2Si_2O_5(OH)_4 + 1.25\,SiO_2 + 4.29HCO_3^- + 0.99\,K^+ + 1.65\,Mg^{+2} + 1.59\,FeOOH$$
(kaolinite) + (silica) + (bicarbonate) + (solute) + (solute) + (limonite)

Based on a similar focused chemical study of the weathering of soil hornblende in an upland forested mountain catchment basin (Cone Pond) in the White Mountains of north-central New Hampshire, Hyman and others (1998), consider $Al(OH)_3$ rather than kaolinite the resistate aluminum product, and hematite rather than limonite the stable iron oxide, and offer the following reaction:

$$(K_{0.10}Na_{0.36})(Ca_{1.90}Mn_{0.043})(Fe(III)_{0.052}Fe(II)_{1.89}Mg_{2.48}Al_{0.63}(Al_{1.09}Ti_{0.062}Si_{6.84})O_{22}(OH)_2 +$$
(hornblende)

$$10.5\,H_2O + 9.55\,H^+ + 0.47\,O_2 = 1.72\,Al(OH)_3 + 6.84\,H_4SiO_4 + 1.90\,Ca^{+2} + 2.48\,Mg^{+2} + 0.63Na^+$$
(water) (oxygen) (silica) (solutes)

$$+ 0.10K^+ + 0.043Mn^{+2} + 0.062Ti^{+4} + 0.97\,Fe_2O_3$$
(solutes) (hematite)

Note that the weathering of complex mafic silicates consumes oxygen and delivers diverse high solute loads to groundwater. The mafic-silicate-derived ferrous iron is immobilized in the stable hydroxylate mineral limonite (or in hematite), thus, these weathering reactions may deplete dissolved oxygen at the rock - water interface. In regard to nitrate reduction; the sub-oxic waters near the interface may host bacterial reducers that attack dissolved nitrate. Stripped of oxygen, the nitrogen is stabilized as N_2 gas by the nitrogen-nitrogen triple-bond. Some glauconitic sediments in the map area, classified here as mafic, have been locally associated with nitrate reduction (Bohlke and Denver, 1995). Substrates for microbial denitrification could include sulfide minerals, organic carbon, and ferrous iron in silicates or iron oxides. Possibly, ferrous iron may reduce and deplete nitrate as in laboratory experiments (J.K. Bohlke, oral communication, 1997).

Chemical Weathering in Relation to Rock Type

In Table 1, rock types on the map (see Explanation) are grouped into five classes based on their mineralogy, thus the map suggests where common reactions (discussed above) between host rocks and their contained waters are likely to be taking place. The five rock classes are: 1) carbonate rocks, including rocks and sediments that contain minor carbonate, which may be rapid acid-neutralizers; 2) mafic rocks and sediments, which may locally deplete oxygen at the weathering interface (but tested waters are well-oxygenated) and also deliver high solute loads to ground water; 3) resistate rocks, including quartzofeldspathic rocks and sediments, which are deemed least reactive with water; 4) carbonaceous-sulfidic rocks, including organic sediments, which may be important oxygen reducers; and 5) the rarer carbonate-sulfidic carbonaceous rocks, which may neutralize acid and reduce groundwater.

Two important water-rock interaction parameters are acid-neutralization capacity and solubility (Stumm and Morgan, 1981). The common calcium and magnesium carbonate rocks, limestones and dolomite, are the most readily soluble and the most acid-neutralizing (Garrels and Mackenzie, 1971; Bricker and Rice, 1989). Limestones typically form valleys or tablelands with thin, clayey residual soils. Dissolution of these rocks results in karst topography, which is

characterized by sinkholes and caves. Much less soluble, acid-neutralizing, mafic silicate minerals such as glauconite, biotite, hornblende, and calcium pyroxenes, weather to yield calcium, magnesium and iron ions. Coarse-grained nonmarine sediments, of the Atlantic Coastal Plain, that are composed of relatively insoluble, resistate minerals such as quartz and feldspar, and metal oxides, may have little capacity to influence water chemistry. However, marine sediments that contain carbonate shell fragments or cement have a greater capacity to neutralize acid waters by dissolution.

Primary and secondary porosity, permeability, grain size, and texture of rocks and minerals affect surface area of rock exposed to water. These influence the rates of hydrochemical reaction and weathering. Fractures, fissility, bedding, and other foliation are surfaces of porosity and permeability that enhance weathering and dissolution. Massive plutonic rocks have lower porosity and permeability with less surface area for hydrochemical reaction than schists, gneiss, and bedded sedimentary rocks.

Reducing environments are likely to be significant sites of chemical reaction. The separation of closely-related chemical elements in the upper lithosphere by oxidation-reduction processes in solution and redeposition is discussed by Mason (1958, p. 160-166) and Drever (1997, p. 159 - 174). Common near-surface reducing environments, and the lithogeochemical codes of rock units associated with these environments, are: 23s, 24s, 32s, 75, the black-line overprint, and greensand, 77. Iron and other metals can be mobilized by organic acids and in oxygen-depleted reducing environments. Wet humic soils and carbonaceous sediments and rocks offer reducing, acidic environments, which in some cases precipitate sulfides. These reducing environments may trap phosphate, vanadium, uranium, selenium, and copper in and near organic accumulations in sediments, black shales and slates, carbonaceous-sulfidic schists, and coals (Mason, 1958). In general, those metals and semimetals whose oxides are soluble (e.g., U, S) in well-oxygenated waters are precipitated from the reduced waters, whereas those metals whose oxides (e.g., Fe, Mn) are insoluble in well-oxygenated waters, may dissolve in oxygen-depleted reduced waters.

Carbonaceous-sulfidic siltstones, shales and schists, peat, coal, and organic muds are most likely to yield reduced, oxygen-poor water.

MAP CHARACTERISTICS

This lithogeochemical map shows the chemical, lithologic, and mineralogic character of near-surface bedrock and unconsolidated sedimentary deposits in the tributary watershed basins that drain to the Chesapeake Bay in Maryland and Virginia. The map was produced as an aid to grouping water quality analyses for ecosystem studies. It may be used as a base for hydrogeologic modeling of nitrate transport within catchment basins of streams flowing to the Bay. It identifies rock units that, upon weathering, may neutralize acid and/or result in reducing conditions. The reducing conditions may lead to the reduction and elimination of nitrate in ground water. The map provides a generalized areal surrogate for pH and Eh, that is potentially useful for ecosystem studies, for grouping water analyses, and for the appraising, testing, and modeling of relationships between rock types and water chemistry (Peper and others, 1997, Peper and McCartan 1997, McCartan and Peper, 1997, McCartan and others, 1998).

Rock types, as depicted on the map, may influence ground and surface water quality in several ways, through chemical weathering reactions and mineral and rock solubility characteristics. Soluble carbonate rocks, and rocks containing minor carbonate, may strongly buffer ground water and neutralize acid (Stumm and Morgan, 1981; Drever, 1997, Chapter 3).

Other rocks, such as the rarer calcareous carbonaceous-sulfidic rocks, and the more abundant carbonaceous-sulfidic rocks (black shales, slates, and schists, and organic coals, peat, and muds) may produce a reducing environment (Mason, 1962, Figure 33, p. 165) resulting in reduced, oxygen-depleted ground water. A reducing environment may immobilize metals (Garrels and Mackenzie, 1971), yielding sub-oxic and anoxic waters that favor bacterial reduction, and inorganic reduction of nitrate (Lovely and others, 1994). Mafic rocks are richer in iron, magnesium, and calcium; and are more readily soluble than the relatively non-reactive and resistant quartzofeldspathic rocks. The solubility of these mafic rocks may allow higher solute loads to enter ground and surface waters. Physical characteristics of rock types other than mineralogy and chemical composition affect rock solubility and susceptibility to weathering. These include degrees of induration and consolidation, primary or secondary porosity and permeability, grain size and texture, character of bedding or layering, and structural fabrics such as metamorphic foliation.

In order to help the reader identify the major rock chemical compositional classes, colors on the map depict general rock composition. Carbonate and calcareous rocks are in shades of blue (units 11, 12, 32c, 41c, 50c). Carbonaceous and sulfidic rocks and sediments are in shades of red (21cs, 23s, 24s, 31s) or orange (32s, 75) A black-line overprint shows carbon-rich soils. Non-calcareous mafic rocks and sediments are in greens (42, 43, 77) or yellow-green (41). Quartz-feldspar rich rocks and sediments, with few mafic or calcareous minerals or materials, and little organic content, are shown in shades of yellow, tan, and brown (22, 32, 33, 34, 61, 61v, 62, 73, 74, 76). A general discussion of major elements and trace elements in rocks in the mid-Atlantic region is given in Appendix 3.

CLASSIFICATION OF ROCK TYPES

Grouping of Map Units

The Explanation of Map Units (on Plate 1) shows the classification of dominant rock types. Table 1 groups the rock types into key reactive-mineral component classes. Appendix 2 shows the individual code assignment of each unit on the original State geologic maps. Three major rock type groups include: (I) sedimentary rocks and metamorphic equivalents, (II) igneous rocks and metamorphic equivalents, and (III) unconsolidated sediments. The rock units are numerically coded on the map. The words rock types, rock units, etc. is used herein to refer to rocks and sediments. Map units coded by letter symbol indicate key water-reactive minerals in the rock, and, specifically, if the rock is calcareous (c), carbonaceous-sulfidic (s) or calcareous-carbonaceous-sulfidic (cs). Calcareous rocks are acid-neutralizing and carbonaceous-sulfidic rocks generate reducing conditions; calcareous-carbonaceous-sulfidic rocks may do both (Garrels and Mackenzie, 1971; Stumm and Morgan, 1981; Bricker and Rice, 1989; Webb and others, 1994; Bohlke and Denver, 1995; Langland and others, 1995; Senior, 1996; Ator and Ferrari, 1997; Drever, 1997).

Sedimentary Rocks and their Metamorphic Equivalents

Carbonate-rich rocks

Carbonate-rich rocks are very soluble, acid-neutralizing rocks (Stumm and Morgan, 1981). Limestones (11) and dolomites (12) form valleys in the Valley and Ridge province, and underlie tablelands and are cliff-formers in the Plateau province. Limestone-pebble

conglomerate (11) is locally present in part of the Mesozoic Culpeper basin of northern Virginia. Narrow valleys underlain by marble (12) are present in the eastern Maryland Piedmont.

Siliciclastic sedimentary rocks

Clastic sedimentary rocks include siliceous-aluminous and siliceous rocks. These rocks range from sandstone, feldspathic sandstone, and conglomerate (22) and gray calcareous mudstone and shale (21cs), to black shale (23s), and the coal-bearing sandstone intervals (24s). Carbonaceous-sulfidic (s), and calcareous-sulfidic (cs) units are identified.

Metamorphosed clastic sedimentary rocks

Metamorphosed clastic sedimentary rocks (30's), consisting of metamorphosed siliceous-aluminous, clastic sedimentary and volcaniclastic rocks, including schists, quartzites, and paragneisses. These rocks are listed in approximate order from fine-grained to coarse-grained. Carbonaceous-sulfidic (s), and calcareous (c) units are recognized.

Igneous Rocks and their Metamorphic Equivalents

Mafic and ultramafic rocks

Mafic rocks (40's), include metavolcanic rocks such as greenstone and metabasalt (41c), and metamorphosed plutonic rocks such as metadiabase and minor metagabbro . These rocks tend to be slightly calcareous where they have been metamorphosed under greenschist-facies metamorphic conditions, because of metamorphic reactions that convert calcic plagioclase to albite + quartz + calcium carbonate + epidote minerals. The carbonate minerals occur as disseminated grains and as fracture-filling veins. Studies indicate that greenschist-facies mafic metavolcanic rocks of the Virgilina Formation buffer groundwater in the southern Virginia Piedmont (LeGrande, 1960), and that those of the Catoctin Formation in the Maryland and Virginia Blue Ridge neutralize and buffer stream water (Bricker and Rice , 1989; Webb and others, 1994). Amphibolite-facies mafic rocks (unit 41), such as hornblende-plagioclase amphibolite, typically contain little carbonate. Mafic plutonic rock masses, gabbro, diorite, diabase (unit 43) are generally not calcareous, except locally where minor carbonate has formed by hydrothermal alteration or by metamorphic reactions. Mesozoic diabase, although massive and unmetamorphosed, commonly contains secondary carbonate minerals along fractures and in veins.

The metamorphic equivalents of ultramafic rocks (50's), such as talc schist, in most cases contain grains and veins of secondary carbonate minerals and are slightly calcareous (50c). Drever (1997, p. 279-280) discusses the high pH characteristic of waters from some ultramafic rocks.

Felsic rocks

Felsic rocks (the 60's series) include the felsic plutonic rocks, granites and granitoids, and the very fine-grained felsic volcanic rocks (61v, not in map area), and the relatively quartz-free alkalic syenitic rocks (62, not in map area). These rocks are mostly mixtures of quartz and feldspars, and have little mineral content that would buffer or reduce water.

Unconsolidated Sediments

Unconsolidated sediments (70's) occur as thick deposits in the Atlantic Coastal Plain Province of Virginia and Maryland. Unconsolidated surficial deposits, such as those along flood plains and river terraces, in other geologic provinces, are not shown on this map because they are not shown on the State maps from which the units were derived. For example, insoluble and resistate lag quartzose gravels of former higher river channels form minor patchy accumulations in the Piedmont. These quartzose lag gravels (currently unmapped) cap denuded and saprolite-covered bedrock in conical hills in the Piedmont. These resistate deposits do not interact much with water. They may form locally important surficial aquifers, but are thin.

Unit 71c (not on map) includes carbonate-rich (>15% carbonate) sediment containing grains of such minerals as calcite, dolomite, and ankerite. Also included are unconsolidated to poorly consolidated shell beds in sandy or muddy marine sediments. The abundance of carbonate suggests that these units would most effectively neutralize hosted acid water.

The mineralogy of units 72 (not on map), 73, and 74 suggests that they may be the least likely rock types in this series to buffer acidity or alter redox states of hosted waters. Unit 72 includes sand with more than 15% feldspar. These sands are generally most abundant south of Washington, D.C., where they are classified as 76 because of the abundance of clay in most samples and the abundance of coarse clasts (gravel) in many samples. Unit 73 includes sediment with more than 15% clay particles.

Much sediment is fine sand, silt, and clay, with minor sand coarser than medium grained. Many Coastal Plain marine formations include at least a few thin intervals characterized by this fine texture and these present a potential barrier to ground-water flow. Only a few geologic formations, however, are dominated throughout by this fine texture. Unit 74 contains mixtures of quartz silt, sand, and gravel, a weathered residuum from which iron and carbonate have been removed. This is typical of the upper weathered part of most upland gravel deposits, which cap many upland terraces of southern Maryland and the high ground of the peninsulas (“necks”) of Virginia.

Geologic materials in unit 75 have high organic content. Low Quaternary terraces in Virginia (State Map unit Qt) are currently assigned to unit 75. One marginal marine formation, the Shirley Formation of Virginia, at an altitude of 35 - 45 feet along the James, York, and Rappahannock Rivers, contains a significant amount of organic plant material and might alternatively be classified as 75 but is currently classified as 76. Sediments similar to unit Qt of the Geologic Map of Virginia (Virginia Division of Mineral Resources, 1993) occur in Maryland but are not delineated there on geologic maps. Other units of high organic content are shown by black-lined overprint designating areas of high soil carbon content from the STATSGO database (U.S. Department of Agriculture, 1994). The overprint delineates significant areas of organic-rich swamp, bog, and marsh sediment and peat, and is a separate digital layer for the map. The organic-rich sediments in these areas, and in unit 76, reduce, de-oxygenate, and contribute to the bacterial denitrification of hosted waters, according to preliminary tests discussed above.

Unit 76 includes significant proportions of both sand and gravel, and silt and clay, and in addition may have some organic material.

Units 77 and 77f (not on map) are greensand and clayey greensand respectively. They contain glauconite, a clay-like iron-rich mafic mineral, and pyrite, which is iron sulfide. Glauconite and pyrite may influence water chemistry by dissolution or oxidation, and may generate substrates with sub-oxic and anoxic conditions. Weathered greensands are documented examples of denitrification and reduction (Bohlke and Denver, 1995). Two marine formations on the state maps, the Aquia and Nanjemoy (mapped as unit 77), are glauconitic, and also contain quartz sand and silt,

and various detrital clay minerals and minor pyrite. The Calvert and Choptank Formations, currently represented by lithogeochemical unit 73, are identified by dispersed glauconite, or glauconite restricted to a few beds.

Carbonaceous and Sulfidic Rocks

In the classification scheme the letter "s" designates rocks that contain iron sulfide and carbon. The sulfide was fixed under reducing anoxic conditions by interaction with biomass, both in modern wet humic soils or ancient deep basins. Water in modern bog sediments, and in black carbonaceous-sulfidic coals, shales, mudstone, slates, and schists can be reducing, oxygen-starved, and may be moderately to strongly acidic (Garrels and MacKenzie 1971, p. 140 - 142; Pettijohn, 1956, p. 622; Mason, 1958, p. 160 - 166). Water hosted by these carbonaceous-sulfidic rocks and sediments in the southern part of the Chesapeake Bay watershed is oxygen-poor, with no nitrate, high dissolved organic carbon, and high dissolved iron (McCartan and others, 1998).

Modern accumulations of organic-and sulfide-rich sediments occur in wet humic bogs and fluvial deposits. They form narrow deposits along major streams through the Piedmont uplands. In the Virginia and Maryland tide-water area, organic- and sulfide-rich sediments occur as swamp, marsh, and bog deposits. These form extensive deposits in the lowland areas of the Delmarva peninsula along the southeast side of the Chesapeake Bay. As fine-grained organic-rich sediments in the subsurface they may locally act as screens and nitrate eliminators for nitrate-laded waters recharged from adjacent agricultural fields and later discharged to the bay. Hosted waters may have sub-oxic dissolved oxygen concentrations of 1mg/L or less, and no detectable nitrate (Speiran and others, 1998, Fig. 2; and Speiran 1996; Focazio and others, 1993; Reay and others, 1992). Similar patterns of nitrate reduction and elimination were noted in studies by Michael J. Focazio, (oral communication, 1997) in association with peat and organic material (unit 75) in low terraces south of the Norfolk area in Virginia. As mentioned above, and shown in the map explanation, many of these areas are shown on the lithogeochemical map by the black- line overprint, based on high soil-carbon content.

Sulfide Mineral Deposits

Metal sulfide mineral deposits, historical mines, and notable metal sulfide occurrences are too small to show as map units, but are shown as a box with central dot on the map (Mason and Arndt, 1996). Many of these symbols are concentrated in an area of predominantly mafic volcanic and plutonic rocks of the central Virginia Piedmont (Pavlides, 1981; Pavlides and others, 1982). The extent to which these individual metal sulfide occurrences, and their mine tailings, act as sources of metal-pollution, and spawn iron-rich, acidified and reduced, surface and ground waters is beginning to be studied (Dagenhart, 1980; Krishnaswamy, 1996; Seal and Wandless, 1997; Seal and others, 1997).

POTENTIAL MAP APPLICATIONS

This map of the Maryland and Virginia part of Chesapeake Bay watershed is intended to be used by hydrologists to test spatial relationships between rock types and water chemistry. The map may be used to evaluate the hypothesis that lithology of rocks and sediments significantly influences the chemistry and quality of waters traveling over and through them on a regional scale. To test this hypothesis, hydrologists in the Chesapeake Bay region could compile existing

ground-water chemical data, from water wells and ground water databases, to compare these data to the map units, specifically to infer nitrate loading to streams. Such comparisons would test the validity of this map and suggest modifications. A map of rock types could then be extended geographically to encompass the entire Chesapeake Bay watershed, including parts of West Virginia, Delaware, Pennsylvania, and New York, in addition to Virginia and Maryland. Ultimately, a digital GIS layer on rock types for the entire watershed could be applied to improve the " hydrogeomorphic units" ("HGMR's", Ator and Ferrari, 1997) presently used in assessments and models for water quality and ecosystems of the Chesapeake Bay watershed.

LIMITATIONS OF THE MAP

Regional water quality patterns can be related in part to the distribution of rock types, so this map (Plate 1) contains potentially useful information, if users are aware of the map's limitations. The map has not been systematically tested lithogeochemical unit by lithogeochemical unit. The map was compiled from State geologic maps at scales of 1:500,000 (VA) and 1:250,000,(MD). Map unit codes are shown in Appendix 2. Detail is limited to those scales and should not be interpolated to greater detail. Additionally, some units are mapped differently in the two states based, in part, on regional variations in lithology or metamorphic grade. In general, the lithologic coding of units is internally consistent within each state, and State-line discrepancies are minor.

The lithogeochemical map portrays near-surface bedrock and major unconsolidated deposits, so small surficial deposits that contain transported materials different from the underlying unit could potentially influence water chemistry in ways not discernible from the map. Most surficial deposits in the map area are residual saprolite and soils derived locally from weathering of the underlying bedrock, except for flood-plain and terrace deposits along the rivers.

The map is based on generalized descriptions of geologic map units, which commonly consist of more than one rock type interlayered or otherwise mixed. Lithologic heterogeneity, unresolved at the scale of regional geologic maps could misrepresent the local lithology and water chemistry at individual sites in ways that cannot be explained by a regional-scale map. The map does not take into account that water may be contained in, and react with, more than one host rock along a given flow path. Nor does it take into account how the chemistry along ground-water flow paths, as in mineralized fractures for example, may differ from the overall chemistry of the rocks. Furthermore, even the smallest watersheds may contain more than one host rock unit, so that waters flowing through the different units may become mixed.

More comprehensive, quantitative testing for spatial correlations and relationships between lithogeochemical units and water quality need to be done in the context of non-geologic variables such as land use. Suggested approaches include statistical principal-component analysis and cluster analysis using the MAIA (= USGS, Water Resources Division, National Water Quality Assessment Program, NAWQA) data set, statistical analysis using Maryland and Virginia State well-water data sets, and targeted networks of new ground water samples accompanied by local studies of flow paths and processes of specific rock-water interactions.

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REFERENCES CITED

Ator, S.W., and Ferrari, M.J., 1997, Nitrate and selected pesticides in ground water of the Mid-Atlantic region: U.S. Geological Survey Water-Resources Investigations Report 97-4139, 8 p.

Berg, T.M., Sevon, W.D., and Abel, Robin, 1984, Rock types of Pennsylvania: Harrisburg, Pennsylvania, Pennsylvania Bureau of Topographic and Geologic Survey, scale 1:500,000.

Bicknell, B.R., Imhoff, J.C., Kittle, J.L., Jr., Donigian, A.S. Jr., and Johanson, R.C., 1993, Hydrologic Simulation Program - FORTRAN, User's Manual for release 10, EPA/600/R-93-174, U.S. Environmental Protection Agency Environmental Research Laboratory, Athens, GA.

Bohlke, J.K., and Denver, J.M., 1995, Combined use of groundwater dating, chemical, and isotopic analyzes to resolve the history and fate of nitrate contamination in two agricultural watersheds, Atlantic Coastal Plain, Maryland: Water Resources Research, v. 31, no. 9, p. 2319-2339.

Bricker, O.P., Godfrey, A.E., and Cleaves, E.T., 1968, Mineral-Water interaction during the weathering of silicates, in Baker, R.A., ed. Trace Inorganics in Water, Advances in Chemistry Series 73: American Chemical Society, Washington, D.C., p. 128 - 142.

Bricker, O.P., and Rice, K.C., 1989, Acidic deposition to streams: Environmental Science and Technology, v. 23, no. 4, pp. 379 -385.

Cleaves, E.T., Edwards J., Jr., and Glaser, J.D., compilers, 1968, Geologic map of Maryland: Maryland Geological Survey, scale 1:250,000, 1 sheet.

Colton, G. W., 1970, The Appalachian basin - its depositional sequences and their geologic relations: in, Fisher, G.W, Pettijohn, F.J., Reed, J.C., Jr., and Weaver, K.N., eds., Studies of Appalachian Geology: Central and Southern: New York, John Wiley and Sons, Interscience Publishers, p. 5 - 48.

Dagenhart, T.V., 1980, The acid mine drainage of Contrary Creek, Louisa County, Virginia: Factors causing variations in stream water chemistry: Unpub. M.Sc. thesis, University of Virginia (Charlottesville), 215 pp.

Donigian, A.S. Jr., Bicknell, B.R., Avinash, S.P, Linker, L.C., and Chang, C.H., 1994, Chesapeake Bay Program -- Watershed model application to calculate Bay nutrient loads: U.S. Environmental Protection Agency, Chesapeake Bay Program, 282 p.

Donigian, A.S., Jr., Bicknell, B.R., and Imhodd, J.C., 1995, Hydrologic Simulation Program -- Fortran (HSPF): [in] Computer Models of Watershed Hydrology, V.P. Singh, (ed), Water Resources Publications, Littleton, CO, p. 395-442

Drever, J. I., 1997, The geochemistry of natural waters; surface and groundwater environments (third edition): Upper Saddle River, New Jersey, Prentice-Hall, 436 p.

Epstein, J.B., 1993, Stratigraphy of Silurian rocks in Shawangunk mountain, southeastern New York, including a historical overview: U.S. Geological Survey Bulletin 1839 - L, 40 p.

Epstein, J.B., Orndorff, R.C. and Rader, E.K., 1995, Middle Ordovician Stickley Run Member (New Name) of the Martinsburg Formation, Shenandoah Valley, Northern Virginia: U.S. Geological Survey Bulletin 2135, p 1-13

Executive Council on Environmental Quality, 1981, Environmental Trends: Washington, D.C., U.S. Government Printing Office, 346 p.

Focazio, M.J., Speiran, G.K., and Rowan, M.E., 1993, Quality of ground water in the coastal plain physiographic province of Virginia: U.S. Geological Survey Water-Resources Investigations Report 92 - 4175, 70 p., 5 plates

Focazio, M.J., Plummer, L.N., Bohlke, J.K., Busenburg, Eurybiades, Bachman, L.J., and Powars, D.S., 1997, Preliminary estimates of residence times and apparent ages of ground water in the Chesapeake Bay watershed, and water-quality data from a survey of springs: Water-Resources Investigations Report 97 - 4225, 75 p.

Froelich, A.J., 1985, Geology of the Culpeper Basin, Virginia and Maryland: U.S. Geological Survey Miscellaneous Investigation Series Map I - 1313 - E, scale 1:125,000.

Garrels, R.M., and Mackenzie, F.T.,1971, Evolution of Sedimentary Rocks: New York, W.W. Norton and Company, Inc., 397 pp.

Grady, S.J., and Mullaney, J.R., 1998, Natural and human factors affecting water quality in surficial aquifers in the Connecticut, Housatanic, and Thames River Basins: United States Geological Survey Water-Resources Investigations Report WRI 98 - 4042, 86 p.

Helsel, D.R., and Hirsch, R.M., 1992, Statistical methods in water resources: New York, Elsevier Science Publishing Company, Inc., 522 p.

Hyman, M.E., Johnson, C.E., Bailey, S.W., April, R.H., and Hornbeck, J.W., 1998, Chemical weathering and cation loss in a base-poor watershed: Geological Society of America Bulletin v. 110, no. 1, p. 85 - 95.

Krishnaswamy, R., 1996, The geochemistry and ecology of a phyco-microbial metal sink: potentials for environmental bioremediation of acidic heavy metal laden leachate from a pyrite mine, Contrary Creek, Louisa County, Virginia: Unpub. M.Sc. thesis, George Washington University (Washington, D.C.), 156 pp.

Lakin, H.W., and Davidson, D.F., 1973, Selenium, in, Brobst, D.A., and Pratt, W.P., eds., United States Mineral Resources: U.S. Geological Survey Professional Paper 820, p. 573 - 576.

Langland, M.J., Leitman, P.L., and Hoffman, Scott, 1995, Synthesis of nutrient and sediment data for watersheds within the Chesapeake Bay drainage basin: U.S. Geological Survey Water-Resources Investigations Report 95-4233, 121 p.

Lee, K.Y., and Froelich, A.J., 1989, Triassic-Jurassic stratigraphy of the Culpeper and Barboursville basins, Virginia and Maryland: U.S. Geological Survey Professional Paper 1472, 52 p.

LeGrand, H.E, 1960, Geology and Ground-water resources of Pittsylvania and Halifax Counties: Charlottesville, Virginia Division of Mineral Resources Bulletin 75, 86 p.

Lovley, D.R., Chapelle, F.H., and Woodward, J.C., 1994, Use of dissolved H_2 concentrations to determine distribution of microbially catalyzed redox reactions in anoxic groundwater: Environmental Science and Technology, p. 1205 - 1210.

Mason, Brian, 1958, Principles of Geochemistry: New York, John Wiley and Sons, 310 p.

Mason, G.T., Jr., and Arndt, R.E., 1996, Mineral Resources Data System (MRDS) with retrieval software by Kim Buttleman: U.S. Geological Survey Digital Data Series DDS-20, (June 1996 - Release 1, CD-ROM)

McCartan, Lucy, and Peper, J.D., 1997, Lithogeochemical map of the Chesapeake Bay watershed: an example of useable repackaging of traditional geologic information: Anoint, R.B. and others, eds., 4th International Symposium on Environmental Geochemistry, Programs with Abstracts, U.S. Geological Survey Open-File Report 97-496, p. 63.

McCartan, Lucy, Peper, J.D., Bachman, L.J., and Horton, J.W., Jr., 1998, Application of geologic map information to water quality issues in the southern part of the Chesapeake Bay watershed, Maryland and Virginia, eastern United States: Journal of Geochemical Exploration, v. 64, p. 355 - 376.

Pavlides, L., 1981, The central Virginia volcanic-plutonic belt; an island-arc of Cambrian (?) age: U.S. Geological Survey Professional Paper 1231-A, 34 p.

_____, Gair, J.E., and Crawford, L. J., 1982, Massive sulfide deposits of the southern Appalachians: Economic Geology, vol. 77, no. 2, p. 233 - 272.

Peper, J.D., Grosz, A.E.., Kress, T.H., Collins, T.K., Kappesser, G.B., Huber, C.M. and Webb, J.R., 1995, Acid deposition sensitivity map of the southern Appalachian Assessment Area: Virginia, North Carolina, South Carolina, Tennessee, Georgia, and Alabama: U.S. Geological Survey On-Line Digital Data series Open-File Report 95-810, scale 1:1,000,000 with text and data.

Peper, J.D., and McCartan, Lucy, 1997, Lithogeochemical map units and water quality patterns in the Chesapeake Bay watershed, in, Horton, J.W., Jr., and Cleaves, E.T., eds., Forum on geologic mapping applications in the Washington-Baltimore urban area: U.S. Geological Survey Circular 1148, p. 46.

Peper, J.D., McCartan, Lucy, Horton, J.W., Jr., Bachman, L. J., Brakebill, J.W., Bohlke, J.K., and Bricker, O.P., 1997, Development of a lithogeochemical map for prediction of water quality patterns in Maryland and eastern Virginia: Geological Society of America Abstracts with Programs v. 29, no. 6, p. 306.

Pettijohn, S. J., 1956, Sedimentary Rocks: New York, Harper and Brothers, 718 p.

Rader, E.K., and Evans, N.H., editors, 1993, Geologic map of Virginia - Expanded explanation: Charlottesville, Virginia Division of Mineral Resources, 80 p.

Reay, W. G., Gallagher, D.L., and Simmons, G.M., Jr., 1992, Ground-water discharge and its impacts on surface water quality in a Chesapeake Bay inlet: Water Resources Bulletin, v. 28, p. 1121 - 1134.

Risser, D.W., and Siwiec, S. F., 1996, Water-quality assessment of the lower Susquehanna River basin: environmental setting: U.S. Geological Survey Water Resources Investigations Report 94-4245, 70 p.

Robinson, G.R., Jr., 1997, Source data for lithogeochemical classification of rock types in watersheds in New England: U.S. Geological Survey Open-File Report 97-154, 18p.

Robinson, G.R., Jr., Peper, J.D. , Desimone, L.A., and Steeves, P.A., 1999, Lithogeochemical character of near-surface bedrock in the Connecticut, Housatonic, and Thames River Basins: Water Resources Investigation Report 99 - 4000, 86 p., 2 maps; lithogeochemical, map scale 1:125,000, physiographic domains, map scale 1:250,000; tables and charts. CD-ROM and web site.

Seal, R.R., II, and Wandless, G.A., 1997, Stable isotope characteristics of waters draining massive sulfide deposits in the eastern United States: In, Wanty, R.B., Marsh, S.P., and Gough, L.P.,eds., 4th International Symposium on Environmental Geochemistry Proceedings, U.S. Geological Survey Open-File Report OF 97-496, p. 82.

Seal, R.R., II, Hammarstrom, J.M., Meier, A.L., and Flohr, M.J.K.,1997, Controls on geochemical signatures of mine drainage from volcanic- and sediment-hosted massive sulfide deposits in the eastern United States: Geol. Soc. Amer. Programs with Abstracts, v. 29, p. A386.

Senior, L.A., 1996, Ground-water quality and its relation to hydrogeology, land use, and surface water quality in the Red Clay Creek Basin, Piedmont physiographic province, Pennsylvania and Delaware: U.S. Geological Survey Water-Resources Investigations Report 96 - 4288, 122 p.

Speiran, G.K., 1996, Geohydrology and geochemistry near coastal ground-water-discharge areas of the Eastern Shore, Virginia: U.S. Geological Survey Water-Supply Paper 2479, 73 p.

_____, Hamilton, P.A., and Woodside, M.D., 1998, Natural processes for managing nitrate in ground water discharged to Chesapeake Bay and other surface waters: more than forest buffers: U.S. Geological Survey Fact Sheet FS-178-97, 6 p.

Stumm, Werner, and Morgan, J.J., 1981, Aquatic chemistry, an introduction emphasizing chemical equilibria in natural waters: New York, Wiley-Interscience Publication, John Wiley and Sons, 780 p.

Trapp, Henry, Jr., and Horn, Marilee A., 1997, Ground water atlas of the United States; Segment 11; Delaware, Maryland, New Jersey, North Carolina, Pennsylvania, Virginia, and West Virginia: U. S. Geological Survey Hydrologic Investigations Atlas 730 - L, 24 p.

U.S. Department of Agriculture, 1994, State Soil Geographic (STATSGO) Data Base: Soil Conservation Service Miscellaneous Publication Number 1492, 33 p. plus CD-ROM.

U.S. National Park Service, 1997, Air quality; Great Smoky Mountains National Park Management Folio no. 2: Gatlinburg, Great Smoky Mountains National Park, Tennessee, 4p.

Virginia Division of Mineral Resources, 1993, Geologic map of Virginia: Charlottesville, Virginia Division of Mineral Resources, scale 1:500,000.

Webb, J.R., Diviney, F.A., Galloway, J.N., Rinehart, C.A., Thompson, P.A., and Wilson, Suzanne, 1994, The acid-base status of native brook trout streams in the mountains of Virginia, Report to the Virginia Department of Game and Inland Fisheries: Charlottesville, University of Virginia, 91 p.

APPENDIX 1. DIGITAL INFORMATION

The preliminary lithogeochemical map of near-surface rock types in the Chesapeake Bay watershed, Virginia and Maryland, was created in two software packages, ABICAS* and ARC/INFO*. Digital geologic maps of Virginia and Maryland were translated into maps of rock types by converting the ABICAS line files to ARC/INFO polygon covers and then reattributing the files according to the lookup table in Appendix 2. The digital version of the 1:500,000-scale Geologic map of Virginia is a joint product of the Virginia Division of Mineral Resources and the U.S. Geological Survey. The digital version of the 1:250,000-scale Geologic map of Maryland (Cleaves and others, 1968) was produced by the U.S. Geological Survey from a scanned paper copy and was edited by the Maryland Geological Survey. The lithogeochemical units and the conversion table in Appendix 2 were edited by the Virginia Division of Mineral Resources and the Maryland Geological Survey. Note: the Martinsburg Formation in the Valley and Ridge of Virginia consists of dark shales and dark greywacke siltstones and some sandstones. A lowest part of the formation in the Winchester-Staunton area is dark calcareous siltstone and thin limestone (Stickley Run Member of Epstein and others 1995). The member is not delineated on the base geologic map for the lithogeochemical map.

*The use of brand names is for descriptive purposes only and does not constitute endorsement by the U.S. Geological Survey

APPENDIX 2. TABLE OF NUMERICAL LITHOGEOCHEMICAL CODES AND ORIGINAL GEOLOGIC MAP SYMBOLS. First entries are symbols on the State geologic maps of Maryland (Cleaves and others, 1968) and Virginia (Virginia Division of Mineral Resources, 1993); numbers and letters show lithogeochemical classification (see Explanation and table 1)

CZa,32
CZac,12
CZba,41
CZc,43
CZcb,43
CZcr,61v
CZcs,22
CZfm,32
CZg,50c
CZh,34
CZhb,43
CZl,33
CZlb,43
CZmd,43
CZmg,31s
CZmi,42
CZmq,33
CZms,32
CZmy,33
CZpb,50c
CZpm,33
CZum,50c
Ca,22
Cbg,34
Cca,32
Ccas,32
Ccfv,61v
Cch,22
Ccmv,43
Cco,11
Ccv,42
Cd,61
Ce,11
Cev,11
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APPENDIX 3. MINERALOGY AND CHEMISTRY OF ROCKS AND SEDIMENTS

Minerals and Major Elements in Igneous Rocks

The igneous rocks in the Blue Ridge and Piedmont Provinces of the mid-Atlantic region range from mafic to felsic in composition. Mafic basalt - gabbro is siliceous-aluminous, with iron, magnesium, and calcium. Some calcium, with alumina and silica, is in plagioclase (sodium-calcium feldspar); some calcium is associated with the iron and magnesium in hornblende and pyroxene. Felsic granodiorite-granite is silicious-aluminous, with silica in the mineral quartz. The soluble alkalies calcium and sodium are in plagioclase, and the potassium is mostly in potassium feldspar or mica, muscovite or lesser dark biotite. Some iron, calcium, and magnesium are in hornblende, and some in biotite. Trace iron is in the oxides magnetite and ilmenite, and trace titanium is in ilmenite and rutile. Trace phosphate (0.3 percent) is in apatite. With increasing iron and magnesium content, and depleted calcium and silica, the igneous rocks range to quartz- and feldspar-free ultramafic (in the Appalachians mostly their metamorphic equivalents), dunite, peridotite and serpentinite. With increasing alumina they range to the rarer feldspar-rich alkalic (sodium and potassium and rare-earths) rocks.

Minerals and Major Elements in Sediments and Sedimentary Rocks

The soluble calcium and magnesium that are carried off the land and trapped in the oceans, may be, in consort with biomass in shallow seas (and possibly in the past with elevated atmospheric carbon dioxide), precipitated or fixed as carbonates. Carbonates form thick and important accumulations as strata in the Valley and Ridge, and Plateau provinces in the central Appalachians (Colton, 1970).

Among the clastic sediments and sedimentary rocks the sandstones are most diverse in major-element chemistry . The graywackes have composition near granodiorite but range to the right, toward "intermediate" igneous rocks in composition. In the central Appalachians metamorphosed graywackes appear in rock packages interlayered with more abundant metashale or schist in the Piedmont. They form minor interlayers with ridge-forming protoquartzites in the Valley and Ridge.

With increasing feldspar and muscovite content, the sandstones range toward arkosic sediments, typically deposited in intermontaine basins as red hematite-stained sediments, under continental conditions, where physical disaggregation was important along with humid chemical weathering. They are the common sediments of the Mesozoic basins in the Appalachian Piedmont, where they range up-paleoslope into arkosic conglomerates (and locally in northern Virginia and southern Maryland) into limestone cobble and pebble conglomerate. Down-paleoslope they merge into black lacustrine mudstone and shale (Froelich, 1985; Lee and Froelich, 1989). In northern Virginia the black shales form thin 0.5m thick cyclothemic accumulations in 1 - 3 m thick fine sandy siltstones over broad 7 - 10 km wide areas.

With long periods of winnowing and reworking, the sands and derived orthoquartzite sandstones range to nearly pure silica (quartz; Pettijohn, 1956), and comprise mostly blanket-like veneer transgressive sheets (beach and dune veneer, near-shore beach deposits), that are common in basal Late-Proterozoic to Middle Cambrian strata, above unconformities in the Appalachia basin. These may be variously porous and have local calcareous, silicious, or ferrugenous secondary cements.

Somewhat more feldspathic and micaceous, the protoquartzites are the distal, fluvial sediments of fans or river-scoured plains. They are components of Lower and Middle Silurian strata in the Appalachians where they merge upslope and laterally with, and enclose, minor red continental sediments (Epstein, 1993); and are major components of Mississippian-Pennsylvanian

strata where they interfinger downslope with bog-sediments and coal, or rare local redbeds and sulfates of marine evaporite origin such as some Maccrady Formation (Colton, 1970) in Virginia.

Shales have compositions more aluminous than granodiorite and range less broadly than do sandstones. The high-grade, mid-crustal, metamorphosed shale equivalents, schists in the Blue Ridge and Piedmont, may be enriched in the resistate aluminosilicate minerals kyanite and sillimanite, or in segregated granite veins where they occur in gneiss-schist sequences. The black shales are suggested important reducers and sulfide, phosphate, and trace-element precipitators. They are common in the Valley and Ridge Province. Deep-water accumulated and metamorphosed black slates and schists form accumulations in the Piedmont.

Trace Elements in Rocks

Processes in relation to biomass and reduction in biogenic deposits concentrate some trace elements many times over general crustal abundance in the rock or sediment. Among others , these may include: boron, germanium, arsenic, bismuth, beryllium, and uranium (Mason, 1958, Table 39) as well as sulfate, phosphate and selenide (Lakin and Davidson, 1973). Few studies in the map area (see for instance Senior, 1996) relate trace elements in rocks to trace elements in water.