

U.S. DEPARTMENT OF THE INTERIOR
U.S. GEOLOGICAL SURVEY

PORTRAYING CHEMICAL PROPERTIES OF BEDROCK FOR WATER QUALITY AND
ECOSYSTEM ANALYSIS: AN APPROACH FOR THE NEW ENGLAND REGION

Gilpin R. Robinson, Jr.¹

USGS Open-File Report 97-154

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¹U.S. Geological Survey, 954 National Center, Reston, Virginia 20192

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ABSTRACT

A classification scheme has been developed to describe bedrock geologic rock units in terms of lithologic units with similar chemical features (termed lithochemical units) that portray the relative reactivity of their constituent minerals to dissolution and other weathering reactions. The lithochemical classification, as developed for the New England Region, consists of 26 lithologic types, which are defined on mineralogy, weathering characteristics, and structural setting. The 26 units can be summarized into 6 major categories, arranged in order of decreasing weatherability or attack by natural waters: (1) carbonate-rich rocks, (2) clastic sedimentary rocks restricted to rift basins, (3) mafic igneous rocks and their metamorphic equivalents, (4) ultramafic rocks, (5) metamorphosed, noncalcareous clastic sedimentary rocks, and (6) felsic igneous and plutonic rocks and their metamorphic equivalents.

This classification was developed to provide the USGS National Water Quality Assessment (NAWQA) Program with a scheme to use bedrock geologic data for analysis of the water-quality characteristics of surface water and shallow ground water.

INTRODUCTION

Bedrock lithologies and other bedrock geologic features are among the significant factors that affect both the chemical quality and modes of transport of surface and ground waters in different hydrologic domains. Knowledge of the composition, geologic character, distribution, and continuity of bedrock and surficial rock units and their relation to the distribution and features of aquifers, discharge and recharge sites for waters, and the chemical character of natural waters is an important part of a regional description of surface and ground water quality and provides a physical framework within which the natural factors that influence water quality can be evaluated and understood. In addition, bedrock lithologies and their response to the climatic regime provide fundamental physical controls on local ecosystem potentials. The nutrient cycle is dependent upon the chemical availability of elements in rocks and soils to waters and vegetation. As such, habitat for numerous terrestrial and aquatic species is either enhanced or limited in association with specific lithologies or geologic environments due to their chemical characteristics. The geological characterization provided in this classification is intended to portray the significant bedrock geologic features that influence water quality in relation to both the mineralogic character and the residence time of waters in relation to the rocks and surficial materials which these waters are in contact. The rock units are defined in ways that portray the variable reactivity of their constituent minerals to weathering dissolution (of significance are carbonates, sulfides and other iron-bearing minerals, ferromagnesian silicates, and aluminosilicate minerals). To the degree that surficial materials are related to their proximal bedrock source, the variations in bedrock geology also provides guidelines to the expected variations in the properties and chemistry of surficial materials. In glaciated areas, the mineralogy of tills and

some stratified drift is related to adjacent bedrock units and bedrock geology has been used to help define their character (Bailey and Hornbeck, 1992). Geologic characterization can also provide a framework to interpret regional elevations, slope gradients, fracture densities, and weathering profiles that influence the residence time of waters in these areas and help define habitat characteristics.

BEDROCK GEOLOGY AND INFORMATION SOURCES

A wide variety of igneous, metamorphic, and sedimentary rocks with varying types and thicknesses of overlying surficial materials are present in the New England region. Statewide geologic maps describing the bedrock rock types at scales of 1:500,000 to 1:100,000 are available for the region (Conn: Rogers, 1985; Mass: Zen and others, 1983; Maine: Osberg and others, 1985; N.H.: Lyons and others, 1986; N.Y.: Fisher and others, 1970; R.I.: Hermes and others, 1994; Vt.: Doll and others, 1961). However, these maps collectively contain many hundreds of rock units that are defined by time-stratigraphic and other geologic criteria that are not generally relevant to water quality or ecosystem analysis. Moreover, the rock units depicted on the state geologic maps are inconsistent across map boundaries in some cases. Thus, a regional coding scheme is developed to reclassify the geologic units according to mineralogical and chemical characteristics that are relevant for water-quality investigations and ecosystem analysis.

PURPOSE AND OBJECTIVES OF THE CLASSIFICATION

This classification was developed to provide the National Water Quality Assessment (NAWQA) Connecticut, Housatonic, and Thames River Basins study unit with an approach to use published bedrock geologic data for analysis of water-quality characteristics of surface water and shallow ground water. The classification system is intended to characterize the bedrock geologic units and their related surficial materials in terms of mineralogic and chemical parameters relevant to water quality, such that the geologic data could be used in a Geographic Information System (GIS) to analyze and interpret water quality and ecosystem conditions.

The objectives of the classification system were to:

1. Characterize the bedrock geologic units and related surficial materials in terms of mineralogic and chemical parameters that may be further related to natural background water quality or to their potential to interact with man-made materials or solutions. Develop a strategy for the compilation of a limited number of lithochemical units for bedrock that can be uniformly applied to the entire study area.
2. Identify geologic features with possible significant hydrologic impact, such as Mesozoic age and other geologically-recent faults that may define significant fracture-controlled aquifers.
3. Develop information that identifies the geologic features that most significantly influence the quality of waters in various aquifers and drainage basins and character of local soils.

4. Provide a classification approach that can be used to develop cartographic information databases and other spatial digital files as part of a Geographic Information System (GIS) to compare and evaluate geologic, geochemical, and other data with water quality and ecosystem conditions.

RATIONALE BEHIND THE LITHOCHEMICAL CLASSIFICATION

The chemical character of surface and ground waters is dependent upon a variety of climatic, geologic, geochemical, biochemical, and anthropogenic factors. However, the ultimate source of most dissolved cations in non-polluted natural waters is the minerals in the sediments and rocks at the earth's surface that, through processes of dissolution and weathering, are in contact with these waters.

Surface and ground waters react with the rock and soil minerals they encounter during flow and incorporate major and trace elements by decomposing and dissolving minerals. Consequently, the chemical character of surface water, soil water, and shallow groundwater in a watershed is often similar. This link between soils, soil-water characteristics, and surface waters is demonstrated by a few studies that have attempted to make direct comparisons between soil water chemistry and surface water chemistry on a watershed scale. For a number of watersheds, average soil solution compositions correspond closely to mean annual surface-discharge chemistry (for example, White, 1995, p. 438-440), implying that both terrestrial and aquatic ecosystems may share linked lithology-based habitat factors. Similarly, a number of studies have demonstrated that, in moist climates, the major element chemistry of streamwaters in individual watersheds is similar to that of shallow subsurface groundwaters that have percolated through weathered rock (Vebel and Dowd, 1983; Vebel, 1985), implying that a similar lithologic classification can be used to characterize both ground and surface waters as well.

The important processes and factors controlling water chemistry include:

1. Relative rates of irreversible dissolution and alteration of silicate and other minerals.
2. Precipitation of sparingly soluble salts and other mineral phases that provide limits to solute concentrations.
3. Selective removal and circulation of nutrient elements and compounds by plants.
4. Biochemical reactions producing carbon dioxide and changes in redox conditions.
5. Sorption and desorption of ions by mineral and organic phase surfaces.
6. Concentration of solutes by evapotranspiration.
7. Residence time of rock-water contact.

Although the interplay between these processes and factors is complex, it is expected that a general relationship should exist between the chemical composition of natural waters and that of the solid materials with which the water has been in prolonged contact.

A water classification scheme based upon geologic criteria needs to address the range of differences in rock weathering products, weathering rates, geologic structural features, and soluble mineral components available to water circulating through the rocks in various hydrologic domains. Dissolution and weathering rates differ greatly for different minerals and therefore for different rock types. The relative relief and topographic elevation of different rock

types in an area usually reflect their relative weathering rates and are an indirect measure of the residence time of water in the hydrologic system. The structural fabrics of different rock types, such as mineral alignment and fracture density and orientation influence the circulation pathways for water and the degree to which this water can interact with the host rock.

Although dissolution and weathering rates are highly variable, laboratory and field studies of dissolution and weathering rates in moist climates tend to show generally consistent relative stabilities of minerals during weathering. The relative stability of common rock-forming silicates undergoing chemical weathering in humid climates observed by Goldich (1938) is portrayed in figure 1.

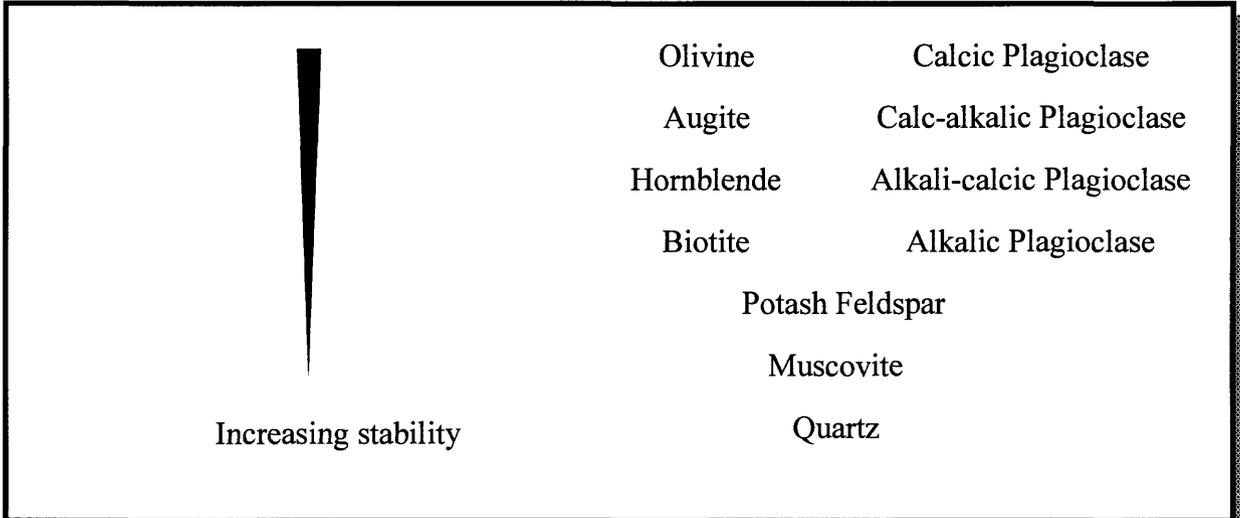


Figure 1. Relative stability of common rock-forming silicates in chemical weathering (after Goldich, 1938 and Rose, Hawkes, and Webb, 1979).

The arrangement is similar to Bowen’s reaction series, which defines the order of successive mineral development during magmatic crystallization (Bowen, 1922). The presence and relative abundance of these minerals provide the basis used to classify most igneous rocks, thereby linking rock classifications of igneous rocks (and metamorphic rocks with similar mineral assemblages) to weathering characteristics. A similar sequence based on weathering of fine-grained minerals in soils was developed by Jackson and others (1948) which is summarized in figure 2. These classifications show similar trends in that salts, gypsum (and other soluble sulfate minerals), and carbonate minerals (to a lesser degree) are more readily dissolved in water generating a high porosity that promotes further water infiltration. Plagioclase and ferromagnesian minerals, such as olivines, pyroxenes, amphiboles, and to a lesser degree, biotite, are weathered more rapidly than alkali-feldspars, muscovite, or quartz which are relatively inert and insoluble. Consequently, in humid temperate climates, rocks rich in carbonates and clastic rocks cemented by carbonates have relatively lower relief and elevation and tend to supply higher solute loads to surface and ground waters than other rock types. In contrast, rocks rich in alkali-feldspar, muscovite, and quartz, such as granites, schists, and quartzites have relatively greater elevation and relief than other rocks types in humid temperate climates and react with

surface and ground waters to a lesser degree at generally slower rates.

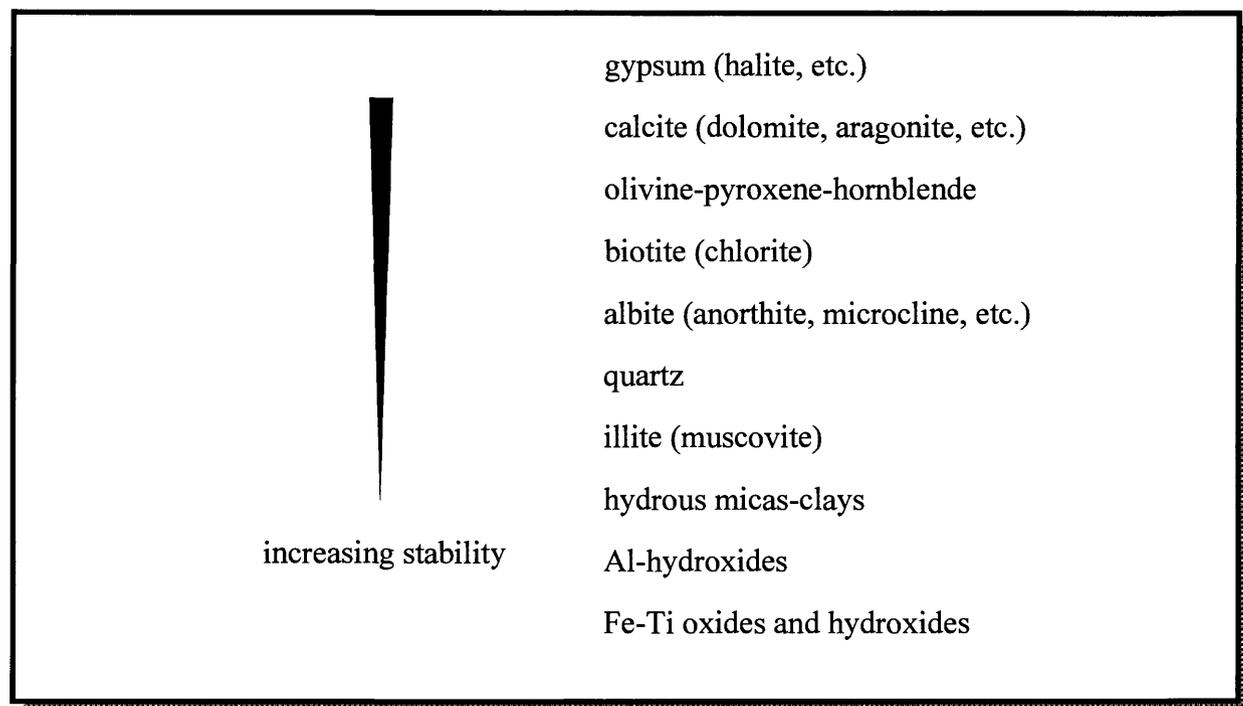


Figure 2. Weathering sequence for clay sized minerals in soils and sediments (modified from Jackson and others, 1948).

Most rocks are complex mixtures of minerals of variable stability (or solubility) in water, although most common rock-forming minerals are only sparingly soluble. The relatively abundant monovalent and divalent cations in natural waters, such as Ca^{+2} , Na^+ , Mg^{+2} , and K^+ , are released from their parent minerals in exchange for H^+ during weathering reactions and enter the aqueous medium, whereas Fe^{+2} released during weathering of iron-bearing minerals is usually oxidized and precipitated as ferric hydroxides in the weathering horizon. The charge of the soluble cations is balanced by that of the anions of the weathering acids, which is generally largely HCO_3^- (carbonic acid). Carbonic acid, either of atmospheric or organic origin, is generally the most abundant and most potent of the agents that dissolve mineral matter from rocks, although the relative balance of anions other than the carbonate species, such as halogens or sulfate, can influence the cation load. The halogens and sulfate may be derived from trace soluble salts present in the rocks or be contaminants from rainwater or dry fallout. Oxidation of sulfides in rocks undergoing weathering can provide significant amounts of sulfate.

As minerals are dissolved, major (and often trace constituents) in the waters tend to be proportionate to the more soluble mineral constituents in the source rocks; these concentrations may vary between different rock types but often have similarities within groups of rock types and show trends where dissolved constituents tend to increase in proportion to the total dissolved solids in waters (c.f. Dall'Aglio and Tonani, 1973).

Although major and trace elements in waters are related to the compositions of rocks and soils in the drainage basin or hydrologic flow path (Rose, Hawkes, and Webb, 1979, p. 352-354), trace elements may show complicated relationships. Trace elements present in trace amounts in one or more major minerals tend to be liberated into waters at essentially the same rate as major elements and tend to show a good correlation with total dissolved solids in solution and with content in the source rocks (c.f. Rose, Hawkes, and Webb, 1979, fig. 14.4, p. 354, from Lopatkina, 1964). However, trace elements that occur as major constituents of trace minerals that are highly reactive with water may be preferentially leached into solution. High calcium and bicarbonate (alkalinity) concentrations can result from the dissolution of relatively sparse carbonate minerals in rocks; high sulfate and metal concentrations can result from trace amounts or local concentrations of sulfide minerals exposed to oxidation and dissolution; high sulfate concentrations can result from the dissolution of gypsum or other relatively soluble sulfate minerals occurring sparingly in sediments; and high salinities can result from the dissolution of trace salts. Therefore, the lithologic classification used here attempts to portray the distribution of gypsum, carbonate minerals, and sulfides in rock types, even when the relative abundance of these constituent minerals may not be large.

However, the relationships of water chemistry with trace minerals can be complex when the reactive minerals are restricted to special rock types that are not mapped at the scale used for the geologic classification or that have a restricted distribution within a larger lithologic package or rock formation. For example, Dall'Aglico (1971) found that within one drainage in the Alpine Range of Italy, very high uranium concentrations were observed in stream waters and sediments; only small pegmatites with trace uranium minerals could be identified as a possible source. The use of broader terrane units and a relatively robust set of rock units classification may be needed to provide an adequate framework for the chemical classification of waters.

The chemical classification and interpretation of natural waters according to the geologic character of their source has been used in a number of studies (c.f. Garrels, 1967; Garrels and MacKenzie, 1967; White and others, 1963), although no completely satisfactory geologic classification scheme has been developed (Hem, 1989, Clarke, 1924, p.8). White and others (1963) present representative chemical analyses of groundwaters of low mineral content associated with common rock types that they grouped into eleven broad categories; their classification scheme and associated chemical characteristics of groundwaters is summarized in table 1. For surface waters in individual catchment areas and watersheds, Stallard and Edmond (1983, 1987) and Stallard (1985) show a good correlation between solute concentrations in runoff and bedrock lithology in the Amazon basin. The highest solute concentrations are associated with evaporites, intermediate concentrations with limestones, and lowest concentrations with silicate rocks. Amiotte-Suchet and Probst (1993), found that for 200 small non-polluted monolithologic catchments in France, that solute fluxes and rates of chemical weathering showed good correlations and similarities within (and significant differences between) seven lithologic groupings (figure 3).

Rock types	chemical characteristics of ground water
waters from igneous terranes	
granite, rhyolite, and similar rock types	generally low solute concentrations; high Na, HCO ₃ ⁻ , and SiO ₂ ; relatively low pH; flouride concentrations may be high; Ca and Mg concentrations are generally low.
gabbro, basalt, and ultramafic rocks	high Ca/Na and Mg/Ca ratios; variable SiO ₂ (sometimes high due to dissolution of reactive silicates); where Eh and pH are low, Fe and Mn are high; sulfate may be high if sulfides are present; very high Mg/Ca ratio in waters from ultramafic rocks.
andesite, diorite, and syenite	generally ranges between granite and gabbro characteristics.
waters from sedimentary terranes	
sandstone, arkose, and graywacke	generally high Ca/Na, K/Na, HCO ₃ /Cl, and SO ₄ /Cl ratios; may have high solute concentrations.
siltstone, clay, and shale	low Ca/Na, HCO ₃ /Cl, F/Cl ratios; high Mg/Ca ratios.
limestone	high alkalinity, Ca, and CO ₂ content; high pH.
dolomite	high alkalinity and CO ₂ content; high Ca and Mg; high pH.
waters from metamorphic terranes	
quartzite	generally low solute concentrations; high K/Na; low pH.
marble	similar to limestone
slate, schist, and gneiss	similar to siltstone, clay, and shale. May have high sulfate or chloride concentrations.
waters from unconsolidated sands and gravels	
	chemical characteristics are similar to those of the source rocks of the sediments, although solute concentrations may be variable.

Table 1. Classification of ground waters of low mineral content associated with common rock types (after White, Hem, and Waring, 1963).

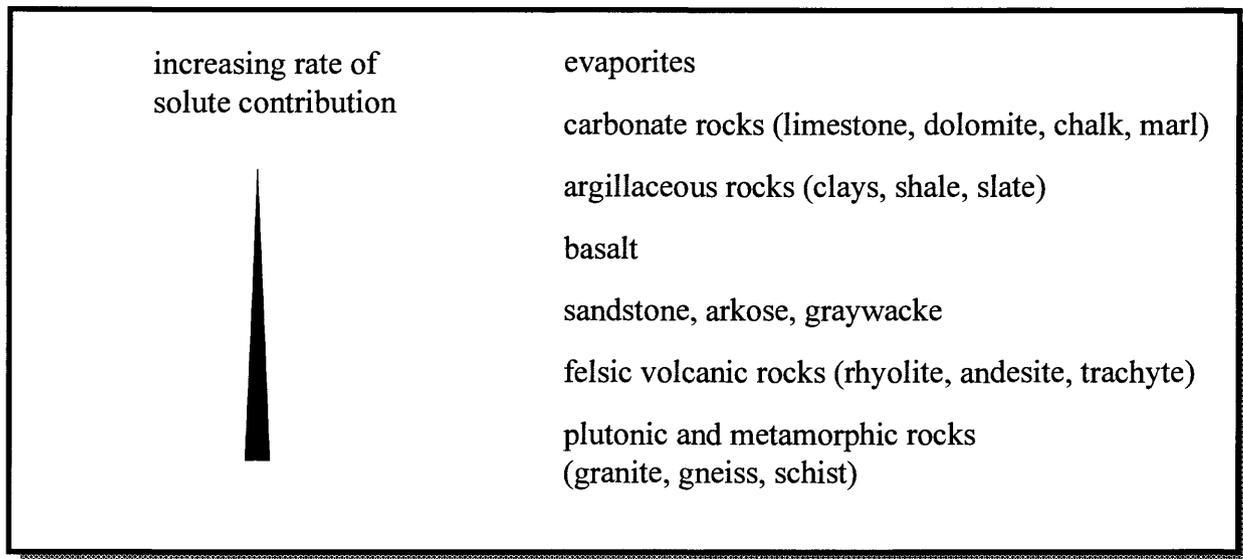


Figure 3. Ranking of relative rates of solute flux and chemical weathering (measured by CO₂ consumption) for monolithologic catchments in France (after Amiotte-Suchet and Probst, 1993 and Meybeck, 1986, 1987).

Glass and others (1982), in an attempt to use bedrock geology to map ecosystem susceptibility to acid rain, developed a four tier classification of rock formations according to their ability to neutralize acid (table 2). These classifications share many similar features.

Type	Buffer capacity classification	Rock types
I	Low or no buffer capacity. Overlying waters very sensitive to acidification.	Granite, syenite, granitic gneisses, quartz sandstones, or equivalents.
II	Medium to low buffer capacity. Acidification restricted to first and second order streams and small lakes.	Sandstones, shales, conglomerates, high-grade metamorphic to intermediate volcanic rocks, intermediate igneous rocks, and calc-silicate gneisses.
III	High to medium buffering capacity. No acidification except in cases of overland runoff in areas of frozen ground.	Slightly calcareous, low-grade intermediate to mafic volcanic, ultramafic, and glassy volcanic rocks.
IV	"Infinite" buffering capacity. No acid precipitation effect of any kind.	Limestones, dolomites, highly fossiliferous sediments or metamorphic equivalents.

Table 2. Classification of rock formations according to their ability to neutralize acid deposition (after Glass and others, 1982).

Within regions of similar relief and climate, differences in water chemistries on a catchment scale appear to correlate with different bedrock lithologies, and these correlations are consistent with the relative differences in dissolution rates measured in the laboratory and observed in field studies for rock types and minerals, although the observed differences in field studies are less dramatic than would be predicted by the laboratory measurements (for reviews and discussion, see Drever and Clow, 1995, and Sverdrup and Warfuinge, 1995).

The lithochemical classification developed for the New England Region is given in Appendix A., incorporates many of the criteria of the classification methods cited above, and consists of 26 lithologic types, which are defined on mineralogy, weathering characteristics, and structural setting, such as the presence of rift basins of Mesozoic age. The 26 lithochemical units can be summarized into 6 major categories, arranged in order of decreasing weatherability or attack by natural waters: (1) carbonate-rich rocks, (2) clastic sedimentary rocks restricted to rift basins, (3) mafic igneous rocks and their metamorphic equivalents, (4) ultramafic rocks, (5) metamorphosed, noncalcareous clastic sedimentary rocks, and (6) felsic igneous and plutonic rocks and their metamorphic equivalents.

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lithochemical unit (rock types)		topographic expression	soil characteristics	chemical character of waters	habitat characteristics
Sedimentary Rocks and their Metamorphic Equivalents					
Unit code	Carbonate-rich Rocks (series 10 units)	generally lowlands and topographic depressions; may be sites of stream and river channels, ponds, lakes, and groundwater discharge.	generally thin alkaline clay soils; high Ca, low K availability; may form Fe- gossan in weathered sulfide-rich facies	high alkalinity, Ca, and bicarbonate (CO ₂) contents; high pH; may have high sulfate and carry elevated concentrations of solute complexed by bicarbonate ion, such as As and U	low to no sensitivity to acid deposition; flora favoring alkaline, high Ca soils; productive aquatic faunas
11	limestone, dolomite, and carbonate-rich clastic rocks; may include fine-grained non-calcareous clastic rocks				
12	marble; may include some calc-silicate rock				
12s	sulfidic marble; may include some calc- silicate rock				
13	calcareous clastic and metaclastic rocks containing approximately 15 to 45% carbonate minerals				

lithochemical unit (rock types)		topographic expression	soil characteristics	chemical character of waters	habitat characteristics
Sedimentary Rocks and their Metamorphic Equivalents					
code	Carbonate-poor Clastic Sedimentary Rocks restricted to rift basins (bedded lithologies below biotite-grade of regional metamorphism) (series 20 units)	variable; generally lowlands with subdued topography in the study area	clay soils; variably neutral to acidic.	Generally high Na and sometimes Ca and SO ₄ concentrations in waters; groundwaters may have moderate to high solute concentrations where acidic or high sulfate concentrations exist. Fe may be high in groundwaters where Eh and pH are low	Low to moderate sensitivity to acid deposition
		21	tan and red mudstone and shale; may include sandstone; locally contains minor carbonate and/or gypsum		
21cs	calcareous, locally sulfidic, gray mudstone and shale				
22	interbedded mudstone, shale, and siltstone; may contain sandstone				
23	sandstone and interbedded sandstone and conglomerate; may contain siltstone, shale, and mudstone				

lithochemical unit (rock types)		topographic expression	soil characteristics	chemical character of waters	habitat characteristics
Sedimentary Rocks and their Metamorphic Equivalents					
code	Metamorphosed Non-calcareous Clastic Sedimentary Rocks ; may include felsic and mafic metavolcanic rocks. Rock bodies may be foliated, recrystallized, highly deformed, and may have a high degree of variability of exposed rock types in individual watershed catchment areas. (series 30 units)	generally uplands with moderate hills and ridges	variable clay to sandy to rock-chip soils. Variable neutral to slightly acid soils; sulfidic units may have acidic soils.	low to moderate solute concentrations	moderate to high sensitivity to acid deposition.
31	Slate and graywacke	uplands and ridges	rocky soils	generally low Ca/Na ratios; variable K/Na ratios. Higher Ca when slightly calcareous.	sensitive to acid deposition. Acidic metal-rich soils developed over sulfide-rich horizons may have endemic floras.
32	pelitic schist and phyllite, may include granofels	moderate hills	clay soils		
33 and 33c	mixed schist, granofels; and gneiss (slightly calcareous - 33c)	low to moderate rolling hills	clay to sandy soils		
34	quartzose metasediment, quartzite, quartz granofels, and quartz gneiss	uplands and ridges	sandy to rocky soils	generally low solute concentrations; low pH; high K/Na	
31s	graphitic and sulfidic slate and graywacke	uplands and ridges	rocky acidic soils	Fe may be high in groundwaters where Eh and pH are low; sulfate may be high	
32s	sulfidic schist; may include sulfidic granofels	low to moderate hills	clay soils		
33s	sulfide-bearing schist and gneiss	low hills	clay to sandy soils		

		lithochemical unit (rock types)	topographic expression	soil characteristics	chemical character of waters	habitat characteristics
Igneous Rocks and their Metamorphic Equivalents						
code	Mafic Igneous Rocks and their Metamorphic Equivalents (series 40 units)	variable	variable	smectite clay soils; poor drainage	high Ca/Na and Mg/Ca ratios; variable SiO ₂ (sometimes high due to dissolution of reactive silicates); where Eh and pH are low, Fe and Mn are high	Low sensitivity to acid deposition; may have endemic flora favoring alkaline, high Mg and low K soils; productive aquatic faunas where Ca is high in surface waters.
			moderate ridges and hills	thin rocky smectite clay soils; high in Mg, low in K		
41	basalt					
42	greenstone, lower greenschist facies metabasalt, and schistose mafic rock with minor dispersed carbonate (Mg-rich)					
43	amphibolite and layered mafic gneiss; may be mixed with other lesser lithologies such as felsic volcanics and metaclastic rocks.	Moderate rolling topography	Fe-rich smectite clay soils, poor drainage;			
44	massive mafic rocks; includes gabbro, diorite, monzodiorite, and diabase	lowlands or uplands, depending upon adjacent lithologies	neutral to basic soils; high Mg.			

lithochemical unit (rock types)		topographic expression	soil characteristics	chemical character of waters	habitat characteristics
Igneous Rocks and their Metamorphic Equivalents					
code	Ultramafic Rocks (Series 50 units)	upland hills, knobs, or ridges	thin rocky Fe- rich soils	Extremely high Mg/Ca; generally high SiO ₂ due to solution of reactive silicates; groundwaters may have low Eh values and high metal contents.	low sensitivity to acid deposition; frequently has endemic flora favoring high Mg, low K, alkaline soils.
50	ultramafic rocks; includes serpentinites, dunites, peridotites, and tremolite-talc schists associated with other ultramafic rocks				
code	Felsic Igneous and Plutonic Rocks and their metamorphic equivalents (series 60 units)	generally uplands and highlands	generally sandy soils	generally low solute concentrations	
61	granitoid rocks; includes granite, quartz monzonite, granodiorite, trondhjemite, and equivalent gneiss	uplands and highlands; uplands may have little internal relief and steep slopes along borders	sandy soils	generally low solute concentrations; high Na, HCO ₃ ⁻ , and SiO ₂ ; relatively low pH; fluoride, U, and radon concentrations may be high; Ca and Mg concentrations are generally low	high sensitivity to acid deposition
61v	fine-grained felsic rocks of volcanic to subvolcanic origin;				
62	quartz-poor plutonic rocks; includes syenite, monzonite, quartz syenite, and anorthosite		thin clay soils		

Appendix A.

lithochemical unit (rock types)		topographic expression	soil characteristics	chemical character of waters	habitat characteristics
Igneous Rocks and their Metamorphic Equivalents					
Felsic Igneous and Plutonic Rocks and their metamorphic equivalents (series 60 units)					
62n	nepheline syenite; includes feldspathoid-bearing syenitic rocks and volcanic rocks	generally lowlands or topographic depressions; may be sites of wetlands, ponds, or lakes.	clay soils, may be somewhat basic.	Generally low Ca/Na; may be alkaline; silicate concentrations may be high due to dissolution of reactive silicates.	low sensitivity to acid deposition