

# 13. Weathering Processes

By W. Ian Ridley

13 of 21

## **Volcanogenic Massive Sulfide Occurrence Model**

Scientific Investigations Report 2010–5070–C

**U.S. Department of the Interior**  
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# 13. Weathering Processes

By W. Ian Ridley

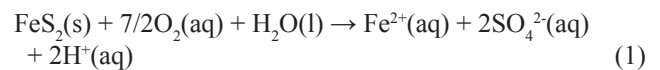
Seafloor massive sulfides (SMS), the presumed precursors of ancient VMS deposits, are unstable in the presence of even small concentrations of oxygen. They are potentially subjected to ambient temperature weathering and other processes that can cause substantial postdepositional changes in mineralogy and geochemistry (Koski and others, 2003). Submarine weathering (halmyrolysis) at the site of ore deposition results from a variety of reactions that are initially mediated by oxygenated seawater that circulates through the deposit. Oxidation begins at the deposit/seawater interface, and the oxidation front gradually moves into the deposit, resulting in mass wasting of the ore deposit at ambient temperatures of 1–2 °C.

In principle, the process of seafloor weathering can produce intermediate stages of supergene enrichments by complete or partial replacement of primary sulfides by secondary sulfides and enriched gossans (Hannington and others, 1988; Herzig and others, 1991), but the continued circulation of oxygenated seawater eventually results in the physical and chemical destruction of the deposit. Consequently, weathering of SMS deposits is an inevitable consequence of exposure to seawater unless the deposit is rapidly covered by sediment and(or) volcanic material that shields sulfides from seawater contact. Anoxic, circumneutral bottom waters also contain a small amount of oxygen so that, under anoxic conditions, the weathering of the deposit may be slowed but not halted.

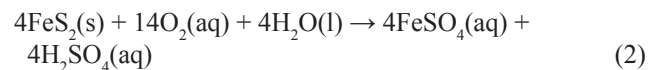
Microbial degradation of seafloor sulfides—for instance, pyrrhotite—also may be an important process of seafloor weathering (Toner and others, 2009). If a VMS deposit is preserved in the rock record, which must be a relatively rare event, it may be subject to subaerial degradation if exposed to abiotic reactions involving surface and near-surface oxygenated fluids, atmospheric oxygen, and biotic reactions involving bacterial activity. Halmyrolysis and subaerial degradation require similar oxidative chemical reactions, the differences being largely determined by the presence or absence of gaseous oxygen, dissolved oxygen and iron concentrations, and hydrologic setting. The deleterious environmental consequences of subaerial degradation of VMS ores and the resulting acid drainage production, has received particular attention from environmental geochemists over the past few decades (Evangelou, 1995; Plumlee, 1999).

## Mineralogic Reactions to Establish Process

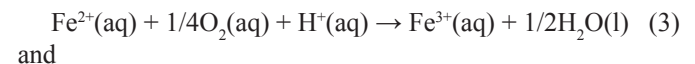
The physical and chemical degradation of a deposit is largely determined by the rates of oxidation of sulfides. There is a substantive amount of literature on the mechanisms and rates of pyrite oxidation (see Evangelou, 1995, for a review) but less information on other sulfides that are commonly found in VMS deposits. Pyrite can be directly oxidized by seawater oxygen depending upon the oxygen concentration, which is a function of the rate of fresh seawater renewal and the degree of bottom water anoxia:



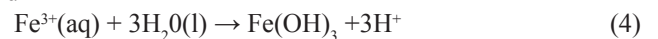
and



Both reactions produce significant acidity, but the extent to which the fluid acidity is maintained is determined by the degree to which these initial reactions occur in a closed system. Pyrite oxidation also can be accomplished through indirect exothermic reactions using oxygen and ferric iron. Solubility of Fe(III) is strongly pH dependent; however, even in circumneutral seawater the concentrations of Fe(III) are sufficient to dominate the oxidation of iron sulfides. In a system that is open to seawater circulation, the acidity and dissolved iron are removed into the large reservoir of ocean water. The presence of a carapace of seafloor gossan, composed principally of ferric oxides and oxy-hydroxides, reflects the low solubility of Fe(III) in solution and implies fluid pH values that are either neutral or slightly alkaline:



and



These reactions continue until the solid pyrite is exhausted or the sulfidic material is isolated from ambient seawater. The presence of a surface in situ gossan may

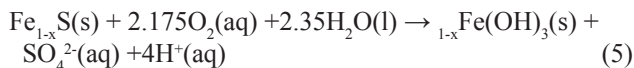
substantially slow down the rate at which the underlying sulfidic material is oxidized. Initially, gossans have a high porosity and permeability, so they do not form an efficient impermeable barrier to the circulation of seawater, but, upon compaction, gossans can form a highly effective impermeable barrier. The slowest step of reactions 1-4, and possibly other intermediate steps, initially determines the rate of pyrite oxidation. However, the rate of oxidation is also a function of available dissolved oxygen and the extent to which ferric-bearing minerals encapsulate, and hence shield, pyrite from reaction with oxygenated seawater.

The origin of gossans associated with VMS deposits is not clearly established. Some appear to have formed on the seafloor whilst others are related to subaerial oxidation. The chemistry of seafloor gossans (Mills and others, 2001) has been interpreted in terms of precipitation from low-temperature vent fluids and hydrogenous reactions involving ambient seawater. However, seafloor weathering of unstable sulfide minerals ultimately produces metal oxides and oxyhydroxides, so some gossans must be a product of halmyrolysis. It seems likely that seafloor gossans represent a spectrum of overlapping processes involving low-temperature vent fluids and ambient seawater.

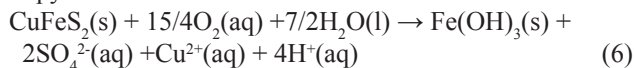
Modern SMS deposits are the sites of abundant micro- and macrofauna, and fossilized macrofauna have been encountered in ancient VMS deposits, such as those in the southern Urals (Little and others, 1997) and the Troodos (Little and others, 1999). Because the food chain for macro fauna begins at the bacterial level, it is reasonable to assume that ancient VMS deposits were also the sites of abundant microfauna. Thus, direct and indirect oxidation of sulfides also may be mediated by chemosynthetic bacteria, which is a common phenomenon in modern SMS deposits (Toner and others, 2009).

Of the major iron sulfides found in VMS deposits (pyrite, pyrrhotite, and marcasite), pyrrhotite is the most reactive and pyrite the least. This appears to be true for both abiotic and biotic oxidation. Other sulfides are also unstable in ambient, oxygenated seawater. The extent to which these sulfides are destroyed is a function of: (1) their iron content and, hence, the extent to which Fe(II) is available for redox reactions; (2) the stability of the crystal lattice, which is partly a function of the degree to which the lattice can accommodate minor and trace elements; and (3) the metal/sulfur ratio that determines the extent of sulfuric acid production (Lottermoser, 2003). Some reactions that involve iron-bearing sulfides and dissolved oxygen under abiotic conditions are shown below, in which ferric hydroxide  $[\text{Fe}(\text{OH})_3]$  is used as a generalized formula for a potential complex series of secondary oxides and oxyhydroxides:

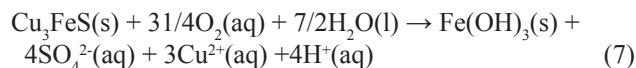
Pyrrhotite:



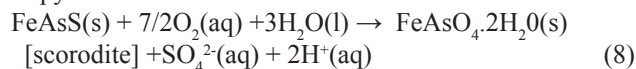
Chalcopyrite:



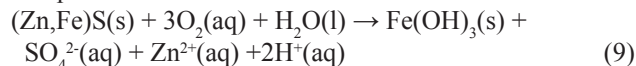
Bornite:



Arsenopyrite:

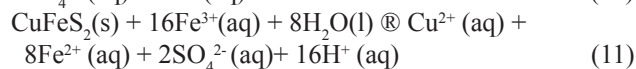
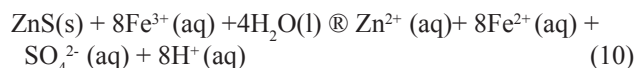


Fe-rich sphalerite:



In these cases, the reduced dissolved metal species are more soluble than dissolved Fe(III) and(or) their precipitation is kinetically inhibited, so that Fe(III)-bearing minerals tend to dominate the mineralogy of seafloor gossans associated with VMS deposits. Initially, however, the presence of cations other than iron in solution results in replacement of iron sulfides by secondary minerals, such as copper, zinc and lead sulfides, and possibly sulfates. The different solubilities of ferric iron and manganese can result in large variations in the Fe/Mn ratios of seafloor gossans (Mills and others, 2001). Common minerals formed during halmyrolysis include goethite, hematite, birnesite, todorike, Fe-smectite, and various silica polymorphs. Iron silicates, usually smectite, can also occur as a major component of several "postdepositional" hydrothermal deposits.

Koski and others (2008) determined a resistance to oxidation in the subaerial environment in the order pyrrhotite < sphalerite < chalcopyrite < pyrite, but it is unknown if this sequence also applies to the seafloor environment. The common presence of sphalerite in seafloor gossans suggests that sphalerite, or at least Fe-poor varieties, may be resistant to oxidation. Some nonferrous sulfides, such as galena, are highly resistant to oxidative weathering. Although pyrite may be the most resistant of the major sulfide components of VMS deposits, it is often the dominant sulfide phase, so frequently pyrite oxidation is the rate-determining step in mass oxidative wasting. Rimstidt and others (1994), Plumlee (1999), Koski and others (2008), and Corkhill and others (2008) consider that the reaction rates in the oxidation of sphalerite, chalcopyrite, arsenopyrite, and enargite are not primarily determined by oxygen but by redox reactions involving bacterially-produced ferric iron; for example:



## Geochemical Processes

Halmyrolic degradation is the rule rather than the exception during the life cycle of a VMS deposit, the corollary being that exceptional circumstances are required to preserve a VMS deposit in the rock record. The most important consequence of seafloor weathering is initial high-grading of the deposit due to supergene replacement processes, but eventually there

is a substantive loss of metals into the water column and(or) a physical degradation of the deposit as it loses coherence (Koski and others, 2003). At an advanced stage of degradation, insoluble oxides and oxyhydroxides precipitate and have a high adsorptive capacity. These minerals scavenge elements, particularly transitional metals, from seawater and(or) from pore fluids after they have been released from sulfides and secondary minerals. The scavenging efficiencies are principally determined by the rate of accumulation of the oxides and oxyhydroxides. Probably ninety nine percent or more of metals are lost during seafloor weathering if gossans are formed.

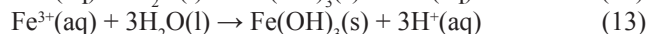
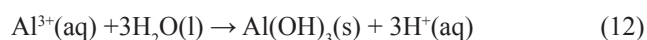
The extent to which the transfer of material to the water column during halmyrolysis contributes to the marine element budget has yet to be assessed, but it may be a significant effect. Precious metals may be high graded in secondary gossans, especially if the original sulfide ore contained Au and Ag primary minerals. For instance, the Letneye deposit in the southern Urals contains a variety of primary precious metal tellurides—such as sylvanite, volynskite, attaitite, and stutzite—that, upon oxidation either released native precious metals or produced secondary, high grade minerals such as hessite and acanthite.

Thus, the common late-stage products of seawater weathering include the formation of gossans that have many physical and chemical features in common with subaerial gossans. In the literature, they have received relatively little attention, except as indicators of subsurface mineralization. Exceptions include the Cretaceous-age ochres of Troodos (Constantinou and Govett, 1972; Robertson and Hudson, 1973; Robertson, 1976; Robertson and Fleet, 1976; Herzig and others 1991), various deposits in the southern Urals (Yaman-Kasy, Sibay, Uchaly, Letneye; Herrington and others, 2005), and the gossans associated with the TAG hydrothermal field (Hannington and others, 1988). Ochres associated with the sulfide deposits in Troodos are economic for precious metals (Constantinou and Govett, 1972).

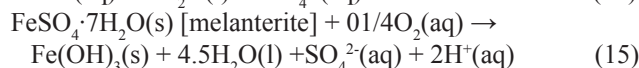
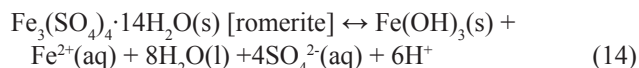
The formation of secondary oxides and oxyhydroxides also produces a substantial reduction in density relative to the original sulfide ore. This property can result in the transport through bottom currents of the secondary products away from the origin site of ore deposition, which in turn results in an increase in the aspect ratio (length:thickness) of the deposit (Herrington and others, 2005). However, the gossans may remain physically associated with sulfide ore if the degree of weathering is limited and the deposit is rapidly covered, for example, the ochres within the Skouriotissa VMS deposit in the Troodos Massif, Cyprus. Gossans also may be preserved if there is an absence of seawater movement in bottom currents. The gossans may be associated with other chemical sediments, such as the umbers of Troodos. The genetic relationships between ochres and umbers is unclear, although the latter appear to be a consequence of low-temperature hydrothermal venting, as observed at the TAG hydrothermal field (Mills and others, 2001), and have many features in common with metaliferous sediments at mid-ocean ridges (Bostrom and Peterson, 1969).

The various reactions highlighted above, which also may be extended to subaerial oxidation, provide a useful general picture of the geochemical changes that occur during seafloor halmyrolysis. Subaerial weathering of exposed VMS deposits and, if mined, their mill tailings and spoil heaps involves processes and products that have commonality with seafloor weathering. Notable differences involve the presence of gaseous oxygen, oxygen-rich meteoric water, variable climate, and hydrology, all of which affect the processes and products of sulfide oxidation. The effect of subaerial weathering is the development of drainage with a high acidity and metal content that may have deleterious environmental effects (Eppinger and others, 2007). The limitations on acidity are provided by the availability of sulfide minerals to suitable oxidation reactions and (or) acid buffering reactions. These latter reactions involve gangue minerals and country rock that consume hydrogen ions, such as silicates and carbonates.

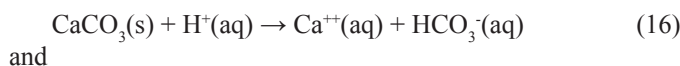
The manganese-rich nature of subaerial gossans contrasts with the manganese-poor gossans developed on the seafloor, where dissolved manganese may be transported away from the site of gossan development. In the subaerial environment, solutions may be more static, so their chemical evolution may result in dissolution of Mn-bearing minerals and precipitation of manganese oxides, hydroxides, and oxyhydroxides at the same site as precipitation of ferric minerals. High acidity develops if reactions take place under lower water/rock ratios, and the weathering process can be considered as a one-pass continuous flow reactor. The reactions described above for seawater weathering are generally applicable for subaerial weathering, but the increased acidity results in increased solubility of cations. In effect, subaerial oxidation of a VMS deposit is a significantly faster process than halmyrolysis. Increased solubility of cations, such as Fe(III) and Al(III), produce additional acidity by precipitation of hydroxides, such as ferric and aluminum hydroxides, and sulfates may precipitate upon fluid mixing and(or) evaporation:



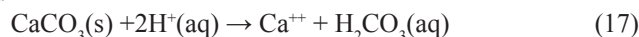
Such phases remain highly stable. These reactions produce a positive redox feedback loop (reduced species in sulfide minerals and oxidized species in solution) that continuously increases acidity in solution. During subaerial weathering, a wide variety of complex sulfates, hydroxysulfates, oxides, hydroxides, carbonates, silicates, and native metals may precipitate as secondary minerals, commonly as a result of evaporation. Over 100 minerals have been recognized, many of which are inherently unstable in an aqueous environment. As noted above, the precipitation of some hydroxides releases acidity, whereas the formation of sulfates and hydroxysulfates—such as jarosite, alunite, schwertmannite, and romerite—consumes protons. Many of these minerals are soluble, whereby acidity is again released; for instance:



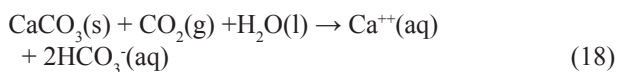
The presence of limestone country rock, or any carbonate-bearing assemblages, can mitigate the effects of acid drainage. Congruent reactions of acid drainage that involve carbonates (calcite, dolomite, siderite, ankerite, magnesite) result in partial or complete mineral dissolution and production of bicarbonate ions or carbonic acid, depending upon the pH of the acidic solution (Sherlock and others, 1995). Calcite is more easily dissolved than other carbonate minerals. In the absence of gaseous  $\text{CO}_2$  in the phreatic zone, the dissolution of calcite occurs in a closed system and the reactions proceed as follows:



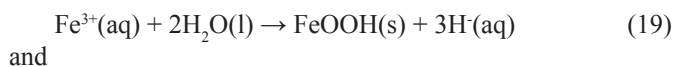
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However, the presence of gaseous  $\text{CO}_2$  in the vadose zone results in open system behavior limited only by the availability of one or more carbonate minerals. Increased calcite dissolution generates more bicarbonate ions and enhances consumption of acidity:



Some VMS deposits contain siderite, whose acid consumption capability is  $E_h$  dependent. Under reducing conditions, iron is released into solution as Fe(II) ions. In the presence of gaseous oxygen, released iron is present as Fe(III) and is subsequently hydrolyzed to ferric oxide or ferric oxyhydroxide (reactions 15,16), which produces acidity. In this case, the presence of siderite has no effect on the acidity of the solution.

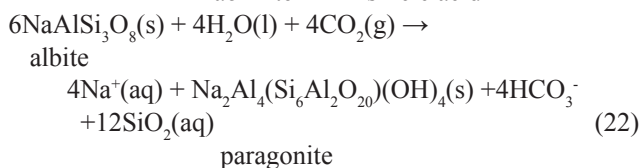
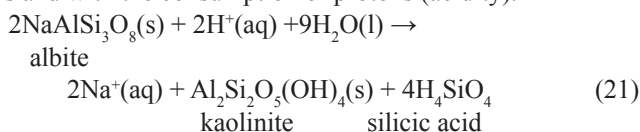


and



Silicate minerals are a ubiquitous part of VMS deposits. They occur as: (1) gangue minerals intimately associated with sulfides; (2) minerals within rocks that form a part of the VMS stratigraphic framework; and (3) secondary minerals developed during hydrothermal, supergene, and weathering processes. A very large variety of silicates are associated with VMS deposits, ranging from ferromagnesian minerals (olivine, pyroxene, amphibole, mica), to alkali-bearing aluminosilicates (feldspar, clay), to simple oxides (magnetite, hematite, quartz). The acid buffering capacity of these minerals and their host rocks vary widely in terms of potential chemical reactions and hydrologic considerations that determine the pathways of fluid movement. Highly siliceous rocks, such as rhyolites, quartzites, and siliceous argillites, have little buffering capacity. In

contrast, basic and ultrabasic igneous rocks and shales have a stronger buffering capacity. Generally, reactions with silicates are incongruent with the formation of secondary minerals (kaolinite, illite, montmorillonite), silicic acid, or bicarbonate ions and with the consumption of protons (acidity).



If dissolved silica in reaction 22 reaches saturation, then either chalcedony or opal may precipitate. The buffering capacity of the system is limited by further reactions that produce protons, such as precipitation of gibbsite.

## Factors Controlling Rates of Reaction

There have been relatively high numbers of experimental studies of the kinetics of sulfide oxidation for those sulfides that are least resistant to oxidation (pyrite, marcasite, and pyrrhotite; Lawson, 1982; Wiersma and Rimstidt, 1984; McKibben and Barnes, 1986; Moses and others, 1987; Moses and Herman, 1991; Evangelou and Zhang, 1995; Janzen and others, 2000). However, there have been fewer studies for sulfides that are common in VMS deposits but are more resistant to weathering (molybdenite, cinnabar; Daskalakis and Helz, 1993; Jambor, 1994; Rimstidt and others, 1994; Weisener and others, 2003). The factors controlling the rates of sulfide oxidation are both chemical and physical. The physical factors include:

11. hydrologic considerations—such as grain and fracture porosity/permeability (Plumlee, 1999) and hydraulic head—that determine the velocity of fluid movement and the extent to which advection moves reactant products from reaction sites and prevents surface poisoning; and
12. the geometry of sulfide minerals—such as crystal form, grain sizes and shapes, surface roughness, fractures, cleavage planes, pits, and edges—that collectively determines the specific surface area of reactant minerals and the presence of high energy domains.

Chemical factors include:

1. the pH of the reactant fluid that determines the solubility of Fe(III);
2. the presence of dissolved oxygen, Fe(II) and Fe(III) ions, and their solution concentrations;



3. mineral phase chemistry;
4. species activation energies for reaction progress;
5. rate laws (equations) for specific oxidative reactions; and
6. the physicochemical prehistory of the solid reactants, particularly temperature.

Non-oxidative reactions are pH dependent. Pyrite and marcasite do not undergo such reactions. Pyrrhotite and some other sulfides, such as sphalerite, can undergo non-oxidative dissolution by acidic solutions in the absence of dissolved oxygen and ferric iron (Janzen and others, 2000). Such conditions are unlikely in nature but might occur in the saturated zone.

The solubility of ferric iron is strongly pH dependent, being inversely correlated. At high initial ferric iron concentrations in acidic systems, the rate of oxidation of iron sulfides ( $\text{FeS}_2$ ,  $\text{Fe}_{1-x}\text{S}$ ) is efficient and obeys a zero order rate law, that is, the rate of oxidation is independent of concentration of reactants. At low ferric iron concentrations, as might be expected in circumneutral and alkaline systems, the oxidation of iron sulfide is dominated by reduction of ferric iron but the rate law is fractional. The rate constant, as measured by the rate of ferrous iron production, is approximated at 0.5, that is, the oxidation rate is proportional to the square root of ferric iron concentration.

Over a wide range of pH conditions and, hence, dissolved ferric iron concentrations, the rate laws are consistent with oxidation that involves complex sorption and desorption processes at the solid crystal surface. For instance, Moses and Herman (1991) demonstrate that ferrous iron adsorbed onto the surface of pyrite is a critical part of pyrite oxidation, as originally proposed by Singer and Stumm (1970). Reactions 1 and 3 indicate the importance of dissolved Fe(II) as an intermediary in electron transfer between pyrite and dissolved oxygen. The overall mechanism takes advantage of the preferential adsorption of Fe(II) onto pyrite surfaces and the preference of Fe(III) as the pyrite oxidant. The surface concentration of Fe(II) determines the reaction rate. Electrons are transferred from the pyrite surface to dissolved oxygen via adsorbed Fe(II) that is consequently oxidized to Fe(III). The latter is subsequently reduced to adsorbed Fe(II) by fast transfer of another electron from the pyrite surface and the cycle of oxidation and reduction is then repeated.

## Effects of Microclimate and Macroclimate

Plumlee (1999) provides a useful summary of the weathering of sulfidic ores in varying climatic zones. A fundamental consideration in the oxidation of such ores in the subaerial environment and the formation and dispersal of acid drainage is the availability and flow of water. The latter is determined by the hydraulic conductivity of the overall system and also

by the hydrologic cycle, both being determined by climate to some degree. The hydraulic conductivity of rocks depends upon: (1) the intrinsic permeability (grain-to-grain, fracture, mine workings); and (2) the degree of fluid saturation, this being determined by the position of the water table, which is a function of climate and local topography. Microclimates are particularly important in areas of significant elevation changes, for example, the Rocky Mountains, where precipitation changes can be extreme and periods of freezing and thawing can produce changes in hydraulic conductivity and increased rock exposure caused by the absence of significant biological groundcover. Extremes of microclimate are also important in remediation efforts where accessibility and biologic activity may be seasonally limited.

The availability of water is determined by the regional and local cycles of precipitation/evapotranspiration and humidity, which are functions of climate. In arid and semiarid climates, the flow of surface water may be seasonal, limited by the duration of wet periods punctuated by periods when surface evaporation exceeds rainfall (Nordstrom, 2009). Under these conditions, acidic surface waters may either disappear to dryness, or be greatly reduced in volume, resulting in precipitation of minerals that carry substantial acidity, for example, melanterite ( $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ) and chalcantite ( $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ). Nordstrom and Alpers (1999) provide a classic description of the processes of evaporation and re-solution at the Iron Mountain, Calif., VMS deposit. Subsequent periods of rainfall may result in re-solution of these minerals and dispersal of acid waters into surface waters and groundwaters. In temperate and tropical climates, abundant rainfall may result in excessive weathering, particularly through the action of organic acids. Flooding may result in physical transport of materials, for instance, downstream movement and dispersal of mine tailings, with the consequent increase in water turbidity and aerial extension of plumes of acidic drainage.

## Effects of Hydrologic Setting

A fundamental consideration in the oxidation of sulfidic ores in the subaerial environment and the formation and dispersal of acid drainage is the availability and flow of water. The latter is determined by the hydraulic conductivity of the overall system and also by the hydrologic cycle, both being determined by climate to some degree. The hydraulic conductivity of rocks depends upon: (1) the intrinsic permeability (grain-to-grain, fracture, mine workings); and (2) the degree of fluid saturation, this being determined by the position of the water table, which is a function of climate and local topography. In arid and semiarid climates, subaerial gossans developed atop VMS ores provide a porous cap that allows further access to the underlying fresh ore.

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