

A deeply weathered granitic outcrop showing the enlargement of joints and fractures by chemical and mechanical weathering. Abundant mineral and rock fragments accumulate at the base and eventually are picked up and transported as sediment. (Siever, 1988, Sand, p. 27; courtesy R. Siever.)

Weathering

If you stroll among the outcrops on a typical granitic batholith, such as the Sierra Nevada, you will notice that most of the rocks are granodiorites and quartz monzonites. In any given sample, the dominant minerals are feldspars, with plagioclases constituting 30%-50% of the rock and K-feldspars typically ranging from 5%-35%. In almost any igneous rock, quartz is typically only 5%-10%, with a maximum of about 25%-30% in a quartz-rich granite and none whatsoever in diorites or gabbros (or their volcanic equivalents, andesite and basalt).

But if you scramble down into the washes and ravines that drain the granitic mountains and examine the sand washing off those same rocks, you will see that quartz is already a much higher percentage of the sand and feldspars are much less common. If you follow a mountain stream down to the ocean and look at the sand on the beach, you will find that nearly all the sand is quartz and feldspars are relatively rare. In most beach sands, quartz may be 80%-95% of the sand-sized fraction. Clearly, some process is at work to decrease feldspar abundance, because feldspars go from being the most abundant mineral in the Earth's upper crust to being one of the scarcest in the detritus that was disintegrated and decomposed from that crust.

Where did all those feldspars (and the enormous quantities of aluminum, calcium, and sodium that make them up) go? Where did all that extra quartz come from? Because quartz is pure silica, we can deduce that some aluminum, calcium and magnesium must have been lost from the initial proportions

found in igneous rocks. Since they can't leave the planet, these chemicals must go somewhere. Most of them end up as components of clay minerals.

The same conclusion could be drawn by examining ancient sandstones. Although the minerals in these rocks were derived largely from igneous and metamorphic parents, much as they are in modern sediments, many ancient sandstones have few feldspars. The average sandstone is 50%-70%quartz, and many sandstones are 99% pure quartz. Just as happens today, some process in the geologic past must have altered the proportion of minerals from a parent rock to a final sedimentary end product. That process is weathering. Sediments and sedimentary rocks would not exist without weathering, the combination of processes by which pre-existing rocks physically disintegrate and chemically decompose into soil, loose clasts, and dissolved components. Weathering products constitute the raw materials from which sedimentary rocks are made.

Weathering is the simple consequence of exposing pre-existing rocks to the conditions at the Earth's surface: low temperature and pressure, organic activity, and chemically active substances such as water and atmospheric gases. Physical and chemical weathering are the means by which pre-existing rocks and minerals change and come into equilibrium with this surface environment.

Soil consists of untransported products of physical weathering, typically loose, unconsolidated, mainly resistant, compositionally altered mineral residue (for example, grains of quartz, feldspar,

mica, and rock fragments). Soil becomes sedimentary rock if it is eroded, transported (generally, by any of four agents: wind, ice, running water, and gravity), and deposited as **sediment**. Compaction and cementation convert sediment to sedimentary rock. Chapter 3 discusses how weathered clastic residues are actually entrained, carried away, and eventually deposited.

Chemical weathering generates various types of material. Some products are ions in solution (for example, potassium, sodium, and silica). These are transported as dissolved constituents in groundwater and surface runoff and are eventually precipitated as sediment. Other chemically weathered material is modified solid mineral residue (for example, clay minerals). Clay minerals are eroded and transported much as are coarser-grained clasts.

This chapter outlines the processes of physical and chemical weathering and summarizes how rocks disintegrate and decompose as a function of climate and topography.

PHYSICAL WEATHERING: DISINTEGRATING ROCK INTO CLASTS

There are four major mechanisms of physical (mechanical) weathering: freeze-thaw, insolation, stress release (unloading), and organic activity. Each is a slow, unspectacular process that leads to the same result. Solid, unyielding, difficult-to-erode rock is converted into smaller, movable, unconsolidated rock and mineral debris.

Freeze-Thaw

In this process, the active agent is water; the active catalyst is hourly, daily, weekly, or longer term temperature changes. Temperatures hovering near 0°C cause water to freeze into ice and melt into water repeatedly. When water freezes, a 9% – 10% volume expansion occurs. Water freezing along cracks and fissures developed in solid masses of rock must expand. Forces as great as several kilograms per square centimeter gradually split the rock apart. The term *ice-wedging* is used interchangeably with freezethaw. It was coined to describe situations in which ponded films of water in fractures transform into solid masses of ice that wedge apart masses of rock.

Several factors promote freeze-thaw. The process works best where fractures are abundant. Fractures might be columnar joints produced when lava cools, joints formed during extension or bending of bedrock, or joints formed along bedding planes. A

moist climate in which the daily temperature range roughly straddles the 0°C mark further increases the likelihood of freeze-thaw. A similar, less common process occurs when salts such as halite and gypsum crystallize in cracks and crevices. Evaporation of trapped brines can lead to the growth of more voluminous crystals that force apart the solid rock mass.

Insolation

Insolation refers to stresses generated when minerals are exposed to changing temperatures and undergo differential thermal expansion and contraction. When the latticework of adjacent minerals enlarges and collapses as bedrock surface temperatures rise and fall, expansion and contraction cracks develop and cause the solid rock to disintegrate. This process is common in arid, dry climates such as the Sahara and Mojave deserts where daily temperature fluctuations of $20^{\circ}-30^{\circ}\text{C}$ are common. In wetter climates, moisture facilitates insolation. Such minerals as clays hydrate and swell, then contract and desiccate, generating additional stress and strain. Insolation creates mechanical weathering products that are indistinguishable from those produced by freeze-thaw.

Stress Release

Stress release occurs when rocks buried beneath overlying material experience high confining pressures. As surface weathering and erosion proceed, overburden is removed, confining pressures drop, and the deeper seated rock mass expands. A series



Figure 2.1

Spheroidal weathering in a boulder of San Marcos Gabbro, Mesa Grande, San Diego County, California. (Photo by W. T. Schaller; by permission of the U.S. Geological Survey.)

of expansion cracks or joints develops roughly parallel to the ground surface; these joints evolve into a series of onionskin-like sheets or slabs of rock separated by crudely curved, subparallel cracks. Because these cracks are likely passageways for water, they become sites of freeze-thaw. Exfoliation—the spalling of curved slabs of rock from bedrock surfaces—and spheroidal weathering (Figure 2.1)—a process in which solid rock masses cut by intersecting, roughly cubical joint patterns weather into spheroidal cores—are attributable to both freeze-thaw and stress release from unloading.

Organic Activity

Organisms that live on or in weathering bedrock promote physical weathering. Plant roots seek out small pockets of soil formed above developing cracks. As plant growth continues, the root system lengthens and thickens, gradually prying apart the crack by generating stresses similar in magnitude and orientation to freeze-thaw stresses. Microscopic and megascopic organisms living within soil and altered bedrock can also fragment them further as they ingest and burrow through the material.

CHEMICAL WEATHERING REACTIONS

Dissolving Constituents

Chemical weathering proceeds in two distinct ways. (1) Some constituents dissolve completely; for example, such minerals as calcite and halite. The constituents dissolved from such minerals are carried away by groundwater and runoff and can be precipitated elsewhere with or without the assistance of organisms. (2) Other constituents, such as feldspars and micas, are altered into new minerals (especially clay minerals). These new minerals, altered or weathered residues, form when selected components are removed and carried away. Because they typically are finer-grained than the original material, they are more readily removed from the weathering site.

Chemical weathering of rocks and minerals involves several simultaneous chemical reactions: hydrolysis, hydration, simple solution, and oxidation-reduction. These reactions proceed most easily in the presence of both water and air.

Simple Solution (Solid Mineral + Acid or Water = Ions in Solution). Simple solution (dissolu-

tion) is the chemical reaction of solid rocks and minerals with water or acid. Bonds between ions in rigid crystalline lattices are broken and the freed ions are disseminated in solution. Solubility can be partial or complete. Let's examine some specific examples.

The mineral quartz is not very soluble. Less than 6 ppm (parts per million) is dissolved in normal fresh water. Crystals of quartz exposed in an outcrop of granite typically show little corrosion because of this minimal solubility. They appear fresh and unscathed by solution, standing out in relief above more easily decomposed minerals such as feldspar. The weathering reaction can be expressed as

$$SiO_2 + 2 H_2O \rightarrow H_4SiO_4$$
 (6 ppm)
quartz water silica in solution as hydrosilicic acid

Calcite is much more soluble than quartz. In the laboratory, dousing a block of limestone with weak acid will result in noticeable, instantaneous corrosion. In the natural world, exposures of limestone become pitted over periods of only days as they react with rainfall. Most natural rainfall becomes carbonic acid as raindrops fall through Earth's atmosphere and absorb small amounts of carbon dioxide gas:

$$H_2O + CO_2 \rightarrow H_2CO_3$$

water carbon carbonic acid
dioxide

Carbonic acid and acids in general contain abundant hydrogen ions. Thanks to their valency and small size, they have a strong affinity for anions and will displace other cations in mineral structures. Limestone dissolves as the hydrogen ions displace calcium ions, generating both dissolved calcium and biocarbonate:

$$CaCO_3 + H_2CO_3 \rightarrow Ca^{2+} + 2HCO_3^-$$

limestone rainfall dissolved dissolved calcium bicarbonate

Halite (NaCl) is extremely soluble, even in distilled water. Grains of halite dropped into a beaker of water disappear completely. A salty taste develops as sodium and chlorine ions become dispersed in the water, producing a brine. The solubility of sodium and chlorine is measured in thousands of parts per million, enormous compared with the solubility of quartz.

$$NaCl + H_2O \rightarrow Na^+ + Cl^-$$

halite water ions dissolved in water

Hydration and Dehydration (Solid Mineral + Water = New Hydrated Mineral; Dehyration is the Reverse). Some weathering

processes involve the chemical combination of preexisting minerals with water (hydration) or the removal of water from some pre-existing mineral (dehydration). These processes produce new minerals in greater equilibrium with the environment. Two common reactions are the dehydration of gypsum to form anhydrite:

$$CaSO_4 \cdot 2H_2O \rightarrow CaSO_4 + 2H_2O$$

gypsum anhydrite water

and the hydration of iron oxide (hematite) to form "limonite" (this is essentially corrosive rusting):

$$Fe_2O_3 + 3H_2O \rightarrow 2Fe(OH)_3$$

hematite water "limonite" (oxidized zone in soil)

A third hydration reaction occurs when the clay mineral kaolinite combines with water to form the clay mineral gibbsite; dissolved silica is released as a by-product.

Hydrolysis (Hydrogen Ion + Mineral with Mobile Cations = Entirely Dissolved Mineral or Partially Altered Mineral in Which Hydrogen Ions Replace Mobile Ions That Are Put Into Solution). Hydrolysis is defined as the replacement of cations in a mineral structure by hydrogen ions derived either from water or, more likely, from acid. Hydrolysis releases to the solution the cations replaced in the mineral structure by hydrogen and either converts the original mineral into a different mineral or dissolves it completely. (Simple solution of such minerals as calcite is really hydrolysis where no solid relict of the original survives.)

Most silicate minerals weather primarily by a series of hydrolysis reactions, and silicate minerals such as pyroxenes, amphiboles, micas, and feldspars, along with quartz, make up the bulk of the Earth's primary crust. The specifics of the hydrolysis process and the extent to which an original mineral is decomposed depend on the material.

Dark-colored (mafic) minerals such as olivine and pyroxene can dissolve completely:

$$Mg_2SiO_4$$
 + $4H^+$ \rightarrow $2Mg^{2+}$ + H_4SiO_4 dissolved silica

 $2CaMgSi_2O_6$ + $16H^+$ \rightarrow $2Ca^{2+}$ + $2Mg^{2+}$ + $4H_4SiO_4$ dissolved silica

Light-colored (felsic) minerals, especially feldspars such as orthoclase and plagioclase, dissolve partially, producing dissolved silica and cations and leaving fine-grained, easily transportable clay minerals:

Oxidation-Reduction (Atmospheric Oxygen Gains Electrons and is Reduced as Mineral Constituents Lose Electrons and are Oxidized, Producing New "Rusted" Minerals). Oxidation and reduction are inexorably linked. Oxidation does not occur without reduction, and vice versa. Oxidation is the process by which an atom or ion loses electrons. Reduction is the process by which an atom or ion gains electrons. The best oxidizing agent is atmospheric oxygen, O2; non-ionized atoms of oxygen (zero valency) in the atmosphere combine readily with other existing ions and gain electrons to become anions of oxygen (O^{2-}) . As a result, oxygen is reduced, but the ion from which the oxygen atoms gains electrons is oxidized. The most obvious examples of this process involve the oxidation of ferrous iron (Fe²⁺) to ferric iron (Fe³⁺). In the natural world, this is the process of rusting, so called because it changes dull, metallic, ferrous iron to reddish-orange ferric iron. For example,

The Controls

Several factors dictate which chemical weathering reactions will be at work. Climate is of paramount importance. Higher temperatures promote chemical weathering because kinetic thermal energy facilitates any reaction. Therefore, chemical weathering should be more extensive in warmer climates (lower latitudes) than in colder climates (higher latitudes and/or higher elevations). Moisture (rainfall) is also important because most chemical weathering requires water. Thus, warm and humid climates will be most favorable for chemical weathering. Even though the temperature is favorable in desert areas, not enough water is present for hydrolysis, solution, and hydration to occur. In arctic regions and high mountainous terrains, abundant precipitation exists, but in the wrong form, falling as snow and ice rather than rain.

Hydrolysis and simple solution depend on the ready availability of hydrogen ions. The abundance

of hydrogen ions—more specifically, the activity of the hydrogen ions in a solution—is controlled by the acidity or alkalinity of a solution; that is, the pH. The pH is a way to designate the concentration of H⁺ ions in solution, or [H⁺].

The pH of a solution expresses hydrogen ion concentration as the negative of the log to the base 10 of hydrogen ion concentration, or $-\log_{10}$ [H⁺]. The pH of solutions can range from 1 to 14 because the ratio of water to hydrogen and hydroxyl (the dissociation constant) is 1×10^{-14} . Solutions with precisely equal amounts of acid components [H⁺] = 10^{-7} and base components [OH⁻] = 10^{-7} have a pH of 7 and are termed neutral. Solutions with an excess of hydrogen ions have pH values from 1 to just below 7 and are called acids. Acids are the most effective agents of hydrolysis because they readily provide hydrogen ions to replace cations in the mineral lattice.

Most natural waters have pH values between 4 and 9. Figure 2.2 shows a graph that displays the pH (and Eh, discussed shortly) of waters in various natural environments. This graph is important because it permits inferences about the likelihood of hydrolysis and oxidation-reduction in waters of particular settings. For example, rainwater, streams, and groundwater are slightly acidic (pH values from 4 to 6.5). This means that they are active agents of hydrolysis and solution. Acidity is directly attributable to the absorption of atmospheric carbon dioxide by water as it falls through the atmosphere. (Recent concerns about acid rain reflect the fact that increased industrialization based on the accelerated combustion of fossil fuels adds ever-increasing amounts such of acid-producing gases as carbon dioxide and hydrogen sulfide to the atmosphere, making falling rain more acidic and corrosive.) Most soils have pH values from 4 to 5, so further chemical decomposition by hydrolysis continues in soil zones. Mine waters generated as groundwater percolates through sulfide-rich mineral deposits are notoriously acidic and corrosive. Conversely, the pH of seawater is slightly higher than 8, so little submarine hydrolysis occurs. (Many low-temperature chemical reactions do occur, however, as pre-existing minerals such as clays equilibrate with seawater.)

The likelihood of oxidation depends largely on the availability of free atmospheric oxygen (the principal natural agent of oxidation). The term Eh expresses the potential for either oxidation or reduction. Eh, short for redox potential, is measured using an electrolytic cell. Its value includes magnitude and sign, either positive (oxidizing) or negative (reducing). The higher the magnitude (in volts), the more likely it is that a particular ion or atom will be either oxidized or reduced. Iron is the most important element affected by the oxidation-reduction process.

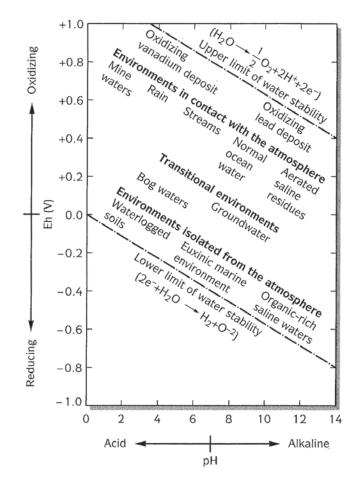


Figure 2.2

Geochemistry of natural waters, showing Eh and pH in various settings. These chemical conditions are classified into oxidizing and reducing conditions (vertical axis) and acidic vs. alkaline (basic) conditions (horizontal axis). (Modified from Blatt et al., 1980, *Origin of Sedimentary Rocks*, Fig. 6-12,p. 241; reprinted by permission of Prentice-Hall, Inc., Englewood Cliffs, N.J.)

Figure 2.2 shows variations in Eh for waters in selected natural environments. Natural waters that are reducing characterize depositional settings physically isolated from the atmosphere. In such settings as the waterlogged soils of swamps or the oxygenstarved, stagnant marine waters at the bottom of the Black Sea, reduction rather than oxidation occurs. Any iron found will be in the form of the ferrous (Fe²⁺) ion (for example, as the mineral pyrite). Any organic matter found therein will not decompose because organic decay is just natural oxidation; that is, the chemical "burning" of hydrocarbons as they slowly combine with free oxygen. Oxidation, iron present predominantly in the form of reddish ferric iron (Fe³⁺), and organic tissue decay characterize settings in which there is free interaction among atmospheric oxygen, rainwater, streamwater, groundwater, and ocean water.

WEATHERING IN THE NATURAL WORLD

The process by which source rock breaks down is complex because it depends on several factors: source composition, climate, drainage, topographic relief, and the relative rates of chemical and physical weathering. Nevertheless, the sedimentary geologist must attempt to infer what is happening at the source from the composition and texture of the material weathered from it.

Source Composition

Source composition—specifically the mineralogy, texture, and rock structure—is of paramount importance. Consider some examples. Two rock types, a marble and a quartzite, might be identical in every aspect but mineral composition. In identical physical settings, however, their styles of weathering will differ dramatically. In a moist, relatively warm climate, calcite grains corrode and dissolve as acidic rainfall washes over the marble. The dissolved components are carried away by groundwater and runoff and might eventually be precipitated as carbonate sediments in a setting such as the modern Bahama Banks. Conversely, the quartz grains composing the quartzite will dissolve slightly, if at all. In colder winter months, ice-wedging along bedding planes and joints may disintegrate the quartzite mechanically, producing an apron of quartz-rich rubble. Most of the quartz grains eventually will be transported away from the weathering site by mass wasting and runoff, perhaps ending up as alluvial or deltaic clastic deposits. Segregation by size might occur during transport; likewise, there might be some additional mechanical weathering by abrasion (quartz is hard and lacks cleavage).

Does physical weathering also affect the marble? Ice-wedging could produce an apron of calcite fragments around the exposed marble. Some of this detritus, like the quartz grains flanking the quartzite, might experience a brief period of clastic transport and deposition. Chemical weathering would continue to corrode this detrital calcite, however. After mechanical disintegration, individual calcite grains would have more exposed surface area, a condition that generally promotes chemical weathering. Corrosion would intensify, producing additional dissolved calcium and carbonate for precipitation elsewhere. Calcite fragments entrained as clasts would abrade rapidly to finer-grained detritus (calcite is soft and has excellent rhombic cleavage).

The details of how source rock lithology controls weathering differ, but there are general rules. Fine-

grained rocks (for example, volcanic rock, slate, and mudrock) decompose chemically more readily than coarse-grained rocks (for example, plutonic rock, gneiss, and sandstone). This tendency reflects the amount of grain surface area per unit volume, which controls the availability of chemical reaction points (that is, incomplete bonds) in a mineral.

In this context, it is useful to think of particular minerals as being *in equilibrium* with certain conditions in the crust or on the surface. Igneous minerals—especially olivine, pyroxene, hornblende, and the plagioclase feldspars—are formed in magma chambers at high temperatures; this is their equilibrium state. Once they are exposed to the Earth's surface conditions (lower temperatures and chemical weathering), they are out of equilibrium and essentially doomed to destruction (however slowly). To reach equilibrium, the silica, aluminum, iron, and other elements must seek a new mineral state that is stable at the Earth's surface. These are mostly quartz, clay minerals, iron oxides, and aluminum oxides.

Decades ago, Goldich (1938) examined the distribution of major rock-forming silicate minerals in several soil profiles and proposed a mineral-stability series that lists minerals in descending order of their propensity to survive chemical decomposition. This listing is almost precisely the same as the listing known as Bowen's reaction series, used to describe the order in which major silicate minerals solidify from igneous magmas. Olivine, pyroxene, and calcic plagioclase feldspar, the higher-temperature, higherpressure minerals that form first from igneous melts, are least resistant to weathering. This is largely because their simple crystal lattices (olivine is composed of simple tetrahedra; pyroxene is a singlechain silicate) are less tightly bonded together, and so the bonds are easily broken. These minerals also have abundant cations (especially iron, magnesium, and calcium) that are subject to chemical weathering and are eagerly grabbed by roots in biological weathering. Quartz, muscovite, and K-feldspar crystallize later from cooler melts in conditions more like those of the surface. These minerals are all complex sheet or framework silicates, with many Si-O bonds that are harder to break. Consequently, they are less susceptible to weathering. Rocks that are aggregates of unstable minerals such as olivine, pyroxene, and calcic plagioclase (basalt, peridotite, dunite, and gabbro) will decompose more easily than rocks composed of resistant minerals such as quartz, muscovite, and K-feldspar (rhyolite, granite).

Fissured and jointed rocks are more susceptible to weathering because they provide access to the fluids that promote chemical decomposition and icewedging. For example, foliated metamorphic rocks and well-bedded sedimentary rocks weather more rapidly than massive coarse-grained igneous rocks.

FOR FURTHER READING 25

Climate

The climate at the weathering site is crucial. Daily temperature fluctuations and the frequency with which the temperature rises above and falls below the freezing point determine the importance of icewedging and insolation. Total precipitation, especially the amount in the form of rainfall, governs the extent of hydrolysis, hydration, and solution. Higher mean annual temperatures increase chemical weathering rates.

Drainage

Like all chemical reactions, weathering reactions are reversible. For reactions to continue, reaction products must be removed. This stops re-reaction of products with one another in the reverse direction. For example, when feldspar weathers by hydrolysis to produce clays and dissolved constituents such as silica, potassium, sodium, and calcium, the reaction products can easily re-react if they remain trapped or ponded at the soil site (LeChatelier's principle). Re-reaction is common in poorly drained soil zones developed above bedrock. Conversely, where drainage is good and reaction products are quickly swept away, re-reaction cannot occur.

Topographic Relief

Topographic relief (the difference in elevation between low and high points in a region) and slope steepness strongly influence weathering. Slope steepness controls the rate at which weathering products are eroded from the weathering site and transported elsewhere. Once material is in transit, little additional chemical weathering occurs.

Mass wasting and runoff occur at higher rates in steep-sloped mountainous areas than in areas of low-lying, monotonous plains. Consequently, in mountainous regions, weathered material is removed rapidly and decomposition is less extensive. Soils developed where slopes are gentle and relief is low remain in place as precipitation continues to filter through them, permitting extensive decomposition.

Relative Rates of Chemical and Physical Weathering

The precise mix of weathering products generated in a region reflects the relative rates of mechanical disintegration and chemical decomposition. Rocks exposed in polar regions and high latitides are

typically mantled with a veneer of physically disintegrated, undecomposed rock rubble. Where topographic relief is high and steep slopes and cliffs are common, aprons of talus develop. Negligible chemical alteration accompanied by significant mechanical disintegration also typifies hot, dry desert climates. Weathering in desert and arctic regions produces large volumes of clastic sediment but few raw materials for chemical and biochemical sediments. Conversely, ice-wedging and insolation are unimportant in low-lying, low-latitude areas with tropical climates, but chemical decomposition is extensive. Tremendous volumes of dissolved silica, potassium, calcium, and sodium are produced and become ready candidates for chemical or biochemical sedimentation elsewhere. Clastic material generated in such tropical settings will be clay minerals, the future constituents of mudrock.

CONCLUSIONS

Physical disintegration and chemical decomposition of pre-existing rocks generate the raw materials from which Earth's sedimentary rock record is built. How the dissolved constituents produced by chemical weathering travel to depositional sites and are precipitated as the various chemical and biochemical sedimentary rock types is discussed in the chapters describing those rocks. The processes by which the physical residues produced by mechanical weathering are entrained at their place of origin, are transported elsewhere, and are eventually deposited are addressed in the next chapter.

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