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Geochemical Release and Environmental Interfaces

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3.1 Introduction

Geochemistry is the study of principles of chemistry which explains the properties and chemical operations of major geological systems within and on the surface of the earth, both in the past and the present (Mather 2013).

The geochemical release is the process of chemical weathering of minerals from their parent materials. These minerals originate from naturally occurring solids, such as sediments, and rocks, which interact with the environment through their surfaces. Depending on different environmental conditions that affect these surfaces, they could release mineral and gases to the environment.

Weathering is a major process in releasing of minerals from natural solids. It is the alternation or breakdown of rocks and other naturally occurring solids in its original form at the earth surface into simpler forms, such as sediments, clay, gases, soils, and substances that dissolve in water (Saunders and Fookes 1970).

Weathering at the earth surface happens in two different pathways namely, physical weathering and chemical weathering as shown in Figure 3.1. Physical weathering is disintegration of rocks by mechanical processes such as rock fracturing, freezing, and thawing, or breakdown in transportation by rivers and glaciers (Saunders and Fookes 1970). Chemical weathering occurs through chemical reactions between minerals and external agents such as air and water (Chung et al. 2020).

Geochemical release is the end product of chemical weathering of many geological systems. It can be separated into two different types, namely mineral release and gas release.



Figure 3.1 Picture of both physical and chemical weathering. Source: U.S. Department of the Interior / Public Domain.

3.1.1 Mineral Release

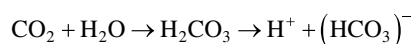
As mentioned earlier, release of minerals from rocks happens due to both chemical and physical weathering. The weathering of rocks occurs due to various factors, such as (Patel 2017):

- Properties of the parent rock: the mineralogy and the structure affect the susceptibility of the weathering process.
- Climate: high temperatures and rainfalls increase the rate of weathering
- Soil: moisture, pH, organisms, and host vegetation in soil form an environment that promotes the weathering of rocks.
- Length of exposure: longer the exposure, higher the rate of weathering.
- Topography: lower the topographic elevations, more susceptible to the weathering.

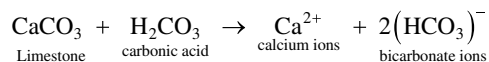
Minerals that weathered chemically from naturally occurring solids are due to many chemical reactions with air and water. These processes may include dissolution of minerals or sometimes combination with other atmospheric components in order to form new minerals, such as clay and oxides. Chemical weathering (Figure 3.2) occurs due to three main reactions, such as (Viers et al. 2007):

3.1.1.1 Dissolution

Carbonic acid forms from carbon dioxide (CO₂) that released from decaying organic matter and the atmosphere, dissolved in rainwater:



This carbonic acid reacts with limestones, dissolving carbonates yielding an aqueous solution of bicarbonate and calcium ions:



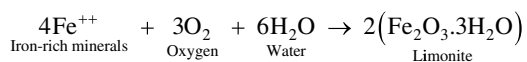
Most of the underground cavern systems are created by the dissolution of limestones.

3.1.1.2 Oxidation and Hydration

Oxidation produces iron oxide minerals (hematite and limonite) in well-aerated soils, usually in the presence of water.

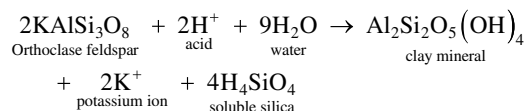
High iron content substances, such as magnetite, pyrite, pyroxene, amphibole, and olivine, are more prone to the oxidation.

These minerals combine with oxygen and water to form hydrated iron oxides as follows:



3.1.1.3 Hydrolysis

This reaction is responsible for the formation of clays, the most important mineral in soils. A typical hydrolytic reaction occurs when orthoclase feldspar reacts with slightly acidic water to form clay minerals, potassium ions, and silica in solution:



The ions released from silicate minerals in the weathering process are sodium, potassium, calcium, iron, and magnesium ions. They are carried away by rain and river waters and become important soil nutrients. (Viers et al. 2007)



Figure 3.2 Chemical weathering. *Source:* Bonnie Moreland / Flickr / Public domain. Accessed from: <https://www.geographyrealm.com/physical-chemical-of-weathering-of-rocks/>

Physical weathering is a mechanical process that fragments minerals and rocks, and this may happen due to certain reasons. Natural zone of weakness is one of the main reasons. Some of the most common processes are bedding planes in sedimentary rocks, joints in massive igneous rocks, and exfoliation in metamorphic rocks. Through uplift and erosion, rocks rise slowly to the earth's surface, where they are free from the weight of overlying rock; thus, their fractures will open slightly. This allows chemical and physical weathering to widen the cracks. Living organisms in the rocks may also promote weathering as shown in Figure 3.3. For instance, tree root may occupy and amplify cracks in rocks (Macheyeki et al. 2020).

Hot and cold cycles can also occupy in weathering of minerals by thermal expansion and contraction depending on the region. Mineral crystallization of aqueous solutions also contributes to the fractures to expand.

The weathered minerals are then transported through erosion. Erosion is a natural process that transports weathered or unweathered materials. It loosens, removes, and



Figure 3.3 Root weathering. *Source:* National Park Service / Jim Peaco / Public Domain.

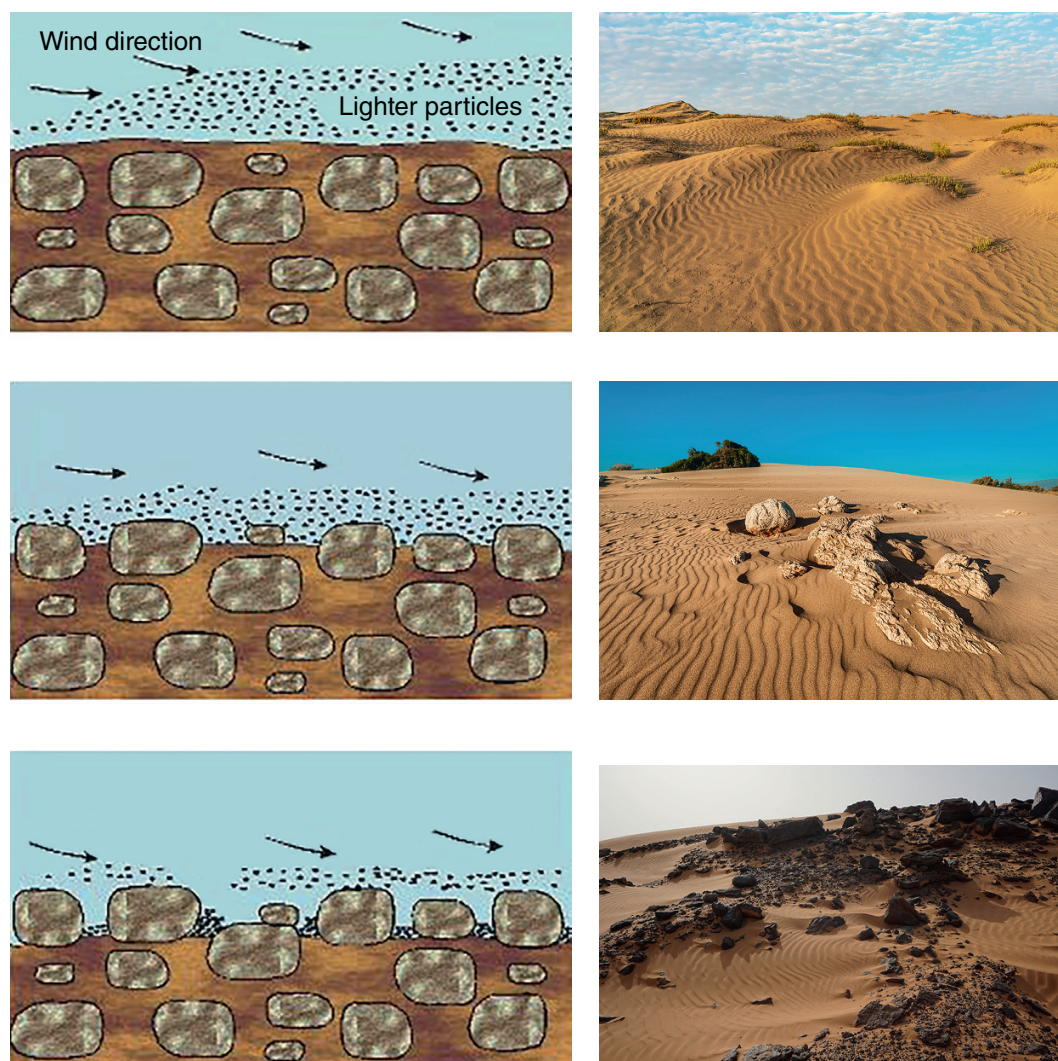


Figure 3.4 Erosion by wind. *Source:* Vastram/Adobe Stock, EdNurg/Adobe stock, maxos_dim / 55 images/Pixabay. Accessed from: https://www.geo.fu-berlin.de/en/v/geolearning/mountain_building/weathering/Erosion/index.html

transports materials like, sand, sediment, soil, mud, and other weathered minerals. Erosion uses mediums, such as wind (Figure 3.4), underground water as well as running water, waves, glaciers, and gravity (Moses et al. 2014).

3.1.2 Gas Release

When it comes to geochemical release of substances, it is very crucial to gain a knowledge about the gases that are released from geological systems, mainly from earth surfaces and also from the deep earth crust. It is a well-known fact that some minerals, such as quartz and pumice rocks, have cavities that contain gases like, CO_2 , hydrogen, and nitrogen. Gases that release from natural disasters, mainly from volcanic eruptions, earthquakes, and anthropogenic

breakage of rocks, also contribute to gas release. Emission of noble gases from geological resources also contributes widely to the geochemical releases.

There are three main hypotheses to explain the states in which the gases exist in rocks. The simplest of all is that the gases in cavities and pores have been entrapped in the rocks during the process of solidification of magma. It is supported with microscopic studies of minerals like quartz and topaz that observe numerous small gas bubbles (Chamberlin 1909).

The gases that present in many minerals are usually CO_2 and hydrogen found in hints enclosed in the cavities of the rock. Many gases are released to the environment with the heat reactions of nongaseous substances of rocks. Hydrogen liberates with temperatures higher than

500 °C. CO₂ is produced when carbonates are heated sufficiently in the presences of iron. CO is formed from the CO₂ when heated. Methane is also produced by decomposition of organic matter and the reaction between CO₂ and water. Likewise, many gases can be obtained with thermal reaction of nongaseous substances of rocks (Chamberlin 1909).

Shale gas (Figure 3.5) is another type of natural gas, which is trapped in the fine-grained sedimentary rocks which act as a reservoir as well as source. Shale is a combination of mud (clay and slit), clay, carbonates (dolomite and calcite), silica, and organic materials. The gas is normally stored in three distinctive ways: (i) free gas, gas within the rock cavity; (ii) adsorbed gas, gas that is absorbed onto the organic materials; and finally, (iii) dissolved gas, gas that is dissolved in the organic materials. These gases are obtained through horizontal drilling and hydraulic fracturing (Zendehboudi and Bahadori 2017).



Figure 3.5 A gas shale bedrock with the layered structure. Source: Zhang et al. 2020/John Wiley & Sons, Inc.



Figure 3.6 Volcanic gases in Hawaii are rich in carbon dioxide and sulfur dioxide. Flank of Kilauea between Pu'u O'o and coast. Source: Tada Images/Adobe Stock. Accessed from: <https://www.sandatlas.org/volcanic-gases/>

When considering geochemical releasing of gases, volcanic gases get an immense place. Relatively, volcanic gases are substances that releases from volcanos or volcanically active areas. Volatile substances are chemical elements that dissolved in magma that forms gases when placed toward low pressure and temperature.

Volcanic gases (Figure 3.6) mainly constitute about 90% of water vapors and 10–40% of CO₂. It also contains sulfur compounds such as sulfur dioxide and hydrogen sulfide (Aiuppa et al. 2005). It also consists of chemical elements like F, Cl, and B and is also a composition of H₂, CO, CH₄, S₂, N₂, NH₃, and O₂. Metals such as Pb, Zn, Cd, Hg, Cu, Bi, Na, and K also present at trace levels (Aiuppa et al. 2007).

The three main reservoirs that contribute to the formation of volcanic gases are as follows (Lin et al. 2010):

- The mantle
- The crust
- The atmosphere

Many volcanos in the continental regions are highly explosive, and the gases that release are more versatile and variable due to their composition. These volcanos contain higher amount of water and thick magma, which expand 1000 times more during an eruption. The water comes from two main sources. Many volcanos carry hydrated minerals beneath the earth crust which releases water under high pressure. Another source of water is meteoric water that derived from precipitation (snow and rain). Since this water contains other dissolved substances such as O₂, the volcanic gas composition is localized to its region.

Another fact worth knowing is that there are many places that release volcanic gases without a magma degassing (Figure 3.7). These types of gases are diffused through



Figure 3.7 Steam and volcanic gases escape from a crack in the roadway in the Leilani Estates neighborhood in the aftermath of eruptions from the Kilauea volcano on Hawaii's Big Island on 9 May 2018 in Pahoehoe, Hawaii. *Source:* U.S. Geological Survey/NASA Earth Observatory.

the ground or may be released through cracks of the earth surface. This is mainly due to the ground water heated by nearby volcanos. These gas vapors mainly constitute water vapor but may contain nonreactive species like CO_2 and He^3 . Volcanic gases: Overview (sandatlas.org).

Another geochemical gas release to be noticed is the gases that are released due to breakages of rocks (Figure 3.8). Slight amount of helium and argon gases released from rocks and earth crust under stress, which can be used to forecast natural disasters such as earthquakes before they happen. Rocks contain slight amounts of geogenic gases like radon, helium and argon that form over many years

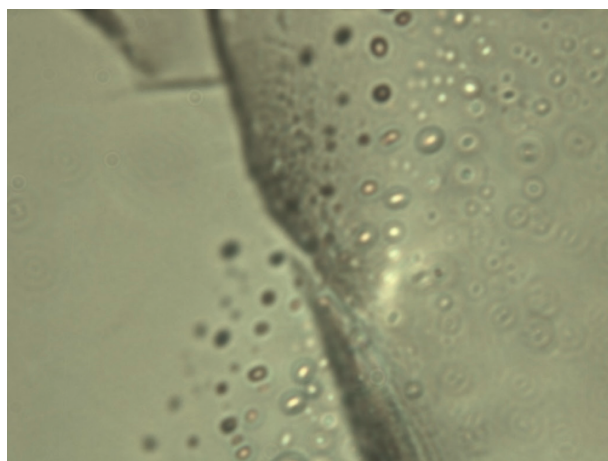


Figure 3.8 A magnified image of tiny gas-filled pores in the rock, with a stress-induced crack. *Source:* Gas released from rocks can predict impending breakage – GeoSpace – AGU Blogosphere. Accessed from: <https://blogs.agu.org/geospace/2016/12/30/gas-released-from-rocks-can-predict-impending-breakage/>

when radioactive compounds decays. The composition of these gases can be considered as a function of mineralogical composition, rock matrix, and the depositional, thermal, erosional, and tectonic history of the formation. Hence, the release of these noble gases gives a precursory signal before the deformation or degradation of rocks (Byerlee 1978).

3.2 Environmental Interfaces

Environmental interfaces are broadly defined as any surface in equilibrium with its surrounding environment. There are various types of environmental interfaces, including geochemical, atmospheric aerosols, nanomaterials, and indoor surfaces. Thus, investigating the connection between geochemical release and these varied and complex environmental interfaces is necessary to understand both beneficial and adverse effects on living organisms.

3.2.1 Atmospheric Aerosol Interface

Atmospheric aerosols are tiny particles of solids and liquids. An atmospheric aerosol interface is an equilibrium of these particles with the surrounding environment. Aerosol particles play an important role in the atmosphere. By absorbing and scattering solar radiation, aerosols reduce the amount of energy reaching the earth's surface, while at the same time they enhance the greenhouse effect by absorbing and emitting long-wave radiation (Pöschl 2005).

The aerosol particles are meticulously related with chemical reactions of gas and liquid phases at the gas-aerosol particle interface. The gas-aerosol interface is a localized region where both inorganic and organic species are enriched with. The reactions take place according to chemical and physical properties of the species. For instance, hydrophobic organic species are favorably absorbing on to the gas-particle interface through the particle phase. There are three main reactions that the gas-aerosol interface experiences, such as gas phase diffusion, interfacial transport, and particle phase diffusion, to achieve the gas-particle equilibrium (Qian et al. 2019).

Aerosols are sites that certain chemical reactions occur in. One of the most abundant reactions is the destruction of the stratospheric ozone. During winter, aerosols form polar stratospheric clouds. These clouds act as a site for the chemical reactions to happen. Volcanic aerosols preferentially contribute for destroying the stratospheric ozone.

There are three types of aerosols that mainly effect the climate. Among them, volcanic aerosols impact enormously on the climate. After a massive volcanic eruption, a large, wide layer of volcanic gases form in the stratosphere. The gases are highly enriched with sulfur dioxide ions.

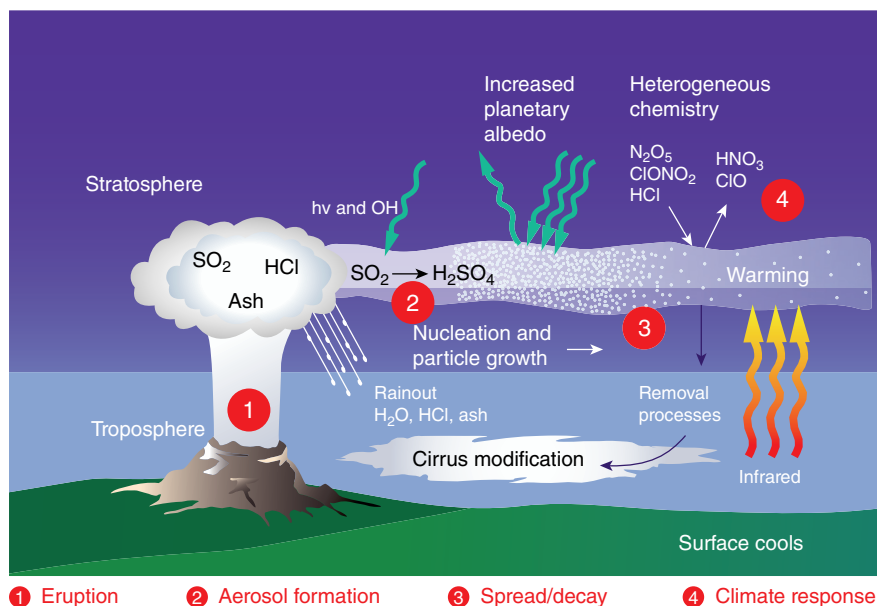


Figure 3.9 Illustration of production and effect of volcanic aerosols, including SO_2 . Source: Windows to the universe staff (Lisa Gardiner) volcanoes influence climate – windows to the universe (windows2universe.org).

Sulfur dioxide is a major substance that contributes to the depletion of ozone. Sulfur dioxide gases formed are converted to sulfuric acid, which condenses to produce aerosol particles that remain in the atmosphere for a vast period of time (Figure 3.9). Volcanic gases also contain hydrochloric (HCl) acid which condenses with water vapor and rained out of volcanic cloud formation. Volcanic aerosols increase the echelons of chlorine (Cl_2) gas that reacts with N_2 in the atmosphere, which is a key donor toward the ozone annihilations (Kirk-Davidoff 2018).

Desert dust is another method that affects the climate. Desert dust is a composition of many minerals which are suspended in the atmosphere (Figure 3.10). The particles are relatively large for atmospheric aerosols and would not remain in the atmosphere for a long time, if they were not launched by intense storms to higher altitudes. Since the dust is made up of minerals, the particles absorb sunlight and disperse it. By absorbing sunlight, the dust particles tend to heat the atmosphere, which in turn inhibits the formation of storm clouds. By suppressing the storm clouds and their rain, it is believed that the veil of dust will continue the expansion of the desert (Mahowald et al. 2014).

The third type of aerosol comes from human activities. While, much of the man-made aerosols come in the form of smoke from the forest fire by burning coal and oil. The concentration of artificial sulfate aerosols in the atmosphere has increased since the beginning of the industrial revolution. At current production level, man-made sulfate particles are believed to be outnumbered the

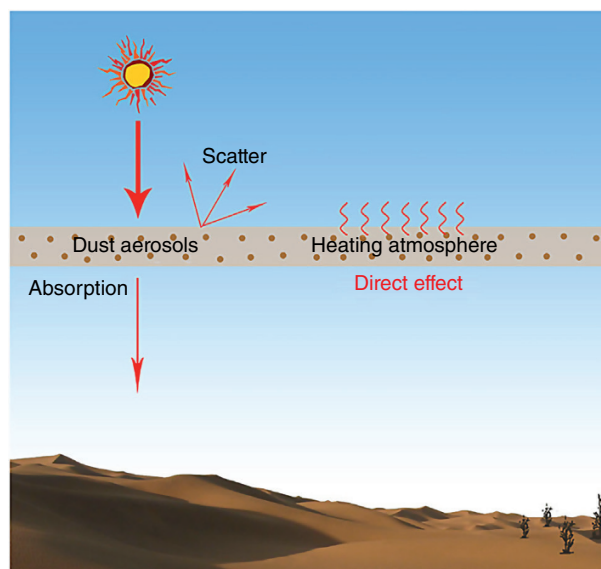


Figure 3.10 A schematic depiction of the direct radiative effect of dust aerosols. Source: Huang et al. (2014) / John Wiley & Sons.

naturally produced particles. Sulfate aerosols do not absorb sunlight but reflect it, which decreases the amount of sunlight reaching the earth.

3.2.2 Nanomaterial Interfaces

Nanoparticles (NPs) are of 1–100 nm in size and composed of organic matter, carbon, metal, metal oxide, or aerosol particles. In this size range, increase in surface area, change

of electronic state, or deficient or development of new lattice structures result in the appearance of unique magnetic, biological, optical, and mechanical properties. The extremely high surface area specifies the importance of the surface of a NP and distinctiveness compared to its core which in various cases is linked to its final application. Therefore, surface functionalization is critical in displaying its distinct properties which in turn would weaken upon aggregation (Perera et al. 2021).

Nanomaterials can be divided into two basic sections, namely natural nanomaterials and synthetic nanomaterials (Ghaemi et al. 2017). Natural nanomaterials are the substances that occur naturally in the earth crust. These particles are generally formed by various geological processes, such as volcanic eruptions, lightning flash pyrolysis, and biochemical processes as well. Thousands of different nanomaterials are added to the atmosphere by each and every active volcano. These materials can spread through a large area with the help of the wind containing elements like Ni, Cd, Pb, S, Fe, Ag, Ca, Si, and Cu. Synthetic nanomaterials are substances that are made through anthropogenic activities, both purposely and inadvertently. Synthetic nanomaterials are classified as engineered nanomaterials and incident nanomaterials (Barhoum et al. 2022).

Nanomaterials from volcanic ash, lightning, forest fire, and even from outer space are naturally present in the atmosphere. For instance, multiwalled carbon nanotubes produced from soot are present in the air in the size range of 15–70 nm (Griffin et al. 2017). Nanomaterials of silicon dioxide are suspended in the atmosphere due to volcanic eruptions (Michel et al. 2013).

Synthetic nanomaterials, both engineered and incident nanomaterials, are dissolved in the atmosphere. They released to the environment by the sources of productions. Gases that release from the road vehicles are considered to be the prime supplier for these engineered nanomaterials to be suspended in the air. Incidental nanomaterials like titanium oxide, that were used in many industries, can be found in water sources contaminated with waste waters from different industries, such as paint industry (Sani-Kast et al. 2015). Titanium oxide nanomaterials mostly accumulated in sludge-treated soils than by landfill and sediments. Zinc oxide (ZnO) is another incidental nanomaterial that accumulates in earth by disposal of electronics, medicines, and cosmetics such as sunscreens containing ZnO (Durenkamp et al. 2016). Carbon NPs, both incidental and engineered nanomaterials, are released mainly due to the emission of carbon from vehicles and industrial wastes, which may be waste water or waste gas. When these nanomaterials suspended in the atmosphere, they will have a direct effect on all geological systems.

3.2.3 Effect of Geochemical Release on Environmental Interfaces

3.2.3.1 Adverse Effects of Geochemical Release on Environmental Interfaces

The release of minerals and gases from the geochemical systems sometimes effects negatively to the whole atmosphere from earth crust to upper atmosphere. This includes air pollution and land pollution, as well as adverse effects on the human health.

One of the main pollutants that cause adverse effects is the release of polluted gases from natural and anthropogenic causes. This may include volcanic gases, desert dusts, carbon emission from road vehicles and industries, smoking, forest fires, etc.

Volcanic gases and dust that are blown to the atmosphere during an eruption have an impact on environment and human health. Despite the distinct locations of the volcanos situated, their effect can be widely spread around the atmosphere. Volcanic gases mainly consist of sulfur dioxide, CO₂, hydrogen sulfides, and hydrogen halides which would affect negatively not only on atmosphere but also on human health, animals, properties, and vegetation. These compounds are potent greenhouse gases. SO₂ is a greenhouse gas having both warming and cooling effects, and it reacts with water to form sulfuric acid which is the key source of acid rain. Acid rain causes many environmental effects like deforestation, corroding buildings, contaminating water ways, and aquatic systems (Tricker and Tricker 1999). CO₂ is another gas that is harmless in small quantities, but when in high quantities, it causes global warming that effects badly on the living organisms. It also has an effect on vegetation and human health as well. At higher concentrations, it may cause coma and sometimes death as well. For instance, the incident in Nyos Lake event killed almost more than 1000 of people in Cameroon (Tchindjang 2018). Fumes that come from volcanos are acidic not only with sulfuric but also with HCL and HF as well (Aiuppa 2009). These also contribute to the acid rain significantly.

Another major adverse effect of geochemical release is an effect due to mineral release through the weathering process, due to human activities like mechanical weathering. Mechanical weathering, if done incorrectly, causes landslides, deformation of rocks, and also the formation of mountains as well.

Release of heavy metals and metalloids such as arsenic, chromium, and lead can cause severe health problems. For example, exposure to arsenic is known to cause health effects from skin tumors, cancers, and children's cognitive developments. Inorganic arsenic has been identified as a carcinogen that can induce cancers in human body (Hong

et al. 2014). Additionally, arsenic is known to effect on major organs such as the dermal system, cardiovascular system, renal system, nervous system, hepatic system, endocrine system, and hematological system (Abdul et al. 2015). Additionally, the release of nonmetallic ions such as fluoride can also cause adverse health effects. Excess amount of fluoride in drinking water can cause dental fluorosis. It is reported that more than 200 million people have dental fluorosis that caused primarily by the excess amount of fluoride in drinking water (Jagadeshan et al. 2015).

3.2.4 Benefits of Geochemical Releases on Environment

Even though there are some of negative effects of geochemical releases, they also have positive effects toward the environment.

The most important benefit is the release of plant nutrients into the environment. These nutrients are including macronutrients such as K, Ca, Mg, P, and S, macronutrients such as B, Cl, Cu, Fe, Mn, Mo, Ni, and Zn, and some other nutrients that are essential for plant life under particular environmental conditions (Co, Na, and Si). These

nutrients are present in rocks, and they are slowly released to the environment during weathering of these rocks. It is suggested that ground rock acts as a slowly release fertilizer that provides the nutrients top soil that can be utilized by plants.

As mentioned earlier, volcanic gases contain SO₂ substances that cause the greenhouse effect but also have a cooling effect to the atmosphere, when SO₂ reacts with water vapor to form sulfuric acid which has a property of cooling the stratosphere by back-scattering the sunlight radiation, making the atmosphere cool. (Burtraw et al. 2005)

Volcanic eruptions are also beneficial. Volcanic rocks and substances are weathered to form most fertile soils in the earth, which can be used in cultivations and forest civilizations. Some of the young volcanos can be used as harnesses to produce geothermal energy. Many volcanic materials are sources to the metallic minerals such as Ag, Au, Cu, Pb, and Zn.

The release of noble gases such as He and Ar from the breakage of rocks are also useful in finding when and where the natural disasters like earthquakes, take place, hence, preventing the loss due to natural disasters before they happen. (Bauer et al. 2016)

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