ENVIRONMENTAL GEOSCIENCES

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Lecture-56

Geochemical Classification of Elements: Interaction of Geochemical Cycles

Welcome to the SWAYAM NPTEL course on Environmental Geosciences. We are discussing the module eleven that is Geochemical Classification of Elements and Geophysical Methods. In the module eleven, we have already discussed in the lecture one. Today we will discuss the lecture two that is Geochemical Classification of Elements in which we will see about the interaction of the geochemical cycles. The important concepts which will be covered in this lecture is the introduction to geochemical cycles, geochemical cycle of carbon, geochemical cycle of oxygen, geochemical cycle of nitrogen, geochemical cycle of sulphur and geochemical cycle of phosphorus.

Now, first of all, we will understand about the geochemical cycles. The concept of geochemical cycles is a comprehensive expression of interactions within the four components of the Earth's super system, that is, geosphere related to the solid Earth, then hydrosphere, biosphere, and atmosphere - in terms of global reservoirs of materials and transfer of materials, from one reservoir to another. Every element has its own unique geochemical cycle and all of these cycles have been operating simultaneously. Each cycle comprises two interconnected components. The first is the an exogenic component that is which operates on the surface of the earth

and second is the an endogenic component that is which operates in the interior of the earth. The two components are linked through tectonics. It is assumed that in the absence of anthropogenic perturbations, chemical mass transfer among global reservoirs is cyclic, which means that the intake of geologically permanent reservoirs is balanced in the long run by their output so that their size and composition remain within rough limits constant over long periods of time. As geochemical processes appear to be cyclic superimposed on the slow secular evolution of the Earth, the modeling of environmental systems boils down to the modeling of cyclic processes or parts of them.

The factors involved in the construction of geochemical cycling models include, first the identification of sources and sinks of the elements. Second, the definition of the boundaries of the reservoirs. Third, the prediction and evaluation of transport paths. Fourth, quantitative knowledge of the masses of the substances in reservoirs and fluxes into and out of reservoirs. And fifth, the appropriate mathematical models relating the various variables.

Based on this, the different types of geochemical cycles are, first, the geochemical cycle of carbon, second, the geochemical cycle of oxygen, third, the geochemical cycle of nitrogen, fourth, the geochemical cycle of sulphur, fifth, the geochemical cycle of phosphorus. These geochemical cycles are of prime importance for the biosphere, the most active geochemical realm at present and the Earth's surface. Now first, the geochemical cycle of carbon. The carbon cycle is important for three reasons. First reason is that carbon is one of the basic elements of the structure of all life on the Earth, making up approximately fifty percent of the dry weight of all living things.

Second, the cycling of carbon approximates the transfer of energy around the earth, the metabolism of natural, human and industrial systems. And third, the carbon dioxide and methane are the two of the most important greenhouse gases. The earth contains approximately ten to the power of twenty three grams of carbon, most of it sequestered in carbonate rocks and buried organic matter such as kerosene, oil, natural gas and coal. Near about zero point one percent of the carbon in the Earth's upper crust is cycled throughout active surface reservoirs. The main exogenic reservoirs are the oceans, the biosphere, the land and the atmosphere.

Carbon fluxes between the atmosphere and the oceans and between the atmosphere and the continental biosphere are very large. The main processes that control the transfer of carbon among these reservoirs are biological i.e. oxygenic photosynthesis and aerobic respiration by terrestrial plants and phytoplankton in the oceans.

$$\textit{Photosynthesis}: CO_{2\,(g)} + H_2O_{(l)} + \text{sunlight} \Rightarrow CH_2O + O_{2\,(g)}$$

In the photosynthesis process, the carbon dioxide plus water in presence of sunlight makes the CH_2O plus oxygen.

$$\boxed{\textit{Respiration}: CH_2O + O_{2(g)} \Rightarrow CO_{2(g)} + H_2O_{(l)} + \text{energy}}$$

In the respiration process, the same CH_2O plus oxygen gives us the carbon dioxide and the water plus energy, where CH_2O stands for organic compound such as carbohydrates. Almost all multicellular life on Earth depends on the production of carbohydrates by photosynthesis and breakdown of those carbohydrates by respiration to generate the energy needed for the movement, growth and reproduction of organisms.

Most of the carbon dioxide extracted from the atmosphere through photosynthesis is returned to the atmosphere through cell respiration and decay of plants. Here you can see the diagram which is showing the simplified geochemical cycle of carbon, some CO_2 and CH_4 are returned to the atmosphere via plant decay and the cycle would be in balance if it were not for human interference such as burning of fossil fuels, cement manufacturing and deforestation. You can see in the diagram from the atmosphere and the land, oceans and mantle, everywhere we are seeing the changing of carbon dioxide, carbon monoxides and the methane in these different spaces. On an annual basis, the amount of carbon involved in photosynthesis and respiration is about one thousand times greater than the amount that moves through the geological component. Non-biological processes that release carbon dioxide to the atmosphere include burning of fossil fuels and biomass, cement manufacturing, decay of organic matter, and breakdown of calcium carbonate.

During the past one fifty years, the atmosphere has registered a thirty percent increase in the amount of carbon, mostly from the combustion of fossil fuels. The main geochemical processes involved in the cycling of carbon include the weathering of rocks exposed by erosion and tectonic uplift, second, precipitation of minerals, burial and subduction of rocks and sediments at convergent plate boundaries, and third, the volcanism. Weathering of rocks containing carbonate and silicate minerals is facilitated by carbonic acid formed by reaction of water with atmospheric CO_2 and by oxidation of organic matter. The precipitation of calcite and silica is predominantly biological in the sense that they are precipitated by reef and planktonic organisms to build their skeletons. When marine animals and plants die, their remain settled toward the sea floor.

Much of this organic debris undergoes decomposition by bacteria and dissolution during their downward journey replenishing the ocean water in dissolved CO_2, calcium, silica, and nutrients. The CO_2 is stored in the deeper waters of the oceans for hundreds to a thousand or so years before being returned to the atmosphere by the upwelling of the deep ocean waters. The organic debris that escapes degradation during downward transit accumulates as part of the seafloor sediments. Burial eventually transforms calcite-rich sediments into limestone and the highly altered, finely disseminated organic matter called kerogen into oil and gas under appropriate temperature-pressure conditions. Burial of terrestrial plant material commonly in swampy environments leads to the formation of different ranks of coal depending on the temperature pressure conditions experienced by the buried material.

The carbon incorporated in sedimentary rocks may be transformed into the anthracite or graphite by thermal metamorphism whereas limestones may recrystallize to form marble. The carbon cycle continues as seafloor spreading leads to subduction of the seafloor under continental margins. The carbon-wearing material in the subducting slab eventually melts and the carbon is incorporated into magma. Part of the carbon enters crustal igneous rocks formed from this magma and some carbon is released through volcanic eruptions through the atmosphere, mostly as CO_2, where the carbon combines with water and returns to the Earth's surface as H_2CO_3 dissolved in rainwater. The widespread occurrence of marine carbonate deposits suggests that dissolution of CO_2 in seawater has played an important role in the removal of carbon dioxide from the Earth's atmosphere.

Now, the geochemical cycle of oxygen. A unique feature of the Earth among celestial bodies is an abundance of free molecular oxygen in its atmosphere. Living organisms depend on oxygen for breathing and for producing energy. Oxygen is also essential for combustion and it is the ingredient for maintaining the stratospheric ozone shield that provides protection from UV rays. Oxygen is a very reactive element and it readily reacts with most elements of the periodic table.

The atmospheric oxygen concentration has been maintained at a fairly constant value for a long time because of a balance between its production and consumption. The main source of atmospheric oxygen is oxygenic photosynthesis by land plants and phytoplankton of the oceans which produces sugars and oxygen from CO_2 and water in the presence of sunlight.

$$CO_{2(g)} + H_2O_{(l)} + \text{sunlight} \Rightarrow CH_2O\ (\text{carbohydrate}) + O_{2(g)}$$

You can see the reaction also CO_2 with water and sunlight making the carbohydrate and oxygen. Here you can see the simplified exogenic geochemical cycle of oxygen that is from atmosphere to land and land to oceans and oceans to again atmosphere. So here it is very nicely dealt about the, taking of oxygen by surface water, groundwater, animals, soil, rocks and then again by weathering it is going to oceans.

So this figure illustrates a geochemical cycle of oxygen among atmosphere, land and oceans. A small amount of oxygen is also produced by photolysis of water vapor, the net reaction for which can be represented as the equation. Here you can see the reaction with water and UV photon giving the hydrogen and oxygen.

$$\boxed{2H_2O_{(g)} + \text{UV photon} \Rightarrow 4H_{(g)} \uparrow + O_{2\,(g)}}$$

Atomic oxygen formed by the photo dissociation of molecular oxygen by ultraviolet radiation is the major form of oxygen above near about one twenty kilometer altitude. The main processes that result in relatively large fluxes of oxygen from the atmosphere to the Earth's surface include the aerobic respiration, that is the oxidation of organic substrates with oxygen to yield chemical energy.

Second, biologically mediated oxidative metabolism of compounds such as methane, methanol and formaldehyde which are common in soils and sediments as the products of anaerobic fermentation and reaction. And third, the various oxidation reactions, that is example of oxidation reactions that consume oxygen include combustion of fossil fuels and biomass, oxidation of sulfide to sulfate, oxidation of iron-II minerals to iron-III minerals, and oxidation of reduced volcanic gases. Aerobic respiration is the most important process of oxygen consumption on the earth. And the crust mental system holds nearly ninety nine point five percent of the Earth's oxygen and is recycled through plate electronics. Now I will discuss the geochemical cycle of nitrogen.

Nitrogen is an essential constituent of DNA, RNA and proteins which are the building blocks of life. All organisms therefore require nitrogen to live and grow. The availability of nitrogen to sustain life should not be a problem considering that it constitutes nearly seventy nine percent by volume of the Earth's atmosphere two point eight two into ten to the power twenty moles of nitrogen gas and much smaller amounts of six other molecular species that is NH_3, NH, N_2O, NO, NO_2 and HNO_3. The N_2 gas is inert and therefore cannot be utilized directly by plants or animals except by a few primitive bacteria that are capable of converting nitrogen gas to NH_3 or NH_4^+, which is the only way organisms can utilize nitrogen directly from the atmosphere. The other significant reservoirs of nitrogen include sediments and sedimentary rocks and to a lesser extent the biosphere and dissolved organic compounds in the oceans.

The oceans contain a relatively small amount of nitrogen as dissolved nitrogen because of its low solubility in water. The nitrogen cycle is a little more complicated cycle because nitrogen exists in both organic and inorganic forms as well as in many oxidation states. Moreover, nitrogen is not involved to any appreciable extent in mineral dissolution and precipitation; it is strictly a biogenic element that is cycled through the action of microorganisms. Thus, microbial processes have a strong, in many cases, controlling influence on the biogeochemistry of nitrogen. Three classes of microorganisms are important in this connection, that is, those that convert N_2 to NH_4^+, those that convert NH_4^+ to NO_3^-, and those that convert NO_3^- back to N_2, and thus completing the cycle.

Nitrogen is cycled through the biosphere, atmosphere and geosphere by six main natural processes which transform nitrogen from one chemical form to another. The six natural processes are first the nitrogen fixation, second the ammonia assimilation, third the nitrification, fourth the assimilatory nitrate reduction, fifth the ammonification and sixth the denitrification. Nitrogen fixation is the process by which N_2 is converted to any nitrogen compound in which nitrogen has a non-zero oxidation state. The most common is the reduction of N_2 to NH_3 mediated by certain bacteria i.e. rhizobium which live in the root nodules of legumes such as peas and beans and cyanobacteria. Here you can see the reaction with the nitrogen and water gives the NH_3 and oxygen.

$$\boxed{2N_{2(g)} + 6H_2O \Rightarrow 4NH_3 \text{ (wihin the organism)} + 3O_{2(g)}}$$

The NH_3 is released following the death of the organism and subsequent hydrolysis of NH_3 produces NH_4^+, which can be assimilated by plants and the reaction is NH_3 plus H_2O giving the NH_4^+ plus OH^-.

$$\boxed{4NH_3 + 4H_2O \Rightarrow 4NH_4^+ + 4OH^-}$$

Over geological history, most reactive nitrogen has been formed by biological mediation. In the latter half of the twentieth century, however, the Haber-Bosch process for manufacturing NH_3, which is used to make fertilizers and explosives, has been the dominant process on continents for creating reactive nitrogen. This process uses nitrogen from the atmosphere and hydrogen from the fossil fuels, usually from the natural gases and operates at high temperature and pressure with a metallic catalyst. Another reactive form of nitrogen, NO gas, is produced by high energy natural events such as lightning or high temperature combustion of fossil fuels. You can see the reactions also.

Ammonia assimilation is the uptake of NH_3 or NH_4^+ by an organism into its biomass in the form of an organic nitrogen compound. All nitrogen obtained by animals can be traced back to the eating of plants at some stage of the food chain. We may not realize it, but the nitrogen in our food was fixed initially by nitrogen fixing bacteria. Nitrification is the aerobic process by which microorganisms oxidize ammonia to nitrate ion and derive energy from the reaction. Nitrification is a combination of two bacterial processes, that is oxidation of ammonium ion to nitrate ion by one group of bacteria, that is nitrosomonas, and oxidation of NO_2^- to NO_3^- by another group of bacteria, that is nitrobacter.

The conversion of nitrites to nitrate is beneficial for plants because accumulated nitrites are toxic to plant life. Assimilatory nitrate reduction is the uptake of nitrate ion by an organism and incorporation as biomass through nitrate reduction. It is an important process for input of nitrogen for many plants and organisms. Ammonification is part of general processes of decomposition that converts reduced organic nitrogen to reduced inorganic nitrogen by the action of microorganisms. Denitrification is the reduction of nitrates back to any gaseous nitrogen species largely N_2.

Here you can see the reaction also which is giving the gaseous nitrogen species. It is an anaerobic process that is carried out mainly in sediments by bacterial species such as Pseudomonas and Clostridium and the conversion takes place following sequence. Being a gas, N_2 is likely to be lost directly to the atmosphere. Here you can see the simplified exogenic chemical cycle of nitrogen. The natural nitrogen cycle has been affected considerably by anthropogenic input of nitrogen gases from various sources.

Denitrification is the only nitrogen transformation process that removes nitrogen from ecosystems, thereby approximately balancing the nitrogen fixed by the nitrogen fixers described. The natural exogenic nitrogen cycle has been affected considerably by anthropogenic input of nitrogen gases from various sources, ammonium-based chemical fertilizers, automobile exhaust, industrial plants, and sewage facilities such as septic tanks and holding tanks. You can see the diagram of the photochemical smog also. The various forms of nitrogen in our ecosystems contribute to a number of environmental problems such as photochemical smog and acid rain and creation and growth of eutrophic lakes and oceanic dead zones through algal bloom-induced hypoxia. Now the geochemical cycle of sulphur.

Sulphur is a very reactive element and combines directly with many elements, especially with hydrogen and oxygen forming H_2S and many oxides of sulphur, the most important of which are the SO_2 and SO_3. Sulphur is also a biologically active element and is cycled readily through the food chain. Some of the earliest organisms on the earth utilize sulfur compounds, particularly through anoxygenic photosynthesis. Sulphur from the mantle enters the hydrosphere as a result of alteration or weathering of mafic and ultramafic rocks in the oceans and on land by emission of SO_2 during volcanic eruptions. In the present oxic state of the atmosphere, any H_2S in the volcanic emissions is rapidly oxidized to SO_2.

Volcanic emissions also release SO_2 directly to the atmosphere. Other sources of sulphur in the atmosphere are biologically produced H_2S, dimethyl sulphide and other organic sulfur compounds which are readily oxidized to SO_2; SO_2 from burning of fossil fuels and biomass and industrial processes and SO_4^- and sulfate ion from sea salt aerosol. Here you can see the simplified geochemical cycle of sulphur, which is telling that how the sulphur is playing important role in the atmosphere, land, mantle and oceans. Most of the sulphate ion re-deposited in the ocean as precipitation and dry-fall. The SO_2 combines with H_2O to form H_2SO_4, which leads to the acid deposition on land and in oceans.

Weathering of Sulphur-bearing sediments releases the stored Sulphur, which is then oxidized into SO_4^-, into sulphate ion. Sulphate ion is taken up by the plants and microorganisms and converted into the organic forms. Animals consume these organic forms through their food, thereby cycling the Sulphur through the food chain. When organisms die and decay, some of the sulphur is again released as sulphate ion and mostly transported as runoff, although some enters the tissue of microorganisms. The fate of sulphate ion that enters the ocean and lakes from the atmosphere and as runoff from the land is dominated by anaerobic bacteria that reduce sulphate ion to H_2S.

These bacteria can tolerate a large range of pH and salinity conditions and they occur widely in marine and lacustrine sediments as well as in the overlying water column if it is sufficiently anoxic. The H_2S reacts with the metals, forming sulphides, predominantly iron sulphide, that accumulates on the seafloor with marine sediments and eventually recrystallizes to pyrite. In addition, sulphate salts such as anhydride and gypsum are precipitated episodically in marine and non-marine evaporite basins. At the present time, sulphate input into the ocean exceeds the output by a large amount, the imbalance being due to excessive inputs of anthropogenic sulphur and the absence of large modern-day evaporite basins. The sulphur incorporated in sedimentary rocks is recycled into the hydrosphere in the form of dissolved sulphate ion when the sedimentary rocks are exposed to chemical weathering.

Now the geochemical cycle of phosphorus. Phosphorus is an essential element for all organisms and is a key player in the fundamental biochemical reactions. It is a critical component of ATP i.e. adenosine triphosphate, the cellular energy carrier. Adenosine triphosphate contains a large amount of energy stored in its high-energy phosphate bonds; the energy is released when ATP breaks down into ADP and utilized for many metabolic processes. Phosphorus like calcium is an essential ingredient for body weights.

In human body eighty percent of the phosphorus is found in teeth and bones as organophosphates and in calcium phosphates such as hydrooxyapatite and fluorapatite. Organisms cannot directly assimilate phosphorus stored in rocks and soils. Conversion to orthophosphate, which can be assimilated directly, occurs through geochemical and biochemical reactions at various stages in the global phosphorus cycle. The simplified geochemical cycle of phosphorus you can see here from the land, oceans, and Earth's surface. Very little phosphorus circulates in the atmosphere because at the earth, normal temperature and pressure, phosphorus and its compounds are not gaseous.

Sedimentary rock constitute the largest reservoir of phosphorus. Weathering of continental bedrock results in the dissolution of phosphorus minerals such as apatite and release of phosphorus as phosphate ion that can be assimilated by organisms. Plant absorb phosphates from soil or water, then bind the phosphate into organic compounds. The phosphorus is passed into the animals through successive steps in the food chain and eventually returned to the soil or water through the excretion of urine and feces, as well as from the decomposition of plants and animals after death. Much of the phosphates delivered to the oceans through runoff, however, are pollutants derived from anthropogenic sources such as mining, leakage of sewage, and use of phosphates for fertilizers, detergents, soft drinks, etc.

The phosphorus is transported as soluble phosphate ion as an adsorb phase on suspended particles of soil clays and ferric oxides and as detrital primary apatite and particulate organic compounds. The solubilization/desorption of some of this phosphorus adds to the phosphorus budget of the oceans. The sole means of phosphorus removal from the ocean or lake water is burial with marine sediments that accumulate on the ocean floor. The phosphatic materials in the sediments include organic phosphorus compounds that survive bacterial decay, finely dispersed authigenic calcium phosphate in marine muds of continental margins; phosphate adsorbed on hydrous ferric oxides and incorporated in $CaCO_3$ during growth of calcareous shells. When sediments are stirred up by upwelling a lot of phosphorus returns to the surface water and re-enters the phosphorus cycle.

As is the case with nitrogen, phosphorus also undergoes many transfers between deep and surface waters before becoming buried permanently in sediments and locked in the resulting sedimentary rocks. This phosphorus would be released only when the rocks are brought to the surface by tectonic uplift and subjected to weathering. Now let us summarize the lecture. We have discussed first about the geochemical cycle. Geochemical cycle describes the movement of chemical elements through Earth's spheres maintaining environmental balance.

These cycles regulate the distribution and recycling of essential elements needed for life. Then we have discussed the geochemical cycle of carbon. We have seen the carbon cycle involves the exchange of carbon among the atmosphere, oceans, biosphere and geosphere through processes like photosynthesis, respiration, decomposition and fossil fuel combustion. It plays a crucial role in regulating Earth's climate and supporting life. Then we have discussed the geochemical cycle of oxygen.

We have seen the oxygen cycle maintains atmospheric oxygen through biological and chemical processes such as photosynthesis, respiration and oxidation. It is vital for sustaining aerobic life and influencing atmospheric and oceanic chemistry. Then we have discussed the geochemical cycle of nitrogen. We have seen the nitrogen cycle involves nitrogen fixation, nitrification assimilation, ammonification and denitrification, facilitating the conversion of nitrogen between its gaseous and usable forms. This cycle is essential for plant growth and ecosystem functioning. Then the geochemical cycle of sulfur, the sulfur cycle transfers sulfur between the atmosphere, lithosphere, and biosphere through processes like weathering, volcanic activity, bacterial activity, and sediment deposition. It influences soil fertility and acid rain formation. And lastly, we have discussed the geochemical cycle of phosphorus. We have seen the phosphorus cycle moves phosphorus through rocks, water, soil, and living organisms without a significant atmospheric phase. It is a key nutrient for DNA, RNA, and ATP, and plays a crucial role in ecosystem productivity. Thank you very much to all.