ENVIRONMENTAL GEOSCIENCES

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Lecture-55

Geochemical Classification of Elements

Welcome to the SWAYAM NPTEL course on Environmental Geosciences. We have discussing module eleven. We have to discuss in module eleven about the geochemical classification of elements and geophysical methods. Now, today we will start the lecture one that is geochemical classification of elements. In this lecture, the important concepts we will cover like introduction to geochemistry, history of geochemistry, the origin of elements, the geochemical classification of the elements.

Here, first of all, we will understand about the geochemistry. In the simplest terms, geochemistry may be defined as the science concerned with the chemistry of the earth as a whole and of its component parts. Geochemistry deals with the, Geochemistry deals with the distribution and migration of the chemical elements within the earth in space and in time. The primary purpose of geochemistry is on the one hand to determine quantitatively the composition of the earth and its parts and on the other hand to discover the laws which control the distribution of the individual elements. The main task of geochemistry can be summarized as the determination of the relative and absolute abundances of the elements and of the atomic species that is isotopes in the earth.

The study of distribution and migration of the individual elements in the various parts of the earth, say the atmosphere, the hydrosphere, crust, etc. and in the minerals and rocks with the object of discovering principles governing this distribution and migration. Now history of geochemistry, just we will understand the history of geochemistry, the science of geochemistry has largely developed during the present century. Nevertheless, the concept of an autonomous discipline dealing with the chemistry of the earth is an old one and the term geochemistry was introduced by Swiss chemist Schonbein, discoverer of ozone in eighteen thirty eight. The history of geochemistry naturally includes much of the history of chemistry and geology. Because geochemistry is basically concerned with the chemical elements, their discovery and recognition are the landmarks in the history of the subject.

Lavoisier recognized the thirty one elements say Oxygen, Nitrogen, Hydrogen, Sulphur, Phosphorus, Carbon, Chloride, Fluoride, Bromide, Antimony, Silver, Arsenic, Bismuth, Cobalt, Copper, Tin, Iron, Manganese, Mercury, Molybdenum, Nickel, Gold, Platinum, Lead, Tungsten, Zinc, Calcium, Magnesium, Barium, Aluminum, and Silicon. Of these, Gold, Silver, Copper, Iron, Lead, Tin, Mercury, Sulphur, and Carbon were already known to the ancient world. The last decade of the eighteenth century saw the discovery of Uranium, Zirconium, Strontium, Titanium, Yttrium, Vanadium, Chromium, and Tellurium.

By nineteen hundred, therefore, the periodic table was essentially complete except for some short-lived radioactive elements and for Europium, Luteinium, Lutetium, Hafnium, and Rhenium Proof of this, however, was first provided in nineteen fourteen when Moseley demonstrated the correlation between X-ray spectra and the atomic numbers of the elements. Throughout the nineteenth century, geochemical data were mainly the byproduct of general geological and mineralogical investigations and comprised more and better analysis of the various units like minerals, rocks, natural waters and gases making up the accessible parts of the earth. In many ways, nineteen hundree twelve can be considered a critical date in the development of geochemistry because of the work of V.M. Goldschmidt and his associates.

In the same year, Von Laue has also shown that the regular arrangement of atoms in crystals acts as a diffraction grating toward X-rays and thus made the discovery that enabled the atomic structure of solid substances to be determined. In the last fifty years, the work and the stimulus of the Goldschmidt have helped geochemistry to develop from a somewhat incoherent collection of factual data to a philosophical science based on the concept of the geochemical cycle in which the individual elements play their part according to established principles. Geochemical speculation has extended beyond the accessible parts of the earth to the nature and constitution of the interior, the development of the earth throughout the geological time and ultimately to its pre-geological history and to the history of the solar system as a whole. Geochemistry is at the threshold of new and exciting discoveries and changes. Now we will understand the origin of the elements.

The structure of the nuclei of the elements as aggregates of protons and neutrons has resulted in theories to explain their origin and their relative abundances by a synthesis or buildup starting with either or both of these basic building blocks. Several theories as to the mode of formation of the chemical elements have been proposed One which may be termed the equilibrium theory proposes that the relative abundances of the elements are the result of a frozen thermodynamic equilibrium between nuclei at some high temperature and density. By suitable assumptions as to the temperature, pressure and density, good agreement with observed abundances is obtained for elements of atomic number up to fourty.

For elements of higher atomic number, however, these assumptions lead to impossibly low abundances. On this account, Theories have been proposed that consider the relative abundances of the elements as resulting from non-equilibrium processes on this type. On this basis, the light nuclei were built up by thermonuclear processes and the remaining nuclei by successive neutron capture with intervening P-disintegrations. This theory predicts the general trend of the observed data but fails to explain some of the detailed features, particularly bridging of the gap caused by the non-existence of nuclei of atomic weights five and eight.

It is apparent that no single process can satisfactorily account for the observed complexity. Advances in nuclear physics allowed Burbidge, Fowler, and Hoyle in nineteen fifty-seven to propose that the general features of the abundance curve could be explained by nuclear reactions taking place in stars. In order to explain the measured distribution, they outlined eight processes for the synthesis. In their model, elemental matter started with hydrogen, which formed the primitive matter from which stars were made. The individual steps in their synthesis are discussed as below.

First, the hydrogen burning to produce helium. Hydrogen burns by successive proton capture to produce three helium. At temperatures of ten to the power of seven degrees centigrade and densities about hundred gram per centimeter cube, three helium nuclei impact and combine to form four helium and two protons. At still higher temperatures, additional nuclear reactions involving three helium, four helium and protons provide alternate mechanisms for producing additional four helium. In older or second-generation stars containing club carbon, a catalytic cycle progressing through six steps allows the overall reaction from four atom of hydrogen to one atom of helium.

The carbon cycle reaction also provides a mechanism for the production of quantities of fourteen nitrogen in the star. Second is the helium burning by three body collisions or triple alpha. The reaction takes place at temperatures in the order of ten to the power eight degree centigrade and densities of about ten to the power five gram per centimeter cube. This process provides a mechanism for skipping the unstable nucleides with masses of five and eight.

A twelve carbon produced can then add four helium to produce sixteen oxygen. At this point in a star's evolution, hydrogen has been converted to helium and the helium into twelve carbon and oxygen with the accumulation of some nitrogen. Further collapse of the star producing higher temperatures and greater densities allows additional reactions sometimes known as the alpha process or the carbon and oxygen burning to take place. In this stage of stellar evolution, twelve Carbon nuclei react to form species such as twenty Neon, Twenty three Sodium, twenty three Magnesium and twenty four Magnesium together with a new supply of alpha particles and protons. In sequence, oxygen nuclei react to produce Silicon-twenty eight, Phosphorus-thirty one, Sulphur-thirty one and Sulphur-thirty two and probably some chloride and argon from secondary reactions involving the alpha particles, protons and neutrons.

As the star evolves further, silicon burning or the equilibrium e- process takes place. Because of the high temperatures, the rate of nuclear reaction is increased and elements with atomic numbers greater than twenty eight silicon come into equilibrium with it. This process is responsible for the nucleosynthesis of the most abundant nuclei between atomic number twenty-eight and atomic number fifty-seven at the Fe peak. With the production of the iron group elements, the star will have run out of the reactions that can supply it with energy since iron is at the top of the curve of binding energy per nucleon. The primary mechanism for the synthesis of elements heavier than iron is by far the capture of free neutrons.

Neutrons are apparently produced by the reaction of alpha particles on thirteen carbon, seventeen oxygen or twenty-one neon. Slow neutron capture or the S-process can produce elements up to and including two zero nine bismuth but many observed nuclei are bypassed. The process is called the S-process because the rate of neutron addition is slow compared with beta decay lifetimes of the nuclei produced. Any unstable nuclei produced generally decay before the next neutron interaction takes place. The isotopes of a given element are built up successively until one is reached that is unstable.

Then beta decay produces the isobaric nucleoid of that element which serves as the target for further isotope building reactions until another unstable species is formed. This process produces peaks in the element abundance curve where there is a buildup of of stable elements with low-neutron capture cross-sections. To produce elements heavier than bismuth and to make neutron-rich elements not made by the s- process, a rapid neutron capture or r- process has been proposed. In this process, neutrons are added to beta decay unstable nuclei before the decay can take place. This allows the production of many nuclei which made through subsequent decay account for the neutron rich isotopes of some elements.

The large neutron fluxes for the r process that is the rapid neutron capture process appear to take place during the massive stellar explosions called supernovas. These explosions provide the large flux of nutrients required and a mechanism for dispersing the elements made by all of the processes into space so that they may be recycled. Now, we will understand the geochemical classification of the elements. Goldschmidt was the first to point out the importance of this primary geochemical differentiation of the elements. He coined the terms siderophile, chalcophile, lithophile, and atmophile to describe elements with affinity for metallic iron, for sulfide, for silicate, and for the atmosphere respectively.

When he put forward this concept in nineteen twenty-three, a few quantitative data were available on which to base his ideas. The geochemical nature of an element could of course be established by measuring its distribution between three liquid phases of metal, sulphide and silicate. He recognized the difficulty of carrying out these measurements in the laboratory, but remarked that meteorites provide us with such an experiment in a fossilized condition. Many meteorites consist of nickel iron, troilite, and silicate, all of which have presumably solidified from a liquid state. The distribution of a particular element between those three phases would be established when the system was in a liquid condition and can be determined by mechanically separating these phases and analyzing them individually.

From such analysis, the partition of the element between metal silicate and sulfite can easily be calculated. The information derived from meteorites was supplemented by that obtained by a study of smelting processes, such as the distribution of elements during the smelting of the Mansfeld copper slate in Germany. The smelting of this slate gives a silicate slag a matte rich in iron and copper sulfide and metallic iron. Spectrographic measurements of the concentration of many minor elements in the different phases have given distribution coefficients agreeing on the whole with those determined from examination of meteorites. On the basis of these results, an element may be classified according to its geochemical affinity into one of the four groups that is siderophile, chalcophile, lithophile and atmophile.

Some elements show affinity for more than one group because the distribution of any element is dependent to some extent on temperature, pressure, and the chemical environment of the system as a whole. For instance, chromium is strongly lithophile element in the earth's crust, but if oxygen is deficient as in some meteorites, chromium is decidedly chalcophile, entering almost exclusively into the sulfo-spinel daubreelite, i.e. FeCr2S4. Similarly, under strongly reducing condition, carbon and phosphorus are siderophile. In the right side of the table, you can see the four different columns telling about the siderophile, chalcophile, lithophile and atmophile and discussing in detail about the geochemical classification of the elements. The mineralogy of an element, although a general guide, may not be altogether indicative of its geochemical character.

For example, all thallium minerals are sulfides, the greater part of the thallium in the earth crust is contained in potassium mineral in which the thallium ion proxies or the potassium ion. In general, the classification of an element as lithophile, chalcophile or siderophile refers to its behavior in liquid-liquid equilibria between melts. When an element shows affinity for more than one group, it is given in parentheses under the group or groups of secondary affinity. The geochemical character of an element is largely governed by the electronic configuration of its atoms and hence it is closely related to its systematic position in the periodic table. In the table you can see the Atmophile is having the single line, Lithophile no line, Chalcophile the double line and Siderophile the triple line.

Here you can see which of the elements belongs to atmophile, lithophile, chalcophile and siderophile in the periodic table. Lithophile elements are those that readily form ions with an outermost eight electron shell; the chalcophile elements are those of the B subgroups whose ions have eighteen electrons in the outer shells; the siderophile elements are those of group eight and some neighboring elements whose outermost shells of electrons are for the most part incompletely filled. These factors are reflected by other properties also. Goldschmidt pointed out the marked correlation between geochemical character and atomic volume. If the atomic volume of the elements is plotted against atomic number the resulting curve shows maxima and minima. All siderophile elements are near the minima; the chalcophile elements are on the sections in which the atomic volume increases with the atomic number; they are followed by the atmophile elements, whereas lithophile elements are near the maxima and on the declining sections of the curve.

If the heat of formation of an oxide is greater than that of iron oxide, the element is lithophile; the difference between the two heats of formation is a measure of the intensity of the lithophile character. Similarly, those elements having oxides with heats of formation lower than iron oxide are chalcophile or siderophile, semi-quantitative measure of lithophile, siderophile or chalcophile character is also provided by the electrode potential. Elements with high positive potentials such as the alkali and alkaline earth metals are lithophile; the noble metals, with high negative potentials, are siderophile; elements falling in the intermediate range are generally chalcophile. Now let us summarize the chapter. Firstly, we have discussed the introduction about the geochemistry in which we have discussed that geochemistry explores the chemical composition and processes of earth's material, studying element distribution and interactions with the lithosphere, hydrosphere, atmosphere, and biosphere.

Secondly, we have discussed about the history of geochemistry. We have seen that geochemistry evolved from early chemical and mineralogical studies, gaining recognition in the nineteenth and twentieth centuries through advancements in analytical chemistry and the study of Earth's elemental cycles. The origin of the elements. Elements originated from stellar nucleosynthesis, where hydrogen and helium formed in the Big Bang, and heavier elements were created in stars through fusion, supernovae, and the neutron capture processes. And lastly, we have discussed about the geochemical classification of elements.

We have seen elements are classified based on their chemical behavior and affinity, categorized as lithophile that is rock loving, chalcophile that is sulfur loving, siderophile that is iron loving and atmophile that is gas loving elements. Thank you very much to all.