

### The Distribution of the Chemical Elements.<sup>1</sup>

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**P**ETROLOGISTS generally agree that the earth contains a core of an iron alloy, most probably nickel iron with about 8 per cent of nickel, in analogy to the most common types of iron meteorites. Below the common silicate rocks of the crust there is probably a region of enrichment of heavier silicates, which have separated by crystallisation from molten silicate magma, and have settled downward owing to their high specific gravity. Probably the mineral olivine is present here in substantially larger amounts than in the average surface rocks.

does not explain the fact that there seems to be a very distinct boundary to the iron core, and also a marked discontinuity against the silicate mantle. It seems also improbable that two substances of so different density as iron and silicate, originally present in a molten state, would not have separated in the earth's field of gravity. The possibility must be considered that this intermediate shell largely, or at least to a considerable part, contains sulphides and oxides of heavy metals, especially the monosulphide of iron, a substance we even observe as a

Radial Thickness.	Density.	Name.	Main Chemical Features.	Main Physical Features.	Which Group of Elements is Concentrated.
Several 100 km.	0.0015	Atmosphere	Nitrogen, oxygen, water vapour, carbon dioxide, rare gases	Gas	Atmophile
0-11 km.	about 1	Biosphere	Organic substances and skeleton minerals	Solid and liquid, often in colloidal division	Biophile
0-11 km.	1	Hydrosphere	Oceanic and fresh water with dissolved salts and gases, snow and ice	Liquid (in part solid)	Atmophile (and some lithophile)
60-120 km.	2.8	Earth's crust of silicates	Ordinary silicate rocks	Solid	Lithophile (of late crystallisations and mother liquors)
1100 km.	3.6-4	Eclogite shell	Silicate rocks, probably rich in $Mg_2SiO_4$	Solid, very dense crystalline arrangements of atoms (eclogite facies)	Lithophile (of early crystallisations)
1700 km.	5.6	Sulphide - oxide shell	Characterised by large amounts of sulphides and oxides of heavy metals, especially iron	Solid	Chalkophile
3500 km.	8-10	Nickel iron core	Alloy of iron and nickel	Solid (in part liquid ?)	Siderophile

Concerning the physical state of matter in this heavier silicate shell underlying the earth's crust, we know with certainty that it is in the solid state, and that certain crystallised silicates and other minerals must be present in a peculiar state of high density owing to pressure, which is characteristic for the eclogite facies, as deduced by Fermor and Eskola, and recently most convincingly demonstrated by P. Wagner.

Between the eclogite shell and the iron core there is still another mighty shell, separated from the eclogite shell and from the iron core by surfaces of discontinuity detected by measurements of the propagation of seismic waves. By many petrologists this shell is considered to be a mixture of silicate and nickel iron. This opinion, however,

distinct separate phase in a very large number of meteorites.

From many basic igneous rocks in the earth's crust molten sulphides segregate as separate sulphide magmas. Any such sulphide magma will tend to migrate towards the zone between the iron core and the silicate mantle, so that in this region of the interior of the earth there would accumulate the major part of sulphidic compounds, mainly iron monosulphide, together with heavy oxidic minerals, especially oxides of iron and chromium, which separate from silicate magmas at early stages of crystallisation.

Outside the silicate shell or lithosphere, there are further envelopes of our earth, the hydrosphere and the atmosphere, and on the boundary between the lithosphere and atmosphere, as well as intergrown through the hydrosphere, there is a

<sup>1</sup> From a discourse delivered at the Royal Institution on Friday, Mar. 15.

last, and from the human point of view a most important sphere, the biosphere, the zone of organised organic substance, the zone of life.

Our earth thus is separated into a number of shells, arranged in the order of density, as shown by the table on p. 15.

Men of science agree that our solid earth must once have been in a molten condition to enable the density distribution which prevails to-day to be formed. Already in times older than geological record, in the early 'astronomical' age of the earth, the subdivision of the molten planet, surrounded by a gaseous envelope, into several liquids, must have begun, followed by separation of the different liquid phases according to gravity. The distribution of chemical elements between the three liquids and one gaseous phase may now be considered from the viewpoint of physical chemistry; we may try to find the quotients of partition in the four-phase equilibrium. Such volatile elements, which have no very great affinity to the substances of the three liquid phases, will accumulate in the gaseous envelope, such as, for example, argon and nitrogen; also compounds with similar properties, as water and carbonic acid, will enter the primordial atmosphere. All these substances may be called *atmosphile*. Many chemical elements gather in the silicate magma; they are *lithophile* elements. The most prominent element is oxygen, constituting 62 per cent of the numbers of atoms present, or even 92 per cent of the volume of the earth's crust. The only heavy metal entering in appreciable amounts into the silicate shell is iron, about 2 atomic per cent of iron being present.

Next we shall consider the elements which are concentrated in the molten iron; we may call them *siderophile* elements. These are elements having a great solubility in molten iron, either as uncombined elements or as chemical compounds, such as nickel, platinum, carbon, phosphorus. Lastly, we may consider the elements which enter into molten iron sulphide; we may give them the name *chalcophile* elements. Such elements are, for example, copper, silver, lead, bismuth, selenium.

The actual amount of metals and of non-metallic elements in the earth as a whole has resulted in sulphuration and oxidation of part of the iron. We find iron in large amounts in the sulphide phase, and even to some extent in the silicate phase. Therefore, the partition of all other metals will be dependent on their affinities to oxygen and to sulphur, compared with those of iron. If an element is more siderophile than iron it will enter into the nickel-iron core; if it is more chalcophile than iron it will concentrate in the sulphide phase; if its inclination to enter into oxygen compounds is greater than that of iron it will accumulate in the silicate slag. Iron, therefore, is a kind of measure of geochemical affinity.

It would be interesting to know whether the rarity of precious metals is real, or if it is due to special quotients of partition which might have concentrated such metals as gold and the platinum metals, in the interior of our planet. Especially

it would be a matter of importance to ascertain if the elements of the platinum group really are so very rare as they appear to be from most analysis of terrestrial matter. The average amount of platinum in the average silicate rocks may be considered to be of the order of 1 to 1000 millions, that is, about 1 gram in 1000 tons of rock. We may, without any doubt, predict that platinum and the other siderophile metals of the platinum group must be found in very much larger concentrations in iron meteorites, if the present distribution of elements is due to an equilibrium of partition. By the microdocimastic methods of analysis, worked out for our geochemical work by Dr. Lunde and Mrs. Johnson Høst, a large number of terrestrial rocks and of meteorites were analysed for precious metals by Mrs. Høst in my laboratory. Some data from her determinations illustrate the amount of platinum metals in meteorites:

Iron Meteorites.	Total Platinum Metals.
Arispe . . . . .	117 grams per ton.
Savik, Cape York . . . . .	75
Mount Joy . . . . .	{ 68
Mukerop . . . . .	{ 54
Toluca . . . . .	38
N'Goureyma . . . . .	25
	{ 2
	{ 2
Silicate Meteorites.	
Juvinas	No platinum metals, no silver, no gold.
	Total precious metals less than 0.05 gm. per ton.
Stannern	No platinum metals, no silver, no gold.
	Total precious metals less than 0.05 gm. per ton.

These data, and many others, demonstrate that the platinum metals are not to be considered as very rare elements, but that their relative rarity in terrestrial surface rocks is only a consequence of their partition between nickel iron and silicates.

The quotients of partition between the different phases for any given element must be dependent on the properties of this element, and we may expect to find general relations between geochemical distribution and the properties of atoms and ions. If we plot a diagram showing the atomic volume of the chemical elements as a function of atomic number (nuclear charge), we find the following correlation between geochemical character and atomic volume. The typical siderophile elements are found at the minima of atomic volume, as, for example, carbon, phosphorus, iron, ruthenium, platinum. The typical atmosphile elements tend towards the maxima of atomic volume, such as hydrogen and the rare gases. Lithophile elements occupy the descending branches, where we find the typical ion-forming elements such as magnesium and calcium. In the ascending branches of the curve we find the typical chalcophile elements, for example, copper and selenium. These regularities seem to be connected with different types of electronic arrangement in the several types of atoms and ions. If there exist elements following after uranium in atomic number, they are probably siderophile, and for this reason they may be absent or nearly absent from the rocks of the earth's crust.

We have seen how the present distribution and

apparent frequency of chemical elements may be largely due to the laws of partition between the four phases, a separation which has taken place in the very early history of our earth. As cooling proceeds there comes into action a new kind of separation, which has no precedents in the earlier history of our earth, namely, *fractional crystallisation*. Among the first products of separation are minerals with low solubility in the silicate magma and high melting points, such as chromite and olivine; then follow other iron ores, together with the bulk of pyroxenes and plagioclase feldspars; later on the pyroxenes are succeeded by amphiboles and biotite; and the basic plagioclases are followed by acid ones and by potash feldspar, with quartz and muscovite. At last only pegmatitic magmas and aqueous solutions remain as a kind of mother liquor of the magma, from which crystallise coarse pegmatitic dikes and hydrothermal mineral veins, and from which also gaseous constituents may escape, giving rise to pneumatolytical minerals.

Whilst the partition into atmophile, lithophile, etc., groups had taken place between amorphous phases, as gases and liquids, the process of fractional crystallisation involves the presence of crystalline phases, and the properties of atoms and ions in crystalline arrangements must be of deciding importance for the fate of the different elements. The distribution of any given element between a liquid phase and a coexisting crystalline phase will depend on isomorphism between the element (or its ions) with the components of the crystalline phase. Now isomorphism, as crystallographers have known for a very long time, is mainly dependent on the volume of the different kinds of atoms or ions, and the question of partition therefore leads to a relation between atomic and ionic sizes and geochemical distribution. Therefore, from the geochemical point of view, it is most important to get exact determinations of the radii of atoms and ions in crystals. The formation of crystals will effect a sieving or sorting of elements, and this process of sieving may determine the fate of any rarer element present, including both lithophile elements and the small amounts of siderophile and chalcophile elements which have entered the molten silicate.

We must also consider the very important case that the rare element does not enter the crystal, but is forced to remain in the liquid. In this manner a number of rare elements are concentrated in the mother liquors of magmas: There they remain until their concentration reaches the saturation limit of their own crystalline phases; then they are precipitated as minerals of rare elements. This explains why, in the mother liquors of silicate magmas, the pegmatite magmas, we encounter such a wealth of rare elements. If our principle concerning the relation between fractional crystallisation and the sizes of atoms and ions is sound, we shall expect to find *two very different types* of rare elements in the mother liquors: those which are of *very small* size compared with current atomic and ionic sizes, and those which have *very large* sizes.

This is in the very best accordance with mineralogical experience.

The specific gravity of the liquid part of an ordinary silicate magma, which undergoes processes of fractional crystallisation, decreases substantially as crystallisation proceeds, owing to the high density of the earlier minerals and to the increase in volatile components (as water and carbonic acid) in the mother liquor. Residual magmas and associated aqueous solution will thus have a strong tendency to migrate upwards to the uppermost levels of the earth's crust, and heavy minerals of early crystallisation will tend to sink down towards deep levels. Therefore, in the highest levels of the silicate shell we encounter a relative enrichment of those elements that are concentrated in the light granitic rocks and residual solutions of the magmatic sequence. For this reason many of the rare elements, which are typical for pegmatitic associations, are found in comparatively high concentrations in the uppermost levels of the atmosphere.

The fact that chemists have been able to detect not less than 89 out of 92 possible elements is surely due to the circumstance that the processes of distribution, acting in a strong field of gravitation, have been very favourable for accumulating even very rare lithophile elements in considerable amounts near the surface of our earth. Also, the distribution of the radioactive elements, with a marked enrichment of uranium and thorium in the light rocks of very high levels, is in complete accordance with the principles of geochemical distribution.

An investigation of the present distribution of chemical elements, however, cannot be limited to the study of inorganic nature; there is at work one more factor—the youngest in the story of geochemical evolution—that is, the organic world, the *biosphere* of the earth. Living organisms need a number of elements for the construction of protoplasm and auxiliary substances; we may mention carbon, hydrogen, oxygen, phosphorus, sulphur, chlorine, together with small but indispensable amounts of rarer elements such as iodine. Under most varying conditions of life, organisms have shown their ability to concentrate and utilise the different types of necessary substances; they have become one of the important factors regulating the distribution of chemical elements. Especially for such elements which in the original inorganic matter are present only in more modest concentrations, such as phosphorus or iodine, or fixed nitrogen, organic Nature has become a dominating factor of distribution.

We may become conscious of the importance of organic life in geochemistry if we consider that our present atmosphere, containing a large amount of oxygen and only traces of carbon dioxide, may have got these features largely through the action of plant life on the primary atmosphere of our planet. We may particularly refer, in this connexion, to the ever-increasing activity of man in utilising the resources of our earth, thereby greatly altering the distribution of elements within the reach of his power.