FACTORS INFLUENCING THE DISTRIBUTION OF THE ELEMENTS

James H. Pannell, *Niagara Falls, New York.*

The relative abundance of the elements in the earth's crust is a subject of fundamental importance to mining geologists but is one which is seldom studied comprehensively. A great number of the elements present in the earth in very low concentration are being used in every day artifacts, and it has become essential to discover the factors causing these metals to become concentrated in certain rocks. The search for many of the rarer metals has been stimulated by their increasing use in the realms of catalysis and electron emission ,where the quantity used is quite small.

At this time, when the search for strategic materials is the basis of production, it would seem advisable to review briefly our knowledge concerning the causes for the present distribution of minerals. Although such knowledge will not lead us immediately to a source of rich ore, it will save us the time which might be spent in prospecting for material in an impossible location.

This study received a great and much-needed impetus between the years 1910 and 1920, due mainly to the work of F. W. Clarke in the U. S. and V. M. Goldschmidt in Germany. The latter, by his use of visual and x-ray spectrography, successfully covered a great deal of ground and eliminated the error introduced in chemical analysis by the impurities in the large quantities of reagents necessary for the treatment of large samples. His determinations of ionic radii, carried out as a part of this work, will stand as a lasting memorial to his perseverance.

The average percentage composition of the earth's crust is now known to a high degree of precision, and the following table is taken principally from the results obtained by Clarke and Washington (1). It is worth remembering that although these figures relate to the lithosphere only, the inclusion of the atmosphere and hydrosphere does not alter them, as they stand.

Many of the elements in this table, for instance radium, beryllium, molybdenum, vanadium and tungsten, which are exceedingly scarce, have become quite familiar to us as a result of their highly important chemical and physical properties. Their use, however, would be prohibited if they had not been concentrated by natural processes in certain parts of the earth's crust to such an extent that their extraction is relatively simple.

In 1922 V. M. Goldschmidt (2) suggested that the scarcity of the precious metals was not an inherent characteristic of planetary bodies, but was caused by a process of selective elimination, because of the large partition ratios of these elements between silicate slags and ferro-compounds.

The Chief Elements of the Earth's Crust in Order of Abundance

1.	Oxygen	46.43	23.	Lithium	0.003
2.	Silicon	27.77	24.	Copper	0.002
3.	Aluminum	8.14	25.	Cerium etc.	0.001
4.	Iron	5.12	26.	Beryllium	0.00xx
5.	Calcium	3.63	27.	Cobalt	0.00xx
6.	Sodium	2.85	28.	Boron	0.000xx
7.	Potassium	2.60	29.	Zinc	0.000xx
8.	Magnesium	2.09	30.	Lead	0.000xx
9.	Titanium	0.629	31.	Arsenic	0.000xx
10.	Phosphorus	0.130	32.	Cadmium	0.0000xx
11.	Hydrogen	0.127	33.	Tin	0.0000xx
12.	Manganese	0.096	34.	Mercury	0.0000xx
13.	Fluorine	0.077	35.	Antimony	0.0000xx
14.	Chlorine	0.055	36.	Molybdenum	0.0000xx
15.	Sulphur	0.052	37.	Silver	0.00000xx
16.	Barium	0.048	38.	Tungsten	0.00000xx
17.	Chromium	0.037	39.	Bismuth	0.00000xx
18.	Zirconium	0.028	40.	Selenium	0.000000xx
19.	Carbon	0.027	41.	Gold	0.000000xx
20.	Vanadium	0.021	42.	Bromine	0.000000xx
21.	Nickel	0.019	43.	Tellurium	0.0000000xx
22.	Strontium	0.018	44.	Platinum	0.0000000xx

A comparison of the lithosphere with iron meteorites reveals a striking richness of the latter with respect to the rarer metals, germanium and gold. Most geologists favor the theory which proposes that the core of the earth consists of an iron-nickel combination similar to that which constitutes the magnetic portion of iron meteorites, although recently a novel hypothesis of an "electronic gas" (3) has been propounded for the earth's centre and its implications may have some effect on this part of our argument. The process of equilibrium between iron and large quantities of silicates was verified by experiments with artificial melts and by a study of the natural iron concretions in the Ovifak basalt on the island of Disco near Greenland. The enrichment of these is illustrated by the following figures, giving amounts in grams per ton: Pt 5, Pd 1, Rh 0.5, Ru 0.5, Au 1–5, Ag 5-10, Ge 1000. Although H. S. Washington (4) discovered an interesting relationship between the periodic classification and the correlation of the elements, this was probably mere happenstance because there is no similar line of demarcation in the long periodic table.

A classification based on the distribution of the elements has been made by Goldschmidt (2) in which he divides them into five groups. The Siderophile, Chalcophile and Lithophile correspond to the Iron, Sulphide and Silicate respectively; the inclusion of the Atmophile and

Biophile would make the range complete, but they are not pertinent to this sketch. The Siderophile includes the transitional metals, iron, nickel, cobalt, etc., and the noble metals. In the Chalcophile are the heavy metals and metalloids, while the Lithophile contains the alkali metals, alkaline earths, halogens and the lighter metals. When considering natural processes of differentiation we must not expect to find any truly perfect separations and thus some elements occur in all classes. According to this plan then, the three concentric spheres of which the world consists are iron-nickel at the centre, sulphide intermediate, and silicate at the surface, with one of the boundaries coinciding with the limiting depth for the propagation of transverse vibrations, and beyond which the texture of the bathysphere must alter considerably. There have been many schemes suggested for the general composition of the earth and these are reviewed by A. F. Buddington (5) who does not belive that the idea of such a large volume of sulphide is tenable. He gives the siderophile a mean thickness of twenty kilometres, and places it at a distance of twenty-nine hundred kilometres from the surface. Nevertheless, the main idea of magmatic differentiation is generally conceded to have been the first step in separating the elements.

During magmatic crystallization, when the space lattices of minerals are being built up of ions or atoms, another course of selection takes place. The growth of a crystal in a saturated solution of the salt can be visualized as an orderly falling into place of alternate positive and negative ions so that each small unit cell is electrically neutral. If one now introduces another cation similar to that already present, but having a smaller ionic radius, it will take the place of the larger ion in the subsequent crystallization. Similarly, in mineralization the smaller ion has a greater chance of going into the crystal, as it permits a tightening up and decrease of lattice energy. In silicates however, when an isomorphous replacement of silicon by aluminum takes place, an alkali metal is also added and this cation merely fits into an interstice and is not close-packed. Base exchange is not a new concept by any means and its importance in agriculture (6) must have been appreciated at an early stage. Instances of this action are so common that one may discern, by the determination of the alkali metals in a mixture of plagioclases for instance, which of them crystallized first. The ionic radii of these cations are: Li 0.78; Na 0.98; K 1.33; Rb 1.49; Cs 1.65 angstrom units. A great deal of controversy has raged over the preferential movement of these alkalis in ionic exchange as some experimentalists found them to be arranged in reverse order to their radii and hence postulated a "hydrated ion" with an envelope inversely proportional to the effective radius (8). A mathematical expression for this mechanism was worked out by Hans Jenny (8) in a

thorough study of the aluminum silicates. Recently Russell and Pearce (7) were able to separate a mixture of the rare earths by percolating their solution through a zeolite and making use of the fact that the smaller ion is extracted first and held out most firmly. An ion of practically the same size but of higher valency than another will also be found in the early crystals of a melt, and an example of this is seen in the preponderance of anorthite-$CaO \cdot Al_2O_3 \cdot 2SiO_2$ in the early fractions of sub-alkaline granodiorites. Similarly, the last crystals of magnesium minerals contain most of the lithium present. The following tables summarize these data, and are from the work of Goldschmidt (2).

DIFFERENTIATION DURING CRYSTALLIZATION
Figures relate to the quotient by weight
$1000 \times Li_2O/MgO$

Early Rocks		*Late Rocks*	
Peridotite	0.12	Syenite	20
Gabbro	3.3	Granite	600
Diorite	10	Trachyte	150
Basalt	3.3	Obsidianite	200
Porphyrite	16		

PERCENTAGES OF CERTAIN OXIDES IN ROCKS

	Peridotite	Gabbro	Diorite	Granite	Nepheline syenite
Early					
Cr_2O_3	0.5	.05	.01	.0003	.0001
NiO	.4	.02	.005	.0003	.0003
CaO	.03	.01	.004	.001	.001
MgO	40.	8.	3.	1.	1.
Late					
BaO	.003	.007	.03	.05	.06
Cb_2O_5	—	.001	.003	.005	.02
La_2O_3	—	.001	.003	.005	.05
K_2O	.1	1.	2.	4.	6.

Early	*Silicate Meteorites*	*Earth's Crust*
Chromium	3,200 grams per ton	200 grams per ton
Magnesium	137,000 grams per ton	21,000 grams per ton
Late		
Zirconium	80 grams per ton	190 grams per ton
Sodium	3,700 grams per ton	21,400 grams per ton
Lithium	5 grams per ton	65 grams per ton
Potassium	1,700 grams per ton	25,900 grams per ton
Strontium	20 grams per ton	420 grams per ton
Barium	5 grams per ton	390 grams per ton

Some idea of the marked effect which a small difference in radii between two cations can have on their separation is gained from the higher gallium:aluminum ratio in later minerals, their respective radii being 0.62 and 0.57 angstrom units.

A comparison of the earth's crust with silicate meteorites shows that the former contains a disproportionately large amount of late crystals in its uppermost layers, and the above table expresses this quantitatively. The effect is mainly due to the low density of the syenites and granites of which the Sial is composed, and is an example of gravity differentiation. Two well-known examples of this are the Lugar Sill, where olivine crystals sank to the lower regions of the magma, and the Murray ore deposits at Sudbury.

Probably the first attempt to correlate the elements was made by Washington (10, 11) but in spite of the number of analyses he made, his knowledge of the chemical compositions of minerals was not comprehensive enough to enable him to arrive at any worthwhile conclusions. At that time the only relationship recognized was that propounded by Vogt (12) which merely indicated which elements were likely to be found in acid or basic rocks. Thus the siliceous rocks will contain higher proportions of aluminum and alkalis, while ferromagnesian minerals will be found in basic rocks, where the term "basic" implies an unsaturated condition with respect to silica. This division is important as a basis for the study of petrology but it is too simple to be used as a guiding rule in an investigation.

Among the many interesting and provocative groups, so far as abundance is concerned, is that containing titanium. This element is ninth in order, according to Clarke, and hence is much more abundant than any of the other members of its class, viz., zirconium, hafnium, and thorium. In fact, the average amount in the earth as a whole is probably less than 0.2% (9); although much of the titanium may crystallize early, it probably associates with zirconium, hafnium and thorium, which are conspicuous members of the later crystals. As the early dense minerals separate out, the residual magma becomes enriched in these elements, and this may account for the statement of Lord Rayleigh, obtained through his study of the thermal equilibrium of the earth, that the proportion of thorium decreases with depth. There are no hafnium minerals, as the concentration in the lithosphere is only about 3.2×10^{-4} and a zirconium:hafnium ratio of about 60:1 prevails. This ratio is not altered by weathering of the minerals, in contrast to the effect on eudialite, in which the $TiO_2:ZrO_2$ ratio may change drastically. Titanium, often in the form of ilmenite ($FeO \cdot TiO_2$), is very widespread but at the same time is so finely divided that at one time it was practically ignored in

the analysis of silicate rocks. Another widespread element, strangely enough, is gold and Newton Friend suggests that in the colloidal form it accounts for the color of celestite.

We have seen how important ionic radius and charge is in the distribution of minerals of magmatic origin, and the quotient of these quantities, Z/r plays a vital part in the reactions which lead to the secondary disposition of the elements (2, 13). This ionic potential serves as a key to their behaviour during the metamorphism of rocks. During the processes of weathering, those of low potential, such as the alkali metals, remain in solution as ions; those of intermediate potential are precipitated as hydroxides, and those of high potential form soluble complex anions with oxygen. Chromium and boron are members of the last group. Whether the first continents were formed by radial or tangential forces may be disputable, but since their inception they have been subjected to a continuous leaching action. The mechanical aspect of this affair is known as erosion but it is not of more importance than the effect of solution. A survey of the balance of elements in sea water leads to some surprising revelations, and these are of particular interest now that it is becoming a source for iodine, bromine, and magnesium, to mention only a few. As rich ores are used up and mechanical treatment is progressively improved to handle the poorer ones, it is inevitable that attention will be drawn to the illimitable reserves which the ocean contains. As a result of the work of Joly (14) and others, it is calculated that six hundred grams of igneous rock have passed into solution for every kilogram of sea water, but of the elements with low potential, sodium alone remains to any extent. Some of the others are readily adsorbed on the hydrolysates; beryllium and gallium necessarily are associated with aluminum and occasionally with vanadium also. The concentration of some anions however, is higher than would result from the weathering of primary rocks and their percentage in fossil shells indicates that this concentration was formerly even higher. One is led to believe that they were original constituents and may have been supplied to a large extent by submarine volcanoes. With regard to the poisonous metallolds and heavy metals, it is clear that sufficient amounts have been supplied to drastically alter marine life and consequently terrestrial life too. Fortunately many metals, among which are selenium, arsenic, lead, antimony, and bismuth, are adsorbed by the precipitate of iron hydroxide and subsequently are found in the sedimentary iron ores. Indeed the removal of this arsenic has presented a problem to the steel maker. Copper remains in the sea to a comparatively large extent, in some inexplicable manner and is even found in the shells of oysters (15). However copper is among the rarer elements, in spite of its familiarity in artifacts. Interest is shifting

more and more to sea water and bitterns as sources of industrial chemicals and the study of oceanography is certain to increase. An exciting speculation might center about the use of alluvial iron ore beds which are formed when the colloidal hydroxide is coagulated by the ionized salt of the sea. In cases where the gangue is relatively innocuous both iron and aluminum may be extracted, although the latter will undoubtedly be the most valuable.

Metamorphism and more particularly metasomatosis, or changes involving chemical transformation, are responsible for most ore bodies, but, like oceanography, this is a vast subject and will not be dealt with here in any detail. Ignoring for the present the possibility of differentiation, we generally picture the formation of a batholith as an injection of a large mass of molten magma into the overlying rock. Occasionally these intrusions are unbelievably large, e.g., the one in British Columbia, but large or small they are all surrounded by areas of contact metamorphism. Pneumatolysis, resulting from the action of the magmatic vapors, gives rise to ore bodies and the formation of such attractive gems as tourmaline and topaz. The presence of water in this residual liquid from the magmatic crystallization plays an important role in lowering the fusion point of the matrix; one to two per cent can effect a lowering of as much as 300°C. The volatile constituents become concentrated as cooling proceeds and the pressure rises, until finally they are injected with great force into the country rock. Rare elements are so concentrated in the resulting pegmatites that they may crystallize as distinct species, and these minerals in turn are often enriched in extremely rare elements, e.g., rhenium in molybdenite. The action of water vapor and hydrogen chloride, fluoride and sulphide, etc., at elevated temperatures is so little understood that we have no fundamental knowledge by which we may distinguish it from earlier magmatic separations. The chemical activity of these substances under such conditions is very intense and does not easily lend itself to laboratory study. The gases emitted by the fumaroles in the Valley of Ten Thousand Smokes, at temperatures as high as 640°C., were analyzed by Allen and Zies (16) with these results:

> 99.5% water vapor
> 0.2% insoluble gases
> 0.3% acid gases

Although the proportions are quite small, the total volumes of acid gases involved are very large, and in 1919 they totalled 1.8×10^6 metric tons per annum, at normal temperature and pressure. At this location it was found that barium and iron oxides had been concentrated to an amazing degree and at the temperature prevailing, the halides and some-

times the sulphides and oxides of the elements encountered were volatile. Although the expulsion of volatile constituents marks the end of igneous activity, it does not terminate the active concentration of elements either by gaseous action or by co-precipitation, which Zies considers to be of great importance. The magnetite found in this valley in 1919 by Fenner was not encountered in 1923, presumably because the temperature had fallen to the point at which condensation of acidic steam took place and decomposed the iron sulphide. In place of this were covellite, chalcocite, and sphalerite which are relatively insoluble in acid and represented a further concentration of copper and zinc.

We would not expect elements which occur in extremely small proportions to be concentrated to an extent that would make their extraction easy, especially when they are so sparsely distributed as to exclude the possibility of forming definite compounds. But, as previously noted, these elements may be trapped or co-precipitated during the formation of other minerals. Among the instances of this are the association of fluorine with barium sulphate and gallium with zinc sulphide. Grimm has also shown how the formation of mixed crystals depends on the dimensions of similar crystals and also on the size of the substituted atomic species. As examples of the combination of rarer elements with common ones having similar characteristics, we may cite aluminum-gallium, magnesium-nickel, zirconium-hafnium, and silicon-germanium. Germanium is also concentrated by certain plants and has been determined to form 1.6% of certain coal ashes. It is interesting to note the association of vanadium, nickel and molybdenum with hydrocarbons, in view of the use of these metals as catalysts in the synthesis of organic compounds. Boron, arsenic, bismuth and beryllium are also present in coal ashes in percentages between 200 and 50 times their percentages in the lithosphere.

Summarizing the three principle factors in the distribution of the elements, they are: the division among the three immiscible spheres of the siderophile, chalcophile and lithophile; separation during crystallization governed by ionic size and charge and the further concentration during the formation of sediments which is controlled largely by the ionic potential. From that point, there are many more factors coming into play which are studies in themselves.

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Volume 54 (1943)

January–June