THE CONCENTRATION OF THE LESS FAMILIAR ELEMENTS THROUGH IGNEOUS AND RELATED ACTIVITY[1]

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Throughout the ages mankind has been striving to increase the usefulness of the tools which he uses for providing himself with sustenance, with greater creature comforts, and with weapons of offense and defense. The archaeologist designates the great historical periods as the stone age, the bronze age, and the iron age, and implies thereby an increase in man's ability to use available materials in the making of his artifacts. We are now living in an age which can no longer be designated with the name of any single material. It is true that the present may still be called the iron age; nevertheless aluminum has become a potent factor in gradually lessening the dominance of iron. Aluminum is even more abundant in the earth's crust than iron and has the desirable property of lightness. Its utilization was delayed until a method was found for obtaining it in a high degree of purity from its ores. This has been accomplished only within the last forty years.

The present age, with its emphasis on speed, demands that the materials used in the construction of its artifacts shall be produced at low cost and shall possess lightness and resistance to deformation and corrosion. In the effort to secure these properties, the chemist is encouraged to study more intensively the chemical and physical properties of elements which are less common in the earth's crust than iron and aluminum. One outstanding result of this effort is the addition of magnesium to the list of commonly used metals. It is useful by itself but is even more useful when alloyed with aluminum.

Table 1 shows that the three elements iron, aluminum, and magnesium are among the most abundant elements. We have learned to use, either by themselves or as alloys, a host of metallic elements that are present in the earth in minor or even very low concentrations. Many of them, on the basis of our chemical and physical knowledge of their properties, are

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TABLE 1

Average composition of igneous rocks

Major and common elements*

ELEMENTS	1	2	3	4
Oxygen	46.59	46.41	47.29	47.2
Silicon	27.72	27.58	28.02	28.0
Aluminum	8.13	8.08	7.96	8.0
Iron	5.01	5.08	4.56	4.5
Calcium	3.63	3.61	3.47	3.5
Sodium	2.85	2.83	2.50	2.5
Potassium	2.60	2.58	2.47	2.5
Magnesium	2.09	2.09	2.29	2.5
Titanium	0.63	0.720	0.46	0.33
Phosphorus	0.13	0.157	0.13	0.22
Hydrogen	0.13	0.129	0.16	0.17
Manganese	0.10	0.124	0.078	0.075
Sulphur	0.052	0.080	0.10	0.06
Barium	0.050	0.081	0.093	0.03
Chlorine	0.048	0.096	0.063	0.04–0.025
Chromium	0.037	0.068	0.034	0.01
Carbon	0.032	0.051	0.13	0.22
Fluorine	0.030	0.030	0.10	0.04–0.025
Zirconium	0.026	0.052	0.017	0.02–0.01
Nickel	0.020	0.031	0.020	0.005
Strontium	0.019	0.034	0.034	0.005
Vanadium	0.017	0.041	0.017	0.00n
Cerium, yttrium	0.015	0.020		0.00nn
Copper	0.010	0.010		0.000,n
Uranium	0.008	0.000,00n		0.000,00n
Tungsten	0.005	0.000,00n		0.000,00n
Lithium	0.004	0.005	0.004	0.004
Zinc	0.004	0.004		0.000,n
Columbium, tantalum	0.003	0.000,00n		0.000,000,n
Hafnium	0.003			
Thorium	0.002	0.000,00n		0.000,000,n
Lead	0.002	0.002		0.000,n
Cobalt	0.001	0.003		0.00n
Boron	0.001	0.001		0.00n
Glucinum	0.001	0.001		0.00n
	100.000	100.000	100.000	100.000

* The data are taken from Clarke and Washington (5) and show the averages obtained by several workers in this field. The reader is referred to the sources cited in the reference for further details. The numbers at the head of the columns refer to authors cited in reference 5.

rated as common elements. Surely copper, silver, gold, the platinum metals, lead, zinc, mercury, bismuth, manganese, titanium, nickel, and chromium are familiar elements, yet as compared with iron, aluminum, and magnesium they are, with respect to the earth's crust, uncommon. They are used either alone or in alloys; the alloys of nickel and chromium with iron have enormously increased the usefulness of this common element. It can be truly said that we are living in an age of alloys.

We are not concerned with the metals only, for many of the elements are most useful to man when they are combined with the two most abundant elements, namely, silicon and oxygen; the enormous development of the ceramic industries is a case in point.

This age is also becoming increasingly more dependent on substances that exercise a controlling influence on both chemical and physical processes. Catalysis and electron emission have assumed an importance that is out of all proportion to the amount of material used. In the constant endeavor to find materials that will increase catalytic action and electron emission and that will increase the usefulness of our commonly employed elements, it is quite natural that more attention will be given not only to the common and abundant ones but also to the rare and less familiar ones.

In this paper an element will be considered as rare when its concentration in the earth's crust (38) falls below 0.01 per cent, as shown in tables 1 and 2. When we consider the mass of the lithosphere (19×10^{18} metric tons) (5), the total amount of any of these is enormous, but this capacity factor is of little use if the cost of extraction is not commensurate with the market value of the product. It is true that gold, one of the rarest of elements, can be extracted economically from rather lean materials, but if all countries were to abandon the gold standard there would be but little gold extracted. Radium, in spite of its great value and usefulness, would remain a fascinating chemical curiosity but for the fact that it has been concentrated in uranium ores which in themselves represent a concentration from leaner material. The elements beryllium, molybdenum, vanadium, tungsten, thorium, the "rare earths," tantalum, and surely radium are very rare elements, but our chemical and physical knowledge of their properties has increased to such an extent that they are less familiar only to those who do not have occasion to work with them; they are now extensively employed in the industries. It is quite possible that cesium, rubidium, columbium, thallium, gallium, and even rhenium will soon be in the same category of useful elements.

None of the rare elements is likely to be useful unless we find it concentrated in nature to such an extent that it can be economically extracted with respect to market conditions. It is opportune, therefore, to review our knowledge, scanty though it may be, of the probable methods of concentration by natural processes.

Igneous rocks constitute 95 per cent of the crust of the earth (5). They are the source of the shales, sandstones, limestones, and soil that make up the remaining 5 per cent. It is obvious, therefore, that they must also be the source of all known elements. The geochemistry of the various elements considers their distribution throughout the earth. Since we have factual knowledge of only 3 per cent of its radius (28), our information concerning the more deeply seated portions must be by analogy with the meteorites or by inference from the data derived from seismological studies (2).

While it is true that the discussion of the distribution of the rare elements deep within the earth and in meteorites does not come within the scope of this discussion, a brief review of the findings of Ida and Walter Noddack (29) will be worth while. They have made analyses of the rare elements in meteorites, in extremely scarce rocks of deep-seated origin, in igneous rocks, and in sedimentary rocks. Their analyses indicate the same low concentrations recorded in tables 1 and 2. It is not at all unlikely, therefore, that most of the concentrations remain low throughout the stages of differentiation indicated below on account of the scarcity of the elements. Every analyst will appreciate the difficulty of removing a slight trace of some impurity which persists no matter how many operations he may use to remove it through concentration, either as a precipitate or by solution. It has been said that the best analysis is only an asymptotic approach to perfection (40). The research worker in seeking for the rare elements must therefore resort to the keenest of analytical tools such as optical and x-ray spectroscopy and must often combine them with chemical methods that permit coprecipitation of the rare with more readily removed elements. Given sufficient material and sensitive methods of analysis it is quite probable that all elements can be determined in any rock, but it is far more important to know how they have been concentrated in nature (23).

Geologists are now in fair agreement that such igneous rocks as are now amenable to investigation have in a great measure been derived from a homogeneous igneous mass by a process of differentiation. The theory of petrographical provinces (21) indicates that this homogeneous mass may have had a uniform bulk composition; nevertheless it gave birth to rock sequences that differed with respect to mineral species in different parts of the original mass. It is well to bear in mind, however, that while it is true that differentiation has taken place in many localities, there are huge igneous masses called batholiths that have been intruded under the crust of the earth and have crystallized and cooled without differentiation (24). Much remains to be done to give us a clearer view of these processes, but even though our knowledge concerning the nature of the materials

TABLE 2

Average composition of igneous rocks

Less common and rare elements*

ELEMENTS	5	6	7
Cerium, yttrium	1.5×10^{-4}	2×10^{-4}	$n \times 10^{-5}$
Copper	1×10^{-4}	1×10^{-4}	$n \times 10^{-6}$
Uranium	8×10^{-5}	$n \times 10^{-8}$	$n \times 10^{-8}$
Tungsten	5×10^{-5}	$n \times 10^{-8}$	$n \times 10^{-8}$
Lithium	4×10^{-5}	4×10^{-5}	4×10^{-5}
Zinc	4×10^{-5}	4×10^{-5}	$n \times 10^{-6}$
Columbium, tantalum	3×10^{-5}	$n \times 10^{-8}$	$n \times 10^{-9}$
Hafnium	3×10^{-5}		
Thorium	2×10^{-5}	$n \times 10^{-8}$	$n \times 10^{-9}$
Lead	2×10^{-5}	2×10^{-5}	$n \times 10^{-6}$
Cobalt	1×10^{-5}	3×10^{-5}	$n \times 10^{-5}$
Boron	1×10^{-5}	1×10^{-5}	$n \times 10^{-5}$
Glucinum	1×10^{-5}	1×10^{-5}	$n \times 10^{-5}$
Molybdenum	$n \times 10^{-6}$	$n \times 10^{-6}$	$n \times 10^{-7}$
Rubidium	$n \times 10^{-6}$	$n \times 10^{-6}$	$n \times 10^{-5}$
Arsenic	$n \times 10^{-6}$	$n \times 10^{-6}$	$n \times 10^{-5}$
Tin	$n \times 10^{-6}$	$n \times 10^{-6}$	$n \times 10^{-5}$
Bromine	$n \times 10^{-6}$	$n \times 10^{-6}$	$n \times 10^{-5}$
Cesium	$n \times 10^{-7}$	$n \times 10^{-7}$	$n \times 10^{-8}$
Scandium	$n \times 10^{-7}$	$n \times 10^{-7}$	$n \times 10^{-12}$
Antimony	$n \times 10^{-7}$	$n \times 10^{-7}$	$n \times 10^{-5}$
Cadmium	$n \times 10^{-7}$	$n \times 10^{-7}$	$n \times 10^{-8}$
Mercury	$n \times 10^{-7}$	$n \times 10^{-7}$	$n \times 10^{-8}$
Iodine	$n \times 10^{-7}$	$n \times 10^{-7}$	$n \times 10^{-5}$
Bismuth	$n \times 10^{-8}$	$n \times 10^{-8}$	$n \times 10^{-9}$
Silver	$n \times 10^{-8}$	$n \times 10^{-8}$	$n \times 10^{-9}$
Selenium	$n \times 10^{-8}$	$n \times 10^{-8}$	$n \times 10^{-9}$
Platinum	$n \times 10^{-9}$	$n \times 10^{-9}$	$n \times 10^{-10}$
Tellurium	$n \times 10^{-9}$	$n \times 10^{-9}$	$n \times 10^{-10}$
Gold	$n \times 10^{-9}$	$n \times 10^{-9}$	$n \times 10^{-10}$
Iridium	$n \times 10^{-10}$		
Osmium	$n \times 10^{-10}$		
Indium	$n \times 10^{-11}$	$n \times 10^{-11}$	$n \times 10^{-11}$
Gallium	$n \times 10^{-11}$	$n \times 10^{-11}$	$n \times 10^{-11}$
Thallium	$n \times 10^{-10}$	$n \times 10^{-10}$	$n \times 10^{-11}$
Rhodium	$n \times 10^{-11}$		
Palladium	$n \times 10^{-11}$		
Ruthenium	$n \times 10^{-11}$		
Germanium	$n \times 10^{-11}$	$n \times 10^{-12}$	$n \times 10^{-12}$
Radium	$n \times 10^{-12}$	$n \times 10^{-14}$	

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* The data are taken from Clarke and Washington (5). The numbers at the head of the columns refer to authors cited in reference 5. The authors obviously consider these values as orders of magnitude. It is quite possible that these figures will have to be changed when more accurate data are obtained, but it is doubtful if the changes will significantly alter these orders of magnitude.

below the earth's crust is limited, considerations based on the study of seismic phenomena, elasticity of rocks (1), and phase rule studies (4, 28) of the rocks that have been brought to the surface have produced theories which, in spite of the fact that they must later be either amplified or discarded altogether, are helpful in giving us a picture of what is probably going on.

On the basis of the known density of the earth taken as a whole, about 5.5, and the density, 2.8, of the known granitic shell which makes up the bulk of the earth's crust, it naturally follows that the earth's core must contain material of higher density. On the basis of analogy with the composition of meteorites it is assumed that the core is composed of the two metals nickel and iron. The study of seismic phenomena, the known compressibility of rocks and their elastic properties, and the analyses of igneous rocks all indicate that there are three principal shells covering the core. The bulk composition of the layer next to the core corresponds to that of a peridotite, the next shell to that of a basalt, and the surface layer to that of a granite. The statistical studies of Clarke and Washington (5) confirm this theory with respect to the surface shell, for they show that in spite of the many different kinds of igneous rocks, the bulk composition corresponds to that of a granite. It is possible that the basaltic shell with its relatively low silica content grades into the siliceous granite.

Geologists believe that rocks of low silica content such as eclogites and peridotites are of deep-seated origin; the physicist has found from his studies that the known rocks that would account for the observed sudden increase in velocity of seismic waves are just these eclogites and peridotites.

The granitic shell is believed to be about 60 kilometers thick and somewhat unevenly distributed. It is thickest in the continental masses and thins out to almost nothing in the great oceanic deeps. The average analysis of the rocks of the earth's crust certainly points to a granitic composition, but the intrusion into the shell and extrusion on the surface by igneous activity of rocks of different composition varying from a basalt to a rhyolite show clearly that a process of differentiation has taken place. The depth (6) at which these changes took place is at present a matter of conjecture, but it quite probably happened below the granitic shell. Our knowledge concerning the distribution of the rare or less familiar elements has been derived, of course, from the layer whose average composition is a granite. Yet the very fact that differentiation has taken place is a matter of considerable interest, for in this manner minerals of economic importance have been concentrated (36).

Poulett Scrope (32) was one of the earliest investigators to promulgate the idea that a huge mass of heated igneous material under the surface of the earth could differentiate. "It is quite conceivable that, when exposed in the focus of a volcano to successive liquefaction and reconsolidation, the heavier minerals may sink by a sort of filtration through the lighter ones, the upper portions of the mass becoming consequently more felspathic, the lower more ferruginous or augitic." This beautifully simple theory was bitterly opposed by many geologists, but the entire problem was once more taken up by Schweig (31) in the light of the advances made in geology and physical chemistry. Relatively little attention was paid even now to this newer presentation of differentiation. About ten years later, the work of Bowen (4) truly aroused the interest of the geologists in this problem. By this time, however, the experimental side of petrography received such decided support from phase rule considerations and from the new experimental technique developed at the Geophysical Laboratory of the Carnegie Institution, that Bowen could with much greater assurance point out to the geologist that fractional crystallization in a large body of molten magma can take place. Objections (10) have been raised to parts of Bowen's theory; nevertheless the definite possibility and probability of such differentiation have been demonstrated.

In this brief résumé of differentiation mention has been made only of siliceous rocks. It is well at this point to call attention to the work of Vogt (35) and Goldschmidt (11), who consider it possible that some basic magmas have become so greatly enriched in sulfur that sulfides of the heavy metals, particularly sulfides of iron and nickel, may have separated on cooling. Goldschmidt (11) postulates that an original fluid globe separated on cooling into three immiscible layers: at the core a metallic melt, which grades into one in which the sulfides dominate, and this in turn grades into a siliceous shell containing a gas phase,—the atmosphere. It is believed by some geologists that the well-known platinum-rich copper nickel sulfide ore bodies of Sudbury have resulted from a process of differentiation through fractional crystallization, but there is as yet no unanimity of opinion on this point. The sulfide ores are, however, associated with a huge mass of intruded igneous rocks, and it is believed that magmatic differentiation played an important rôle in their origin. This also seems to apply to the segregation of the platinum metals in many basic rocks of the Ural Mountains in Russia, Columbia, California, and South Africa, and to the segregation of chromite, magnetite, and the titanium-iron mineral ilmenite (24), but even here the influence of post-magmatic effects of aqueous solutions and volatile constituents is not denied.

Considerable impetus has recently been given to the elucidation of the theory of segregation and concentration of the sulfides by Merwin and Lombard (25). This is the first attempt to apply phase rule principles to these vaguely understood processes. The three-component system, copper, iron, and sulfur, was studied at various temperatures and at a definite vapor pressure of sulfur. The region of stability of the iron sulfides, the copper sulfides, the copper–iron sulfides, and of a series of solid solutions of the various sulfides was thereupon determined.

As differentiation progresses in the more acidic portions of the large igneous masses that have been considered in this review, the volatile constituents, such as water, hydrogen chloride, hydrogen fluoride, hydrogen sulfide, and carbon dioxide, that were present in solution begin to assert themselves by virtue of their becoming more concentrated. It is now well established that water to the extent of about 1 or 2 per cent can lower the fusion point of difficultly fusible rocks such as a granite by over 300°C. Morey (26) and Goranson (19) have shown that as crystallization and cooling in a closed system continue, the volatile constituents, especially water, can generate enormous pressures on the constraining mantle. If the mantle is not strong enough to withstand the pressure it will be ruptured, and igneous materials, including the gases, will be injected through volcanic activity. It is also possible that the constraining mantle may be strong enough to withstand rupturing, but the boiler pressure, so to speak, is great enough to permit the injection of the siliceous mass of material into weaker layers of the mantle. It is by some such mechanism as this, together with probable chemical activity on the surrounding rock, that it is believed the end products of differentiation, namely, the pegmatite dikes (24), are formed. These masses of material injected under high gas pressure are the happy hunting ground for those in search of rare elements (14). Many of these elements have reached such a high degree of concentration that when combined with other elements they crystallize as distinct mineral species. The boron-bearing minerals, the rare earths, the cesium mineral pollucite, the lithium- and cesium-rubidium-bearing micas, the fluoborates, the fluorides, and the beryllium minerals are examples. They also contain many minerals such as molybdenite, within which have been concentrated some of the extremely rare elements of which rhenium is an example. We have now reached a stage in the differentiation in which volatile constituents, especially water, play an important rôle. It was said above that there are relatively few sulfide deposits whose origin by magmatic segregation is unambiguous. The reason is that near the end of the various processes of differentiation water and other volatile constituents, such as carbon dioxide, hydrogen chloride, hydrogen fluoride, boron, and hydrogen sulfide, at temperatures which we know from field and laboratory evidence may be as high as 650°C., accumulate and produce an intensely chemically active environment. Very little of a fundamental nature is known of this complicated system. At present it can not be studied as an entirety and must be broken down into a simpler form. This has been done for part of the system iron–chlorine–water by Stirnemann (33). Similar fundamental studies of vapor phase activity are now being carried out by Morey and his coworkers (27). The problem, by virtue of the intense chemical activity of its components, is extremely difficult, but at least an attempt must be made to obtain its solution if we wish to coördinate field evidence with laboratory investigation.

The term "water" was applied to one of the constituents in the igneous materials, but it is perhaps best to give it its usual designation of H_2O, for in the environment mentioned above it is above its critical temperature and the properites of liquid and vapor become indistinguishable. As cooling takes place it will exist in both phases, and all the active chemicals referred to may be either in solution or in the vapor phase. Naturally the intensity of the chemical activity will depend on temperature and percentage concentration. This point will be discussed again later in this review. It must be obvious from what has been said that the record of any magmatic segregation of constituents that may have taken place can be destroyed in its entirety by virtue of the chemically active gases that are produced in the last stages of differentiation. It is not amiss to call attention to the fact that "geological field research deals with end phenomena of completed reactions but with a very imperfect record of the earlier steps in the earth-making process" (7).

On page 54 the condition was postulated that the pressure of the vapor phase generated on crystallization of the silicate magma may reach such proportions that rupturing of the constraining mantle may take place. We thus have in its simplest form the beginning of volcanic activity which is, therefore, the surface manifestation of more deep-seated activity. We no longer have a completely closed system, and all the changes brought about by virtue of change in pressure and lowering of temperature will take place. The phenomena are not necessarily confined to the surface, for the hearth of the volcano may still be several miles below the orifice; nevertheless the physical-chemical environment is that of an essentially open system in which chemical changes may take place quite rapidly.

We have reached a stage in the history of an igneous body which is more or less amenable to direct study. Volcanic phenomena have been observed for a long period of time and naturally more attention has been given to the description of types of solid materials, the dust clouds, the lava, and the fragmental material which contribute to the construction of the volcanic edifice. Some of the earlier writers on volcanic activity realized that the extrusion of solid materials certainly accounts for the bulk of the material brought to the surface, but they also recognized the fact that at many volcanoes vapors, especially water, played a very important part in providing the mechanism by which the solid materials were brought to the surface (28, 32). In the course of the early part of this century attention was directed specifically to these vapors and to the minerals which were formed by the interaction of the vapors with the constituents in the extruded rocks. The story is not quite so simple as just stated. The rock materials that are brought to the surface are not necessarily composed of the minerals and constituents in the last stages of differentiation. Interaction with the constraining mantle may take place in the hearth of the volcano and introduce material which may have quite a different composition. Then, too, interaction of the chemical vapors with this material may bring about a sequence of changes quite different from those peculiar to the unaltered segregation. The possibility, however, exists of coordinating field studies in nature's laboratory at volcanoes with fundamental studies carried out under carefully controlled conditions.

The volcanic eruption that took place in 1912 in the Valley of Ten Thousand Smokes (3, 9, 39) located on the Alaskan Peninsula offered an unusual opportunity for studying the chemical aspects of the later stages of igneous activity. The activity in the Valley was, according to Fenner (9), brought about by the injection of the very siliceous lava, rhyolite, under the old floor of the Valley. The pressure exerted by the volatile constituents was sufficient to rupture the floor and permit the igneous materials to reach the surface. The lava was highly charged with volatiles which on sudden relief of pressure escaped into the atmosphere and deposited a great mass of hot and very porous glassy pumice. The Valley is roughly four miles wide and twelve miles long, and it is estimated that a cubic mile of material was extruded. Thousands of fumaroles (steam vents) were situated in this rhyolitic pumice, and in 1919, seven years after the eruption, were quite active both thermally and chemically. Steam temperatures as high as 640°C. were found, indicating that the temperature of the more deeply buried material was still quite high. Allen and Zies (3) collected and analyzed the fumarole gases and found that they contained about 99.5 per cent of water, 0.2 per cent of gases insoluble in water, and a total of 0.3 per cent of the acid gases hydrogen chloride, hydrogen fluoride, and hydrogen sulfide. The bulk of the gas is obviously steam, but we must not be misled by the low concentration of the other gases. An estimate (39) was made of the total amount of gases that would be emitted if the rate observed in 1919 were to continue. This is only an estimate, to be sure, but reasons have been given in the references cited for believing that it is of the right order of magnitude. It is seen from table 3 that even though the percentage concentration of the dominant acid constituents is small, yet the total amount from this single volcanic area is enormous. It is essential, therefore, in dealing with these natural phenomena to keep both the intensity and the capacity factors clearly in mind.

The presence of large total amounts of fluorine is particularly noteworthy, for it is one of the most active of the acid gases in decomposing silicates. The interaction of the acid gases with the extruded pumice decomposed the latter and set free a host of halides, sulfides, and oxides whose presence in the pumice was not even surmised. The reader is referred to the original articles (39) for the detailed account of the investigations. It will suffice for our present purpose to call attention to a few items of geochemical importance. Our interest was first directed to the concentration of minor elements when we found barium in the incrustations around the vents in amounts that represented a hundredfold increase over that determined in the pumice itself. Magnetite (Fe_3O_4) was found in many of the vents, and, although no reliable estimate could be made of the total amount, it was obvious that it must be thought of in terms of tons rather than a few pounds. The evidence is also clear that the magnetite was derived through a vapor phase activity and represents, therefore, the concentration of the iron derived from the more deeply seated portions of the pumiceous deposit. The magnetite was so beautifully crystallized that one might easily assume that we were dealing with a relatively pure material. The analysis in table 4 shows, however, that this was far from the truth.

TABLE 3

Amount of acid gases emitted in 1919 by the fumaroles in the Valley of Ten Thousand Smokes (39)

Estimated volume of steam calculated at 100°C. and 760 mm. = 26×10^6 liters per second

GAS	PER CENT	GAS CONTAINED IN STEAM	METRIC TONS OF GAS PER YEAR
		kg. per second	
HCl	0.117	36.0	1.3×10^6
HF	0.032	5.6	0.2×10^6
H_2S	0.029	8.4	0.3×10^6

When it was found that a well-crystallized mineral such as magnetite could contain so many extraneous minor elements, it was decided to subject the other incrustations that had been collected to detailed chemical and spectrographic analysis. It was then discovered that many elements were present other than those found in the magnetite. Thus bismuth, gallium, thallium, boron, germanium, arsenic, selenium, and tellurium were definitely proved to be present. Molybdenum was found not only in the magnetite but in the other incrustations as well, often in the form of the hydrated oxide molybdenum blue. The concentration of this compound was great enough to color areas covering half an acre.

The pumiceous material in its purest form was next subjected to the same analytical procedure, and every element found in the incrustations was shown to be present in the pumice. The concentration in the incrustations was almost one hundred times that in the pumice. Practically all the elements mentioned above have one characteristic in common: namely, their halides, and, in some cases, their sulfides and oxides are volatile at the temperatures prevailing in the Valley of Ten Thousand Smokes. We obviously have here a mechanism by which large amounts of elements present in traces in the igneous materials can be concentrated at or near the surface and brought up from more deeply buried materials. The condition is here met that in order to bring about this type of concentration there must be a constant shifting of equilibrium due to lowering of the pressure and temperature. Niggli (28) has given considerable thought to the volatile products of igneous materials and has clearly presented the theories underlying the probable changes that take place on the cooling

TABLE 4

Foreign constituents in the fumarolic magnetite found in the Valley of Ten Thousand Smokes (39)

WEIGHT OF SAMPLE	WEIGHT OF SUBSTANCE AS DETERMINED	CALCULATED AS	PER CENT
grams	*grams*		
10		Hg	None
10	0.0007 PbO	Pb	0.005
10		Bi	None
10	0.0233 Cu	Cu	0.23
10	0.0054 MoO_3	Mo	0.04
10	0.0005 SnO_2	Sn	0.004 (approximate)
10		As	None
10		Sb	Present*
10		Cr	None
10		V	None
10	Colorimetrically	TiO_2	0.005
10	0.0474 Zn	Zn	0.47
10	0.0005 $NiC_8H_{14}N_4O_4$	Ni	0.01
10	0.0003 CoO	Co	0.02
1	Colorimetrically	MnO	0.13
1	0.0196 $BaSO_4$	S	0.27
20	0.0110 NaCl + KCl	NaCl	0.05
10	0.0530 siliceous residue		0.53
1	0.0005 Al_2O_3†		

* Definitely identified spectroscopically and not present in the blank.

† Present in the portion of fumarolic magnetite soluble in hydrochloric acid, and indicates that alumina was not present as part of the magnetite molecule.

of a magma. It will repay those interested in this phenomenon to study his presentation carefully.

In a sense this period of expulsion of volatile constituents is the last stage of what may be called true igneous activity, but it is by no means the last chapter in the study of concentration of the elements. One illustration will suffice. In 1923 Fenner continued his studies in the Valley of Ten Thousand Smokes and at our request made an effort to collect more of the magnetite found in 1919, but none was found. The temperatures had fallen to a point where active condensation of the steam was taking place; the acid gases were now in solution, and the magnetite was decomposed. The influence of hydrogen sulfide was now apparent, for in the new chemical environment only such compounds could persist as are relatively insoluble in acid. In place of magnetite, such minerals as covellite (CuS), chalcocite (Cu_2S), and sphalerite (ZnS) were found. These represent a further concentration of the copper and zinc. This illustration is cited to show the complex mechanism by which concentration is brought about.

These are in brief the methods by which concentration of the elements may be attained in nature. We have seen, however, that many of the rare and less familiar elements are present in igneous materials in such extremely low concentrations that it is possible for them to be dragged along as persistent impurities, so to speak, throughout the process of rock differentiation. It would seem almost futile to hope to find them in the rocks in any concentration of economic importance, no matter how valuable their chemical or physical properties may be. The case is not so hopeless, however, as it may seem.

In the discussion of the formation of the pegmatite dikes it was stated that some of the rare elements may be too dilute to form a definite mineral yet may be trapped by other minerals. Every analyst is familiar with a related process. For instance, extremely minute amounts of fluorine can be carried out of a neutral solution if barium is added and subsequently precipitated as barium sulfate. Gallium often escapes detection when present in low concentrations, but it can be concentrated by hydrogen sulfide if zinc is present. This phenomenon of coprecipitation is but little understood, but in the writer's opinion it is an important agency in concentrating some of the rare elements. There is still another mechanism by which minerals can gather up elements that exist in solution at low concentration. The magnetite found in the Valley of Ten Thousand Smokes contained appreciable amounts of manganese and zinc within the magnetite itself. This reminds one of the important mineral group called the spinels, of which magnetite and the zinc- and manganese-bearing franklinite are examples. Still another example: the cesium, rubidium, and gallium often found in lepidolite, one of the many minerals found in pegmatite dikes, can be fairly easily concentrated in the alums that are readily obtained after the mica is decomposed.

Grimm (20) has shown that the ability to form such mixed crystals depends on the dimensions of similarly constructed crystals and also on the dimensions of the substituted atom species. Goldschmidt (11 to 18), a most indefatigable worker on the problem of the distribution of the elements, has in a series of articles called attention to the high degree of probability that the segregation of the elements in crystals is governed by the relation between crystal structure and the dimensions of the atom and ion species. If this is true, then in the course of the crystallization of the various mineral species all extraneous elements whose atomic or ionic dimensions are either too small or too large to be taken up by the crystals are concentrated in the mother liquor. Perhaps the finest contribution made by Goldschmidt (12) is his determination of the ionic radii of many of the elements in Angström units. The values of the radii are based on x-ray studies of crystal structure, which furnish the so-called lattice dimensions, and on the determinations by Wasastjerna (22) of the ionic dimensions of F^- and O^{--}. The assumption is also made that in general the anion–cation distances of closest approach should be given by the sum of the corresponding radii (22). X-ray studies of a large number of combinations of the elements with oxygen, fluorine, and sulfur were made by Goldschmidt in order to obtain a basis for his calculations. Pauling also calculated the ionic distances from different data and obtained results that agree well with those of Goldschmidt. These results are tabulated in the International Tables for the Determination of Crystal Structure (22). They apply to distinct crystal groups, and due regard must be given to the structure type, valency, and coördination number. The interested reader is referred to the citations for the necessary details. These ionic and atomic dimensions provide us with a powerful tool for following the

TABLE 5

*Lattice dimensions of similar compounds of aluminum and gallium**

ALUMINUM COMPOUNDS	LATTICE DIMENSIONS	LATTICE DIMENSIONS	GALLIUM COMPOUNDS
	Å.	Å.	
Al_2O_3	5.13	5.28	Ga_2O_3
$LaAlO_3$	3.78	3.89	$LaGaO_3$
AP	5.451	5.436	GaP
AlAs	5.628	5.635	GaAs
AlSb	6.091	6.093	GaSb

* Taken from Goldschmidt (13).

probable course of the segregation of the elements that exist in minor concentration in the rocks, and have enabled Goldschmidt (17) to make several trenchant observations. The lattice dimensions of similar aluminum and gallium compounds are shown in table 5. This striking similarity in dimensions is also reflected in the similarity of the ionic radii.

In table 6 are shown the ionic radii of a few elements of equal valency. They are arranged in groups of similar dimensions, and a common element is associated with an element whose average concentration in the earth's crust is low. They have been selected for this presentation because this same association is repeatedly found in nature.

TABLE 6

*Similarity in ionic radii of rare elements of equal valency camouflaged by the common elements**

ELEMENT	IONIC RADIUS	ELEMENT	IONIC RADIUS	ELEMENT	IONIC RADIUS	ELEMENT	IONIC RADIUS	ELEMENT	IONIC RADIUS
	Å.		Å.		Å.		Å.		Å.
Mg	0.78	Si	1.27	Al	0.57	Si	0.39	Zr	0.87
Ni	0.78	Pb	1.32	Ga	0.63	Ge	0.44	Hf	0.86

* Taken from Goldschmidt (13).

TABLE 7

*Similarity in ionic radii of the yttrium elements**

ELEMENT	IONIC RADIUS	ELEMENT	IONIC RADIUS	ELEMENT	IONIC RADIUS
	Å.		Å.		Å.
Gd	1.11	Y	1.06	Ho	1.05
Tb	1.09			Er	1.04
Dy	1.07			Yb	1.00
				Cp	0.99

* Taken from Goldschmidt (13).

The same striking similarity in ionic radii obtains for the trivalent yttrium series of elements (see table 7). The analyst finds it extremely troublesome to separate these elements, and nature has had the same difficulty. The average percentage concentration of these elements in the earth's crust is extremely low; they are not removed by the usual processes of differentiation and therefore are concentrated in the mother liquor,—the pegmatites. Many other examples could be cited, but for our purpose the above will suffice.

Goldschmidt (17) has given the name "Tarnung" or "camouflage" to this tendency for the rare elements to be associated with and obscured by some more common element whose concentration in the siliceous igneous fluids is high enough to form a distinct mineral. He has also shown that extraneous elements whose valencies differ but whose ionic radii are similar may also be concealed or camouflaged within some common mineral. Table 8 contains several examples for both the common and the rare elements.

Many years ago Washington (37) called attention to the fact that calcium is frequently found with sodium in the soda feldspars, and barium with the potassium feldspars. Goldschmidt's work, based on x-ray studies of crystal structure and x-ray analysis, now provides an explanation for the association of the elements referred to and has thereby given great impetus to the study of their geochemistry.

The geochemical cycle of germanium as worked out by Goldschmidt and Peters (15) is of unusual interest. The former, on the basis of similarity in dimensions of ionic radii, had indicated that this element should be associated with silicon in the silicates. Papish (30) by means of his spectrographic analyses showed that germanium is in fact widely distributed in silicate minerals. Goldschmidt and Peters (16) showed that germanium could probably be absorbed by the roots of plants. They found for instance 1.6 per cent of GeO_2 in the ashes derived from some English coals, surely an extraordinary concentration of what is usually called a rare element.

TABLE 8

*Similarity in ionic radii of elements differing in valency camouflaged by the common elements**

ELEMENT	IONIC RADIUS	VALENCY	ELEMENT	IONIC RADIUS	VALENCY
	Å.			Å.	
Li	0.78	1	Ca	1.06	2
Mg	0.78	2	Y	1.06	3
Na	0.98	1	Sc	0.83	3
Ca	1.06	2	Zr	0.87	4
K	1.33	1	Ti	0.64	4
Ba	1.43	2	Nb	0.69	5

* Taken from Goldschmidt (13).

The geochemistry of rhenium has been studied very thoroughly by its discoverers, Ida and Walter Noddack (29). A truly enormous number of substances have been analyzed by them within a comparatively short time both by x-ray and by optical spectroscopy. No claim seems to be made by them for great accuracy of the determinations; nevertheless their work brings out clearly where this extremely rare element is likely to be found in nature. Here, again, similarity in ionic radii seems to be the guiding principle in showing that the greatest concentrations will be found in the molybdenites associated with pegmatitic minerals. Molybdenum and rhenium are much alike in their chemical properties and in the dimensions of their ionic radii. The work of Ida and Walter Noddack also brings out a point that has been frequently referred to, namely, the investigation of the by-products and so-called waste materials in the industries. Rhenium has been extracted from a molybdenum by-product in amounts that definitely take this element out of the category of a chemical curiosity (8).

Even though the useful elements found in ore bodies were derived from igneous materials through the processes of differentiation referred to in this review, yet their present concentration has in most cases been obtained through a complicated process of decomposition of the original materials and their reconcentration from solution in a favorable physical-chemical environment. The rare elements camouflaged in some mineral may also be reconcentrated when this mineral is decomposed through subsequent geochemical alteration.

It would behoove those who are interested in searching for the rare elements that are not found as distinct mineral species to sharpen their quantitative physical and chemical analytical tools and search for these less familiar elements in the minerals and waste products within which the guiding principle of similarity in ionic radii has shown they may be concealed. It will also be desirable to take cognizance of the chemical principles referred to in the discussion of the concentration of the elements in volcanic areas through vapor phase activity and through the solvent action of acid or even alkaline waters.

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