

*The Principles of Distribution of Chemical Elements in Minerals and Rocks.*

THE SEVENTH HUGO MÜLLER LECTURE, DELIVERED BEFORE THE CHEMICAL SOCIETY ON MARCH 17TH, 1937.

By PROF. DR. V. M. GOLDSCHMIDT.

WHEN, eight years ago, I had the honour of presenting a lecture ("The Distribution of the Chemical Elements," Friday Evening Lecture, March 15th, 1929) in this same room before an audience of the Royal Institution concerning geochemical research work at the University of Oslo, I explained some views on a problem, the study of which is interesting both for chemists and geologists, namely, the distribution of the chemical elements. I then gave some outlines of the problems involved, and also described examples of systematic relations.

Meanwhile, the general programme for geochemical research work indicated then has largely been followed; results have been obtained concerning the actual amount and distribution of nearly all the chemical elements, this having, in many cases, been rendered possible by new and improved methods of analysis. At the University of Göttingen, during the years 1929—1935, continuing and extending previous work at Oslo, I again had the privilege of co-operating with a number of young mineralogists, chemists, and physicists engaged in the problem of determining the composition of minerals and rocks, especially with regard to rare constituents.

For many years the methods of spectrographic analysis had been of great utility in ascertaining the presence of rare elements—I need only mention in this connection the important work in your country of Sir William Crookes, of W. N. Hartley, and H. Ramage. More recently, improved methods, in many cases combining chemical and optical work, have made it possible to collect numerous data with regard to the exact amounts of the constituents, through a large range of percentages.

During the first years of my research work, analysis by means of *X*-ray spectra, initiated by my friend Professor A. Hadding of Lund (Sweden), made possible several investigations upon rare constituents of minerals down to 0.1% or even to 0.01%; and during the Göttingen years, in co-operation with Dr. R. Mannkopff, assisted by a number of young research workers, methods of quantitative analysis by means of the arc spectrum were developed so as to be capable of determining 0.001% (or even less) of most elements. Apart from the publications of Dr. Mannkopff, I have to mention the work of my young friends Drs. Peters, Bauer, von Engelhardt, Hörmann, Noll, Minami, Strock, and Witte in developing and improving the new methods of analysis and co-operating in the collection of data. Of course, during our work the general advance in optical spectrographic methods, especially through the work of Professor Walther Gerlach in Munich, has been of much importance.

Our methods of analysis, either by physical means, such as optical and *X*-ray spectra, or by quantitative chemical work, have generally been directed to the development of those methods which permit the detection and determination of small amounts of various elements in rather small amounts of substance. We have purposely avoided those methods involving the working up of considerable amounts of substance, for the following reason: if we have to determine the distribution of substances between minerals of different kinds, particularly if very small percentages are involved, we have to take care that we really are studying the single pure mineral, and not a mixture containing contaminations from other minerals. This end is most readily attained if only small amounts of any mineral are needed for examination; as soon as we have to work up many grams or even kilograms, in most cases it becomes almost impossible to secure pure material for analysis.

Much has been said recently about the so-called "omnipresence" of all chemical elements, the supposed common level of the presence of a given element in any matter, especially in minerals. I feel sure that much, if not all, of this "omnipresence" of elements in crystallised minerals is due to their contamination by inclusions, surface adsorption, and other accidental impurities. In rocks, however, the omnipresence of elements has a reasonable meaning.

One great advantage of using only small amounts of substance for our investigation is

that one avoids the introduction of large amounts of laboratory reagents. The degree of impurity of even so-called fine chemicals is often astonishing, and in several cases we have found that in traditional methods of analytical determination of minor constituents a higher percentage of, for instance, barium has been contributed from the reagents than from the rock specimen.

Our methods of analysis have in many cases been founded on optical spectrography, based on the intensity of spectrum lines in the carbon arc, the Mannkopff-Peters effect of ionic concentration in the surface layer of the negative electrode being particularly used. Optical spectrographical methods also have been invaluable in the control of purity of reagents and efficiency of chemical separations.

*Abundance of Elements.*

		Earth's crust (g. per ton as unit).	Sun's atmosphere (0.1 mg. per sq. metre as unit).*			Earth's crust (g. per ton as unit).	Sun's atmosphere (0.1 mg. per sq. metre as unit).*
1	H	—	6,000,000	44	Ru	—	5
2	He	—	800,000	45	Rh	0.001 (G)	0.3
3	Li	65 (G)	0.6	46	Pd	0.01 (G)	1.2
4	Be	6 (G)	0.6	47	Ag	0.1 (G)	1
5	B	3 (G)	300 ?	48	Cd	0.5 (G)	15
6	C	—	300,000	49	In	0.1 (G)	0.1
7	N	—	500,000 ?	50	Sn	40 (G)	2
8	O	494,000	3,200,000	51	Sb	1 ?	1
9	F	270	—	52	Te	—	—
10	Ne	—	—	53	I	0.3 (L)	—
11	Na	28,300	400,000	54	X	—	—
12	Mg	21,000	1,500,000	55	Cs	7 (G)	—
13	Al	88,200	60,000	56	Ba	390 (G)	250
14	Si	276,000	600,000	57	La	19 (G)	8
15	P	786 (G)	—	58	Ce	44 (G)	40
16	S	500	—	59	Pr	5.6 (G)	1
17	Cl	480	—	60	Nd	24 (G)	15
18	Ar	—	—	61	—	—	—
19	K	25,900	250,000	62	Sm	6.5 (G)	5
20	Ca	36,300	200,000	63	Eu	1.0 (G)	4
21	Sc	5 † (G)	200	64	Gd	6.3 (G)	2
22	Ti	6,300	8,000	65	Tb	1.0 (G)	—
23	V	100	5,000	66	Dy	4.3 (G)	6
24	Cr	200	25,000	67	Ho	1.2 (G)	—
25	Mn	930	40,000	68	Er	2.4 (G)	0.2
26	Fe	51,000	1,000,000	69	Tu	0.3 (G)	—
27	Co	40 (G)	25,000	70	Yb	2.6 (G)	—
28	Ni	100 (G)	60,000	71	Cp ‡	0.7 (G)	—
29	Cu	100	6,000	72	Hf	3.2 (H)	0.4
30	Zn	40 (G)	5,000	73	Ta	—	—
31	Ga	15 (G)	6	74	W	69 (H)	0.3
32	Ge	7 (G)	80	75	Re	0.001 (N)	—
33	As	5	0.3	76	Os	—	—
34	Se	0.6 (G)	—	77	Ir	0.001 (G)	0.1 ?
35	Br	—	—	78	Pt	0.005 (G)	8
36	Kr	—	—	79	Au	0.005 (G)	—
37	Rb	310 (G)	4	80	Hg	0.5 (S)	—
38	Sr	420 (G)	150	81	Tl	0.3 (G)	5 ?
39	Y	31 (G)	30	82	Pb	16 (H)	3
40	Zr	190 (H)	30	83	Bi	0.2 (G)	—
41	Nb	15 (G)	1	90	Th	11 (G)	—
42	Mo	15 (H)	3	92	U	4	—
43	Ma	—	—				

G, data determined in the laboratories of the Mineralogical Institutes of Göttingen and Oslo; H, data determined by Prof. von Hevesy and co-workers; L, determination of iodine in rocks by G. Lunde; N, data of I. and W. Noddack; S, determination of mercury in rocks by Prof. A. Stock.

\* Data due to H. N. Russell (*loc. cit.*). The data for H, He, and O are possibly somewhat too low. The elements P, S, Yb, and Cp have since been found in the sun's atmosphere.

† The data for scandium are under revision; our earlier estimate, 5 g., is possibly too low.

‡ Cp = Lu.

Much work had to be done in the development of methods, in the purification of electrodes, in finding standards of comparison, and, in many cases, in combining suitable methods of chemical concentration with a spectrographic examination of the concentrates.

The abundance of most elements in the surface matter of the earth is now known with some degree of accuracy. The preceding table demonstrates our present knowledge with regard to the rocks of the earth's surface as far as reliable data are available; these data are based partly upon the pioneer work of Clarke and Washington, and partly upon later investigations with regard to rare elements, many having been found at the Göttingen laboratory, others at Oslo, and others by von Hevesy and his co-workers or by I. and W. Noddack.

I have omitted data for hydrogen, carbon, nitrogen, and inert gases, as they are not significant for the analyses of the primary rocks, the hydrosphere and atmosphere being neglected.

A few years ago, the results of a chemical analysis of a composite sample of magmatic rocks were published by I. and W. Noddack (*Svensk Kem. Tids.*, 1934, **46**, 173), and in many cases they agree with other determinations, but for certain elements (Y, Rh, Ir, Pt) their data appear to be decidedly too high, and for others (Co, Rb, Sr, Nb, Ag, Sn, I) they are lower than our data. The special assemblage of their composite sample of rocks may be the cause of some of the differences.

A most interesting basis for comparison between terrestrial and cosmic matter is given in Russell's data on the composition of the sun's atmosphere (*Astrophys. J.*, 1929, **70**, 11).

If we examine the results concerning the material in the surface rocks of the earth, we find that some elements are present in large percentages, such as silicon, aluminium, magnesium, and potassium; others are rather rare, *e.g.*, zirconium, scandium, beryllium, and rubidium; and some exceedingly rare, *e.g.*, platinum metals and gold, or selenium.

One of the most important problems in geochemistry is to find the true relative abundance of the chemical elements in the world as a whole, and from that point of view it is interesting to test whether the relative amounts of the elements in the earth's crust are truly representative of their primary proportions or whether these amounts have been modified by selective elimination of certain elements or groups of elements.

As I mentioned in my previous lecture (*loc. cit.*), some very suitable elements for a study of selective behaviour are those of the platinum and palladium families, or even the entire group of the precious metals. These metals are very rare in the earth's crust, and even 15 years ago, in a lecture at Leipzig, I had ventured the hypothesis that this rarity had been caused by a process of selective concentration into the interior of the earth, owing to the

*Precious Metals in Meteoric Iron (Goldschmidt and Peters).*

Locality.	Structure.	G. per ton.							
		Ru.	Rh.	Pd.	Ag.	Os.*	Ir.	Pt.	Au.
Coahuila, Mexico .....	Hexaedrite	10	5	10	5	?	10	10-100	5-1
São Julião de Moreira, Portugal...	Octaedrite <i>cc</i>	10	10	10	5	5	1	10-100	10
Mount Joy, Pa., U.S.A. ....	"	5-10	5	10	5	<5	1	10-100	5-10
Arispe, Mexico .....	"	10	5	10	5	?	10	10-100	5-1
"	"	10	5	10	1-5	5	10	10-100	5
Corrizatillo, Chile .....	"	5	5	10	5-10	<5	5	10	5-10
Magura, Czechoslovakia .....	Octaedrite <i>c</i>	10	5	5-10	5	<5	5	10-100	5
Cañon Diablo, Ar., U.S.A. ....	"	10	5	5-10	5	5	5	10-100	5
Rust Crust, Cañon Diablo .....	"	10	5	5	1	5	5	10	5
Cranbourne, Victoria, Australia ...	"	10	5	10	1	—	5	10	5
Rust, Cranbourne .....	"	10	5	10	10	—	—	10	5
Saviik, Cape York, Greenland ...	Octaedrite <i>m</i>	10	5	5	10	<5	10	10-100	5
Toluca, Mexico .....	"	5	0-5	10	1	—	1	1	10
"	"	10	5	10	1	—	1	10	10
Henbury, Central Australia .....	"	10	5-10	10	5	5	10	10-100	5
N'Goureyma, Sudan .....	Octaedrite <i>b</i>	5	1-5	5	1	—	1	5-10	1
Morradal, Norway .....	Ataxite	5	5	10	5	—	1	10	5
"	"	5	5	10	1-5	<5	1	10-100	5-10
Capland .....	"	10	5-10	10	5-10	5	10-100	100-10	1
Rust Crust, Hoba, S.W. Africa ...	"	10	5-10	10	1	<5	10	100-10	0-5
"	"	10	5-10	10	1	5	10	100-10	0-5
Medwedew, Krasnojarsk, Siberia	Iron from pallasite	5	5	10	5-1	—	—	5	5
"	"	5	1-5	10	1-5	<5	1	5	5
Brenham, Kansas, U.S.A. ....	"	5-10	5	10	1	<5	5-1	10-100	10-5
Estherville, Iowa, U.S.A. ....	Iron from siderolite	10	5	10	1	<5	1	10	1-5
Knyahinya, Czechoslovakia .....	Iron from chondrite	10	5	10	5	<5	5	10-100	10
Holbrook, Arizona, U.S.A. ....	"	10	10	10-100	1	<5	5	100-10	10

\* The data for osmium are minimum amounts, as part of the metal is lost as volatile OsO<sub>4</sub>.

large partition ratios of these metals between silicate slags and iron alloys, and I recommended a systematic search for the platinum metals in meteoric irons. Eight years ago I was able to give many new examples to demonstrate the abundance of platinum metals in meteoric iron, and to-day our question can be answered in much greater detail by a number of analyses of meteoric irons for platinum metals; these were made partly in the Göttingen laboratory, and partly by I. and W. Noddack in Berlin. The table on p. 657 gives the data from Göttingen.

The following table averages the data from Göttingen and from Berlin.

*Meteoric Iron (Average).*

*Precious metals, g. per ton.*

	I. and W. Noddack.					I. and W. Noddack.			
	G. and P. 1932. <sup>1</sup>	1930. <sup>2</sup>	1931. <sup>3</sup>	1934. <sup>4</sup>		G. and P. 1932. <sup>1</sup>	1930. <sup>2</sup>	1931. <sup>3</sup>	1934.
Ru	10	23·9	20·30	12—13	Os	>3	8·8	25·30	9
Rh	5	5·0	4	4—5	Ir	5	2·3	5	3·6
Pd	10	19	15—20	10—11	Pt	20	17·7	10—22	23
Ag	5	3·2	6—8	3—4	Au	5	1·4	0—1	2—3

<sup>1</sup> Goldschmidt and Peters, *Nachr. Ges. Wiss. Göttingen, Math.-phys. Kl.*, 1932, 377.

<sup>2</sup> *Naturwiss.*, 1930, **18**, 757.

<sup>3</sup> *Z. physikal. Chem.*, 1931, *A*, **154**, 207; *ibid.*, Bodenstein-Festband, 1931, 890.

<sup>4</sup> *Svensk Kem. Tids.*, 1934, **46**, 173.

From the tables, we see that concordant data exist with regard to the amounts of platinum metals in meteorites, and that these are in full agreement with prediction. A very interesting result of investigations during recent years is our discovery that gold also is concentrated in meteoric iron in very considerable amounts. If the nucleus of the earth is as rich in gold as the average meteoric iron, about 5 g. per ton, then the interior contains enough gold to make a coating of the metal 1 m. thick over the entire surface of our globe.

Still another element which has hitherto been considered as very rare has been found by us in large amounts in meteoric iron: that is germanium. We have found this in small amounts (a few g. per ton) in all terrestrial and meteoric silicate rocks,\* but most of the germanium in the world has been concentrated in certain metallic alloys, such as meteoric iron. The following table affords a comparison between the concentrations (in g. per ton) in the earth's crust and in meteoric iron.

	Earth's crust.	Meteoric iron.	Factor.		Earth's crust.	Meteoric iron.	Factor.
Pt	0·005	20	4000	Au	0·005	5	1000
Ir	0·001	5	5000	Ni	100	80,000	800
Rh	0·001	5	5000	Ge	7	500	70
Pd	0·01	10	1000	Ag	0·1	5	50

Now, we can further test our hypothesis concerning the distribution of precious metals and of germanium by means of experiments which Nature itself has performed. If our silicate rocks have been deprived of precious metals and of germanium by some process of equilibrium of partition between silicate slag and iron alloy, then we could reproduce practically the same equilibrium by bringing a large amount of fused silicate rock into contact with a very small amount of metallic iron, and we should expect concentration of the same rare elements in the iron as have been concentrated in iron meteorites. Such experiments which establish the equilibria of partition between large amounts of fused silicate and small amounts of iron have been made by Nature in the cases of the iron lumps in the basalt of Ovifak, on the island of Disco, near Greenland, and of the iron-nickel alloy josephinite in olivine rock from Oregon, U.S.A. The following data demonstrate that precious metals and germanium have been concentrated effectively in the Ovifak iron, and our investigation of precious metals in josephinite revealed about 5 g. of platinum, 10 g. of palladium, and 1 g. of gold per ton, besides much silver.

\* Important observations on the occurrence of germanium in certain silicates have been made also by J. Papish.

*Iron from Basalt, Ovipak, Disco, Greenland (g. per ton).*

Pt.	Pd.	Rh.	Ru.	Au.	Ag.	Ge.
5	1	0.5	0.5	5—1	5—10	1000

We may take these data as a confirmation of our hypothesis that equilibria of partition between metallic or semi-metallic phases and silicate phases have been responsible for a more or less effective elimination of certain elements from the material of the earth's crust. We may summarise our knowledge concerning these equilibria in the following table, where the first three columns refer to the equilibria of partition between liquid iron, liquid sulphides, and fused silicates.

Iron, siderophile.	Sulphide, chalcophile.	Silicate, lithophile.	Gases, atmophile.	Organisms, biophile.
Fe, Ni, Co	((O)), S, Se, Te	O, (S), (P), (H)	H, N, C, (O)	C, H, O, N, P
P, (As), C	Fe, Cr, (Ni), (Co)	Si, Ti, Zr, Hf, Th	Cl, Br, I	S, Cl, I (B)
Ru, Rh, Pd	Cu, Zn, Cd, Pb	(Sn)		(Ca, Mg, K, Na)
Os, Ir, Pt, Au *	Sn, Ge, Mo	F, Cl, Br, I	He, Ne, Ar	(V, Mn, Fe, Cu)
Ge, * Sn *	As, Sb, Bi	B, Al, (Ga), Sc, Y	Kr, X	
Mo, (W)	Ag, (Au), Hg	La, Ce, Pr, Nd, Sm		
(Nb), Ta	Pd, Ru, (Pt)	Eu, Gd, Tb, Dy		
(Se), (Te)	Ga, In, Tl	Ho, Er, Tu, Yb, Cp		
	(Cr)	Li, Na, K, Rb, Cs		
		Be, Mg, Ca, Sr, Ba		
		(Fe), V, Cr, Mn		
		((Ni)), ((Co)), Nb, Ta		
		W, U, ((C))		

\* That germanium, tin, and gold are distinctly siderophile elements has recently been proved by independent studies on meteorites and on metallurgical products.

The principle of partition of elements between a metallic liquid, rich in free electrons, a sulphidic liquid of a semi-metallic nature, and an ionic liquid affords a classification in three groups of elements, with regard to their geochemical affinities, these three groups being accompanied by a fourth, including the elements which are accumulated in gas phases, either as free volatile elements or as gaseous compounds. A fifth group contains those elements which are concentrated by living organisms in later stages of terrestrial evolution.

The partition of elements according to the first four groups of geochemical affinity is closely related to the structure of the electron shells of the atoms. Ions of the rare-gas type, *e.g.*, those of sodium, calcium, and aluminium, enter preferentially into the ionic phases of the silicate shell; the metallic elements of the transition groups, such as nickel, palladium, and platinum, enter preferentially into the iron alloys; and elements of the 18-electron shells, such as copper, lead, etc., into sulphide melts, if the potential of reduction is not high enough to permit formation of their iron alloys. A corresponding classification of all elements in two groups, metallogenetic and petrogenetic, was proposed by Washington in 1920.

The classification into the groups of different geochemical affinity, a division connected with potentials of ionisation and with the type of ionic structure, is not exclusively restricted to the time of the formation of the principal shells of the earth, but may take place at any time when an element has to be distributed between ionic, metallic, and semi-metallic phases. Therefore, we find iron, nickel, and gold in native platinum, and nickel, copper, and platinum metals in iron monosulphide ores, and I think that even the concentration of gold in pyrites and in arsenopyrites may be an analogous process of concentration of siderophile precious metals in semi-metallic phases. In this connection, it may be interesting to note that gold and even platinum metals have been concentrated in hydrothermal nickel arsenide minerals, as might have been expected.

Of course, the quotients of distribution into the primary geochemical affinity groups are dependent on the temperature; also, the degree of reduction of the system is often of importance. For instance, chromium is a strongly lithophile element under ordinary terrestrial conditions. If, however, oxygen is deficient, as in iron meteorites, chromium is decidedly chalcophile, entering almost exclusively into the sulpho-spinel daubréelite, FeCr<sub>2</sub>S<sub>4</sub>.

Our first principle of geochemical distribution, the principle of the four primary geochemical affinity groups, accounts for the scarcity of certain elements in the earth's crust, and its validity has been verified by us and others by means of analyses of the different phases of meteorites.

In comparing the composition of meteorites with that of the earth's crust, we have to distinguish between three different assemblages of elements in the meteorites; as pointed out in my 1929 lecture, these are the silicates of the stony meteorites, the iron-nickel alloy of the iron meteorites and of the stony meteorites, and the sulphide phase (troilite) of both. Our knowledge of the relative abundance of elements in meteorites is due mainly to the early compilations of Farrington and of Merrill, and to numerous determinations of rarer elements in the Göttingen laboratory and by I. and W. Noddack, von Hevesy, Paneth, and others.

An important verification of our geochemical classification has been obtained by the study of certain metallurgical products from the copper industry of the Mansfeld district in Germany; Cissarz and Moritz have studied the sulphide phase, the pig iron and the silicate slags from Mansfeld, and have found a distribution of elements representative of the partition into the corresponding geochemical groups. It may be noted that the elements gold, tin, and germanium, once considered by me to be dominantly chalcophile, have been found to be siderophile with regard both to behaviour in industrial separation and to separations in meteoric matter.

We understand clearly why the typical siderophile and chalcophile elements are only sparsely represented in the silicate crust of the earth, and how they are distributed between minerals of different bond type, and our knowledge has advanced so far as to permit a successful prediction of hitherto unknown modes of occurrence. The processes of mineral formation and of the partition of elements between different minerals are, however, not limited to the separation of metallic, semi-metallic, and ionic substances, for a number of other mineral-forming and differentiating processes have been, and still are, operating.

The processes mentioned above have not been directly connected with or restricted to the crystalline state of matter. The partition into chalcophile and lithophile elements takes place between amorphous, liquid phases, as well as in interactions in which crystalline substances are involved. We shall now, however, study some processes which are directly related to properties of crystalline matter, *i.e.*, the processes of formation of crystallised minerals from liquid or gaseous systems.

The formation of crystalline minerals involves the building up of space lattices of atoms or ions, in a regular arrangement, depending upon the size, or we may say the radii, of the individual atoms or ions. Into such a lattice only those particles can enter which are of a size appropriate to the lattice spacings. Therefore the crystals act as a kind of sorting or sieving mechanism, allowing certain particles to enter, and excluding others of unsuitable size.

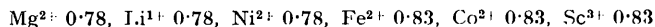
Any process which involves the formation of crystalline minerals, whether from molten magmas, from aqueous solutions, or from gases, involves a sorting of elements according to the radii of their atoms or ions, and one of the most important principles for the distribution of the elements, therefore, is the grading according to size, especially as compared with the lattice spacings or interatomic distances of rock-forming minerals of the most ordinary elements.

The following table gives a list of elements, or rather of their ions, arranged according to their radii. It is noteworthy that the importance of these dimensions for the connection between chemical composition and crystal structure emerged primarily from our geochemical work on the distribution of particles between crystalline minerals.

Radius, A.	Ions.
0.1—0.3	B <sup>3+</sup> , C <sup>4+</sup> , N <sup>5+</sup> , S <sup>6+</sup>
0.3—0.5	Be <sup>2+</sup> , Si <sup>4+</sup> , Ge <sup>4+</sup> , P <sup>5+</sup> , V <sup>5+</sup> , Mo <sup>6+</sup> , W <sup>6+</sup>
0.5—0.7	Al <sup>3+</sup> , Ga <sup>3+</sup> , Fe <sup>3+</sup> , Cr <sup>3+</sup> , V <sup>3+</sup> , Ti <sup>4+</sup> , Nb <sup>5+</sup> , Ta <sup>5+</sup>
0.7—0.9	Li <sup>1+</sup> , Mg <sup>2+</sup> , Ni <sup>2+</sup> , Co <sup>2+</sup> , Fe <sup>2+</sup> , Zn <sup>2+</sup> , Sc <sup>3+</sup> , In <sup>3+</sup> , Zr <sup>4+</sup> , Hf <sup>4+</sup> , Sn <sup>4+</sup>
0.9—1.1	Na <sup>1+</sup> , Ca <sup>2+</sup> , Cd <sup>2+</sup> , Y <sup>3+</sup> , Gd <sup>3+</sup> —Ce <sup>3+</sup> , Ce <sup>4+</sup> , Th <sup>4+</sup> , U <sup>4+</sup>
1.1—1.4	K <sup>1+</sup> , Sr <sup>2+</sup> , La <sup>3+</sup> —Eu <sup>3+</sup>
1.4—1.7	Rb <sup>1+</sup> , Tl <sup>1+</sup> , Cs <sup>1+</sup> , Ba <sup>2+</sup> , Ra <sup>2+</sup>

In the group of the lanthanides I have drawn the subdivision between Eu (radius 1.13) and Gd (radius 1.11) instead of between Gd and Tb, in order to follow the traditional division between cerium and yttrium earths.

Given a table of radii of ions, we can as a rule predict into which minerals any given element is entering; for instance, we may predict a connection between magnesium and a number of other elements :



Now the question arises as to the order of preference in which the different ions, being of suitable size, will enter into a crystal lattice : not all guests are equally welcome in a lattice, and the crystal in many cases makes a choice between them. Let us first consider the simplest case. In the pair magnesium–nickel the radii are alike, and also the charges of the ions, both metals being bivalent, and therefore the nickel ions pass into the crystals of magnesium silicate with about the same probability as the magnesium ions; consequently, the amount of nickel in a number of magmatic minerals is roughly proportional to that of magnesium.

If radii, charges, and the ionic type of two elements are exactly alike or very similar, then no separation takes place at all; I may refer to the pair zirconium–hafnium, known through the work of von Hevesy and Coster, or to the pair yttrium–holmium, which is never separated in Nature. The rare elements hafnium and holmium are hidden away by “camouflage” in minerals of more common elements (zirconium and yttrium).

If there is some small difference of ionic radius, the bond is weakened for the larger ion; therefore the melting point of iron olivine is lower than that of magnesium olivine, and the larger ion is concentrated in the mother-liquor as compared with the smaller ion according to the fusion diagram found by Bowen and Schairer. The following data illustrate the difference of melting points :

Mineral	Formula.	M. p.	Mineral.	Formula.	M. p.
Forsterite	Mg <sub>2</sub> SiO <sub>4</sub>	1910°	Fayalite	Fe <sub>2</sub> SiO <sub>4</sub>	1205°

Even small differences in radii may thus make possible an enrichment of the larger component of such a pair in late crystallates and in mother-liquors, as, for instance, in the pair aluminium–gallium, the radii of the trivalent ions being 0.57 A. (Al) and 0.62 A. (Ga).

	Ga <sub>2</sub> O <sub>3</sub> , %.	Al <sub>2</sub> O <sub>3</sub> , %.	Ga : Al (atoms).
Bytownite, Sogndal, Norway .....	0.0005	32	1 : 120,000
Nephelite, Langesund, Norway .....	0.01	32	1 : 6,000
Diasporite, Langesund, Norway .....	0.2	80	1 : 800
Opalised wood, Yellowstone Park, U.S.A. ....	0.1	0.7	1 : 13

Another example is furnished by certain univalent followers of potassium in *late* crystals of potassium minerals; for instance, in the potash feldspars of pegmatites we find considerable amounts of rubidium, caesium, and thallium, according to the relation of the radii of the univalent ions : K 1.33 A., Rb 1.49 A., Tl 1.49 A., Cs 1.65 A.

Now a crystal may extend its hospitality even to ions having a fitting radius but a different charge (of the same sign); for instance, magnesium minerals may take up scandium or lithium. In what sequence do such ions of different charge enter a crystal structure? We have found that this order depends upon the magnitude of the electrostatic charge of the ion, as long as simple atomic ions are concerned. The ion which has a larger charge has the preference over other ions of the same size but of lower charge. For instance, the atoms of scandium enter into early crystallisations of magnesium minerals, especially into the pyroxenes of gabbros and basalts.

A very well-known analogous example is offered by the groups of soda–lime feldspars, the plagioclases, the bivalent ions preferentially entering the crystal, and giving rise to the well-known crystallisation diagram of the lime–soda feldspars as found by Bowen :

Mineral.	Formula.	M. p.
Anorthite .....	Ca <sup>2+</sup> (Al <sub>2</sub> Si <sub>2</sub> O <sub>8</sub> ) <sup>2-</sup>	1550°
Albite .....	Na <sup>+</sup> (AlSi <sub>3</sub> O <sub>8</sub> ) <sup>1-</sup>	1090

Therefore calcium is concentrated in early fractions of plagioclase crystals, sodium in late fractions.

In the same manner strontium and barium enter early crystals of potash feldspars, as found by Noll and von Engelhardt at Göttingen. We have given the phenomenon the name of " capturing " (" Abfangen ") of highly charged ions.

Correspondingly, ions of fitting radius, but having a *lower* charge are only reluctantly admitted into the same crystals, owing to correspondingly weakened electrostatic bonds. Therefore lithium is concentrated not in the first but in the *last* crystallates of magnesium minerals, as shown by the very accurate studies of Strock at Göttingen.

Quotient (by weight),  $\frac{\text{Li}_2\text{O}}{\text{MgO}} \times 10,000$ , according to Strock.

Early :	{ Peridotite .....	0.12	Early :	{ Basalt .....	3.3
	{ Pyroxenite .....	0.17		{ Porphyrite and andesite ...	16
	{ Gabbro .....	3.3			
	{ Diorite .....	10			
Late :	{ Syenite .....	20	Late :	{ Trachyte .....	150
	{ Nephelite syenite .....	70		{ Phonolite .....	140
	{ Granite .....	600		{ Liparite and obsidianite ...	200

Generally, in the series of magmatic rocks and minerals, these rules enable us to discriminate between elements of early and those of late introduction into the crystals of common rock-forming minerals. In the following table, the examples are taken mostly from investigations in collaboration with Dr. Bauer, Dr. Hörmann, and Dr. Witte ; the barium data are due to Dr. von Engelhardt.

Rock.	Early.				Late.			
	Cr <sub>2</sub> O <sub>3</sub> , %	NiO, %	CoO, %	MgO, %	BaO, %	Nb <sub>2</sub> O <sub>5</sub> , %	La <sub>2</sub> O <sub>3</sub> , %	K <sub>2</sub> O, %
Peridotite (dunite) ...	0.50	0.40	0.03	40	0.0003	—	—	0.1
Gabbro .....	0.05	0.02	0.01	8	0.007	0.001	0.001	1
Diorite .....	0.01	0.005	0.004	3	0.03	0.003	0.003	2
Granite .....	0.0003	0.0003	0.001	1	0.05	0.005	0.005	4
Nephelite syenite .....	0.0001	0.0003	0.001	1	0.06	0.02	0.05	6

If, now, we compare the chemical composition of the earth's crust and of silicate meteorites, we find the well-known differences clearly explained as a consequence of selective enrichment of late crystallates in the uppermost crust of the earth :

	Grams per ton.			Factor.	
	Silicate meteorites.	Earth's crust.			
Cr .....	3,200	200	0.06	} Early crystallisation.	
Mg .....	137,000	21,000	0.15		
Zr .....	80	190	2.3		
Na .....	3,700	21,400	2.5		
Li .....	5	65	13	} Late crystallisation.	
K .....	1,700	25,900	15		
Sr .....	20	420	21		
Ba .....	5	390	78		

The enrichment of late crystallates in the uppermost crust of the earth is effected by the relatively low specific gravity of granite magmas, nephelite syenite magmas, and aqueous residual solutions, which all tend to migrate towards the surface of our planet.

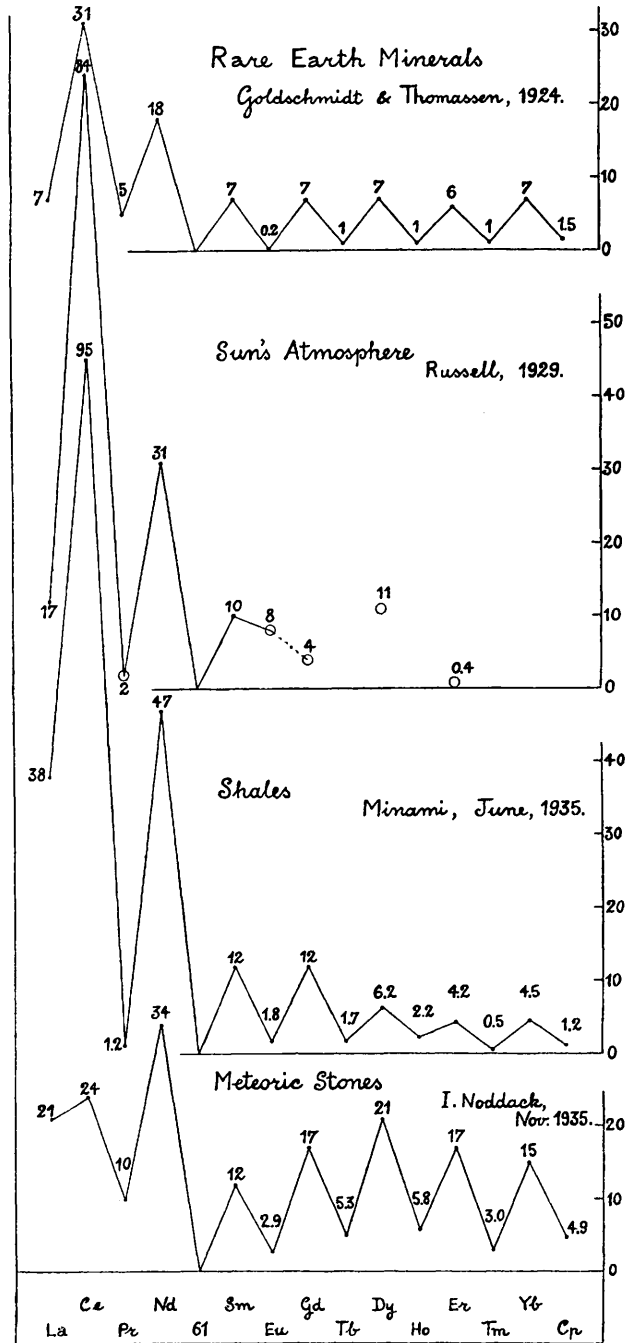
In order to ascertain the original proportions between elements, we have to search for " coherent groups " of elements, *i.e.*, elements which, owing to their similarity in radius and in valency, enter into the same minerals at about the same stage of fractional crystallisation. Zirconium and hafnium are one such coherent pair. A large rather coherent group is furnished by the rare-earth elements, comprising the lanthanide family (elements of atomic number from 57 to 71) and yttrium.

The data in Fig. 1 embody determinations of the proportions of these elements, as



found in rare-earth minerals by me and Thomassen (*Vid. Selsk. Skr., Math. Naturv. Kl., 1924, No. 5*), in the sun's atmosphere (still somewhat incomplete data) by Russell (*loc. cit.*),

FIG. 1.



in average samples of sedimentary rocks (shales) by my co-worker Minami, (*Nachr. Ges. Wiss. Göttingen, Math. Phys. Kl., 1935, 1, 155*), and somewhat later in stone meteorites by

I. Noddack (*Z. anorg. Chem.*, 1935, **225**, 337) : the coherency of the group is distinctly visible. All data are referred to 100 atoms of yttrium as the unit.\*

Some differences are of interest. The relatively small amount of cerium, as compared with the trivalent rare-earth elements, given by I. Noddack for the meteorites may be caused, I think, by a partial loss of that element, probably in the separation of thorium, due to the hydrolytic precipitation of ceric hydroxide.

More interesting are the differences concerning the element europium. In rare-earth minerals this metal is usually present only in very minor amounts, even in comparison with other elements of odd atomic number. However, in the assemblage of rare-earth elements, which is found in sedimentary rocks and represents an integration or re-assembling of all the rare-earth atoms of primary minerals and rocks, europium is found in similar amounts to, for instance, terbium. Also, in the solar atmosphere as well as in many stellar atmospheres, europium is found in amounts not less than those of other odd rare-earth elements.

Unpublished investigations by me and Dr. Bauer at Göttingen have revealed terrestrial assemblages rich in europium, for instance in certain pyromorphites, many titanites, potash feldspars, and some strontianites. Many years ago I predicted close isomorphism between bivalent europium and strontium, a prediction which has been verified by the Noddack's experimental work on the isolation of europium by means of mixed crystals of the sulphates at the Freiburg laboratory.

As a summary of all investigations on crystallised minerals of magmatic origin, we may state that the radii and valency properties of the atoms and ions regulate the distribution of elements in the primary magmatic rocks and in the minerals of those rocks. Also, these principles have made possible the prediction of unknown facts, and the systematic investigation of the composition of magmatic minerals and rocks with regard to minor constituents has greatly augmented our knowledge of geochemistry. I may mention the important comprehensive investigations made by Russian geochemists, especially A. E. Fersman.

As a third, most important field of research, the geochemistry of sedimentary rocks has been studied in more detail during the last eight years. The importance of this field of geochemistry may be judged by the fact that a very great percentage of ores and other useful minerals and rocks is associated with sediments. According to available statistical data, about 85—90% of the annual yield of mineral products comes from sedimentary mineral and ore deposits, and this fact emphasises the great practical importance of the geochemistry of sediments.†

The processes of weathering, transportation, and redeposition of matter at the surface of the earth's crust involve a great number of chemical reactions concerning all chemical elements. The importance of the geochemistry of sediments has long been recognised by Russian scientists, particularly Vernadsky.

For the processes in igneous rocks and their derivatives we have learnt to consider the effects of atomic and ionic properties, *e.g.*, ionic size and charge, as most important factors in the distribution of the elements. In the processes of sediment-making also, ionic size and charge are of the utmost importance, especially in a certain mutual relation, *viz.*, the ionic potential, given by the quotient between ionic charge,  $Z$ , and ionic radius,  $r$ . The importance of this function in physical chemistry has been demonstrated by Cartledge (*J. Amer. Chem. Soc.*, 1928, **50**, 2855).

Besides the ionic potential and the deformability of ions, their polarisability is of importance as a controlling factor in certain phenomena of ionic adsorption, as demonstrated by Noll.

We give a table and a graph (Fig. 2) illustrating the ionic potential.

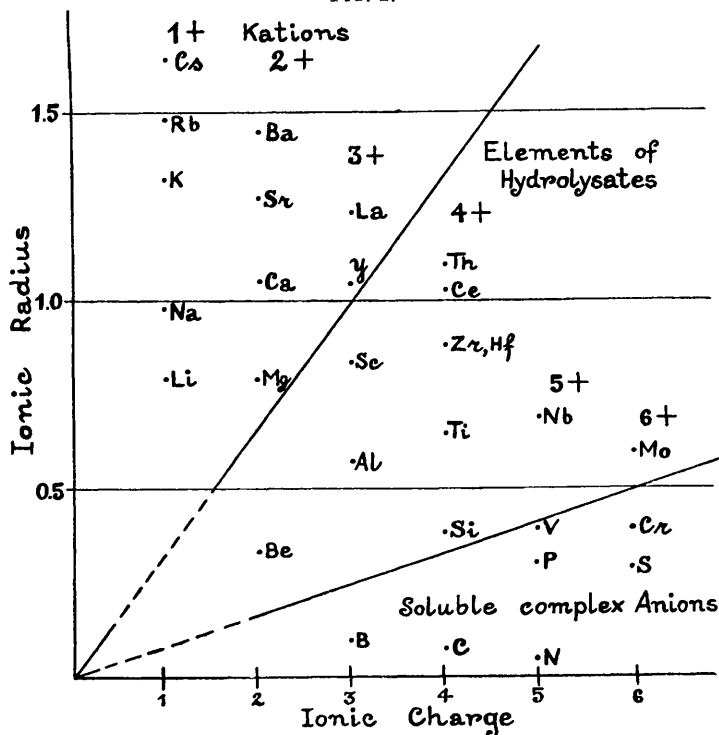
The ionic potential is important not only for the distribution of chemical elements during the formation of sedimentary rocks, but also for other mineral-forming processes,

\* Quite recently, data on the amounts of rare-earth elements in iron ores from Sweden have been published by Landergrén (*Jernk. Annaler*, 1936, 711), which afford another welcome confirmation of the "geochemical coherency" of the rare-earth elements.

† For a number of ores the importance of sedimentary deposits has recently been pointed out by Brinkmann.

Ionic potential, $Z/r$ .									
Cs <sup>1+</sup>	Rb <sup>1+</sup>	K <sup>1+</sup>	Na <sup>1+</sup>	Li <sup>1+</sup>	Ba <sup>2+</sup>	Sr <sup>2+</sup>	Ca <sup>2+</sup>	La <sup>3+</sup>	Mg <sup>2+</sup>
0.61	0.67	0.71	1.0	1.3	1.4	1.6	1.9	2.5	2.6
Sm <sup>3+</sup>	Y <sup>3+</sup>	Cp <sup>3+</sup>	Sc <sup>3+</sup>	Th <sup>4+</sup>	Ce <sup>4+</sup>	Zr <sup>4+</sup>	Al <sup>3+</sup>	Be <sup>2+</sup>	
2.7	2.8	3.0	3.6	3.7	3.9	4.6	5.3	5.9	
Ti <sup>4+</sup>	Nb <sup>5+</sup>	Mo <sup>6+</sup>	Si <sup>4+</sup>	B <sup>3+</sup>	P <sup>5+</sup>	S <sup>6+</sup>	C <sup>4+</sup>	N <sup>5+</sup>	
6.3	7.3	9.7	10	15	15	20	27	45	

FIG. 2.



especially those connected with aqueous solutions. The same principle also regulates the base exchange of zeolite minerals: natural zeolite crystals collect ions the potential of which does not exceed 2.0.

The potential is very important also for the chemical behaviour of elements: I may mention the similarity of the hydrated ions of trivalent scandium and quadrivalent thorium, of bivalent beryllium and trivalent aluminium.

Substances with low ionic potential, such as sodium, calcium, and magnesium, remain in true ionic solution in the process of weathering and transportation; those with intermediate ionic potential are precipitated by hydrolysis, their ions being associated with hydroxyl radicals from aqueous solutions; and substances with still higher ionic potential form anions containing oxygen and usually again soluble to give true ionic solution. The field of elements is therefore divided into three parts with respect to ionic potential.

We can illustrate sediment-forming processes by the following classification of their products, showing the analogy between these processes and a chemical analysis.

*Succession of sediments.*

	Examples.
1. Residua	Quartz, zircon.
2. Hydrolysates	Bauxite, clays.
3. Oxydates	Limonite, psilomelane.
4. Carbonates	Calcite, dolomite.
5. Evaporates	Chlorides, sulphates, borates.

First of all, insoluble substances remain as residua, mostly as granular material which form sands, grits, etc. Next, the fine mud of hydrolysates settles down; it contains hydroxy-silicates or hydroxides of aluminium, finely divided micas and chlorites, and finely divided silica, forming clays, bauxites, shales, etc. Another stage consists in the precipitation of hydroxides of ferric iron and of tervalent and quadrivalent manganese; such precipitation has to be preceded by a process of oxidation, mostly in shallow surface waters, whereby the ferrous and manganous ions are converted into the higher state of valency, which has a much higher ionic potential, and this in turn causes precipitation. In a great many cases, such as in ordinary mudstones, the hydrolysates and oxydates are associated in the same sediment.

Our studies in Göttingen had as one principal aim to account for a quantitative balance of substances through the process of sedimentation. Following an early attempt by Joly (*Sci. Trans. Roy. Dublin Soc.*, 1899, 7, 23), one can calculate the amount of matter in the sedimentary cycle by means of the sodium content of the ocean; calculation based upon our new material furnishes and uses the following data. For each kg. of sea water about 600 g. of primary rocks have passed through the cycle of weathering, disintegration, and sedimentation.

*Amounts (kg.) of Rocks of Sedimentary Cycle and of Surface Waters per cm.<sup>2</sup> of the Surface of the Earth.*

Shales and sandstones .....	155	Sea water .....	268.5
Limestone .....	10.2	Fresh water .....	0.1
Dolomite .....	4.4	Continental ice .....	4.5
Total .....	169.6	Water vapour .....	0.003

For a number of elements, *e.g.*, carbon and oxygen, we have attempted quantitative balances to account for the amounts involved and recovered. Here I shall only point out one single aspect of the balances, *viz.*, the amounts of several elements which have entered into and remained in solution in sea water.

*Balance of Various Univalent, Bivalent, Tervalent, and Quadrivalent Metals in Sea Water, per Kg. of Sea Water.*

	Supplied.	Present.	Percentage.		Supplied.	Present.	Percentage.
Na .....	16.8 g.	10.7 g.	66	Al .....	52.6 g.	0.6 mg.	0.0012
K .....	15.0 g.	0.37 g.	2.5	Sc .....	3 mg.	0.04 $\gamma$	0.0013
Li .....	39 mg.	0.11 mg.	0.2	Y .....	19 mg.	0.3 $\gamma$	0.0016
Rb .....	200 mg.	0.2 mg.	0.1	La .....	11 mg.	0.3 $\gamma$	0.003
Cs .....	6 mg.	0.002 mg.	0.03	Si .....	160 g.	1 mg.	0.0006
Mg .....	12.6 g.	1.3 g.	10	Ce .....	26 mg.	0.4 $\gamma$	0.002
Sr .....	250 mg.	10 mg.	4				
Ca .....	21.6 g.	0.42 g.	2				
Ba .....	23.4 mg.	0.05 mg.	0.02				

We shall first discuss elements of low ionic potential, beginning with the alkaline metals. We see that sodium alone remains to any great extent in the sea; potassium remains only in some few units %, owing to the very strong adsorption of its ions on the finely divided hydrolysate sediments. Still more effectively the *rare* alkaline ions are being eliminated from the sea water; also direct experiments have shown that rubidium and caesium are adsorbed to a higher degree than potassium.

The same sort of balance for the bivalent alkaline-earth elements demonstrates that the amounts left in sea water are conspicuously less than the relative amounts of the alkaline metals. It is interesting that strontium remains in sea water to about double the extent of calcium.

A comparison of tervalent elements\* with regard to marine concentration reveals that the rare-earth metals are somewhat favoured as compared with aluminium, probably owing to their smaller ionic potential. The presence of rare-earth metals in sea water is,

\* This is based on some still unpublished investigations from the Göttingen laboratory concerning rare-earth elements.

of course, interesting in connection with the findings of Sir William Crookes concerning the presence of minute amounts of, *e.g.*, yttrium and samarium in the lime carbonate of marine organisms. In Göttingen, we have been able to prove the presence of all rare-earth metals in, for instance, the lime carbonate of corals or very pure chalk from Southern Sweden. In this connection I may mention that the calcites of mineral veins, too, always contain determinable amounts of rare-earth metals.

A study of some quadrivalent elements in sea water similarly indicates a preference for those elements having small ionic potentials. However, the ionic potential of these elements is generally so high that it causes almost quantitative precipitation with the hydrolysate sediments. For the same reason we find a number of rare quadrivalent elements concentrated in the hydrolysate sediments. For instance, besides beryllium and gallium, which follow aluminium, the elements titanium, zirconium, tin, and quinquevalent niobium are found to be concentrated in bauxite, together with aluminium hydroxide, and the factor of concentration is about the same as for that of alumina, being as a rule about 4—5-fold as compared with their mother rock.\* In some cases vanadium also is somewhat concentrated in the bauxites. The trivalent elements with somewhat lower ionic potential, such as the lanthanides, yttrium, and even scandium, are as a rule not concentrated in typical bauxites, because their lower ionic potential permits their removal in aqueous solutions.

*Balance of Various Elements forming Anions in Sea Water, per Kg. of Sea Water.*

	Supplied.	Present.	Percentage.		Supplied.	Present.	Percentage.
B .....	2.4 mg.	6 mg.	260	I .....	0.18 mg.	0.05 mg.	28
Cl .....	0.29 g.	19.3 g.	670	F .....	150 mg.	1 mg.	0.7
S .....	0.3 g.	0.88 g.	290	P .....	470 mg.	0.06 mg.	0.013

A study of the balance of the common anions in sea water, such as chloride, iodide, sulphate, and borate, reveals the very interesting fact that certain of these elements are found in sea water in such large amounts that a derivation from the primary rocks through weathering processes seems impossible. We are led to believe that chlorine, boron, and probably sulphur have been primary constituents of oceanic waters, for the amounts derived from primary rocks are smaller than the amounts present in the sea water of to-day, and the percentages of boron and sulphur in fossil sediments are so large that the proportion of these elements in the ocean was probably still higher in earlier geological periods than now. However, we have to consider the possibility of large supplies of chlorine, sulphur, and boron from volcanic gases and volcanic springs.

*Balance of Various Heavy Metals and Metalloids in Sea Water, per Kg. of Sea Water.*

	Supplied.	Present.	Percentage.		Supplied.	Present.	Percentage.
V .....	60 mg.	0.3 $\gamma$	0.0006	Hg * .....	0.3 mg.	0.03 $\gamma$	0.01
Mn .....	0.56 g.	4 $\gamma$	0.0007	Pb .....	10 mg.	?	?
Fe .....	31 g.	60 $\gamma$	0.0002	Cu .....	60 mg.	10 $\gamma$	0.017
Ni .....	60 mg.	0.07 $\gamma$	0.0001	Se .....	0.4 mg.†	4 $\gamma$	1
Mo .....	9 mg.	0.7 $\gamma$	0.008	As .....	3 mg.	20 $\gamma$	0.7
Zn .....	24 mg.	7 $\gamma$	0.03				

\* Data by Stock and Cucuel (*Naturwiss.*, 1934, 22, 391).

† From the selenium percentages in sedimentary rocks; the values from igneous rocks might probably be somewhat lower.

Important results are being obtained concerning the percentage of certain poisonous metals and metalloids in sea water. We find that the amounts which potentially have been supplied from the primary rocks to sea water during geological times are so considerable that a serious poisoning of the ocean would have been caused if some phenomena of elimination of poisonous substances had not been in action; this applies, for instance, to copper, lead, arsenic, selenium, and mercury.

We find that a number of poisonous elements, among them selenium, arsenic, lead,

\* I may mention that the alkali aluminate solutions of the Baeyer process for making alumina are a potential source for very large quantities of gallium.

antimony, and bismuth, have been removed from aqueous solution by means of a process also known in practical medicine, that is, adsorption on freshly precipitated hydroxides of iron. We find considerable concentrations of selenium, arsenic, and lead in the sedimentary iron ores. The arsenic content of these ores in most cases is so high that it brings a very notable quantity of arsenic even into iron and steel, from which this element is difficult to eliminate by the usual technical processes of refining. Molybdenum is concentrated in oxidate sediments of manganese compounds.

One very interesting, and as yet unexplained, fact of the marine balances of minor constituents is that copper is present in sea water in relatively large amounts as compared with most other heavy metals. I do not know the cause for the exceptional concentration of copper as compared, *e.g.*, with the apparently almost complete elimination of nickel, and I think that continued investigations might be worth while.

A number of rare elements from sea water are concentrated in marine phosphate deposits. I may mention that one of our co-workers at Göttingen, Mr. Brundin from Lund, found large percentages of zinc in marine phosphates; and even cadmium, indium, and bismuth have recently been found to be concentrated in oceanic phosphate sediments.

Indium also is concentrated in sedimentary siderite rocks as well as in siderites of hydrothermal origin, probably because of the similarity of ionic radii between trivalent indium and bivalent iron. The presence of indium in siderites was noticed by Hartley and Ramage many years ago. Some data in connection with the occurrence of indium in siderite are appended:

Ionic radii, A. ....	In <sup>3+</sup> 0.92.	Fe <sup>2+</sup> 0.83.	Mn <sup>2+</sup> 0.91.
	InBO <sub>3</sub> .	FeCO <sub>3</sub> .	MnCO <sub>3</sub> .
Lattice constants $\left\{ \begin{array}{l} a, \text{ A.} \\ a \end{array} \right.$ .....	5.84	5.75	5.84
	48° 10'	47° 52'	47° 46'

We see that in the third stage also of geochemical processes, *i.e.*, the cycle of sediment formation, the distribution of the chemical elements is regulated by the properties of their atoms and ions, the ionic potential being the most important property deciding the distribution in that stage.

As a next stage of geochemical evolution we may consider the processes of concentration due to the action of living organisms. Many such processes are well known to science, and Vernadsky, in particular, has called attention to their importance.

The elimination of phosphorus or of nitrogen compounds from sea water is the object of study by oceanographers and marine biologists, as shown in the admirable work of British biochemists among whom I may mention Dr. W. R. G. Atkins; and so also is the general circulation and balance of carbonic acid in sea water, which has been studied extensively by many investigators, lately especially by Dr. Wattenberg, of the Meteor Expedition.

The iodine cycle, the concentration of iodine in organisms, has been studied by von Fellenberg in Switzerland; the iodine metabolism of the marine bios has been investigated by Dr. G. Lunde and Dr. C. Closs in Norway, demonstrating in considerable detail the faculty of certain marine organisms to concentrate iodine up to several hundred thousand fold, as compared with sea water.

Other interesting phenomena are the accumulation of copper or vanadium by marine organisms.

If we study the single crystalline minerals of sedimentary rocks, we again recognise the importance of atomic and ionic radii in the distribution of rare elements between different minerals. One interesting feature is the accumulation of cobalt in the pyrites of shales, just as in those of hydrothermal origin.

Some very remarkable concentrations of rare elements are met with in the hydrocarbons, as well as in bituminous rocks; this applies to the accumulation of vanadium, molybdenum, and nickel, which doubtless form organometallic compounds and migrate together with the hydrocarbons. In collaboration with Professor K. Krejci-Graf, I am now engaged in a study of these elements in connection with bituminous substances.

The connection between vanadium, nickel, molybdenum, and natural hydrocarbons is the more interesting, for it is just these elements which are the most effective catalysts for

the industrial synthesis of hydrocarbons, and they may have been active in Nature by facilitating reactions between hydrogen sulphide and organic substances. Without doubt in these cases special atomic properties, especially valency forces, are controlling the association between these metals and the hydrocarbons, an association which has caused the formation of the famous Minas Ragras deposit of vanadium sulphide in Peru. The correlation of vanadium and asphaltites has recently been studied in much detail by G. Fester in Argentina.

In the phenomena of concentration and selective distribution of rare elements treated above, we have in a great many cases found clear and simple connections to be operative between special atomic and ionic properties and the processes of concentration. There is, however, one field of concentration of rare elements where such a simple connection with specific atomic properties is not so obvious—that is the concentration of rare elements in the ashes of certain coal deposits. About seven years ago I found the rare element germanium to be concentrated in certain coal ashes; \* the maximum amount, more than 1%, has been found in the ash of certain British coal seams from the Hartley district. Our further study of the matter revealed that other rare elements also have been concentrated in just those types of coal which are rich in germanium. The following elements have been found to be concentrated in such coal ash: Li, Be, Sr, Ba, B, Sc, Y, La—Cp, Zr, Hf, V, Co, Ni, Mo, Rh, Pd, Pt, Cu, Zn, Ga, Ge, As, (Se?), Ag, Cd, In, Sn, Sb, I, Au, Tl, Pb, Bi.

These observations agreed with older data on the occurrence of, *e.g.*, zinc, cadmium, lead, nickel, copper, molybdenum, tin, and lead in coal ash and flue dusts, and as the investigations were continued, nearly all rare elements were found concentrated in certain coal ashes. The following table summarises some of the results.

*Rare Elements in Ashes of Coal (g. per ton).*

Element.	Maximum.	Average of "rich" ashes.	Earth's crust.	Factor of enrichment.	
				Maximum.	Average.
B .....	3,000	600	3	1000	200
Ge .....	11,000	500	7	1600	70
As .....	8,000	500	5	1600	100
Bi .....	200	20	0·2	1000	100
Be .....	1,000	300	5	180	50
Co .....	1,500	300	40	35	8
Ni .....	8,000	700	100	80	7
Zn .....	10,000	200	40	250	5
Cd .....	50	5	0·5	100	10
Pb .....	1,000	100	16	60	6
Ag .....	5—10	2	0·1	50—100	20
Au .....	0·2—0·5	—	0·005	40—100	—
Pt .....	0·7	—	0·005	120	—
Li .....	500	—	65	8	—
Sc .....	400	60	5	80	3—12
Ga .....	400	100	15	27	7
Y .....	800	100	31	26	3
Zr .....	5,000	—	190	26	—
Mo .....	500	200	15	33	15
In .....	2	—	0·1	13	—
Sn .....	500	200	40	13	5
Tl .....	5	1	0·3	17	3

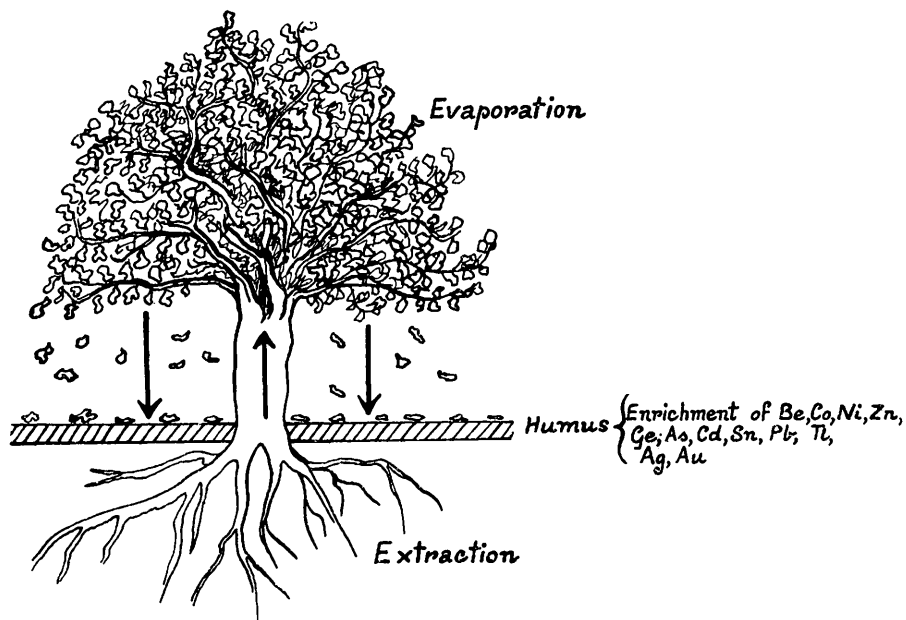
The most remarkable feature of these data seems to be that the concentration is operative on a great number of elements, belonging to the most diverse groups of the periodic system, with regard both to their chemical affinity properties and to their atomic radii and valency or ionic charge. Typical lithophile elements, such as beryllium and rare-earth

\* Our first results concerning the enrichment of germanium in coal ash date from 1930; among the first specimens studied was a very rich coal from the collections of the Mineralogical Institute at Göttingen, labelled "Coal from the Main Seam, Hartley, near Newcastle." Through the kindness of British colleagues we have been able to study also further samples from the same district. I may mention that the incineration of the coals has to be made in very thin layers, preferably after moistening with nitric acid, in order to avoid loss of volatile germanous compounds, such as germanous oxide and sulphide, from the ashes.

elements or zirconium and niobium, are being concentrated together with siderophile and chalcophile elements, such as precious metals, lead, bismuth, and arsenic. Typical cation elements such as lithium, and complex anions, such as those of boric acid, are concentrated.

Most interesting is the circumstance that the factor of enrichment is about the same in a great many cases, a coincidence which is the more remarkable in view of the extreme chemical diversity of the elements involved. One has to consider whether some simple process has been operative, a process not of a chemical but of a physical nature, which involves many elements jointly.

FIG. 3.



I think one could imagine some process which may be effective in that manner, a process connected with plant life, for instance in a forest. The soil solutions dissolve the inorganic constituents of the sub-soil according to their solubility, as we normally only have a small amount of solvent compared with the bulk of mineral matter. These solutions enter the plant organism through the roots of the plants, and at the place of strongest evaporation, especially in the leaves, the greater part of the mineral matter is deposited. The dead leaves accumulate at the surface of the ground, decaying into humic substances. The most soluble mineral constituents of the leaves and of their products of decay, such as carbonates and sulphates of lime, magnesium, sodium, and potassium, and humates of iron, are swept downwards by circulating rain water, and insoluble or sparingly soluble compounds are filtered off in the humus layer, perhaps in some cases being precipitated as organic complex compounds. By such processes many different chemical elements have been found to become concentrated in the uppermost humus layer of forest soils; we may illustrate this by data from a very old forest of beech and oak in Germany (Sababurg, north of Cassel).

*Enrichment of Elements during Decay of Oak and Beech Humus (g. per ton).*

	B <sub>2</sub> O <sub>3</sub> .	MnO.	NiO.	GeO <sub>2</sub> .	As <sub>2</sub> O <sub>5</sub> .	Ag.	Au.
Mineral soil (sand) .....	7	400	20	5	—	—	—
Ash from fresh oak leaves .....	5,000—10,000	20,000*	50	5	—	—	—
Ash from oak humus .....	200	2,400	100	70	—	1	—
Ash from beech humus .....	30	1,400	100	70	500	5	0.5

\* Ash from fresh beech leaves; in leaves from the previous year, MnO = 7700 g.

Other elements concentrated in the humus are : Be, Co, Zn, Cd, Sn, Pb, and Tl.

We find in the humus ashes enrichment of many different elements, in many respects



analogous to the concentration of rare elements in coal ash. I consider it most likely that the concentration of rare elements in coal ash could have arisen in the same manner as the concentration in ashes from humus soil. The conclusion is that such "rich" coals may have been formed wholly or partly from fossil humus soils. Of course, biological processes also may, in some cases, be involved in the acts of concentration, especially with regard to some elements placed at the beginning of our table, elements which show the greatest factor of concentration, especially boron, an element which in many cases is strongly concentrated in the ashes of living plants.

For most of the elements, however, the process seems to be essentially an inorganic physical process. The function of the plants seems mainly to be that of a filtering and evaporating apparatus, which delivers its products to the uppermost stratum of the soil, where the products of evaporation again are partly dissolved, mainly as bicarbonates, and where the most insoluble compounds are filtered off from the more soluble ones, which re-enter the circulation in soil and plants.

Here we have a process of concentration, by means of fractional extraction by a kind of countercurrent leaching, evaporating, and redissolving device, which to a considerable extent is independent of special chemical properties of the elements involved and generally tends to concentrate rare elements relatively to the common ones. The end product of the process will be a sub-soil deprived of most of the rarer constituents, and an uppermost humus layer rich in rare elements. I think the common association of coal seams together with underlying refractory sands and clays deprived of soluble components may be indicative of the existence of such processes.

It would be worth while to investigate these processes also in present forest soils of wet and hot tropical regions. Even if a typical humus layer is not present in such soils, it might be important to compare the percentages of rarer elements in the sub-soil and in the surface layer. Biological observations on the sterile mud bottoms of some tropical forests might suggest the existence of such phenomena. Also the influence of rare soil constituents, such as zinc and arsenic, on the micro-flora of humus soils might be worth an investigation.

One question, which of course must be answered in connection with these phenomena, from a geochemical point of view, is why such processes of local concentration of rare elements by leaching and redeposition are not found more generally also in vein formation. The answer might be as follows. In order to make possible a leaching of compounds of rare elements corresponding, not to their percentages, but to their solubilities, the raw material must be present, not as the usual crystalline isomorphous mixtures, in which the rare elements are shielded against leaching actions, but as a finely disintegrated, preferably amorphous, material which is easily percolated by solutions. This condition generally obtains only in the zone of mineral weathering, not in compact crystalline rocks. Therefore, we find it as a soil phenomenon, not as a common geological process of deeper strata of the earth's crust.

Perhaps some of my audience may think that the subject of the last discussion is rather far removed from chemical mineralogy and chemical geology. However, some beautiful processes of mineral formation or even ore formation are connected with the same processes. The fine crystal needles of nickel monosulphide, millerite, often found in connection with coal seams, the cobalt nickel sulpho-spinel linnaeite, found in many British coal seams, and the arsenopyrites of coal are all connected with the same process of enrichment of rare elements. Moreover, one very important ore deposit may wholly or partly owe its existence to the erosion and redeposition of old enriched humus soils: that is the bituminous copper shale of Germany and Russia, in which we find associations of rare elements which have much in common with the element assemblages of humus soils and humus coals.

Of course, it is scarcely possible, within one single hour, to give an exhaustive report of the processes of element migration and element distribution involved in geology, mineralogy and even biology. However, I have attempted to give a sketch of our growing knowledge of geochemistry, of the principles governing the distribution of the chemical elements, and the application of these principles to some important stages of evolution of terrestrial matter.

I have tried to demonstrate four principal stages of geochemical evolution of matter.

The first stage represents the partition according to affinity properties, which govern the partition between ionic, semi-metallic, and metallic phases, besides eventually a vapour phase, having come into action during the very early history of the earth. The second stage during processes of crystallisation represents the sifting and sorting of elements by crystals, according to particle size, especially ionic size, the order of introduction into fitting crystal lattices being controlled according to ionic charges. In the third stage of geochemical evolution, represented principally by the formation of sedimentary rocks, the quotient between ionic charge and ionic radius, the ionic potential, is a most important principle, governing the distribution of elements in the sediments. The fourth stage, controlled by the activities of living organisms, again furnishes remarkable concentrations and assemblages of elements, in part governed by special chemical valency properties, and in part directed by dominantly physical principles.

During the last year, new research facilities for geochemistry have been opened at the laboratories of the Geological Museum at the Royal Frederiks University at Oslo, in co-operation with the Royal Norwegian Ministry of Trade and Industry. I hope that the coming years may bring further advances in our knowledge concerning the distribution of the elements.

## APPENDIX.

*Publications on Geochemistry from the Mineralogical Institute of the University of Göttingen, 1930—1936.*

*Nachrichten von der Gesellschaft der Wissenschaften zu Göttingen, Math.-phys. Kl., Fachgruppe IV (Geologie u. Mineralogie).*

- V. M. Goldschmidt : Elemente u. Minerale pegmatitischer Gesteine, 1930, 370.  
 V. M. Goldschmidt : Ueber das Vorkommen des Germaniums in Steinkohlen und Steinkohlen-Produkten, 1930, 398.  
 V. M. Goldschmidt : Zur Kristallchemie des Germaniums, 1931, 184.  
 V. M. Goldschmidt and Cl. Peters : Zur Geochemie des Galliums, 1931, 165.  
 V. M. Goldschmidt and Cl. Peters : Zur Geochemie des Scandiums, 1931, 257.  
 V. M. Goldschmidt and Cl. Peters : Zur Geochemie des Berylliums, 1932, 360.  
 V. M. Goldschmidt and Cl. Peters : Zur Geochemie der Edelmetalle, 1932, 377.  
 V. M. Goldschmidt and Cl. Peters : Zur Geochemie des Bors, I und II, 1932, 402 and 528.  
 V. M. Goldschmidt and Cl. Peters : Zur Geochemie des Germaniums, 1933, 141.  
 V. M. Goldschmidt and Cl. Peters : Zur Kenntnis der Troilitknollen der Meteoriten, 1933, 278.  
 V. M. Goldschmidt and Cl. Peters : Ueber die Anreicherung seltener Elemente in Steinkohlen, 1933, 371.  
 V. M. Goldschmidt and Cl. Peters : Zur Geochemie des Arsens, 1934, 11.  
 V. M. Goldschmidt, Cl. Peters, H. Berman, and H. Hauptmann : Zur Geochemie der Alkalimetalle, 1933, 235.  
 V. M. Goldschmidt and H. Hauptmann : Isomorphie von Boraten u. Karbonaten, 1932, 53.  
 V. M. Goldschmidt and O. Hefter : Zur Geochemie des Selens, 1933, 245.  
 V. M. Goldschmidt and L. W. Strock : Zur Geochemie des Selens, II, 1935, 123.  
 V. M. Goldschmidt, H. Bauer, and H. Witte : Zur Geochemie der Alkalimetalle, II, 1934, 39.  
 E. Minami : Selen-Gehalte von europäischen und japanischen Tonschiefern, 1935, 143.  
 E. Minami : Gehalte an seltenen Erden in europäischen und japanischen Tonschiefern, 1935, 155.  
 L. W. Strock : Zur Geochemie des Lithiums, 1936, 171.  
 Th. Ernst and H. Hörmann : Bestimmung von Vanadium, Nickel und Molybdän im Meerwasser, 1936, 205.

*Zeitschrift für anorganische und allgemeine Chemie.*

- E. Thilo : Ueber die Resultate der Analysen zweier Kohlenaschen, 1934, 218, 201.  
 H. Bauer : Quantitative Analyse schwer verdampfbarer Stoffe im Lichtbogen, untersucht am Lanthanoxyd, 1934, 221, 209.

*Industrial and Engineering Chemistry.*

- V. M. Goldschmidt : Rare Elements in Coal Ashes, 1935, 27, 1100.

*Chemie der Erde.*

- W. Noll : Geochemie des Strontiums, 1934, 8, 507.  
 W. v. Engelhardt : Geochemie des Bariums, 1936, 10, 187.

*Fortschritte der Mineralogie.*

- V. M. Goldschmidt : Grundlagen der quantitativen Geochemie, 1933, **17**, 112.  
V. M. Goldschmidt : Grundlagen der quantitativen Geochemie, II, 1935, **19**, 183.

*Geologiska Föreningens i Stockholm Förhandlingar.*

- V. M. Goldschmidt : Drei Vorträge über Geochemie, 1934, **56**, 385.

*Teknisk Ukeblad, Oslo.*

- V. M. Goldschmidt : Geokjemiske Forskningsarbeider i Göttingen, 1936, **83**, No. 11.

*Die Naturwissenschaften.*

- V. M. Goldschmidt : Geochemische Verteilungsgesetze und kosmische Häufigkeit der Elemente, 1930, **18**, 999.  
V. M. Goldschmidt : Geochemische Leit-Elemente, 1932, **20**, 947.  
V. M. Goldschmidt, H. Hauptmann, and Cl. Peters : Ueber die Berücksichtigung seltener Elemente bei Gesteins-Analysen, 1933, **21**, 363.

*Zeitschrift für physikalische Chemie.*

- V. M. Goldschmidt : Ueber das Vorkommen des Germaniums im Meteoriten von Cranbourne, 1930, *A*, **146**, 404.

*Handwörterbuch der Naturwissenschaften, 2nd ed., Jena.*

- V. M. Goldschmidt : "Geochemie," 1933.

For a table of ionic radii, see V. M. Goldschmidt : "Kristallchemie," 1934.

Concerning the methods of quantitative spectrum analysis by means of the carbon arc, reference is given to articles by R. Mannkopff, Cl. Peters, H. Witte, H. Hörmann in *Zeitschrift für Physik* and to a summary by L. W. Strock, published by Adam Hilger, Ltd., 1936.

Numerous data from investigations made together with Dr. Bauer, Dr. Hörmann, and Dr. Witte on the geochemistry of various elements will be published in the near future, as well as the investigations jointly with Prof. K. Krejci-Graf on rare metals in bituminous substances.

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