THE TERRESTRIAL DISTRIBUTION OF THE ELEMENTS

By David T. Gibson, D.Sc.

(Senior Lecturer in Chemistry, Glasgow University)

Geochemistry may be described as the Natural History of the chemical elements. The crystal form of naturally occurring compounds has long served to direct attention to minerals of economic value. Only since the detailed structure of such crystals has become known, has it been possible to elicit the laws which govern the formation and disintegration of minerals. Consequently, although many relevant data had been accumulated, no comprehensive account of the principles, on which the segregation and aggregation of terrestrial elements take place, could be made until someone equally experienced in mineralogy, petrology, and X-ray crystallography could turn his attention to the problem. The scientific antecedents, which enabled Victor Moritz Goldschmidt to make this study and thereby establish the science which will always be associated with his name, will be found in the Memorial Lecture delivered by J. D. Bernal.[1]

It is all the more regrettable that Goldschmidt did not live to produce a comprehensive account of his work, since so much of it was published in comparatively inaccessible journals. Important references to the work of other investigators will be found in the Faraday Society discussion on igneous rocks,[2] Berg's " Vorkommen der mineralischen Rohstoffe," [3] Vernadsky's " Geochemie ",[4] Holmes's " Age of the Earth ",[5] and in the discussion on the minor elements in *Soil Science*.[6] E. S. Larsen [7] gives a historical sketch covering the last 50 years and G. W. Tyrrell [8] summarises a number of recent papers.

The Three Major Partings of the Elements

Originally a uniform gas mixture, the constituents of the Earth, in cooling, pass through the phases :

$$\text{Gas} \xrightarrow{\text{I}} \text{Liquid} \xrightarrow{\text{II}} \text{Solid} \xrightarrow{\text{III}} \text{Solution}$$

Each change of phase is governed by a characteristic property of the atom, and represents a major parting of the elements, some undergoing the change before others.

I. *The First Parting.*—This was originally pictured by V. M. Goldschmidt [6, 9] as resulting in the condensation of the gaseous substance of the Earth into an iron core, an intermediate sulphide–oxide zone, a siliceous envelope, and an atmosphere. He showed that similar artificial melts

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[1] *J.*, 1949, 2108. See also C. E. Tilley, *Obituary Notices of Fellows of the Royal Society* 1948, **6,** 51.

[2] *Trans. Faraday Soc.*, 1925, **20,** 413.

[3] G. Berg, " Vorkommen der mineralischen Rohstoffe ", Leipzig, 1929.

[4] W. J. Vernadsky, " Geochemie ", Akad. Verlag, Leipzig, 1930.

[5] A. Holmes, " Age of the Earth ", Nelson, 1937.

[6] V. M. Goldschmidt *et al.*, *Soil Sci.*, 1945, **60,** 1.

[7] *Amer. Geol. Soc., Ann. vol.*, 1941, 391.

[8] *Sci. Progress*, 1948, **36,** 506.

[9] V. M. Goldschmidt, *Z. Electrochem.*, 1922, **28,** 411.

separated during cooling into three phases, and that individual elements were concentrated preferentially in one or two of these phases. He classified the elements as siderophil (core), chalcophil * (intermediate zone), lithophil (crust), and atmophil. As may be seen from the accompanying Periodic Table (Table I), these designations correspond to typical electronic configurations :

TABLE I

H																	He
Li	Be	B											C	N	O	F	Ne
Na	Mg	Al											Si	P	S	Cl	A
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo		Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	Rare earths	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
lithophil						siderophil					chalcophil or thiophil					lithophil atmophil	

These allocations are, of course, not rigid. As a result of variability of valency, mutual solubility of layers, and change of partition coefficients with temperature, many elements enter more than one phase. The classification of elements as " lithophil " etc. is not in any way invalidated by recent Swiss work discussed below.

II. *The Second Parting.—Formation of igneous rocks.* The solidification of the crust is really fractional crystallisation on a cosmic scale over a considerable time, and is governed by ionic size. Cations which may be compactly incorporated in a silicate lattice are accepted early in the crystallisation, those less suitable are accepted later or rejected completely. " Stable " and " unstable " are terms related to environment. Rocks formed at high temperature (500—1200°) and pressure fall ready victims to the effect of ice, air, and carbon dioxide.

III. *The Third Parting.—Weathering. Formation of sedimentary rocks.* Igneous rocks are now subject to selective dissolution leaving silica and alumina as residue. From this solution the other constituents are severally removed by hydrolysis, adsorption, biological action, or even by crystallisation. These accumulated residues and precipitates form sedimentary rocks, and the residual solution is sea water. The third parting is governed by the intensity of ionic charge. For comparative purposes this may be expressed as charge/radius of the ion.

The connexion between weathering and biological activity has been extensively investigated in Russia by Vernadsky,[4] A. P. Vinogradov,[11] and A. E. Fersman.[12] Much interesting information has also been accumulated by O. Baudisch,[13] E. J. Conway,[14] and M. D. Kamen,[15] but, as yet, no

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[10] S. J. Shand, " Eruptive Rocks ", Murby, London, 1947.

[11] *Nature,* 1943, **151,** 659.

[12] See S. Tomkeieff, *ibid.*, 1944, **154,** 814.

[13] *Soil Sci.*, 1945, **60,** 173.

[14] *Quart. Rev. Biol.*, 1943, **18,** 337.

[15] *Bull. Amer. Museum Nat. Hist.*, 1946, **87,** 109.

* Shand's term " thiophil " is much better.[10]

answer can be given to the question : What specific character of the atom makes it suitable for participation in biological reactions ?

IV. *Metamorphic Rocks.*—As is well known, the compacted products of physical and chemical weathering, when subjected to heat and pressure, are recrystallised. This transformation is not merely physical, involving the loss, at most, of simple volatile materials like carbon dioxide and water, but has been shown by D. L. Reynolds [16] to involve the replacement of certain ions by others. Metamorphic rocks are, of course, similarly formed (and to a very much greater extent) by the same forces acting directly on igneous rocks. In fact, a number of geologists (see A. Holmes [17]) envisage granitisation as a basic " front " invading pre-existing rock. Ahead of the front will be found mobile ions expelled by the process, followed by the less mobile which have taken their place. There will be a " chromatographic " effect in which sorting in terms of ionic mobility [18] will have taken place. A fuller understanding of the process will reveal novel segregations, but work on these lines is only just beginning [21] and will not be considered further in this review. The process is evidently one of solid diffusion. In this connexion the behaviour of silver iodide, quoted by Wells,[19] is probably relevant. At the transition point (146°) the iodine ions suddenly re-arrange to form a new stable lattice, but the lattice of the silver ions breaks down. From 146° to the melting point (555°) the silver is in a fluid form in the solid iodine lattice.

The First Parting

Goldschmidt's conception of the segregation of the constituents of the Earth into three concentric zones has formed the basis of geochemical work for the last 25 years. It was well-known to metallurgists that a melt consisting of iron sulphide, soda, sand, and (insufficient) coke would form, on cooling, three layers, slag, ore, and metal. G. Tammann [20] and V. M. Goldschmidt [6] further showed that those elements which react with oxygen more exothermally than iron will tend to accumulate in the slag. Those which react less exothermally than iron will concentrate in the metallic phase. V. M. Goldschmidt [21] was able to determine the zonal affinity of many elements by adding them to such artificial melts and then finding the distribution between the zones by actual analysis. He found that meteoric iron and the native iron of Disco (Greenland) are much richer than ordinary pig iron in the precious metals, because they have concentrated the precious-metal content of a large body of surrounding rock during formation. The enrichment factor

$$\% \text{ M in meteoric iron}/\% \text{ M in ordinary iron}$$

is large (Pt 4000, Ir 5000, Pd 1000, Au 1000, Ag 50).

The most important consequence of this conception is that lithophilic

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[16] *Proc. Royal Irish Acad.*, 1943, *B*, **48,** 231.

[17] *Nature*, 1943, **155,** 412.

[18] P. Lapadu-Hargues, quoted by D. L. Reynolds, *Sci. Progress*, 1947, **35,** 212 ; cf. also D. L. Reynolds, *Geol. Mag.*, 1946, **102,** 389.

[19] A. F. Wells, " Structural Inorganic Chemistry ", Oxford, 1945, p. 165.

[20] *Z. anorg. Chem.*, 1924, **134,** 276.

[21] *J.*, 1937, 655.

elements enjoy a seeming abundance simply because their locus is ours also. Conversely, those which are not lithophilic seem to us rarer than they actually are, because their main depot is inaccessible, but no element is completely excluded from the lithosphere because, at the temperature of segregation, silicate, sulphide, and metal phases have an appreciable mutual solubility.

In this connexion the " Abundance of the Elements in the Earth's Crust ", originally determined by F. W. Clarke and H. S. Washington,[22] is of very great interest. Their figures formed the basis of Goldschmidt's work, and, in turn, were greatly amplified by him. A recent study from the Geophysical Laboratory in Washington [23] concludes that " whilst it is quite possible that these figures will have to be changed when more accurate data are obtained, it is doubtful if this change will significantly alter the orders of magnitude ". This conclusion is confirmed by the more restricted, but very thorough, work of S. R. Nockolds and R. L. Mitchell ; [24] however, in the case of two very important elements, fluorine and potassium, the accepted values have already been called in question.[25, 26] The following Table of abundance of elements in the Earth's crust is adapted from data published by Berg.[3]

Relative abundance of the elements in the Earth's crust

Oxygen	50%	Potassium	2·4%
Silicon	26	Magnesium	1·9
Aluminium	7·5	Hydrogen	0·9
Iron	4·7	Titanium	0·6
Calcium	3·4	Chlorine	0·2
Sodium	2·6	Phosphorus	0·1
	Total	99·5%	

The abundance of the remaining elements is more conveniently expressed in g./ton of the crustal rock :

less than 1 kg./ton (1 kg./ton = 0·1%) ; Mn, C, S, Ba, Cr, N, F, Zr, Zn, Ni, Sr, V (total 0·45%)
less than 100 g./ton ; Cu, Y, W, Li, Rb, Hf, Ce, Pb, Th, Nd, Co, B (total 0·04%)
less than 10 g./ton ; Mo, Br, Sn, Sc, Be, La, . . . As, A, Ge (total 0·01%)
less than 1 g./ton ; Se, . . . Nb, Sb, U, Ta, Ga, In, Tl, Cd
mg./ton ; I, Pt metals, Ag, Bi, Hg, Te, Au, rare gases
mg./1000 tons ; Ra, Ac, Po.

A number of interesting points is revealed by these data.

(*a*) Many of the " common " metals, *e.g.*, Cu, Hg, Sn, and As, are really very scarce. Their familiarity is due to their ores being conspicuous, concentrated in a few favoured localities, and readily reduced. (*b*) On the other hand, many elements not naturally concentrated, are regarded as scarce even though they are abundant in the aggregate. (*c*) Some of the lighter elements are surprisingly scarce. This may be due to the sensitivity of their atoms to disruption, the consumption of their atoms in the synthesis of more complicated atoms, or, more prosaically, to their inclusion in the

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[22] *U.S. Geol. Svy.*, 1924, Professional paper 127.
[23] E. G. Zies, *Amer. J. Sci.*, 1938, **35,** 385.
[24] *Trans. Roy. Soc. Edin.*, 1948, **61,** 533.
[25] E. S. Shepherd, *Amer. J. Sci.*, 1940, **38,** 117.
[26] J. H. J. Poole, *Nature*, 1948, **162,** 775.

analyses of more abundant elements, *e.g.*, beryllium included with aluminium or strontium with calcium. (*d*) There is a marked falling off in abundance of all elements having an atomic number greater than nickel. (*e*) Elements of even are more abundant than those of odd atomic number. This is not because the even-numbered elements are more accessible. The question may most suitably be examined using the lanthanons. In them we have a chemically coherent group of elements in which no geochemical process operates to effect selective enrichment. There are minerals in which the abundance rises (or falls) with rising atomic number, but, in all of these, the elements show an alternating abundance.

It may also be mentioned that the abundance of a rarer element is estimated, not by summing the contents of those few favoured localities where mineralogical treasures containing a high proportion of the rare element exist, but by determining into which common minerals the rare element preferentially enters, and in what proportion it exists there.

W. Kuhn and A. Rittmann's Views.—In view of the wide acceptance of Goldschmidt's three-zone theory of the Earth, it is surprising that quite recently two Swiss workers have put forward what seems, at first sight, to be a completely different hypothesis. Kuhn and Rittmann [27] point out that, as there is general agreement that the Earth is derived from the Sun, the initial material of the new planet must have been very rich in hydrogen. Under its relatively tiny gravitational force, the early history of the planet must have been dominated by the loss of hydrogen and resultant superficial cooling. The mechanism of this escape had been discussed by Niggli [28] who indicated that a selective transport of less volatile materials to the surface would be effected thereby.

The result would be the formation of a composite crust the outer part rich in the more volatile, silicon and aluminium compounds, the inner in the less volatile compounds, those of iron and magnesium. Thus far the new view is in agreement with the older ideas. The essential novelty is the insistence that with the high temperature and viscosity obtaining, and the decreasing efficacy of gravity as the centre of the Earth is approached, there will be *no force adequate* to bring about the separation into definite zones of the whole material of the Earth. In particular, the idea of an *iron core* must be abandoned. Just inside the crust, Kuhn and Rittmann suppose that a silicate–metal zone exists as an undifferentiated emulsion. The depth of this transition zone is small, and within a distance from the centre corresponding to half the Earth's radius there is only undifferentiated solar material.

They regard the loss of hydrogen and resultant cooling as an entirely superficial phenomenon. The contrast between the old and the new conceptions will be seen in Fig. 1. The first parting, as regards the segregation of the elements of the Earth as a whole, is therefore :

$$\text{gas} \longrightarrow \text{siliceous segregate} + \text{undifferentiated material}$$

and not :

$$\text{gas} \longrightarrow \text{three concentric phases}$$

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[27] *Geol. Rundschau*, 1941, **32**, 215 ; W. Kuhn, *Experientia*, 1946, **2**, 10.

[28] P. Niggli, *Z. anorg. Chem.*, 1912, **75**, 162.

Kuhn and Rittmann are careful to point out that this drastic reconsideration of Goldschmidt's original ideas does not, in any way, invalidate them, so far as preferential concentration or elimination of elements in the *lithosphere* is concerned; nor does it affect any surface phenomena which bring molten sulphide, silicate, and metallic phases into contact. The most important *geochemical* consequence of the Swiss view is that it points to a completely different set of values for the abundance of elements in the Earth *as a whole.* Several workers, notably F. W. Clarke,[29] H. S. Washington,[30] and H. N. Russell [31] have attempted to arrive at such values. They all agree in allotting a very subordinate position to hydrogen. It is the essence of the new view that a large core of completely undifferentiated solar material, containing approximately 30% of hydrogen exists in the Earth. Not only in this, but also in their deductions from the weighed average composition of meteorites, Kuhn and Rittmann differ from previous workers. The relative abundance and the composition of iron meteorites have frequently been used as an index of the size and actual composition of the Earth's core. Kuhn and Rittmann point out, however, that the iron meteorites, being far more conspicuous and durable than the stony meteorites, have exerted a correspondingly exaggerated influence on the estimates of the internal composition of the planetary bodies, and hence

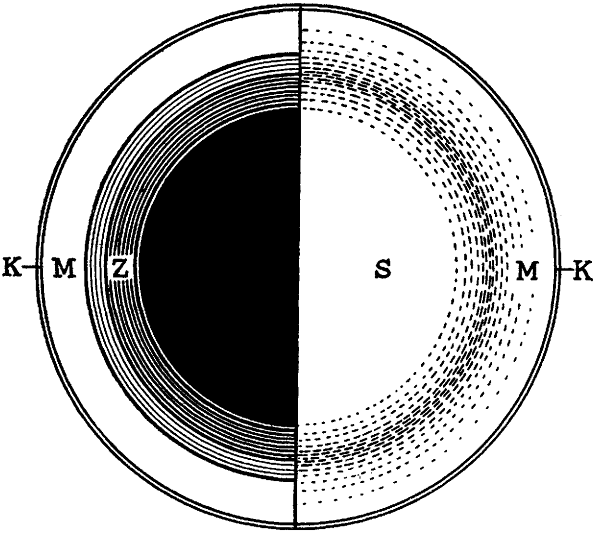

FIG. 1

Old and new conception of the interior of the Earth. Old (left): solid crust K; silicate shell M; intermediate zone Z; iron core. New (right): solid crust K; magma zone M, composed of molten silicates with increasing Fe–Mg–H *content downwards; practically unaltered solar material S.*

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[29] *U.S. Geol. Svy.*, 1924, **132,** *D,* 76.

[30] *Amer. J. Sci.*, 1925, **9,** 351.

[31] *Science*, 1941, **94,** 375.

of the Earth. We are not here concerned with their extremely interesting *geophysical* conclusions. The cosmic implications of the Swiss view have since been briefly considered by R. Wildt.[32]

The Second Parting

This parting may be further subdivided into three stages :

(*a*) The first crystallisation, (*b*) the main crystallisation, and (*c*) the final crystallisation and the residual liquors.

To understand the second parting, igneous-rock formation (cf. P. Niggli,[33] Shand [10]) must be considered. Although very many silicates and aluminosilicates are known, igneous rocks are composed of a very small number of mineral species of which pyroxenes, amphiboles, micas, felspars, and quartz are by far the most important. These represent, however, only a part, albeit a very large part, of the original magma. Volatile constituents, which may represent only 1% of the whole, exercise a quite disproportionate effect on the behaviour of the mass, in lowering viscosity and the temperature range of crystallisation. Their fate will be considered later.

The crystallisation of silicates results, as W. L. Bragg [34] has shown, in the formation of one-, two-, or three-dimensional giant anions in which the Si–O ratio may be 1/4, 1/3, 2/5, 4/11, etc. The negative charges on the lattice are balanced by cations of size suitable to the interstices in the Si–O pattern. The fundamental distinction between the chemist's and the geologist's viewpoint is that the former regards such crystals as pure only if the cationic points are occupied by two or three cations at most, in *molecular proportions.* To the geologist it is the Si–O pattern which is critical. The negative charges on the lattice will be balanced by cations A, B, C . . ., but they may be present in any proportions say 1A, mB, nC . . . so long as the total charge is neutralised. The over-riding consideration is the economical use of space. Goldschmidt [21] has provided detailed evidence of the operation of this principle.

The Conditions of the Second Parting.—The progress of crystallisation is conveniently divided into three stages corresponding to three substantially distinct physical environments in which it takes place.

The First Crystallisation.—In the first crystallisation the parent magma —homogeneous at greater depths—wells up to fill subsidiary reservoirs at perhaps 2—3 miles depth. In these, differentiation must be effected by crystallisation of the higher-melting constituents from the excess of molten silica. These crystals sink and, if they melt again at lower levels, they do not mingle again perfectly with the melt from which they separated. Thus is explained the composite character of the crust : a comparatively infusible " sial " outer layer in which *si*lica and *al*umina are predominant, and an inner crustal " fema " layer made up of *fe*rro*ma*gnesian minerals. These two layers are separated by a comparatively more fusible " sima " layer. Further differentiation may be produced by subterranean movement of the

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[32] *Month. Not. Roy. Astr. Soc.*, 1947, **107**, 97.

[33] " Ore Deposits of Magmatic Origin ", Murby, London, 1929.

[34] *Nature*, 1927, **120**, 410.

partly crystallised magma resulting in a filterpress action, the molten material being strained off from the crystalline, resulting in the formation of an acid magma (the melt) and a basic one (the crystals). The immediate cause of igneous action is relief of pressure rather than supply of heat; [35] the ultimate cause is the potential energy of the hydrogen of the Earth's core.[27]

The natural silicates are, generally, completely miscible not only when molten, but also in the solid state. As G. W. Tyrrell [36] has pointed out, it is unusual for their cooling curves to show an eutectic minimum. Such curves have been extensively investigated by N. L. Bowen [37] whose well-known "reaction principle" indicates that if a mixture of silicates cools sufficiently slowly to establish true equilibrium, the solid will be homogeneous and of the same composition as the melt. However, since movement is so often associated with cooling, it is evident that equilibrium will often not be established. It is therefore important to know in what sequence and in what combinations the major components of the magma will separate when conditions are favourable for differentiation. Further, it is of interest to know how the minor constituents will be distributed throughout the mass.

The Main Crystallisation.—This takes place when the magma is either (*a*) injected into fissures comparatively near the surface, forming intrusive rocks, *e.g.*, granite or (*b*) ejected at the surface forming extrusive rocks, *e.g.*, basalt. The essential difference is that the intrusive rocks cool slowly under pressure retaining their volatile constituents, and consequently forming large crystals. Extrusive rocks cool rapidly and volatile constituents are lost. The consequent fine-grained character of the product is much less efficient in parting the elements. The first and the main crystallisations may be summarised in the following scheme.

BASIC	INTERMEDIATE		ACID ROCKS
Refractory oxides, Olivines	Amphiboles, Pyroxenes	Micas, Felspars	→
	← — — QUARTZ — — — — — — — — — →		
	corresponding to the chemical types:		
R_2SiO_4	R_2SiO_3	$R_2O, Al_2O_3, 6SiO_2$	
	in which the predominant cations R are:		
Fe Mg	Fe Mg Ca	Ca Na K	

Harker [35] and Niggli [38] give a series of graphs detailing the variation in percentage of all these cations with increasing "acidity" of various types of rock. From these graphs it is evident that the formation of the different silicates during the crystallisation overlaps extensively.

[35] A. Harker, "Natural History of Igneous Rocks", Methuen, 1909.

[36] *Trans. Faraday Soc.*, 1925, **20,** 418.

[37] "The Evolution of Igneous Rocks", Princeton, 1928.

[38] P. Niggli, ref. 33, p. 15.

In the first and the main crystallisations, the solvent is molten silica, whilst the solutes are iron oxide, magnesia, lime, alumina, soda, potash, and a small admixture of supercritical gases, CO_2, SO_2, HF, B_2O_3, H_2S, H_2O, etc. Niggli [33] has emphasised that in the cooling of an intrusive magma containing such volatile materials "the process of consolidation cannot terminate with the formation of ordinary igneous rocks. The residual solutions continuously change in composition, and the melt gradually assumes the character of a pegmatitic, pneumatolytic,* and finally hydrothermal solution, while progressively decreasing in quantity." So much silica and basic oxides have separated that water, previously a minor solute, has accumulated in the residues to such an extent as to become the effective solvent. In supercritical water silica is not only soluble, but actually volatile.[39] Thanks to this dissolved silica, the vapour pressure of the system, in spite of the temperature (500°), remains comparatively low. Below this, the solubility of silica falls off so rapidly that the vapour pressure of the system rises with falling temperature. Such a state of affairs has been called by Niggli [40] "retrograde boiling". It has the very important consequence that the residual liquors of crystallisation of the magma are forced into every cranny which cooling is producing in the surrounding rocks. The minerals which then separate are a minute fraction of the original intrusion, but by reason of accessibility, characteristic appearance, and efficient differentiation, they are of the utmost economic

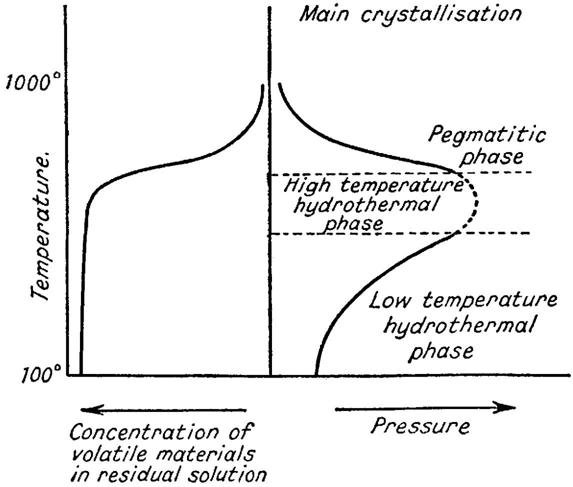

Fig. 2

[*After Niggli.*]

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[39] C. J. van Nieuwenburg and P. M. van Zon, *Rec. Trav. chim.*, 1935, **54,** 129.

[40] P. Niggli, "Die leichtfluchtige Bestandteile im Magma", Teubner, Leipzig, 1920.

* Shand [10] suggests that this term should now be discarded, having been used in different senses by Bunsen, Brogger, and Niggli. He prefers "high and low temperature hydrothermal".

and scientific importance. The geologist is primarily concerned with the products of the first and main crystallisations, the mineralogist and chemist with the final one; the geochemist finds them all significant.

The Products of the Second Parting.—The three environments, in which solidification takes place, give rise to distinct types of mineral:

Above 1200°	—first crystallisation—	refractory oxides and pyrites.
1200—500°	main ,,	ortho-, meta-, and alumino-silicates; predominant cations: Fe, Mg, Ca, Na, K.
Below 500°	final ,,	cations too large or too small to be accepted earlier, and anions similarly rejected.

Shand distinguishes between the formation of sulphide and oxide ores. He considers that, while there is ample evidence for the claim that the ores of such outsize cations as tin, tantalum, tungsten, and beryllium are deposited in the final crystallisation, the very low solubility of the sulphides in silicate melts shows that they must be eliminated as a liquid phase during the first crystallisation. On the other hand their solubility is not *nil*. There must be some remaining in solution to give rise to a second crop of sulphide ores at the very end of the final crystallisation. The amount then deposited will make up in accessibility what it lacks in quantity.

The First Crystallisation.—This, accordingly, affords two distinct types:

(*a*) Refractory oxides—magnetite, chromite, ilmenite, spinel, apatite, and to a certain extent, olivine [$(FeMg)SiO_4$]. Owing to their density, these sink and become accessible only in special circumstances. Ferruginous sands of this origin give such viscous slags that, as yet, they defy economic exploitation; but, for this very reason, chromite finds its major use as a material for furnace linings.

(*b*) The pyrites of the first crystallisation probably separates as a liquid phase and becomes trapped in the mass of more refractory crystals. The importance of this phase depends on the impurities which it carries, particularly copper and nickel. It is interesting that, whilst gold occurs in pyrites from both the first and the final crystallisations, platinum occurs in the former only.

The Main Crystallisation.—The subsequent process of crystallisation may be described as consisting essentially of the adjustment of the composition of the magma to that required for the separation of the felspars. Accordingly, in the main crystallisation the first minerals to separate are pyroxenes [$(Mg,Ca)SiO_3$], followed by lime, soda and potash felspars. Whilst these, together with quartz, make up approximately four-fifths of the Earth's crust, other minerals are important and widespread:

(*a*) Those which arise when the parent magma is poor or rich in the ions which make up pyroxenes and felspars. Thus an excess of aluminium results in its being accepted into the metasilicate crystals with the formation of augite (Al_2 for MgSi). An even greater excess of aluminium may result in its separation in the first crystallisation as spinel. A deficit of aluminium is correspondingly compensated by the formation of alkali-augite. These are in a sense compensatory minerals.

(*b*) Those which have remained in suspension until the residual melt has a composition substantially different from that in which they were produced. Thus olivines may, at a lower temperature, react further with silica. At the other end of the main crystallisation, by the separation of the principal silicates, the volatile constituents become more significant components of the magma, and accordingly silicates with hydroxyl and fluoride groups are produced, *e.g.*, mica and tourmaline. The conditions for such components have been extensively studied by Bowen.[37]

Such variants differ substantially from the minerals from which they are theoretically derived. They involve much more drastic modifications of the lattice than the quantitatively less extensive replacements of common ions by rarer ions which occur at the same time. These formed the theme of Goldschmidt's [21] Lecture to the Chemical Society in 1937, and are described shortly below.

TABLE II

Average percentage composition of rocks compared with the economic requirement of profitable minerals

	SiO_2.	Al_2O_3.	Fe_2O_3.	CaO.	NaCl.
Average	50—80	15—20	7	5	5
Economic	98—99	40—60	50	50—55	90—95

It is evident from Table II that only in rare cases are common elements concentrated by igneous action to an extent sufficient to form economic sources of supply. Nevertheless, the partial concentrations which do take place at this stage exercise a profound influence on the course of weathering. As will be seen later, the products of weathering provide the main sources of our economic minerals. Quite apart from the direct utilisation of the products of igneous action, an understanding of the principles by which the common elements are accumulated provides an insight into the fate of those elements which are present in amounts too small to yield characteristic minerals. It also enables a distinction to be made between those which are hard to procure, because they are nowhere concentrated, and those which are intrinsically in short supply at the Earth's surface. The distribution of those minor constituents is no longer the academic question it might seem, for they are the source of the trace elements indispensable to fertile soils.

The Fate of the Rare Elements in the Second Parting.[24, 21] *The Crystal Sieve.*—Table III [21] gives a list of the ions of the elements arranged according to their radii.

The rarer elements fall into two categories. (*a*) Those whose ionic radius is very much greater or much less than that of Mg, Fe, Ca, Al, Na, or K. Such elements cannot be accommodated in any of the main lattices and they accumulate in the final liquors, often forming typical compounds with rarer anions which have been rejected for similar reasons. (*b*) Those whose ionic radius is approximately equal to that of one or other of the major

TABLE III

Radius, A.	Ions.								
0·1—0·3 . . .	B^{3+}	C^{4+}	N^{5+}	S^{6+}					
0·3—0·5 . . .	Be	Si^{4+}	Ge	P^{5+}	Mo^{6+}	V^{5+}	W^{6+}		
0·5—0·7 . . .	Al	Ga	Fe^{3+}	Cr^{3+}	V^{3+}	Ti^{4+}	Nb^{5+}	Ta^{5+}	
0·7—0·9 . . .	Li	Mg	Ni	Co	Fe^{2+}	Zn	Sc	In	
	Zr	Hf	Sn	Mn					
0·9—1·1 . . .	Na	Ca	Cd	Y	Gd—Lu		Ce	Th	U
1·1—1·4 . . .	K	Sr	La	Eu					
1·4—1·7 . . .	Rb	Tl	Cs	Ba	Ra				

constituents. Such rarer ions crystallise in the appropriate fraction of the common minerals as will now be described.

" The formation of crystalline minerals involves the building up of space lattices of ions . . . depending on the size of the individual ions. Into such a lattice only particles which are of a size appropriate to the lattice spacings can enter. Therefore the crystals act as a kind of sieving mechanism allowing certain particles to enter, excluding others of unsuitable size." Goldschmidt [21] terms this " the crystal sieve ".

Consequently, minor constituents tend to enter the lattice most suited to their size and valency, and to act as deputies for the major constituent as far as the amount available will allow.

Thus, in the crystallisation of the felspars, cations are incorporated in order of increasing size : Ca, Na, K. It is observed that barium is to be found mainly in the potash felspars, and this is entirely in keeping with the relative ionic radii of the four elements :

$$\mathrm{Na/Ca} = 0{\cdot}98/1{\cdot}06 = 0{\cdot}925, \quad \mathrm{K/Ba} = 1{\cdot}33/1{\cdot}43 = 0{\cdot}93$$

The deputy is, however, seldom both the right size and of the right valency, and Goldschmidt considers three possibilities :

(1) The deputy has the right valency but is slightly too large, and will therefore enter the later-forming fractions of a mineral. It may even be found in the *outer* layers of large crystals. Thus rubidium will be found preferentially in the latest crystals of a potash felspar.

(2) The deputy is the right size but has a higher valency. Such a deputy, *e.g.*, Sc$^{\cdot\cdot\cdot}$ for Mg$^{\cdot\cdot}$, will be held more firmly in the lattice and will accordingly be accepted preferentially to the major constituent. In fact, magnesium ortho- and meta-silicate minerals are richer than lime felspars in scandium. Deputies of the right size, but of a lower valency will obviously be accommodated in the later fractions of a mineral.

(3) The deputy has the right valency and the right size. Here two subsidiary possibilities exist. (*a*) The major constituent or the deputy has a slight tendency to exhibit a higher or lower valency than normal. (*b*) The valency of both elements is constant. In the latter case we have the very interesting situation of an element present to the extent of say 0·01—0·001% in igneous rocks, ubiquitous in distribution, not by any means negligible in aggregate amount, but everywhere swamped (and camouflaged) by the major partner from which no natural process of crystallisation, solution,

or precipitation can separate it. Thus is explained the amazing fact that an element as abundant as hafnium remained unsuspected till 1923 in zirconium minerals.

The swamping of gallium by aluminium is not quite so perfect. It exemplifies the possibility (*a*). The deputy has a slight tendency to exhibit a lower valency. Accordingly, whilst the main bulk of gallium is swamped by aluminium in felspars and their products of weathering, a very minor amount not so incorporated manifests the latent thiophilic character of gallium by entering into certain zinc ores. As is well known, it was in such form that the element was first discovered. Even more interesting is the biological concentration referred to later. Similar considerations account for the occasional juxtaposition of such unexpected pairs as lead and strontium (cf. Goldschmidt [6]). Moreover, it often happens that a rock contains two sets of crystals of the same mineral, some large, even several centimetres long, others barely visible. Evidently the magma had cooled slowly forming the large crystals and then, before the crystallisation was complete, the rate of cooling had greatly increased, perhaps by the eruption of the magma. Two things are certain: the large crystals must have been formed earlier than the small, and the outside layers of the large crystals must be later than the inside layers. Consequently we expect enrichment of preferred deputies in the inside of the large crystals and enrichment of deferred deputies in the mass of small crystals. The very interesting work of C. W. Bunn [41] on two-dimensional isomorphism suggests still another possibility for which as yet no mineralogical data are available.

If an element $E^{\cdot\cdot\cdot}$ or $E^{\cdot}$ deputises for the normal lattice tenant $E^{\cdot\cdot}$, some adjustment of the anionic charges is demanded. If deputising is only to the extent of say 5% there may actually be vacant cationic positions, *e.g.*, $Y^{\cdot\cdot\cdot}$ replacing $Ca^{\cdot\cdot}$ in CaF_2, or vacant anionic positions, *e.g.*, $K^{\cdot}$ replacing $Mg^{\cdot\cdot}$ in $MgCl_2$. If, however, the increment in cationic charge is balanced by a corresponding increment in anionic charge there need be no limit to the extent of the replacement, *e.g.*, ferrous tungstate for scandium niobate.

It must be emphasised that, although such enrichments are often of the order of a hundred- to a thousand-fold over the *average* concentration of the element in the lithosphere, they are nevertheless of no immediate importance. Their true significance is appreciated when the parent rock is weathered. Then these minimal concentrations supply the trace elements indispensable to agriculture. Moreover, E. B. Sandell and S. S. Goldich,[42] who have, by an independent method, confirmed many of Goldschmidt's data and conclusions, point out that a deputy accepted in a lattice may, at a later stage in the crystallisation, be re-absorbed into the liquid phase.

The Final Crystallisation.—The products of the final crystallisation are called pegmatites. In the aggregate they amount to only a minute fraction of the total magma, but they have a much greater economic and scientific value because they are more accessible and more differentiated than the products of the first and the main crystallisations. The reason for the greater differentiation of minerals in pegmatites is that the viscosity of the

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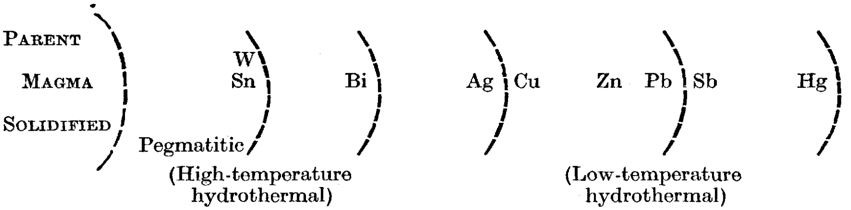
[41] *Proc. Roy. Soc.*, 1933, *A*, **141**, 567.

[42] *J. Geol.*, 1943, **51**, 115, 167.

solution has decreased so much. Not only has water assumed the role of solvent, but thiophilic elements which were too large or too small to be accommodated in any of the main lattices, have now (by disappearance of the major constituents) become sufficiently abundant to form lattices suited to their own dimensions, in combination with anions which were likewise rejected by the silicate lattice, *e.g.*, borate, phosphate, sulphide, niobate, and molybdate. The solution is moving and cooling so that the temperature proper to the crystallisation of each metal corresponds to a spatial separation. In the ideal case there is a zonal distribution of minerals about the igneous rock.



In the high-temperature hydrothermal zones the temperature is still high enough for the solvent to react with the rock walls through which it is passing; in the low-temperature hydrothermal zone the country rock is merely an inert container of the solution.

The high-temperature phase, though it deposits directly less than 1% of the material of the original intrusion, exerts a quite disproportionate effect on the country rock. In earlier stages of the intrusion the conductivity of the rock is too poor, and the viscosity of the magma is too great, for the effect to be widespread, and in the very last stage the solutions are too cool to effect drastic change; but in the high-temperature phase, corresponding to the pressure maximum, deposition of minerals is accompanied and even facilitated by the absorption of acid from the supercritical solution. In this way tin and tungsten are deposited as oxides:

$$SnF_4 + 2H_2O \rightleftharpoons SnO_2 + 4HF$$

$$4HF + 2CaCO_3 \longrightarrow 2CaF_2 + 2H_2O + 2CO_2$$

The oxides of these metals are frequently accompanied by such accessory minerals as fluorite, fluorapatite and tourmaline. At the very end of the crystallisation the deposition of mercury may, in favourable cases, be actually observed.[43] It is present in solution as a complex sulphide, influenced by the equilibrium:

$$Na_2S + H_2O + CO_2 \rightleftharpoons Na_2CO_3 + H_2S$$

Mercuric sulphide is not soluble unless sodium sulphide is present; hence, since $([Na_2S][CO_2])/([Na_2CO_3][H_2S])$ is a constant the higher the concentration of carbon dioxide the lower is that of sodium sulphide. Mercuric sulphide therefore tends to be deposited under impermeable shelves of rock where carbon dioxide accumulates. Just because it is a peripheral deposit, it is the first to be lost on subsequent erosion.

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[43] G. Berg, ref. 3, p. 266.

In addition to the thiophilic elements, which are thus often far more accessible than their overall abundance in the lithosphere would suggest, many very small or very large lithophilic cations are not deposited until the final crystallisation. They are often found combined in phosphates, borates, titanates, and tantalates—acidic oxides likewise unacceptable in the silicate lattices. One of the most interesting of the rejected cations is uranium. The geochemistry of this element has recently been described by S. Tomkeieff,[44] who showed that it is deposited entirely during the final crystallisation. In the earlier phase it separates before tin as a dioxide along with ceria and thoria, all of which form similar lattices of the fluorite type. Again, at the end of the hydrothermal phase it appears as trioxide in complicated carbonaceous minerals.

In addition to metallic minerals, pegmatites contain quartz, fluorspar, and barytes. Barytes results from interaction between the ascending sulphide solutions and descending aerated rain-water. The sulphuric acid formed is immobilised by the small amount of barium in the ascending solution. Consequently a vein will carry quartz all the time, fluorspar at deeper levels, and barytes towards the surface.

It now remains to consider the results of weathering on the igneous rock. This is particularly important, for, whereas 95% of the Earth's crust consists of igneous rock, 90% of our mineral resources are derived from the remaining 5% which has undergone weathering.

The Atmosphere and the Ocean

The disintegration of igneous rocks is intimately bound up with the atmosphere which " weathers " them, and with the ocean which ultimately receives all the soluble constituents and much of the sediments. The origin of these masses of gas and water is therefore of great interest to the geochemist and also to the biologist, for the development of air and sea is a clue to the origin of life itself.[45, 46]

Two fundamentally distinct views would account for the atmosphere. The simpler supposed that all the oxygen of our planet would be locked up in combination with reactive metals. The fact that iron was known to exist uncombined, although in the siderosphere, indicated that there was insufficient oxygen. The original atmosphere would consist of the less reactive gases, including nitrogen, water, and carbon dioxide. According to this view, photosynthesis has ever since been progressively replacing the carbon dioxide by an equal volume of oxygen :

$$CO_2 + H_2O \rightarrow (CH_2O) + O_2$$

Consequently, allowing for the carbonate locked up in limestones and the oxygen withdrawn from the atmosphere to convert igneous ferrous into sedimentary ferric iron, there should be one gram-molecule of oxygen in the atmosphere for every 12 grams of sedimentary organic carbon—coal, oil, shale, living matter. It has, however, been objected that to suppose

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[44] *Sci. Progress*, 1946, **34**, 696.

[45] R. Wildt, *Rev. Mod. Physics*, 1942, **14**, 151.

[46] G. A. Riley, *Amer. Scientist*, 1944, **32**, 132.

all the present organic carbon once formed the primæval atmosphere would be to postulate an atmosphere so rich in carbon dioxide that no known form of life present or extinct could have existed in it. J. H. J. Poole [47] goes further and suggests that the great "excess of fossil carbon over atmospheric oxygen" indicates that the original oxygen must have been consumed by some such reaction as:

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$$

A different origin for atmospheric oxygen was suggested by G. Tammann [49] who pointed out that at the temperature of molten magma all terrestrial water would be vaporised and slightly dissociated:

$$2H_2O \rightleftharpoons 2H_2 + O_2$$

In the Earth's gravitational field hydrogen is not stable, and consequently the equilibrium will be displaced more and more to the right by the escape of hydrogen. In fact there would be a race between total disappearance of all water and the retention of hydrogen as water, resulting from the falling temperature—the dissociation of water below 2000° being negligible.

Any theory of the atmosphere should be able to indicate how the three planets, Venus, Earth, and Mars, which obviously had a similar origin, and are of approximately equal size, nevertheless have respectively, a dense carbon dioxide atmosphere, a cloudy aqueous atmosphere, and scarcely any atmosphere at all.[32]

Confining our attention to the Earth, it is obvious that the two extreme views sketched above are not mutually exclusive, for, whilst much of our oxygen may have been derived from dissociated water, much may have come photosynthetically, not from a huge original carbon dioxide atmosphere but from carbon dioxide continually fed into the atmosphere by volcanic discharge. Incidentally, Tammann's view does not account for the very great rarity of neon if it did not escape from the Earth's gravitational field. If it did escape, why should water, a molecule slightly lighter than neon, not likewise have escaped even without dissociation?

In one of the early calculations of the Age of the Earth J. Joly [50] assumed the original Ocean to have been fresh water, and estimated the annual contribution of salt by the rivers of the world. His value was widely accepted at the time but many factors are now recognised as complicating the original simple concept. E. J. Conway,[51] in a careful analysis of the problem, shows that not only has the rate of supply of sulphate and chloride to the sea not been constant, but that these two anions and possibly others participate in cyclic processes, going down to the sea, returning to the atmosphere, and participating once more in the attack on igneous rock. Obviously, if the chloride anion takes part in cyclic processes, some process must withdraw its cation. This, Conway considers, is effected by the formation of glauconite, potassium being withdrawn from solution and forming an insoluble potash iron silicate on the ocean floor. Conway con-

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[47] *Proc. Roy. Dublin Soc.*, 1941, **222,** 345.

[48] V. M. Goldschmidt, *Geologiska Feren. Stockholm,* 1934, 409.

[49] *Z. physikal. Chem.*, 1924, **110,** 17.

[50] *Phil. Mag.*, 1911, **22,** 357.

[51] *Proc. Roy. Irish Acad.*, 1942–43, *B*, **48,** 119, 161.

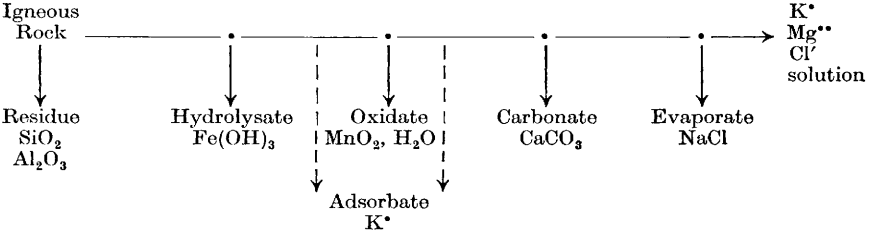
siders that the Ocean is being continually replenished with both chloride and water by volcanic action. The primæval ocean was not substantially less saline than it is to-day ; a conception which casts doubt on the frequently suggested idea that the salinity of body fluids corresponds to that of the Ocean at the period when life began on the planet.

The Third Major Parting of the Elements. Weathering

Weathering is a physical and mechanical process as well as a chemical one ; the former predominantly in a dry climate, the latter in a moist climate, but seldom exclusively either. In general terms weathering, in so far as it is chemical, effects a selective extraction of the constituents of igneous rock, leaving some as residue (TiO_2, Fe_2O_3, SiO_2, clay) and transporting others away in solution ($Na^{\cdot}$, $Ca^{\cdot\cdot}$, $Fe^{\cdot\cdot}$, $Mg^{\cdot\cdot}$ ions). These elements which have passed into solution are then selectively removed by adsorption (*e.g.*, K), or hydrolysis (*e.g.*, Fe), or interaction with anions yielding insoluble precipitates (*e.g.*, Ca), or by biological intervention (*e.g.*, Ca) until only sodium, magnesium, chloride, and sulphate and mere traces of other ions remain.[52] These constitute sea water. Further, under favourably arid conditions, a fractional crystallisation may result in separate beds of common salt and of magnesium and occasionally even of potassium salts being formed. A convenient summary of Van't Hoff's classical work on the formation of the Stassfurt salt deposits has been given by A. W. Stewart.[53]

Since these various methods of abstracting ions from solution are not simultaneous, and since the solution is moving (seawards), the various ions may be deposited in different localities constituting important commercial deposits. The aqueous medium being far more mobile than magma, weathering is often a very efficient type of economic segregation. Such, in general terms, is the fate of all igneous rock. Its stability is relative to its environment, and so with change of temperature, pH, and oxygen availability quite different types of molecule are favoured. This is not to say that it matters little what type of rock is undergoing weathering. The ultimate fate will be the same, but the rate of disintegration and the relative importance of the physical and the chemical types of weathering will be very different.

Therefore the effect of weathering on the silicate containing the oxides which are common to all but the most extreme types of rock, may be summarised :



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[52] H. Wattenberg, *Z. anorg. Chem.*, 1938, **236,** 339.

[53] " Some Physico-Chemical Themes ", Longmans, London, 1922.

Before discussing the mechanism of weathering in detail, two cognate problems must be considered:

(i) the atomic characteristic which controls these separations, and (ii) the fate of minor constituents of the rock.

It was shown that in the first parting the type of bond which the element formed determined its siderophilic, thiophilic, or lithophilic character. In the second parting, the formation of igneous rocks, the governing factor is *ionic radius*. In weathering both valency and size are significant.[48] Ionic potential, expressed by the quotient, ionic charge/ionic radius, is a measure of the density of the charge at the surface of an ion. If this is low, (< 4) electrons are easily lost, and the ion goes readily into solution and remains in solution. If the ionic potential is high (> 12), electrons are more readily shared. The element accordingly appears as an oxygenated anion, *e.g.*, SO_4'', PO_4'''. Elements with intermediate ionic-potential values go into solution in reducing media and suffer reprecipitation in oxidising media. The conversion of an ion into one of higher valency results in an increase in the ionic potential, because the numerator (valency) increases while the denominator (radius) decreases since the ion has fewer electrons. The fate of the minor constituents is controlled by these considerations also; but, since we have to do with a quotient, in sedimentary deposits elements may be associated which have neither the same valency nor ionic size, but for which the quotient is similar, *e.g.*, scandium and thorium. It will be realised that in the crystallising magma such elements will show little tendency to foregather, for at that stage similarity in radius is required to bring about juxtaposition. When, however, similar valency and similar ionic radius combine to give similar ionic potential, the elements concerned are separated neither in the second nor in the third parting as, *e.g.*, Al/Ga or Zr/Hf which are mentioned above. The latter case is interesting, for it was only the clamant demand of an important theoretical inquiry which led to the detection of hafnium; and it was only by a physical separation of similar *covalent* derivatives that a complete purification was effected. It has been suggested that, given suitable commercial or scientific stimulus, a modification of the purification of bauxite would make available considerable quantities of gallium.

The process of chemical weathering may be divided into three sections.

(*a*) Weathering of the main igneous rock in so far as it concerns oxides of major importance: silica and alumina; iron and manganese oxides; lime and magnesia; soda and potash.

(*b*) Weathering as it affects the anions; the nitrogen, carbon, iodine, etc., cycles in Nature.

(*c*) Weathering of the constituents of pegmatites. This is of the greatest mineralogical interest and economic importance, but, in view of the preponderance of highly insoluble derivatives formed by heavy metals, it is much more restricted in scope and might even be regarded as a kind of outdoor analytical chemistry. The study of the resulting secondary-ore deposits finds a key in the electrochemical series, for many of the reactions involve alternate oxidation and reduction. It will suffice to consider the mechanism of the formation of " zones of secondary enrichment ".

The Main Oxides.—*Aluminium and Silicon Oxides.*—As mentioned above, the various silicates formed at high temperatures in the absence of oxygen fall ready victims to cold oxygenated water containing carbon dioxide. Dissolution of the rock proceeds even more rapidly if the rain has percolated through peat and become charged with humic acids or attacked pyrites and carried away dilute sulphuric acid. Moreover, it has long been recognised that volcanic hydrogen chloride and sulphur dioxide would locally and spasmodically supplement the action of these weaker acids. It is now evident from Conway's calculations that a far more substantial supply of these ions participates in a natural cycle, being returned by the sea to the atmosphere and so, in rain, attacking a fresh quota of rock and assisting its transport seawards.

The geochemistry of the most abundant metal of the lithosphere has been exhaustively treated by G. E. Hutchinson.[54] Vernadsky [4] states that " alumino-silicates form the skeleton of the biosphere ", natural zeolites providing a " *bureau de change* " where biologically active fluids can collect cations most suited to their natural reactions. This is not to say that aluminium compounds never participate *per se* in organic development, the well-known mordanting action of lichens being due to the alumina they contain, whilst in certain soils pink hydrangeas are turned blue. Nevertheless, compared with iron, magnesium, potassium, and calcium, aluminium plays, we believe, a quite insignificant rôle. There is, however, one very interesting possibility suggested by Hutchinson, *i.e.*, that aluminium may be an important factor in minimising silicosis, for in mines and quarries where it is a severe hazard, intentional admixture of aluminiferous dust has been found to reduce the incidence of this disease. The weathering of micas and felspars is in effect an exhaustive extraction in which all the soluble constituents are elutriated leaving a residue of alumina and silica (clay) with variable, lesser amounts of iron oxide. It is, however, not merely a matter of removing the soluble from the insoluble. Interesting and important as are the reactions of the ions which go into solution, the nature of the clay which results depends naturally on the severity of the conditions under which it has been formed, and the nature of the clay is of paramount importance to the fertility of the soil. In temperate climates weathering takes place with rain-water containing sulphate and chloride ions, carbon dioxide, and humic acids, the colloidal products of plant decay. It is believed that *initially* both silica and alumina go into solution. Subsequently the former develops into a negative, the latter into a positive colloid. In this form a certain amount of migration is possible especially if the alumina is protected by humic acid. So long as either oxide is in great excess, no precipitation occurs, but eventually a gel forms by mutual precipitation and this gel contains varying amounts of iron. Such a gel has the very important property of adsorbing cations from solutions percolating the soil whilst allowing anions to pass on. The essential condition

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[54] *Quart. Rev. Biol.*, 1943, **18** *passim.*

is that the soil should possess a fine granular structure so that it may have the maximum porosity. If it should be drenched with water it becomes peptised and finally non-porous.[3]

The main direct source of carbon dioxide for weathering is decaying humus which plays the triple rôle of supplying carbon dioxide, being a protective colloid, and acting as a reducing agent whereby much iron is removed. If there should be a deficit of electrolyte to precipitate the humus sol, the whole products of weathering may escape downwards to the water table where an overpowering concentration of electrolyte will bring about immediate precipitation as a thin, hard, impervious layer bonding all the rubble that happens to be at that level, a disastrous situation agriculturally. The significance of normal temperate weathering is that it does *not* separate silica from alumina, but recombines them into a porous framework wherein a variety of cations, the essential nutrients of plant life, are held in a form available for use. Under tropical conditions the two oxides are extensively separated. It has been suggested that this is owing to the absence of humus and/or the presence of nitric acid (tropical thunder-storms), but neither of these would indicate why *silica* should be removed. It would seem more probable that under arid conditions, the alkali leached from the rock would remain nearby in undiluted solution and so would remove the more acidic oxide, *i.e.*, silica, leaving laterite. This mixture of alumina, ferric oxide, and titania has no base-exchange properties, but provides the raw material for the manufacture of aluminium.

The importance of trace elements in fertile soils is now well known.[6] These trace elements are ultimately derived from the igneous rocks from which, by weathering, the soils were produced. An early example was provided by the prevention of grass sickness in New Zealand by dressing the pasture with " iron ore ". Only when the local supply was exhausted and a neighbouring supply proved ineffective was the real prevention traced to cobalt. Again it is well known that V, Ni, Co, Mo, Ge, Ga, and As are concentrated in certain coals. This may well be the reason why some coals are superior for hydrogenation ; but it is certainly a serious factor in atmospheric pollution and is one cause of the difficulty in obtaining carbon pure for spectroscopy.[55] The non-metals also are essential in minimal amounts in fertile soils. The indispensability of boron has been well publicised, whilst on the other hand vast areas occur where selenium in the soil makes agriculture impossible.[56]

Iron and Manganese Oxides.—Owing to its abundance in the lithosphere and to its ready change of valency, iron plays a very important part in weathering. Iron occurs in two main forms :

(*a*) In the first crystallisation with Ti, Ni, Cr, and S. These are heavy refractory minerals which sink to the bottom of the magma reservoir and are there shielded from weathering till very extensive erosion has occurred. From the resistant residue of such rocks titaniferous sands and chromite form the main sources of these two metals. The iron–nickel is of a different

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[55] V. M. Goldschmidt, *Ind. Eng. Chem.*, 1935, **37**, 1100.

[56] W. V. Searight *et al.*, *Soil Sci.*, 1946, **61**, 455.

character, for it is produced by the segregation of that part of the sulphide zone (chalcosphere) which is soluble at high temperature in the lithosphere. This iron-nickel sulphide separates in the first crystallisation, and contains too much sulphur to be a desirable ore of iron, but frequently contains important concentrations of thiophilic and even siderophilic elements, *e.g.*, Sudbury platinum.

(*b*) In the main crystallisation along with Mg, Ca, Mn, and Al. Here ferrous iron is associated with magnesium, calcium, and manganese, ferric iron with aluminium. The first effect of weathering is to remove lime and magnesia as hydrogen carbonates and to immobilise iron and manganese by oxidation. Subsequent action by reducing media, *e.g.*, peaty water, results in reduction of the last two elements to the bivalent state again, and their removal in solution as hydrogen carbonates or as organic complexes.

In the absence of decaying organic matter, iron and manganese do not long remain in solution, for the predominant surface environment is an oxidising one. Of the two, iron is the more readily oxidised. Ferric hydroxide is a positive colloid and therefore tends to adsorb anions, in particular phosphate, *e.g.*, Lorraine ores, whereas manganese hydroxide (a negative colloid) tends to adsorb cations, *e.g.*, Cu and Ba, providing a valuable natural mechanism for removing poisonous heavy metals from sea water. The precipitation of iron is not always a purely inorganic process, but one in which bacteria may play a part, feeding on the humic acid which has brought about the solution of the iron. Vernadsky [4] has paid special attention to the rôle of manganese in the biosphere, where it resembles iron in being a transporter of oxygen, particularly in making it available at depth in the Ocean. In igneous rock manganese is always bivalent, and, as such, it goes into solution. When the pH of the solution rises, manganese is more readily oxidised. As the colloidal hydrated dioxide carries a charge opposite to that of hydrated ferric oxide, the two oxides mutually precipitate and, as " wad ", are accumulating in enormous quantities on the Ocean floor. There it serves to oxidise decaying organic sediments. It is thus itself reduced and so the cycle begins once more.

Lime and Magnesia.—Although approximately equally abundant in the lithosphere, lime is much more familiar and available than magnesia. At least three factors are responsible. First, although they are indeed approximately equally abundant in the layer of the earth's crust for which analyses are available, nevertheless, since magnesium minerals separate early in the main crystallisation along with iron, they sink. Consequently they are less exposed to weathering than the felspars which contain most of the calcium. Further, both enter into biological processes, calcium to form bone and shell, magnesium to form chlorophyll. Both elements are thus in steady circulation and demand in the biosphere, but whereas magnesium is widely used in low concentration and in ephemeral form, calciferous " disjecta membra ", having in life served to sustain and protect the organism, are themselves durable after its death and accumulate as bone beds and coral islands. Ultimately so far from being dissipated by geological action, they are consolidated, forming limestones and even, under pressure, marble.

Another reason for the apparent scarcity of magnesium is that much that is commonly called limestone and regarded as $CaCO_3$ contains appreciable amounts of $MgCO_3$ without actually reaching equimolarity as in dolomite. This does not mean that magnesium carbonate has partly gone to the make-up of the shell, for the organism uses aragonite, the form of calcium carbonate with which magnesium carbonate is *not* isomorphous. The replacement has taken place at a later stage. Consolidation of coral to limestone results in the change, aragonite to calcite. Thereafter, if the limestone is percolated by solutions containing magnesium, partial or even complete replacement will occur with the formation of dolomite or (more rarely) magnesite. Strontium carbonate is, however, capable of entering into the composition of shells. Its solubility product is greater than either of the others, consequently magnesian limestone will probably be poor in strontium, as it will be the first to be replaced.

The solutions containing lime and magnesia as hydrogen carbonates produced in weathering are deprived of these elements by adsorption on clay. Thence *via* plants they pass into animals. Another less important mechanism sometimes removes calcium hydrogen carbonate from solution. It has been known for many years that aquatic plants flourish on dissolved carbon dioxide. In so doing they disturb the equilibrium which maintains calcium in solution :

$$Ca(HCO_3)_2 \underset{\text{excess of } CO_2}{\overset{\text{removal of } CO_2 \text{ by plants}}{\rightleftharpoons}} CaCO_3 \downarrow + H_2O + CO_2$$

A particularly interesting example of this is described by F. Darling [57] as causing seasonal turbidity in a lochan on Lismore island.

The most drastic separation of calcium from magnesium is purely physical in operation. Joseph Black, who first clearly discriminated between these two elements, emphasised the difference in solubility of the sulphates. An important consequence of this difference is that when land-locked seas are subjected to severe evaporation, the first salt to separate is calcium sulphate. On the other hand, magnesium salts are intensely soluble and therefore accumulate as an invisible asset in the Ocean—one of the few major raw materials which are in no danger of being cornered.

Nickel, which has an ionic radius nearly equal to that of magnesium,[6] accompanies it in igneous rocks. Being a much weaker base it is separated on weathering, magnesium passing into solution leaving, in favourable cases, nickel silicate as a residual concentrate, as in the well-known ores of New Caledonia.

Soda and Potash.—These resemble the previous pair in being approximately equally abundant, but most unequally available. The sodium ion being the smaller, is, according to Fajans's rule, the more heavily hydrated, in fact the effective radius of a hydrated sodium ion is greater than that

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[57] " A Naturalist in the Highlands ", Nelson, London, 1948.

of the non-hydrated potassium ion, as may be seen from the respective ionic mobilities. Goldschmidt calculates that the radius of K^+ is approximately equal to that of $[OH_3]^+$. An important consequence of this is that clays are flocculated by K^+ rather than by hydrated Na^+ ion, because the water envelope round the sodium ions would tend to prevent the clay micelles from coalescing. Hence potassium ions are preferentially adsorbed on clays, as was shown in Way's classical experiments.

Further, D'Arcy Thompson [57a] mentions that, in a growing cell, cations are attracted to the site of growth. Potassium is therefore at a double advantage over sodium, being more abundant in the clay and therefore in the sap and being more mobile in the solution. E. J. Conway [58] has, moreover, illustrated the significance of ionic size in fermentation ; a yeast cell will develop if given glucose and potassium phosphate ; glucose combined with phosphate and potassium can penetrate the cell. Fermentation breaks down the glucose releasing phosphate, which leaves the cell to combine with more glucose and so on. If sodium phosphate is used, the hydrated sodium ion is too large to enter the cell. Therefore the phosphate ion, to preserve electrical neutrality, must also stay out and fermentation cannot proceed.

A consequence of these and other biological processes is that whereas the sodium : potassium ratio in igneous rocks is approximately 1 : 1, the solution which reaches the sea contains about thirty times as much sodium as potassium.

Although potassium salts are in general the more soluble, it is actually they which are being steadily removed from the sea, as mentioned above, to form glauconite, permitting the release of a corresponding amount of chloride to the weathering cycle.

Only under exceptionally long continued arid conditions, *e.g.*, the Dead Sea, can evaporation bring about the separation of solid sodium chloride. This has often happened in the past, but only with advanced concentration can potassium and magnesium salts crystallise out. Even if they do, they will form the uppermost layer of the deposit. If the arid conditions continue, it will be potassium salts which will be blown away. If rainy conditions ensue, they will be washed away.

Weathering of Non-metals.—Whilst all the major constituents of igneous rocks, with the possible exception of aluminium, play an essential part in the economy of living organisms, it is really only of calcium that it may be said that biological concentration is characteristic and extensive, indeed nearly exclusive. The situation with the important non-metals other than silicon is quite opposite. They are not lithophilic and, since they have high ionic potentials, they appear as acidic radicals in pegmatites, or, as vapours, escape into the atmosphere from centres of igneous activity. Initially the acids to which they give rise supplement the action of carbon dioxide in the weathering of the lithosphere. Thus some anions, *e.g.*, chlorine, find a life partner with which to accumulate in the Ocean. As

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[57a] " On Growth and Form ", Cambridge, 1942, p. 459.

[58] *Nature*, 1942, **150**, 461.

such, sodium chloride plays an extremely important rôle in biology, lowering the freezing point of plant fluids, providing a source of strong acid in the digestive tract, and regulating the osmotic pressure in other media. Nevertheless in its many forms of usefulness it may be regarded as a passive electrolyte returning to its dead level concentration of a 3% solution. No biological process concentrates any appreciable amount of chloride, or concentrates it permanently. The purely physical process of evaporation to dryness, as in the Dead Sea area, is the only form of concentration. Nothing emphasises so forcibly the difference between our small-scale rapid laboratory technique and the slow cosmic processes than the differing geochemical behaviour of elements which we are used to regard as closely allied. The differing rôles of sodium and potassium have already been discussed. No less significant are the fate of fluorine, chlorine, and iodine.

Thanks to the extreme insolubility of calcium fluoride and to its stability over a wide range of temperature, fluoride escaping from magmatic solution is rapidly and permanently immobilised by reaction with limestone. For this reason fluorine is not, in the true etymological sense, a halide, for none can exist as an ion in sea water.

The position with iodine is the opposite. Here is the classical case of biological concentration, but of the mechanism whereby the thyroid gland and certain seaweeds preferentially extract iodine from solutions containing less than $10^{-x}\%$, very little is known. The remaining halogen, bromine, is also susceptible to biological concentration as in the mollusc from which Tyrian purple was obtained. Nowadays it is being extracted much more prosaically from sea water by careful pH and redox control for industrial purposes.[59]

Another acid which supplements carbon dioxide in weathering processes is sulphuric acid, locally produced by the weathering of pyrites and the hydrolysis of the resulting ferric sulphate, or, more generally and in widespread effect, by the dissolution of volcanic sulphur dioxide in rain. Such sulphate in arid regions may (rarely) produce deposits of natural Glauber's salt, or more commonly react with clay to produce alum shale, or simply contribute to the sulphate content of the Ocean. In one important respect SO_4'' differs from SiO_4'''': it is susceptible to biological reduction. It is not too much to say that whereas the geologist looks on life as a process of reduction, the biologist knows that all life involves oxidation. Thus, in putrefaction, sulphate supplies the bacteria with oxygen, being itself reduced to sulphide. E. J. Conway[60] has recently shown that it thus returns to the atmosphere, where it is again oxidised, and attacks the rocks *de novo*.

The contrast between metal and non-metal stands out most markedly in consideration of the carbon cycle. It was mentioned earlier that there is reason to believe that in earlier stages of this planet's history, the atmosphere contained more carbon dioxide than now. There is, in fact, a progressive replacement of silica in the lithosphere by carbon dioxide. This

[59] L. C. Stewart, *Ann. Repts. Smithsonian Inst.*, 1934, 153.

[60] *Quart. Rev. Biol.*, 1943, **18**, 337.

is, however, not the only process whereby carbon dioxide is abstracted from the atmosphere. Of far more immediate importance to us is the photosynthetic reduction of carbon dioxide resulting in the production of carbohydrates :

$$n\mathrm{CO_2} + n\mathrm{H_2O} \longrightarrow (\mathrm{CH_2O})_n + n\mathrm{O_2}$$

Such carbohydrate then has two routes to comparative permanence. More familiarly, *via* peat, brown coal, and coal, it may, under certain conditions, form anthracite. Less familiarly, carbon may be locked up in oil derived from the decomposition of fish protein. This may have a bearing on the frequent association of brine with oil-fields.

These two mechanisms for abstracting carbon dioxide from the atmosphere are most effectively controlled by the hydrogen carbonate content of the Ocean :

$$\mathrm{Ca(HCO_3)_2} \rightleftharpoons \updownarrow \mathrm{CaCO_3} + \mathrm{H_2O} + \mathrm{CO_2}$$

The amount of calcium hydrogen carbonate held in solution is regulated by the partial pressure of carbon dioxide in the atmosphere. Should this decrease, dissolved carbon dioxide will escape to replenish the atmospheric store and the equilibrium will move to the right. The resulting precipitation is effected, not in the ordinary sense of a chemical precipitation, but as increased biological activity, the enhanced growth of coral-building organisms, or, to a lesser extent, by aquatic plants as mentioned above. On the other hand, the increased pressure of atmospheric carbon dioxide will be relieved by increased dissolution of the gas in the Ocean. Equilibrium will move to the left, and an equivalent amount of coral will pass into solution.

These and other well-known aspects of the carbon cycle in Nature are summarised in Table IV.[61] Whilst the numerical data are admittedly tentative, they illustrate the sort of balance sheet which will one day be available for all the elements.

The chloride cycle has already been considered in connexion with the origin of the Ocean, and the nitrogen cycle is too well-known to require recapitulation, but the phosphorus cycle is worth discussion. It was considered from the geological point of view by J. W. Gregory.[62]

The ultimate source of all our phosphate is the apatite of igneous rock. This mineral has been synthesised in the laboratory by the action of phosphorus chloride vapour on red-hot lime. There seems little doubt that the natural mineral is similarly produced from phosphorus trichloride or trifluoride vapour and lime-silicates. It is thus widespread in occurrence, but as the average phosphorus pentoxide content of rocks is only 0·25%, and as the mineral is very resistant to weathering, we can only admire the excellence of the natural device for ensuring a constant supply of an indispensable element, however prodigal any generation might incline to be.

The geochemistry of phosphorus is the story of its concentration from this wide diffusion into rich beds and veins. Appropriate to an element

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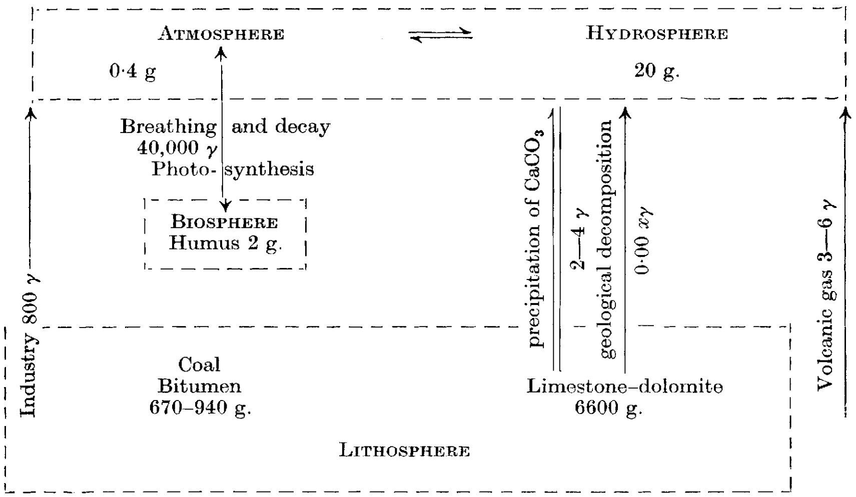
[61] V. M. Goldschmidt, *Geologiska Foren. Stockholm*, 1934, 416.

[62] *Trans. Geol. Soc. Glasgow*, 1917, **16**, 115.

of which it has been said " ohne Phosphor, kein Gedenken ", the mechanism involves not merely biological intervention, but very intelligent intervention.

TABLE IV



Annual balance sheet per sq. cm. of the Earth's surface.

The richest sources of phosphate lie in tropical or in semi-tropical zones. Their origin may be summarised thus : Weathered apatite . . . phosphate ion in solution . . . marine organisms . . . larger organisms . . . fish. . . . Thus far the concentration is merely biological. Where small arid islands lie off a fertile coast, myriads of fish-eating birds resort there to nest. The climatic conditions protect them from molestation at the nesting season, and also preserve the valuable, highly soluble mixture of ammonium salts, including phosphate, of their excreta. The ammonium salts are eventually leached away, and in a less arid climate the phosphate too is gradually washed down into the crevices of the underlying rock. On coral islands the product is rock phosphate, which may contain up to 95% of calcium phosphate. On volcanic islands the phosphate is naturally immobilised by the bases which form the least soluble phosphates, *e.g.*, ferric and aluminium oxides. It would not be surprising if the mineral was also found to be substantially enriched in zirconium.

Not all the phosphate is thus concentrated. Very important amounts react directly with the shelly detritus of the sea floor partly forming calcium phosphate and partly acting as a colloid in cementing together particles of inert minerals on the sea floor. Phosphate of such origin is of the greatest historical interest, for it was from beds of such origin in Cambridgeshire that phosphate for the earliest experiments at Rothamsted was obtained. It formed the basis for the English superphosphate (and indirectly sulphuric acid) industry.

Phosphate in the animal body has two distinct rôles, as a capital store of which the mechanical structure of the body is constructed and as a transport agent, carrying the fat and carbohydrate to the site of combustion and carrying off wastes, as phosphoric esters. Recent experiments with radio-phosphorus [63] have shown that bone is continually being renewed so that there must be a steady flow of phosphorus through the system and a continuous enrichment of the surface of the soil with phosphate in excreta ; much of the richest arable land in Australia was infertile until this was realised : there had been no small mammals so that the phosphate had to be supplied artificially.

Phosphate, so interestingly concentrated, is as yet largely dissipated in sewage. Owing to the fact that it is a tribasic anion it is more extensively adsorbed on the sludge and therefore not so completely lost as the equally essential potassium.

The frequent occurrence of vanadium in the soot of oil burners indicates that it also is probably of marine origin. In fact, certain marine organisms do effect the oxidation–reduction cycle in their blood through the changing valency of a vanadium complex. As will be seen from the table of abundance of the elements, vanadium is by no means as scarce as might be supposed from the rarity of its ores and in analysis it is probably often included with phosphate. In one important respect it differs markedly from phosphorus ; it does not form a volatile hydride. Consequently in reducing media, such as decaying organic matter and particularly protein, phosphorus may be removed as a gaseous hydride whilst vanadium combines with simultaneously-formed sulphide to give ores of the patronite type.

Among the rare amphoteric elements Goldschmidt [21, 55] has discovered a special type of physical concentration in which plant growth plays an important part. His findings may be summarised :

(*a*) The roots of trees extract a variety of elements from a large bulk of rock ; (*b*) the sap transports them in solution to the leaves ; (*c*) the leaves fall, and the resulting humus contains (i) Na, Fe, Ca, Mg, etc., (ii) As, Ga, Ge, etc. ; (*d*) the common elements are leached out by rain, whilst the rarer ones are retained in the humus, possibly as complexes with tannin ; and (*e*) the humus forms peat and finally coal.

This explains why the ash of many coals is enriched many-fold, even as much as a thousand-fold, in the rarer elements, particularly in gallium and germanium.

Weathering of Pegmatites.—The weathering of the products of the crystallisation of the final liquors (pegmatites) cannot occupy such a conspicuous part in the economy of Nature, since these form merely 1% of the products of the solidification of the magma. Moreover, the heavy metals, which constitute such a significant part of pegmatites, are characterised by the variety of insoluble salts which they form. Consequently, if any of the heavy metals are weathered, the material is seldom transported far in solution before it encounters an anion capable of immobilising it once more. The phenomena are therefore similar to those encountered in weathering iron pyrites, leading to secondary enrichment. In Fig. 3 the

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[63] G. von Hevesy, *Nature*, 1937, **139**, 149.

dotted zone represents a vein of pyrites reaching the surface *SS*. Aerated rain-water will convert iron sulphide into soluble ferric sulphate and wash it downwards till, at the level *AB*, the oxygen supply is exhausted. Further oxidation of the iron sulphide is brought about by reduction of ferric to ferrous sulphate. At a slightly lower level *A′B′*, the ferric sulphate too will be exhausted. Now, the aerated rain-water will extract not only iron, but also copper, silver, and gold and will carry them down in solution so long as an excess of oxygen is present. Consequently the whole precious-metal content of the upper part of the vein will be reprecipitated as soon as the oxygen supply is exhausted, *i.e.*, between level *AB* and *A′B′*. Further, erosion, by lowering the level of the hill surface to *S′S′*, will obviously lower the reduction level by a corresponding amount. In course of millions of years the surface may fall hundreds of feet. The precious-metal content of all this pyrites will be concentrated in a shelf 5—10 feet thick. Once below the zone of secondary enrichment, the precious-metal content is low ; it has not yet been concentrated. Such a deposit has often an iron cap at the surface, formed by ferric sulphate ascending in solution by capillarity and then undergoing hydrolysis.

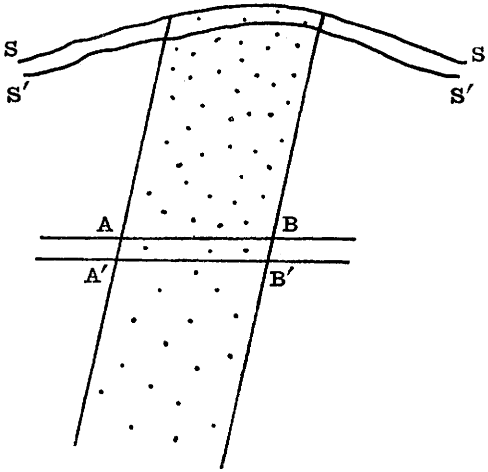

FIG. 3

[*After Berg.*]

Quite a different manner of selective concentration of elements is discussed by R. A. Mackay.[64] Relatively impermeable barriers, such as exist at the contact of shale with limestone, can so impound solutions as to cause some metals to be deposited within the structure, and allow the ore-carrying fluid to pass on *through* the barrier. If the metal is in colloidal solution, this is called dialysis ; if in true solution, it is exosmosis, removal of solvent by application of pressure at a semipermeable barrier. Mackay is concerned with the order of deposition of heavy-metal ores from aqueous

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[64] *Econ. Geol.*, 1946, **41**, 13.

solution. The larger an ion, the less it will be hydrated. Consequently, in the series : Hg, Pb, Zn, Cu, Sn, the larger ions will be least impeded by an " entourage " of water molecules, and will penetrate furthest, *i.e.*, Hg will penetrate further than Sn. On the other hand, where migration takes place in the vapour phase or in anhydrous melts, the largest ions will penetrate *least* as was pointed out by Lapadu-Hargues [18] in his studies on metamorphic rocks. It is therefore not surprising that mineral sequences are observed which conform neither to the order of increasing nor to the order of diminishing ionic radius, for it is quite conceivable that deposition may have occurred at an intermediate temperature, so that the two effects are superimposed.

W. Q. Kennedy [65] suggests that the original ore concentrations may have been formed in the granite layer. The rôle of igneous rock is a secondary one involving transport and reconcentration of ores previously localised within specific sectors of the crust.

These, and other schemes whereby the separation of metallic ions from solution, and from each other, may be envisaged are not mutually exclusive. It is for the chemist to call attention to such as are *possible*, and for the geologist to decide which, if any, are exemplified in Nature.

The author is greatly indebted to Dr. G. W. Tyrrell for access to his unique collection of reprints and to Dr. Walther Bierther for having called attention to the work of Kuhn and Rittmann.

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[65] *Schweiz. Mineralogist,* 1948, **28,** 1.