

Liversidge Research Lecture

No. 4a
1942

CHEMISTRY OF THE EARTH

J. S. ANDERSON



The Royal Society of New South Wales



John Stuart Anderson

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JOHN STUART ANDERSON 1908-1990

John Stuart Anderson was born on 9 January 1908 at Islington, London (U.K.). At the age of 11 he obtained an L.C.C. Junior Country Scholarship to attend the boy's school section of the Northern Polytechnic (Highbury County School) from 1919 to 1924. He passed the Schools Certificate examination with Distinction or Credits in every subject, and was awarded an Intermediate County Scholarship to enroll for the B.Sc. course at Northern Polytechnic for the period 1924-1926. Then, with a Royal Scholarship (he was top of the list) he entered the Royal College of Science (Imperial College) where, in his second year (1928) he was top of the class, and was awarded the Frank Hutton Prize in Advanced Chemistry. For his third year, involving research, he worked under the supervision of Professor H.B. Baker, and graduated B.Sc. (1st. class Hons.) in 1929. In continuation of research at Imperial College, he worked on nickel carbonyls, and graduated Ph.D in 1931. Then, with a University of London Travelling Scholarship, he went to Heidelberg (Germany) to work for a year with Hieber on iron carbonyls. In 1932 Anderson returned to Imperial College as a Demonstrator, and began research on the X-ray crystallography of organic compounds, and on hydrogen isotope studies of hydrogen exchange in metal amines. In 1936 he and Emeleus collaborated in the writing of 'Modern Aspects of Inorganic Chemistry', a seminal textbook published in 1938.

In 1938 Anderson obtained a Senior Lectureship at the University of Melbourne, replacing Noel Bayliss (later Sir Noel, FAA) who had accepted the Chair of Chemistry at The University of Western Australia. He turned his attention to searching for a natural source of technetium, an element that had been made artificially in 1937, and also on chemical methods for the separation of zirconium and hafnium. Partly as a result of constraints imposed by the Second World War (1939-1945) the research interests of John Anderson (often referred to as 'JS') moved more to solid-state chemistry, the subject of his Liversidge Lecture in 1942.

In 1946 he was invited to join the newly set up Chemistry Division at the Atomic Research Establishment at Harwell, and in 1947 he moved to Harwell to exercise general oversight of broad-ranging research in inorganic chemistry, and to run, directly, a small and quite uncommitted research group. He continued work on the solid state and non-stoichiometry, including work on oxides and hydrides of uranium. With state-of-the-art X-ray diffraction instruments at Harwell he was able to make important progress in studies of the solid state.

When Professor Hartung retired at the end of 1953, 'JS' was appointed to replace him, and took up the position of Professor and Head of the Chemistry School, University of Melbourne, in 1954. In 1959 he moved back to the U.K. to become Director of the National Chemical Laboratory, and in 1963 he accepted the invitation to take up the Chair of Inorganic Chemistry at Oxford University. He held this position until he retired in 1975. He remained actively interested in chemistry. During 1974-6 he was President of the Dalton division of the Chemical Society, London, and for the period 1975-1982 he was at the University College of Wales, Aberystwyth working in collaboration with J.M. Thomas (now Sir John, FRS); then he came back to Australia as a Visiting Fellow at the Research School of Chemistry, Australian National University. He remained there until 1989 when illness overtook him, and he died on Christmas Day 1990.

Honours and Awards

1942	Liversidge Research Lecture, Royal Society of New South Wales
1944	H.G. Smith Medal, Royal Australian Chemical Institute
1945	Syme Research Prize, University of Melbourne
1953	Tilden Lecture, Chemical Society (London)
1953	FRS
1954	FAA (a Foundation Fellow of the Australian Academy of Science)
1958	Masson Lecture, Australian New Zealand Association for the Advancement of Science (ANZAAS)
1963	Liversidge Lecture, Chemical Society (London)
1964	Fellow of the Imperial College
1966	Matthew Flinders Lecture, Australian Academy of Science
1973	Davy Medal, Royal Society of London
1975	Award for Solid State Chemistry, Chemical Society (London)
1975	Longstaff Medal, Chemical Society (London)
1978	Honorary Fellow, Indian Academy of Science
1979	Hon. D.Sc., University of Bath (U.K.)
1980	Hugo Muller Medal / Lecture, Chemical Society (London)
1984	Liversidge Research Lecture, ANZAAS

Biographical Sources

1. Hyde, B.G. and Day, P., 'John Stuart Anderson 1908-1990', *Historical Records of Australian Science*, 1992, **9**, 127-149.
2. Hyde, B.G. and Day, P., 'John Stuart Anderson, 9 January 1908 - 25 December 1990, elected F.R.S. 1953', *Biographical Memoirs of Fellows of the Royal Society*, 1992, **38**, 3-26.
3. Hyde, B.G., 'John Stuart Anderson 1908-1990', *Chemistry in Australia*, 1991, **58**, 406-407.

Scientific Publications of J.S. Anderson

John Stuart Anderson was the author / co-author of 160 papers and 10 monographs. These are listed as an appendix to the biographical article (1) listed above.

CHEMISTRY OF THE EARTH*

J. S. ANDERSON

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It is laid down in the terms of the Liversidge Lectureships that the lectures shall deal with new knowledge, and shall serve to promote research. Few developments in science have made so vital a contribution to chemical theory as has the knowledge that has been acquired, since Laue's discovery of the diffraction of X-rays, as to the constitution of the crystalline state of matter. This is especially true of inorganic chemistry, dealing, as it does, with compounds existing for the most part in the solid state as ionic or homopolar aggregates, rather than as molecular units. In this and the subsequent paper, therefore, the relation between crystalline structure and chemical theory will be taken as the general underlying theme.

The close association between chemistry and mineralogy obtaining in the early part of the last century is familiar to every chemist; nevertheless, with the passage of the years this association, so fruitful for the early growth of chemical theory, weakened, few chemists and geologists perceiving the fruitful fields of investigation that lay on the borders of the two sciences. Within recent years, however, and especially during the last two decades, there has been a greatly renewed interest in geochemistry - the chemistry of the earth whereby the subject has been brought, in large measure, within the ordered domain of theoretical physical chemistry. This advance is due, in the main, to the work of a few schools of research - those of von Hevesy at Freiburg, I. and W. Noddack at Berlin, Clarke and Washington in America, and - above all - V.M. Goldschmidt at Göttingen and Oslo. The new subject so created, impinging on fields as diverse as nuclear physics, geology and metallurgical industry, appears eminently appropriate for a lecture which commemorates the work of Liversidge, who himself made so many contributions to Australian mineralogy.

The Data of Geochemistry

The basic data of geochemistry are the analytical data of the world around us, the world of air and oceans and rocks immediately accessible to our investigation. Of this accessible world, by far the greatest mass is made up of the rocks of the *lithosphere*, represented by the exposed rock sections amounting to between 16 and 30 kilometres in aggregate thickness. About 95% of the lithosphere is composed of igneous rocks, with 4% of schists, 0.75% of sandstones, and 0.25% of limestones. Since, however, the materials of the sedimentary rocks must have been derived, in the first place, from the igneous rocks, as also was (for the greater part, at least) the solute of the oceans, it is clear that we may formulate as the first major task of geochemistry the establishment of the mean composition of the igneous rocks.

On this purely analytical question, finality has not yet been reached, in spite of the vast number of rock analyses that have been performed. Whereas there is substantial

* Liversidge Research Lecture delivered on October 27th, 1942, at Science House, Sydney, arranged by the Royal Society under the terms of the Liversidge bequest. Reproduced by permission of the Royal Society of New South Wales from *J. Proc. Roy. Soc. N.S.W.*, 1942, **76**, 329-344.

TABLE 1.
Relative Abundance of the Elements
 (Composition of the earth's crust, including the oceans and the atmosphere, in percentage by weight.)

1. Oxygen	49.5 %		49. Praseodymium	3.5×10^{-4} %
2. Silicon	25.7		50. Argon	3.5×10^{-4}
3. Aluminium	7.5		51. Cassiopeium*	1×10^{-4}
4. Iron	4.7		52. Germanium	1×10^{-4}
5. Calcium	3.39			
6. Sodium	2.63	99.51%	53. Selenium	8×10^{-5} %
7. Potassium	2.40		54. Caesium	7×10^{-5}
8. Magnesium	1.93		55. Terbium	7×10^{-5}
9. Hydrogen	0.87		56. Holmium	7×10^{-5}
10. Titanium	0.58		57. Thulium	7×10^{-5}
11. Chlorine	0.19		58. Niobium	6×10^{-5}
12. Phosphorus	0.12		59. Antimony	3×10^{-5}
			60. Uranium	2×10^{-5}
13. Manganese	0.09		61. Tantalum	2×10^{-5}
14. Carbon	0.08		62. Gallium	2×10^{-5}
15. Sulphur	0.06		63. Europium	1.4×10^{-5}
16. Barium	0.04		64. Indium	1×10^{-5}
17. Chromium	0.033		65. Thallium	1×10^{-5}
18. Nitrogen	0.030	0.45%	66. Cadmium	1×10^{-5}
19. Fluorine	0.027		67. Illinium*	$<1 \times 10^{-1}$
20. Zirconium	0.023			
21. Zinc	0.02		68. Iodine	7×10^{-6} %
22. Nickel	0.018		69. Platinum	ca. 5×10^{-6}
23. Strontium	0.017		70. Palladium	ca. 5×10^{-6}
24. Vanadium	0.016		71. Osmium	ca. 5×10^{-6}
			72. Ruthenium	ca. 5×10^{-6}
25. Copper	0.010		73. Silver	4×10^{-6}
26. Yttrium	0.007		74. Bismuth	3×10^{-6}
27. Tungsten	0.005		75. Mercury	3×10^{-6}
28. Lithium	0.004		76. Iridium	ca. 1×10^{-6}
29. Rubidium	0.0033		77. Rhodium	ca. 1×10^{-6}
30. Hafnium	0.0025	0.04%	78. Tellurium	ca. 1×10^{-6}
31. Cerium	0.0022			
32. Lead	0.002		79. Helium	8×10^{-7}
33. Thorium	0.002		80. Neon	5×10^{-7}
34. Neodymium	0.0012		81. Gold	1.5×10^{-7}
35. Cobalt	0.0012		82. Masurium*	ca. 1×10^{-7}
36. Boron	0.001		83. Rhenium	ca. 1×10^{-7}
37. Molybdenum	7.5×10^{-4} %		84. Krypton	1.9×10^{-8} %
38. Bromine	6×10^{-4}			
39. Tin	6×10^{-4}		85. Xenon	2.9×10^{-9} %
40. Scandium	6×10^{-4}			
41. Beryllium	5×10^{-4}		86. Radium	7×10^{-12} %
42. Lanthanum	5×10^{-4}		87. Protactinium	2.6×10^{-12} %
43. Samarium	5×10^{-4}			
44. Gadolinium	5×10^{-4}		88. Actinium	2.3×10^{-14} %
45. Dysprosium	5×10^{-4}			
46. Ytterbium	5×10^{-4}			

47. Arsenic	4.5×10^{-4}	89. Polonium	$1.4 \times 10^{-15} \%$
48. Erbium	4×10^{-4}	90. Niton*	$4 \times 10^{-17} \%$

* **Note by the transcriber:** The modern names for the element names asterisked in Table 1 are: -

*Cassiopeium = Lutecium; *Illinium = Promethium; *Masurium = Technetium; *Niton = Radon

agreement as to the concentration of the major constituents of the lithosphere, such as are ordinarily determined directly in rock analyses, there have been far too few analyses in which those elements occurring only in minute amounts in igneous rocks have also been determined. The development of optical and X-ray methods of spectrochemical analysis has greatly extended the range of available data, and has led to a marked revision of the table of abundance of the elements. Much more work is needed, however, and some differences will be found between authoritative authors as to the abundance of the rarer elements in the lithosphere. Table I, based largely on the data of Washington and Clarke (1924), as revised by Noddack (1930, 1936a), sets out the present state of our knowledge.

Certain of the main features of Table 1 are familiar to most chemists, but there are a few points to which it is desirable to draw attention. There is, in the first place, the overwhelmingly predominant rôle played, in the lithosphere, by a small number of elements. About 99.5% of the entire mass of the igneous rocks is made up of twelve elements. Sixty-four out of the eighty-eight known elements together make up less than 0.04% of the total mass of the lithosphere.

Secondly, we may notice that some of the "common" elements that play the most important rôles in economic life, and that have been long known to and used by man, are actually comparatively rare. As examples one may cite copper, lead and antimony. Copper is less abundant than vanadium; lead is comparable in abundance with thorium and molybdenum; antimony is rarer than germanium or caesium. Bismuth, mercury and gold are less abundant than any of the platinum metals. Although familiar to every student of chemistry, they rank in actual fact amongst the very rarest constituents of the lithosphere.

Complementary to the point just discussed is the abundance of certain elements far less familiar to most chemists - elements discussed in text books under the heading of the rarer elements. Most notable is the great importance of titanium in the composition of igneous rocks. Similarly, zirconium and vanadium are commoner than any of the heavy metals of commerce, other than iron, while the rare earths, taken as a group, are about as abundant as copper.

Consideration of these matters leads us to the conclusion that we must draw a clear distinction between the *abundance* of the elements and, their *accessibility*. The elements that have been longest known, and that are most familiar to the student of chemistry, are those that occur in Nature as the major constituents of easily recognised minerals. We may distinguish between the *mineral occurrence* of elements and their *disperse occurrence*, and may trace a gradation in the measure of their dispersion in the earth's crust and in their accessibility. At the head of the list stands the occurrence of the elements in ore bodies - i.e., as major constituents of minerals which, through the mode of their formation, or through secondary processes, have been segregated in masses large enough for economically practicable working. Instead of being so segregated, however, many minerals are systematically dispersed as crystalline constituents of the rocks. This may be strikingly exemplified by the occurrence of titanium. Rutile, ilmenite, sphene, etc., are amongst the most widely spread of minor rock-forming minerals. Generally, however, it is only where

these heavy minerals have been left as a mechanically resistant residue from the weathering and elutriation of rock masses that - as in our own valuable beach sand deposits of the New South Wales coast - we find titanium minerals segregated in considerable masses.

So far we have considered the occurrence of an element in its own crystalline minerals. Experience shows, however, that absolutely homogeneous crystalline minerals are of rare occurrence. They grew in nature from complex mixtures, and it is the rule, rather than the exception, to find in mineral crystals inclusions of foreign minerals, ranging in size from visible or microscopic crystals to regions on the microscopic verge of colloidal dimensions. In this connection, the application of the electron microscope, with its great resolving power, to mineragraphic problems, holds promise of interesting information as to the gradation between such colloidal dispersions of one mineral in another and the atomic dispersion of the elements. This latter represents the ultimate degree of dispersion - the inclusion of foreign atoms, by isomorphous replacement, within the crystal lattice of the host.

Between these degrees of dispersion in the earth there is no sharp division. Every stage from the high grade ore to the atomic dispersion is represented in nature. One consequence - of philosophical rather than practical importance, perhaps - is the difficulty caused thereby in defining what is meant by a "pure mineral species". No mineral analyses to an ideally simple formula, and even the diamond leaves a trace of ash when it is burned.

The Omnipresence of the Chemical Elements

The foregoing considerations have been further developed by I. and W. Noddack (1936*b*) into an interesting, if controversial, hypothesis. Very few analyses of minerals have been made without any preconceived assumption as to the number of elements present. When such analyses are made, the results are somewhat surprising; they show clearly that the range of elements detected depends solely on the limits of analytical sensitivity. Such an analysis of a zinc blende, reported by Noddack, is reproduced in Table 2.

In this table, column I records the major and column II the minor constituents determined by the ordinary methods of analysis. In column III are the constituents determined by optical or X-ray spectroscopy, either directly or after suitable chemical enrichment processes. In column IV are certain elements made the subject of special search by highly sensitive enrichment methods. Taking into account that the detection of any of the rare earths or the platinum metals connotes the presence of the whole group, and that the presence of uranium implies the presence of all its disintegration products, it will be seen that 75 elements were detected directly or indirectly in this sample. The only elements not found, in fact, were those for which a sufficiently sensitive analytical technique is lacking. The conclusion drawn by the Noddacks (1936*b*) from such results as these is that every "pure" mineral contains every element. Whether, as these authors consider, the conclusion can be extended to "pure" chemicals depends on the quantitative efficiency of chemical separation processes.

Their extensive work on the geochemistry of rhenium (Noddack, 1931) gave I. and W. Noddack the opportunity to amass a considerable body of data on the minor constituents of

TABLE 2.
Analysis of a Zinc Blende.

I	II	III	IV
Zn = 63.55%	H = 0.09%	Co	$\Sigma Y, \text{La-Cp} = 0.00004\%$
S = 31.92%	Ca = 0.08%	Ni	$\Sigma \text{Platinum metals} = 0.0007\%$
O = 1.15%	Cd = 0.08%	Cr	Re = 0.00001%
Fe = 1.57%	Al = 0.05%	Mo	
Si = 0.34%	Mg = 0.04%	Ge	
Mn = 0.27%	Se = 0.04%	Sn	
Pb = 0.15%	Cl = 0.03%	Ag each 0.01-0.001%	
As = 0.14%	Sb = 0.03%	Hg	
Cu = 0.13%	C = 0.02%	V	
	P = 0.02%	Te	
	Na = 0.01%	Ga	
	K = 0.01%	In	
	Ti = 0.01%	Zr	
	Bi = 0.01%	Sr	
		Sc	
		W	
		Au	
		Hf	
		Th each 0.001-0.0001%	
		U	
		Ba	
		Tl	
		Br	

Their extensive work on the geochemistry of rhenium (Noddack, 1931) gave I. and W. Noddack the opportunity to amass a considerable body of data on the minor constituents of minerals, and this they have treated statistically from the standpoint of the omnipresence of the elements. There are, according to these authors, about 1,800 distinct mineral species known. If, for each element, there is plotted a distribution curve, showing the number of minerals containing more than 1 %, 0.1 %, 0.01 %, etc., of that element, the curves so obtained have a similar form for all the elements (Fig.1). Two points on the curves have particular significance: (a) the point of inflexion, marking the concentration below which the disperse occurrence of any element is observed; and (b) the intersection of the curve with the ordinate at N = 1800, which represents the probable minimum concentration of that element in any mineral. For example, it is said that there are 360 minerals rich in iron, 700 with more than 1%, 1,250 with more than 0.1%. For molybdenum, a relatively rare element, there are 11 molybdenum minerals proper, with 25-70% Mo, 6 minerals with 1-3%, and (by inference from the 600 mineral species actually examined for molybdenum), 30 with 0.1-1%, 80 with 0.01-0.1%, 180 with 0.001-0.01%, 400 with 0.0001-0.001%. The

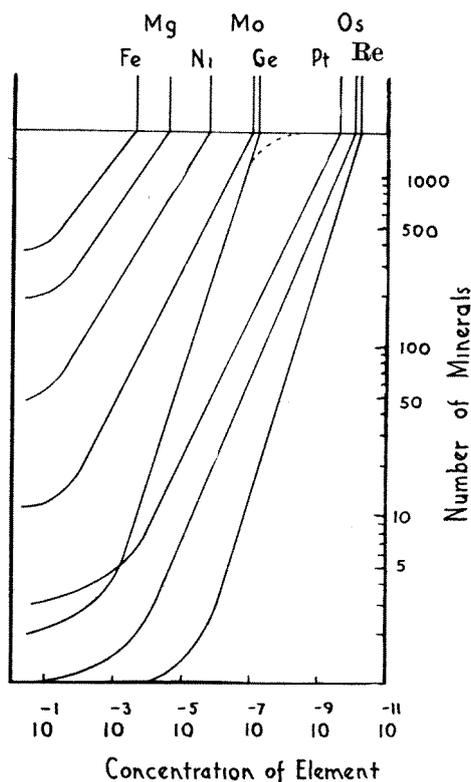


FIGURE 1.- Statistics of distribution of elements in minerals.

Noddacks' figures are open to criticism on a number of counts; thus, the concentration of any trace constituent in any one mineral taken from different sources varies over a very wide range, so that mean values have little significance. For example, the indium content of zinc blende varies from 0.1% to less than 0.0001%. Nevertheless, the general concept is worth some attention, and the idea of the "omnipresent concentration" of the elements in minerals has some meaning. The complementary idea is that of the probability of occurrence of any element above a certain concentration. For example, from the data given above regarding the concentration of iron in minerals, there is a probability of about 0.7 that any mineral taken at random will contain at least 0.1% of iron.

A further point brought out by the Noddacks' statistical treatment is that the number of minerals formed by any element is roughly a function of its abundance. $M = k.A^x$, where M is the number of minerals formed, A is the abundance of the element, and the exponent x has about the same value (0.3-0.5) for all the elements (Noddack, 1936a). This relation is not absolutely rigid - if it were, one would expect that elements rarer than, say, antimony (Table I) would form no minerals of their own at all. This is not true, for the formation of compounds out of the originally uniform planetary matter must have depended on the chemical individuality of the elements, as well as on random fluctuations of composition of the mass. Thus, elements as rare as mercury and the platinum metals form their own characteristic minerals (native metals, sulphides, etc.), in virtue of their chemical inertness, affinity for sulphur, etc. On the other hand, rhenium and indium form no minerals of their own, and seem never to enter into the minerals of other elements to the extent of more than 0.01% and 1% respectively.

The chemical individuality of the elements, in so far as it conditions their mode of occurrence, can be measured by the ratio of their omnipresent concentration to their

terrestrial abundance. This ratio, for a few elements, is listed in Table 3. It is clear that elements prone to mineral formation - e.g., silicon, oxygen, magnesium - occur almost exclusively in that manner, and are impoverished as regards their dispersed occurrence. With increasing rarity, the ratio must necessarily diminish, and for an element that was uniformly dispersed it would reach the value unity. Rhenium comes very close to this, and other rare elements, such as indium and germanium, may be seen also to be comparatively uniformly distributed throughout the material of the earth's crust.

TABLE 3.

Abundance. Element.	Omnipresent Concentration.	Lithosphere Abundance.	Lithosphere Omnipresent Concn.
Fe	2.5×10^{-4}	1.50×10^{-2}	60
O	2.0×10^{-4}	5.49×10^{-1}	2745
Mg	2.7×10^{-5}	1.42×10^{-2}	526
Si	6.5×10^{-5}	1.63×10^{-1}	2500
Al	1.5×10^{-5}	4.96×10^{-2}	3300
Ni	1.7×10^{-6}	6.47×10^{-5}	3.8
Mo	1.0×10^{-7}	5.77×10^{-7}	5.8
Ge	6.6×10^{-8}	2.46×10^{-7}	3.7
Sn	1.5×10^{-8}	9.01×10^{-7}	61
In	8.0×10^{-9}	1.61×10^{-8}	2
Pt	2.8×10^{-10}	2.66×10^{-9}	9.5
Os	1.0×10^{-10}	1.24×10^{-9}	12.4
Re	7.0×10^{-11}	9.34×10^{-11}	1.3

The foregoing considerations are not simply of academic interest. They are directly relevant to the problem of isolating the elements from natural sources. This is true even of the "common" elements; the amount of any metal contained in the total ore deposits of the world is exceeded, by a vast factor, by the amount dispersed less accessibly through the rocks of the lithosphere. The problem of extracting aluminium is an obvious illustration. In felspars and clay minerals aluminium is widely and abundantly spread, but the segregation of aluminium in simple ores (i.e. high grade bauxite) is comparatively rare. Development of technically practicable methods of extracting aluminium from clay minerals is an urgent problem of the present day. Analogous problems relating to the other technically important metals will certainly confront the chemist of the future.

For the rare elements the matter is especially important, since these may, in many cases, be recovered solely, or at least most readily, as by-products of the extraction of base metals. The minute concentrations of rare elements in base metal ores (cf. Table II) are compensated by the large scale of metallurgical operations, whence suitably enriched products may be obtained from which to extract the rare constituents. A few examples may be cited to illustrate the realisation and the possibilities of such sources of rare elements. Thus, about half the world's platinum output is obtained as a by-product of the extraction of nickel from the Sudbury ore, which contains one part of platinum in two or three million of ore. Equally striking is the production of rhenium at low cost (Feit, 1930). The ultimate source of this has not been made clear, but it is probably the Mansfeld copper schist, which contains only about $4 \times 10^{-5}\%$ Re. The residues from which rhenium is

extracted are themselves by-products of the recovery of molybdenum, which itself is present only to the extent of 0.08% in the original ore. Undeveloped potentialities are numerous. Sir Gilbert Morgan (1937; cf. Goldschmidt, 1935) has pointed out that, in consequence of the occurrence of gallium and germanium in significant amounts in the ash of British coals, upwards of a thousand tons of each of these rare elements are probably lost annually in smoke and flue dusts. Nearer home, we may cite the case of indium, which has recently attained a certain economic importance. The zinc blende and galena of Broken Hill both contain small but detectable amounts of indium, as recent Melbourne investigations have shown. The concentration in the ore is minute, but the quantities of material involved are such that, on a conservative estimate, about a ton of indium must pass through the flowsheets of the zinc and lead extraction plants each year.

The Absolute Abundance of the Elements

The determination of the absolute abundance of the elements in the universe may be taken as one of the primary objectives of geochemistry, because the proportions in which the various species of atoms have been formed are presumably a measure of their relative nuclear stability. In so far as the data for the lithosphere are relevant, they show evidence of a regular periodicity to which attention was first drawn by Harkins; namely, that elements with odd atomic numbers tend to be less abundant than those of even atomic number.

We cannot, however, assume that the rocks of the lithosphere are a representative sample of cosmic matter. In fact, such an assumption would be at variance both with the data of geophysics, as will be considered later, and with analyses of extraterrestrial matter, such as meteorites. The latter, and spectrographic evidence as to the composition of the sun, would lead beyond the bounds of the present discussion. We may note, however, that the mean composition of meteorites (Noddack, 1930; Hevesy, 1932) differs from that of the lithosphere in such a way as to accord more closely with Harkins' rule.

All the evidence points to the conclusion that the composition of the lithosphere differs from that of the earth as a whole. This being so, any relationship between the relative abundance of elements can be strictly valid only for groups of elements so alike chemically that they will not have been separated in any physico-chemical process of differentiation. The rare earths provide an excellent illustration of such a coherent group (Fig. 2); their relative proportions are practically the same in the lithosphere, in meteorites, and in the sun (Noddack, 1935). It is worth noting that these data refer to the whole elements; between the abundance ratios for each isotope individually, the regularities are far more obscure. Harkins' rule owes its validity, in part, to the fact that, whereas elements of odd atomic number have only one isotope (or at most two), multiplicity of isotopes is common amongst elements of even atomic number.

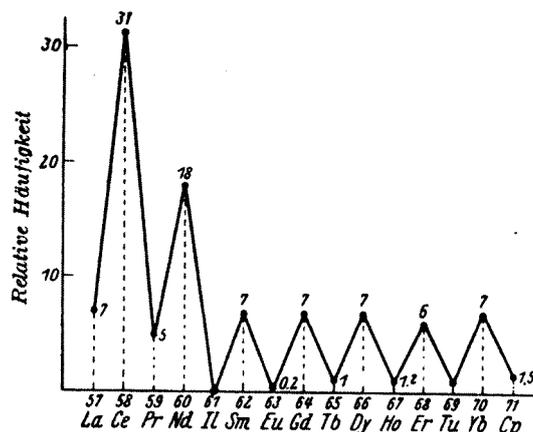


FIGURE 2.- Relative abundance of rare earth elements.

In considering the relation between abundance and nuclear stability, it is fitting to touch briefly on the problem of the missing elements. In spite of the claims that have been made, it is fairly clear that four elements still remain to be isolated - those of atomic numbers 43, 61, 85 and 87. The entries for 43 (masurium) and 61 (illinium) in Table I should therefore be deleted. It will be noted, in the first place, that all are "odd" elements. Elements 85 and 87, from their position in the Periodic Classification, are unlikely to possess any non-radioactive isotopes, and may well be elements of short life. They do not belong to any of the three main disintegration series, so that if they now exist at all they must be derived from some improbable branching process or a rare isotope of the long-lived radio elements. Practically, then, only ekamanganese (Noddack's masurium) and the rare earth metal (Smith-Hopkins' illinium and Rolla's florentium) remain to be isolated. What are the prospects for their discovery?

The study of isotope statistics has revealed a number of regularities which, although only empirical rules, do nevertheless accord with all the known elements. Mattauch (1934) has pointed out (a) that every element has at least one "odd" isotope; (b) that elements with odd atomic numbers are limited to nuclei with odd atomic weights; and (c) that of two isobares differing only by one unit of nuclear charge, one is invariably unstable - as, for example, the the β -active ^{87}Rb , isobaric with ^{87}Sr . Isotope data for the known elements adjacent to elements 43 and 61 are set out in Tables 4 and 5. In each case, as was pointed out by Jensen (1937), all the likely nuclei are already represented among the stable isotopes of known elements. Thus ^{95}Mo , ^{97}Mo , ^{99}Ru , ^{101}Ru block the most probable nuclei for element 43, as do ^{143}Nd , ^{145}Nd , ^{147}Sm , ^{149}Nd and ^{149}Sm those likely for No. 61. Unless the atomic weights of these elements are abnormal, they come within the scope of Mattauch's rule, which would suggest that they must be very rare, that they may be radioactive, and that they may, in fact, not exist.

TABLE 4.

Mass	Z = 36	37	38	39	40	41	42	43	44	45
Number.	Kr Pd	Rb	Sr	Y	Zr	Nb	Mo		Ru	Rh
84	57		0.5							
85		73								
86	17		10							

87		27	7.5						
88			82						
89				100					
90				48					
91				11.5					
92				22		14			
93					100				
94				17		10			
95						15.5			
96				1.5		18		5	
97						10			
98						23		?	
99								12	
100						10		14	
101								30	0.1
102								22	
	1								
103									99.9
104								17	
	9								
105									
	23								

TABLE 5.

Mass Number	Z =	58 Ce	59 Pr	60 Nd	61	62 Sm	63 Eu	64 Gd
140		89						
141			100					
142		11		36				
143				11				
144				30		3		
145				5				
146				18				
147						17		
148				1		14		
149				1		15		
150						5		
151							51	
152						26		
153							49	
154						20		
155								17

The Distribution of the Elements

The second main problem of geochemistry concerns the distribution of the elements amongst the materials of the universe, and of our earth in particular. It has already been

stated that the rocks of the lithosphere cannot be taken as representative of the whole earth, as simple geophysical considerations show. In the first place, as Cavendish found, the mean density of the earth is about 5.8, whereas the density of the silicate rocks is about 2.6 - 2.8. Hence the interior of the earth must be composed of denser materials than the crust. Seismic evidence is in accord with this view, for the propagation of earthquake waves through the earth can be accounted for only if there are fairly abrupt discontinuities in the density and the elasticity of the earth at depths of 2,900 km. and 1,200 km. below the surface, as well as a less marked change at a depth of about 120 km. These discontinuities can only represent changes in material composition. What further evidence can be gained as to these materials of the earth's interior?

V.M. Goldschmidt, regarding meteorites as representative samples of planetary matter, has pointed out that in addition to the well known division into stony and iron meteorites, it is necessary to recognise a third meteoric material, troilite, which is associated with both iron and stony meteorites. Troilite is, predominantly, ferrous sulphide, together with other sulphides, such as daubréelite, FeCr_2S_4 ; upwards of thirty other elements have also been detected in minor amounts. The view may reasonably be advanced (Goldschmidt, 1922; Tammann, 1923, 1924) that the material of the earth initially underwent a similar separation into a four-phase system, consisting of a gaseous atmosphere and three immiscible liquid phases: a metallic liquid, consisting of a nickel-iron alloy by analogy with the siderites, a sulphide phase, mostly composed of ferrous sulphide, and a fused silicate phase. These, separating under the influence of gravity, would confer on the earth a structure (Fig. 3) compatible with all the geophysical evidence. In the meteorites, on account of the smallness of the masses involved, gravitational separation did not occur, so that the three phases, although very different in density, are frequently found intermingled physically.

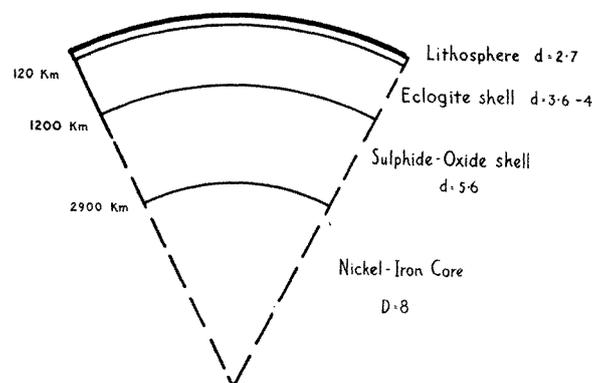


FIGURE 3 - Section through the earth.

Evidence in support of Goldschmidt's view is found in the observation that just such a separation - into metal, matte and slag - is common in the metallurgy of sulphide ores, where it represents the phase equilibrium attained on the hearth of the furnace. In a three-liquid equilibrium of this kind there is a systematic distribution of the minor constituents between the phases, as was pointed out by Goldschmidt and Tammann (*loc. cit.*). For example, we have observed in Melbourne that in the lead blast furnace the trace of indium present is virtually absent from the silicate slag, and is strongly concentrated in the sulphide phase.

Laboratory experiments also show that the same separation of phases and partition of elements between them takes place in relatively simple mixtures, as for example in a

mixture of iron, ferrous sulphide and a fusible silicate. When solidification commences, a further differentiation occurs (cf. Paneth, 1925); a minor sulphide fraction separates from the silicate melt, owing to the decreasing miscibility of the liquids, while the initial, middle and final crystal fractions from the silicate phase differ systematically in composition.

From a study of the distribution of the minor constituents of a mixture in such laboratory experiments, in metallurgical processes, in meteorites, and in terrestrial minerals, the elements may be classified, following Goldschmidt, as *siderophile*, *chalcophile*, *lithophile* or *atmosphile*, according as they are concentrated preferentially in the metallic, the sulphide, the silicate or the gaseous phase (Table 6). For example, nickel, gold and the platinum metals are enriched 1,000-5,000 fold in meteoric or native iron, as compared with the earth's crust. Other elements classed as siderophile display the same preferential concentration.

TABLE 6.

Goldschmidt's Classification of the Elements.

Iron, Siderophile.	Sulphide, Chalcophile.	Silicate, Lithophile.	Gases, Atmosphile.	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), Se, Y	Kr, X (<i>sic</i> , =Xe)	
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.

Physico-Chemical Factors Underlying the Distribution

In broad outline we can perceive the factors that determine the distribution of the elements in the kind of system under consideration. Iron, because, of its preponderant abundance, is common to all the condensed phases - the metallic melt, rich in free electrons, the ionic silicate melt, and the semi-metallic sulphide melt, concerning the constitution of which we have as yet no satisfactory physical model. Elements higher in the electromotive series than iron must displace iron from the ionic melt, in which they are, accordingly, preferentially concentrated. The strongly electropositive elements are therefore

lithophile in character. Conversely, the nobler metals are necessarily *siderophile*, being displaced by iron from the ionic liquid. The third main group, of *chalcophile* elements, contains those which form essentially homopolar compounds with the metalloids, and which cannot coexist in an ionic environment (melt or solution) with appreciable concentrations of metalloid ions. This group therefore comprises, in the main, the metals of the sulphide groups of analytical chemistry.

Whilst this qualitative treatment of the Goldschmidt classification is broadly correct, there are a number of outstanding problems regarding the magnitude of the distribution coefficients. In fact, very few quantitative studies of this kind have been made. Jander (1925) measured the partition of gold between molten iron and fused silicates; Noddack, Noddack and Bohnstedt (1940) that of gold, rhenium, molybdenum and the platinum metals between iron and ferrous sulphide. Jander and Rothschild (1928) examined equilibria between fused silicates and sulphides, and recently the author and Mr. M. J. Ridge have examined the distribution of several metals between the two coexisting liquid phases in the system tin-stannous sulphide. The general conclusions to be drawn from all these experiments are, firstly, that distribution is invariably more uniform than would be expected from simple thermodynamic calculation, and secondly, that the problem opens the whole question of the general theory of liquids. The chemistry and physics of fused salts and semi-metallic compounds is an outstanding field of fundamental research which impinges also on the province of the metallurgist. It would be a worthy object both for the research of the academic scientist and for the support and encouragement of the industrialist.

The Crystallisation of the Silicate Melt

Our accessible world is derived from the crystallisation of the silicate phase, so that the geochemist is most closely concerned with the sequence of events in that process. With the onset of crystallisation, a process of differentiation must have commenced through the operation of gravitational forces. The first materials to crystallise from such a melt would be the heavy metallic oxides, such as magnetite and chromite, together with the denser silicates such as olivine, Mg_2SiO_4 , and the magnesium metasilicate minerals (pyroxenes). All of these, we may note, are characterised by close-packed anion lattices, so that they represent the structures attaining the maximum density amongst silicates and oxides. Such minerals, settling through the melt, must have gone to build up the denser silicate-oxide shell of the earth. Included in this shell there are undoubtedly crystalline materials that could not be formed by crystallisation under ordinary pressures; for example, the diamond, crystallised originally under enormous pressure, is brought to the earth's surface along with the typical silicate minerals referred to above.

The further course of crystallisation, as the temperature fell and the composition of the melt changed, can be correlated with the building of crystal lattices of increasing complexity of ordering, and higher lattice energy, the general sequence being:

orthosilicate unit lattices \rightarrow one-dimensional chains \rightarrow
(pyroxenes)

two-dimensional sheet structures \rightarrow three-dimensional networks
(aluminosilicates, feldspars)

\rightarrow three-dimensional openwork structures
(zeolites)

Distribution of Minor Elements During Fractionation

To the free energy of formation of any solid ionic compound from its elements, factors of two kinds contribute. These are (a) those specific to the elements concerned - ionisation potentials, electron affinities, heats of sublimation and dissociation; and (b) the cohesive energy or lattice energy of the compound, involving the structure and dimensions of the lattice unit. Where the thermodynamic quantities listed under (a) are known, the lattice energy may be derived by means of the Born-Haber cycle. Alternatively, following Madelung, it may be calculated (for simple structures, at least) from the laws of force between ions

$$U_L = \frac{N.A.z^2.e^2}{R} \left(1 - \frac{1}{n}\right)$$

where A = Madelung constant.

z = valency of ions.

R = cell dimension.

n = repulsion exponent.

This expression for the Madelung energy* involves, as will be seen, the valency of the ions and the interionic distances in the lattice.

The sequence of crystallisation from a cooling melt follows, as was indicated above, the order of increasing lattice energy. It follows that, even between the major constituents of a complex melt, there must be a sorting process as crystallisation proceeds, according to the contribution of their ions to the cohesive energy of the solid phase.

The variation of cohesive energy with the ionic radius of the cation is typically exemplified by the orthosilicates of magnesium and iron:

Mg ₂ SiO ₄	m.p. 1910°	radius	Mg ₂ ⁺	0.78 Å
Fe ₂ SiO ₄	1205°		Fe ₂ ⁺	0.83 Å.

Thus, magnesium has been concentrated preferentially in the earlier, and iron in the later crystallates from the magma. On the larger scale, magnesium must be relatively more abundant in the deeper silicate shell of the earth than in the lithosphere.

When we turn to the minor elements, present in atomic dispersion in minerals, we may infer that here again ionic radius has been one significant factor governing their distribution. The growth of our knowledge of chemical crystallography has shown that isomorphous replacement must be interpreted on a wider basis than is envisaged by Mitscherlich's law. Provided that an ion is metrically compatible with the lattice dimensions of a crystal, it may be able to replace another ion of different valency, the electrostatic balance between cationic and anionic charges being compensated either by another replacement elsewhere in the lattice, or else by the occurrence of one or more vacant lattice sites. This process, very clearly demonstrated by the chemistry of the silicates (cf. Bragg, 1937), we may conveniently term isomorphous replacement of the second kind. It follows that the mineralogical behaviour of the elements - i.e. their association with other elements and their role in mineral structures - is determined by their

* This term is convenient, since there are several correction terms, some not inconsiderable in magnitude, that must be taken into account in a rigorous computation of lattice energy.

ionic radii rather than by their ordinary chemical characteristics, as is shown, for example, by the coordination numbers of the ions in oxide structures (Table 7).

From Table 7 we may note how aluminium can replace, in silicate structures, either the silicon in 4-coordinate positions, or magnesium in 6-coordinate positions. Lithium, in virtue of its small ionic radius, necessarily replaces magnesium in 6-fold coordination, and cannot play the same part as do the other alkalis (coordination number 8). Titanium, similarly, must occupy 6-coordinate lattice positions, and cannot replace silicon, even though it is formally quadrivalent.

TABLE 7

Coordination Numbers of Ions in Oxide Structures.

Ion.	Radius Ratio.	Coordination Number.	
		Observed.	Predicted.
B ³⁺	0.20	3 and 4	3 or 4
Be ²⁺	0.25	4	4
Si ⁴⁺	0.38	4	4
Al ³⁺	0.41	4 and 6	4 or 6
Li ⁺	0.44	6	6
Mg ²⁺	0.47	6	6
Ti ⁴⁺	0.55	6	6
Na ⁺	0.56	6	6
Se ³⁺	0.61	6	6
Zr ⁴⁺	0.63	6 and 8	6
K ⁺	0.76	8	8

Note. - These radius ratios are based on Pauling's univalent ionic radii; radii quoted in the text are effective, or Goldschmidt radii.

Although ions of different valency and slightly different size from those proper to a given lattice site can thus be incorporated in a growing crystal, it is evident that such isomorphous replacement will not be without effect on the cohesive energy. The sense of this effect may be seen from the expression given for the Madelung energy of the lattice. Hence, in the crystallisation of the earth's minerals from a complex melt there was a sorting action exercised on the basis of ionic radii and ionic charge of the minor constituents.

In the first place, amongst ions of the same valency, the smaller ions must have been taken up preferentially into the crystal. Larger ions, in consequence accumulated in the mother liquors. For this reason, rubidium, caesium and thallium did not normally replace potassium in silicate minerals (ionic radii: K⁺, 1.37Å.; Rb⁺, 1.49Å. ; Cs⁺, 1.65Å. ; Tl⁺, 1.49Å.), and were ultimately concentrated almost exclusively in the minerals of the pegmatite dykes and other late crystal fractions. Conversely, where (as in the pairs nickel-magnesium, zirconium-hafnium) the ionic radii were very similar, little separation could arise during crystallisation. Thus, the magnesium-nickel ratio remained fairly uniform throughout all stages of crystallisation of silicate magmas.

The valency effect is even more significant than the ionic radius in determining the ease with which isomorphous replacement occurs. As between two ions of similar radius

but different valency, the ion of higher valency is taken up preferentially in the earlier crystallate, that of lower valency accumulating in the mother liquors. The ions of scandium and lithium differ little in radius from the magnesium ion (radii: Sc⁺⁺⁺, 0.83Å.; Li⁺, 0.78Å.). Scandium was therefore incorporated preferentially in place of magnesium in the early crystallates (e.g., early pyroxenes). We may logically infer that scandium is actually more abundant in the earth than analyses of the lithosphere suggest, most of the scandium having been taken up in the formation of the rocks of the deeper silicate shell. Lithium, on the other hand, replaces magnesium to an increasing extent in the later crystallates, as the following figures, taken from Goldschmidt (1937), show:

	Ratio $\frac{\text{Li}_2\text{O}}{\text{MgO}} \times 10^4$
EARLY crystallates Peridotite	0.12
Pyroxenite	0.17
Diorite	10 (upper limit)
LATE crystallates Syenite	20
Nepheline syenite	70
Granite	600

It is interesting to note, in passing, that the presence of all the rare alkalis in certain minerals, such as lepidolite, is accidental in that it arises from two causes. In the case cited, lithium has accumulated to replace magnesium because of its lower valency, while rubidium and caesium have replaced potassium because of their larger ionic radii.

The figures just quoted show how our conclusions can be put to the test of experiment over a limited range amongst the materials of the lithosphere. On a much larger scale, the selective incorporation or rejection of minor elements between the deeper silicate shell and the lithosphere must have removed certain elements in large measure from our accessible world, while disproportionately increasing the concentration of others. Evidence that this has been done is obtained when we compare the abundance of the elements in the lithosphere and in stony meteorites which, for reasons mentioned earlier, are probably representative of the whole silicate phase. As Table 8 shows, elements that should have entered the early crystallates are, in fact, impoverished in the lithosphere, those that should have remained for the last crystallates are relatively enriched.

For the chemist, these data have interest as bearing on the question of the mutual association of the elements, and the sources from which rare elements may be obtained. It has been pointed out by various workers (Papish and Holt, 1930; Brewer and Baker, 1936) that the association of elements within the same horizontal period of the Periodic System is frequently more striking than that of elements of the same group - for example, the occurrence of every element from copper to selenium in zinc blende, and the customary association of indium with tin.

TABLE 8

Comparative Compositions of Lithosphere and Meteorites.

		Silicate Meteorites. (Concentrations in Grams per Ton.)	Lithosphere. (Concentrations in Grams per Ton.)	Ratio.
Early	Cr	3,200	200	0.06
Crystallates	Mg	137,000	21,000	0.15
	Zr	80	190	2.3
	Na	3,700	21,400	5.8
Late	Li	5	65	13
Crystallates	K	1,700	25,900	15
	Sr	20	420	21
	Ba	5	390	78

In the light of Noddack's arguments this loses some of its force, but it probably does reflect the systematic change in ionic radius which makes isomorphous replacement possible. Where, as in the transition series, a sequence of elements can display the same valency, with a very gradual decrease in ionic radius, the mutual association is particularly marked. The rare earths, of course, exemplify this very clearly.

The progressive rejection of certain elements by the growing solid phase must have led to their accumulation in the residual mother liquors of the magma. The elements concerned will have been those that cannot readily be built into ordinary silicate structures on account of their excessively small (e.g., B³⁺) or excessively large ionic radius. In the latter category belong the rare alkalis, the rare earths, thorium, niobium, tantalum, tungsten and uranium. The material of these mother liquors is found in the minerals of the pegmatite dykes, which have therefore become the collectors of rare elements in the lithosphere. It is proverbial that the typical minerals of these elements (e.g. samarskite, tantalite, uraninite) are extremely complex, and the local association of these minerals in a few regions, such as the Scandinavian mountains, is very striking.

In conclusion, we may notice that these elements, which we know only as very minor constituents of our world even after the gigantic enrichment experiment of the earth's solidification, must be truly rare in the cosmic sense. Among them, because derived from uranium and thorium, are the radioactive elements, so that the consequential phenomena of radioactivity - for example the development of heat within the earth's crust - must be largely concentrated within the lithosphere.

The subject of our consideration in this lecture lies, as was said at the outset, on the border of several sciences. Much of it, no doubt, belongs to the proper province of the geologist, and may bulk large in the geology of the future. Nevertheless, its recent rapid growth has come largely from the hands of the physical chemist. To both chemist and geologist, it sets old facts in a new light, and opens up vistas of problems not soon to be exhausted.

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