THE RELATIVE ABUNDANCE OF THE ELEMENTS

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Interest in the elemental composition of his surroundings must have developed in man almost as soon as the concept of elementary forms of matter was originated. Empedocles (450 B. C.) is supposed to have been the first to propose the four elements air, earth, fire and water; he attempted to state the composition of flesh and bones in terms of these elements. But accurate methods of chemical analysis had to come before the quantitative study of the rocks which make up the earth's crust. After Bunsen turned his attention from organic to inorganic chemistry he developed an interest in petrology, studying in particular the composition of rocks he had observed in Iceland. A table derived from Bunsen's data of the average composition of the solid crust of the earth was published in Newth's *Inorganic Chemistry*:

Relative abundance of the elements

	Percent	
O	44.0—	47.7
Si	22.8—	36.2
Al	9.9—	6.1
Fe	9.9—	2.4
Ca.	6.6—	0.9
Mg	2.7—	0.1
Na	2.4—	2.5
K	1.7—	3.1
	100.0	100.0

Many other determinations of the elemental composition of the earth's crust have been made since the time of Bunsen, but one of the most comprehensive was that of F. W. Clarke and H. S. Washington published in 1924 (1). Their figures, which were based on some 5,000 ''superior'' analyses selected from more than 8,000 analyses of igneous rocks, have been widely quoted in chemistry textbooks. The rocks came from every continent and major island group. Clarke and Washington assumed that the composition of the crust to a depth of 10 miles below sea level would not vary greatly from that of the volcanic outflows and other rock forms observable at the surface. The volume of matter involved, including the mean elevation above sea level, amounted to 1.6×10^9 cubic miles; matter had an average specific gravity of about 2.6. The surface layer was estimated to consist of 93 percent solid and 7 percent liquid, the atmosphere making up a scant 0.03 percent by weight. It was observed that the average composition of the lithosphere was very nearly the same as the composition of the igneous rocks alone. This is due to the great preponderance of the latter. The estimate given for the relative abundance of the rock types follows:

	Percent
Igneous	95
Sedimentary	5
Shale	4
Sandstone	0.75
Limestone	0.25

The metamorphic rocks were not included since their quantities were presumed to be too small to seriously modify the final averages. The adjusted figures as given by Clark (2) agree quite well with later figures by other investigators. They show 99.5 percent of the outer ten miles of the earth to be made up of eighteen elements as follows:

	Percent
Oxygen	49.20
Silicon	25.67
Aluminum	7.50
Iron	4.71
Calcium	3.39
Sodium	2.63
Potassium	2.40
Magnesium	1.93
Hydrogen	0.87
Titanium	0.58
Chlorine	0.19
Phosphorus	0.11
Manganese	0.09
Carbon	0.08
Sulfur	0.06
Barium	0.04
Nitrogen	0.03
Fluorine	0.03

The relative abundance of the elements in terms of the number of atoms can be derived by dividing the weight percentages by the atomic weights. When this is done the greatest differences are observed in the case of hydrogen and other light elements such as carbon and nitrogen. The first eighteen elements on this basis are shown below. The figures are derived from the data of Anderson published in 1942 (3).

	Relative no. of atoms ×10⁻⁵
Oxygen	3094
Hydrogen	863
Aluminum	278
Sodium	114
Calcium	84.6
Iron	84.1
Magnesium	79.3
Potassium	61.4
Titanium	12.1
Carbon	6.66
Chlorine	5.36
Phosphorus	3.87
Nitrogen	2.14
Sulfur	1.87
Manganese	1.64
Fluorine	1.42
Chromium	0.634

These are followed by lithium, vanadium, nickel, zinc, barium, zirconium, strontium, and copper, in that order.

The composition of the earth below the region of igneous rocks is largely speculative. Estimates of volume and mass of the earth lead to the conclusion that the density of the earth as a whole is considerably greater than the density of the surface rocks. The overall density appears to be 5.52 g./cm.³ whereas the density of granite and basalt are 2.75 and 3.3 g./cm.³ respectively. To account for this a region of much higher density must be assumed.

The composition of meteorites has led to the conclusion that an iron-nickel core is present in the earth. V. M. Goldschmidt proposed (4) a series of layers (fig. 1) which could have been formed by the cooling of a
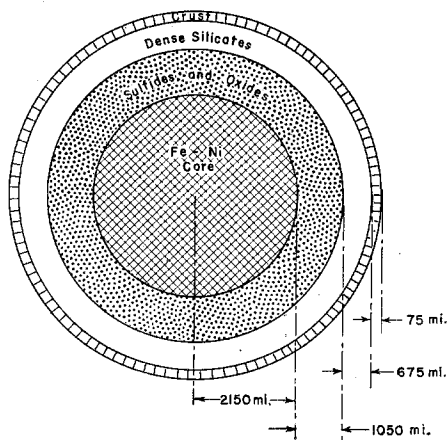

FIG. 1.—Layers formed by cooling of a gaseous or fused mass. (After V. M. Goldschmidt.)

gaseous or fused mass. The inner iron-nickel core has a radius of approximately 2150 miles. Above this is a layer of oxide and sulfide ores of density 5-6 g./cm.³ extending outward for another 1000 miles Surrounding this sulfide layer is a dense layer of highly compressed solid silicates having a density of 3.6-4 g./cm.³ This eclogitic layer extends to within 75 miles of the surface. Goldschmidt compares this system to the layers formed during the metallurgy of copper. The lower layer of metal is covered with a copper matte made up of metallic sulfides and above that floats a slag made up of silicates. The composition of the crust is thus determined by the ability of the slag or silicate layer to extract the various metals and oxides.
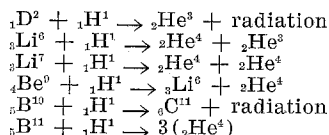
Goldschmidt believed that meteorites may have solidified with separation in a similar way but that the eclogitic layer was not possible because of insufficient pressure in small meteorites. There is some speculation that meteorites tend to lose their silicate shells while passing through the outer atmosphere of the earth. Maskelyne (5) proposed that the frictional heating of the meteorite due to its high velocity causes the shell to be heated to incandescence and to expand and fly away from the central mass with explosive violence. Thus the surface layer has been left as a trail of meteoric dust and only the core reaches the earth's surface. The composition of meteorites classes them as iron, stony, or carbonaceous metorites. The last class is very small, although it is possible that very few carbonaceous meteorites reach the earth's surface without

being completely consumed by the oxygen in the atmosphere. The other two classes merge into one another. For instance the stony meteorites almost invariably contain nickel-iron. The almost total absence in meteorites of quartz and feldspars, the most common minerals in the earth's crust, is further evidence of the disintegration of the outer shell of the meteorite. An average of 318 analyses of iron meteorites gives 90.85 percent iron, 8.52 percent nickel and 0.59% cobalt which is in fair agreement with analyses of terrestrial iron found in Greenland.
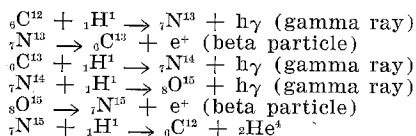
It is apparent, then, that with such inadequate data on the composition of all but 0.1 percent of the radius of the earth it is difficult to arrive at an overall abundance ratio. Clarke (2) roughly estimates iron 67.2 percent, oxygen 12.8 percent, silicon 7 percent, and nickel 4 percent. The percentages of all the other elements are small.

The first adequate and complete tabulation of modern universal relative abundances was made by Goldschmidt (6) in 1938. His sources were principally analyses of meteoric composition and stellar spectra. Still more recently Brown (7) worked out new tables of stellar abundances of the lighter elements, meteoric abundances, cosmic abundances of the elements, and cosmic abundances of nuclear species. In general there is reasonably good agreement between the relative abundances determined in various regions of the universe. Terrestrial and meteoric composition differs from stellar principally in the more volatile elements hydrogen and the rare gases. Varia-

tions in the percentages of the light elements with atomic numbers 1 through 7 (including deuterium) are accounted for by the thermonuclear reactions between protons and the nuclei of the lightest elements of the periodic system. Gamow (8) postulates the following reactions as occurring successively as the temperature of a steller body heats up from 1 million to 20 million degrees:

$$_1D^2 + {_1}H^1 \rightarrow {_2}He^3 + \text{radiation}$$
$$_3Li^6 + {_1}H^1 \rightarrow {_2}He^4 + {_2}He^3$$
$$_3Li^7 + {_1}H^1 \rightarrow {_2}He^4 + {_2}He^4$$
$$_4Be^9 + {_1}H^1 \rightarrow {_3}Li^6 + {_2}He^4$$
$$_5B^{10} + {_1}H^1 \rightarrow {_6}C^{11} + \text{radiation}$$
$$_5B^{11} + {_1}H^1 \rightarrow 3({_2}He^4)$$

The processes of energy formation in the sun and other stellar bodies which have passed the 20 million degree temperature mark do not consume the lighter elements other than hydrogen if the carbon-nitrogen cycle of Bethe and Weizsäcker proposed in 1938 is correct. This cycle, which requires five million years, consists of the following six reactions in which four hydrogen atoms (protons) are converted into one helium atom with the evolution of two beta particles and three quanta of energy as gamma rays:

$$_6C^{12} + {_1}H^1 \rightarrow {_7}N^{13} + h\gamma \ (\text{gamma ray})$$
$$_7N^{13} \rightarrow {_6}C^{13} + e^+ \ (\text{beta particle})$$
$$_6C^{13} + {_1}H^1 \rightarrow {_7}N^{14} + h\gamma \ (\text{gamma ray})$$
$$_7N^{14} + {_1}H^1 \rightarrow {_8}O^{15} + h\gamma \ (\text{gamma ray})$$
$$_8O^{15} \rightarrow {_7}N^{15} + e^+ \ (\text{beta particle})$$
$$_7N^{15} + {_1}H^1 \rightarrow {_6}C^{12} + {_2}He^4$$

Having established that the relative abundance of the elements is very nearly uniform throughout the universe it becomes desirable to learn the rules controlling the abundances and the theoretical explanations of these rules. One of the first rules to be observed is that abundance decreases with either increasing atomic
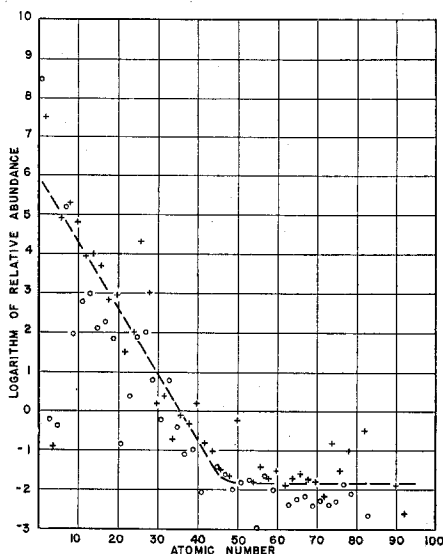

FIG. 2.—A plot of the logarithm of relative abundance vs. atomic number.

number or atomic mass. A plot of the logarithm of relative abundance vs. atomic number is given in fig. 2. The data are from Brown (7); the relative abundance is taken with respect to 10,000 atoms of silicon. An outstanding feature of the plot is the rapid decrease in abundance up to atomic number 45. From that point on the abundance is nearly constant.

Another rule, which has long been observed, is the greater abundance of elements of even atomic number over those of odd atomic number immediately preceding or following. This is particularly noticeable if the elements of the transition groups are investigated. In fig. 3 the logarithm of the abundance is plotted against atomic number. The elements of the third, fourth, and fifth periods of the periodic chart are superimposed (with adjusted scale to bring the fourth and fifth period elements in line with those more
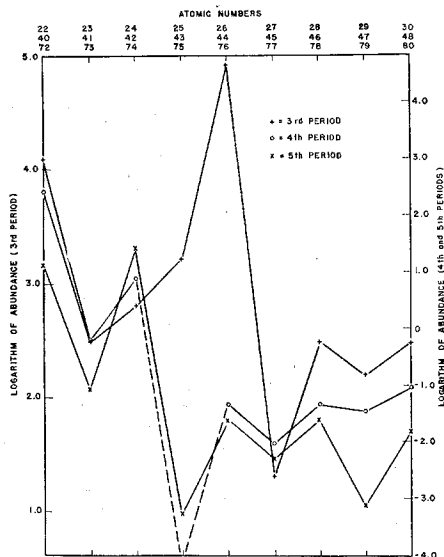
FIG. 3.—Logarithm of abundance plotted against atomic number.

FIG. 4.—A plot of packing fraction against atomic mass.

abundant members of the third period). The data are those of J. S. Anderson (3). The abundances are derived from percentages by dividing by the atomic weights and multiplying by 10^8. It is observed that the values for manganese and iron are out of line. This "superabundance" of elements with masses in the neighborhood of 50 has been explained in terms of their low packing fractions. A plot of packing fraction against atomic mass (fig. 4) shows a minimum for elements with atomic masses of the same order as iron and manganese. Packing fraction is de-
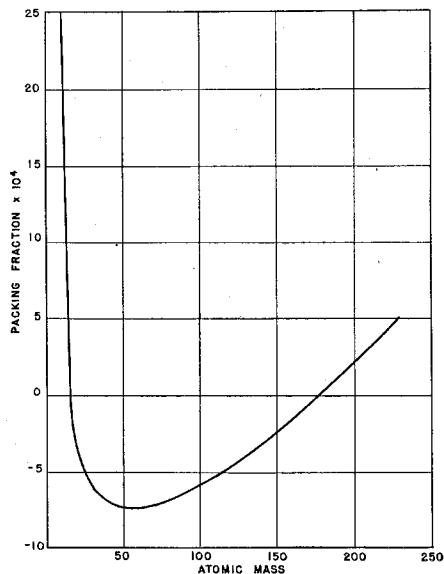
fined as the ratio of mass excess to mass number.

Not only are atoms of even atomic number usually more abundant than those adjacent atoms of odd atomic number, but atoms of even mass number are commonly more abundant than atoms of mass number one greater or one less. In this connection it is interesting to note that of 40 elements of odd atomic number listed in isotope tables, 23 are believed to exist in only one isotopic form with odd mass numbers and 12 others show only two isotopes both having odd mass

$$\text{Packing fraction} = \frac{M - A}{A}$$

where M = actual mass of a particular isotope (equal to the sum of the masses of the protons and neutrons in the nucleus)

A = The mass number of the isotope (the whole number nearest to the actual mass)

For example, the packing fraction of oxygen is:

$$\frac{(8 \times 1.00812) + (8 \times 1.00893) - 16.00}{16.0000} = \frac{0.13640}{16.0000} = 00.008525$$

numbers. Of the remaining five (hydrogen, lithium, boron, nitrogen, and potassium) nitrogen is the only one whose principal isotope is of even mass (99.62% N^{14}) and potassium is the only one known to have three natural isotopes. The potassium isotope of even mass (0.012%) is radioactive.
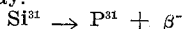
On the other hand, the 43 atoms of even atomic number whose isotopic composition has been determined, show an average of slightly over 5 isotopes per atomic species. Furthermore, among these isotopes of even-numbered atoms, the ones of even mass number exceed those of odd mass number by 3:1 (166 to 56).

A partial explanation of these factors lies in the instability of atoms of uneven number. They may undergo three types of changes:
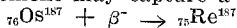
As early as 1873 Clarke (9) indicated the probability that the elements were originally developed by a process of evolution from much simpler forms of matter, as is indicated by the progressive chemical complexity observed in passing from the nebulae through the hotter stars to the cold planets.

In 1930 Goldschmidt (10) proposed that the frequency of occurrence of each type of atom, which appears to be the same in all parts of the cosmos, is determined by properties of the nucleus.

One of the early theories to explain the origin and abundance of the elements was that of Sterne (11) who showed that it was possible to consider by statistical mechanics an assembly containing radiation, atomic nuclei, electrons and neutrons

1. If the element has too little mass for its charge it will decay and liberate a positron.
$$Si^{27} \rightarrow Al^{27} + \beta^+$$
2. If the element has too little charge for its mass it will liberate an electron on decay.
$$Si^{31} \rightarrow P^{31} + \beta^-$$
3. The element may capture a K electron.
$$_{76}Os^{187} + \beta^- \rightarrow _{75}Re^{187}$$
   (This was the first example of K-capture actually observed with a natural isotope.)

Furthermore, for a nucleus to be stable it must have less mass than the combined masses of any pair of nuclei resulting from its subdivision. This would account for the absence of nuclei with masses of 5 or 8 as well as the fact that stable nuclei with even mass number almost invariably have even atomic number. A nucleus with even mass number and odd atomic number usually has an atomic mass greater than one or both of its neighbors and may change into one of both by β-emission or K-capture.

wherein all possible transmutations of the nuclei occur without the "annihilation" of any ultimate particles. He proposed that one could calculate the abundance of the various nuclei in such an assembly, provided it was in equilibrium, in terms of the atomic masses and packing fractions. Sterne believed that these equilibria were established inside of many or perhaps all stars. He concluded that if all nuclei are composed ultimately of electrons and protons then the most abundant element, when equilibrium is estab-

lished at densities between one and one million grams per cubic centimeter and at temperatures which are "not too high," would be the element of even mass number and smallest packing fraction.

Weizsäcker (12) and Chandrasekhar and Henrich (13) believed the equilibrium state represented by the observed abundance curve was determined by nuclear binding energies at some very high temperature and density. Gamow (14) disputes this on the ground that since binding energy is approximately a linear function of atomic weight a rapid exponential decrease of abundance through the entire natural sequence of elements would be required by the equilibrium theory. This could account for the abundance of the lighter elements (fig. 2) but would not account for the approximately constant abundance of the heavier elements. It is not possible to assume that heavy nuclei were formed at higher temperatures and their abundances "frozen" while lighter nuclei were being formed since at 10^{10} degrees K. and 10^6 g/cm^3 density nuclear transformations are mostly caused by the processes of absorption and re-evaporation of free neutrons.

Thus the rates should be essentially the same for light or heavy elements. Gamow further postulates that the conditions necessary for rapid nuclear reactions were existing only for a very short time, perhaps considerably shorter than the β-decay period of free neutrons (about one hour). If free neutrons were present in large quantities in the beginning of the expansion of the universe, the mean density and temperature of expanding matter must have

dropped to comparatively low values before these neutrons had time to turn into protons. The neutrons forming this comparatively cold cloud were gradually coagulating into larger and larger neutral complexes which later turned into various atomic species by subsequent processes of β-emission. The decrease of relative abundance of the elements with increasing atomic mass must have been due to the longer time required for formation of heavy neutronic complexes by radiative capture. The high abundance of hydrogen must have resulted from the competition between the β-decay of original neutrons, resulting in inactive protons, and the coagulation process by which these neutrons were incorporated into heavier nuclei.

Alpher and Herman (15) carefully reviewed all aspects of the equilibrium theory of element formation. They point out that at high concentrations of neutrons the capture probabilities would increase as the material cooled, so that the distribution of elements would be radically changed, especially at high densities. In fact neutron capture reactions give important changes in element abundances even at densities of the order of 10^{-8} g/cm^3.

Alpher and Herman conclude that equilibrium theory applied to an assembly at a single density and temperature does not reproduce the observed relative abundance distribution and that a non-equilibrium theory of element formation requires the specification of detailed nuclear processes, principally successive radiative capture of neutrons with intervening β-disintegration. One difficulty of this

theory is the absence of nuclei with masses 5 and 8 and the high proportion of iron. The polyneutron fission theory which proposes, among other things, that the heavy nuclei are fragments resulting from the breakup of a "cold" nuclear fluid consisting primarily of neutrons does not seem consistent with the conditions which may have existed when the elements first came into being.

It is obvious from this brief discussion that the subject is far from being in a settled state. Part of the difficulty, as pointed out by Brown (16), is that the questions overlap so many of the scientific disciplines. In an age of increasing specialization in science, broad problems of this type cannot be solved rapidly.

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