Astrochemical Problems in the Formation of the Earth

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THE ASSUMPTION that the earth was formed by condensation of a cold cosmic cloud appears to offer a more satisfactory explanation of its composition than does the assumption that the earth was condensed directly from a mass of hot gas.[1] On the latter assumption, it is difficult to account for such facts as the presence of water but the absence of quantities of the noble gases, the constant isotopic composition of matter in the earth and meteorites, and the presence of both metallic and oxidized iron.

The composition of the earth is essentially that of the solid particles which may be presumed to be present in a cold cosmic cloud. The process of condensation then must separate these particles from the large excess of gaseous material and bring them together to form a mass with the characteristics which the geologists ascribe to the earth in its initial state. The essential features of this geological picture[2] are a central core of iron (with about 8 percent nickel), surrounded by a mantle of magnesium and iron meta- and orthosilicates and an outer layer of basalt. In the initial stages there was no surface water, no atmosphere, and no granite masses on the surface—that is, no continents.

Initial Composition of the Cosmic Cloud

Brown (*3*) has summarized the data on the relative abundances of the elements in the sun and stars. His values are given in Table 1. At a temperature of not more than a few hundred degrees Kelvin, a cosmic cloud formed from the elements with these abundances would consist of solid particles and gases. The weight of the gaseous materials was several hundred times that of the solids. Chemical thermodynamics permits definite conclusion as to the compounds present in both the gas and the solid particles. The more important materials are summarized in Table 2, and the thermodynamic data relating to their stabilities at 298° K are given in Table 3. It may be presumed that the average composition of the solid particles was constant throughout the cloud. Because of the large excess of hydrogen and water, stabilities are determined by oxidation-reduction potentials relative to these substances. Oxygen will be present either in very stable solid oxides or as water; the nitrogen as nitrides or ammonia; and the carbon as carbides or methane. A very important problem is that of iron and ferrous oxide.

$$FeO + H_2 = Fe + H_2O,\ \Delta F_{298} = 3.8\ \text{kcal};$$

$$k = \frac{P(H_2O)}{P(H_2)} = 1.6 \times 10^{-3}.$$

From the relative abundances of H and O (Table 1) the ratio $\frac{P(H_2O)}{P(H_2)}$ in the gas phase is 5×10^{-4}. Hence, at 298° K the equilibrium favors the reduction and FeO is unstable. However, if the FeO is combined with SiO_2 to form $FeSiO_3$, the equation becomes

$$FeSiO_3 + H_2 = Fe + SiO_2 + H_2O,\ \Delta F_{298} = 12\ \text{kcal};$$

$$k = \frac{P(H_2O)}{P(H_2)} = 10^{-7}.$$

Hence, $FeSiO_3$ (also Fe_2SiO_4) is stable at 298° K and would remain so below 600° K. This becomes an extremely significant fact, since the amount of oxidized iron will depend upon the SiO_2 available for the formation of the iron silicates. $MgSiO_3$ and Mg_2SiO_4 appear to have equal or greater stability than $FeSiO_3$ and Fe_3SiO_4, and the amount of oxidized iron should therefore depend upon the relative abundance of Mg and Si. From Table 1 the relative abundances are found to be 8870 and 10,000, respectively. The meteoric silicates are approximately 45 percent *ortho*. Hence 8870 Mg would tie up only 6865 SiO_2 and leave 3135 SiO_2 for the formation of iron silicates. Assuming the percentage of the ortho and meta silicates is the same for both Mg and Fe, the ratio of magnesium to oxidized iron is then $\frac{6865}{3135}$, or 2.2. Brown (*2*) has given the weight percentages of magnesium and oxidized iron in the silicate phase of meteorites as 16.62 and 13.23, respectively. The corresponding atomic ratio is 2.9, which is in approximate agreement with the value calculated above, and if a correction is made for the SiO_2 combined with Ca, Na, and K, the agreement would be even better.

[1] This point of view was expressed by Harold Urey, Harrison Brown, and the author at the Rancho Santa Fe Conference on the Formation of the Earth, held under the sponsorship of the National Academy of Sciences, January 23–25, 1950.

[2] The geologists present at the Rancho Santa Fe Conference were in general agreement on the broad aspects of this picture.

TABLE 1

COSMIC RELATIVE ABUNDANCES

Element	Abundance*	Element	Abundance
H	3.5×10^8	A	130–2,000
He	3.5×10^7	K	69
C	80,000	Ca	670
N	160,000	Sc	0.18
O	210,000	Ti	26
F	90	V	2.5
Ne	$10^4 - 10^5$	Cr	95
Na	462	Mn	77
Mg	8,870	Fe	18,300
Al	882	Co	99
Si	10,000	Ni	1,340
P	130	Cu	4.6
S	3,500	Zn	1.6
Cl	190	Ga	0.65

* Atoms per 10,000 atoms of Si.

Condensation of the Earth Cloud

It may be assumed that the initial diameter of the earth cloud was less than half the distance between the orbits of Mars and Venus, or 5×10^{12} centimeters. During the condensation of the cloud under gravitational forces to form the earth, two important processes occurred: one, the loss of the gaseous material and, two, a concentration of the iron particles toward the center of the mass.

The gaseous material escaped even if the total mass (gas plus solids) was several hundred times the present mass, since the gravitational force at the surface of the mass was insufficient to hold the gases until the diameter was greatly reduced. The problem cannot be stated exactly without a knowledge of the surface temperature. The surface toward the sun would be heated, and the gravitational heating would be considerable, as will be discussed later. A temperature of not less than 400° K (*1*) will be taken as a rough estimate (*5*). At that temperature a gas with a molecular weight of 40 would escape until the radius was reduced at least 100 times. It seems probable, then, that in the condensation from a radius of about 2.5×10^{12} cm to 6.37×10^8 cm, even the heavier gases were lost and the earth as originally formed was without an appreciable atmosphere. This is in agreement with the conclusions of Brown (*1*).

During the major portion of the condensation

TABLE 2

PRINCIPAL SUBSTANCES PRESENT IN INITIAL CLOUD

Gases	*Solids* (*continued*)
H_2	Oxides or their compounds of Fe, and all elements more electropositive than Fe, e.g., Fe_2SiO_4, $MgSiO_3$, $Ca_3(AlO_3)_2 \cdot nH_2O$, $Al(OH)_3$
H_2O	
CH_4	
NH_3	
He, Ne, etc.	
Solids	Nitrides, Fe_2N, etc.
Metals (Fe and all less electropositive elements)	Carbides, Fe_3C, etc.
	Halides, CaF_2, NaCl, NH_4Cl, etc.
	Sulfides, FeS, PbS, etc.

process the particles are "falling" through an appreciable concentration of gases. By Stokes' law the velocity of fall is given by the expression

$$V = \frac{2a^2(d - dm)G}{9\zeta}$$

where a is the radius of the particle, d is density, dm the density of the medium, G the acceleration of gravity, and ζ the viscosity coefficient. The density of the particles varies from about 8 for the iron-nickel to 3.5 for olivine and 2.9 for the basalt. Thus from the density difference, the iron-nickel particles would fall with a velocity two to three times that of the silicate mineral. However, it is likely that the iron particles with a simple crystal lattice grew to much greater size than the more complicated silicates, and, since the velocity is proportional to the square of the radius, this factor could have produced large differences in velocities. An iron particle with $a = 10^{-2}$ cm would fall three million times faster than a silicate particle with $a = 10^{-5}$ cm. It seems likely, then, that the process of condensation concentrated the metals toward the center of the earth and also concentrated the heavier orthosilicates around the metal core with the lighter basalt nearer the surface.

TABLE 3

ΔH, ΔF, AND S AT 298° K

Compound	ΔH (kcal)	ΔF (kcal)	S (cal/deg)
H_2	0	0	31.21
NH_3	−11.04	−3.976	46.11
CO	−26.41	−32.81	47.3
H_2O (gas)	−57.80	−54.63	45.10
H_2O (liquid)	−68.31	−56.69	16.71
SiO_2	−205.4	−192.4	10.0
FeO	−63.7	−58.4	12.9
CO_2	−94.45	−94.26	51.06
CH_4	−17.89	−12.14	44.50
$FeSiO_3$	−276	−258.8	(22)
Fe_2SiO_4	−343.7	−319.8	35.4
Fe_3C	5.0	3.5	25.7
Fe_2N	−0.9	2.6	24.2
TiN	−73.0	−66.1	7.20
TiC	−54	−53	5.8

It is possible that the moon was formed in the later stages of condensation. When the diameter was several times that of the final value, tidal waves in the "loose material" may have been sufficient to cause a rupture. Since the heavier iron and mineral particles had already been concentrated toward the center of the earth, the composition and density of the moon formed at that stage would correspond to that of the outer layers of the earth.

The most difficult point to understand in the condensation process is how the enormous gravitational energy could have been dissipated to such an extent that the earth condensed comparatively cold. The total gravitation energy of condensing the solid particles is 2.6×10^{39} ergs, or 10^4 calories per gram. In the early stages of the condensation the escaping gases certainly carried away large amounts of energy, but in the final stages the particles are presumably falling in a near vacuum, and a body falling from only a few miles out from the earth's surface would acquire a kinetic energy sufficient to heat it to several thousand degrees.

The answer lies in the fairly high viscosity coefficient of a cloud of small dust particles even with no gas present and the low terminal velocity which the particles of the cloud would therefore possess. From kinetic theory the viscosity coefficient of a system of particles with a thermal velocity V_k, mass m, and radius a, is:

$$\zeta = \frac{mV_k}{16\,\pi\,a^2}$$

Assuming the thermal velocity for a temperature inside the cloud of 600° K, which is below the temperature at which the hydrated silicates would lose water, the value of the viscosity coefficient for particles of $a = 10^{-5}$ cm is about 10^{-4}. Using this value to calculate the terminal velocity of particles of this size and density $\rho = 3$, one finds

$$V_t = \frac{2a^2\rho g}{9\zeta} = 6.5 \times 10^{-4} \text{ cm/sec.}$$

In view of this low velocity of fall of the cloud, one feels justified in equating the rate of decrease of gravitational energy to the decrease in energy by radiation:

$$\frac{Gm_0m_1dR}{R_0^2} = 4\pi r^2 cT^4 dt,$$

where G is the gravitational constant, m_0 the mass of the earth, m_1 the mass of the particle, R_0 the radius of the earth, c the radiation constant, and t is time. Substituting $V_t dt$ for dR, and simplifying:

$$\frac{T^4\zeta}{a^3\rho^2} = \frac{2}{27}\,\frac{G^2m_0^2}{cR_0^4} = 1.2 \times 10^{10}.$$

This equation assumes that each particle is radiating into space—an assumption that is, of course, not true. And a knowledge of the coefficient of opacity is required for an exact solution (*4*). However, a cloud of particles with radii less than 10^{-3} cm would apparently not acquire a high temperature in slowly falling to the earth's surface.

Heating of the Earth

If the earth was formed as a comparatively cold mass, we must next consider the problem of how its present internal temperature was attained. A calculation of the energy produced by the radioactivity of K^{40} shows that this source of energy is very appreciable. The calculation, using Brown's (*3*) values for the abundance of potassium, follows:

Abundance of K, 0.12 percent.

Total $K = 0.0012 \times 6.1 \times 10^{27} = 0.73 \times 10^{25}$ grams.

K^{40} at present, 0.012 percent of total $K = 0.88 \times 10^{21}$ grams.

Half-life of K^{40}, 1.5×10^9 years, uncorrected for K-capture.

Assumed age of earth, 3×10^9 years.

Amount of K^{40} at time of earth's formation, $4 \times 0.88 \times 10^{21} = 3.52 \times 10^{21}$ grams.

Maximum energy from K^{40} β^-, 1.3 Mev. Mean energy from K^{40} β^-, 0.5 Mev. Energy corrected for K-capture, 0.6 Mev.

Heat produced by reduction of K^{40} from 3.52×10^{21} grams to 1.76×10^{21} grams $= \frac{1}{40} \times 1.76 \times 10^{21} \times 0.6 \times 10^6 \times 2.3 \times 10^4 = 6.1 \times 10^{29}$ calories.

Assuming all K is in the mantle, and weight of mantle is 50 percent of weight of earth:

Heat per gram of mantle $= \frac{6.1 \times 10^{29}}{3.05 \times 10^{27}} = 200$ cal/g.

Specific heat of mantle material 0.2 cal/g.

Rise of temperature $\frac{200}{0.2} = 1000°$ C.

Thus in the first 1.5×10^9 years the K^{40} alone would have increased the temperature of the mantle to about 1300° C. If most of the potassium were concentrated in the outer basalt layer, this region could easily attain temperatures above 2000° C. In addition to the K^{40} effect, the heat liberated by the uranium radioactive series must be considered. A calculation for the decomposition of U^{235} to lead over the period 2.8×10^9 to 9×10^8 years ago gives as the heat produced 3×10^{29} calories, or about 50 percent of that liberated by K^{40}, and a summation of the heat from all the radioactive series would probably add another 25 percent.

Formation of the Atmosphere

As the temperature of the interior of the earth increased, various chemical reactions occurred, a number of which liberated the materials now forming our atmosphere.

1. A portion of the basalt decomposed to give the granite, which rose to form the continents, and dunite, which tended to sink to lower levels.

2. The hydrated silicates and aluminates were broken down with the liberation of steam, which rose to the surface to form the present water.

3. Ferrous oxide oxidized many of the carbides to form CO_2, e.g.,

$$Fe_3C + 2FeO = 5Fe + CO_2;\ \Delta F_{298} = 19{,}000 \text{ calories.}$$

The free energy of the reaction is positive at 298° K, but the entropy of the reaction is about 50 cal/deg; hence, the reaction will go above 500° K.

4. Since the excess of hydrogen has been lost, the newly formed steam will oxidize more Fe:

$$Fe + H_2O = FeO + H_2;\ \Delta F_{298} = -3800 \text{ calories.}$$

Most of the free iron which remained in the outer layers was thus oxidized.

5. Nitrides were hydrolyzed by steam to ammonia:

$$2Fe_2N + 3H_2O = 3FeO + Fe + 2NH_3;\ \Delta F_{298} = -21{,}900 \text{ calories.}$$

Free Fe_2N would have been unstable in the original cloud, but considerable quantities doubtless were present as a dilute solution in Fe. The same is true of the Fe_3C. The ammonia would decompose in the hot regions into N_2 and H_2. Urey has suggested that ammonia was also liberated from NH_4Cl by reaction with basic oxides.

Later Changes in the Atmosphere

At this stage the atmosphere consisted of water vapor, carbon dioxide, nitrogen, hydrogen (which was slowly lost from the gravitational field), and possibly some ammonia. Photochemical changes have added our present supply of oxygen. The hydrolysis of the complex silicates freed basic oxides such as CaO and MgO, which absorbed large amounts of the CO_2. Any ammonia has been oxidized to nitrogen by the oxygen. Argon has been added by the β-decomposition of K^{40}.

The Origin of the Earth Cloud and the Other Planets

Since the earth cloud of gas and dust particles was unstable with respect to its ability to retain the gas, it must have been formed by the breakup of a larger cloud, and the other planets were doubtless formed in the same manner from the same cloud. The characters and origin of the larger cloud are open to considerable conjecture. Von Weizsäcker (*6*) has discussed the mechanics of the condensation of a cosmic cloud to form a sun and planets. The problem has also been treated by Whipple (*7*), and the following postulate is somewhat along the lines suggested.

In the process of condensation of the cosmic cloud (*A* in Fig. 1), it may be assumed that the sun acquired a small diffuse companion (*B*, Fig. 1), either in the original condensation process or from one or two smaller neighboring clouds. This diffuse companion would have condensed to a small companion star, but its rotational and orbital velocities were so large that it was distorted (*C*, Fig. 1), and broke up into smaller clouds (*D*, Fig. 1). The minor planets were formed from the tail or winglike portion of the cloud, and the major planets from the more massive portion. All the minor planets should have condensed to bodies without an atmosphere. The major planetary clouds were all of sufficient mass to hold the lighter gases, and their composition should approximate the total composition of the initial cloud, i.e., the sum of the gases plus the solid particles. Pluto, on the other wing, is presumably more like the earth, and any more distant planets would be expected to be smaller.

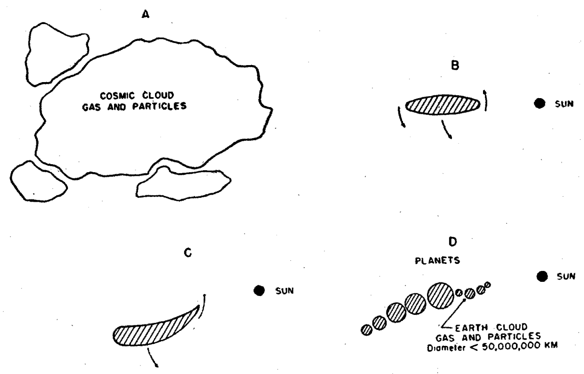

FIG. 1.

The suggested formation of the earth cloud from a diffuse companion of the sun is not essential to the arguments with regard to the development of the earth in its present state; however, the hypothesis does give a reasonable picture of the distribution of mass among the various planets, and some picture is required that gives a common origin of all the solid material of the earth and meteorites to account for their constant isotopic composition.

References

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