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The deficiency of siderophile elements in the Moon

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The deficiency of siderophiles in the crust of the Earth is customarily attributed to leaching by metallic nickel-iron, which eventually sank to form the core. A similar deficiency exists in the Moon, which has, at best, a very much smaller core. Hence it is logical to consider the hypothesis that the Moon formed from the mantle of the Earth, after the siderophiles had been removed.

It is shown that the non-hydrostatic figure of the Moon, and the requirement that the mascons must be supported, together with the high heat-flow, imply that the metal of the Moon is collected in the core. It probably amounts to less than 1 % of the Moon's mass.

Calculations show that if the core is in chemical equilibrium with the lunar silicates, then the nickel has been removed from the Moon as a whole to an extent which is greater than can be explained by theories of direct formation from a nebula.

The only salvation for the idea of direct formation from a nebula appears to be an efficient process of extraction of the siderophiles by successive passage of small amounts of reduced metal through the silicate portion of the Moon.

Since natural processes do not usually operate with the required efficiency, it can be concluded that the formation of the Moon by the fission of the Earth is geochemically plausible.

Introduction

A qualitative argument for the origin of the Moon can be given as follows:

(*a*) By comparison with the cosmic composition (see figure 1) the Earth's crust is deficient in siderophile elements.

(*b*) The usually accepted explanation is that at an early stage in the Earth's history, the metallic and silicate portions of the Earth, which had condensed into liquids or solids, were mixed. At this time, the siderophile elements migrated into the metal, following well-established laws. Eventually, the metal separated from the silicate and sank to the core.

(*c*) The Moon's crust is similarly deficient in siderophiles (see figure 2). These witness, by the above principles, to an early mixture of metal and silicate in the Moon, either as solids or as liquids.

(*d*) But the Moon now has no core; hence a bodily separation of metal from the silicate mass of the Moon is suggested; this points to fission of the Earth as the origin of the Moon.

(*e*) The fission origin cannot be summarily rejected on the ground that the Earth's mantle is richer in volatiles than the Moon (see figure 3); dynamical calculations in fact predict the loss of something like 90 % of the mass of the proto-moon after fission.

In the above comparisons, we have followed the ideas of Wänke (1973) in using a lunar basalt (Apollo specimen 12018) for the lunar crust. We have used a terrestrial flood basalt (BCR-1, Flanagan 1973) for the terrestrial rock. Logically, the comparison should be between lunar mantle material and terrestrial mantle material; but this is impossible. We have therefore compared terrestrial with lunar basalts, in order to minimize effects of differences in petrogenetic processes. One effect of this choice has been to lose track of the lunar iron deficiency; the lunar basalts tend to be higher in iron than terrestrial basalts, for reasons connected with the low oxygen fugacity. For the cosmic composition, we have used the data of Cameron (1975).

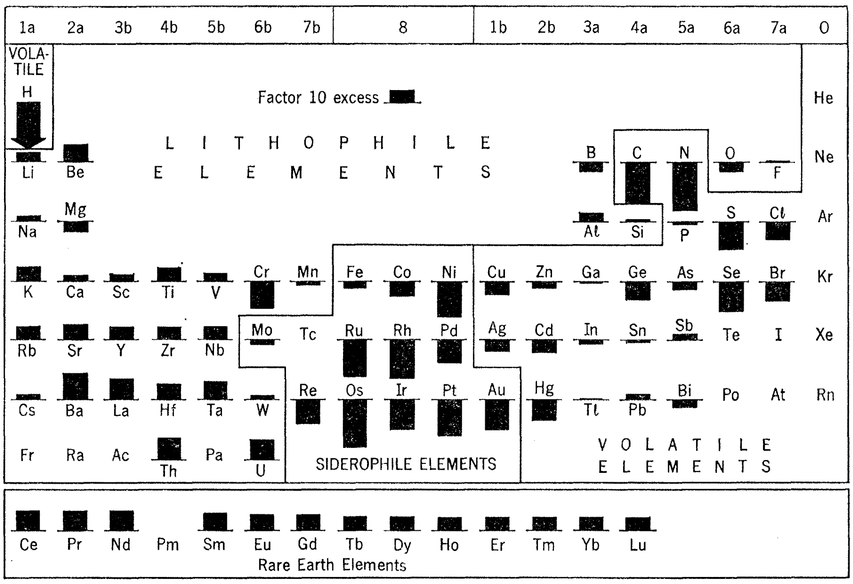

Figure 1. Comparison of standard basalt BCR-1 with cosmic abundances, converted to weight fractions, taking Si as 0.206. Bars proportional to the logarithm of the ratio (BCR-1)/cosmic.

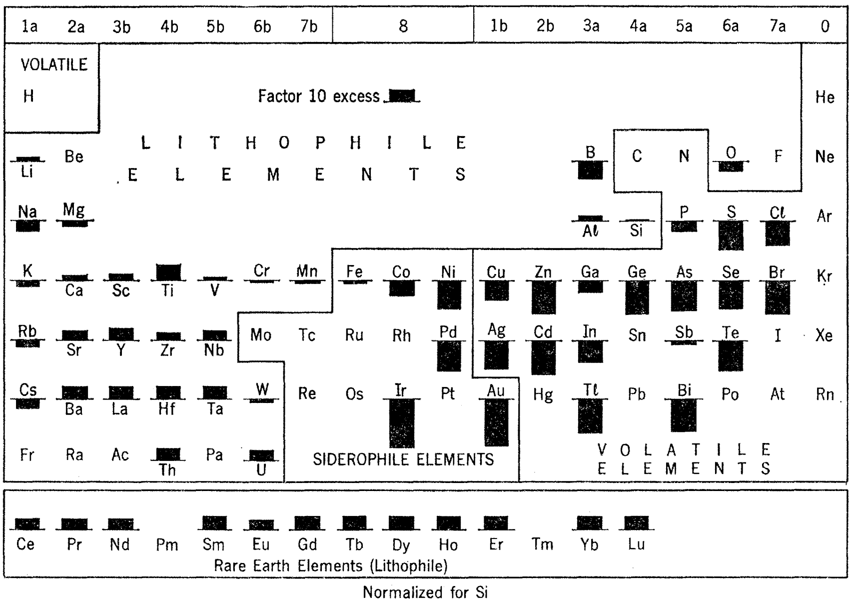

Figure 2. Comparison of lunar sample 12018 with the cosmic abundances converted as in figure 1 above. Wänke (1973) took the analyses of the sample found in the second volume of Levinson (1971) as representing the lunar crust. We have omitted Bouchet *et al.* (1971), which is discordant, and have added the siderophiles from Anders *et al.* (1971) although these do not include 12018. Bars are proportional to the logarithm of the ratio 12018/cosmic.

The loss of matter mentioned under (*e*), which even includes the alkali metals, may have been due to a T Tauri stage in the Sun (Herbig 1954). Alternatively, it may have been caused by intense heating from a common atmosphere surrounding Earth and Moon, as in the double star Beta Lyrae. Both gas and solid matter may have been lost in this process.

Since the sinking of iron to the core is an essential preliminary to fission, it is well to keep in mind the possibility that there may also have been upward mantle differentiation and even crustal formation on the Earth prior to fission. The calculations of Rubincam (1975) suggest that shortly after fission, the Earth's viscosity may have been greater than 10^{15} Pa s, which seems to mean that some crystallization had occurred. Then the fission process may have skimmed off a component enriched in crustal rock.

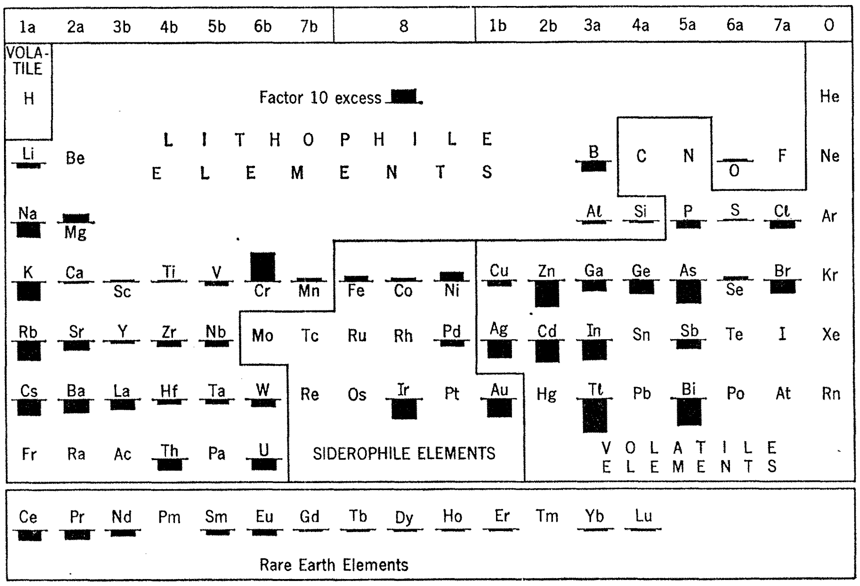

FIGURE 3. Comparison of lunar sample 12018 with BCR-1. Bars proportional to the logarithm of the ratio 12018/BCR-1.

LIMITS ON THE AMOUNT AND DISTRIBUTION OF METAL IN THE MOON

The lunar metal must, at the present time, be concentrated in the core, apart from the small amount (less than 0.1 %) distributed through the rock (Herzenberg *et al.* 1971). The argument is as follows:

(*a*) The non-hydrostatic figure of the Moon, and the mascons, indicate the presence of stress-differences in the interior of the Moon of not less than 20–100 bar (2–10 MPa) (Urey 1952; Urey & MacDonald 1971). The survival of the stress-differences for billions (10^9) of years (at least since the filling of the maria) indicates an effective viscosity near 10^{26} Pa s (Urey & MacDonald 1971) unless they are supported by convection. Since lunar seismic activity is about 10 orders of magnitude below that of the Earth, active convection is not plausible.

(*b*) The observations of shear waves which must have passed through regions as much as 800 km below the surface, and the observations of quake hypocentres at similar depths also imply temperatures below the melting point (Nakamura *et al.* 1974).

(*c*) Thermal history calculations, on the other hand, show that if the heat sources were uniformly distributed at the present time, then the observed 3 μW/cm² of heat flow would imply melting at depths less than 300 km.

(*d*) Therefore the heat sources must now be concentrated near the surface. Urey & MacDonald (1971) emphasized that even with a chondritic rate of heat generation (about half of that observed, i.e. near 1.5 W cm^{-2}) only a very small fraction of the radioactive material can be below the crust. Toksöz & Johnston (1974) point out that no reasonable thermal history of the Moon can be given, consistent with the observed heat flow, which does not concentrate the radioactive elements in the crust.

(*e*) It seems to follow that there was a time, early in the Moon's history, when it was so weak throughout that the forces of magmatic differentiation, working on density differences of the order of 0.4 g cm^{-3}, were effective in moving nearly all the radioactive material to the surface.

(*f*) Then at this time the interior must also have been weak enough to permit nearly all the metal, with a density difference of about 4.4 g cm^{-3}, to move to the core.

We next consider the amount of metal which might exist at the centre of the Moon. Kaula *et al.* (1974) give $C/Ma^2 = 0.395 \pm 0.005$, where C is the Moon's moment of inertia, M its mass, and a its radius. This figure corresponds to a metallic core in the Moon, they find, containing at most 3 % of the total mass. The expected amount is about 0.8 %. (For a homogeneous body the figure would be 0.400; with a crust 60 km thick but no core, the figure is about 0.397.) Kaula *et al.* also consider, and prefer slightly, a model with no core.

From seismic data, Nakamura *et al.* (1974) find that the radius of the metallic (or sulphide) core can be at most about 360 km, corresponding to about 0.9 % of the Moon's volume. This core cannot be pure metal, however, since the seismic compressional wave velocity is at most 5.1 km s^{-1}, they find. Pure metal would give 6 km s^{-1}. The plausible values of 270 km radius and 4.5 km s^{-1} for the compressional wave velocity imply that the mass of metal in the lunar core is less than 0.5 % of the Moon's total mass.

GEOCHEMICAL CONSIDERATIONS

(*a*) *The process of extraction*

The most abundant of the siderophile elements (apart from iron itself) is nickel. Because of its similarity to iron in many respects, the marked fractionation between iron and nickel in the Earth and the Moon is a critical phenomenon for understanding the geochemistry of the Moon.

Since we are interested in setting a lower limit to the amount of free metal which must be present, we suppose the extraction to occur with high efficiency. A small quantity of free iron is produced by the reduction of the iron oxide during the heating event early in the Moon's history. The free iron trickles down through the body of the Moon, and comes into equilibrium with the nickel; a quantity n of the nickel, measured in number of atoms per unit volume, is reduced. Suppose that the remaining number of iron atoms is f, again per unit volume. Then the ratio of free nickel to free iron is n/f; let this be K times the ratio of nickel oxide, N, to iron oxide, F. If the amount of metal trickling through is infinitesimal, then we can write, for a single step

$$n/f = \mathrm{d}N/\mathrm{d}F = K(N/F), \tag{1}$$

since the number of atoms of nickel reduced equals the number of molecules of nickel oxide lost; and the same is true for iron and FeO. Then the result of repeating this process a very large number of times can be approximated by solving the differential equation. Doing so implies that each small increment of liquid metal reaches equilibrium with the silicate mass before trickling down. This approach is useful because it yields the least amount of metal that would suffice to extract the nickel. Solving:

$$\ln N - \ln N_0 = K\,(\ln F - \ln F_0). \tag{2}$$

We want to find out how much iron will be needed to extract the nickel; accordingly we solve for F/F_0, thus:

$$\ln N - \ln N_0 = (K-1)\,(\ln F - \ln F_0) + \ln F - \ln F_0,$$

whence

$$\ln\,(F_0/N_0) - \ln\,(F/N) = (K-1)\,\ln\,(F/F_0). \tag{3}$$

The final amount of metal formed includes both the amount of iron formed by reduction, $F_0 - F$, and the initial nickel supply, N_0, since the nickel is effectively entirely reduced. In terms of the ratios, it is convenient to write the total metal as

$$F_0\{(1 - F/F_0) + N_0/F_0\},$$

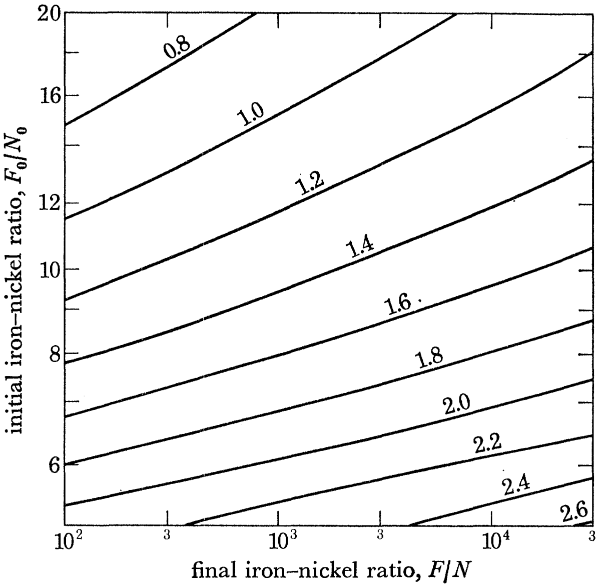

Figure 4. The amount of metal (iron plus nickel) which is needed to reduce the iron/nickel ratio in the lunar silicates from an initial ratio (the cosmic ratio, for example) to the observed final ratio, F/N by an efficient leaching process.

(*b*) *Reaction constant for the reduction of nickel*

The oxidation of nickel is controlled by the availability of oxygen (the redox potential) and this in turn is controlled by the state of oxidation of iron. If oxygen from nickel is made available, it will be used up chiefly in oxidizing iron; and if nickel is to be oxidized, the most easily reduced oxide which is available in quantity is iron oxide. We consider the reaction $\mathrm{NiO} + \mathrm{Fe} \rightarrow \mathrm{FeO} + \mathrm{Ni}$.

From very simple calculations, by using handbook values for the free energies and entropies, and assuming perfect solutions, we obtain, at 2000 K, for the equilibrium constant

$$K = (\mathrm{FeO}/\mathrm{NiO})\,(\mathrm{Ni}/\mathrm{Fe}) = 92.$$

Here the fractions in parentheses are the ratios of the concentrations of the substances. The resulting value of K falls close to the centre of the determinations, experimental and theoretical, cited by Schenck *et al.* (1968). As is clear from their figure and our calculations, the result is not significantly dependent on temperature in the relevant range (2000–1800 K).

(*c*) *Numerical values*

Consider first the results of the efficient extraction process. If we accept the values of iron and nickel concentrations found in lunar specimen 12018 (which Wänke adopted as representing the lunar crust) namely 16.4 % and 78 parts/10^6 respectively, the ratio FeO/NiO is 2100. If we assume an initial ratio of 17, which is near the cosmic ratio, and a total lunar iron content of 9 %, as suggested by Urey & MacDonald (1971), and Parkin *et al.* (1973), we find by solving (3) for the total metal, that at least 1 % metal is needed to extract the nickel successfully from the Moon (see figure 4).

In contrast to the efficient extraction process, an equilibrium relation at 2000 K between iron, nickel and their oxides, would yield a ratio of iron to nickel in the metal of 2100/92 = 23.

APPLICATION TO THEORIES OF THE MOON'S ORIGIN

Clearly the deficiency of lunar siderophiles can be explained on the basis of the fission hypothesis, whether the fission leads directly to two bodies, or indirectly by way of a sediment ring thrown out from the mantle, as Ringwood (these Proceedings) suggests.

Can it also be explained on the hypothesis of the formation of the Moon by accretion from a circumsolar nebula?

Theories which attribute the Moon's origin to accretion must explain the deficiency of iron, compared with the solar or terrestrial iron content, by some kind of fractionation of metal from silicate in a solar nebula. This is awkward, because in the observed nebulae of the dusty kind the optical properties are remarkably uniform from nebula to nebula. The absorption follows a $1/\lambda$ curve over a wide range in wavelength (Heiles 1971; Annestad *et al.* 1973) as if fractionation were a minor process.

Calculations, particularly by Larimer (1967) indicate that if segregation does nevertheless take place, then the siderophile elements will condense preferentially on the iron particles, rather than on the silicate particles. From the thermodynamic standpoint, that is logical; the iron/nickel equilibrium in metals versus silicates will in principle be the same whether they are physically in contact, as in a magma, or only in contact by way of an intervening gas, as in a condensing nebula. But in the real world it does not always work out that way. In condensation from atomic explosions (Norman & Winchell 1966; Winchell 1969) it is observed that one element may coat the surface of a particle which has already condensed, instead of penetrating to the interior. In this case, further preferential condensation of the new element would stop.

If, nevertheless, the processes of nebular fractionation work, then, accoring to Ganapathy & Anders (1974) we should not expect that metal–silicate segregation in the nebula would be complete. It is expected that a minimum of 25 % of the iron, along with its train of siderophiles, will remain in the metallic form mixed with the silicate. The metal, they suggest, is later partly oxidized; they propose models in which either 6 or 4 % of the Moon's mass remains in the metallic form.

Clearly these models do not fit the observations, which suggest that the metal in the Moon's core is less than 1 % of the Moon's mass. The calculations of the percentage oxidized are admitted to be rather shaky, however, and perhaps we should consider the possibility that

90 % or more of the metal is oxidized, leaving only about 1 % of the Moon's mass, or not over 10 % of the iron as metal. Then if the core is in equilibrium with the lunar silicates, it must be about 95 % iron, as noted above. This leads to a contradiction, since the nebular fractionation idea requires us to find a place for about 0.5 % of the Moon's mass as nickel; only 0.05 % is then in the core, and even less in the silicate.

If the metal was once completely or nearly completely oxidized, then it could be re-reduced by the efficient extraction process, as described here. Then the total amount of metal required would be only about 1 %, and this would remove the nickel from the silicate even if it amounted to 0.5 % of the Moon's mass.

Conclusion

The deficiency of siderophile elements in the Moon suggests leaching by liquid metallic iron. The small amount of metal in the Moon then suggests that the leaching took place in the protoearth, and that the Moon thereafter formed from it by fission.

Our analysis indicates that this conclusion is difficult to escape unless the leaching-out of the siderophiles took place by a highly efficient process.

References (O'Keefe & Urey)

Anders, E., Ganapathy, R., Keays, R. R., Laul, J. C. & Morgan, J. W. 1971 *Proc. 2nd Lunar Sci. Conf.* **2**, 1021–1036.

Annestad, P. A. & Purcell, E. M. 1973 *A. Rev. Astr. Astrophys.* **11**, 309–362.

Bouchet, M., Kaplan, G., Voudon, A. & Bertoletti, M.-J. 1971 *Proc. 2nd Lunar Sci. Conf.* **2**, 1247–1252.

Cameron, A. G. W. 1975 *Space Sci. Rev.* **15**, 121–146.

Flanagan, F. J. 1973 *Geochim. cosmochim. Acta* **37**, 1189–1200.

Ganapathy, R. & Anders, E. 1974 *Proc. 5th Lunar Sci. Conf.* **2**, 1181–1206.

Heiles, C. 1971 *A. Revs. Astr. Astrophys.* **9**, 293–322.

Herbig, G. H. 1954 *Astrophys. J.* **119**, 483–495.

Herzenberg, C. L., Moler, R. B. & Riley, D. L. 1971 *Proc. 2nd Lunar Conf.* **3**, 2103–2123.

Jeffreys, H. 1959 *The Earth* (4th ed.). Cambridge University Press.

Kaula, W. M. 1971 *Physics Earth Planet. Interiors* **4**, 185–192.

Kaula, W. M., Schubert, G. & Lingenfelter, R. E. 1974 *Proc. 5th Lunar Sci. Conf.* **3**, 3049–3058.

Larimer, J.W. 1967 *Geochim. cosmochim. Acta* **31**, 1215–1238.

Levinson, A. A. (ed.) 1971 *Proc. 2nd Lunar Sci. Conf.* Cambridge, Mass.: M.I.T. Press.

Nakamura, Y., Latham, G., Lammlein, D., Ewing, M., Duennebier, F. & Dorman, J. 1974 *Geophys. Res. Lett.* **1**, 137–140.

Norman, J. H. & Winchell, P. 1966 *Gulf General Atomic Rep. GA* 7051, 42 pp. P.O. Box 608, San Diego, California.

Parkin, C. W., Dyal, Palmer & Daily, W. D. 1973 *Proc. 4th Lunar Sci. Conf.* **3**, 2947–2961.

Press, F. 1966 *Handbook of physical constants* (ed. S. P. Clark), pp. 195–218. New York: Geological Society of America.

Rubincam, D. P. 1975 *J. geophys. Res.* **80**, 1537–1548.

Schenck, H., Steinmetz, E. & Grundmann, R. 1968 *Arch. EisenhüttWes.* **39**. 895–902.

Toksöz, M. N. & Johnston, D. H. 1974 *Icarus* **21**, 389–414.

Urey, H. C. 1952 *The planets*, Yale University Press..

Urey, H. C. & MacDonald, G. J. F. 1971 *Physics and astronomy of the Moon* (ed. Z. Kopal), pp. 213–289, 2nd ed. New York: Academic Press.

Wänke, H. 1973 *Top. Curr. Chem.* **44**, 115–154.

Winchell, P. 1969 *High Temp. Sci.* **1**, 200–215.