be maintained. The meager evidence which might be used for a qualitative estimate of the pressure points toward a much lower value. The figure of  $1.5 \times 10^5$ atm quoted by Brown and Patterson is based on an assumed equilibrium temperature of 2,000° K. From the considerations outlined above, it is apparent that the temperature figure should be very much higher, and hence the pressure values considerably lower, perhaps even near 1 atm. There is certainly no convincing basis for a proposal of  $10^5$ – $10^6$  atm. On the contrary, the evidence points toward pressures much too low to be "comparable to the internal pressures existing within Mars."

Thus, even if we grant (for the purposes of the present discussion) the questionable assumptions on the basis of which the computations have been made, we come to the conclusion that the more reliable of the data presented lead to temperatures far higher than the 3,000° reported by Brown and Patterson. Furthermore, their estimate of a pressure of  $10^5-10^6$  atm, calculated from an assumed temperature of 2,000° instead of 3,000°, cannot be maintained; for, as has been pointed out, the temperature calculations of greatest significance lead to values about five

times higher than the assumed  $2,000^{\circ}$ ; consequently, the pressures must be far below  $10^{5}$  atm, and a figure as low as 1 atm is entirely consistent with the available data.

Since the temperature and pressure values reported by Brown and Patterson are at variance with those obtained from a careful, critical analysis of the same basic data, any conclusions of cosmological significance drawn from their figures can hardly be proposed as compelling, let alone "irrefutable." While the hypothesis of a single planet of origin for meteorites may be an attractive one (5), as indeed its popularity for almost a century (4) testifies, there is as yet no thermodynamic basis for justifying this assumption.

#### References

- BICHOWSKY, F. R., and ROSSINI, F. D. Thermochemistry of chemical substances. New York: Reinhold, 1936.
- BROWN, HARRISON, and PATTERSON, CLAIRE. J. Geol., 1948, 56, 85.
- 3. KELLEY, K. K. J. Amer. chem. Soc., 1943, 65, 339.
- OLIVIER, C. P. Meteors. Baltimore: Williams and Wilkins, 1925. Pp. 255-263.
- WATSON, F. G. Between the planets. Philadelphia: Blakiston, 1941. Pp. 200-205.

# The Composition of Meteoritic Matter and the Origin of Meteorites

## Harrison Brown

## Institute for Nuclear Studies, University of Chicago

Professor Klotz (6), in his interesting and vigorous discussion of the chemical interpretation by Patterson and the writer (2) of the composition of meteoritic matter, has undertaken an analysis of the possibilities of determining the temperatures within the planet from which meteorites may have had their origin. It is unfortunate that Professor Klotz' discussion evidences misinterpretation of the intent of our survey, of the methods used by us in arriving at our conclusions, of the validity of the data accumulated, and of the relative stress placed by us upon the various points in our argument. Each of these items deserves further comment.

In our investigations an effort was made primarily to see whether or not some sort of chemical order might exist in a field of inquiry where heretofore little order has been found. Our work was stimulated by the hope that, should indications of order become apparent, paths might be opened for fruitful and informative meteoritic research guided by sound chemical principles.

The sources of information utilized in our investigations of meteoritic relationships were varied, including notably:

(1) The variation of the nickel content in the metal phase of stony meteorites with the metal phase content and the relationships between the metal phase of stony meteorites and iron meteorites.

(2) The variation of the distribution coefficient of nickel between metal and silicate phases as a function of metal phase content.

(3) The dependence of the distribution coefficients of various elements between the silicate and metal phases upon the enthalpy change of the general reaction  $M + FeSiO_3 \rightleftharpoons MSiO_3 + Fe$  or  $M + FeO \rightleftharpoons MO + Fe$ .

(4) The major differences existing between the me-

teoritic distribution coefficients of nickel between silicate, metal, and sulfide phases compared with those measured in the laboratory.

(5) The composition of the silicate phase of stony meteorites with respect to eight constituents as a function of metal phase content, and comparison with the composition of plateau basalt and igneous rock.

(6) The ratio of combined iron to metallic iron as a function of metal phase content.

(7) The atomic ratio of silicon to magnesium as a function of metal phase content.

(8) Frequency distribution relationships for various elements in meteorites as compared with distributions in igneous rocks.

(9) The frequency distribution of the metal phase of stony meteorites.

Given the various relationships mentioned above, the problem is to see whether any theory of meteorite origin is consistent with the data accumulated. We attempted to demonstrate that, from the chemical and geological points of view, the century-old planetary origin theory is quite consistent with the data available, *assuming* internal planetary temperatures of the order of those existing within the earth.

One of the more striking meteoritic regularities we stressed was the strong and surprisingly smooth dependence of the distribution coefficients between metal and silicate phases upon the affinities of the various elements for oxygen. In spite of the crudity of the available data, the necessary use of heats of formation of oxides rather than silicates, and the necessary ignoring of entropy and other corrections, this dependence is most marked, covering a range between platinum and magnesium of over  $10^5$ . The dependence of the distribution coefficient upon  $\Delta H$  suggests that elements distributed themselves between meteoritic phases under conditions approaching equilibrium, the appreciable scattering about any smooth curve that might be drawn through the points resulting from a combination of possible effects, notably: (a) The crudity of distribution coefficient data; (b) entropy effects; (c) change of  $\Delta H$  with temperature; (d) pressure effects; (e) the use of oxide rather than silicate data, and (f) the necessary consideration of gross meteoritic matter instead of the stony and iron phases of individual meteorites. (See for example the strong dependence of the distribution coefficient of nickel upon the metal phase content in Fig. 2 in our paper in the Journal of Geology.)

Nickel is the only element for which adequate data exists, for comparison of meteoritic distribution coefficients with those observed in the laboratory. Zur Strassen measured the equilibrium  $Ni + FeSiO_3 \rightleftharpoons$ NiSiO<sub>3</sub> + Fe at 1,840° K and found a value for the equilibrium constant of  $7.25 \times 10^{-3}$ , which is nearly 40 times smaller than the corresponding value of 0.24 observed in gross meteoritic material. One must ask : At the temperatures which one might expect to find in the interiors of the inner planets, can this major difference be explained in a manner which is consistent with the other sources of evidence outlined above? The line of reasoning used by us was as follows:

It seems probable that the temperature at the *center* of the earth is closer to  $2,000^{\circ}$  C than to  $3,000^{\circ}$  C (4). On the basis of considerations by ter Haar and others (5) on the mechanism of planet formation, it would appear unreasonable to expect temperatures much higher than this to exist in the interiors of any of the inner planets. In view of the relatively low mean temperatures to be expected for the *silicate mantle* of the earth (of the order of  $2,000^{\circ}$ - $3,000^{\circ}$  K) and even lower temperatures to be expected for the silicate mantle of the smaller planets, the major discrepancy existing between zur Strassen's measured equilibrium value and the observed meteoritic value appears to be difficult to explain on a temperature increase basis alone.

Prof. Klotz is apparently under the misconception that we estimated the temperature at which equilibrium might have occurred purely on thermodynamic grounds, and then used that calculated temperature in order to estimate the pressure that would be required in order to elevate zur Strassen's observed equilibrium value to that value observed in gross meteoritic matter. Actually, realizing that any estimate of temperature on thermodynamic grounds would be crude at best, we chose a reasonable temperature of an order of magnitude based upon two limits: (a) the lower limit is set by the fact that the material must have been molten, and (b) on the basis of geophysical and astronomical evidence, the estimated internal temperatures within the earth may be used to set an upper limit.

Fortunately zur Strassen measured the nickel-iron silicate equilibrium at two temperatures, thus permitting one to estimate roughly whether or not, by increasing the temperature to a value which is reasonable from the geophysical point of view, an equilibrium constant of the correct order of magnitude could be obtained. Actually, even assuming a substantial value for  $\Delta$ Cp for the system, the temperature required becomes unreasonably high.

We demonstrated that if on the other hand one maintained temperatures not much higher than those útilized by zur Strassen in his experiments (temperatures of reasonable order of magnitude from the geophysical and astronomical points of view), the discrepancy could be explained on the basis of a pressure effect of the order of magnitude of  $10^5$  atmospheres acting upon the system. This one case would of course not be important in itself. It is significant to note, however, that in the only other case where comparison of meteoritic data with laboratory experiment is possible, namely, the distribution of nickel between the metal and *sulfide* phases, a similar discrepancy exists which is even more difficult to explain on a temperature change basis alone.<sup>1</sup> Indeed, it appears that the two effects together cannot be explained on a temperature change basis alone. Yet, as in the case of the silicate equilibrium, the assumption of a pressure effect of the order of 10<sup>5</sup> atmospheres is sufficient to decrease zur Strassen's measured value to the observed meteoritic value. The nickel distribution between sulfide and metal (on which Prof. Klotz did not comment) is all the more significant because the discrepancy is in a direction opposite to the silicate case, and the molar volume change of the reaction is also of opposite sign. Thus the pressure effect estimated from the sulfide case is nearly identical to that estimated from the silicate case. In the silicate case one might conceivably rationalize the data by making rather drastic assumptions as to temperature and  $\Delta Cp$ . But to do so in the nickel-sulfide case becomes difficult in the extreme.

It must be emphasized at this point that nickel distributions in meteorites do not constitute the only source of evidence for a pressure effect. There are several regularities, among them, the combined iron to metallic iron ratio, and the silicon to magnesium ratio, both as a function of metal phase content, which can be understood if one assumes a pressure effect, but which are difficult to understand if it is assumed that meteorites were formed in the absence of a gravitational field of substantial order of magnitude.

Concerning Prof. Klotz' objection to our estimate of temperature by means of the demonstrated increase of distribution coefficient with increasing enthalpy change in the reaction  $M + FeO \rightleftharpoons MO + Fe$ , it must be repeated that no effort was made to determine the precise temperature of the presumed parent body. Indeed, how can one determine the precise temperature of a body which may vary in temperature from a few hundred degrees at its surface to perhaps a few thousand degrees in its interior? Rather, it was our intention to see whether the order of magnitude of the temperature indicated by the gross meteoritic distribution data is consistent with the order of magnitude of temperatures generally believed to exist in the interiors of the inner planets, among them the earth, assuming the various contributions to  $\Delta F$  to be statistically distributed.

In Fig. 3 in our paper in the Journal of Geology we plotted the various distribution coefficients against the enthalpy changes. Weighting each point according to our evaluation of the experimental precision of the distribution coefficients, we estimated the most reasonable slope to be one yielding a temperature of about  $3,000^{\circ}$  C, stressing that "the crudity of such an estimate cannot be over-emphasized." Unfortunately, we did not discuss the method by which we weighted the precisions of the points, believing it to be obvious to anyone reasonably familiar with the difficulties involved in meteorite analysis.

Prof. Klotz has attacked this estimate essentially on the grounds that the greater the enthalpy change, the less important become the other contributions to the free energy change. He suggests that, if one is to estimate temperatures, considerably more weight should be placed upon those cases possessing large enthalpy changes (negative or positive).

This would be correct were it not for an important fact completely ignored by Prof. Klotz: Very large and very small distribution coefficients between meteoritic phases are difficult to determine, the errors being such that large coefficients as determined are usually too low, and the low coefficients are usually too high, by as much as several orders of magnitude. The reasons for this are twofold. First, it is exceedingly difficult to obtain either the metal or the silicate phase in pure form. The metal phase in particular is difficult to obtain completely free of silicate. Second. most meteorite constituents exist in exceedingly small abundance. In such cases, if the distribution coefficient is either very large or very small, the analytical problems become almost insurmountable. As the result of these considerations, the distribution coefficients for those elements possessing high coefficients must be considered lower limits; the distribution coefficients for those elements possessing low coefficients must be considered upper limits. Taking into account the objection to drawing a slope through points possessing low  $\Delta H$  values, the best slope that one can draw in all fairness to the data is one yielding a temperature of the order of 3,000° C. It was our intention to point out only that this is of a reasonable order of magnitude and is consistent with the other points of our argument.

Meteoritic data in their present form are both too crude and too sparse to permit the development of a quantitative proof on chemical grounds alone of the

<sup>&</sup>lt;sup>1</sup>V. M. Goldschmidt (3) was the first to recognize that the nickel content of troilite is in reality quite low ( $\sim 0.1\%$ ). Previously determined high values were obtained probably due to contamination of the troilite by schreibersite.

relationships between meteoritic matter and the earth. In particular, one cannot base conclusions (either pro or con) concerning the planetary origin hypothesis on the basis of an isolated consideration, such as Prof. Klotz has attempted. If this were possible, the planetary origin theory would long ago have been completely discounted on the very real and serious astronomical ground that it is difficult to understand how a single body in our solar system could have been shattered into pieces of meteorite dimensions. Rather, the field of meteoritics is like a complicated mosaic in which the various component parts must be pieced together into a reasonable pattern, and then examined for consistency. We found that on the basis of existing data, from the chemical point of view the planetary origin hypothesis is consistent, as distinct from other hypotheses we examined in the same light.

Much chemical data must be accumulated before one can say definitely that meteorites did or did not have their origin in a planet. It is difficult to believe that, on the basis of existing data, the hypothesis can be refuted. However, with the development of new methods for studying meteorites (1), the time should not be too far distant when precise distribution coefficients are available together with adequate information on distribution coefficients as a function of temperature.

#### References

- 1. BROWN, H., and GOLDBERG, E. Science, in press.
- 2. BROWN, H., and PATTERSON, C. J. Geol., 1948, 56, 85.
- GOLDSCHMIDT, V. M. Geochemische Verteilungsgesetze der Elemente. Oslo: I. kommission, Los J. Dybwad. 1938.
- GUTENBERG, B. (Ed.) Internal constitution of the earth. New York: McGraw-Hill, 1939. Pp. 153-163.
- TER HAAR, D. Det. Kgl. Danske Videnskabernas Selskab, 1948, 25, No. 3.
- 6. KLOTZ, I. M. Science, 109, 248.

