Meteorites

H. J. Hall

graphite → diamond
phase trans

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Comments on two papers by John F. Lovering concerning a typical parent meteorite body

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IN a recent paper, LOVERING (1957b) has presented data and arguments in regard to the subject of this note. He summarizes his conclusions in Table 6 (p. 260). I believe that the conclusions presented in this table are most doubtful or that they have been presented previously. I shall take up the items in this table in the order in which he lists them.

(1) *Silicate/metal nickel fractionation in stony meteorites*

Some years ago BROWN and PATTERSON (1948) attempted to estimate the pressures within a primitive planet assumed to be the parent of the meteorites, from the distribution of nickel between the silicate and metal phases of stone meteorites. LOVERING notes that the chondrites are secondary objects and that the previous estimate is unreliable. He then presents new data on nickel in the olivine and metal phases of pallasites. He finds 150 p.p.m. of nickel in Admire and Allim and 350 p.p.m. in Brenham and Springwater. He averages these to secure 250 p.p.m. and points out that this is three times the amount expected on the basis of ZUR STRASSEN's observations. It seems possible and perhaps likely that some metallic impurity was included in the olivine samples. This was the criticism of UREY and CRAIG (1953) in regard to the BROWN and PATTERSON work. At least a variation by a factor of 2·3 between the amount of nickel in Brenham and Spring-water and that of Admire and Albin needs to be explained in some way, which LOVERING does not attempt to do. Moreover, the temperature chosen by LOVERING is arbitrary in the extreme. He assumes 2000°K for this at some time in the past, but also assumes that cooling to 700°K occurred during some 10^9 years or so. Surely diffusion of nickel over some millimetres or a centimetre would occur during this time and no well-defined equilibrium temperature could exist. Moreover, he uses volume data for pure phases at ordinary temperatures instead of partial molal volumes at high temperatures. Any deduction of pressures on such a basis is so doubtful as to be meaningless.

(2) *Metal/sulphide nickel fractionation in stony-iron meteorites, and*

(3) *Metal/sulphide nickel fractionation in iron meteorites*

LOVERING reports analyses for nickel in the troilite and metal phases of the Rio Loa, Henbury and Toluca irons and the Brenham and Springwater pallasites, and calculates a mean distribution coefficient for each group, namely 0·06 and 0·03 respectively. (I cannot repeat his calculation of these averages from his data.) The differences of these two averages is puzzling, but the differences between the individual distribution coefficients calculated from the five sets of data are even larger, i.e. by about a factor of 10. Thus, if equilibrium was established and if the data are reliable, these iron and stony-irons must have been formed under very different conditions and averaging equilibrium constants can give only doubtful results. Moreover, I cannot repeat the calculation he uses for ZUR STRASSEN's equilibrium constant. JANDER and ROTHSCHILD (1928) give values for $([FeSiO_3][NiS])/([NiSiO_3][FeS])$ at various concentrations of nickel in an equilibrium mixture. The values

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vary, but an extrapolation to zero nickel content gives ~ 1 for the equilibrium constant of the reaction

$$\text{NiSiO}_3 + \text{FeS} = \text{FeSiO}_3 + \text{NiS}, \qquad K = 1$$

ZUR STRASSEN (1930) gives many data for the reaction

$$\text{Ni} + \text{FeSiO}_3 = \text{Fe} + \text{NiSO}_3, \qquad K = 6\cdot53 \times 10^{-3}$$

and finds no trend with concentration. The first reaction was studied at 1700°C* and the second at 1480°C. Calculating the constant for the latter temperature to its value at 1700°C, assuming that the entropy change for the reaction is zero, gives $2\cdot5 \times 10^{-2}$. Now, adding the equations gives

$$\text{Ni} + \text{FeS} = \text{Fe} + \text{NiS}, \qquad K = 2\cdot5 \times 10^{-2}$$
$$T = 1973°\text{K}.$$
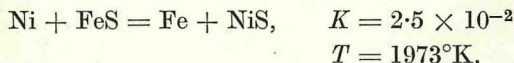
Thus the calculated equilibrium constant and LOVERING's very rough observed values agree without pressure correction of any kind at $\sim 2000°$K. LOVERING gives $K = 1$ at 1200°K in his Table 1, but uses 2000°K in Table 6.† At lower temperatures the higher value of K may be correct, but the imperfections of solid solutions are so great that equilibrium constants extrapolated from the liquid state or calculated from thermodynamic data for pure phases are so uncertain that any conclusions in regard to the effect of pressure on the distribution would be quite inconclusive.

(4) Depression of the γ–α transformation temperatures in the iron meteorites and time to form Widmansättten pattern

LOVERING accepts the high pressures suggested by UHLIG (1954) and reviews further data on the temperature pressure coefficient. So far as the writer is aware, the argument for high pressures is given by UHLIG (loc. cit. pp. 289, 293), and this argument can hardly be regarded as certain. In fact, UHLIG says, "The factor of pressure, therefore, may conceivably prevent transformation of >13 per cent alloys (which at 10^5 atm transform below 460°C) even though the alloys cool slowly through the pressure-depressed transformation temperatures, just as the 34 per cent Ni alloy at 1 atm cools without change below 460°C". Iron–nickel meteorites containing between 13 and 27 per cent nickel consist of finely divided mixtures of kamacite and taenite and are known as the nickel-rich ataxites. UHLIG tries to account for this by high pressures. However, the composition of the octahedrite kamacite and taenite is consistent with crystallization at $\sim 450°$C and low pressure (PERRY, 1944) or at $\sim 250°$C and high pressure, i.e. about 10^5 atm, but not at 700°K (423°C) and 7×10^4 atm pressure, as LOVERING assumes. Diffusion times would be very long if the temperature were 250–300°C. It may be that the nickel-rich ataxites were formed at high pressures and that the octahedrites were formed at low pressures. The possible effect of impurities on these processes is not completely determined. An attempt to decide between 10^5 atm and 7×10^4 atm pressure is most unrealistic in regard to the present state of the problem.

LOVERING refers only to the dates of Thompson and Mayne for the Brenham pallasite

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* JANDER and ROCHSCHILD do not state whether their temperatures are on the Kelvin or centigrade scales, but since they studied liquid equilibria and FeSiO_3 melts at 1455°C, I conclude that the temperatures are on the centigrade scale. The extrapolated value for K was secured by plotting apparent values of K against the nickel concentration in the sulphide phase.

† ZUR STRASSEN's discussion of this equilibrium is very brief and obscure to me. In a footnote he says, "Auf eine Anfrage wegen elticher Unstimmigkeiten, auf die hier nicht eingegangen werden kann, war Herr Priv.–Doz. Dr. JANDER so freundlich uns mitzuteilen, dass die Arbeit einen mehr orientierenden Charakter trage und nur einen Überblick über die Verhältnisse bei Sulfid–Silikatgleichgewichten geben sollte. Deshalb sind aus den Zahlen keine weitergehenden Schlüsse zu ziehen."

and neglects other data in the literature. These dates of Thompson and Mayne are doubtful. Since this work was done, Turkevich, Reed and Hamaguchi have shown that there is very little uranium in the metal of meteorites, as must be expected on thermodynamic grounds. Hence their helium age is doubtful. Their potassium argon age is highly uncertain because of the difficulty of analysing for potassium. They give 0·019 per cent; EDWARDS (1955) found 0·01 per cent. (A repetition of this work by GEISS (unpublished) using different samples resulted in no check on either the argon or potassium analyses.) Any history proposed on the basis of this data is uncertain.

(5) *Graphite–diamond phase transformation in iron meteorites*

The conclusions in regard to this problem are identical with those reached previously by UREY (1956), except for slight differences in pressures and temperatures proposed.

LOVERING credits UREY with reporting the presence of pseudomorphs of diamonds in iron meteorites. This is incorrect. It is unfortunate if an incorrect impression was given. The observations were made in the 1880's, as could easily have been verified by a study of the literature. (This is summarized with detailed references by FARRINGTON (1915), a reference indicated by UREY.)

In discussing high pressures in connection with the meteorites, the writer did not refer to the work of BROWN and PATTERSON, because it seemed pretty well understood that their conclusions were not valid, as LOVERING agrees. I believe that LOVERING's revised figures are inconclusive and that the best evidence for high pressures is given by the presence of diamonds. No other high-pressure minerals are reported. Since diamonds are partly converted to graphite, even this record has been partially lost. It may be that only this most durable mineral, namely diamond, has survived and that all other records, such as the equilibria discussed by LOVERING, have been destroyed.

LOVERING assumes in another paper (LOVERING, 1957a) that the parent of the meteorites was a large object with an iron–nickel core, presumably some 500 km in diameter. He ignores arguments that have been advanced against this. For example, the number of stony irons observed to fall is about 0·3 as many as the observed falls of irons. Since the stony irons are characteristic of the boundaries between the silicate and iron phases, this indicates that the parent bodies were small, perhaps some metres or tens of metres in dimensions. If the stony-iron layer were even a kilometre thick on the surface of a sphere of 500 km radius, only 1/160 of the volume would consist of this material and even small gravitational fields would prevent a mixture of melted iron and solid silicate remaining intact, so that the layer cannot have been so thick. Some specimens of Brenham are partly pallasite and partly quite typical octahedrites, so that a surface region has been observed, which is most improbable if the parent object was large. Also, many iron meteorites have holes and pits which HENDERSON regards as primordial surfaces. These holes have smaller openings than their interior dimensions and they could not have been produced as the broken surfaces from a large iron body. Again, the iron meteorites are comparatively free of gross distortions. Yet any process which would disrupt an object some hundreds of kilometres in diameter would probably produce many pieces of distorted metal! So far as can be seen, LOVERING's discussion of the crystallization of an iron–nickel melt could be applied to a comparatively small mass. In addition, much evidence exists for chemical fractionation of the iron–nickel in meteorites (UREY and CRAIG, 1953). It is most unlikely that the entire variation in nickel content is due to fractional crystallization of an iron–nickel melt containing 11 per cent nickel.

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