(1) Meteorites (3) minerals
(2) Cohenite (4) Geology

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Cohenite as a pressure indicator in iron meteorites—III

Comments on a paper by Lipschutz and Anders

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Introduction

Ringwood (1960) pointed out that the mineral "cohenite" $(Fe, Ni)_3C$, which occurs in many iron meteorites, is highly metastable and in view of the very slow cooling to which irons have been subjected, should have decomposed into graphite plus metal. It was shown that the stability of cohenite was favoured by high pressure. Thermodynamic calculations revealed that a minimum pressure of 25,000 atm would have been required to maintain the thermodynamic stability of cohenite in the temperature range through which irons are known to have slowly cooled.

Lipschutz and Anders (1961a) argued that natural cohenite had been thermodynamically stabilized by the presence of phosphorus in solid solution and that high pressure was not necessary to explain its presence in iron meteorites. This was disproved by Ringwood and Seabrook (1962) who showed that cohenite contains only very small quantities of phosphorus. The observed concentrations are far too small to cause appreciable stabilization. In their latest paper, Lipschutz and Anders (1964) have retracted their previous view and agree that cohenite in iron meteorites is indeed a highly metastable phase and that an explanation for its survival is required.

Lipschutz and Anders (1964) have attempted to provide such an explanation. Their arguments fall into two classes, the first of which is concerned with the thermodynamics and phase equilibria of the iron–carbon system and the second with the kinetics of cohenite decomposition. It will be convenient to consider these separately.

Phase Equilibria and Thermodynamics in the Iron–Carbon System

In the following discussion the term "cohenite" is used to designate the natural mineral whereas "cementite" is used with reference to the corresponding isostructural synthetic phase Fe_3C. Lipschutz and Anders (1961b) carried out an experimental investigation of the decomposition of cementite at high pressures. From their results they concluded that the pressure stabilization of cementite predicted by Ringwood (1960) on the basis of Darken and Gurry's (1951) thermodynamic data did not occur. Accordingly they constructed a revised P, T phase diagram (Fig. 4 in their paper) for the iron–carbon system in which the stability field of cementite was severely restricted. They proceeded to discuss the significance of the occurrence of cohenite in iron meteorites on the basis of their new phase diagram. Their procedure is open to a number of serious objections.

(a) The experimental data used by LIPSCHUTZ and ANDERS were mostly obtained between 450 and 650°C. They concluded from these results that the stability boundary for cementite should be shifted towards higher pressures. By comparing the positions of the $Fe_3C \rightleftarrows 3Fe_\alpha + C$ (graphite) boundaries (AB) in their new phase diagram (Fig. 4) with the position of the same boundary in the phase diagram calculated from DARKEN and GURRY's data (Fig. 3), it can readily be shown that the new diagram requires a change in the *free energy of formation of cementite at zero pressure* of about 2·3 kcal/mol over the whole temperature range. It is inconceivable that an error of this magnitude should have remained undetected in the iron–carbon system which has received more intensive investigation from metallurgists and chemists than perhaps any other comparable system. Some comparisons are illuminating. DARKEN and GURRY (1951) give the free energies for the formation of cementite from carbon-saturated iron and graphite as 0·4 and 0·2 kcal at 700 and 800°C respectively. According to LIPSCHUTZ and ANDERS, the corresponding values would be 2·7 kcal and 2·9 kcal respectively.

(b) LIPSCHUTZ and ANDERS (p. 704) claim that their thermodynamic proposals which are based upon the experimental behaviour of Fe_3C at high pressures "should perhaps be given greater weight than stability relations derived by indirect methods". This statement ignores the fact that DARKEN and GURRY used precise equilibrium measurements of phase boundaries in the iron–carbon system at zero pressure to refine the basic thermochemical data. DARKEN and GURRY's thermodynamic data accordingly are closely consistent with the observed equilibria. On the other hand, LIPSCHUTZ and ANDERS' revised thermodynamic data are grossly *inconsistent* with the 1 atm phase diagram.

A particularly serious discrepancy concerns the position of the cementite-α iron eutectoid. This is experimentally observed to lie about 10°C below the graphite-α iron eutectoid (DARKEN and GURRY, 1951). The small magnitude of this difference shows clearly that the free energy of formation of cementite from graphite and carbon-saturated iron is also small in the vicinity of the eutectoid (0·25 kcal according to DARKEN and GURRY). LIPSCHUTZ and ANDERS would increase this value to approximately 2·55 kcal/mol. This would make it impossible to understand and interpret the observed close proximity of the two eutectoids. In fact, using the LIPSCHUTZ and ANDERS diagram the Fe_3C–Fe_α eutectoid should occur about 100°C *below* its observed temperature. Furthermore, it would result in a eutectoid composition which differed seriously from the observed composition.

(c) In Fig. 4 LIPSCHUTZ and ANDERS have displaced the $Fe_3C/Fe_\alpha + C$ boundary (AB) corresponding to an increase in free energy of cementite of 2·3 kcal/mol. But they have not altered the position of the Fe_γ(C sat.)/$Fe_3C + Fe_\alpha$ boundary JB. Yet such a change in the free energy of formation of cementite as that proposed must necessarily affect this boundary to a comparable degree. On Fig. 4 of their paper the boundary JB must be moved to the left by a considerable amount. The stability field of cementite in Fig. 4 would then disappear.

(d) However, these consequences are in direct conflict with the measured effect of pressure on the cementite eutectoid as determined by HILLIARD and

CAHN (1961), HILLIARD (1963) and RADCLIFFE *et al.* (1963). These authors observed displacements of eutectoid temperature and composition as a function of pressure which were closely consistent with the thermodynamic data of DARKEN and GURRY. On the other hand, they were completely incompatible with the proposals of LIPSCHUTZ and ANDERS.

In Table 1, thermodynamic calculations on the variation of eutectoid temperature and composition with pressure in the iron–carbon system by KAUFMAN (1963)

Table 1. Comparison of thermodynamic calculations on the pressure dependence of eutectoid composition and temperature in the iron–carbon system (KAUFMAN, 1963, p. 343) with values derived from the experimental determinations of HILLIARD, 1963, especially Table 1, p. 434

Pressure (kbar)	Eutectoid composition (calculated) (at. % carbon)	Eutectoid composition (observed) (at. % carbon)	Eutectoid temperature (calculated) (°K)	Eutectoid temperature (observed) (°K)
0	3·61	3·56	996	1000
35	1·57	1·72	938	928
50	1·10	1·16	902	883
65	0·61	0·79	861	853

are given. They may be compared with the experimental results of HILLIARD (1963). The agreement is excellent. Yet KAUFMAN's calculations were based upon thermodynamic data which yielded DARKEN and GURRY's values for the free energy of formation of cementite. The calculations were also performed *prior* to the experimental measurements. LIPSCHUTZ and ANDERS have stated their preference for thermodynamic results based upon direct experiments at high pressure. Why do they ignore the comprehensive experimental investigations mentioned above?

This list of gross conflicts between the thermodynamics of the iron–carbon system as proposed and implied by LIPSCHUTZ and ANDERS with the results of a score or more well known metallurgists of the highest repute could be extended. LIPSCHUTZ and ANDERS are claiming in effect that their own experimental results deserve precedence over the combined results of virtually all previous investigators. It is therefore fitting that we should examine their experimental results and technique.

LIPSCHUTZ and ANDERS (1961b) subjected samples of cementite to varying pressures and temperatures in a squeezer apparatus (Fig. 2 of their paper). The cementite powder was sandwiched between two discs of platinum foil and the sandwich was then compressed to the desired pressure between two chrome carbide pistons. An external furnace provided the desired temperature. After completion of a run the whole sample plus platinum wafers (plus any pieces of adhering decomposed piston) was dissolved in acid and the residue examined by X-ray diffraction. In all runs the authors found some graphite or amorphous carbon, which they attributed to the decomposition of cementite. They also observed in all runs some chromite which they attributed to oxidation of pistons and diffusion of iron through the platinum.

These experiments are open to some obvious objections. The cementite was placed in contact with platinum* which is able to form solid solutions with iron, thereby lowering its activity. The authors noticed that iron diffused from the sample, through the platinum wafer and reacted with the chrome carbide piston. Since one of the reaction products was chromite, $FeCr_2O_4$, it is clear that the system was also open to oxygen from the air.

It is difficult to attach any significance to the inferred decomposition of cementite under the experimental conditions described by the authors. The system which they investigated was not closed to iron and the activity of iron was lowered by reaction with platinum, oxygen and chromium. In such circumstances, partial decomposition of cementite was only to be expected, with iron migrating out of the system and graphite remaining. The observation that oxygen from the air was able to enter the system to form chromite suggests the possibility that it may have gained direct access to the cementite sample causing selective oxidation of iron and leaving residual graphite. Finally, there is no guarantee that the graphite observed was not derived from the piston, and liberated during the selective oxidation of chromium to form chromite.

Lipschutz and Anders claim that they are observing an isochemical equilibrium decomposition of cementite according to the equation

$$Fe_3C \rightarrow C(\text{graphite}) + Fe_\alpha$$

The minimum requirement if this claim is to be sustained would be an unambiguous demonstration of the equilibrium coexistence of the pure phases on the right-hand side of this equation after completion of the experiment. Their experimental technique did not permit this requirement to be established, since after an experiment, the sample was dissolved in acid leaving only carbon (plus chromite) to be identified.

The experiments and interpretation described by Lipschutz and Anders (1961b, 1964) are clearly of a highly dubious nature. It is indeed difficult to accept the claim of these authors that their experimental results call for a revolution in the thermodynamics of the iron–carbon system.

3. Kinetics of Decomposition of Cementite

Lipschutz and Anders (1964) claim that cohenite, although admittedly thermodynamically unstable, has not decomposed during the slow cooling experienced by iron meteorites because of slow nucleation of graphite in the cohenite. They make the statements (pages 709 and 710) "Our own experiments show that absence of nucleation centres inhibits graphitisation of cementite at 680°C by a factor of $>6 \times 10^4$. Data from other authors (Hickley and Quarrell, 1954)

* Lipschutz and Anders (1961b) mentioned that they had carried out a few runs using low carbon steel foil instead of platinum, with no apparent difference to the results. It is to be regretted that the specific results of these experiments were not reported. Results from such runs remain open to the objections stated above—namely, the evidence that the system was not closed to chromium and oxygen and the absence of a demonstration of the presence of *pure* iron coexisting with graphite at the end of the experiment. Under the experimental conditions described, the iron foil would have become seriously contaminated by reaction with the chrome carbide piston.

indicate factors of $>10^5$. In meteorites, factors of 10^{10}–10^{11} are needed. "To sum up the matter: if relatively imperfect cementite crystals heat-treated in the laboratory show inhibition by factors of $>10^5$, is it entirely unreasonable to suppose that the larger and much more perfect meteoritic cohenite crystals were inhibited by factors of 10^{10}–10^{11}?"

We will leave readers to ponder the latter question and reserve comment for the first part which claims that variations in graphitisation rates of cementite of greater than 10^5 *have been experimentally observed.*

ANDERS and LIPSCHUTZ obtain the factor of 10^5 by comparing their own results on the heat treatment of a pure iron–carbon alloy composed of iron and cementite with the results of KLEIN (1934) who determined the rate of decomposition of cementite in the presence of graphite nuclei. The information is plotted in Fig. 5 of their paper, which is accompanied by the caption "Cementite samples heated at 680°C for 1946 hr failed to show any graphitisation whatsoever although *similar* (my italics) samples with pre-formed nucleation centres show one per cent of graphitisation in 0·03 hr." (The former results are those of LIPSCHUTZ and ANDERS, whilst the latter are those of KLEIN.)

Now in a kinetic study aimed at investigation of the effects of the presence or absence of graphite nuclei on decomposition rate it is essential to keep other variables such as composition constant if valid comparisons are to be made. Yet, on consulting Klein's original paper we find that he worked on an impure cast iron containing 1·65% Si, 0·5% Mn, 0·18% P and 0·13% S. It is well known that silicon behaves as a graphitising agent in steels. *It is completely invalid to compare reaction rates in two steels of such contrasting compositions and then to attribute differences observed solely to the presence or absence of graphite nucleation centres.* LIPSCHUTZ and ANDERS in the caption to Fig. 5 (quoted previously) state that the samples which they investigated were *similar* to those which Klein investigated, differing only in the presence of pre-formed nucleation centres. This statement is incorrect and seriously misleading.

LIPSCHUTZ and ANDERS (p. 709) claim that experiments by other authors (HICKLEY and QUARRELL, 1954, is the only reference given) have "indicated" that the presence or absence of nucleation centres affects graphitisation rates by factors $>10^5$. After studying the reference, I find acceptable evidence for variations in graphitisation rates of the order of 100, not 100,000.

One further point: On page 710 LIPSCHUTZ and ANDERS attempt to explain why cohenite does not decompose in the absence of graphite nuclei. "Finally, the free energy difference between cementite and graphite is so small near the formation temperature that it may be more than offset by the surface energy which will favour millimeter sized cohenite crystals over angstrom-sized graphite nuclei." The first phrase of this statement is correct if the thermodynamic results of DARKEN and GURRY are used. However, the authors appear to have forgotten that earlier in their paper they claimed that DARKEN and GURRY's value for the free energy of formation of cementite was wrong by 2·3 kcal/mole.

4. CONCLUDING REMARKS

The authors have drawn attention to the possible role of kinetics in explaining

the survival of cohenite in iron meteorites. This is an important suggestion which deserves careful study. It is to be regretted that the authors have chosen to support it by a combination of dubious experiments and clearly fallaceous thermodynamic and kinetic arguments. Regardless of the merits of the suggestion, such arguments could not be permitted to stand without challenge.

Whether or not the survival of cohenite can be attributed to a difficulty in the nucleation of graphite remains unresolved and requires further investigation. Brett and Ringwood are currently studying the thermal decomposition of meteoritic cohenite. They have found that cohenite from Cosby's Creek completely decomposed to iron plus graphite after 180 days at 650°C. Cohenite (*in situ*) in Coolac was extensively graphitised in the same interval. We noticed that graphitisation was initially more rapid along cracks. Ultimately, however, graphitisation commenced at centres which were scattered approximately randomly throughout the crystal. In some regions, the nucleation showed a crystallographic control, the centres following one of the principal crystallographic planes in the cementite structure. Nucleation in the bodies of these natural cohenite crystals occurred at points for which no evidence of previous cracks or inhomogeneity was present at the highest optical magnification. These observations do not support the views of Lipschutz and Anders (1964, p. 707) regarding the decomposition of meteoritic cohenite.

The observation that natural cohenite decomposes completely or extensively in 6 months at 650°C and that the decomposition is not obviously controlled by pre-formed nuclei must surely be relevant to the problem of its occurrence in irons which have probably cooled through the temperature interval 700–600°C over a period of 10^6–10^7 years. Whilst there is no doubt that nucleation is an important, probably the most important, rate controlling factor in the decomposition of cohenite, it will require a much more competent and comprehensive investigation than that of Lipschutz and Anders to make plausible the view that a nucleation difficulty is solely responsible for the enormous discrepancy between the observed decomposition times and the inferred slow cooling of meteorites. Differing nucleation conditions have been observed to change graphitisation times by a factor of approximately 100 (Hickley and Quarrell, 1954); to explain the survival of cohenite in meteorites, a factor greater than 10^6 is needed.

Until such evidence is produced the pressure stabilization hypothesis is to be preferred in the author's opinion. However, it is desirable to reconsider some quantitative aspects of this hypothesis in the light of the current uncertainty concerning kinetics. Previously, it was assumed that equilibrium was maintained down to a temperature of 450°C. At this temperature a pressure of 25,000 bars is required to stabilize cementite (Ringwood, 1960). A more conservative view would be to restrict the assumed lowest temperature of equilibration more closely to the temperature interval in which meteoritic cohenite can be decomposed in laboratory experiments. To stabilize cohenite at 650°C, a minimum pressure of 8 kbar would be required (Ringwood, 1960). If the present results can be extended to 600°C, a minimum pressure of 12 kbar is indicated.

Note added in proof

LOVERING (1964) has recently described the occurrence of cohenite in the metallic masses found in basaltic rocks at Disko Island, Greenland. The basalts have crystallized under comparatively shallow (i.e. low pressure) conditions and may have cooled over intervals varying from weeks to years. Despite the long cooling times, decomposition of cohenite into graphite was not observed. LOVERING concluded that the presence of cohenite in meteoritic irons could not therefore be used as an unequivocal pressure indicator.

On the other hand RAMDOHR (1960, p. 340) observed that the decomposition of cohenite into graphite was quite common in irons from Disko. This observation is clearly of crucial importance to the problem. The cooling histories of Disko specimens have clearly varied widely. It is not impossible that the samples examined by LOVERING cooled comparatively rapidly whilst those referred to by RAMDOHR cooled more slowly. It seems that a study of the phase assemblages of Disko specimens in relation to their probable cooling histories, as given by locations within the enclosing basalts, might resolve the controversy.

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REFERENCES

DARKEN R. S. and GURRY R. W. (1951) Free energy of formation of cementite and the solubility of cementite in austenite. *J. Metals* **3,** 1015–1018.

HICKLEY R. H. and QUARRELL A. G. (1954) The graphitisation of steel at subcritical temperatures *J. Iron St. Inst.* **178,** 337–346.

HILLIARD J. E. (1963) Iron–carbon phase diagram: Isobaric sections of the eutectoid region at 35, 50, and 65 kilobars. *Trans. Amer. Inst. Mech. Engrs* **227,** 429–437.

HILLIARD J. E. and CAHN J. (1961) The effect of high pressures on transformation rates, in *Progress in Very High Pressure Research* (Eds. F. P. Bundy, W. R. Hibbard and H. M. Strong) pp. 109–125. John Wiley, New York (1961).

KAUFMAN L. (1963) Phase equilibria and transformations in metals under pressure, in *Solids under Pressure* (Eds. W. Paul and D. Warschauer), Chapter II, pp. 303–356. McGraw-Hill, New York.

KLEIN E. H. (1934) Der zeitliche Verlauf des Zementitzerfalls im Gusseisen *Stahl und Eisen.* **54,** 827–830.

LIPSCHUTZ M. E. and ANDERS E. (1961a) The record in the meteorites—IV. Origin of diamonds in iron meteorites. *Geochim. et Cosmochim. Acta* **24,** 83–105.

LIPSCHUTZ M. E. and ANDERS E. (1961b) On the mechanism of diamond formation, *Science* **134,** 2095–2099.

LIPSCHUTZ M. E. and ANDERS E. (1964) Cohenite as a pressure indicator in iron meteorites? *Geochim. et Cosmochim. Acta* **28,** 699–712.

LOVERING J. F. (1964) Electron microprobe analyses of terrestrial and meteoritic cohenite. *Geochim. et Cosmochim. Acta* **28,** 1745–1756.

RADCLIFFE S. V., SCHATZ M. and KULIN S. A. (1963) The effects of high pressure on the isothermal transformation of austenite in iron carbon alloys. *J. Iron St. Inst.* **201,** 143–153.

RAMDOHR P. (1960) *Die Erzmineralien und Thre Verwachsugnen.* Akad-Verlag, Berlin.

RINGWOOD A. E. (1960) Cohenite as a pressure indicator in iron meteorites. *Geochim. et Cosmochim. Acta* **20,** 155–158.

RINGWOOD A. E. and SEABROOK M. (1962) Cohenite as a pressure indicator in iron meteorites—II. *Geochim. et Cosmochim. Acta* **26,** 999–1010.