

A study of some iron meteorites of the Gibeon association

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SUMMARY. The macroscopic features of a number of Gibeon meteorites have been reviewed and selected specimens have been examined in more detail by metallographic, microprobe, and X-ray diffraction techniques.

A number of specimens appear to have been reheated by man and in these cases reheating temperatures are indicated. Specimens that show no signs of artificial reheating are discussed in relation to the form, distribution, and structure of the kamacite, daubréelite, and troilite. X-ray examination of the kamacite reveals partly annealed shock damage. Small monomineralic inclusions of daubréelite appear to be concentrated in the non-octahedral kamacite and show no signs of alteration. By contrast all the troilite has been remelted and has dissolved contiguous plessite and daubréelite. The remelting of troilite appears to have been induced by shock at temperatures below about 450 °C.

THE association of iron meteorites from Gibeon, South-west Africa, has been known since before 1836 and Gibeon is catalogued by Hey (1966) as a fine octahedrite with a true band width of 0.25 mm and a nickel content of about 8 % for Lion River, Bethany, and Mukerop, and 8.29 % for Amalia Farm. More than 15 tons of this material has been collected and is now widely distributed in museums. An account of the Gibeon meteorites has been given by Spencer (1941), who has drawn attention to the fact that the significance of the individual names may be somewhat uncertain in terms of the original location of fall. Some of the Gibeon irons show macroscopic twin boundaries or large-scale grain boundaries of the parent taenite and recent discussions of this effect have been presented by Hey (1942), Frost (1967), Axon (1967), Axon and Faulkner (1967), and Aladag and Gordon (1969). In addition to the usual Widmanstätten precipitation of kamacite on octahedral planes of the parent taenite a number of instances have been noted of earlier plates that are oriented parallel to the cube face of the parent taenite, and this effect has been reviewed recently by Axon and Faulkner (1967).

A study of the sulphides in Gibeon has been made by Frost (1967), who has drawn attention to the fact that in many samples the sulphide nodules appear to have been remelted by shock heating; these nodules contain daubréelite and often seem to be similar to the Reichenbach lamellae, indeed nodules may grade into lamellae. Although there appear to be exceptions, the majority of Reichenbach lamellae that were studied by Frost appear to be oriented either parallel to the cube faces of the parent taenite, in which case they may occupy the centres of cubic kamacite plates, or, in specimens that have been subject to repeated spinel twinning, they appear to have formed on a cube face that was present in the parent taenite before the onset of twinning or kamacite

precipitation. On the basis of metallographic and microprobe examination Frost describes the Reichenbach lamellae in Goamus (B.M. 1910, 753) in terms of a complex mixture of nickel-free daubréelite containing 20 % iron, kamacite with about 1.9 % nickel, and taenite with about 56 % nickel. El Goresy (1965) has described a similar structure in Bethany, which he describes as a sieve-like region of daubréelite from which troilite has been completely resorbed and replaced by kamacite. A detailed metallographic and microprobe investigation of a complex sulphide area in a sample of Mukerop from the University of Naples mineral collection has been reported by Orsini (1967) and by Orsini and Cento (1967). They described the juxtaposition of the sulphide area with the kamacite matrix and showed that at such a location the sulphide area consisted of reasonably well-formed crystals of daubréelite, having polygonal outlines and diameters of about 10 μm , which were embedded in a very fine duplex background of troilite and kamacite. Orsini and Cento (1967) suggested a build-up of nickel-rich phase where the sulphide area came into contact with the kamacite matrix but Orsini (1968) kindly provided the unpublished original photograph of the nickel distribution in the area studied by Orsini (1967) and it appears that nickel rich areas (containing more than 37 % nickel) were also scattered about within the sulphide region. Thus we suggest that a detailed description of the sulphide region in the Naples specimen would not differ greatly from that given by Frost (1967) for the situation in Goamus (B.M. 1910, 753).

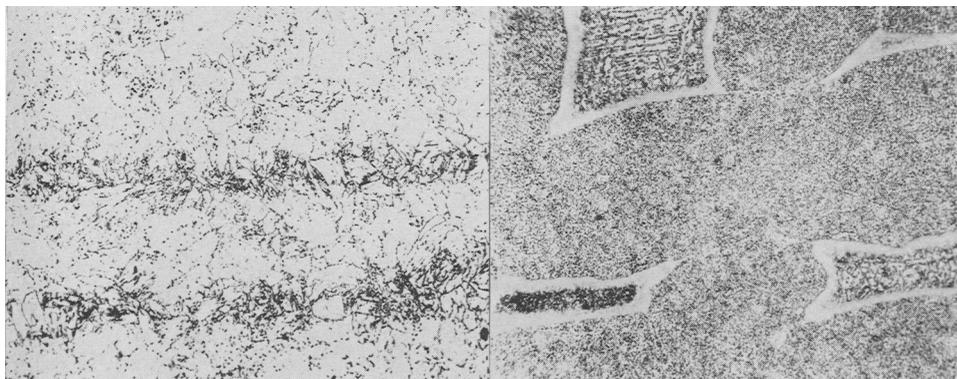
The trace element chemistry of Gibeon has been investigated by Lovering, Nichiporuk, Chodos, and Brown (1957), who reported also 7.96 % nickel and 0.39 % cobalt, by Smales, Mapper, and Fouché (1967), and by Wasson (1967) and there is general agreement that the meteorite belongs to group IVA and that it contains a large (200 ppm) amount of chromium. It is unfortunate that no analysis of phosphorus content is available, particularly in view of the very marked absence of solid phosphides from most samples of this meteorite. Reed (1969) has noted that rhabdite is absent from the kamacite of Bethany (B.M. 1930, 422) and has reported the kamacite to contain 7.2 % nickel and 380 ppm phosphorus. Reed (1965) has also reported an Agrell depletion of 0.6 % nickel at the kamacite-taenite interface of another Gibeon specimen. Using a band width of 0.35 mm and a nickel content of 7.9 % Goldstein (1969) has proposed a cooling rate of 50 °C per million years, although care should be exercised in using this value in view of the exceptionally low phosphorus (and high chromium) content of Gibeon in comparison with other octahedrites for which cooling rates have been estimated.

In the present work an examination has been made of the holdings of Gibeon in the British Museum and the authors wish to express their thanks to the museum authorities and in particular Drs. Hey and Frost for help and advice. In addition two small pieces of Bethany, H74.22 and H74.16 of the American Meteorite Laboratory have been examined.

A macroscopic examination of the deeply etched surfaces of Mukerop (B.M. 85891), Mukerop (B.M. 1921, 190), Goamus (B.M. 1910, 753), Goamus (B.M. 1921, 386), Kameelhaar Farm (B.M. 1941, 1), Great Namaqualand (B.M. 54729), and Lion River (B.M. 32048) was made and in all of these instances macroscopically visible sulphide

areas displayed the ragged outline similar to that reported by Orsini (1967) and described by Frost (1967) as shock melted.

In addition Mukerop (B.M. 1959, 159) and pieces cut from Goamus (B.M. 1910, 753 and B.M. 1921, 386) and from Kamkas (B.M. 1941, 2) were reprepared for metallographic examination by the optical microscope and the electron-probe microanalyser (S.E.M. 2), as was Bethany H74.22.



FIGS. 1 and 2: Fig. 1 (left). Microstructure of Kamkas (B.M. 1942, 2) etched 1% nital $\times 110$. Relics of the original taenite ribbons are indicated by the acicular martensite, which forms in the regions where the nickel content of the metal is highest. The relics of kamacite have a lower nickel content and the martensite is therefore less acicular. Fig. 2 (right). Microstructure of Goamus (B.M. 1921, 386) etched 1% nital $\times 85$. Plesite is tempered, taenite-kamacite interfaces are thermally diffused and a fine uniform precipitate of 'isothermal taenite' is present throughout the kamacite. Evidence for reheating.

The macrostructure of Kamkas (B.M. 1941, 2) can be developed by etching in nital and shows the thermally diffused relics of a Widmanstätten structure, although the etch-relief normally produced between kamacite and taenite does not develop. On microscopic examination the structure appears as in fig. 1; in this figure the whole of the metallic material consists of tempered martensite and the macroscopically visible relics of the taenite ribbons can be seen as narrow bands, within which the martensite has the acicular morphology characteristic of nickel-rich alloys. By contrast, the broader bands, which are the relics of the original kamacite, have the more massive, ragged, transformation product that arises from the quenching of material with a lower nickel content. The macro- and micro-structure of Kamkas (B.M. 1941, 2) is therefore consistent with the reheating of ordinary Gibeon material into the temperature range where only the parent taenite is stable but below the melting point of the metal. This temperature range would be approximately 800–1400 °C. The period of reheating was long enough to resorb the taenite ribbons but not long enough to homogenize the metal completely with respect to nickel content. Reheating treatments considerably more severe than those employed by Brentnall and Axon (1962) in their laboratory reheating experiments on Cañon Daiblo are necessary. No sulphides and no relics of pre-existing sulphides were present in the sample of Kamkas we had

available for examination. It is possible that the reheating of Kamkas may have been done by human agency but our investigations are not able to give a conclusive answer on this point.

A history of terrestrial reheating and hammering by human agency is more reasonably established in the case of Goamus (B.M. 1921, 386) of which the British Museum Collection contains a 1.2 kg end slice that shows signs of hammering on its outer surface. We have made a detailed metallographic and microprobe examination of a 98 g piece from the edge of B.M. 1921, 386. This material is in a heavily cracked and corroded condition, although in all cases the cracks follow the Widmanstätten pattern and in many cases the invasion of corrosion product appears to have followed Reichenbach lamellae in the original structure. A number of sulphide nodules are also present but in each case the invasion of corrosion product was too great to allow a clear and unambiguous description of the sulphide itself. The macro-etched surface showed a fairly well defined Widmanstätten structure but microscopic examination of the nital-etched material revealed the structure shown in fig. 2. This structure is characteristic of normal octahedrites that have been reheated within the field of the phase diagram where both kamacite and taenite are stable. Reheating causes the kamacite-taenite interfaces of the original Widmanstätten structure to become thermally diffused and also allows particles of taenite to exsolve from the body of the kamacite to produce the 'isothermal taenite' of Brentnall and Axon's (1962) reheating experiments. Microprobe analyses were made of the nickel content of the exsolved 'isothermal taenite' particles and an average of $14 \pm 1\frac{1}{2}$ % nickel was obtained. According to the binary phase diagram of the iron-nickel system taenite of this composition corresponds to a reheating temperature of about 650 °C. It thus appears that Goamus (B.M. 1921, 386) was reheated to an effective temperature of about 650 °C for a period of several hours. This reheating treatment was probably given by man in an attempt to forge the material and it is probable that the combination of reheating and hammering so damaged the original integrity of the structure as to facilitate the invasion of corrosion products into the sulphide lamellae. The reheating temperature was probably too low to melt the sulphides, but this point is not absolutely certain for two reasons: Firstly, in samples of Gibeon that have not been subjected to terrestrial reheating the sulphides show certain peculiarities, which have been described by Frost (1967) and by Orsini (1967), and which make terrestrial reheating somewhat difficult to identify. Secondly, the sulphide nodules (in B.M. 1921, 386) are heavily invaded by terrestrial corrosion products, which makes an unambiguous description of the sulphide structures difficult. However, subject to these uncertainties, our examination of the least corroded sulphide nodules (in B.M. 1921, 386) does not suggest that they were remelted as a result of the terrestrial reheating. This is consistent with our estimate of 650 °C reheating.

Metallographic investigations have been made on another Goamus specimen (B.M. 1910, 753), which shows no signs of terrestrial reheating. The British Museum holding of this material consists of a slice measuring 17 in by 12 in across its largest dimensions and weighing 6.6 kg. Our own examination was made on a 2 in by 1 in piece of this material, which was partly bounded by a portion of the outer surface of the meteorite. It appears from the condition of this outer surface that material has been removed by

terrestrial corrosion, but the extent of this loss cannot have been great since microscopic examination of the etched specimen reveals the remains of a heat altered zone. The macrostructure shows a well-developed Widmanstätten pattern but there is no macroscopically visible phosphide. Lamellae and nodular inclusions of sulphide are visible in the macrostructure and in all instances they show the ragged outline described in this specimen by Frost (1967).

Detailed microscopic examination confirmed the absence of phosphide phases either as schreibersite or as rhabdite but revealed the presence of many small crystals of daubréelite within the kamacite. A number of small ragged sulphide areas, which were not obvious to the naked eye, became visible on microscopic observation and these showed the same general features as were displayed on a larger scale by the macroscopically visible Reichenbach lamellae and sulphide nodules. A detailed description of the sulphides will be given when the Mukerop specimen is discussed.

A detailed metallographic examination was made of a 2.2 in by 1.2 in etched surface of Bethany H74.22 from the American Meteorite Laboratory and this specimen showed the general structural features noted in Goamus (B.M. 1910, 753) with the additional effect of at least nine plates of kamacite that had formed parallel to the cube face prior to the more general precipitation of octahedral kamacite. The central spines of the non-octahedral plates appear to be particularly rich in small crystals of daubréelite and of what appears to have been daubréelite associated with troilite. The monomineralic daubréelite crystals had an average diameter of about $70\ \mu\text{m}$ with regular outlines, and showed no signs of reheating. By contrast the daubréelite-troilite associations were slightly larger and showed very ragged outlines. Altogether 66 daubréelite crystals in this size range were encountered at the centres of the 9 cubic plates of kamacite. A further 148 monomineralic daubréelite crystals were encountered, but these were generally smaller ($10\text{--}50\ \mu\text{m}$) and were distributed in approximately equal proportions in each of three other locations: within the bulk of the octahedral plates of kamacite (of which there were more than 240), at kamacite-taenite interfaces, and within the fields of coarsest plessite. Since the ratio of plate kamacite to all forms of plessite is 4:1 there is a considerable concentration of daubréelite at the centres of the cubic plates of kamacite, where the crystals are generally larger than those elsewhere, and there is a deficiency of daubréelite within the octahedral kamacite by comparison with that present in the coarse plessite and at the taenite boundaries. No phosphide was encountered in this specimen.

A further slice of Bethany H74.16 from the American Meteorite Laboratory shows a region of heat alteration zone.

Mukerop (B.M. 1959, 159) is an almost square slice of approximately 2-in side, which does not include material from the outer surface of the meteorite. The general metallographic features of the metal and sulphide phases are similar to those in other unheated Gibeon specimens and one sulphide area is in a particularly convenient position for microprobe examination. With the permission of the Museum authorities this sulphide and its surrounding metal was cut out by electrochemical machining and prepared for microprobe examination.

Metallographic examination of the metal in Mukerop reveals that there is a range

of plessite structures from very coarse comb or granular plessites in the larger fields to fine bainitic plessites in the smaller fields. Some of the granular plessites consist of 'picture-frame' rims of taenite, within which relatively small proportions of globular taenite bodies are distributed in a predominantly kamacite background. Small isolated daubréelite crystals are an occasional feature of such areas. Thick ribbons of taenite and the swollen taenite component of coarse plessite show martensitic decomposition at their centres. Rhabdites and all forms of schreibersite are absent from the structure and the kamacite is often remarkably free from Neumann lines and shows no microscopically visible indication of shock polymorphism. However the condition of the kamacite does in fact differ from that of normal unshocked kamacite in two respects. Firstly, its microhardness is somewhat high, although it is considerably less than that of acicular kamacite produced by shock metamorphism.¹ Secondly, back reflection X-ray photographs from the kamacite of Mukerop show the range of disordered microcrystallinity that has been used by Jaeger and Lipschutz (1968) as an indication of shock history.

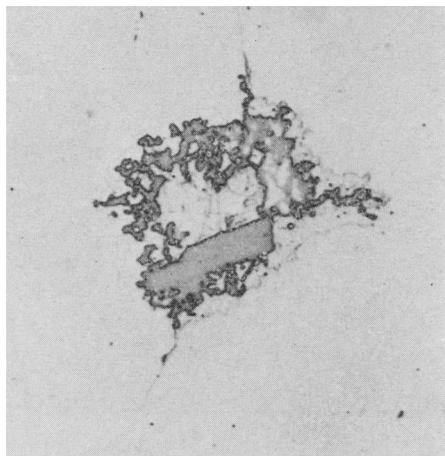


FIG. 3. Microstructure in Mukerop (B.M. 1959, 159) etched 1% nital $\times 450$. Small crystal of daubréelite (dark) within and partly attacked by pool of troilite-kamacite eutectic liquid. The matrix is kamacite.

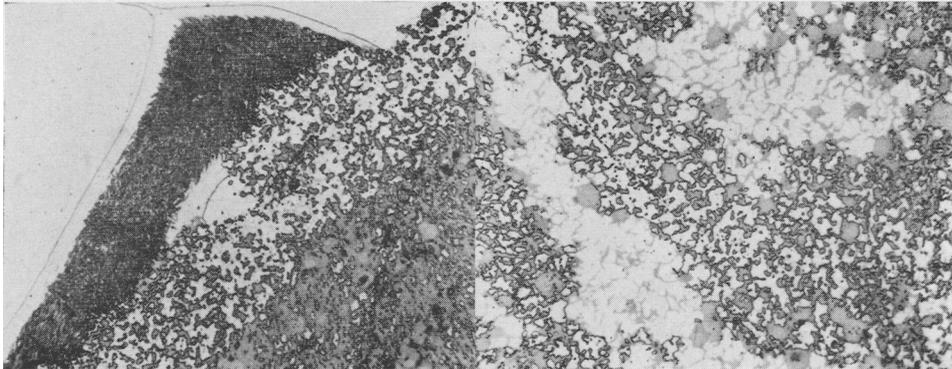
Microprobe examination of kamacite-taenite interfaces at positions well removed from sulphide inclusions show sharply defined interfaces with a small Agrell depletion of about 0.3% nickel in the kamacite and a maximum nickel content in the taenite of about 36%. According to the binary equilibrium diagram of the iron-nickel system taenite of this nickel content would correspond to equilibrium at about 450 °C.

In so far as microscopic observation of the sulphides is concerned the small monomineralic daubréelites appear with sharp interfaces to the kamacite matrix. In other meteorites daubréelite is also found in association with troilite, but in samples of Gibeon it is rare to find daubréelite in contact with conventional troilite. The more usual situation is represented in fig. 3 where a small crystal of relatively unchanged daubréelite appears to be surrounded by a resolidified pool of kamacite-troilite eutectic. The most reasonable way by which the structure of fig. 3 may have arisen is by the shock-induced melting of troilite and a portion of the surrounding kamacite to form a eutectic liquid. Rapid resolidification of the eutectic pool then produces the structure shown.²

¹ Microhardness values for kamacite obtained on the Reichert instrument may be quoted for purposes of comparison: ordinary Cañon Diablo 178, artificially shocked 138 kb Cañon Diablo 250, artificially shocked 228 kb Cañon Diablo 293, acicular kamacite in Trenton 300, Goamus (B.M. 1910, 753) 213, Mukerop (B.M. 1959, 159) 198, Bethany H74.22 205.

² Similar structures have been observed by Axon, Boustead, and Yardley (1968) in Willamette (B.M. 86945).

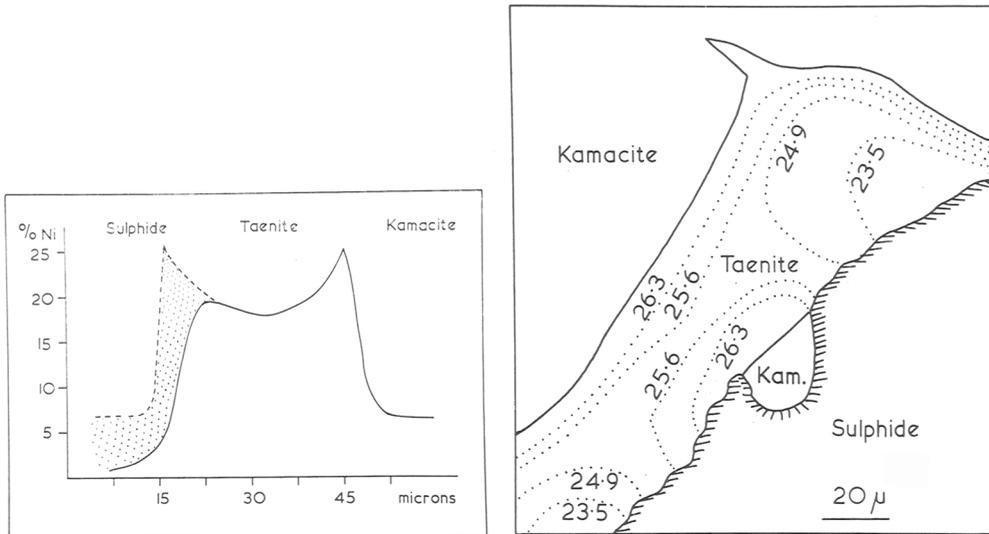
It can be seen that a certain amount of reaction has in fact taken place between the daubréelite and the pool of eutectic liquid and this phenomenon is also encountered in the large sulphide nodules and Reichenbach lamellae where, presumably on account of the greater heat content of the larger pools of liquid, it is usual for the original massive daubréelite component to be more extensively attacked than in the microscopic area of fig. 3. However, fairly large areas of original parent daubréelite are occasionally encountered that show signs of dissolution in the adjacent liquid and daubréelite that has dissolved in this way is the first phase to crystallize out when the



FIGS. 4 and 5: Fig. 4 (left). Mukerop (B.M. 1959, 159) etched 1% nital $\times 450$. A pool of molten metal-troilite has invaded and partly dissolved a plessite field. Fig. 5 (right). Mukerop (B.M. 1959, 159) etched 1% nital $\times 550$. The structure within another pool of resolidified liquid showing relatively large crystals of 'daughter' daubréelite within light taenite and intermingled with duplex troilite-kamacite eutectic.

complex liquid resolidifies. Thus small polygonal or rounded crystals of daughter phase (which has essentially the same chromium content as the massive parent daubréelite) occur embedded in a fine troilite-kamacite background in the manner described by Orsini and Cento (1967). The nickel-rich phase that these authors have noted is taenite, the origin of which is clarified by reference to figs. 4 and 5. Fig. 4 shows the way in which liquid metal-sulphide has eaten into the taenite rim and some of the plessite interior of a pre-existing field of plessite that was situated adjacent to the original troilite-daubréelite nodule, while fig. 5 shows, in a similar area and at higher magnification, the nickel-rich component of the finally solidified liquid. Melting and resolidification were too rapid to allow proper homogenization of composition within the liquid pool and this effect in another area is illustrated in fig. 6 where a microprobe line analysis for nickel content is made from the sulphide area into the plessite at a location where dissolution of plessite has operated. Fig. 7 shows the lines of equal nickel content within the damaged plessite area of fig. 4 and indicates that heat from the liquid has allowed some solid-state diffusion of nickel to take place within the plessite near the contact area of liquid-solid interaction. In this instance it is clear that the final distribution of nickel within the plessite of fig. 4 is a slightly modified version of what would be expected in conventional unaltered plessite. It is

thus clear that the plessite was fully and completely formed some time before it suffered attack by the sulphide liquid and we have already noted that for unaltered regions of the Widmanstätten structure in Mukerop a kamacite-taenite equilibrium temperature of about 450 °C seems appropriate.



FIGS. 6 and 7: Fig. 6 (left). Microprobe trace for nickel content at the edge of a sulphide area. Remelted troilite-kamacite has invaded a plessite area. This trace is at a location different to the areas shown in figs. 4, 5, or 7. Fig. 7 (right). Microprobe examination of the nickel content within the plessite region of fig. 4.

Discussion. Subsequent to their unknown date of fall it appears that at least some of the Gibeon irons have been subject to unrecorded transport, mechanical attack, or heating by man and in addition they have all lost material from their outer surfaces through weathering and corrosion. However, a number of Gibeon irons appear to be free of mechanical or thermal alteration by man and in some of these cases the weathering has not been sufficiently severe to remove all traces of the heat-alteration zone produced during the passage of the material through the earth's atmosphere. Axon (1969) has drawn attention to the value of heat-alteration zones in helping to distinguish between terrestrial and pre-terrestrial phenomena in meteorites that have had an uncertain history.

The Gibeon irons appear to have a relatively high content of chromium and, as judged by the marked absence of phosphide phases, a remarkably low content of phosphorus. However, bulk analyses of material that embraces the sulphide phases do not appear to have been conducted on Gibeon and new bulk analyses for these elements and for sulphur would be valuable. Daubréelite is one of the important minor phases of the Gibeon irons and it appears not only as a component of the macroscopic nodules and Reichenbach lamellae but also as microscopic crystals. On the microscopic

scale isolated crystals of daubréelite are concentrated at the centres of the cubic plates of kamacite and smaller crystals are distributed throughout the rest of the structure. The cubic plates of kamacite formed earlier than the octahedral plates and Axon and Faulkner (1967) have suggested that the nucleation of the cubic plates may have been assisted by slip deformation in the high-temperature parent taenite. Two possible explanations are available for the concentration of larger daubréelites within the cubic kamacite: either they precipitated at an early stage within the kamacite or, perhaps more probably, they precipitated on the cubic slip planes of the parent taenite and so, in turn, helped to nucleate the cubic kamacite.

The condition of the sulphide phases in Gibeon is significant. On the microscopic scale isolated monomineralic crystals of daubréelite show no signs of reheating although in all cases where troilite is present the troilite exists as a finely dispersed component of a troilite–kamacite eutectic, which sometimes also contains particles of taenite. The macroscopically visible nodules and Reichenbach lamellae usually show a more complex structure of fine daubréelite crystals embedded in a troilite–kamacite–taenite eutectic and in some instances it is obvious that the fine daubréelite crystals are the re-precipitated daughter products from massive parent daubréelite that has been partially dissolved by a troilite–metal liquid. It thus appears that the original structure of the Gibeon sulphides was a conventional association of daubréelite with troilite, but at a fairly late stage the troilite remelted and dissolved a portion of the adjacent kamacite to form a pool of eutectic liquid, in which more or less daubréelite dissolved according to the size and heat content of the liquid pool. The eutectic temperature for the binary iron–iron-sulphide system is 988 °C at atmospheric pressure, but this temperature would be altered to an uncertain extent by the presence of nickel and chromium and an imposed pressure. Nevertheless if the troilite had been remelted by the uniform reheating of the whole meteorite the process would have left very obvious signs of reheating in the metallic structures. The highly local pools and fine scale distribution of the resolidified eutectic structures, coupled with the disordered microcrystallinity of the bulk kamacite when examined by X-ray diffraction, suggest that the preferential melting of the troilite arose through shock pressure operating on the low density, high compressibility, and favourable shock impedance of this phase in the manner indicated by Heyman, Lipschutz, Nielson, and Anders (1966). Some limits can be placed to the stage of cooling history at which Gibeon encountered the shock reheating. It must have been above room temperature since there is no sign of the acicular shock-hardened kamacite that accompanies the remelted troilite of La Primitiva (B.M. 1927, 77). On the other hand the shock must have been experienced subsequent to the stage at which the meteorite had cooled to about 450 °C since the molten sulphide has cut into taenite that corresponds to this temperature.

In addition to the obviously complex cosmic history of Gibeon the situation in some samples is further confused by terrestrial reheating, mechanical damage, and corrosion.

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