

## A metallographic and microprobe study of the Barranca Blanca meteorite

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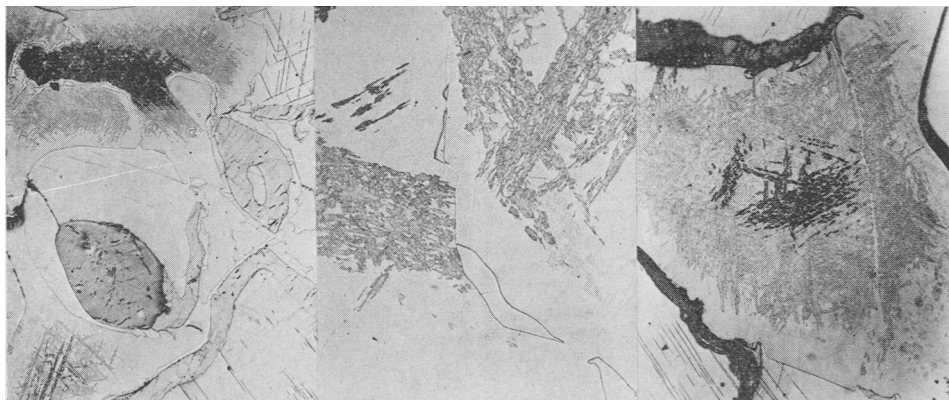
**SUMMARY.** The distribution of kamacite, taenite, and plessite suggests that kamacite nucleated at the sulphides, which appear to have been plentifully dispersed in the parent taenite. Such a process could take place without the undercooling that is usually assumed in normal octahedrites. The plessite fields show internal boundaries that are probably relics of grain boundaries in the parent taenite-sulphide aggregate. Microprobe investigations have been made of nickel distributions in and between kamacite, taenite, plessite, and schreibersite, and particular attention has been paid to the nickel distribution at the internal grain boundaries in the plessite. Evidence is presented for the diffusion of nickel along these boundaries and for their migration during the later stages of formation of the microstructure.

**BARRANCA BLANCA** was found in 1855 between Copiapo and Catamarca, Atacama, Chile. The meteorite as found weighed about 12 kg and the main mass is now preserved as B.M. 41187 in the British Museum Collection. It is recorded by Hey (1966) as a brecciated octahedrite with a nickel content of 8.01 % and trace element analyses have recently been reported by Smales, Mapper, and Fouché (1967) and by Wasson and Kimberlin (1967) who report a nickel content of 7.96 % and show that Barranca Blanca is somewhat different from the majority of medium octahedrites in its trace-element chemistry.

The outer surface of the meteorite has an unusual pattern of overlapping half-centimetre pits, which produces a three-dimensional scalloped effect. A similar effect is found on approximately half of the external surface of Puquios No. 154 in the collection of the American Museum of Natural History, New York. The surface features of Barranca Blanca may have arisen in part by the removal of material during the earth residence of the meteorite but the depth of material so removed cannot have been very great since unconsumed portions of the superficial heat-altered zone may be detected on the etched specimen at  $\times 100$  although it is not generally visible to the naked eye.

A moderately flat surface of approximately 10 in<sup>2</sup> had at some time been prepared on the main mass and had been deeply macro-etched. This macro-surface shows no distinct Widmanstätten structure but the situation is somewhat confused by the presence of massive cracks and heavy penetration of corrosion product. A new surface of approximately 2 in<sup>2</sup> was prepared for macro- and microscopic examination and a  $\frac{1}{4}$  in<sup>2</sup> of surface was examined by the microprobe technique, using an A.E.I. S.E.M. 2 instrument. The macrostructure is dominated by massive sulphides, which

appear within the kamacite grains and not at kamacite grain boundaries. Indeed the sulphides, although present to a much less extent, appear to act like the olivine crystals in a pallasite and most of the kamacite in Barranca Blanca is swathing kamacite around these sulphides. Relatively small quantities of plessite and taenite appear scattered through the macro-structure and have a rounded outline rather than the more usual angular form that is characteristic of ordinary octahedrites.



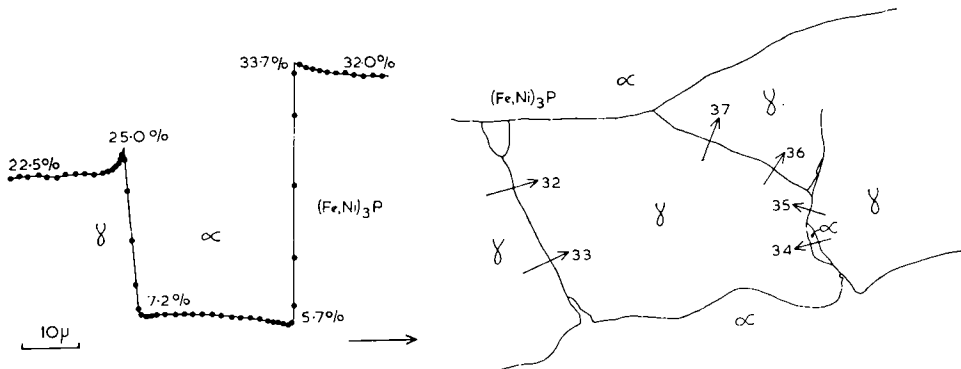
FIGS. 1 to 3: Fig. 1 (left). Etched 1% nital  $\times 20$ . Troilite (dark) surrounded by kamacite, strings and a hollow nodule of schreibersite (cracked), and martensitic plessite showing internal grain boundaries with kamacite precipitation along some of the boundaries. Fig. 2 (middle). Etched 1% nital  $\times 175$ . Kamacite spindles precipitated at internal boundaries of plessite. Note that under certain circumstances plessite may extend right up to the boundary without the intervention of taenite. Evidence for grain boundary migration. Compare fig. 5. Fig. 3 (right). Etched 1% nital  $\times 50$ . An internal grain boundary in plessite. The martensitic plessite shows a different orientation on either side of the boundary.

On microscopic examination of the nital-etched specimen the massive sulphides appear twinned and the kamacite contains Neumann lines, although these are not profuse and vary in quantity from grain to grain. Schreibersite occurs in massive form bordering the sulphides and within the kamacite; it also occurs as smaller crystals in association with plessite. Ordinary rhabdites are not present but one large, hollow, giant rhabdite was encountered with good straight outer edges free of diffusion effects and it appears that Barranca Blanca was not significantly reheated after this crystal formed.

In ordinary octahedrites each plessite area consists of a continuous and uninterrupted pattern. This indicates that the plessite formed from residual taenite which, although not chemically homogeneous, yet had a single unique crystallographic orientation. The situation is very different in Barranca Blanca, where the larger areas of plessite often have a patchwork form such that the pattern of the plessite structure is interrupted by grain boundaries of the pre-existing parent taenite. The effect is shown at the top of fig. 1, where it may also be seen that kamacite has precipitated at some positions along these grain boundaries of the parent phase. A similar effect is shown at higher magnification in fig. 2. Smaller areas of plessite may show internal

grain boundaries or subgrain boundaries, which interrupt the plessite pattern although they are not decorated by precipitated kamacite; this situation is illustrated in fig. 3.

Microprobe investigations were made on an unetched section and calibrations were made with the series of standard alloys used by Axon and Yardley (1969). Nickel concentration profiles at simple kamacite-taenite interfaces consistently gave the rather high nickel content of  $7.5 \pm 0.2\%$  in the kamacite, which appeared to be homogeneous apart from a small Agrell depletion of approximately  $0.4\%$  nickel over a distance of about  $10\ \mu\text{m}$  at the kamacite-taenite interface. The maximum nickel content of the taenite is  $31\%$  at the interface and this nickel content falls steeply but smoothly as the



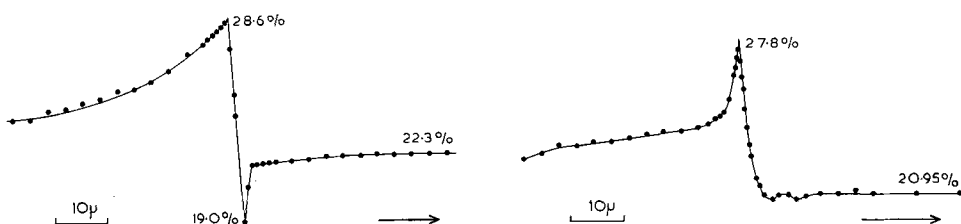
Figs. 4 and 5: Fig. 4 (left). Distribution of nickel between taenite, kamacite, and schreibersite. The schreibersite is not chemically homogeneous. Fig. 5 (right). Sketch of the distribution of precipitates and internal boundaries in a plessite field. The positions of microprobe traces are indicated.

microprobe trace proceeds into the plessite region, where it reaches a constant value of  $22.5 \pm 2\%$  at a distance of about  $25\ \mu\text{m}$  from the interface. The plessite areas are remarkably homogeneous with respect to nickel content and the plessite is typically of the martensitic form, as shown in figs. 1, 2, and 3.

A more complex situation arises when massive schreibersite is present in the neighbourhood of taenite. Fig. 4 shows a nickel concentration profile that extends from plessite (which is bordered by taenite) into kamacite and then into massive schreibersite. From this figure it appears that schreibersite is in competition with plessite for the available supply of nickel, hence the maximum nickel content at the edge of the taenite reaches a value of only  $25\%$  and, with a content of  $7.2\%$  nickel in the adjacent kamacite, there is no Agrell effect. The interface relationships between this kamacite and the schreibersite are particularly suggestive. Not only is there, in the kamacite, a pronounced gradient of nickel concentration as the schreibersite interface is approached but, very unusually, there is a significant build-up of nickel at the edge of the phosphide phase. It thus appears possible that nickel diffusion into the phosphide continued to operate at a stage when diffusion into the taenite had ceased. It is usually assumed that diffusion is more rapid in the phosphide phase than in taenite but the conditions under which the Barranca Blanca structures were formed seem to be

unusual in that the nickel was not allowed sufficient time to become uniformly distributed throughout the mass of the phosphide phase.

Fig. 5 is a sketch of the arrangement of boundaries within a rather complex area of plessites and it may be noted that the microstructure at the right of fig. 5 is shown in fig. 2. Six microprobe traces (numbers 32-7) were made for the distribution of nickel across these boundaries at the locations shown in fig. 5. Attention should be drawn to the fact that a precipitate of phosphide has grown into the taenite at the top of the nearly vertical boundary on the left of fig. 5 and, furthermore, a finger of kamacite has grown along the bottom end of this boundary. Fig. 6 shows the measured microprobe trace number 32, from which it can be seen that the material to the left of the boundary



FIGS. 6 and 7: Fig. 6 (left). Distribution of nickel at trace 32 of fig. 5. Nickel appears to have drained down the boundary towards the schreibersite particle in fig. 5. Fig. 7 (right). Distribution of nickel at trace 35 of fig. 5. The migration of the boundary (from right to left in fig. 7 and in the direction of the arrow in fig. 5) appears to have swept nickel behind the moving interface.

has a fairly conventional type of nickel distribution with a maximum of about 28-9 % nickel. However, on the boundary itself there is a pronounced and unusual minimum in the nickel content. The trace number 33, which, of course, is at a position considerably removed from the phosphide precipitate, shows only a very slight (1 % nickel) minimum on the boundary whereas the adjacent maximum at the left of the boundary reaches the more usual value of 32-3 % nickel. The nickel distribution to the right of this boundary is homogeneous at about 22 % in both traces 32 and 33.

Trace number 34 of fig. 5 was taken across the large spindle of kamacite shown in fig. 2 and the form of this trace is pretty conventional. There is a nickel content of 7.7 % at the centre of the kamacite spindle, a small Agrell effect, and a pronounced and symmetrical concentration gradient of nickel in the taenite at each side of the 30- $\mu$ m wide spindle. The maximum nickel content at each taenite interface is 32-3 % and this decreases to about 22 % over a distance of approximately 15  $\mu$ m. This is essentially the same arrangement as is encountered when massive kamacite is in juxtaposition with taenite but it may be worthy of note that this is the only trace in which a nickel concentration gradient was detected when approaching the boundaries of the large central grain of plessite shown in fig. 5.

Trace number 35 of fig. 5 is shown in fig. 7 and corresponds to the concentration gradients encountered when the analysis spot moves from the clear taenite at the centre of fig. 2 across the boundary into the martensitic plessite, which comes into contact with the left side of the boundary. The maximum nickel content in trace 35

is lower than is usually found when taenite comes into equilibrium with kamacite; similar observations are also true of traces numbered 36 and 37.

*Discussion.* In the light of the metallographic and microprobe observations reported above an attempt will be made to discuss the conditions under which the structure of Barranca Blanca may have formed.

It appears, from the shape and distribution of both the kamacite and the residual taenite-plessite aggregates, that the nucleation of kamacite was controlled by the sulphide nodules distributed within the parent taenite. Thus in Barranca Blanca the kamacite is 'swathing' in the same sense that in a pallasite such as Brenham (Axon and Yardley, 1969) the kamacite is swathing about the pallasitic olivines. However, there exists a marked difference between the proportions of sulphide in Barranca Blanca and olivine in a typical pallasite. Indeed the pallasite structure is essentially composed of olivines in near contact with an infilling of metal, whereas in Barranca Blanca the continuous metallic matrix predominates and the sulphide inclusions are dispersed within this matrix. In the metallurgy of man-made alloys a distribution of non-metallic inclusions has the effect of slowing down or preventing the growth of grains in a single-phase alloy, and in view of this it would not be surprising to find that, in Barranca Blanca, the high-temperature parent taenite had a polycrystalline microstructure in which the grains were prevented from growing because the grain boundaries were pinned in position by the sulphide particles. The boundaries that are now observed in the plessite of Barranca Blanca (figs. 1, 3, 5) are presumably relics of these high-temperature boundaries of the parent taenite.<sup>1</sup>

As the parent taenite cooled it is reasonable to suggest that swathing kamacite nucleated easily at the sulphide inclusions without having to undergo the 110 °C undercooling that Goldstein and Short (1967) propose for the formation of ordinary octahedral kamacite when centres for heterogeneous nucleation are absent. This means that in Barranca Blanca the kamacite-taenite distribution could have formed at a relatively high temperature by comparison with what would apply in a normal octahedrite of the same nickel content. On this model the precipitation of kamacite would commence at about 750 °C and would probably continue under conditions of approximate (macroscopic) equilibrium with the co-existing taenite down to a temperature of about 580 °C, at which temperature the composition of the residual taenite would be a uniform 20 % nickel.

The build-up of the 'M profile' of nickel around the homogeneous 20 %-nickel plessite shows that cooling below 580 °C does not proceed according to macroscopic equilibrium conditions. Because of the relative rates of diffusion in the two phases the composition of the kamacite continues to adjust itself *homogeneously* to equilibrium at much lower temperatures, whereas the composition *gradients* that arise in the outer regions of the residual taenite allow interface equilibrium to be maintained between the kamacite and taenite according to the equilibrium phase diagram.

<sup>1</sup> In this context it may be worth noting that polycrystalline parent taenite is a marked feature of the silicate-bearing octahedrite Kodaikanal (Axon, 1968) and, on a larger scale, distinct grain boundaries are found within the occasional large and continuous metal regions of Brenham; a good instance is in the New York Collection, A.M.N.H. (Mason, 1962).

The rather high (7.5 %) nickel content of the kamacite and the unusually low (31 %) maximum nickel content at the taenite–kamacite interfaces are consistent with an effective temperature of frozen equilibrium (Axon, 1967, p. 211) of about 450 °C according to the binary iron–nickel equilibrium diagram of Goldstein and Ogilvie (1965). The smallness of the Agrell effect suggests that the material then cooled more rapidly below 450 °C.

The suggestion that the effective rate of cooling may have increased when this meteorite reached 450 °C is supported by the observations on phosphide–kamacite disequilibria illustrated by fig. 4. Phosphide is normally homogeneous with respect to nickel content because diffusion rates within the phosphide phase are sufficiently rapid to allow a homogeneous distribution of nickel to become established with the common meteoritic cooling processes. However, in Barranca Blanca it appears that in the final stages of cooling insufficient time was available to allow the nickel to become homogeneously distributed within the massive phosphide.

The growth of phosphide depends upon the acquisition of nickel, and, to this extent, phosphides are in competition with other nickeliferous phases. An interesting example of nickel diffusing along a plessite boundary towards a growing phosphide is provided at the left of fig. 5, since, from traces 32 and 33, there appears to be a general decrease of nickel about this boundary as the phosphide particle is approached.

Finally, it is interesting to consider the status of the plessite boundaries in fig. 5 that mark out the large central grain. It has already been noted that this grain is extraordinarily uniform at about 22 % nickel and this uniform composition extends right up to the boundary unless there are secondary effects such as the precipitation of kamacite spindles at the boundary. The microprobe trace of fig. 7 is taken at position 35 on fig. 5 and this region is also shown in fig. 2. From the latter figure it can be seen that at trace 35 martensitic plessite of 21 % nickel extends right up to the boundary of the large central grain. By contrast, the nickel within the next grain on the right of the boundary shows a distribution rather similar to the so-called 'M profile' that arises when taenite is in contact with growing kamacite. The particular profile of trace 35 must, however, have a different origin, since the cliff edge of the distribution is in contact with material of 21 % nickel and this is the same composition as that into which the smooth curve of the profile merges at the left of trace 35. A possible explanation for this particular boundary distribution of nickel is that the boundary was moving to consume the central grain at the same time that excess nickel from the outside of the plessite field was diffusing along the boundary. Such movement of the boundary would sweep up nickel from the grain that was being consumed and pile it up in the grain that was growing. In this way the symmetrical cusp distribution of the stationary boundary is re-distributed to a pseudo 'M profile' under the influence of boundary migration. It appears that this process was finally brought to a halt by the precipitation of phosphide and of kamacite spindles at the left and right boundaries respectively. Such precipitation would lock the moving boundary in position to give the structures shown in fig. 5.

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