

A metallographic study of the Angra dos Reis (iron) meteorite

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SUMMARY. The Angra dos Reis (iron) has been studied metallographically and an attempt has been made to discuss the circumstances under which the following elements of structure formed: clear etching and frosty etching kamacite, decorated Neumann lines, giant rhabdites, plate rhabdites, rhabdite clusters, microrhabdites, cohenite, and remelted troilite. The remelted troilite is taken to indicate a shock event. However, since there are no metallographically visible indications of shock in the kamacite and since the back reflection X-ray diffraction pattern shows only very faint Debye-Scherrer arcs superimposed on a pattern of sharp spots, it is concluded that the shock event took place at a temperature that allowed shock effects to anneal out of the kamacite almost completely. A sub-microscopic precipitate in the metallic matrix is observable with the electron microscope and may represent the final precipitation of phosphide from shocked kamacite.

THE Angra dos Reis (iron) is recorded by Hey (1966) as a nickel-poor ataxite. The main mass is in the Vatican collection and Salpeter (1957) has recorded it as a hexahedrite under the name Pseudo-Angra dos Reis. Our own examination indicates a hexahedrite structure. Salpeter reports that a complete individual of 6175 g and clearly showing flight markings was part of a collection, which was sent from Brazil in 1888 as a donation to Pope Leo XIII. The circumstances under which this meteorite was originally discovered are not recorded and it is unfortunate that it has been given the same name as a well-established stone meteorite. Further confusion arises from the improbable suggestion that the iron was observed to fall on the same day as the stone.

A polished end-piece was made available to the British Museum for analysis and study and Hey (1966) reports that a nickel content of 5.44% was determined by A. J. Easton. In a personal communication Dr. Hey has indicated that the analysis figures reported for Angra dos Reis (iron) on p. 609 of Hey (1966) are also due to the same analyst. The analysis was conducted on 2 g of material selected as free from visible inclusions and gave Ni 5.44%, Co 0.33%, P < 0.01%, Cu 136 ppm, Cr 40 ppm, Ga 64 ppm, Ge 148 ppm (A. J. Easton, anal.). Thus, like most hexahedrites, the Angra dos Reis (iron) belongs to Ga-Ge class II. No analyses are available for sulphur but the absence of massive sulphide and phosphide bodies from the present section indicates a rather low total content of sulphur and phosphorus. On the other hand, the small sulphide bodies that are occasionally present contain chromium in the form of daubréelite.

By arrangement with Fr. Salpeter and the British Museum a 70-g sample (BM 1970, 26) was made available to us for metallographic examination and we wish to express our gratitude for the loan of this material.

Experimental

An area of approximately 17 cm² was prepared for metallographic examination. In the polished condition no significant macrostructure was visible although a range of fine structural detail became visible to the naked eye after the sample had been lightly etched in 1% nital. The kamacite showed an uneven etching response and it was possible to identify areas of 'bright' and 'frosty' kamacite. The areas of bright kamacite appeared relatively free of macroscopically visible structure whereas the frosty kamacite displayed a variety of effects, which included thin oriented laths of phosphide, specks of sulphide, and decorated relics of Neumann lines. These features are illustrated in fig. 1, in which it should be noted that the shaded areas represent *clear* kamacite. The laths of phosphide are probably identical with the rhabdite plates studied by Bøggild (1927) in Coahuila and a single-surface analysis of their orientations showed that they were not incompatible with the (100) and (221) habits that Bøggild proposed. In Angra dos Reis (iron) the rhabdite plates occasionally reach a length of 4 mm, and in general are surrounded by shells of bright etching kamacite. Most rhabdite plates occur within 5 mm of a sulphide nodule and many appear to radiate from, or be associated with, such a nodule. In general a hand lens was required to make the sulphide nodules easily visible.

On detailed microscope examination at magnifications up to $\times 600$ it appeared that in all cases but one the sulphides consisted of fairly well-formed aggregates of small daubréelite crystals embedded in a fine troilite-kamacite eutectic, fig. 2, and the interface at which the troilite eutectic came into contact with the metallic matrix was ragged and appeared to indicate the penetration of a sulphide-rich liquid into the kamacite matrix. On a larger scale these effects have been reported by Axon and Smith (1970) in samples of Gibeon and have been identified as sulphide aggregates in which the troilite has been remelted by a shock event. Two additional effects in the vicinity of the sulphide areas became visible on microscope examination, namely the presence of cracked and partially graphitized cohenite around some of the sulphides and, in some instances, clusters of well-formed rhabdites near to, and apparently radiating from, the sulphides. A particularly interesting area is shown in fig. 3 where the only unmelted sulphide in the section is surrounded by an unusually large area of cracked and partially graphitized cohenite in which a number of rhabdites and rhabdite plates are wholly or partly embedded.

Microscopic examination showed that the pattern of bright and frosty kamacite areas was associated with a marked difference in the size of rhabdites. The bright kamacite was characterized by normal, well-formed, rhabdites, which ranged in size from 1 to 5 μm with an average diameter of 3 μm and were distributed in the arrangement Bøggild (1927) described for Coahuila. The average population density was about 100 rhabdites per mm². In general these areas have a relatively simple structure free of other features. By contrast the areas of frosty kamacite contained predominantly microrhabdites which ranged in size from 0.5 to 2.5 μm with an average diameter of 0.8 μm . The average population density of microrhabdites in the frosty areas reached 2500 per mm². Rhabdite clusters and decorated Neumann lines were confined to the

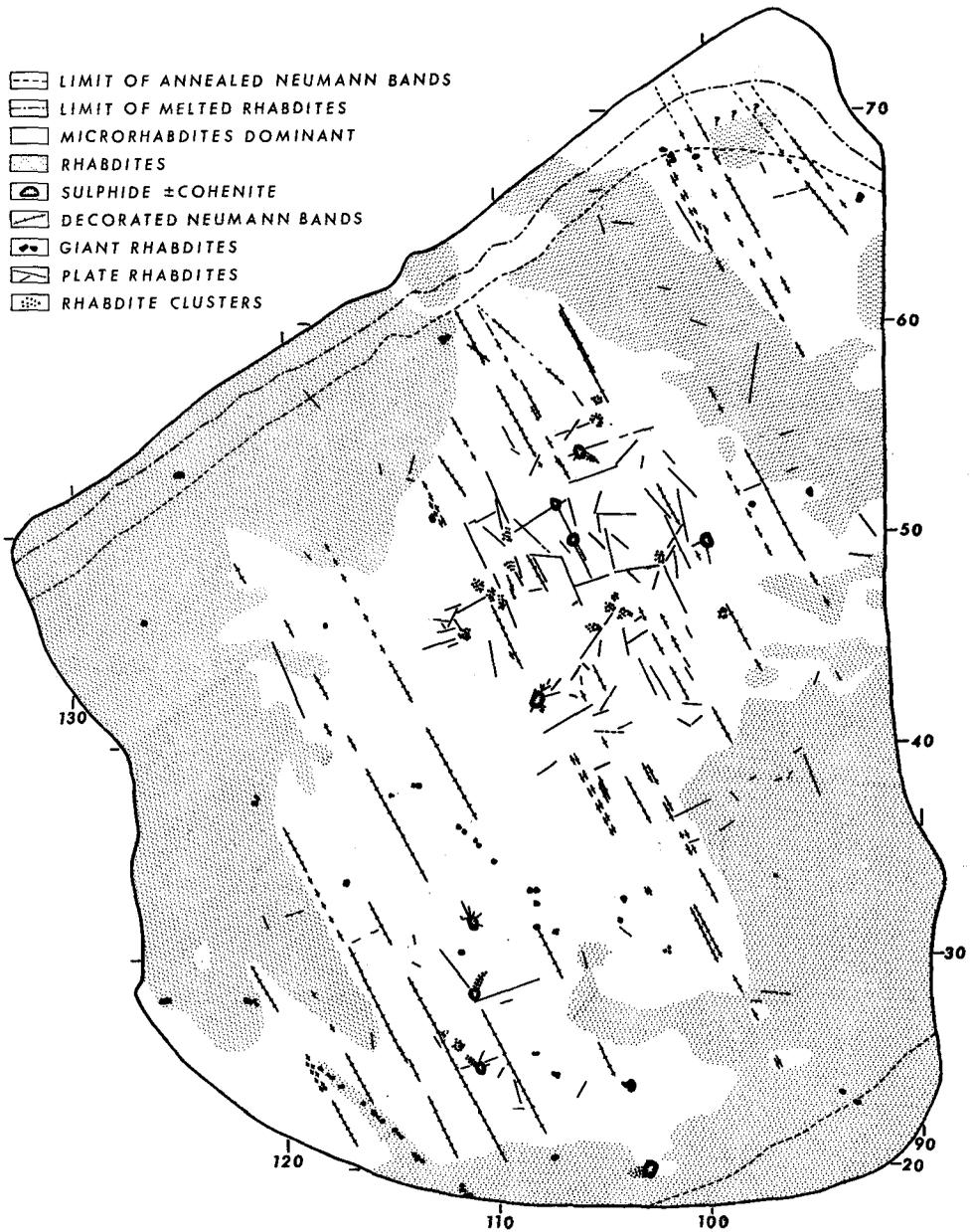
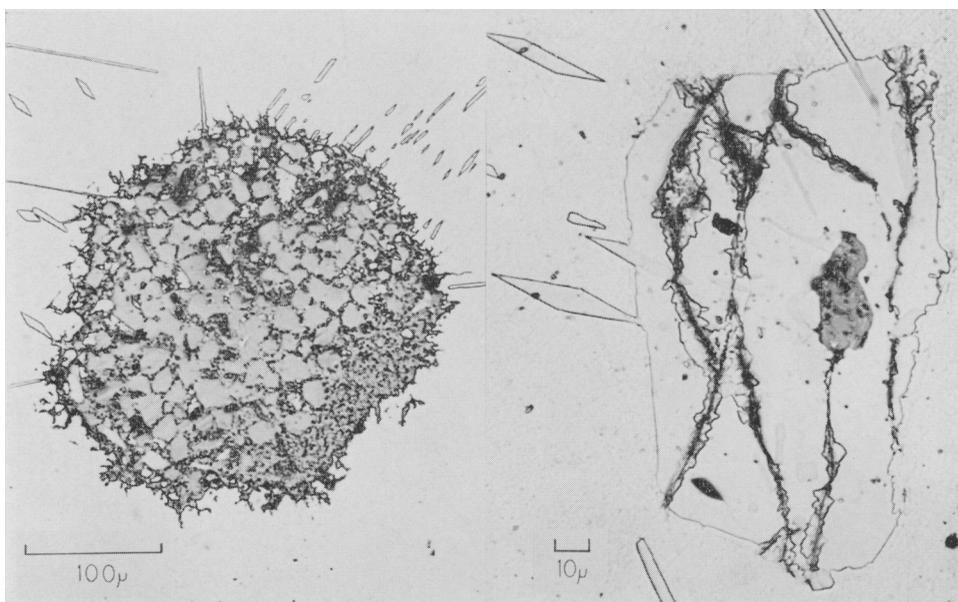


FIG. 1. Map of the microstructural features visible at $\times 300$ on the etched 70-g end-piece of the Angra dos Reis iron. Note that the shaded areas represent clear kamacite. The numbered index marks about the edge of the plot are graduations on the microscope stage at intervals of 10 mm.

frosty areas whereas rhabdite plates and giant rhabdites were found predominantly in the frosty areas but with a minor, sporadic, distribution in the areas of clear kamacite. At the boundary between clear and frosty areas the size of the rhabdites decreases and the population density increases rapidly, but the boundary between the two types of kamacite may be placed at approximately 225 rhabdites per mm^2 .



FIGS. 2 and 3: 2 (left). Etched in Nital. A sulphide nodule in kamacite. Rhabdites and rhabdite plates are present in the surrounding kamacite. Within the nodule fairly well-formed crystals of bright grey daubréelite are embedded in a fine kamacite-troilite eutectic. The ragged edge of the nodule suggests that molten eutectic liquid has penetrated into the solid kamacite. 3 (right). Etched in Nital. A small and apparently unmelted bean-shaped area of sulphide surrounded by cracked and partly graphitized cohenite. The cohenite has grown around pre-existing rhabdites and plate rhabdites.

Fig. 1 shows a map of the metallographic features visible at a magnification of $\times 300$ and the numbered scale marks around the figure represent distances in the two perpendicular directions of the microscope stage at intervals of 10 mm. In fig. 1 the shaded areas represent clear kamacite and, although the centres of features are correctly located on this map and the lengths of rhabdite plates and decorated Neumanns are to scale, it must be emphasized that the widths and diameters of the various microscopically visible features have been exaggerated considerably. Of the features in fig. 1 *giant rhabdites* occur sporadically in both clear and frosty kamacite but distinct belts of giant rhabdites are confined to frosty areas and are parallel to one family of the decorated Neumann lines. The giant rhabdites are usually subhedral and often embayed, they range in size from 23 to 108 μm with an average diameter of about 40 μm and they are usually surrounded by a zone of about 100 μm free of microrhabdite precipitation. *Rhabdite plates* range in size up to 3 and occasionally 4 mm in length

and are usually about $4\ \mu\text{m}$ thick, although the longest may reach a thickness of $9\ \mu\text{m}$ at their mid points, tapering towards the ends. Occasionally, as in fig. 4, the rhabdite plates show short gaps and, in particular, where two plates approach one another with different orientations they usually stop a short distance apart, although occasionally

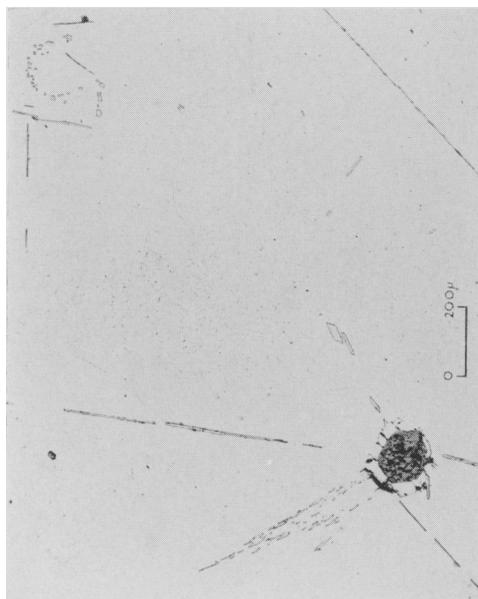


FIG. 4. Etched in Nital. A region from an area of frosted kamacite. At the bottom right is a sulphide-cohenite nodule with radiating rhabdites in the form of plates and a longitudinally sectioned cluster. At the top left, a cluster of rhabdites sectioned transversely. A finely dispersed array of microrhabdites forms the general background.

'L' and 'T' shapes are formed between rather short plates. *Rhabdite clusters* contain up to twenty closely packed individuals that have formed with a common crystallographic axis. The individual rhabdites are usually separate, although occasionally individuals may grow together to form a twin. Clusters appear most frequently in the neighbourhood of sulphide nodules, from which they often radiate. A range of size is shown by the individual rhabdites within a cluster but the usual diameter is about $5\ \mu\text{m}$. Two clusters are shown in fig. 4 cut at different angles by the plane of section. The cluster at the top left of fig. 4 is sectioned perpendicular to the common axis whereas the cluster at the bottom right is sectioned more obliquely and is obviously associated with the neighbouring sulphide-cohenite nodule. *Decorated Neumann lines* are visible in the areas of frosted kamacite because pre-existing Neumann lines have partially annealed out of the structure but have in part become

decorated by the precipitation of euhedral to subhedral rhabdites of average size $2\ \mu\text{m}$ diameter. The decoration is often sparse and gaps are common where the twin annealed out before it became decorated. A careful search was made to see if extensions of the Neumann lines could be detected in the clear kamacite but no really satisfactory evidence of extension was obtained. Since some of the decorated Neumann lines are parallel to the belts of giant rhabdites it is tempting to assume that the belts of giant rhabdites were also nucleated at pre-existing Neumann lines and that the decorating phosphide formed at a higher temperature.

Other microstructural features encountered were conventional (undecorated or 'fresh') Neumann lines throughout the section and a zone of heat alteration along part of the edge of the specimen. Within the zone of heat alteration two temperature contours could be identified, namely the temperature at which fresh Neumann lines began to be altered and, nearer to the outside surface, that at which rhabdites commenced to melt. These features are represented in fig. 1.

In addition to the metallographic investigation the specimen was examined by electron microscopy using gold-shadowed carbon replicas, by microhardness, X-ray, and electron-microprobe methods. The electron probe microanalysis was hampered by the fact that the specimen could not be cut and special arrangements had to be made to introduce the whole section of fig. 1 into the sample chamber of an S.E.M. 2 microprobe analyser. Because of the difficulty of accurately positioning the large specimen it is probably not safe to rely upon quantitative analyses but qualitative results confirmed the optical identifications of phases already reported. Electron microscopy of replicas was employed to examine the microrhabdites in more detail and to investigate whether there was any precipitate finer than that visible optically. Examination of gold-shadowed replicas at magnifications of $\times 32\,000$ indicated that both the clear and the frosty kamacite of the Angra dos Reis iron contained a very fine background precipitate ranging in size from 0.05 to 0.1 μm diameter in addition to the rhabdites and microrhabdites.

Microhardness tests gave no evidence of shock hardening in the kamacite and back reflection X-ray diffraction patterns were dominated by an array of sharp single-crystal diffraction spots. However, in addition to the sharp diffraction spots the X-ray photographs always showed faint arcs of Debye-Scherrer rings similar to those observed by Boustead (1962) from the shock-hardened La Primitiva BM 1927, 77 after it had been almost completely recrystallized by laboratory heat treatment.

Discussion

Only one section of the Angra dos Reis iron is available for study but our observations on this section indicate that the material has a low sulphur and phosphorus content, corresponding to the marked absence of massive phosphides and sulphide nodules. Some chromium is present as daubr elite within the small sulphides present and carbon is present in small quantities as cohenite.

Our observations suggest that this meteorite had a fairly complex history and a possible sequence of events may be outlined:

The mass of material presumably existed at some time in the high-temperature condition of essentially homogenous parent taenite but it is probable that the small inclusions of iron-chromium sulphide were already present in this taenite. On cooling it is likely that the first crop of kamacite nucleated at about 750 $^{\circ}\text{C}$ and grew around the existing sulphide inclusions. This early formed kamacite would be less rich in nickel than the parent taenite and, in this sense, would be analogous to the swathing kamacite that is found around some of the massive sulphide nodules in octahedrites. The volume change that accompanies the transformation of taenite to kamacite may set up stresses with the production of transformation twins in the kamacite. According to Hutton, Coleman, and Leslie (1959) transformation twins in commercial steels take the form of partially annealed Neumann lines and Axon (1969) has suggested that the decorated Neumanns in some meteorites may arise through the precipitation of phosphides upon such transformation twins. The bands of giant rhabdites may represent an extreme instance of this effect in which phosphorus precipitates at a temperature of about 700 $^{\circ}\text{C}$ on an early generation of transformation twins. The sequence

of phosphide precipitation probably continued at temperatures above 600 °C by the nucleation of the rhabdite plates and rhabdite clusters about the sulphide particles. The rhabdites in the clusters and the rhabdite plates are larger than the isolated rhabdites found in the areas of clear kamacite and presumably formed at a higher temperature. Moreover, the tapered form of some of the plates suggests that they developed over a range of temperatures. As the material cooled further the next generation of rhabdites to develop would be those in the clear areas of kamacite.

At this stage of the cooling sequence it seems likely that small amounts of cohenite precipitated at locations on the sulphide–kamacite interfaces and occasionally the cohenite areas grew sufficiently to enclose nearby particles of phosphide. Also at about 600 °C the high-temperature iron–chromium sulphide phase would have decomposed into a probably lamellar array of daubréelite and troilite (El Goresy and Kullerud, 1969) and the main features of the areas of clear kamacite would have been established, as would the features of the areas of frosty kamacite with the exception of the precipitation of the microrhabdites that form the groundmass in frosty areas and the decorated Neumanns. Axon (1969) has suggested that the origin of Neumann lines decorated by phosphide precipitates may lie in the deformation of high-temperature kamacite, induced either by transformation stresses or by other means, and it has already been suggested that the belts of giant rhabdites in the Angra dos Reis iron arise from high-temperature precipitation of phosphide at the sites of early transformation twins. It is not clear, in the Angra dos Reis iron, whether the deformation twins that evolve into decorated Neumanns were produced by transformation stresses or by external forces; however, they must have been present before the microrhabdites began to precipitate in the frosty kamacite region. Thus the next stage in the precipitation of optically visible phosphide is the nucleation of rhabdites at the twin interfaces and this is followed by the general precipitation of microrhabdites to form the background of the frosty kamacite areas.

In addition to the precipitation sequence, which can be discussed in terms of a fairly straightforward and uninterrupted cooling process, there are a number of effects that indicate a history of rather severe mechanical damage. For instance, the cohenite bodies have been fractured at a temperature sufficiently high to allow a small amount of cohenite to decompose into graphite. Also many, but not all, of the sulphide bodies have remelted and, since there is no visible sign of reheating in the phosphide bodies—other than those in the heat alteration zone—it seems likely that the sulphides were melted not by uniform reheating of the whole body but by a local, shock-induced, increase of temperature due to the favourable compressibility and shock impedance of the troilite. It appears probable that this shock event was experienced when the bulk of the kamacite was at a sufficiently high temperature for shock effects to anneal out of the metal phase almost completely, leaving no metallographically observable effects and only minor effects in the X-ray diffraction pattern. A temperature in the region of 400–500 °C would appear not unreasonable, thus the shock that remelted the troilite occurred while the Angra dos Reis iron was still part of its parent body. The submicroscopic precipitate visible on electron microscope examination of both clear and frosty areas of kamacite is unusual, but it may represent the ultimate

exsolution of phosphide from shocked kamacite as the material continued its cooling history.

These events were eventually followed by the production of conventional Neumann lines, presumably by secondary collision processes and, finally, by the formation of the heat alteration zone during the flight of the meteorite through the earth's atmosphere.

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