

## A metallographic study of some hexahedrites

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**SUMMARY.** Large samples of the hexahedrites Scottsville, Indian Valley, Okano, Puripica, and Hex River Mountains from the British Museum Collection and a sample of Lombard have been prepared for metallographic examination and details of their structures have been mapped with the aid of a specially constructed *X-Y* plotting device that is geared to the stage of a metallurgical microscope. The following elements of structure have been studied and an attempt has been made to discuss the circumstances under which they were formed: clear etching and frosty etching kamacite, decorated Neumann lines, giant rhabdites, plate rhabdites, rhabdite clusters, microrhabdites, cohenite or decomposed cohenite, and troilite (which in some instances is recrystallized or remelted). In general the range of structural effects is similar to that previously reported for the Angra dos Reis hexahedrite (*Min. Mag.* 1971, **38**, 94-101). The variations of structure are discussed in relation to nickel content and trace element chemistry of the meteorites.

THE chemical composition and geographical distribution of hexahedrites has been discussed by Henderson (1941, 1965). Buchwald (1967) has examined the macro- and microstructures of Indian Valley and of Scottsville. Wasson and Goldstein (1968) have investigated the chemical composition and microstructure of the North Chilean hexahedrites using 1 g. samples for chemical analysis and approximately 2-3 cm<sup>2</sup> of microstructure. They have concluded that Puripica may differ microstructurally from the five meteorites (Rio Loa, San Martin, Filomena, Coya Norte, Tocopilla) that share with it identical chemical analyses. Wasson (1969), from the analysis of 1 g. samples, has arranged the hexahedrites in chemical group IIA and has shown that within this group they may be further characterized by their content of iridium. Moore, Lewis, and Nava (1969) included Scottsville and Hex River Mountains in a group of 100 iron meteorites analysed for macrostructural contents of Ni, Co, P, C, S, and Cu. Nickel analyses by A. A. Moss have been reported by Hey (1966) for both Okano and Lombard while a more detailed analysis of Angra dos Reis (iron) by Easton has been reported by Axon and Waine (1971). Analytical information from these sources is collected in Table I for the meteorites examined in the present work.

No iridium value is available for the Angra dos Reis (iron), which, in Table I, we have placed between Scottsville and Indian Valley because of its nickel content and structure. In their study of the Angra dos Reis (iron) Axon and Waine (1971) identified the following structural features after etching with 1% Nital: on macroscopic examination the kamacite showed 'bright' areas, occupied by general groundmass rhabdites, and 'frosty' areas, occupied by microrhabdites; within the frosty areas decorated Neumann bands were encountered. Frosty areas appeared in locations appropriate to swathing or early formed kamacite. The phosphide bodies were

classified as microrhabdites, general groundmass rhabdites, rhabdite clusters, rhabdite plates, giant rhabdites, swathing schreibersite, and massive schreibersite. Troilite was encountered in a shock-melted and, in some instances, in an unmelted condition. Carbide was observed in a cracked and partly graphitized condition. In Angra dos Reis (iron) the carbide phase encloses rhabdite; it therefore must have formed later than the general groundmass rhabdites but was subsequently subject to cracking and partial decomposition into graphite and a low-nickel kamacite.

TABLE I. *Chemical data for the hexahedrites studied*

	Wasson's analyses				Other analyses			Ref.	Total area of surface examined
	Ni	Ga	Ge	Ir	Ni	P	Co		
Scottsville	5.31	60.4	172	49	{ 5.48 5.52	{ 0.23 0.19	{ 0.44 0.43	Moore	156 cm <sup>2</sup>
Angra dos Reis	—†	64†	148†	—	5.44	0.01	0.33	Easton	17
Indian Valley	5.48	61.4	174	11	5.64	0.27‡	0.45	Lovering	64
Okano	5.55	59.9	180	11	5.4	—	—	Moss	48
Lombard	5.59	58.0	174	2.3	5.6	—	—	Moss	45
Puripica	5.58	59.5	174	3.8	5.77	0.19	0.26	Henderson	73
Hex River Mts.	5.59	60.7	181	4.4	{ 5.65 5.72	{ 0.25 0.25	{ 0.45 0.46	Moore	55

† Easton anal., see Axon and Waine, 1971.

‡ Eakins, 1892.

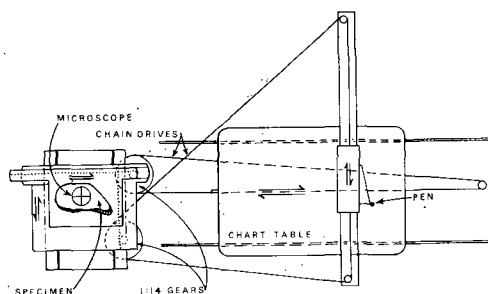


FIG. 1. Schematic view of automatic X-Y plotting table driven from stage controls of metallurgical microscope.

*Experimental methods and results.* The largest surfaces of Scottsville B.M. 62871, Okano B.M. 1923, 1016, Puripica B.M. 1959, 921, Hex River Mountains B.M. 77098, and the three surfaces of Indian Valley B.M. 1959, 920 available on specimens loaned from the British Museum collection together with the surface of Lombard from the American Meteorite Laboratory (658-32) were prepared for metallographic examination. The total area studied is recorded in Table I. It should be noted that only

the largest surface of Indian Valley and a portion only of the surfaces of Scottsville and Hex River Mountains are illustrated in figs. 2 to 7. The surface of Scottsville was too large for our polishing machines so it was prepared by a small polishing wheel fitted to an electric drill. After metallographic polishing each specimen was lightly etched in 1% Nital and examined under a metallographic microscope attached to the X-Y automatic chain-driven plotting table of fig. 1. This plotting table continuously reproduces on paper, at a (mechanical) chart magnification of 14 times, the details

of structure that the operator follows with his microscope cross-wires using a selected (optical) magnification between  $\times 75$  and  $\times 300$ . After the main structure in a particular area had been identified and plotted, the whole area was scanned by making regular passes to ensure that no detail had been missed. A major advantage of this method of mapping large surfaces is that fine grain boundaries and other microstructural features that are visible only at high magnifications may be identified and plotted simultaneously with the coarser macrostructural features. Thus the interrelation of coarse and fine structures may be recorded in a manner that is not possible with either microphotography or macrophotography alone. On the 14-fold magnification of the working charts the larger features can be plotted to scale but the finer details have to be plotted diagrammatically, for instance the true lengths of plates may be shown but their widths will be exaggerated. The greatly reduced versions of the charts, used as illustrations here, are possible because the space between structures is large enough for them to be exaggerated without overlapping on to adjacent structures.

The essential results are illustrated in figs. 2 to 7 and in Table II an attempt is made to tabulate for each specimen the relative abundance of the various features (Profuse (P), Dominant (D), Equal (E), Subordinate (S), subsidiary (ss), trace (tr), absent (abs)) together with the *average* dimensions in  $\mu\text{m}$  of the diameters or thickness of the phosphide precipitates. The table also indicates the presence of melted (m) or granulated (gr) troilite (t) or daubréelite (d) and the extent to which Carbide (C) has decomposed to low nickel kamacite (k), with or without the presence of Graphite (G).

From the sequence of figs. 2 to 7 and from the information in Table II it appears that when sufficiently large sections are examined the hexahedrites show a sequence of macro- and microstructural features that in general change according to composition.

It must be emphasized that the dimensions of phosphide precipitates recorded in Table II are *average* values and there is a considerable spread of measured values for each phenomenon.

Massive schreibersite in Lombard is located at the bottom right-hand corner of the map and appears to have formed along the boundaries of a small rectangular field of residual taenite.

Belts of giant rhabdites are observed in all specimens except Puripica, although they are sparse in Scottsville. Along the length of a belt the giant rhabdites are larger in the areas of clear kamacite than in the frosty kamacite.

Plate rhabdite is abundant in Hex River Mountains but uncommon in Okano. Small plates are often found at the boundary between clear and frosty kamacite. At this boundary there is an abrupt change in the population density from several thousand microrhabdites per  $\text{mm}^2$  in the frosty areas to 250–300 rhabdites per  $\text{mm}^2$ , falling over a distance of several mm to about 50–100 per  $\text{mm}^2$  in the areas of clear kamacite. Within the frosty areas are decorated Neumann lines and also rhabdite clusters, which are found characteristically associated with small sulphide bodies less than 1 mm diameter.

A different form of microrhabdite precipitation occurs in the nickel-depleted vicinity

TABLE II. *Relative proportions and average sizes ( $\mu\text{m}$ ) of precipitates and microstructural features in hexahedrites*  
*(for symbols see text)*

Meteorite	Kamacite		Dec. Neu.	Massive schreib.	Giant rhabd.	Rhabd. cluster	Plates	Rhabd.	Micro-rhabd.	Sulphides	Carbide
	Frosty	Clear									
Scottsville	D	S	P	abs	tr	ss	tr			ss m	ss (k)
Angra dos Reis	E	E	4 P	abs	44 ss	5 ss	5 S	6	~1	ss m	ss GkC
Indian Valley	S	D	2 S	abs	39 S	5 abs	4 S	3			
Okano	S/SS	D	1.4 abs	abs	53 S	ss	3 tr	5	1	S m	tr (k)
Lombard	ss	D	tr	tr	192 S	4 abs	4 ss/S	11		ss td	tr (k)
Puripica	tr	D	4 tr	300 abs	75 tr	tr	S (20†)	5	1-2	S tdgr	tr C
Hex River Mts.	tr	D	5 tr	abs	172 S	1.5 tr	6 D	10	1	ss td	ss (k)
			3		81	9	10	8	1	S tdm	ssGk

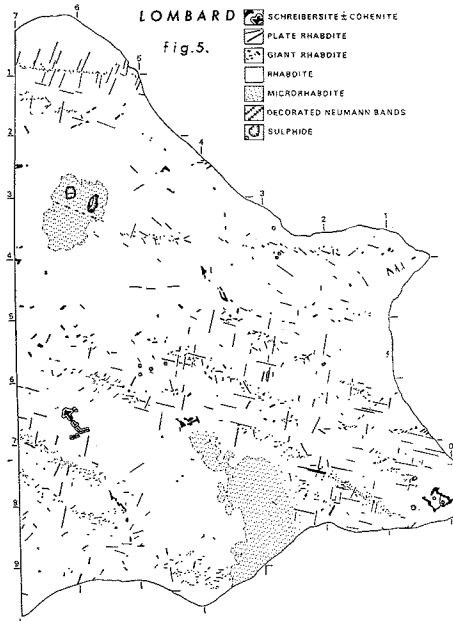
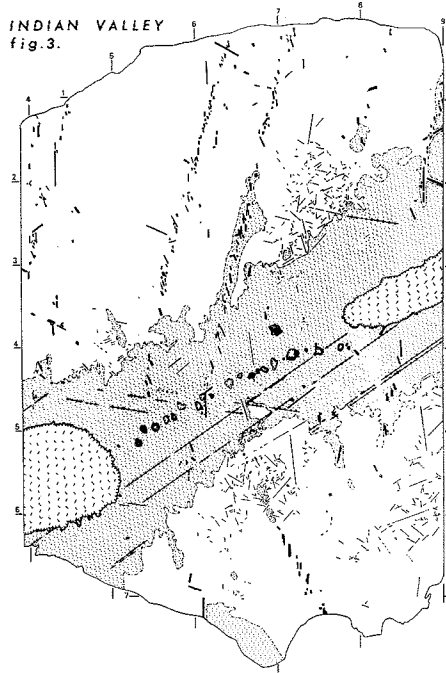
† Includes plates of large size in giant rhabdite belts.

of large schreibersite bodies. It is less dense and the distribution is more uneven than in the areas of frosty kamacite and does not give rise to a frosty appearance in the macrostructure. The two types of microrhabdite areas are well illustrated in Okano, where a sparse distribution of microrhabdite is found as a sheath about the line of giant rhabdites but the true frosty kamacite is associated with a group of small sulphides placed well away from the giant rhabdite belt.

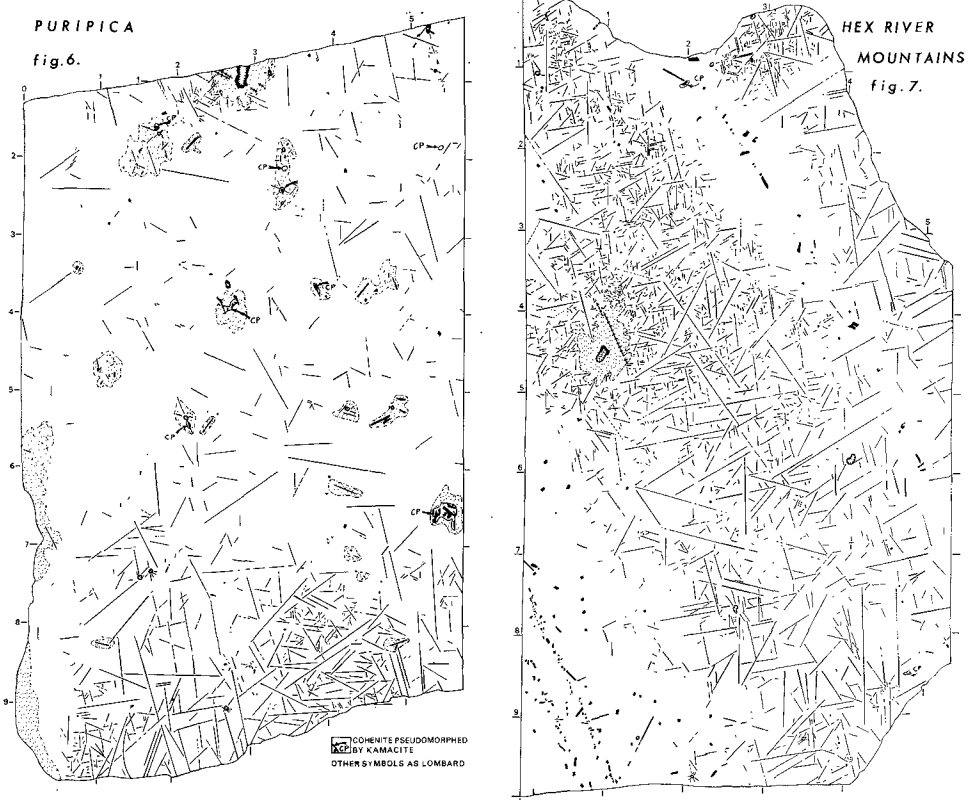
Shock-melted troilite is encountered in Scottsville, Angra dos Reis (iron), Indian Valley, and Hex River Mountains; granulated troilite is observed in Lombard; apparently unaltered assemblies of troilite with daubréelite lamellae are found in Okano and Puripica.

Cohenite is present in a cracked but undecomposed condition swathing schreibersite in Lombard; it is found in a cracked condition in Angra dos Reis (iron), where some decomposition to graphite and a low-nickel kamacite has taken place along the cracks. In Hex River Mountains pre-existing cohenite has completely decomposed to graphite and low-nickel kamacite while in Scottsville, Indian Valley, Okano, and Puripica there are regions of granulated and sometimes finely decorated low-nickel kamacite, within which are embedded particles of schreibersite; these areas, figs. 8 and 9, in which the nickel content of the kamacite is about  $1\frac{1}{2}\%$ , may be interpreted as the sites of pre-existing cohenite from which all the carbon has been removed.

Special features arise in the structure of some of the meteorites. Okano, which was reported to have been recovered in 1904 following the appearance of a fireball, shows a well-developed heat-alteration zone, which has not been marked on fig. 5; it also shows occasional traces of ablation deposit and the outer surface of the meteorite shows little sign of terrestrial corrosion. However, Okano has suffered very severe cracking at a late stage of its history and two of the cracks are plotted in fig. 5. In B.M. 1923, 1016, in its present state of preparation a considerable amount of infilling material has chipped out from the cracks and has been lost. Thus it is not possible to give an unambiguous description of the true condition of the material that occupied the cracks. However, the absence of heat-alteration effects in the small metal fragments that are occasionally found in the crack and the absence of dendritic structures in the infilling material suggest that there was little if any penetration of ablation-melted material into the crack. By contrast there is much evidence, particularly filling the more narrow fissures at the interior root of the cracks, of terrestrial corrosion product and there remains much metallographic evidence of severe mechanical distortion at the fracture surfaces. The amount and depth of penetration of terrestrial corrosion in the cracks is surprisingly great for a meteorite recovered and carefully preserved immediately after fall and raises the question whether or not Okano was associated with the observed fireball of 7 April 1904. On the other hand the corrosion is concentrated within the cracks, at the locations where metal is particularly susceptible to corrosion on account of being deformed, and one must not overlook the possibility that the corrosion could have taken place during the original cutting and macroetching processes. It is therefore in order to advocate the utmost care in cutting and etching any newly fallen or supposedly newly fallen iron meteorite, particularly if the material has been subject to mechanical deformation or cracking.



FIGS. 2 TO 5: Maps of hexahedrite samples; symbols on fig. 5 (bottom right). Scale marks are centimetres.



FIGS. 6 and 7: Maps of hexahedrite samples; for symbols see fig. 5. Scale marks are centimetres.

There are special features in both the macrostructure and the microstructure of Indian Valley. On the macroscopic scale (fig. 3) specimen B.M. 1959, 920 shows a pronounced concentration of both large and small nodules of melted troilite located on an internal surface of the sample. In fig. 3 portions of large melted nodules occur at each of the parallel cut edges of the sample with a string of small nodules stretching between. The present-day orientation of the kamacite appears to be identical on both sides of this sulphide-enriched surface since at least one of the belts of giant rhabdite, several of the decorated Neumann lines, and all of the late-stage undecorated Neumann lines cross the surface without deviation. Thus an explanation has to be sought for this surface of sulphide enrichment within a single crystal of kamacite. It is possible to interpret the effect as either a high-temperature slip plane of the parent taenite that provided the site for massive troilite precipitation or as a grain boundary of the parent taenite. On the grain boundary hypothesis one must assume either that the  $\gamma\gamma$  boundary unpinned at a high temperature and moved away from the surface on which the sulphides precipitated or that kamacite nucleated at the  $\gamma$  boundary and grew equally into the two (differently oriented) grains of parent taenite. The

high-temperature slip or fracture plane has been invoked by Brett and Henderson (1967) to rationalize the distribution of massive sulphides and this hypothesis favours the development of unigrain kamacite insofar as kamacite would be expected to nucleate at the plane of sulphide particles within the unigrain parent taenite. Insufficient evidence is available to distinguish between the various possibilities but the slip plane hypothesis provides the most simple mechanism.

On the microscopic scale Indian Valley is unusual in that considerable recrystallization or grain growth has taken place in the mechanical twins (Neumann lines) and this aspect has been well studied by Buchwald (1967). Similar effects are present in Scottsville and arise through a late-stage sequence of bulk reheatings after the Neumanns had been produced by a deformation process.

*Discussion.* In the present work we have prepared for microscopic examination sections very much larger than the one or two cm<sup>2</sup> that are ordinarily employed in metallographic examination. The results, figs. 2 to 7, demonstrate that there may be considerable variation of microstructure from one location to another. All the specimens used in the present work demonstrate this effect to some extent but it is particularly marked for Indian Valley and Okano. The case of Puripica, fig. 6, is interesting since it shows that large areas may be entirely free of plate rhabdite whereas other areas are heavily loaded with this form of phosphide. This casts doubt on Wasson and Goldstein's (1968) suggestion, based on the examination of small microsections, that Puripica is free of plate rhabdite and reopens the possibility that Puripica may be structurally as well as chemically associated with Rio Loa, San Martin, Filomena, Coya Norte, and Tocopilla.

When our results are considered in the sequence of figs. 2 to 7 there appears to be a progressive decrease of frosty kamacite from Scottsville to Hex River Mountains and a corresponding increase of plate rhabdite. However, as may be seen from Table I this structural sequence is not in exact conformity with the iridium content at the low-iridium end of the sequence, and if the sequence is altered to conform with iridium content Hex River Mountains and Lombard become interchanged so that a sharp and sudden peak occurs in the content of plate rhabdite at Hex River Mountains and decreases through Puripica to Lombard. Further work on both structure and iridium content would obviously be desirable for meteorites at the low iridium end of the sequence.

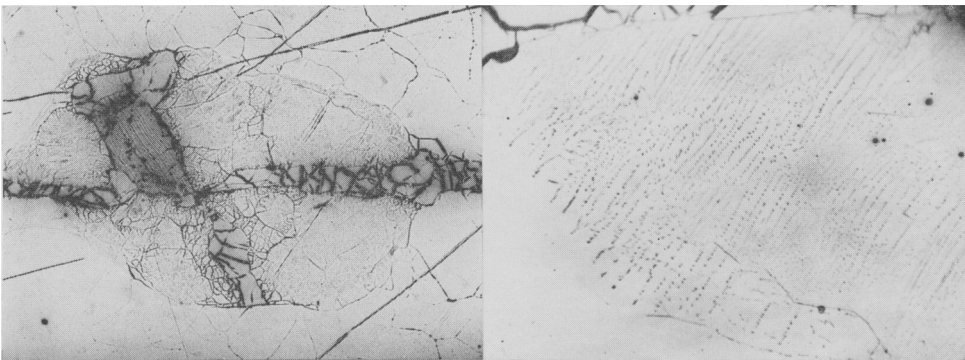
In Table I we have placed Angra dos Reis (iron) between Scottsville and Indian Valley and all the elements of structure observed by Axon and Waine (1971) in Angra dos Reis (iron) are present to a greater or less extent in the meteorites now under study and the general scheme whereby the macrostructure of the Angra dos Reis iron developed appears applicable also to the present specimens.

At a temperature of about 900 °C the meteorites consisted of sulphide particles in a taenite matrix. On cooling to about 800 °C the first crop of kamacite would be expected to nucleate and grow about the sulphide bodies and would have a low nickel content, whereas later crops of kamacite would be more distant and richer in nickel. Axon and Waine (1971) suggested that the first crop of nickel-poor kamacite



precipitated microrhabdites at a low temperature to produce frosty kamacite, whereas the later, more nickel-rich, areas precipitated rhabdite and rhabdite plates at a somewhat higher temperature to form clear kamacite.

The influence of sulphides on the distribution of frosty kamacite is well illustrated in Indian Valley. In Scottsville, which has a low nickel content and a widely scattered distribution of small sulphides there is a large proportion of frosty kamacite but in Lombard, Puripica, and Hex River Mountains smaller quantities of sulphide and a higher nickel content are associated with small quantities of frosty kamacite.



FIGS. 8 and 9: FIG. 8 (left). Cohenite pseudomorph in Puripica;  $\times 57$  Nital etch. A patch of veined, reticulated, low-nickel kamacite surrounded by normal kamacite. The area of low-nickel kamacite contains cracked crystals of schreibersite and a laminated association of troilite and daubréelite. FIG. 9 (right). Low-nickel kamacite in Puripica;  $\times 300$  Nital etch, showing very fine precipitation within the low-nickel kamacite.

However, the belts of giant rhabdites grew at a much higher temperature than that at which microrhabdites, rhabdite plates, and ordinary rhabdites formed. To explain the presence and location of giant rhabdites it is tempting to assume that some deformation effect arose in the kamacite of the parent body at a temperature of about  $600^{\circ}\text{C}$  and triggered off the precipitation of giant rhabdites along the belts that are present in all specimens except Puripica. These belts run through both clear and frosty kamacite but, following the interpretation of these as nickel-rich and nickel-poor areas, the giant rhabdites in any one belt reach a larger size in clear than in frosty kamacite.

At about the same time as the belts of giant rhabdites were induced massive schreibersite precipitated at any available locations and at this stage cohenite precipitated around or in association with either giant rhabdites or schreibersite.

Undisturbed cooling then took place for about  $200^{\circ}\text{C}$ , during which time rhabdite clusters, plate rhabdites, and ordinary groundmass rhabdites precipitated. Some cohenite redissolved at this stage leaving patches of  $1\frac{1}{2}\%$  nickel kamacite (figs. 8, 9). At this stage no precipitation of phosphide had taken place in areas that were eventually to become frosty kamacite but a second mechanical distortion took place,

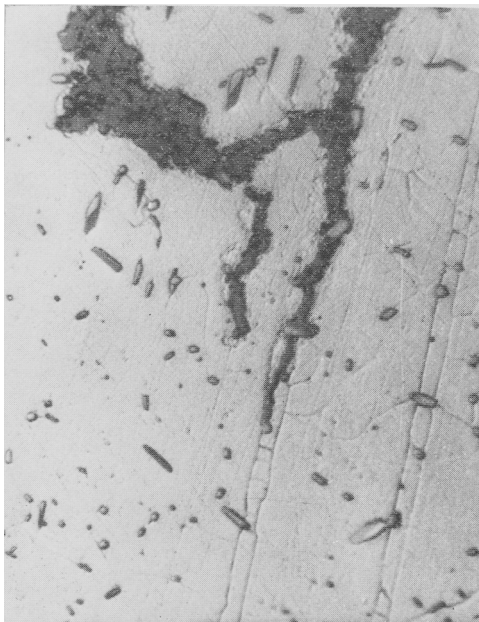


FIG. 10. Indian Valley;  $\times 300$  Nital etch. Finger of remelted troilite penetrating along a decorated Neumann band.

producing twins in the kamacite, which immediately became decorated in areas where phosphorus and nickel precipitation had not occurred. Thus the decorated Neumann lines were produced in the frosty kamacite and the precipitation of microrhabdite took place immediately afterwards.

At about this time a shock occurred that was sufficient to remelt the troilite in a number of hexahedrites. This shock clearly did not produce the decorated Neumann lines in Indian Valley since the sulphide melt penetrated along the already decorated twins (fig. 10). Melted sulphide eutectics are also present in Scottsville and Hex River Mountains. Troilite in Lombard shows marked granulation of the type produced by shock while in Puripica and Okano it shows only slight strain. No metallographic evidence of shock is present in the kamacite of any of these hexahedrites, hence the event that melted the

troilite must have taken place while the meteorite masses were still at a sufficiently high temperature for the deformation effects to anneal out of the metal in the manner indicated for the Gibeon octahedrite by Axon and Smith (1970).

A final shock at relatively low temperature produced the clean, undecorated Neumann lines that are a feature of all the specimens. This was followed by ablative flight through the earth's atmosphere followed by earth residence, corrosion, and the danger of damage by man.

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