Seven Shock-transformed Hexahedrites, Sensitive to Grainboundary Corrosion

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Dedicated to Professor H. Hintenberger on the occasion of his 70th birthday.

Seven polycrystalline iron meteorites (Forsyth County, Holland's Store, Wathena, Pima Co., Chico Mountains, Kopjes Vlei and Mejillones), of bulk composition as normal hexahedrites of group II A, are shown to be severely altered hexahedrites. Microprobe examination and various heat treatments of synthetic alloys support the conclusion that the meteorites after a primary slow cooling were subjected to shock-reheating above 800 °C. Thereby the following transformations took place $\alpha \rightarrow \gamma \rightarrow \alpha_2 \rightarrow \alpha$, and an unequilibrated structure, very sensitive to grain-boundary corrosion was formed.

Introduction

The last ten years have seen a very significant progress with respect to understanding the structure and composition of iron meteorites. The efforts in analysing for main and trace elements have resulted in a classification system [1, 2] that may form the basis for all further discussions. Mass-spectrometric work [3, 4] has provided valuable insight in the isotopic composition and the content of noble gases, data which allow us among other things to deduce the age of meteorites, and the intensity of the cosmic radiation.

However, certain meteorites have for various reasons been difficult to handle. One such group consists of seven polycrystalline iron meteorites, Table 1, which because of their enigmatic structure, that sets them apart from the more familiar hexahedrite or Widmanstätten structures, only rarely have been included in systematic investigations. Apart from brief descriptions with photomicrographs [5, 6] and more extended ones by Buchwald [2], the meteorites in question have only been cursorily examined [7 – 9]. In the Hey-Catalogue [10], they are indiscriminately labelled nickel-poor ataxites, brecciated hexahedrites or granular metabolites.

The purpose of this paper is to explain the structure and by experiments to support the presentation. It will be shown that the microscopic holes, that have

Table 1. Weight and bulk composition of the seven polycrystalline iron meteorites. Other important elements are iron (about 93%), cobalt (0.5%) and sulfur (0.1%).

	Weight	percent		ppm		
	kg	Ni	P	Ga	Ge	Ir
Forsyth County	23	5.54	0.21	60	176	31
Holland's Store	12.5	5.35	0.25	61	184	20
Wathena	0.57	5.54	0.27	60	184	7.0
Pima County	0.21	5.60	0.25	60	181	8.9
Chico Mountains	0.21	5.56	0.33	59	176	6.2
Kopjes Vlei	abt. 8	5.65	0.3	59	181	3.1
Mejillones	abt. 15	5.67	0.33	60	177	2.3

The analyses are weighted averages as reported in [2].

long puzzled scientists, are mainly artefacts, and that the extreme sensibility to terrestrial corrosion is due to a high degree of unequilibrium, which has sensitized the grain boundaries. Finally, an attempt will be made to present an evolutionary path that might lead to the observed structures.

Structure

While the seven meteorites do have some structural characteristics that may serve to distinguish them from each other, the following presentation will emphasize what they have in common: The polycrystalline kamacite, the shock-melted troilite aggregates, the resorbed phosphides, and the general unequilibration of all structural elements.

Polished sections show a massive material in which are embedded scattered diffuse patches of troilite and minute particles of graphite.

Upon etching a grain structure, which is unique to these iron meteorites, develops. Almost equiaxial grains, 0.3 – 3 mm in diameter, constitute the bulk of the specimens. Each kamacite grain is differently oriented as deduced from the oriented sheen from etching, and from the presence of occasional Neumann bands.

Each grain is divided into many thousands almost equiaxial subgrains, 30 – 50 μm in diameter, Figures 1 – 2. Within each main-grain the subgrains are uniformly oriented, since Neumann bands pass the subgrain boundaries with shifts of directions that are less than 1°.

The hardness of the metalphase is 190 ± 20 (Vickers DPN, 100 g load), somewhat dependent on the local coldwork from late splitting in the atmosphere in connection with the fall.

Grainboundaries and subboundaries are all very dirty, rich in tiny precipitates, 0.2 – 2 μm across, which on the microprobe could be shown to be mainly iron-nickel-phosphides. It is, however, possible that some of the smaller ones are carbides.

Equally distributed throughout the sections with a frequency of 300 – 500 pr. mm^2 there occurs a puzzling unit, a rounded or elongated metal grain 3 – 15 μm across, normally associated with tiny phosphide particles. These "unequilibrated loops" may be situated on grainboundaries or away from them, Figure 3.

There are no rhabdite-prisms or -plates in these meteorites. There is, however, occasional large schreibersite crystals, up to 10×1 mm in size. These are severely damaged and partially dissolved. Around them are zones with steep gradients of nickel and phosphorus, and the structure shows a corresponding zonation in grain size, and frequency and type of the tiny precipitates, Figure 8. Nearest the phosphide are equal numbers of amoeboid taenite particles and angular phosphides, farther away only phosphides occur.

Cm-sized troilite-daubreelite aggregates of the usual lamellar development, as seen in e.g. Coahuila, were once present. Now they have been transformed into intricate intergrowths of 1 – 10 μm grains of ironsulfide, iron-nickel-sulfide and iron, with dispersed fragments of daubreelite, and of schreibersite, which once rimmed the troilite nodule, Figure 4.

Graphite occurs as angular or spheroidal, often zoned aggregates, 10 – 150 μm across. The spherules are composed of anisotropic, radiating crystallites and are most common near the schreibersite remnants, presumably because the graphite was derived from cohenite, previously rimming the schreibersite, Figure 5.

Two of the meteorites, Mejillones and Kopjes Vlei, are no more corroded, than the heat-affected α_2 zone and an occasional patch of the fusion crust have been preserved. The others are rather heavily corroded. Cohen [11, 12] and others after him, believed that the strong corrosive attack was due to lawrencite, $FeCl_2$, a mineral which was assumed to be part of the meteorite structure. As discussed previously [13] the chlorine is, however, not of cosmic origin, but has entered the grain boundaries during a long exposure to terrestrial groundwater.

Pima County and Chico Mountains, which are very small and of a fragmental nature, have an obscure origin and may very well have come from the same, now lost meteorite [2, p. 976].

Forsyth County and Holland's Store have, in addition to the structures discussed above, at one end a different, more hexahedrite-like structure. The two structural types are separated by a wavy boundary. Forsyth County and Holland's Store are in all details so similar that they, too, might come from the same original fall.

The problematic pits

The structural description above was based upon the study of perfect sections. However, upon routine polishing and etching the sections always become pitted, wherefore most published photomicrographs (e.g. [5, 6]) show a profusion of black dots. There has been considerable confusion as to the cause of the pits; it has thus been proposed that they represented oxides, magnetite [5], altered rhabdites [2], or were pores in non-massive meteorites [7].

The first result of this investigation is that the pits are artifacts. They are not genuine and the meteorites are not porous. Careful cutting and polishing, supported by impregnation, and performed with small load and good cooling and lubrication, will usually result in perfect samples with no pitting.
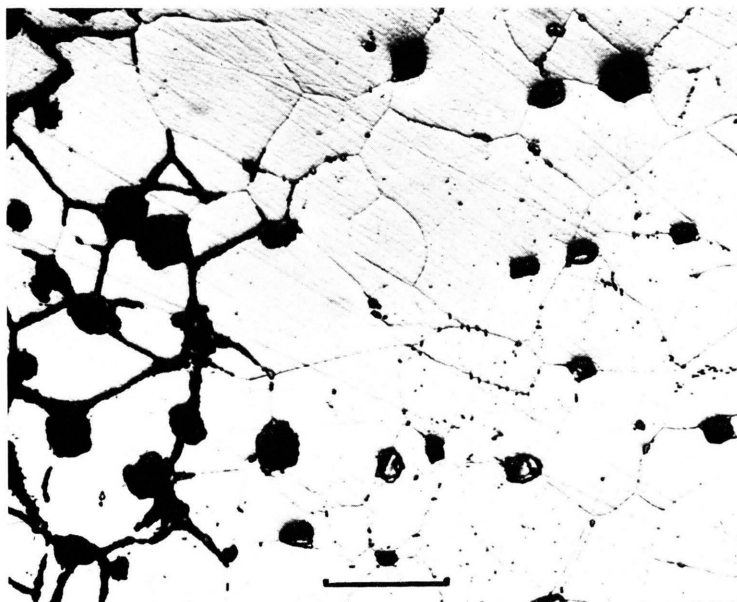
Fig. 1. Forsyth County. Corrosion penetrates from the surface (left) along the grain boundaries. The unequilibrated loops are selectively attacked and the polished surface becomes pitted (black). Etched. Scale bar 40 μm.
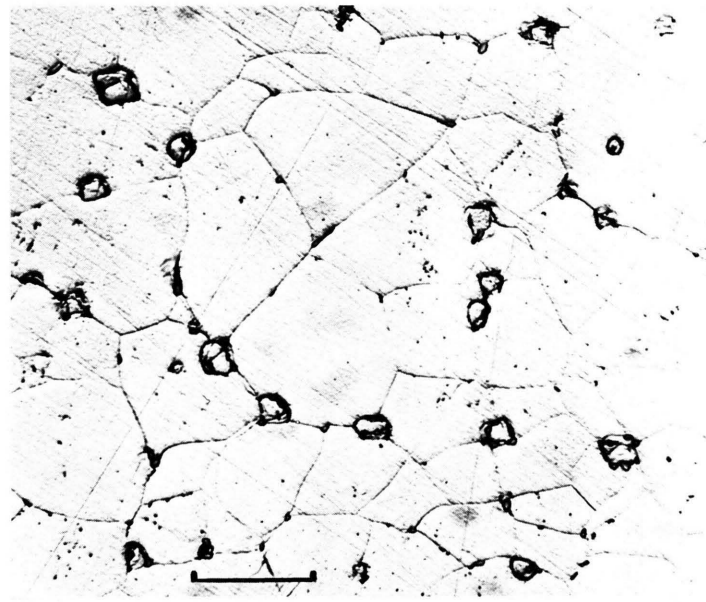

Fig. 2. Forsyth County. The uncorroded interior displays a polycrystalline kamacite structure with a significant number of sensitive, unequilibrated loops. Lightly etched. Scale bar 40 μm.
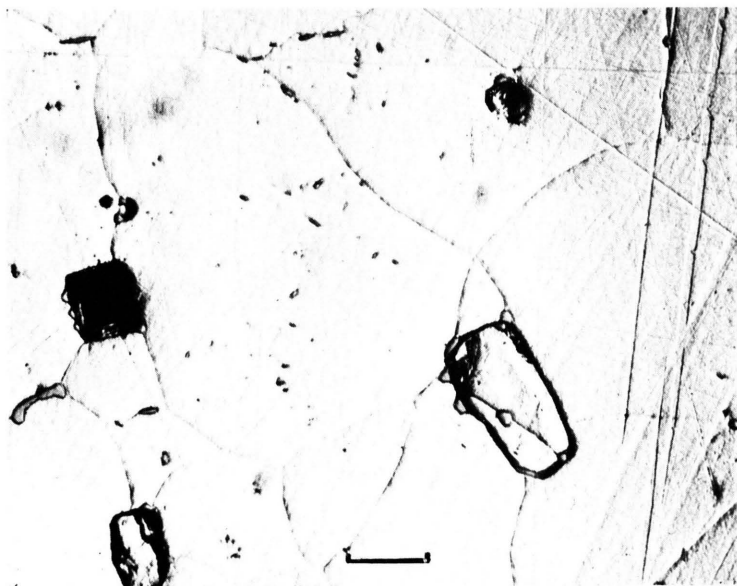
Fig. 3. Forsyth County. Four unequilibrated loops showing various stages of destruction, caused by polishing and etching. To the right several indistinct Neumann bands. Oil immersion. Scale bar 10 μm.

Fig. 4. Wathena. Detail of a shock-melted troilite nodule. The rapid melting and solidification produced a fine-grained eutectic of iron and ironsulfide with dispersed daubreelite (dark grey) and schreibersite fragments (white). Etched. Oil immersion. Scale bar 10 μm.

However, since the pits develop so easily in these irons and not in others of the same bulk composition, some explanation must be sought.
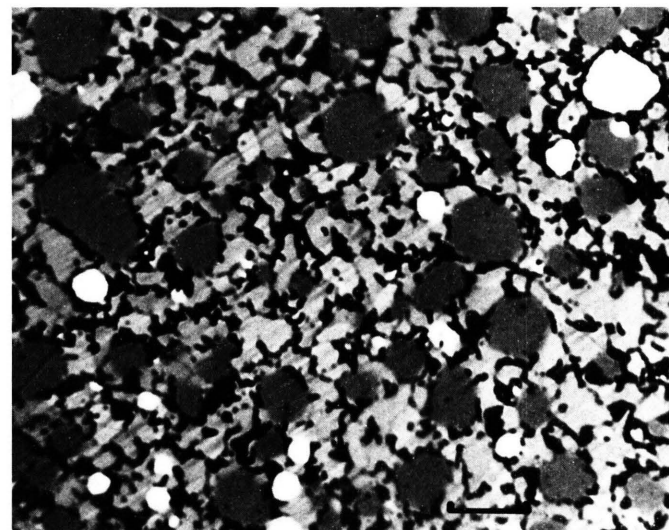
The perfect polished section is massive and it is hardly possible to predict that pits will occur during subsequent handling. Already a very weak etching with 1% Nital (1% nitric acid in ethanol) will reveal the grain- and subgrain boundaries, and their associated precipitates. A somewhat longer etching deepens the grain boundaries, and especially the "unequilibrated loops" are severely attacked. Finally, the loops become undercut and $1-15$ μm large grains easily pop out, leaving the characteristic rounded pits. The phosphide particles usually remain in situ. After prolonged etching, the pits may assume angular outlines, corresponding to the crystallographic orientation of the kamacite grains. It appears that there is a $1:1$ correlation between the unequilibrated loops and the pits.

Microprobe work only revealed the usual components, kamacite and phosphide, plus occasional graphite and sulfide. The phosphides have a frequency and distribution reminiscent of rhabdites in hexahedrites. They are, however, much smaller than in hexahedrites and usually occur as angular, irregular blebs in $\alpha - \alpha$ grain boundaries.

Results from microprobe work on three of the seven meteorites are shown in Table 2; work on Boguslavka and North Chile has been included for comparison. These two are hexahedrites of the same bulk composition, but monocrystalline and presumably representing a much better state of equilibrium because they have a very low cooling rate, on the order of $1°$ per million year [14] (this reference discussed Quillagua and Tocopilla, which both are fragments of North Chile). The normal hexahedrites

are soft, about $145-150$ Vickers, except when they have been cold-worked by fragmentation in the atmosphere.

The table shows that phosphorus is increased by about a factor five in the pitted meteorites. Simultaneously the volume-percent of phosphides is significantly decreased. Clearly, the kamacite of the polycrystalline meteorites is supersaturated with respect to phosphorus.

There are indications that the metallic phases are supersaturated with respect to carbon and sulfur atoms too, but this assumption could not be verified with the microprobe. However, in at least one of the seven meteorites, Kopjes Vlei, carbon is clearly concentrated in the unequilibrated loops. The carbon reveals itself in the heat affected α_2 zone where the loops now are surrounded by darketching nickel-bainite zones, created by diffusion of carbon away from the loops during the brief atmospheric reheating, Figure 6.

Optical examination, hardness testing and microprobe work thus all lead to the same conclusion, that the seven meteorites are unequilibrated and inhomogeneous, both in structural, mechanical and chemical respects. It is this lack of equilibration that leads to the pitting. The chemical gradients around the grain boundaries, possibly aided by ultrathin graphite films on some boundaries and by mechanical stress-concentration, concentrate the attack along the sensitized boundaries and loosen the coherence. Pits develop where the small grains become undercut, otherwise only heavy grain boundary etching develops.

During exposure to terrestrial ground water a similar attack, albeit more slowly, develops. Chloride-containing waters are particularly active and pene-

Table 2. Three of the polycrystalline meteorites compared to two normal hexahedrites, Boguslavka and North Chile.

	Bulk composition[a]		Kamacite composition[b]		Phosphide type[c]	Reference
	%Ni	ppm P	%Ni	ppm P		
Forsyth County	5.54	2100	5.4	2010 ± 220	GBP	9
Forsyth County	5.54	2100	5.3 ± 0.2	2200 ± 500	GBP	this work
Kopjes Vlei	5.65	3000	5.4 ± 0.3	2000 ± 500	GBP	this work
Mejillones	5.67	3300	5.81 ± 0.4	2620 ± 300	GBP	8
Mejillones	5.67	3300	5.72 ± 1.2	2850 ± 700	GBP	8
Boguslavka	5.42	2000	5.2 ± 0.1	500 ± 100	R	this work
North Chile, Puripica	5.59	3000	5.28 ± 0.2	400 ± 100	R	8
North Chile, Yungay	5.59	3000	5.30 ± 0.1	500 ± 100	R	this work

[a] Data as compiled in [2];   [b] Microprobe data;   [c] GBP, mainly grain boundary precipitates. R mainly rhabdites.

trate from the surface along the grain boundaries. The small loops are most readily converted to limonite, later follows the bulk of the material ([2], Figures 1024, 1905).

Experimental Verification

In order to establish a better understanding of the formation of the unequilibrated structure, extensive experiments on synthetic alloys have been performed. In this connection only a few pertinent data will be discussed.

The alloys (Table 3) were produced from powders of carbonyl iron, carbonyl nickel and iron phosphide [15].

Compression, followed by sintering for at least 24 hours in hydrogen at 1100 °C, and ending with quenching in water, resulted in alloys, that under microprobe examination proved to be homogeneous within ± 0.05% nickel and phosphorus.

A) Rapid heating followed by rapid cooling

Samples were then reheated above the $\alpha \rightarrow \gamma$ transformation temperature, which for these alloys is $750 - 850°$. They were held for half an hour and again quenched in water. The resulting structure was the well-known α_2 structure, a rather hard, unequilibrated structure, which is typical for the heataffected α_2 zone on fresh falls of hexahedrites. It did, however, not correspond to the structure of the polycrystalline meteorites in question.

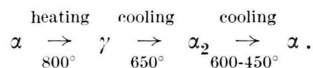### B) Rapid heating followed by slow cooling

Alloys of the same composition were reheated to similar high temperatures in the γ-region, and then left to controlled, slow cooling. In a typical experiment the cooling from $900°$ to $450°$ lasted 20 days, whereafter the furnace was held at $450°$ for an additional 5 days. Then the batch was quenched.

Table 3. Composition of synthetic alloys, weight %.

	% Ni	% P	% C	% Si	% Cu
E 3	3.0	0.5	0.03	0.10	0.02
G 46	4.0	0.6	0.03	0.10	0.02
G 57	5.0	0.7	0.03	0.10	0.02
E 6	6.0	0.5	0.03	0.10	0.02

The resulting structure was in all essential features identical to that of the meteorites: Polycrystalline ferrite with fine phosphide precipitates and a dense population of unequilibrated loops, Figure 7.

The heat treatment is an example of the solid-state transformations

$$\alpha \underset{800°}{\overset{heating}{\rightarrow}} \gamma \underset{650°}{\overset{cooling}{\rightarrow}} \alpha_2 \underset{600-450°}{\overset{cooling}{\rightarrow}} \alpha \, .$$

On cooling, the polycrystalline γ first transforms diffusionless to α_2. Then, on further slow cooling, the α_2 grains proceed towards a polycrystalline, equiaxed α structure of improved equilibrium. The impurity atoms, P and C, interfere with the grain boundary movements and prevent, under these cooling rates of about $25°$ per day, the formation of perfect grains. Instead a large number of unequilibrated loops are left pinned in the structure, as seen in Fig. 7, which should be compared to Fig. 2 of the meteorites.

The alloys contained as an impurity 1000 ppm Si max. While this is about a factor 50 more than is usual for iron meteorites [2, 16], the concentration of silicon is still too low to have had any significant effect on the equilibrium diagrams here in question. However, the silicon atoms, which are substitutional in the Fe-Ni-lattice, may be assumed to have reinforced the pinning of the P and S atoms.

Discussion

The seven enigmatic meteorites have bulk compositions and trace element concentrations, which within the limits of analytical error place them in group II A [1, 2]. They thus constitute a significant subset of the total population of about 45 meteorites in group II A.

It is generally assumed that the hexahedrites have had a very small cooling rate whereby they developed a coarse kamacite structure with grain-sizes of at least 30 cm diameter [2, 14]. It might be postulated therefore that the fine-grained meteorites here discussed represent material which had been subjected to a much more rapid primary cooling.

This appears, however, not to be the case, since remnants of troilite and schreibersite are present in a morphology and size which are typical of hexahedrites. The centimetersized inclusions of schreibersite must have been precipitated by very slow solid-state reactions below about 600 °C [17]. Therefore,
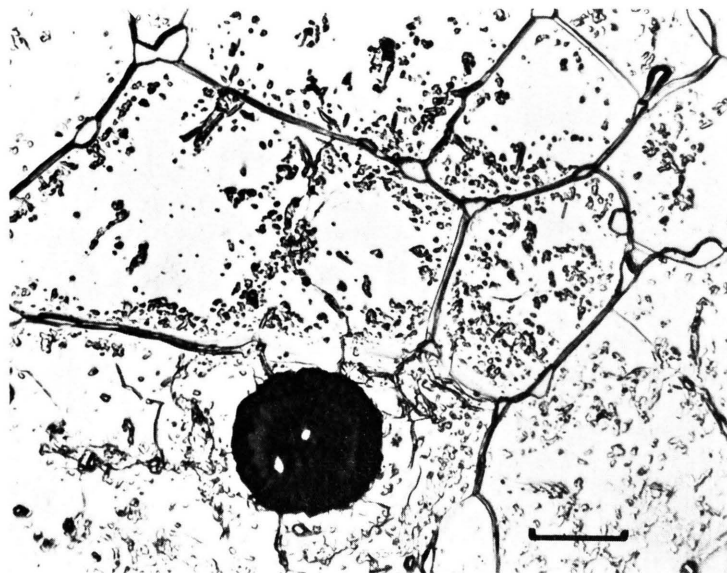
Fig. 5. Mejillones. Polycrystalline kamacite with numerous angular phosphides in the deep-etched grain boundaries. Below, a zoned graphite precipitate. Etched. Scale bar 25 µm.
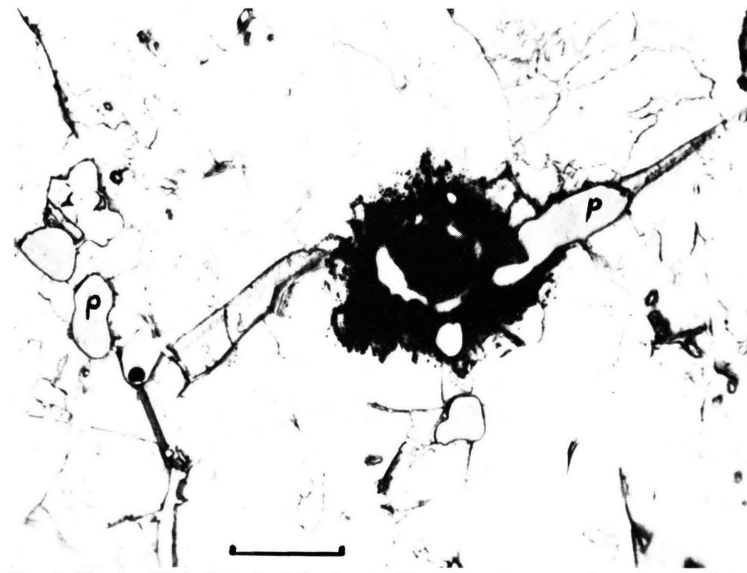

Fig. 6. Kopjes Vlei. Detail of the heat-affected α_2 rim zone from atmospheric flight. The brief reheating to above 1000°C here melted and rounded the phosphides (P), and carbon diffused away from the unequilibrated loop and formed darketching nickel-bainite. Etched. Oil immersion. Scale bar 20 µm.
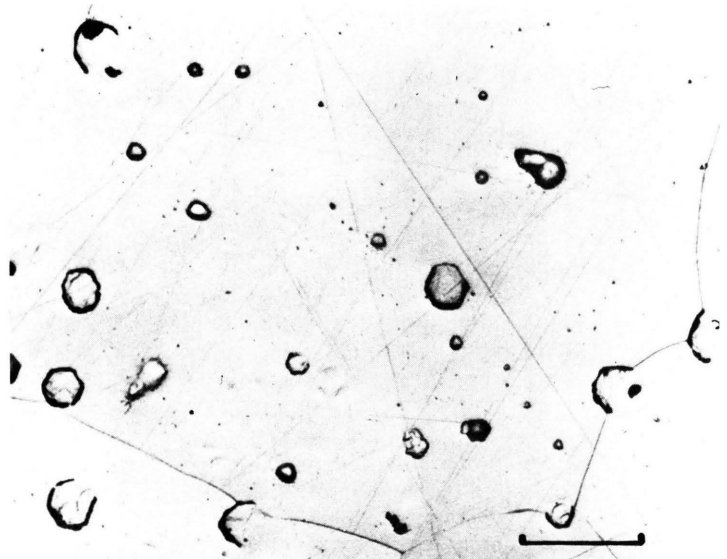

Fig. 7. Alloy E 3, subjected to 20 days of slow cooling from 900 to 450°C. Polycrystalline ferrite with a number of unequilibrated loops, which upon further polishing and etching will develop into pits. Slightly etched. Scale bar 20 µm.
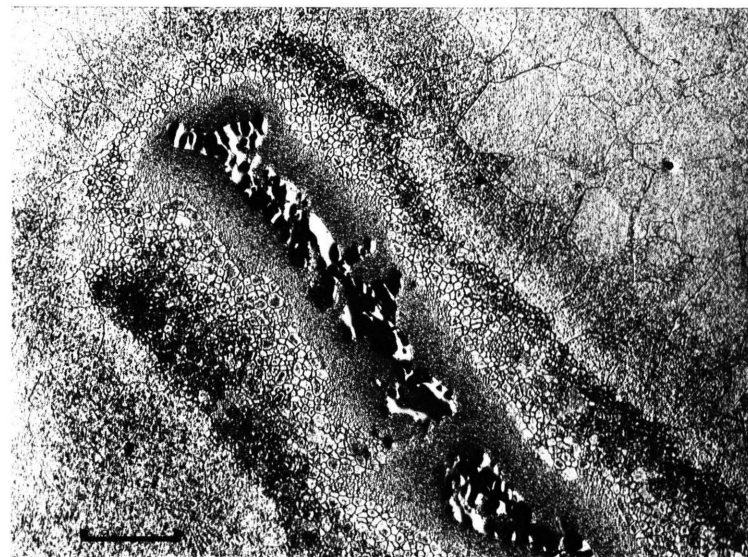

Fig. 8. Mejillones. Around a primary schreibersite crystal there is a strongly zoned variation in the phosphorus and nickel concentration, apparently caused by a brief, secondary, non-equilibrium thermal cycle. Etched. Scale bar 1 mm.

the fine-grained meteorites must at an earlier time have been coarse-grained.

In the following model an attempt is made to incorporate all relevant structural and compositional observations. A primary slow cooling generated typical, coarse-grained hexahedrite material with occasional nodules of cm-sized troilite, and with mm-cm-sized schreibersite crystals. Thin cohenite rims developed around some of the crystals, and in the matrix a heavy population of micron-sized rhabdites precipitated. This structure is well-exemplified by, e. g., North Chile ([2], Figures 1288 – 1298).

A severe shock with elements of shearing reheated the material to above 800 °C bulk temperature. In this phase, which probably lasted less than an hour, the schreibersite and rhabdite in the metal phase started to dissolve, and cohenite decomposed. The monocrystalline kamacite recrystallized to polycrystalline γ, which grew to mm-sized grains. The pulse of heat sent waves of P-, Ni- and C-atoms away from the preexisting inclusions, but equilibrium was not achieved before cooling set in again, Figure 8.

Even if the bulk temperature attained was only about 800 °C, the compressible troilite inclusions reached temperatures above 1000 °C, sufficient to melt them. The associated daubreelite and adjacent schreibersite rims were fragmented and disseminated into the melt, Figure 4.

Very soon the material started to cool, with a cooling rate about 25° per day. Thereby the numerous γ-crystals independently transformed to α_2, whereupon these slowly changed to more equiaxed α-grains. Part of the phosphorus reprecipitated as phosphide particles, while part of the carbon reprecipitated as graphite nodules and ultrathin films on some grain-boundaries. The cooling-rate was high enough to prevent equilibrium with respect to phosphorus, wherefore about 0.2% P remained in solid solution. The impurity atoms and precipitates interfered strongly with the grain boundaries and resulted in a large number of unequilibrated loops.

This shock-metamorphism will thus fit into our general understanding of shock-processes, but adds a new dimension, in which α via γ forms α_2, which then approaches equilibrium α, of a peciliar appearance and of an easily corroded character.

Since the material, after having reached the maximum temperature, cooled rather rapidly it must be assumed that it was no longer part of a large,

asteroidal-sized body, but rather a meter-sized fragment. In other words, the shock that produced the structural alterations, also fragmented the parent body and released the meteorites which from now on were exposed to cosmic radiation.

The only later event, which there is evidence for in the meteorites, is the penetration of the atmosphere, during which the already small masses were further reduced and fragmented. The surface was reheated and ablated, and Neumann bands formed in grains along the intergranular cracks [2].

The stages of shock-metamorphism and hexahedrites may be illustrated by Figure 9. After a slow primary cooling the meteorites-to-be are cool, soft, well-annealed, coarse-grained and with equilibrium precipitates, point A. The shock-event deforms and reheats the material to a degree which depends on distance from the impact point and on the local geometry and shielding. The distant part will be only slightly reheated, leading to recovery. Another part will be reheated above 500 °C and thereby recrystallize provided previous cold-work were sufficient. Finally, a small part will be reheated above the $\alpha \rightarrow \gamma$ transformation temperature and behave as discussed in the present paper.

If the meteorites of group II A are subjected to a structural reevaluation, we see that we have samples of all categories, Table 4. The total population may therefore be taken to represent a parent body which at one time was subjected to a violent shock, and was split and transformed. Of course, some of the material melted and vaporized, but of this nothing has survived, or at least has not been identified as meteorites so far.

The situation has a certain similarity to the impact event at Barringer Crater, Arizona. Around this crater a large number of metallic fragments, the Canyon Diablo meteorites, are scattered. Metallographic analysis ([2], page 390) shows that these fragments represent all stages of shock-transformation and many of them display steep temperature gradients. In addition, also the shock-melted remnants have survived and may be distinguished as tiny, metallic droplets scattered over the arid plain.

The boundary, that in Holland's Store and Forsyth County separates coarse- and fine-grained material, suggests that we also here have had steep temperature gradients. In the coarse-grained end the temperature did not exceed about 750 °C, therefore the α-structure did not transform to γ which was the
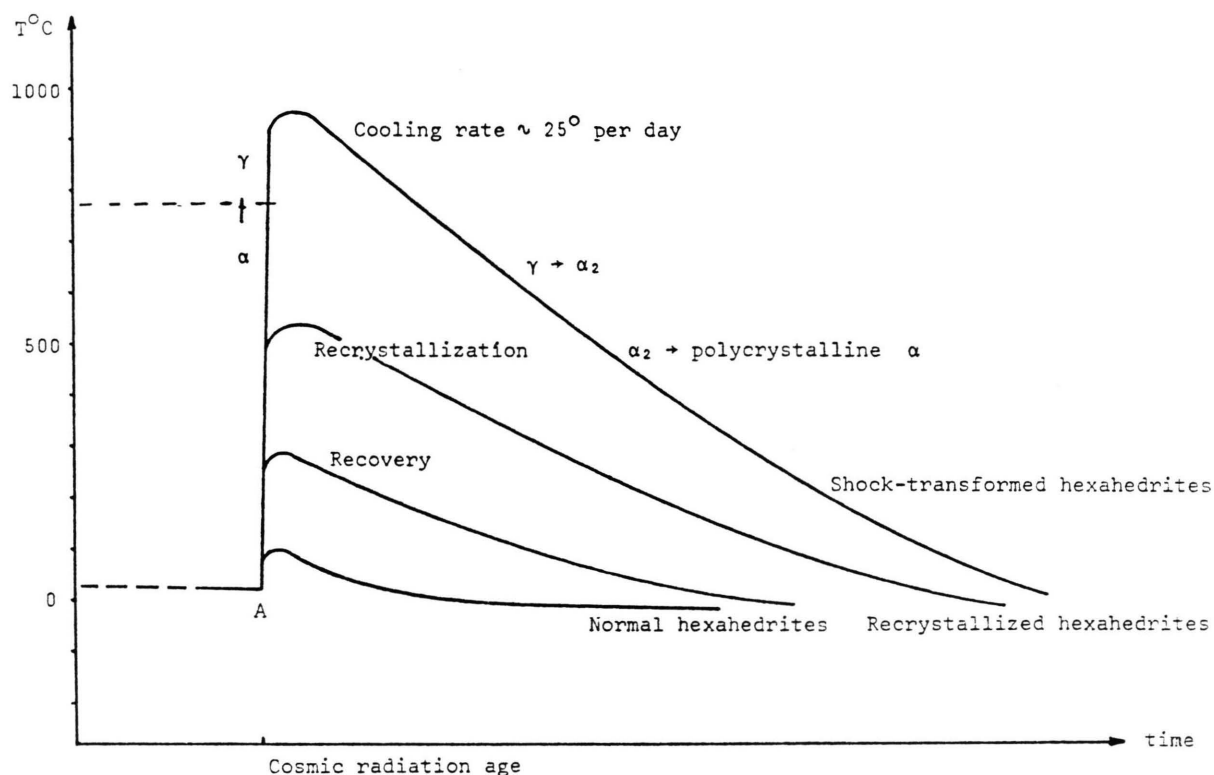
Fig. 9. Sketch suggesting the various reaction paths resulting from shock-reheating. The thermal cycle leads to significantly different structures for the same bulk composition.

Table 4. Some hexahedrites of group II A, arranged according to the extent of secondary changes in the primary structure.

Structural alterations	Examples
Only small structural changes	North Chile, Walker County, Murphy, Smithonia
Increasing recovery, recrystallization and decomposition of minerals	Bruno, Bennett County Angra dos Reis Scottsville, Edmonton Boguslavka Sierra Gorda, Negrillos Cedartown
$\alpha \to \gamma$ transformation, decomposed minerals, and unequilibrated matrix	Forsyth County, Holland's Store Wathena, Pima County, Chico Mountains, Kopjes Vlei Mejillones

necessary step for further decomposition to α_2. In the opposite end, 20 cm away, the temperature was high enough for the transformations to take place.

Conclusions

i) The seven fine-grained meteorites belong to the hexahedrite class, chemical group II A.

ii) They cooled slowly together with the bulk of group II A and developed an annealed coarse-grained hexahedrite structure.

iii) A shock event disrupted the parent body, and steep temperature- and pressure gradients developed. The fine-grained meteorites represent a case of severe alteration, where the reaction path α (monocrystalline) $\to \gamma$ (polycrystalline) $\to \alpha_2 \to \alpha$ (polycrystalline) was followed.

iv) The included minerals decomposed, and the cooling-rate, of the order of $25°$ per day, was so high that a significant proportion of the phosphorus remained in solid solution.

v) The impurities of phosphorus and carbon prevented a full equilibration of grain boundaries. Tiny phosphides and carbides, and graphite segregates, line many of the grain boundaries.

vi) Terrestrial corrosion attacks preferentially along these unequilibrated grain boundaries.

vii) Routine cutting and polishing develop a large number of micron-sized pits, conditioned by the said lack of equilibration.

viii) Lawrencite was never present as a cosmic mineral; the chlorine in the grain boundaries is derived from terrestrial groundwater.

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