Mineralogy of a unique graphite-containing fragment in the Krymka chondrite (LL3)

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Abstract

The Krymka chondrite contains an exotic graphite-bearing fragment that appears to be of a new type of material added to unequilibrated LL-chondrite during agglomeration on the surface of the parent body. The fine-granular texture without chondrules, two morphological groups of graphite crystals which differ in size and occurence, high content of troilite (11.3 vol.%), the high Ni (55.5–66.6 wt.%) and Co (1.59–2.87 wt.%) contents of the taenite and absence of kamacite, the presence of F-apatite, which is rare for meteorites but common for lunar and terrestrial igneous rocks, are the main features of the fragment.

The mineralogy and texture indicate: (1) the fragment probably formed by crystallization from a highly reduced silicate melt, which had been enriched in carbon; 2) the subsequent metal sulphidization lowered its abundance and resulted in the formation of troilite and the compositional features of the residual metal; (3) terrestrial weathering of an exotic fragment and the host part of the chondrite produced iron hydroxides, pentlandite and quite possibly magnetite.

KEYWORDS: chondrite, fragment, graphite, filiform crystals.

Introduction

THE meteorite collection of the Natural History Museum of the National Ukrainian Academy of Sciences contains 50 individual samples of the Krymka meteorite with a total mass of about 26 kg. An overwhelming majority of them show evidence of shock metamorphism and terrestrial oxidation, which vary in intensity from sample to sample. Comparison of the effects of shock metamorphism with experimental data indicates a shock pressure up to 25–45 GPa and the shock heating of the main part of these samples up to 500°C and local parts more than 950°C (Semenenko *et al.*, 1978; 1987). The Krymka sample studied by Stöffler *et al.* (1991) has evidence of a shock pressure of 10–15 GPa (shock stage S3).

On studying sample N1290/29, we found an exotic graphite-rich fragment with mineralogical peculiarities that corresponds neither to the carbonaceous fragments with mysterite in Krymka (Higuchi *et al.*, 1977; Lewis *et al.*, 1979; Grossman *et al.*, 1980; Semenenko *et al.*, 1991*a*, *b*), nor to any other known type of cosmic matter including carbon-rich aggregates (Fodor and Keil, 1978; Scott *et al.*, 1981*a*,*b*; Taylor *et al.*, 1981; Brearley *et al.*, 1987; Scott *et al.*, 1988). The sample also contains completely shock-melted regions. The latter testify that the sample N1290/29 was shocked more intensely than the rest of Krymka.

Analytical procedures

The graphite-bearing fragment was found on a broken surface of sample N1290/29. Splinters from it (less than 0.5 × 0.3 mm in size) were examined by X-ray diffraction (Fe-*K*α, β, ASTM card index) and SEM (REM-100u and JCXA-733) techniques. A polished section (13 × 10 × 4 mm) of the sample was prepared for petrographic study by reflected light microscopy and electron microprobe analysis. Evidence of shock metamorphism was also obtained by transmitted light microscopy for olivine grains separated by crushing some splinters. The graphite-bearing fragment was studied with a CamScan

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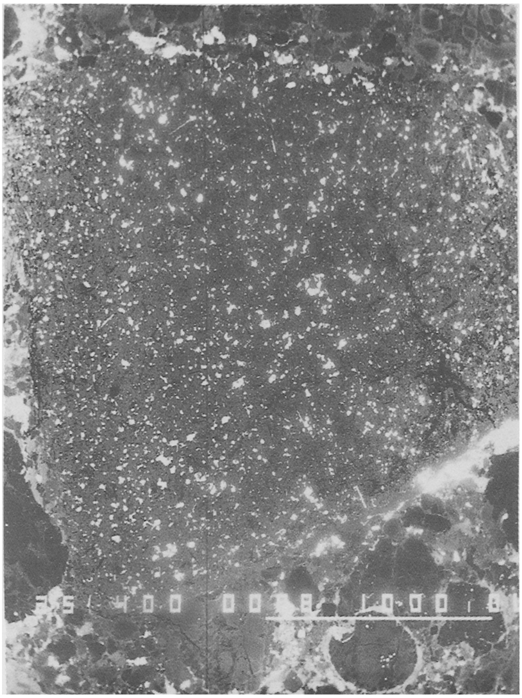

FIG. 1. Low magnification, back scattered electron image of the Krymka graphite-containing fragment. Note some troilite-metal plates (white) and uniformly distributed graphite filiform crystals (black) in the fragment. The scale bar is 1 mm.

SX-50, Camebax-36 and JCXA-733 (Jeol Superprobe) electron microprobes, using 10 kV accelerating voltage for graphite crystals, 15 kV for silicates and 25 kV for metallic phases and beam currents of 50 nA for graphite and 10 nA for the other minerals, with 2 μm diameter electron beam, and ZAF data correction. Analytical errors are 1.5% relative for major elements and 0.02% absolute for minor ones.

Results

The graphite-bearing fragment (Fig. 1) is characterized by its black colour, fine-granular texture and the presence of abundant holes in the polished section. The irregular shapes of the holes indicate formation by plucking of mineral grains during grinding and polishing of the sample. The fragment is triangular (2.8 × 2.1 mm) and has a sharp boundary with the host. One side of the fragment is bounded by troilite with a quench texture.

The polished fragment contains 14.1 vol.% of artificial holes and the following minerals (vol.%): silicates (olivine, pyroxene and plagioclase feldspar) 78.7; troilite 11.3; graphite 3.0; taenite 2.2; magnetite 2.9; both chromite and phosphates less than 1 and rare grains of pentlandite, total (excluding holes) = 100%.

A SEM study of a fracture surface shows the following features:

1. The presence of regular hexagonal plates (less than 2 μm), with a morphology typical of graphite (Fig. 2). The absence of the characteristic pinacoidal cleavage on prismatic faces (Fig. 2*a*) may be due to transformation during shock metamorphism. Microcrystals of graphite protrude from the surfaces of silicate grains (Fig. 2*b*), metal (Fig. 2*c*) and troilite globules or are scattered over their surfaces (Fig. 2*d*) and on the walls of silicate voids (Fig. 2*a*). Many microcrystals, presumably of graphite, have sizes of less than 0.3 μm (Fig. 2*c,d*). It is interesting that the size and morphology of the microcrystals are similar to those of regular hexagonal plates of Solar System graphite, which have been chemically isolated from Murchison (CM2), but have never been observed *in situ* in the chondrite (Amari *et al.*, 1990; Zinner *et al.*, 1990).

2. The presence of rounded plagioclase grains protruding from the surfaces of olivine grains.

3. Single prismatic crystals of pyroxene (?).

4. Troilite and metal globules without microcrystals of graphite. The globules have smooth, sometimes undulating and porous surfaces.

5. Growth steps, brittle fractures and adhering melt drops on some crystal faces of the silicates. The faces of some olivine crystals contain many holes, which belong probably to dissolution figures. Outline and mode of disposition of the holes are similar to those on the metal grain surfaces of intensely shocked chondrites (Semenenko *et al.*, 1987).

6. Partly devitrified glass between silicate crystals.

7. Rosettes of needlelike fine crystals of iron hydroxides presumably formed by terrestrial alteration.

X-ray and microscopic observations indicate that olivine and troilite are the most abundant minerals in the fragment. Most subhedral to anhedral silicate grains are less than 20 × 30 μm in size. Small grains (<5 μm) are of olivine or pyroxene and the larger ones are polymineralic and consist of olivine and/or pyroxene and plagioclase. A small quantity of partly devitrified interstitial glass of variable composition is also present. Based on the small size, microprobe analyses of the minerals in many cases give poor totals and stoichiometry that restrict the quantity of acceptable data. An accurate composition of the glass was obtained for only one point (Table 1). Most olivine grains exhibit evidence of shock metamorphism (undulatory and mosaic extinction), while some euhedral grains are optically uniform (strain free). Olivine is inhomogeneous, but this

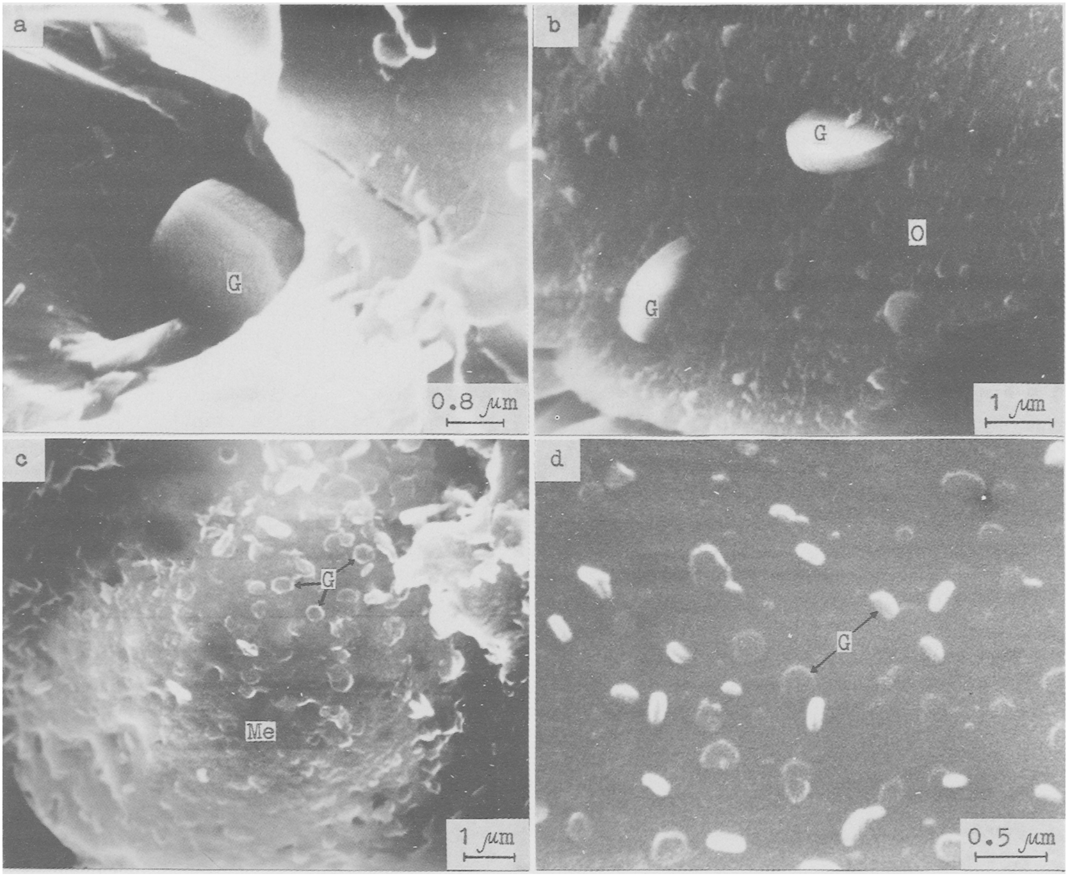

FIG. 2. SEM images of graphite microcrystals in the fragment of the Krymka chondrite. G, graphite; O, olivine; Me, metal. (*a*) Graphite microcrystal without pinacoidal cleavage, located inside a void in silicate. (*b*) Protruding microcrystals of graphite (white, grey) on the surface of an olivine grain. (*c*) Hexagonal microcrystals on the surface of a metal globule. (*d*) Microcrystals on the surface of an olivine grain, partly (white and light grey) protruding from the host mineral. Note the multiple graphite (?) nuclei on the surface of the metal globule (*c*) and especially on the olivine grain (*d*).

variability is less visible among grains. The variation is less than 2 mol.%. The largest variations (up to 4 wt.% FeO) occur between grains in different parts of the fragment (Table 1). The olivine contains higher FeO than that in equilibrated LL-chondrites (Fig. 3*a*). One olivine grain (SiO_2 36.2, TiO_2 0.05, Cr_2O_3 0.06, FeO 27.8, MnO 0.36, MgO 32.8, CaO 0.09, P_2O_5 3.00, total 100.40 wt.%, Fa 32.2) resembles phosphoran olivine in pallasites (Buseck, 1977). Some olivine grains contain rounded inclusions (<1 μm) which are enriched in P_2O_5.

Pyroxene is less abundant than olivine; Ca-poor and Ca-rich pyroxenes are equally abundant. Study of some silicate grains in transmitted light revealed the presence of clinopyroxene twins. Both pyroxenes have variable compositions (Table 1, Fig. 3*a,b*). FeO content in the Ca-poor pyroxene is similar to that in equilibrated LL-chondrites (Fig. 3*a*). Olivine (26–30 wt.% FeO) and Ca-poor pyroxene (13–19 wt.% FeO) compositions correspond to the upper limits of those (0–34 and 0–21 wt.% FeO, correspondingly) in the host part of Krymka (Dodd *et al.*, 1967). The five grains of plagioclase studied have slight compositional inhomogeneity (Table 1).

Phosphate grains are distributed between the silicates. Most grains are rounded but some are subhedral and less than 6 μm in size. An accurate composition (Table 1) was obtained for four grains only. One is fluorapatite, extraordinary for chondrites, but the others are merrillite, which is typical

TABLE 1. Electron microprobe analyses (wt.%) of silicates and phosphates in graphite-containing fragment of the Krymka chondrite

	Olivine		Ca-poor pyroxene		Ca-rich pyroxene		Plagioclase feldspar		Mesostasis	F-apatite	Merrillite
	range (50)[1]	average	range (7)	average	range (6)	average	range (5)	average	(1)	(1)	average (3)
SiO_2	35.5–38.2	37.0	51.4–55.9	54.1	50.9–54.7	53.5	61.4–64.7	63.1	47.6	0.45	0.16
TiO_2	n.d.–0.17	<0.02	0.12–0.24	0.18	0.46–0.62	0.53	n.d.–0.11	0.06	<0.01	n.d.	<0.03
Al_2O_3	n.d.	n.d.	0.29–0.62	0.41	1.12–3.00	1.54	20.9–22.7	22.1	17.9	0.14	0.24
Cr_2O_3	n.d.–0.33	0.05	0.14–0.37	0.22	0.52–0.88	0.71	n.d.–0.09	<0.03	0.14		
FeO	26.1–30.2	27.9	13.2–18.7	15.3	5.61–9.37	6.57	1.04–1.71	1.29	13.5	1.38	1.74
MnO	n.d.–0.44	0.29	0.29–0.44	0.36	n.d.–0.22	0.15	n.d.–0.04	n.d.	0.12	0.05	<0.02
MgO	31.8–36.7	34.6	27.1–29.8	28.3	15.3–16.7	15.8	0.01–0.82	0.45	8.89	0.18	2.92
CaO	n.d.–0.50	0.09	0.59–2.04	0.97	19.2–21.9	20.6	3.41–3.66	3.53	2.10	52.6	44.8
Na_2O	n.d.	n.d.	n.d.–0.10	0.06	0.67–0.87	0.78	8.96–10.1	9.32	8.39	<0.01	2.55
K_2O	n.d.	n.d.	n.d.	n.d.	n.d.–0.13	<0.03	0.03–0.10	0.06	0.79	<0.02	<0.03
P_2O_5	n.d.–0.22	0.04	n.d.–0.20	0.04	n.d.–0.13	0.07	0.03–0.21	0.08	0.06	41.7	45.3
F										5.23	0.64
Cl										0.41	<0.01
S										0.05	n.d.
Total		99.99		99.94		100.28		100.02	99.53	102.22	98.4
			Wo 1.0–4.0	1.9	40.1–45.6	43.2	Ab 81.2–83.9	82.3			
	Fa 28.8–35.0	31.3	Fs 20.8–25.9	23.0	9.1–14.7	10.7	Or 0.2–0.6	0.4			
			En 73.1–77.3	75.1	44.5–48.5	46.1	An 15.7–18.2	17.3			

( )[1] – number of analyses.
< – within error limits.

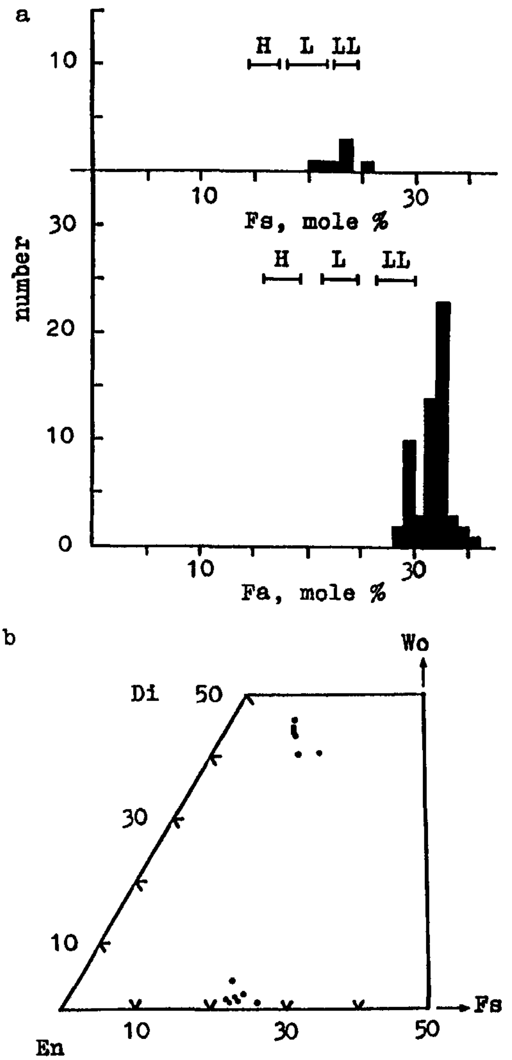

FIG. 3. Composition of silicates in the Krymka graphite-containing fragment: (*a*) Histogram showing the iron:magnesium ratio of Ca-poor pyroxene and olivine grains. H, L and LL compositional ranges for olivine and Ca-poor pyroxene from Keil and Fredriksson (1964) are shown for comparison. (*b*) Chemical composition of Ca-poor and Ca-rich pyroxene.

for LL-chondrites (Van Schmus and Ribbe, 1969). The fluorapatite grain contains some FeO, MgO, SiO_2, and Cl. The merrillite is essentially homogeneous but has variable concentrations of FeO and F (Table 1). The phosphate grains contain SiO_2 which may be due to the substitution of PO_4 groups by SiO_4 groups in the phosphate structure as the consequence of the substitution of Ca^{2+} ions by REE^{3+} and Y^{3+} (Frondel, 1978).

Irregular, sometimes prismatic, hexagonal and cubic troilite grains are present (Fig. 4). The irregular grains are associated with taenite (Fig. 4*a*) and the prismatic (Fig. 4*b,c*) with graphite. Cubic crystals of troilite with regular octagonal and tetragonal shapes contain metal relics (Fig. 4*d*). The troilite composition varies from grain to grain and small amounts of Ni and Co are present in some points (Table 2).

Metal particles (less than 20 × 30 μm) occur associated with troilite (Fig. 4*a,d*), sometimes with graphite and chromite or as separate irregular grains. The particles are taenite with very high concentrations of Ni and Co, which vary from grain to grain (Table 2). The concentration of Co is close to that in kamacite and some taenite particles in the matrix of Krymka (Fig. 5). In most cases the taenite in the graphite-containing fragment is characterized by a positive correlation of Ni and Co (Fig. 5). It approaches the composition of awaruite and differs from taenites in chondrules and in most cases in Krymka matrix (Rambaldi and Wasson, 1984; Semenenko *et al.*, 1987).

Regular prismatic crystals of graphite, varying in size from 80 × 6 to 20 × 5 μm, are uniformly distributed in the fragment. Idiomorphism of graphite is higher than for silicates, which are located on the phase boundary. An overwhelming majority of crystals have an anomalous shape with a length/width ratio greater than 10 (Fig. 6). This morphological feature allows us to classify them as filiform crystals (Givargizov, 1977). Rare grains have irregular shapes. From their bireflection, two types of graphite are observed: crystals with uniform grey colour (Fig. 6*a,b*) and those with 'spotty' colour (from gray to greyish brown) (Fig. 6*b*) apparently linked to their polycrystalline structure. Some filiform crystals alternate with metal and/or troilite plates (Fig. 4*c*). Graphite consists mainly of C with small amounts of other elements (Table 3). Variation of the composition is negligible within graphite crystals and greater between crystals. Some crystals are slightly curved and distorted.

Chromite occurs as separate rounded grains up to 20 μm in diameter in association with troilite, graphite, taenite and plagioclase. The composition of chromite grains in the fragment differs from that in the host (Bunch *et al.*, 1967) and is characterized by higher concentrations and variation of TiO_2 (Table 4). The former are zoned, with TiO_2, MgO, MnO and V_2O_3 decreasing towards the grain rim. Two groups of chromite grains can be distinquished. Most grains inside the fragment contain up to 13.0 wt.% Al_2O_3, 4.2% TiO_2, 3.5% MgO and are classified as Al-chromite, similar to those found in

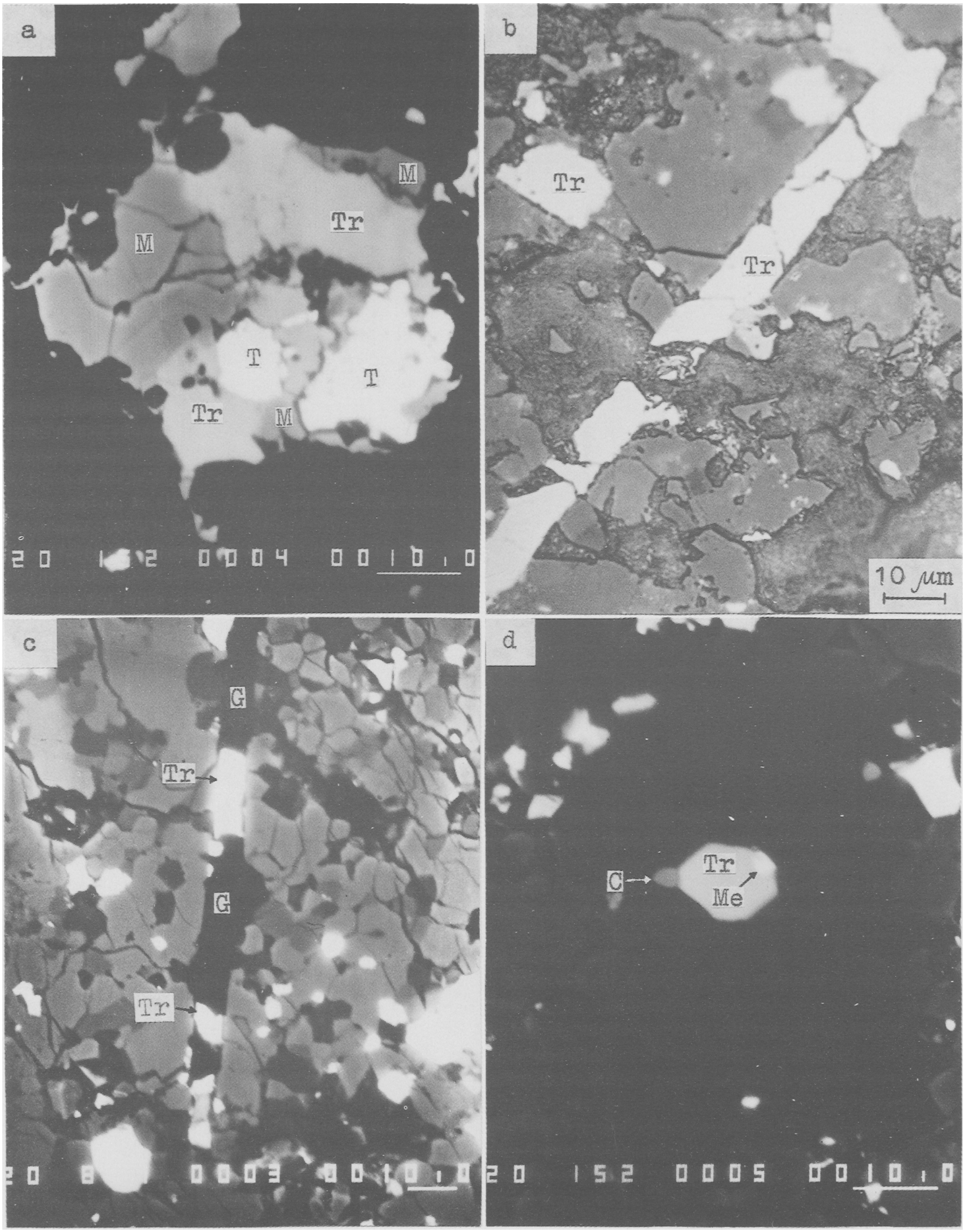

FIG. 4. Backscattered electron images (except *b*) of opaque minerals in the fragment of the Krymka chondrite. M, magnetite; Tr, troilite; T, taenite; G, graphite; Me, metal; C, chromite. (*a*) Association of taenite, troilite and magnetite in silicates (black). Metal is probably older than troilite and replaced by it. Simultaneously magnetite substitutes for the troilite owing to weathering. (*b*) Reflected light image of the troilite plate and grains. Note the artificial holes (dark grey) in silicates (grey). (*c*) Graphite filiform crystal (black) alternating with troilite plates (white). Silicates – grey, dark grey. (*d*) Cubic troilite crystal with metal relic and chromite grain in silicates (black).

TABLE 2. Electron microprobe analyses (wt.%) of taenite, troilite and pentlandite in the fragment of Krymka.

	Taenite		Troilite		Pentlandite
	range (19)[1]	average	range (31)	average	(1)
Fe	31.6–41.7	35.8	60.6–64.1	62.7	50.6
Ni	55.5–66.0	61.1	n.d.–0.45	0.06	15.1
Co	1.59–2.87	2.39	n.d.–0.12	<0.03	0.45
Cu	n.d.–0.26	0.07	nd.–0.07	<0.01	0.19
Cr	n.d.–0.11	<0.03	0.01–0.10	0.04	<0.03
P	n.d.	n.d.	n.d.–0.02	n.d.	n.d.
S	n.d.–0.30	0.07	34.6–39.1	36.6	33.0
Si	n.d.–0.05	n.d.	n.d.–0.13	<0.03	<0.03
Total		99.46		99.47	99.40

()[1] – number of analyses.
< – within error limits.

lunar rocks (Haggerty, 1974; Frondel, 1978). Two chromite grains on the periphery of the fragment contain variable but lesser concentrations of Al_2O_3, TiO_2 and MgO than Al-chromite. Two compositionally distinct chromites (A, B) have been reported in the host part of Krymka (Table 2) (Bunch *et al.*, 1967). The composition of chromite in the matrix near the fragment is nearly identical to that of chromite (A).

Many troilite and kamacite grains in the host meteorite and troilite in the fragment are associated with magnetite. Magnetites are located on the rims of troilite grains and have inherited outlines of their irregular shape (Fig. 4*a*). In some cases magnetite crystals with a hexagonal shape like that of troilite, but not of cubic magnetite, are observed (Fig. 6*b*). Microprobe data of the magnetites, which have the same range in both fragment (14 measured grains) and host part (11 grains), show the following concentrations (wt.%) of FeO (89.4–94.0); Cr_2O_3 (n.d.–0.58); MgO (n.d.–0.42); Al_2O_3 (n.d.–0.17); TiO_2 (n.d.–0.06); Ni (n.d.–0.55) and S (n.d.–0.38).

The fragment contains evidence of terrestrial oxidation, which is especially distributed around the

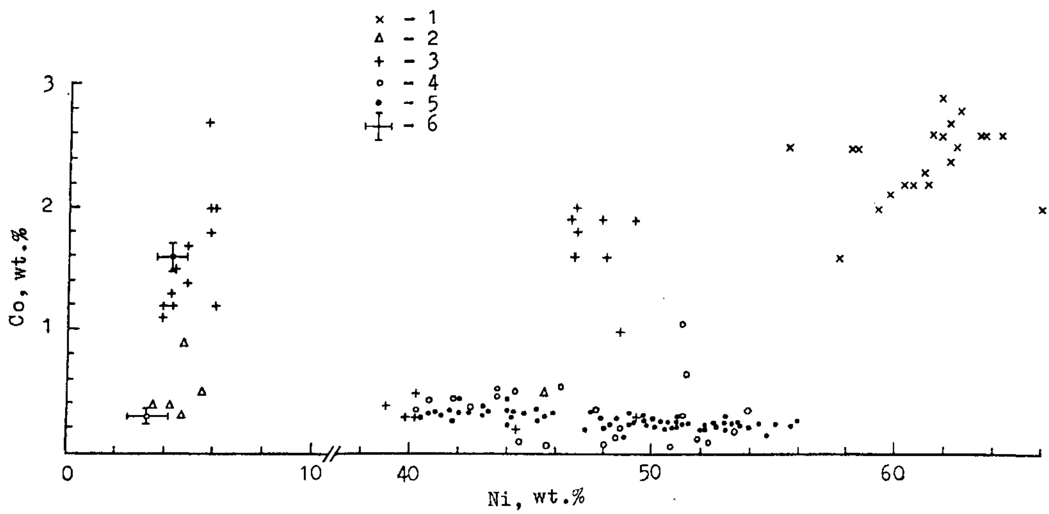

FIG. 5. Ni *vs*. Co plot for Krymka metal particles in: 1, graphite-containing fragment; 2, 4, chondrules; 3, 5, matrix; 6, average data of Ni and Co concentrations in kamacite. 1, our data; 2, 3 data from Semenenko *et al.* (1987); 4–6 data from Rambaldi and Wasson (1984).

TABLE 3. Electron microprobe analyses (wt.%) of graphite in the fragment of Krymka

	Range (13)[1]	Average
C	95.3–99.9	98.6
Si	0.12–0.85	0.41
Al	0.01–0.29	0.05
Fe	0.59–1.98	1.03
Ni	n.d.–0.31	0.08
Mg	0.08–0.30	0.17
Ca	0.04–0.18	0.08
Na	0.02–0.26	0.10
K	n.d.–0.08	<0.03
S	0.02–0.08	<0.03
Cl	0.01–0.05	<0.03
Total		100.61

()[1] – number of analyses.
< – within error limits.

fragment and in the host. The silicates are penetrated by veins of iron hydroxides, which partially replace the troilite. A unique prismatic grain of troilite is associated with pentlandite (Table 2). This association is located on the fragment margin where there is a high content of iron hydroxides, which testifies to the secondary origin of the pentlandite due to terrestrial oxidation.

It is necessary to point out the presence of completely shock-melted regions in the host part of sample N1290/29. These are lightly coloured, chondrule-free and crystalline with isolated metal-troilite mixtures. The host part of the sample has a chondritic texture and also contains quenched troilite melt, which is absent within the graphite-bearing fragment. The latter shows some evidence of shock metamorphism, such as brittle and plastic deformation of minerals, dissolution figures on the surface of some olivine crystals and melt structures such as troilite and metal globules (Fig. 2*c*). Melt drops adhering to the surfaces of some crystals are considered to have been formed by shock.

In summary, the fragment is characterized by the following features which distinguish it from the host chondrite: 1, absence of chondrules, fine-granular texture and black colour; 2, high content of troilite; 3, presence of graphite and F-apatite; 4, absence of kamacite and plessite; 5, distinct composition of taenite and chromite; 6, less compositional variation

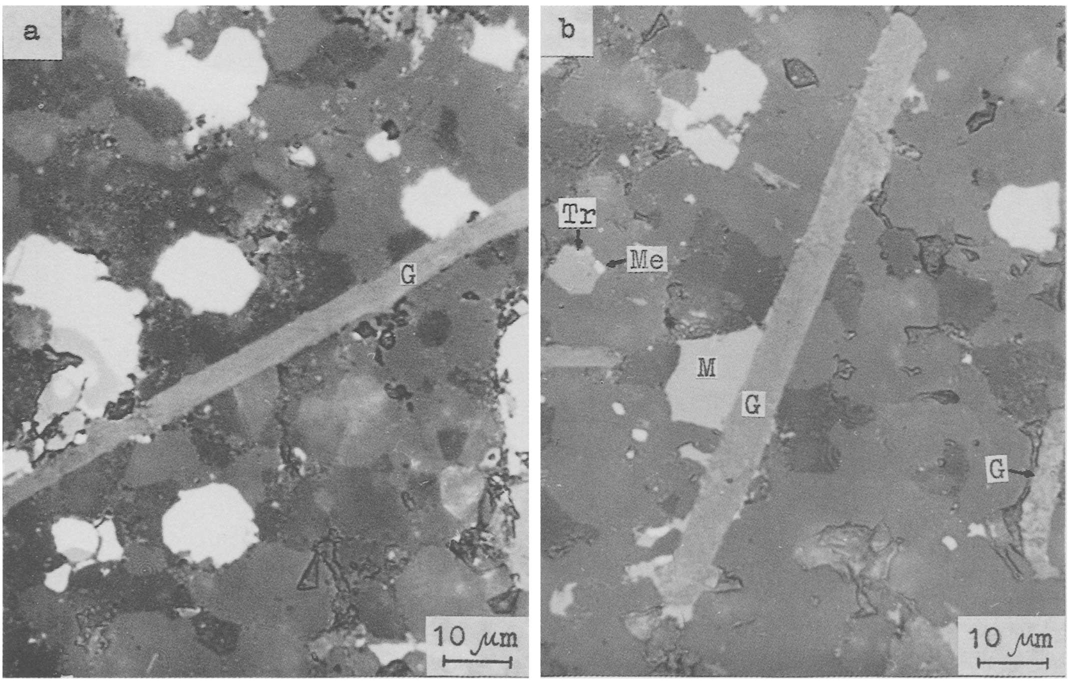

FIG. 6. Reflected light images of graphite filiform crystals, occurring in silicates (grey, dark grey) of the fragment in the Krymka chondrite. G, graphite; Me, metal; M, magnetite; Tr, troilite. (*a*) Part of a graphite crystal with anomalous form and uniform structure. (*b*) Uniform and polycrystalline structure of graphite crystals (central and right part, correspondingly). The latter is characterized by high bireflection. The uniform crystal is associated with a hexagonal grain of magnetite. Note the hexagonal crystal of troilite with metal relic (left part).

TABLE 4. Electron microprobe analyses (wt.%) of chromite in the fragment and the host part of Krymka

	Fragment			Host part		
	I[1]		II	(1)	A[3]	B
	range (11)[2]	average	average (3)			
SiO_2	n.d.–0.29	0.04	0.27	0.17		
TiO_2	3.33–4.19	4.00	1.50	0.24	0.49	0.60
Al_2O_3	10.9–13.0	11.4	3.79	n.d.	0.10	12.6
Cr_2O_3	44.4–47.3	46.4	58.3	63.7	62.7	53.2
V_2O_3	0.40–0.71	0.48	0.71	0.58	0.37	0.82
Fe_2O_3	3.21–6.36	5.10	3.09	1.65		
FeO	27.6–28.9	28.1	29.2	30.0	35.4	23.4
MnO	0.26–0.40	0.30	0.44	0.48	0.66	0.59
MgO	2.66–3.53	3.46	1.82	0.47	0.41	8.40
CaO	0.03–0.21	0.08	0.17	0.27		
Total		99.36	99.29	(97.56)	100.13	99.61
Calcul. Fe_2O_3					4.45	2.45

[1] I, II – two compositionally distinct chromites in the fragment.
()[2] – number of analyses.
[3] A, B – two compositionally distinct chromites (Bunch *et al.* 1967)

of olivine and pyroxene; 7, less shock metamorphism and weathering.

Discussion

The graphite-containing fragment is different from the host Krymka chondrite and from any known type of cosmic matter with graphite (Fodor and Keil, 1978; Ramdohr, 1973; Higuchi *et al.*, 1977; Berkley *et al.*, 1980; Scott *et al.*, 1981*a,b*; Taylor *et al.*, 1981; Brearley *et al.*, 1987; Scott *et al.*, 1988). These data indicate that the exotic fragment was probably added to unequilibrated LL-material during agglomeration on the surface of the parent body.

The mineralogical data without isotopic or TEM characteristics allow us to determine only some aspects of the pre-accretion history of the fragment. It is characterized by its uniform fine-granular texture, some variation in mineral composition but does not contain direct structural or compositional evidence of agglomeration. In contrast to the host (Dodd *et al.*, 1967; Huss *et al.*, 1981; Nagahara, 1984), the olivine and Ca-poor pyroxene in the graphite-containing fragment are fairly homogeneous and their compositions correspond to those in lithic fragments in the Olivenza (LL5) and St. Mesmin (LL6) chondrites (Fodor and Keil, 1978). The compositional variations in the olivine and Ca-poor pyroxene are slightly larger than those (Fig. 3*a*) in equilibrated LL-chondrites (Keil and Fredriksson, 1964).

The principal difference in mineralogy between the fragment and any known type of cosmic matter is the presence of graphite. The occurrence of graphite is not known in equilibrated chondrites and is very limited in the unequilibrated ordinary chondrites. The crystalline graphite in the Krymka fragment is dissimilar to graphite of the ureilites, enstatite chondrites, iron meteorites and especially to C-rich aggregates. The latter consist of aggregates of Fe-rich poorly graphitised carbon grains of micron and submicron sizes (Lumpkin, 1986; Brearley *et al.*, 1987), comprising clasts or matrix of unequilibrated chondrites and are classified as a new kind of type 3 chondrites (Scott *et al.*, 1981*a, b*).

The graphite in the Krymka fragment is characterized by the following main features (Figs. 2, 4*c*, 6): 1) the presence of two groups of grains with different sizes, morphology and occurrence: large crystals with predominant occurrence as the anomalous form (filiform) located among silicate grains, and microcrystals of regular hexagonal plates arranged on the edge or on the surface of silicate, metal and troilite grains; 2) uniform distribution of the large crystals inside the fragment. The anomalous form of graphite grains testifies that large crystals in the fragment were dominantly formed as fibres or lamellae.

The experimental data of Berezhkova (1969) and Givargizov (1977) have shown that anomalously shaped crystals are typically formed by fast growth from a saturated melt at an early or late stage of crystallization, or from a gas. According to those authors the growth rate of fibres is 10–100 times higher than that of normal crystals, promoting crystallization of metal crystals with extraordinary shape (plates) from the melt. In this sense it is interesting to point out the presence in the fragment of metal and troilite as plates alternating with filiform graphite crystals.

The foregoing experimental data allow us to explain the many features of the graphite crystals in the fragment. The occurrence of intact graphite crystals between silicate grains in most cases in fair preservation indicates that graphite in the fragment was probably formed from a melt. We exclude graphite crystallization from a gas, since in this case we must assume later agglomeration and compression of graphite crystals with silicates. It is known that agglomeration and compression in most cases are responsible for the cracks and destruction of chondrules and silicate grains of chondrites. So, it is very difficult to explain the preservation of intact graphite lamellae and fibres during such intensive processes. The morphology of the large graphite grains, their uniform distribution inside the fragment, higher idiomorphism than the other minerals and the presence of multiple nuclei of graphite microcrystals suggest early and fast graphite crystallization from a silicate melt saturated in C. The presence of polysynthetic twins of clinopyroxene, small sizes of monomineralic silicate and opaque grains and their disposition on the graphite phase boundaries testify to fast crystallization of the melt after the formation of the graphite fibres.

The occurrence of graphite as microcrystals protruding from the grain edges or grain surfaces of different minerals (Fig. 2*b–d*) testifies to their formation after the formation of silicates and metal on phase boundaries, probably as a result of melt crystallization or shock-metamorphic processes. The latter could stimulate precipitation of a second generation of graphite during slow cooling of minerals containing dissolved carbon.

The absence of kamacite and the anomalous composition of taenite (Fig. 5) are important features of the mineralogy of the fragment. The constant association of taenite with troilite suggests a genetic relationship (Fig. 4*a,d*). We do not know accurately the abundances of the minerals in the fragment, because 14 vol.% of the surface of the polished section had crumbled out during grinding and polishing. The Krymka host chondrite has lower contents (vol.%) of metal (0.9) and especially troilite (4.3) (Semenenko *et al.*, 1978) than the fragment and the high content of troilite (11.3) in the fragment is an important characteristic. The association of metal and troilite, the absence of kamacite, the high Ni and Co contents of the taenite with a positive correlation, the cubic form of some sulphide crystals, the presence of metal relics within cubic troilite crystals and the association of sulphide and metal plates with graphite crystals are evidence for troilite formation by metal sulphidization in an H_2S-rich environment. Considerable sulphidization of metal lowered its abundance and resulted in an increase in Ni and Co concentrations in the residual metal (Rambaldi and Wasson, 1980). The presence of troilite crystals with a cubic shape, which is typical for metal but not for troilite, indicate the sulphidization of metal after the melt had crystallized.

It is necessary to note that Ni-rich taenite (awaruite) occurs in terrestrial rocks in association with serpentine and probably formed below 200°C (Ramdohr 1962). The equilibrium terrestrial assemblages of awaruite (about 62 at.% Ni) with troilite–pentlandite are also in accord with the phase diagram at low temperature (Misra and Fleet, 1973). Unlike the terrestrial rocks the fragment with Ni-rich taenite has significantly different characteristics that indicate that taenite formed in a highly reduced environment by metal sulphidization.

Another feature of the mineralogy of the fragment is the presence of F-apatite, which unlike Cl-apatite (Van Schmus and Ribbe, 1969) is rare in meteorites but common in lunar (Frondel, 1978) and terrestrial igneous rocks (Fuchs, 1968). Fluorine contents are very low in ordinary chondrites, but it occurs in fluor-richterite in more reduced meteorites: enstatite chondrites, enstatite achondrites and iron meteorites (Bevan *et al.*, 1977). The presence of fluorapatite in the Orgueil (Cl) chondrite was suggested by Jungck *et al.* (1981). Unfortunately, we have too few data from which to determine the genesis of the F-apatite. It is possible that highly reduced conditions were favourable for the formation of F-apatite in the fragment.

The presence of magnetite is of special interest owing to the discussion about its cosmic or terrestrial formation, especially in C-rich aggregates (Scott *et al.*, 1981*a,b*; Taylor *et al.*, 1981; Brearley *et al.*, 1987; Scott *et al.*, 1988; Alexander *et al.*, 1989). Fibrous magnetite has been observed in the troilite of the Krymka matrix and has been interpreted as having formed by the oxidation of sulphide and of preterrestrial origin (Alexander *et al.*, 1989). Taylor *et al.* (1981) noted that "weathering of meteoritic metallic Ni,Fe produces hydrated iron-oxides, not magnetite". At the same time many data indicate that there are uncertainties and that magnetite may have formed on Earth in many weathered meteorites (Ramdohr, 1973; Yudin and Kolomensky, 1987). For example, Yudin *et al.* (1983) observed grains and veins of magnetite in the Tzarev chondrite.

The magnetite in Krymka has the following features: 1) It occurs both in the fragment and in the host with identical composition. 2) It is always associated with troilite and preferentially with Ni-poor metal, but not with Ni-rich taenite. As a consequence magnetite is less abundant in the fragment than in the host. 3) There is morphological evidence of the replacement of troilite by magnetite (Fig. 4*a*, 6*b*). 4) Deformation lamellae are absent in the magnetite, which is very sensitive to shock pressure, although magnetite is accompanied by silicates, which have deformation structures. Taking these characteristics into account, we conclude that the formation of magnetite is probably due to terrestrial oxidation in the fragment mainly of troilite and in the host, of troilite and kamacite.

Thus, texture and mineralogy indicate that the material of the fragment probably formed by crystallization from a highly reduced melt, which had been enriched in C. We have no data on the nature of the C-rich silicate melt but C-rich aggregates could have been its precursor.

After agglomeration the Krymka chondrite underwent complicated shock metamorphism (Semenenko *et al.*, 1987). According to the experimental data of Stöffler *et al.* (1991), the structure and composition of completely shock-melted regions of sample N1290/29 testify to shock pressures of about 75–90 GPa and a peak temperature of over 1500°C. The presence of shear deformation in minerals in these regions indicates that after solidification of the melted regions the chondrite has undergone repeated light shock, which caused the mechanical deformation of the minerals. The graphite-bearing fragment contains evidence of shock metamorphism which is less intensive than in sample N1290/29. Owing to the lack of a thin section and too few olivine grains studied in transmitted light, we have no possibility of estimating the shock pressure inside the fragment. The abundant melt structure of troilite outside the fragment points to shock heating to over 988°C, but the peak temperature within the fragment was below 988°C.

Conclusions

1. The Krymka chondrite contains an exotic graphite-bearing fragment which is dissimilar to any previously described type of cosmic matter.

2. The graphite-containing fragment was probably formed by crystallization from a highly reduced silicate melt which had been enriched in C. Considerable sulphidization lowered the abundance of metal and resulted in the formation of troilite and the compositional features of the residual metal. The fragment was added to unequilibrated LL-material during agglomeration and mixing of chondritic matter probably as result of shock on the surface of the parent body.

3. Weathering of the exotic fragment and of the host chondrite produced iron hydroxides, pentlandite and quite possibly magnetite.

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