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# METALLIC SPHEROIDS FROM METEOR CRATER, ARIZONA[1]

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ABSTRACT

The mineralogy, texture, and chemical composition of metallic spheroids from Meteor Crater, Arizona, were studied in detail. The spheroidal to elongate particles studied average 0.5 mm across and characteristically are coated by siliceous glass containing numerous minute fragments of quartz. Some spheroids consist of a fine-grained granular kamacite core, commonly intergrown and surrounded by a goethite-like iron oxide and maghemite. Associated with the kamacite is an interstitial pink mineral optically similar to the pink schreibersite inclusions in the metallic spherules in philippinites and indochinites. *X*-ray powder patterns of this pink mineral from the Meteor Crater spheroids are also identical to that of schreibersite.

Electron microprobe analysis shows:

| | Ni% | Fe% |
|---|---|---|
| Kamacite | 2–24 | 74–97 |
| Maghemite | 5–6 | 59–62 |
| Goethite-like mineral | 2–14 | 45–60 |

The wide range of nickel content in kamacite, the fine-grained texture, and the siliceous glass coating on the spheroids indicate that the Meteor Crater spheroids probably condensed from a vapor or melt produced during impact of the meteorite. The range in nickel content in the kamacite of the Philippine and Indochina tektite spherules is nearly identical to that of the kamacite in the spheroids from Meteor Crater, whose meteoritic origin is certain.

## INTRODUCTION

As part of a systematic study of particles formed by fusion from the impact of a meteorite, the magnetic metallic spheroids collected by Dr. H. H. Nininger from Meteor Crater, Arizona were studied in detail. These spheroids were obtained with the kind permission of Dr. Carleton Moore, Director and Custodian of the Nininger Meteorite Collection at the Arizona State University, Tempe, Arizona. Zaslow and Kellogg (1961) published a short note on the study of these spheroids, but to our knowledge, no detailed study has been undertaken.

In this study, nearly 50 different spheroids most of them about half a millimeter but a few as large as 2 to 3 millimeters in diameter were studied in polished sections, by *x*-ray diffraction, and by the electron microprobe, or by a combination of all three methods. The shape of these sphereoids varies from irregular, to elongate, to spherical.

Nearly all the spheroids which were examined under the binocular microscope were coated on the outside by brown iron oxide, which can easily be removed by treatment with dilute acetic acid and gentle rubbing

[1] Publication authorized by the Director, U. S. Geological Survey.

with a glass rod in a spot plate. Removal of this brown iron oxide revealed that directly below this oxide, most if not all the spheroids have a fragile thin white coating of silica or siliceous glass generally a fraction of a millimeter thick (Fig. 1). This white isotropic glass coating, with an index of refraction from 1.47 to 1.49 contains numerous powdery angular fragments of quartz. Inside the siliceous glass coating of the spheroids, commonly a layer of gray iron oxide of variable composition and thickness wraps around a core of metallic nickel iron. That these spheroids are

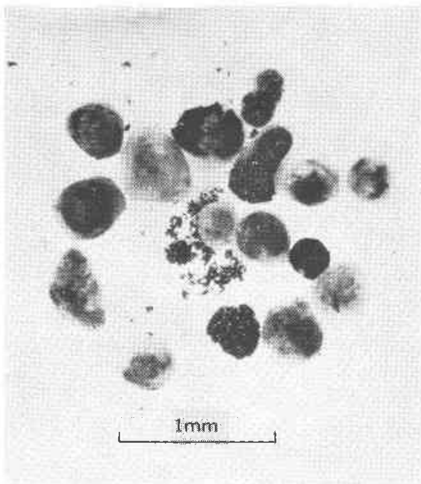


FIG. 1. Photomicrograph of several spheroids showing siliceous glass coating (light colored grains). Dark grains are uncoated.

results of impact induced fusion of the Canyon Diablo iron meteorite is unmistakably indicated by their close association with the Meteor Crater of Arizona, the presence of the glass coating, the notable nickel content in both the gray oxide phase and the metallic core, the fine grained texture and the mineral assemblage of the core.

## MINERALOGIC AND PETROGRAPHIC STUDIES

In polished sections and under the reflecting microscope, most of the spheroids consist of the following mineral assemblage: a gray goethite-like iron oxide commonly intergrown with light gray maghemite, bright creamy white kamacite and more rarely white schreibersite. In many spheroids an intergrowth of troilite and pink schreibersite occurs interstitially among the fine-grained kamacite. In most spheroids the gray oxide phases grade into or interlock with the nickel-iron core. In a few spheroids however the order is reversed, the core being gray iron oxide rimmed by creamy white nickel iron.

*Goethite-like mineral.* This is a gray iron oxide phase which generally occurs around the creamy white nickel-iron core; sometimes intimately intergrown with it in a fingerprint or pearlitic texture. It also occurs as alternating bands in maghemite and is referred to as a goethite-like mineral on the basis of its color (Figs. 2, 3, 4, and 10). Strong lines of goethite were detected on the powder pattern of only 2 of the 15 spheroids which were $x$-rayed. The goethite-like mineral however, is observed optically in all the polished sections of the spheroids. The identification of this phase is uncertain because of the poor $x$-ray data owing principally to the poor crystallinity of this phase. Furthermore, as shown by microprobe analysis, this gray iron oxide is also deficient in iron as compared to the composition of goethite.

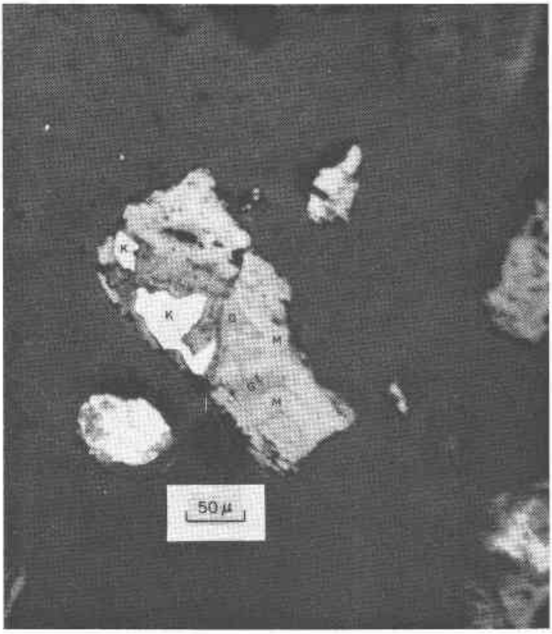


FIG. 2. Photomicrograph of grain 1 in polarized reflected light showing low nickel kamacite (K), maghemite (M), and goethite-like iron oxide (G).

*Maghemite.* Maghemite is light gray in reflected light and generally occurs in elongate isotropic grains alternating in bands with the goethite-like iron oxide (Figs. 2 and 4). Traces of maghemite based on the presence of only the strong reflections were detected by $x$-ray in 8 spheroids (Table 1).

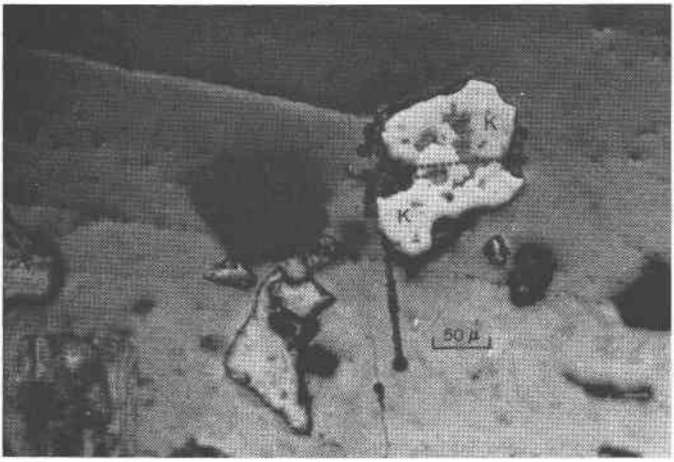


FIG. 3. Photomicrograph of grain 2 in polarized reflected light showing contamination spots left in a point-by-point traverse made by the electron probe on kamacite (K) and goethite-like iron oxide (G).

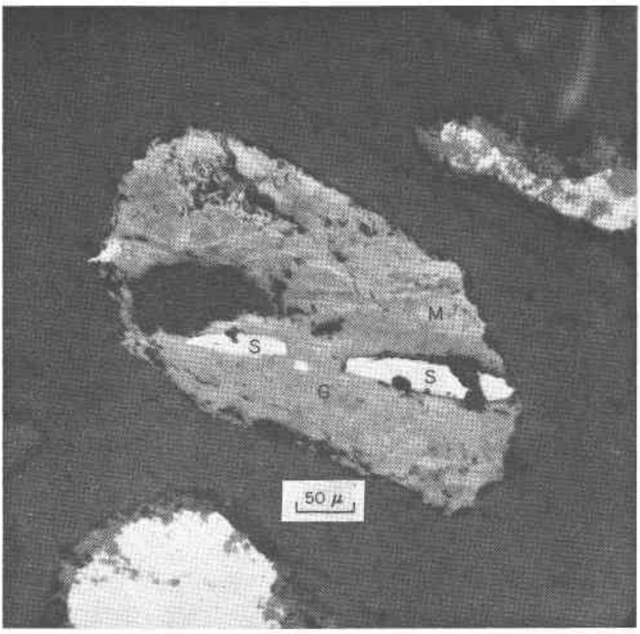


FIG. 4. Photomicrograph of grain 3 in polarized reflected light showing elongated bodies of schreibersite (S), goethite-like iron oxide (G), and minor maghemite (M).

TABLE 1. MINERAL ASSEMBLAGES OF UNTREATED SPHEROIDS EXAMINED BY X-RAY DIFFRACTION

| Film No. | Spindle No. | Relative Abundance[1] | | | | |
|---|---|---|---|---|---|---|
| | | Kamacite | Taenite | Maghemite | Quartz | Goethite |
| 17855 | 118 | M | m | tr | tr | tr |
| 17860-a | 128 | M | m | m | tr | — |
| 17861-a | 129 | M | tr | tr | tr | — |
| 17862-a | 130 | M | m | m | m | — |
| 17863-a | 131 | M | m | — | m | — |
| 17864 | 132 | M | m | m | m | — |
| 17865-a | 133 | M | m | — | m | — |
| 17866 | 134 | M | m | tr | — | — |
| 17867 | 135 | m | — | — | M | — |
| 17883 | 147 | M | tr | — | m | m |
| 17884 | 148 | M | m | m | M | — |
| 17886 | 150 | m | tr | — | M | — |
| 17887 | 151 | M | m | m | M | — |
| 17888 | 152 | M | m | — | M | — |
| 17890 | 154 | M | — | — | M | — |

[1] M—major constituent.
m—minor constituent.
tr—trace constituent.

*Kamacite.* This mineral is commonly the major constituent in the core of the spheroids. It is creamy white, highly reflecting, and extremely fine-grained. Being isotropic, the fine-grained nature was revealed by interstitial pink schreibersite which marks the grain boundaries, and by its excellent homogeneous, nonspotty $x$-ray powder pattern. Because of extremely fine grain size and random orientation of kamacite, the texture (Figs. 5 and 6) is interpreted as one of rapid quenching. There is no widmanstätten structure.

*Taenite.* Taenite is difficult to detect in polished sections. Trace amounts are commonly detected in most of the spheroids by $x$-ray. Taenite becomes a major phase of the residue, after the spheroids have been treated with hydrochloric acid and the kamacite and iron oxide phases are removed.

*White schreibersite.* These white grains are believed to be relict grains, not completely destroyed or transformed by the impact-induced fusion (Fig. 4). Large schreibersite grains are however rarely found in the smaller spheroids which we have studied and in only one of the grains was

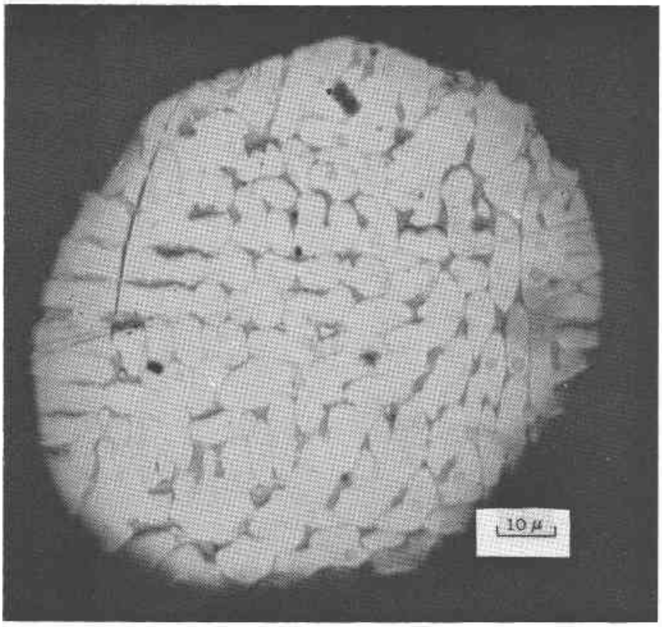


FIG. 5. Photomicrograph of a grain in polarized reflected light showing interstitial pink phase (light gray) and troilite (dark gray) outlining the boundaries of the kamacite grains.

schreibersite observed; here, as a white elongated phase surrounded by an intergrowth of nickeliferous maghemite and goethite-like iron oxide. It is identified chiefly on the basis of its chemical composition and optical properties.

*Pink schreibersite.* This pale pink phase occurs interstitially alone or intergrown with troilite along the grain boundaries of the kamacite (Figs. 5, 6, 7 and 8). It is distinctly anisotropic and appears in strong relief when etched for 10 seconds with 5 per cent nital (5% nitric acid in alcohol) (Fig. 7). It has a completely different habit from the rhabdite[1] that occurs as rhombs throughout the Canyon Diablo iron and which is not present in the spheroids. It is identified principally by its $x$-ray diffraction powder pattern obtained from material in the residue sample after the spheroids were digested with cold 1:1 HCl.

*Troilite.* Troilite is brownish-pink in color and is observed at high mag-

[1] Rhabdite is needle- or rod-shaped schreibersite. It is observed in cross section in the form of squares or rhombs.

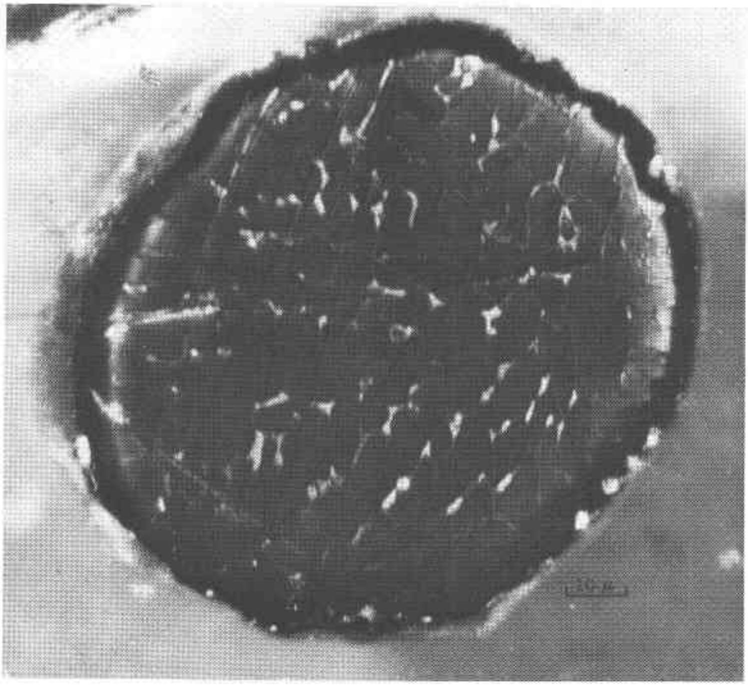

FIG. 6. Photomicrograph of the same grain as in Fig. 5 under crossed nicols illustrating the anisotropism of the schreibersite and troilite.

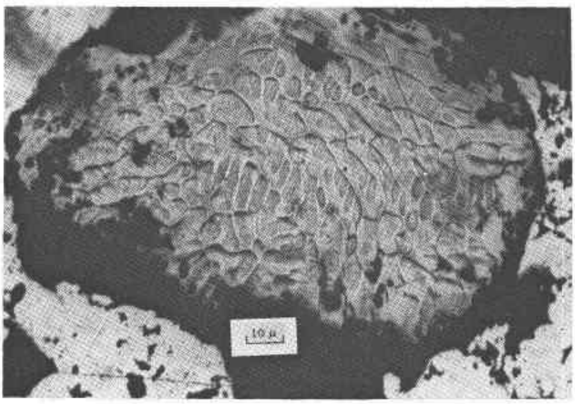


FIG. 7. Photomicrograph of an etched kamacite in polarized reflected light showing a network of the interstitial pink mineral in relief

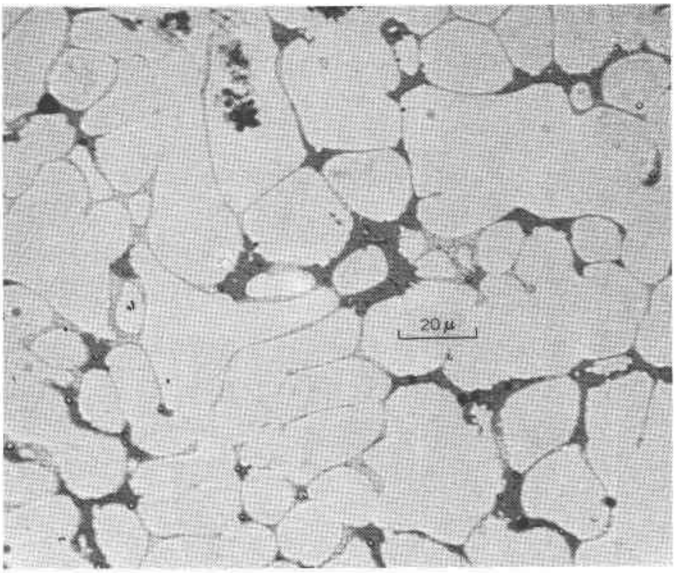


FIG. 8. Photomicrograph showing fine intergrowth of troilite (dark) and schreibersite (light) in a matrix of kamacite. Width of the fine schreibersite filaments is about 1 micron.

nification as an intergrowth with pink schreibersite (Fig. 8). Its identification is based on its optical properties and the presence of major iron and sulfur in the microprobe analysis. Because of the small amount present, it was not detected by the $x$-ray method.

## $X$-ray Investigation

In order to check the optical identification and to correlate the mineralogical and chemical data, 15 spheroids were $x$-rayed. The spheroids were gently rubbed by a glass rod in a spot plate, removing essentially the outer brown iron oxide and silica glass coating. Each spheroid was then mounted on top of an ethyl cellulose spindle and $x$-rayed in a Debye-Scherrer powder camera of 114.49 mm diameter using Fe K$\alpha$ radiation and Mn filter. The major phase of all the spheroids $x$-rayed was the body-centered cubic $\alpha$-iron with a unit-cell size of approximately 2.86 Å. It is not the distorted body-centered cubic $\alpha 2$. Traces of quartz and the strong lines of maghemite and taenite were generally detected. Troilite and schreibersite were not detected in any of the untreated spheroids. Results of the $x$-ray analysis which show the relative abundance of the mineral phases present are given in Table 1. Wüstite, lepidocrocite, as well as hematite and magnetite were not detected by the $x$-ray studies of these spheroids.

TABLE 2. MINERAL ASSEMBLAGES OF THE RESIDUE OF 5 TREATED SPHEROIDS AS DETERMINED BY X-RAY DIFFRACTION

| Film No. | Spindle No. | Relative abundance[1] | | |
|---|---|---|---|---|
| | | Schreibersite | Taenite | Quartz |
| 17850 | 117 | M | — | — |
| 17857 | 120 | m | M | — |
| 17900 | 155 | M | — | — |
| 17901 | 156 | M | — | — |
| 17902 | 157 | M | M | — |

[1] M—major constituent.
m—minor constituent.

Five spheroids were treated with cold 1:1 HCl which dissolved away the kamacite and iron oxide phases leaving a dark colored, soft, friable spongy mass as a residue. *X*-ray powder data show that the residue consisted essentially of schreibersite (Table 2). From 2 of the 5 residues, a pattern of taenite was obtained. The residue of two additional spheroids treated this way were prepared for polished section and microprobe study. Because of the friable and spongy nature, the resulting mount was not satisfactory either for optical study or for quantitative microprobe analysis.

## ELECTRON MICROPROBE ANALYSIS

The electron microprobe of the same type as the one described by Castaing (1951, 1960) built at the U. S. Geological Survey was used for the chemical analysis of the spheroids. In this study, three crystals and three detectors were used to measure three elements simultaneously. Two lithium fluoride crystals and two geiger counters were used to measure Fe and Ni concentrations. A mica crystal and a proportional counter which were placed in a vacuum were used for the measurement of either phosphorus or sulfur.

Prior to quantitative analysis, spectrometer traces for each mineral were made. These traces gave qualitative information as to the elements present and their relative amounts, which helped in the selection of standards used. An example of the kind of information obtained from qualitative scans is presented in Fig. 9. This figure shows the relative intensities of the Fe K$\beta$ and the Ni K$\beta$ peaks obtained from spectrometer traces made on the white areas of grains 1, 2, and 3 (Figs. 2, 3, 4). Optically these three areas look similar but the qualitative spectrometer scans with a lithium fluoride crystal quickly indicated that all three white areas are different in chemical composition. Spectrometer scans using the mica

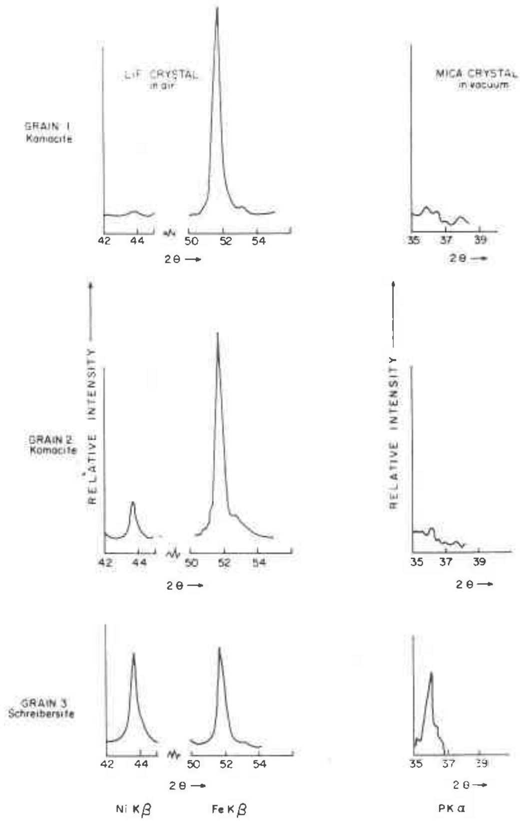


FIG. 9. Relative intensities of Fe K$\beta$ and Ni K$\beta$ peaks obtained from spectrometer traces of the kamacite in Figs. 2, 3, and schreibersite of Fig. 4.

crystal showed the presence of phosphorus in grain 3. There is no detectable phosphorus in grain 1 or 2. A slight suggestion of a P peak at 36° in these grains occurs on the descent of the large FeK$\alpha$ peak at 33.9°.

Pure iron and pure nickel, analyzed kamacite from the Canyon Diablo iron meteorite (Fe=93; Ni=7), goethite (Fe=61.1), hematite (Fe =69.9), pyrite (Fe=46.2, S=53.6), and rhabdite from the Canyon Diablo iron meteorite (Fe=42, Ni=44, P=15) were used as standards in the study.

The precision for the quantitative analysis of Fe in nickel-iron and iron oxides using the above standards is generally in the order of $\pm 5\%$ of the amount present, and for the nickel analysis, for the range of concentration less than 30%, is in the order of $\pm 10\%$ of the amount present.

Results of the microprobe analysis for the spheroids which were not

TABLE 3. ELECTRON PROBE DATA FOR THE SPHEROIDS WHICH WERE NOT X-RAYED

| Sample No. | Mineral | No. of Analyses | % Fe | % Ni | Total |
|---|---|---|---|---|---|
| MS-1 Grain 1 | Kamacite | 8 | 98.3 | 2.3 | 100.6 |
| | Light gray oxide | 6 | 61.6 | 5.7 | 67.3 |
| | Dark gray oxide | 5 | 51.7 | 3.0 | 54.7 |
| MS-1 Grain 2 | Kamacite | 9 for Fe<br>7 for Ni | 74.1 | 23.5 | 97.6 |
| | Dark gray oxide | 2 | 33.3 | 5.1 | 38.4 |
| MS-1 Grain 3 | Schreibersite | 8 | 41.3 | 40.7 | 101.10[1] |
| | Dark gray oxide | 16 for Fe<br>12 for Ni | 45.3 | 2.2 | 47.5 |
| MS-1 Grain 4 | Pink | 10 for Fe<br>9 for S<br>6 for Ni | 43.7 | 6.4 | 74.6[2] |
| MS-1 Grain 5 | Kamacite | 3 | 82.5 | 12.8 | 95.3 |
| | Dark gray oxide | 4 | 42.1 | 8.6 | 50.7 |
| MS-1 Grain 6 | Light gray oxide | 5 | 59.0 | 5.1 | 64.1 |
| MS-1 Grain 7 | Pink | 10 | 53.4 | 16.0 | 98.0[3] |

[1] Contains 19.0% P.
[2] Contains 24.6% S.
[3] Contains 28.6% S.

$x$-rayed are given in Table 3 and results of the microprobe analysis for the $x$-rayed spheroids are given in Table 4.

The nickel values, obtained by both random spot analysis and by point by point traverse for the kamacite in grain 1 (Fig. 2) are consistently low,

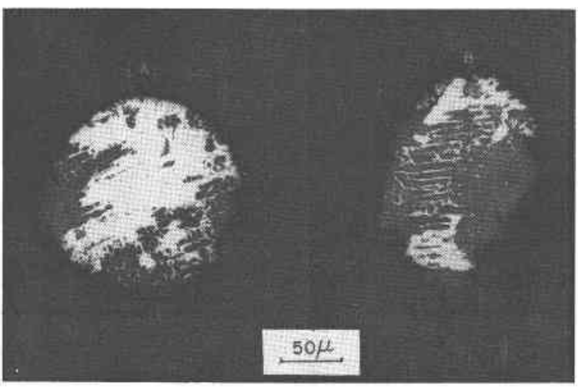


FIG. 10. Photomicrograph of 2 of the $x$-rayed spheroids in polarized reflected light showing typical sizes, shapes and textures. The dark gray mineral is goethite-like iron oxide, white is kamacite and the light gray inclusions in the kamacite are schreibersite. A-spheroid 129, B-spheroid 131.

TABLE 4. ELECTRON PROBE DATA FOR X-RAYED SPHEROIDS

| Sample No. | Mineral | No. of Analyses | % Fe | % Ni | Summation |
|---|---|---|---|---|---|
| 118 | Kamacite | 13 for Fe, 14 for Ni | 83 | 17 | 100 |
| | Predominantly dark gray oxide | 14 | 45 | 7 | 52 |
| 128 | Kamacite | 3 | 78 | 18 | 96 |
| | Predominantly dark gray oxide | 2 | 45 | 5 | 50 |
| 129 | Kamacite | 3 | 83 | 17 | 100 |
| | Predominantly dark gray oxide | 3 | 47 | 8 | 55 |
| 130 | Kamacite | 3 | 88 | 13 | 101 |
| | Predominantly dark gray oxide | 5 | 56 | 3 | 59 |
| 131 | Kamacite | 3 | 83 | 17 | 100 |
| | Predominantly dark gray oxide | 3 | 46 | 8 | 54 |
| 132 | Kamacite | 3 | 81 | 17 | 98 |
| | Predominantly dark gray oxide | 3 | 53 | 9 | 62 |
| 133 | Kamacite | 5 | 82 | 18 | 100 |
| | Predominantly dark gray oxide | 3 | 48 | 5 | 53 |
| 134 | Kamacite | 3 | 83 | 15 | 98 |
| | Predominantly dark gray oxide | 3 for Fe, 2 for Ni | 56 | 7 | 63 |
| 135 | Kamacite | 3 | 83 | 17 | 100 |
| | Predominantly dark gray oxide | 3 | 53 | 14 | 67 |
| 147 | Kamacite | 3 | 82 | 17 | 99 |
| | Predominantly dark gray oxide | 4 | 47 | 10 | 57 |
| 148 | Kamacite | 3 | 86 | 12 | 98 |
| | Predominantly dark gray oxide | 3 | 53 | 7 | 60 |
| 150 | Kamacite | 5 | 83 | 17 | 100 |
| | Predominantly dark gray oxide | 3 | 44 | 12 | 56 |
| 151 | Kamacite | 5 | 81 | 15 | 96 |
| | Predominantly dark gray oxide | 11 | 52 | 4 | 56 |
| 152 | Kamacite | 8 | 81 | 15 | 96 |
| | Predominantly dark gray oxide | 7 | 46 | 5 | 51 |
| 154 | Kamacite | 4 | 84 | 18 | 102 |
| | Predominantly dark gray oxide | 3 | 35 | 5 | 40 |

never exceeding 3 per cent. The kamacite in grains 2, 5, and in all the $x$-rayed spheroids which appear to be optically very homogeneous, contains an unusually high nickel content for kamacite. The $x$-ray data confirm that $\alpha$ iron or kamacite is the major phase in all the $x$-rayed spheroids. The high nickel content could be partially caused by a fine intergrowth of taenite with the kamacite which is not resolved optically.

The dark gray mineral which occurs in all the spheroids studied and is referred to as a goethite-like mineral was deficient in iron as compared to goethite (Table 3, 4). In addition to the iron deficiency, the nickel content of this goethite-like mineral in some of the spheroids was as much as 14 per cent. Because of the fine-grained and poorly cyrstalline nature of this dark gray phase, it can not be certain whether this dark phase consists of a single phase or a mixture of more than one phase.

The light gray iron oxide or maghemite is usually finely intergrown with the dark gray iron oxide and the analysis of a pure area of it is difficult. It generally contains more iron than the dark gray iron oxide.

The white mineral in grain 3 (Fig. 3) is described as schreibersite. In addition to a higher reflectivity than normal schreibersite, analysis of this mineral indicated that it is enriched in phosphorus by about 4 weight per cent as compared to the stoichiometric composition of schreibersite (Table 3). This enrichment in phosphorus suggests a possibility that this phase could be $(Fe, Ni)_2P$ rather than $(Fe, Ni)_3P$. However, owing to the small size of the sample, identification of this phase by $x$-ray diffraction was not possible.

The pink interstitial mineral identified by $x$-ray as schriebersite is commonly less than 5 $\mu$ wide and occurs in nearly every spheroid studied (Figs. 5 and 6). It is intimately associated with troilite and kamacite, so that generally Fe, Ni, and S are detected over such an area. In some spheroids, the pink schreibersite and the brown troilite are clearly resolved (Fig. 8). It is observed that the pink schreibersite also occurs interstitially as spongy filaments between the kamacite grains. The holes are filled with kamacite and because the width of the filaments is less than a micron, it is extremely difficult to obtain an analysis of only this material (Fig. 8). Very small quantities of phosphorus have been detected with the microprobe. In grains 4 and 7 of Sample MS-1, this "impure" pink phase was analyzed and the results show major Fe and S and minor nickel, and little or no phosphorus (Table 3). In an attempt to locate larger areas of the pink mineral, several larger spheroids were prepared for microprobe analysis but it was found that the grain size of the pink mineral seemed to remain constant regardless of the size of the spheroid. Attempted microprobe analysis of the pink phase in the $x$-rayed spheroids proved inconclusive because it was not possible to obtain an analysis on the pure material.

## Conclusions

As a result of meteorite impact-fusion, the spheroids which were originally part of the Canyon Diablo iron meteorite[1] are completely

[1] The Canyon Diablo meteorite is classified as a coarse octahedrite. It has the usual widmanstätten structure consisting or oriented bands of kamacite and taenite. Numerous rhombs of rhabdite occur within the kamacite. Minor amounts of other minerals such as graphite, troilite, diamond, cohenite, and olivine are present as inclusions.

changed in texture. Except for the addition of iron oxide phases the mineral assemblages while differing in composition remain essentially the same in both the iron meteorite and the spheroids.

The widmanstätten structure present in the Canyon Diablo iron meteorite is completely destroyed in the spheroids. High temperature heating and quenching caused the destruction but at the same time gave rise to the fine-grained quenched texture which is partly pearlitic in nature. The numerous rhabdite rhombs present throughout the kamacite in the unshocked meteorite are no longer present in the spheroids and the shreibersite, which is generally present, occurs as a fine network outlining the kamacite grain boundaries.

The siliceous glass coating on the spheroids indicates that they must have consolidated and cooled in an environment where a great deal of silicate vapor was also condensing. The sharp angular fragments of quartz which they contain, probably came from the sandstone in the area of Meteor Crater which was pulverized by the impacting Canyon Diablo iron meteorite.

The compositional variation among the spheroids can best be seen in the variability of the Ni content in the body-centered $\alpha$-iron and the various iron oxide phases. Both the low nickel (up to 3 per cent) and the high nickel (up to 24 per cent) content in the kamacite indicate the drastic change in the composition of phase in the Canyon Diablo iron meteorite as the result of impact.

These spheroids are notably different from all the alleged cosmic magnetic spherules which have been examined at the U. S. Geological Survey. Many of the latter are hollow and none of them contain detectable nickel or any phase resembling kamacite in composition.

By comparison, the texture and mineral assemblages of the Meteor Crater spheroids are nearly identical to those of the Philippine and Indochina tektite spherules (Chao *et al.*, 1962, 1964). In all these spheroids or spherules, anisotropic schreibersite and troilite occur interstitially as a network within a fine-grained matrix of kamacite. Kamacite, the major phase in all these particles, is isotropic, body-centered cubic $\alpha$-iron with a unit-cell size of approximately 2.86 Å. The grain size of the minerals is not dependent on the size of the spheroids or spherules. The extremes of the high and the low nickel content of kamacite is also characteristic of the spherules from the Philippine and Indochina tektites. Thus, the results of this investigation indicate that the metallic spherules in the Philippine and Indochina tektites, when compared to the spheroids from Meteor Crater whose meteoritic origin is certain, must also have a similar, *i.e.* meteoritic, origin.

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