

CONTRIBUTIONS TO THE STUDY OF THE CANYON DIABLO METEORITES

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PART I

BY GEORGE P. MERRILL

Attention was first called to the remarkable distribution of meteoric irons in the vicinity of Canyon Diablo, Coconino County, Arizona, at the 1891 meeting of the American Association for the Advancement of Science, held in Washington.¹

Since that time the physical and chemical characteristics of the irons have been described by numerous workers, including Huntington,² Cohen,³ Brezina,⁴ and Derby,⁵ while others have discussed the subject with reference to the occurrence of diamonds in the iron, the origin of the crater, etc.; these papers, for the present, need only incidental reference. The matter will be taken up more in detail in a final paper which is in process of preparation.

Interest, almost to the point of sensationalism, has recently been revived in the occurrence through the publication of Messrs. D. M. Barringer and B. C. Tilghman,⁶ of Philadelphia, who have shown the meteoric hypothesis of the origin of the crater to have had a much more substantial basis than many, including the writer, were at first disposed to admit. Correspondence and interviews with the writers of this paper led to the acceptance on the part of the present writer of an invitation to visit the crater, and the placing in his hands, for study, of a complete series of the meteoric products and other materials found associated therewith. One of these products, an altered sandstone, has been already described.⁷ The present paper

¹ Proc. Am. Assoc. Adv. of Sci., August, 1891, p. 277; Am. Jour. Sci., vol. 42, 1891, p. 413.

² Am. Acad. Arts and Sciences, vol. 22, 1892, and 1894.

³ Meteorischen Studien, iv, 1895.

⁴ Die Meteoritensammlung des k. k. Nat. Hof. Mus., 1895.

⁵ Am. Jour. Sci., vol. 49, 1895, p. 101.

⁶ Proc. Acad. Nat. Sci. Phila., December, 1905.

⁷ A Peculiar Form of Metamorphism in Sandstone. Proc. U. S. Nat. Mus., vol. XXXI, 1907, p. 547.

has to do principally with a singular type of meteoric iron which for evident reasons was overlooked by earlier observers.

In stating the facts bearing upon the origin of the crater, Mr. Barringer¹ writes of disinterring from pits and open cuts numerous nodular masses of oxidized meteoric material, or "shale balls" of all weights up to fifty pounds. These were usually roughly globular in outline, and consisted exteriorly of hydrated oxide of iron which served as a cement, loosely binding together the adjacent rock fragments (see pls. XVIII and XIX). In a number of instances such were found to contain still unoxidized iron centers or nuclei, the intermediate zone showing a green hydroxide of nickel mingled with oxides of iron. Several of these "shale balls" were given the writer for examination and study, and it is to them in particular and their bearing upon the problem that the present paper has reference.

The occurrence of the balls is sufficiently described in the paper of Mr. Barringer. The writer, while on the ground, saw several of them exhumed, and can corroborate his description in every detail. It will be well, incidentally, however, to emphasize the fact that the balls with iron centers have been found mainly on the north side of the crater and in the trenches, rarely on the surface.² The apparent significance of this will appear later.

The appearance of the freshly exhumed shale ball is that of a rough and friable mass of iron oxide encrusted with bits of sandstone and limestone, and in the case of those found but a short distance below the surface, thickly entangled with grass roots (pl. XVIII, fig. 1).

In the case of the smaller, superficial masses, oxidation has usually progressed to the extent that no metallic residue remains, and the nodule quickly falls to pieces on exposure. The larger and deeper-seated nodules, as their weights indicate, still retain unaltered nuclei. Such, cut in halves, are shown in fig. 2, pl. XVIII, and figs. 1 and 2, pl. XIX. The rounded mass of iron is surrounded by a crust of oxide, some 10 to 15 mm. in thickness. Mr. Tassin's examinations show this oxide to consist of both limonite and turgite. Beyond this is an indefinite zone of iron oxide and rock fragments. The inner zone of oxide is identical in composition and physical properties with much of the iron shale so common on the surrounding surface, and suggests at once a like origin for both. An etched surface of the

¹ Proc. Acad. Nat. Sci. Phila., 1905, pp. 878, 879.

² Since the above was put in type Mr. Barringer has informed the writer that one shale ball has been found on the east side of the crater, and one completely oxidized form on the south.



FIG. 1



FIG. 2

CANYON DIABLO METEORITES

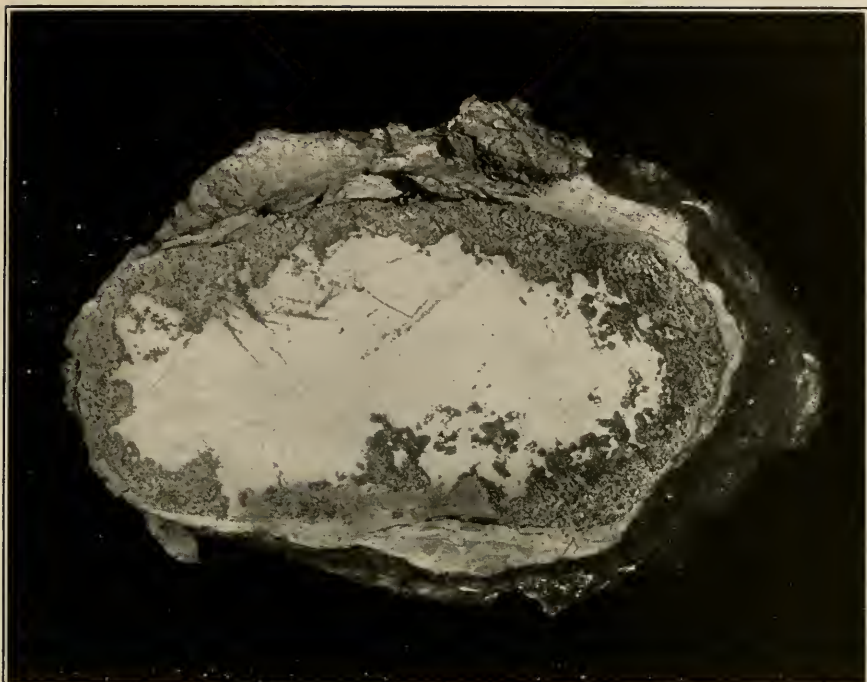


FIG. 1



FIG. 2

CANYON DIABLO METEORITES



CANYON DIABLO METEORITES

unaltered iron shows a structure quite unlike that of the typical iron, as described (see pl. xx), a difference so striking that one unacquainted with the conditions under which they were found would certainly be justified in pronouncing them independent falls. This difference, which is further accentuated in composition, as shown in Mr. Tassin's paper (p. 209), is very evident in the illustrations (compare pls. xix and xx).

As noted by Mr. Tassin and as is readily evident on even a casual inspection, the shale iron differs from the other irons in the relatively large proportion of iron chlorides and phosphides and in the lack of the broad kamacite plates so conspicuous in pl. xx. So abundant are the first mentioned that a polished surface soon tarnishes, the chloride, as is usual in chloride-rich irons, exuding in the form of greenish drops which quickly oxidize, coating it with a layer of "rust." Fig. 2 of pl. xviii and fig. 1 of pl. xix show polished surfaces with oxidized coatings produced by an exposure of but a few days in the atmosphere of this office. The common type of the Canyon Diablo iron (pl. xx), on the other hand, is very stable, withstanding the warm, damp atmosphere of Washington, for a prolonged period without serious oxidation.

The writer believes that the discovery of these shale balls explains the origin of the widely disseminated iron shale which is found on the plain and which has been the subject of discussion by other writers, particularly Derby,¹ Barringer,² and Farrington.³

The explanation now given is not new or, at least, not wholly so, but is emphasized here and apparently substantiated by the finding of the shale actually in contact with an unaltered nucleus and in process of formation. The shale, according to this view, originates through the oxidation of a peculiarly susceptible variety of the iron and is not to be explained, as does Dr. Farrington, on the basis that such were derived from buried irons, which would receive a larger amount of water from being covered with soil and rock fragments, and hence would oxidize more rapidly. That, however, the protective covering was instrumental in producing this particular type of shale is probable, since the gradually oxidizing material would be held in place rather than fall away to powder, as would be the case if the decomposition took place on the surface.

The presence of the shale scattered so widely over the plain, usually in fragments rather than in the form of balls with metallic nuclei, the writer would explain as follows:

¹ Am. Jour. Sci., vol. 49, 1895, p. 102.

² Proc. Acad. Nat. Sci. Phila., December, 1905, p. 879.

³ Am. Jour. Sci. (4), 17, 1907, p. 300.

It must be remembered that this fall is very old; just how old it is impossible to say, but on the now apparently plausible assumption that it was contemporaneous with the formation of the crater, it must antedate the latest eruption of the volcanoes north of Flagstaff, since, as Mr. Tilghman informs me, the borings have shown that the fine lapilli, scattered universally over the plain, occur likewise over the bottom of the crater. This places it back several hundred years at least. During this period the general surface of the plain must have been cut down appreciably, both by wind and water action, and the irons and heavier pebbles and boulders are thus left exposed.

Dr. Farrington's statement¹ that the meteoric irons "are found only at the surface" is, if not founded upon a misapprehension, at



FIG. 48

least misleading. It is true that those thus far found lay on or near the surface, but this the writer believes is due to their having been uncovered by erosion. As a matter of fact, nearly all—even those of but a few ounces in weight—are still covered by earth, with only a mere point of iron projecting, and one not experienced in finding them may pass repeatedly over a given area without success, while the experienced will pick them up almost under his very eyes.

The shale balls, in varying stages of formation and destruction, are thus gradually brought to light, and, no longer confined by the compact envelope of earthy matter, go quickly to pieces, and no recognizable trace of the metallic portion remains.

¹ *Am. Jour. Sci.* (4), 17, 1907, p. 308.



CANYON DIABLO METEORITES

There are yet to be considered in this connection the small pear-shaped and oval balls of oxide which have been found by Mr. Barringer and others far out on the plain and wholly independent, so far as locality is concerned, of either the shale ball just described or the irons. These, as shown in text figure 48, are, as a rule, more or less flattened and with surfaces much checked. Exteriorly they are composed of platy iron oxide indistinguishable, either chemically or physically, from that of the typical shale balls. These were considered by Mr. Barringer as solidified drops of fused oxide stripped off from the main mass by atmospheric friction.¹

Several of these forms were found by the writer, and other more typical forms were generously placed in his hands by Messrs. Barringer, Tilghman, and Holsinger. These have been cut in halves by a diamond saw and have been found in their more solid parts to retain still recognizable traces of the original crystalline structure of the iron, and also still unoxidized particles of iron phosphides. But it has been shown by Berwerth² and Mr. Tassin's work in the Museum laboratory that the heating of meteoric iron, even at a temperature far below the point of fusion, completely changes its structure. We are forced to conclude therefore that these forms are also products of terrestrial oxidation of small sulphur-chlorine-rich individuals once buried in the soil, but in which the material, before exposure by erosion, had so far adjusted itself to atmospheric conditions that no subsequent disintegration has taken place.

There remains for the present to be discussed only the relationship in origin between these chlorine-phosphorus-rich varieties and the normal irons.

As is well known, the fall is remarkable for the large number—several thousand at least—of independent individuals which have been found, and which show no evidence of atmospheric friction such as is common to meteorites, and by which one is enabled to judge of their orientation during the latter part of their flight through the air.

Such forms as those shown in pl. XXI, for instance, could not have escaped the loss of some of their exposed edges and points had they, unprotected, been subjected to any long frictional action. Yet these are no exception to the rule, sharp angles prevailing, and the individual irons showing further no torn nor broken edges such as to suggest that they once formed portions of a larger mass.

¹ Such an origin would apparently have been considered as possible by Lockyer. See his *Meteoric Hypothesis*, p. 69.

² Sitz. du Kaiserl. Akad. der Wiss., v. CXIV, 1905, p. 345.

An attempt has been made by at least one writer to account for these forms, some of which are of not over a gram in weight, on the supposition that they were flaked off from the cold parent mass through the superficial heat suddenly developed after the meteorite entered our atmosphere. It is, perhaps, not safe, without experimental work, to say how a mass of iron might behave under these conditions. It should be borne in mind, however, that the Canyon Diablo iron is one of the hardest and toughest of known meteorites, and that, moreover, as has been apparently definitely shown, the depth of the penetration of heat in such cases is extremely slight, owing to the rapid stripping off of the burned or fused material during its passage through the air. The discovery of this readily oxidizable variety of what is apparently a part of the same fall¹ may, perhaps, enable us to account for this phenomenon otherwise.

The possibility of the irons being but residuals out of a large and coarse-grained stony meteorite or pallasite has often been considered by the writer and is discussed by Mr. Barringer. He fails to find any evidence in favor of such a supposition. With these conclusions the writer agrees. In comparing the large number of irons which the Messrs. Barringer and Tilghman have placed in our hands we think, however, we have been able to trace a tendency toward gradation of one form into another. In cutting several which seemed nearly identical with the well-known types, we found here and there apparent intermediate structures (see upper right of pl. xx), and portions rich in iron phosphide, with thin particles of shale adhering. We have therefore come to the conception of a large heterogeneous mass of nickel-iron with segregation masses rich in chlorides, phosphides, and sulphides. Such would naturally rupture most readily along the line of contact with the more homogeneous portions, and, moreover, the results of atmospheric frictional heat would ignite and burn away the sulphide portions. Even where the heterogeneous masses of considerable size fall to the earth it is possible that these susceptible portions would oxidize and wholly disappear, leaving the more refractory to be found later. This would account for the almost constant association of shale and irons of the type shown in pl. xxi at various points out on the plain.

The occurrence of the still incompletely oxidized forms—shale balls—as described, is due to the protective action of the dry soil in a region of great aridity, the annual precipitation, as recorded by the Weather Bureau, being but about 8 inches. It has been shown by the Bureau of Soils that under such conditions soils rarely or never become saturated with moisture for more than a few inches below

¹ The possibility of an independent fall has been considered.

the surface, and that this moisture is brought back by capillarity and evaporated rather than drained off at lower levels, as in more humid regions. An iron thus buried, even though rich in chloride and sulphide, would therefore endure for a long period.

PART II.

By WIRT TASSIN

A. THE SHALE-BALL IRON

Several sections of the "shale balls" having iron centers were polished and etched. These etched surfaces were apparently so different in appearance from the ordinary Canyon Diablo irons that had their locality not been known they would not have been regarded as parts of the same fall. Sections of the Canyon Diablo meteorite, which had been in the possession of the Museum since 1894, were found which showed areas having the usual very coarse octahedral structure, with broad kamacite plates, together with small areas having a structure closely comparable with those of the shale-ball irons (pl. xx). Further, the analysis of the shale-ball iron compared with those of the well-known Canyon Diablo agrees as closely as could be expected in a heterogeneous mass subject to segregation. Thus:

Constituents.	A.	B.	C.	D.
Fe	95.370	91.396	93.510	94.030
Ni	3.945	7.940	5.600	5.320
Co	0.044	0.020
Cu	trace	0.010
P	0.144	0.179	0.156	0.235
S	trace	0.004	0.010	0.005
C	0.417	0.512	0.121
Si	trace	0.047	0.050	0.020
Cl	0.000	0.120
Insol	0.260
Total	99.719	99.983	99.882	99.881

Analysis "A" was made by Moissan,¹ "B" by Booth, Garrett, and Blair,² "C" and "D" by myself. The analyses "A" and "B" were made prior to the discovery of the shale-ball irons, and, like "C," which was made on an iron collected by Mr. G. K. Gilbert in 1892, are of Canyon Diablo irons of the ordinary type. "D" is that of a shale-ball iron. It will be noted that "A," "B," and "C" are distin-

¹ Compt. Rend., 1904, CXXXIX, 776.

² Proc. Phila. Acad. Sci., 1905, LVII, 875.

guished by the absence of chlorine, and in "C" at least this element was especially looked for, while "D" contains 0.120 of a per cent; also that the amount of phosphorus in "D" is much greater than in the others. To this difference in the chlorine and phosphorus content is due the difference between the two types of iron in their degree of oxidation, and to a certain extent their difference in structure.

The surface developed by etching a polished section of a shale-ball iron is characterized by the absence of the coarse lamellar structure with broad plates of kamacite, and by the presence of numerous schreibersite areas, more or less regularly arranged. Nodules of carbon and troilite are generally absent (see pl. XIX).

The mass of the etched area is seen to be made up of a darker-colored alloy, or eutectic (plessite), containing numerous masses or plates of schreibersite in parallel arrangement, oriented in the directions of the sides of triangles which correspond to three directions of the octahedron. These schreibersite areas are seldom less than a millimeter in width, and vary in length from two millimeters to thirty millimeters, with an average of about five millimeters.

Associated with and next to the schreibersite areas, and commonly bounding them along their longitudinal directions, may often be seen a more or less narrow band of cohenite. This cohenite area is more or less interrupted and has not been observed to form a continuous border to the schreibersite. Only occasionally has the cohenite been seen independently of the schreibersite, and then only in very small quantities. Small areas of kamacite may also be seen in the eutectic. These kamacite areas occur very sparingly and are rarely over a millimeter along their maximum diameters. Bounding the kamacite is a very fine hair-like line of a tin-white alloy which is regarded as tænite. This alloy occurs elsewhere apparently not associated with kamacite and seemingly developed in thin plates or sheets along the planes of irregular and much-interrupted octahedral cleavages of the eutectic, and which have an orientation identical with that of the schreibersite masses as above mentioned. Further, the tænite may occasionally be found arranged concentrically and outside of some of the smaller schreibersite masses at a distance of about a millimeter therefrom.

Troilite was not observed as visible segregations in the section under discussion, but under the microscope its presence was occasionally shown by treating the eutectic with an acid and cadmium chloride.

Carbon, as graphite, diamond, or in the amorphous form, could not be detected. The above statement is also true of lawrencite.

although the iron oxidizes, with extreme ease and a very short exposure to the atmosphere of the room, will cause it to sweat (fig. 2, pl. XIX).

A metallographic description of the eutectic itself cannot satisfactorily be made, since it was found almost impossible to resolve it under the microscope. Practically all that can be said is that the darker-colored alloy is fine granular; that the grains are apparently homogeneous, and are probably made up of minute octahedra arranged in very fine lamellæ.

The mineralogical separations made on the shale-ball iron did not yield the varied material that the ordinary Canyon Diablo irons have

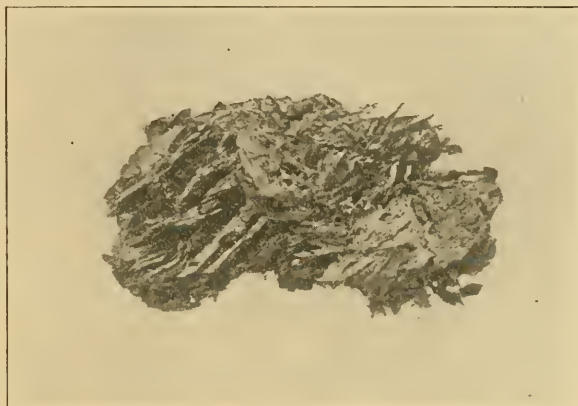


FIG. 49

yielded. Troilite, magnetite, chromite, diamond, and graphite were not found.

Schreibersite occurs abundantly in three distinct forms. The most common occurrence is as broad, thin, dark steel-gray, flexible magnetic lamellæ. These are often felted together to such an extent that in one case a mass of them weighing 26 grams has been preserved intact (text fig. 49). They have a specific gravity of 7.090 and the following composition:

P	13.80
Fe	63.04
Ni	23.07
Co	0.03
Cu	0.00

The second occurrence of this phosphide is as more or less flattened and angular nodules and rounded grains having a brilliant

steel-gray to nearly tin-white color, quite brittle and strongly magnetic. Their specific gravity is 7.20, and on analysis gave:

P	15.370
Fe	58.540
Ni	26.080
Co	0.052
Cu	trace.

The third form of the phosphide is as the lath-shaped form called rhabdite. This form occurs very sparingly free, and not enough of it was secured to do more than make a qualitative test to prove its identity. It is abundant as a constituent of the schreibersite lamellæ, and under the microscope, using a vertical illumination, the characteristic flat prisms are readily seen. In addition to the above forms of schreibersite, there is left a black non-magnetic residue having the following composition:

P	8.77
Fe	84.29
NiCo	5.00
C	2.16

Very little can be said concerning this material except that it may be a decomposition product resulting from the prolonged treatment of schreibersite with dilute acid.

Cohenite occurs in thin plates and rounded grains, none of which show any evidence of crystallization. When fresh, the mineral is dull tin-white in color, but soon changes to a bronze-yellow. The material analyzed contained some schreibersite, as shown by the phosphorus content: Its density was 7.612 and had the following percentage composition:

Fe	91.290
Ni	2.480
Co	0.100
C	5.060
P	0.015

The nickel-iron alloy, tænite, occurs as very thin tin-white flexible lamellæ having a brilliant metallic luster. An analysis gave:

Fe	72.160
Ni	27.750
Co	0.020
Cu	0.000
P	0.045
C	0.120

A small amount of olivine was noticed as occurring in rounded grains of a pale greenish-yellow color having the following composition:

SiO ₂	41.51
MgO	52.70
FeO	5.89
NiO	0.29

B. THE IRON SHALE

That the oxidized portions of the shale balls (pl. xviii, fig. 2) and the pear-shaped schistose masses of iron oxide shown in fig. 48 are the result of weathering subsequent to the fall of the mass, as stated by Derby¹ and Farrington,² does not seem to me to be open to question when their field occurrence is known. That both have the same origin is to me demonstrated by the following analyses:

Constituents.	A.	B.	C.
Fe ₂ O ₃	74.63	78.82	81.07
FeO	3.91	0.65	0.00
NiO	9.79	8.85	4.66
CoO	0.49	0.39	0.00
CaO	1.27	0.00	0.00
MgO	0.00	0.02	0.00
H ₂ O	8.02	10.00	12.81
SiO ₂	1.09	0.76	1.47
CO ₂	0.35	0.00	0.00
Al ₂ O ₃	0.05	0.00	0.00
S	trace	0.01	0.00
P	0.10	0.20	0.09
Cl	0.08	0.031	0.00
C	0.15	0.100	0.00
	99.93	99.831	100.10

CuO, SO₃ and P₂O₅ absent.

Analysis "A" was made by Mr. H. W. Nichols,³ "B" and "C" were made by me; "B" on one of the inner layers of a shale ball having an iron center; "C" on a shale ball similar to that shown in fig. 49.

These analyses, which while in the aggregate are alike, differ in certain particulars to which attention should be called. Thus, Nichols finds 3.91 per cent of FeO; I find but 0.65 per cent in that made

¹ Am. Jour. Sci., 1895, 3d series, vol. 49, p. 101.

² Am. Jour. Sci., 1906, 4th series, vol. 22, p. 309.

³ Am. Jour. Sci., 1906, 4th series, vol. 22, p. 306.

on the shale ball having an iron center, and none in that of the shale found on the plains. Farrington, combining his analysis, finds 42.39 per cent of magnetite, basing his figures upon the assumption that the protoxides of iron and nickel are so combined, and thus accounting for the magnetic character of the shale. I find no protoxide of iron in "C," and therefore have no reason for assuming the presence of magnetite in that case, at least. I am inclined to regard the iron shale as being made up essentially of limonite with some turgite, basing my opinion upon the physical characters of the shale in preference to data derived from combining the results of the analyses—a method admittedly speculative. Further, in the portions analyzed by me the magnetic character of the material is certainly due in part at least to the relatively large amount of unaltered schreibersite present and which is plainly visible in many sections of the iron shale.

EXPLANATION OF PLATES

PLATE XVIII

FIG. 1. A typical "shale ball," consisting of a residual nucleus of metallic iron surrounded by a crust of iron oxide, to which are adhering fragments of sandstone and limestone. The crust has been broken away at the right just above the center, exposing a portion of the nucleus. (Cat. No. 76,843, U. S. N. M.)

FIG. 2. A shale ball similar to that shown in Fig. 1 cut in halves, showing the metallic nucleus with its crust of "iron shale." The dark marginal areas are due to the exudation and oxidation of iron chloride after cutting. (Cat. No. 76,842, U. S. N. M.)

PLATE XIX

Shale ball cut in halves to show structure of the metallic nucleus and to illustrate the rapid oxidation which takes place along the outer margin. In the plate the two halves are oriented as laid open by the saw, the oxidation products and adhering rock fragments having broken away somewhat unequally. The outline between the metallic and oxidized products is very conspicuous. Fig. 1 shows a freshly polished surface, while Fig. 2 shows the second half after being for some days exposed to the air. The illustration shows the rapidly oxidizing ferrous chloride as it exudes around the outer margin. (Cat. No. 76,946, U. S. N. M.) Dimensions of metallic nucleus, 88 millimeters by 187 millimeters.

PLATE XX

Etched slice of the common type of Canyon Diablo iron, showing the thick plates of kamacite and nodules of troilite. At upper right a small area of transition toward the structure of the shale ball iron. (Cat. No. 85,833, U. S. N. M.)

PLATE XXI

Six characteristic pieces of the smaller Canyon Diablo irons of the common type, selected to show forms and lack of fusion effects on sharp angles. All reproduced on same scale. Actual length of central specimen, 170 millimeters. (Cat. No. 76,841, U. S. N. M.)