

## METALLIC SPHERULES IN IMPACTITE AND TEKTITE GLASSES<sup>1</sup>

ROBIN BRETT, *U. S. Geological Survey, Washington, D. C.*

### ABSTRACT

Electron microprobe analyses indicate that Ni-Fe spherules within impactite glass bombs from the Meteor Crater area, Arizona, contain from 20 to 65 weight percent Ni. Spherules from impactite glass at Wabar, Saudi Arabia, contain 8 to 41 percent Ni. The parent meteorites contain 7 to 8 percent Ni. The analyses indicate that glass in the vicinity of the spherules is enriched in Fe. Spherules in philippinite and indochinite tektites contain 1 to 3 and 4 to 6 percent Ni, respectively. The glass in the vicinity of tektite spherules is not enriched in Fe and contains from 3 to 6 percent Fe.

It is proposed that spherules in impactite glasses were partially oxidized prior to or during incorporation into impactite bombs. The almost Ni-free Fe oxide diffused into the glass, thus depleting the metal in Fe, and enriching the glass. Carbon dioxide and water may have contributed to the oxidation at Meteor Crater.

Spherules in tektites were not oxidized because the tektites were formed in an atmosphere with extremely low partial pressure of oxygen. A less likely alternative is that the spherules were incorporated into the tektite glass instantaneously so that oxidation was prevented.

### INTRODUCTION

Impactite bombs consist predominantly of glass that formed from rock and soil when a meteorite hit the earth. These impactite bombs, commonly contain small Ni-Fe spherules.

Previous analyses of metallic spherules from meteorite impact craters indicate that the spherules are richer in Ni than the parent meteorite from which they were derived. The Ni content of metallic spherules in tektites is consistently low with respect to impactite spherules.

It is the purpose of the present paper to examine the processes contributing to the Ni enrichment and to propose that the cause is oxidation, which the spherules in tektites have not undergone.

### DESCRIPTION OF SPHERULES

Ni-Fe spherules in impactite bombs from the Wabar and Meteor Crater meteorite impact craters have been described by several authors (e.g. Spencer, 1933; Nininger, 1954; Park and Reid, 1964; Larson *et al*, 1964). The spherules consist of Ni-Fe finely intergrown with subordinate troilite (FeS) and schreibersite (Fe, Ni)<sub>3</sub>P in a fine-grained texture characteristic of rapid cooling from a melt.

Spherules occur both within impactite glass bombs (Spencer, 1933) and as discrete individuals coated with a thin layer of oxide and siliceous glass

<sup>1</sup> Publication authorized by the Director, U. S. Geological Survey.

(Mead, *et al.*, 1965). The spherules within the impactite glass bombs commonly occur in dark- rather than light-colored glass. Spherules range in diameter from 0.5 mm to less than a micron. Within any given impactite bomb, spherules are highly irregular in size and concentration; they occur as commonly near the surface of bombs as in the interior. Unlike spherules in tektites, not all metal particles in impactites are spherical; a small percentage of those seen in Meteor Crater impactites are irregular in shape; that of a dumbbell is especially common.

There is no doubt that metallic spherules in the Wabar and Meteor

TABLE 1. ANALYSES OF NICKEL IN METALLIC SPHERULES FROM IMPACTITE GLASS AND TEKTITES

Locality	Ni, wt. percent	Reference
Wabar Crater	8-11	Park and Reid (1964)
	10-48	Larson <i>et al.</i> (1964)
	8.8*	Spencer (1933)
Bosumtwi Crater	5.2	El Gorsey (1966)
Philippinites	1.2- 3.2	Chao <i>et al.</i> (1962)
	2.1- 4.9	Chao <i>et al.</i> (1964)
Indochinites	4.4-13.2	Chao <i>et al.</i> (1964)

\* Wet chemical analysis, all others by electron microprobe.

Crater impactites are of meteoritic origin, since metallic meteorites are the only available source of Ni-Fe.

Spherules similar in size and mineralogy to those in impactites occur within tektites from Dalat, South Viet Nam, and Mandaluyong, Philippine Islands (Chao, *et al.*, 1964). They have also been reported in australites by Schüller and Ottemann (1963). Spherules are considerably rarer in tektites than in impactite glasses. The presence of coesite, which appears to be indicative of meteoritic impact (Chao, *et al.*, 1960), in tektites (Walter, 1965) and the resemblance of the metallic spherules in tektites to impactite spherules suggests that the spherules are of meteoritic origin.

#### IRON AND NICKEL CONTENT OF SPHERULES AND GLASS

*Previous work.* Analyses by previous workers of the Ni content of impactite and tektite spherules are given in Table 1. Some Wabar spherules are greatly enriched in Ni with respect to the parent meteorite which contains 7.3 weight percent Ni (Spencer, 1933). One spherule in suevite glass

from the Bosumtwi Crater (El Goresy, 1966) is low in Ni with respect to impactite spherules from other craters. The composition of the parent meteorite is, however, unknown.

Analyses of Meteor Crater spherules that were not enclosed in glass also show enrichment of Ni with respect to the composition of the parent meteorite. Ni contents are as high as 45 percent (Nininger, 1956; Park and Reid, 1964; Mead, *et al.*, 1965).

TABLE 2. COMPOSITION OF SELECTED TEKTITES, IMPACTITES AND IMPACTITE SOURCE MATERIAL (TEKTITE ANALYSES FROM CHAO (1963), WABAR ANALYSES FROM SPENCER (1933))

	Indochinites	Philippinites	Avg. Tektite	Wabar white glass	Wabar black glass <sup>1</sup>	Wabar sand- stone
SiO <sub>2</sub>	73.0	70.8	73.87	92.88	87.45	92.06
Al <sub>2</sub> O <sub>3</sub>	12.83	13.85	12.69	2.64	1.77	2.80
NiO	—	—	—	—	0.35	—
Fe <sub>2</sub> O <sub>3</sub>	0.64	0.70	0.47	0.23	0.28	0.60
FeO	4.37	4.30	4.16	0.53	5.77	0.19
MgO	2.48	2.60	2.18	0.47	0.60	0.45
CaO	1.91	3.09	2.23	1.46	1.90	1.19
SrO	—	—	—	—	—	0.01
Na <sub>2</sub> O	1.45	1.38	1.38	0.42	0.39	1.03
K <sub>2</sub> O	2.40	2.40	2.28	1.61	0.58	1.04
TiO <sub>2</sub>	0.73	0.79	0.75	0.12	0.15	0.12
P <sub>2</sub> O <sub>5</sub>	—	—	—	tr.	tr.	—
CO <sub>2</sub>	—	—	—	—	—	0.59
MnO	0.09	0.09	0.10	0.01	0.01	0.01
H <sub>2</sub> O <sup>+</sup>	—	—	—	0.32	0.04	0.20
H <sub>2</sub> O <sup>-</sup>	—	—	—	0.11	0.08	0.22
Total	99.90	100.00	100.11	100.80	99.37	100.50

<sup>1</sup> Includes Ni-Fe spherules.

No analyses have been made of the Fe or Ni content of the impactite or tektite glasses containing spherules, although Spencer (1933) includes a bulk analysis of Wabar black glass with spherules (Table 2). Spencer has calculated that the Fe-Ni ratio in the black glass (including spherules) is close to that of the parent meteorite. Table 2 also lists analyses of some tektite glasses.

*Present analyses.* In the present study glass and spherules from both the Mandaluyong, Philippine Islands, and Dalat, South Viet Nam, tektite localities and impactite glass from the meteorite craters at Wabar, Saudi

Arabia, and Meteor Crater, Arizona, were examined for Fe and Ni with an ARL electron microprobe. Some spherules were also analyzed for Si, using pure Fe as a standard. The spherules analyzed had not been oxidized by weathering, since they showed no characteristic oxide veinlets or preferential oxidation of troilite.

Fe-Ni standards for spherule analysis were those used by Goldstein and

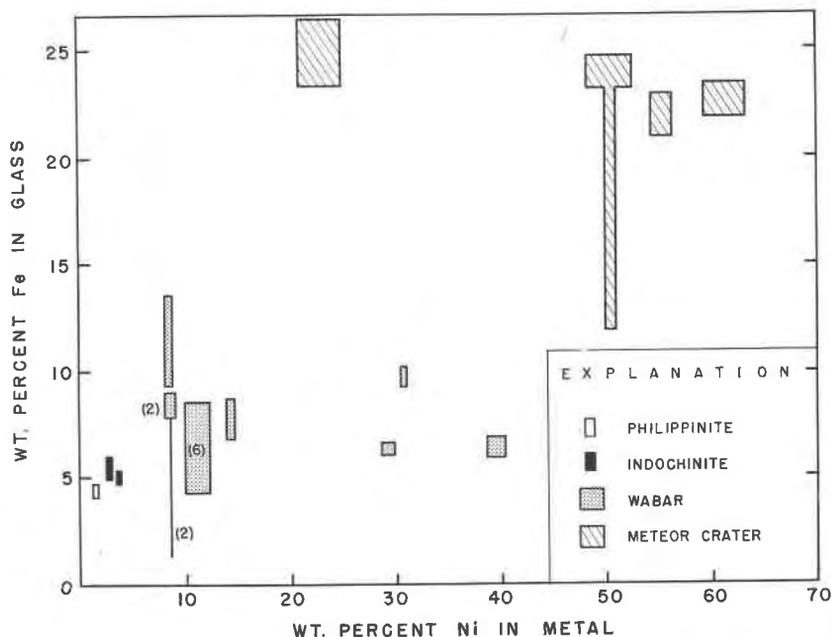


FIG. 1. Plot of Ni in metallic spherules versus Fe content of surrounding glass for indochinite, philippinite, Meteor Crater impactite and Wabar impactite specimens. The range of values for any given measurement represents the standard deviation from the mean for the analysis. Figures in parentheses refer to the number of different spherule measurements which plot within the area shown.

Ogilvie (1965). Synthetic glasses (total Fe = 1.4, 3.1, 4.2, 4.4, 4.9, 6.7 wt. %), pyroxenes (total Fe = 8.5, 14.7, 16.5, 19.9, 24.3 wt. %), chromite (total Fe = 10.9 wt. %), and fayalite (total Fe = 44.2 wt. %), were used as standards in determining the Fe content of the impactite and tektite glasses. The accuracy for the quantitative analysis of Ni in the Ni-Fe spherules is conservatively estimated as within  $\pm 5$  percent of the amount present, and for the Fe analyses of the glasses within  $\pm 10$  percent of the amount present.

Results are listed in Table 3 and Figure 1. At least 10 points were ana-

TABLE 3. MICROPROBE ANALYSES OF Ni IN SPHERULES AND Fe IN SURROUNDING GLASS OF TEKTITES AND IMPACTITES

Locality	Ni in metal	Fe in glass	Fe content of glass at least 500 microns from any spherule	Comments
Philippinite A	1.5± 0.1 ( 1.3— 1.7)	4.4± 0.2 ( 3.8± 4.8)	4.0± 0.5 ( 3.3± 4.5)	
Philippinite B	2.7± 0.3 ( 2.5— 3.5)	5.4± 0.5 ( 4.8— 5.8)	5.4± 0.3 ( 5.0— 5.7)	
Indochinite A	5.0± 0.5 ( 4.5— 6.5)	3.6± 0.2 ( 3.2— 4.0)	3.5± 0.2 ( 3.3— 3.7)	
Meteor Crater A	22.8± 1.9 (19.7—23.5)	24.9± 1.6 (23.2—27.4)	—	Ni content of Canyon Diablo meteorite is 7–8.5 wt. percent (Prior, 1953)
Meteor Crater A	55.2± 1.1 (53.6—56.6)	21.8± 1.0 (21.5—22.7)	—	
Meteor Crater A	50.6± 2.3 (47.1—53.6)	17.1± 5.4 (11.5—22.8) 24.0± 0.7 (22.7—25.0)	—	Fe content of glass on one side of spherule differs markedly from that on the other
Meteor Crater B	50.7± 0.6 (50.0—51.6)	22.8± 0.6 (22.2—23.5)	17.4± 7.2 ( 0.8—23.2)	
Meteor Crater C	61.3± 2.0 (57.6—64.7)	22.6± 0.8 (21.4—24.3)	—	
Wabar A	14.1± 0.3 (13.5±14.7)	7.7± 1.0 ( 6.3— 8.6)	5.6± 2.8 ( 0.3— 8.0)	Ni content of parent meteorite is 7.3 wt. percent (Spencer, 1933)
Wabar A	12.5± 0.2 (12.2—12.7)	5.7± 1.4 ( 2.5—7.6)	5.6± 2.8 ( 0.3— 8.0)	
Wabar A	14.4± 0.3 (14.2—14.7)	—	5.6± 2.8 ( 0.3— 8.0)	
Wabar A	31.8± 0.3 (31.2—32.1)	9.7± 0.4 ( 9.1—10.4)	5.6± 2.8 ( 0.3—8.0)	
Wabar B	39.5± 0.9 (38.3—40.6)	6.3± 0.4 ( 5.8— 7.0)	4.2± 2.4 ( 1.6— 6.5)	
Wabar C	11.0± 0.7 ( 9.8—13.3)	4.4± 0.6 ( 3.0— 5.3)	3.3± 3.6 ( 0 —13.9)	
Wabar C	11.1± 0.5 (10.7—12.0)	7.2± 1.0 ( 5.5— 9.7)	3.3± 3.6 ( 0.0—13.9)	
Wabar C	10.0± 0.2 ( 9.9—10.2)	6.3± 1.3 ( 4.6—10.7)	3.3± 3.6 ( 0.0—13.9)	
Wabar C	10.2± 0.4 ( 9.9—10.8)	6.5± 1.8 ( 4.2— 9.2)	3.3± 3.6 ( 0.0—13.9)	
Wabar C	29.4± 0.5 (28.2—30.5)	7.6± 0.5 ( 6.3— 8.6)	3.3± 3.6 ( 0.0—13.9)	
Wabar D	8.4± 0.4 ( 7.9— 9.0)	8.4± 0.6 ( 6.7— 9.1)		Light-colored glass of Park and Reid (1964). Spherules so abundant that all glass lay within 500 microns of a spherule
Wabar D	11.5± 0.1 (11.3—11.7)	7.3± 1.3 ( 4.6— 9.2)		Light colored glass, as above.
Wabar D	8.5± 0.3 ( 8.3— 8.7)	11.5± 2.1 ( 7.8—14.2)		Light colored glass, as above.
Wabar D	8.6	4.2± 3.7 ( 0.1—8.8 )		Light colored glass, as above. One spot analysis of metal only.

More than one listing for a given specimen corresponds to analyses of more than one spherule in that specimen. All analyses in wt percent, given as mean plus std. deviation and range of values. Ranges of values are in parentheses.

lyzed within each spherule, both by traverse and spot analysis. At least 12 points were analyzed within the glass surrounding each spherule by traversing from 0–100 microns out from the spherule at either 2- or 5-micron intervals. At least 10 spot analyses of glass more than 500 microns distant from any spherule were also made for most specimens. The above figure of 500 microns is correct only if it is assumed that there were no spherules within 500 microns below the surface analyzed. The assumption is probably not correct in some measurements of impactite glass, which explains the high Fe content of some of the glass.

Analysis of tektite and impactite glasses showed greater contents of Fe and Ni in glass within 8 microns of the spherule boundaries than in glass farther from the spherule, presumably because of excitation from part of the spherule below the surface. No gradients in Fe content of glass were observed within 100 microns of any spherule. If any gradients exist within 8 microns they are masked by the excitation effect. Analyses within 8 microns of a spherule are therefore not included in Table 3.

Variation ranges of the contents of Ni in metal and Fe in glass in any given impactite bomb are considerably larger than the estimated analytical error. Part of the variation in Ni content of any given spherule may be due to accidental analysis of the tiny troilite and schreibersite particles that occur in these spherules, but the major part of observed analytical differences probably reflect real differences in the Ni content of the metal phase.

The analytical results can be summarized as follows:

1. In any given tektite, the Fe content of glass is fairly uniform throughout (4 to 6 wt. % in the philippinites, and 3 to 4 wt. % in the indochinite specimen). The Fe content of impactite glass in the vicinity of spherules is considerably higher than that of tektite glass. It is fairly constant within 100 microns of any given impactite spherule but diminishes, in some specimens to the limit of detection (0.01 wt. %), at distances 500 microns or more from any spherule. Unfortunately, no continuous profile showing these gradients was obtained.

2. No relation between the size of spherules and their Ni content was found (Table 4). Spherules vary widely in their Ni contents within any given impactite bomb, but the amount is fairly constant in any individual spherule.

3. The Ni content of impactite spherules (Meteor Crater, 20 to 65 wt. % Ni; Wabar, 8 to 41 wt. % Ni) is considerably higher than that of tektite spherules (philippinites, 1 to 3 wt. % Ni; indochinites, 4 to 6 wt. % Ni). The impactite spherules are depleted in Fe with respect to the parent meteorite.

4. The Fe content of Meteor Crater impactite glass in the vicinity of

TABLE 4. AVERAGE Ni CONTENT OF SPHERULES IN WABAR IMPACTITE GLASS ARRANGED IN ORDER OF INCREASING SPHERULE DIAMETER

Spherule diameter (microns)	Ni content (wt percent)
8	8.4
10	8.2
10	32.0
12	12.7
15	10.0
20	8.5
20	10.2
25	11.5
28	39.8
30	11.1
36	14.0
57	11.0
105	29.4

spherules (11 to 27 wt. %) is higher than that of Wabar glass (0 to 10 wt. %), even though the Ni contents of the parent meteorites are approximately the same. The Fe content of the glass near spherules in any given bomb is reasonably constant.

5. Neither the spherules in impactites nor tektites showed silicon contents above the silicon background measured for a pure Fe standard.

6. The Ni content of spherules in light-colored Wabar glass reported here is in agreement with the analyses of Park and Reid (1964).

The Ni content of tektite glass was no greater than that of a glass standard in which the Ni content is a few parts per million. The Ni content of the impactite glasses was as much as three times greater than that of the standard.

#### THE SYSTEM Fe-Ni-O

To interpret the above results it is necessary to have some understanding of the phase equilibria of the system Fe-Ni-O. Unfortunately, data on the system are insufficient to derive thermochemical conclusions for the the present study; in addition, neither the time of heating nor the maximum temperature reached during the formation of impactite and tektite glass has been definitely established. The temperature was above about 1500°C, as at that temperature Ni-Fe alloys of composition similar to those in impactites and tektites melt (Hansen and Anderko, 1958).

Brabers and Birchenall (1958) have published the only phase diagram (1050°C isotherm) of the Fe-rich portion of the system Fe-Ni-O (Figure 2). Progressive oxidation of Fe-Ni alloys containing less than 55 atom

percent Ni results in the formation of wüstite ( $\text{Fe}_{1-x}\text{O}$ ) in which Ni is virtually absent and in the progressive enrichment of the metal phase in nickel. Continued oxidation caused the formation of a nickel-iron spinel  $[(\text{Fe}, \text{Ni})\text{O} \cdot \text{Fe}_2\text{O}_3] + \text{metal} + \text{wüstite}$  and, for alloys with an original Ni content greater than about 24 atom percent Ni, the equilibrium assemblage becomes Ni-rich metal plus Ni-rich spinel.

No details exist on phase equilibria at temperatures other than  $1050^\circ\text{C}$ , but Fechtig and Utech (1964) have shown that molten Fe-Ni alloys become progressively enriched in nickel during oxidation.

In the present study, the metal in the Bogou iron meteorite (total Ni

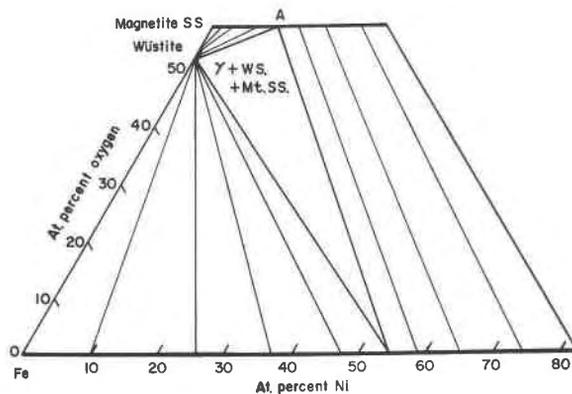


FIG. 2. Phase diagram of the Fe-rich portion of the system Fe-Ni-O at  $1050^\circ\text{C}$  (after Brabers and Birchenall, 1958). Symbols:  $\gamma = \gamma\text{-Fe, Ni}$ ; Mt. ss. = magnetite solid solution  $[(\text{Fe}, \text{Ni})\text{O} \cdot \text{Fe}_2\text{O}_3]$ , ws. = wüstite ( $\text{FeO}$ ).

7.2 wt. %, E. P. Henderson and R. S. Clarke, Jr., oral commun., 1966) within a few microns of the ablation crust caused by oxidation upon entry into the earth's atmosphere was analyzed by the methods described earlier. The Ni content of this metal is consistently high compared to that in the interior of the meteorite, and is locally as high as 65 weight percent where the metal penetrates the oxide at acute angles. The iron oxide contains less than 2 weight percent Ni. Oxidation during ablation therefore depletes Fe in the metal, as in the experimental observations.

#### EXPERIMENTAL WORK

Some simple heating experiments were made to examine possible mechanisms of Ni enrichment in metallic spherules. Metallic filings of composition approximating that of a coarse octahedrite (Fe 92.3, Ni 7.0, Co 0.5, C 0.2 wt. %) were obtained from Manlabs Inc., Cambridge,

Mass. A portion of these filings was partially oxidized by heating in air, another portion was left unoxidized. The two batches of filings were then placed in two silica glass tubes in the narrow space between the tube wall (1.3 mm thick), and a tight-fitting silica glass rod. The tubes were then evacuated and sealed. The part of each tube containing filings was then heated in a hydrogen-oxygen blowtorch flame for approximately 30 seconds. The maximum flame temperature attained in this way is 2660°C (Lurie and Sherman, 1933); temperatures in the silica glass tubes probably were about  $2000 \pm 300^\circ\text{C}$ .

The tube containing metal plus oxide melted more readily than the one containing just metal and vesiculated vigorously locally, with rapid diffusion of the oxidized metal through the glass, causing it to become dark in color. There was little or no change in color or appearance of the tube containing unoxidized metal after heating, except for the formation of a few small vesicles. Both runs were cooled in air.

Polished sections were made of both runs, which were then examined microscopically. Spherules had formed by melting of the metal filings. Devitrified glass surrounded the numerous vesicles and the contact of spherules with dark glass in the specimen which had been prepared from partially oxidized filings.

A further run prepared with unoxidized filings and heated for 2 minutes gave results similar to those of the run held at temperature for only 30 seconds. The spherules and glass were then analyzed by the same methods and standards described previously. The Ni content of the metal in the unoxidized run remained unchanged within the limits of detection and no Fe was detectable in the silica glass. In the partially oxidized run, the remaining metal was enriched in Ni (Ni=8 to 10 wt. %) and the Fe content of the glass ranged from 0 to 14 weight percent.

#### CONCLUSIONS

Oxidation of Ni-Fe has been shown to enrich Ni in the metal phase. The Ni enrichment in the ablation rim of the Bogou meteorite is caused by this process. Castaing and Frederiksson (1958) proposed oxidation to account for the high Ni contents of some spherules of supposed cosmic origin. It is proposed that the high Ni contents of spherules in impactite glass compared to the parent meteorite are due to loss of the iron component of the alloy by oxidation. The loss of Fe in the spherules with resultant enrichment in Ni can be accounted for by incorporation of iron in the glass. Spencer (1933) and Taylor and Kolbe (1965) showed that the chemical composition of dark glass of the Wabar and Henbury impactites, respectively, corresponds closely to that of the rock from which the glasses were formed, with the addition of Ni-Fe in meteoritic proportions.

The Ni enrichment cannot be explained by fractionation due to partial vaporization or melting of meteoritic metal as this demands a very narrow range of impact temperatures, which is highly unlikely.

I have considered four possible processes to explain oxidation of metallic spherules in impactites:

1. Atmospheric oxidation after the spherules were incorporated into the molten silicate bombs.

Had this occurred, then oxidation would have taken place progressively from the surface of the glass inwards, so that the outer portion of each glass bomb would be totally depleted in spherules which should be increasingly rich in Fe (less oxidized) toward the center of any given bomb. Observation and electron microprobe analyses in the present study have shown that spherules are distributed uniformly throughout each bomb and that the Ni content of any spherule is not related to its distance from the surface. The heating experiments reported here have shown that 1.3 mm of silica glass prevents atmospheric oxidation of Ni-Fe for times of at least 2 minutes, even at temperatures in the vicinity of 2000°C. This process may therefore be rejected.

2. Oxidation of the spherules by CO<sub>2</sub>. Any carbonate minerals present in rock from which the impactite bombs formed would decompose at the temperatures which occur during impact, and the metallic oxides so formed would be incorporated into the glass. The Fe in the spherules would simultaneously be oxidized by the reaction:  $\text{Fe} + \text{CO}_2 = \text{FeO} + \text{CO}$ . Dolomite (in the Kaibab Limestone) was available for such reaction at Meteor Crater at the time of impact; however the rock at Wabar is almost pure quartz sand. Hence CO<sub>2</sub> may have contributed to oxidation at Meteor Crater, but not at Wabar.

3. Oxidation by H<sub>2</sub>O in the rock from which the impactites were derived. Calculation shows that to oxidize sufficient Fe-Ni by the reaction  $\text{Fe} + \text{H}_2\text{O} = \text{FeO} + \text{H}_2$ , to enrich the glass by 10 weight percent FeO would require several wt. percent H<sub>2</sub>O. Geological evidence indicates that at least part of the Coconino Sandstone at Meteor Crater was saturated with water at the time of impact (E. M. Shoemaker, oral commun., 1966). The impactite bombs from Meteor Crater which I examined in the present study consisted partly of fused Coconino Sandstone, so that the above mechanism may have contributed to the oxidation of spherules there. The time of the Wabar impact has not been established, but all available evidence indicates that it is of recent origin (V. E. Barnes, written communication). The meteorite therefore fell in a desert environment, so that oxidation of the spherules by water at Wabar is dubious.

4. Atmospheric oxidation of spherules prior to their incorporation in impactite bombs. The spherules were partially oxidized in the extremely

short period prior to their incorporation in the bombs. Upon incorporation into the bombs the FeO skin surrounding each spherule diffused into the glass, enriching it in Fe, leaving a clean glass-metal interface. Alternatively the oxidation may have occurred subsequent to incorporation in the silica melt, while the melt was undergoing turbulent flow.

I consider this process to be dominant in the oxidation of impactite spherules as it is the only one which satisfactorily accounts for oxidation at Meteor Crater and Wabar.

The higher Ni content of metal and accompanying higher Fe content of the surrounding glass from the Meteor Crater impactites with respect to the Wabar impactites indicates that the Meteor Crater material is more oxidized. This suggests that the partial pressure of oxygen at Meteor Crater was higher than that at Wabar during the meteoritic explosion, or that the molten Meteor Crater spherules were exposed to oxidation for a longer time before they were incorporated into the glass bombs, or, more likely, the CO<sub>2</sub> and H<sub>2</sub>O assisted oxidation at Meteor Crater.

An enrichment of Ni in metallic spherules from an original 10 to a final 50 weight percent requires that four-fifths of the original iron in the spherule was oxidized and dissolved in the glass.

Spherules in indochinites, unlike those in impactite glasses, have a lower Ni content than almost any iron meteorite. Spherules from philippinites have a lower Ni content than any reported iron meteorite.

The Ni-Fe ratio of metal in spherules from philippinites may be low because the ratio in the metallic portion of the meteorite which formed them was low. An alternative hypothesis compatible with the above discussion is that the tektites and spherules were formed in a reducing environment such that liquid Fe was exsolved from the silicate melt which formed the tektites, and incorporated into the spherules derived from the parent meteorite, thus diluting their Ni content. Reid, *et al* (1964) have shown that metallic Fe separates from a tektite melt at high temperatures under reducing conditions.

Unlike the impactite glasses which contain spherules, tektite glasses containing spherules are no richer in Fe than those free of spherules. The above facts suggest that metallic spherules in tektites did not oxidize. The spherules and tektite glass were formed in an environment in which the partial pressure of oxygen was so low that the reaction Ni-Fe alloy + oxygen  $\rightarrow$  wüstite + Ni-rich alloy was prohibited. This low oxygen pressure during tektite formation is compatible with the results of Rost (1964), who found a total pressure corresponding to only 35 mm Hg in an undamaged moldavite bubble, and those of Thorpe *et al.* (1963), and Walter and Carron (1964), who suggest that tektites may have formed under reducing conditions on the basis of Fe<sup>2+</sup>/Fe<sup>3+</sup> ratios in tektite

glasses. Suess (1951), O'Keefe *et al.* (1962), and Zähringer (1963) also found low gas pressures inside tektite bubbles. Such low pressures perhaps occur in the center of an explosion caused by meteoritic impact with the earth (Vand, 1965), but on the present evidence the tektites may equally well have been formed in an extraterrestrial environment in which oxygen pressures were low. A less likely alternative is that the spherules may have been formed in an environment with high partial pressure of oxygen but were incorporated into the glass almost instantaneously so that no oxidation could occur. If oxidation of Ni-Fe spherules can be effected by CO<sub>2</sub>, H<sub>2</sub>O, and air as suggested earlier, then it follows that the material from which tektites were formed contained little carbonate and water.

#### ACKNOWLEDGMENTS

I thank F. Wood, Goddard Space Flight Center, NASA, Greenbelt, Maryland, for help in the analytical work, and T. J. Abercrombie, National Geographic Society, Washington, D. C.; T. E. Bunch, University of Pittsburgh; E. C. T. Chao, U. S. Geological Survey, Washington, D. C.; and E. P. Henderson, U. S. National Museum, Washington, D. C., for supplying specimens for study. I am grateful to E. M. Shoemaker, U. S. Geological Survey, for helpful suggestions.

#### REFERENCES

- BRABERS, M. J. AND L. E. BIRCHENALL (1958) High temperature oxidation of iron-nickel alloys. *Corrosion* **14**, 179t-182t.
- CASTAING, R. AND K. FREDERIKSSON (1958) Analyses of cosmic spherules with an X-ray microanalyser. *Geochim. Cosmochim. Acta* **14**, 114-117.
- CHAO, E. C. T. (1963) The petrographic and chemical characteristics of tektites, J. O'Keefe, ed., *Tektites*, Univ. Chicago Press, Chicago, Ill. 51-94.
- CHAO, E. C. T., I. ADLER, E. J. DWORNIK, AND J. LITTLER (1962) Metallic spherules in tektites from Isabela, the Philippine Islands. *Science* **135**, 97-98.
- CHAO, E. C. T., E. J. DWORNIK, AND J. LITTLER (1964) New data on the nickel-iron spherules from southeast Asian tektites and their implications. *Geochim. Cosmochim. Acta* **28**, 971-980.
- CHAO, E. C. T., E. M. SHOEMAKER, AND B. K. MADSEN (1960) First natural occurrence of coesite. *Science* **132**, 220-222.
- EL GORESEY, A. (1966) Metallic spherules in Bosumtwi Crater glasses. *Earth Planet. Sci. Lett.* **1**, 23-24.
- FECHTIG, H. AND K. UTECH (1964) On the presence or absence of nickel in dark magnetic cosmic spherules and their mechanics of origin. *Ann. N. Y. Acad. Sci.* **119**, 234-249.
- GOLDSTEIN, J. I. AND R. E. OGILVIE (1965) Fe-Ni phase diagram. *Amer. Inst. Mining Met. Eng.* **233**, 2083-2087.
- HANSEN, M. AND K. ANDERKO (1958) *Constitution of binary alloys*. McGraw-Hill, New York, N. Y., 1305 p.
- LARSON, R. R., E. J. DWORNIK, AND I. ADLER (1964) Electron probe analysis of "cosmic" spherules. *Ann. N. Y. Acad. Sci.* **119**, 282-286.

- LURIE, H. H. AND G. W. SHERMAN (1933) Flame temperatures of combustible gas-oxygen mixtures. *Ind. Eng. Chem.* **25**, 404-409.
- MEAD, C. A., E. C. T. CHAO AND J. LITTLER (1965) Metallic spheroids from Meteor Crater, Ariz. *Amer. Mineral.* **50**, 667-681.
- NININGER, H. H. (1954) Impactite slag at Barringer Crater. *Amer. J. Sci.* **252**, 277-290.
- NININGER, H. H. (1956) *Arizona's meteorite crater*. Amer. Meteorite Museum, Sedona, Ariz. 232 p.
- O'KEEFE, J. A., L. A. DUNNING AND P. D. LOWMAN, JR. (1962) The composition of gases in a tektite bubble. *Science* **137**, 228.
- PARK, F. R. AND A. M. REID (1964) A comparative study of some metallic spherules. *N. Y. Acad. Sci. Annals* **119**, 250-281.
- PRIOR, G. T. (1953) *Catalogue of meteorites*. 2nd ed. rev. by M. H. Hey. Trustees Brit. Mus., London, England. 472 pp.
- REID, A. M., F. R. PARK AND A. J. COHEN (1964) Synthetic metallic spherules in a Philippine tektite. *Geochim. Cosmochim. Acta* **28**, 1009-1010.
- ROST, R. (1964) Surfaces and inclusions in moldavites. *Geochim. et Cosmochim. Acta* **28**, 931-936.
- SCHÜLLER, A. AND J. OTTEMANN (1963) Vergleichende Geochemie und Petrographie meteoritische und vulkanische Gläser (ein Beitrag zum Briefproblem). *Neues Jahrb. Mineral. Abh.* **100**, 1-26.
- SPENCER, L. J. (1933) Meteoric iron and silica-glass from the meteorite craters of Henbury (central Australia) and Wabar (Arabia). *Mineral. Mag.* **23**, 387-404.
- SUESS, H. E. (1951) Gas content and age of tektites. *Geochim. Cosmochim. Acta* **2**, 76-79.
- TAYLOR, S. R. AND P. KOLBE (1965) Geochemistry of Henbury impact glass. *Geochim. Cosmochim. Acta* **29**, 741-745.
- THORPE, A. N., F. E. SENFTLE, AND F. CUTTITA (1963) Magnetic and chemical investigations of iron in tektites. *Nature* **197**, 836-840.
- VAND, V. (1965) Astrogeology: Terrestrial meteoritic craters and the origin of tektites. *Advan. Geophys.* **11**, 1-114.
- WALTER, L. S. (1965) Coesite discovered in tektites. *Science* **147**, 1029-1032.
- AND M. K. CARRON (1964) Vapor pressure and vapor fractionation of silicate melts of tektite composition. *Geochim. Cosmochim. Acta* **28**, 937-951.
- ZÄHRINGER, J. (1963) K-Ar measurements of tektites, in *Radioactive Dating*, Int. At. Energ. Agency, Vienna, Austria, 289-308.

*Manuscript received, June 10, 1966; accepted for publication, September 3, 1966.*