Fictitious occurrences of iron silicide (ferrosilicon).

By L. J. Spencer, M.A., Sc.D., F.R.S.
Formerly Keeper of Minerals in the British Museum.

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FERROSILICON is occasionally found under circumstances that suggest that it is a natural mineral. Twice during the past quarter of a century it has been described as a *new* mineral, and the error was detected only after preliminary accounts had been published. It has also at times been thought to be meteoric. A supposed meteoric iron from North Carolina was described by C. U. Shepard in 1859 as composed of a material to which he gave the name 'ferrosilicine'.

The following notes collected during several years contain nothing new. They are merely brought together to serve as a warning against an error that may recur.

On several occasions between 1924 and 1929 Mr. H. N. G. Cobbe, a consulting mining engineer, sent to me for identification rounded pieces of a metallic substance that had been picked out from the concentrates of the gold dredgers on rivers and creeks in British Guiana. After some trouble we were able to match these with the nodules of ferrosilicon sometimes present in commercial calcium carbide. Evidently the spent carbide from the acetylene flares was emptied out into the river to be collected again by the dredgers.

For comparison, Mr. Cobbe obtained samples from the works of Messrs. Allen Liversidge. Another sample was obtained through Prof. V. M. Goldschmidt from the calcium carbide works of the Aktieselskabet Meraker Smelteverk at Kopperå in Norway. A larger broken fragment (67·23 grams), found in a large container of carbide used for acetylene welding, was given by Mr. R. G. Thomson of Birmingham.

This material usually has the form of more or less spherical pellets up to a centimetre in diameter; but some irregular pieces up to 4½ cm. across, broken from larger slabby masses, were seen. It is

steel-grey to tin-white with a bright metallic lustre. A bronze-yellow tarnish is sometimes shown; but there is no rust. It is very hard (H. 6½) and brittle, and is readily powdered with a hammer. The fracture is uneven. The specific gravity is variable, 5·8–6·8, due partly to cavities in the mass. Some of these cavities are bubbles with smooth surfaces, and others are partly filled with feathery and platy agregates of minute tetrahedra. The magnetic character is also variable: some pieces are attracted by a magnet, while others are not. Some pieces are slightly attacked by hydrochloric acid, but usually they are not affected even by aqua regia. The material is decomposed by hydrofluoric acid or by fusion with caustic soda. An approximate analysis of a pellet from British Guiana gave Fe 65, Si 35 % corresponding nearly to the formula FeSi.

Nodules of ferrosilicon occurring as an impurity in commercial calcium carbide were described by Vivian B. Lewes[1] in 1898 and with some further details in his book 'Acetylene', in 1900. He distinguished two kinds: (1) grey, sp. gr. 3·5–5·8, non-magnetic, not oxidized before the blowpipe; (2) steel-grey, sp. gr. 6·3–6·8, strongly magnetic, slowly oxidized by air and water. His analysis (of which kind not stated) gave Fe 58·07, Si 30·76, Ca 2·65, Al 3·01, Mg 0·64, C &c. 4·87 = 100·00. Analyses quoted by J. H. Vogel[2] show the following extremes: Fe 62·7–82·1, Si 16·3–33·5, C 0·1–2·2.

'A supposed new mineral', said to have been found in the basalt of County Antrim, was briefly described in 1909 as a compound of iron, silicon, and carbon. Mention was made of the fact that when the material was powdered, or even scratched, it emitted an odour like that of acetylene prepared from commercial calcium carbide. The finding of this material in basalt could not be confirmed, and a later note admitted that it was very probably an artificial product.[3] The characters, so far as stated, agreed with those of ferrosilicon.

Another 'new mineral?'[4] was found in 1911 as small pellets on the separating tables at the Kimberley diamond mines in South Africa. It was slightly magnetic, with sp. gr. 6·7, H. '6–9', and contained Fe 71·39, Si 20·03, C 8·41 %. When broken, it gave off

[1] V. B. Lewes, Journ. Soc. Chem. Industry, London, 1898, vol. 17, p. 532; 'Acetylene', London, 1900, p. 331.

[2] J. H. Vogel, Handbuch für Acetylene, Braunschweig, 1904, p. 13.

[3] R. J. Moss and H. J. Seymour, Nature, London, 1909, vol. 81, p. 518; 1910, vol. 82, p. 280.

[4] J. R. Sutton, A new mineral?, Nature, London, 1911, vol. 87, p. 314.

a strong smell of carbide. A further examination[1] proved the identity of this material with the pellets of iron carbide and iron silico-carbide found in commercial calcium carbide. At that period the blue ground from the diamond mines was disintegrated by the action of the weather, for which purpose it was spread out on extensive 'floors'. To prevent any thefts of diamonds these floors were surrounded by a barbed wire fence and at night lit by acetylene flares. The spent carbide was no doubt emptied out on the spot and so got mixed with the blue ground.

A magnetic nodule found near Renison Bell in Tasmania, which was thought to be perhaps a meteorite, when shown to Mr. G. W. Card, Curator of the Mining and Geological Museum at Sydney, was at once recognized by him as a calcium carbide residue—a pitfall that he had met before.[2]

An alleged meteorite from Greece was offered to the British Museum in 1929. It weighed 140 grams and an analysis made in Athens showed Fe 74·03, Si 19·76, Ni 0·10 %, sp. gr. 7. When received, it was found to have the characters of the ferrosilicon from calcium carbide.

Crystallized compounds of iron and silicon are Fe_3Si (cubic;[3] containing Si 20·0 %), FeSi (tetrahedral-cubic; Si 33·3 %), and $FeSi_2$ (tetragonal; Si 50·0 %). Other compounds have been suggested and there is a continuous series of alloys Fe-Si. Ferrosilicon containing about 15 % Si was made commercially in the blast furnace, and more recently higher grades containing 25–95 % have been made in the electric furnace. These are used in the manufacture of steel. Some of them are unstable, especially that containing about 56 % Si, which may decompose with explosive violence, and shipwrecks have been so caused. The most stable is FeSi, which is not attacked by acids (except HF). This retains its metallic appearance when exposed to the weather, and for this reason it would be likely to be found in odd situations.

Calcium carbide was first manufactured commercially in 1895, and it will be noticed that the fictitious occurrences of ferrosilicon men-

[1] B. de St. J. van der Riet, A supposed new mineral from Du Toitspan, Kimberley. Trans. Roy. Soc. South Africa, 1912, vol. 2, Proc. pp. xxix–xxx; Nature, London, 1911, vol. 88, pp. 166–167.

[2] H. Conder, Geological pitfalls. Industrial Australian and Mining Standard, 1926, vol. 76, p. 6; reprinted in Mining Magazine, London, 1926, vol. 35, p. 190.

[3] E. S. Greiner, J. S. Marsh, and B. Stoughton, The alloys of iron and silicon. New York and London, 1933, p. 66.

tioned above are all subsequent to that date, except the 'ferrosilicine' of C. U. Shepard[1] in 1859. Two analyses of this gave Fe 84·00, Si 13·57, C trace, P 1·31; and Fe 87·10, Si 10·60, C 0·40, P trace; sp. gr. 6·745. C. F. Rammelsberg[2] determined Si 15·7, and he concluded that the material was a white cast iron of poor quality.

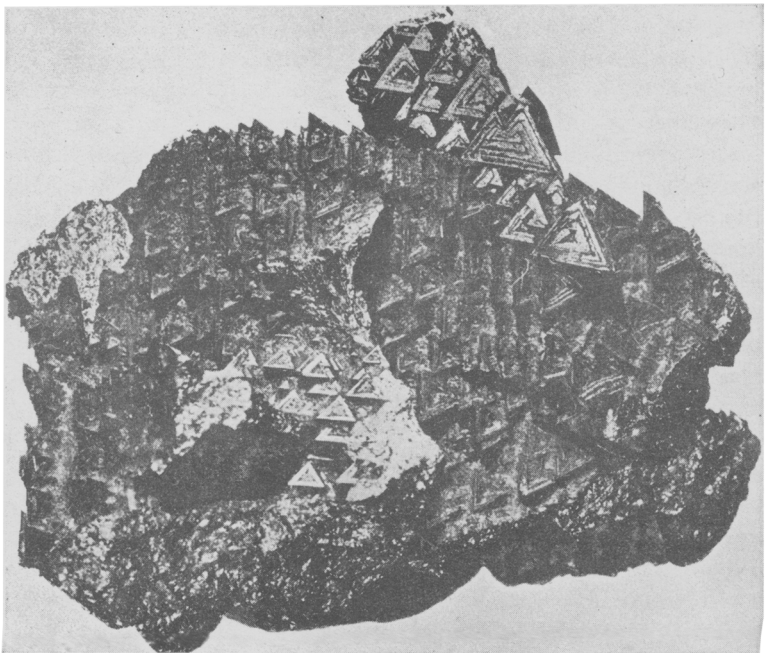

FIG. 1. Parallel grouping of tetrahedral-cubic crystals of iron silicide (FeSi). ×4.

Rutherfordton, where the specimen was found, was the centre of an iron mining district and there were furnaces in the neighbourhood. A fragment of the specimen, acquired by the British Museum from C. U. Shepard in 1860, is strongly magnetic and on the steel-grey fractured surface has quite the appearance of ferrosilicon. This, as well as some other pseudo-meteorites,[3] must then be referred to blast

[1] C. U. Shepard, Examination of a supposed meteoric iron, found near Rutherfordton, North Carolina. Amer. Journ. Sci., 1859, scr. 2, vol. 28, pp. 259–270.

[2] C. F. Rammelsberg, Journ. Prakt. Chem., 1862, vol. 85, p. 88.

[3] L. J. Spencer, Pseudo-meteorites. Nat. Hist. Mag. (British Museum), 1931 vol. 3, pp. 44–56 [Min. Abstr., vol. 5, p. 9].

furnace products. Some of these have been produced accidentally, often in blast furnace 'bears'.[1] They are materials likely to be carried about by persons with magpie propensities, and when lost to be found again in strange situations.

A crystallized 'silico-ferro-manganese' was described in this Magazine[2] in 1903. This is triclinic and has the composition Fe 67·40, Mn 20·10, Si 10·50, C 1·63, P 0·17, S trace. It belongs to the orthorhombic and triclinic series $(Fe,Mn)_3(C,Si)$, which include ferro-manganese and Spiegeleisen. These also have masqueraded as meteorites.

The crystallized furnace products which I described in 1903 were mostly supplied by the late Dr. J. E. Stead. Subsequent to that date he sent, in 1906, a beautifully crystallized specimen of ferro-silicon (FeSi), which may be briefly described in this place. This is tetrahedral-cubic[3] and is identical with the main part of the material found in calcium carbide residues. This specimen (fig. 1; B.M. 1906,394) shows over areas up to $2\frac{1}{2} \times 1\frac{1}{2}$ cm. a strictly parallel grouping of large numbers of sharply developed regular tetrahedra. These measure 1–2 mm. along the edge and show brilliant facets with sunken, step-like surfaces. They build up larger, but distorted and flattened, tetrahedra which are irregularly grouped together. Another more compact specimen (B.M. 1906,395) shows feathery aggregates of minute tetrahedra crystallized on the surface and in a cavity in the mass. This material is steel-grey with bright metallic lustre and strongly magnetic. It is very hard (H. $6\frac{1}{2}$) and brittle, sp. gr. (D^{24}_4) 6·46, and is not attacked by acids. It came from a melt containing 26 % Si.

[1] 'Bears' are masses of metal (sometimes weighing hundreds of tons) found in the foundations of dismantled furnaces, and represent the accumulation of molten metal that has corroded through the furnace lining. These also have often been thought to be 'meteorites'.

[2] L. J. Spencer, Crystalline forms of carbides and silicides of iron and manganese ('ferro-manganese', &c.). Min. Mag., 1903, vol. 13, pp. 296–302.

[3] FeSi was first determined to be tetrahedral-cubic by A. de Schulten, Compt. Rend. Acad. Sci. Paris, 1911, vol. 152, p. 1107, and this has since been confirmed by X-ray examination by G. Phragmén (1923, 1926; M.A. 3–337) and H. Möller (1930; M.A. 4–361, 4–460).