Table 1. Compositions of the Grant, Canyon Diablo and Breece meteorites

Meteorite	Type	wt.% Fe	wt.% Ni	wt.% Co	wt.% P	wt.% S	Reference
Grant	Med. octahedrite	88·63	9·35	0·63	0·57	0·03	HENDERSON (1941)
Canyon Diablo	coarse octahedrite	89·17	7·33	0·51	0·26	0·01	MERRIL (1013)
		—	7·15	0·50	—	—	GOLDBERG et al. (1951)
Breece	Med. octahedrite	89·63	9·17	0·64	0·57	trace	HENDERSON and PERRY (1958)

It has been shown in this laboratory that correct surface preparation is extremely important in obtaining reliable data from the electron probe. Therefore the meteorite specimens and standards were carefully polished down through $\frac{1}{4}\mu$ diamond paste and the usual etching procedure was eliminated. The samples were examined under the microscope and certain areas were picked for analysis. These areas were taken marked by microhardness indentations so that they could be readily identified in the light optics of the electron probe.

C. Determination of chemical compositions

The intensity ratio $I_A/I_A{}^0$, where $I_A{}^0$ is the intensity from the pure element A, is not directly proportional to the composition C_A. The intensity ratio must be corrected for X-ray absorption and X-ray fluorescence because of the other elements present in the specimen. For binary systems a correction curve can be determined by using standard alloys. In some cases, this may not be practical, especially when working with ternary systems. For these situations calculations can be made which correct for X-ray absorption and fluorescence (CASTAING, 1952; CASTAING and DESCAMPS, 1955).

The ratio of measured intensity of radiation from element A in an alloy containing i elements is given by:

$$I_A/I_A{}^0 = \frac{C_A f_A(\chi)}{f_A{}^0(\chi)} \left[1 + \sum_i \frac{I_A{}^i}{I_A} \right]$$

where the fluorescence term must be summed for all elements in the alloy which fluoresce element A. The above terms have their usual meanings as given in the literature (CASTAING, 1960).

The correction curve for Fe–S was calculated and checked by two standard alloys. Fig. 1 shows the correction curves for the ternary Fe–Ni–P. The Fe, Ni and P intensities are measured with the electron microanalyzer and any two intensity ratios are sufficient to determine the composition of a given area. However, the composition was determined by the intersection of the three intensity ratios. A correlation of $\pm\frac{1}{2}$ weight per cent is the accuracy that was obtained.

IV. RESULTS

Electron microanalyses of numerous phosphide and sulfide precipitates were made. Many of the phosphides had so many cracks in them that accurate X-ray intensities could not be measured. Fig. 2 shows the position of an electron probe

trace across a phosphide in the Breece meteorite 100 μ in width. Fig. 3 gives the results of the scans of Co, Fe and Ni across the area. The large fluctuations in intensity within the phases are due to the presence of cracks within the phosphide. The composition of the precipitate as determined from the correction curves are 34·8 wt.% Ni, 49·5 wt.% Fe, 15·6 wt.% P and 0·1 wt.% Co. This gives a molar composition of 29·9 at.% Ni, 44·8 at.% Fe and 25·3 at.% P, which is almost exactly the stoichiometric composition of (Fe–Ni–Co)$_3$P. The swathing kamacite is 20 to 30 μ
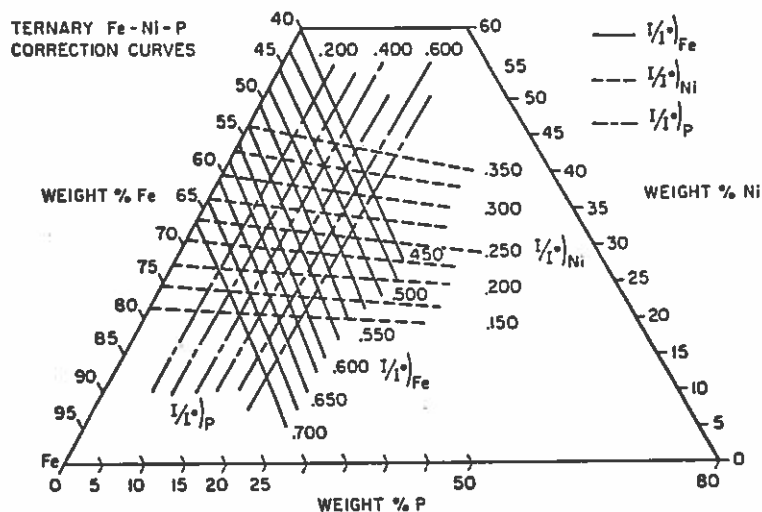

Fig. 1. Ternary Fe–Ni–P correction curves.

in width and shows a depletion of nickel from 7·0 wt.% in matrix kamacite to 6·3 wt.% at the phosphide-kamacite boundary.

A phosphide about 85 μ in width gave scans with large variances in the X-ray intensity due to the presence of cracks. However, a steady intensity was obtained in non-cracked areas and the composition of the phosphide is 36·7 wt.% Ni, 48·0 wt.% Fe, 15·2 wt.% P, and 0·1 wt.% Co. The molar composition is 31·6 at.% Ni, 43·5 at.% Fe, 24·9 at.% P, which is again in good agreement with the composition of (Fe–Ni–Co)$_3$P. The region of swathing kamacite was 30 μ wide and shows a decrease in Ni content fron 7·0 to 6·0 wt.%.

In the Grant meteorite, a large phosphide band was studied (Fig. 4). It is 500 μ wide and has a swathing kamacite border 40 μ in width. The nickel content exhibits a gradient in the border from 6·9 wt.% in the matix kamacite to 6·0 wt.% at the kamacite-phosphide interface. On the basis of the correction curves, the composition of the band is 23·4 wt.% Ni, 61·2 wt.% Fe, 15·3 wt,% P and 0·15 wt.% Co (19·8 at.% Ni, 55·4 at.% Fe, and 24·8 at.% P). The Fe, Ni, Co and P intensities were constant across the phosphide.

Figure 5 shows a large troilite precipitate (160 μ) in the Grant meteorite which was scanned with the electron probe. The troilite was in part surrounded by a phosphide 70 μ wide. The Ni, Fe and S traces taken across this area are shown in
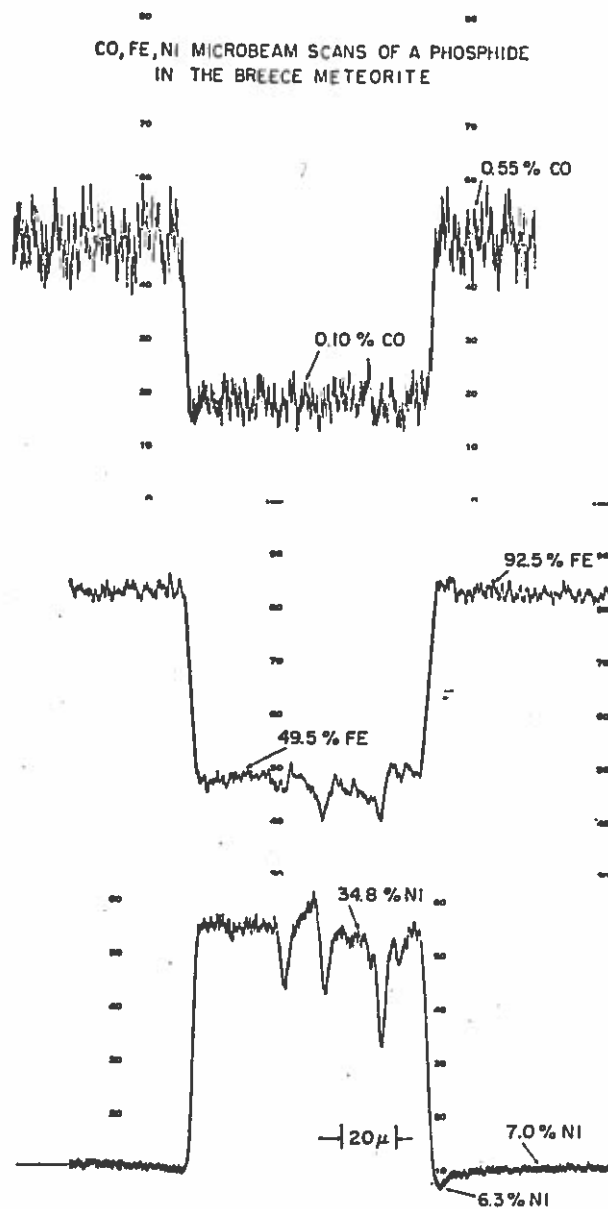
Fig. 3. Co, Fe, Ni microbeam scans of a phosphide in the Breece meteorite.

Fig. 6. There is no sulfur present in the phosphide and the sulfide contains no nickel.

The phosphide has a gradient of Ni and Fe within it. The Ni is highest at the troilite-phosphide interface and lowest at the phosphide-kamacite interface. The Fe gradient is exactly opposite, having the highest amount of Fe at the phosphide-kamacite interface. The phosphorus content is constant across the phosphide and the sulfur and iron content is constant across the sulfide. At the kamacite-phosphide border, the composition of schreibersite is 36·3 wt.% Ni, 48·3 wt.% Fe, and 15·4 wt.% P (31·3 at.% Ni, 43·6 at,% Fe, 25·1 at.% P), and at the phosphide-troilite border the composition is 38·1 wt.% Ni, 46·5 wt.% Fe and 15·4 wt.% P (32·8 at.% Ni, 42·1 at.% Fe, 25·1 at.% P). The precipitate is identified as $(Fe-Ni)_3P$ with variable amounts of Fe and Ni.

Using correction curves for the binary system Fe–S, the Fe and S intensity data give the composition of troilite as stoichiometric FeS. Swathing kamacite is present on both sides of the scan. There is a decrease in the Ni content of 1·4 wt.% in the zone on the phosphide side and 1·9 wt.% on the sulfide side of the scan. These gradients are 20 and 30 microns wide respectively.

Another phosphide in the Grant meteorite shows a gradient of Fe and Ni across its 75 μ width. At the high Ni end the composition is 37·5 wt.% Ni, 47·4 wt.% Fe 15·0 wt.% P (33·0 at.% Ni, 42·0 at.% Fe, 25·0 at.% P). At the low Ni end the composition was found to be 34·3 wt.% Ni, 50·7 wt.% Fe and 15·0 wt.% P (29·0 at.% Ni, 46·0 at.% Fe 25·0 at.% P). The Co content is 0·05 wt.%. The swathing kamacite is 15 μ wide and shows a Ni decrease of 1·2 wt.%.

Several rhabdite particles from the Canyon Diablo meteorite were examined. One precipitate is 15 μ in width (Fig. 7) and has a composition of 43·6 wt.% Ni, 41·2 wt.% Fe and 15·2 wt.% P (37·7 at.% Ni, 37·4 at.% Fe, 24·9 at.% P) corresponding to schreibersite. The swathing kamacite is 18 μ wide and the concentration of Ni decreased from 6·8 to 6·0 wt.% at the interface between kamacite and the phosphide.

Other precipitates which were less than 10 μ wide gave unreliable results. The composition of these phosphides indicated that they were low in phosphorus, for example, one gave 43·9 wt.% Ni, 43·2 wt.% Fe and 12·9 wt.% P. The composition determination may be inaccurate by as much as 5 weight per cent. The swathing kamacite in this case was 10 μ wide and the Ni content decreased by 0·6 wt.% over the zone.

V. Discussion

The phosphides identified in the three meteorites were all of a composition $(Fe-Ni-Co)_3P$ corresponding to that of schreibersite. They contained 15·5 ± 0·5 wt.% phosphorus with variable amounts of iron and nickel. It has been claimed that meteorites contain no more than 0·75 wt.% phosphorus (KRINOV, 1960) and according to the Fe–P phase diagram (HANSON, 1958), phosphorus of this amount is soluble in alpha iron at temperatures below that of the eutectic (1050°C). The influence of Ni should be to lower the solubility of phosphorus. However, phosphorus, in the amount found in iron meteorites, is still soluble in the metallic Fe–Ni below the temperature at which the liquid phase is present (VOGEL, 1958). Therefore, if phosphides formed directly from the melt non-equilibrium solidification must have

NI, FE, S MICROBEAM SCANS OF A SULFIDE SURROUNDED
BY A PHOSPHIDE IN THE GRANT METEORITE

39.1 % NI

36.3 % NI

KAMACITE   SULFIDE   PHOSPHIDE

6.9 % NI

5.0 % NI

55 % NI

92.5 % FE

63.5 % FE

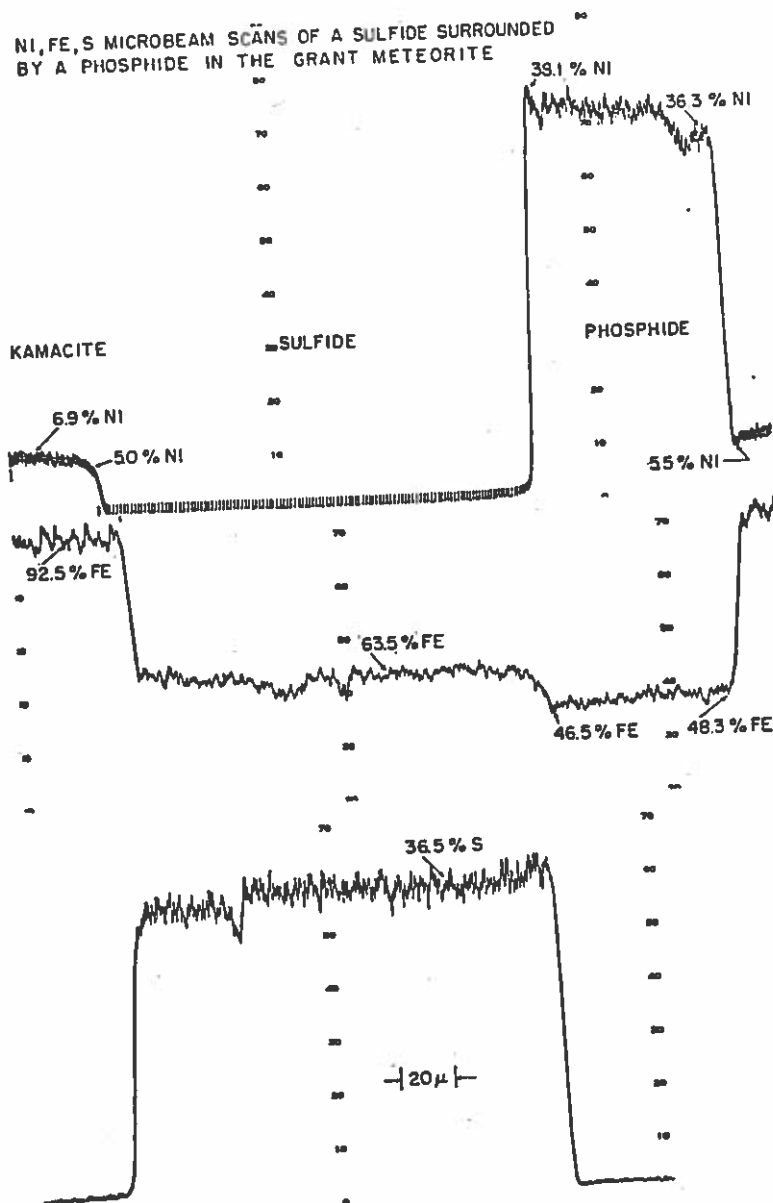46.5 % FE   48.3 % FE

36.5 % S

20μ

Fig. 6. Ni, Fe, S microbeam scans of a sulphide surrounded by a phosphide in the
Grant meteorite.