Cape York: The extraordinary mineralogy of an ordinary iron meteorite and its implication for the genesis of III AB irons

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A study of accessory minerals in the Cape York iron meteorite has been carried out with the electron microprobe. Phases analyzed include chromite, sphalerite, two closely related potassium-bearing sulfides, silica, and native copper. In addition, four phosphate minerals were found: One chemically similar to buchwaldite, but rather rich in iron, one corresponding to terrestrial maricite, and two more, which seem to be new minerals on the basis of microprobe analysis. Evidence from the composition of accessory minerals as well as texture elucidates some details of the fractional crystallization of the group III AB parent melt. A modification of the fractional crystallization model is therefore proposed. We suggest that sulfide nodules have originated as droplets of an immiscible sulfur-rich liquid that continuously segregated from the parent melt during crystallization of the metal. The modified model also explains the Ni/Cr anticorrelation and the high abundance of sulfur in group III AB irons which could not be satisfactorily explained by previous models.

INTRODUCTION

The Cape York iron meteorite is the second largest recovered iron, and the largest meteorite of group III AB. This group, as defined by SCOTT et al. (1973), is the largest chemical group of iron meteorites, comprising 157 members, or 33% of all irons (BUCHWALD, 1975). In the present study interest will be focused on accessory minerals found in samples of the Cape York fragment Agpalilik (C3W/1 through 3), obtained from the Geological Museum, Copenhagen, and jointly examined by the Max-Planck-Institut in Mainz and us (preliminary results: JOCHUM et al., 1975).

ANALYTICAL METHODS

Microprobe analyses were performed with an ARL-SEMQ automated microprobe (15 kV acceleration voltage, 15 nA sample current, except where indicated otherwise in the text). In order to minimize sample decomposition phases rich in volatiles, such as alkali phosphates, were analyzed by scanning (in TV mode) an area previously checked for homogeneity. Automatic procedures that correct on-line for background, dead-time, and drift were used wherever applicable. Matrix effects of oxide minerals were corrected for by applying the method of BENCE and ALBEE (1968), and

the compilation of alpha factors by ALBEE and RAY (1970). For other minerals a correction program by WEINKE et al. (1974) based on standard ZAF-correction procedures was used.

THE CAPE YORK METEORITE

Metallographic descriptions, photomicrographs and -macrographs, and a detailed discussion of the large, oriented sulfide inclusions of the Cape York meteorite have been presented by BUCHWALD (1975: 410-425). The reported shock-induced alterations of the troilite correspond to peak shock pressures of 130 - 800 kbar according to LIPSCHUTZ (1968) and JAIN and LIPSCHUTZ (1969). Apparently, differences in peak shock pressures between different locations in a piece as large as the Cape York (Agpalilik) fragment can be quite large.

The minor element content of the troilite is low. Aside from Fe, S, and about 0.13% Cr all other elements are below 0.02% by weight. A special high-sensitivity microprobe technique was used for the determination of manganese in troilite. Values found range from 180 to 195 ppm, which is in good agreement with the results of JOCHUM et al. (1975).

Accessory phases found to date are listed in Table 1. With the exception of carlsbergite,

Table 1. Accessory minerals in the Cape York (III A) iron meteorite

Name	Formula	Reference (1)	
Phosphates			
Buchwaldite	$NaCaPO_4$	a	table 2
I (2)	$Na_4Ca_3(Fe, Mg)(PO_4)_4$?	x	table 2
II (maricite ?)	$NaFePO_4$	x	table 2
III	$Na_4Mn(PO_4)_2$?	x	table 3
IV	not known	x	table 3
Sulfides			
Daubréelite	$FeCr_2S_4$	b, d (3)	
Chalcopyrrhotite	$(Fe, Cu)S$	b (3)	
Djerfisherite	$K_3(Fe, Ni, Cu)_{13}(S, Cl)_{14 \pm x}$	x	table 4
K-bearing sulfide	$K_3(Fe, Ni, Cu)_{13}S_{14 \pm x}$	x	table 4
Sphalerite	$(Zn, Fe)S$	b, x	table 5
Ferroan-alabandite	$(Mn, Fe)S$	x	see text
Other			
Chromite	$FeCr_2O_4$	(4)	see text
Silica	SiO_2	x	see text
Copper	Cu	b, d, x	see text
Carlsbergite	CrN	c	

(1) x = this work, a = OLSEN et al. (1977), b = RAMDOHR (1973), c = BUCHWALD and SCOTT (1971), d = BUCHWALD (1975), (2) = may be ferroan buchwaldite, (3) = not found in present samples, (4) = abundant.

which occurs exclusively within the metal phase, all others are concentrated either within the troilite nodules or along their rims. Daubreelite is present only in smaller sulfide aggregates.

MINERALOGY OF ACCESSORY PHASES

1) *Chromite*   Clusters of chromite crystals ranging from 0.2 to 2mm in size are frequently observed near one end of troilite nodules, most commonly lined up directly at the rim or parallel to it a few millimeters away. Occasionally similar clusters are also found deep within nodules. Shapes vary from perfectly euhedral to spherical, at the troilite-metal interface sometimes taking the form of mushrooms, the thin "stem" protruding into the metal, and the rounded "head" into the troilite.

Chemically all chromite is almost pure stoichiometric $FeCr_2O_4$, the only detectable minor elements being ZnO (average 0.16 weight %), MnO (0.58%), and V_2O_3 (0.27%).

Essentially the same composition has been found by BUNCH and KEIL (1971) for chromites from the Bagdad (III A) and Putnam County (IV A) iron meteorites. Chromite of this composition seems to be very common in group III AB (our unpublished results).

The asymmetrical distribution of chromite along the long axis of the troilite nodules has been ascribed to the influence of a gravitational field during solidification (BUCHWALD, 1971b). As a consequence of this distribution, certain trace elements have been found by JOCHUM et al. (1975) to be enriched near this end. Taking their mass spectrometric data one can infer a Ga-content of the chromite of about 130ppm, and calculated concentrations of Mn and V are in excellent agreement with our microprobe data. Zn, however, is more enriched than can be explained by the presence of chromite alone.

2) *Phosphates*   As already reported in preliminary form (KRACHER and KURAT, 1975) there are at least four different phosphate phases present, none of which has been observed in other meteorites. They tend to occur along or very close to the troilite-metal boundary of some of the nodules, but opposite to the chromite-rich end. They form aggregates up to 100µm in size, but are intimately intergrown with each other, and the size of individual grains hardly exceeds 20µm. This small grain size has up to now made it impossible to obtain X-ray data.

Phosphate I is similar to buchwaldite, $NaCaPO_4$, (OLSEN et al., 1977) except for appreciable contents of FeO and MnO (see Table 2, first and second columns). Although the former might be just a ferroan variety of the latter, the possibility that they are two different minerals cannot be excluded, owing to the uncertainties concerning synthetic $NaCaPO_4$ (KLEMENT and DIHN, 1938; BREDIG, 1942). MOORE (pers. comm.) has pointed out that Na_4Ca_3

Table 2. Averages of microprobe analyses and cation proportions of chemically well characterized phosphates in the Cape York (III A) iron meteorite (in weight %)

	I	(1)	II
P_2O_5	44.6	44.9	42.3
Cr_2O_3	–	–	0.57
FeO	6.9	–	33.5
MnO	1.76	0.06	7.1
MgO	2.39	–	1.45
CaO	27.1	35.6	0.36
Na_2O	17.9	19.5	15.6
K_2O	0.14		
Total	100.79	100.16	100.88
Ions on the basis of 16 O			
P	3.98	4.00	4.04
Cr	–	–	0.05
Fe	0.61	–	3.16
Mn	0.16	0.01	0.68
Mg	0.38	–	0.24
Ca	3.06	4.01	0.04
Na	3.66	3.98	3.41
K	0.02	–	–
sum M^{2+}	4.21	4.02	4.12
sum M^+	3.68	3.98	3.41

(1) Buchwaldite (OLSEN et al. 1977).

Table 3. Compositional ranges and analyses by (1) of chemically poorly characterized phosphates in the Cape York (III A) iron meteorite (electron microprobe analyses, in weight %)

	III	(1)	IV	(1)
SO_3	2.5 - 3.7	–		
P_2O_5	41.5 - 44.3	41.1	45.3 - 47.8	46.0
Cr_2O_3	0.62 - 1.65	3.2	14.2 - 15.0	16.1
Al_2O_3		0.2		
FeO	1.24 - 4.0	3.0	0.52 - 0.75	
MnO	15.8 - 19.2	20.1	1.20 - 1.85	1.5
ZnO			ca. 0.26	
MgO	0.42 - 1.54	–		
CaO	0.05 - 1.49	–	10.4 - 12.0	11.3
Na_2O	30.9 - 35.8	28.8	15.3 - 19.8	19.3
K_2O	0.11 - 0.20	0.3	6.2 - 6.9	5.3

(1) OLSEN (pers. comm.), analyses of phases intergrown with buchwaldite, of which X-ray patterns could not be obtained.

$(Fe, Mg)(PO_4)_4$ should constitute a stable phase, possibly isostructural with bredigite, $Ca_7Mg(SiO_4)_4$. Our analysis is rather close to this formula, except for a considerable Na deficiency.

Phosphate II (Table 2) is compositionally close to $NaFePO_4$, with some Mn and Mg substituting for Fe. It is believed to be identical to the terrestrial mineral maricite recently described by STURMAN et al. (1977). Maricite and buchwaldite have different structures, and can be expected to display little mutual solubility.

The sodium-rich phosphate III is very difficult to analyze due to rapid decomposition under electron bombardment. The compositional data given in Table 3 would be consistent with the tentative formula $Na_4(Mn, Fe)(PO_4)_2$. In reflected light it is darker than $NaCaPO_4$, less transparent, nearly or completely isotropic and difficult to polish adequately, which has been found to be due to chemical reaction with the polishing lubricant. An unusual feature of this phosphate is the presence of sulfur. The relative positions of the SK_α line were compared in this mineral and in troilite and anhydrite standards. Radiation from the phosphate was found to be closer to anhydrite, suggesting the presence of SO_4^{2-} in the phosphate structure.

Phosphate III adjacent to the silica inclusion described below is transsected by numerous very fine veins of native copper, occasionally replaced by nickel-iron.

Although most analyses are not very satisfactory either because of intergrown foreign minerals or rapid decomposition under the electron beam, a general anticorrelation of Na and Mn has been noticed. Since this is highly implausible to result from solid solution substitution, phosphate III might in fact be an intergrowth of two phases - perhaps $Na_4M(PO_4)_2$/ $NaMPO_4$, where M = Mn, Fe, etc. - although optically and electron optically it appears to be a single phase.

The greenish, highly birefringent, rather transparent phosphate IV poses so much analytical difficulty that no definite formula could be established yet. One atom equivalent each of Ca and Cr is present per three PO_4 units, and Na+K makes up most of the rest, but no further information could be obtained. The Na/K-mole ratio is somewhat variable, but close to about 5, and the presence of a detectable amount of ZnO seems worth mentioning (Table 3). Further elucidation of this rather enigmatic mineral depends on the discovery of larger inclusions. A typical intergrowth of three of these phosphates (I, III, and IV) is shown in Fig. 1.

3) *Djerfisherite and related mineral*   Two very similar potassium-bearing sulfides are present in the nodules, one generally forming small irregularly shaped specks, the other one a continuous rim between phosphate III and
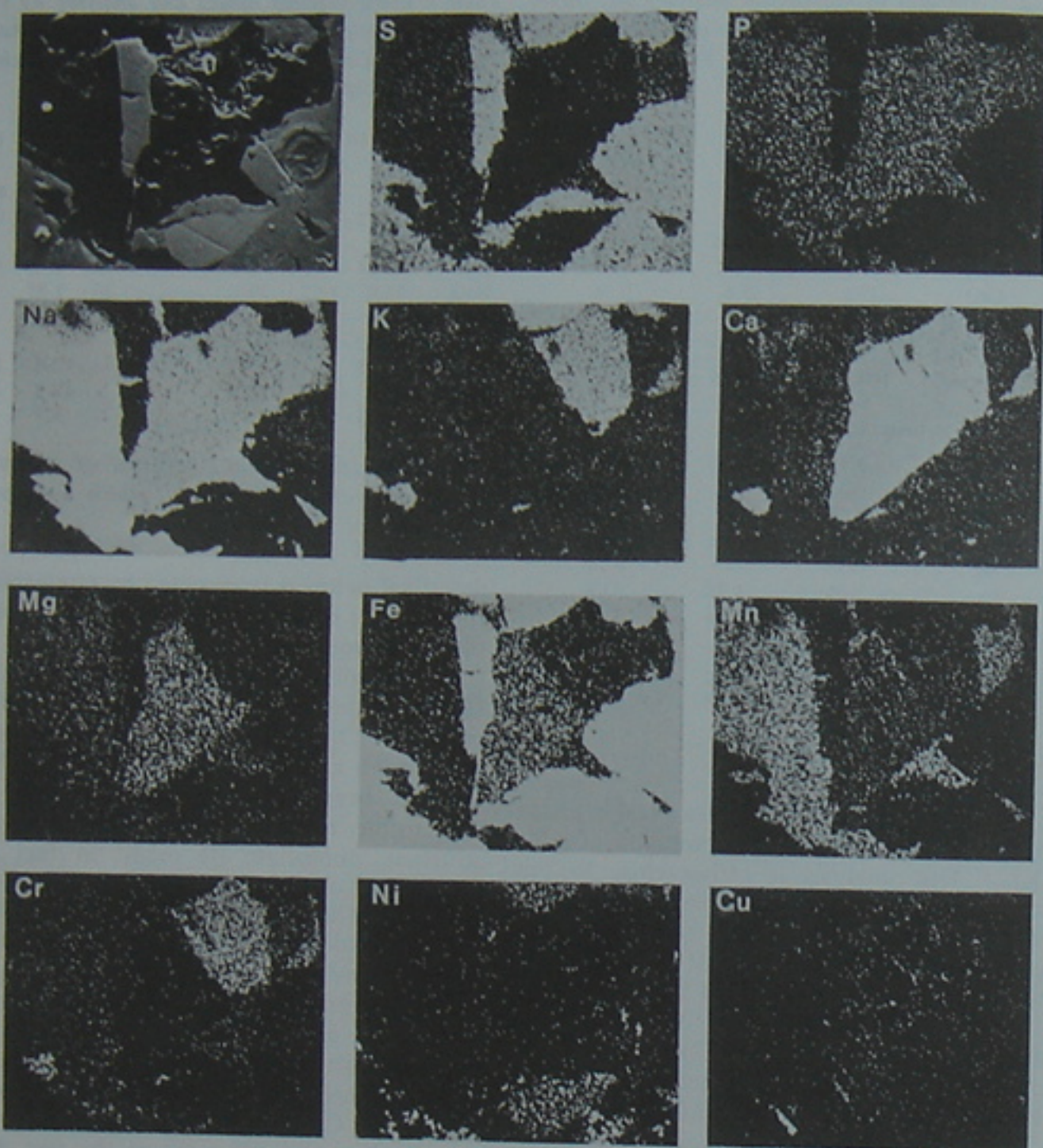
Fig. 1. Secondary electron image and X-ray scans of selected elements of a phosphate intergrowth containing phosphates I (very high Ca), III (Mn) and IV (K and Cr). Note presence of S in phosphate III. At the central top edge scans of K and S indicate the presence of djerfisherite. A small grain of native copper is also present. Width of field (each frame) 150 μm.

troilite. Optically they are nearly indistinguishable, and Table 4 shows that they are very similar chemically as well, the main difference being recognized in the chlorine content. Whereas the variety occurring in specks is with minor differences chemically identical to the mineral djerfisherite found in enstatite meteorites (FUCHS, 1966), and the I A iron Toluca (EL GORESY et al., 1971), the rim mineral occurring along the phosphate interface does not contain appreciable amounts of chlorine.

The latter phase could be identical with the unidentified djerfisherite-like mineral of EL GORESY et al. (1971). The higher sulfur content suggests replacement of $2 Cl \rightleftarrows S$. The formulae in Table 4 have been calculated to give a total of 16 cations in accordance with EL GORESY et al. (1971). Ni concentrations are identical in both phases within sampling error (caused by some grain - to - grain variability of Ni content),

Table 4. Chemical composition of djerfisherite and related mineral in the Cape York (III A) iron meteorite (electron microprobe analyses, in weight %)

	(1)	(2)
Fe	48.9	49.3
Ni	7.0	7.4
Cu	2.5	1.3
K	9.3	9.0
S	32.4	33.5
Cl	1.4	–
Total	101.5	100.5

formulae on the basis of 16 cations:
(1) $K_{2.992}(Fe_{11.014}Ni_{1.500}Cu_{0.495})_{13.008}(S_{12.710}Cl_{0.479})_{13.207}$ (2) $K_{2.924}(Fe_{11.215}Ni_{1.601}Cu_{0.260})_{13.076}S_{13.273}$. (1) = djerfisherite, (2) = unknown Cl-free djerfisherite-like mineral.

Fig. 2. Sphalerite in a troilite nodule, finely intergrown with troilite and nickel-iron. Reflected light, Width of field 120 μm.

but the difference in K-content is marginally significant. Since native copper is often found in the immediate vicinity, the lowest value rather than an average has been adopted for Cu in Table 4. The value given is considered to be an upper limit.

The fact that the two minerals have been found in contact with each other, and the existence of a definite hiatus in the Cl-contents suggest that the two phases encountered are two distinct minerals.

4) *Sphalerite and ferro-alabandite* Occasional sphalerite grains of very characteristic appearance are present within the troilite nodules. They form oval to crescent-shaped inclusions with jagged, irregular rims and are intimately intergrown with other sulfides, suggesting breakdown of a solid-solution (see Fig. 2). Veins of troilite which appear to be exsolved, and tiny aggregates of ferroan alabandite are common. Ferroan alabandite has not been found outside sphalerite grains, and no quantitative analysis was possible due to small grain size. The analysis of sphalerite is given in Table 5.

Table 5. Chemical composition of sphalerite from the Cape York (III A) iron meteorite (electron microprobe analysis).

	Weight %		Mole fractions
Zn	56.9	ZnS	0.820
Fe	8.1	FeS	0.137
Mn	2.5	MnS	0.043
S	32.5		
Total	100.0		

SCHWARCZ et al. (1975) proposed a cosmobarometer based on the iron content of meteoritic sphalerite. The pressure is recorded when the assemblage is cooled below about 350°C, at which temperature diffusion becomes negligible. No troilite can be exsolved or dissolved by sphalerite below that point. Only grains that are in contact with troilite are suitable for barometry. The pressures indicated by our analyses (Table 5) are between 10 and 15 kbar, much higher than the expected lithostatic pressure in an asteroid-sized parent body. As will be discussed below, the high confining pressure may have been the result of the way of solidification rather than lithostatic pressure in the parent body.

5) *Native copper* Native copper is ubiquitous in some troilite nodules where it is concentrated along the rim or near inclusions of other accessory minerals. One copper inclusion near a metal-chromite aggregate in the center of one nodule was sufficiently large to be analyzed for Fe, Ni and Zn. Fe contents were measured at five different acceleration voltages between 8 and 20 kV in order to estimate the contribution of secondary fluorescence of Fe (excited by CuK_α) to the FeK_α counting rate. The Fe contents measured that way were identical within analytical precision (0.75%). An appreciable contribution of FeK_α counts by secondary fluorescence can therefore be excluded. The Ni content averages 1.52%, being slightly higher near the nickel-iron interface than near the chromite interface. Zn was below the detection limit (0.1%). The Fe content is

lower than that obtained by KRACHER *et al.* (1975) for the I A iron Landes, but still too high to satisfy the Fe-Ni-Cu phase diagram. No sulfide resembling chalcopyrrhotite as described by RAMDOHR (1973) has been encountered.

6) Silica A rather large subhedral bleb of a silica polymorph (diameter almost 1mm) has been found attached to phosphates at the rim of a troilite nodule (Fig. 3). Most of the rim to troilite consists of phosphates III with copper veins, and a narrow band of djerfisherite. Schreibersite is attached to the silica inclusion opposite to the phosphate. The thin (1.2mm) specimen slice contains an intergrowth of phosphates on the face opposite to the silica. There is obviously a complicated mineralogical assemblage present.

Aside from the mere fact that silica is present in a III AB iron meteorite, where it has not been found previously (WASSON, 1974; BUCHWALD, 1977), the most surprising feature is its purity: typical results of microprobe analysis are 0.08% FeO, and Na, K, Ca, Mg, Al, Mn, Cr, Ti all below detection limit (about 0.02%).

No attempt has been made yet to separate silica for determination of the particular polymorph because of the danger of losing the adherent phosphate material, which is thought to be more valuable.

Fig. 3. Silica at the troilite (left) - iron (right) interface. Rim towards troilite is phosphate III, which has partly fallen out, and is intergrown with native copper. Arrow points at djerfisherite with a similar Cl-free mineral, which also forms a thin rim between the phosphate and troilite. Heavily fractured grain at lower right of silica is schreibersite. Reflected light. Width of field 2mm.

7) Unidentified phases A grain of nickel-iron near the center of one nodule, associated with chromite, sphalerite, and copper, was found to be partly rimmed by layers of unidentified oxide minerals. Optically the rim is darker than chromite, and element scans show Fe as a dominant element, with some Ca, and local enrichments of Cu, Ni, K, and Cl but little S. The whole assemblage would be suggestive of weathering, were it not for its location in the middle of a specimen that shows little other signs of weathering and that, according to the dissection map, has been cut from deep inside the 1.20 × 1.80m object. It is, however, possible that phases similar to weathering products could result from prolonged exposure of a mineral readily decomposed under these conditions to aqueous abrasive slurry during cutting. Dissecting of the Agpalilik iron took 180 hours net cutting time for each 1.4m² section (BUCHWALD, 1971a).

DISCUSSION

1) Fractional crystallization model It is now almost generally accepted that group III AB iron meteorites originated by fractional crystallization of a parent melt (WASSON, 1972; SCOTT, 1972; KELLY and LARIMER, 1975), commonly described as a "core". Other possibilities for producing such a nickel-iron melt should be considered, however, and we would prefer calling it a "pool" whether or not it was originally located in the center of the parent body. Most properties of group III AB iron meteorites can be understood by assuming slow crystallization of this parent melt. An idealized model assuming a completely homogeneous liquid in equilibrium with a solid phase in which diffusion is negligible leads to predictions that are in good agreement with observations (SCOTT, 1972).

2) Modification of the model In trying to explain our observations two additional assumptions had to be made for the following discussion, the feasibility of which will be discussed in turn below:
a) Crystallization proceeded "from top to bottom" i.e. from the outer boundary of the parent melt closest to the surface of the parent body towards the center.
b) The amounts of minor elements present in the system are sufficient to cause liquid immiscibility.
Given a chemically homogeneous melt, crys-

tallization must start where the heat of crystallization can dissipate into cooler surroundings. Therefore, metal will nucleate on the wall silicates rather than within the melt, where nucleation would require substantial supercooling. The metal-silicate interface closest to the surface of the parent body will always be the preferred site of crystallization, since it provides the most efficient heat sink, and metal will continue to crystallize there. This metal may be prevented from sinking towards the center by a number of effects, such as adhesion to the mantle material, surface tension, trapping of phases lighter than the melt, etc. Once a continuous solid layer has formed, its cohesion would in itself be sufficient to prevent crystallizing metal from sinking to the bottom. Also, the gravitational field is likely to have been quite weak, in spite of the pronounced effect it had on the shape of the troilite nodules. Thus, assumption (a) does not seem entirely unreasonable.

The possibility that liquid immiscibility influenced the formation of melts in iron meteorite parent bodies was amply discussed by VOGEL (1961). Although liquid Fe and FeS are miscible in all proportions at high temperatures (> 980°C) in the absence of impurities, he assumed that the bulk composition of the real multi-component system present in a meteorite parent body was close to, or even within a two-liquid-stability-field. Trace elements most likely to be responsible for the liquid immiscibility are P, Cr, and Mn. Even if these elements were not present in sufficient amounts at the onset of solidification, fractional crystallization would lead to their enrichment in the remaining liquid, and the border of the two-liquid field would eventually be reached.

Whether or not VOGEL's (1961) assumption is correct can only be established by experiment. In the absence of experimental data we take our observations as an indication that assumption (b) is also valid.

3) Nodule formation From the preceding assumptions the following mechanism can be derived, on the same assumptions of negligible diffusion in the solid and complete mixing in the liquid as SCOTT (1972): Consider crystallization of a small amount of practically sulfur-free nickel-iron from a homogeneous melt. If no trace elements besides sulfur were present, this would simply increase the bulk sulfur content of the remaining liquid. If this liquid was saturated with sulfur, however, when crystalliza-

tion began, then this increase in sulfur content will shift the composition of the liquid into the 2-phase field. Therefore, the formation of solid will be accompanied by the formation of a second, sulfur-rich liquid phase, while the bulk sulfur content of the original, metal-rich liquid will remain virtually constant. Designating the fraction of parent liquid to be converted to solid as α, the mass balance for a small increment of crystallization is given by

$$\Delta M_{L1} + \alpha.\Delta M_S + (1 - \alpha).\Delta M_{L2} = 0 \qquad (1)$$

where the subscripts refer to metal-rich melt (L1), solid (S), and sulfur-rich liquid (L2).

Of the total surface area A of the metal-rich parent melt, a fraction α.A will be in contact with solid, and (1 − α).A in contact with sulfur-rich liquid. As both phases grow simultaneously from the parent melt, the solid will tend to grow around the drops of sulfur-rich liquid, incorporating and finally shielding them from further contact with the parent melt (Fig. 4). Formally, such a process is identical with the simultaneous growth of two different mineral species from a melt, one of which happens to be a liquid in our case, and the appropriate treatment for element fractionation (e.g. GREENLAND, 1970) can be applied accordingly.

As has been explicitly stated by SCOTT *et al.* (1973), fractional crystallization without any specific mechanism for sulfur enrichment in the solid is incompatible with the abundance of large sulfide nodules in group IIIAB. For this reason, BUCHWALD (1975) proposed that some
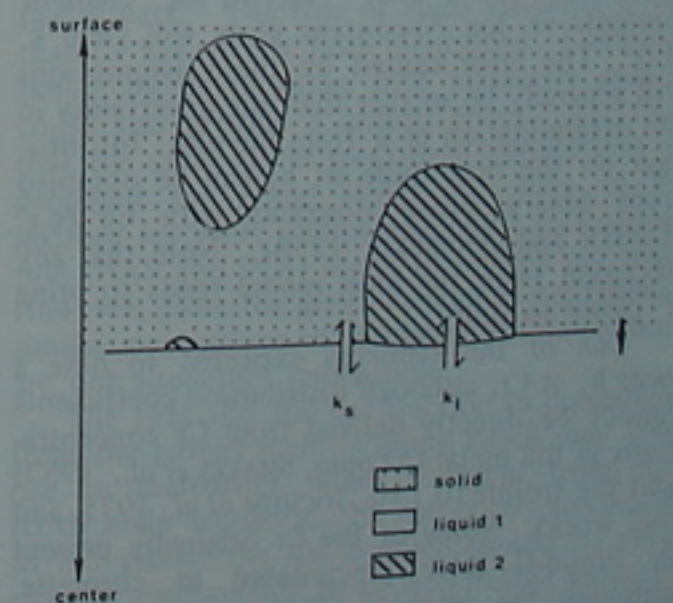

Fig. 4. Formation and trapping of sulfur-rich liquid during fractional crystallization of metal (schematic).

parent melt was trapped between growing metal dendrites. The efficiency of such a process is limited to below 10% trapping as judged from the Ni/P correlation through group IIIAB (SCOTT, 1972) and the Fe-Ni-P phase diagram (DOAN and GOLDSTEIN, 1970). Consequently, BUCHWALD'S (1975) model requires a very high sulfur concentration in the parent melt. In the course of fractional crystallization, the melt would reach the eutectic point long before the observed spread in Ni values is attained. Thus, the models of SCOTT (1972) and BUCHWALD (1975) are mutually exclusive.

4) *Partitioning of trace elements*   Partitioning of trace elements in the system can be described by two coefficients, k_s and k_1, for solid/liquid-I and liquid-II/liquid-I distributions, respectively. On the (admittedly overly simplistic) assumption that liquid-II is quantitatively trapped by the solid, and no trapping of liquid-I occurs, the apparent distribution coefficient k' will be:

$$k' = \alpha . k_s + (1 - \alpha) k_1$$

If α does not vary greatly with the fraction already solidified, k' will remain reasonably constant during crystallization. This seems to be a reasonable approximation, as studies of large sections reveal practically no systematic variation of S with Ni (BUCHWALD, 1975 : 83). Since α is assumed to be close to unity, the only elements for whick k' will significantly differ from k_s are the strongly chalcophilic ones, for which k_1 is very large. Assuming constant α and k' (Ni) = k_s(Ni), log *element contents vs.* log *Ni-content* plots will yield k' (El). The error caused by these assumptions will generally be smaller than the uncertainty in the determination of k' from the plot. Information on the magnitude of k_s can be obtained from binary phase diagrams with Fe (e.g. HANSEN and ANDERKO, 1958). Note that any deviation from the ideal model tends to bring k' closer to unity.

One of the elements expected to have a large k_1 is Cr, although distribution coefficients cannot be directly derived from Cr concentrations in the metal (51ppm, SMALES *et al.*, 1967) and the troilite (0.13%, JOCHUM *et al.*, 1975, and this work). Some of the Cr originally present in liquid-II later precipitated as chromite, although the estimate (JOCHUM *et al.*, 1975) that 85% of the chromium present in the non-

metallic inclusions is located in the chromite, seems to be too high, and abundant carlsbergite inclusions (BUCHWALD and SCOTT, 1971) make the Cr determination in the metal difficult.

The numerical value of α can be estimated from the total sulfur content of Cape York (1.3%, BUCHWALD, 1975) and by assuming a composition of liquid-II close to a Fe-FeS eutectic to be about 0.96. Taking k' to be 2.1 (SCOTT, 1972) and k_s between 0.6 and 0.9, the value of k_1 must be between 30 and 40, and the original concentration of Cr in liquid-II prior to precipitation of chromite a few tenths of a percent.

If data were available on other elements that can be expected to have a large k_1, e.g. Mn and Zn, their correlation with Ni could provide a check of the model.

5) *Formation of chromite and phosphates* There is a temperature interval of about 500° between the solidification of metal and troilite. In this range chromite and phosphates formed. An oxygen fugacity, fO_2, leading to equilibrium between phosphates and P dissolved in metal (OLSEN and FUCHS, 1967) must have prevailed at that time. The phosphates scavenged the system for lithophile trace elements in a similar way as they do in terrestrial pegmatites (cf. MOORE, 1973). If the process takes place in a gravitational field (BUCHWALD, 1971b), phosphates will float on the sulfide, whereas, according to experimental results of EWERS *et al.* (1976), chromite will sink to the bottom of the sulfide liquid. This behaviour is also expected from the fact that pure $FeCr_2O_4$ has a higher density at room temperature than troilite, and a lower thermal expansion coefficient. These relations are not expected to change significantly within the pressure range indicated by the sphalerite barometer. The textural evidence suggests that the phosphates formed within the still molten sulfide nodules as an immiscible liquid layer resembling the formation of phosphate slags in steelmaking.

According to the stoichiometric proportions of elements present, an assemblage of Na, Ca, Fe, Mn-phospahtes would be formed. This "dephosphorization of iron" with Na_2O was studied by OELSEN and WIEMER (1942), and with CaO most recently by TRÖMEL *et al.* (1969), who found in both cases enrichment of manganese in the phosphate which increases as the ratio A_2O/P_2O_5 (A = Na or ½Ca) is changed from 1 to 2. If a mixed phosphate of inter-

mediate A_2O/P_2O_5-ratio is cooled, one can expect a breakdown to a mixture of $NaMPO_4$ and $Na_4M(PO_4)_2$, with M predominantly being Fe in the former, and Mn in the latter. This is in very good agreement with our observations, although the partition coefficient defined as

$$k_D = \frac{(Mn/Fe)III}{(Mn/Fe)II}$$ (where subscripts refer to the observed phosphate phases as numbered in the text) of about 60 is surprisingly high. Apparently the numeric value of k_D is a very sensitive function of equilibration temperature. Since the solubility of Ca in $NaFePO_4$ seems to be very low, an additional Ca-bearing phosphate has to be formed. Fluctuations in bulk composition and/or differences in nucleation temperature may account for the differences in composition between buchwaldite as observed by OLSEN *et al.* (1977) and our phosphate I.

The presence of Cr in the phosphate layer, however, is somewhat surprising, since it does not normally occur in terrestrial phosphates (MOORE, 1973). Although the green colour of phosphate (IV) seems to indicate that at least part of the chromium is trivalent, the possibility that most of it is present in the divalent state has to be considered. OELSEN and WIEMER (1942) found that under their experimental conditions chromium was never present to an appreciable extent in the slags, and speculated that neither Cr (II) nor Cr (III) had a tendency to enter the phosphate layer. However, since they worked under air ($pO_2 = 0.21$ atm), the concentration of Cr (II) in their experiments was probably negligible, and Cr (III) was removed as solid $FeCr_2O_4$ before the liquids could equilibrate, so that their results are not strictly applicable to the conditions under which the meteoritic phosphate mineral formed.

It is not yet clear at which point in this sequence silica nucleated. Its high purity seems to point at low temperature equilibration, but since physico-chemical conditions during formation are not known, low activity of potential contaminants is a possible alternative explanation.

6) *Sphalerite equilibration*   Another surprising result of our analyses is the low iron content of sphalerite, which indicates high pressure prevailing during equilibration with troilite (SCHWARCZ *et al.* 1975). This, however, can also be explained by the model proposed here. Within large homogeneous single crystals of nickel-iron, which made up the Cape York

parent body, inclusions may have been subjected to high confining pressures by differences in thermal expansion coefficients and/or volume changes associated with phase transformations.

The situation is different, however, for group IA meteorites with nickel-iron single crystals of only a few tens of centimeters in size, and ubiquitous large non-metallic veins. It is understandable that in the parent body of group IAB, which may never have been molten (WASSON, 1972; SCOTT, 1972), a high confining pressure of the kind proposed above could not build up, but would be dissipated by gliding along grain boundaries and veins.

These differences in the mechanical way of crystallization are believed to cause the large difference in pressure recorded by sphalerite compositions in IA meteorites (0 - 3kbar, SCHWARCZ *et al.* 1975) and Cape York (12 - 15kbar, this work).

Ascribing the low iron content of sphalerite to lithostatic pressure would lead to an unreasonable estimate for the size of the Cape York parent body (over a thousand km in diameter), in contradiction to chemical and mineralogical features (ANDERS, 1964) as well as astronomical data (CHAPMAN and DAVIS, 1975). Alternatively, there might be some as yet unexplained reason rendering the sphalerite barometer inapplicable to the present system.

EPILOGUE

The validity of the proposed model of liquid segregation during crystallization will have to be verified by comparison with additional observational data. The role of trace elements other than Cr has already been mentioned. Compositional trends in other iron meteorite groups could also provide a critical check. The fact that the same rather specialized assumptions as proposed for group IIIAB also have to be invoked for other groups with Ni/Cr anticorrelation (IIAB and IVA) seems to weaken our case. However, given the general chemical similarities, similar mechanisms of fractional crystallization are not altogether implausible.

The first and the last fraction to crystallize from the parent melt of group IIIAB may give rise to meteorites rather different from the IIIAB main sequence. In particular, according to our model the last fraction should be very close in composition to an iron-troilite eutectic close in composition to siderophiles. Of all troilite-strongly depleted in siderophiles. Of all troilite-rich meteorites known so far, none is close

enough in composition to group IIIAB to meet this requirement. One meteorite, Soroti (WASSON and SCHAUDY, 1971), may have been produced by a similar process, although its composition precludes a close relationship to group IIIAB.

It is to be hoped that further work will bear out the validity of this model, and explain some of the more enigmatic aspects of the mineralogy of IIIAB irons, which has previously been thought to be uninterestingly simple.

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