

## CONDENSATION AND THE COMPOSITION OF IRON METEORITES

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The pressure-temperature conditions in the primordial nebula which could produce the observed Ni, Ga and Ge abundances in the major iron meteorite groups have been calculated assuming equilibrium condensation. Included in these calculations are the effect on the metal composition of Fe oxidation and sulphide formation during accretion, GeS and GaCl in the nebula gases and pressure variations in the nebula. It was found that the IIAB irons had their abundances of these elements fixed at the low-pressure extreme of the range which gives the IAB irons, but at  $50 \pm 10$  K higher temperatures. IIIAB and IVA formed over the same temperature range as IAB ( $600\text{--}670\text{--}660$  K) in regions where the pressure was lower by a factor of 20 and  $10^4$  respectively. Group IVB accreted soon after condensation of the metal and at pressures of less than  $10^{-3}$  atmosphere. The distribution of sulphur and carbon are consistent with this. The abundance of carbon in group IAB suggests that this and group IIAB accreted at about  $10^{-4}$  atmosphere, so that IIIAB and IVA accreted where the pressure was  $5 \times 10^{-6}$  and  $10^{-8}$  atmosphere, respectively.

### 1. Introduction

Goldberg et al. [1] first observed that the abundance of Ga in iron meteorites did not vary randomly over all samples examined, but tended to take “preferred values”. Lovering et al. [2] found that Ge did likewise, and Scott [3,4] has observed that to some extent most of the relatively volatile elements (e.g. Sb, Zn, Cu and Au) were similar in this respect. Over the iron meteorites as a whole, the abundance of Ga and Ge varies over four and five orders of magnitude respectively, but within the groups shows less than a factor of two variation. This is in sharp contrast to many other trace elements, particularly the refractory ones, which show no tendency to take preferred values and within the Ga-Ge groups usually show many orders of magnitude variation. Nickel, Pd and Co show intermediate behaviour between that of Ga and Ge, and of Ir. A detailed classification scheme

for iron meteorites has now been developed based essentially on Ga, Ge and Ni content [5]. The four major groups are IAB, IIAB, IIIAB and IVA, which, together with the small but important group IVB, contain some 70% of all iron meteorites. An additional 15% are contained in seven minor groups and the remainder appear anomalous. It is generally believed that each group formed in a discrete region of the nebula, presumably in a discrete parent body. Members of groups IIIAB and IVA cluster in exposure age at about 650 and 400 m.y., respectively. This is taken as evidence that prior to exposure they were part of the same parent body so that a single event could release them all.

The two types of element abundance trend observed in iron meteorites are generally interpreted as evidence for two processes. The one which most affected refractory elements, and which operated within the groups, is generally thought to be a melting process – refractory elements have very large liquid-solid partition coefficients – such as fractional crystallisation [3] or some variant of partial melting

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[6]. The process which affected mainly the more volatile elements, and which gave rise to the groups, is generally assumed to be condensation and accretion in the primordial solar nebula. It is these processes which we will be concerned with here.

The combination of low volatile element abundance and high Ni abundance has led Scott [3] and Kelly and Larimer [6] to suggest that group IVB is an early, high-temperature condensate; Grossman [7] showed that the first-formed metal was nickel-rich. Even so, in Wasson and Wai's [8] calculations the low Ga and Ge abundances in IVB, and IVA, could only be achieved with mechanical help, for example by assuming that an aerosol rich in these elements was blown away from the accreting parent body by the solar wind. This conclusion was based on an assumption – that Ga and Ge form ideal solutions with Fe – which I will not need to make. Detailed calculations concerning the formation conditions of the other groups have never been presented, although Kelly and Larimer's results show that most groups could have formed by a condensation process. These authors preferred a value of  $10^{-5}$  atmosphere for the nebular pressure. Larimer and Anders [40] have proposed that Ga and Ge vary in abundance in chondritic meteorites because they are depleted in chondrules but not in matrix. Their abundance in a body may therefore be due to a combination of volatility and chondrule/matrix ratio in the body. The variations shown by Ga and Ge in iron meteorites are over several orders of magnitude, rather than a factor of two or so observed in chondrites, and it seems the situation is quite different. In fact the model proposed here is essentially that advocated by Larimer and Anders for Pb, Bi and Tl in chondrites, in which variations over several orders of magnitude are achieved by assuming accretion occurred during condensation.

Here I am concerned with the condensation and accretion conditions of the four major iron meteorite groups and group IVB, or, more precisely, their parent bodies. I have included a quantitative treatment of sulphide formation and oxidation as part of the condensation process – just as it appears to have been for chondrites – and I have allowed for the possibility that the meteorite parent bodies formed in different regions of the primordial nebula. I have also included a consideration of the minor elements, C, P and S, because they too show abundance variations between the groups.

## 2. Methods

The methods by which calculations applicable to condensation in the primordial nebula may be performed were originally described by Urey [9,10]. More recently they have been refined and utilised by Lord [11], Larimer [12] and Grossman [7]. The methods are therefore well documented and only a brief outline is necessary here. Equilibrium condensation processes are assumed. The composition of the gas phase was calculated by a series of mass-balance equations which set the abundance of the 15 most common elements equal to the sum of their abundance in every species they occur, gaseous and condensed. Most of the species Grossman [7] listed in his table 1 were included and a number were added which became important at low temperatures, notably several hydrogen compounds. Standard computer programs were used to solve these equations iteratively. After each condensed species appeared, that is when its partial pressure exceeded its vapour pressure, an equation was added which kept the condensed phase at equilibrium with the gas. This step was introduced by Grossman and can be very important. Generally, the condensation of a species may be delayed  $30\text{--}50^\circ$  if an element it should contain has previously condensed in another phase, and in certain cases the condensation may be prevented altogether [42]. Calculations were performed at  $25^\circ$  or  $100^\circ$  intervals depending on the temperature region in question. The equilibrium constant–temperature relationships were determined by fitting linear equations to the published data over the temperature range concerned, using the method of least squares, or they were calculated from the enthalpies and entropies of reaction where tabulations of equilibrium constants were not available. The calculations were performed at  $10^{-3}$  atmosphere nebula pressure over the temperature range  $300\text{--}2000$  K and  $1$  and  $10^{-6}$  atmosphere over certain temperature ranges. Condensation equations of the kind described by Urey [9,10] and Larimer [13] allowed an infinite degree of interpolation to intermediate pressures and temperatures. The sources of thermodynamic data of relevance here are given in Table 1. The abundance tables were those of Cameron [14]. It should be noted that, although equilibrium models remain most popular, the concept of equilibrium has been challenged by a number of authors [15–17,8]. Serious objections have been

TABLE 1

Sources of thermodynamic data

System	Source
Fe, Ni, Co, Ga, Ge	Hultgren et al. [21]
C, P, S	Stull and Prophet [30]; Chase et al. [31]
GaO(g), GaCl(g), GaBr(g), GaH(g), GeS(g), GeO(g), GeCl <sub>4</sub> (g), GeBr <sub>2</sub> (g), GeBr <sub>4</sub> (g), GeI <sub>2</sub> (g), GeI <sub>4</sub> (g)	Wagman et al. [32]
GaOH(g)	Battat et al. [39]
MgGeO <sub>3</sub> (s), Mg <sub>2</sub> GeO <sub>4</sub> (s) *	Navrotsky [33]; Stull and Prophet [30]; Wagman et al. [32]
Ca <sub>2</sub> (PO <sub>4</sub> ) <sub>2</sub> (s)	Robie and Waldbaum [34]
Fe <sub>3</sub> P(s), Ni <sub>3</sub> P(s) **	Kubachewski and Evans [35]; Komarek [36]
P (ideal solution assumed)	see text
C activity coefficients	Natesan and Kassner [28]
S (ideal solution assumed)	Turkdogan et al. [37]

\* Entropies calculated by summation of oxides [35].

\*\* Entropy of Ni<sub>3</sub>P taken to be equal to that of Fe<sub>3</sub>P.

raised to a number of these [18] but, in any event, equilibrium models seem to represent a good starting point.

### 3. Results and discussion

I will consider the results in four sections which deal in turn with the Ni content of the metal, the Ga and Ge content of the metal, the pressures and temperatures which give the observed Ni, Ga and Ge contents of the metal, and finally the predicted behaviour of the minor elements.

#### 3.1. Nickel

The Ni content of the metal as a function of temperature is shown in Fig. 1. The high-temperature region of the curve is pressure dependent and the results are shown for three nebula pressures. The effect of errors in the thermodynamic data are indicated by dotted lines. Below about 700 K these effectively move the curve on the temperature axis and

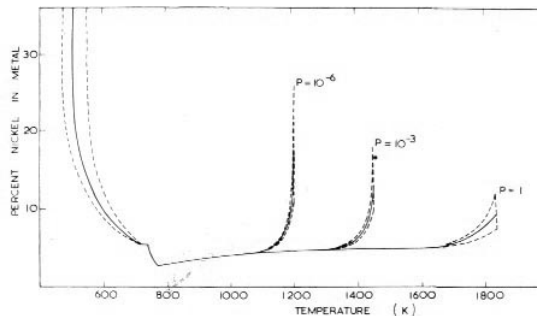


Fig. 1. Variation in the Ni content of the metal during condensation in the solar nebula. The  $P$  values refer to nebula pressures in atmospheres. The pressure-dependent condensation branch (right) reflects the fact that Ni is more refractory than Fe. The pressure-independent low-temperature branch (left) is caused by preferential removal of Fe by oxidation and FeS formation. The broken lines represent uncertainty due to errors in the thermodynamic data.

change its shape very little. Consequently the absolute error in the temperature equivalent to any two Ni contents, is much greater than the error in the difference between their values ( $\pm 60$  K compared with less than  $\pm 10$  K).

The curve is characterised by two temperature regions in which the Ni content of the metal is high. At high temperatures the high Ni is the result of Ni being less volatile than Fe and the enrichment is less at higher pressures. At low temperatures the high Ni is primarily the result of reactions with the gases which remove Fe faster than Ni (to give FeS and Fe silicates). The curve differs slightly from previous

TABLE 2

Condensation temperatures of phosphide [(Fe, Ni)<sub>3</sub>P] and metal \*

Nebula pressure (atm)	Phosphide		Metal	
	start of condensation	50% condensation	start of condensation	50% condensation
10 <sup>-8</sup>	1125	1122	1077	1061
10 <sup>-6</sup>	1241	1238	1201	1181
10 <sup>-4</sup>	1392	1385	1358	1332
10 <sup>-2</sup>	1579	1570	1561	1526

\* Uncertainty varies from  $\pm 10$  K at 10<sup>-8</sup> atmosphere to  $\pm 15$  K at 10<sup>-2</sup> atmosphere.

TABLE 3

Accretion temperatures (K) based on Ni content and Fig. 1 \*

	Low temperature **	High temperature ***			
		$P = 10^{-2}$	$10^{-4}$	$10^{-6}$	$10^{-8}$
IAB	600–670	–	–	–	–
IIAB	665–740	–	–	–	–
IIIAB	595–650	–	–	–	–
IVA	595–650	1460–1480	1280–1295	1140–1155	1030–1040
IVB	–	–	1334–1350	1190–1205	1070–1080

\* The range given includes error in the thermodynamic data and one standard deviation on the mean Ni content of each group.

\*\* Relative error  $\pm 10$ , absolute error  $\pm 60$ . Pressure independent.\*\*\* Range includes absolute error.  $P$  is the nebula pressure in atmospheres.

calculations [6] because I have allowed for the formation of  $(\text{Fe,Ni})_3\text{P}$  which condenses ahead of the metal (Table 2). This lowers the Ni content of the high-temperature branch by about 20% below the value it would have if  $(\text{Fe,Ni})_3\text{P}$  were ignored and causes the Ni content of the metal between the branches to drop below the cosmic Fe/Ni value it would otherwise have, corresponding to 5.5% Ni. Ideal solution between  $\text{Fe}_3\text{P}$  and  $\text{Ni}_3\text{P}$  has been assumed. This produces  $(\text{Fe,Ni})_3\text{P}$  with similar Ni contents to the meteorite phosphides. There is, however, no implication that the  $(\text{Fe,Ni})_3\text{P}$  which condensed in the nebula is that currently observed in the meteorites. The phosphides observed are almost certainly the result of the secondary igneous processes [19,20]. The step at 770 K in Fig. 1 is caused by the oxidation of phosphide to phosphate  $[\text{Ca}_3(\text{PO}_4)_2]$ . I will defer further discussion of P, in particular the reason for the differences between my results and those of Wai and Wasson [23], until later.

There appear to be two opportunities for obtaining the observed Ni contents in each group by condensation and accretion. If accretion occurred on the low-temperature branch of the Ni curve the accretion temperatures obtained are pressure independent and are given in Table 3. High accretion temperatures are pressure dependent and are also given.

### 3.2. Gallium and germanium

Data could be found for the gaseous oxide, sulphide, halides and hydrides of Ge and the gaseous

oxide, halides, hydrides and hydroxide of Ga. By way of illustration the results of calculations at  $10^{-6}$  and  $10^{-4}$  atmosphere nebula pressure are shown in Fig. 2 and their distribution over a number of gas phases is given in Table 4. At all the pressures and temperatures considered Ge is present in the gas phase primarily as  $\text{GeS}(\text{g})$  – even after the formation of  $\text{FeS}$  – which makes it more volatile than previously assumed. It is even possible that, at temperatures below those of interest here, the even more volatile  $\text{GeBr}_2(\text{g})$  may become important. Kelly and Larimer [6] and Wasson and Wai [8] assumed Ge was present in the gas as the less volatile  $\text{GeO}$ . Ga is primarily present as the monatomic gaseous element until just

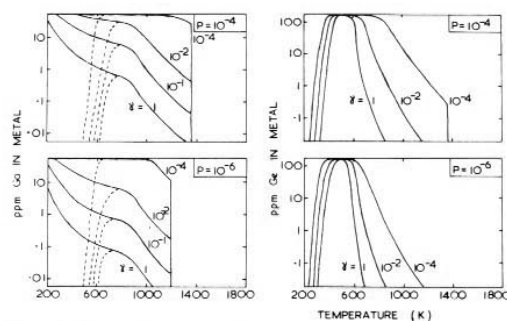


Fig. 2. Curves showing the fraction of Ga and Ge in the metal for nebula pressures of  $10^{-6}$  and  $10^{-4}$  atmosphere, and a variety of activity coefficients. Both elements are siderophile during condensation but become lithophile and transfer to the silicates at lower temperatures. The dotted portion of the Ga curves result if the thermodynamic data for  $\text{Ga}_2\text{O}_3$  is assumed to equal that of Ga-feldspar and assuming ideal solution in feldspar.

TABLE 4

Distribution of Ga and Ge over the gaseous phases at  $10^{-6}$  atmosphere nebula pressure

Germanium		Gallium		
species	$T = 650$ K fraction	species	$T = 650$ K fraction	$T = 1000$ K fraction
Ge	$0.14 \times 10^{-1.5}$	Ga	$0.66 \times 10^{-8}$	$0.16 \times 10^{-1}$
GeO	$0.37 \times 10^{-4}$	GaO	$0.29 \times 10^{-3.0}$	$0.95 \times 10^{-1.7}$
GeS	0.98	GaH	$0.11 \times 10^{-8}$	$0.96 \times 10^{-4}$
GeH <sub>4</sub>	$0.14 \times 10^{-1.5}$	GaCl	0.99	0.16
GeCl	$0.35 \times 10^{-1.7}$	GaOH	$0.14 \times 10^{-1}$	0.82
GeCl <sub>4</sub>	$0.19 \times 10^{-2.9}$			
GeBr <sub>2</sub>	$0.21 \times 10^{-1}$			
GeBr <sub>4</sub>	$0.92 \times 10^{-3.5}$			
GeI <sub>2</sub>	$0.21 \times 10^{-1.5}$			
GeI <sub>4</sub>	$0.11 \times 10^{-5.9}$			

before Fe, Ni alloy condenses, when GaOH(g) takes over as the most stable species [41]. However, its dominance is short-lived and below 870 K, independent of pressure, GaCl(g) becomes the most stable gas phase. This again makes it more volatile than previously supposed, because previous authors had assumed that Ga was present in the gas as the monatomic element at all temperatures.

It is known that Ga does not form ideal solutions with Fe [21] and it is almost certain that Ge is similar in this respect [6]. The extent of departure from ideality is expressed by the activity coefficient,  $\gamma$ , where  $a = \gamma N$ ,  $a$  being the activity of the element in solid solution, equal to its partial pressure in the nebula divided by the vapour pressure of its solid, and  $N$  the mole fraction in the solid solution.  $\gamma$  is primarily a function of temperature and secondly of composition, and to a good approximation there is usually a relationship such as:

$$\log \gamma = (A/T) + B \quad (1)$$

where  $A$  and  $B$  are constants and  $T$  is temperature. For substances such as Ge and Ga which go into solid solution more readily than ideality would predict,  $\gamma$  is less than unity (say  $10^{-2}$  or  $10^{-4}$ ). A family of curves assuming various values for  $\gamma$  are given in Fig. 2.

There would be a small rise in Ge/Fe and Ga/Fe ratios above their cosmic values if Fe transfers to FeS before Ga and Ge are oxidised. However, for any reasonable values for their activity coefficients Ga and Ge will not have fully condensed when FeS formed,

and it is doubtful that Ge/Fe and Ga/Fe ratios much in excess of cosmic will occur. Over the lower-temperature portions of the curves the Ge content of the metal drops because Ge transfers to the silicates (becomes lithophile) as MgGeO<sub>3</sub> and Mg<sub>2</sub>GeO<sub>4</sub> form ideal solid solutions with MgSiO<sub>3</sub> and Mg<sub>2</sub>SiO<sub>4</sub> respectively. Gallium probably also becomes lithophile somewhere around similar temperatures. The silicate phase to which Ga is most likely to transfer is feldspar but thermodynamic data for the Ga analogue of feldspar could not be located. Wasson and Wai [8] assumed the thermodynamic data for Ga<sub>2</sub>O<sub>3</sub> for this calculation and the portions of the curves shown with broken lines have been made with this assumption. There is an additional uncertainty because we do not know the activity coefficient for the formation of Ga-feldspar solid solution in feldspar. For the present calculations I have assumed Ga will remain siderophile until below the accretion temperatures indicated by the Ni.

From the data in Table 1 and curves like those shown in Fig. 2, it is apparent therefore that the Ga and Ge abundance of the metal during condensation passes through the values observed in all of the groups. This is also true for Ni (Fig. 1) so we now want to know under what conditions, if any, we can obtain metal with the appropriate abundance of all three elements in all five groups. I will consider first the possibility of producing the groups IAB, IIAB, IIIAB and IVA as low-temperature accretions, on the upward swing of the Ni curve (Fig. 1). For reasons

that will become apparent I defer discussion of group IVB until later.

### 3.3. Relative pressure-temperature conditions of condensation and accretion

Fig. 3 shows the pressure-temperature conditions in which metal giving the observed Ga, Ge and Ni contents in these four groups exists at equilibrium with the nebula. We may consider the derivation of these plots as follows.

(1) Temperatures are fixed by the Ni content of the groups. For a low-temperature origin, that is for all groups except IVB, they are independent of pressure.

(2) We must now find the pressure required to produce, say, the observed Ge content of any given group. I need to know  $\gamma_{Ge}$ , but for the purposes of illustration I will assume  $10^{-2}$ . I can now calculate pressure-temperature boxes for each group. Considerable pressure differences are required. Had we chosen a smaller, or larger, value for  $\gamma_{Ge}$  the boxes would have moved to lower, or higher, pressures, but their relative positions are unchanged.

(3) I now assume that the Ga contents were fixed at the same time as Ge. This was either because at this time microscopic dust became accreted into

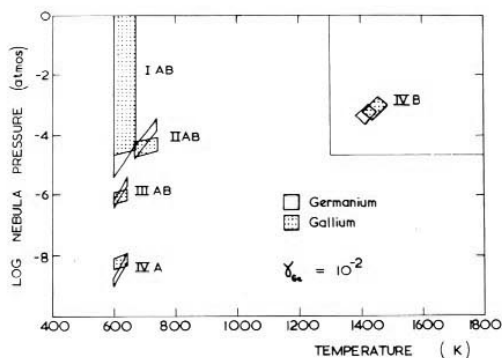


Fig. 3. Pressure-temperature conditions in the solar nebula which produce metal with the Ga, Ge and Ni contents observed in IAB, IIAB, IIIAB, IVA and IVB iron meteorites. The activity coefficients for Ge in Fe,Ni alloy ( $\gamma_{Ge}$ ) has been arbitrarily taken as  $10^{-2}$  — which also fixes  $\gamma_{Ga}$  (see text) — however the same spacings are observed for any other value (Fig. 4). The pressure-temperature conditions for group IVB are not fixed in relation to the others.

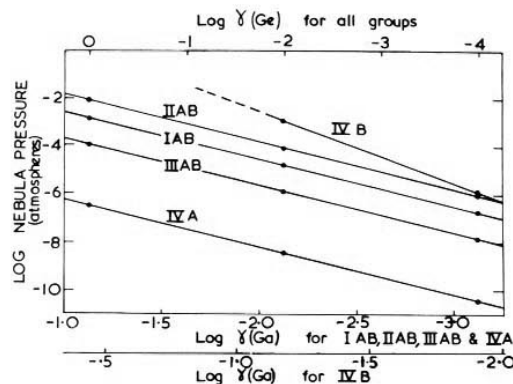


Fig. 4. Relationship between pressure and activity coefficients ( $\gamma_{Ge}$  and  $\gamma_{Ga}$ ) for each iron meteorite group. Note that the relative pressures applicable to the condensation of each group are independent of the activity values. The values for IAB are lower limits because Ga and Ge are fully condensed in this group. The apparent relationship between  $\gamma_{Ge}$  and  $\gamma_{Ga}$  is caused by the Ge and Ga contents being fixed at the same temperature.

macroscopic objects, or because diffusion became too sluggish — most probably it was a combination of the two. This assumption means that we have no choice over the selection of  $\gamma_{Ga}$ . In short, for a given group, a selected value of  $\gamma_{Ge}$  fixes the nebula pressure, which in turn fixes  $\gamma_{Ga}$ . The values of  $\gamma_{Ga}$  are also given in Fig. 4. The significant point is, that when a pair of values for  $\gamma_{Ge}$  and  $\gamma_{Ga}$  gives the observed Ga and Ge content of one group, they also succeed for the others (except IVB); i.e., the Ge and Ga boxes in Fig. 3 overlap when we use the same  $\gamma_{Ge}$  and  $\gamma_{Ga}$  values for all groups. This comes as no surprise, because I argued from the Ni content that these groups formed at similar temperatures.

This may be put another way. By trying different values it is found (Fig. 4) that there is an empirical relationship between  $\gamma_{Ge}$  and  $\gamma_{Ga}$ :

$$\log \gamma_{Ge} = 2 \log \gamma_{Ga} + (2.3 \pm 0.3) \quad (2)$$

The only way we can explain this is by assuming that the Ga and Ge contents were fixed at the same temperature, and that it was the same in each group. In this case we could write equation (1) for Ga and Ge, eliminate  $T$ , and obtain an expression resembling equation (2).

Wai and Wasson [23], using the abundance pat-

terns in ordinary chondrites, have developed a model in which the efficiency of condensation and accretion decreases with time due to the continual separation of gas and dust. The agreement over the relative pressures required by the Ga and Ge abundances (Fig. 3) shows that if this model is true, the extent of gas-dust fractionation was the same in each group. There would still need to be large pressure variations. The main difference between this model, and that of Wai and Wasson, is that here I explain the variations in Ni content as part of the same overall process – this is thought to have been the case for chondrites. There is some doubt, however, as to whether the abundance data support Wai and Wasson's model, or the Larimer-Anders model similar to that used here [24].

To summarise, this model yields the result that groups IAB, IIAB, IIIAB and IVA were in equilibrium with the nebula until accretion at a temperature of 600–700 K, and that there were significant pressure differences in the nebula at the location of the accretion of their parent bodies. IAB could have formed over a wide range of pressure and we have been able to fix only a lower limit. This is because Ga and Ge are fully condensed in this group. IIAB formed at the lower end of this range, IIIAB and IVA formed in regions where the pressure was  $1/20$  and  $10^{-4}$  of this value respectively.

The only way in which these groups could have formed under equilibrium conditions at the same pressure would be if there were very large variations in the activity coefficients which seem very unlikely. The Ni content (Fig. 1) and the agreement between the Ga and Ge boxes in Fig. 3 shows that these groups accreted at similar temperatures, and that the same values of  $\gamma_{\text{Ga}}$  and  $\gamma_{\text{Ge}}$  applied. Compositional variations are also unlikely to be responsible for the pressure differences in Fig. 3. The abundance of Ga and Ge ( $8 \times 10^{-4}$  and  $5 \times 10^{-4}$  mole fractions, respectively) is too small to affect activity coefficients. Nickel cannot explain the apparent pressure differences either, as even qualitative assessment will show. IIAB has lowest Ni, but similar pressures to IAB, while IVA has the same Ni as IAB but the lowest apparent pressure. I conclude that if these groups formed at low temperatures, there were significant pressure differences in the locations where their parent bodies accreted.

I will now consider the possibility of the forma-

tion of meteorite parent bodies on the high-temperature, downward swing of the Ni curve. IAB, IIAB, and IIIAB require pressures greater than 1 atmosphere and  $\gamma_{\text{Ge}}$  less than  $10^{-4}$  to form at high temperatures and their accretion temperatures are then greater than 1500 K. These values seem exceedingly unlikely but cannot be ruled out altogether. Scott [3] and Kelly and Larimer [6] have argued that group IVB is an early condensate because it is rich in refractories and low in volatiles. The evidence seems fairly convincing and we will adopt this conclusion here. IVA and IVB can form as high-temperature accretions at pressures and temperatures given in Table 3. The choice between a high- or low-temperature origin for IVA can be made and the implausibility of such an origin for IAB, IIAB and IIIAB affirmed by a consideration of the minor elements. However, the same values of  $\gamma_{\text{Ge}}$  and  $\gamma_{\text{Ga}}$  will not give the observed compositions in both IVA and IVB so that markedly different pressure and temperatures between the two groups would be required. For example, if IVB accreted under a pressure of  $10^{-4}$  atmosphere its accretion was 1310 K. Then for IVA to accrete at 1400 or 1200 K the pressure must have been  $10^{-3}$  or  $3 \times 10^{-6}$  atmosphere respectively. IVB is also plotted in Figs. 3 and 5, but there is no reason to suppose the same  $\gamma$  values applied to this group.

### 3.4. Minor elements – sulphur, carbon and phosphorus

Before we can compare the predicted minor element abundances with those observed it is necessary to make some attempt at estimating their relative abundance in the five iron meteorite classes we are discussing. This is particularly difficult because these elements tend to concentrate in macroscopic and sparsely distributed inclusions and we therefore have to utilise both mineralogical and chemical data (Table 5).

*Sulphur.* Sulphur begins condensing as FeS at a pressure-independent temperature of 695 K and 50% is condensed by 657 K. Meteorites belonging to parent bodies which accreted above this temperature can only acquire S by non-equilibrium mechanisms or by the formation of solid solutions of S in the metal. However, this is negligibly small – less than  $10^{-6}$

TABLE 5

Range and mean values for Ni, Ga, Ge and minor elements in iron meteorite groups IAB, IIAB, IIIAB, IVA and IVB \*

	Ni **	Ga **	Ge **	S ***	S †	C †	P †
IAB	6.4–8.7	55–100	190–520	0.4–2.0	0.002–0.056	0.005–0.063	0.16–0.61
(106)	7.53	74	289	0.88 (8)	0.009 (12)	0.029 (15)	0.25 (17)
IIAB	5.3–6.4	46–62	107–185	0.08–0.30	0.003–0.032	0.002–0.002	0.13–0.44
(62)	5.73	58	170	0.17 (8)	0.018 (17)	0.008 (17)	0.26 (18)
IIIAB	7.1–10.5	16–23	27–47	0.1–2.0	0.001–0.032	0.002–0.040	0.08–0.26
(158)	8.27	19.7	38.6	0.77 (16)	0.018 (17)	0.014 (42)	0.21 (46)
IVA	7.4–9.4	1.6–2.4	0.09–0.14	0.04–0.5	0.001–0.063	0.003–0.043	0.02–0.15
(38)	8.23	2.08	0.120	0.21 (3)	0.012 (31)	0.017 (13)	0.07 (13)
IVB	16–18	0.17–0.27	0.03–0.07	0.02–0.05	0.002–0.032	0.004–0.005	0.05–0.10
(12)	16.81	0.220	0.054	0.03 (3)	0.011 (11)	0.004 (3)	0.07 (3)

\* Ga and Ge values in ppm, others in weight percent. Numbers of specimens in parenthesis.

\*\* Wasson [38].

\*\*\* Planimetric estimates from Buchwald [25].

† Chemical estimates from Moore et al. and Lewis and Moore [26] excluding one anomalously high S value from IAB and two from IIAB and two high C values from IAB.

wt.% at all temperatures and pressures considered.

From both mineralogical [25] and chemical [26] observations S appears to be abundant in all classes except IVB. This is what we would predict from the condensation/accretion model above in which IVB accreted before FeS condensed (695 °K) and the others after. IAB, IIAB, IIIAB and IVA therefore accreted on the low-temperature arm of the Ni curve. The small differences that are present cover a factor of two or three, rather than the two orders of magnitude difference observed between these and IVB. These are so much smaller fractionations that I am inclined to ascribe them to a different process, and differentiation during the melting process would seem a good candidate. Fractionations of a similar order are observed with P. Other evidence in support of the conclusion that IAB, IIAB, IIIAB and IVA formed on the low-temperature arm are firstly, that the same  $\gamma_{\text{Ga}}$  and  $\gamma_{\text{Ge}}$  values apply in each group (Fig. 3), and secondly, the prime evidence that IVB is an early condensate is that it is enriched in refractory and depleted in volatile elements and there is no evidence that this is the case for the other groups. For example the Ir and Au contents of IVA are 0.4–4.0 and 0.5–8.0 ppm respectively while for IVB these are 13–38 and 0.07 ppm. For comparison, cosmic values,

normalised to Ni, are about 2 and 1 for Ir and Au respectively.

**Carbon.** Carbon is particularly interesting because only a small range of pressure-temperature conditions can produce metal which contains appreciable amounts of this element. Carbon will condense as graphite at very low temperatures and pressures (Fig. 5).  $\text{Fe}_3\text{C}$  is unstable under all conditions considered and the presence of cohenite  $[(\text{Fe},\text{Ni})_3\text{C}]$  in some iron meteorites is ascribed to kinetic rather than thermodynamic considerations applicable after the secondary (melting) fractionation event [27]. There is, however, a limited range of pressures and temperatures over which significant quantities of carbon may go into solid solution [10]. These conditions are shown in Fig. 5. The solution is non-ideal and activity coefficients were calculated from the expression given by Natessan and Kassner [28]. The experimental data were obtained over the range 700–1060 °C and require some extrapolation to the temperatures applicable here (600–700 K). This may introduce an error of a factor of ten or so, but the overall symmetry and gross features of the contours would be unchanged. These are governed by the composition of the gas, or more specifically by the change from CO to  $\text{CH}_4$



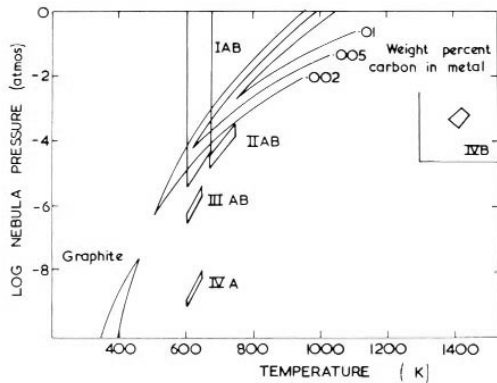


Fig. 5. The pressure-temperature conditions in which C forms solid solution in the metal or condenses as graphite. The region giving metal with the observed iron meteorite composition (from Fig. 3) are superimposed. These calculations predict most carbon in group IAB, with IIAB and IIIAB having less and IVA and IVB virtually none. This is the observed pattern.

being the dominant gas phase. Superimposed on Fig. 5 are the pressure-temperature boxes for  $\gamma_{Ge} = 10^{-2}$ . Any reasonable value of  $\gamma_{Ge}$  puts IAB in the pressure-temperature regions where metal richest in C would be formed, IIAB and IIIAB would have slightly less and IVA and IVB considerably less.

Group IAB is undoubtedly rich in C and it contains abundant carbides and graphite nodules [22]. Many of group IIAB also contain carbides and graphite. Buchwald [25] mentions cohenite or cohenite which has decomposed to graphite in at least 27 out of 50 IIAB iron meteorite descriptions. However, he was unable to find these minerals in any IIIAB irons despite the fact that in many cases (Canton, Cleveland, Duketon, Gundaring, Lexington County . . .) they had previously been reported and were therefore specifically being sought. It would appear from mineralogical observations that IIAB should be intermediate between IAB and IIIAB in its C contents. IVA and IVB do not contain graphite, carbides or C in solid solution.

These mineralogical observations fit the condensation model rather well. The C-rich IAB irons can be formed under pressure-temperature conditions which give C-rich metal. The lower abundance of carbon in the groups IIAB and IIIAB, and absence in IVA and IVB could therefore also be a condensation/accretion

effect rather than the result of any subsequent differentiation. To move IIIAB and IVA into the C-rich pressure-temperature region and still have the observed Ga and Ge abundances would require  $\gamma_{Ge}$  of 1 and 100 respectively, both of which are extremely unlikely. Unlike IAB, group IIAB may well have been completely melted [22,3,6], but this has not apparently removed the carbon acquired during condensation and accretion, presumably because carbon is very soluble in liquid iron.

**Phosphorus.** Phosphorus condenses as  $(Fe,Ni)_3P$  ahead of the metal (Table 2). As a consequence of this stable reservoir the amount of P in solid solution never exceeds  $10^{-5}$  wt.%. At the pressure-independent temperature of 770 K  $(Fe,Ni)_3P$  is converted to whitlockite by reaction with the nebula gases and below this the P in solid solution in the metal is even lower. The presence of P in the iron meteorites involves incorporation of phosphate or phosphide in the meteorite parent bodies, but since it is in the condensed phase over a very wide range of pressures and temperatures, the abundance of P in iron meteorites is not difficult to understand.

The results of the present P calculations differ in two respects from those of Wai and Wasson [23]. Firstly, P condenses as a solid solution with Fe rather than as schreibersite, and, secondly, after the condensation of  $Fe_3P$  in Wai and Wasson's calculations most of the P goes into solid solution in the metal rather than in forming  $(Fe,Ni)_3P$ . Phosphorus has a particularly complex history in the nebula gases; each of  $P(g)$ ,  $P_2(g)$ ,  $PH_3(g)$ ,  $PN(g)$  and  $P_4O_6(g)$  is at some time the major component of the gas phase. During  $Fe_3P$  and Fe condensation I find  $P_2(g)$ , whilst Wai and Wasson find  $PN(g)$ , to be the dominant species. Even so, they would still have found schreibersite condensed ahead of the metal had they assumed solid solution between  $Fe_3P$  and  $Ni_3P$ . The difference in the calculated distributions after Fe and schreibersite condensation arises from our use of different activity coefficient data. Wai and Wasson take  $10^{-5}$  from Komarek's data [36] — this is in fact a Henrian coefficient (i.e. with respect to a solution of 1% P on liquid Fe), rather than a Raoultian coefficient (i.e. with respect to pure solids). For the moment, I have assumed ideal solution and my figures may require some revision when better

activity coefficient data are available. It will not affect my main conclusions, however.

Phosphorus is of little value in deciphering condensation and accretion conditions because, unlike S and C, it can enter the condensed phase at most pressures and temperatures. Assuming the condensate could accrete each phase equally there would be no difference in the P contents of the iron meteorite parent bodies at the end of condensation and accretion at any temperature or pressure. In fact IVA and IVB have somewhat lower P contents than IIIAB and IAB which in turn are lower than IIAB but these differences are considerably less than for C and S. Olsen and Fuchs [29] have shown that substantial redistribution of the P between silicates and metal probably occurred during differentiation, which is probably the cause of these differences.

#### 4. Summary and conclusions

There are two temperature regions at which the Ni contents of the iron meteorites IAB, IIAB, IIIAB, IVA, and IVB can be produced by equilibrium processes; soon after condensation of the metal, and below 750 K. The Ga and Ge contents of IAB, IIAB and IIIAB are too high for early condensates and these most probably formed over the lower-temperature region. The IVB parent body was an early condensate. The Ni, Ga and Ge contents of IVA can be explained by its parent body also being an early condensate but at different pressures to IVB. However, the other trace elements and the S abundance in IVA suggest that it accreted at similar temperatures to IAB, IIAB, and IIIAB. The differences in Ga and Ge abundance between IAB, IIAB, IIIAB and IVA are due to differences in pressure and, in the case of IIAB, temperature conditions. IIAB formed at the low-pressure extreme of the range for IAB and at about 50 K higher temperatures while IIIAB and IVA formed at similar temperatures but pressures which were lower by factors of 20 and  $10^4$  respectively. The S and C abundances are consistent with this model, but P condenses too readily to be a useful measure of condensation and accretion conditions. The abundance of C in group IAB suggests it formed at about  $10^{-4}$  atmosphere, so that IIAB formed in regions where the pressure was  $5 \times 10^{-6}$  and IVA where the pressure was  $10^{-8}$  atmosphere.

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