

PART VII
DIFFERENTIATED
METEORITES

1

THE ORIGIN OF IRON METEORITES

W. R. KELLY, E. R. RAMBALDI, and J. W. LARIMER

The chemistry of iron meteorites is compared to predictions of the chemical fractionations that develop during the cosmic history of the metal phase, from condensation and accretion through melting, segregation and freezing. Of the 12 resolved iron meteorite groups, 3 appear to have evolved in bodies which accreted at $T > 1000^{\circ}$ K. In several cases, the core-forming process seems to have ceased prematurely, just as the metal began to melt and flow (group IAB with its silicate inclusions) or after the metal aggregated into pods but before it sank to form a core (group IVA, with groups IIAB and IIIAB being in more advanced stages). The Shaw chondrite contains residual metal from a partial melting process, as required to complement the fractional melts which refroze prematurely in the case of group IAB meteorites.

INTRODUCTION

Iron meteorites probably represent the only tangible evidence bearing on the question of how metal-rich cores form and evolve in planetary objects. Anders (1964) reviewed the evidence on the origin of iron meteorites, concluding that many small bodies, presumably the asteroids, rather than one large body were involved. All of the evidence accumulated since then supports this view. Their trace element contents vary by up to factors of 10^4 , but tend to cluster or display correlations indicative of groupings. Scott and Wasson (1975), on the basis of Ga, Ge, Ir and Ni contents in nearly 500 iron meteorites, resolved 12 groups, implying at least that many parent bodies. But 14% of the meteorites studied do not fit into one of these groups, suggesting that many more bodies are represented.

The chemical trends between and within groups are complex, reflecting the effects of various processes that have left their imprint. An important interpretative step was taken by Scott (1972). Noting that the content of 15 additional elements supports the groupings, he points out that two fractionations must be explained: those within groups and those between groups. Within a group, pairs of elements tend to correlate logarithmically over wide concentration ranges. Such trends are best explained by a fractional crystallization process, one that operated during cooling and freezing in the cores of the parent bodies. The fractionation between groups must predate those within groups and probably reflects chemical differences between the bodies.

Following this reasoning, Kelly and Larimer (1976) approached the problem from a somewhat different perspective. The cosmochemical history of the metal phase was traced through four stages: 1) condensation, nebular fractionation and accretion, 2) oxidation or reduction, 3) melting and segregation of metal from silicates and

4) fractional crystallization during cooling. Changes in composition at each stage are predictable and can be compared to the end-product, the iron meteorites.

COSMIC HISTORY OF THE METAL PHASE

Only elements more noble than Fe (Au, Co, Cu, Ga, Ge, Ir, Mo, Ni, Os, Pd, Pt, Re, Rh and Ru) were considered. Including Fe, these fifteen siderophile elements differ considerably in their volatilities and melting-freezing behavior, providing a means to resolve trends that arise at each stage.

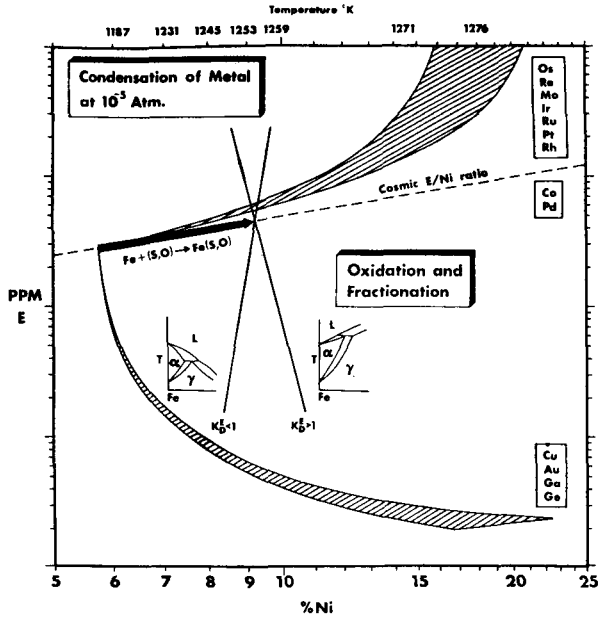


Figure 1. During condensation, the composition of cosmic metal changes continuously. The Ni content decreases from 19% ($P_T = 10^{-5}$) to 5.5%, the refractory element contents decrease along a line in the upper shaded region, the volatile contents increase along a line in the lower shaded region, and Co and Pd retain their cosmic proportions relative to Ni. The temperature scale is tied to the Ni content; it does not apply for the vertical portion of the volatile element curves. The size of the shaded region reflects uncertainties in the thermodynamic data. Oxidation of Fe shifts the composition along the heavy arrow, or a line parallel to it. Fractional crystallization of a melt with a composition at the tip of the arrow spreads out the trace element contents along lines of positive or negative slope, depending on their phase relations with Fe.

The predicted changes in composition during stages 1, 2 and 4 are shown in Figure 1. Stage 3, melting and segregation, will be covered later. The nebular condensation temperature of FeNi metal is about 1276° K ($P_T = 10^{-5}$ atm.). This metal contains 19% Ni; it is rich in refractories (Os, Re, etc.) and depleted in volatiles (Au, Cu, etc.). Three elements--Co, Ni and Pd--condense almost simultaneously; they retain their cosmic proportions during condensation. As the temperature falls below 1276°, the fraction of Fe and Ni condensed increased rapidly. Both are 99.9% condensed at 1135°. Since the refractories are almost totally

ORIGIN OF IRON METEORITES

condensed at 1276°K, their concentration in the metal decreases over this interval. Elements more volatile than FeNi metal condense on the metal grains along with the major elements and continue to condense at even lower temperatures.

When the temperature in the nebula falls to 680°K, some of the metallic Fe is converted to FeS according to the reaction $\text{Fe} + \text{H}_2\text{S} \rightarrow \text{FeS} + \text{H}_2$ (Urey, 1952). With FeS forming at the expense of metallic Fe, the unreacted metal shifts in composition toward higher Ni and trace element contents along the cosmic ratio line, or one parallel to it if condensation was incomplete. At lower temperatures, additional Fe is converted to FeO (Larimer, 1968) or Fe_3O_4 (Urey, 1952) with similar effects.

Accretion at this point will yield a body containing a mixture of silicates, sulfides and metal, just as in the H or L chondrites, with the metal having a composition near the tip of the arrow in Figure 1. Let's assume that this metal melts and sinks to form a core. To keep the discussion simple, we'll keep track of only two trace elements, Au and Ir. As the molten core cools, crystals begin to form and each element will distribute itself between solid and liquid, according to its distribution coefficient:

$$k_D^E = C_E^S / C_E^L,$$

where C_E^S and C_E^L are the concentrations of element E in the solid and liquid. Elements with higher melting points than Fe (Ir) will have k_D^E values greater than 1 and vice versa. During fractional crystallization, the composition of the solid changes:

$$C_E^S / C_E^0 = k_D^E (F)^{k_D^E - 1},$$

where C_E^0 is the initial bulk concentration of the element and F is the fraction of liquid remaining ($0 < F < 1$). Such a relationship can be combined with a similar one for Ni, yielding:

$$\log C_E^S = A \log C_{\text{Ni}}^S + B.$$

The A term equals $(k_D^E - 1) / (k_D^{\text{Ni}} - 1)$ and defines the slope of the fractionation trend. The Fe-rich portion of the Fe-Ni phase diagram resembles the left one in Figure 1, that is, $k_D^{\text{Ni}} < 1$. Therefore, elements with $k_D^E < 1$ (Au) will be positively correlated with Ni and elements with $k_D^E > 1$ (Ir) will be negatively correlated.

Scott (1972) has shown that the k_D values inferred from the slopes of the correlation lines are in qualitative agreement with the known phase relations. Note that k_D^E may be dependent on both temperature and composition. But lacking experimental data, it is here assumed to remain constant.

IRON METEORITE COMPOSITION

A representative sample of Au, Ir and Ni data from iron meteorites is compared to the predictions in Figure 2. The data on the remaining elements are consistent with these patterns (Scott, 1972; Kelly and Larimer, 1976).

One group of iron meteorites, IVB, stands out. The metal contains 16-18% Ni; it is rich in refractories and depleted in volatiles. In fact, the composition with respect to all 15 elements is nearly identical to the predicted composition of metal just below the condensation temperature of FeNi metal in the nebula (Table 1). No other combination of the processes considered can produce a metal of this composition. It thus appears that this metal, and presumably the parent body, accreted at a very high temperature. This does not rule out a melting and segregation stage

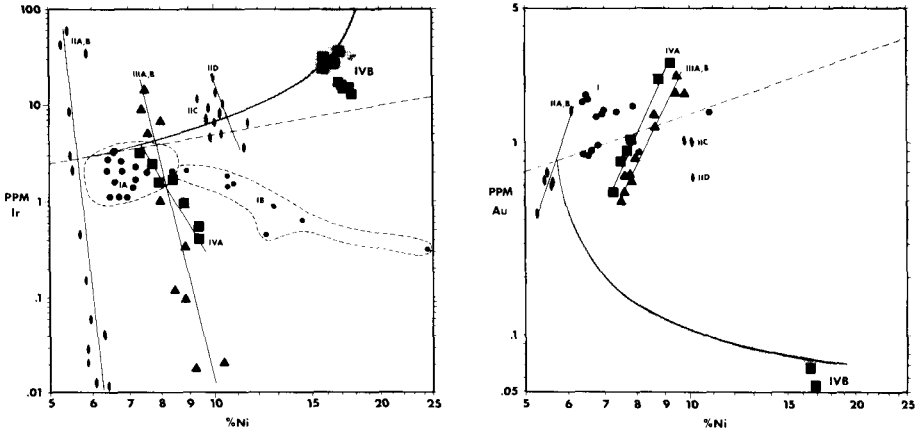


Figure 2. a) Ir is negatively correlated with Ni in several groups (II AB, III AB), as predicted (Fig. 1). Group IV B is unusual: its composition falls on the condensation curve at high temperatures. Group I AB displays a unique fractionation trend. b) Au is positively correlated with Ni, as expected. Group IV B again falls on the condensation curve at high temperatures and group I AB displays a unique fractionation trend.

TABLE 1

Comparison of Predicted Metal Composition During Condensation ($T = 1270^{\circ} \text{K}$, $P_T = 10^{-5} \text{atm}$) and Group IVB Iron Meteorites

Element ppm (%)	Observed IVB Metal	Predicted Metal
Au	.06 - .07	.07
Co (%)	.68 - .72	.69
Cu	1 - 5	5
Fe (%)	82 - 84	85
Ga* ($\gamma = 3 \times 10^{-2}$)	.17 - .27	.006 (.20)
Ge ($\gamma = 3 \times 10^{-4}$)	.03 - .08	2×10^{-5} (.07)
Ir	4.0 - 36	27
Mo	22 - 30	70
Ni	16 - 18	17
Os	19 - 40	28
Pd ($\gamma = 0.4$)	5.6 - 6.6	1.2 (3.0)
Pt	11 - 21	50
Re	2.2 - 4.0	2.0
Rh	1.8	8
Ru	13 - 30	37

* Predicted metal composition using activity coefficient data rather than assuming ideality.

ORIGIN OF IRON METEORITES

in this body. But if such processing did occur, the effects were small in comparison to those observed in other groups of iron meteorites. Another group, III F, containing only 5 members, appears to have accreted at a somewhat lower temperature, -1180° K. Yet a third group, IV A, also appears to have accreted in this range (-1220° K), but in this case subsequent processing was more extreme as discussed below.

Two of the most populous groups, II AB and III AB, seem to have had a more traditional history. The chemical trends match those illustrated schematically in Figure 1, the only difference being the degree of oxidation in the parent body. In these cases, fractional crystallization evidently led to the most extreme ranges in trace element content observed, by factors of 10^3 to 10^4 .

The chemical trends in group I AB differ from those in any other group. These meteorites are also unusual in containing abundant silicate inclusions with chondritic compositions. This raises the interesting possibility that these meteorites are derived from a body, or a portion of a body, in which the metal-silicate segregation process did not go to completion.

MELTING-SEGREGATION PROCESSES

The chemical fractionations that could arise during the melting-segregation stage in the evolution of iron meteorites has not previously been considered. Yet in most models, it is implicit that the metal pass through this stage. In fact, in any model where the segregation takes place in a parent body, partially molten metal should be as abundant, or more abundant, than totally molten metal. For example, consider a spherical body of homogeneous composition consisting of N shells of equal thickness. The outermost shells contain the largest fraction of the total mass, and metal, in the body. If the inner $1/3$ of the body completely melts and the outer $2/3$ partially melts, with an average F value of 0.3, then 92% of the molten metal in the body would be derived from partial melts. Thus, many iron meteorites must consist of partially molten metal and it is not unlikely that in some cases this metal did not drain to the center and become homogenized.

The composition of the liquid and solid during partial melting can be predicted in a manner analogous to the fractional crystallization stage. The problem is similar to the terrestrial and lunar one of generating basaltic liquids by partial melting (Gast, 1968; Shaw, 1970). Three steps in the melting process may be distinguished (Shaw, 1970):

1. Melting proceeds to some finite extent, the liquid and solid remaining in contact and in equilibrium until migration begins.
2. Once migration begins, pores and channels become available and the melt flows away continuously as it forms.
3. The increments of melt aggregate into larger masses which become homogenized.

In the first step, when fraction F has melted, the concentration of element E in the liquid, C_E^L , is obtained by substituting K_D into the mass balance equation:

$$C_E^L / C_E^0 = [K_D^E + F (1 - K_D)]^{-1}.$$

As the melt begins to flow continuously, the composition varies according to

$$C_E^L / C_E^0 = \frac{1}{K_D^E} (1 - F)^{\frac{1}{K_D^E} - 1}$$

where C^k is used to distinguish this melt from that of the first step. The composition of the aggregate melt is obtained by integration:

$$\bar{C}_E^g / C_E^0 = \frac{1}{F} [1 - (1 - F)^{1/K_D^E}]$$

where \bar{C}_E^g is used to distinguish this liquid composition from the others.

If the metal in group I AB represents a partial melt that refroze in the process of segregating itself from the silicates, then it should have the compositional trend associated with the second step. The predicted trends are compared to the Ir-Ni data from group I AB in Figure 3. Note that the slope of this linear trend is $(1/K_D^{Ir} - 1) / (1/K_D^{Ni} - 1)$ in contrast to the relationship for fractional melting. However, when K_D values of 20 ($= K_D^{Ir}$) and 0.5 ($= K_D^{Ni}$) are used, there is good internal agreement with the data for both the fractional melting and crystallization trends.

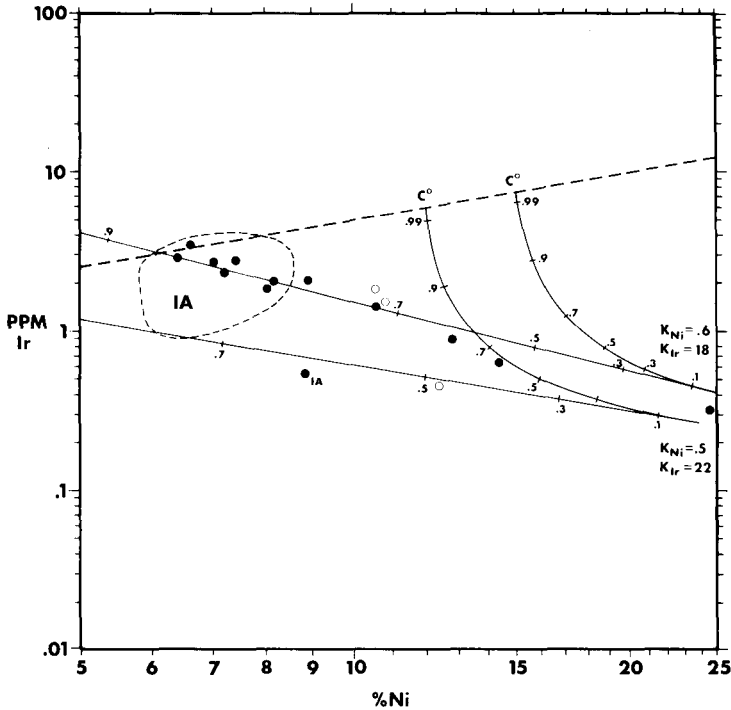


Figure 3. The Ir-Ni data from group I AB are linearly correlated, as predicted for a fractional melting process. The curved lines trace the composition of a homogenized, aggregate melt. A starting composition at C^0 is assumed; filled circles indicate I AB members known to contain silicate inclusions.

It is obviously of interest to look for chondrites which may have experienced a partial loss of metal. If the model is correct, any metal that remains should have a composition complementary to that which was lost, or group I AB metal. The

ORIGIN OF IRON METEORITES

chondrite Shaw, a highly metamorphosed L group meteorite, deficient in metal and sulfide, is a potential candidate (Fredriksson and Mason, 1967). The metal in Shaw is enriched in refractories and depleted in volatiles, just the reverse of the trend observed in group I AB (Fig. 4). In fact, the metals from Shaw and San Cristobal, the extreme end-member of group I AB, are quantitatively complementary with respect to all elements for which data exist (Rambaldi and Larimer, 1976).

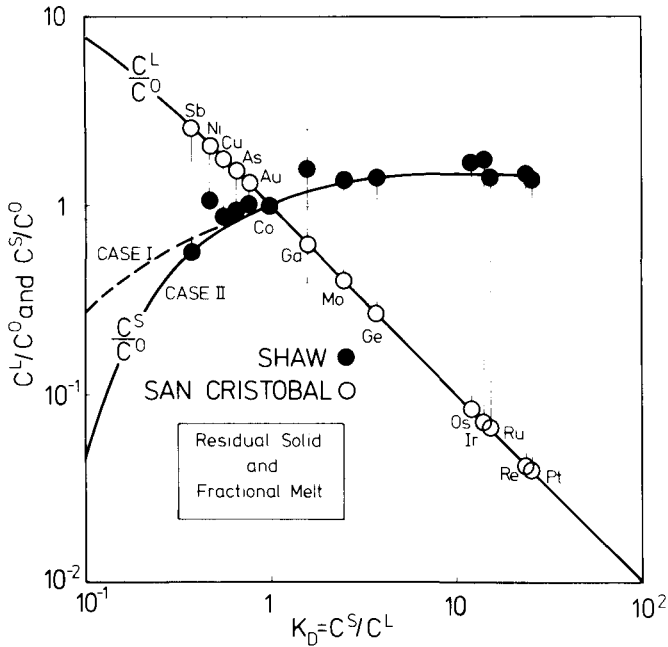


Figure 4. The metals in the chondrite Shaw and the group I AB iron meteorite San Cristobal are complementary in composition. The curves indicate the dependence of composition of a liquid ($F = 0.1$) and residual solid ($F = 0.3$) on K_D values (dashed = step I, solid = step II; see text). All trace element data are normalized to Co, an element which is little fractionated in iron meteorites and whose K_D value is assumed to equal 1. The C^0 values are the average composition of metal in 3 highly metamorphosed chondrites.

IMPLICATIONS FOR CORE FORMATION

Independent evidence on the origin of iron meteorites comes from cooling rate estimates (Wood, 1964; Goldstein and Ogilvie, 1965; Goldstein and Short, 1967a,b). These estimates are made by measuring the diffusion profile of Ni across the γ -FeNi grains in iron meteorites. The data indicate that most iron meteorites cooled at a rate of between 1^0 and 10^0 per Myr. In some groups the data cluster, suggesting an origin at similar depths in the parent bodies. But in other groups, the cooling rates differ implying an origin at different depths.

An interesting situation arises in comparing chemical trends and cooling rate estimates in groups III AB and IV A. Both have similar chemical trends (Fig. 2) but not cooling rates. In group III AB, the Ni-rich members cluster around $1.5^0/\text{Myr}$ while the Ni-poor members spread out between 2 and $10^0/\text{Myr}$. In group IV A, the

spread is even larger, 7° to 200° /Myr. (Scott and Wasson, 1975), indicative of origins at different depths. This indicates that meteorites belonging to group IV A did not originate in a single core while many, but not all, of group III AB did. One solution to the problem is to find a process which produces trends nearly identical to the fractional crystallization process. The cooling rate data from group IV A, coupled with the chemical trends, suggest an origin in the same body, perhaps as several molten pools of metal distributed throughout the body. These pools might be considered aggregates of metal that become segregated, possibly homogenized, but did not sink to form a single core. The chemical trends, probably modified by mixing and subsequent fractional crystallization, might resemble those predicted for step III in the partial melting process (Fig. 5). The predicted trends are nearly linear and essentially indistinguishable from the fractional crystallization trends.

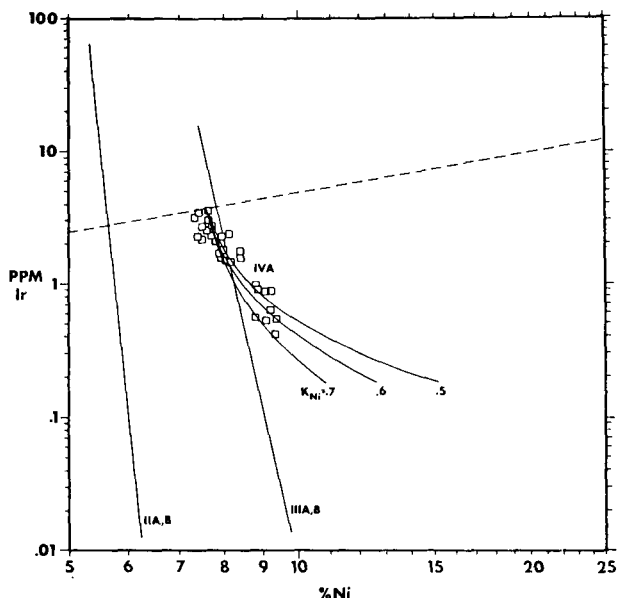


Figure 5. Ir and Ni are negatively correlated in most iron meteorite groups, but along lines of different slope. The correlation in group IV A can be approximately duplicated by a predicted trend for homogenized aggregates of partial melts. Such a trend, expected if the molten metal collects into a number of pools radically distributed in the parent body, is consistent with both the chemistry and cooling rates of group IV A.

This interpretation of the chemistry of iron meteorites implies that core formation and evolution can be considered a series of steps: molten metal begins to flow and segregate itself from the surrounding silicates; it aggregates or coalesces into larger masses which sink to form a core, and subsequent cooling leads to fractional crystallization. In the meteorites, each of these steps is represented: group I AB, group IV A and group III AB.

ACKNOWLEDGEMENTS

This work was supported in part by NASA Grant NSG 7040. The financial sup-

ORIGIN OF IRON METEORITES

port of The Deutsche Forschungsgemeinschaft is gratefully acknowledged by one of us (E.R.R.).

REFERENCES

- Anders, E. 1964, *Space Sci. Rev.* 3, 583.
Fredriksson, K., and Mason, B. 1967, *Geochim. Cosmochim. Acta*, 31, 1705.
Gast, P. W. 1968, *Geochim. Cosmochim. Acta*, 32, 1057.
Goldstein, J. I., and Ogilvie, R. E. 1965, *Geochim. Cosmochim. Acta*, 29, 893.
Goldstein, J. I., and Short, J. M. 1967a, *Geochim. Cosmochim. Acta*, 31, 1001.
Goldstein, J. I., and Short, J. M. 1967b, *Geochim. Cosmochim. Acta*, 31, 1733.
Kelly, W. R., and Larimer, J. W. 1976, *Geochim. Cosmochim. Acta*, (in press).
Larimer, J. W. 1968, *Geochim. Cosmochim. Acta*, 32, 1187.
Rambaldi, E., and Larimer, J. W. 1976, *Earth Planet. Sci. Lett.*, (in press).
Scott, E.R.D. 1972, *Geochim. Cosmochim. Acta*, 36, 1205.
Scott, E.R.D., and Wasson, J. T. 1975, Submitted to *Rev. Geophys. Space Sci.*
Shaw, D. M. 1970, *Geochim. Cosmochim. Acta*, 34, 237.
Urey, H. C. 1952, *The Planets*, New Haven: Yale University Press.
Wood, J. A. 1964, *Icarus*, 3, 429.