INVITED REVIEW
Iron meteorites: Crystallization, thermal history, parent bodies, and origin
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Abstract

We review the crystallization of the iron meteorite chemical groups, the thermal history of the irons as revealed by the metallographic cooling rates, the ages of the iron meteorites and their relationships with other meteorite types, and the formation of the iron meteorite parent bodies. Within most iron meteorite groups, chemical trends are broadly consistent with fractional crystallization, implying that each group formed from a single molten metallic pool or core. However, these pools or cores differed considerably in their S concentrations, which affect partition coefficients and crystallization conditions significantly. The silicate-bearing iron meteorite groups, IAB and IIE, have textures and poorly defined elemental trends suggesting that impacts mixed molten metal and silicates and that neither group formed from a single isolated metallic melt. Advances in the understanding of the generation of the Widmanstätten pattern, and especially the importance of P during the nucleation and growth of kamacite, have led to improved measurements of the cooling rates of iron meteorites. Typical cooling rates from fractionally crystallized iron meteorite groups at 500–700 °C are about 100–10,000 °C/Myr, with total cooling times of 10 Myr or less. The measured cooling rates vary from 60 to 300 °C/Myr for the IIIAB group and 100–6600 °C/Myr for the IVA group. The wide range of cooling rates for IVA irons and their inverse correlation with bulk Ni concentration show that they crystallized and cooled not in a mantled core but in a large metallic body of radius 150 ± 50 km with scarcely any silicate insulation. This body may have formed in a grazing protoplanetary impact. The fractionally crystallized groups, according to Hf–W isotopic systematics, are derived originally from bodies that accreted and melted to form cores early in the history of the solar system, <1 Myr after CAI formation. The ungrouped irons likely come from at least 50 distinct parent bodies that formed in analogous ways to the fractionally crystallized groups. Contrary to traditional views about their origin, iron meteorites may have been derived originally from bodies as large as 1000 km or more in size. Most iron meteorites come directly or indirectly from bodies that accreted before the chondrites, possibly at 1–2 AU rather than in the asteroid belt. Many of these bodies may have been disrupted by impacts soon after they formed and their fragments were scattered into the asteroid belt by protoplanets.

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1. Introduction

Recent studies have argued that the iron meteorites, like stony-irons and achondrites, come from solar system bodies that melted allowing mm-sized and smaller metal and silicate grains in chondrite material to segregate into much larger domains (e.g., Krot et al., 2008; Weisberg et al., 2006). According to the textbooks, iron meteorites are derived from over 50 bodies that were 5–200 km in size, most of which melted to form metallic cores and silicate mantles. These bodies are thought to have accreted in the asteroid belt after the chondrites and to have been broken open by impacts long after the bodies had cooled slowly.

Other studies suggest that almost all of these statements may be incorrect. Iron meteorites may have been derived originally from bodies as large as 1000 km or more in size that melted. There is a growing consensus that most iron meteorites come from bodies that accreted early – even before the parent bodies of the chondrites – and that 26Al, which has a half-life of 0.7 Myr, is the major heat source that melted them. Evidence from Hf–W radiometric dating of irons and chondrites shows that most irons come from bodies in which metallic cores formed <1 Myr after the growth of the oldest objects, Ca–Al-rich inclusions in chondrites (Kleine et al., 2005; Markowski et al., 2006a, b; Qin et al., 2008; Burkhardt et al., 2008). The early accretion of igneously differentiated asteroids is also inferred from consideration of the heating effects of 26Al in planetesimals. Homogeneity of Mg isotopic compositions of diverse meteorite parent bodies suggests that 26Al was homogeneously distributed in the solar system (Thrane et al., 2006). Therefore there would have been sufficient thermal energy from 26Al to melt cold planetesimals that accreted within 1.5 Myr of CAI formation and were large enough (> 20 km radius) so that little heat was lost for several half-lives of 26Al (Hevey and Sanders, 2006). In addition, chondrule ages determined by Al–Mg and Pb–Pb dating are 1.5–5 Myr after CAI formation indicating that chondrules accreted after differentiated parent bodies when 26Al concentrations were no longer adequate to melt asteroids (see Scott, 2007).

The requirement that iron meteorite parent bodies accreted before those of the chondrites is one of several arguments advanced by Bottke et al. (2006) for their claim that these bodies accreted not in the asteroid belt but closer to the Sun at 1–2 AU where planetesimals accreted faster (see Section 7.7). Thus, the parent bodies of the iron meteorites could have been much more diverse than those of the chondrites and the irons may tell us more about the bodies that accreted to form the terrestrial planets than the chondrites.

In this paper we discuss how this new view of the formation of the iron meteorites was developed. We review the general structure and classification of iron meteorites and outline the crystallization and formation of the iron meteorite chemical groups and their thermal history as revealed by metallographic cooling rates. We discuss other evidence, chiefly isotopic, that elucidates the thermal and igneous histories of irons, and finish with conclusions about the possible origins and formation of their parent bodies.

2. Composition, structure, and chemical groups of the iron meteorites

2.1. Composition and structure

Iron meteorites are Fe–Ni alloys containing minor amounts of Co, P, S, and C. The Ni content varies from a minimum of 5.1 up to 60 wt% although the vast majority of irons have between 5 and 12 wt%. The 10 largest irons, which each weigh more than 10 tons (e.g., Buchwald, 1975), are meter sized and most were large single crystals of taenite (fcc Fe–Ni) after solidification and at high temperatures in their parent bodies. The Widmanstätten pattern of the irons was revealed independently by Thomson and by von Widmanstätten in 1804 and 1808, respectively (see review by Clarke and Goldstein, 1978) when polished sample surfaces were etched by various chemicals (Fig. 1). This structure can be used to determine the cooling rate of each meteorite, as discussed in Section 4.

The Widmanstätten pattern develops as a two-phase intergrowth of kamacite (α-bcc, ferrite) and taenite (γ-fcc, austenite), and forms by nucleation and growth of kamacite from taenite during slow cooling of the parent body (Owen and Burns, 1939). The conventional explanation of Widmanstätten pattern formation, which is only partly correct but will suffice for this introduction, is based on the binary Fe–Ni equilibrium phase diagram (Yang et al., 1996). A meteorite of a given Fe–Ni content cools from the one-phase taenite (γ) region into the two-phase α + γ region, where kamacite (α) nucleates and grows as the meteorite continues to cool. Kamacite nucleates on the close packed octahedral {1 1 1} planes of taenite, forming a Widmanstätten pattern (Fig. 1). In three dimensions, kamacite grows as two-dimensional plates into the surrounding taenite. As cooling continues, kamacite grows at the expense of taenite and the Ni content of both kamacite and taenite increases.

The nature and scale of kamacite has led to a structural classification of iron meteorites. Hexahedrites (H) are one-phase kamacite with Ni of 5–6.5 wt% Ni. Octahedrites (O) have visible (to the eye) Widmanstätten...
patterns with kamacite widths of 0.2–3 mm and Ni concentrations of 6 to 12 wt% that are generally inversely related to kamacite width. Ataxites (D) have microscopic Widmanstätten patterns where kamacite is similarly oriented and <0.2 mm in width (Fig. 1d) and Ni contents of ~10 to >20 wt%.

The presence of P, S, and C in iron meteorites leads to the formation of precipitates of schreibersite \((\text{FeNi})_3\text{P}\) (Figs. 1a, c, d), troilite \((\text{FeS})\) (Figs. 1b, c), cohenite \((\text{FeNi})_3\text{C}\) (Fig. 1b) and other Fe–Ni carbides. The bulk concentrations of these and other elements are compiled by Buchwald (1975). P and C are very soluble in the liquid phase and at high temperatures, fcc taenite can accommodate ~1 wt%. In most cases, phosphides and carbides exsolve in the solid state during cooling. S is less soluble in taenite and sulfides usually form as the liquid metal solidifies. As discussed in Section 3, the concentration of these elements in the liquid, particularly S, has a major effect on the solidification behavior and the eventual distribution of major, minor, and trace elements in the meteorite. These elements tend to segregate to the liquid phase during solidification, lowering the melting point of the liquid and allowing for the formation of eutectic material at the lowest temperatures. As discussed in Section 4, the amount of P present in the metal greatly influences the nucleation temperature, the reaction process, and the diffusion rate of Ni as the Widmanstätten pattern develops. Silicates are present in some iron meteorites, mainly groups IAB, IIICD, and IIIE (Mittlefehldt et al., 1998) and their

Fig. 1. Polished and etched slices of iron meteorites showing Widmanstätten patterns. (a) Carlton – group IIICD, Of. Kamacite plates (blue) formed on the close-packed planes of the parent taenite phase. Plessite, a fine mixture of kamacite and tetrataenite, formed in the prior taenite regions between the kamacite plates. Schreibersite precipitates are observed in the centers of some of the kamacite plates. Scale – 1 cm along the bottom. (b) Canyon Diablo – group IAB, Ogg. Note cohenite precipitates in the centers of several kamacite plates. A large rounded sulfide occurs in the right-hand bottom corner. Scale – 10.5 cm along the bottom. (c) Mt. Edith – group IIIAB, Om. Narrow bands are kamacite, gray angular areas enclosed by these are plessite. Short angular bands surrounded by kamacite are schreibersite \((\text{Fe–Ni})_3\text{P}\); rounded black inclusions are troilite, \(\text{FeS}\). Scale – 19 cm along the bottom. (d) Tawallah Valley IVB, D. Kamacite plates form on the close packed planes of the parent taenite phase. The matrix is plessite, a fine mixture of kamacite and tetrataenite. Numerous schreibersite precipitates are observed in or near kamacite plates. (b and c: Courtesy of Smithsonian Institution). (For abbreviations, Of, Om, etc., see Table 1 footnotes.)
composition and significance are discussed in Sections 3 and 5.

### 2.2. Trace elements and chemical groups

Early measurements of Ga and Ge in iron meteorites showed that their concentrations fall into four distinct groups, labeled I–IV, in order of decreasing abundances (Goldberg et al., 1951; Lovering et al., 1957). Subsequently, Wasson (1967) and Wasson et al. (1998) analyzed ~700 iron meteorites, initially for Ni, Ga, Ge, and Ir and later for Cr, Co, Cu, As, Sb, W, Re, Pt, and Au, using instrumental neutron activation analysis. The original four Ga–Ge groups were resolved into 14 clusters labeled with additional letters A–G attached to the Roman numerals (Table 1). About 15% of the irons do not fit these groups and are labeled as ungrouped. Ga and Ge are the most useful elements to classify irons, because the range within most groups is only a factor of less than 2.5, whereas the total range between all groups varies by factors of 10³–4. The power of this classification to reveal correlations between numerous diverse properties including mineralogical, chemical and isotopic parameters shows that the members of each group are closely related and formed together in one parent body (Buchwald, 1975; Scott and Wasson, 1975; Haack and McCoy, 2004). Figs. 2a,b show the variation of Ge vs. Ni and Ir vs. Ni for the groups and ungrouped irons. The abundances of these elements in CI chondrites normalized to Ni are also shown.

Gallium and Ge vary between groups because they are the most volatile siderophile elements and the range increases with increasing volatility. In group IAB, element/Ni ratios for siderophiles are broadly comparable to CI chondritic values, but in groups IVA, IVB and the ungrouped irons, with similarly low concentrations of Ga and Ge, element/Ni ratios are depleted relative to CI chondrites and decrease in order of increasing volatility: Au, P and As, Cu and Ga, and Ge (Wasson, 1985; Scott, 1977a). Two possible explanations for the depletion of volatile elements have been proposed: in the solar nebula before accretion, or during major planetary impacts prior to metal solidification. Ga and Ge show small variations within groups because, unlike Ir (Fig. 2), they are not fractionated significantly between solid and liquid metal. Comparisons of the chemical trends within groups and their mineralogy suggests that there are two very different types of groups: (1) groups IIAB, IID, IIIAB, IVA, IVB, and possibly the smaller groups such as IC and IIIF, which are very largely free of silicates, have compositional trends that can be explained by chemical fractionation during solidification of molten iron; (2) groups IAB, IIICD, and IIE, with more abundant silicates, the chemical trends are very different and commonly much weaker (Scott, 1972). In the first type, chemical variations are largely consistent with fractional crystallization modeling using experimentally determined solid metal/liquid metal partition coefficients, whereas in the second, the trace element distribution

<table>
<thead>
<tr>
<th>Group</th>
<th>Number</th>
<th>Ni (wt%)</th>
<th>Structure</th>
<th>Example</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>IABc</td>
<td>~110</td>
<td>6–60</td>
<td>Og-D</td>
<td>Canyon Diablo</td>
<td>Choi et al. (1995)</td>
</tr>
<tr>
<td>IC</td>
<td>11</td>
<td>6–7</td>
<td>Ogg, Og</td>
<td>Bendego</td>
<td>Scott and Wasson (1976)</td>
</tr>
<tr>
<td>IIAB</td>
<td>78</td>
<td>5.3–6.5</td>
<td>H, Ogg</td>
<td>Coahuila</td>
<td>Wasson et al. (2007)</td>
</tr>
<tr>
<td>IIC</td>
<td>8</td>
<td>9.3–11.5</td>
<td>Opl</td>
<td>Ballinoo</td>
<td>Wasson (1969)</td>
</tr>
<tr>
<td>IID</td>
<td>21</td>
<td>9.6–11.1</td>
<td>Om, Of</td>
<td>Carbo</td>
<td>Wasson and Huber (2006)</td>
</tr>
<tr>
<td>IIE</td>
<td>17</td>
<td>7.2–9.5</td>
<td>Og-Off</td>
<td>Weekeroo Sta.</td>
<td>Wasson and Wang (1986)</td>
</tr>
<tr>
<td>IIF</td>
<td>6</td>
<td>11–14</td>
<td>Opl, D</td>
<td>Corowa</td>
<td>Kracher et al. (1980)</td>
</tr>
<tr>
<td>IIG</td>
<td>6</td>
<td>4.1–4.9</td>
<td>H</td>
<td>Bellsbank</td>
<td>Malvin et al. (1984)</td>
</tr>
<tr>
<td>IIAB</td>
<td>~220</td>
<td>7.1–10.6</td>
<td>Om</td>
<td>Cape York</td>
<td>Wasson (1999)</td>
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<tr>
<td>IIICDc</td>
<td>12</td>
<td>12–23d</td>
<td>Of-D</td>
<td>Tazewell</td>
<td>Choi et al. (1995)</td>
</tr>
<tr>
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<td>14</td>
<td>8.1–9.6</td>
<td>Og</td>
<td>Kokstad</td>
<td>Malvin et al. (1984)</td>
</tr>
<tr>
<td>IIIF</td>
<td>8</td>
<td>6.8–8.5</td>
<td>Og, Om</td>
<td>Clark Co.</td>
<td>Kracher et al. (1980)</td>
</tr>
<tr>
<td>IVA</td>
<td>61</td>
<td>7.5–12</td>
<td>Of</td>
<td>Gibeon</td>
<td>Wasson and Richardson (2001)</td>
</tr>
<tr>
<td>IVB</td>
<td>14</td>
<td>16–18</td>
<td>D</td>
<td>Hoba</td>
<td>Walker et al. (2008)</td>
</tr>
<tr>
<td>Ungroupedc</td>
<td>~110</td>
<td>6–35</td>
<td>Ogg-D</td>
<td>Butler</td>
<td>Scott (1979), Wasson (1990)</td>
</tr>
</tbody>
</table>

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*bStructure: H, hexahedrite; Ogg, Og, Om, Of, Off – coarsest, coarse, medium, fine, and finest octahedrites; Opl, plessitic octahedrite, D, ataxite. See Buchwald (1975, Table 26a) for definitions.

*cWasson and Kallemeyn (2002) define 120 irons from groups IAB and IIICD and ~35 ungrouped irons as a “group IAB complex”. IIIC and IIID irons are included in their scheme as sLM and sLH subgroups, respectively. The silicate-bearing groups IAB and IIICD did not form by fractional crystallization.

*dIrons with lower Ni concentrations are excluded.
cannot be modeled by fractional crystallization alone (Chabot and Jones, 2003; Chabot and Haack, 2006). These two types of iron meteorite groups were called “magmatic” and “non-magmatic” (Wasson, 1985). However, it is likely that metal in groups IAB, IIICD, and IIE was once molten, so this terminology, although widespread, is rather misleading. We refer to groups IAB, IIICD, and IIE as the “silicate-bearing groups”, and the “magmatic” groups are called the “fractionally crystallized groups”. Note, however, that there are two silicate-rich IVA irons and one silicate-bearing IIIAB iron. Fractionally crystallized iron meteorite groups are widely thought to be derived from the cores of asteroids that melted, whereas the silicate-bearing groups may come from bodies that were not heated sufficiently for metallic cores to have formed (Haack and McCoy, 2004). In this case, a group of iron meteorites from the core of a differentiated body should have cooled at virtually identical rates because of the high thermal conductivity of metal compared with mantle and crust materials. However, there is evidence in several fractionally crystallized groups for diverse cooling rates so these irons could not have cooled in an insulated metallic core. At least one group, IVA, appears to have formed in a metallic body that crystallized and cooled with virtually no silicate mantle.

The classification and number of parent bodies represented by the silicate-bearing groups is more uncertain as their chemical trends are ill-defined. Groups IAB and IIICD contain assemblages of graphite, troilite and silicates like those in chondrites and might have formed in the same body (McCoy et al., 1993; Benedix et al., 2000), whereas group IIE irons mostly contain differentiated silicates and lack graphite (Mittlefehldt et al., 1998). Wasson and Kallemeyn (2002) defined a “group IAB complex” consisting of 156 meteorites previously classified in groups IAB and IIICD plus a number of ungrouped irons. These were reorganized into a main group of 70 irons with 6.4–7.5 wt% Ni (previously called group IA), five subgroups (two being IIIC and IIID), 2 grouplets and 27 more distantly related irons. Although Wasson and Kallemeyn (2002) recognized that these irons could come from several bodies (as suggested by O isotopes), they argued that they formed in similar ways. We follow Krot et al. (2008) and Weisberg et al. (2006) and use the earlier definitions for groups IAB and IIICD.

3. Crystallization of iron meteorite groups

3.1. Introduction

By studying the chemical variations within a group of related irons, we can gain insight into the bulk composition of the metallic liquid from which they solidified since the relative concentrations of siderophile elements in the core reflects the bulk composition of the parent asteroid. In addition we can learn about the process by which the irons crystallized, and the environment on the parent asteroid in which they formed. The groups show surprisingly large differences in bulk compositions and their internal chemical variations, so that it is not possible to identify a typical
group of iron meteorites. Consequently, we explore the solidification of iron meteorites using a group-by-group approach. The bulk composition of a metallic liquid has a crucial influence on the trace element chemistry during crystallization and the evolution of the metallic melt. Thus, before examining individual iron meteorite groups, we briefly discuss the importance of bulk compositions as related to the evolution of iron meteorites.

3.2. Effects of bulk composition during crystallization

Experiments to measure how diverse elements partition between coexisting solid metal and liquid metal show that the partition coefficient (D) is greatly affected by the concentration of S, P, or C in the metallic liquid (Willis and Goldstein, 1982; Jones and Drake, 1983). Additionally, some elements are especially sensitive, e.g., the partition of Ni varies little with changing composition of the metallic liquid, while that for Ir can change by orders of magnitude during crystallization in the Fe–Ni–S system. During fractional crystallization of the metallic melt, the non-metals are largely excluded from the crystallizing solid metal and consequently enriched in the metallic liquid. Thus, during crystallization, the metallic liquid composition is continuing to evolve to higher non-metal contents, which in turn influences the chemical partitioning of elements between the crystallizing solid metal and the residual liquid metal. This changing metallic liquid composition must be taken into account when attempting to understand the behavior of elements during the crystallization of iron meteorites.

Fig. 3 shows experimentally determined solid metal/liquid metal partition coefficients for Au, Ge, Ir, and Ni in the Fe–Ni–S (Chabot et al., 2003; Chabot and Jones, 2003), Fe–Ni–P (Corrigan et al., 2006), and Fe–Ni–C (Chabot et al., 2006) systems. The non-metals S, P, and C can affect partitioning behavior during the crystallization of the metal. However, S can have a much larger influence than either P or C if all three elements are present in significant amounts (Fig. 3). For example, D(Ge) increases by two orders of magnitude from the S-free system to the Fe–FeS eutectic composition of 31 wt% S. In contrast, D(Ge) only increases by a factor of 3 from a P-free to a Fe–Fe3P eutectic composition (10 wt% P) and about a factor of 5 from the C-free to the Fe–C eutectic composition of 4.3 wt% C.

Unlike the binary Fe–S and Fe–P systems, the Fe–S–P system shows a large liquid immiscibility field (Raghavan, 1988). Thus, as fractional crystallization proceeds and the liquid is enriched in non-metals, the bulk composition may enter the immiscibility field, causing two immiscible molten phases to form, one S-rich, P-poor and one S-poor, and P-rich. A similar liquid immiscibility field exists in the Fe–S–C system (Raghavan, 1988). Chabot and Drake (2000) conducted experiments that suggested the liquid immiscibility field in the part of the Fe–S–P system that is relevant to the

![Fig. 3](image_url). Experimental determinations of solid metal/liquid metal partition coefficients (D) for Au, Ge, Ir, and Ni are shown in (a) Fe–Ni–S, (b) Fe–Ni–P, and (c) Fe–Ni–C systems. References for the data are in the sources shown on the figure. The addition of non-metals to the metallic liquid can cause large changes in the partition coefficients, which are crucial to understanding chemical variations in iron meteorite groups (Corrigan et al., 2009).
crystallization of iron meteorites is actually smaller than shown by Raghavan (1988). Yet Chabot and Drake (2000) still concluded that some iron meteorite groups, despite the smaller liquid immiscibility field, might still have encountered liquid immiscibility in the Fe–S–P system. Thus, it is important to understand the bulk non-metal composition of the iron meteorite parent melts and to assess if immiscible liquids may have formed, especially during the later stages of fractional crystallization.

The bulk S content of the parent melt of an iron meteorite group cannot be inferred from measurements of the bulk S content of iron meteorites themselves, sulfur is virtually insoluble in solid metal, and thus is found only in inhomogeneously distributed troilite nodules that likely represent melt trapped during the crystallization process. Instead, the S concentrations of the melt have to be inferred by studying distributions of other elements most sensitive to the amount of S present in the liquid during crystallization.

Fig. 4a shows calculated fractional crystallization trends for Ir vs. Au using the partitioning values of Fig. 3 and for different bulk S concentrations. Traditionally, element trends for iron meteorites were plotted vs. Ni content, due in part to the much higher Ni concentrations than other elements, making Ni contents easier to measure. However, D(Ni) has a value close to unity at all S concentrations (Fig. 3), resulting in limited Ni variations during crystallization of iron meteorite groups. Therefore, Ni is a poor choice for assessing the success of crystallization models and Au is commonly used instead (Haack and Scott, 1993; Wasson, 1999; Wasson and Richardson, 2001).

For higher bulk S concentrations, the Ir vs. Au trend becomes steeper and shows a larger overall fractionation of Ir (Fig. 4). The Ir vs. Au trends for five iron meteorite groups are also shown in Fig. 4, plotted on the same overall scale as the models in Fig. 4a. Fig. 5 shows similar model and iron meteorite plots for Ge vs. Au. As shown by the models in Figs. 4a and 5a, simple fractional crystallization can produce large fractionations in Ir and distinctly non-linear Ge trends, both of which are sensitive to the bulk S concentration. Ir and Ge are thus good choices for deducing constraints on the crystallization history of iron meteorites. The chemical trends for the five groups (Figs. 4 and 5) suggest a wide range of bulk S compositions from essentially S-free to about 18 wt% S. The estimated S

![Fig. 4. Logarithmic plots of Ir vs. Au. (a) The solid composition during simple fractional crystallization of Fe–Ni liquids with 3–18 wt% S; (b–f) data for groups IIAB, IIIAB, IVA, IID, and IVB. All graphs are scaled with a factor of 20 on the Au x-axis and a factor of 10,000 on the Ir y-axis, to enable comparisons between the calculated curves and the different iron meteorite groups. Simple fractional crystallization models were run until the Fe–FeS eutectic composition of 31 wt% S was reached. On (d–f), model curves have tick marks (x-marks) that correspond to every 10% of crystallization. Sources for the iron meteorite data: IIAB (Wasson et al., 2007), IIIAB (Wasson, 1999), IVA (Wasson and Richardson, 2001), IID (Wasson and Huber, 2006), and IVB (Walker et al., 2008).]
values are dependent on the crystallization model utilized.

3.3. Crystallization of the chemical groups

Different types of crystallization models have been used to gain insight into the evolution of iron meteorite groups. Some of the earliest attempts to model the crystallization of iron meteorites used best-fit curves to experimentally determined solid metal/liquid metal partition coefficients in simple fractional crystallization calculations (e.g., Jones and Drake, 1983). Subsequent work, noting the shortcomings of simple fractional crystallization, added complexities to model additional effects that might be caused by assimilation of additional metal to the core during crystallization (Malvin, 1988), dendritic crystallization of the core (Haack and Scott, 1993), the onset of liquid immiscibility (Ullf-Møller, 1998), and incomplete mixing in the molten core (Chabot and Drake, 1999). Mathematically, these models resembled the simple fractional crystallization calculations, using fits to experimental partition coefficients, but with appropriate modifications. More recently, crystallization models have been developed that are mixtures of fractionally crystallizing solid and liquid trapped during the crystallization process (e.g., Wasson, 1999; Wasson and Richardson, 2001; Wasson and Huber, 2006; Wasson et al., 2007). The trapped melt model offers an attractive explanation for the scatter within iron meteorite groups. However, in contrast to previous models, the partition coefficients used in these trapped melt models are not set by best-fits to the experimental values but, rather, are determined using estimates of the amount of trapped melt in individual iron meteorites; the partitioning values determined by this method do not always agree with the experimental values (for reviews, see Chabot and Haack, 2006).

3.3.1. Crystallization of the IIIAB group

The crystallization history of the IIIAB group has been investigated by many workers because this is the largest iron meteorite group, its elemental trends are well defined, and the crystallization trend appears to be well sampled (e.g., Wasson, 1999). Using a simple fractional crystallization model, based on parameterizations of experimentally determined solid metal/liquid metal partition coefficients, the IIIAB Ir vs. Au and Ge vs. Au trends are fairly well matched by a bulk S content for the IIIAB parent melt of about 12 wt%. This model can explain the three orders of magnitude variation in Ir.
in IIIAB (Fig. 4c), and the curved Ge trend (Fig. 5c), which arises due to changes in D(Ge) with changing S content during fractional crystallization. Thus, to first order, the IIIAB group seems to represent a metallic melt that began with about 12 wt% S and experienced simple fractional crystallization as the melt solidified.

More complex models have addressed the shortcomings of the simple model, which misses the high-Au, low-Ir, later crystallizing portion of the IIIAB trend (Fig. 4c). Models involving liquid immiscibility in the Fe–S–P system (Ulff-Møller, 1998) or incomplete mixing in an inwardly crystallizing core (Chabot and Drake, 1999) matched the low-Ir portion of the IIIAB trend. There is also a considerable amount of scatter around the general IIIAB trend, especially for Ir (Fig. 4c), which is reflected in the two-fold variations of Ir in the Cape York shower (Esbensen et al., 1982). These local variations may result from inward dendritic crystallization of the core (Haack and Scott, 1993) or trapped melt (Wasson, 1999), the latter using assumed partition coefficients, suggesting a much lower initial S content for the IIIAB bulk composition of 2.4 wt% S.

### 3.3.2. Crystallization of the IVB group

Though there are only 12 well-analyzed members of the IVB group, their chemical data suggest a simple crystallization history (Rasmussen et al., 1984; Campbell and Humayun, 2005; Walker et al., 2008). The Ir vs. Au (Fig. 4f) and Ge vs. Au (Fig. 5f) IVB trends are both well matched by simple fractional crystallization in a S-free system. Campbell and Humayun (2005) fit the IVB trends for a number of elements and calculated partition coefficients that are in good agreement with the experimentally determined ones. Small troilite nodules are present, but their abundance suggests that these irons have the lowest S concentrations of any group (0.02–0.05 wt% S; Buchwald, 1975, Table 3). Chabot (2004) demonstrated that crystallization trends were very similar for S contents from 0 to 2 wt% and that the IVB Ge vs. Au and Ir vs. Au trends were equally well fit with a S content of 2 wt% as in a S-free system. Overall, the crystallization of the IVB group appears to be consistent in every aspect with simple fractional crystallization of a nearly S-free metallic melt. The well-behaved nature of the group may suggest that the crystallization process is simpler in general for a system essentially free of non-metals such as S. However, the sub-chondritic Re/Os and Pt/Os inferred from fractional crystallization models remain a mystery (Walker et al., 2008).

### 3.3.3. Crystallization of the IIB group

Figs. 4b and 5b show that the IIB Ir and Ge trends are well defined (Wasson et al., 2007) and generally consistent with simple fractional crystallization from a metallic melt with an initial S content of about 18 wt%. Given this high S content, it seems likely that liquid immiscibility in the Fe–S–P system would have been encountered during the fractional crystallization (Chabot and Drake, 1999). Having the metallic liquid separate into two immiscible liquids, one S-rich and one P-rich, would affect the elemental crystallization trends (Ulff-Møller, 1998). However, the first-order simple fractional crystallization model does quite well at fitting the IIB trends and no discontinuity in either the Ge or Ir trend is observed (Figs. 4b and 5b). Additionally, the IIB trends actually show considerably less scatter than observed for the IIIAB group. Having a bulk S concentration of 18 wt% also raises the question of where is that S now, since less than 45% of the melt will crystallize before the Fe–FeS eutectic composition of 31 wt% S is reached by the liquid. The lack of S-rich meteorites may reflect the friable nature of such materials, causing them to not survive the journey to Earth’s surface (Kracher and Wasson, 1982). The trapped melt model of Wasson et al. (2007), using assumed rather than experimentally determined partition coefficients, suggests a much lower bulk S concentration of 7.5 wt% and is able to explain the low-Ir members not reproduced by simple fractional crystallization on Fig. 4b. However, even with an initial S content of 7.5 wt%, Wasson et al. (2007) concluded that the IIB melt experienced liquid immiscibility during crystallization.

### 3.3.4. Crystallization of the IVA group

The elemental trends in group IVA (e.g., Wasson and Richardson, 2001) are less consistent with simple fractional crystallization than trends in groups IIIAB, IVB, and IIB. The Ir vs. Au trend appears to be formed by fractional crystallization of a metallic melt with a bulk S content of 3 wt% (Fig. 4d). However, the Ge vs. Au trend is not matched by fractional crystallization with 3 wt% S but, rather, by a significantly higher S content of 9 wt% (Fig. 5d). If the Ge and Ir trends were established during the simple fractional crystallization process, both elements should exhibit partitioning behavior consistent with the single S content of the bulk metallic liquid. The discrepancy between the Ge–Au and Ir–Au trends suggests that simple fractional crystallization was modified significantly by some other process. Using an initial S content of 0.4 wt%, the trapped melt model of Wasson and Richardson (2001) had success at matching the Ir–Au IVA trend but has not been applied to the Ge–Au trend.

### 3.3.5. Crystallization of the IID group

Although a small group with 21 members, group IID shows well defined and interesting chemical trends (Wasson and Huber, 2006). As in the IVA group, the Ir (Fig. 4e) and Ge (Fig. 5e) trends suggest different bulk S contents when fit by simple fractional crystallization. As with the IVA group, the inferred initial bulk S content consistent with the Ge trend (12 wt%) is about
6 wt% higher than the S content consistent with the Ir trend (6 wt%). However, due to the small number of IID members, only two meteorites are inconsistent with the Ge trend as modeled with 6 wt% S. Overall, the IID group, like the IVA group, appears to have solidified in a process that was more complicated than simple fractional crystallization. The trapped melt model of Wasson and Huber (2006) suggests an initial S content of 0.7 wt% and formation by crystallization of a P-rich lower liquid in a stratified, two-layer core. The trapped melt model nicely reproduces the Ir–Au IID trend but has not been used to model the IID trends of Ge–Au.

3.3.6. Crystallization of the IAB group

The IAB group is a “silicate-bearing group” rather than a “fractionally crystallized group.” Fig. 6 plots the Ir–Au and Ge–Au trends, and also included are IIICD and other irons that were classified as belonging to the larger “IAB complex” of Wasson and Kallemeyn (2002). By comparing these trends to those of Figs. 4 and 5, it is clear that the IAB group shows considerable scatter in the compositional values of its members in comparison to the previously discussed groups. Despite these compositional variations, it is still interesting to examine if any of the trends are consistent with simple fractional crystallization. Fig. 6 shows that many of the IAB group irons, but not the lower Ge members, are generally consistent with simple fractional crystallization of a metallic melt with a very high bulk S content.

The formation and evolution of the IAB group continues to be debated. Wasson and Kallemeyn (2002) argued that the main group was not formed by fractional crystallization but, rather, involved crystal segregation with solid and melt essentially in equilibrium and multiple impact induced melting events to create the different subgroups. Others have suggested fractional crystallization of melts in parent bodies that were disrupted during the crystallization process, incomplete differentiation of the parent asteroid, partial melting followed by mixing events, the crystallization of S-rich cores, or a combination of multiple processes (Kracher, 1985; McCoy et al., 1993; Benedix et al., 2000; Takeda et al., 2000). The common presence of silicate inclusions is an important constraint on the history of these meteorites. Overall, there is agreement that the IAB iron meteorites experienced a crystallization history and environment substantially different from the “fractionally crystallized” groups and from just simple fractional crystallization of an undisturbed metallic melt.

4. Cooling rates

4.1. Formation of the Widmanstätten pattern

4.1.1. Binary Fe–Ni

The conventional explanation for the formation of the Widmanstätten pattern is based on the binary Fe–Ni...
equilibrium phase diagram (Fig. 7, Yang et al., 1996) in which a meteorite cools from the one-phase taenite (g) region of the diagram into the two-phase \( \alpha + \gamma \) region where kamacite (\( \alpha \)) nucleates and grows. However, the Widmanstätten pattern does not form by this process.

Experimental evidence shows that for Fe–Ni alloys, the g-solid solution transforms to a supersaturated \( \alpha \)-solid solution, \( \alpha_2 \), martensite during cooling (Allen and Earley, 1950). No composition change takes place. Only during reheating from low temperatures does the supersaturated solid solution \( \alpha_2 \) decompose into \( \alpha + \gamma \) (kamacite + taenite), with equilibrium compositions given by the \( \alpha + \gamma \) tie line at the reheating temperature. \( T_c^\gamma \) is the Curie temperature of the \( \gamma \) phase. \( T_c^\gamma \) is the ordering temperature of FeNi, \( \gamma'' \).

Fig. 7. Fe–Ni binary phase diagram (Yang et al., 1996). \( \alpha \) is a low-Ni bcc phase, \( \gamma \) a high-Ni fcc phase, \( \gamma_1 \) a low-Ni paramagnetic fcc phase, \( \gamma_2 \) a high-Ni ferromagnetic fcc phase, \( \gamma' \) is ordered Ni,Fe, \( \gamma'' \) is ordered FeNi–tetrataenite, and \( M_s \) is the martensite starting temperature. \( T_c^\gamma \) is the Curie temperature of the \( \gamma \) phase.

4.1.2. Effect of P and the Fe–Ni–P phase diagram

In a study of the effect of P on the formation of the Widmanstätten pattern in iron meteorites, Goldstein and Doan (1972) produced Widmanstätten kamacite in the intergranular or matrix region of the original taenite with an Fe–Ni alloy containing as little as 0.1 wt% P. Fig. 9 shows the microstructure of a 9.8 wt% Ni, 0.3 wt% P alloy slowly cooled from the all taenite field to 650 °C. A Widmanstätten pattern of kamacite plates is observed in the intragranular (matrix), which was fcc taenite at higher temperatures. In this alloy kamacite formed by the reaction path \( \gamma \rightarrow \gamma + \text{Ph} \rightarrow \alpha + \gamma + \text{Ph} \), where Ph is schreibersite, (Fe–Ni)\(_3\)P. As suggested by Narayan and Goldstein (1984a), the nucleation of intragranular kamacite in low P alloys does not begin...
when the alloy enters the two-phase $\alpha + \gamma$ field, but starts only when the alloy enters the three-phase $\alpha + \gamma + \text{Ph}$ field. It is clear that P has a very important role in the nucleation of the Widmanstätten pattern in iron meteorites and also in metal particles of stony-irons containing P (e.g., pallasites, mesosiderites).

### 4.1.3. Nucleation of the Widmanstätten pattern in high and low P meteorites

The ternary Fe–Ni–P phase diagram has been determined experimentally to temperatures below 500 °C (Doan and Goldstein, 1970; Romig and Goldstein, 1980). The formation of the Widmanstätten pattern is determined by the bulk Ni and P content of the meteorite and by its path through the ternary Fe–Ni–P phase diagram as the meteorite cools from the taenite field at high temperatures. Depending on the Ni and P content, the kamacite nucleation temperature can be determined from either the $\gamma$ boundary, the $\alpha$ boundary, or the martensite start temperature, $M_s$, where $\alpha_2$–martensite forms (Yang and Goldstein, 2005). As an example, Fig. 10 shows an iso-Ni concentration section at 8.5 wt% Ni from the Fe–Ni–P diagram (Doan and Goldstein, 1970). Alloy “a” is a high P meteorite as it passes first through the $\gamma + \text{Ph}$ phase field before $\alpha$-kamacite nucleates. The mechanism for Widmanstätten pattern formation is: $\gamma \rightarrow \gamma + \text{Ph} \rightarrow \alpha + \gamma + \text{Ph}$ (Mechanism II, Yang and Goldstein, 2005). Fig. 9 illustrates a Widmanstätten pattern, which formed by Mechanism II in an experimental alloy.

Narayan and Goldstein (1984a) determined experimentally that the $\alpha$ phase does not nucleate when the P content is too low to enter the three-phase $\alpha + \gamma + \text{Ph}$ field via the $\gamma + \text{Ph}$ phase field. The $\alpha$ phase nucleates only when $\gamma$ is saturated in P and enters the $\alpha + \gamma + \text{Ph}$ field upon cooling. The reaction path for low P meteorites is shown for alloys “b” and “c” in Fig. 10. For a meteorite which cools below the $(\alpha + \gamma)/(\alpha + \gamma + \text{Ph})$ boundary before the Ms temperature is reached (alloy “b” in Fig. 10), the reaction for forming the Widmanstätten pattern is $\gamma \rightarrow \alpha_2 + \gamma \rightarrow \alpha + \gamma + \text{Ph}$. The designation $(\alpha + \gamma)$ indicates that the alloy passes through the $\alpha + \gamma$ two-phase field but kamacite nucleation is suppressed. This reaction scheme is called Mechanism III (Yang and Goldstein, 2005). For a meteorite which cools below Ms before it reaches the $(\alpha + \gamma)/(\alpha + \gamma + \text{Ph})$ phase boundary (alloy “c” in
Fig. 10), the reaction for forming the Widmanstätten pattern is $\gamma \rightarrow \alpha_2 + \gamma \rightarrow \alpha + \gamma$, Mechanism V (Yang and Goldstein, 2005). The $\alpha_2$ martensite starts to form below Ms, the martensite start temperature (Fig. 7). As cooling proceeds, newly formed martensite begins to decompose into $\alpha + \gamma$. Some of the high-temperature $\gamma$ phase may also be retained.

The bulk Ni and P contents of the meteorite determine which of the three reactions control the formation of the Widmanstätten pattern. Fig. 11 shows the Ni and P contents of chemical groups IIIAB and IVA as well as the Ni–P boundaries for the region of applicability of mechanism II for high P irons and of mechanisms III and V for low P irons using the Fe–Ni–P phase diagram. This diagram shows that the Widmanstätten structure in the high P members of group IIIAB forms by mechanism II, $\gamma \rightarrow \gamma + \text{Ph} \rightarrow \alpha + \gamma + \text{Ph}$. Mechanism III represents the reaction $\gamma \rightarrow (\alpha + \gamma) \rightarrow \alpha + \gamma + \text{Ph}$, and Mechanism V represents the reaction $\gamma \rightarrow \alpha_2 + \gamma \rightarrow \alpha + \gamma$.

4.1.4. Growth of the Widmanstätten pattern

The formation of the Widmanstätten pattern in iron meteorites is controlled initially by nucleation as discussed in Section 4.1.3 and then by kamacite growth.
in the surrounding taenite as temperature decreases. Experiments have been performed to nucleate and grow intragranular \( \alpha - \) kamacite as a function of cooling time and temperature in Fe–Ni–P alloys (Narayan and Goldstein, 1984a, b). Fig. 12a shows an \( \alpha \)–kamacite crystal that nucleated and grew in taenite and Fig. 12b shows the Ni concentration profile measured across the \( \alpha \)–kamacite/\( \gamma \)–taenite interface of the kamacite crystal. Narayan and Goldstein (1984b) observed that growth kinetics are dictated by the bulk diffusion of Ni in taenite and equilibrium partitioning of Ni and P between kamacite and taenite takes place at the \( \alpha \)/\( \gamma \) interface. A numerical model to simulate growth of this kamacite crystal was developed based on these observations. The solid line on Fig. 12b is the profile predicted by the numerical model and forms an excellent fit with the measured data. The numerical model used to simulate Ni redistribution and kamacite growth of the experimental alloys is the same model used to simulate the formation of the Widmanstätten pattern in iron meteorites. Although the numerical model used for Widmanstätten pattern growth extrapolates Ni distributions for a process that takes millions of years, it has validity based on its successful application to experimental alloys.

4.2. Metallographic cooling rates

4.2.1. Cooling rate model

The metallographic cooling rate model simulates growth of the Widmanstätten pattern and distribution of Ni content in kamacite and taenite phases during growth. The model considers five major factors: (1) mechanism for Widmanstätten pattern formation, (2) kamacite nucleation temperature, (3) effect of impingement, (4) Fe–Ni and Fe–Ni–P phase diagrams, and (5) interdiffusion coefficients.

Depending on the bulk Ni and P content of a meteorite, the reaction that controlled Widmanstätten formation and the appropriate nucleation temperature for the Widmanstätten pattern can be determined (Fig. 11). Impingement is caused by overlapping Ni gradients from the growth of adjacent kamacite plates spaced apart by a distance \( L \). The effect of impingement is to restrict the growth of kamacite and increase the amount of Ni in taenite during formation of the Widmanstätten pattern (Saikumar and Goldstein, 1988). The Fe–Ni and Fe–Ni–P phase diagrams can be used to obtain the equilibrium phase compositions of kamacite and taenite for the P-bearing metal phases during the cooling process. The interdiffusion coefficients of Ni in kamacite and taenite control the rate at which Ni can be transferred between the two phases. P has the effect of increasing the diffusion rate of Ni in taenite significantly (Dean and Goldstein, 1986; Yang and Goldstein, 2006).

Numerical models have been developed which simulate diffusion controlled kamacite growth in taenite (Widmanstätten pattern development) in the Fe–Ni–P phase system. A constant cooling rate is usually assumed for the temperature range in which the Widmanstätten pattern forms. The model includes the applicable nucleation mechanisms (II, III, and V) for Widmanstätten pattern formation and the kamacite nucleation temperature for the bulk Ni and P content of a specific iron meteorite. The model also includes the equilibrium tie lines in the Fe–Ni and Fe–Ni–P phase diagrams and the binary and ternary diffusion coefficients as a function of temperature and composition. Impingement is considered by assuming or measuring the distance (\( L \)) between adjacent kamacite plates. As \( L \) decreases, overlapping Ni gradients in the taenite between two kamacite plates are calculated. The Ni profile in kamacite and taenite for a specific cooling rate and bulk meteorite Ni and P content is the output of the computer model. Fig. 17 shows calculated Ni profiles for IVA irons Bishop Canyon and Duchesne, each with a different cooling rate and impingement distance. [For detailed discussions, see Hopfe and Goldstein (2001), and Yang and Goldstein (2006)].

4.2.2. Compositional measurements

Ni, Fe, Co, and P compositions are measured across kamacite–taenite–kamacite areas using the electron probe microanalyzer (EPMA) on properly prepared iron meteorite samples (Fig. 13). A typical M shaped Ni profile is obtained across each taenite band. Measurements of the central taenite Ni content and the corresponding taenite half-width are also made (Fig. 13). The half-width of the taenite band can only be measured after the kamacite/taenite band orientation with respect to the analyzed surface is obtained (Yang and Goldstein, 2006).

4.2.3. Methods for the measurement of metallographic cooling rates

A variety of metallographic methods have been used to determine the cooling rates of the Widmanstätten pattern in iron meteorites. The taenite profile matching and the taenite central Ni content methods are the most accurate. In the taenite profile-matching method, the Ni content vs. distance profile in taenite is computed for several cooling rates from the cooling rate model as a function of bulk Ni and P content and taenite half-width. The calculated Ni composition profile in taenite (Ni vs. distance) is then plotted and compared with Ni composition profiles measured for a given meteorite with the EPMA (Goldstein and Ogilvie, 1965). For each taenite band the orientation of the kamacite plates must be measured in order to obtain accurate distances.
traversed by the EPMA. Fig. 13 shows measured and calculated Ni composition profiles for the Bishop Canyon and Duchesne IVA irons that have different compositions and cooling rates. The measured cooling rate of Bishop Canyon is 3000 °C/Myr, while that of Duchesne is 200 °C/Myr. To obtain a statistically accurate cooling rate for a meteorite, measured and calculated Ni profiles from a minimum of three kamacite bands need to be compared.

In the taenite central Ni content method, the Ni content in the center of taenite is computed for several cooling rates from the cooling rate model as a function of bulk Ni and P content and taenite half-width. The calculated central Ni content is then plotted vs. the half-width of the taenite for several cooling rates (Wood, 1964). Ni contents in the center of taenite phases of various half-widths are measured for a given meteorite with the EPMA. These data are plotted on the same graph as the computer simulated iso-cooling curves of central Ni content vs. taenite half-width. The measured data should fall along one of the computed iso-cooling rate curves (Wood, 1964). A variation of this cooling rate method was developed by Rasmussen (1981), who measured the local bulk Ni and bulk P contents for each taenite lamella. Fig. 14 shows computed iso-cooling rate curves and measured taenite central Ni contents for the Bishop Canyon and Duchesne IVA irons. The data follow iso-cooling rate curves from which a cooling rate can be measured. A cooling rate of 2500 °C/Myr with a 2σ uncertainty range of 1.3, 1920–3250 °C/Myr, for Bishop Canyon and a cooling rate of 100 °C/Myr with a 2σ uncertainty range of 2.9, 30–290 °C/Myr, for Duchesne were measured (Yang et al., 2007). These values compare well with those obtained for these meteorites from the profile-matching method (Fig. 13).
Central Ni content measurements of about 10 taenite bands are needed to obtain a statistically accurate cooling rate. For each band the orientation of the kamacite plates must be measured to determine accurate taenite half-widths. The measured data for the taenite central Ni content method is usually easier to obtain than for the taenite profile-matching method. Therefore, the taenite central Ni content cooling rate method is usually employed.

Other metallographic cooling rate methods (kamacite bandwidth, taenite maximum Ni, and kamacite central Ni content) have been developed, although they have limited applicability. The kamacite bandwidth method of Short and Goldstein (1967) relates the width of the Widmanstätten kamacite to the cooling rate. The method cannot be employed since the effects of impingement are not considered and a constant amount of undercooling before nucleation of the Widmanstätten pattern is assumed (Saikumar and Goldstein, 1988). The taenite maximum Ni method of Short and Goldstein (1967) relates the maximum Ni content in the taenite next to the kamacite/taenite border measured with the EPMA with the cooling rate. The method has fallen out of favor because it is sensitive to impingement effects and to the exact placement of the electron beam close to the kamacite/taenite interface. A correlation between the measured and calculated Ni content in the center of a kamacite band for a given cooling rate has been observed (Powell, 1969; Haack et al., 1996a). Unfortunately the uncertainty in the detailed shape of the $\alpha/(\alpha + \gamma)$ solvus line for the Fe–Ni–P phase diagram leads to errors in the predicted Ni variation in the kamacite phase as a function of cooling rate. This method is also relatively insensitive to cooling rate variations (Hopfe and Goldstein, 2001).

The hexahedrites, which have Ni contents of 5–6.5 wt%, do not form a Widmanstätten pattern on cooling. These meteorites contain sufficiently high P so that it is possible to obtain cooling rates by measuring Ni gradients across kamacite–phosphide–kamacite regions with the EPMA. A comparison is made using these data with computer simulated Ni profiles of phosphide growth in the Fe–Ni–P system as a function of cooling rate (Randich and Goldstein, 1978). For each phosphide, the orientation of the plates must be measured in order to obtain accurate distances to use in comparing measured and simulated Ni growth profiles.

4.3. Measured cooling rates

Since the early studies of Wood (1964) and Goldstein and Ogilvie (1965), metallographic cooling rates have been measured for a large number of irons. The computer simulation methods have become more accurate as the major effect of P on the nucleation and growth of the Widmanstätten pattern has been recognized. For example, the measured cooling rates of IVA irons Bishop Canyon and Duchesne have increased over the last 40 years by a factor of 10–50 (Goldstein and Short, 1967; Yang et al., 2008a) as the accuracy of the method has improved. The latest cooling rate measurements for the IIIAB and IVA chemical groups (Yang and Goldstein, 2006; Yang et al., 2007, 2008a) are the most accurate to date, as all five major factors for the measurement of cooling rates are considered in the simulation model and kamacite/taenite orientations are measured. Potential inaccuracies in each of these factors are discussed for the IIIAB irons by Yang and Goldstein (2006).

To establish whether there is any variation of cooling rate within a given chemical group, it is important to minimize the uncertainty in the cooling rate measurement of each meteorite and to evaluate their accuracy. The major uncertainty is due to measured deviations from the calculated iso-cooling curve for the taenite central Ni content method. For example, each data point for Bishop Canyon or Duchesne in Fig. 14 represents one measurement from a single taenite band. The deviation from the average iso-cooling curve, the cooling rate of the meteorite, gives the uncertainty in the cooling rate. Recent measurements list the cooling rate measurement along with the $2\sigma$ uncertainty in the cooling rate determination, which range from a factor of 1.3 for Bishop Canyon to 3.0 for Duchesne, with an average of 2.0 for 24 IIIAB and IVA irons (Yang and Goldstein, 2006; Yang et al., 2007, 2008a). Clearly, to establish cooling rate trends in chemical groups, careful attention must be paid to determining errors in the measurement of each individual cooling rate. At this time it is not possible to determine if cooling rates vary within a chemical group, unless the individual cooling rates vary by more than a factor of 2.

Measured variations in cooling rates for a specific chemical group that exceed the statistical uncertainty in the cooling rate of 2.0 provide strong evidence that the parent asteroid does not have a conventional metal core surrounded by a silicate mantle. The highest quality cooling rate measurements have been obtained for groups IIIAB and IVA (Fig. 15), particularly studies in which the orientation of kamacite/taenite interfaces have been measured (Yang and Goldstein, 2006; Yang et al., 2007, 2008a). Cooling rates vary from 56 to 338 °C/Myr for the IIIA irons and from 100 to 6600 °C/Myr for the IVA irons, variations of 6 and 66, respectively. In both cases, the cooling rate ranges exceed those expected for samples from a core enclosed by a silicate mantle, as such samples should have indistinguishable cooling rates.

Table 2 summarizes the measured cooling rate data for chemical groups IIIAB, IVA, IAB, IIICD
(a subgroup of the group IAB complex, Wasson and Kallemeyn, 2002), IIAB, and IVB. Much of the older cooling rate data (chemical groups IAB, IIICD, IVB) were obtained using the kamacite bandwidth method (Short and Goldstein, 1967). The kamacite bandwidth method cannot be used as discussed in the previous

Fig. 15. Cooling rate measurements for iron meteorites in chemical groups IIIAB and IVA (Yang and Goldstein, 2006; Yang et al., 2007). Variations of a factor of 6 and 66 are observed in Groups IIIAB and IVAB, respectively. The error bar for each meteorite represents the 2σ uncertainty range.

Table 2. Cooling rate variations in iron meteorite chemical groups.

<table>
<thead>
<tr>
<th>Group</th>
<th>Cooling rate variation (°C/Myr)</th>
<th>Authors</th>
<th>Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>IAB</td>
<td>2–3</td>
<td>Goldstein and Short (1967)</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>63–980</td>
<td>Rasmussen (1989)</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>25–70</td>
<td>Herpfer et al. (1994)</td>
<td>2</td>
</tr>
<tr>
<td>IIICD</td>
<td>87–480</td>
<td>Rasmussen (1989)</td>
<td>1</td>
</tr>
<tr>
<td>IIAB</td>
<td>0.8–10</td>
<td>Randich and Goldstein (1978)</td>
<td>3</td>
</tr>
<tr>
<td>IIIAB</td>
<td>1.0–10</td>
<td>Goldstein and Short (1967)</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>21–185</td>
<td>Rasmussen (1989)</td>
<td>2</td>
</tr>
<tr>
<td>IVA</td>
<td>7–90</td>
<td>Goldstein and Short (1967)</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>2–96</td>
<td>Rasmussen (1982)</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>19–3400</td>
<td>Rasmussen et al. (1995)</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>100–6600</td>
<td>Yang et al. (2008a)</td>
<td>2</td>
</tr>
<tr>
<td>IVB</td>
<td>2–25</td>
<td>Goldstein and Short (1967)</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>110–450</td>
<td>Rasmussen et al. (1984)</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>1400–17,000</td>
<td>Rasmussen (1989)</td>
<td>1</td>
</tr>
</tbody>
</table>

2. Taenite central Ni content method (includes effects of P on phase diagram and on diffusion coefficients for Ni in taenite).
3. Phosphide growth simulation.
section, since the effects of impingement are not considered and a constant amount of undercooling before nucleation of the Widmanstätten pattern is assumed. It is possible that the IVB cooling rates obtained by the kamacite bandwidth method may be useful, but only if the orientation of the bands with respect to the polished surface are measured so that accurate bandwidths are obtained. From the best-quality data given in Table 2, it appears that there are significant, $2\sigma > 2$, variations in cooling rates not only for IIIAB and IVA irons but possibly for IIAB and IVB irons.

Possible cooling rate variations for chemical groups IIAB and IVB (Table 2) need to be re-investigated in order to learn more about the size, silicate mantle, etc. of their parent asteroidal bodies. The number of measured cooling rates for Group IAB (Herpfer et al., 1994) is limited and the cooling rates for subgroup IIICD of the group IAB complex (Table 2) need to be remeasured. The effect of C content on the IAB and IIICD irons may also have an effect on phase boundaries and interdiffusion coefficients. It is important to obtain cooling rates for the IAB irons as this is the second largest chemical group and is silicate rich. This chemical group experienced a crystallization history different from the “fractionally crystallized” groups such as IIIAB, IVB, and IVA. Measured cooling rates will help in understanding how silicates were incorporated in the parental melt, the nature of the mantle, and the nature of the solidification process in the parent asteroidal body.

4.4. Cooling rates obtained from the cloudy zone structure

Although most studies of the thermal history of metallic Fe–Ni grains have focused on the metallographic cooling rates applicable at $\sim 650–400$ °C, relative cooling rates at lower temperatures can also be obtained by analyzing the microstructure of taenite rims. During cooling to low temperatures ($< 400$ °C), several phase transformations take place within the Ni gradient in the taenite phase (Fig. 13). Fig. 16a shows an optical micrograph of the microstructure of decomposed taenite near the kamacite–taenite boundary of the Dayton IIICD iron meteorite (Yang et al., 1997a). (b) TEM bright field image of a kamacite/decomposed taenite region in the Tazewell, IIICD iron meteorite (Reuter et al., 1988). K is kamacite, CT1 is the outer taenite rim, CZ is the cloudy zone region, CT2 is an unetched part of the cloudy zone called clear taenite 2, and M is finely decomposed martensite (high-Ni plessite). Fig. 16b displays a bright field transmission electron microscope image of the CT1/CZ microstructure in a thin section of the Tazewell IIICD iron at much higher magnification. The clear taenite zone, CT1, contains FeNi, $\gamma_2$, which is sometimes ordered as tetrataenite. The cloudy zone, CZ, is two phase with a high-Ni fcc FeNi island phase surrounded with a low-Ni honeycomb phase, which is usually bcc martensite (Reuter et al., 1988). Fig. 17a shows Fe and Ni scanning X-ray maps of a $2 \times 2 \mu$m kamacite-clear taenite–cloudy zone interface region in a thin section of the Carlton IIICD iron meteorite. A two-phase structure of the cloudy zone and the chemical composition of the island and honeycomb phases are observed. Fig. 17b shows the Ni and Fe variation along a line scan across the kamacite-clear taenite–cloudy zone. The Ni content of the clear taenite region varies from $> 50$ wt% at the kamacite–taenite interface to $\sim 45$ wt% at the boundary with the cloudy zone.
The cloudy zone region has ~42 wt% Ni at the boundary with tetrataenite and grades to ~30 wt% at its boundary with the decomposed martensite. The structure of the cloudy zone develops by a spinodal reaction in which a high-Ni phase ($\gamma_2$) (island phase) forms in a matrix of low-Ni kamacite or taenite ($\gamma_1$) (honeycomb phase) (Yang et al., 1997a). The spinodal reaction occurs at low temperatures <350 °C (Fig. 7). Both the formation of tetrataenite and the spinodal reaction are cooling rate dependent. Tetrataenite increases in width, and the size of the high-Ni island phase in the cloudy zone increases with decreasing cooling rate; both these microstructures can give cooling rate information at low temperatures <350 °C (Yang et al., 1997b). At Ni contents below ~30 wt%, plessite, a fine mixture of kamacite and tetrataenite forms at low temperature and is observed in the centers of taenite regions between the plates (Fig. 1). The structure of plessite and the mechanism of formation are discussed in detail by Buchwald (1975), Zhang et al. (1993), Yang et al. (1997a), and Goldstein and Michael (2006). 

Yang et al (1997b) proposed an empirical cooling rate indicator for meteoritic metal based on the size of the high-Ni particles, island phase, in the cloudy zone, which together with the surrounding low-Ni phase form a “honeycomb” structure (Figs. 16 and 17). They measured the size of the high-Ni taenite particles, island phase, in the cloudy zone of various iron, stony-iron, and stony meteorites by high-resolution scanning electron microscopy (SEM) at the outer edge of the cloudy zone adjacent to the tetratenite rim and showed that the size increased with decreasing cooling rate. They found that the size of the high-Ni particles ranges from 400 to 450 nm in mesosiderites, which cooled very slowly, to ~20–40 nm in the rapidly cooled IVA iron meteorites. Since the inverse relationship between high-Ni particle size (island phase size) and metallographic cooling rate holds not only for iron meteorites but also for metal in stony-irons, and stony meteorites, the scale of the cloudy taenite microstructure provides a valuable guide to relative cooling rates of metal-bearing meteorites at 350–200 °C.

Measurements of the high-Ni particle size are more difficult to obtain with the SEM for fast-cooled meteorites. As the island phase size approaches the resolution of the SEM (≤10 nm), specimen preparation becomes more critical. The amount of chemical attack or etching used to develop the cloudy zone microstructure can affect the apparent size and also the visibility of the microstructure as observed even in a high-resolution SEM. In addition, the finest cloudy zone particles are especially sensitive to shock heating, which can cause the cloudy zone to quickly coalesce or even disappear. High-Ni particle sizes <10 nm are measured by making electron transparent thin sections and analyzing the cloudy zone region using the TEM (Figs. 16 and 17).

Since Yang et al. (1997b), more accurate metallographic cooling rates have been measured (Hopfe and Goldstein, 2001; Yang and Goldstein, 2006; Yang et al., 2007, 2008a) and more high-Ni particle sizes have been measured (Yang et al., 2007; Goldstein et al., 2008). The direct relation between decreasing island phase size and increasing cooling rate in the IVA irons (Fig. 18) is the same as that observed by Yang et al. (1997b) for the overall trend for iron, stony-iron, and stony meteorites. This variation takes place over a cooling rate range of 4 orders of magnitude (0.2–6600 °C/Myr). As recognized by Wasson and Richardson (2001), a straight line relationship fits the data in Fig. 18. Cooling rates cannot be derived directly from cloudy taenite particle sizes because there is no effective model currently available for spinodal growth in the Fe–Ni system. However, the relative cooling rates of two meteorites,
(CR₁) and (CR₂), can be estimated from the ratio of their respective island phase or high-Ni particle sizes (IPS₂/IPS₁), namely: \( \frac{CR₁}{CR₂} = \left( \frac{IPS₂}{IPS₁} \right)^n \). The parameter \( n \) obtained from Fig. 18 equals 2.4±0.4.

This equation can be used to obtain relative cooling rates, for example, between meteorites in the same chemical group. For the IVA irons, the differences in the high-Ni particle sizes vary by 2.9±0.5, indicating that cooling rates in the temperature range where the Widmanstätten pattern forms vary by about a factor of 5 (Yang et al., 2007). For the IIIAB irons, the differences in the high-Ni particle sizes vary by 1.75±0.5, indicating that the cooling rates in the temperature range where the Widmanstätten pattern forms vary by about a factor of 5.

In TEM studies of IVA irons, Goldstein et al. (2008) observed that the widths of the tetrataenite, CT₁ regions (Figs. 16 and 17) correlate directly with the island phase size in the cloudy zone and with the cooling rate of the meteorite. The measurement of tetrataenite widths can be easily corrected for orientation effects, since the electron transparent thin section obtained by focused ion beam (FIB) techniques is cut normal to the kamacite/taenite interface. Measurement of the widths of tetrataenite regions can provide another independent measurement of relative cooling rates at low temperatures.

### 5. Iron meteorite ages

Radioactive isotopes with diverse chemical properties and half-lives of 4 Myr to 40 Gyr have decayed in iron meteorites or their progenitor materials, providing constraints on many different stages in their formation (e.g., Chabot and Haack, 2006; Wadhwa, 2007). The

<table>
<thead>
<tr>
<th>Isotopic system</th>
<th>Process dated</th>
<th>Group</th>
<th>Age (Myr)</th>
<th>Age since CAI (Myr)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>¹⁸²Hf–¹⁸⁵W</td>
<td>Core formation</td>
<td>IIAB, IID, IIIAB, IVB</td>
<td>4567±1.2</td>
<td>−0.2±1.2</td>
<td>Markowski et al. (2006a, b)</td>
</tr>
<tr>
<td>¹⁸⁷Re–¹⁸⁷Os</td>
<td>Crystallization of molten Fe–Ni</td>
<td>IIAB</td>
<td>4530±50</td>
<td>37±50</td>
<td>Cook et al. (2004)</td>
</tr>
<tr>
<td>¹⁴⁷Sm–¹⁴³Nd</td>
<td>Silicate closure at ~1000 K</td>
<td>IAB (CC)</td>
<td>4530±20</td>
<td>40±20</td>
<td>Stewart et al. (1996)</td>
</tr>
<tr>
<td>⁵³Mn–⁵³Cr</td>
<td>Phosphate closure at ~1000 K</td>
<td>IIIAB</td>
<td>4563±1</td>
<td>4.1±0.5</td>
<td>Sugiura and Hoshino (2003)</td>
</tr>
<tr>
<td>¹²⁹I–¹²⁹Xe</td>
<td>Silicate closure at ~1100 °C</td>
<td>IAB (CC)</td>
<td>4557±0.1</td>
<td>9</td>
<td>Bogard et al. (2005)</td>
</tr>
<tr>
<td>⁴⁰K–⁴⁰Ar</td>
<td>Silicate closure at ~575–700 K</td>
<td>IAB</td>
<td>4527±1</td>
<td>40±11</td>
<td>Bogard et al. (2005)</td>
</tr>
<tr>
<td>⁴⁰K–⁴⁰Ar</td>
<td>Impact reheating</td>
<td>IIE (Watson)</td>
<td>3676±7</td>
<td>890</td>
<td>Bogard et al. (2000)</td>
</tr>
</tbody>
</table>

Meteorite abbreviation: CC, Caddo County.

- Absolute ages for HF–W and Al–Mg chronometers assume CAI formation at 4567.1±0.16 Myr (Amelin et al., 2002, 2006).
- Using the angrite LEW 86010 to anchor the Mn–Cr chronometer (see Kita et al., 2005). The age decreases by 1 Myr if the carbonaceous chondrite initial ⁵³Mn/⁵⁵Mn is used as a proxy for the CAI initial (Shukolyukov and Lugmair, 2006).
- Age increases by 1 Myr if the Shallowater age of Gilmour et al. (2006) is used.
- Age increased by 21 Myr using new ⁴⁰K decay constant for consistency with Vogel and Renne (2008).
ages in Table 3, are representative of those providing the best constraints on their formation. Absolute ages are listed as well as ages relative to CAIs, which formed 4567 Myr ago according to U–Pb dating (Amelin et al., 2002, 2006).

### 5.1. Hf–W metal–silicate fractionation ages

$^{182}$Hf decays into $^{182}$W with a half-life of 8.9 Myr. Since Hf is lithophile and W is siderophile, the ratio of $^{182}$W in irons to the stable reference isotopes $^{183}$W and $^{184}$W may constrain the time at which metal and silicate were separated so that they were no longer able to equilibrate. For irons derived from bodies that were melted sufficiently to form cores (probably all major groups except IAB and IIE), metal–silicate equilibrium probably ceased when metal droplets settled through silicate melt to form a core, as in the terrestrial magma ocean (Rubie et al., 2003). After allowance for cosmic-ray effects, the $^{182}$W/$^{184}$W ratio in these irons is remarkably similar to the inferred initial ratio of Ca–Al-rich inclusions (CAIs), which are the first objects formed in the solar system (Markowski et al., 2006a, b; Kleine et al., 2005; Scherstén et al., 2006; Qin et al., 2008; Burkhardt et al., 2008). For Negrillos (IIA) and Gibeon (IVA), where the cosmic-ray effects are best constrained, the model ages for core formation in their parent bodies are $-1.0 \pm 1.3$ Myr after crystallization of CAIs (Markowski et al., 2006b; Burkhardt et al., 2008). (A negative age would imply that core formation preceded CAI formation!) For eight fractionally crystallized groups, Burkhardt et al. (2008) infer that core formation took place $<1$ Myr after CAIs. Irons in silicate-bearing groups IIE and IAB tend to have lower $^{182}$W/$^{184}$W ratios, implying more recent metal–silicate exchange (Markowski et al., 2006a). This might reflect younger formation by impact melting of chondritic material after cores formed in other bodies, or more plausibly, partial metal–silicate exchange during cooling (Markowski et al., 2006a). [Note that the three irons listed by Markowski et al. (2006a, b) as IICD (See Choi et al., 1995) are now included in the main IAB group (Wasson and Kallemeyn, 2002).]

Some irons have especially low $^{182}$W/$^{184}$W values, suggesting they may be older than CAIs. However, such low abundances of $^{182}$W are almost certainly a result of cosmic-ray effects during long space exposure, not from early silicate–metal separation (Markowski et al., 2006b; Qin et al., 2008). Nevertheless, Humayun et al. (2007) have raised concerns about the accuracy of the CAI initial $^{182}$W/$^{184}$W ratio obtained from Allende CAIs, as aqueous fluids have caused alteration in Allende. The W contents of some CAIs in Allende have definitely been disturbed by alteration, however, the $^{182}$W/$^{184}$W value for CAIs derived by Kleine et al. (2005) was obtained from both separated minerals and bulk CAIs and has been confirmed by Burkhardt et al. (2008).

Studies of Hf–W systematics of CAIs in less altered chondrites and $^{182}$W/$^{184}$W ratios in irons with short cosmic-ray exposure ages would clearly be invaluable to constrain more precisely when cores formed in asteroids. However, except possibly for IAB and IIE members, it is reasonably certain that iron meteorites come from the first bodies that accreted. Asteroids larger than $\sim 30$ km across that accreted $<1$ Myr after CAIs would have been heated sufficiently by $^{26}$Al to melt and form cores (Sanders and Taylor, 2005; Scherstén et al., 2006). Chondrites probably come from bodies that accreted $>1.5$ Myr after CAIs formed when there was insufficient $^{26}$Al to melt asteroids as chondrule formation ages are $2–5$ Myr after CAIs (Fig. 19). In addition, there is an inverse relationship between peak metamorphic temperature in a chondrite group and the chondrule formation age, supporting the concept that differentiated bodies accreted before the chondrite parent bodies (Scott, 2007).

### 5.2. Re–Os metal solidification ages

Re and Os are highly siderophile elements but small differences in their preference for solid and liquid Fe–Ni cause the Re/Os ratio to rise during crystallization. Strong correlations between the abundance of $^{187}$Os, which is the decay product of $^{187}$Re, and the Re/Os ratio among the bulk compositions of irons in groups allow their crystallization times to be inferred (Smoliar et al., 1996). Since the decay constant for $^{187}$Re is poorly known, absolute ages have been derived by pegging the Re–Os age of IIIAB irons to the Pb–Pb crystallization age of coarse-grained angrites. The inferred Re–Os ages of 4530 $\pm 50$ and 4517 $\pm 32$ Myr for IIAB and IIIAB irons, respectively in Table 3 from Cook et al. (2004) are consistent with earlier studies by Smoliar et al. (1996) and others. These data do not reveal any significant differences between the low- and high-Ni ends of individual groups nor between groups, but they do limit the duration of core crystallization to a period of less than 30 Myr.

### 5.3. Mn–Cr cooling ages

Mn-bearing phosphates in IIIAB irons show a correlation between the $^{55}$Cr/$^{52}$Cr ratio and the Mn/Cr ratio, implying that $^{53}$Mn (half-life 3.7 Myr), decayed in the phosphates to $^{53}$Cr (Sugiura and Hoshino, 2003). The slopes of the isochrons for the phosphate sarcopside in four IIIAB irons (all with bulk Ni of $\sim 9–10\%$) give the $^{53}$Mn/$^{55}$Mn ratio when the mineral cooled through the isotopic closure temperature of $\sim 1000\, \text{K}$. Using the
LEW 86010 angrite to anchor the Mn–Cr relative ages to the Pb–Pb absolute ages (Fig. 19) gives a time of 4 Myr after CAIs for the IIIAB phosphates to have cooled through $300^\circ$C. This Mn–Cr age would probably require a metallographic cooling rate of $1500^\circ$C/Myr (cooling from $1500^\circ$C to $700^\circ$C in 2 Myr assuming that cooling started 2 Myr after CAI formation). This rate is rather higher than the rate of $100^\circ$C/Myr calculated by Yang and Goldstein (2006), but given the uncertainties in the Mn–Cr anchor age and the metallographic cooling rate, the Mn–Cr cooling time is not implausible.

5.4. Ar–Ar cooling and impact reheating ages

The decay of $^{40}$K to $^{40}$Ar in K-bearing silicate minerals in irons provides constraints on the time of isotopic closure. Because the closure temperature in feldspar of $\sim 600$–$700^\circ$K is lower than for most other chronometers, this chronometer can be readily reset by impact heating (e.g., Bogard et al., 2000, 2005). Ar–Ar ages of around 4.5 Gyr for IAB silicates are thought to reflect primary cooling at this time while the 3.7 Gyr age of the Watson IIE iron probably reflects late impact reheating (Table 3).

6. Relationships with other meteorites

Possible links between iron meteorite groups and various stony and stony-iron meteorites have been proposed primarily on the basis of O isotopic compositions of silicates, phosphates, and chromites (Franchi, 2008). However, many differentiated meteorites have rather similar O isotopic compositions so that improvements in the precision of the O isotopic analyses have caused some interpretations to be revised. For example, Clayton and Mayeda (1996) found that IIIAB irons had O isotopic compositions indistinguishable from those of eucrites, mesosiderites, and main-group pallasites from which they inferred that the four types could all be derived from a single body. However, more precise measurements using laser fluorination showed that main-group pallasites and eucrites had distinctly different O isotopic compositions from eucrites and mesosiderites and could not be from the same differentiated body (Greenwood et al., 2006). We conclude that except for the link between group IAB irons and winonaites, the iron meteorite groups are probably not derived from bodies that supply us with other kinds of meteorites.

6.1. Group IAB irons and winonaites

Silicates in certain group IAB irons are most commonly angular inclusions with approximately chondritic mineralogy, but also occur as grains in sulfide and graphite nodules and non-chondritic inclusions such as gabbroic clasts (Benedix et al., 2000; Takeda et al., 2000). The chondritic silicate inclusions are closely similar in mineralogy and O isotopic composition to winonaites, which are strongly metamorphosed and partly melted, metal-bearing meteorites, some of which appear to contain relict chondrules (Clayton and Mayeda, 1996; Benedix et al., 1998). There is additional evidence for a strong link between these two groups as the Mount Morris (Wisconsin) meteorite, classified as a winonaites, may actually be a large silicate clast from the Pine River IAB iron that was found nearby (Bevan and
Grady, 1988). In addition, the Winona meteorite itself may be a silicate inclusion from the Canyon Diablo IAB iron (J.T. Wasson, private communication).

6.2. IIE irons and H chondrites

Similarities in the O isotopic and mineral compositions of silicate inclusions in IIE irons and H chondrites (Fig. 20) have persuaded many authors that the IIE irons formed on the H chondrite body by impact melting (e.g., Casanova et al., 1995; Clayton and Mayeda, 1996; Ikeda and Prinz, 1996; Gaffey and Gilbert, 1998). However, Bogard et al. (2000) inferred from differences in exposure ages and mineralogy that IIE irons and H chondrites came from separate bodies. High-precision analyses of H chondrite falls by Folco et al. (2004) suggest that IIE irons and H chondrites have different O isotopic compositions (Fig. 20). Although Folco et al. (2004) favored a common parent body in view of some similar degassing ages of ~3.7 Gyr, Franchi (2008) concluded that this is unlikely unless the internal structure and isotopic variation in the H chondrite body is poorly understood. We need high-precision analyses of IIE silicates to allow us more insight into the potential relationship between IIE irons and H chondrites.

6.3. Group IIIAB irons and main-group pallasites

The composition of metallic Fe–Ni in main-group pallasites is similar to that of Ni-rich IIIAB irons and comparable to the calculated liquid composition after most of the IIIAB core had crystallized and the liquid was near eutectic composition (Scott, 1977b; Wasson and Choi, 2003). The major discrepancies are some high-Ir pallasites and the relatively high concentrations of Ga and Ge in pallasite metal. A common origin for IIIAB irons and main-group pallasites has also been inferred from the O isotopic compositions of chromites and phosphates in IIIAB irons (Clayton and Mayeda, 1996; Fig. 21). However, laser fluorination analyses are needed to test this. Strong evidence against formation of IIIAB irons in the main-group pallasite body comes from studies of the cloudy zone microstructure showing that the pallasites cooled more slowly than the IIIAB irons (Yang et al., 2008b; Fig. 18).

6.4. Group IVA irons and L chondrites

The O isotopic compositions of silica and orthopyroxene inclusions in IVA irons are surprisingly heterogeneous and overlap those of L and LL chondrites, suggesting that the irons may have formed from
L/LL-like material (Clayton and Mayeda, 1996; Wang et al., 2004; Franchi, 2008). However, it seems unlikely that these irons and chondrites come from the same body as the former are derived from a body that was almost entirely molten, whereas the latter were not melted significantly. Group IVA irons were not associated with L or LL chondrites when they cooled as the thermal model of Yang et al. (2007, 2008a) precludes the presence of significant amounts of silicate around the source of the IVA irons when the Widmanstätten pattern formed. The heterogeneity among the IVA irons may be attributed to incomplete homogenization during parent body accretion, heating, and differentiation.

7. Formation of iron meteorite groups

Here we integrate chemical and isotopic constraints on the origins of groups IAB, IIE, IIIAB, IVA, and IVB, and the ungrouped irons. The first two groups are the “silicate-bearing” groups, whose origin has not been reviewed recently; the last three are the best-studied “fractionally crystallized” groups.

7.1. Group IAB irons

Several unique features of IAB irons are difficult to reconcile with formation in a single metallic core: the high abundance of chondritic silicates, the lack of clear fractional crystallization trends like those in other groups (Fig. 6), and the close association with the winonaites, which were strongly metamorphosed but not extensively melted (Benedix et al., 1998). Kracher (1985) argues that IAB irons might come from a single S-rich core, but most authors favor an origin in metallic pools. These are thought to have formed either by impact melting of cold chondritic material (Choi et al., 1995; Wasson and Kallemeyn, 2002) or by catastrophic impact fragmentation and reassembly of a body that was already hot and partly molten (Benedix et al., 2000, 2005).

Cooling rates of IAB irons during kamacite growth are too poorly constrained to make definitive statements about burial depths and body sizes (Table 2). Radiometric ages of silicates are somewhat inconsistent, but Bogard et al. (2005) infer that partial melting and impact disruption and reassembly of the IAB body occurred at 4.56 Gyr and that metamorphism lasted until 4.52 Gyr. However, they also speculate that the IAB body may have experienced a more complex history with milder impact heating around 4.52 Gyr. Vogel and Renne (2008) Ar–Ar dated plagioclase grains from four IAB irons and found that some contained plagioclase grains with a range of ages that were uncorrelated with grain size. For example in Caddo County, they found a range from 4.47 ± 0.02 to 4.56 ± 0.02 Gyr. They inferred that the silicate grains in a single iron cooled at different rates to below 350 °C (the approximate blocking temperature for K–Ar) at different locations prior to an impact that mixed metal and silicate. However, this seems unlikely as it would appear to require steep thermal gradients in the meteorites when they cooled through 350 °C after the Widmanstätten pattern formed. Group IAB irons are largely unshocked, so localized impact heating also appears unlikely and the explanation for the very diverse Ar–Ar ages is unclear.

7.2. Group IIE irons

IIE irons contain silicate inclusions of chondritic and differentiated composition (Wasson and Wang, 1986; Mittlefehldt et al., 1998; Bogard et al., 2000) as well as Ge isotopic compositions uniquely light and variable (Luais, 2007). Because of their complexity, we list the IIE irons in Table 4 together with some of their characteristic properties. Four have heterogeneously distributed angular silicate inclusions 1–10 cm in size broadly chondritic in composition – mostly olivine and orthopyroxene with minor plagioclase and phosphates (Buchwald, 1975; Olsen et al., 1994; Casanova et al., 1995). Another five have 5–10 vol% globular silicate inclusions up to 1 cm in size that are gabbroic in composition containing plagioclase (or glass), K-feldspar, pyroxene with only trace amounts, if any, of olivine (Wasserburg et al., 1968; Ikeda and Prinz, 1996; Ruzicka et al., 1999). In addition, crystals of nearly pure potassium feldspar up to 11 cm in length were found on the exterior of Colomera (Wasserburg et al., 1968).

Mittlefehldt et al. (1998) suggest that IIE inclusions should be viewed as a sequence extending from primitive to highly differentiated: (1) chondritic inclusions like those in Netschaev that contain chondrules (2) clasts like Techado that lack chondrules and appear unmelted, (3) totally melted, silicate clasts like the one in Watson that lack metal but are roughly chondritic in composition, (4) plagioclase–orthopyroxene–clinopyroxene clasts that could represent basaltic partial melts as in Miles and Weekeroo Station, and (5) plagioclase–clinopyroxene clasts like those in Colomera, Kodaikanal and Elga.

Group IIE irons can also be divided into an old group with formation ages of 4.5±0.1 Gyr and cosmic-ray exposure ages of 50–600 Myr, and a young group (Netchaëvo, Watson, Kodaikanal) with ages of 3.7±0.1 Gyr resulting from late impact heating and cosmic-ray exposure ages of 3–15 Myr (Bogard et al., 2000; Table 3). These subgroups can also be distinguished on the basis of their N and Ge isotopic compositions (Mathew, 2000; Luais, 2007). However,
there is no simple relationship between the nature of a silicate clast, its age, and the composition of the associated metal. Oxygen isotopic compositions of the silicate inclusions suggest that all silicate-bearing IIE irons could come from a single body, but high-precision laser fluorination analyses are needed to check this (Fig. 20).

Given the heterogeneous distribution of silicates in many IIE irons, it is not surprising that some lack silicates (Table 4). However, the composition of the metal in IIE irons is not especially unusual (there are several ungrouped irons that are compositionally similar) so the classification of these silicate-free IIE irons is less secure.

Although there are many radiometric ages for IIE irons, there are no modern determinations of metallographic cooling rates to constrain parent body size or burial depths. However, kamacite bandwidth variations suggest that IIE irons cooled at diverse rates and burial depths, not in a core. The uniquely high concentration of IIE members impact heated during the Late Heavy Bombardment at \(3.8 \text{ Gyr}\) suggests that the IIE parent body was large at that time, conceivably as large as Vesta (Bogard, 1995).

Group IIE was excluded in the discussion in Section 3 of chemical variations due to crystallization because the IIE irons show complex patterns and their analytical data are somewhat incomplete. Although As, Au, and Ni vary systematically among IIE irons in a similar fashion to their behavior in IIIAB irons, Wasson and Wang (1986) argued against a fractional crystallization origin for IIE as the variations of W and Ir with Ni are much smaller than those in IIIAB and resemble those in IAB irons. They concluded that IIE irons formed in individual pools of impact-produced melt, consistent with the diverse cooling rates discussed above.

The remarkable diversity of properties has lead to a wide range of models for the formation of IIE irons, and two ungrouped irons, Guin and Sombrerete, which have similar silicate inclusions. These include (1) an intermediate stage in the gravitational separation of metal and silicates before the core had formed (Wasserburg et al., 1968), (2) impact mixing of materials from a single body that was undergoing igneous differentiation (Bogard et al., 2000; Ruzicka et al., 2006), (3) near-surface impact melting of a chondritic body (Wasson and Wang, 1986; Rubin et al., 1986), and (4) impact mixtures from collisions between metallic projectiles with a target of H chondrite affinity (Ruzicka et al., 1999). Given the increasing evidence for impacts during differentiation caused by \(^{26}\text{Al}\) heating, early formation of IIE irons by impact mixing of materials from a single partly melted body appears most plausible. However, it is possible that impacts mixed materials from several asteroid-sized bodies or that protoplanetary collisions were involved.

### 7.3. Group IIIAB irons

This group has chemical trends consistent with a S-rich molten metallic core in a differentiated body that was undisturbed when it fractionally crystallized and cooled. However, the range of cooling rates of \(~60–300 \text{ °C}/\text{Myr}\) in IIIAB irons exceeds the error limits of \(2\sigma = 2.0\) (Fig. 15a). After allowance for the change in kamacite nucleation mechanism that causes a step in the cooling rate vs. bulk Ni curve, the IIIAB irons appear to show an inverse correlation between bulk Ni and

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**Table 4.** Group IIE irons and their properties.

<table>
<thead>
<tr>
<th>Meteorite</th>
<th>Ni (wt%)(^a)</th>
<th>Silicates(^b)</th>
<th>Ages (Gyr)(^c)</th>
<th>Technique(^c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Arlington</td>
<td>8.42</td>
<td>Absent</td>
<td>4.5</td>
<td>Ar–Ar, Rb–Sr</td>
</tr>
<tr>
<td>Barranca Blanca</td>
<td>8.07</td>
<td>Absent</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Colomera</td>
<td>7.86</td>
<td>Differentiated</td>
<td>3.68</td>
<td>Pb–Pb, Rb–Sr</td>
</tr>
<tr>
<td>Elga</td>
<td>8.25</td>
<td>Differentiated</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Garhi Yasin</td>
<td>8.3</td>
<td>Chondritic(^b)</td>
<td>4.41</td>
<td>Ar–Ar</td>
</tr>
<tr>
<td>Kodaikanal</td>
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<td>Differentiated</td>
<td>3.74</td>
<td>Ar–Ar</td>
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<tr>
<td>Leshan</td>
<td>9.5</td>
<td>Absent</td>
<td></td>
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<tr>
<td>Miles</td>
<td>8.6</td>
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<td>4.49</td>
<td>Ar–Ar</td>
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<td></td>
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<tr>
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<td>Chondritic</td>
<td>3.68</td>
<td>Ar–Ar</td>
</tr>
<tr>
<td>Watson 001</td>
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<td>Differentiated</td>
<td>4.4–4.5</td>
<td>Ar–Ar, I–Xe, Rb–Sr</td>
</tr>
</tbody>
</table>

\(^a\)Wasson and Wang (1986).  
\(^b\)Bogard et al. (2000), Buchwald (1975).  
\(^c\)Bogard et al. (2000) for references.
cooling rate (Yang and Goldstein, 2006), similar to the IVA group though with a smaller range. The most likely explanation is that the body in which the IIIAB irons cooled had a small silicate mantle that was thicker than the IVA mantle (<1 km), but much thinner than the tens of kilometers expected for an undisturbed differentiated body. Detailed thermal models are needed to establish the dimensions of the core and silicate mantle. These data will help to constrain the nature of the impact — whether asteroidal or protoplanetary — and whether the core crystallized before or after the impact. The antiquity of the phosphate in IIIAB irons — only 4–5 Myr younger than CAIs (Fig. 19) — and its low temperature of isotopic closure (~750 °C) imply that the core crystallized only a few Myr after CAIs formed. Such rapid core crystallization would be aided by an impact that removed all but a few kilometers of silicate from a molten metallic body, perhaps several tens of kilometers in radius.

One IIIAB iron, Puente del Zacate, contains a single 7 mm wide silicate clast in a troilite nodule. Most surprisingly, these silicate minerals resemble those in group IAB irons in that they are a chondritic mixture of olivine, pyroxene, and plagioclase mixed with graphite (Olsen et al., 1996), and their O isotopic composition closely matches that of the phosphates and chromites in IIIAB (Fig. 21). How a small chondritic fragment could be added to core material during an impact is not known. However, its presence in sulfide suggests that it was trapped in residual melt and was therefore added to the liquid prior to rapid crystallization of the IIIAB metal, as inferred above.

7.4. Group IVA irons

According to conventional models, the average cooling rate for IVA irons of 200–1500 °C/Myr implies that they are derived from the core of a differentiated body of radius 10–20 km (Chabot and Haack, 2006). However, Yang et al. (2007, 2008a) rejected this model as the cooling rates of 13 IVA irons at 650–500 °C decreased systematically from 6600 to 100 °C/Myr with increasing bulk Ni (Fig. 15) and measurements of the size of the high-Ni particle size in the cloudy zone showed that cooling rates at 300 °C decreased with bulk Ni by a factor of ~15. In addition, a mantled core that cooled at 3000 °C/Myr (a lower limit for the fast cooled, low-Ni IVA irons) would require a differentiated body only 4 km in radius, yet a body of this size would not have been melted sufficiently by 26Al to form a core (Yang et al., 2007).

The only plausible explanation for the IVA cooling rates is that the irons did not cool in a mantled core or a disrupted and reaccreted body (Haack et al., 1996b), but in a large metallic body with scarcely any silicate insulation. Yang et al. (2007, 2008a) calculated that a metallic body of 150 ± 50 km radius would accommodate the ranges of cooling rates they inferred for IVA irons from both kamacite growth modeling and cloudy taenite intergrowth at Tcz. (b) Comparison between calculated cooling rates for IVA irons (Fig. 20b) with two theoretical curves derived from the thermal model in (a) and a fractional crystallization model for the Ni distribution assuming an initial bulk S content for the IVA body of 3 and 9 wt%.

![Fig. 22. Models for crystallization and cooling of a 150 km radius metallic body to explain the thermal histories and bulk Ni of IVA irons (Yang et al., 2007, 2008a).](image-url)
A possible mechanism for making such a body was proposed by Asphaug et al. (2006), who suggested that the parent bodies of iron and stony-iron meteorites were formed in grazing impacts between protoplanets. Their numerical models suggested that such impacts could convert the central part of the projectile into a string of metal-rich bodies. Inwards fractional crystallization of one of these molten metallic bodies would ensure that the early-formed low-Ni IVA irons would cool quickly near the surface and that bulk Ni would be correlated inversely with cooling rate.

Yang et al. (2008a) tested this model further by using the fractional crystallization model for IVA irons to calculate how bulk Ni would vary with burial depth in a 150 km radius metallic body that crystallized inwards. Since no single S concentration for group IVA satisfies the simple fractional crystallization model, values of 3 and 9 wt% were used (Figs. 4d and 5d). The variation of Ni with burial depth was then combined with the thermal model in Fig. 22a to infer how cooling rate varied with bulk Ni. Fig. 22b shows that this modeling for a 150 km radius metallic body provides a very good match for the IVA cooling rates.

Two silicate-rich irons, Steinbach and Sao Joao Nepomuceno, have metal compositions and cooling rates indicating that they come from the IVA body. How these silicate-rich irons could have formed has been a major mystery because the silicates, silica and pyroxene, should have quickly floated up to the core–mantle boundary of a differentiated body. A protoplanetary impact of the kind envisaged by Asphaug et al. (2006) may provide an environment for trapping silicates under an advancing solidification front, as well as producing the silicates from magmas with more chondritic compositions (Ruzicka and Hutson, 2006).

A very different impact model for formation of IVA irons and stony-irons infers that they were produced by impact melting of L/LL chondrite material near the surface of an asteroid that generated an asteroidal core (Wasson et al., 2006). They argued that the inferred cooling rates were incorrect and that the irons cooled at the same rate, contrary to Fig. 15b.

Group IVA, like IVB irons, have extraordinarily low concentrations of moderately volatile siderophile elements. Fig. 2a shows that Ge/Ni ratios in these irons (and some ungrouped irons) are more than a factor of 1000 lower than in CI chondrites. Given the evidence for impacts during the formation of IVA irons, loss of volatiles like Ga, Ge, and S from molten iron may have occurred during asteroidal or protoplanetary impacts (Wasson et al., 2006; Yang et al., 2007).

7.5. Group IVB irons

The remarkable depletion of Ga and Ge in IVB irons (Fig. 2) is clearly a result of high-temperature metal–vapor equilibration (Kelly and Larimer, 1977; Campbell and Humayun, 2005; Walker et al., 2008). Most authors have invoked condensation and accretion at high nebular temperatures, rather than impact volatilization, as the mean group IVB composition matches that predicted by equilibrium condensation calculations. Depletion of W and some other less siderophile elements may reflect oxidation in the IVB body. Chemical trends suggest that these irons come from a fractionally crystallized core with <2 wt% S. However, two characteristics of the cooling rate data are difficult to reconcile with crystallization and cooling in the core of a differentiated body: the high cooling rates of $10^{-3}$–$10^{-4}$°C/Myr (Rasmussen, 1989), which require a differentiated body that was too small to be melted by $^{26}$Al heating, and the diverse cooling rates that are incompatible with an insulated core. However, unlike group IVA, the IVB irons may show a positive correlation between cooling rate and bulk Ni. A proposed link between IVB irons and angrites (Campbell and Humayun, 2005) needs further testing.

7.6. Ungrouped irons

There does not appear to be a fundamental difference between the ungrouped irons and those in groups. It is unlikely, for example, that a significant number are chemically reprocessed members of other groups. Some small irons weighing <20 g could be impact-produced metallic slugs from chondritic asteroids (Wasson, 2000). However, most of the larger ungrouped irons appear to have experienced chemical fractionation processes like those that produced the groups (Scott, 1979). Abundances of volatile siderophile elements like Ga, Ge, Cu, and As among both ungrouped and grouped irons tend to be correlated. Deviations of the ungrouped irons from the overall As–Ga trend are inversely related to their Ir concentrations, consistent with the inverse As–Ir trends and small Ga variations within fractionally crystallized groups. This suggests that most ungrouped irons were fractionally crystallized, like most grouped irons.

The ungrouped irons contain sets of two to four related irons that may well achieve group status as more irons are discovered. The arbitrary minimum number for a group is set at five. In addition, some of the ungrouped irons that Wasson and Kallemeyn (2002) include in their IAB complex may come from the same body. The total number of parent bodies currently sampled by the ungrouped irons is probably somewhat higher than earlier estimates of 40–50 (Scott, 1979; Wasson, 1990). Interestingly, the fraction of ungrouped irons recovered from Antarctica (~0.35) is much higher than for non-Antarctic irons, even after excluding the smallest samples (Wasson, 1990, 2000). The high
proportion of ungrouped Antarctic irons is probably related to their much smaller mean mass (~100 × smaller than for non-Antarctic ones). Smaller meteoroids may sample more diverse locations in the asteroid belt, because they are ejected with higher impact velocities (Wasson, 1990) or because they drift slower into resonances.

7.7. Source of iron meteorites

Since the ungrouped and grouped irons probably come from over 60 different asteroids, about two-thirds of all the asteroids sampled by meteorites were melted sufficiently to allow metal-silicate segregation. However, this high proportion is not reflected in the spectral properties of large intact asteroids or their fragments (Bottke et al., 2006). Types C and S asteroids, generally considered to be chondritic, dominate over likely igneous types such as A and V types, which are composed of olivine and basalt, respectively. (Note that nearly all V types probably come from Vesta.) The virtual absence of stony and stony-iron meteorites that are related to the irons likely reflects the much greater strength of metallic Fe–Ni than rock and its longer impact lifetime (Burbine et al., 1996).

A possible explanation for the abundance of igneous meteorites, the scarcity of igneous asteroids, and the early formation of iron meteorite parent bodies is that melted planetesimals were formed at 1–2 AU from the Sun and their fragments were scattered into the asteroid belt by protoplanets (Bottke et al., 2006). Since most irons cooled in 10 Myr or less (rather than 100 Myr or more, as inferred ~30 years ago), it becomes more plausible that the iron meteorite parent bodies were disrupted in the first few Myr inside 2 AU (Bottke et al., 2006). Disruption by grazing protoplanetary impacts rather than bombardment by smaller projectiles might help to explain how many differentiated bodies were disrupted while Vesta’s crust was preserved (Asphaug et al., 2006). Note that disruption inside 2 AU may have produced bodies that were ~1–10 km in size; disruption during the past 1 Gyr into meter-sized fragments that were exposed to cosmic rays occurred in the asteroid belt.

8. Summary

Contrary to traditional views about their origin, iron meteorites may have been derived originally from bodies as large as 1000 km or more in size. Most iron meteorites come directly or indirectly from bodies that accreted before the chondrites, possibly at 1–2 AU rather than in the asteroid belt. Many of these bodies may have been disrupted by impacts before they cooled slowly.

Chemical variations within the larger chemical groups, excluding IAB and IIE, are broadly consistent with fractional crystallization implying that each chemical group comes from a single molten metallic pool or core. However, the groups differ considerably in bulk composition and crystallization conditions. Only the nearly S-free group IVB is well modeled by simple fractional crystallization of an isolated metallic melt using experimentally determined partition coefficients. The presence of S complicates the crystallization history of the other groups and there are unresolved issues about the scatter in chemical trends (IIIAB), liquid immiscibility (IIAB), trapping of liquid (IIAB, IIIAB, IV, IID), and formation of late stage members (IIIAB, IIAB). The IVA and IID groups have well-defined chemical trends but no crystallization model has explained both the Ir and Ge trends with a single bulk S content.

The irons in groups IAB and IIE, many of which contain silicates, show considerable scatter on most binary elemental plots; neither formed from a single isolated metallic melt. Impacts were involved in their formation but whether they generated molten metal pools or merely mixed preexisting molten metal with silicate is not certain. The IAB silicate inclusions are cogenetic with the winonaites, which are strongly metamorphosed chondrites. No other group of silicate or metal-silicate meteorites is strongly linked to any group of irons.

The cooling rates of irons determined from kamacite growth models have increased over time (in one case by a factor of 50) as models have become ever more sophisticated. Typical cooling rates for irons in their parent asteroidal bodies at ~500–700 °C are 100–10,000 °C/Myr with cooling times of 10 Myr or less. This increase in measured cooling rate is due largely to the recognition of the importance of P in the nucleation and growth of the Widmanstätten pattern.

The highest quality cooling rates are those for groups IIIAB, ~60–300 °C/Myr, and IVA, ~100–6600 °C/Myr. These variations greatly exceed a factor of 2, which is the uncertainty of the cooling rate method. The wide range of cooling rates for IVA irons shows that these meteorites cooled not in a mantled core but a large metallic body of radius 150±50 km with scarcely any silicate insulation. The correlation between bulk Ni and cooling rate requires inwards crystallization of a molten metallic body, which may have formed by a grazing impact between protoplanets. Protoplanetary impacts may have also been involved in the formation of IIIAB irons; thermal histories of groups IIAB and IVB, need to be re-investigated to see if they formed in a similar way. Impact volatilization and high-temperature nebular condensation have been invoked to explain the depletions of Ga, Ge and other volatile siderophiles in groups IVA and IVB, respectively.
After excluding ungrouped irons weighing < 20 g that may be simple impact melts, silicate-bearing irons, and others loosely linked to group IAB, we infer that the remaining ungrouped irons probably come from at least 50 other bodies that formed in analogous ways to the fractionally crystallized groups. They have $^{182}\text{W}/^{184}\text{W}$ ratios showing they were derived originally from bodies that were melted by $^{26}\text{Al}$ to form cores < 1.5 Myr after CAI formation and before the formation of chondrites. These constraints, the evidence for rapid cooling of many irons in a few Myr, the lack of other kinds of meteorites related to the irons, and the small fraction of differentiated bodies in the asteroid belt all suggest that irons could be derived from fragments of planetesimals or protoplanets that formed and broke up at 1–2 AU and were subsequently scattered into the asteroid belt by protoplanets.

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