COOLING RATE VARIATIONS OF GROUP IVA IRON METEORITES

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Cooling rates of eight group IVA iron meteorites were determined using a modification of the Wood method where cooling rate curves are calculated as a function of central taenite Ni content and taenite half-width. The major modification of the Wood method was to include the effect of P on the Ni solubility limits and Ni diffusion coefficients in the kamacite phase for each meteorite studied. The Borg and Lai binary kamacite Ni diffusivities were judged to be the best quality data available for the calculations. The calculated cooling rates range between 3 and 65°C/Myr. A correlation between decreasing cooling rate and increasing Ni content within the group IVA iron is observed. This cooling rate variation agrees closely with the 6–70°C/Myr range calculated by the independent bulk Ni–kamacite bandwidth method. Such a large variation in cooling rate within the group IVA argues against formation within the core of a single parent body.

Willis and Wasson in the preceding paper found only a factor of 2 variation in cooling rate for the six IVA iron studied. The differences between the results of Willis and Wasson and this study are due mainly to the choice of the Ni diffusion coefficients in α and to the choice of the expressions for the effect of P on both the diffusion coefficients and the Ni solubility in kamacite. The Hirano et al. diffusivities used by Willis and Wasson were judged to be incorrect particularly because they are significantly higher than diffusivities in kamacite and taenite measured by other investigators. The assumption of Willis and Wasson that the same P content (0.03 wt.%) can be used for the low-Ni IVA’s and that the same P content (0.16 wt.%) can be used for the high-NI IVA’s was judged to be a serious oversimplification.

1. Introduction

The Widmanstätten pattern of the group IVA iron shows a slight increase in bandwidth with increasing Ni content [1]. Goldstein and Short, using the bulk Ni–kamacite bandwidth method showed that this bandwidth variation can be explained by cooling rates which decrease by almost a factor of 10 as Ni content increases across the group [1]. Such a cooling rate variation has also been calculated by the profile-matching technique of Goldstein and Short [2]. In the preceding paper by Willis and Wasson [3] cooling rates for the IVA iron were remeasured using a pseudo-binary calculation employing the Wood [4] method. Willis and Wasson calculate a varying cooling rate of a factor of 2 but find no correlation between cooling rate and bulk Ni content. Their interpretation is that of a uniform cooling rate for the group.

The purpose of this paper is twofold. Firstly we will comment on the method and results of Willis and Wasson. We will show that cooling rate variations of up to a factor of 4 are calculated for the IVA’s when using their pseudo-binary calculation scheme. Secondly we will show that better-quality diffusion coefficients and better representations of the effect of P on diffusion coefficients and Ni solubilities in kamacite should be used for the cooling rate calculations. The use of these improved input parameters leads to significant cooling rate variations of a factor of ~15 across the IVA group.

2. Willis-Wasson computer simulations

Our computer simulation scheme is similar to that used by Randich and Goldstein [5] to calculate phos-
Fig. 1. Cooling rate determinations for four low- and four high-Ni IVA irons using the Wood method [4] and the Wills-Wasson input parameters [3]. Microprobe data from Wills and Wasson [3] and this study are plotted on the wt.% Ni vs. taenite half-width diagrams for each meteorite.
phide growth in hexahedrites. It uses a Crank-Nicholson technique for solving the diffusion equations and a Murray-Landis grid transformation for calculating the effect of the kamacite-taenite interface movement. We have incorporated the Hirano et al. [6] diffusion coefficients modified by a factor of 1.88 for high-Ni IVA's and the pseudo-binary kamacite solubility curves of Willis and Wasson [3] for low-Ni IVA's (0.03 wt.% P) and for high-Ni IVA's (0.16 wt.% P).

With these input parameters, we generate the same cooling rate curves via the Wood method of central Ni content vs. taenite half-width as given by Willis and Wasson [3, fig. 6].

Fig. 1 shows these curves for the six meteorites analyzed by Willis and Wasson as well as for one additional low-Ni IVA, Signal Mountain, 7.84 wt.% Ni, and one additional high-Ni IVA, Chinautla, 9.48 wt.% Ni. The measured microprobe data of Willis and Wasson are plotted for each meteorite as well as our own data for Signal Mountain and Chinautla. In addition we have added our own data for Para de Minas and Hill City to that of Willis and Wasson. The effect of undercooling was also calculated. For a high-Ni IVA, Hill City, undercooling of \(<120^\circ\text{C}\) only affects the cooling rate curves at taenite half-widths greater than 8 \(\mu\text{m}\) (Fig. 1). On the other hand for a low-Ni IVA, Para de Minas, undercooling of \(<120^\circ\text{C}\) only affects the cooling rate curves at taenite half-widths greater than 10 \(\mu\text{m}\). The data for Gibeon, Harriman and New Westville do not plot along one cooling rate curve (Fig. 1) and the effect of undercooling of \(>120^\circ\text{C}\) may cause the variation in the data. The lack of a significant number of data points for Harriman and New Westville makes it difficult to determine the cooling rates of these two meteorites very accurately.

One can obtain average cooling rates from these curves using the points between 2 and 6 \(\mu\text{m}\) as suggested by Willis and Wasson [3] since these show the least effects of undercooling. In cases where there is a lack of a significant number of data points, Harriman and New Westville, the cooling rates can only be estimated. The results are listed in Table 1. For the same meteorites, the calculated cooling rates from Willis and Wasson [3] and this study are quite similar.

As shown in Table 1 group IVA irons have cooling rates ranging between 15 and 50 \(^\circ\text{C}/\text{Myr}\). We found a variation of a factor of 3—4, whereas Willis and Wasson [3] found a variation of a factor of 2 for the same Ni range. We do not observe the same decrease in cooling rate with increasing Ni content as shown by Goldstein and Short [1]. However, considering the four low-Ni IVA's and the four high-Ni IVA's separately (Fig. 1), the low-Ni IVA's have a cooling rate approximately two times that of the high-Ni IVA's. Therefore even using the Willis-Wasson calculation scheme, our results are consistent with a variation in cooling rates for the group IVA meteorites.

3. Input parameters for computer simulation

3.1. Procedure for selection

The correct choice of diffusion coefficients and phase boundaries to be used in the computer simulations is absolutely critical if the method is to yield correct cooling rate values. Differences in cooling rates of up to a factor of 4 for a single meteorite can occur if an incorrect choice of input parameters is made. Willis and Wasson [3] have used consistency arguments, some containing circular reasoning, to determine which set of diffusion coefficients and phase boundaries should be used for the simulations. For example, two experimental sets of data are available, Hirano et al. [6] and Borg and Lai [9] for the

<table>
<thead>
<tr>
<th>Meteorite</th>
<th>Ni content * (wt.%)</th>
<th>Cooling rate (°C/Myr)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>this work</td>
<td>Willis and Wasson [3]</td>
</tr>
<tr>
<td>Gibeon</td>
<td>7.68</td>
<td>30</td>
</tr>
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<td>Signal Mountain</td>
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<td>50</td>
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<td>Harriman</td>
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<td>20</td>
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<td>Para de Minas</td>
<td>7.99</td>
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<tr>
<td>Mantos Blancos</td>
<td>8.88</td>
<td>15</td>
</tr>
<tr>
<td>Hill City</td>
<td>9.09</td>
<td>20</td>
</tr>
<tr>
<td>New Westville</td>
<td>9.36</td>
<td>15</td>
</tr>
<tr>
<td>Chinautla</td>
<td>9.48 **</td>
<td>25</td>
</tr>
</tbody>
</table>

* Schaudy et al. [7], except Chinautla.
** Moore et al. [8].
diffusion coefficient, of N in kamacite, \( D_\alpha \). The major reason for their choice of the Hirano et al. coefficients was that they yielded better matches between calculated cooling rate curves (Wood method) and the experimental points for Gibeon, and that they minimized the cooling rate range [3]. As stated previously the most probable reason that the Gibeon data do not plot along one cooling rate curve is that severe undercooling effects have occurred. For the phase boundaries Willis and Wasson have chosen to use two pseudo-binary phase diagrams to reflect the different P contents of the low- and high-Ni IVA irons. Their choice of the best \( \alpha/\alpha + \gamma \) phase boundaries is based on iterative fits of calculated Ni profiles for the kamacite phase to measured Gibeon and Hill City Ni profiles for the kamacite phase [3]. To use this iteration technique Wasson and Willis assumed that both the diffusion coefficients and the cooling rate are known. The diffusion coefficients were, however, determined using an assumed phase diagram.

Our approach to obtaining the input parameters is to evaluate the two sets of kamacite diffusivities on the basis of the quality of the data available to date. To obtain the pseudo-binary \( \alpha/\alpha + \gamma \) phase boundaries, extrapolation from experimental data was used. After this first step, we adopted the iteration technique of Wasson and Willis [3] to determine the final position of the phase boundaries.

### 3.2. Diffusion coefficients

The diffusion coefficient of Ni in taenite is a function of temperature and Ni concentration. The most recent determination is by Goldstein et al. [10]. Since the P solubility in taenite is much lower than that of kamacite [11], the binary diffusivities of Goldstein et al. in taenite were used in this study as well as in the study of Willis and Wasson [3].

The major coefficient of Ni in the kamacite phase, \( D_\alpha \), has been a subject of controversy among researchers who have simulated kamacite growth. The central issue involves the choice of binary diffusion coefficients in the \( \alpha \) phase for the ferromagnetic region \((T < 750^\circ C)\). The diffusion coefficients of Ni in \( \alpha \) were determined by Hirano et al. [6] and by Borg and Lai [9]. Fig. 2 displays all the pertinent data from Hirano et al. [6] and Borg and Lai [9]. The temperature region covers the \( \gamma \) phase, \( \alpha \) phase-

paramagnetic and \( \alpha \) phase-ferromagnetic. The data of Hirano et al. [6] was measured over the entire temperature range while that of Borg and Lai [9] was measured over the \( \alpha \) phase-paramagnetic with one value below the anomalous region and in the \( \alpha \) phase-ferromagnetic temperature range. As observed in Fig. 2, the diffusion coefficients of Borg and Lai are smaller than those of Hirano et al. at all temperatures. Goldstein et al. [10] also determined Ni diffusion coefficients in the \( \alpha \) phase at 800 and 700\(^{\circ}C\). These values are shown by the X's in Fig. 2. There is excellent agreement between these data and the data of Borg and Lai [9] in the \( \alpha \) phase. Since Hirano et al. [6] and Borg and Lai [9] both agree on the magnitude of the shift in activation energy (2.7 kcal for Hirano et al., 2.4 kcal for Borg and Lai) from \( D_\alpha \) ferromagnetic to \( D_\alpha \) paramagnetic, the lack of significant low-temperature data by Borg and Lai [9] still allows one to evaluate \( D_\alpha \) ferromagnetic.

It can be shown that the diffusion coefficients determined by Hirano et al. [6] are too large. The \( \gamma \)
phase Ni diffusion coefficients from Hirano et al. [6] are significantly higher than those of Goldstein et al. [10] (Ni = 5 at.%; Fig. 2). Heyward and Goldstein [12] have also calculated some binary coefficients and the value for 0% P, 8 at.% Ni at 1100°C is shown in Fig. 2. This value agrees with the previous binary results of Goldstein et al. [10]. Clearly the diffusion coefficients determined by Hirano et al. [6] are higher than the more recent diffusion work in both the α and γ phases. Hirano et al. did, however, make measurements at low temperatures, within the ferromagnetic range at 600 and 680°C where kamacite growth occurs. This fact and the existence of duplicate measurements at these temperatures are a major reason for the selection of the Hirano et al. data by Wasson and Willis [3]. However, Hirano et al. used the surface decrease technique for their radioactive 63Ni tracer work at 710°C and below [6]. This technique was calibrated empirically with their data at 750 and 840°C obtained by another diffusion technique. Since the Hirano et al. data at 750 and 840°C, as well as other temperatures in both the α and γ phase fields, lie above the Goldstein et al. data, it is not surprising that the Hirano et al. data within the ferromagnetic range also lie above that of Borg and Lai. We therefore argue that the Hirano et al. coefficients are incorrect and should not be employed.

We have chosen the binary diffusivities of Borg and Lai [9] as the best experimental values available for calculation purposes. In the ferromagnetic range:

$$D_\alpha = 10.5 \exp(-64,300/RT) \text{ cm}^2/\text{s}$$

(1)

where $R$ is the gas constant (1.987 kcal/K) and $T$ is the diffusion temperature in K.

The effect of P on $D_\alpha$ in the kamacite phase can be determined using the ternary diffusion data of Heyward and Goldstein [12]. The 1100°C data of Heyward and Goldstein shows that increasing the P content will increase $D_\alpha$ while increasing the Ni content will have little influence on the value of $D_\alpha$. Since the only isotherm that gives $D_\alpha$ values for various P contents is at 1100°C, it is assumed that the $D_\alpha$ dependence on P is similar at lower temperatures. Using the 1100°C data, an expression of the functional dependence of $D_\alpha$ on P content can be written as:

$$D_\alpha = [1 + A_1C_P + A_2C_P^2] \times 10.5 \exp(-64,300/RT) \text{ cm}^2/\text{s}$$

(2)

where $C_P$ is the P content (wt.%), $A_1 = 1.2665$ and $A_2 = 0.6231$. For 0.16 wt.% P in the kamacite phase, the diffusion coefficient is increased by only a factor of 1.22. This P effect is much smaller than the factor of 1.88 used by Willis and Wasson [3]. These authors incorrectly interpreted the original ternary diffusion data for Ni diffusion in kamacite from Heyward and Goldstein [12]. They quote results at 770°C which were in fact never measured by Heyward and Goldstein [12]. The calculated effect of P on $D_\alpha$ [$D_{\text{NiNi}(\alpha)}^\text{Fe}$] in the kamacite phase for the maximum P solubility in kamacite as a function of temperature is shown in the ferromagnetic range in Fig. 2.

### 3.3. Phase diagram

The Fe-Ni binary phase diagram over the temperature range 900—500°C is given by Goldstein and Ogilvie [13]. Since the IVA's have low P contents and the solubility of P is much lower in the taenite phase [11], the $\gamma/(\alpha + \gamma)$ boundary of the Fe-Ni diagram was not altered for the presence of P. This same assumption was used by Willis and Wasson [3].

The kamacite phase can contain appreciable amounts of P. The presence of P will change the maximum Ni solubility in kamacite and in turn effect the cooling rate curves obtained from the Wood method. In order to obtain an analytical expression relating Ni solubility in the α phase to temperature the experimental data of Goldstein and Ogilvie was plotted over the temperature range 750—500°C. A peak in the Ni solubility in α occurs between 500 and 400°C [13] with the Ni solubility decreasing below this range. A trial curve, defining the $\alpha/(\alpha + \gamma)$ phase boundary, called ALN, from 750 to 300°C, was drawn through the experimental data having a peak Ni solubility (<7.5 wt.%) between 500 and 400°C. A parallel procedure was used in determining the Ni solubility of the point defining the α corner of the three-phase reaction field, $\alpha + \gamma + \text{Ph}$, called AUN. The experimental data from Doan and Goldstein [11] were used over the temperature range 750—550°C. The presence of P increases the Ni solubility over that of the pure Fe-Ni binary. As temperature decreases the P solubility in α decreases and one would expect the Ni solubility of the point AUN to parallel that of the binary point ALN and to converge on it at low tempera-
tures. Again a trial curve was drawn through the experimental data having a Ni solubility peak (<8.0 wt.% Ni) between 500 and 400°C and converging on the binary solubility limits as temperature is decreased.

The variation of ALN and AUN give the Ni solubility limits for 0% P and for the maximum P soluble in kamacite. The Ni and P contents of the IVA irons vary between 7.5 and 9.5 wt.% Ni and 0.02 and 0.2 wt.% P [14]. Therefore each meteorite will have kamacite Ni solubility values which are unique and which lie between the ALN and AUN limiting cases. We have determined unique Ni solubility curves for each IVA iron of interest. As a first approximation a trial curve is drawn. This curve moves towards the binary solubility curve (ALN) as temperature is decreased.

Willis and Wasson [3] have suggested a means of improving the kamacite Ni solubility curves for each meteorite by matching simulated Ni concentration profiles in kamacite with experimentally measured ones. This iterative procedure was also used in this study. The simulation model incorporating the trial solubility curve and the Borg and Lai diffusivities modified for P effects, equation 2, is used to generate cooling rate curves according to the Wood method and a tentative cooling rate is determined. Using phase dimensions measured from each meteorite as inputs to the simulation model a Ni concentration

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**Fig. 3.** Kamacite Ni concentration profiles in Signal Mountain, a low-Ni, low-P IVA iron and in Hill City, a high-Ni, high-P IVA iron. Electron microprobe data are shown as filled circles, calculated profiles as lines. The error bars are estimates of the 95% confidence limits on the precision of the microprobe measurements. The composition profiles were calculated using phase diagrams developed in this study and diffusion coefficients of Borg and Lai [9] modified for the influence of P. The calculated and measured profiles are used to derive the a/(a + γ) phase boundary.

**Fig. 4.** Kamacite Ni solubility curves for two IVA irons, Signal Mountain and Chinaulta, containing 0.04 and 0.17 wt.% P, respectively. The low- and high-P kamacite Ni solubility curves of Willis and Wasson are also shown for comparison purposes.
profile is generated. A corresponding Ni concentration profile in kamacite is measured with the microprobe on the meteorite and the two profiles are compared. The phase diagram is then modified in order to produce a simulated profile more closely approximating the measured one. This phase diagram modification, however, shifts the cooling rate curves in the Wood method, yielding a new cooling rate. The entire process is repeated anew. This technique should not be used repeatedly as the Ni concentration profile in kamacite is also sensitive to changes in other input parameters, such as nucleation temperature or distance between kamacite bands. Two simulated and measured kamacite Ni concentration profiles are shown in Fig. 3 for Signal Mountain a low-Ni, low-P IVA member and for Hill City a high-Ni, high-P IVA member. The kamacite Ni solubility curves for two IVA irons of differing Ni and P content are shown in Fig. 4. The two solubility curves of Willis and Wasson (0.03, 0.16 wt.% P) \[3\] are also shown in Fig. 4 for comparison purposes. Matched Ni solubility curves from the two studies do not differ greatly, \(<0.3\) wt.% at most. The successful match of the computer profile with the experimental profile shows that we have selected self-consistent phase boundaries for these meteorites.

4. Results and discussion

4.1. Cooling rates

Cooling rate curves for the application of the Wood method were calculated for the eight meteorites considered in this study. The Borg and Lai \[9\] P modified diffusivities, equation 2, and the best fit kamacite Ni solubility curves were used in the calculation. The diffusivities and Ni solubilities in this study are sensitive to bulk Ni and P content. Therefore selected bulk Ni and P values were obtained from the literature for each meteorite. Particular attention was paid to studies such as Moore et al. \[8\] where both bulk Ni and P were measured on the same sample. For two meteorites, where P contents were not well established, values were taken from the linear variation of log wt.% P vs. log wt.% Ni for the IVA irons. The selected Ni and P compositions chosen are listed in Table 2. It is interesting to note that the

<table>
<thead>
<tr>
<th>Meteorite</th>
<th>Willis-Wasson study [3]</th>
<th>This study</th>
<th>Bandwidth [14]</th>
<th>Cooling rate ((^{°})C/Myr)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ni content (^{a}) (wt.%)</td>
<td>cooling rate (^{c}) ((^{°})C/Myr)</td>
<td>Ni</td>
<td>P</td>
</tr>
<tr>
<td>Signal Mountain</td>
<td>7.84 (^{a})</td>
<td>0.04 (^{d})</td>
<td>0.28</td>
<td>65</td>
</tr>
<tr>
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<td>7.93 (^{d})</td>
<td>0.035 (^{f})</td>
<td>0.30</td>
<td>35</td>
</tr>
<tr>
<td>Harriman</td>
<td>7.96 (^{a})</td>
<td>0.045 (^{f})</td>
<td>0.30</td>
<td>20</td>
</tr>
<tr>
<td>Para de Minas</td>
<td>8.19 (^{g})</td>
<td>0.06 (^{e})</td>
<td>0.33</td>
<td>25</td>
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<tr>
<td>Mantos Blancos</td>
<td>8.83 (^{e})</td>
<td>0.10 (^{g})</td>
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<td>4</td>
</tr>
<tr>
<td>Hill City</td>
<td>9.2 (^{d})</td>
<td>0.12 (^{d,f})</td>
<td>0.38</td>
<td>6</td>
</tr>
<tr>
<td>New Westville</td>
<td>9.40 (^{d})</td>
<td>0.14 (^{d})</td>
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<td>4</td>
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<tr>
<td>Chingaoula</td>
<td>9.48 (^{e})</td>
<td>0.165 (^{g})</td>
<td>0.35</td>
<td>7</td>
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</tbody>
</table>

\(^{a}\) Schaudy et al. \[7\].
\(^{b}\) Calculated with Wasson equation \[15\] using bandwidth measurements from Buchwald \[14\] and Ni contents used this study.
\(^{c}\) Cooling rates determined in this study using the input parameters of Willis and Wasson \[3\].
\(^{d}\) Buchwald \[14\].
\(^{e}\) Moore et al. \[8\].
\(^{f}\) This study, see text.
\(^{g}\) Fletcher \[16\].
Fig. 5. Cooling rate determinations for four low- and four high-Ni IVA irons using the Wood method [4] and the input parameters developed in this study. Microprobe data from Willis and Wasson [3] and this study are plotted on the wt.% Ni vs. taenite half-width diagrams for each meteorite.
Gibeon Ni value used in this study is significantly higher than that used by Willis and Wasson [3]. Except for the Ni value of Para de Minas the Ni and P values are very close to those given by Buchwald [14].

Taenite step scans were performed with the electron probe for four IVA iron using essentially the same procedures as Willis and Wasson [3]. These data and central Ni concentration vs. taenite half-width data for the six meteorites studied by Willis and Wasson were used to determine cooling rates. Calculated cooling rate curves were generated for the eight IVA iron and are plotted in Fig. 5 along with the appropriate microprobe data. An average cooling rate was obtained by interpolating between the calculated curves using the points between 2 and 6 μm to minimize undercooling effects as suggested by Willis and Wasson [3]. Since there are so little data for Harri man and New Westville, only cooling rate ranges were obtained for these meteorites.

The measured cooling rates are listed in Table 2. Group IVA iron have cooling rates ranging from ~4 to 65°C/Myr. In addition the cooling rates increase with increasing Ni content. The cooling rates for these eight meteorites range from 6 to 70°C/Myr using the bulk Ni—kamacite bandwidth method of Goldstein and Short (Table 2). According to Willis and Wasson [3], however, the cooling rates for the six meteorites they studied vary from only 13 to 25°C/Myr.

Fig. 5 shows the effect of undercooling before the nucleation of the Widmanstätten pattern on the cooling rate curves of Gibeon and New Westville. Cooling rate curves including undercooling of 150°C for Gibeon and 190°C for New Westville pass through almost all the data points. Data beyond taenite half-width of ~4 μm are affected by severe undercooling. Based on these results, data for Gibeon and New Westville for taenite half-widths less than ~4 μm, yield cooling rates of 35 and 3°C/Myr, respectively. Clearly Willis and Wasson [3] should not have chosen Gibeon data to determine the best diffusion coefficients for Ni in kamacite.

4.2. Comparison of cooling rate calculation schemes

Uncertainties in the cooling rate determinations due to experimental errors and the computer model-
curve at 25°C/Myr on the Willis-Wasson curves falls at ~6°C/Myr on our curves. This decrease in cooling rate of a factor of ~4 is obviously very significant. This shift in cooling rate curves involves both a lateral translation and a rotation. If the Borg and Lai diffusion coefficient [9] multiplied by 1.88 for the high-Ni IVA's is substituted for the Hirano et al. [6] coefficient, no change in the cooling rate is observed. This result is consistent with that reported by Willis and Wasson [3]. This could be due in part to the near doubling of the original Borg and Lai [9] $D_\alpha$ values even though P solubility in $\alpha$ is rapidly decreasing with decreasing temperature. In fact, when the same calculation is made using the measured P-content of Hill City (0.12 wt.%) and the Borg and Lai diffusion coefficient [9] including the effect of P (equation 2) the cooling rate is decreased by a factor of ~4. In this last case the value of $D_\alpha$ is much smaller and has the effect of greatly decreasing the cooling rate. Clearly the choice of the diffusivity in kamacite has a major influence on the measured cooling rate.

To investigate the effect of changing the Ni solubility in kamacite we can hold the diffusivity constant. First for high diffusivity, Hirano et al. [6] X 1.88, changing the phase diagram from Willis-Wasson to that used in this study, yields a decrease in cooling rate of approximately a factor of 5. Secondly for lower diffusivity, Borg and Lai [9] including the effect of P (equation 2), changing the phase diagram from Willis-Wasson to that used in this study does not change the cooling rate at all. Therefore the effect of changing Ni solubility in kamacite is only significant at the high diffusivities of Hirano et al. [6]. Since the Borg and Lai coefficients are more correct, the effect of $a/(\alpha + \gamma)$ phase diagram differences (Fig. 4) need not be considered for the IVA's.

The slight bulk Ni variation for Hill City between Willis-Wasson [3] (9.09 wt.%) and Moren-Goldstein (9.20 wt.%) does not cause a noticeable cooling rate curve shift. However, the variation in the bulk P content does produce a significant cooling rate curve shift when P-sensitive parameters are employed, i.e., the kamacite Ni solubilities of Moren-Goldstein and/or the Borg and Lai [9] $D_\alpha$ values as given by equation 2. To investigate the effect of changing the bulk P content we can hold the diffusivity constant. When using the Moren-Goldstein kamacite Ni solubilities and the Hirano et al. [6] $D_\alpha$ values x 1.88 an increase in the bulk P content from 0.12 to 0.16 wt.% changes the Ni solubility and causes a decrease in the cooling rate. Likewise, using the high-P phase diagram of Willis-Wasson [3] and the Borg and Lai [9] $D_\alpha$ of equation 2, an increase in the bulk P content changes the diffusivities and decreases the cooling rate. Therefore the assumption of the same bulk P value for each high-Ni IVA meteorite (0.16% P as given by Willis and Wasson [3]), is a serious oversimplification of the real case.

4.3. Ternary model for the IVA's

A new ternary model for the growth of the Widmanstätten pattern has been developed by Moren and Goldstein [17,18] and Moren [19]. This model incorporates the effect of P on the kamacite and taenite Ni solubility limits and on the diffusion of Ni in both kamacite and taenite. It also allows tie line shifting for mass balance during precipitate growth [5] which is important in the initial growth period. Both the Wood method [4] and the profile-matching technique of Goldstein and Short [2] are used to obtain cooling rates. Only preliminary results using this technique are available at this time. Using the ternary calculation with the Wood method as well as the data of Willis and Wasson [3], Moren and Goldstein reported cooling rates of 30°C/Myr for Gibeon, 10°C/Myr for Harriman, 25°C/Myr for Para de Minas, 4°C/Myr for Mantos Blancos, 7°C/Myr for Hill City and 3°C/Myr for New Westville [18]. These cooling rate values compare favorably with those of our present study (see Table 2) using a pseudo-binary calculation scheme and also show approximately a factor of 10 variation in cooling rate within the IVA iron. 

5. Origin of group IVA

The results obtained in this work show a large range in the cooling rates of group IVA iron meteorites. The cooling rates vary by a factor of ~15 times and decrease from 65°C/Myr at the low-Ni end of the group in a regular fashion to ~4°C/Myr at the high-Ni end of the group. The large variation in cooling rates within the group IVA iron meteorites argues against the formation of the group IVA meteorites within the core of a single parent body.
Acknowledgements

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